

Radiation synthesis of stimuli-responsive membranes, hydrogels and adsorbents for separation purposes

*Final report of a coordinated research project
2000–2004*



IAEA

International Atomic Energy Agency

August 2005

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RADIATION SYNTHESIS OF STIMULI-RESPONSIVE MEMBRANES, HYDROGELS AND
ADSORBENTS FOR SEPARATION PURPOSES

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FOREWORD

Radiation synthesis of stimuli-responsive membranes, hydrogels and adsorbents for separation purposes is a wide field of important applications for radiation technology. Stimuli-responsive membranes have emerged in recent years as a unique class of materials that can offer many advantages over the conventional materials in a number of applications. Radiation processing techniques have been applied for synthesis of new materials with specific separation features and for their characterization. Exploration of areas where such materials can be beneficially utilized has shown that stimuli-responsive membranes manufactured by radiation processing are being developed and commercialized in many developed and developing Member States.

The International Atomic Energy Agency (IAEA) has launched a Coordinated Research Project (CRP) on Radiation Synthesis of Stimuli-responsive Membranes, Hydrogels and Adsorbents for Separation Purposes to further develop this technology. The first research coordination meeting (RCM) of the CRP, held at the IAEA in Vienna, 12–14 December 2001, recognized the growing interest in the development of such novel materials using radiation techniques, and made suggestions and recommendations to achieve these objectives. They included the development of new synthesis and characterization methods, and exploration of areas where such materials could be beneficially utilized. Accordingly, the principal investigators engaged in the project have initiated work on the development of radiation-processed materials in different forms such as hydrogels, ion track membranes, monoliths, nanoparticles and nanogels for developing applications in various areas. Network cooperation was established among participants to share experiences and exchange information.

The second RCM, held in Budapest, 2–6 June 2003, reported on the progress achieved since the first meeting, critically evaluated the results obtained by different groups and formulated the work programme and networking activities for the next year. The participants representing Egypt, France, Germany, Hungary, India, Japan, Kazakhstan, Republic of Korea, Poland and Turkey presented satisfactory reports.

The third and final RCM was held at the IAEA in Vienna, 22–26 November 2004. The participating chief investigators discussed the results obtained during the CRP and drafted the final report with main achievements, conclusions and recommendations for the practical applications and for future cooperation.

The highlights of results include production of single and multi-pore polyamide membranes, fast thermo-responsive hydrogels, porous polymer monoliths, stimuli-responsive hydrogels based on natural polymers, polymeric nanogels and novel non-ionic thermo-sensitive hydrogels. The application areas explored for beneficially utilizing these novel materials included specialized drug delivery systems (DDS), selective adsorbents, nanopores for single molecule detection and membranes for separation and concentration of solutes.

The report provides basic information on radiation processing and promotes experience exchange for further developments of radiation technology. Protocols and procedures of preparation of various stimuli responsive membranes and their actual and perspective applications are described in the report. Public awareness and technology acceptance are other factors to be considered for further dissemination.

The IAEA wishes to thank all the participants in the CRP for their valuable contributions. The IAEA officer responsible for this publication was A.G. Chmielewski of the Division of Physical and Chemical Sciences.

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SUMMARY

1. INTRODUCTION

The contributions presented in this technical publication describe the work and the results of the research groups involved in the implementation of the Coordinated Research Project (CRP) on Radiation Synthesis of Stimuli-responsive Membranes, Hydrogels and Absorbents for Separation Purposes. It emphasizes the emerging applications of new materials prepared by radiation techniques (membranes, nano- and microgels, hydrogels, beads and monoliths) in separation technology. It also outlines the present status of the field of research.

1.1. Existing challenges

Environment (removal of toxic substances – heavy metal ions, dyes)

Environmental pollution remains one of the major problems both on the national and international level. There is a need for developing new, effective and cost-efficient technologies for removal of pollutants from wastewaters. One of the most severe problems with this respect is the presence of toxic substances such as heavy metal ions, anions and dyes in the industrial wastewaters. It is expected that selective, stimuli-sensitive polymer-based absorption systems can provide technologically and economically sound solution of some of these problems. An important aspect is that these materials with stimuli-sensitive, reversible adsorption properties can be easily regenerated and used for a large number of sorption-desorption cycles.

Recovery of uranium from seawater

It is foreseen that nuclear power plants, along with renewable resources, will continue to be a very important source of energy when compared with burning fossil fuels. The uranium necessary to operate the nuclear power plants is currently acquired from uranium ore. However, it seems reasonable to investigate also alternative sources and technologies. One of them is recovery of uranium from seawater. Due to the low concentration of uranyl ions in seawater and the presence of high concentrations of other ions, highly effective and selective separation systems must be applied. Radiation-formed hydrogels, polymeric resins and mesoporous materials are believed to be potential materials of choice for these purposes. Therefore, extensive research to design, test and optimize hydrogel-based uranium recovery systems is needed.

Biomedical and biological applications

Health care is the field where fast progress and increasing quality of services is of very high social importance. Disease prevention, diagnostics as well as fast and efficient cure, besides its human and social impacts, is also of great importance from the economic point of view. Therefore it is of utmost importance that high-quality medicaments, biomaterials and elements of diagnostic systems can be produced by modern techniques that are at the same time economically sound and safe for humans and environment. Within this project, two main aspects have been addressed: i) developing new biomaterials, sensors and controlled drug-delivery systems, ii) separation, purification and analysis of biopolymers (DNA, proteins, viruses...). In all these cases ionizing radiation offers a convenient means to develop unique alternative solutions e.g. nanogels, hydrogels, single pore membranes, monoliths, grafted membranes, hollow membranes, biochips.

1.2. Radiation based technologies and products as a solution

Temperature-sensitive as well as pH-sensitive membranes and gels have been suggested for use in a variety of novel applications including controlled drug delivery, immobilized enzyme reactors, chemo-mechanical devices, artificial muscles, and separation processes. Radiation based technologies (gamma rays or electron beam) are considered to be among the most convenient ways to produce and sterilize polymer gels and membranes. There are many advantages of the radiation-based technologies of polymer-based stimuli-responsive materials over the conventional techniques. Since the chemical reactions in the processed materials are initiated by radiation, there is no need to use (usually toxic) initiators, crosslinking agents or other auxiliary substances. This helps to reduce costs, makes the technology simple, does not lead to by-products and waste, and the resulting product is of high purity. Radiation-based technologies can easily be handled also by small companies and the costs of production, being an important component of the final shelf-price of the product, are considerably lower than for the corresponding conventional procedures, as proven by the already implemented radiation-based technologies, e.g. hydrogel wound dressings. Moreover, some of these products cannot be synthesized by conventional methods.

Nowadays special radiation sources such as heavy ion beams produced from accelerators can also be used to synthesize different kinds of membranes. To control the transport of ions and/or molecules as a function of external parameters such as electrical field, pH, and concentration, novel membranes should be developed. For this purpose, the fabrication process of solid state nanopores in polymer films, which are able to regulate the ion flow based on similar principles as function of the biochannels (asymmetrical pores of nanometer scale) has to be studied and optimized. Asymmetric pores are also characterized by a lower resistance than the corresponding cylindrical pores of the same limiting diameter. Lower resistance assures higher ion current and therefore easier detection. From the few techniques currently available to fabricate a pore of these characteristics, the combination of heavy ion irradiation and chemical etching constitute a unique tool.

It was shown in this CRP that this latter technique allows the creation of polymeric nanochannels with apertures of only few nanometers. Synthetic nanopores have also significant potential applications in biosensing and genomics. The main advantages of this technique over current technologies are its high speed, very low detection limit, together with the capability to analyze biomolecules without prior marking, quantitative amplification, or chemical modification. Separation of ions and proteins is also of interest in other applications such as kidney dialysis. In this case, heavy ion beam irradiation followed by chemical etching provides a solution for the fabrication of hollow membranes. Polymeric templates with parallel pores of controlled diameter are produced, on which a suitable monomer is polymerized. After decomposition of the template a hollow membrane is formed. These artificial membranes are presently the ones offering the characteristics the closest to the natural systems.

In order to develop new technologies and products utilizing this technology, it was necessary to coordinate the activities of research groups at an international level. The current coordinated research project was intended to stimulate research activities in this field and provide a forum for information exchange and cooperation between the specialized research teams from 10 countries.

2. OBJECTIVES

The overall objective of the CRP was to develop new materials by using radiolytic methods for practical applications in various fields. The developed techniques are environment-friendly techniques that help to keep the environment clean e.g. by collecting hazardous materials from wastewaters, by simplifying the uranium recovery technology or by replacing poisoning organic solvents used in separation by water, etc.

The following were the specific objectives of the CRP:

- Development of new functionalized hydrogels, partly by using natural polymers for collecting hazardous heavy metals, dyes and other organic compounds from wastewaters.
- Synthesis of polymers with high selectivity for collecting uranium from wastes and also from sea-water.
- Synthesis of new polymeric materials (nanogels, membranes) for separation of biomolecules or biopolymers, such as amino acids, nucleic acids, proteins, etc.
- Synthesis of stimuli responsive nano- and microgels, hydrogels for controlled drug delivery. Production of polymers with special properties for biomedical applications.

3. SUMMARY OF THE COORDINATED RESEARCH PROJECT

3.1. Egypt

A great deal was focused on the wastewater treatment from heavy and toxic metals because of the severe problems of environmental pollution. Among many sorptive materials, various forms of synthetic polymers containing complexing molecule, which are abundantly at low cost, have emerged as one of the most important materials for the synthesis of new sorbents. The use of high-energy radiations in the grafting and copolymerization processing is known to improve the physicochemical qualities of many polymer products to expand their utilizations. One of the important materials which could be used for the wastewater treatment is the stimuli-responsive functionalized copolymers that are capable for metal chelation and/or complexation with their reactive functional groups such as carboxylic acid, amide, nitrile, oxime, quaternized pyridine groups etc. Such functionalized reactive membranes and hydrogels were prepared by radiation-induced grafting and radiation copolymerization of different monomers and polymers. In this respect, great efforts were focused on the search and development of new materials more efficient and stimuli-responsive for many applications such as separation and purification purposes.

During this CRP, studies have been made for the preparation and characterization of different hydrogels and membranes which are prepared by γ -radiation-induced copolymerization and grafting of vinyl and acrylic monomers such as acrylic acid (AAc), 4-vinylpyridine (4-VP), AAc/ 4-VP, N-vinyl pyrrolidone/acrylic acid (NVP/AAc) and NVP/Acrylamide NVP/AAm) for the purpose of separation and extraction of heavy metals and dyes from wastewater. The factors affecting the preparation and homogeneity of such prepared materials were thoroughly investigated. Characterization, stimuli-responsiveness and some selected properties of the prepared hydrogels and membranes were studied. Accordingly, the possibility of its practicable uses in separation processes and wastewater treatment were thoroughly studied and evaluated. Also, several trials were made to improve the chelation affinity and adsorption capacity to the metals by further introduction of certain reactive chelating groups via the functional groups of the prepared hydrogels and membranes. It is worthy to mention that different natural ligno- cellulosic materials were also used for the preparation of super-adsorbent materials suitable for separation and purification processes of wastewater. Also, trials were made for the recovery of valuable metals such as Au, Ag and Ru from their wastes. Some of the radiation prepared hydrogels and membranes showed very promising stimuli-responsive properties which make them useful for practical applications.

3.2. France

Ionizing radiation is usually considered to induce damages in organic materials. However, these radiolytic damages can beneficially be used. As an example, new materials to be used in membrane technology can be produced using heavy ion beams.

Several steps are required: i) irradiation of polymeric films (formation of latent tracks), ii) selective chemical attack of the latent tracks to produce pores (etched tracks), iii) polymerization of a suitable monomer onto the porous membrane, iv) removal of the template (porous membrane).

Different polymers can be used as templates. Poly (ethylene terephthalate) (PET) and polycarbonate are the most used membranes. They are commercially available in pore diameters in the micrometer range down to the nanometer range. Poly (vinylidene difluoride) (PVDF) membranes exist with micrometer pore diameters. The etching of PVDF films in order to obtain pores of much lower diameter was studied. By oxidative etching in highly concentrated basic solution at moderate temperature, pores with diameters of 50 to 400 nm were produced.

On the other hand, the polymerization of pyrrole onto PET templates was carried out. Track-etched membranes of 8 to 14 μm thickness and 2 to 5 μm pore diameter were used as templates. Pore density ranged from 10^6 to 10^8 ions per cm^2 . Diaphragmatic method was chosen among the several polymerization methods available. It was shown that the pyrrole oxidative polymerization is diffusion-limited and takes place from the middle of the film.

Once the poly(Pyrrole) (PPy) polymerization is achieved, the template membrane is decomposed using highly concentrated sodium hydroxide at high temperature. The PPy membrane is constituted of two parallel surfaces linked by cylindrical and parallel microtubing of typically 500 nm thickness, though 150 nm thicknesses are obtainable. It exhibits extremely high mechanical properties that render them valuable for applications that need cycling. PPy membranes are porous and their porosity may be controlled by the chemical nature and the size of the counterion used in the polymerization.

Such membranes can be arranged in stack to produce a filtration module. PPy polymerization was achieved throughout the stack of membranes. But the best way for achieving the prototype of filtration module is to achieve the PPy polymerization on individual membrane, to paste the modified membranes together so that the feeding of fluids is possible, and thereafter decompose the PET templates. Such modules could be observed by SEM which gives indication on its highly mechanical strength. Such PPy membrane assemblies which possess high specific surface area of the order of 100 to 10,000 m^2/l will be tested in kidney dialysis.

3.3. Germany

The research work was focused on the production of single conically shaped nanopores in polymer films and on the characterization of their ionic transport properties.

Poly (ethylene terephthalate) (PET) and polyimide (PI) foils were irradiated with GeV single heavy ions, and by subsequent one-side etching, single asymmetric nanopores were produced. The diameter of the conical pores in PET varied between 4-20 nm at the small opening and several hundred nm at the large opening. In the case of PI, due to the higher bulk etching rate, the large aperture reached a few μm .

The current-voltage (I-V) characteristics were measured at symmetric electrolyte conditions of KCl at various concentrations and pH values. It was found that conical nanopores with charged surfaces are cation selective and show preferential cation flow (i.e. rectification) from the narrow entrance to the wide opening of the cone. Concentration and pH influence the rectification properties for both polymers. The mechanism of rectification is based on (i) asymmetry of electrostatic interactions inside a nanopore and (ii) electromechanical gate, which changes the pore diameter at various voltages applied.

The transient transport properties of single PET and PI pores were also investigated. The ion current through PET nanopores fluctuates considerably, the fluctuation depending on the voltage, whereas PI nanopores display a stable current signal for KCl concentrations between 0.1 and 3 M, and pH values between 2 and 8. This different behaviour has been attributed to the chemical structure of the two polymers influencing surface characteristics of the resulting nanopores.

The ability of polyimide conical nanopores to detect individual plasmid DNA molecules has been demonstrated. The molecules were electrophoretically driven through the nanopore at a constant voltage, while a time series of ion current was recorded simultaneously. The presence of these molecules inside the pore was detected as a transient decrease of the ion current, whose duration and shape was tentatively related to the structure of the molecules. For low biomolecule concentration and very narrow pores, each decrease in ion current (referred to as an “event”) should correspond to a single molecule. Nanopore biomolecule detection and analysis is a rapidly developing field, with significant potential applications in biosensing and genomics. The main advantages of the nanopore detection technique over current technologies are its high speed, very low detection limit, together with the capability to analyse biomolecules without prior marking, quantitative amplification, or chemical modification.

Finally, the suitability of etched ion track membranes for production of metallic, semi-metallic and semiconducting nanostructures (e.g. nanowires and nanospheres) should be mentioned. At GSI nanowires of different sizes, shapes and materials have been created by electrochemical deposition in the pores of polycarbonate and PET membranes. These nanowires have many potential applications in fields such as nano-electronics, opto-electronic and sensorics.

3.4. Hungary

Radiation initiated synthesis of diethyleneglycol dimethacrylate (DEGDMA) based polymer was carried out by simultaneous polymerization and crosslinking. The synthesis was performed in situ in the chromatographic columns and monoliths of good flow-through characteristics, containing both mesopores and macropores in the micrometer range, were obtained. Systematic investigations were made in order to clarify the effect of variables on the properties of the final polymer; these variables included the monomer concentration, type of solvent, irradiation temperature, dose and dose rate. Using DEGDMA as monomer, monoliths with good structure were obtained when low molecular weight alcohols (methanol, isopropanol) were applied as solvents in the 20 to 40 volume % range. The optimum dose was in the range of 20 to 40 kGy, and the optimum dose rate was of 10 to 16 kGy/h. Under the conditions applied DEGDMA was easily copolymerized with glycidyl methacrylate (GMA), hydroxyethyl acrylate (HEA) and N-isopropyl acrylamide (NIPAAm). These comonomers were used to functionalize the monoliths in order to make them applicable for given separation tasks. Increasing the GMA/DEGDMA ratio in the starting solution decreased the pore size of monoliths, while increase of the HEA/DEGDMA and NIPAAm/DEGDMA ratios resulted in larger pores and higher flow-rates. The columns prepared showed good HPLC properties in separating amino acids, proteins and nucleic acids.

The research and development work enables now to produce chromatographic columns with tailor-made properties. Future development work should be needed to adjust the column properties to a large number of specific separation tasks.

3.5. India

Stimuli-responsive crosslinked poly(vinyl methyl ether) (PVME) and N-isopropyl acrylamide (NIPAAm) based polymers were synthesized by irradiation methods. Post-irradiation grafting to polypropylene and cellulose was carried out at different temperatures, in the presence of different solvents (irradiation dose-range of 10 to 60 kGy).

After characterizing and optimizing the synthesis conditions, the prepared grafted polymers were tested in several practical applications. The polymers were characterized by a number of methods including positron annihilation lifetime spectroscopy (PALS) and dynamic swelling experiments.

The work demonstrated that the synthesis conditions such as type of radiation and the dose-rate highly affect the swelling characteristic of the polymer because of the microstructure formed. In the case of polymers, gamma irradiation resulted in higher gel fractions than electron irradiations; however the electron-beam synthesized gel showed higher thermo-responsiveness. The abruptness of the thermo-responsiveness was lost with increased crosslinks density.

NIPAAm was also copolymerized with ionic monomers in order to increase the ionic strength of the gel. The presence of small amounts of ionic groups into the poly(NIPAAm) matrix affected the equilibrium degree of swelling and lowered the low critical solution temperature (LCST).

The poly(NIPAAm) gels prepared by gamma irradiation were tested for proteins separation. Proteins are more excluded at higher pH which is well above the isoelectric point probably due to electrostatic interactions in the molecules which keep them in the extended form. At low solute concentrations the proteins are more excluded implying that exclusion efficiency decreases with increasing concentration. It was also shown that this method cannot be applied for exclusion of very low molecular weight proteins like lysozymes.

New absorbents for the protein adsorption were prepared also by mutual radiation grafting of vinylbenzyltrimethylammonium (VBT) on cotton matrix. The binding capacity of the grafted matrix increased with the extent of grafting. The equilibrium capacity and elution percentage of the VBT-g-cellulose anion exchange absorbent was found to be 40 mg/g and 94%, respectively.

The PVME polymers were tested in purification of wastewaters containing either hexacyanoferrite or potassium thiosulfate. The polymer forms a complex with such ionic compound. These complexes are very stable and do not decompose in the solution. However, they dissociate if strong electrolytes are added. This gives the possibility for the collection of these compounds from the wastewater and transferring solution with much smaller volumes.

3.6. Japan

Principles of pH- and electro-responsiveness of polyelectrolytes and polyampholytes, and pH- and temperature-responsiveness of poly(dimethylaminoethyl methacrylate) gels as well as their intelligent drug release functions were clarified as a base for biomedical applications. IPN (interpenetrating networked) hydrogels were studied and a remarkable improvement in the stimuli-responsive properties was found. Natural polyelectrolytes such as polysaccharides and proteins were immobilized into polyacrylamide hydrogels by radiation entrapping polymerization to confer stimuli-responsive properties. Stimuli-responsive hydrogels, especially poly(N-isopropyl acrylamide), could be polymerized to form nano- and microspheres by precipitation polymerization method in the presence of specific solvents. Such precipitation polymerization can be used to fabricate pro-drug spheres.

Stimuli-responsive hydrogels were coated on drug-containing polymeric films and cured using EB and UV radiation to produce intelligent membranes and chips. An efficient radiation curing processing with conveyer system was developed. The substrates were produced using ion-beam or excimer laser lithography. The effective intelligent drug release functions of those chips and membranes were clearly proved. The temperature responsive fragrance release systems, glucose responsive insulin release system and glucose responsive nicotine release system were developed. Computer programming control techniques for the intelligent releases were developed as the base of drug delivery chip, a new kind of biochip. The effectiveness of program control for multi environmental signal response multi feedback release was proved.

3.7. Kazakhstan

The stimuli-responsive hydrogels and film materials have been obtained for application in separation process. Novel polycationic and polyampholyte hydrogels were synthesized by gamma-radiation copolymerization of vinyl ether of monoethanolamine (VEMEA) with vinyl ether of ethyleneglycol or with acrylic acid. The complex formation of the prepared hydrogels with various metal ions and linear polyelectrolytes has been studied. The research of interaction with proteins has been started.

Water soluble and crosslinked thermo-sensitive cationic copolymers based on 2-[(methacryloyloxy)ethyl]trimethylammonium chloride and N-isopropyl acrylamide (MADQUAT-NIPAAm) were obtained and their interactions with poly(acrylic acid) (PAA) and potassium hexacyanoferrates (II, III) were studied. It was found that the composition of copolymer significantly affects the composition of polyelectrolyte complexes and that PAA molecular weight influences their aggregation stability. The rate of contraction and the final swelling degree of the gel-polymer complexes depend on PAA initial concentration and molecular weight. The hydrogels of copolymers absorb potassium hexacyanoferrates (II, III) and undergo contraction. The sorption ability of hydrogels depends on MADQUAT content in copolymers and is higher with respect to $K_3[Fe(CN)_6]$ than to $K_4[Fe(CN)_6]$. The study of interaction MADQUAT-NIPAAm copolymers with proteins has been started.

Novel non-ionic thermo-sensitive linear and crosslinked polymers have been obtained by gamma-irradiation copolymerisation of hydrophilic (ethylene glycol, 2-hydroxyethylacrylate) and hydrophobic comonomers (vinyl butyl ethers, vinyl isobutyl ethers, 2-hydroxyethylmethacrylate, butylacrylate). It has been found that these soluble copolymers exhibit a LCST in water. Hydrogels based on these copolymers undergo thermo-induced contraction or collapse. The sorption processes of surfactants by novel thermosensitive copolymers have been studied.

Stimuli-responsive films were prepared by gamma-radiation cross-linking of the blends based on PAA and poly(vinyl methyl ether). The environmental pH affects significantly the swelling of the films. The films have lower swelling ability in acidic media, due to suppression of carboxylic groups ionization and to the formation of additional physical cross-links via interpolymer hydrogen bonding.

Novel polymeric film materials were prepared by radiation grafting of cationic monomer VEMEA on the surface of polyethylene and polypropylene films. The prepared graft copolymers showed a good affinity towards the investigated metal ions (Pb^{2+} , Cd^{2+} , Zn^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Ag^+) chelation and/or complexation. Treating of the saturated films with 0.01 HCl at room temperature for one hour easily recover the absorbed metals and accordingly the films can be reused for the resorption of metal ions.

Copolymeric hydrogels based on polyethylene glycol (PEG) and methacrylic acid (MAA) have been synthesized by using γ -irradiation copolymerization. Physico-chemical characteristics of obtained networks were studied. A comparative study of uranyl ions adsorption by PEG-MAA and polymethacrylic acid (PMAA) hydrogels was carried out. It was shown that the sorption characteristics depend on pH and ionic strength of solution as well as uranyl ions concentration. The higher stability in the regeneration processes and possibility of repeated use of copolymeric hydrogel of PEG-MAA for uranyl ions adsorption in comparison to homopolymer PMAA were demonstrated.

3.8. Republic of Korea

In order to recover uranyl ion (UO_2^{2+}) from sea water, chelate-type resins with hydrophilic amidoxime (AO) and amidoxime/carboxylic acid (CA) groups were prepared by radiation-induced polymerization of acrylonitrile (AN) and AN/acrylic acid followed by subsequent amidoximation of cyano group of poly(AN), respectively.

The hydrophilic amidoxime resins were characterized by FT-IR, FT-Raman, solid-state ^{13}C -NMR, SEM, and elemental analysis. The adsorption rate of uranyl ions by resins with the amidoxime/carboxylic acid groups was higher than that of resins with the amidoxime group. The uranyl ion uptake for resins with AO and AO/CA groups was approximately 914 and 924 mg/g, respectively.

MCM-41 materials were synthesized using cetyl tetramethyl ammonium bromide (CTAB), dodecane tetramethyl ammonium bromide (DTAB) and eicosane tetramethyl ammonium (ETAB) as structure directing surfactants to tune the experimental conditions for the preparation of mesoporous materials to make effective entrapment of uranyl ions in the pores of the materials. X ray diffraction (XRD) analysis and nitrogen adsorption measurements reveal that the pores are hexagonal with tunable textural properties through the choice of surfactant and experimental condition. These MCM-41 materials are suitable for application as adsorbent. Studies on sorption of uranyl ion was made. N_2 -adsorption measurements, XRD and FTIR spectroscopic analysis of uranyl ion loaded MCM-41 confirm the entrapment of uranyl ion in the pores of MCM-41. The adsorption rate and efficiency of uranyl ion adsorption with MCM-41 were comparatively more (nearly 99 % at 24 h of adsorption) than reported for the polymeric resin. This informs that adsorption capability of MCM-41 is superior over the polymeric resins. After 24 h of contact time, the amount of UO_2^{2+} loaded into MCM-41 materials takes the order: ETAB > CTAB > DTAB.

3.9. Poland

The research was focused on basic and practical aspects of the radiation-assisted formation and properties of stimuli-responsive hydrogels and membranes.

The main results were:

- Broadening the basic knowledge on the mechanism of radiation-induced processes in aqueous solutions of poly(vinyl methyl ether) – PVME – and on the radiation-induced formation of thermo-sensitive PVME hydrogels
- Elaboration of new products: two types of composite thermo-sensitive membranes based on PVME
- Elaboration of a new, monomer-free, radiation-based method for synthesis of microgels and nanogels of stimuli-sensitive polymers, with the options of using individual polymers or interpolymer complexes as substrates
- Modification of the previous technique allowing to synthesize nanogels of independently chosen molecular weight and dimensions (tailored internal density)
- Elaboration of new, stimuli-sensitive hydrogels based on p(MADQUAT-co-NIPAAm) and detailed characterization of their properties
- Contribution to the understanding of the polymer-polymer interactions in aqueous solutions. This knowledge may be useful in elaborating products where polymer substrates are designed to selectively bind biological macromolecules
- Formulating the ideas of two new biomedical products (synovial fluid supplement and fat-binding diet additive) based on the knowledge gained during the realization of the project and initiating preliminary tests of their performance

The reported basic and application-oriented research on stimuli-responsive hydrogels for separation purposes is a step towards the planned future applications of radiation technologies in modern controllable separation, binding and filtration processes, especially in the biomedical field. A part of the presented work was performed in close co-operation with the research group of Kazakhstan. Moreover, the network cooperation has stimulated interesting ideas for R&D.

3.10. Turkey

The radiation synthesis, characterization of swelling behavior and network structure of poly(N,N-dimethylaminoethyl methacrylate) (P(DMAEMA)), and poly(N, N-dimethylaminoethyl methacrylate-co-N-vinyl 2-pyrrolidone) (P(DMAEMA-co-VP)) hydrogels as well as their use for the separation and recovery of water pollutants were studied. The influence of irradiation dose, VP concentration, cross-linking agent content on the total gelation percentage and monomer conversion was investigated. The effect of pH and temperature on the swelling behavior of hydrogels has also been examined. Hydrogels showed typical pH and temperature response i.e. low-pH and low temperature swelling, and high-pH and high temperature deswelling. Polymer-solvent interaction parameter (χ) and enthalpy (ΔH) and entropy (ΔS) changes appearing in the χ parameter for the P(DMAEMA-co-VP)-water system were determined using Flory-Rehner theory of swelling equilibrium. The negative values obtained for ΔH and ΔS indicate that P(DMAEMA) and P(DMAEMA-co-VP) hydrogels have LCST. Experimental data are in good agreement with the values calculated from Flory-Rehner theory of swelling equilibrium.

For the investigation of heavy metal ion adsorption, characteristics of P(DMAEMA) hydrogels and adsorption of Pb(II), Cd(II), Ni(II), Zn(II), Cu(II) and Co(II) ions by P(DMAEMA) hydrogel were investigated. Langmuir type adsorption isotherms were observed for the adsorption of Cu(II), Pb(II) and Cd(II), Co(II), Ni(II) ions for all prepared hydrogels. The adsorption capacity of hydrogels depends on the type of heavy metal ion and the medium pH. It was found that the metal ion uptake by P(DMAEMA) hydrogel gradually increased with increasing initial metal ion concentrations and not reaching adsorption equilibrium even at 2000 ppm metal ion concentration. The order of adsorption affinity based on the amount of metal ion uptake (mg metal ion / g dry gel) is as follows: Cu(II) > Zn(II) \cong Co(II) > Pb(II) >> Ni(II) > Cd(II).

The removal of nitrite ions from aqueous solutions was investigated by using protonated P(DMAEMA) hydrogel. It was shown that P(DMAEMA) hydrogel containing protonated pendant amine group is very efficient and highly selective for the removal of nitrite ions from aqueous solutions even at very high concentrations. Adsorption studies have shown that pH of the nitrite solution influences the nitrite ion uptake by P(DMAEMA) hydrogel. The adsorption capacity of hydrogel has been increased up to 3100 mg NO₂⁻ /g dry gel by changing pH of the solution. FTIR studies have shown that nitrite binding onto hydrogels occurs through the formation of N-nitroso groups and that these hydrogels can be regenerated by treatment with acid solutions.

4. CONCLUSIONS

Stimuli-responsive hydrogels and membranes have emerged in recent years as a unique class of materials that can offer many advantages over the conventional ones in a number of applications of radiation processing techniques. New synthesis and characterization methods were developed and areas for applications where such materials can be beneficially utilized were explored. Accordingly, the teams engaged in this project have carried out the development of radiation processed materials in different forms such as hydrogels, grafted membranes, ion track membranes, beads, monoliths, nanoparticles and nanogels for emerging applications in various areas. The work done in frame of the CRP can be classified according to the following areas:

A. Development of novel materials

- Fast stimuli-responsive hydrogels based on natural and synthetic polymers
- Novel non-ionic thermosensitive hydrogels based on hydrophilic/hydrophobic ratio
- Temperature and pH responsive membranes
- Single asymmetric nanopore membranes for ion flow regulation

- Thermo and pH-sensitive nano- and microgels of independently controlled density and dimensions
- Porous polymer monoliths and beads with specifically tuned morphology of any desired size and shape
- Hollow membranes with high specific surface area

B. Advanced methods for the synthesis and exploration of the microstructure and properties of novel materials:

- ion beam irradiation and asymmetric chemical etching for the production of single conical nanopore membranes
- template synthesis for the production of hollow membrane
- monomer-free nanogels synthesis by radiation-induced intramolecular crosslinking
- excimer laser and ion beam lithography combined to EB and UV curing for the production of membranes and biochips
- positron annihilation spectroscopy (PAS) adopted to demonstrate the different microstructure of the hydrogels formed under different conditions of irradiation
- SEM-ion conductance hybrid method for determination of single conical pore geometry and transport properties

C. Exploring the applications of developed novel materials

The application areas being explored for beneficially utilizing these novel materials included specialized drug delivery systems (DDS), selective adsorbents, membranes for separation and concentration of biological solutions. These applications include:

- Fast separation of proteins and peptides (DEGMA or its copolymers)
- Drug delivery based on PC-programmed controlled systems responding to very small changes in the pH as well as temperature (DDS chips).
- Single biomolecule detection with asymmetric Kapton nanopores.
- Ion flow control with asymmetric nanopores.
- Removal of toxic metals by stimuli-responsive DMAEMA/VP, AAm/NVP, AAc/NVP, VEMEA based hydrogels possessing simultaneous temperature and pH sensitivity and stimuli-responsive membranes based on grafted natural lignocellulosic and synthetic polymers
- Selective removal of toxic anions from wastewaters with P(DMAEMA) hydrogels
- Uranium recovery from sea water by amidoximated copolymeric adsorbents and mesoporous materials
- Removal of textile dyes using stimuli-responsive membranes based on grafted natural lignocellulosic polymers
- Temperature-controlled solid-liquid filtration by composite membranes of PVME hydrogel grafted onto the surface and/or in the pores of ion-track PET membranes
- Kidney dialysis using hollow membrane obtained from track-etched polymers as templates
- Production of synovial fluid substitutes based on PVP/PAA microgel
- Production of nanowires using track-etched membranes as templates

5. POSSIBLE AREAS OF FURTHER RESEARCH

Further research in this field is possible in the following areas:

- Optimization of the synthesis of the novel materials to meet the requirements of practical applications

- Development of integrated systems based on the novel materials
- Continuation of the laboratory and animal tests towards clinical assays is needed in order to validate the commercialization of the healthcare products
- Field studies for the recovery and removal of heavy metals and other pollutants with applications of sorbents and membranes
- Improvement of the nanopore DNA sensors

The established network expressed their willingness to continue R&D in this field, especially regarding some aspects of nano and grafted materials.

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REPORTS BY PARTICIPANTS IN THE COORDINATED RESEARCH PROJECT

RADIATION SYNTHESIS OF STIMULI-RESPONSIVE MEMBRANES AND HYDROGELS FOR WASTE TREATMENT AND SEPARATION PROCESSES

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Abstract

Studies have been made for the preparation and characterization of different hydrogels and membranes which are prepared by γ -radiation-induced copolymerization and grafting of different vinyl and acrylic monomers such as acrylic acid (AAc), 4-vinylpyridene (4-VP), AAc/ 4-VP, N-vinyl pyrrolidone/acrylic acid (NVP/AAc) and NVP/Acrylamide NVP/AAm) for the purpose of separation and extraction of some heavy and toxic metal ions as well as dyes from wastewater. The factors affecting the preparation and homogeneity of such prepared materials were thoroughly investigated. Characterization, stimuli-responsive and some selected properties of the prepared hydrogels and membranes were studied and accordingly the possibility of its practicable uses in separation processes and wastewater treatment were thoroughly studied and determined. Also, several trials were made to improve the chelation affinity and adsorption capacity to the metals by further introduction of certain reactive chelating groups via the functional groups of the prepared hydrogels and membranes. It is worthy to mention that different natural lingo- cellulosic materials were also used for the preparation of super-adsorbent materials suitable for separation and purification processes of wastewater. Also, trials were made for the recovery of valuable metals for their waste such as Au, Ag and Ru. Some of the radiation prepared hydrogels and membranes showed very promising stimuli-responsive properties which make them of practicable uses.

1. OBJECTIVE OF THE RESEARCH

Environmental pollution is one of the most important problems of this century. Heavy metals such as lead, cadmium and copper, and different types of dyes in wastewater are hazardous to the environments. Because of their toxicity, their pollution effect on our ecosystem presents a possible human health risk. Among many sorptive materials, various forms of synthetic polymers containing complexing molecule, which are abundantly at low cost, have emerged as one of the most important materials for the synthesis of new sorbents. The use of high-energy radiations in the grafting and copolymerization processing is known to improve the physicochemical qualities of many polymer products to expand their utilizations. This trend is envisaged to be continuously growing to form a big application field of polymeric products. The grafting of hydrophilic monomers into polymeric substrates generates perm-selective membranes with interesting properties for the use in different separation processes such as in reverse osmosis desalination of saline water and wastewater treatments.

2. INTRODUCTION

Recently, the removal of heavy and toxic metals from wastewater using functionalized polymers is under research and development in many laboratories. Functional groups can be introduced in the polymeric materials by radiation grafting technique. The membrane selectivity towards some heavy and toxic metals which may exist in the wastewater and low level nuclear waste is very important factor to be investigated. Several trials are made to improve the chelation affinity to the metals by further introduction of certain reactive chelating groups via the functional groups of membranes. The possible use of such functionized graft copolymers in the field of waste water and low level nuclear waste treatments is one of the main goals for this research project.

Hydrophilic polymers when crosslinked chemically or physically forming three-dimensional networks swell but do not dissolve in water [1]. They are termed hydrogels when the amount of water retained is between 20-100 % of the total weight, and when water content exceeds 100% these hydrogels are called super adsorbent hydrogels. A hydrogel can be considered as a container of water made of three- dimensional mesh [24]. Many materials both naturally occurring and synthetic fit the definition of hydrogels. Dextranes, starch, alginates and collagens are examples of natural polymers that can be crosslinked to hydrogels.

Hydrogels based on synthetic polymers include; poly (hydroxyalkyl methacrylates) polyacrylamide, polyethylene oxide, poly N-vinyl -2-pyrrolidone and poly (vinyl alcohol). The most characteristic property of hydrogel is its ability to swell in the presence of water and to shrink in the absence of it. Among the factors controlling the extent of swelling are the hydrophilicity of polymer chains and the crosslink density [5]. By incorporating some stimuli-responsive comonomers either into the backbone of the network structure or as pendant groups, it is possible to prepare hydrogel with responsive properties [6]. These hydrogels possess the ability to swell, shrink, bend or even degrade in response to a signal [7]. These stimuli-responsive hydrogels are also called intelligent hydrogels [8]. They reversibly swell and shrink with small change in the environmental factors that causes an abrupt volume changes in hydrogels such as pH, temperature, electric field, ionic strength and type of salt [9]. In addition to wide range of applications of these hydrogels in biomedical applications, they are also used in the separation and purification processes.

Hydrogels are typically synthesized by one of the two well-established procedures: (a) polymerization and simultaneous or post-polymerization cross-linking of hydrophilic monomers and (b) modification of hydrophilicity [11] of existing polymers with potential hydrogel properties [12]. The preparation of hydrogels by radiation treatment of aqueous solution of hydrophilic monomers or polymers carries some advantages over the conventional techniques, it doesn't require initiators, crosslinkers and can be used practically with any vinyl monomer and both polymerization and crosslinking reactions can be initiated at ambient or sub-ambient temperatures [13].

3. MATERIALS AND METHODS

3.1. Materials and monomers

- Low density polyethylene (LDPE), polypropylene of thickness 35 and 20 μm , respectively supplied by El-Nasr Company for medical supplies, Egypt.
- The fibrous raw materials used in this work were depithed Egyptian Bagasse obtained from El-Nasr Company for Sugar and Pulp Industry at Edfo and Rice straw.
- Acrylic acid (AAc), Acrylamide (AAM), Acrylonitrile (AN), Methylmethacrylate (MMA), 2-Hydroxyethylmethacrylate (HEMA) Styrene (Sty) and N-Vinyl-2-pyrrolidone (NVP) (Merck, Germany) of purity 99 % were used without further purification. Other chemicals such as solvents, inorganic salts and acids were reagent grade.

3.2. Preparation of hydrogel

Different comonomer compositions were prepared and subjected to γ - irradiation to different doses at fixed dose rate of 1.43 Gy/s. Distilled water and water / methanol - mixture were used as diluents for the copolymerization processes. The prepared copolymer hydrogels were then dried at room temperature and weighed (w_d).

3.3. Gel Determination in the Co-polymerized hydrogels

The dried hydrogels were extracted with water for 48h at 100°C in order to extract the insoluble parts of the hydrogel. The insoluble parts, i.e., the gelled parts were taken out and washed with hot water to remove the soluble part, then dried and weighed. This extraction cycle was repeated till the weight became constant. The gel fraction yield in the hydrogel was determined from the following equation:

$$\text{Gel (\%)} = \frac{w_e}{w_d} \times 100$$

Where w_d and w_e represent the weights of the dry hydrogel and the gelled part after extraction, respectively.

3.4. Grafting techniques

The direct radiation grafting method was used as a technique in which the polymer and monomer solutions were subjected at the same time to ionizing radiation. The dose rate used here in the range of 2.2 to 2.8 Gy/s. Mohr's salt with concentration 2.5 wt % was added to minimize the homopolymerization of the monomer during radiation. The glass ampoules containing monomers and LDPE, PP films were bubbled by nitrogen gas for 5-8 min. The glass ampoules were subjected to cobalt-60 gamma rays and total doses of 5 to 40 kGy were used. After graft copolymerization, grafted films were washed with distilled water and extracted with hot distilled water to remove the homopolymer formed. The films dried in vacuum oven at 30-40°C for 2 hour and weighed. The degree of grafting was determined by percentage increase in weight using the following equation:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_o}{W_o} \times 100$$

where W_o and W_g represent the weight of initial and grafted films respectively.

3.5. Metal uptake measurement

The fixed weight of the prepared hydrogel was immersed in the metal feed solution of definite concentration (100 ppm). Merck atomic absorption standard solutions of these metals were used for the calibration process. The pH and temperature of metal feed solutions were adjusted before applying the hydrogels for treatment processes. The remaining metal ions in its feed solution were determined by an atomic absorption instrument (Unicam Model Solaar 929).

The metal uptake (E) was calculated as follows:

$$E \text{ (mmole/g)} = \frac{C_i - C_f}{W \times A \times 10}$$

Where:

- W is the weight of the dry hydrogel (g)
- A is the atomic weight of metal ion.
- C_i and C_f are the initial and remaining concentrations of metal ions in mg/l (ppm)

100 ml of the metal ions solution was used instead of one liter, so we divide by 10. The total uncertainty for all experiments ranged from 3-5%

4. RESULTS AND DISCUSSION

4.1. Radiation synthesis of functionalized polymers

The functionalized polymers that capable for metal chelation and/or complexation with their reactive functional groups such as carboxylic acid, amide, nitrile, oxime groups were prepared by radiation technique. Radiation copolymerization of different monomers as well as modification of some membranes by grafting method was selected to prepare functionalized polymeric materials. The selectivity of the prepared functionalized polymers towards some heavy and toxic metals, which may exist in the wastewater and low-level nuclear waste, was investigated. Several trials were made to improve the chelation affinity to the metals by further introduction of certain reactive chelating groups via the different reagents.

The possible use of such functionalized copolymers in the field of separation and removal of low-level nuclear waste treatments as well as dyes and toxic heavy metals from wastewater is one of the main goals for this research project.

The summary of the results obtained is presented in the following:

Preparation of hydrogels and graft copolymer by radiation

Hydrogels were prepared by γ -radiation induced copolymerization of binary monomer mixtures. The factors affecting the hydrogel properties such as irradiation dose comonomer and solvent composition were investigated. The influence of NVP/AAc and NVP/AAm composition on the gel percent, i.e., the insoluble part in the NVP/AAc and NVP/AAm hydrogels, was determined by extraction in boiled water for 48 h. It was found that as the N-vinyl-pyrrolidone (NVP) content increases the gel percent increases Figure 1. This behavior is observed for both NVP/AAc and NVP/AAm binary monomers system in which the content of gel is higher for AAc at a given composition. It is taken into consideration that the copolymerization process was carried out in water for NVP/AAm and in methanol/H₂O (20/80) for NVP/AAc. This behavior is due to the higher affinity of AAc to crosslinking rather than AAm.

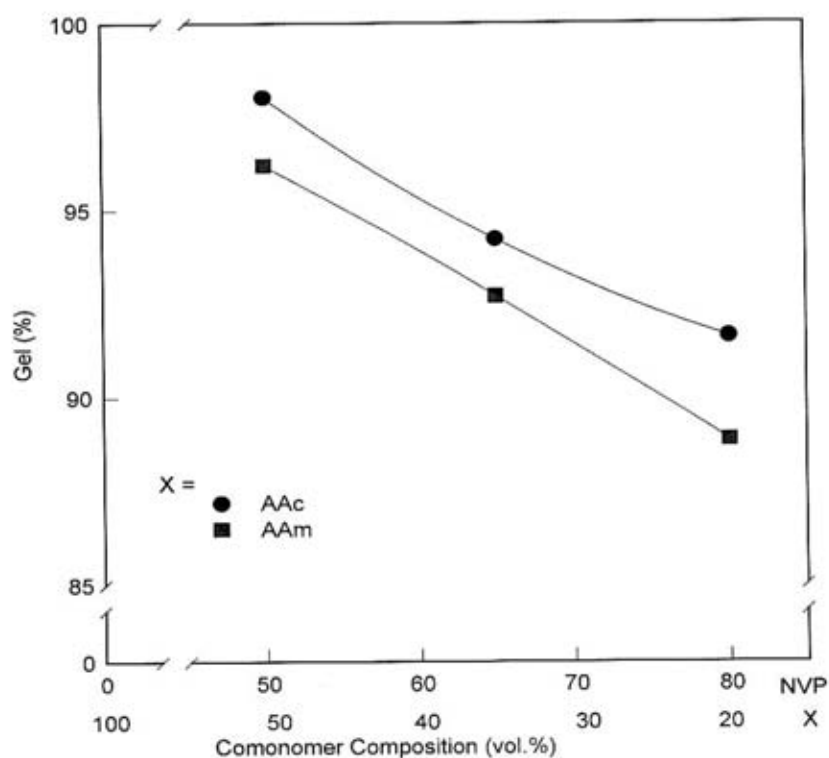


FIG. 1. Effect of NVP content on Gel% for (NVP/AAc) copolymer hydrogel in (H₂O/MeOH) and (NVP/AAm) copolymer hydrogel in (H₂O). Dose 15 kGy

In the direct radiation method, the total dose determines the number of initiated sites able to be copolymerized. The effect of radiation dose on the conversion yield in NVP/AAc is shown in Figure 2. It is observed that the higher the dose, the higher the gel percent obtained, at a given comonomer composition. Results indicated also that the crosslinking process in the prepared hydrogel is enhanced at higher doses. Meanwhile, the higher NVP content in the comonomer composition, the higher the gel percent obtained. This behavior is observed for both NVP/AAc and NVP/AAm systems.

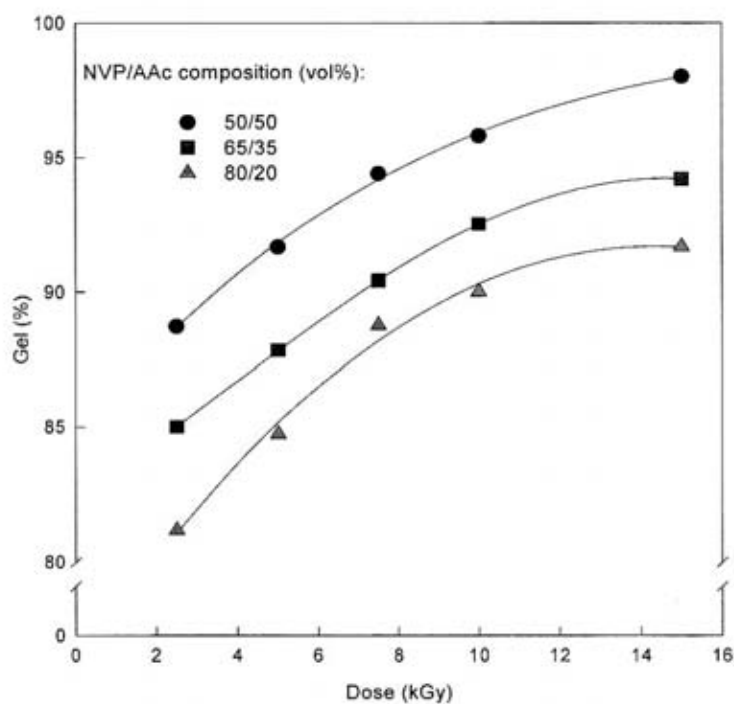


FIG. 2. Effect of Dose on the Gel% for the (NVP/Ac) copolymer hydrogel at different NVP/Ac compositions; comonomer concentration (80 vol%) in H_2O

Figures 3 shows the effect of comonomer composition on the grafting of (AAm/Ac) reaction onto low-density polyethylene (LDPE). It is found that, the degree of grafting of (AAm/Ac) onto LDPE and PP films increases as the AAm content increases in the solution till the optimum value reached at certain composition.

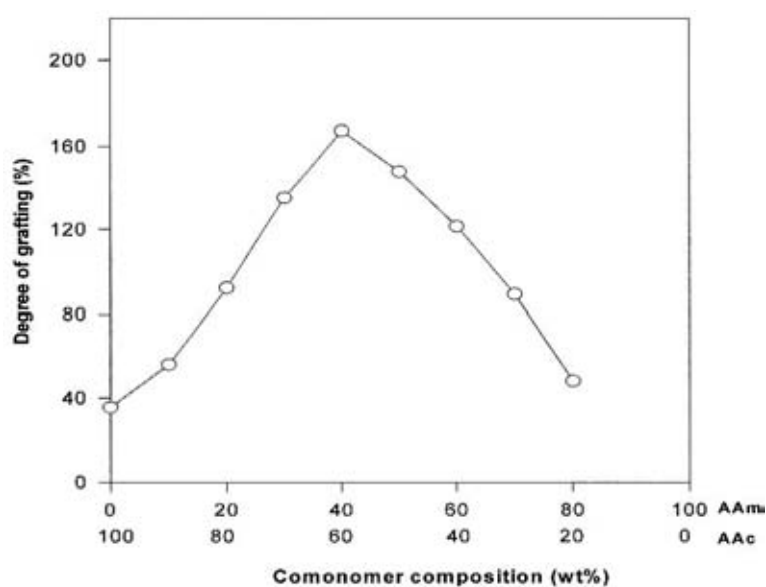


FIG. 3. Effect of comonomer composition (AAm/Ac) onto the grafting yield for LDPE at irradiation dose 20 kGy, comonomer concentration (50 wt %)

4.2. Radiation induced grafting of vinyl monomers onto natural polymeric materials

Natural cellulosic material is considered, as a convenient way to impart desired properties. The effect of irradiation time on the grafting yield of comonomer (AAm/AAC) 50/50 wt % grafted at different comonomer concentrations onto pulped bagasse and rice straw at various comonomer concentrations was investigated. It can be seen that the degree of grafting initially increases with irradiation time for all comonomer concentrations and thereafter it tends to be a curvature relationship. This is due to the behavior and characteristic of free radicals formation in polymers with irradiation time, which in general increases at first then it tends to level off at higher doses. Meanwhile, the higher the comonomer concentration the higher the degree of grafting obtained (Fig.4). This behavior is observed for both substrates (bagasse and rice straw), in which they almost gained the same degree of grafting.

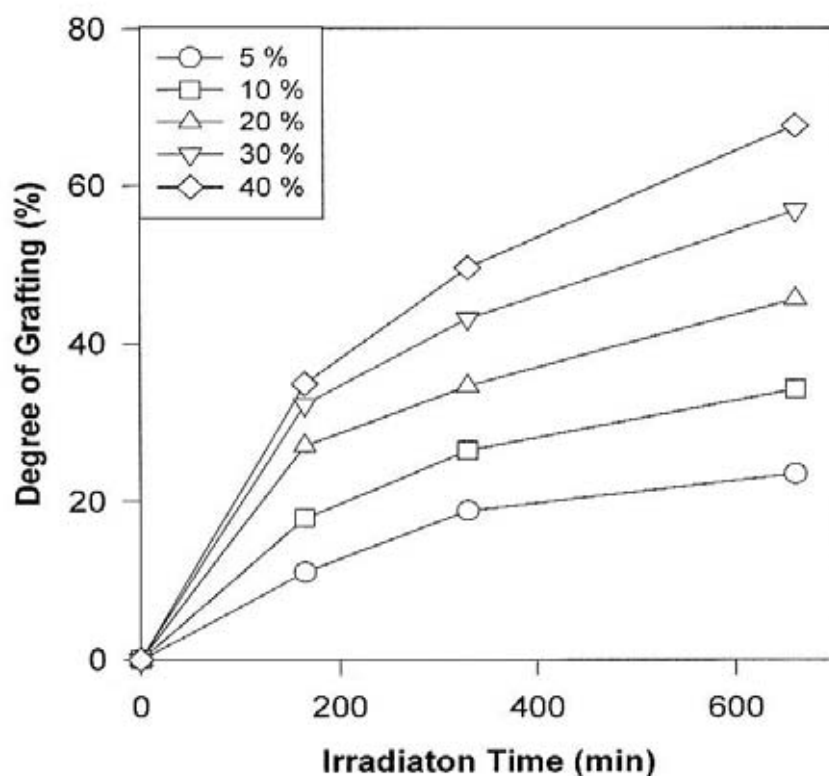


FIG. 4. Effect of irradiation time on degree of grafting of (AAm/AAC) binary monomer mixture of composition (50/ 50) wt % onto Bagasse at various comonomer concentrations (wt %).

4.3. Characterization and some selected properties of the prepared hydrogels

Swelling behaviours

Swelling is one of the most important parameters affecting on the characteristic properties of the hydrogel and accordingly determining its applicability for practical use. The influence of soaking time on the water uptake is investigated for NVP/AAC and NVP/AAm hydrogels prepared at different irradiation doses as shown in Table I. It can be seen that the water uptake percent increases as the soaking time increases to reach a certain limiting value after almost 8 to 10 hrs, which is called the maximum swelling at equilibrium (S_{max}).

This behavior is observed for all hydrogels prepared at different doses that ranged from 5 to 15 kGy. Meanwhile, the S_{\max} increases with irradiation dose up to 15 kGy and thereafter it decreases. This is due to the enhancement of crosslinking process at higher doses, and as a consequence the diffusion and swelling properties are hindered by network structure formation. This is clearly shown in Table (1), which shows the effect of irradiation dose on the S_{\max} for hydrogels prepared from different comonomer compositions.

TABLE I. EFFECT OF COMONOMER COMPOSITION AND DOSE (KGY) ON WATER UPTAKE %; SWELLING TIME 6 H.

Dose (kGy)	Water uptake (%)					
	NVP/Aam vol.%			NVP/AAC vol.%		
	50/50	65/35	80/20	50/50	65/35	80/20
2.5	381	520	487	46	76	119
5	396	556	542	53	81	157
7.5	405	578	553	62	98	169
10	427	638	570	79	120	172
15	456	592	594	95	125	180
20	354	562	561	85	116	150

The alkaline treatment of NVP/AAC copolymer resulted in a very pronounced increase in its swelling behaviours (almost 20 times) higher than that for the untreated one (Fig.5). This is reasonably due to the conversion of free –COOH groups of AAC into its Na – salt, which possesses electrolytic groups and having much higher hydrophilic properties if compared with that of free carboxylic groups.

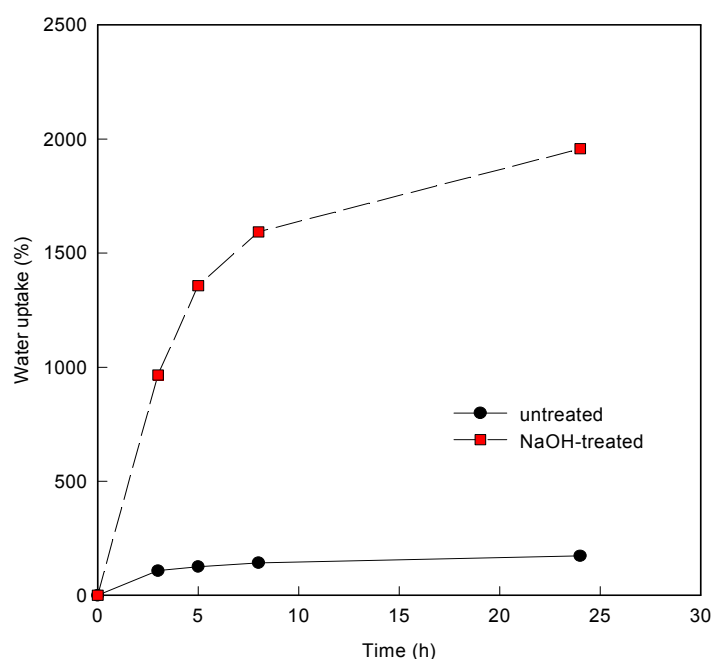


FIG. 5. Effect of swelling time on the water uptake% for NaOH- treated and untreated (NVP/AAC) (80/20 vol%) copolymer hydrogel prepared at 15 kGy.

The results suggested that the hydrogen bonding formed in hydrogel that contained free –COOH groups result in a cross-linking network structure. As a consequence the water uptake is reduced. However, the chemically treated hydrogel possessed higher water uptake due to the formation of easily ionizable –COO⁻Na⁺ group, which have good hydrophilic properties.

Surface Morphology

The surface characteristics of ungrafted and different levels of grafted pulped bagasse and rice straw are investigated by scanning electron microscopy and are represented in Figures (6,7), in order to elucidate the topological changes occurring under grafting reactions. The results show that the diameter of individual fibers seems to become thicker with the degree of grafting indicating that grafting occurred mainly on the surface of the fibers [14].

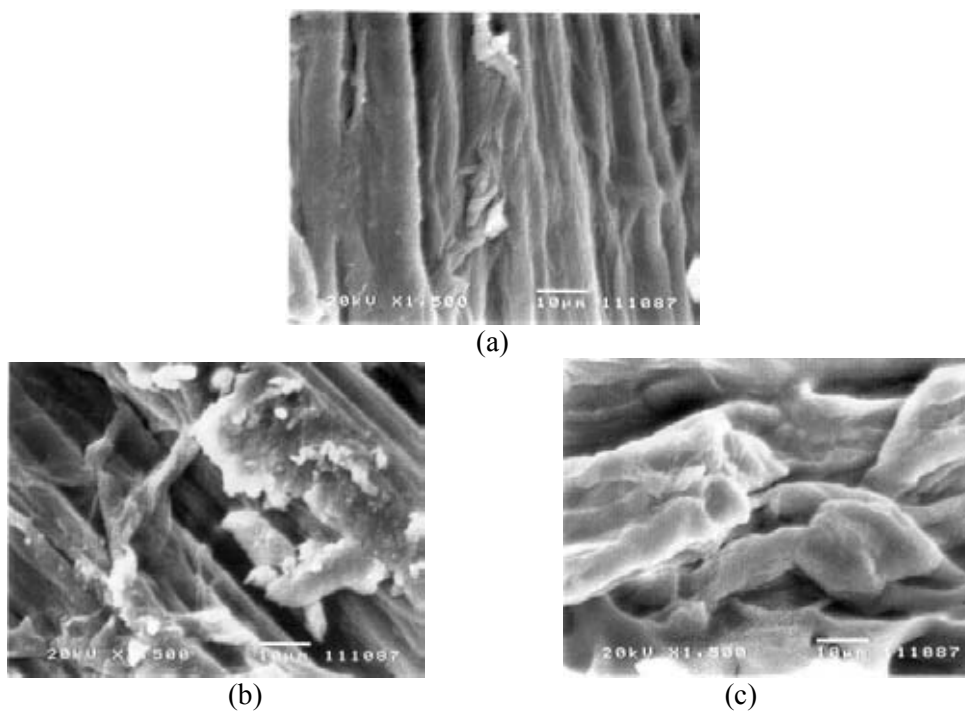


FIG. 6. SEM for (a) Pulped Bagasse; (b) 23% grafted Bagasse; (c) 56% grafted Bagasse.

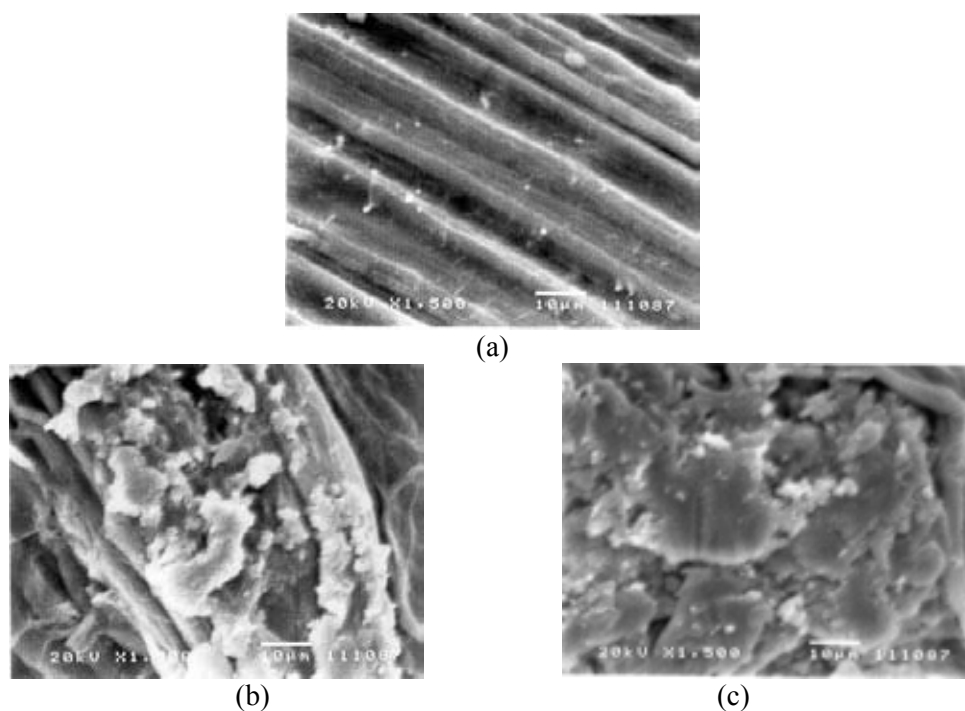


FIG. 7. SEM for (a) Pulped Rice Straw; (b) 39% grafted Rice Straw; (c) 71% grafted Rice Straw

Permeability measurement

The solution and transport behavior of low molecular weight substances in polymeric materials has become increasingly important in recent years with the widespread use of polymer films and membranes in different fields of application such as filtration and packaging processes.

The permeation and release control of substances have been recently investigated on the basis of the change of conformation, chain extension, hydrogen bonding and hydrophilicity of the polymeric material. In this respect, permeability measurement was performed for the original and grafted LDPE and PP using PMI autocapillary flow porometer. The permeability increases with increasing the graft percent for both grafted LDPE. That is due to hydrophilic nature of both acrylamide and acrylic acid comonomer. It is also observed that the permeability of grafted LDPE is very high than that of PP films. This may be due to the highly amorphous structure of LDPE if compared with that highly crystalline PP structure. Such permeability experiments proved clearly that the obtained grafted films possessed membrane quality and can be act as a semi permeable membrane.

Control of pore size by changing the length and the density of a grafted monomer onto polymers have been reported on the basis of water permeability [15]. They found that, the water permeability through membranes grafted with acrylic acid increased sharply below pH 4, representing the expansion of pores. Also they concluded that very high density of graft chains or very long graft chains restricted the mobility of PAAc chains.

Thermal gravimetric analysis (TGA)

Investigating the change in thermal properties of the prepared hydrogels is important for its application as well as characterization and determination of the chemical and physical changes occurring by copolymerization. From the practical point of view, the prepared hydrogel should possess good thermal stability in the range of applicable temperature. TGA curves of different hydrogels reveal that there are two distinct steps of weight loss. It is suggest that the initial stage of thermal diagram in the range from ambient temperature to 250°C, the weight loss is due to dehydration process of the water contained in such hydrophilic hydrogel. At the second stage from 250 to 450°C, there is decomposition in the side groups and branches of the hydrogel. However, at the third stage above 450°C, the weight loss is due to the main chain scission in the polymer chain and matrices. For pure PNVP shows characteristic single step degradation with maximum at 458°C and 98% of a weight loss [16]. It was also observed that as the NVP content in the copolymer increases the thermal stability increases. Results showed that such hydrogel is thermally stable at temperature up to about 200°C, which is suitable for its practical uses.

4.4. Application of prepared hydrogels in metal and dye removal from wastewater

The present study is designed to investigate the efficiency of prepared hydrogels and grafted copolymers in the removal of different metals and dyes from their wastes. The factors affecting the treatment process of such metal ions from their wastes using the prepared hydrogels as well as the graft copolymers are investigated and presented in the following:

1. Operation time.
2. pH of metal ion solution
3. Effect of initial concentration.
4. Degree of grafting.
5. Operation temperature.
6. Selectivity of the graft copolymers towards metal ions was investigated.

Effect of initial metal ion concentration.

Sorbent hydrogels, it was informative to obtain knowledge on its sorption capacity towards different metal ion concentrations. Figure 8 shows that the increasing in concentration of metal ions results in increasing the amount of metal ions uptake to reach a certain limiting value. Thereafter, it levels off at higher feed concentration (> 1000 ppm). These results revealed that the chelating sites of the sorbent become saturated when the concentration of the feed solution is reached 1000 ppm above which no more metal ion uptake was occurred.

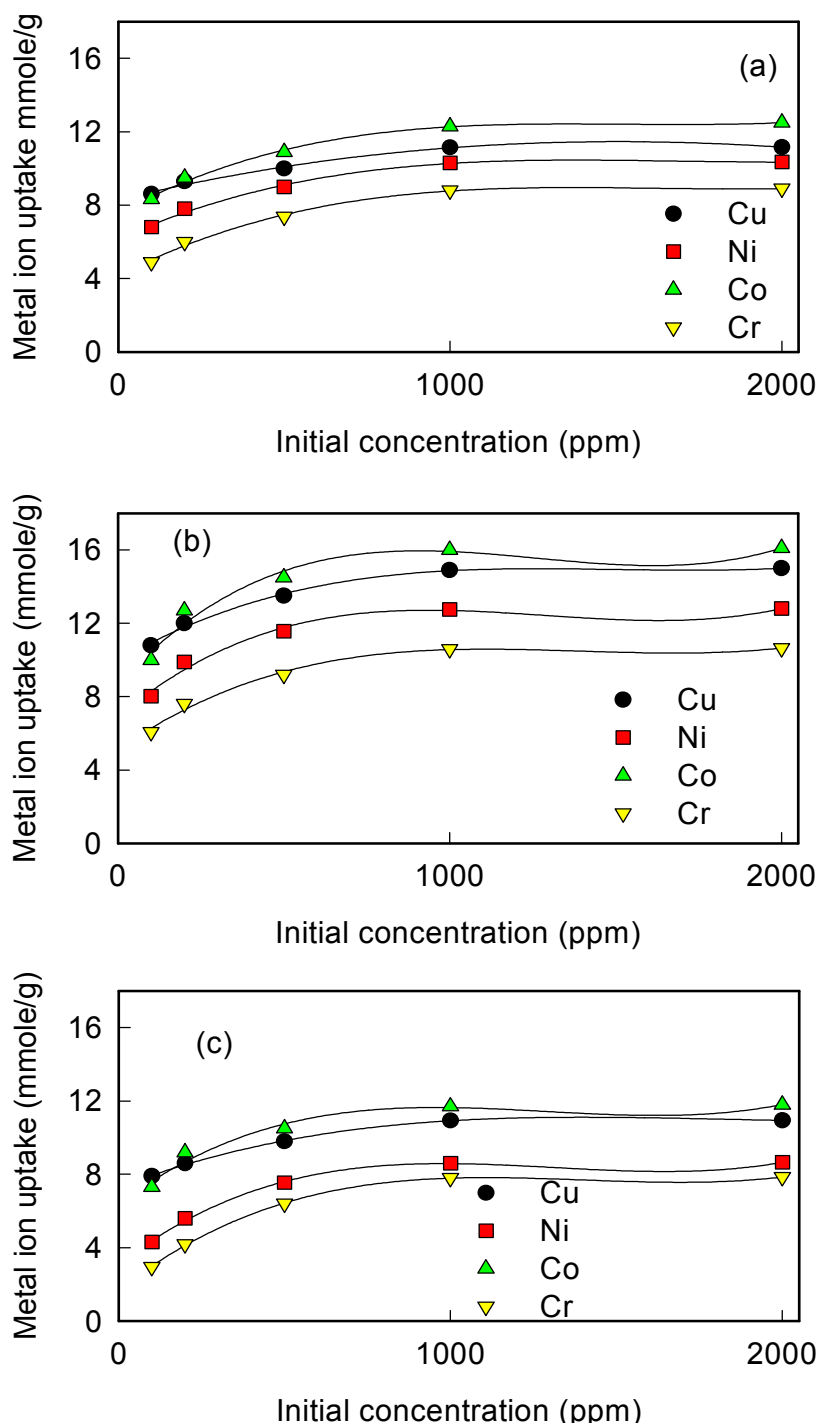


FIG. 8. Effect of initial concentration on Metal uptake for different hydrogels: a- NVP/AAC, b-NVP/AAC treated, c- NVP/AAm, Swelling time; 7hr.; pH = 5 temp.; 70°C

Effect of temperature

Figure 9 (a-c) shows the relation between the amount of metal ion uptake expressed in (mmole/g) and temperature for prepared hydrogels: NVP/AAC, NVP/AANa and NVP/AAM. It can be seen that, the amount of metal ions uptake increases with increasing temperature for all kind of hydrogels investigated. This is attributed to the increase in kinetic energy of the metal ions with temperature and the flexibility of the hydrogels increase as well. Consequently, the diffusion of the metal ion solution in the hydrogel increases with temperature and the amount of metal ion uptake increase as well. It was observed that, the maximum metal ions uptake obtained at the boiling point at which the highest diffusion is occurred.

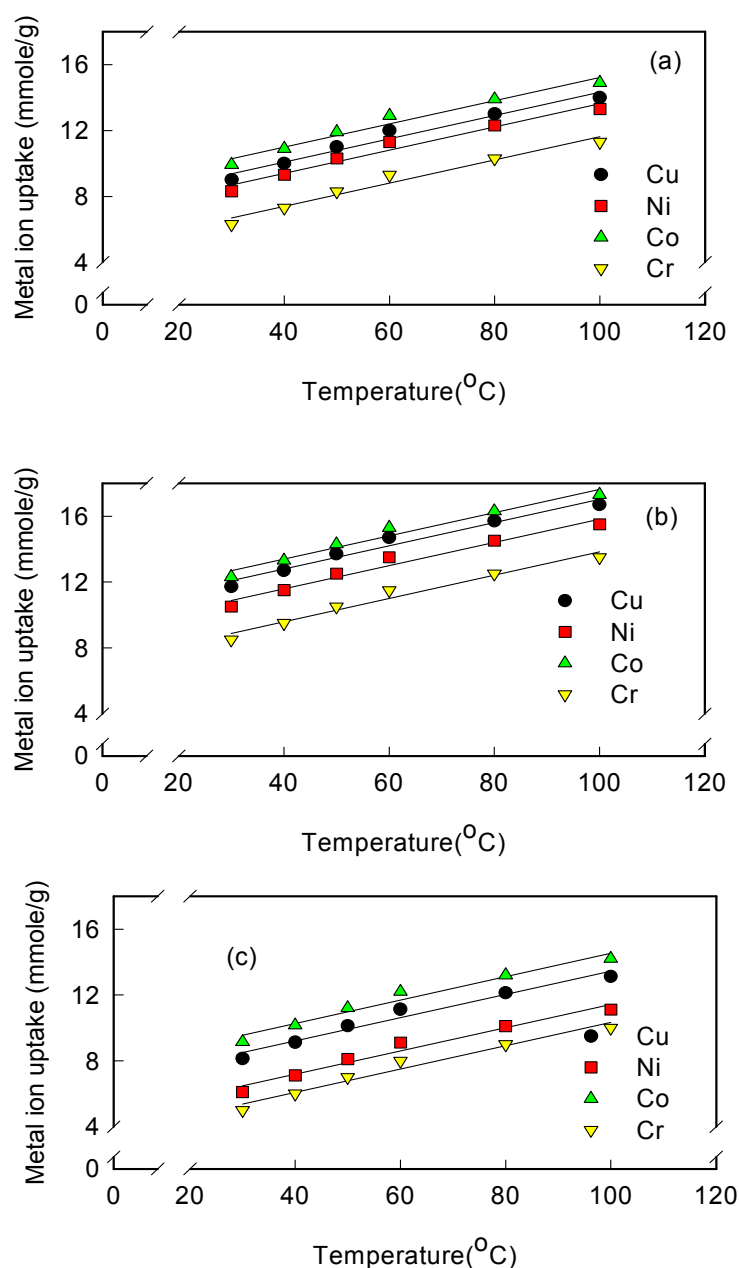


FIG. 9. Effect of Temperature on the Metal uptake for different hydrogels: a- NVP/AAC, b- NVP/AAC treated, c- NVP/AAM, Initial Metal ion concn.; 100ppm pH = 7

Effect of pH of feed solution

The availability of hydrogels under investigation for metal ion complexation is pH dependent. The sorption characteristics of hydrogels from NVP toward Cu^{2+} , Ni^{2+} , Co^{2+} and Cr^{3+} metal ions are investigated over pH that ranged from 1-7. The sorption affinity of the prepared hydrogels are plotted as a function of pH and shown in Fig. 10. It can be seen that, the amount of metal ions uptake by chelating polymer increases significantly as the pH increases for Ni^{2+} , Co^{2+} and Cr^{3+} up to pH = 7. However, for Cu^{2+} its maximum uptake reaches at pH = 5 there after it decrease due to formation of their hydroxides. On the other hand, the metal ion uptake under high acidic conditions is sharply decreased for almost every chelating exchanger due to competition from hydrogen ions. The abovementioned results indicated that, each metal ion has its optimum pH at which it can be easily extracted by these hydrogels, i.e. the metal uptake is very dependent on pH of its feed solution.

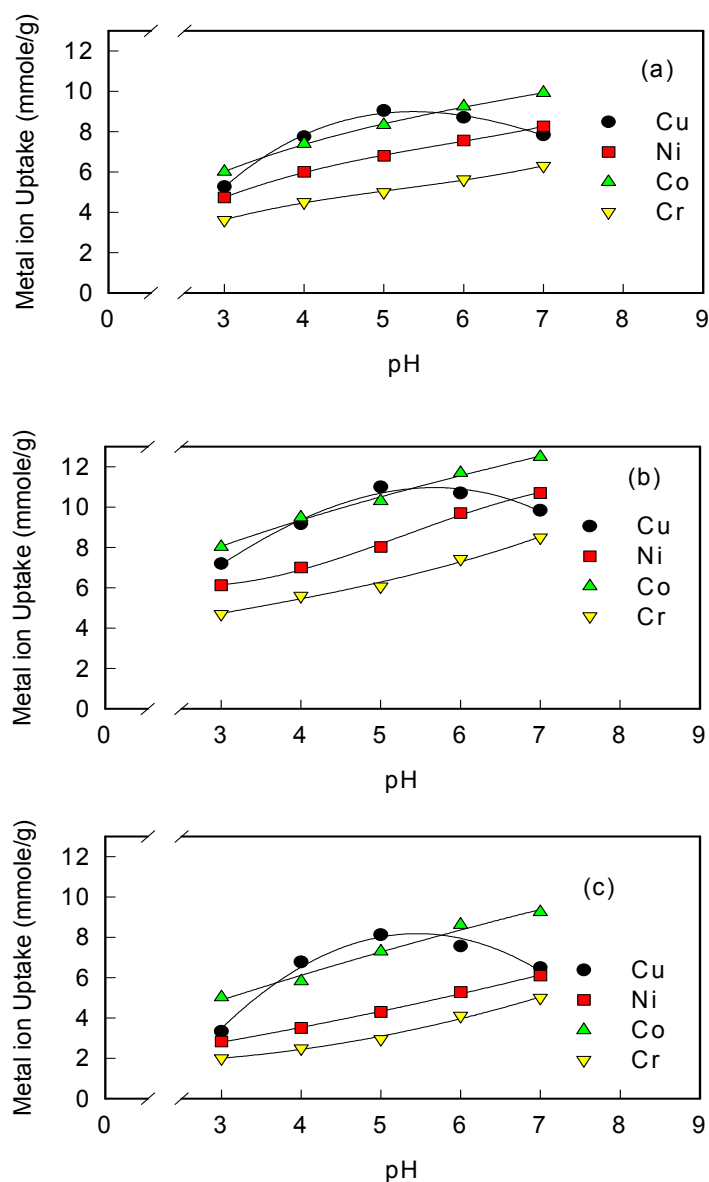


FIG. 10. Effect of pH on the Metal ion uptake for different hydrogels: a- NVP/AAc, b- NVP/AAc treated, c- NVP/Aam. Initial metal ion concn.; 100 ppm, Swelling time; 7 hr.

The sorption affinity of the grafted and cellulosic materials for metal ion complexation are also listed as a function of pH and shown in Table II.

From the data in Table II it can be concluded that, the adsorption of metal ion was remarkably affected by the pH of the solution. Metal ions were adsorbed rapidly from weakly acidic solution and the adsorbed amount increased with the pH value. Modification of adsorption ability of lignocellulosic materials towards metal ions uptake by pulping has been studied by many authors [17, 18]. Also, it has been reported that the natural fibers grafted with different monomers effectively adsorb heavy metal ions from aqueous solution than that of pulped materials which, is in good agreement with the results obtained in our investigated materials.

TABLE II. EFFECT OF PH ON THE ADSORPTION OF VARIOUS DIVALENT METAL IONS (Pb^{2+} , Cu^{2+} , AND Ni^{2+}) ON PULPED AND 67% GRAFTED BAGASSE, RICE STRAW; INITIAL METAL ION CONCENTRATION OF 40 PPM; REACTION TIME 24 HRS.

Metal Ion	pH	Metal ions Uptake (%)			
		Pulped bagasse	Grafted Bagasse	Pulped rice straw	Grafted rice Straw
(Cu^{2+})	2	32	37.6	38.4	41.8
	4	47	52.3	49.2	57
	6	58.3	67.9	63.2	70.1
(Pb^{2+})	2	23	37	29	43.2
	4	50	63	54	69.5
	6	62.5	81.3	69.6	90.5
(Ni^{2+})	2	26	36	31	39.4
	4	38	45	43	49.3
	6	49.2	60.5	52.7	68.7

Effect of treatment time

The efficiency of hydrogels or graft copolymer in waste treatment can be determined from the time required to adsorb the maximum capacity of metal ions by chelation or complexation with its functional groups. From the economical point of view, the time of treatment is an important factor for metal uptake percent. The metal uptake as a function of time for Cu^{2+} , Ni^{2+} , and Pb^{2+} using pulped and grafted bagasse and rice straw was studied to find that, the metal uptake increased with time to reach its maximum value (which is termed here as the maximum capacity) at almost 8 hrs of treatment time. This behaviour is observed for all metal ions investigated here: Cu^{2+} , Ni^{2+} and Pb^{2+} .

Table III represents the maximum uptake (%) of metal ions. It can be seen that order of metal uptake the sequence of $Pb^{2+} > Cu^{2+} > Ni^{2+}$. The initial rate of adsorbed metal ions and the maximum value of uptake are very dependent on the type of metal ions and the steric effect of the copolymer [19]. Also, the ionic size of the investigated metal ions has a great influence not only on its maximum uptake but also on its initial rate of adsorption.

This is reasonably explained by considering the diffusion coefficient of these metals through the porous ionic cellulosic materials which is mainly dependent on their polarity, electronic configuration, ionic radii, etc., and also importantly on the nature of interaction with the functional groups of the cellulosic materials.

TABLE III. MAXIMUM CAPACITY OF METAL UPTAKE (%) FOR DIFFERENT METALS BY PULPED AND GRAFTED BAGASSE AND RICE STRAW, TREATMENT TIME 8HRS, AND INITIAL CONCENTRATION OF METAL ION SOLUTION 40 PPM AT PH 6.

Metal Ion	Metal ions uptake (%)			
	Pulped Bagasse	Grafted Bagasse	Pulped rice Straw	Grafted rice Straw
(Cu ²⁺)	59.8	70.5	62.7	87
(Pb ²⁺)	71.4	86	74.6	92.5
(Ni ²⁺)	51.3	63.9	53.17	70.1

Fig. 11 shows the effect of treatment time on the dye uptake % of Sty/AAC copolymer, at comonomer composition 20/80 wt %, initial concentration of dye metal chelation or complexation due to the free penetration of metal ions and the high surface area of the adsorbent materials that having functional groups suitable for adsorption and chelation processes.

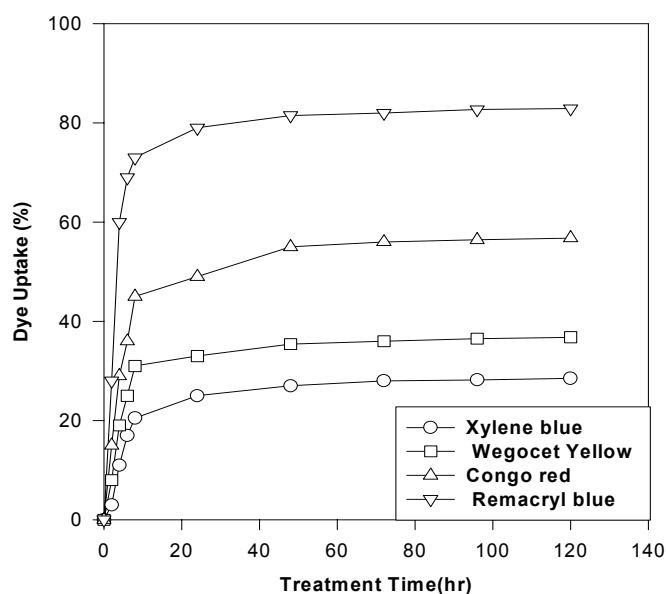


FIG. 11. Effect of treatment time on the dye uptake % of Sty/AAC copolymer, at comonomer composition 20/80 wt %, initial concentration of dye

The affinity of the pulped and grafted cellulosic materials to recover acid blue 7 (Xylene blue), Wegocet yellow 4GL (direct yellow 44), Congo red (direct red 28) and Remacryl Blue 3G (basic blue3) from their aqueous solutions was also studied. Also, the study was carried out to determine the appropriate reaction conditions such as treatment time and pH at which the recovery is performed successfully. The efficiency of the prepared copolymer in wastewater treatment can be determined from the time required for adsorbing the maximum capacity of dyes by chelating or complexation with its functional groups. In this respect, the effect of treatment time on the rate and maximum uptake for different dyes was investigated (Fig. 11).

Membranes prepared by radiation grafting:

Low-density polyethylene was grafted with acrylic acid and chemically treated with different reagents. Metal uptake by complexation with the free carboxylic acid groups of the grafted membranes is determined using two techniques; flame photometer (FP) and X ray fluorescence (XRF). The percent uptake of the prepared metal solutions containing the simulated medium active waste is determined by immersing the grafted membranes for about 24 h. (to reach equilibrium) and then measured by XRF. The ion selectivity is clearly shown in Table IV, in which the concentration of metal uptake or complexation with the membrane is highly dependent on the chemical form of carboxylic acid group derivatives. The order of metal uptake for the different carboxylic acid acrylate membranes is shown to be as follows:

Ni (20%) > Fe(19.7%) > Cr (16.7%) > Zn(14.3%) > Ca(8.5%) > Cu(7.5%) > Cs(6.2%) > Zr (1.7%).

This order is changed by converting the carboxylic acid groups into their sodium carboxylates (-COONa) to be as follows:

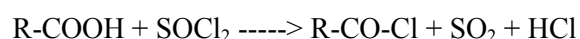
Cu (31.8%) > Ni(14.8%) > Fe(13.7%) > Cr(12.9%) > Ca(8.4%) > Zn(4.8%) > Mo(4%) > Zr(3.5%).

TABLE IV. EFFECT OF REACTIVE FUNCTIONAL GROUP ON THE METAL UPTAKE PERCENT BY LDPE-G- AAC MEMBRANES FROM SIMULATED MAW AQUEOUS SOLUTION AS DETERMINED BY XRF

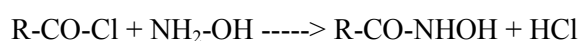
Membrane Form	Degree of Grafting (%)	Metal uptake (%)										
		Ca	Cr	Fe	Ni	Cu	Zn	Sr	Zr	Mo	Cs	U
LDPE-g-PAA _{COOH}	95	8.5	16.7	19.7	20	7.8	14.3	N	1.7	4.5	6.2	0.5
LDPE-g-PAA _{COONa}	95	8.4	12.9	13.7	14.8	31.8	4.8	N	3.5	4	N	0.4
LDPE-g-PAA _{CONHOH}	120	8	5.5	6.3	3.9	1.1	1.5	N	64	8.8	N	0.3
LDPE-g-PAA _{COONa}	1000	10	7.9	39.4	12.4	6.2	5	N	5.7	10	N	2.3

N-Negligible uptake

It is noted that, the order is not only changed by such chemical conversion but also the percentage of metal uptake is differed. This is due to the change in ion exchange properties and selectivity of membrane towards the metal ions by its conversion into Na-acrylate form. The carboxylic acid group of membrane was converted into -NHOH group by acylation reaction, in which the acid chloride is prepared by reacting the carboxylic group with thionyl chloride then treated with hydroxylamine to give hydroxamic acid as follows:



Acyl chloride reacts rapidly with compounds containing active hydrogen e.g. (oxygen, nitrogen, sulphur). After the treatment of membranes with thionyl chloride, membrane is treated with hydroxylamine to give hydroxamic acid as follows:



Such conversion resulted in a surprise change in ion selectivity towards zirconium, which is the most contaminant element for uranium in its recovery process from waste solution and competes strongly with other metals in the simulated waste solution. This is a good advantage for the practical use of such membrane in the recovery process of uranium by the removal of zirconium from its solution, specially this membrane has no affinity towards uranium. It is interesting also to find that all membrane forms do not absorb the monovalent metals (Na, Cs), which exist in the simulated mixture solution. This is due to their weak complexation with the membrane and they are replaced by multivalent ions. The other multivalent ions form strong chelating or complexation bonds with the membrane and as a consequence their uptake is highly pronounced.

Recovery of zirconium and uranium by LDPE-g-PAAc membranes

Extra batch investigations were carried out to test the feasibility of zirconium separation from solution containing uranium, where the uptake % was determined by UV spectrophotometer at λ_{\max} 415 nm for U and at λ_{\max} 520 nm for Zr using alizarin red-S monohydrate (3,4-dihydroxy-9,10-dioxo-anthracene sulfonic acid sodium salt). The effect of treatment time on the uptake percent of Zr and U from a feed solution containing 0.5 g/l Zr and 8 g/l U using LDPE-g-PAAc membrane was investigated to find that the uptake percent of Zr gradually increases with immersion time at 1 and 3 M HNO_3 in which the higher values of uptake % is found at 1 M HNO_3 . The maximum uptake reaches at about 15 h. However, there is no detected uptake for U by such membrane.

Cationic/ Anionic Membranes Prepared by Direct Radiation Graft Copolymerization of AAc/4-VP Binary Monomers onto LDPE Films:

Cationic/ anionic membranes were prepared by the direct radiation-induced graft copolymerization of AAc/4-VP binary monomers onto LDPE films. A trial was made to investigate such prepared grafted membranes for possible use in wastewater treatment from industrial heavy and toxic metals.

The prepared graft copolymers of different grafting yields that having anionic and cationic characters were investigated for waste water treatment. The metal uptake from such waste by the functional groups of membrane is determined using the atomic absorption and XRF to identify the adsorbed metal ions. Some selected metals, which commonly exist in wastewater, are investigated. The selectivity of the different prepared membranes towards Pb, Cd, Zn, Mn, Fe, Co, Cu and Ni is determined (Tables V-X).

In general, the cationic and anionic membranes showed a good affinity towards the chelation and/ or complexation with different heavy or toxic metals investigated here (Pb, Fe, Cu, Zn, Mn, Cd, Co, and Ni). The efficiency of such membrane is high and the maximum metal uptake reached fast within 2h, indicating that the functional carboxylic acid and vinyl pyridine groups have a good affinity towards metal chelation and/ or complexation. The exchange properties and/ or complexation between the ionic membrane and the existing metals in the feed solution seems to be changed by introducing both anionic and cationic characters together in the grafted membrane. It is suggested that the stability constant and complexation bound strength between the metals and functional groups are increased due to the incorporation of pyridine rings that having nitrogen atoms of lone pair of electrons which can easily form a quaternary pyridinium metal salts or chelation. These results are in a good agreement with Irving-Williams series for the stability of various ligand with nitrogen and/ or oxygen as coordinating atoms for divalent metal ions with an exception of Co(II) and Fe(III). Irving-Williams series; for a given ligand, the stability of complexes with dipositive metal ions follows the order of; $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$.

Under competitive conditions, a selectivity factor could be observed in the preferential extraction of Fe(III) over Cu(II) and Pb(II) ions by the sorbent membrane. Meanwhile, in case of other mixtures containing Cd, Co and Ni, the selectivity towards Cd(II) is higher than that for the other two metal ions. Although the ionic radii is the effective factor in case of Cd(II).

The prepared cationic/anionic membranes possessed good properties of great interest in separation of Fe (III) ions from a mixture of other metal ions. These synthetic grafted membranes can be also applied for the treatment of contaminated water resources from heavy and toxic metals such as Pb, Cd, Fe, Cu, etc. They possessed high thermal stability and good hydrophilic properties. Such grafted membranes could be regenerated easily by treating them with dilute HCl for their reuse.

TABLE V. SELECTIVITY RATIO OF LDPE-G-PAAC GRAFTED MEMBRANE TOWARDS TWO METAL IONS EXIST IN A MIXTURE OF FEED SOLUTION, DEGREE OF GRAFTING; 177%.

Metal Feed Solution Mixture	Metal Uptake (m.mol/g)	Selectivity Ratio (M1/M2)
Fe(III) +	3.15	2.6
Co(II)	1.21	
Fe(III) +	3.35	1.6
Ni(II)	2.12	
Fe(III) +	3.84	192
Mn(II)	0.02	
Ni(II) +	3.12	1.1
Co(II)	2.88	
Zn(II) +	2.56	1.4
Cd(II)	1.89	
Pb(II) +	1.14	1.1
Cd(II)	1.01	

TABLE VI. SELECTIVITY RATIO OF LDPE-G-P(AAC/4-VP) GRAFTED MEMBRANE TOWARDS TWO METAL IONS EXIST IN A MIXTURE OF FEED SOLUTION AND MEASURED BY ATOMIC ABSORPTION, DEGREE OF GRAFTING; 121%.

Metal Feed Solution Mixture	Metal Uptake (m.mol/g)	Selectivity Ratio (M1/M2)
Fe(III) +	3.88	1.4
Co(II)	2.85	
Fe(III) +	4.27	6.2
Ni(II)	0.69	
Fe(III) +	4.07	13.6
Mn(II)	0.3	
Ni(II) +	3.02	1.4
Co(II)	2.2	
Zn(II) +	1.89	0.7
Cd(II)	2.85	
Pb(II) +	1.15	1.1
Cd(II)	0.87	

TABLE VII. SELECTIVITY OF LDPE-G-P(AAC/4-VP) MEMBRANES TOWARDS DIFFERENT TWO METALS IN A MIXTURE OF THEIR FEED SOLUTION DETERMINED BY XRF. DEGREE OF GRAFTING; 237%.

Metals mixture	Metal uptake (%)
Fe(III) - Cu(II)	97 - 3
Fe(III) - Pb(II)	87 - 13
Pb(II) - Cu(II)	51 - 49
Fe(III) - Cu(II)- Mn(II)	99- 1-0
Fe(III)- Cu(II)- Pb(II)	94-4- 2
Cd(II)-Ni(II)- Co(II)	85-9-6
Fe(III)-Cd(II)-Pb(II)-Cu(II)	68-14-11-7
Zn(II)-Ni(II)-Mn(II)-Co(II)	71-18-6-5

TABLE VIII. MAXIMUM METAL UPTAKE (M.MOL./G) FOR DIFFERENT IONIC HYDROPHILIC MEMBRANES AS MEASURED BY ATOMIC ABSORPTION TECHNIQUE AT 30 °C. INITIAL CONCENTRATION OF METAL FEED SOLUTION; 2000 PPM, TIME OF TREATMENT; 2H.

Membrane type	Degree of grafting (%)	Maximum Metal Uptake (m.mol./g)							
		Pb	Fe	Cu	Cd	Co	Ni	Zn	Mn
LDPE-g-Aac	177	1.8	3.7	2.9	2.3	5.1	3.6	3.6	3.5
LDPE-g-(Aac/4VP)	121	2.3	4.2	5.3	2.7	3.9	5.1	4.5	3.8
LDPE-g-(Aac/4VP)	130	2.1	3.8	4.2	2.5	3.6	5.4	4.1	3.1

TABLE IX. SELECTIVITY RATIO OF LDPE-G-P(AAC/4-VP) GRAFTED MEMBRANE TOWARDS TWO METAL IONS EXIST IN A MIXTURE OF FEED SOLUTION, DEGREE OF GRAFTING; 121%.

Metal Feed Solution Mixture	Metal Uptake (m.mol/g)	Selectivity Ratio (M1/M2)
Fe(III) + Co(II)	3.88 2.85	1.4
Fe(III) + Ni(II)	4.27 0.69	6.2
Fe(III) + Mn(II)	4.07 0.3	13.6
Ni(II) + Co(II)	3.02 2.2	1.4
Zn(II) + Cd(II)	1.89 2.85	0.7
Pb(II) + Cd(II)	1.15 0.87	1.1

TABLE X. SELECTIVITY OF DIFFERENT IONIC MEMBRANES TOWARDS DIFFERENT THREE METALS IN A MIXTURE OF THEIR FEED SOLUTION.

Mixture of Metals	Metal Uptake (m.mol/g)	
	LDPE-g-PAAc	LDPE-g-P(AAc/4VP)
	Degree of Grafting%	
	177	121
Fe(III) +	2.1	2.8
Cu(II) +	0.3	1.2
Pb(II)	0.8	1.0
Cd(II) +	1.1	1.7
Co(II) +	1.8	1.1
Ni(II)	0.8	1.1

Recovery and concentration of valuable metals

The recovery and concentration of metal ions from aqueous solution has been the subject of much effort by both industry and government, especially for important metal ions such as gold (Au^+), silver (Ag^+) and rhodium (Rh^{2+}). Because of the large volumes of liquids involved, solvent extraction has not generally been applied successfully to very dilute solutions. Ion exchange graft copolymers are a perfect method of metal recovery.

In this respect, the radiation graft copolymers that prepared by radiation grafting of Styrene/Vinyl acetate (Sty/VAc) binary monomers system onto polypropylene followed by sulfonation and alkaline treatments to obtain graft copolymers having more polar groups than untreated ones and to improve their applicability in extraction and separation processes. Some selected metals, which are expensive and exist in wastewater, are investigated. The selectivity of the prepared graft copolymers towards Ag^+ , Au^+ , and Rh^{2+} is determined.

The initial rate of chelated metal ions and maximum value of uptake are very dependent on the type of metal ions and its coordination, stability constant and the steric effect of these copolymer complexes. On the other hand, the ionic size of the investigated metals has a great influence not only on its initial rate but also on the maximum uptake's. This is reasonably explained by considering the diffusion coefficient of these metals through the porous ionic film which is mainly dependent on their polarity, electronic configuration, ionic radii, and also importantly on the nature of interaction with the functional groups of the grafted films.

Table XI shows the atomic radii of the investigated metal ions. The maximum metal uptake observed for such metal ions depend not only on the ionic radii but also on the electronic configuration and their affinity to make complexation and/ or chelation with the functional groups added to the polymer by grafting and chemical treatment. The highest metal uptake observed for Rh^{2+} and the lowest one for Au^+ . In other words, the lower the ionic radii, the higher the metal uptake occurred. Therefore, the ionic size is very important factor because of permeability and diffusivity problems through the porous films of certain diameter and pore size. In general, the grafted and treated films showed a good affinity toward metal ions investigated here, in sequence order $\text{Rh}^{2+} > \text{Ag}^+ > \text{Au}^+$. The efficiency of such films is high and the maximum metal uptake reached after 8 hr.

The sorption characteristics of grafted sulfonated and hydrolyzed film toward Rh^{2+} , Ag^+ and Au^+ metal ions are investigated over pH that ranged from 1-6 (Fig.12). The amount of metal ions uptake by chelating polymer increases significantly with increasing the pH for Rh^{2+} , Ag^+ and Au^+ up

to pH=6. However, the maximum metal uptake reaches at pH=5, thereafter, it decreases due to the formation of their hydroxides. On the other hand, the metal ion uptake under high acidic conditions is sharply decreased due to competition from hydrogen ions. The above results indicated that, each metal ion has its optimum pH at which it can be easily extracted by these films, i.e. the metal uptake is very dependent on pH of its feed solution.

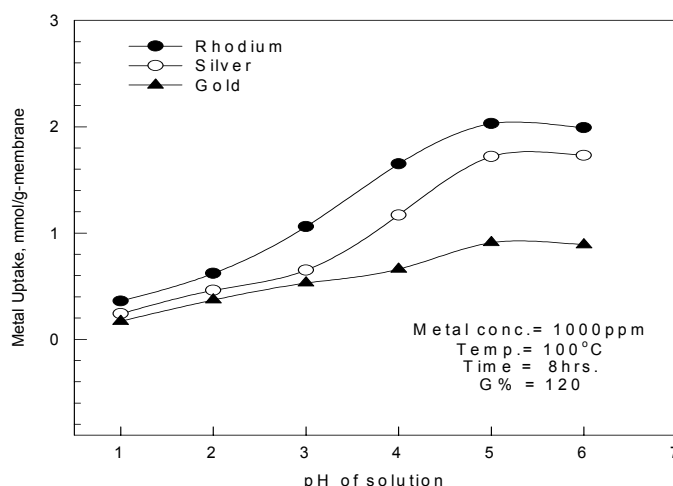


FIG. 12. Effect of pH on metal uptake

Effect of initial concentration of metal feed solution, degree of grafting and temperature on the metal uptake is also investigated and shown in Figs.13-15, respectively. Increasing the concentration of metal ions results in increasing the amount of metal ions uptake to reach a certain limiting value. Thereafter, it levels off at higher feed concentration (>1000 ppm). The amount of metal ions uptake increases with increasing the graft percent for graft copolymers investigated. This confirmed that, the metal chelation or complexation is mainly dependent on the amount of functional reactive groups in the treated grafted films. The amount of metal ions uptake increases with increasing temperature. It was observed that, the maximum metal ion uptake obtained at the boiling point at which the highest diffusion is occurred.

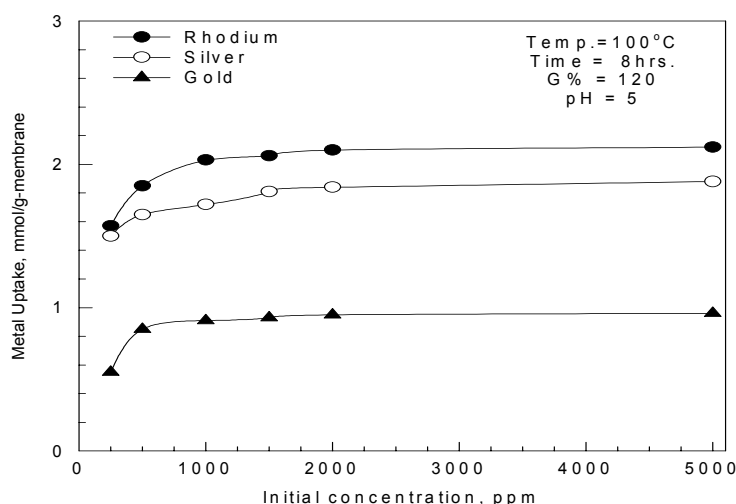


FIG. 13. Effect of initial feed concentration on metal uptake

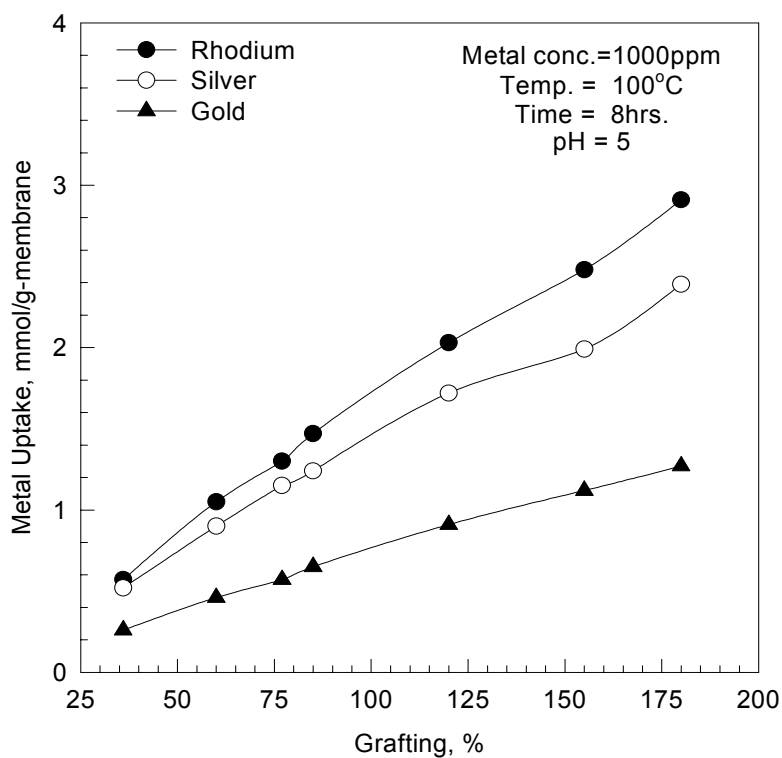


FIG. 14. Effect of grafting percent on metal Uptake

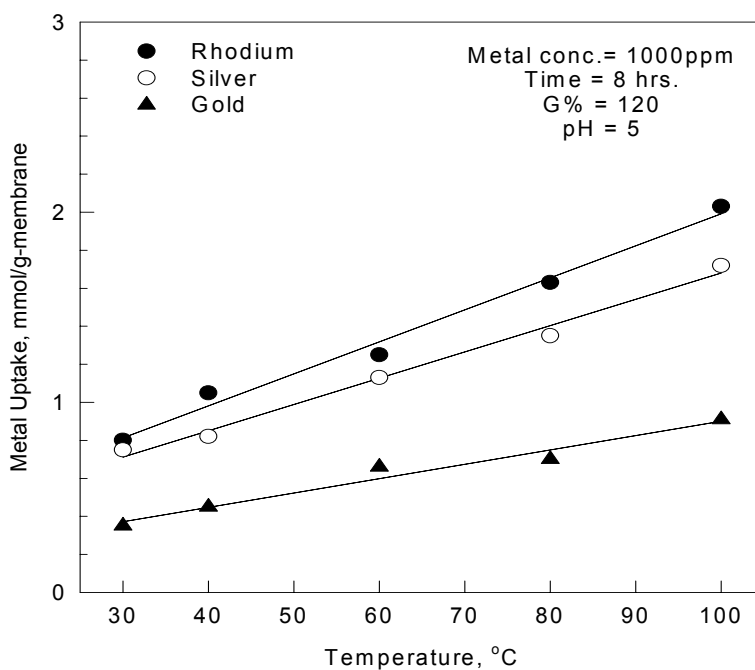


FIG. 15. Effect of temperature on metal Uptake

The aforementioned results suggested that, the diffusion of the metal ion solution in the graft copolymer (i.e. to the functional groups) plays an important role. In the films having high graft yield, the crosslinking formation hinders the diffusion of metal ions. Consequently, at high graft percent, the metal ion uptake increased to small extent with degree of grafting.

The selectivity of different ionic prepared films which are sulfonated and hydrolyzed are investigated using mixtures of the three metal ions in the same feed solution at pH=5 (Fig. 16). The chelating sorbent under investigation demonstrated some selectivity towards three metal ions namely; Rh^{2+} , Ag^+ and Au^+ , the selectivity of sorbent towards Rh^{2+} is higher than Ag^+ and Au^+ . The results can be reasonably explained by considering the valence of metals, their radii and electronic configuration. However, Rh^{2+} ions have a higher valence than the others. On the other hand, the selectivity of sorbent towards Ag^+ is higher than Au^+ due to Ag^+ having smaller ionic radii than Au^+ ions (Table XI).

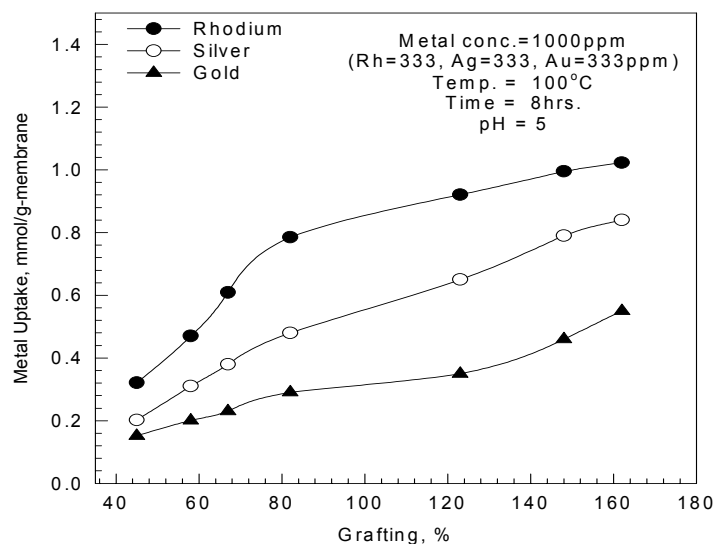


FIG. 16. Effect of selectivity as a factor of grafting percent on metal Uptake

TABLE XI. ATOMIC, IONIC RADII AND ELECTRONIC CONFIGURATION FOR DIFFERENT METAL IONS INVESTIGATED, (EMSLEY, 1991).

Element	Valence	Atomic radius, Å	Ionic radius, Å	Ionic electronic configuration
Rh	2+	1.34	0.86	[Kr]4d ⁷
Ag	1+	1.44	1.26	Kr]4d ¹⁰
Au	1+	1.44	1.37	[Xe]4f ¹⁴ 5d ¹⁰

Recovery of valuable metals from the real waste solutions

Recovery of Ag^+ , Au^+ , Rh^{2+} from real waste solutions was carried out at the optimum conditions (pH = 5, temperature = 100°C and time = 8 hr) and shown in Table XII. Silver ion concentration of the developer and its wash water are 4000 and 350 ppm, respectively. Meanwhile, the wash water of rhodium and gold electroplating processes after evaporation are 500 and 800 ppm, respectively. It is clear that, the prepared film played an excellent role in metal uptake from wastewater. One gram of the film can catch 0.1672 g of silver ions from the developer solution. On the other hand, it can catch about 0.2 and 0.1 gram of rhodium and gold from their wastewater, respectively.

TABLE XII. METAL UPTAKE FOR THE REAL WASTE WATER.

Sample	Metal type	Conc., ppm	Degree of Grafting (%)	Uptake, mmole/g	Uptake, g metal/g
Developer	Ag	4000	187	1.55	0.1672
Wash, Ag	Ag	350	187	1.01	0.1091
Wash, Rh	Rh	500	162	1.05	0.2048
Wash, Au	Au	800	156	0.49	0.0965

5. CONCLUSIONS

- Direct radiation copolymerization is considered an environmentally acceptable technique for preparation of stimuli-responsive hydrogels and membranes for separation and purification.
- Prepared hydrogels and membranes by means of radiation-induced copolymerization of NVP/AAc and NVP/AAm solutions is of interest in some practical uses such as in industrial wastewater treatment from heavy and toxic metals. They possessed good hydrophilic properties and thermal stability, which may make them acceptable for practical uses. The maximum metal uptake is ordered in the sequence of, $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cr}^{3+}$. The treated hydrogel (NVP/AA-Na) showed greater affinity to adsorption of such elements than the untreated hydrogel (NVP/AAc).
- Prepared membranes by direct radiation grafting of binary monomers mixture onto polymer substrates have proved to be promising. The results indicated that the prepared membranes possessed high thermal stability and good hydrophilic properties. Also, they possessed great interest in removal of heavy metals and toxic dyes.
- Modification of properties of lignocellulosic materials by radiation grafting technique using selected binary monomers mixture (AAm/AAc) impart new chemical properties which were proved by physical tools (FTIR, SEM). The alkaline pulping and grafting processes have great effect on the adsorption capacity of different pollutants.
- The different prepared copolymer hydrogels have good chemical and thermal stability. The capacity of the obtained hydrogels towards different pollutants (heavy metal and dyes) is mainly dependent on the amount of the active groups present in the copolymer.-The change in pollutant adsorption by the different adsorbents used resulting from change in reaction conditions is dependent on the number and strength of groups present, whereas the maximum pollutant adsorption depends on the total number of both weak and strong groups present.

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TRANSPORT OF IONS AND BIOMOLECULES THROUGH ASSYMETRIC SINGLE NANOPORES FABRICATED BY HEAVY ION IRRADIATION AND CHEMICAL ETCHING

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Abstract

In the framework of the CRP "Radiation Synthesis of Stimuli-responsive Membranes, Hydrogels and Adsorbents for Separation Purposes", GSI has worked on the production of polymeric single conical nanopores and the study of the ionic transport through these pores. To produce single-pore membranes, polyethylene terephthalate (PET) and polyimide (PI) foils were first irradiated with GeV single heavy ions. By subsequent one-side etching, asymmetric nanopores were created. The diameter of the conical pores in PET varied between 4-20 nm at the small opening and several hundred nm at the large opening. In the case of PI, due to the higher bulk etching rate, the large aperture reached a few μm . The current-voltage (I-V) characteristics were measured at symmetric electrolyte conditions of KCl at various concentrations and pH values. It was found that conical nanopores with charged surfaces are cation selective, and show preferential cation flow (i.e. rectification) from the narrow entrance to the wide opening of the cone. Concentration and pH influence the rectification properties for both polymers was studied. The experimental results are in agreement with existing models. The transient transport properties of single PET and PI pores were also investigated. The ion current through PET nanopores fluctuates considerably, the fluctuation depending on the voltage, whereas PI nanopores display a stable current signal for KCl concentrations between 0.1 and 3 M, and pH values between 2 and 8. This different behavior has been attributed to the chemical structure of the two polymers influencing surface characteristics of the resulting nanopores. Finally, the application of polyimide conical nanopores as single-molecule-DNA sensors is being investigated. First results demonstrate their ability to detect individual plasmid DNA molecules. The nanopore sensor is also able to discriminate between DNA fragments of different lengths [7].

1. OBJECTIVE OF THE RESEARCH

Nowadays, membrane separation processes are applied in fields as various as water treatment, food and chemical processing, biotechnology and medicine. In all processes, e.g. ultrafiltration, nanofiltration, electrolysis, and electrofiltration among others, selectivity, efficiency, and economics of the separation are decisively influenced by the membrane properties.

For several decades, etched ion track membranes have been employed as filters for diverse separation applications. The combination of ion track membranes and responsive gels lead to responsive membranes with pores that open and close as a function of external conditions such as temperature and pH. The aim of the most recent work performed at GSI was to develop a membrane that permits the passage of ions and/or molecules as a function of external parameters such as electrical field, pH, and concentration. We wanted to create an abiotic analogue of biochannels, focusing on voltage-gated channels, which would regulate the ion flow based on similar principles as function of the biochannels. For this purpose, the fabrication process of single nanopores in polymer films had to be studied and optimized. In order to prepare a synthetic voltage-gated pore we chose an asymmetric – tapered-cone shape of the nanopore, in accordance with the recent finding that biological voltage-gated channels are asymmetric in shape. Asymmetric pores are also characterized by a lower resistance than the corresponding cylindrical pores of the same limiting diameter. Lower resistance assures higher, therefore easier to detect, ion currents. Careful studies of average and transient transport properties of conical pores at various electrolyte concentrations and pH values were performed.

2. MATERIALS AND METHODS

2.1. Single-pore fabrication and characterization

Two polymer films, polyethylene terephthalate (Hostaphan RN12, Hoechst) and polyimide (Kapton 50 HN, DuPont), both 12 μm in thickness are mainly used.

The foils are irradiated with single swift heavy ions (Au, U, Pb) of energy 11.4 MeV per nucleon at the UNILAC linear accelerator (GSI, Darmstadt). The irradiations are performed through a mask with an aperture of diameter 0.1 mm. A detector placed behind the sample together with a fast beam switching system allows the controlled production of a single track per foil.

To obtain conical nanopores, the irradiated foils are etched from one side only in a purposely designed conductivity cell, schematically depicted in Fig. 1(a) [3]. 9 M sodium hydroxide at room temperature, and sodium hypochlorite (13% active chlorine content) at 50 °C, are used for etching PET and Kapton, respectively. A stopping solution (1 M KCl + 1M formic acid, and 1 M KI are used for PET and polyimide, respectively) placed on the other side of the foil, neutralizes the etchant in the pore tip when the track becomes completely etched through, thus helping to keep the diameter small. This is supported further by applying +1 V on the etchant side using Pt or Au electrodes, so that once the pore opens, the active OH^- / ClO^- ions are also swept back from the pore tip. The cell is connected to a I/U converter of pA sensitivity, controlled by software written in Lab View 5.0 (National Instruments) [2-8]. Fig. 1 (b) shows a typical current-versus-time curve recorded during the last 10 minutes of etching of a single pore in a polyimide foil [6]. The breakthrough occurred after 244 minutes of etching. Shortly after the breakthrough, the etching is interrupted and the membrane is rinsed first with the stopping medium and then with distilled water. After the pore is etched through, its diameter increases proportional to the etching time.

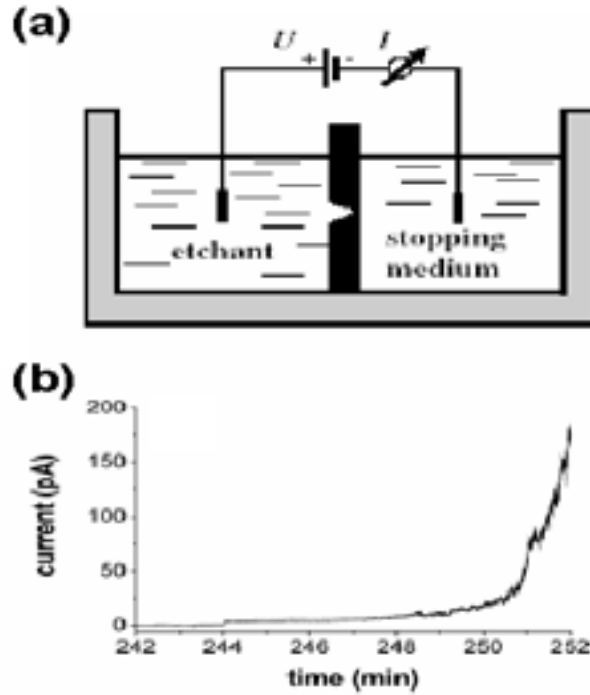


FIG. 1. (a) Schematic of the experimental set-up used for etching [3]. (b) Current-versus-time curve recorded during etching of a single latent track in polyimide [6].

The large openings D of the pores in PET and PI foils (irradiated with 10^7 ions/cm² and subsequently etched under the same conditions), were imaged by SEM (Fig. 2) [6]. In PET, the large opening of the pores after 2 h of etching have a typical diameter of ~ 500 nm (a). In PI, after 4 h of etching $D \sim 2400$ nm (b). This variation is due to the different bulk vs. track etch rates for each polymer [6,8]. The SEM images shown in Fig. 2 also indicate a rough surface in the case of the PET and a smoother surface in the case of PI. In both cases, the small opening d is estimated from conductivity measurements [3].

For a conical pore, d is related to the measured current, I , via:

$$d = \frac{4LI}{\pi\kappa DU},$$

where L is length of the pore (thickness of the membrane), κ is the specific conductivity of the electrolyte, and U is the applied transmembrane potential. Using this method, asymmetric pores with narrow-end diameters of ~ 5 -20 nm are produced [6,8].

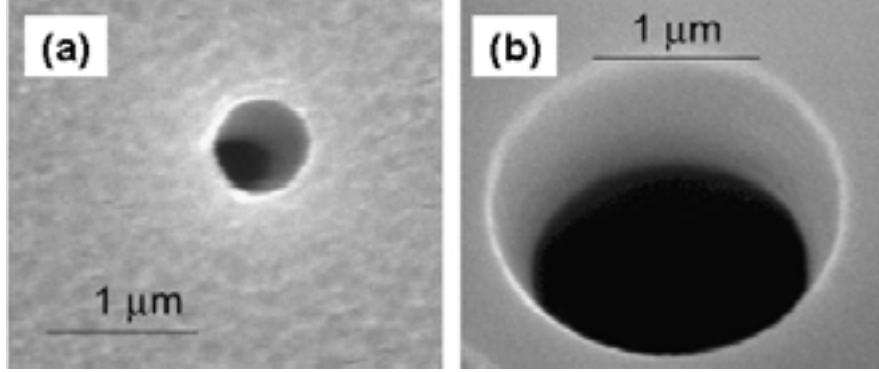


FIG. 2. (a) Scanning electron microscopy (SEM) images of the etched side of a PET (a) and a Kapton foil (b), showing the large opening of a conical pore [6].

The surface corrugation of PET and PI films was studied by scanning force microscopy (SFM) in water (Fig. 3) [3]. The surface of the PI foils is smoother than that of PET, in agreement with the SEM images. We assume that the higher smoothness of the Kapton foil also holds for the nanometer scale. During the chemical etching, polymer chains are broken and modified, forming so-called "dangling ends", i.e., chains with carboxylate end groups. For PET numerous dangling ends are expected, which perform random movements when the foil is immersed in a solution. In contrast to that, the chemical structure of Kapton is based on a planar sequence of aromatic rings, which renders rigidity and smoothness to the pore structure [3].

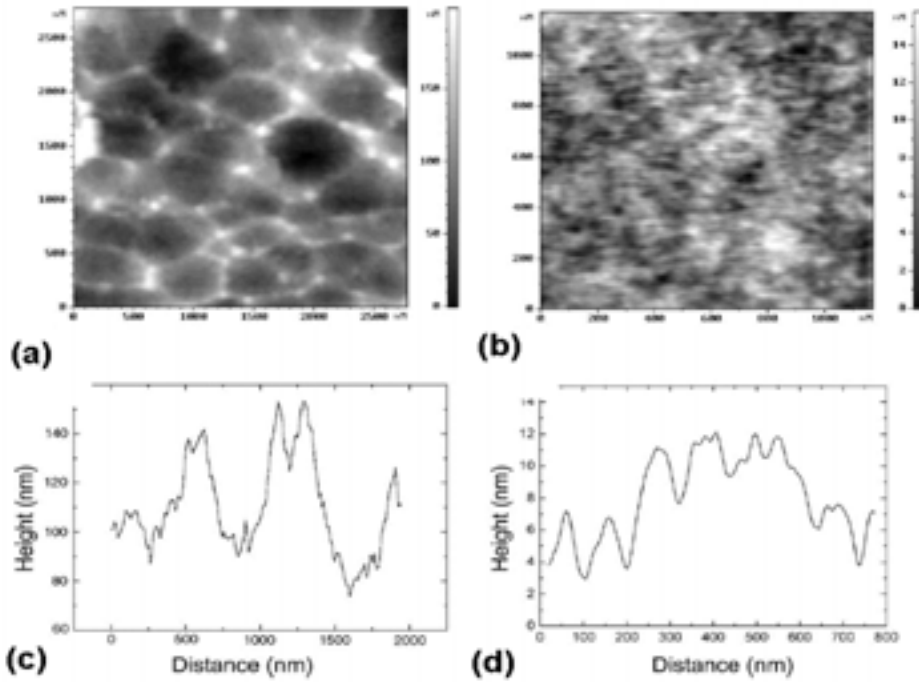


FIG. 3. Surface scans of etched PET (a) and PI (b) foils immersed in water, recorded by SFM. The foils were etched on one side for 2 h in 9M NaOH (PET) and in NaOCl (Kapton). The line plots show the degree of roughness of the etched PET (c) and Kapton (d) foils [3].

2.2. Ion transport

Average transport properties

Transport properties of the single conical pores were studied in the same conductivity cell in which the etching was performed using two Ag/AgI electrodes. Both sides of the cell were filled with KCl solutions of various concentrations and pH values.

Fig. 4(a) shows a typical I-V characteristic of a single conical PET pore, recorded in 0.1 M KCl at pH 7, 5 and 3. The narrow opening of the pore was ~ 2 nm. At pH = 7, when the PET surface is negatively charged, the ratio of the conductivities for negative and positive voltages equals 6. Since conical nanopores are cation selective, the curve indicates preferential cation flow (i.e. a degree of rectification) from the narrow entrance to the wide opening of the cone [2]. By lowering the pH, the carboxylate groups on the surface become protonized which lowers the excess negative charge on the pore walls. Therefore, the degree of rectification decreases. For pH = 3, the PET surface is neutral and the I-V characteristic becomes linear. Fig. 4 (b) presents the I-V characteristics of a single conical Kapton nanopore, measured under the same symmetric electrolyte conditions (0.1 M KCl). Qualitatively, the I-V characteristics display the same behaviour as the PET pores. Due to the larger opening angle, the ion currents through the pore are higher [3].

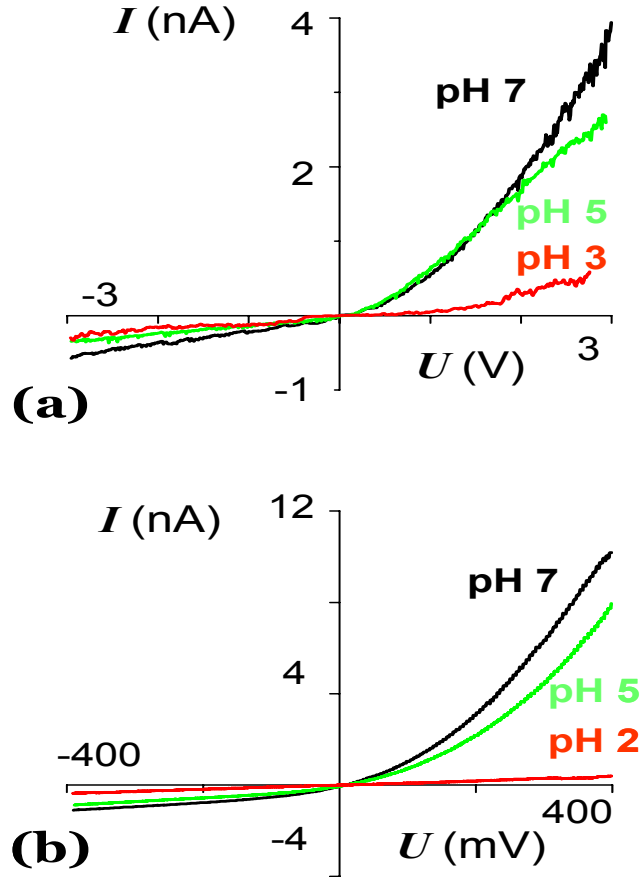


FIG. 4. Current-voltage characteristics of PET (a) and Kapton (b) single pore membranes, measured in 0.1 M KCl at different pH. The diameter of the narrow opening of the PET pore is ~ 2 nm, and that of the PI pore is ~ 8 nm [3].

Figure 5 (left) shows a series of current-voltage (I - V) curves, recorded from a single asymmetric nanopore, at different concentrations in the range of 0.01 M to 3 M KCl, at room temperature [4]. It has been shown that the profile of electrostatic potential inside a conical nanopore with charged surfaces has an asymmetric tooth shape, and it was predicted that the depth of this tooth depends on the electrolyte concentration [5]. For lower salt concentrations, the electrical double-layer at the pore walls is thicker, i.e. fewer counter-ions are screening the surface charges, so their effect is more pronounced. Therefore, one would expect that lowering the electrolyte concentration will enhance the rectification effect. Surprisingly, however, for PET pores the rectification increases with decreasing concentration only up to 0.1 M KCl (Figure 5). As the concentration is decreased further, the degree of rectification drops again for the majority of the pores examined. The origin of this effect is not yet clear, but it seems to be related to the presence of polymer ‘dangling’ ends, since conical, negatively charged Au nanotubes do not show this effect [9]. These dangling ends could act as an electromechanical gate, changing the pore diameter for different applied voltages [2].

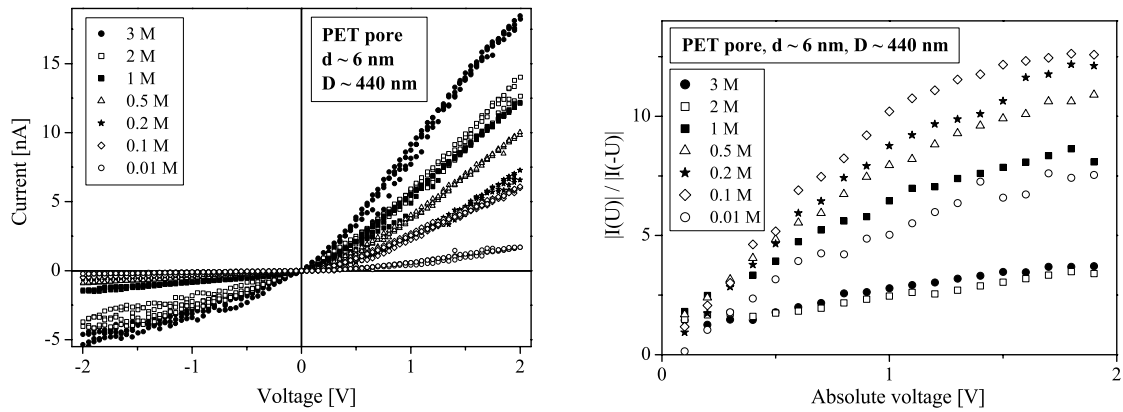


FIG. 5. (left) Asymmetric current-voltage-characteristics of a conical PET nanopore with $d \sim 6$ nm, $D \sim 440$ nm for concentrations in the range 0.01 M–3 M KCl. (right) Variation in the degree of rectification with concentration [4].

Since biological pores show a saturation in conductance when the concentration is raised well above the physiological level, either due to limited geometry or a limiting binding-unbinding rate, it was an interesting question as to whether these rectifying track-etched pores would show similar behaviour. Figure 6 shows ion current measurements at various voltages as a function of electrolyte concentration. As one see from the figure, we do not observe saturation *per se*, but the increase in ion current with KCl concentration clearly has two regimes. For lower concentrations, the ion current rises rapidly, compared to slower increases for concentrations higher than 0.25–0.5 M [4].

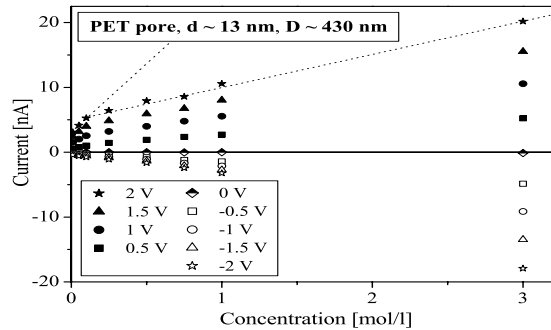


FIG. 6. Ion current versus concentration [4].

Fig. 7 shows current-versus-time curves recorded for both PET and Kapton at constant voltages in a 0.1 M KCl solution at pH 7 [3]. In the case of PET (Fig. 7(a)), the pore exhibits a voltage-dependent ion-current behavior. At 60 mV, the current is considerably stable. At 200 mV, the ion current fluctuates between two conductance states, one close to 0 pA and a second one at around 15-20 pA. The two peaks of the histogram correspond to the low and high conductance states, respectively. At 250 mV, and for higher voltages, the current signal becomes again stable (after a delay of several seconds). The existence of discrete conductance levels for an asymmetric PET nanopore was also observed using a patch-clamp pipette set-up [2].

In the case of Kapton the current signal is very stable over the whole voltage range up to 2 V, and in the KCl concentration ranges between 0.1 M and 3 M for pH between 2 and 8. [6]. An example of the current-versus-time behavior for a single conical Kapton nanopore is shown in Fig. 7(b). The higher stability of the current signal has been attributed to the smoother surface of the membrane [3].

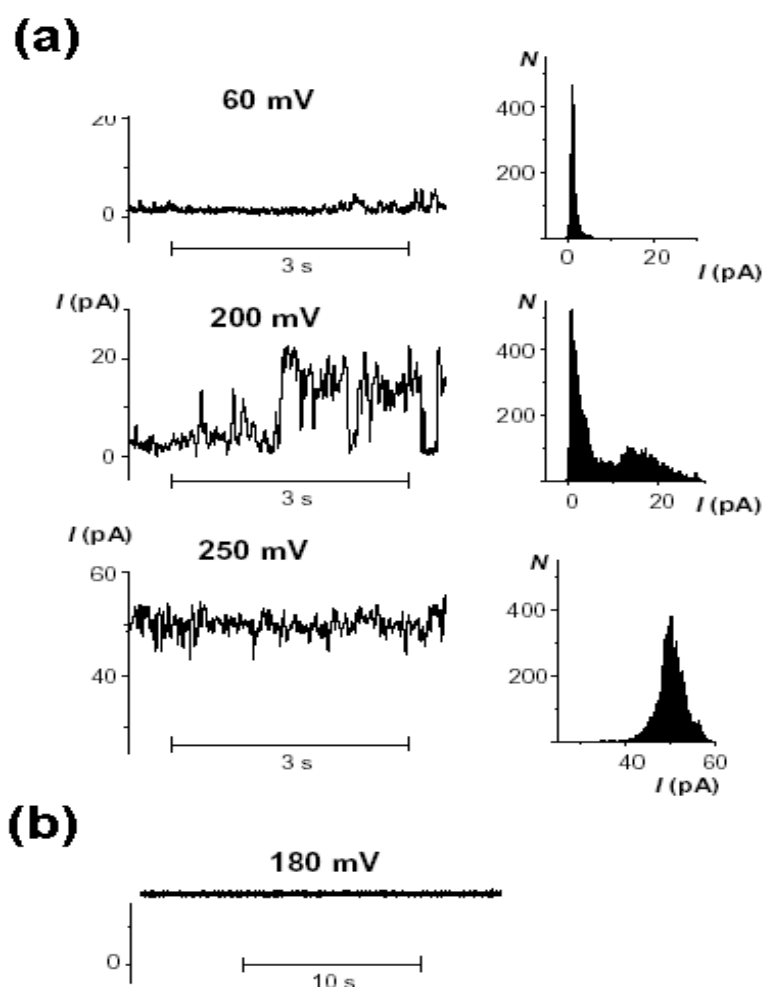


FIG. 7. (a) Ion current versus time for three different values of applied voltage (60, 200 and 250 mV) for a single conical PET pore. Histograms of ion current values (right) are deduced from current signals over a time period of 10 s, with N representing the frequency count of ion current amplitudes. (b) Ion current versus time for a single asymmetric pore in Kapton recorded at 180 mV. In both cases, the electrolyte solution is 0.1 M KCl, pH = 7 [3].

2.3. Similarities to biological channels

It should be pointed out that the synthetic asymmetric nanopores have many features in common with biological channels, which control and select the flow of ions in all living cells [2,10]. It has been shown that voltage-gated ion channels, e.g. Na^+ , K^+ , and Ca^+ channels, are constituted by charged amino acid residues on the interior wall of the channel. In an electrical field, a force is exerted on these charged residues, which results in a change in the shape and diameter of the channel, thereby defining their voltage-dependent ion-transport characteristics [11].

In [12], current-voltage characteristics of the K^+ channel in lipid bilayers, measured in solutions of 0.15 M KCl at *pH* 7, exhibit a clear current rectification. Besides, when applying a constant voltage, the ion current switches between different levels in a voltage-dependent manner. X-ray studies of the *Streptomyces lividans* K^+ channel [13,14] have revealed that the channel with four identical subunits is conically shaped and carries charges on both openings. This suggests that the synthetic nanopores may function in a similar fashion since it is also a conical structure with electrical charges, even though the length of the synthetic pores is much larger than that of an ion channel. It is presumed that the carboxylate groups formed during the track etching, in an electrical field are able to undergo movements and to contribute to the voltage dependence of the pore's diameter [2]. An abiotic nanotube system, which rectifies according to the electromechanical gate principle has been recently designed.

Transport of biomolecules through single asymmetric nanopores

Nanopore biomolecule detection and analysis is a rapidly developing field, with significant potential applications in biosensing and genomics. Molecules are electrophoretically driven through the nanopore at a constant voltage, while a time series of ion current is recorded simultaneously. The presence of these molecules inside the pore is detected as a transient decrease of the ion current, whose duration and shape is related to the structure of the molecules [15, 4, 7]. For low biomolecule concentration and very narrow pores, each decrease in ion current (referred to as an “event”) should correspond to a single molecule. The main advantages of this technique over current technologies are its high speed, very low detection limit, together with the capability to analyse biomolecules without prior marking, quantitative amplification, or chemical modification [4, 7].

The application of our polyimide nanopores as DNA sensors is being explored, and their ability to detect dsDNA has been demonstrated. Polyimide pores are used due to the very stable transport properties reported above [8]. Figure 8 (top) shows the ion current recorded through a single conical polyimide pore (tip diameter 20 nm), with a voltage of 300 mV applied before adding DNA (control measurement or baseline). After adding the DNA to the solution on the narrow side of the pore, numerous ‘events’ are observed (Fig. 8 (center)). The majority of them are of very short duration (< 0.1 ms) and do not correspond to DNA translocations but rather to short collisions of DNA molecules with the pore. This effect has been reported also by other groups with both protein and solid-state nanopores [16, 17].)

The events that correspond to molecules actually translocated through the pore (based on thresholds of minimum depth and duration, derived from previous estimates of translocation speed through these pores [7]), have an average depth of 328 pA (3.5 % of the open-pore current) and an average duration of 11.9 ms. The events have various shapes (Fig. 4), which was expected due to the range of supercoiled and relaxed configurations in which the plasmid molecules exist. One can imagine therefore that DNA enters the pore in various configurations, some more tightly packed that will pass through quickly, and others in irregular, complex configurations that will be pass more slowly, with erratic current signals due to varying degrees of blockage [4].

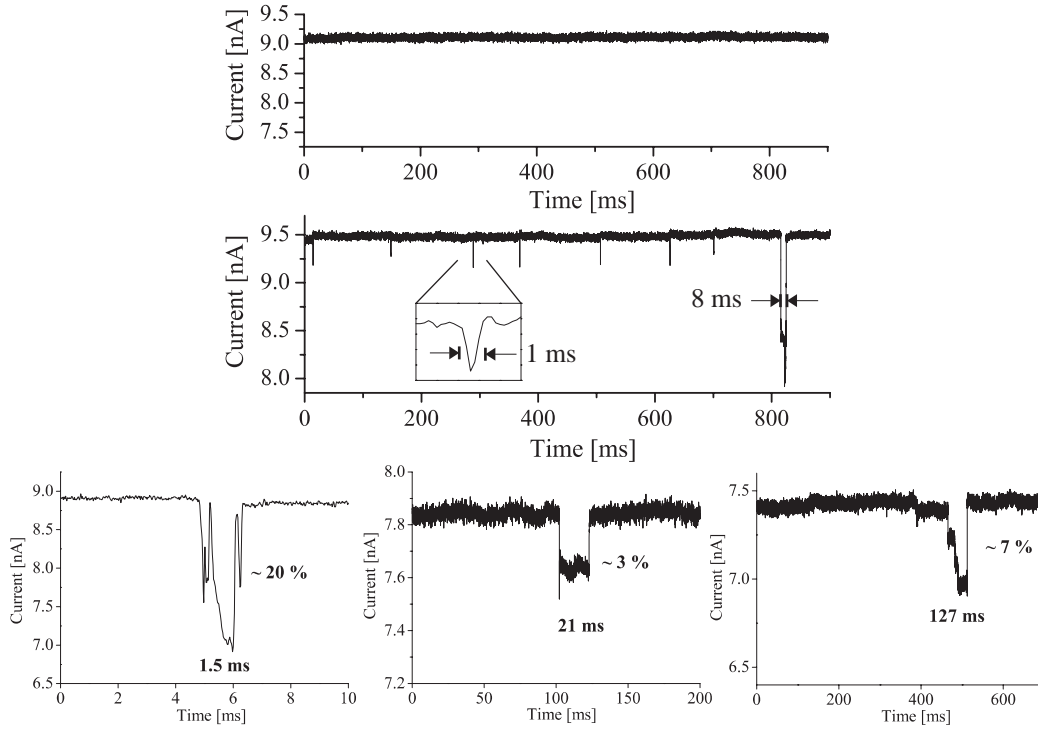


FIG. 8. *Current blockages caused by DNA (top) Reference measurements with electrolyte only do not show any current “events” comparable to those observed in the presence of DNA. (center) Transient decreases in the ionic current in the presence of DNA indicate translocations (e.g. 8.3 ms) or collisions of molecules with the pore without translocation (e.g. 0.1 ms). (bottom) Examples of DNA translocation events of different sizes and shapes that most likely correspond to DNA molecules passing through the pore in different conformations. These measurements were done with a pore of $d \sim 20$ nm at 300 mV [4].*

As reported in [7], the ability of an asymmetric Kapton nanopore not only to detect individual double-stranded DNA molecules but also to differentiate between DNA molecules of different lengths has been investigated. A 4.4 kb plasmid was used, which was cut with restriction enzymes to produce two sticky-end fragments, 284 bp and 4.1 kb. This large ratio of DNA fragment lengths was utilized to enhance the separation in the expected distribution of blockage durations. The conductivity cell, specially designed for the measurements, was filled with 1 M KCl, buffered to pH 7.2 with phosphate buffered saline. Further, 0.01% Triton-X100 was added to prevent adsorption of DNA onto the Kapton film and the surfaces of the cell. A voltage of 120 mV was applied across the nanopore, which is typical of previous investigations on DNA translocations through an α -hemolysin pore [18]. The baseline current was 710 pA and no deflections in current flow were seen (Fig. 9(a)). After adding DNA to a final concentration of 0.5 $\mu\text{g}/\mu\text{L}$ on the side of the Kapton foil with the small opening, the current trace shown in Fig. 9(b), displaying numerous events was recorded.

Figure 9(c) shows the blockage duration histogram of a 10 minute recording, a part of which is shown in Fig. 9(b). A total of 266 blockade events were considered. The histogram presents the distribution of events shorter than 1.6 ms, fitted to the sum of two Gaussians, whose peaks correspond to the mean blockage times. The first peak at 0.16 ms was attributed to bumping of the polymer, i.e. interaction of the DNA with the pore without translocation, as described as well for α -hemolysin. The second Gaussian has a peak at 0.42 ms, which was attributed to the translocation of the 284 bp DNA fragment. Events of several ms were also recorded and attributed to the translocation of 4.1 kb DNA fragments. By this and other analyses, it was demonstrated that a 4-nm pore in Kapton film is able to detect DNA molecules and to distinguish between DNA polynucleotide of different lengths based on the translocation times [7].

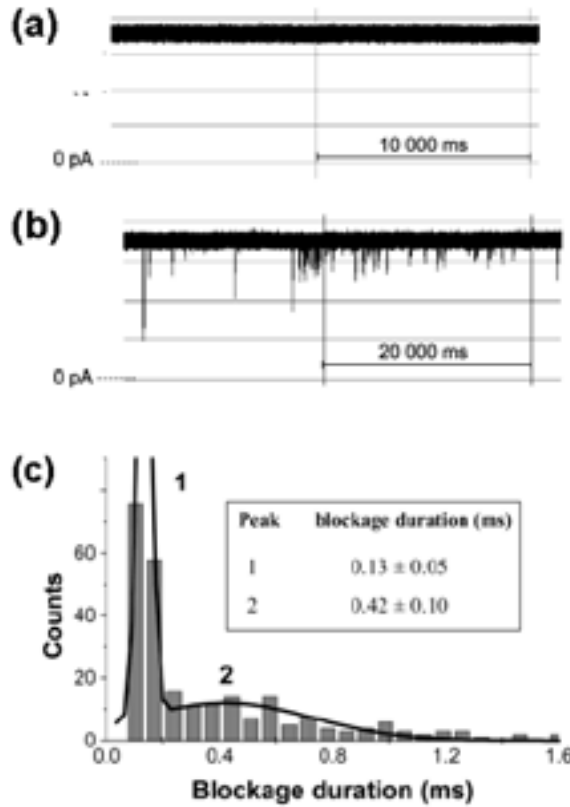


FIG. 9. (a) Ion current versus time measured in 1M KCl pH 7.2 as a control. (b) Current blockages caused by DNA containing 284 bp and 4.1 kb ds DNA fragments. (c) Histogram of blockage durations for the data from the recording in (b) [7].

3. CONCLUSIONS AND FUTURE WORK

Single conically shaped nanopores in polymer films have been prepared and their transport properties characterized. It has been shown that asymmetric charged nanopores function as an ionic diode transporting cations preferentially from the narrow entrance towards the wide opening of the pore. The mechanism of rectification is based on (i) asymmetry of electrostatic interactions inside a nanopore and (ii) electromechanical gate, which changes the pore diameter at various voltages applied.

The future work will be continued in two directions: (i) fundamental studies of ion transport through nanopores and (ii) improving functioning of the DNA sensor. There are still many fundamental phenomena, which have not been studied with asymmetric nanopores. So far we have focused on transport of ions through nanopores. As the next step we plan to study transport of neutral molecules through a membrane with conical pores. It has not been checked yet how the restricted geometry of nanopores influences transport of neutral species; we plan to investigate this issue with pores of various diameters.

We would also like to improve functioning of the nanoporous DNA sensor. The emphasis will be given on studies of dependence of translocation (event) duration on applied voltage, as well as dependence of event frequency on DNA concentration. Translocation of proteins of various isoelectric points will also be accomplished.

Finally, we would like to mention the suitability of etched ion track membranes for the production of metallic, semi-metallic and semiconducting nanostructures (e.g. nanowires and nanospheres). At GSI nanowires of different sizes, shapes and materials have been created by electrochemical deposition in the pores of polycarbonate and PET membranes [19-21]. Investigation of the physical properties of the nanowires (e.g., electrical, optical, thermal) relevant for applications in fields such as nanoelectronics, optoelectronic and sensorics will be continued [22-23].

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RADIATION SYNTHESIZED FUNCTIONAL POLYMER SUPPORTS WITH TAILOR-MADE PROPERTIES FOR SEPARATION AND PURIFICATION

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Abstract

In the framework of the CRP we have worked on the synthesis of porous polymer supports by in-situ radiation initiated polymerization and crosslinking of monomer solutions. The results of our systematic investigation of the pore formation during the radiation-initiated synthesis is reported here. The characteristics of this reaction are that no initiator is needed, and monoliths with the same chemical structure but of various sizes, shapes and porous characteristics can be prepared. The variables affecting the properties of the final polymer are: monomer concentration, type of solvent, irradiation temperature, dose and dose rate. We have showed that when diethyleneglycol-dimethacrylate (DEGDMA) is used as the monomer, monoliths of good flow-through characteristics (with large channel-like pores in the μm range) and appropriate rigidity can be prepared when lower alcohol (methanol, 2-propanol) is used as a solvent, and the monomer concentration is between 20 – 40 v %. The optimum dose is between 20 and 40 kGy, at a dose rate between 10 – 16 kGy/h. Copolymer monoliths from DEGDMA and glycidyl methacrylate (GMA), DEGDMA and hydroxyethyl methacrylate (HEA) and DEGDMA and N-isopropylacrylamide(NIPAAm) were also obtained. Increasing GMA ratio in the feed solution decreased of the pore size of the monolith, while increase in HEA and NIPAAm ratio resulted in higher flow-rate. All columns were tested for applicability in HPLC separation of proteins, amino acids and nucleic acids.

1. OBJECTIVE OF THE RESEARCH

The main objective was synthesis of porous functional supports in shape of monoliths by radiation initiation, starting from single and two monomer solutions, as well as the preparation of radiation-grafted monoliths. The aim of the study was to show the effect of the synthesis conditions on the properties of monoliths, predominantly with respect to size, porous structure and flow characteristics. Monolithic columns may have potential application in size-exclusion chromatography, hydrophobic chromatography and affinity chromatography of large molecules, for separation and purification proteins, antibodies and viruses.

2. INTRODUCTION

In the past several decades macroporous cross-linked polymers mostly in form of spherical particles have been used in a variety of applications including chromatographic separation and purification, detection, immunodiagnosis, adsorbents and combinatorial chemistry. The important characteristic of such polymers is the retention of the porous structure even in the dry state. Their morphology is rather complex, it consists of microglobules aggregated in larger clusters, and the pores are actually the irregular voids between clusters (macropores), between globules (mesopores) or within globules (micropores). In a search for enhanced and simpler chromatographic separation media, it was realized that a macroporous polymer in a form of a continuous rod could be a useful alternative to columns packed with mono-sized particles [1,2]. Such a porous polymer rod, often called "monolith" is characterized by a system of interconnected pores of bimodal distribution, with small pores providing the surface area for specific interactions, while the larger channels allow a high flow rate at moderate pressures.

Therefore the advantages of using such monoliths in chromatography include speed, capacity and resolution. The nature of the pores allows easy permeability for large molecules. Monolith is therefore the column of choice for separation of proteins, pDNA and viruses. Moreover, it eliminates all problems related to the column filling procedure and shattering of beads resulting from osmotic shocks during cycling. These macroporous polymeric rods are usually prepared by a simple molding process that was introduced in the early 1990s [3, 4].

The general procedure of this method consists in polymerization of a monomer (or a monomer mixture) and a cross-linker by an initiator in the presence of at least one porogenic solvent in an unstirred mold. Cleavage of the initiator for radical polymerization is usually induced thermally at a particular temperature. The variables that control pore size distribution are the percentage of the monomer, the type of the porogen, the concentration of the free radical initiator in the reaction mixture and the reaction temperature. Photo-induced decomposition of the initiator can also be used in which case the synthesis is much faster and can be used at any desired temperature [5,6].

We have shown that it is also possible to prepare monoliths in molds by generating radicals with ionizing radiation [7,8]. We had been using the method of radiation-initiated precipitation polymerization to prepare microspheres for biomaterial immobilization and diagnostic purposes [9] as well as for protein purification [10], and have found out that by irradiation of a same monomer solution, either microspheres or porous polymer, so called "monolith" can be obtained. This method has the advantage of generating radicals directly on the monomer, and therefore no initiator is needed. The synthesis can be done at any desired temperature and in a very short time, even within minutes. Owing to the greater penetration depth of ionizing radiation over photo-initiated polymerization, the size and shape of the monoliths can be optimized for the intended application. Functional groups can be introduced either during the synthesis or in a separate step. The characteristics of this method (modification of the radiation-initiated precipitation polymerization used successfully to prepare monodisperse polymer microspheres [11-13]) are that a homogeneous solution of a bi-functional monomer in an organic solvent is irradiated without stirring, and that phase separation occurs because of the insolubility of cross-linked particles. The monomer concentration and the type of porogenic solvent(s) are considered as the factors most profoundly influencing the properties of the final product. Other important factors are the irradiation temperature, the dose and the dose rate.

This report presents the systematic study to develop a radiation-initiated polymerization and cross-linking method for preparation of macroporous polymer rods. The aim of this study was to define the relationship between the porous properties and the synthesis parameters that control them, and to test the prepared monolithic columns for chromatographic applications.

3. MATERIALS AND METHODS

3.1. Synthesis of the monoliths

Teflon tubes filled with deoxygenated solutions containing different concentrations of diethyleneglycoldimethacrylate (DEGDMA), DEGDMA-hydroxyethylmethacrylate (HEA), DEGDMA-glycidylmethacrylate (GMA) and DEGDMA- N-isopropylacrylamide (NIPAAm) in various solvents were placed in plastic bags, filled with nitrogen and irradiated on a ^{60}Co gamma source with doses from 1 to 50 kGy, at different dose rates and temperatures. Grafted monoliths were prepared by simultaneous irradiation of a DEGDMA monolith in various monomer solutions.

Alternatively, used stainless steel chromatographic columns (225 mm x 4 mm ID and 450 mm x 4 mm ID) were cleaned, sealed on one side, filled with the monomer solution, sealed on the other side and irradiated. After the irradiation, the column was directly connected to a chromatograph by standard column fitting. First the solvent was pumped through for cleaning purposes then acetonitrile, tetrahydrofuran, water or methanol was used as the mobile phase for back-pressure measurements and separation experiments.

3.2. Characterization of porous monolith samples

The characterization was performed by spectroscopy (ATI Mattson RS-1 FTIR spectrometer, equipped with an MTEC 300 photoacoustic detector) and electron microscopy (JEOL JSM 5600LV). For spectroscopy and microscopy, 1 mm thick samples were cut from the tube.

To measure the flux, the tubes were provided with fittings, attached to a chromatographic pump, and solvent was pumped through them. The time needed for 5 ml solvent to pass through the column at constant pressure was measured. Usually several different pressures were used, and all measurements were done in triplicate. The pore size distribution was determined by using a mercury intrusion porosimeter (courtesy of Dr. Frantisek Svec, University of California, Berkeley, USA), and the surface area was calculated from the BET isotherms of nitrogen adsorption (courtesy Dr. Krisztina Laszlo, Technical University Budapest). Samples were also prepared to test the mechanical properties by stress-strain measurements and calculating the Young modulus.

4. RESULTS AND DISCUSSION

Radiation initiation has the advantage of much faster preparation over the most often used thermally initiated radical polymerization as well as the possibility of in-situ preparation of porous supports at any desired temperature. This method also has the advantage of the greater penetration depth of ionizing radiation over photo initiated polymerization, thus monoliths of any desirable size can be prepared. Another important advantage of the preparation inside the actual column is to avoid all the problems associated with column filling.

A great number of monomers can be used for preparation of monoliths, and here we report results obtained with DEGDMA and its copolymers with HEA, GMA and NIPAAm. For practical purposes, the most important property of the monolith is the permeability to liquids at as low pressure as possible, and this can be achieved with large pores. At the same time, some applications require large surface area for high capacity, a requirement that needs small pores [5]. Therefore, the monoliths should be tailored for each specific application with suitable pore size or pore size distribution. The pore size is a function of the monomer type and concentration, the type of the solvent, the total absorbed dose and dose rate, and the irradiation temperature.

4.1. Monoliths prepared from single monomer (DEGDMA)

When a monomer is irradiated in an organic solvent, radicals are generated homogeneously in the whole solution. These radicals start the polymerization forming linear, branched and finally cross-linked molecules. Since the monomer used in this paper has two functional groups, the polymerization and cross-linking are almost simultaneous reactions. Being insoluble, the cross-linked molecules precipitate, forming the nuclei of the growing particles. With further irradiation, radicals are generated both on the monomer in solution and in the precipitated globular nuclei that continue to grow in size, interconnect with neighbors, and finally form the porous matrix. Fig.1 shows the conversion of DEGDMA monomer into cross-linked polymer when irradiated in methanol at a dose rate of 16 kGy/h. It is seen that although the cross-linking is faster in the more concentrated solutions, the complete transformation of the monomer into cross-linked polymer is accomplished within less than one hour in all cases.

Since the conversion influences the porous properties of the monoliths (generally at lower conversion the monolith has larger pore [14]), the effect of monomer content on the pore size distribution was determined on monoliths irradiated with 30 kGy, at a dose that is higher than needed for complete conversion.

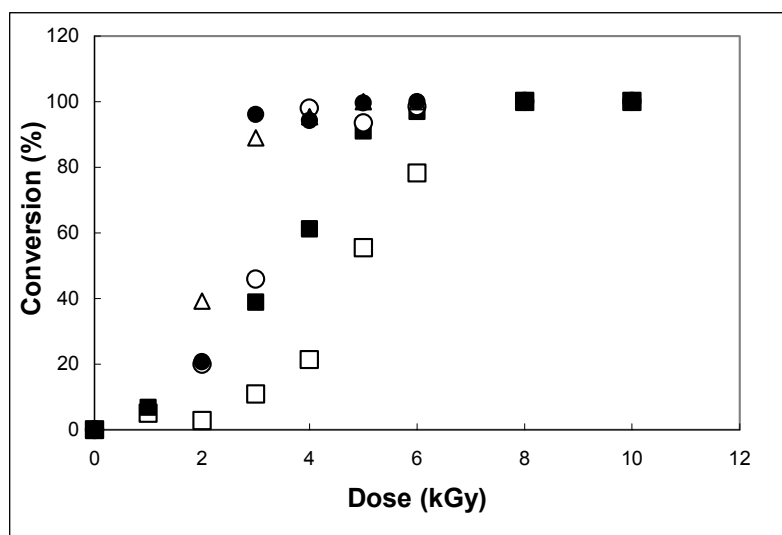


FIG. 1. Reaction kinetics of polymerization/cross-linking in solutions of: (a) different DEGDMA content in methanol: 10 v% (open square), 20 v% (full square), 30 v% (open circle), 40 v% (full circle), and 50 v% (triangle).

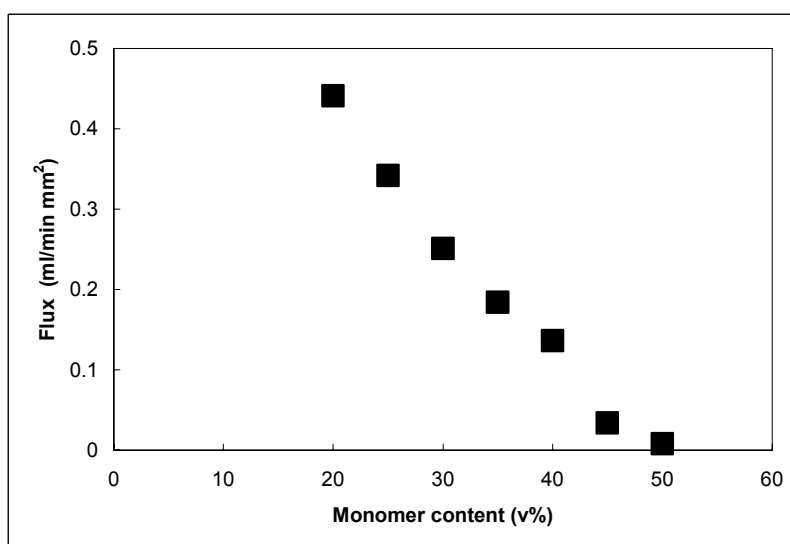


FIG. 2. Flux dependence on the monomer content in the feed solution in methanol. The irradiation was done at 25 °C, with dose rate of 16 kGy/h, up to a total dose of 30 kGy. The flux was measured with acetonitrile pumped through the column at different pressures between 0.1 and 0.4 MPa, then recalculated to 0.1 MPa.

The results of the effect of the monomer concentration on the flux are given on Fig.2. All data points were obtained by measuring the flow rate at several different pressures, then normalizing the data for the pressure of 0.1 MPa. We have also investigated whether the monoliths can be kept dry, so we have measured the flux trough the columns kept in closed (wet) state and in open (dry) state. Each point represents the average of at least four measurements. No real difference was seen between wet and dry samples As the results show, monoliths prepared from solutions with increasing monomer concentration show lower flux, and no measurable flow could be obtained with the column prepared from 50 v % monomer with pressure up to 0.4 MPa.

More accurate information about the pore sizes and their distribution as well as the surface area could be obtained by mercury porosimetry and nitrogen adsorption measurements. Mercury porosimetry monitors the changes in big and medium sized pores, and nitrogen adsorption method sees the small pores that are important in the calculation of the specific surface area. Figure 3 shows the results obtained on selected samples. Additional data are summarized in Table I.

TABLE I. EFFECT OF MONOMER CONCENTRATION ON THE MONOLITH PORE VOLUME AND SURFACE AREA

DEGDMA in methanol [%]	Pore volume [mlg ⁻¹]	Median pore diameter [μm]	S _{BET} [m ² g ⁻¹]
10			3.7
20	2.46	2.91	2.6
25			2.1
30	1.72	3.54	1.7
40	1.27	3.88	0.8
45	0.94	2.52	0.8
50	0.69	0.17	11

The pore volume and diameter were calculated from mercury porosimetry, while the surface area was calculated from the BET isotherm of nitrogen adsorption measurements. It is seen, that those data confirm the previously obtained flow-data and SEM picture results.

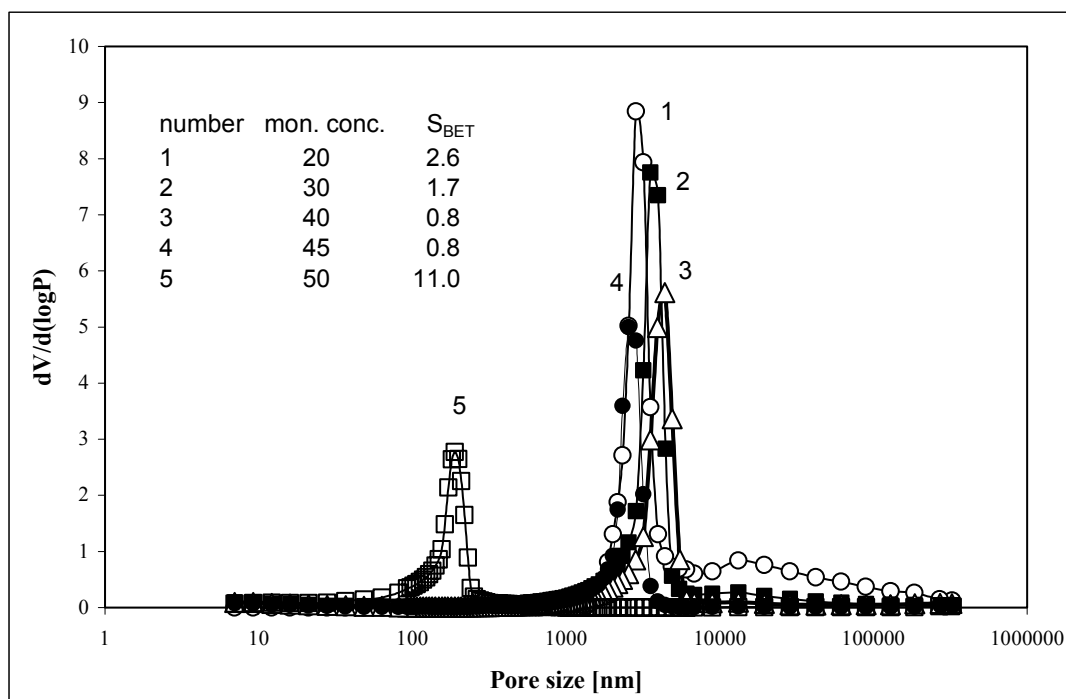


FIG. 3. Differential pore size distribution profile determined by mercury intrusion porosimetry for monoliths prepared by irradiation of solutions with following DEGDMA content in methanol: 20 v% (1), 30 v% (2), 40 v% (3), 45 v% (4) and 50 v% (5). The irradiation was done at 25 °C, with dose rate of 16 kGy/h, and dose of 30 kGy.

For chromatographic application, it is necessary for a liquid to be able to flow through the pores at a pressure as low as possible. To test our samples, they were connected to an HPLC pump. Acetonitrile and THF were used as solvent to obtain the flow rate – pressure diagrams, some of which are shown on Figure 4.

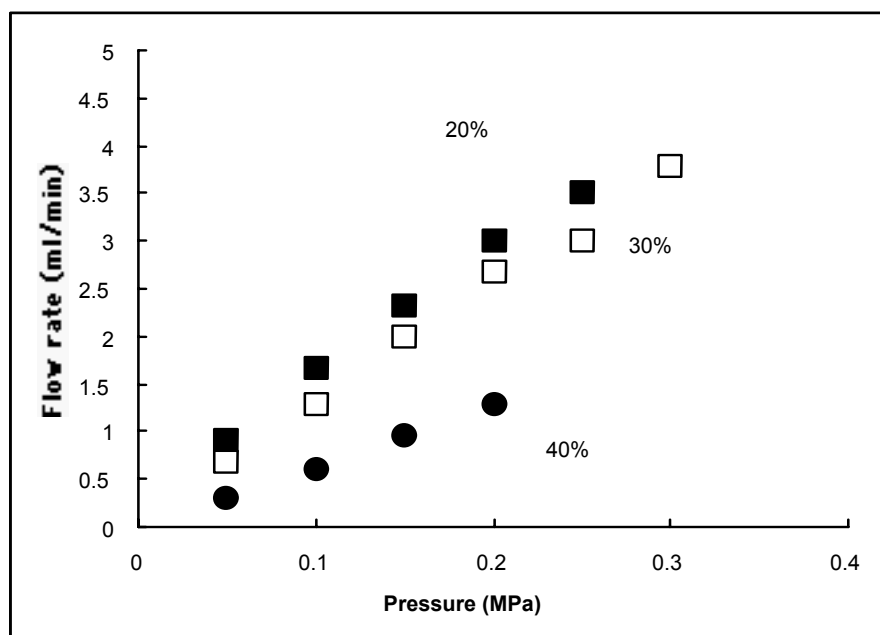


FIG. 4. Flow rate dependence on the pressure for columns with monoliths synthesized from solutions with different DEGDMA content. Acetonitrile was pumped through the tubes.

The solvent has immense effect on the porous structure of the monoliths. We have found that alcohol leads to big pores, while solvents as acetone, THF, ethylpropionate and dioxane lead to monoliths with very small pores that require high pressure for solvents to pass through, thus makes them almost useless in flow-through applications. This fact can be explained with better solubility of the monomer in the organic solvent [5]. The polymerization starts from an initially homogeneous solution and the growing polymer precipitates at some point. Further polymerization and crosslinking continues both in the swollen nuclei and in solution. When the solvent is a good solvent for the polymer, phase separation occurs later, the nuclei are smaller in size but larger in number, and the resulting pores will thus be smaller. Fig. 6 shows some examples of the pore structure of monoliths obtained from different solvents under identical synthesis conditions.

The porosity of these samples was also investigated (Figure 6 and Table II). Again, the pore volume and diameter were calculated from mercury porosimetry, while the surface area was calculated from the BET isotherm of nitrogen adsorption measurements. It is seen, that those data confirm the SEM picture results.

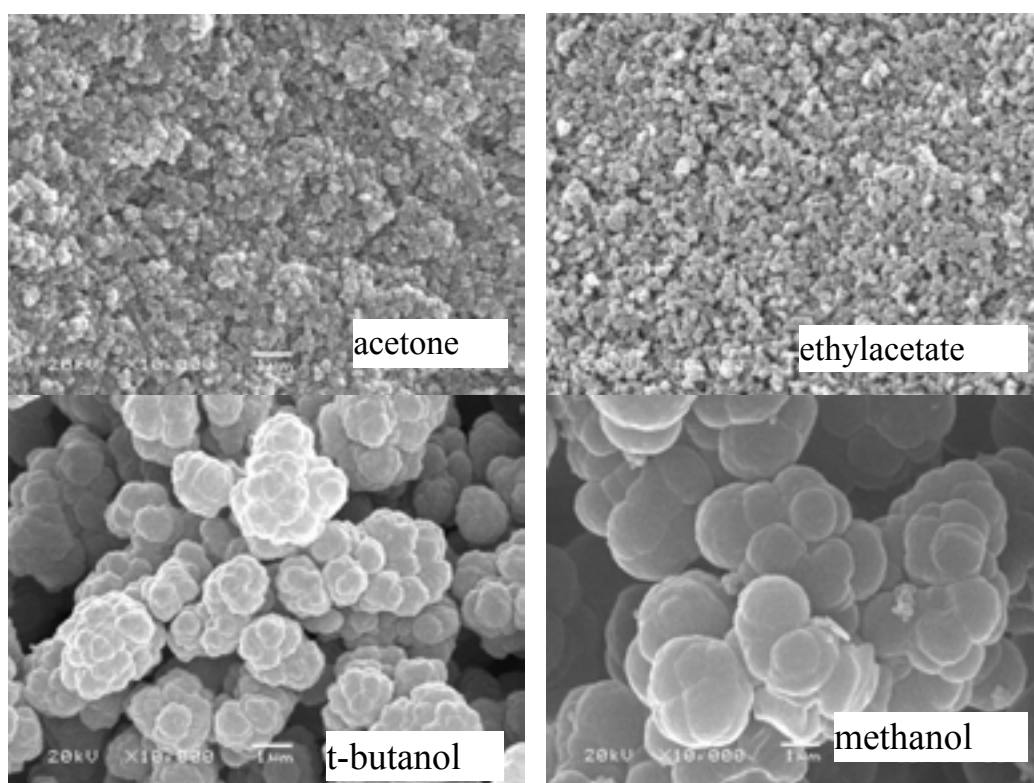


FIG. 5. Solvent effect on the pore size of the monoliths

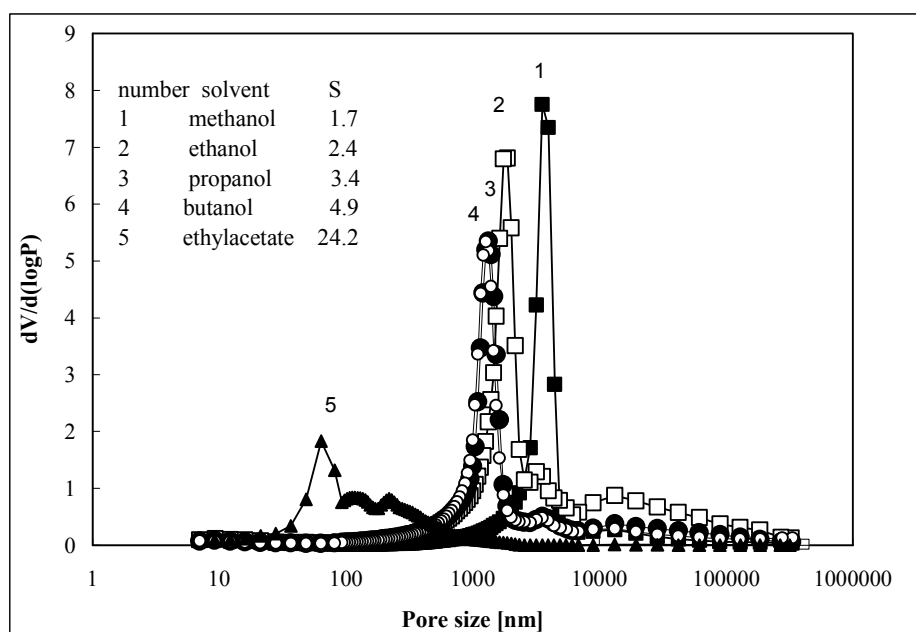


FIG. 6. Differential pore size distribution profile determined by mercury intrusion porosimetry for monoliths prepared by irradiation of 30 v% DEGDMA solutions in the following solvents: methanol (1), ethanol (2), 2-propanol (3), tert-butanol (4), and ethylacetate (5). The irradiation was done at 25 °C, with dose rate of 16 kGy/h, and dose of 30 kGy.

Additional data on the pore volume and diameter calculated from mercury porosimetry and surface area calculated from the BET isotherm of nitrogen adsorption measurements are summarized in Table II.

TABLE II. SOLVENT EFFECT ON THE MONOLITH PORE SIZE AND SURFACE AREA

30% DEGDMA in solvent	Pore volume [ml g ⁻¹]	Median pore diameter [μm]	S _{BET} [m ² g ⁻¹]
Methanol	1.72	3.54	1.7
Ethanol	2.91	1.91	2.4
2-propanol	1.81	1.34	3.5
tert-butanol	1.74	1.27	4.9
Ethylacetate			24.2
Aceton	1.21	0.085	67.7

To test the samples in real flow-trough application, they were again connected to the HPLC pump. The flow rate-pressure curves for two solvents are given on Figure 7. Only samples prepared in alcohol could be used for such a test.

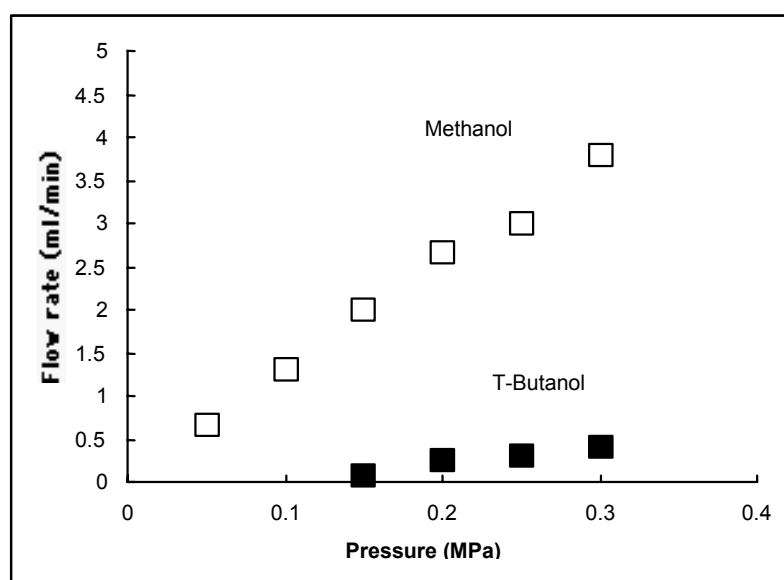


FIG. 7. Solvent effect on the flow characteristics of monoliths

Dose and dose rate effects on the monolith morphology is a unique tool of this method to tailor the polymer porosity without changing the composition of the feed solution. Increased absorbed dose and lower dose rate will produce smaller pores. Higher absorbed dose means higher degree of crosslinking that decreases the pore size and increases the rigidity of the matrix. Accordingly, the flux was also reduced through monoliths with high crosslink density (Fig. 8).

As mentioned earlier, although the dose when complete conversion of monomer is attained is about 7 kGy, monoliths irradiated with less than 10 kGy are too weak to withstand even the low pressure needed in a flow-trough application. Therefore, only columns irradiated with doses in the range of 20-40 kGy were used for testing them by connection to the HPLC pump (Fig. 9) As seen, all columns tested show similar and good characteristics.

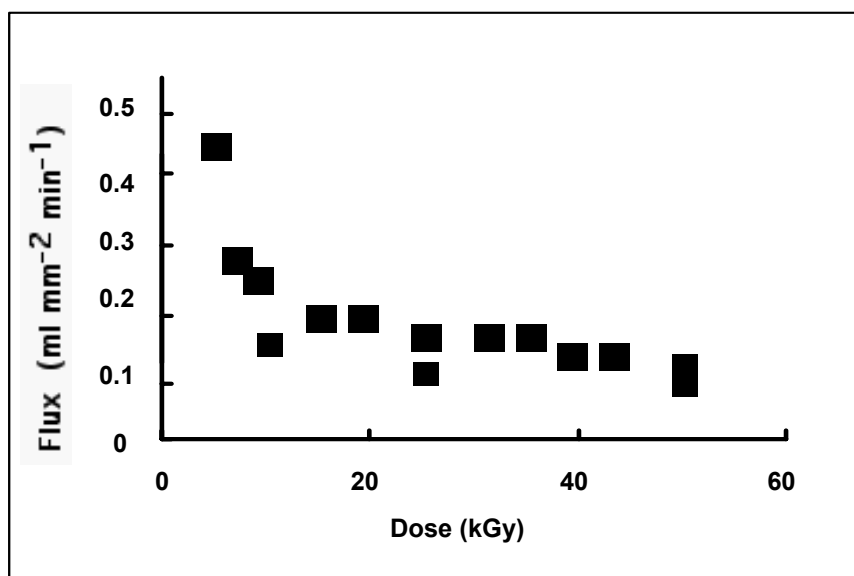


FIG. 8. Flux dependence on the dose when irradiating a solution of 30 v% DEGDMA in methanol. The irradiation was done at 25 °C, with dose rate of 16 kGy/h. The flux was measured with acetonitrile pumped through the column at different pressures between 0.1 and 0.4 MPa, then recalculated to 0.1 MPa.

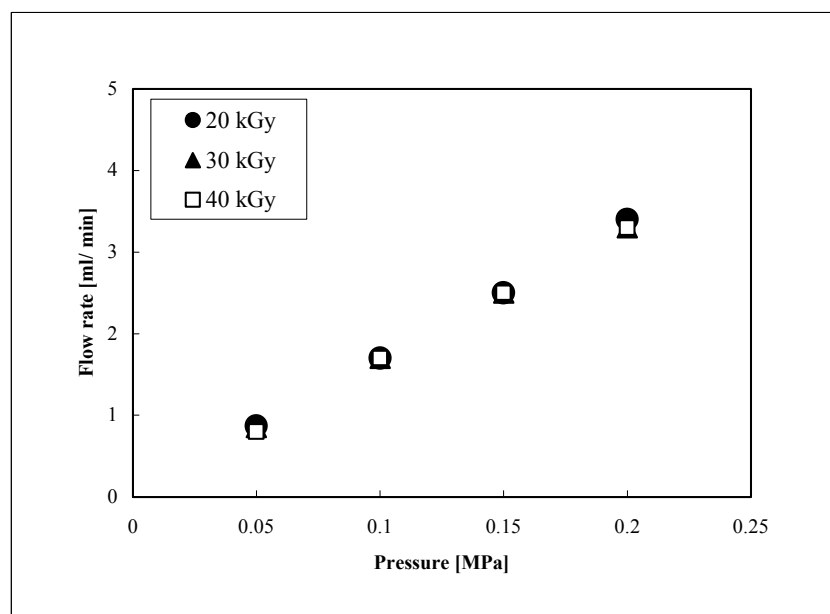


FIG. 9. Flow rate dependence on the pressure for monoliths synthesized from 30 v% DEGDMA in methanol with different doses. Acetonitrile was used as eluent.

As mentioned, the dose rate is another tool in radiation initiation for tailoring the polymer porosity without changing the composition of the feed solution. Monoliths prepared with low dose rate have smaller pores than monoliths obtained at higher dose rate.

Since higher dose rate means increased rate of radical formation, but also to increased rate of termination, which in turn may mean shorter time for monomer incorporation before precipitation. Therefore the pores will be larger. Both flow-trough experiments and SEM photographs show this fact (Fig. 10).

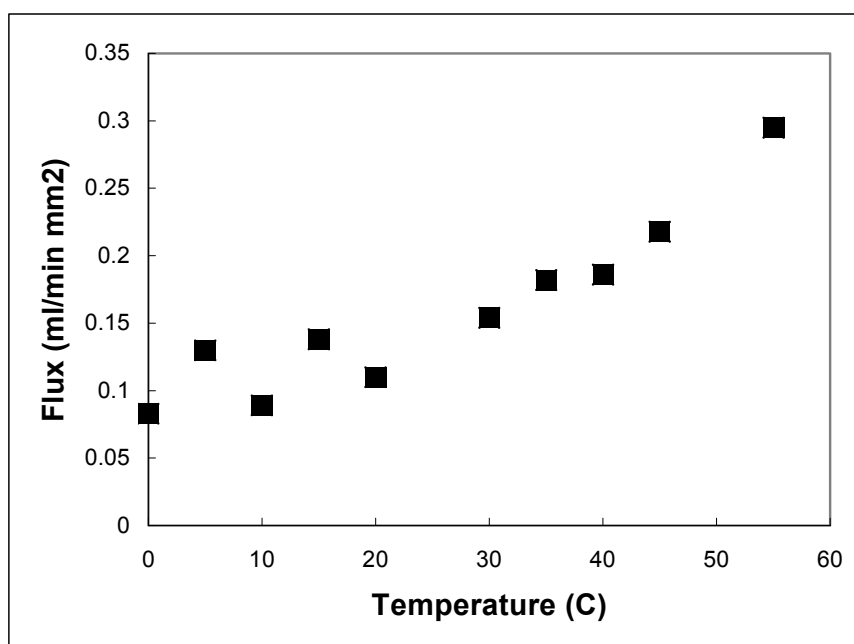


FIG. 10. Flux dependence on the irradiation temperature when irradiating a solution of 30 v% DEGDMA in methanol with dose rate of 16 kGy/h. The flux was measured with acetonitrile pumped through the column at different pressures between 0.1 and 0.4 MPa, then recalculated to 0.1 MPa.

4.2. Monoliths prepared by copolymerizing DEGDMA and another functional monomer

Monoliths prepared by copolymerizing DEGDMA with GMA

Because of their macroporous inner structure, monoliths provide both significant adsorption capacity and improved mass transport of biomolecules. As all biological interactions taking place *in vivo* are based on the formation of specific biomolecule complexes, such as enzyme-substrate, antigen-antibody and receptor-ligand pairs, affinity chromatography is based on the natural affinity of a substance to its complement immobilized on the stationary phase. We have used glycidylmethacrylate (GMA) for co-polymerization with DEGDMA in order to introduce epoxy groups to our monoliths that can react with the amino groups on the ligand. Depending on the amount of added GMA however, not only the amount of epoxy groups on the column, but the pore size was also changed.

Smaller pores certainly influence the flow characteristics but with sufficient epoxy groups on the surface, still sufficient flux could be obtained, as shown on Fig. 11 and Fig. 12.

Epoxy-containing monoliths were shown to have great potential in immunoaffinity separation [15]. When short monolithic columns were used, the method provided a unique possibility of evaluating the formation of bioaffinity pairs in real time by using high flow rates up to 10 ml/min. The dissociation constants of such affinity complexes have been found to be 10^{-7} M for protein-protein and 10^{-6} M for protein-peptide systems. These values are practically identical to those obtained in free solution.

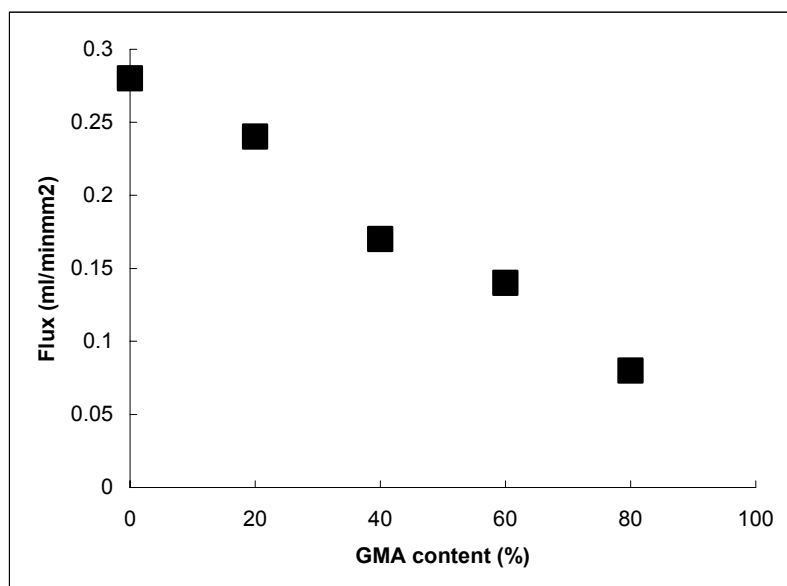


FIG. 11. Flow characteristics of the monoliths synthesized with different GMA content in the feed solution of 30 v% DEGDMA+GMA in methanol, irradiated at dose rate of 16 kGy/h and dose of 30 kGy. The flux was measured with acetonitrile pumped through the column at different pressures between 0.1 and 0.4 MPa, then recalculated to 0.1 MPa.

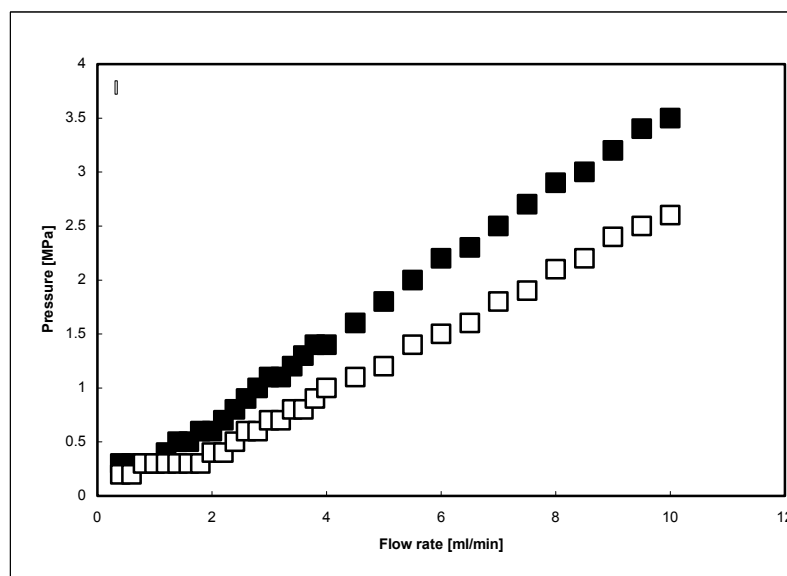


FIG. 12. Pressure response at increasing flow rate for a monolith synthesized by irradiating a 30 v% DEGDMA/GMA (18/12) in methanol solution in a stainless steel column (225 mm x 4 mm) at 25 °C, with dose rate of 16 kGy/h, and dose of 30 kGy. Two different eluents, water (black) and methanol (white) were used.

Another important use of the epoxy-functionality containing monolithic systems is in solid phase peptide synthesis (SPPS). It is possible to carry out synthesis in situ on monolithic disc and to use these units in affinity separations [16]. Other rapidly-growing areas that might use monoliths are enzyme bioreactors and microfluidics.

Monoliths prepared by copolymerizing DEGDMA with HEA

We have also prepared DEGDMA monoliths of different hydrophilicity by co-polymerization of DEGDMA and HEA. Increasing HEA concentration does not only changes the pore size, but the monolith becomes more gel-like, and at HEA concentrations above 20% turns to a soft gel that swells greatly, but is unsuitable for applications as chromatographic column.

Monoliths prepared by copolymerizing DEGDMA and NIPAAm

PolyNIPAAm is a well-known thermoresponsive polymer, having LCST at around 32 °C. When co-polymerized or grafted on a monolith, the pore sizes can be varied with changes in the temperature, and with this also the separation procedure can be altered. Besides, instead of organic solvents, water can be used as eluent, and this has numerous advantages, for example in environmental protection. The results of flux dependance on the NIPAAm content in the copolymer monolith are similar to those obtained with HEA. With increasing NIPAAm concentration, the gel-properties of the monoliths increase leading to higher swelling. We have also prepared monoliths grafted with NIPAAm. The NIPAAm-grafted monoliths change their pore size and hydrophobicity with changes in temperature, making protein separation easier and with minimum damage. According to our first results, the grafted samples open the pores of the monolith and allow about three times higher flux at 40 °C then at 20 °C. These measurements are in progress and will be continued.

4.3. Testing of the monoliths for separation of proteins

All the various types of monolithic columns prepared were tested for separation of proteins, amino acids and nucleic acids by using various eluents, such as THF and acetonitrile, but most successful separations were achieved with water and methanol. As illustration, the separation of HAS and Thymine on a DEGDMA/HEA column is shown on Fig. 13.

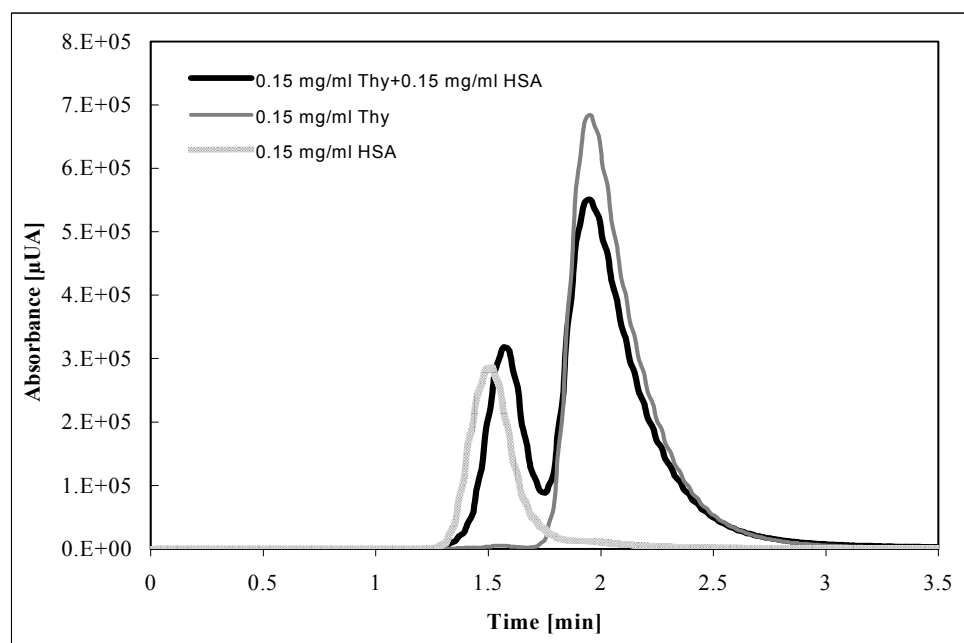


FIG. 13. Separation of HAS and Thy on the DEGDMA/HEA column (black curve). Individual HAS and Thy trace is shown by gray color. The eluent was water, flow rate 0.8 ml/min.

Future plans include the continuation of the work started so far, with special emphasis on the environmental-friendly water-based separation, and synthesis of supports with multifunctional (multiaffinity) properties. Such columns could be used for the quantitative comparison of biological complementary pairs formed under dynamic conditions. This would allow the selection from a group of possible candidates of the affinity ligand which will most efficiently isolate the biomolecule of interest.

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SYNTHESIS, CHARACTERIZATION AND UTILIZATION OF RADIATION SYNTHESIZED STIMULI-RESPONSIVE HYDROGELS AND MEMBRANES

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Abstract

The techniques of gamma and electron beam irradiation have been used to synthesize stimuli response gels and grafted membranes. Fast response thermo-sensitive gels of poly (vinyl methyl ether) (PVME) and poly (N-isopropyl acrylamide) (PNIPA) gels were synthesized using gamma and electron beam irradiation under well defined conditions. The gels were characterized for their swelling-deswelling kinetics and their swelling behaviour was related to their microstructures by studying the pore size distribution using positron annihilation lifetime spectroscopy. Linear poly (vinylbenzyltrimethylammonium chloride) and its gel, responsive to ionic concentration, were prepared by gamma irradiation. NIPA-co-ionic gels were prepared by gamma ray co-polymerization of NIPA with Vinylbenzyltrimethylammonium chloride (VBT) and *p*- sodium styrene sulphonate (SSS) in order to study the effect of incorporation of ionic groups on various characteristics of the responsive hydrogels. The synthesized gels were tested for their usefulness especially for concentration of dilute biological solutions. The results of these studies are presented in this paper.

1. INTRODUCTION

The stimuli-responsive hydrogels are crosslinked polymers that undergo abrupt reversible changes in mass and volume in response to minor changes in the gel's environment such as temperature, pH, ionic concentration, solvent composition, electric field, light intensity or a specific chemical trigger like glucose. The devices based on these gels can be made to function reversibly in response to a specific trigger and are therefore being probed worldwide as potential materials for novel applications such as drug delivery systems, mechano-chemical actuators in robotics, as artificial nerves and for concentrating protein/enzyme solutions near room temperature[1]. Radiation crosslinking of polymer offers several distinct advantages over conventional crosslinking methods [2]. In recent years interest has also been evinced to use electron beam (EB) machines for irradiating water soluble polymers such as poly (vinyl alcohol) to form hydrogels that can be used as burn dressing [3]. The major difference between gamma and EB irradiation is the dose rates at which the radiation dose can be delivered by the two sources. Typical dose rates with gamma radiation sources are in the range 0.1-5 kGy^h⁻¹, whereas with EB accelerators the dose rate are in the range ~kGys⁻¹. Therefore rate of radical formation may be many orders of magnitude higher in EB irradiation as compared to gamma ray irradiation [4]. Irradiation of concentrated solutions of PVME in aqueous solutions (30% w/v) by gamma radiation to a dose of 100 kGy has been reported to form a crosslinked gel [5-6]. Gel preparation by gamma ray irradiation of dilute aqueous NIPA solution and irradiation studies of NIPA in other solvents has also been reported [7-9]. Thermo-responsive gels of NIPA/PVME prepared at low radiation doses possess poor strength due to low crosslinking and therefore gels of better strength need to be prepared by imparting higher radiation doses. However, this results in a decrease in equilibrium degree of swelling (EDS) of the parent matrix. It has been reported that this decrease in EDS can be overcome to some extent by introducing ionic monomers in NIPA matrix as ionic systems are known to absorb more water because of their inherent characteristic [10,11] Also the copolymer matrices having ionic monomers and NIPA will show thermo-response as well as pH or response to ionic concentration. Therefore gels prepared by introducing ionic monomers like VBT (vinylbenzyltrimethylammonium chloride) or SSS (*p*-sodium styrene sulphonate) in NIPA matrix are expected to show higher EDS, good thermo-response as well as response to types and concentration of ions present in the swelling medium. The ionic interaction between ionic gels and ions in the medium can be utilized for effective separation of ions in the medium.

The work done during this project was aimed at the following:

- Utilization of EB and gamma radiation sources for synthesizing fast response thermo-responsive hydrogels of different microstructures.
- Characterization of the gels produced by their swelling characteristic and exploring the micro structure of these gels by positron annihilation life time studies (PALS).
- Co-polymerization of ionic polymers such as VBT and SSS along with thermo-responsive polymers like NIPA using gamma radiation and subsequently studying the swelling behaviour of copolymers in different mediums.
- Investigating the complexation behavior of gamma radiation synthesized linear PVBT and crosslinked PVBT in presence of various anions.
- Grafting of VBT onto cotton to achieve a matrix for bio-chemical separations
- Exploring the feasibility of these crosslinked or grafted matrices for separation and concentration purposes from dilute solutions.

2. MATERIALS AND METHODS

Reagents and chemicals

All polymer/monomer solutions were prepared using water purified by Barnstead nanopure system. For swelling /deswelling studies triply distilled water was used. The poly (vinylmethyl ether) (PVME) solution was prepared by diluting 50 % w/w solution of PVME ($M_w=90,000$), N-Isopropylacrylamide (NIPA) (Mol wt. 113.16, purity >99%), Vinylbenzyltrimethylammonium chloride (VBT)(Mol wt.= 211.74), *para*-Sodium styrene sulphonate (SSS) (Mol wt = 206.20), N, N-Methylene-bis-acrylamide (MBA) were used as received. All other chemicals used were of AnalaR grade. The cotton cloth used for VBT grafting procured, from a local supplier was boiled in NaOH solution, thoroughly washed with liquid detergent and then vacuum dried prior to grafting studies.

Radiation sources

Gamma radiation from ^{60}Co radiation source in a GC-5000 or GC-900 gamma chamber supplied by BRIT, Mumbai, INDIA and having a dose rate of 6 kGy.hr^{-1} and 0.15 kGyhr^{-1} as determined by Fricke dosimetry with suitable lead attenuators was used for imparting gamma dose to samples. Electron beam irradiation of samples was carried out using an industrial ILU-6 accelerator from Budker Institute of Nuclear Physics, Russia at a dose rate of 10 kGy/pass .

Gel sample preparation

For synthesizing gels by gamma irradiation monomer/monomer mixture/polymer solution of known concentrations were filled in glass tubes (ID=2 cm and l=7-8 cm), deaerated at less than 10^{-3} torr vacuum at liquid nitrogen temperature and sealed. Polymerization was carried out by irradiating the sealed samples at desired dose rates in gamma chamber. The cylindrical gels obtained were soxhlet extracted with water to extract any trapped monomer. The gels so obtained were sliced to thin samples and used for studies. To synthesize gels by EB irradiation flat sheets of gels were obtained by irradiating monomer/polymer solution in polished aluminium moulds of dimension 5 cm x 5 cm x 0.2 cm. The sheets were peeled off from trays soxhlet extracted and used for studies.

Grafting of PVBT on to cotton cellulose matrix

Grafting reaction was carried out by mutual radiation grafting technique using ^{60}Co gamma radiation source. Washed cotton cellulose matrix was completely immersed in known volume of 20 % aqueous solution of VBT in stoppered glass bottles and left for an hour to facilitate the swelling of cotton fabric in monomer solution. The bottles containing cellulose samples and monomer solution were then irradiated in ^{60}Co -gamma chamber for required doses at a dose rate of 2.5 kGyh^{-1} . The grafting yield was determined gravimetrically using equation (1). The detailed study of the radiation grafting of VBT on cotton substrate has been described in our earlier work [12].

$$\% \text{ Grafting} = \frac{\text{Weight of grafted film} - \text{Weight of ungrafted film}}{\text{Weight of ungrafted film}} \times 100 \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. Equilibrium swelling and swelling-deswelling kinetics of thermo-responsive gels

Stimuli responsive gels poly (vinyl methyl ether) and poly (N-Isopropyl acrylamide) whose structures are given below have LCST of 37°C [6] and 34°C[8] respectively.

Figure 1 and 2 show the difference in the equilibrium swelling NIPA gels prepared by gamma and EB irradiation to different doses. Similar differences in equilibrium swelling were seen for PVME gels obtained by gamma and EB irradiation. It was seen that though the gel content for the gels didn't change much for these gels with radiation dose the swelling ratio decreased significantly with increase in dose indicating further irradiation beyond gelation dose contributed to increase in crosslink density of the gels. The swelling curve showed sharp discontinuity in the swollen mass at about 34°C (LCST of NIPA) as observed by earlier workers [13,14].

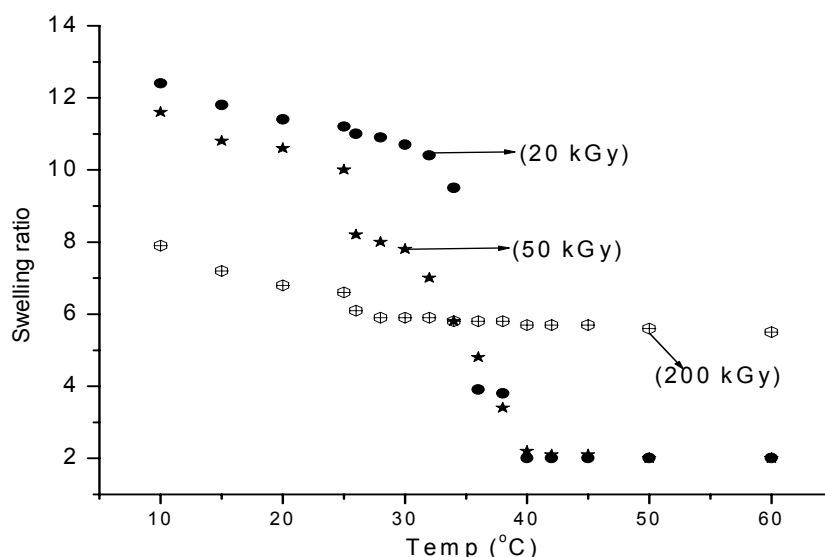


FIG. 1. Equilibrium swelling of gamma crosslinked PNIPA gels at different temperatures

The difference in the equilibrium swelling extent and sharpness in the discontinuity was attributed to the difference in microscopic structure of the gels, induced during synthesis of these gels. For gamma crosslinked radicals are uniformly generated on the polymer chains and inter molecular crosslinking is predominant, resulting in homogeneously crosslinked gels probably with uniform pore size throughout the matrix. On the other hand fast response of EB crosslinked hydrogels was attributed two factors (i) polymerization and crosslinking at extremely high dose rate may result in intra molecularly crosslinked gels and (ii) temperature during EB irradiation may rise above LCST resulting in phase separation in polymerization during crosslinking reaction. Both these factors may result in non-homogeneously crosslinked gels having bigger pore size and hence faster response.

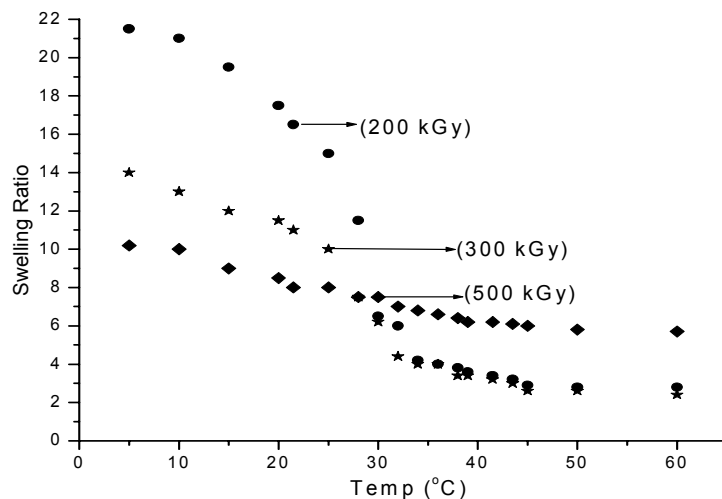


FIG. 2. Equilibrium swelling of EB crosslinked PNIPAA gels at different temperatures

In order to substantiate this hypothesis, PVME gels were prepared under following conditions (i) γ -irradiation at 298 K (i.e. below LCST) (ii) γ -irradiation at 318 K (i.e. above LCST) at a dose rate of 1.5 kGy hr^{-1} (iii) EB irradiation at a dose rate of $10,800 \text{ kGyhr}^{-1}$. Figure 3 shows volume change kinetics of these gels.

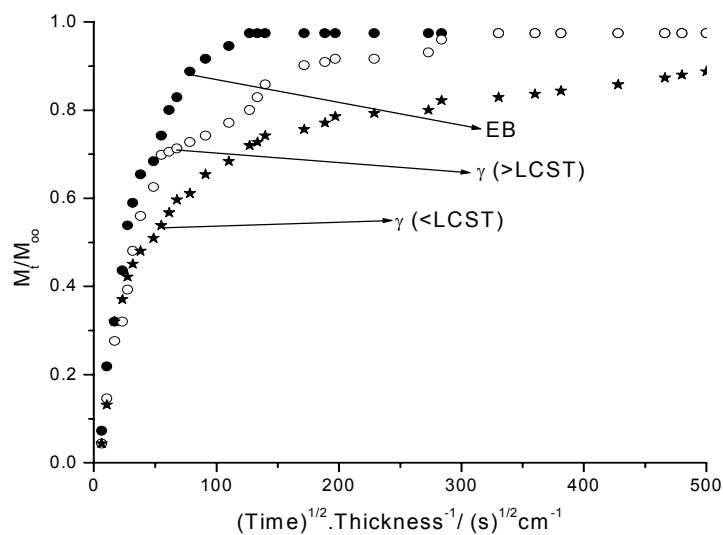


FIG. 3. Shrinking kinetics of gels prepared under different conditions

The figure clearly shows that the deswelling rates for the gels prepared under different conditions followed the order

$$\text{EB} > \gamma \text{ above LCST} > \gamma \text{ below LCST}$$

Indicating higher the inhomogeneity in the crosslinked gels higher the rate of deswelling.

3.2. Positron annihilation spectroscopic studies on radiation crosslinked poly (N-isopropylacrylamide) hydrogels in aqueous solutions and in mixed solvents

Positron annihilation spectroscopy has emerged as a powerful microscopic probe for investigating the subtle differences in the structure of the polymers as it provides direct information regarding the size, concentration and electronic nature of the microscopic holes [15-16]. Positron annihilation lifetime spectroscopy (PALS) was used for investigating poly (N-isopropylacrylamide) hydrogels, prepared by gamma and electron-beam (EB) irradiation. The effect of water content in the hydrogel on the ortho-positronium (o-Ps) lifetime and intensity was investigated. The gels having swelling ratio ~11 were chosen for PALS studies. The lifetime measurements were carried out using a spectrometer with 2 plastic scintillation detectors and having a resolution of 285 ps. The measurement time was adjusted to accumulate a minimum of 106 counts under the peak. The data analysis was carried out using PATFIT to give discrete life time values and code CONTIN was used to get the lifetime distribution.

The lifetime spectra showed three components: a short lived component (τ_1 : 187 to 276 ps) due to annihilation of p-Ps; an intermediate component (τ_2 : 480 ps) due to free annihilation of positrons with electrons belonging to atoms in the bulk; and a long lived component (τ_3 : 1.52 to 3.06 ns) associated with a pick-off reaction with o-Ps in free volume holes. The following semi-empirical relation between o-Ps lifetime (τ_3) and mean free-volume hole radius was used to calculate the radius of free-volume hole.

$$\tau_3 = \frac{1}{2} [1 - (R/R + \Delta R) + 1/(2\pi) \cdot \sin \{2\pi R/R + \Delta R\}]^{-1}$$

Where τ_3 is the o-Ps lifetime in nano-second, R is the mean radius of free-volume holes in nano-meters and ΔR is an empirical electron layer thickness of 0.166 nm.

The results of o-Ps lifetime (τ_3) as a function of water content in PNIPA gels synthesized by gamma and electron beam accelerator showed that in the dried samples of PNIPA, o-Ps life times are similar for both gamma and electron beam irradiated samples (about 1.88 ns), while they are very different in swollen samples of PNIPA for gamma (2.10 ns) and electron beam (2.27 ns) irradiated samples with about 100% water content. This has been attributed to the formation of a gel having a higher degree of intra-molecular crosslinking occurring in the case of EB irradiation (high dose rate) as compared to a uniformly intermolecular crosslinked sample formed at a lower dose rate (gamma irradiated) [17]. Free-volume hole size distribution showed that the distributions for hydrogel prepared by gamma irradiation were more symmetric and Gaussian in nature in both dry and swollen state.

The EB synthesized hydrogels in dry showed only marginal broader distribution as compared to gamma-irradiated sample. However, in the swollen state, a pronounced difference could be seen in EB irradiated hydrogel indicating a non-homogeneity of hole size distribution. The observed positronium lifetime measurements therefore confirmed that micro structural differences existed between gamma and EB-synthesized hydrogels resulting in their very different swelling kinetics. The distribution in positronium lifetime indicated non-homogeneity in the distribution of free-volume holes in EB-synthesized hydrogels. An attempt was also made to study the volume phase transition behavior of PNIPA hydrogels in ethanol-water mixtures with PALS. The o-Ps lifetime (τ_3) was found to depend more on the composition of the gel rather than the degree of the equilibrium [18].

3.3. Swelling of NIPA-co-ionic monomer hydrogels

Ionic monomers vinylbenzyltrimethylammonium chloride (VBT) (an anion releasing monomer) and *p*-sodium styrene sulphonate (SSS) (a cation releasing monomer) were co-polymerized with NIPA in presence of 0.3 % of crosslinking agent N, N -methylene bisacrylamide (MBA).

Gel fraction of NIPA was found to decrease in presence of VBT and SSS. The extent of decrease in gel fraction was more profound in case of SSS as compared to VBT. This was attributed to the predominantly crosslinking/degradation behaviour of the ionic polymers PVBT/PSSS in aqueous solution. It has been reported that PVBT predominantly undergoes crosslinking [19] unlike PSSS, which undergoes degradation [20]. Figs. 4 and 5 show swelling extent of NIPA gels when ionic monomers were introduced in the poly (NIPA) matrix. It was observed that introduction of a small amount of ionic monomer units into pure NIPA matrix affects equilibrium degree of swelling (EDS) and lower critical solution temperature (LCST) to a great extent. On introduction of ionic monomers the volume phase transition does not remain abrupt on temperature scale as well as on time scale.

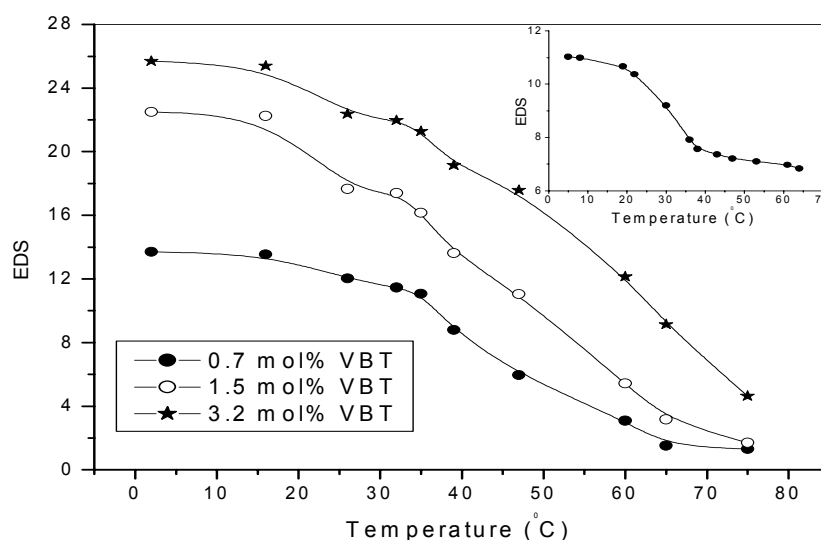


FIG. 4. Thermo-sensitivity of NIPA-co-VBT hydrogels. Inset: Pure Poly(NIPA)

It was found that the EDS increased with the increase in ionic content in the gel. The EDS of gels containing VBT was more than that of gels containing SSS. This observation was similar to reported earlier where introduction of same amount of VBT and SSS in other matrix have been shown to increase EDS by different extents [20].

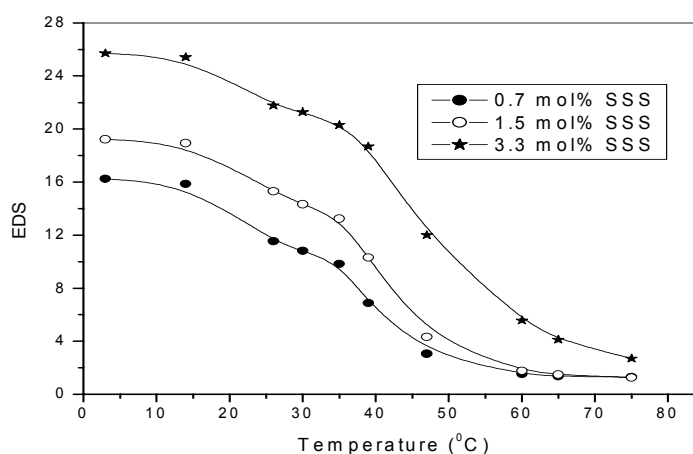


FIG. 5. Thermo-sensitivity of NIPA-co-SSS hydrogels.

Complexation behavior of radiation synthesized PVBT and its gel with ions: Metal ions can be separated from aqueous solution by complexing them with suitable oppositely charged ionic polymers or their crosslinked gels. Complexation behavior of radiation polymerized PVBT and its gel with potassium hexacyanoferrates (II, III) and $K_2S_2O_8$ were investigated by viscometric, turbidity measurements and EDS measurements. These salts were chosen since they generated tetra, tri, and divalent anions for complexation in aqueous medium and because of their bulkier size can imitate drug molecules.

Figure 6 shows effect on viscosity of the polymer solution in presence of these salts. The stoichiometry of the complexes, in terms of $[Salt]/[PVBT]$ ratios were estimated at precipitation and the numerical values were found to be in the range estimated to be in the range 0.4-0.45, 0.25-0.3 and 0.2-0.25 for $K_2S_2O_8$, $K_3[Fe(CN)_6]$ or $K_4[Fe(CN)_6]$ respectively. The complexes of PVBT with these ions were quite stable and were not dissociated upon dilution.

The experimental data indicates that the interaction of PVBT these salts lead to formation of polymer complexes in which the $S_2O_8^{2-}$ is linked to 2.2 - 2.5 monomer units, $[Fe(CN)_6]^{3-}$ to 3.3-4.0 monomer units and $[Fe(CN)_6]^{4-}$ to 4-5 monomer units. The association of these negative ions to cationic polyelectrolytes can be expected as a result of electrostatic interaction. In case of crosslinked gels at a certain $[Salt]/[Gel]$ ratio the hydrogels are characterized by their completely collapsed state and a further increase in this ratio does not influence the swelling of the hydrogels. The most noticeable aspect in deswelling of PVBT gels was that the value of the ratio $[Salt]/[Gel]$ for complete deswelling in presence of different salts were same as the values at which precipitation occurred for linear PVBT value for these salts [22].

From these complexation studies following conclusion were made: (a) linear and crosslinked PVBT prepared by irradiation formed stable complexes with potassium hexacyanoferrate (II, III) and $K_2S_2O_8$. The interaction of linear PVBT with these salts resulted in decrease in the hydrodynamic volume of polyelectrolytes and ultimately precipitation of polymer complexes from the solution. (b) The stoichiometry of the complex formed depended on the charge of the anion from the complexing salts. (c) Crosslinked PVBT hydrogels desorb the embedded water when placed in these salt solutions. The complexes of linear and crosslinked PVBT are fairly stable on dilution and get dissociated only when strong electrolytes are introduced in the medium.

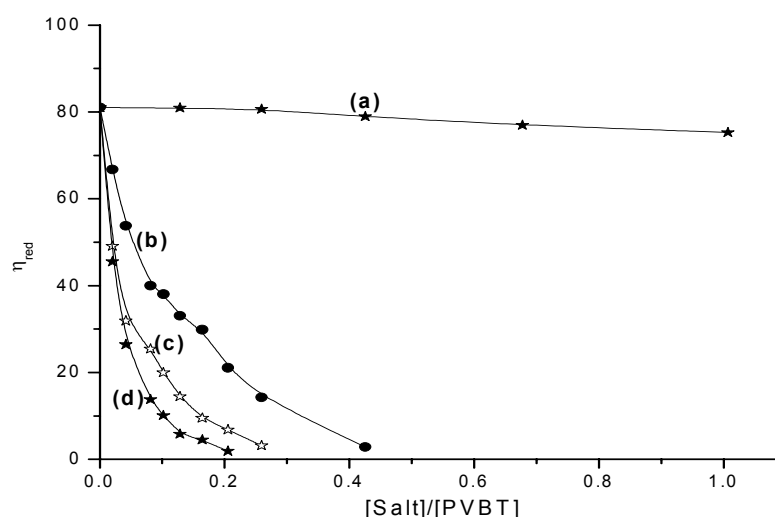


FIG. 6. Viscometric titration of $1 \times 10^{-3} \text{ mol dm}^{-3}$ PVBT with $1 \times 10^{-3} \text{ mol dm}^{-3}$ of salts. (a) H_2O (b) $K_2S_2O_8$ (c) $K_3[Fe(CN)_6]$ (d) $K_4[Fe(CN)_6]$

4. APPLICATIONS OF RADIATION PROCESSED POLYMER MATRICES

4.1. Studies on concentration of protein solution using gamma crosslinked poly(NIPA) gels

For separation studies poly (NIPA) gels deswelled at 318 K were immersed in the protein solution and allowed to equilibrate at room temperature. After the gel has reached the swelling equilibrium, it was removed from the solution. The gel swells by absorbing water and low molecular weight compounds while large molecules (high molecular weight) are excluded. Then, the swollen gels were regenerated by collapsing them at 318 K. The concentration of protein remaining in solution was determined by measuring absorbance of solution at 280 nm.

The exclusion behavior of the gels was studied as a function of

- crosslinking density of the gel,
- solute concentration,
- pH of solution and (iv) molecular weight of the protein.

The selectively results are evaluated in terms of the distribution coefficient, K_d , defined as the ratio of the solute concentration in the gel phase (C_g) to that in the raffinate (C_R) using the following equation.

$$K_d = (V_f C_f - V_R C_R) / V C_R$$

Where V_f and C_f are feed volume and concentration respectively V_R and V are the retentate volume and swollen gel volume respectively.

TABLE I. EXCLUSION BEHAVIOR OF GELS SYNTHESIZED BY GAMMA IRRADIATION

Protein (M.W.)	pH	Dose (kGy)	Protein concentration (%)	K_d
Bovine serum albumin (66,000)	11	15	1	0.122
	5.8	15	1	0.268
	3.8	15	1	0.388
	11	15	0.5	0.094
	11	15	1.5	0.356
Chicken egg albumin (45000)	11	15	1.0	0.326
	5.8	15	1.0	0.533
	3.8	15	1.0	0.737
		05	1.0	0.536
		10	1.0	0.532
		20	1.0	0.444
Lysozyme (14300)	5.8	15	1.0	1.000
α -amylase (50,000-55,000)	11	15	1.0	0.506
	5.8	15	1.0	0.565
	3.8	15	1.0	0.846
	11	05	1.0	0.702
	11	05	1.0	0.565
	11	05	1.0	0.442

The results of these studies, shown in Table I, indicate the following:

- Proteins are more excluded at higher pH which is well above their iso-electric point, probably due to electrostatic interaction within the protein molecules which keeps them in extended form.
- At low solute concentrations, the proteins are more excluded implying that exclusion efficiency decreases with increasing concentration.
- Exclusion of proteins increases as total dose increases during gel formation. This can be attributed to higher crosslinking density of the network structure formed at higher doses.
- Lysozyme having molecular weight 14,300 could not be concentrated at all indicating that proteins below 45000 molecular weight are difficult to concentrate.

4.2. Concentration of serum phase protein from Natural rubber latex using PNIPA gels

Natural rubber latex (NRL) is a milky white fluid obtained from Rubber Tree (*Hevea brasiliensis*) by controlled tapping. NRL is defined as a colloidal suspension of rubber particles in water medium. It is composed of rubber hydrocarbon ($-(C_5H_8)_n$), Protein, Sugar, fatty acids, resins and water. Natural Rubber is mainly a polymer of *cis*-isoprene. There are more than 200 types of proteins present in NRL but the principal one associated with rubber hydrocarbon is α -globulin. Total protein content of the fresh latex is 1-1.5(w%) of which 27% is adsorbed on the rubber particles, 25% present in the bottom fraction (B serum) and remainder 48% in the serum phase (C serum) [23]. Carrillo et. al.[24] were the first to report that water-soluble proteins in the latex are allergens, and they demonstrated that 30 kDa protein from the saline extract of the gloves showed allergenicity. So it is desirable to extract protein from the NRL. Also fresh rubber latex collected from rubber trees contains 30% DRC. For preservation of NRL, it has to be concentrated upto 60% DRC. Trials were carried out to utilize the radiation crosslinked temperature sensitive hydrogels for concentrating natural rubber latex having dry rubber content around 30% and simultaneous removal of proteins from the latex.

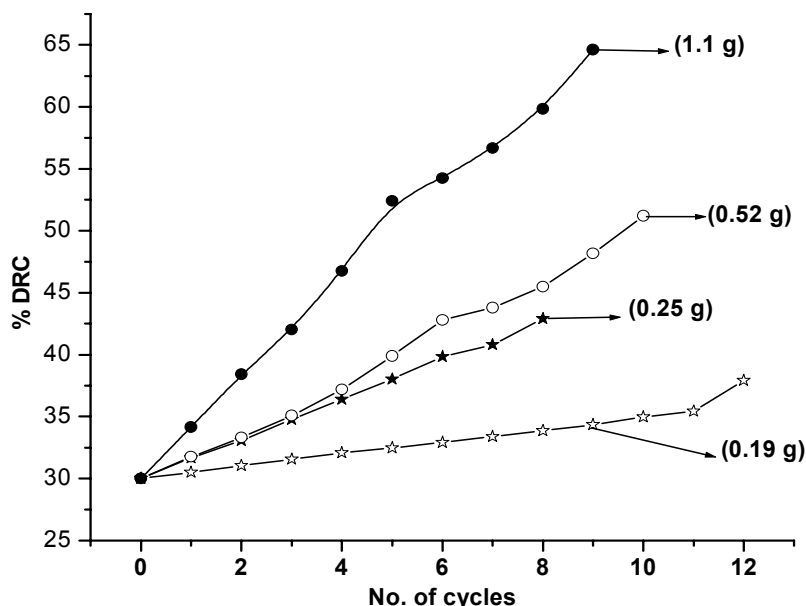


FIG. 7. Increase in DRC content of natural rubber latex

For these studies a known amount of poly(NIPA) hydrogel was swelled in known amount of NRL (DRC 30%) for 3 hours the swelled gel was deswelled at 400C. The extracted solution was tested for proteins using modified Folin Lowry Method [25]. DRC of the rubber was estimated gravimetrically after each cycles. Figure 7 and Table II show results of these studies. It could be concluded that to a great extent only water from latex is absorbed by the gel the rubber chains as well proteins remain back in serum phase. Probably the pore size of the gels is less than the size of the protein molecule in serum phase or may be hydrocarbon rubber chains preferably adhere to the gel surface to choke the pores.

TABLE II. CHANGE IN CONCENTRATION OF SERUM PHASE PROTEIN AND DRC OF NRL

Wt. of gel (g)	Initial DRC content	Final DRC content	Wt. of water removed (g)	Expected decrease in protein content	Actual decrease in protein content
0.19	30 %	37.61 %	4.9	29.17 %	2.4 %
0.25	30 %	42.00 %	6.9	41.07 %	2.6 %
0.52	30 %	51.00 %	9.9	58.93 %	2.8 %
1.10	30 %	64.50 %	12.8	76.19 %	2.9 %

4.3. Adsorption behavior of Bovine albumin serum by radiation grafted cellulose matrix having vinylbenzyltrimethylammonium group

The purification process of protein in biological fluids governs the production cost of the protein in the pharmaceutical and food industries. Therefore, there is a constant demand for efficient recovery of proteins. Among the various recovery techniques, chromatography is a powerful and versatile technique for protein purification in which various functional moieties such as ion-exchange groups, hydrophobic and affinity ligands immobilized onto solid matrices were used.

An efficient recovery system should fulfill the three basic criteria (i) high uptake rate (ii) high uptake capacity (iii) repeated use without loss in the capacity. In the case of conventional gel-bead-packed column, the proteins, driven by a concentration gradient, diffuse into the beads and reach the functional groups. In most of the case rate of diffusion of the proteins governs the overall adsorption rate. On the other hand, uniformly fictionalized polymer brushes prepared by radiation grafting methods do not suffer from the diffusional mass-transfer resistance of proteins. The grafted polymer brushes have high uptake capacity because of multiplayer binding of proteins on the grafted chains extended over the polymer backbone support [26].

Polymer containing a vinylbenzyltrimethylammonium group, as an anion-exchange group is capable of collecting proteins dissolved in biological fluids. Radiation grafting leads to highly functional polymer carriers, which have got many applications, high performance separation and immobilization of proteins is one of them [27]. In the present work, new adsorbent for recovery of proteins was prepared by mutual irradiation grafting of Vinylbenzyltrimethylammonium chloride (VBT) on to cotton cellulose matrix. It is a single step process to incorporate desired anion exchange quaternary ammonium group, unlike earlier work in which first step is the grafting and second step is chemical reaction to modify the grafted chains [28]. Protein molecule may acquire anionic (COO-) as well as cationic (NH₃⁺) charge, depending on the solution condition like pH. The ion exchange reaction between the ion-exchange matrix and protein will depend on the solution condition (like pH, ionic strength) to a greater extent. Therefore, adsorption behavior of anion-exchange cellulose matrix (VBT-g-cotton) for BSA was investigated under various conditions in column process. The details of the radiation grafting of VBT on cotton substrate was described in our earlier work [12].

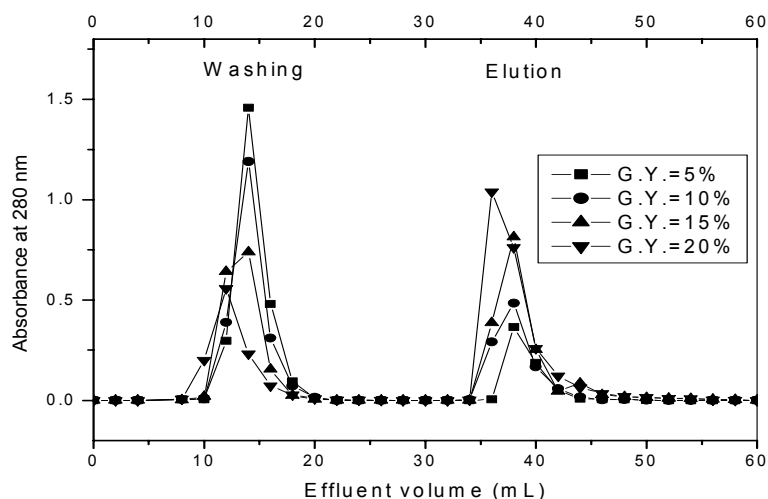


FIG. 8. Adsorption behavior of VBT-g-cellulose for BSA as a function of grafting yield, pH~ 7.0 in 10 mM Phosphate buffer, protein loaded = 8.9 mg, flow rate = 0.5 ml/min.

The adsorption behavior of anion exchange matrix with different grafting yields for BSA is shown in Figure 8. It can be seen from figure that height of washing peak decreased and that of elution peak increased with the increase in grafting yield. The binding capacity (BC) of grafted matrix increased with extent of grafting. Effect of pH and strong electrolytes on binding capacity was also studied. At higher concentration of NaCl complete elution of protein was observed indicating electrostatic interaction between BSA and grafted chains. Figure 9 shows breakthrough curve for 20 % grafted matrix. The equilibrium binding capacity and elution percentage of the VBT-g-cellulose anion exchange adsorbent, estimated from breakthrough curve was found to be 40.0 mg/g and 94% respectively.

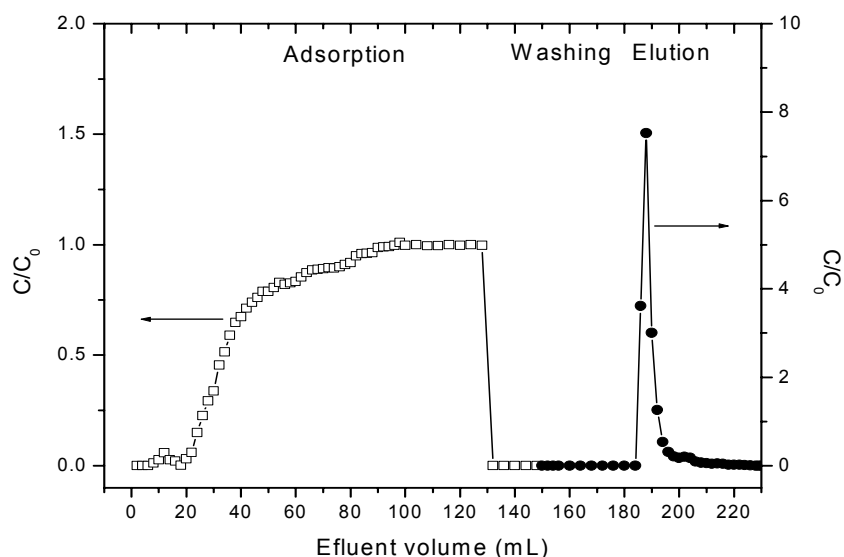


FIG. 9. Breakthrough plot of BSA for anion exchange VBT-g-Cotton cellulose (20% grafted) matrix. BSA concentration in feed solution = 0.4 mg/ml in 10 mM Phosphate buffer (pH~7.0), Flow rate=0.5 mL/min, weight of dry anion exchange matrix=0.2 g.

5. CONCLUSIONS

Gamma and EB irradiation of thermo-responsive monomers/polymers like NIPA and PVME results in gels of different microstructure that can have extremely fast swelling/deswelling kinetics. The decrease in EDS of thermo-responsive gels due to their higher crosslinking can be compensated by introduction of ionic monomers like VBT and SSS in the parent matrices. The introduction of ionic monomers however increases response times of the gels. The thermo-responsive gels can be efficiently used to concentrate dilute protein solution and biological slurries rich in water. Radiation grafted cotton surface effectively captures proteins like BSA from the dilute solutions with high efficiency and such materials may emerge as useful materials for separation of proteins.

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RADIATION SYNTHESIS OF STIMULI-RESPONSIVE HYDROGELS AND THE APPLICATION TO INTELLIGENT DRUG DELIVERY SYSTEMS

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Abstract

Radiation-prepared synthetic and natural polyelectrolyte and polyampholyte hydrogels were applied to the intelligent drug delivery systems (DDS). The intelligent membranes and chips were prepared by nano-porous fabrication with Exima-laser and ion-beam irradiations and the coating of stimuli-responsive hydrogels. This coating was efficiently carried out by curing processing with conveyor system. Computer programming control of intelligent drug releases was studied for the design of DDS chips to carry out the multiple drug delivery in response to multiple environmental changes.

1. OBJECTIVE OF RESEARCH

The research aims to the principle clarification of stimuli-responsive behaviour of hydrogels and the extended development of new material and new synthetic method of hydrogels, as the bases for applications. The research aims to the applications of stimuli-responsive hydrogels to the intelligent DDS membranes and chips produced by radiation curing processing and the integrated DDS chips controlled by computer technology and nano-technology as the final goal.

2. INTRODUCTION

The authors studied and developed the immobilization of enzymes, proteins and cells in 1970's by means of radiation entrapping polymerization method and applied to biosensors and bioreactors [1]. Then the immobilization of drugs and hormones was studied and applied to drug delivery systems in 1980's [2,3]. The authors noticed to the stimuli-responsive polymers in 1990's, because those polymers can be applied to the intelligent type DDS which can deliver the drug with on-off switching of release timing, in response to the environmental signals. However, in recent years, the DDS chips as a new kind of biochips have been the important research subjects for the authors as the future goal to realize the multi-signals responsive multi-drug delivery. Nano-fabrication and computer programming control would be the two key technologies for the purpose. In this report, recent research results in this direction were described as well as the basic findings on the new stimuli-responsive hydrogels and the new methods of synthesis and processing for the application to intelligent DDS chips.

3. MATERIALS AND METHODS

Materials such as monomer and polymer were used special grade commercial products without further purification. Methylene blue was mainly used as the model drug and the released amount of drug was evaluated colourimetrically by the absorption intensity at 663 nm. UV irradiation was carried out using 400W Lamp of Riko-kagaku sangyo Co Ltd. irradiator. The computer program was settled using the system of x 86. Intelligent membranes and chips were holed by means of conventional lithography method with Exima-laser irradiation and ion beam etching using commercially available polymeric films and silicone wafers.

4. RESULTS AND DISCUSSION

4.1. Principle clarification, new synthesis method and new materials of stimuli-responsive hydrogels.

Synthetic polyelectrolytes and polyampholytes as electro- and pH responsive hydrogels.

Since the stimuli-responsive hydrogel phenomena were found by Tanaka in MIT, a lot of works have been reported on this area. But the main interest of researchers has been concentrated in the temperature responsive polymers from the early stage of this research field.

However, the authors have noticed to the importance of polyelectrolytes as electro- and pH sensitive and responsive polymers and chips [4, 14], because the authors intended the application to the intelligent type DDS which can be used in connection with the electrical signals from the sensor and computer. Therefore, the responsive properties of polyelectrolytes and polyampholytes were mainly clarified.

It was found that polyanion and polycation showed the volume changes between shrinkage and expansion toward anode and cathode with the on-off switching of electro-field owing to the ionic interaction between the polymeric ion and the electrode charge.

Polyanion and polycation showed the volume changes between swelling and deswelling in response to the pH changes oppositely. Those changes can be explained by the conformational changes of polymer network between stretched and coiled forms due to ionic repulsion and ionic neutralization. The pH responsiveness of typical polyanion and polycation copolymer hydrogels was shown in Fig.1. In the case of polyampholytes, pH responsive swelling occurred both in the strongly acidic and alkaline regions showing an apparent minimum swelling at certain pH.

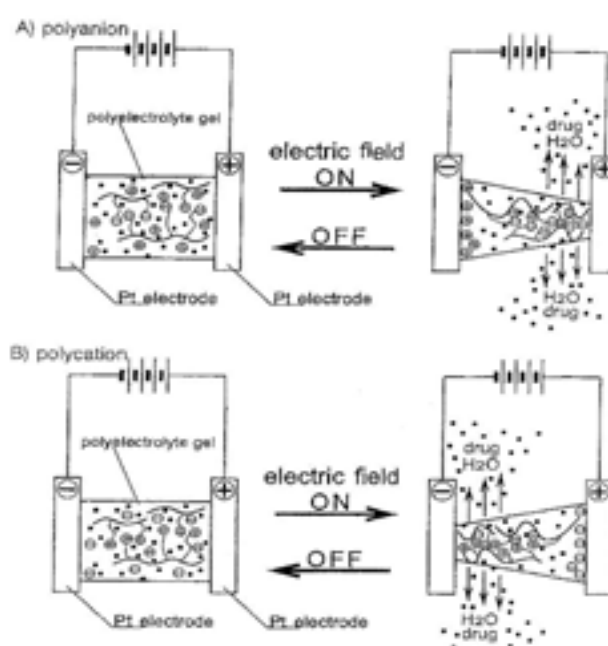


FIG. 1. Electro-responsiveness of polyelectrolyte hydrogel

In general electro- and pH responsiveness of polyelectrolytes and polyampholytes can be explained by the ionic interactions and the resulting conformational extension - relaxation changes of polymeric chains.

On the other hand, it is generally known that the temperature responsive polymer has the chemical structure consisting of hydrophobic segment, hydrophilic group site and again hydrophobic group. N-isopropyl acrylamide is a typical monomer in this category. However, the number of this kind of monomer is very limited in comparison with polyelectrolytes. However, if the polyelectrolyte has the hydrophobic-hydrophilic balanced structure, it can be the electro- pH- responsive and temperature responsive hydrogel. Polydimethylaminoethyl methacrylate (DMAMA) was found as an example of temperature responsive polycation and studied for the pH responsiveness as the function of temperature and the temperature responsiveness as the function of pH. The results could be explained as the summation of pH and temperature responsiveness.

Natural stimuli-responsive polymer hydrogels are the unclarified research area and include unutilized useful materials potentially. Polysaccharides can be typical natural polyelectrolytes and proteins were found as the typical polyampholytes. However, it is not always easy to obtain the stable and strong natural hydrogels. Therefore, the authors used the entrapping polymerization method with the small amount of vinyl monomers for the gelation of natural polyelectrolytes and polyampholytes [6, 8]. It was found that all kinds of natural stimuli-responsive polymers could be entrapped effectively into the formed hydrogels showing the electro and pH responsiveness as well as the intelligent drug release functions.

It was also found that some natural polysaccharides such as cellulosic derivatives can also be the temperature responsive polyelectrolyte hydrogels, showing the electro – pH and temperature responsiveness (Fig. 2). The authors studied and developed radiation degradation with the immobilized of cellulosic wastes such as bigasse, chaff, rice straw and waste papers, in 1980's and enzymatic saccharification with the immobilized cellulase and cellulase producing cells [5]. The protein wastes such as soybean from waste bean and keratin from waste wool were also studied recently. The use of such natural wastes as polyelectrolytes and polyampholytes would be investigated importantly further by the authors.

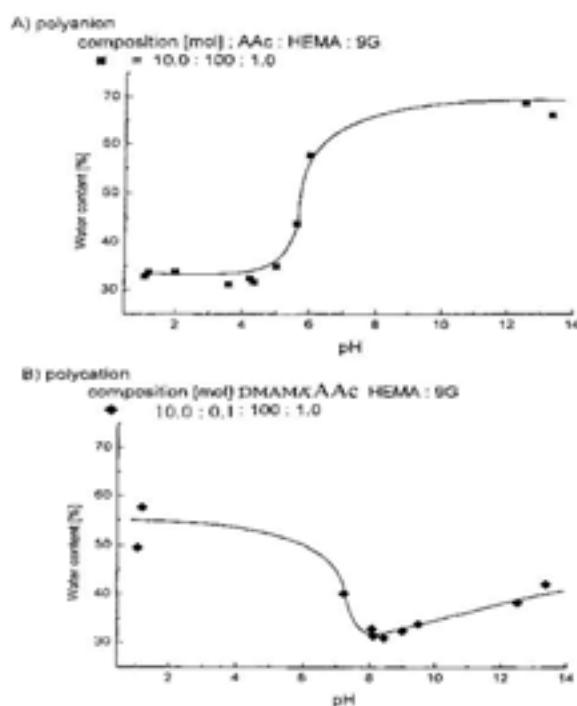


FIG. 2. The pH responsiveness of typical polyanion and polycation copolymer hydrogels

Stimuli-responsive nano-spheres and prodrugs.

Micro-and nano-spheres have the advantage of injectable form and can be used effectively for the targeting type DDS. The authors studied and developed the precipitation polymerization method to prepare the monodispersed micro-and nano particles by choosing the specific combination of monomer and solvent [9]. All kinds of stimuli-responsive hydrogels can be formed into the nano-spheres by this method. Polyelectrolyte such as polyacrylic acid were easily converted into the pH responsive nano-sphere and poly-N-isopropylacrylamide could be converted into the temperature responsive nano-sphere in the presence of hexyl acetate.

Important application is the copolymerization of stimuli-responsive monomer with a biofunctional monomer such as prodrug monomer to form a stimuli-responsive and biomedical nano-sphere. As an example, acrylic acid was copolymerized with methacryloxy testosterone into the pH responsive prodrug to release testosterone by enzymatic chain scission. N-isopropyl acrylamide can be copolymerized with the same prodrug monomer to give the temperature responsive prodrug for targeting. The nano-sphere of natural stimuli-responsive polymer would also be possible entrapping the prodrugs and other biomedical components.

Stimuli-responsive and biodegradable hydrogels.

Most materials for biomedical applications are required highly biocompatibility and DDS materials are usually required both biocompatibility and biodegradability or bioerosibility. The nano- and micro- spheres for targeting and the biological surfaces for cell and tissue culture often need the biodegradability or bioerosibility. Therefore, the stimuli-responsive and biodegradable polyesters were searched for the intelligent nano-spheres and intelligent biological surfaces. The formed polyester hydrogels obtained from polyol and dibasic acid showed the both pH and electro-responsiveness and the good biodegradability.

3.2. Construction and processing of intelligent membranes and chips for drug delivery.

Intelligent membranes and chips by lithography fabrication method.

Based on the research findings on the stimuli-responsive hydrogels in the previous section, the construction of intelligent systems such as intelligent membranes with polymeric films and intelligent chips with silicone wafers was studied for the application to drug delivery [10-13]. In principle, the intelligent systems should be consisted of the sensor part to monitor the environmental changes and the actuator part to carry out the on-off switchings of drug release from the reservoir. Furthermore, in order to treat the multiple feedback releases in response to the inputs of multiple environmental signals, the inclusion of computer part is essentially necessary.

It was developed the construction method of such intelligent systems by means of lithography fabrication and radiation curing of stimuli-responsive hydrogels. The technical process for the preparation of intelligent membranes and chips was shown in Fig.3. Base films and wafers were fabricated into the nano- porous membranes and chips by means of Exima-laser or ion-beam irradiations.

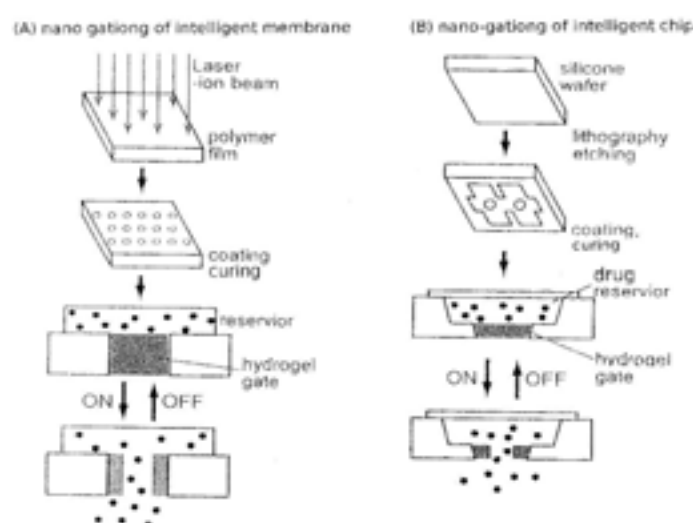


FIG. 3. Nano-gate fabrication for the intelligent DDS membranes and chips

Then the fabricated membranes and chips were coated with stimuli-responsive monomers and cured by UV or electron beam (EB) irradiations (Fig. 4). The formed hydrogel layer could act as the nano-gates to open and shut the nano-holes as the drug release channels. The gates open and close in response to the environmental signals such as pH, temperature, electro-field changes, photo-irradiations and substances additions .to cause the on-off switchings of drug release. All research results using those intelligent membranes and chips clearly proved the effective functions of nano-gating for the intelligent drug delivery.

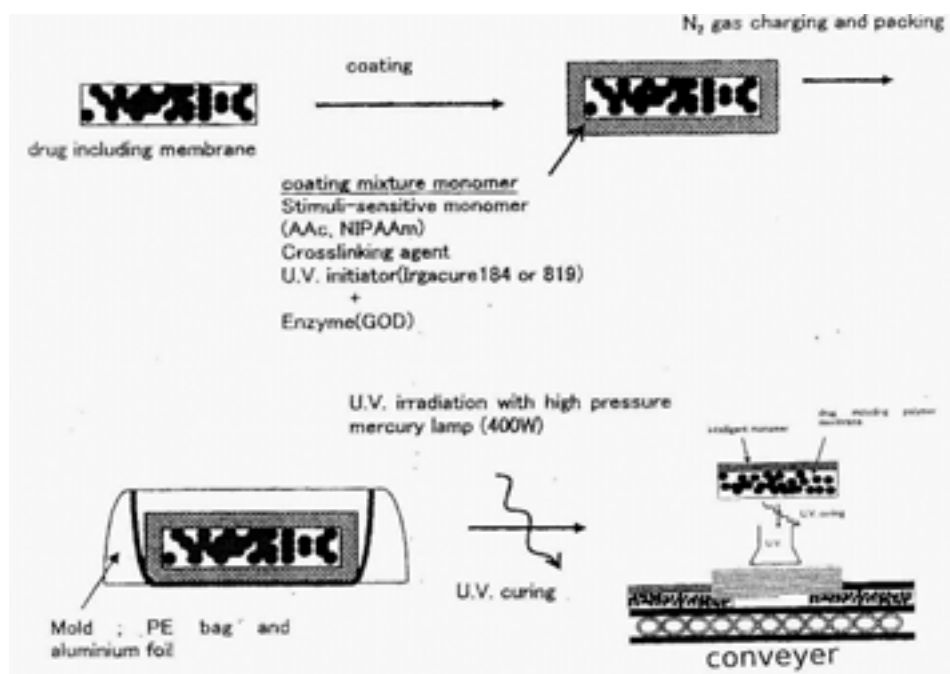


FIG. 4. UV coating and curing processing for intelligent DDS membranes and chips

Intelligent coatings and the UV or EB curing processings.

The authors studied and developed the new processing for the efficient production of intelligent membranes and chips [15, 16]. Fig.4 showed the model scheme and flow diagram of this processing with the conveyer systems. As well known, UV and EB curing processing with conveyer system has been already established and effective used one for the industrial production of various coatings such as paint coatings and magnetic coatings. But no report has been known for the application of this successful processing to the biological and biomedical coatings such as intelligent drug delivery coatings.

3.3. PC programming control of intelligent drug delivery functions for the integrated DDS chips.

PC program design for the intelligent drug releases

The final goal of intelligent DDS is the integrated DDS chips as the new kind of biochips to realize the multi environmental signals responsive multi-feedback drug releases as shown in Fig.5 schematically. Two kinds of key technologies are essentially required for this purpose, the nano-fabrication technology for the integrated chips and the computer technology to control the multiple drug delivery programs. In principle, such an integrated DDS chips have the multiple layer structure consisting of sensor chip for the multiple sensing, PC programming chip and drug release chip for multiple intelligent releases with the nano-gates and nano-channels.

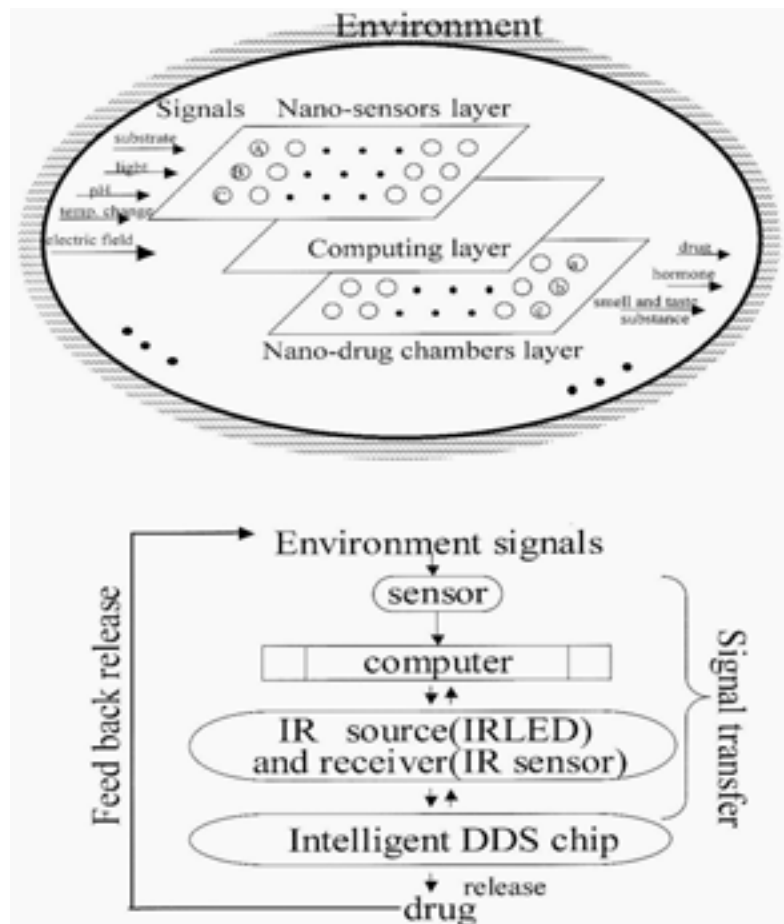


FIG. 5. Flow diagram of computer programming control for intelligent drug release

Among the biochips, DNA chips have been studied and developed extensively by the companies already. But the DDS chip has still been unknown and undeveloped one and can be the further frontier area. The authors have investigated on this subject in recent years. Fig.6 shows the result of program designed releases in response to the small temperature difference by the threshold design with the computer program. Fig.7 presents the result of photo-irradiation and electro-field binary signals responsive binary drug releases with the different on-off switching timings and periods. The program was designed to cause the on-switching of drug only when the two kinds of signals came overlappedly. The result clearly proved the effectiveness of program control for such specific releases.

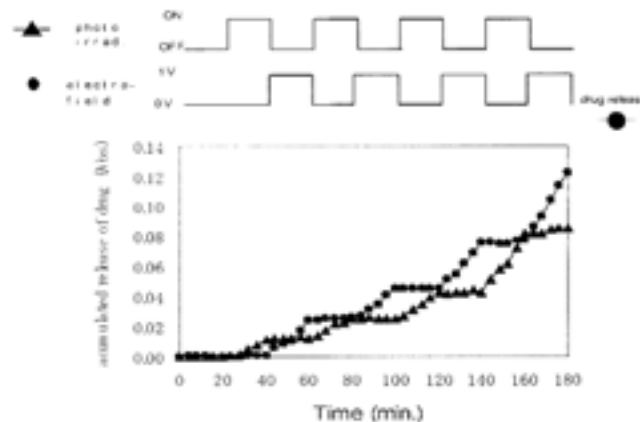


FIG. 6. Intelligent mutual release of binary drugs

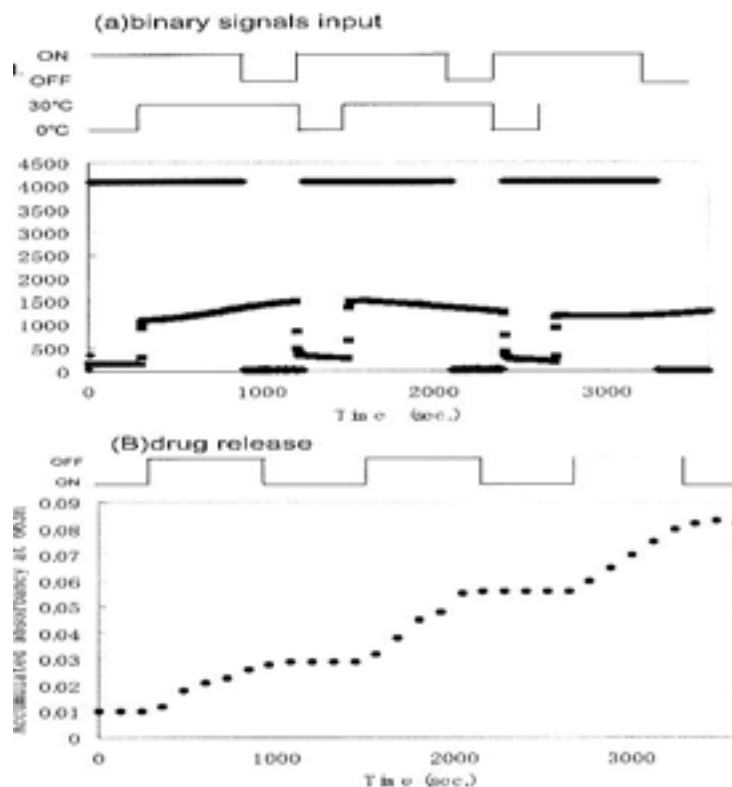


FIG. 7. Intelligent drug release in response to the overlapped inputs of binary signals by computer program

PC program modification for the intelligent releases by wireless communication.

The practical environmental conditions in the living body are always very changeable continuously and complicatedly with the time. Therefore, it is necessary to modify and adjust the settled program according to the real time changes of situation. The authors noticed to the use of wireless communication such as infrared data communication for this purpose. Some practical results to modify the program by the infrared data communication are shown in Figs. 8 and 9 [18].

Fig.8 showed the result of modification of PC program by infrared data communication for the amount of drug releases. The release result proved clearly and accurately the effectiveness of program control on the releases according to the modified amounts by the infrared data communication. Fig.9 showed the result of program modification by the infrared data communication for the threshold temperatures in the temperature responsive drug releases. The threshold values were changed three times and the practical drug release occurred accurately at the differently modified threshold temperatures, 40°C, 50°C and then 30°C. It can be concluded that the program control for the design and modification of intelligent drug release proved the effectiveness clearly and accurately. Those results can be used for the integrated intelligent DDS chips as the essential base techniques.

5. CONCLUSION.

Basic researches on the principle mechanism, characteristic behaviors and the finding of new materials and methods were carried out on the natural and synthetic polyelectrolytes and polyampholites.

Especially, many natural polyelectrolytes and polyampholites including natural wastes could be used as the stimuli-responsive hydrogels by entrapping polymerization method. Stimuli-responsive nano-spheres could be prepared by precipitation polymerization method. Stimuli-responsive and biodegradable hydrogels were synthesized.

Various intelligent membranes and chips were developed using nano-gates fabrication with radiation lithography method by Exima-laser and ion beam and using stimuli-responsive hydrogel coating for the application to drug delivery. All intelligent systems proved the intelligent drug release functions. The UV and EB curing processing with the conveyor system was applied to the efficient production of intelligent membranes and chips effectively. Some applications to nicotine and herb delivery were investigated using the UV curing processing. PC programming control method was developed for the design and modification of threshold programs for the intelligent drug releases. The program control proved the exact effectiveness for the multiple intelligent releases in response to the multiple inputs of environmental signals. Those results are essentially useful for the design and construction of integrated DDS chips as the next generation of intelligent DDS and the new frontier of biochips.

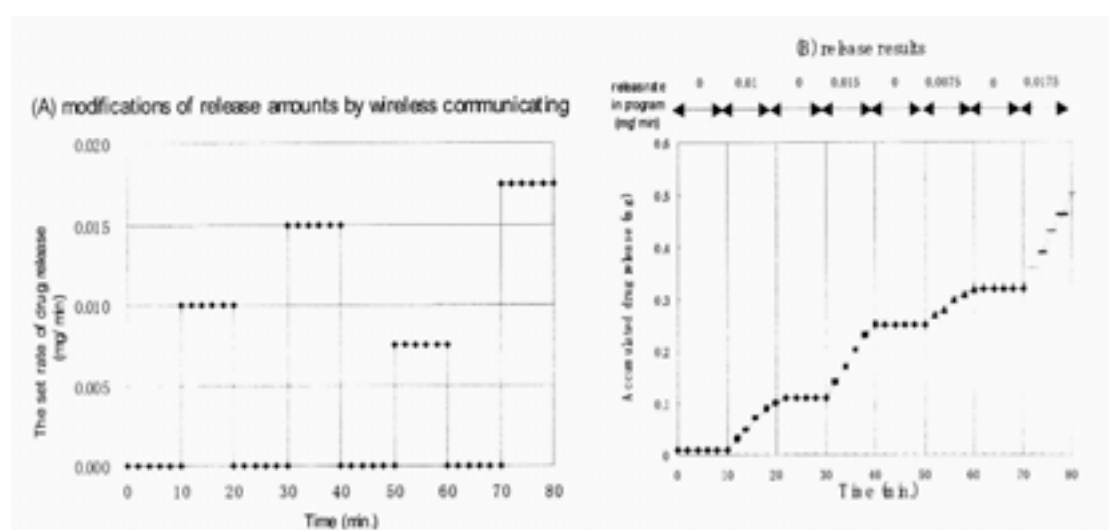


FIG. 8. Computer programming control of drug release rates

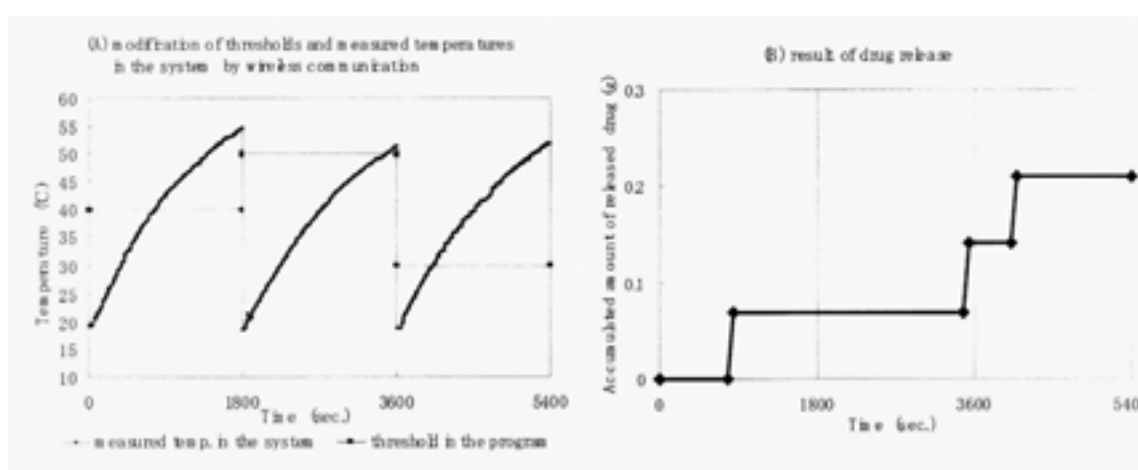


FIG. 9. Computer programming control of temperature responsive drug releases

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GAMMA RADIATION SYNTHESIS OF STIMULI-RESPONSIVE MEMBRANES AND HYDROGEL SORBENTS BASED POLYMERS OF VINYL ETHERS AND THEIR INTERPOLYMER COMPLEXES FOR APPLICATION IN SEPARATION PROCESSES

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Abstract

Stimuli-responsive hydrogel and film materials have been obtained for application in separation process. Novel polycationic and polyampholyte hydrogels were synthesized by gamma-radiation copolymerization of vinyl ethers of monoethanolamine (VEMEA) and ethyleneglycol as well as VEMEA and acrylic acid. The complex formation of the obtained hydrogels with various metal ions and linear polyelectrolytes has been studied. Water soluble and crosslinking thermo-sensitive cationic copolymers based on 2-[(methacryloyloxy)ethyl]trimethylammonium chloride and N-isopropylacrylamide (MADQUAT-NIPAAM) were obtained and their interaction with poly(acrylic acid) (PAA) and potassium hexacyanoferrates (II, III) were studied. It was found that the composition of copolymer significantly affects the composition of polyelectrolyte complexes and molecular weight of PAA influences their aggregation stability. The study of interaction MADQUAT-NIPAAM copolymers with proteins has been started. Novel non-ionic thermo-sensitive linear and crosslinked polymers have been obtained by gamma-irradiation copolymerisation hydrophilic. The sorption processes of surfactants by novel thermosensitive copolymers have been studied. Stimuli-responsive films were prepared by gamma-radiation cross-linking of the blends based of poly(acrylic acid) and poly(vinyl methyl ether). The environmental pH affects the swelling of the films significantly. In acidic media the films have lower swelling ability because of suppression of carboxylic groups ionisation and formation of additional physical cross-links via interpolymer hydrogen bonding. Novel polymeric film materials were prepared by radiation grafting of cationic monomer vinyl ether of monoethanolamine on the surface of polyethylene and polypropylene films. The prepared graft copolymers showed a good affinity towards the chelation and/or complexation with different metals investigated here (Pb^{2+} , Cd^{2+} , Zn^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Ag^{+}). Treating of the saturated films with 0.01 HCl at room temperature for one hour easily recover the absorbed metals and accordingly the films can be reused for the resorption of metal ions. The copolymeric hydrogels based on polyethylene glycol (PEG) and methacrylic acid (MAA) have been synthesized by using γ -irradiation copolymerization. Physical chemical characteristics of obtained networks were studied. The comparative study of uranyl ions adsorption by PEG-MAA and polymethacrylic acid (PMAA) hydrogels was carried out. It was shown that the sorption characteristics depend on pH and ionic strength of solution as well as uranyl ions concentration. The higher stability in the regeneration processes and possibility of repeated use of copolymeric hydrogel of PEG-MAA for uranyl ions adsorption in comparison to homopolymer PMAA were shown.

1. INTRODUCTION

Among all stimuli-responsive polymers and interpolymer complexes, those demonstrating pH and temperature dependent behaviour attract a great attention from both fundamental and practical points of view. They may find widespread application as sensors, sorbent, actuators, controlled and targeted drug delivery systems, non-viral vectors for gene therapy, attachment/detachment of cultured cells [1, 2]. Weakly cross-linked macromolecules of hydrophilic polymers loss the ability to dissolve in water but are able to swell and form soft and elastic materials or so-called hydrogels. Hydrogels have very high sorption ability with respect to small- and macromolecules. The main purpose of this research is obtain new stimuli-sensitive polymers, hydrogels and interpolymer complexes for application in separation process

2. MATERIALS AND METHODS

2.1. Materials

Vinyl ether of monoethanolamine (VEMEA), vinyl ether of ethylene glycol (VEEG) and divinyl ether of diethyleneglycol (DVEDEG), vinyl butyl ether (VBE), vinyl isobutyl ether (ViBE) as the commercial products of Alash Ltd. (Temirtau, Kazakhstan) were used in the present work. They were dried in the presence of dry K_2CO_3 and purified by double distillation.

N-isopropylacrylamide (NIPAAM) was purchased from Japan Co. and purified by triple dissolving in n-hexane at 40°C under stirring followed by precipitation at room temperature. The resulting precipitate was filtered out and dried on open air for 10 hours and then under vacuum for 24 hours.

2-methacryloyloxyethyltrimethylammonium chloride (MADQUAT) was supplied as 75 % aqueous solution (Aldrich). It was purified by precipitation in acetone, dried in a vacuum oven at 45°C and stored in a dessicator at -5°C. Commercial 2-hydroxyethylacrylate (HEA), 2-hydroxyethylmethacrylate (HEMA), butylacrylate (BA) were purchased from Aldrich Chemical Co. HEA, HEMA and BA were purified by vacuum distillation under argon atmosphere. The polyethylene and polypropylene films classified as "for food packaging" obtained from Munai Plastik Ltd. (Kazakhstan) were used in the study. Before experiments each sample was cleaned by acetone. The sample of PAA with weight-average molecular weight 250000 Da was purchased from Aldrich and used without further purification. All the chemicals used in the study were of analytical grade.

2.2. Methods

The copolymerization was performed in sealed glass ampoules using MRX- γ -25M setup equipped by ^{60}Co source with a dose rate 0.9 Gy/s. Before synthesis the feed mixture was saturated by argon. The synthesized hydrogels were purified by washing them with distilled water during 2 weeks. The composition of copolymers was determined by potentiometric titration.

The equilibrium swelling degree of the hydrogels was determined gravimetrically by the following formula:

$$\alpha = (m - m_{\text{dry}}) / m_{\text{dry}}$$

where m and m_{dry} are the weights of the samples swollen in water and in dry state, respectively.

The swelling ratio V/V_0 , where V_0 and V are the volumes of the polymer network immediately after synthesis and in the moment of measurements, respectively, was used for characterization of the hydrogels swelling in dynamics. The diameter of samples was measured using V-630 cathetometer (USSR) with the accuracy of measurements ± 0.01 mm.

The grafting was performed in the sealed glass ampoules with polyethylene films immersed in monomer saturated by argon using an MRX- γ -25M setup equipped by ^{60}Co source with a dose rate 0.3 Gy/s. The dose rate was determined by a Fricke dosimeter.

The grafted films were removed and washed in distilled water for 1 day in order to remove unreacted monomer. The removing of impurities from the grafted films was checked gravimetrically.

The grafting degree was determined by gravimetric and potentiometric techniques and calculated by the following formula:

$$\text{GD} = [(m_{\text{graft}} - m_0) / m_0] \cdot 100 \% \quad (1),$$

where m_{graft} and m_0 are the weights of the films after and before grafting, respectively. For potentiometric determinations the grafted films were immersed in excessive amounts of 0.01 M solution of HCl and the excess is titrated by 0.01 M solution of NaOH. The value of m_{graft} was calculated from the titration results.

The water uptake was determined gravimetrically by the following formula:

$$\alpha = (m - m_{\text{dry}}) / m_{\text{dry}} \quad (2),$$

where m and m_{dry} are the weights of the films swollen in water and in dry state, respectively.

In experiments with copper uptake the samples of the grafted films were soaked into 0.1 M aqueous solutions of CuCl_2 for 1 day. The copper uptake was determined gravimetrically by the following formula:

$$\text{Copper uptake} = [(m_{\text{Cu}} - m_{\text{graft}}) / m_{\text{graft}}] \cdot 100 \% \quad (3)$$

where m_{Cu} and m_{graft} are the weights of the dry films, after and before sorption, respectively.

The potentiometric titration was conducted with a digital ionometer (JenWay, UK). The FTIR spectra of the films were recorded with the help of FTIR-Satellite spectrophotometer (Mattson, USA).

The synthesis of MADQUAT-NIPAAM copolymers was conducted in 10 % aqueous solutions using ^{60}Co MRX- γ -25 radiation facility with the dose rate 0.3 Gy/s. The hydrogels were synthesized by three-dimensional copolymerization in the presence of $3.84 \cdot 10^{-3}$ g/mL N,N'-methylenebis(acrylamide) as the cross-linking agent.

The compositions of the copolymers were determined by elemental analysis (PERKIN 85 ELMER Series II CHNS/O Analyzer 2400), IR-spectroscopy (FTIR Satellite "Mattson", USA) and ^1H and ^{13}C NMR-spectroscopy (Bruker ARX300 spectrometer at 300 and 75 MHz, respectively).

The release of pilocarpine hydrochloride was studied by immersion of dry films saturated with the drug into water and analysing the change in pilocarpine concentration in solution using Shimadzu UV2401PC spectrophotometer (Japan) at the wavelength 215 nm.

3. RESULTS AND DISCUSSION

3.1. Radiation synthesis of cationic and ampholyte hydrogels based on copolymers monoethanolamine and its sorption capability in respect to linear polyelectrolytes and metall ions

Cationic hydrogels have been prepared by copolymerization of vinyl ethers of monoethanolamine (VEMEA) and ethyleneglycol (VEEG) in the presence of divinyl ether of diethyleneglycol (DVEDEG) as a crosslinking agent.

The (co)polymerization of hydrophilic monomers in the presence of bifunctional cross-linkers is one of the methods for preparation of hydrogels. In most cases N, N'-methylene-bis-acrylamide (BAA) is used as a crosslinker for these purposes. However, in the case of vinyl ethers monomers BAA is not suitable because vinyl ethers have very low activity in reactions of radical polymerization and the hydrogels formed have inhomogeneous structure. The mentioned structure can be considered as an interpenetrating network, which incorporates highly cross-linked network composed mostly of BAA and weakly crosslinked network of vinyl ether. In this connection we have used divinyl ether of diethyleneglycol for synthesis of the hydrogels, which reactivity is similar to the reactivity of the monomers used.

The hydrogels were synthesized in the presence of 15 vol. % of water because according to our previous data the addition of water to the feed accelerates the radiation polymerization of the monomers. The main reason of this acceleration is a formation of hydrogen bonds between water and

monomer molecules. The effects of absorbed dose and monomer ratio in the feed on the gel and sol fractions as well as the swelling properties of the hydrogels have been studied.

It was demonstrated that the gel fraction increases with increase in absorbed dose. At the same time a decrease in sol fraction is observed, which is connected with formation of hydrogel having more cross-linked structure. Earlier in the study of binary copolymerization of VEEG with VEMEA [3] we have found that the latter monomer is characterized by lower reactivity. By this reason an increase of VEMEA content in the feed mixture leads to a decrease in the gel fraction and increase in the sol fraction. However, the higher content of VEMEA in the feed results in the formation of hydrogels with higher swelling ability due to the ionic contribution of cationic monomer to the total swelling pressure. The presence of primary amino-groups in VEMEA allows supposing the possible pH-sensitivity of the synthesized hydrogels. In acidic media the hydrogel is characterized by higher swelling ability because of the appearance of additional network charge due to the protonation of amino-groups.

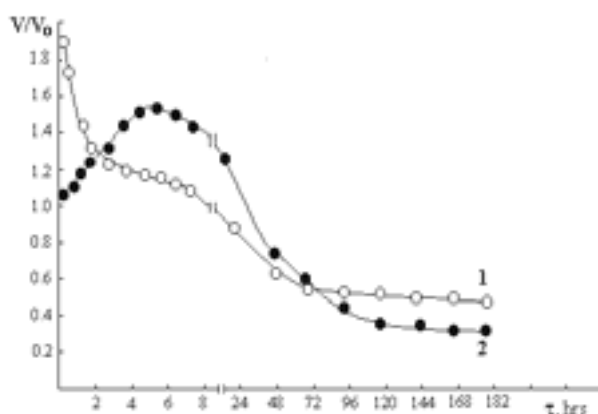


FIG. 1. Effect of pH on the swelling kinetics of VEMEA-VEEG (15 : 85 mol.%) hydrogel in 0.1 M solution of PAA. pH = 2.2 (1), 8.0 (2)

Earlier we studied the interactions of linear copolymers of VEMEA-VEEG with poly(acrylic acid) (PAA) in aqueous solutions [4]. Formation of compact interpolyelectrolyte complexes, which composition depends on pH was shown. In the present work we have studied the swelling behavior of the synthesized hydrogels in solutions of PAA at different pH (fig.1). It can be seen from the figure that the hydrogel undergoes considerable contraction after immersion into the solution of PAA at pH=2.2 due to the formation of interpolyelectrolyte gel-polymer complex and neutralization of the hydrogel charge. Earlier Kabanov et al. [5] have reported the similar behavior of polyelectrolyte hydrogels in solutions of oppositely charged ionic polymers. However, at higher pH values (pH=8.0) in the first stage of interaction the hydrogel swells additionally then reduces its volume. Probably this unusual behavior is connected with recharging of the gel surface by PAA macromolecules having higher charge density in these pH conditions. Then PAA macromolecules penetrate deeply into the network, the charges are neutralized and the gel volume decreases.

In order to confirm the mechanism of PAA interaction with the hydrogel the FTIR spectra of the starting polymers as well as the gel-polymer complex were recorded. For this purpose the hydrogel as well as the gel-polymer complex were dried and molded. The presence of the bands at 1710 cm^{-1} and 1556 cm^{-1} of unionized and ionized carboxylic groups in the spectrum of gel-polymer complex, respectively, confirms the sorption of PAA by the gel and electrostatic mechanism of this interaction.

PAA and VEEG-VEMEA are weak anionic and cationic polyelectrolytes, respectively. Therefore pH should affect considerably on their ionization degree and hence on the swelling behavior of gel-polymer complex. In this connection we studied the effect of pH on the swelling behavior of gel-polymer complex. For this purpose the sample of VEEG-VEMEA gel was immersed into

0.1 mol/L solution of PAA for 10 days. Then the gel-polymer complex obtained was immersed into solutions with different pH.

The gel-polymer complex is characterized by extreme swelling behavior in the media with different pH. The observed dependence of equilibrium swelling degree on pH is typical for polymers having polyampholyte properties. In acidic media the additional protonation of primary amino-groups is occurred resulting in an increase of the hydrogel charge and additional swelling. In basic region the part of unbound carboxylic groups of PAA are ionized and hydrogel attains the negative charge, which leads to its swelling. The pH value (pH=5.4), at which the hydrogel is characterized by minimal swelling degree, can be considered as the isoelectric point of the gel-polymer complex. In this point the negatively charged PAA groups neutralize the positively charged groups of VEMEA and the structure of the gel-polymer complex is relatively compact.

The interaction of copolymers VEMEA-VEEG hydrogels with transition metal ions and gold ions at varying conditions (pH, ionic strength, initial concentration of salt solution) have been investigated. For example it was shown that samples of equilibrium swollen VEMEA-VEEG hydrogel in water solution of CuCl_2 become deep blue and solution is decolorized. The observed phenomenon is connected with the complex formation between copper ions and VEMEA-VEEG hydrogel. that polymer network undergo nonmonotonous alteration of volume in the complexation process: contraction of the gel appear at the initial stage of complexation and then gel significantly swells. This unusual phenomenon of repeated swelling is obviously caused by additional cross-linking of the network by formation of coordination bound at the complexation and appearance of additional charge on the surface of hydrogel. Hydrogel can swell or contract depending on which factor dominates. It was shown that VEMEA-VEEG hydrogels undergo monotonous contraction in KCl solution (0,05 mol/L) because of repression of polyelectrolyte effect in the presence of low molecular weight salt concerning the absence complexation in the system KCl – cationic gel.

Varying of pH in the range from 2 to 6 leads to contraction of hydrogel network in acid media, but no complexation is observed. Apparently, it is caused by competition of protons with metal ions and increasing of ionic strength due to presence of CuCl_2 salt ions of external solution. Sorption process goes more intensively at increasing pH and phenomenon of repeated swelling even at initial stage of the process. Desorption of Cu^{2+} ions from hydrogel polymer matrix ([VEMEA]:[VEEG]=13:87 mol.%) readily undergoes in acid media (pH=2,2). During this process hydrogel swells and loses blue colour, and external solution is significantly coloured. Sorption – desorption processes can be multiple reproduced concerning possibility of using VEMEA-co-VEEG hydrogels as sorbents of transitional metals. It was found also good sorption capability of VEMEA-co-VEEG hydrogels in respect to gold ions.

3.2. Complex formation of temperature-responsive cationic linear copolymers and hydrogels based on [2-(methacryloyloxy)ethyl]trimethylammonium chloride and N-isopropylacrylamide with potassium hexacyanoferrates (II, III) and acrylic acid

Water-soluble and weakly cross-linked cationic polyelectrolytes have attracted considerable attention of researchers because of their ability to form polycomplexes with various large and small molecules. These complex formation reactions can be successfully utilized in purification of wastewater and enrichment technologies. Complexation of polymers with inorganic ions occurs due to two possible mechanisms – donor-acceptor bonding and electrostatic interactions. The first kind of polycomplexes is formed between polymers having electron-donating groups and transition metal ions. The second kind of interactions is realized, when the polyelectrolyte and inorganic ions are oppositely charged. In some cases the binding of inorganic ions by polyelectrolytes occurs by two mechanisms simultaneously.

Some industrial processes involving application of iron-cyanide complexes have led to contamination of ground water with wastes which are potentially hazardous, because they can be

converted to extremely toxic free cyanides (CN^- , HCN) in the presence of UV-light. Different sorbents of inorganic and organic nature were suggested to remove these contaminations.

In the present work the temperature-responsive cationic polyelectrolytes were synthesized by copolymerization of 2-(methacryloyloxy)ethyltrimethylammonium chloride (MADQUAT) with N-isopropylacrylamide (NIPAAm) and the water-soluble copolymers and hydrogels obtained were studied as complex forming reagents in respect to potassium hexacyanoferrates (II, III).

Complex formation of linear MADQUAT-NIPAAm copolymers with potassium hexacyanoferrates (II, III) was studied in aqueous solutions by viscometric and turbidimetric methods. It was found that an addition of $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution to the solution of the copolymer is accompanied by drastic decrease in viscosity caused by compaction of macromolecules in course of complex formation reaction. The same phenomenon is observed upon addition of $\text{K}_4[\text{Fe}(\text{CN})_6]$. However, unlike homopolymer PMADQUAT the mixing of the copolymers with potassium hexacyanoferrates (II, III) in dilute solutions (0.001 M) is not accompanied by phase separation. The appearance of the turbidity becomes seen in more concentrated solutions (0.01 M). Such difference between complexation behavior of PMADQUAT and the copolymers synthesized can be explained by the presence of NIPAAm units, which do not complex with $\text{K}_3[\text{Fe}(\text{CN})_6]$ or $\text{K}_4[\text{Fe}(\text{CN})_6]$ and provide higher solubility of polycomplexes in water. However, since the copolymers of MADQUAT and NIPAAm undergo separation upon heating the polycomplexes can precipitate forming yellow sediments at higher temperatures.

The behavior of polycomplexes in solutions was studied in a wide temperature intervals. It was shown that the polycomplexes aggregate and loose solubility at lower temperatures in comparison with starting polymer. The aggregation of polycomplexes is due to the presence of NIPAAm in copolymer as well as additional hydrophobization caused by complexation.

The hydrogels MADQUAT-NIPAAm have been synthesized and characterized. We studied the complexation of these hydrogels with potassium hexacyanoferrates (II, III). It was found that the volume ratio V/V_0 of the starting hydrogels depends strongly on the composition of copolymers. An increase in MADQUAT content increases the swelling ability of the samples due to ionic contribution to the total swelling pressure. The gel samples immersed in aqueous solutions of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$ undergo contraction and acquire green-yellow color, which is caused by complexation. The amplitude of contraction depends on MADQUAT content in copolymers and is maximal for hydrogels with highest MADQUAT content.

The contraction curves of the samples also depend on MADQUAT content in copolymers. The higher the NIPAAm content the higher the final DS of the hydrogels saturated by potassium hexacyanoferrates (II, III) because NIPAAm does not participate in complexation and remains relatively hydrophilic after the process. In addition an increase in NIPAAm content in the hydrogels shifts the saturation point to the lower relative concentration of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$.

Sorption ability of copolymeric hydrogels was evaluated by spectrophotometric method. We listed the data on the weight of absorbed salt per 1 gram of dry gels and also indicated the results in mol of the salt per mol of MADQUAT unit in the network in parentheses. The hydrogels bind more amount of $\text{K}_3[\text{Fe}(\text{CN})_6]$ than $\text{K}_4[\text{Fe}(\text{CN})_6]$ because every coordination ion $[\text{Fe}(\text{CN})_6]^{3-}$ interacts with three units of MADQUAT but the ion $[\text{Fe}(\text{CN})_6]^{4-}$ requires four MADQUAT units for binding. It can be seen that the higher MADQUAT content in copolymers leads to a greater sorption ability. Besides the amount of the salt absorbed by hydrogel containing 1 mol of MADQUAT units is not constant and depends on the composition of copolymers.

The polycomplexes of gels with the coordination compounds were thoroughly washed by distilled water, dried and analyzed by FTIR spectroscopy. The appearance of the band at 2117 cm^{-1} resulting from the vibrations of $-\text{CN}$ groups in the coordination compound in the spectrum of polycomplex confirms the presence of $\text{K}_3[\text{Fe}(\text{CN})_6]$ inside the gel.

In the present work we have studied also the interaction between hydrogels of MADQUAT-NIPAAm (26:74 mol.%) and linear PAA with different molecular weights (2000, 250000, 450000, 750000 Da).

Fig.2 shows the dependence of the relative volume of the gel samples immersed in aqueous solutions of PAA on time. It can be seen that the hydrogel sample immersed into solution of PAA with lowest molecular weight (2000 Da) undergo contraction with the highest rate. The sample reaches the equilibrium for 40-60 mins. The gel samples immersed into PAA solutions with 250000 and 450000 Da also reduce their volume gradually but their final equilibrium swelling is much higher. The PAA with the highest molecular weight 750000 Da also causes the volume changes of the gel sample. However in the first stage of interaction (first ten minutes) the gel sample increases its swelling degree slightly. Then the gel begins to contract reaching the equilibrium during 60-70 mins. In summary, the molecular weight of linear PAA strongly affects the interaction. The higher the molecular weight of PAA the lower the amplitude of hydrogel contraction as a result of interpolyelectrolyte interaction. This trend can be explained by decrease in penetration ability of linear macromolecules through the network. A slight increase in the first 10 mins of interaction observed for PAA with 750000 Da can be explained by temporary increase in the hydrogel surface charge density caused by local contraction of the surface. After the macromolecules penetrate deeper they neutralize the inner part of the gel charge and the sample undergo contraction.

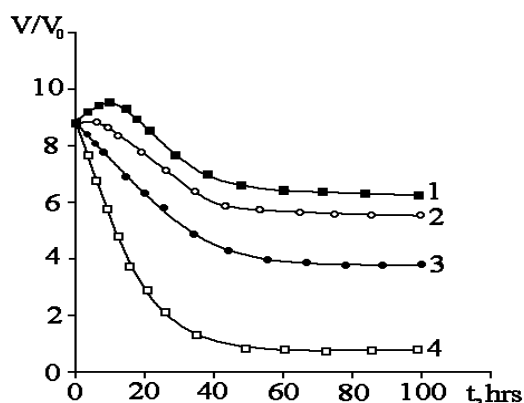


FIG. 2. Swelling behavior of MAD-NIPAAm hydrogels in PAA aqueous solutions. $C_{PAA}=0.01M$; $[MAD]:[NIPAAm]=26:74$ mol.%; $M_w=750000$ (1); 450000 (2); 250000 (3) 2000 (4).

The effect of polymer concentration on the kinetics of hydrogel contraction was studied for PAA with the lowest molecular weight 2000 Da. It was found that if the concentration of PAA is very low (0.001 M) the contraction of the gel sample is slower. However there is practically no difference in contraction kinetics for 0.01 M and 0.1 M solutions of PAA. It is likely that above 0.01 M concentration there is saturation.

The effect of environmental pH at constant ionic strength on the gel contraction kinetics as a result of interpolyelectrolyte reaction have been studied. An increase in solution pH accelerates the contraction process. Such a trend can be explained by dissociation of carboxylic groups of PAA. At low pH value (2.8) the dissociation of carboxylic groups of PAA is completely suppressed, hence the linear polymer interacts with NIPAAm units of hydrogel mainly through hydrogen bonding. The MADQUAT units do not participate in this interaction and remain charged, which leads to a relatively higher swelling degree of the sample. At higher pH (6.7 and 8.4) the ionisation of carboxylic groups is very high and they are able to interact with MADQUAT units of hydrogel and reduce the gel volume very efficiently.

3.3. Hydrophilic stimuli-responsive films based on poly(acrylic acid)-poly(vinyl methyl ether) blends cross-linked by gamma-radiation

Poly(vinyl methyl ether) (PVME) is a non-ionic water-soluble polymer with unique ability to lose its solubility in water at higher temperatures. This property has attracted attention of different researchers and a lot of studies have been performed on temperature-induced phase separation in PVME-water system recently. In the present work we have prepared PAA-PVME cross-linked films, studied their swelling properties in solutions with different pH and the possibility of their use as drug delivery system. PVME as well as copolymers of vinyl methyl ether with maleic anhydride are important components of pharmaceutical formulations for controlled release of some drugs. The low value of glass transition temperature of PVME provides materials containing this polymer softness, elasticity and high adhesiveness, which is very important for their application as biomaterials. However the high adhesive ability of PVME is one of the difficulties in preparation of polymeric films by casting because of difficult detachment of these materials from the casting surface. In this connection the blending of PVME with other polymers is of considerable interest.

It is known that the mixing of aqueous solutions of PVME and PAA is accompanied by appearance of turbidity and precipitation of interpolymer complex (IPC), stabilized by hydrogen bonds, which disturbs the homogenous film formation. There are two possibilities to prevent the complex formation between PVME and PAA. The first one includes the neutralization of PAA by addition of some strong base. In these conditions the IPC will not be formed because the hydrogen bonding is possible with participation of unionised groups only and the mixture of solutions will not undergo phase separation. However, the films prepared by this technique would not be homogenous because of the complete immiscibility of the polymers. The second possibility is addition of organic solvents, which can prevent complexation because of their strong hydrogen bonding ability with respect to polymers. In the present work we have used dimethylformamide (DMF) as an additive, which prevents complexation. The films based on compositions with 10 and 20 mol.% of PVME were cast from 0.3 M aqueous solutions of polymers containing 30 vol.% DMF. The blends with higher PVME content could not be prepared because they were very adhesive and could not be detached from the surface of a Petri dish. After evaporation of the solvent the films obtained were homogenous and very elastic.

In order to prepare cross-linked materials the films were subjected to gamma-irradiation. It was shown that an addition of PVME to the composition increases the gel fraction considerably. It is well known that the gelation dose is inversely proportional to the molecular weight of a polymer, i.e. the higher the molecular weight of the polymer the lower the gelation dose. However, in our case an addition of lower molecular PVME to the mixture enhances the gelation. Cowie et al [6] have reported that the blends of PAA with PVME are characterized by lower glass transition temperature (T_g) than pure PAA. It is likely that a decrease in T_g favours the formation of the gel at lower doses because of the higher flexibility of the composition.

The cross-linked PAA-PVME blend films are able to swell in water and form hydrogels. It was found an increase in absorbed dose decreases the swelling ability of the materials considerably, which is connected with increase in cross-linking degree. An addition of PVME to the composition also decreases the swelling ability of the films because of its higher hydrophobicity and more ability for cross-linking.

The kinetics of hydrogels swelling is a parameter, which is very important for application of these films as biomaterials. We have studied the swelling kinetics of cross-linked films in solutions of different pH. In acidic medium (pH 2.2) the films achieve its equilibrium swelling for 20-30 min but the values of their water sorption capacity are relatively low. The equilibrium swelling degree (α) of pure PAA film is 6.6 g/g but the compositions containing PVME are characterized by even lower values of α . These low α values are caused not only by higher hydrophobicity of these blends but also by the possibility of interpolymer complex formation between unionised carboxylic groups of PAA and ether groups of PVME via hydrogen bonding and appearance of additional physical cross-links.

In solutions with higher pH the films swell to a significantly higher extent. In this case the swelling degree of the hydrogel films is due to dissociation of carboxylic groups of PAA and appearance of the network charge. Besides the interpolymer hydrogen bonding is not possible in these conditions. The structure of the films purified from linear un-cross-linked polymers was evaluated by FTIR spectroscopy. The spectrum of PAA is characterized by the presence of the band at 1711 cm^{-1} , which is typical for carbonyl stretching of COOH-groups. The bands at 1111 and 1086 cm^{-1} observed in the spectrum of PVME are related to vibrations of ether groups. The same bands are observed in the spectrum of PAA-PVME film confirming that both polymers are cross-linked within one network. Some broadening of these bands is likely related to the hydrogen bonding between COOH-groups of PAA and ether-groups of PVME. Soft and elastic consistency of PAA-PVME films in dry and in swollen state is an important property, which is typical for blends of PAA with poly(vinyl ethers).

The materials obtained in the present work can be used as bioadhesive films in ophthalmic applications, where the high elasticity of a polymer is required. Pilocarpine hydrochloride is an effective drug, which is widely used in human and veterinary medicine for treatment of glaucoma. The films containing pilocarpine hydrochloride were obtained in the present work by immersion of the dry cross-linked samples into 1 % aqueous solutions of pilocarpine for several days. Then the films were removed and dried. The release of the drug from the films into water was studied by UV-spectroscopy at the wavelength 215 nm. It was found that the amount of the drug released as well as the release rate are strongly dependent on the content of PVME in the film. An increase in PVME content in the film decreases these release parameters considerably. There are several possible reasons responsible for this regularity. First, the films containing higher amount PVME exhibit less swelling degree, which can delay the release of the drug from the polymer blend. Second, the films containing lower amount of PAA can absorb less amount of pilocarpine hydrochloride since the drug strongly interacts with carboxylic groups of polyacid via electrostatic contacts. Taking into account the specific interaction between the drug molecules and PAA one can suppose that even after 300-400 mins of release a significant amount of the drug is still retained in the polymeric matrix.

3.4. Radiation grafting of vinyl ether of monoethanolamine on polyolefine films

The use of ionizing radiation is preferred for grafting of polymers on different surfaces. The advantages of radiation technique include the possibility to regulate the grafting process and in some cases to initiate the polymerization of monomers, which cannot be prepared by other ways. In recent years, there has been an increasing interest of researchers to the radiation grafting of functional polymers on different surfaces. This technique can be successfully utilized for preparation of selective sorbents, hydrophilization of surfaces, modification of membrane properties of different materials, enhancing the biocompatibility of medical devices.

The irradiation of polyethylene films immersed into the monomer results in the grafting of VEMEA. In order to characterize the obtained materials as well as to confirm grafting we have recorded the FTIR spectra of the films. In the spectrum of the starting polyethylene there are bands 2915, 2848, 1463 and 719 cm^{-1} , responsible for valent and deformation vibrations of CH-groups. New bands in the area 1089-1110 cm^{-1} , characteristic for vibrations of ether groups of VEMEA, 1576-1595, 3368 and 3300 cm^{-1} , responsible for deformation and valent vibrations of VEMEA primary amino-groups, are appeared in the spectra of grafted films. The presence of these new bands in the spectra confirms the grafting process. Moreover, an increase of absorbed dose leads to the increasing of the intensity of these bands.

The grafting degree of VEMEA as a function of the absorbed dose has been determined by two different methods – gravimetric and potentiometric ones. The results are summarized in table I. The gravimetric and potentiometric data are in close agreement. It can be seen that unlike of active monomers the grafting of VEMEA required considerably higher values of absorbed doses and even in these conditions the grafting degree values are comparatively low. In addition the appearance of grafted species on polyethylene films requires some minimal dose, which is within 54-108 kGy.

This "inhibition period" is caused by the low activity of VEMEA in radiation polymerization. Besides the grafting process is not very effective and is always accompanied by the formation of PVEMEA homopolymer.

TABLE I. DEPENDENCE OF GRAFTING DEGREE AND WATER UPTAKE OF GRAFTED FILMS ON ABSORBED DOSE

Absorbed dose, kGy	Grafting degree, %		Water uptake, g/g
	Gravimetric data	Potentiometric data	
54	0	0	0
108	0.75	0.6	0.75
162	4.35	4	1.32
270	9.4	8.1	2,73
324	11.4	12.5	3,05
378	12.8	14	3,75
432	18.1	16.9	4

The grafting of hydrophilic monomer of a hydrophobic polyethylene surface results in the enhancing ability to absorb water. Thus, the values of water uptake by the grafted films reach 4 g per 1 g of dry material. It should be noted that the formation of a hydrogel layer on a surface of polyethylene is observed at doses higher than 400-450 kGy.

In order to increase the efficiency of grafting we have studied the effect of water addition to the monomer taking into account the following: first; it was shown that the water added to the feed mixture accelerates radiation polymerization of VEMEA, second; the presence of water in monomer should increase the number of active radicals in the system because of the radiolysis of water.

The dependences of grafting degree on the water content in the feed at various absorbed doses have been studied. It is obvious that the presence of 10 vol. % of water in the feed increases the grafting degree to reach maximum value. However, the further addition of water from 10 to 50 vol.% leads to a decrease in the grafting degree value to reach a lower one than without water addition. This dependence can be explained by the action of two factors: first is the favourable effect of water, second is the dilution of the feed or enhancing the formation of homopolymer. The similar trends are also observed for the values of water-uptake by the grafted films. The addition of 10 vol.% of water to the feed results in the growth of water uptake, and then it decreases with increasing of water percentage because of dilution of the feed.

As a weak cationic polyelectrolyte the PVEMEA demonstrates the ability for reversible conformation transitions in respond to the change of pH. The water uptake of the grafted films was studied as a function of pH medium. It was found that from the figure that the water uptake is increased upon shifting to the acidic pH region due to the protonation of primary amino-groups and appearance of the additional positive charge on the surface.

In order to increase the grafting degree of VEMEA on a polymeric surface we selected polypropylene as a new substrate for grafting because its structure affords to suppose the higher reaction ability in respect to irradiation.

Polypropylene films were immersed in VEMEA and irradiated in a wide range of the absorbed dose. The grafting degree of VEMEA on PP as a function of absorbed dose is summarized in table II. An increase of the grafting degree is observed in the whole range 54-432 kGy. The appearance of VEMEA species on PP film causes the increase in water uptake by the prepared material because of the hydrophilization of its surface (table II).

An increase of the grafting degree is observed in the whole range 54-432 kGy. The grafting of VEMEA onto polympropylene is more effective than onto polyethylene. Polymer –metal ions

complexation is attractive approach for preparation of functional sorbents for waste water treatment. The presence of electron-donating primary amino- and ether-groups in VEMEA provides the ability of its polymers to form polycomplexes with various metal ions.

TABLE II. DEPENDENCE OF GRAFTING DEGREE AND WATER UPTAKE OF GRAFTED POLYPROPYLENE FILMS ON ABSORBED DOSE

Absorbed dose, kGy	Grafting degree, %	Water uptake, g/g
54	3.00	0.50
108	4.41	1.52
162	6.80	2.00
216	8.13	2.12
270	14.11	2.60
324	18.00	3.31
378	19.20	4.00
432	25.70	4.98

Ability of the grafted films to absorb various heavy metals in order to evaluate the possibility of their uses in waste water treatment was studied. Figure 3 shows the ability of the grafted films for metals uptake. Films with a higher grafting degree are characterized by considerable higher binding ability in respect to heavy metals. Nature of metal ion also has a great importance in the binding to the polymeric material. The affinity of the metal ions to VEMEA is decreased in the following direction:

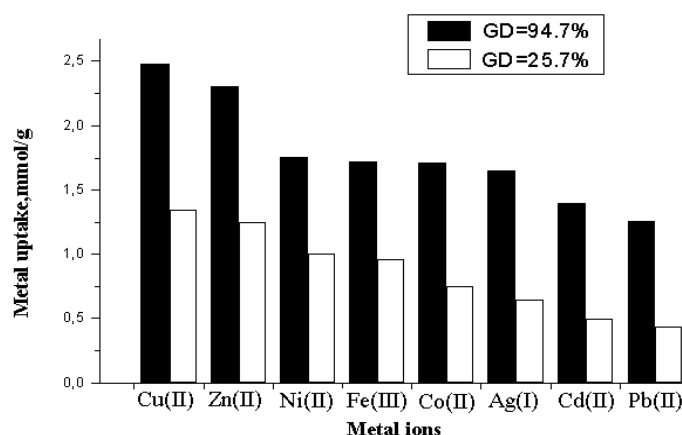
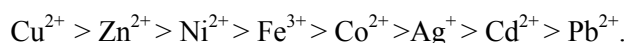


FIG. 3. Sorption of metal ions by grafted films

Thus, the maximum value of metal uptake is very dependent on the type of metal ions and its coordination as well as the ionic size of the metal, which affect the permeability and diffusion of these metals through the porous ionic films. The latter parameter is mainly dependent on the polarity, electronic configuration and ionic radii of these metal ions.

The possibility to use the obtained materials repeatedly was evaluated in the several sorption-desorption cycles. The kinetics of sorption/desorption of metal ions could not be followed by gravimetric studies because it requires removing and drying the samples periodically that affects the accuracy of results. So, the spectrophotometric technique is applied. In this technique it is easy to determine the desorbed/absorbed amounts of metal ions without removing and drying the samples.

The grafted film immersed into metal salt solution starts to absorb metal ions. Therefore the concentration of metal ions in solution decreases with sorption process and this decrease was

monitored using spectrophotometer. The metal sorption increases with time and reaches the maximum after about 2 hours, when the chelating sites of the film are saturated. The maximal amount of absorbed metal salt, which was determined spectrophotometrically and expressed in mmol/g units, coincides well with the metal uptake obtained by gravimetric technique.

The recovery and separation of absorbed metals can be easily carried out by treating the films with 0.01 M HCl for one hour. Desorbed metal ion concentration increases in solution of HCl with time and then reaches the maximum when desorption process is completely done. The regenerated films are again effective for resorption of metal ions with the same efficiency as checked for our films for 5 times.

Studies on the effect of pH on sorption characteristics of grafted film were carried out by metal uptake measurements over pH that ranged from 1 to 6. It was found that the metal sorption process increases with increasing of pH for Cu^{2+} , Ni^{2+} , Co^{2+} and reaches the maximum at pH=5 then decreases. In acidic solutions, the metal uptake decreases due to the competition with protonation reaction. On the other hand, at pH higher than 5 the metal uptake decreases due to the precipitation of hydroxides. Generally each metal ion has its own pH at which it shows maximal sorption.

One of the approaches that can be used to enhance the radiation grafting of VEMEA is to perform the process in the presence of more active monomer. In this work we have studied the preparation of novel materials by γ -initiated radiation grafting of cationic monomer VEMEA from its mixtures with vinyl ether of ethyleneglycol (VEEG) onto polyolefin films. We studied the effect of VEEG addition on the grafting of VEMEA onto polyethylene films. Table III presents the data on total grafting degree GD_{total} of VEMEA and VEEG at different absorbed doses and monomer ratios. It can be seen that an increase of absorbed dose considerably increases the total grafting degree. A significant increase in grafting is observed with addition of VEEG to the commoner mixture. Thus, the grafting degree, which is observed at 216 kGy for pure VEMEA, is 7.9 %. However, in the presence of 50 mol.% of VEEG the value of GD_{total} is increased to 258.5 %. Such a considerable enhancement is likely to be due to higher reactivity of VEEG in copolymerization.

TABLE III. DATA ON TOTAL GRAFTING DEGREE GD_{TOTAL} OF VEMEA AND VEEG AT DIFFERENT ABSORBED DOSES AND MONOMER RATIOS

Absorbed dose, kGy	Total grafting degree, %			
	100 mol. % VEMEA	90 mol. % VEMEA 10 mol. % VEEG	70 mol. % VEMEA 30 mol. % VEEG	50 mol. % VEMEA 50 mol. % VEEG
54	0	2.0	4.1	4.7
108	0.8	3.9	6.0	33.9
162	4.4	9.3	19.6	58.7
216	7.9	12.6	78.6	258.5

FTIR spectra of virgin polyethylene (PE) film, PE grafted with VEEG, PE grafted with VEMEA as well as the film grafted with mixture of the two monomers were recorded in order to characterize the materials obtained. PE film shows several distinct bands at 2908, 2869, 1464, 1376 and 723 cm^{-1} , responsible for valent and deformation vibrations of CH-groups. Grafting of VEMEA onto PE is accompanied by appearance of the new bands at 3367 and 1579 cm^{-1} , responsible for stretching and bending of primary amino groups, and the band at 1108 cm^{-1} , typical for vibrations of ether groups.

The spectrum of VEEG grafted material has very broad new absorption band centred at 3366 cm^{-1} , characteristic for hydrogen-bonded hydroxyl groups' vibrations, new bands at 1095 and 1072 cm^{-1} , responsible for symmetric and asymmetric vibrations of ether groups.

The spectrum of the materials obtained by grafting from binary monomer mixtures shows the presence of amino groups in the sample (1557 cm^{-1}), confirming the grafting of VEMEA. The new characteristic bands are observed at 3361 cm^{-1} (hydroxyl- and primary amino-groups) and 1107 cm^{-1} (ether bonds), which can be characteristic for both monomers.

Using a combination of gravimetric technique for determination of the total grafting degree and potentiometric titration method for determination of ionic monomer VEMEA grafting degree we have determined the grafting degrees of individual monomers in the graft copolymer (Table IV).

As in the case of conventional copolymerization VEEG has higher reactivity in grafting than VEMEA. For all absorbed doses (162 and 216 kGy) an increase of VEEG content in the feed mixture leads to an increase in the grafting degree of both monomers VEEG and VEMEA. Such behaviour can be attributed to the increasing of the copolymerization rate with addition of VEEG, which in turn increases the grafting of both monomers and the total grafting degree. It can be said that the presence of more active monomer in the feed mixture enhances the grafting of the less active monomer due to the significant increase in total grafting degree resulting from the increasing of copolymerization rate.

TABLE IV. DEPENDENCE OF GRAFTING DEGREE OF VEEG AND VEMEA ON THE FEED MIXTURE COMPOSITION

Dose, kGy	FEED MIXTURE COMPOSITION, MOL. %		Total grafting degree, %	Grafting degree of VEMEA, %	Grafting degree of VEEG, %
	VEMEA	VEEG			
162	90	10	9.3	1.1	8.2
	70	30	16.9	1.4	18.2
	50	50	58.7	9.4	49.3
216	90	10	12.6	1.6	11
	70	30	78.6	7.2	71.4
	30	50	258.5	26.7	231.8

The presence of amino- and hydroxyl-groups will modify the hydrophilic properties of the graft copolymer. The obtained materials were evaluated for their sorption ability in respect to water and copper (II) ions.

Table V presents the data on water and copper (II) ions uptake by the films obtained at different monomer ratios in the feed mixture. It is clearly seen that an increase of VEEG content in the feed leads to the higher value of water uptake, i.e. the film becomes more hydrophilic. The uptake of copper (II) ions was controlled by two different methods - gravimetric measurements of the dry film weight increase after sorption and spectrophotometric monitoring of residual copper (II) ions in solution. The results obtained by two methods are in good agreement and indicate the higher copper (II) uptake for films prepared from the mixtures of higher VEEG content. In order to clarify the mechanism of copper (II) binding by the grafted films we have studied the effect of pH on absorption. It was shown from the figure that the uptake of copper (II) ions increases with increasing pH, reaching a maximum at pH 5.0, then decreases. In acidic solutions, the uptake is low due to competition with the protonation reaction. On the other hand, at pH higher than 5.0, the metal uptake decreases due to the precipitation of copper (II) hydroxide on the pH. This result is in good agreement with that obtained in our previous work and confirms that the binding of copper (II) ions by VEMEA-VEEG grafted film takes place mainly due to donor-acceptor interaction with unprotonated amino-groups of VEMEA.

TABLE V. DEPENDENCE OF WATER AND COPPER (II) IONS UPTAKE BY THE GRAFTED FILMS ON THE COMPOSITION OF FEED MIXTURE AT ABSORBED DOSE 216 KGY

Feed mixture composition, mol. %		Water uptake, g/g	Copper (II) ions uptake, %	
VEMEA	VEEG		Gravimetric determination	Spectrophotometric determination
100	0	1.48	0.25	0.21
90	10	2.30	1.20	1.12
70	30	75.00	19.00	18.32
50	50	103.00	23.50	22.76

3.5. Synthesis and characterization of hydrogels based on copolymers of polyethylene glycol and methacrylic acid as sorbent of uranyl ions

The using of high energies irradiation for synthesis of polymers has a number of advantages in comparison to other methods of synthesis: obtaining of polymers free of initiators, easy control of irradiation process and carrying out of polymerization at low temperatures. In the present work the copolymeric hydrogels were synthesized by γ -irradiation of water-ethanol of polyethylene glycol and methacrylic acid (PEG-MAA) in presence of crosslinking agent threethyleneglycol dimethacrylate (TEGDMA) and physical chemical characteristics were studied. The comparative study of uranyl ions adsorption by PEG-MAA and polymethacrylic acid (PMAA) hydrogels was carried out using UV-, FTIR spectroscopy methods. From the structural point of view, in the obtained PEG-MAA hydrogels the one end of PEG chain probably is bound or grafted to the PMAA chain. Such assumption about the structure of polymer network was done because in absence of crosslinking agent obtaining of hydrogels was not possible.

Figure 4 shows the change of gel-fraction yield (CR (%)) of hydrogels with irradiation dose (from 1.4 to 20 kGr), composition of feed monomer mixture and molecular weight of PEG. It can be seen, that highest yield of copolymers is achieved at dose 5 kGr. The following small decrease of CR (%) can be attributed to the scission of methacrylic acid chains. It is known from the literature that polymers, containing quarter carbon atom in its structure under ionizing irradiation undergo to destruction processes and the sharp decrease of the yield of PMAA hydrogel after irradiation dose 5 kGr confirm this supposition. Also it should be noticed that decreasing of CR (%) for copolymeric hydrogels PEG-MAA is less pronounced then for PMAA what is probably due to the template mechanism of copolymerization of the last. As a result, additional physical crosslinks appear in the system because of the formation of interpolymer complexes of hydrogen bonds. Increasing of concentration of MAA in the feed monomer mixture results in increase of their yield. There are two possible reasons of it, the first one is due to enhance of the template copolymerization and the second is because crosslinking of PEG chains at such conditions of experiment was not observed, increasing of PEG content in the feed monomer mixture decrease conversion of PEG-MAA.

The swelling characteristics of PEG-MAA networks with different molecular weight of PEG were studied in the present work. It has been found that hydrogel samples with the smallest PEG chain length have the highest swelling degree. Obtained results can be attributed to decrease of the amount of hydrogen bonds between PEG ether oxygen and PMAA carboxylic groups which play role of additional crosslinks in the network structure. Polymeric hydrogels containing ionic functional groups are widely used materials for different metal ions adsorption due to high adsorption ability, possibility of regeneration and repeated use.

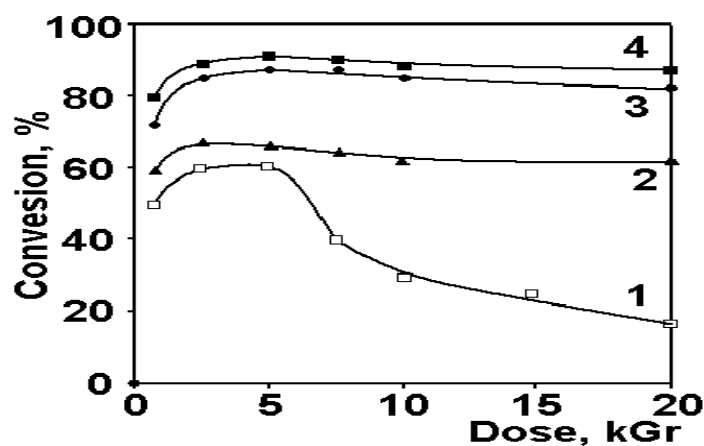


FIG. 4. Conversion (yield of gel-fraction) of PEG-MAA hydrogels of different composition irradiated to various dose.

Uranyl ions sorptions by PEG-MAA and PMAA hydrogels were compared. Structural feature of hydrogels based on PEG-MAA copolymers is the possibility of specific interactions between unionised carboxylic groups of MAA and ether oxygen of PEG via hydrogen bonding at low pH values. Taking into account the possibility of interpolymer complex formation within the network of PEG-MAA the sorption of uranyl ions by these hydrogels and pure poly(methacrylic acid) (PMAA) were studied additionally as a control network without interpolymer interaction.

Figure 5 shows adsorption isotherms of hydrogels of PEG-MAA and PMAA network obtained by plotting its adsorption capacities versus equilibrium UO_2^{+2} ions concentration. The sorption of uranyl ions by hydrogels is accompanied by acquiring of yellow colour by the samples. It can be seen from figures that adsorption becomes more pronounced at higher concentration of the uranyl ions. Besides, composition of copolymers does not affect significantly on its adsorption capacity. It can be seen from the figure that both hydrogels adsorb almost the same amount at low concentration of uranyl ions (100-200 ppm) in spite of the lower content of carboxylic groups of MAA in copolymer then that is in PMAA hydrogel. It can be attributed to conformational peculiarities of the first network. Besides the coordination binding interaction of ether oxygen with UO_2^{+2} can play some role in adsorption.

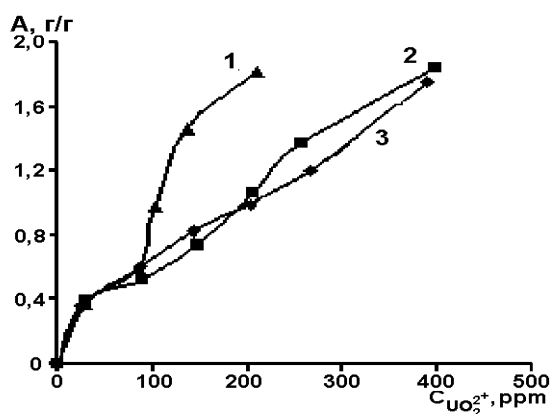


FIG. 5. Adsorption isotherms of UO_2^{+2} ions adsorption onto PMAA (1) and PEG-MAA (2,3) hydrogels

The sorption of uranyl ions by the hydrogels can be followed by FTIR spectroscopic analysis of dried samples. It was shown that the FTIR spectra of initial PMAA and PEG-MAA hydrogels as well as of samples after sorption from solutions with different uranyl ions concentration. The appearance of new band at 1539 cm^{-1} and 1532 cm^{-1} in the spectra of PMAA and PEG-MAA hydrogels saturated by UO_2^{+2} ions, respectively, responsible for asymmetric vibration signals of carboxylate anions indicates the ionisation of carboxylic groups caused by formation of ionic bonds with uranyl ions.

Also a new band in the spectra of hydrogels after sorption of uranyl ions at 937 cm^{-1} belongs to uranyl nitrate hexahydrate. The stability of PEG-MAA and PMAA hydrogels in regeneration processes for repeated using in adsorption processes was studied (Fig. 6). For desorption of uranyl ions from hydrogels the 0.1 M solution of HCl acid was used.

It was found that PMAA network undergo to destruction after the second cycle of regeneration and became not suitable for adsorption purposes. At the same time, copolymeric hydrogels PEG-MAA can be used in sorption-desorption processes more then 5 times. The stability of copolymers to desorption processes in comparison to PMAA is probably attributed to the formation of interpolymer complexes between COOH groups of PMAA and ether oxygen of PEG which enhance the mechanical strength of hydrogel.

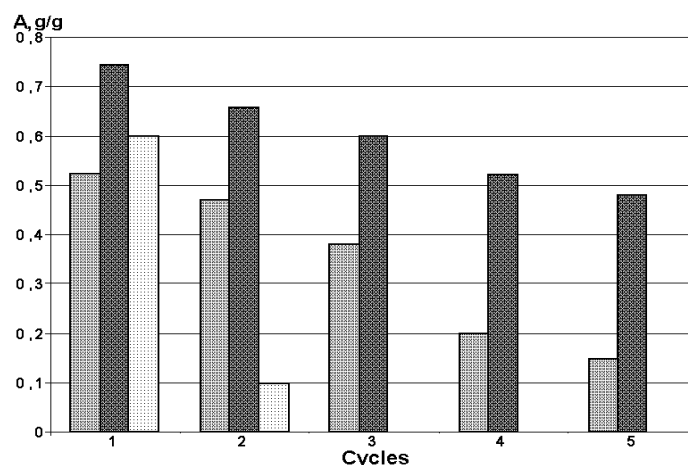





FIG. 6. Adsorption capability of PEG-MAA hydrogels in the sorption-desorption processes; PEG-MAA -  (200 ppm);  (100 ppm); PMAA -  (100 ppm) [PEG]:[MAA]=40:60 mol %

4. CONCLUSIONS

Novel cationic and ampholyte hydrogels were synthesized by gamma-radiation copolymerization of vinyl ethers of monoethanolamine and ethyleneglycol in the presence of cross-linking agent. The cationic hydrogels are able to bind various metal ions and poly(acrylic acid) to form interpolyelectrolyte complexes having swelling properties typical for polyampholytes. The interactions of the synthesized polyampholyte hydrogels and linear poly(acrylic acid) or poly(vinyl ether of monoethanolamine) are accompanied by contraction of the networks independently on pH. However the mechanism of interpolyelectrolyte interactions can be different at different pH.

Temperature-responsive complex forming linear polyelectrolytes of high molecular weight and their hydrogels were synthesized by γ -irradiation copolymerization of MADQUAT and NIPAAM. It was shown that the linear copolymers are able to form polycomplexes with potassium hexacyanoferrates (II, III), which solubility greatly depends on concentration of the reagents and temperature. Using the temperature-sensitivity of the copolymers it is possible to regulate the solubility of polycomplexes. The hydrogels of copolymers absorb potassium hexacyanoferrates (II, III) and undergo contraction. The sorption ability of hydrogels depends on MADQUAT content in copolymers and is higher with respect to $\text{K}_3[\text{Fe}(\text{CN})_6]$ than to $\text{K}_4[\text{Fe}(\text{CN})_6]$. Water-soluble copolymers as well as hydrogels based on MADQUAT and NIPAAM are able to interact with linear PAA and form polycomplexes. The nature of interaction is different at different pH. In acidic media the polycomplexes are stabilized by hydrogen bonds but at higher pH the electrostatic forces play the major role. The molecular weight of PAA as well as the composition of copolymers affects the aggregation stability of polycomplexes and their composition.

Stimuli-responsive hydrogel films were prepared by gamma-radiation cross-linking of the blends based of poly(acrylic acid) and poly(vinyl methyl ether). The films containing higher amount of poly(vinyl methyl ether) are easier cross-linked and have lower swelling ability. The environmental pH affects the swelling of the films significantly. In acidic media the films have lower swelling ability because of suppression of carboxylic groups ionisation and formation of additional physical cross-links via interpolymer hydrogen bonding. The possibility for application of the films as drug delivery systems is demonstrated with anti-glaucoma medicine pilocarpine hydrochloride.

Novel polymeric materials were prepared by radiation grafting of cationic monomer vinyl ether of monoethanolamine on the surface of polyethylene and polypropylene. The grafting degree and water uptake of films are function of absorbed dose. The addition of water to feed mixture up to 10% increases the grafting degrees and water uptake as well as addition of 5% hexane did the same trend. The prepared graft copolymers showed a good affinity towards the chelation and/or complexation with different metals investigated here (Pb^{2+} , Cd^{2+} , Zn^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Ag^+). Maximal sorption for Cu^{2+} , Ni^{2+} , Co^{2+} is achieved after treating time 2 hours in feed solution of pH 5. Treating of the saturated films with 0.01 HCl at room temperature for one hour easily recover the absorbed metals and accordingly the films can be reused for the resorption of metal ions.

Novel non-ionic thermo-sensitive linear and crosslinked polymers have been obtained by gamma-irradiation copolymerisation hydrophilic (of ethylene glycol, 2-hydroxyethylacrylate) and hydrophobic comonomers (vinyl butyl ethers, vinyl isobutyl ethers, 2-hydroxyethylmethacrylate, butylacrylate). It was found that soluble copolymers are characterized by LCST in water, and polymer hydrogels based this copolymers undergo thermo-induced contraction or collapse. The sorption processes of surfactants by novel thermosensitive copolymers have been studied.

The copolymeric hydrogels based on PEG and MAA were synthesized by using γ -irradiation method in presence of crosslinking agent triethyleneglycol dimethacrylate. Physical chemical characteristics of obtained networks were studied. It was found that the swelling and structural characteristics of PEG-MAA hydrogels depend on composition of reaction mixture, PEG molecular weight and pH of solution. The comparative study of uranyl ions adsorption by PEG-MAA and polymethacrylic acid (PMAA) hydrogels was carried out using UV-, FTIR, TGA spectroscopy methods. It was shown that the sorption characteristics depend on pH and ionic strength of solution as well as uranyl ions concentration. The higher stability in the regeneration processes and possibility of repeated use of copolymeric hydrogel of PEG-MAA for uranyl ions adsorption in comparison to homopolymer PMAA were shown.

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PREPARATION AND CHARACTERIZATION OF THE SPHERICAL MESOPOROUS SILICA (MCM-41) FOR RECOVERY OF URANIUM IONS FROM SEA WATER

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Abstract

MCM-41 materials were synthesized using alkyl (decosane, dodecyl and eicosane) trimethyl ammonium bromide as structure directing surfactants. X ray diffraction (XRD) analysis and nitrogen adsorption measurements reveal that the pores are hexagonal with tunable textural properties through the choice of surfactant and experimental condition. MCM-41 materials suit for application as adsorbent. Studies on sorption of uranyl ion were N_2 -adsorption measurements, XRD and FTIR spectroscopic analysis of uranyl ion loaded MCM-41 confirm the entrapment of uranyl ion in the pores of MCM-41.

1. OBJECTIVE OF THE RESEARCH

The objective of the present investigation was to tune the experimental conditions for the preparation of mesoporous materials to make effective entrapment of uranyl ions in the pores of the materials.

2. INTRODUCTION

In recent years, articles related to the various aspects of the mesoporous materials can be found quite frequently in leading journals. The application potentialities and possibilities of tailor making the synthesis to produce mesoporous inorganic material with defined morphology and pore sizes, generate continuing interest on that type of materials. Certainly, the discovery of mesoporous MCM-41 offers the possibility for synthesizing 3D hetero structures in otherwise inaccessible size range by the self-assembly of surfactants as templates at the fluid/solid interface [1-3]. MCM-41 is a porous amorphous silica material with a hexagonal honey comb structure and can be prepared with controllable pore diameters by judicious manipulation of conditions of synthesis. The application superiority of MCM-41 and related inorganic porous products as ceramics, catalyst supports, biomedical implants, and membranes for high-temperature separation technology etc. has well been established [4,5].

In the process of using MCM-41 for specific applications, many different synthetic means have been formulated and attempted for the control of size, shape, orientation, and polymorphic structure [6-9]. Various templates such as microemulsion [10], block copolymers [11], latex particles [12], colloidal crystals [13], sponge-like polymer gels [14] and bacterial superstructures [15] have been tried for modulating the periodicity and regularity of the porous structure in MCM-41. Also, studies have been directed to modulate the pore size without affecting the structural stability of the material [16,17]. Specifically, MCM-41 with tailor-made pore sizes can be a suitable material for testing as an adsorbent.

In an attempt to solve the environmental problems, efforts have been made on extracting various heavy metal ions like mercury ion, using different porous adsorbents [18,19]. For the sorption of uranyl ion, several adsorbents like montmorillonite clays [20], silica gels [21], diatomite (kieselguhr) [22], hydrous oxides [23], etc. have been tried. The remarkable features of MCM-41 such as large surface area ($1000\text{--}1400\text{ m}^2\text{g}^{-1}$) and uniform pores with well defined and controlled sizes (2–10 nm) provide the superiority of using for the removal/entrapment of heavy metal ion from aqueous solution. Shin have proved the efficiency of surfactant-free (calcined) mesoporous titanium based material for the adsorption of uranyl ion (UO_2^{2+}) [24]. Vidya et al. [25] explained the high efficiency for trapping uranyl ion by as-synthesized MCM-41 and MCM-48 due to strong binding between uranyl ion and defective sites in the three dimensional pore system. A comparative account on the extraction efficiency of uranyl ion with MCM-41 synthesized with different textural properties has not been attempted.

Here, we report the synthesis of few spherical MCM-41 materials and their utilities for the entrapment of uranyl ion in the pores. Cetyl tetramethyl ammonium bromide (CTAB), dodecane tetramethyl ammonium bromide (DTAB) and eicosane tetramethyl ammonium bromide (ETAB) were used as structure directing surfactants for the preparation of MCM-41. DTAB and ETAB were synthesized. The calcined materials prepared with CTAB, DTAB and ETAB are designated as MCM-41(C), MCM-41(D) and MCM 42(E) respectively. X-Ray diffraction (XRD), N₂-adsorption measurements and FT-IR spectroscopy were used for the characterization. Entrapment of uranyl ion in MCM-41 was verified by characterization of uranyl ion loaded MCM-41 with inductively coupled plasma- mass spectrometer (ICP-MS) analysis.

3. MATERIALS AND METHODS

3.1. Materials

Tetraethyl orthosilicate (TEOS), cetyl trimethyl ammonium bromide (CTAB), 1-bromodecane, 1-bromoeicosane, and tri ethyl amine were purchased from Aldrich chemicals Co, Milwaukee, USA. Uranyl acetate Merck, Germany was used as received. High purity ethanol, ammonia and chloroform were of analytical reagent grade.

3.2. Synthesis of MCM-41

Synthesis of MCM-41 was performed as detailed elsewhere. 26-29 Different calcined mesoporous materials (MCM-41) were prepared employing CTAB, DTAB and ETAB as surfactants. DTAB and ETAB were synthesized.

Synthesis of DTAB and ETAB

For the synthesis of DTAB and ETAB, 1-bromodecane 7.5 (mL) or 1-bromoeicosane 13.0 (mL) was mixed with 5.0 (mL) of triethyl amine in 30 (mL) of chloroform. The mixture was refluxed at 80°C with stirring for 24 h. The surfactants were obtained (Fig. 1) as white powder after evaporation of chloroform and drying at vacuum oven.

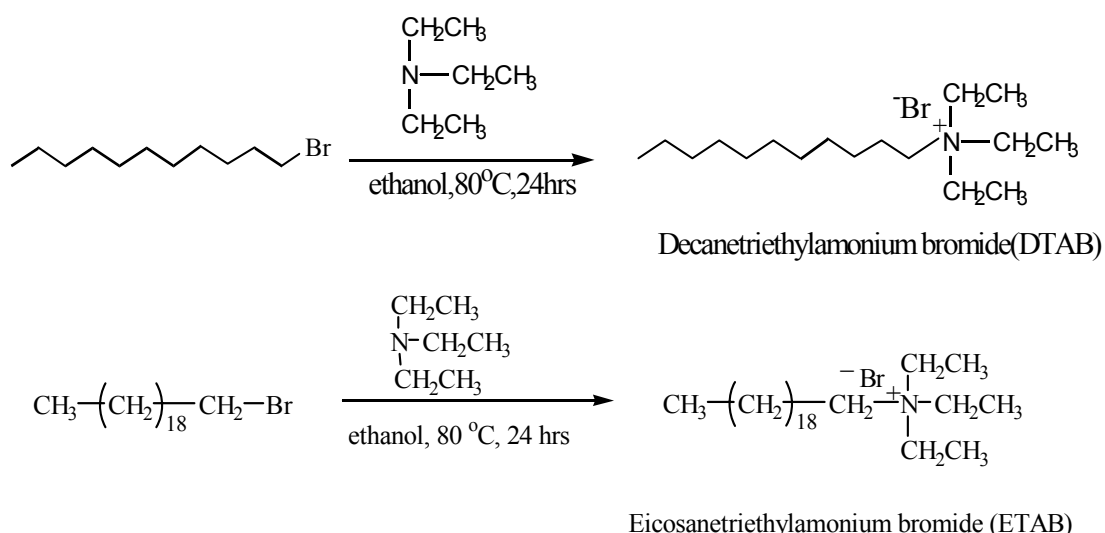


FIG. 1. Preparation of ETAB and DTAB

Preparation of gel for MCM-41

A typical procedure for the preparation of precursor gel is outlined here. The surfactant was diluted with water and stirred for 10 min. Ammonia and ethanol were then added successively under stirring to result a clear solution. An aqueous solution of TEOS was prepared. The surfactant solution was added drop wise to TEOS. After continuous stirring for 210 min, a gel (molar) was resulted. The gel was having the following composition:

- 0.024 teos; 0.0024 surfactant(ctab/dtab/etab); 0.14 ammonia; 2.568 water; 1.284 ethanol.
- formation of MCM-41 from the gel
- the gel samples were calcined in an oven at 550 °c. we designate the calcined materials as MCM-4.

3.3. Adsorption of uranyl ion in MCM- 41

An aqueous solution containing 100 ppm of uranyl ion was prepared using uranyl acetate. 0.25 g of MCM-41 was added slowly to the uranyl solution and the mixture was stirred for 24 h at room temperature. Stirring was continued for different time intervals (2-24 h) to adsorb uranyl ion into the pores of MCM-41. The concentration of the uranyl ion was determined by using inductively coupled plasma mass spectrometer -MS, Perkin-Elmer optima 3000). (ICP)

3.4. Characterization

The powder XRD patterns of the as-synthesized and calcined MCM-41 materials, MCM-41 loaded with uranyl ion were recorded in the 2θ region on a Rigaku diffractometer using a Nickel filtered $\text{CuK}\alpha$ radiation. Thermogravimetry and differential thermal analysis (TG-DTA) measurements were carried out on a Dupont 9900/2100 TG and DTA system in nitrogen atmosphere (50 mL min^{-1}) with a heating rate of 10 K min^{-1} in the temperature range of 300-1037 K. The template contents in the as-synthesized MCM-41 were found to be approximately 40%. The surface area was determined by nitrogen adsorption-desorption method using a Sorptomatic at 77K that was found to be 848 and $990 \pm 20 \text{ m}^2 \text{ g}^{-1}$.

FT-IR spectra of the samples were recorded in mid IR ($400\text{-}4000 \text{ cm}^{-1}$) region on a Jasco 610 spectrometer at 4 cm^{-1} resolution. Compressed KBr pellets containing 6% sample were used for this purpose. Each spectrum was collected after 100 co-added scans. The amount of uranium loaded in the samples was estimated by ICP-AES, using Labtam plasma 8440 equipment. A known amount of the sample was placed in a weighed platinum crucible and was dissolved in aqua-regia and 40% HF to obtain a clear solution. It was then diluted with hot water.

4. RESULTS AND DISCUSSION

4.1. Characterization of MCM-41

There are variations in the morphology of MCM-41 prepared with DTAB, CTAB and ETAB for various conditions.

SEM photographs of MCM-41 (Fig. 2-4) reveal that the materials prepared with ammonia rather than with NaOH are having spherical morphology [samples D6 (Fig. 1d), C6 (Fig. 2d) and E5 (Fig. 2c)]. Knowing the fact that particle morphology and surface texture could be varied depending on the experimental condition, optimum condition for obtaining spherical morphology were deduced.

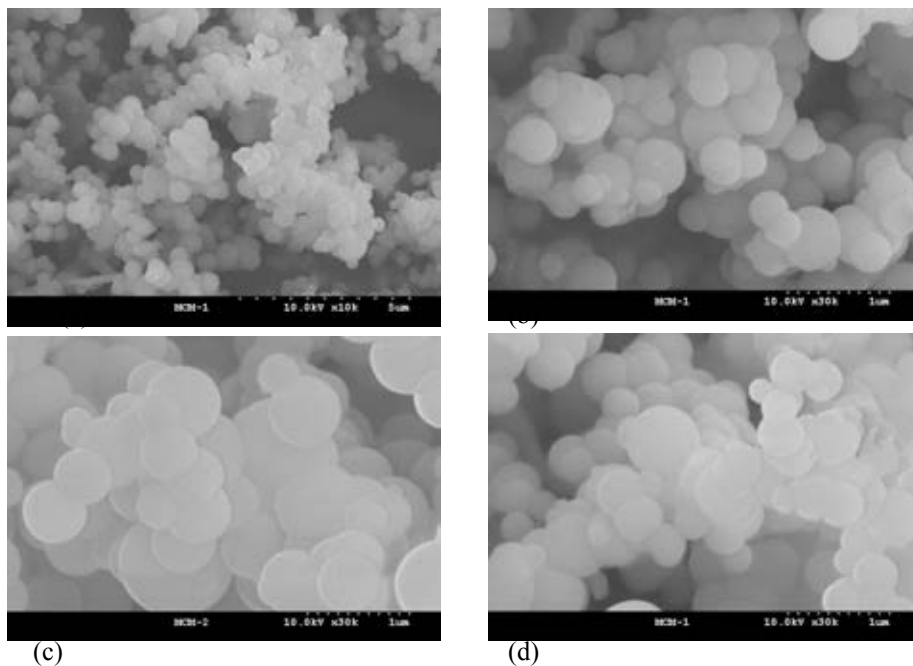


FIG. 2. SEM micrographs of MCM-41 prepared with DTAB as surfactant

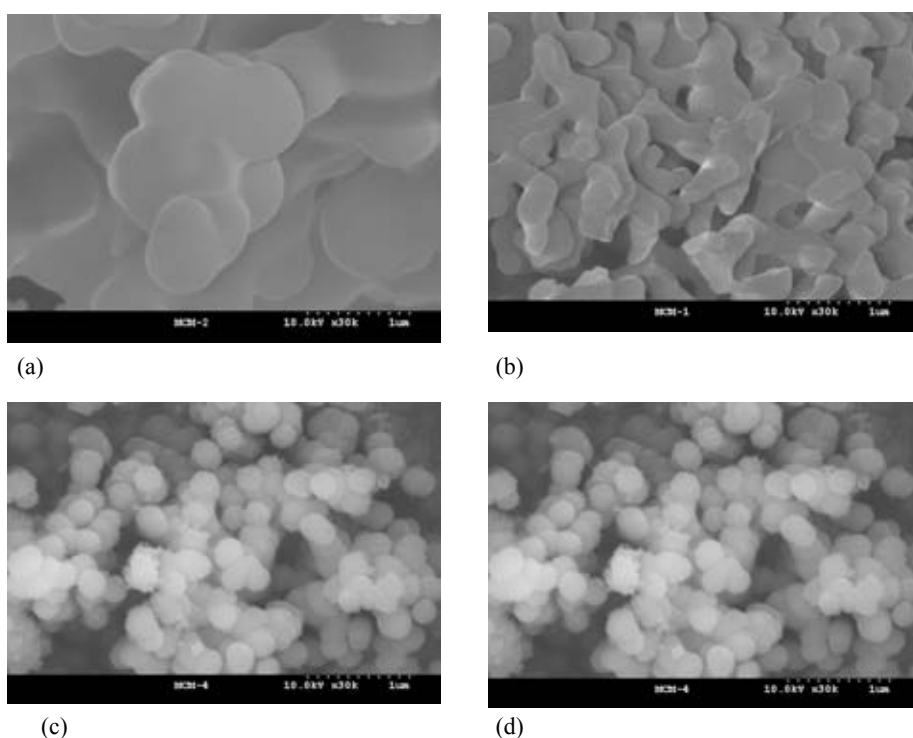


FIG. 3. SEM micrographs of MCM-41 prepared with CTAB as surfactant: C1 (a); C2 (b); C4 (c); C6 (d).

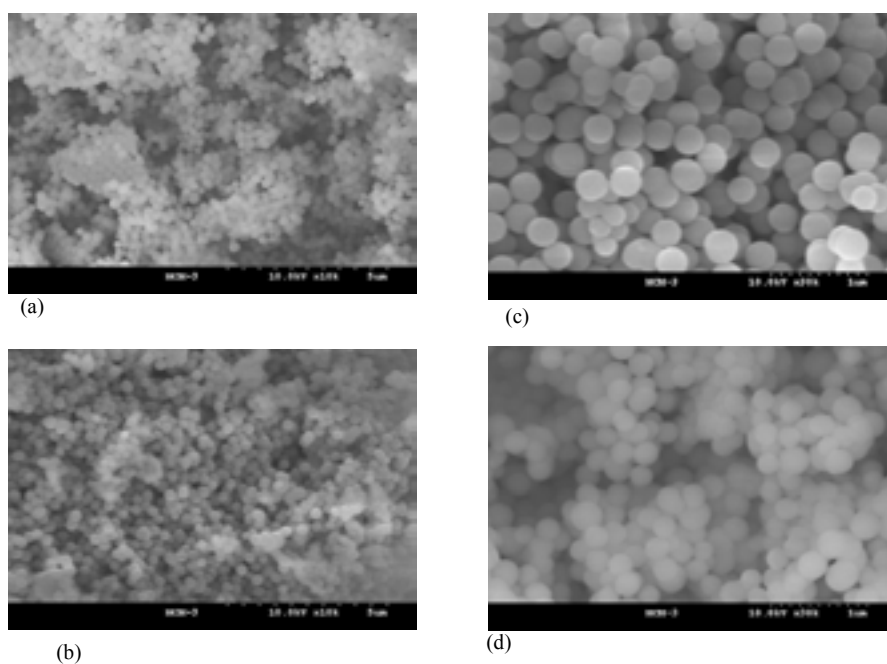


FIG. 4. SEM micrographs of MCM-41 prepared with ETAB as surfactant: E3 (a); E4 (b); E5 (c); E6 (d).

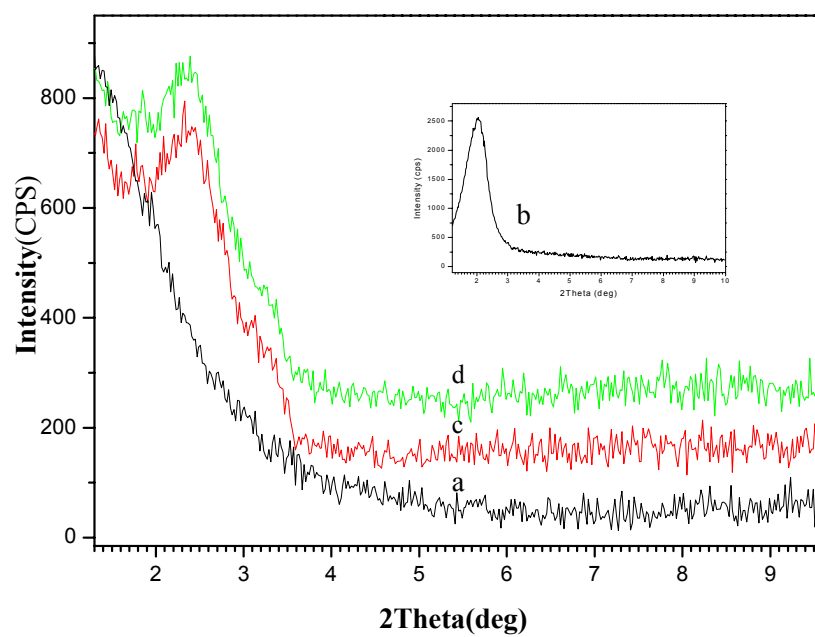


FIG. 5. XRD pattern of MCM-41 prepared with DTAB as surfactant: D3 (a); D4 (b); D5 (c); D6 (d).

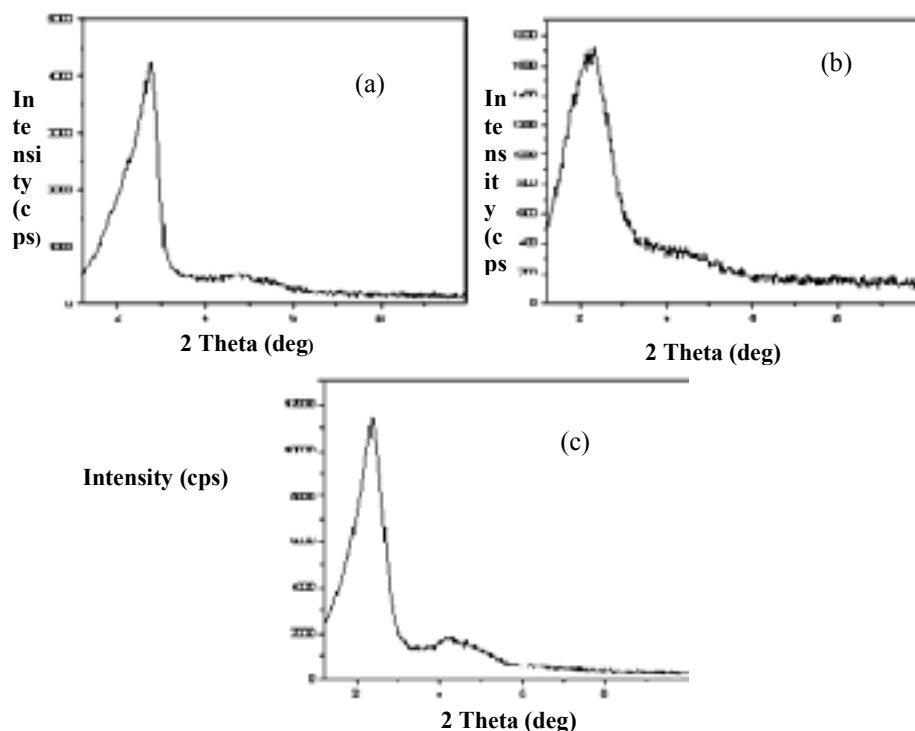


FIG. 6. XRD pattern of MCM-41 prepared with CTAB as surfactant: C2 (a); C3 (b); C6 (C).

Nitrogen adsorption isotherms of MCM-41 were used to evaluate pore size, pore volume and surface area. The morphological variation of MCM-41 with experimental conditions of preparation (as observed through SEM photographs) also result variations in pore size, pore volume and surface area. MCM-41 materials prepared with different experimental conditions show differences in pore sizes and pore volumes. Typically, there can be secondary mesopores in pore structure of MCM-41. This is inferred by presence of hysteresis in adsorption-desorption isotherm at higher pressure regions. Hence, useful correlation could not be obtained between experimental conditions and textural parameters. However, a comparison of pore size, pore volume and surface area could be made between MCM-41 prepared with DTAB, CTAB and ETAB under similar condition. D5, C4 and E5 were prepared under similar conditions. Pore volume and pore size of MCM-41 prepared with ETAB (E5) were found to be low in comparison to MCM-41(C6) and MCM-41(D5). This might be due to limitations of obtaining MCM-41 from surfactants having long aliphatic chain with alkyl trimethylammonium head [32, 33]. Pore size and pore volume of MCM-41 (C) was found to be higher than MCM-41 (D) as a result of the additional presence of $-(CH_2)_6-$ units in the alkyl chain. This observation is in accordance with pore size variation noticed by M. Kruk et al [34] for MCM-41 materials prepared with surfactants having different lengths of alkyl chains. The unit cell parameter (calculated from XRD) of MCM-41 prepared under identical conditions with DTAB, CTAB and ETAB also show variations.

Fig. 7 depicts the FTIR spectra of MCM-41 prepared with DTAB, CTAB and ETAB. Bands representing Si-O-Si stretching (around $1090-1120\text{ cm}^{-1}$ and $800-810\text{ cm}^{-1}$) could be seen as reported for mesoporous silicate frame work. There are variations in the position of the bands between the MCM-41 materials. The band around 1630 cm^{-1} is due to the overtone of Si-O stretching vibrational band [35, 36].

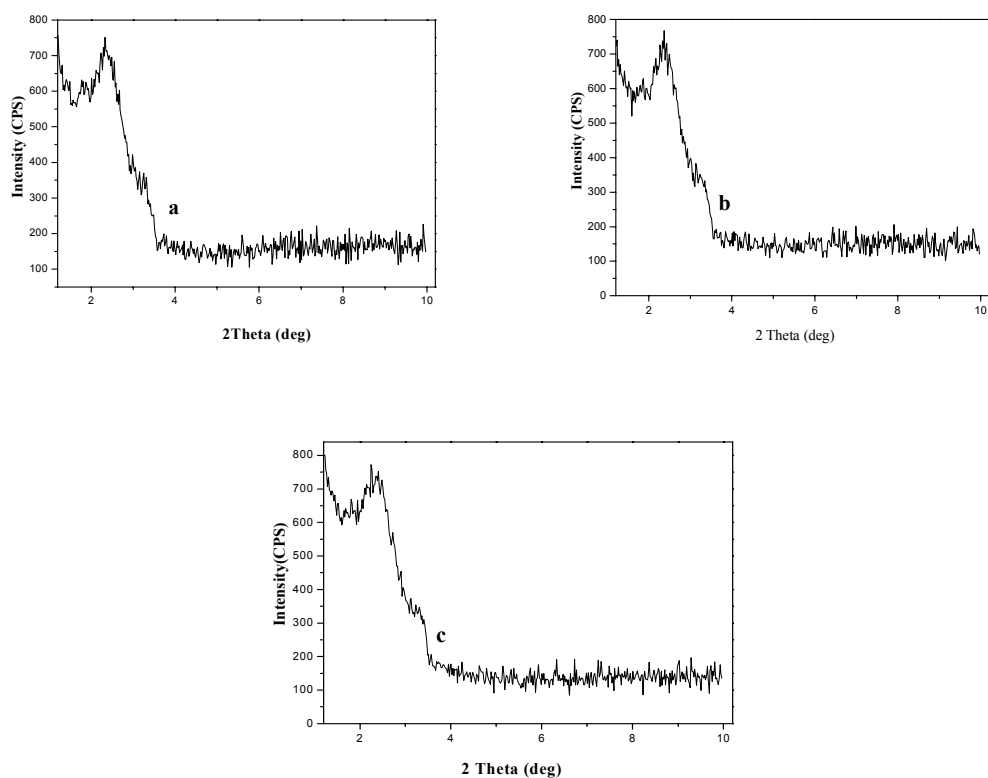


FIG. 7. XRD pattern of MCM-41 prepared with ETAB as surfactant: E3 (a); E4 (b); E6 (c).

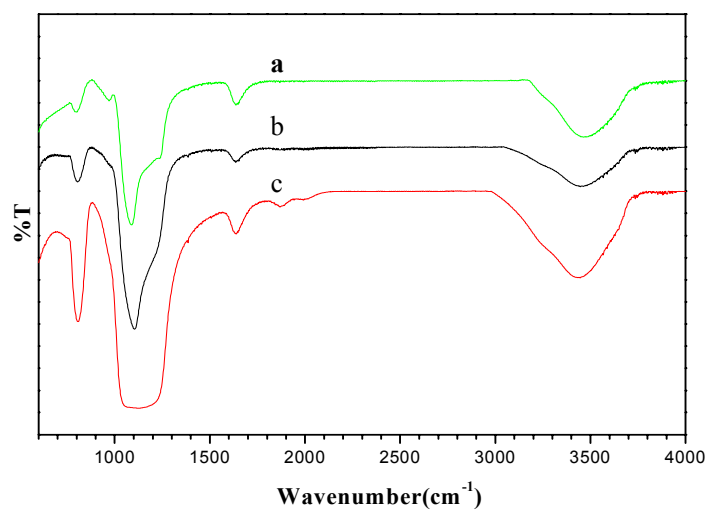


FIG. 8. FTIR spectrum of pristine MCM-41 prepared with DTAB, CTAB and ETAB as surfactant: D6 (a); C6 (b); E6 (c).

4.2. Entrapment of uranyl ion in the pores of MCM-41

Evidences could be obtained for the entrapment of uranyl ion in MCM-41 through XRD measurements and FTIR spectroscopy. The extent of loading of uranyl ion into MCM-41 materials was followed by ICP measurements.

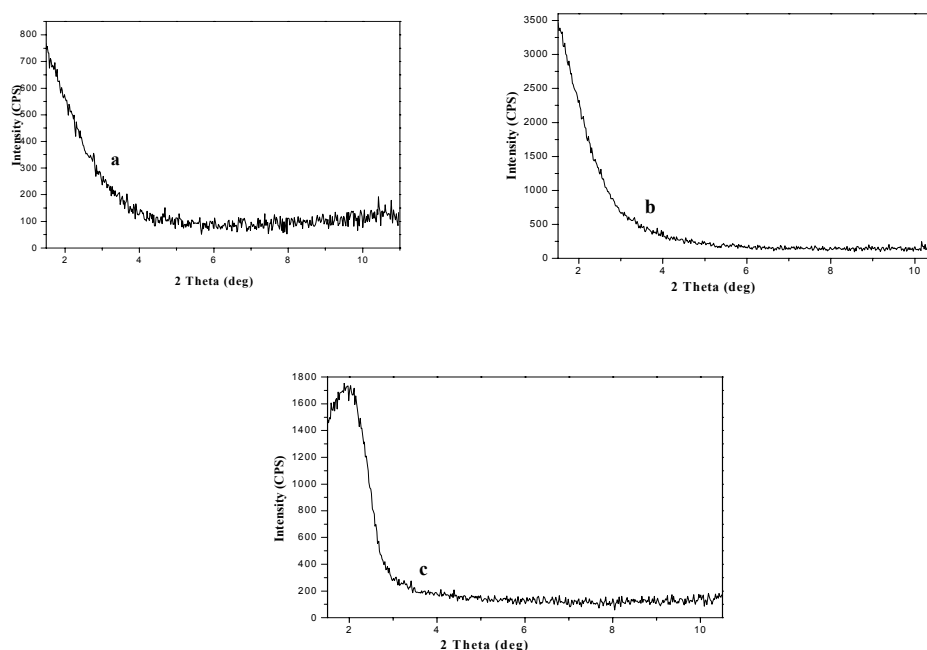


FIG. 9. XRD pattern of uranyl ion loaded MCM-41: D6 (a); C6 (b); E6 (c).

The XRD pattern of uranyl ion loaded MCM-41 (Fig. 9) shows loss of intensity for most of the reflection in comparison to pristine MCM-41. Hence, it is inferred that loading of uranyl ion leads to loss of crystallinity in comparison to pristine MCM-41. 2, 30, 31 FTIR spectra of uranyl ion loaded MCM-41 (Fig. 10) show the clear presence of vibrational bands around 900 cm^{-1} characteristics of U=O stretching of uranyl ion.³⁵

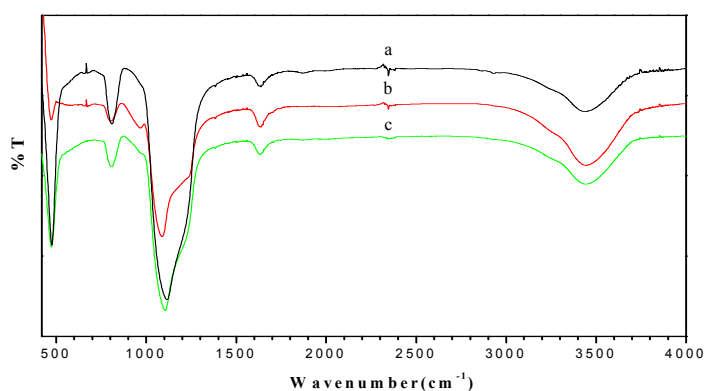


FIG. 10. FTIR spectrum of uranyl ion loaded MCM-41: D6 (a); C6 (b); E6 (c).

There are variations in the intensities of bands corresponding to pristine MCM-41 upon loading with uranyl ions. The Si-O-Si stretching band (around 1220 cm^{-1}) has variation in intensities upon loading uranyl ion and inform that uranyl ion may be found to Si-O-Si units in MCM-41.

ICP data was used to estimate the amount of uranyl ion loaded into MCM-41 (D6, C6 and E5) prepared under similar experimental condition. Results reveal the following information. Firstly, uranyl ion can be loaded gradually with increasing contact time of MCM-41 with uranyl ion (Fig. 11). Recently, polymeric resins with chelate forming functional groups resins were employed by our research group to extract uranyl ion [37].

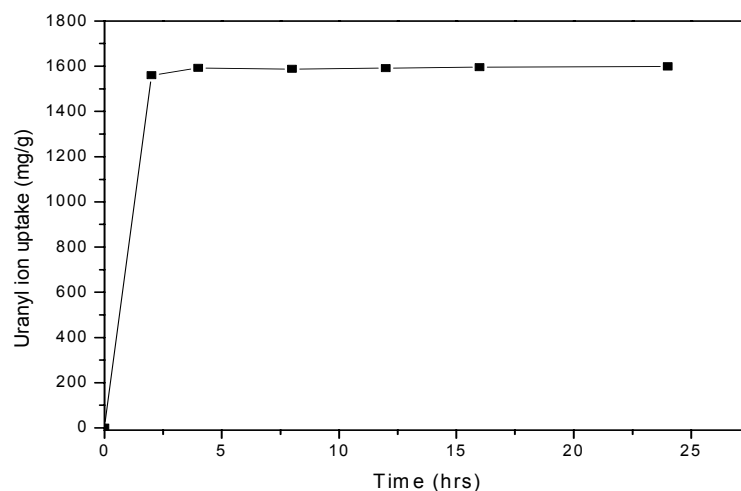


FIG. 11. *Uranyl ion uptake (mg/g) of the MCM-41 (C6).*

The adsorption rate and efficiency of uranyl ion adsorption with MCM-41 were comparatively more (nearly 99% at 24 h of adsorption) than reported for the polymeric resin(chelate-type resins with hydrophilic amidoxime (AO) and amidoxime/carboxylic acid (AC) groups prepared by radiation-induced polymerization. This informs that adsorption capability of MCM-41 is superior over the polymeric resins. After 24 h of contact time, the amount of uranyl ion loaded into MCM-41 materials takes the order: ETAB> CTAB> DTAB.

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STIMULI-RESPONSIVE HYDROGELS FOR SEPARATION PURPOSES

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Abstract

The activity was focused on the radiation-assisted formation and properties of stimuli-responsive hydrogels. Significant part of efforts was devoted to developing stimuli-sensitive gels and membranes based on poly(vinyl methyl ether) – PVME. In the first step, detailed studies on the radiation-induced reactions in PVME in aqueous solution were performed, leading to the formulation of radiolysis mechanism and quantification of kinetic parameters and yields. This was followed by more application-oriented study on the radiation synthesis of hydrogels based on PVME and on obtaining composite membranes by radiation-induced grafting and cross-linking of PVME on poly(ethylene terephthalate) ion-track membranes. Radiation-chemical yields of intermolecular cross-linking and hydrogel formation were analyzed at various synthesis conditions. Swelling properties of PVME hydrogels and their dependencies on dose and temperature were evaluated. Several methods of radiation modification of the track membranes by means of grafting/cross-linking of PVME were elaborated. It has been demonstrated that, by applying various synthesis conditions, two distinct kinds of thermo-sensitive membranes can be obtained, which either increase or decrease their permeability when temperature is risen above the phase transition temperature of the PVME gel. In co-operation with the research team from Kazakhstan, novel cationic, thermoresponsible hydrogels were synthesized by γ -irradiation copolymerization of [2-(methacryloyloxy) ethyl] trimethylammonium chloride – MADQUAT - with N-isopropylacrylamide - NIPAAm. The swelling behavior of hydrogels was evaluated as a function of copolymers composition and temperature. It was shown that the temperature-responsive properties of the synthesized hydrogels considerably depend on the content of ionic comonomer in copolymers. Separation properties of these materials have been studied. Formation of polyelectrolyte complexes between linear copolymers and hydrogels based on MADQUAT-NIPAAm copolymers and PAA has been studied. It was found that the composition of copolymer significantly affects the composition of polyelectrolyte complexes and molecular weight of PAA influences their aggregation stability. The rate of contraction and the final swelling degree of the gel-polymer complexes depends on concentration of PAA in solution and its molecular weight.

1. INTRODUCTION

Research on the radiation-based synthesis and properties of stimuli-responsive hydrogels for separation purposes must be composed of two stages - basic and applied studies. In order to utilize safely and efficiently the radiation technique for the fabrication of stimuli-sensitive hydrogels, the underlying basic chemistry must be known in some detail. Within this field, we have performed detailed studies on the radiation-induced processes in two hydrophilic, stimuli-sensitive polymers: poly(vinyl methyl ether) - PVME - and poly(acrylic acid) - PAA.

PVME is less known and investigated temperature-sensitive polymer than the popular poly(N-isopropyl-acrylamide), while being at least equally well suited for biomedical binding / separation purposes due to its lower critical solubilization temperature close to the temperature of human body. Poly(acrylic acid), being a weak polyelectrolyte, is especially suited for fabricating pH- and ion-sensitive hydrogels. The research work was focused on regular, macroscopic PAA gels, but rather on microscopic gel structures. Micro- and nanogels may have significant advantages over macroscopic hydrogels in some binding / separation applications (*e.g.* much faster reaction to stimuli due to larger surface-to-volume ratio). Up to now, such structures have been mainly synthesized by cross-linking polymerization, using monomers and cross-linking agents. This method may lead to problems if the products are intended as biomaterials due to the presence of residual monomer and/or cross-linker.

An original method of nanogel synthesis was proposed, totally eliminating the use of monomers and cross-linking agents, where the only substrates are polymer chains in aqueous solution, while cross-linking is induced by short pulses of high-energy electrons. The new method has been first tested on simple, neutral hydrophilic polymers. The first successful synthesis of nanogels of a polyelectrolyte - poly(acrylic acid) - using the above mentioned technique is reported.

As a further development of this method, we utilized the process of spontaneous complex formation between two different polymers in solution. Such a complex, when irradiated, may be transformed into a stimuli-sensitive copolymer microgel. Stimuli-controlled separation processes can

be realized with hydrogels sensitive to temperature, pH, ionic strength etc. in many ways. One of them is reversible binding of the substrate within the hydrogel structure or at its surface, while the binding / release behaviors may be controlled by external stimuli. Another way is to use “smart” hydrogels as components of membranes of controlled permeability. Both of these approaches have been addressed in our study. The synthesis and properties of composite temperature-controlled membranes based on poly(vinyl methyl ether) hydrogel have been investigated.

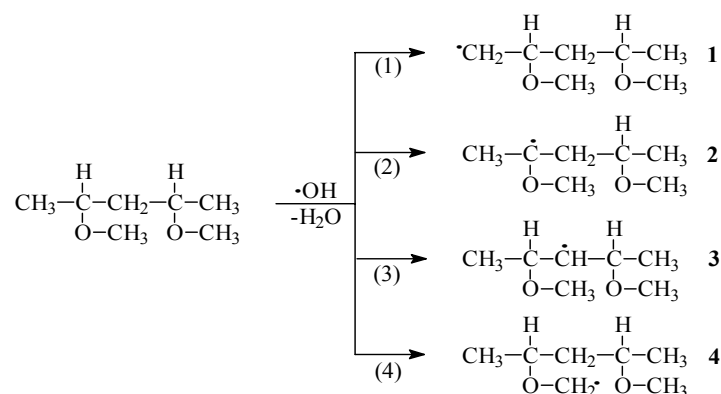
2. SUMMARY OF RESULTS

2.1. Basic studies on the radiation-induced reactions in poly(vinyl methyl ether) – PVME – a thermo-sensitive polymer (selected aspects) [1, 2]

Poly(vinyl methyl ether), PVME, is one of the simplest water-soluble polymers. Its aqueous solutions have the unusual property of reverse temperature solubility, *i.e.* the polymer precipitates at around 34 - 37 °C. Its interactions with water and the mechanism of the phase transitions are presently the subject of considerable interest.

Hydrogels, *i.e.* water-swollen, covalently cross-linked polymer networks, made of poly(vinyl methyl ether) are also heat-sensitive. This property, as well as the fact that the gel collapses at a temperature close to body temperature, has elicited a number of studies on its possible use as a stimulus-sensitive biomaterial, *e.g.* as a thermosensitive (and/or bioadhesive) drug-delivery system and even as an artificial muscle. Other interesting applications of poly(vinyl methyl ether) hydrogels are recyclable separation systems and chemomechanical valves.

Ionizing radiation is a very efficient tool for the formation of hydrogels. The reaction can be carried out at room temperature, is easy to control and environment-friendly. Using γ -irradiation, homogeneous products of any desired shape and size can be produced. For biomedical applications, the radiation technique allows one to carry out in one step the formation of the hydrogel as well as its sterilization. For a further development of this promising technique, it seems worthwhile to investigate in some detail the underlying radiation chemistry of poly(vinyl methyl ether) in aqueous solution. In order to facilitate the study on the mechanism of radiolysis of poly(vinyl methyl ether) - PVME, we first used a low-molecular-weight model of this polymer, 2,4-dimethoxypentane –DMP. Hydroxyl radicals were generated radiolytically and reacted with DMP. Using the pulse radiolysis technique and specific radical scavengers, it has been shown that OH radicals react by H-abstraction ($k = 3.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), generating primary (4, ~45%) and tertiary (2, ~35%) α -alkoxyalkyl radicals as well as secondary and primary β -alkoxyalkyl radicals (1, 3).

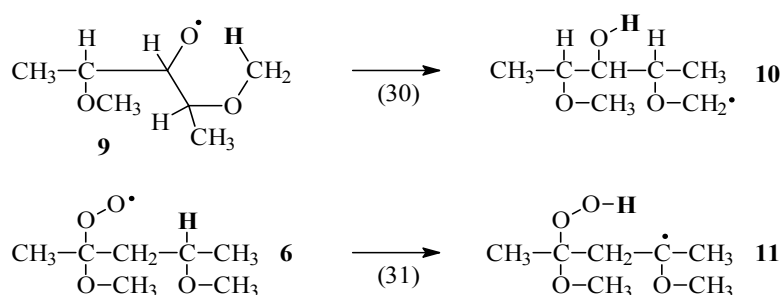


In the absence of oxygen, radicals 1 – 4 decay ($2k = 1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) by recombination and disproportionation yielding dimers and vinyl ethers in nearly equal amounts (Table I).

TABLE I. PRODUCTS AND THEIR G VALUES IN THE γ -RADIOLYSIS OF N_2O -SATURATED SOLUTIONS OF 2,4-DIMETHOXYPENTANE

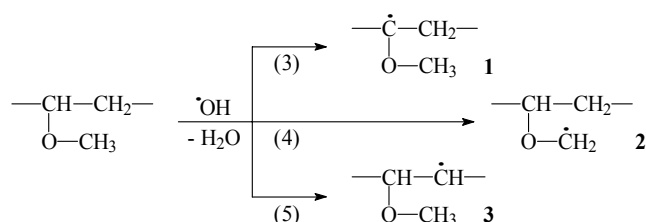
Product	G value / 10^{-7} mol J $^{-1}$
2,4-Dimethoxypent-2-ene	0.86
4-Methoxypentan-2-one	0.53
Dimers	1.55

In the presence of oxygen, four different peroxy radicals are formed. They decay bimolecularly by non-uniform kinetics (initially, $2k \approx 7 \times 10^7$ dm 3 mol $^{-1}$ s $^{-1}$). Especially at low dose rate, they also undergo (mainly) intramolecular H-abstraction.



This leads to an increased autooxidation, *e.g.* oxygen uptake reaches values more than three-times the initial radical yield. Based on these data, the major reaction pathways as well as some side- and consecutive reactions have been elucidated [1]. Product analysis for the model compound following irradiation in anoxic conditions allowed determining the proportion between disproportionation and recombination of radicals. Since recombination occurs with *ca.* 50 % probability, it is expected that no more than a half of the polymer radicals would recombine. This limits the maximum possible yield of intermolecular crosslinks to *ca.* 1.5×10^{-7} mol dm $^{-3}$, a relatively high value when compared to the other water-soluble polymers [*ca.* 15 % recombination has been found in the poly(vinyl alcohol) system and *ca.* 40 % in poly(acrylic acid)]. This is an important parameter for the radiation-induced formation of poly(vinyl methyl ether) hydrogels

The next step was to study the mechanism of radiation-induced reactions in PVME. Hydroxyl radicals were generated radiolytically in N_2O -saturated aqueous solutions in the presence of PVME. As measured by pulse radiolysis, they react ($k = 2.2 \times 10^8$ dm 3 mol $^{-1}$ s $^{-1}$) with PVME by giving mainly rise to α -alkoxyalkyl radicals ($\sim 72\%$) that reduce ($k \approx 2 \times 10^9$ dm 3 mol $^{-1}$ s $^{-1}$) $\text{Fe}(\text{CN})_6^{3-}$, IrCl_6^{2-} or tetranitromethane. Based on the formaldehyde yield in the presence of the latter two oxidants (~ 40 % of OH), it is concluded that OH radicals undergo H-abstraction at $\text{ROCH}_2\text{-H}$, $\text{R}_3\text{C-H}$ and $\text{R}_2\text{HC-H}$ with probabilities of $\sim 40\%$, $\sim 32\%$ and $\sim 28\%$, respectively.



The momentary rate constant of the decay of the PVME radicals depends on the number of radicals per polymer chain and drops as they decay (Fig. 1).

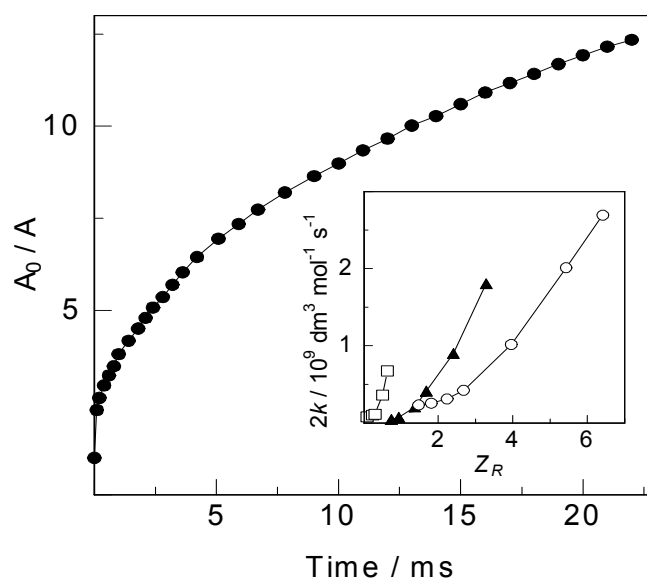


FIG. 1. Pulse radiolysis of PVME ($1 \times 10^{-3} \text{ mol dm}^{-3}$) in N_2O saturated aqueous solution. The ratio of absorbance at 290 nm after pulse (A_0) to absorbance (A) at a given time after the pulse. Inset: momentary second-order rate constants as a function of concentration of radicals per macromolecule Z_R . Polymer concentration: $2 \times 10^{-3} \text{ mol dm}^{-3}$ (\square), $1 \times 10^{-2} \text{ mol dm}^{-3}$ (\blacktriangle) and $1 \times 10^{-1} \text{ mol dm}^{-3}$ (\circ)

The yield of intermolecular crosslinks, as measured by an increase of the molecular weight, strongly increases with decreasing dose rate, and it is concluded that the majority of crosslinks occur intramolecularly, even at the lowest dose rate used [0.0015 Gy s^{-1} , $G(\text{intermolecular crosslinks}) = 0.62 \times 10^{-7} \text{ mol J}^{-1}$] (Fig. 2).

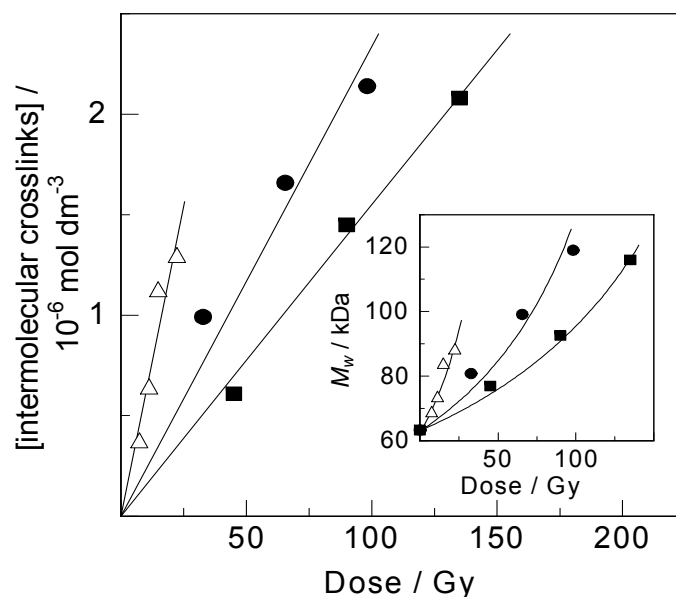
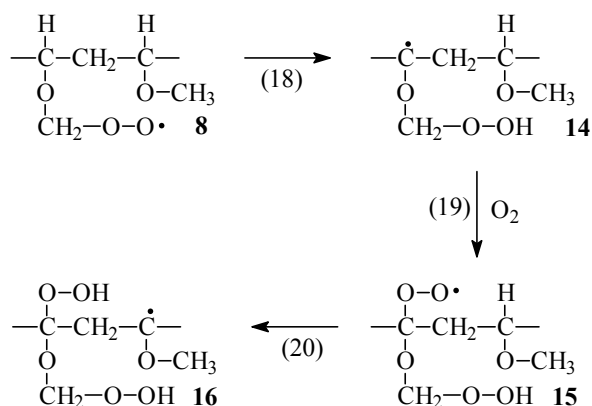


FIG. 2. γ -Radiolysis of PVME ($1 \times 10^{-2} \text{ mol dm}^{-3}$) in N_2O -saturated aqueous solutions. Concentration of intermolecular crosslinks (main graph) and weight-average molecular weight (inset) as a function of dose. Dose rates: 0.15 Gy s^{-1} (ν), 0.013 Gy s^{-1} (λ) and 0.0015 Gy s^{-1} (Δ).

Due to its compactness in aqueous solutions, PVME has properties that enable reactions to occur that may also be undergone by other polymers, but to a lesser extent. For example, there is now evidence that intramolecular cross-linking can be of much greater importance than intermolecular cross-linking even at very low radical steady-state concentrations. Thus conditions can be chosen easily that favor e.g. nanogel formation. This raises the question, whether compaction of other water-soluble polymers, e.g., by the addition of salt or by lowering the temperature could be beneficial if nanogel formation is desired.

In the presence of oxygen, the primary PVME radicals are converted into their corresponding peroxy radicals. They undergo efficient autooxidation via intramolecular H-abstraction [e.g. $G(\text{oxygen uptake}) \approx 110 \times 10^{-7} \text{ mol J}^{-1}$ at 0.0015 Gy s^{-1}].



Most of the hydroperoxides are unstable, *i.e.* the high oxygen-uptake yield is not matched by the organic hydroperoxide yield [$G(\text{organic hydroperoxide}) \approx 34 \times 10^{-7} \text{ mol J}^{-1}$ at 0.0015 Gy s^{-1}]. As a consequence of the instability of some of the organic hydroperoxides, chain scission also strongly depends on dose rate [e.g. $G(\text{chain breaks}) \approx 15 \times 10^{-7} \text{ mol J}^{-1}$ at 0.0015 Gy s^{-1}] (Fig. 3), and prompt chain breakage due to processes occurring in the bimolecular decay of the peroxy radicals is minor compared to the former pathway.

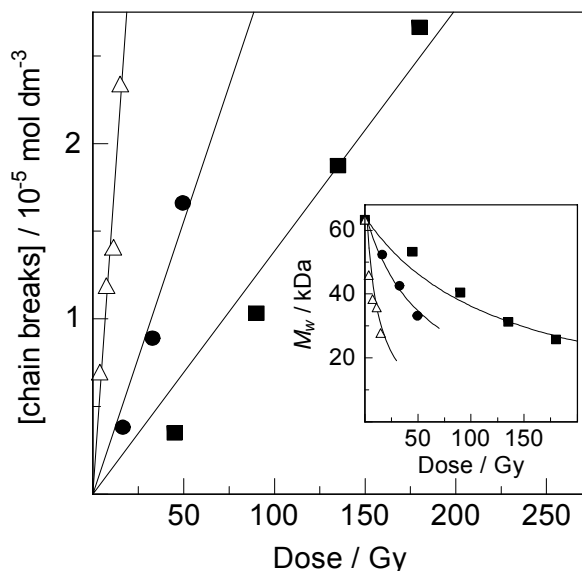


FIG. 3. γ -Radiolysis of PVME ($1 \times 10^{-2} \text{ mol dm}^{-3}$) in $\text{N}_2\text{O}/\text{O}_2$ -saturated aqueous solutions. Formation of chain breaks and decrease of molecular weight (inset) as a function of dose at 0.15 Gy s^{-1} (\blacksquare), 0.014 Gy s^{-1} (\bullet) and 0.0015 Gy s^{-1} (Δ).

2.2. Formation and properties of thermo-sensitive hydrogels of PVME [3, 8, 9]

Temperature-sensitive gels have been suggested for use in a variety of novel applications including controlled drug delivery, immobilized enzyme reactors, chemo-mechanical devices, artificial muscles, and separation processes. One of such materials is poly(vinyl methyl ether), PVME, gel based on the polymer that undergoes a coil-globule transition in water at approximately 34 °C. A hybrid material combining the responsive properties of hydrogels with the mechanical properties of a sturdy ion track membrane can also find application in many separation devices. The combination of a thermoresponsive hydrogel with an ion track membrane leads to a thermoresponsive membrane with pores able to open/close above a certain threshold temperature.

One of the most convenient ways to produce and sterilize polymer gels is to irradiate their aqueous solutions by gamma rays or electron beam. The mechanism and kinetics of the radiation induced transformations of PVME in dilute and semidilute solutions were already discussed. The main aim of this part of our study was to characterize radiation transformations of PVME before and after gelation point and to determine the most effective synthesis parameters for stimuli responsive hydrogel materials for separation purposes.

Experimental

Poly(vinyl methyl ether) supplied by Aldrich (50 % w/w aqueous solution, $d = 1.03 \text{ kg/dm}^3$) has been purified by precipitation in water above LCST (34 °C). Weight-average molecular weight (M_w) and number-average molecular weight (M_n) of polymer after purification were 53.6 kDa and 27 kDa, respectively, as determined by GPC.

Known amount of polymer aqueous solutions was irradiated in Gammacell at a dose rate of 0.1 kGy h^{-1} (Fricke dosimeter). Prior to irradiation solutions were bubbled 60 minutes with argon and sealed in glass ampoules. Samples irradiated with doses below gelation dose were dried under vacuum. Appropriate volume of THF was then added to the resulted polymer to get concentration approximately 15 g dm^{-3} and such solutions were analyzed with GPC system. Samples irradiated with doses above gelation were swelled with large amount of water. After achieving the equilibrium state (approximately 3-4 weeks) hydrogels were weighted (to get equilibrium degree of swelling) and dried under vacuum to constant weight (to get weight of gel fraction, g). The gel sol analysis was performed with the aid of GelSol95 software, a program elaborated in our group (available on home page - mitr.p.lodz.pl/biomat).

A Viscotek GPC system fitted with two thermostated Polymer Laboratories linear columns (Plgel Mixed-BLS 10 μm) and a set of three detectors, including a light scattering detector (Viscotek), differential refractometer and viscometer (Viscotek) was used with THF as the effluent. The molecular weight distribution curves of the PVME samples were analyzed using Viscotek Trisec software and poly(methyl methacrylate) standard of 60 kDa from Polymer Laboratories was used for calibration.

Radiation transformation of PVME

In anoxic PVME aqueous solutions 2% weight to bulk polymer were subjected to gamma irradiation. In such conditions irradiation causes polymer chain cross-linking. With increase dose PVME chains undergo branching and average molecular weight of polymer increases as well.

Above some dose, as called gelation dose (D_g), branched polymer forms three-dimensional network as called hydrogel. Results presented concern changes of PVME aqueous solutions that undergo before and after gelation point.

Cross-linking of PVME chains before gelation point

The changes in irradiated PVME solutions were monitored with using of triple detector GPC system. Samples with wide range of concentrations varied from 2% weight to bulk polymer were irradiated with distinguish doses before gelation point. Unirradiated solutions were measured as well for reference.

With increasing dose the changes of average molecular weights, size of polymer chain, level of branching and increase of polymer solution viscosities were observed. On the base of molecular weight changes basic parameters for PVME cross-linking process were determined i.e. gelation doses and the yields of radiation cross-linking for studied polymer concentrations.

With increasing dose of irradiation one can observe large effect of dose on distribution of molecular weight of polymer in spite whether it is polymer with lowest concentration (Fig. 4) or polymer in bulk state (Fig. 5). With bigger doses chromatographic signal shifts to higher molecular weight range. It is related with increasing degree of cross-linking of irradiated polymers in solution. Crosslinking process proceeds faster in diluted solutions as at lower doses one can observe rapid increase of molecular weight.

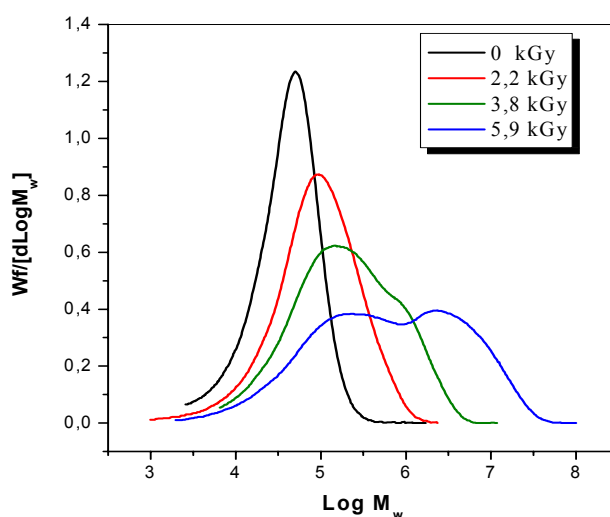


FIG. 4. Distribution of molecular weights of 2% PVME solutions irradiated in anoxic conditions. Range of doses in inset.

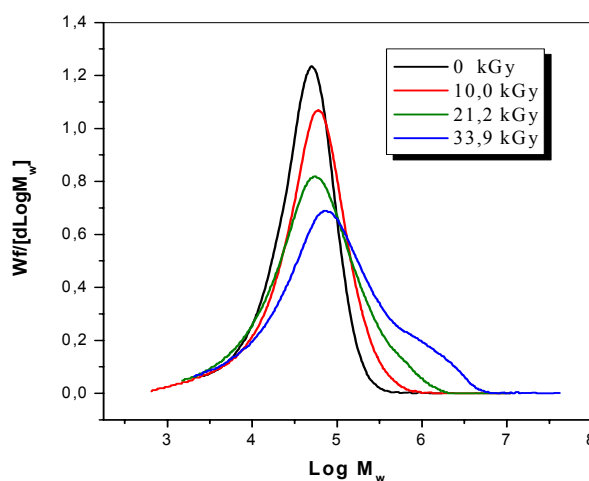


FIG. 5. Distribution of molecular weights for bulk polymer irradiated in anoxic conditions. Range of doses in inset.

Changes of average molecular weights of PVME

Range of PVME solutions 2%, 5%, 10%, 15%, 20%, 50% and bulk polymer were irradiated in anoxic conditions. Results presented in Fig. 6 shows that number average molecular weight (M_n) of PVME does not change much. However weight average molecular weight (M_w) increases with dose and approaches infinity at doses close to gelation point (Fig. 7).

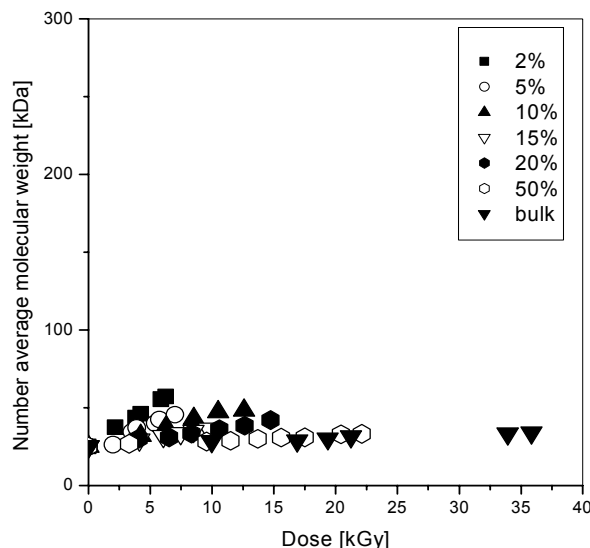


FIG. 6. Changes of number average molecular weight of PVME solutions irradiated in anoxic conditions. PVME concentrations in inset.

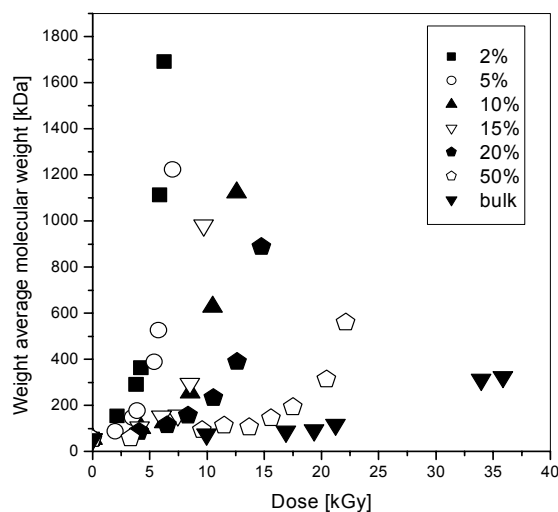


FIG. 7. Changes of weight average molecular weight of PVME solutions irradiated in anoxic conditions. PVME concentrations in inset.

Changes of PVME chain size

Simultaneously with molecular weights change sizes of polymer chain change as well as a result of cross-linking processes. One of the parameter describing average size of polymer coil in solution is z-average radius of gyration, R_g [nm], i.e. a square root of average square lengths of vectors linking center of gravity of macromolecule with its base units:

$$R_g = \left(\frac{1}{N} \sum_{i=1}^N s_i \cdot s_i \right)^{1/2}$$

where s_i is vector linking base polymer units with the center of macromolecule gravity, and N is number of base units. Results concerning radius of gyration for studied polymer solutions are presented in Fig. 8.

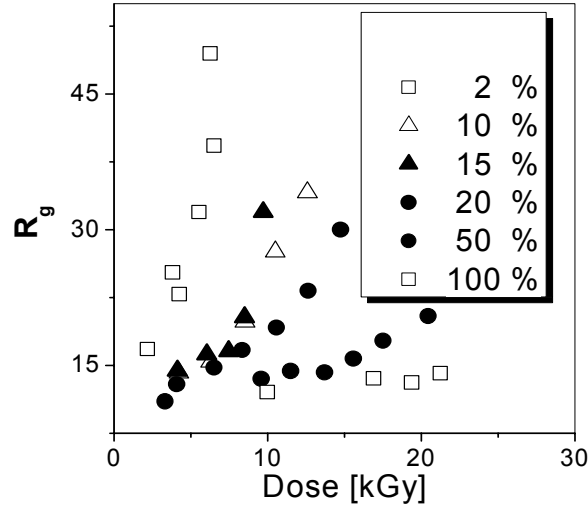


FIG. 8. Changes of PVME radius of gyration, R_g , as a function of dose applied. PVME concentrations in inset.

For linear noncrosslinked polymer increasing of molecular weight involve increasing of radius of gyration of macromolecules. During irradiation sizes of PVME coils undergo considerable enlargement with simultaneous increase of weight average molecular weights. It is characteristic for intermolecular cross-linking of polymer chains. However, with increasing polymer concentration slow down of these processes is observed as a result of increased density of system and decrease mobility of polymer chains carrying radical sites.

Changes of degree of branching of PVME chains

Cross-linking of linear polymer chain should lead to statistically branched polymers with a wide distribution of molecular weights. As a measure of branching content in the system the degrees of branching have been introduced g' and g :

$$g' = \frac{[\eta]_b}{[\eta]_l}; \quad [\eta]_b < [\eta]_l$$

$$g = \frac{\langle R_G^2 \rangle_b}{\langle R_G^2 \rangle_l}; \quad \langle R_G^2 \rangle_b < \langle R_G^2 \rangle_l$$

where: $[\eta]_b, [\eta]_l$ are intrinsic viscosity of macromolecules branched and linear with the same molecular weight, respectively, and $\langle R_G^2 \rangle_b, \langle R_G^2 \rangle_l$ - radii of gyration polymer chains branched and linear within the same molecular weight, respectively.

The above equations are related in the following way:

$$g' = g^a$$

where factor a ranges from 0 to 1.5 and depends on type of branching. For linear polymers $a = 0$ and for statistically branched macromolecules a take values from the range $<0 - 0.6>$.

On the base of GPC measurement the factors g and g' as well as a were determined. Basing of g values one can determinate the average number of branches per macromolecule, B_n .

$$g = \left[\left(1 + B_n/7 \right)^{1/2} + 4B_n/9\pi \right]^{1/2}$$

Resulted values of factor describing type of branching, a , as well average number of branches per macromolecule, B_n , for chosen concentrations shows Fig. 9 as a function of applied dose.

From calculation based on the GPC data results that PVME chains undergo statistical branching during irradiation. Degree of brnching increases steply with applied dose what agrees well with theory of cross-linking. For more concentrated solutions and for bulk polymer branching/cross-linking proceeds much slower as a result of more limited mobility of polymer chain and polymer segments.

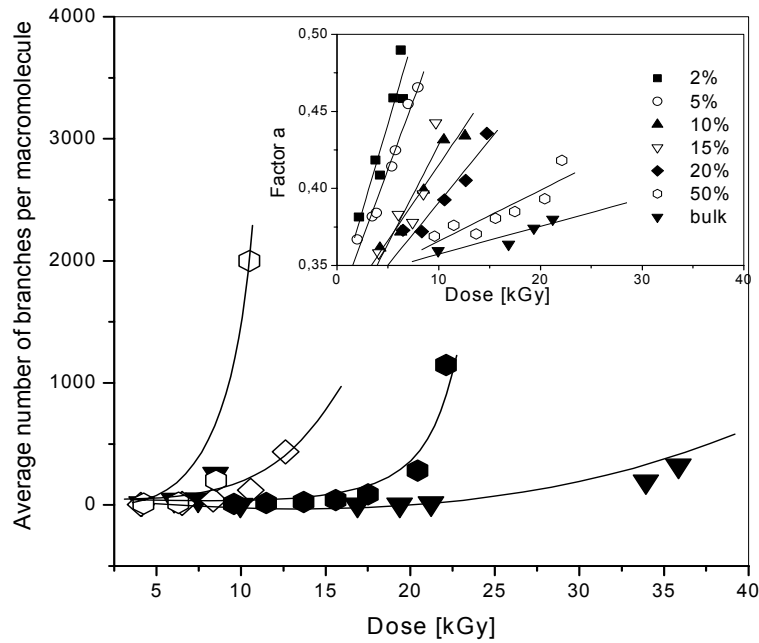


FIG. 9. Average number of branches per macromolecule PVME versus applied dose. Inset: Changes of factor a , describing type of branching in polymer chain.

Determination of G_x in pregelation region

On can specify that in the polymer solution with concentration c (g dm⁻³) ionizing radiation causes formation of c_X (mol dm⁻³) and breaking of c_S (mol dm⁻³) polymer bonds as a result of intermolecular cross-linking and scission in the main polymer chain. It can be described in the terms of the average molecular weights changes according to the following equations:

$$c_X - c_S = c \left(\frac{1}{M_{n,0}} - \frac{1}{M_n} \right) \quad 4c_X - c_S = 2c \left(\frac{1}{M_{w,0}} - \frac{1}{M_w} \right)$$

where M_n and M_w means number and weight average molecular weight of irradiated polymer, respectively. Subscripts 0 denote initial weights of polymer before irradiation. Above equations are valid for polymers with initial most probable molecular weight distribution and degree of polydispersity equal $M_{w,0}/M_{n,0} = 2$. Converting c_X and c_S to radiation yield of cross-linking G_X (mol J⁻¹) and of scission G_S (mol J⁻¹) the above equations obtain following forms:

$$G_X - G_S = \frac{c}{Dd} \left(\frac{1}{M_{n,0}} - \frac{1}{M_n} \right) \quad 4G_X - G_S = \frac{2c}{Dd} \left(\frac{1}{M_{w,0}} - \frac{1}{M_w} \right)$$

where D is absorbed dose (Gy) and d is solution density (kg dm⁻³). If polymer undergoes simultaneous cross-linking and degradation, this set of equations (8) and (9) have to be solved as both G_X and G_S are unknown. For correct calculations both of weights have to be monitored by separate techniques as light scattering (M_w) and osmometry (M_n) for instance. However, if there is no scission processes in the system ($G_S = 0$) one can use only one of the equations and monitor, for example, only changes in weight average molecular weight to determine radiation yield of cross-linking.

Basing on the previous findings, we assumed lack of scission processes in studied PVME solutions under anoxic conditions. We noted linear dependence of $(1/M_{w,0} - 1/M_w)$ as a function of dose at given concentration (Fig. 10), thus the intramolecular cross-linking has no influence on molecular weight changes like it was observed for more diluted solutions during e-beam irradiation. From the slopes the radiation yield of cross-linking was determined for studied polymer solution. The G_X value increases with concentration (Fig. 10) and rises from 0.34×10^{-7} to 2.18×10^{-7} mol·J⁻¹ for sample with concentration 2 % (w/w) and for bulk polymer, respectively.

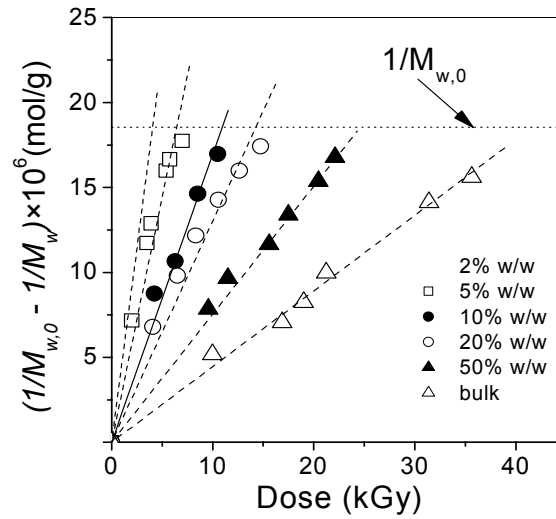


FIG. 10. Reciprocals of PVME weight average molecular weights versus applied dose in anoxic aqueous solutions (concentration given in the figure).

2.3. Radiation formation of PVME hydrogels and studies of their properties

Determination of G_X after gel point. Gel-sol analysis

If there is no possibility to perform molecular weight measurements, a gel sol analysis can be applied to estimate radiation cross-linking and scission parameters for irradiated polymers. Since M_w tends to infinity at D_g (gelation dose, the critical D for gelation), equations given above are valid only for doses ranged from 0 to D_g . From boundary condition one may thus derive the following equation:

$$4G_X - G_S = \frac{2c}{D_g dM_{w,0}} \quad \text{or} \quad G_X = \frac{c}{D_g dM_{w,0} (2 - \lambda/2)}$$

where λ is scission/cross-linking radiation yields ratio (G_S/G_X). Irradiation with doses above D_g increases the fraction of the gel, g , while the remaining soluble fraction, s , decreases: $s+g = 1$. The relation between s and dose D depends on the molecular weight distribution of initial polymer. The general formula, which always allows plotting the relation between sol and dose irrespective of initial molecular weight distribution in form of the straight line, was proposed as a modification of classical Charlesby-Pinner equation:

$$s + \sqrt{s} = \lambda/2 + (2 - \lambda/2) \frac{D_v + D_g}{D_v + D}$$

where D_v is the virtual dose, i.e. a dose needed for changing the distribution of molecular weight of polymer under study to the most probable one ($M_{w,0}/M_{n,0} = 2$).

Application of the modified Charlesby-Pinner equation allowed us to calculate λ , D_v , D_g for series of PVME gels obtained after irradiation of solutions at concentrations varied between 2 and 50 weight % and bulk polymer in anoxic conditions (Table II). The typical plot of experimental points for 10 % PVME solution is presented in Fig. 11. It is worth to note that for correct gel-sol analysis the experimental points should cover at least 50% of sol values range in the $s = f(D)$ coordinate system, and D should be taken from range app. $1.1 \div 3 D_g$. For all studied concentrations such condition were fulfilled. In all irradiated PVME solution there are no degradation processes as irradiation yield of scissions resulted from λ value is zero in all cases. It confirms our previous results for radiation induced changes of PVME in diluted solutions where no degradation products were observed after irradiation in anoxic conditions. The negative value of D_v is connected with narrower then the most probable initial molecular weight distribution of PVME used. The virtual doses remain on the same level for all samples that indicate correctness of proceeded analysis (because starting polymer was the same). Gelation doses increase with the concentration (Fig. 12) and changes from 6 to 48 kGy, for 2 % (w/w) PVME solution and bulk polymer, respectively.

Using D_g values we calculated the yields of cross-linking on the base of the Charlesby-Pinner equation for all studied polymer concentrations. The G_X values increase with PVME concentration and agree well with G_X values determined on the base of molecular weight changes. The slight difference is related to the accuracy of D_g values determination. As we mentioned above, the Charlesby-Pinner equation is derived from changes of irradiated polymer M_w before gelation point and is valid only for doses ranged from 0 to D_g . Thus it is possible to evaluate D_g values by applying G_X determined initially from M_w changes. It can be presented graphically as a intersection of line $(1/M_{w,0} - 1/M_w) = f(D)$ with line $1/M_{w,0}$ (Fig. 11). The D_g values evaluated on this way agree well with values determined on the base of gel-sol analysis (Fig. 13). The differences in G_X values for each PVME concentration determined on two ways reflect differences in the D_g values estimated with these two methods.

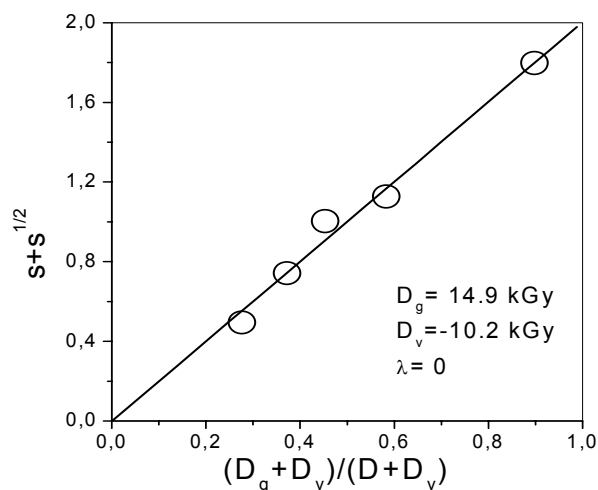


FIG. 11. Typical plot of experimental data in coordinates of equation (6) for 10% (w/w) PVME anoxic aqueous solution (solid line – the best fit calculated by GelSol95 computer program).

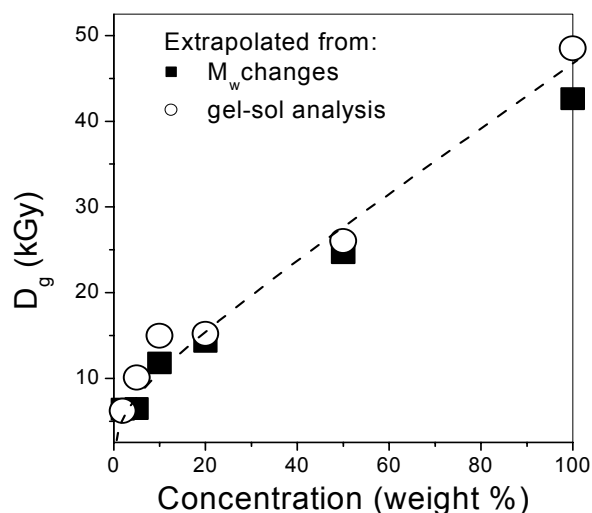


FIG. 12. Dependence of gelation dose on PVME concentration.

2.4. Equilibrium swelling experiments

Swelling measurements were performed to explain the dose nad temperature dependence on equilibrium degree of swelling (DS). In the given conditions (temperature, pressure, humidity) exists certain maximal gel degree of swelling (equilibrium degree) depending on the average distance of the chains between crosslinks. After formation gels need some time to swell and attain the equilibrium level of swelling. To obtain the average time of swelling a degree of swelling were monitored as a function of time for PVME gels irradiated with different doses and concentrations (2-50% and bulk PVME).

Typical shape of swelling kinetic for hydrogel irradiated with various doses is shown in Fig. 13. For all samples such dependence were recorded and one could assume that the average time to get equilibrium degree of swelling varies between 21-28 days depending on the concentration of gel and the dose applied. Increase of dose causes decrease of equilibrium degree of swelling for all analysed gels (Fig. 14).

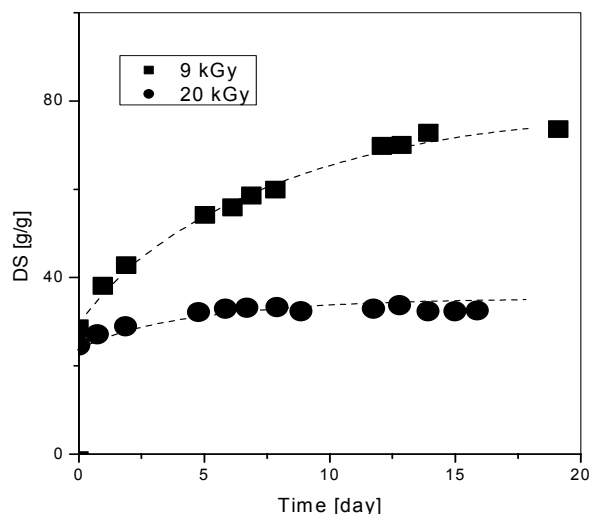


FIG. 13. Degree of swelling 5% PVME gel as a function of time ($t = 25\text{ }^{\circ}\text{C}$).

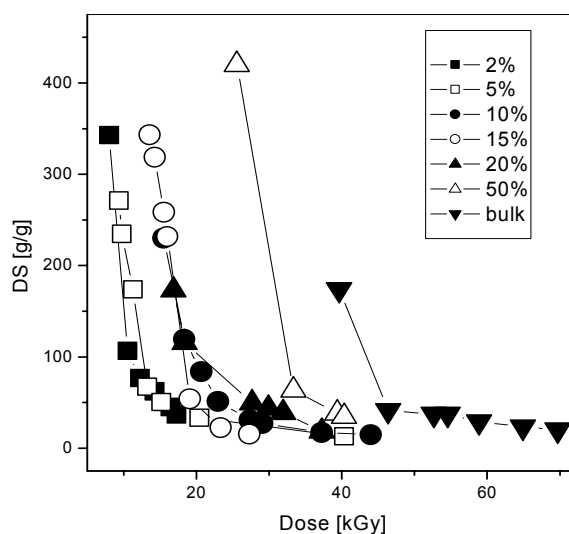


FIG. 14. Equilibrium degree of swelling PVME gels as a function of dose.

Then higher dose absorbed then gel structure is more cross-linked. By choice of irradiation dose one can control cross-linking density of gel and related parameters like equilibrium degree of swelling or pore size for instance.

The network structure homogeneous fourth-functional junctions, and low/moderate degrees of cross-linking can be predicted using the analysis of equilibrium swelling based on Flory's development modified by Peppas for swelling of networks formed in the presence of a diluent. A gel will swell to an extent depending on concentration of effective chains, V_e , which is itself related to the number average molecular weight between crosslinks, M_c :

$$V_e = -\frac{\frac{v}{V_1} [\ln(1 - V_{2,s}) + V_{2,s} + \mu V_{2,s}^2]}{V_{2,r} \left[\left(\frac{V_{2,s}}{V_{2,r}} \right)^{1/3} - \frac{V_{2,s}}{2V_{2,r}} \right]} = \frac{1}{M_c} - \frac{2}{M_{n,0}}$$

where v is the specific volume of polymer; μ is Flory-Huggins the polymer-solvent interaction parameter, V_1 is the molar volume of the solvent; $V_{2,r}$ and $V_{2,s}$ are polymer volume fractions of the gel samples in both the relaxed and swollen state. The polymer volume fractions of the gel samples ($V_{2,s}$; $V_{2,r}$) can be calculated on the basis of simple gravimetric measurements as elsewhere.

Due to Flory's theory of network formation at the gelation point the number of cross-linking bonds have to be equal statistically to the number of macromolecules. At the same point the relation between initial number average molecular weight and the number average molecular weight between successive crosslinks is $M_{n,0} = 2M_c$. Taking into account the Charlesby-Pinner equation for gelation point and relation between $M_{w,0}$ and M_c for polymer with most probable distribution of molecular weight ($M_{w,0}/M_{n,0} = 2$) one can derived following relation:

$$G_x = \frac{c}{4M_c D_g d(2 - \lambda/2)}$$

and the concentration of effective chains is related then with M_c and G_x as follows:

$$V_e = \frac{1}{M_c} - \frac{2}{M_{n,0}} = \frac{4G_x D d(2 - \lambda/2)}{c} - \frac{2}{M_{n,0}}$$

If system under study undergoes only cross-linking the value $\lambda = 0$; for solid polymers c equals density of polymer. Thus if V_e is plotted against dose a straight line should be obtained with slope that gives G_x value. According to Charlesby it is not appropriate to attach much attention to the quantitative results obtained just after gelation-point. In practical terms the gels with $g \geq 0.1$ may be considered as appropriate for this type of analysis.

Fig. 15 presents the changes in the concentration of effective chains deduced from swelling experiments as a function of absorbed dose for PVME gels. One can observe linear dependence V_e on the absorbed dose as well as changes in the slope lines as a function of polymer concentration. All lines meet the value of $-2/M_{n,0}$.

The slopes were determined with last square method with fixed zero point, and the appropriate G_x values are shown in Fig. 16. The character of changes resembles the changes observed for other method of calculation. However, the values are lower than in previous cases (Table II, column C). It is the result of change in the object subjected to irradiation. In case of polymer solution the mobility of chains is much higher then in the hydrogel network where chains as well as their segments are in 'frozen' state (due to cross-linking bonds). For higher polymer concentrations mobility of chains in solution is much lower and for bulk polymer (at room temperature bulk PVME is still liquid as its melting point is -34°C) it can be compared to hydrogel network. It reflects in the G_x values which for higher polymer concentrations compare well irrespective of calculation method applied. In addition, Flory-Huggins factor is not fixed in the broad range of calculation (as we assumed in our calculations).

Table II presents cross-linking and scission parameters calculated on the base of gel-sol analysis.

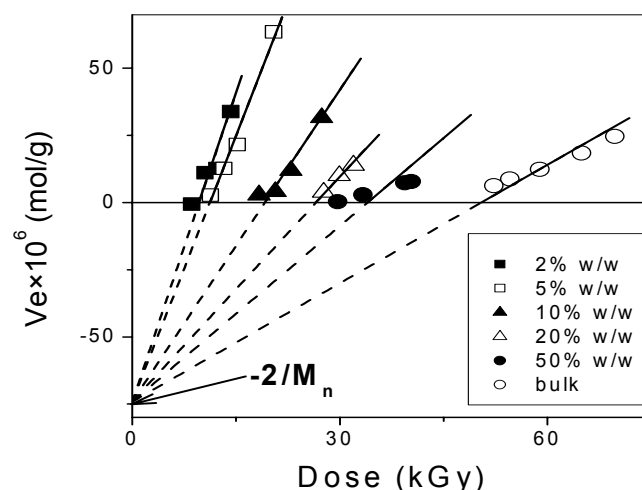


FIG. 15. Dependence of effective chains concentration on absorbed dose for PVME gels obtained in aqueous solutions (concentration given on the figure).

Radiation yields of cross-linking are calculated on the basis of the changes of weight average molecular weight before the gel point; B -the determination of the gelation dose, C -equilibrium swelling experiments resulted hydrogel. A – radiation yield of scission (in the presence of oxygen)

TABLE II. RADIATION YIELDS OF CROSS-LINKING

Concentration (% w/w)	λ	D_g (kGy)	D_i (kGy)	$G_x \cdot 10^7$ (mol J ⁻¹)		
				A	B	C
2	0	6.2	-0.73	0.34	0.30	0.19
5	0	10.1	-8.3	0.72	0.46	0.41
10	0	14.9	-10.2	0.79	0.62	0.48
20	0	15.2	-4.9	1.36	1.22	0.70
50	0	26.0	-8.5	1.88	1.79	1.37
Bulk	0.6	48.5	-43.1	2.18	2.01 (1.2) ^a	1.81

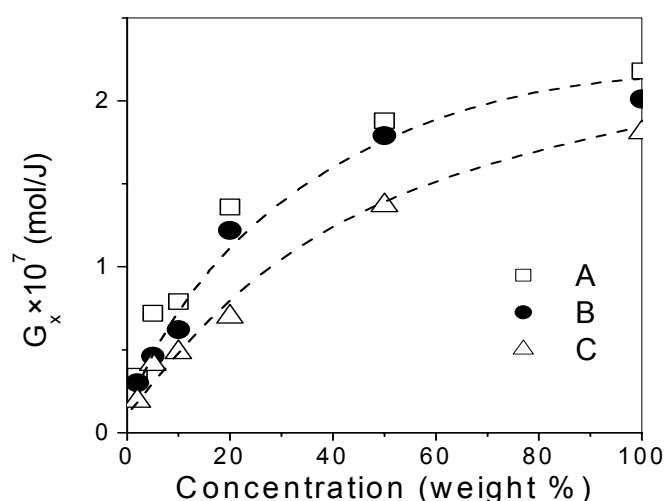


FIG. 16. Dependence of the radiation yields of cross-linking (G_x) on polymer concentration (argon saturated). Values calculated on the basis of: A- changes in the molecular weight before reaching gel point, B- determination the gelation dose value, C- equilibrium swelling experiments.

2.5. Equilibrium degree of swelling as a function of temperature

Lower critical solution temperature, (LCST), for linear polymers strongly depends on degree of polymerisation of given polymer. Increasing degree of polymerisation LCST increases as a result of cooperative interactions between base units of polymer chain and structured solvent molecules. Thus, rise of degree of polymerisation (or molecular weight) increases stability of solution. Hydrogel as a specific form of branched macromolecule should exhibit similar tendency, i.e. dependence of LCST versus degree of cross-linking. Typical changes of equilibrium degree of swelling for 20% PVME gels as a function of temperature is shown in Fig. 17.

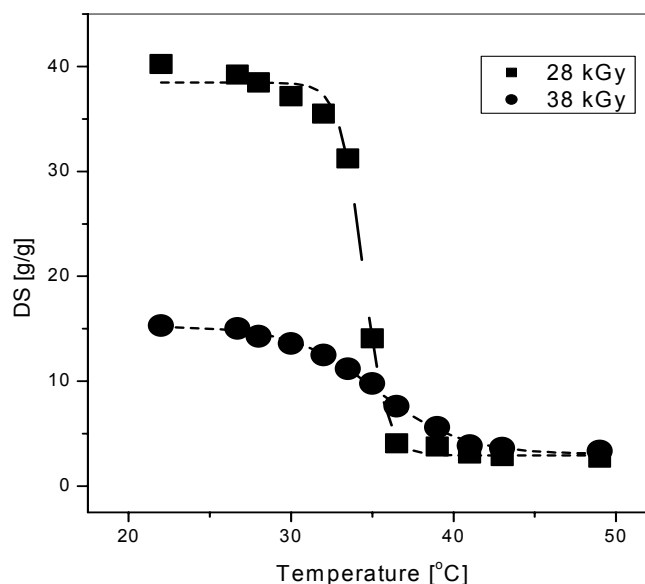


FIG. 17. Dependence of equilibrium degree of swelling of 20% PVME gels versus temperature.

For series of various samples of PVME gels marked from 1 to 9 changes of LCST were observed (Fig. 18).

TABLE III. DESCRIPTION OF SAMPLES TAKEN TO LCST MEASUREMENTS.

Sample no	Concentration [%]	Dose [kGy]	LCST [°C]
1	20%	27,67	35,88
2	100%	52,69	36,12
3	10%	44,02	36,50
4	10%	29,06	36,70
5	2%	17,29	37,18
6	5%	20,44	37,38
7	10%	37,25	37,47
8	5%	40,31	37,75
9	20%	37,26	39,94

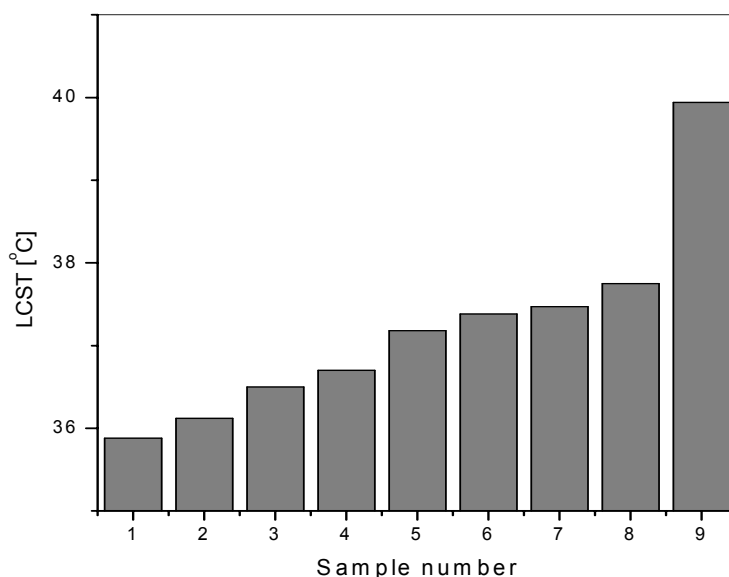


FIG. 18. Changes of LCST for different PVME gel samples

There have been taken attempts to connect values of LCST with some parameter describing hydrogel structure, i.e. concentration of effective chains. However, results were not satisfied and this studies need to be further performed for full explanation of described phenomena. Hydrogel networks obtained from different polymer concentrations are likely different in structural type, and they should not be compared. As a confirmation there can be results obtained for hydrogels obtained from the same polymer concentrations irradiated with different doses (Table III). For given concentrations of PVME (5 %, 10 %, 20 %) LCST rise with increase of applied dose.

2.6. Synthesis of composite thermo-sensitive membranes based on PVME [8]

On the base of PVME cross-linking data, we performed more application-oriented study on obtaining composite membranes by radiation-induced grafting and cross-linking of PVME on poly(ethylene terephthalate) ion-track membranes.

Experimental

Poly(vinyl methyl ether) supplied by Aldrich (50 % w/w aqueous solution, $d = 1.03 \text{ kg/dm}^3$) has been purified by precipitation in water above LCST (34 °C). Weight-average molecular weight (M_w) of polymer after purification was equal to 53.6 kDa and number-average molecular weight (M_n) 27 kDa as determined by GPC. Ion track poly(ethyleneterephthalate) (PET) foils used to synthesis of responsive membranes had average pore size 1.3 μm , thickness 10 μm and porosity 10%.

PET membranes were covered (on the surface and/or inside the pores) with PVME aqueous solution (10 % weight). Then membrane was subjected to irradiation of accelerated electrons with dose 40 kGy. Depending on the covering procedure, it was possible to obtain membranes with the gel located predominantly in the pores (type A) or forming a continuous layer on the surface of PET membrane (type B). After irradiation membranes were immersed into the water for one day. In order to characterize modified membrane the permeability measurement of NaCl through membrane was carried out. As a reference similar measurement was performed for non modified membrane. Presence of polymer on the surface and in pores was confirmed by scanning electron microscopy (Fig. 19).

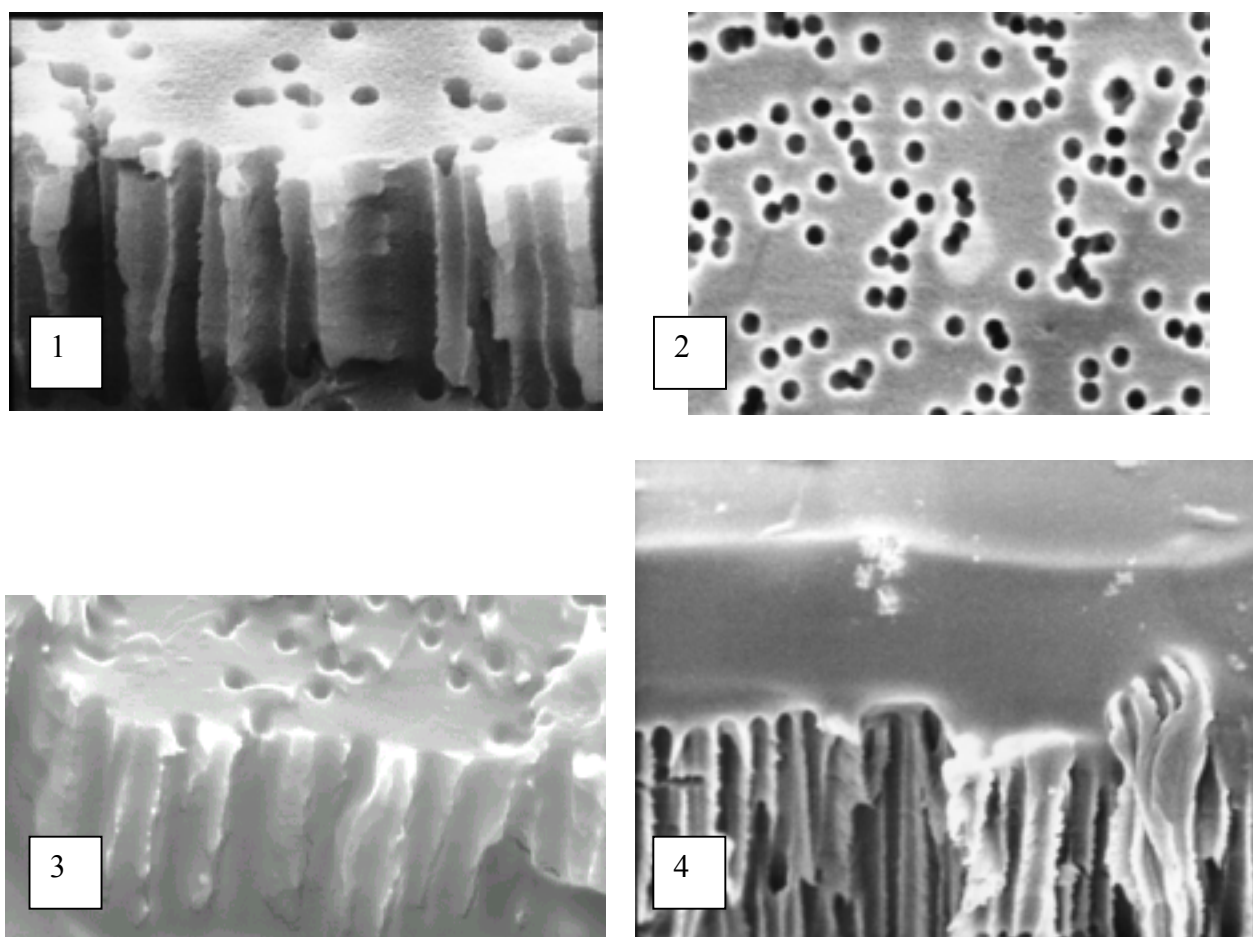


FIG. 19. SEM picture of PET membranes: (1), (2) non-modified, and (3), (4) grafted with PVME hydrogel. In sample (3) gel is predominantly grafted in the pores of PET membrane (composite membrane type A); in sample (4) a gel layer is grafted on the surface of PET membrane (type B).

The diffusion experiments were performed with standard diffusion cell with magnetic stirrers in each half cell (Fig. 20). The diffusion permeability of the membrane was determined by measuring the increase in solute concentration on one side of the membrane after solute had been introduced into the other side and using the data in a mass balance. The solutes used were NaCl and styrene sulfonate. During experiments both sides of the cell were sealed and the build up of electrode in the measuring side was monitored by changes in the solution conductivity which was measured using conductivity meter (CDM83, Radiometer Copenhagen). Measuring cell was thermostated by water bath connected to external thermostat. In defined period of time the conductivity in the measurement cell was monitored.

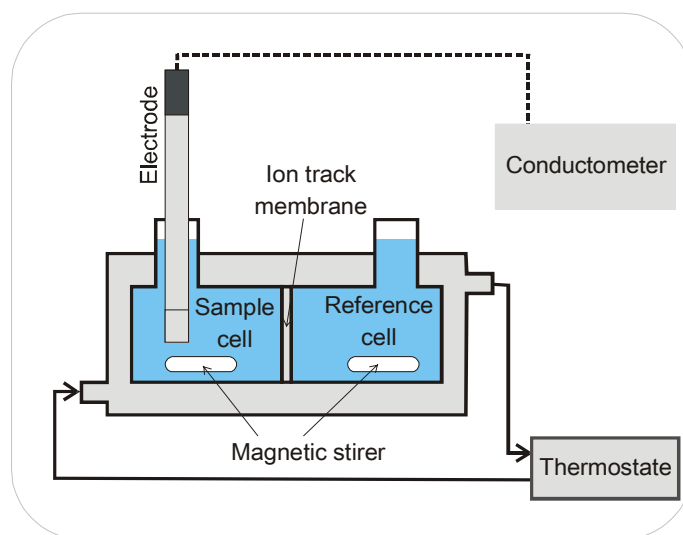


FIG. 20. Schematic representation of instrument for measurements of permeation through porous membrane.

Fig. 21 illustrates the effect of temperature on the permeability of type A and type B composite membranes.

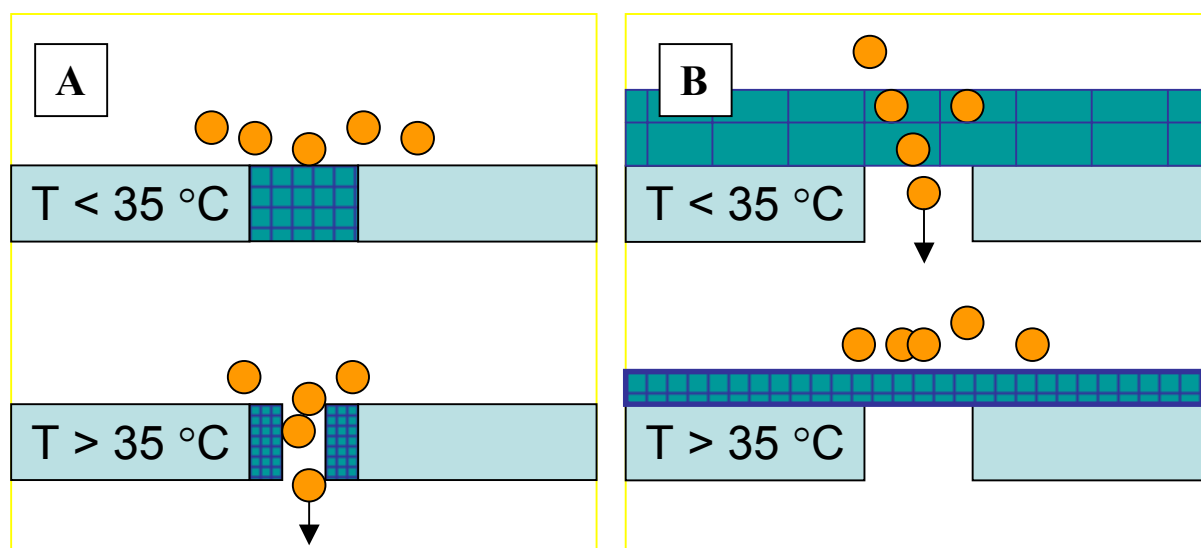


FIG. 21. Effect of temperature on the permeability of type A and type B composite membranes. Hatched areas represent the PVME gel.

For type A membranes (PVME gel grafted predominantly in the pores) an increase in temperature above LCST leads to the shrinkage of the gel in the pores. The volume fraction of a pore occupied by the gel decreases and the solute can penetrate through the pores more easily. This is illustrated by exemplary data shown in Fig. 22.

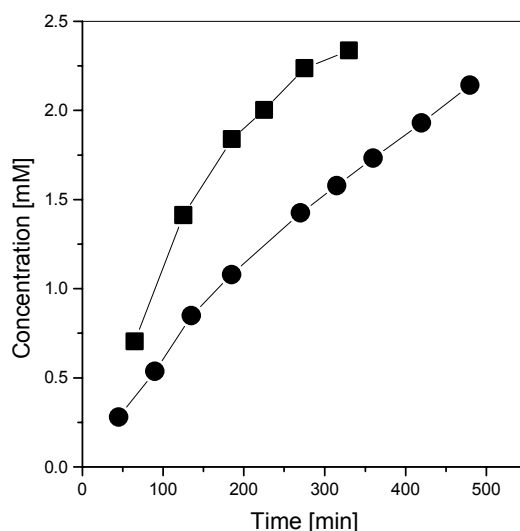


FIG. 22. Diffusion profiles of styrene sulfonate through a composite membrane (type A) at room temperature (circles) and at 48 °C (squares).

For type B membranes (gel layer grafted on the surface on PET membrane), the situation is different. Fig. 23 shows concentration changes of solute (NaCl) permeated through membrane modified and unmodified as a function of time at two distinguish temperatures 25 °C and 40 °C, respectively. Analyzing presented graph one can see difference in diffusion profiles of membrane non- and modified. Process of NaCl permeation through original PET membrane proceed with apparent temperature effect as with rise of temperature solute permeates faster. Grafting of PVME gel on the original PET membrane causes decrease of NaCl permeation at 25 °C since the solute has to diffuse through the pores of the gel layer. Increase of temperature above LCST *i.e.* about 40 °C causes shrinking of thermosensitive PVME gel and results in decrease of effective pores of the gel layer. Gradual increase of temperature results with rise of solute diffusion through original PET membranes. However, in case of modified membrane above LCST (about 38 °C) the rate of diffusion decreases almost 4 times.

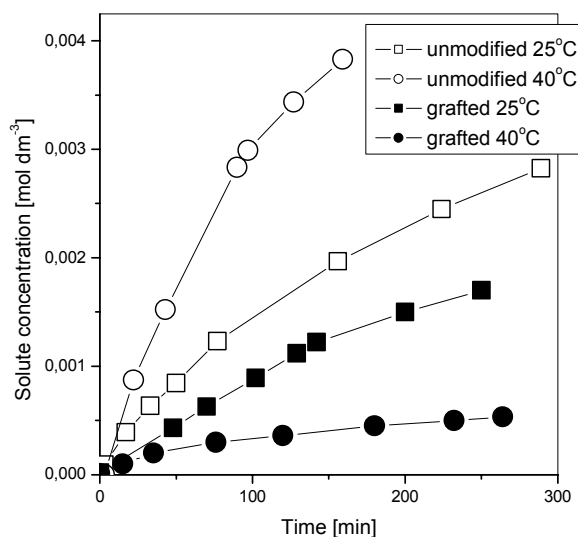


FIG. 23. Changes of NaCl concentration in measurement cell after permeation through PET membrane (non modified and modified) as a function of time at 25°C (squares) and 40°C (circles). Open and solid symbols denote non-modified and modified membranes, respectively.

In order to control influence of cross-linking density of PVME gel on permeation of solute through modified membranes various doses (20, 40, 60, 80 kGy) were applied to graft/crosslink

PVME onto PET ion-track membranes. Changes of diffusion constants of NaCl permeated through membranes grafted at chosen range of doses is shown in Figs. 24 and 25. One can note that dose as low as 20 kGy is not accurate to modify PET ion track membranes with PVME because the diffusion coefficient versus temperature does not change in comparison to non-modified membrane. Rest of membranes were modified and their dependence of $D = f(\text{temp})$ for permeating solute look very similar i.e. have characteristic discontinuous point in the vicinity of LCST of PVME gel. Additionally, there is apparent influence of cross-linking density on permeability of membranes below and above LCST. Increasing dose applied diffusion coefficients decrease slightly (Fig. 25) especially, in the range of temperatures above LCST.

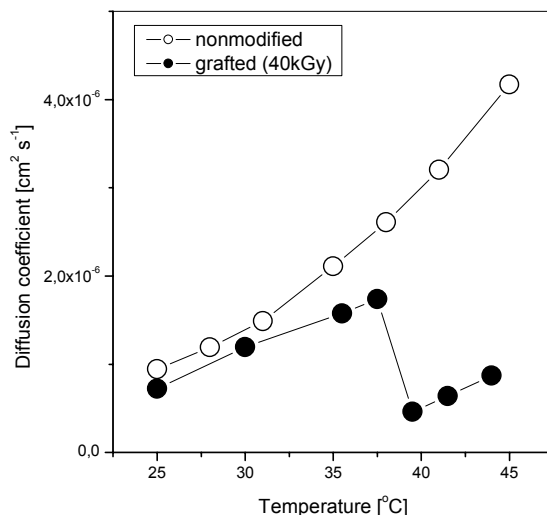


FIG. 24. Changes of diffusion coefficient of NaCl permeated through PET membranes non grafted (open circles) and grafted with PVME (solid circles, dose 40 kGy) as a function of temperature.

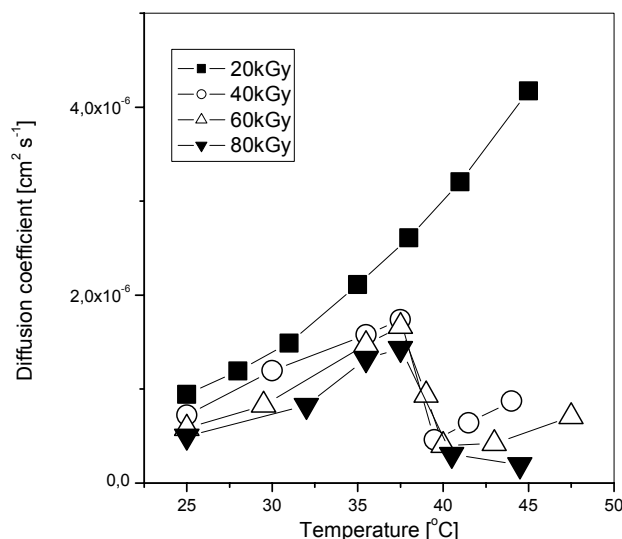


FIG. 25. Changes of diffusion coefficients of NaCl permeated through PET membranes modified with PVME solutions and irradiated with different doses (denoted in inset) as a function of temperature.

For membrane irradiated with 80 kGy there is no further increase of diffusion coefficient with temperature after crossing critical point. Thus, it means that pores in the collapsed gel layer are completely blocked for even such small species like ions. Such results suggest possibility of applying an appropriate dose of ionizing irradiation for easy regulation of diffusion of solutes with temperature-controlled membranes for selective separation purposes. Further studies on selective separation of substances on the modified membranes are in progress.

2.7. Synthesis and properties of nanogels and microgels based on a stimuli-sensitive polymer poly(acrylic acid) [6, 7, 12]

Soft nanomaterials - polymeric nanogels and microgels - have made a fast and brilliant career, from an unwanted by-product of polymerization processes to an important and fashionable topic of interdisciplinary research in the fields of polymer chemistry and physics, materials science, pharmacy and medicine. Together with their larger analogues – macroscopic gels, most known in the form of water-swallowable hydrogels – they have a broad field of actual and potential applications ranging from filler materials in coating industry to modern biomaterials.

A distinct class of microgels are stimuli-sensitive (“smart”, “intelligent”) structures. They are able to react, usually by a pronounced change in dimensions and swelling ability, to external stimuli such as temperature, pH, ionic strength, concentration of a given substance, electric field, light etc. It is believed that nano- and microgels made of stimuli-sensitive polymers may be used in separation, selective absorption and controlled drug release.

A multitude of techniques has been described for the synthesis of polymeric microgels. Most of them can be classified in two groups. The first one are techniques based on concomitant polymerization and cross-linking (where the substrates are monomers or their mixtures), called by some authors “cross-linking polymerization”. The second group are methods based on intramolecular cross-linking of macromolecules (where the starting material is not a monomer, but a polymer).

In our work we try to utilize the latter technique to synthesize nanogels sensitive to pH, ionic strength and temperature. An obvious and important advantage of this method is the absence of monomer. This is of great value when the product is intended for biomedical use, where even small quantities of residual monomer may be potentially harmful and thus unacceptable. In this approach, pure aqueous solution of a polymer is subjected to a short (a few microseconds), intense pulse of ionizing radiation. In this way, many radicals are generated simultaneously along each polymer chain, and their intramolecular recombination leads to the formation of nanogels. This approach has been first tested on neutral water-soluble polymers: poly(vinyl alcohol) and polyvinylpyrrolidone. Our current work extends its applicability to stimuli-sensitive polymers like poly(acrylic acid). Similar approach can be also used to synthesize nanogels of poly(vinyl methyl ether).

The main parameter influencing the competition between inter- and intramolecular recombination of polymer radicals in dilute solutions is the average number of radicals present at each macromolecule at the same time. If this number, under the given synthesis conditions, is much lower than 1, there is only a meager chance that a radical will find a reaction partner within the same chain. In such cases, recombination is only possible between radicals localized on two separate macromolecules. On the other hand, when there are tens of radicals present along each chain, the probability of intramolecular encounters and reactions is higher than that of intermolecular ones. The latter processes are relatively slow, since they require that two large entities – polymer coils – diffuse towards each other. In the case of the radiation-induced radical formation, these two opposite conditions, *i.e.* a very low or very high number of radicals per chain, can be fulfilled by means of a proper choice of irradiation conditions. Continuous irradiation at a relatively low dose rate, such as typical irradiation with gamma rays from isotope sources, leads to a steady-state concentration of polymer radicals in the order of 10^{-7} M.

When the concentration of polymer coils is significantly higher than this value (this condition is usually easily fulfilled), the average number of radicals per chain is much lower than unity and intermolecular cross-linking is observed (Fig. 26a). In order to promote intramolecular cross-linking, short, intense pulses of radiation can be employed, such as pulses of fast electrons from an accelerator, generating radical concentrations in the order of $10^{-4} \div 10^{-3}$ M. If the concentration of polymer coils is low (that is to say, $10^{-6} \div 10^{-4}$ M), many radicals are generated on each macromolecule (typically many tens or even over a hundred), and the conditions for intramolecular recombination are fulfilled (Fig. 26b). Certainly, this does not mean that intermolecular reactions are totally eliminated in such a case. Some coils may come into contact before all the radicals decay, and if there is an uneven number of radicals on a chain, at least one of them must finally find a reaction partner at a neighboring macromolecule.

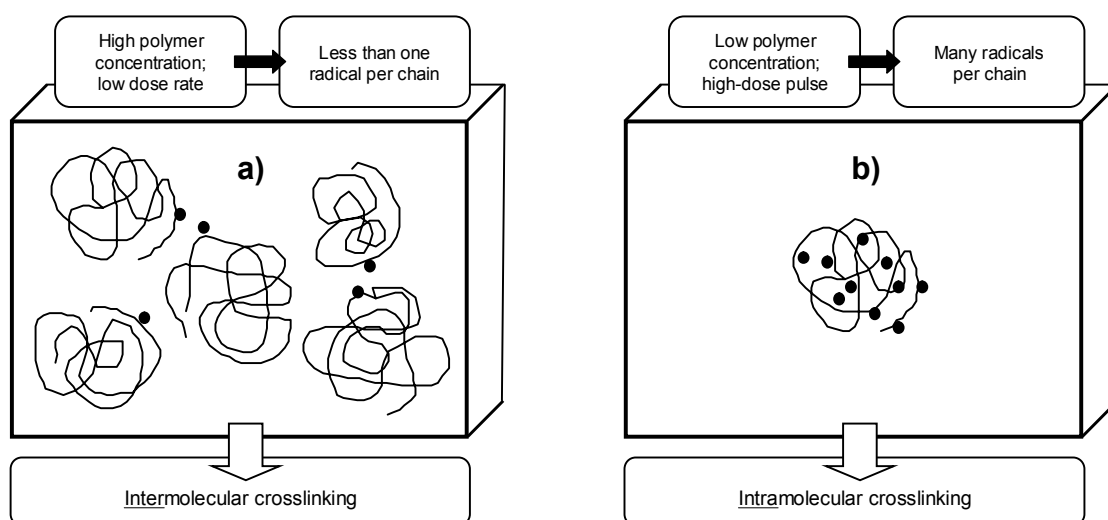


FIG. 26. Irradiation conditions promoting: a) inter- and b) intramolecular recombination of polymer-derived radicals in solution.

2.8. Radiation synthesis of poly(acrylic acid) nanogels

Experimental

Poly(acrylic acid) (PAA, Aldrich, nominal $M_w = 2.5 \times 10^5$ Da) was purified from traces of volatile impurities (water, monomer and solvent) by heating at 40 °C in vacuum for 2 hours. The actual M_w , as determined by multi-angle laser light scattering (see below), was 5.2×10^5 Da. Solutions of PAA were prepared by overnight stirring at 50 °C.

Pulse irradiation was conducted in a setup shown schematically in Fig. 27. Aqueous PAA solution (pH = 2.0, HClO_4), saturated with oxygen-free argon (saturation started 1 h before the irradiation and continued during the process), was circulating at $1 \text{ cm}^3 \text{ s}^{-1}$ in a gas-tight, closed-loop system, passing through a quartz cell (effective volume: 0.7 cm^3) that was subjected to short pulses of fast electrons [pulse duration: 2 μs , pulse frequency: 0.5 Hz, electron energy: 6 MeV, absorbed dose of ionizing radiation per single pulse: 1.15 kGy ($1 \text{ Gy} = 1 \text{ J kg}^{-1}$)], generated by an ELU-6 linear accelerator (Eksma, Russia). Knowing the parameters of the system, it was possible to set the total irradiation time so as to assure that on average each volume element (0.7 cm^3) of the solution absorbed one shot (average absorbed dose equal to a dose in a single shot, this corresponds to the lowest doses shown in Figs. 28-30), or any other desired number of shots.

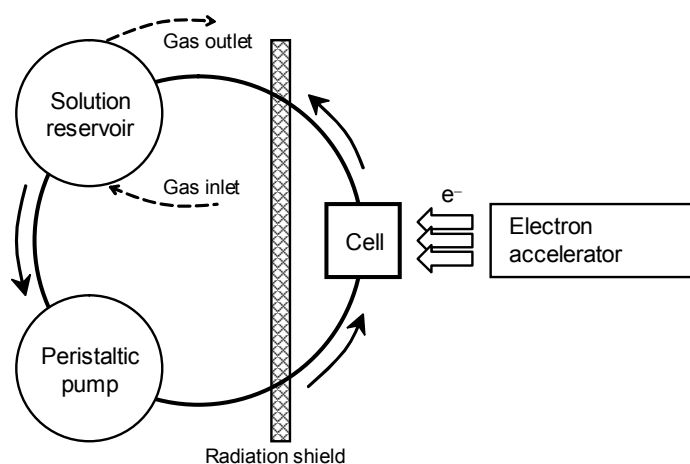


FIG. 27. A schematic diagram of the pulse-irradiation setup used in the synthesis of nanogels. Solid-line arrows indicate the flow of polymer solution in the closed loop.

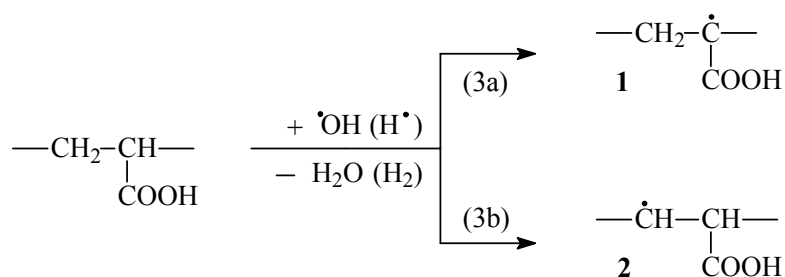
Tests on the radiation-induced degradation of linear and cross-linked PAA were performed on the same setup as used in the synthesis, but the solutions were saturated with oxygen and the dose per pulse was lowered to 20 Gy.

Molecular parameters of the products were determined by static multi-angle laser light scattering (BI-200SM Brookhaven goniometer with a Lexel 95E Ar-ion laser $\lambda = 514.5$ nm), at 25.0 ± 0.1 °C, in aqueous solution of pH 10.0 (NaOH) containing 0.5 M NaClO₄. Viscosities were measured on an automatic Ubbelohde viscometer AVS-310 (Schott) at 25.0 ± 0.1 °C.

Visualization of nanogels was performed by Atomic Force Microscopy. The films cast from 10% (w/v) salt-free solutions of linear PAA and nanogels were air-dried in a dust-free atmosphere at RT. All measurements were done in the contact mode.

Generation and recombination of PAA radicals

Hydroxyl radicals and hydrogen atoms formed by radiolysis of water react rapidly with PAA by hydrogen abstraction and in this way polymer-derived mid-chain radicals 1 and 2 are formed, their initial molar ratio being *ca.* 1:2.



The fate of the PAA-derived radicals 1 and 2 had been studied before in some detail. As can be expected, it depends strongly on pH. In neutral and alkaline solutions, where the carboxylic groups are deprotonated and there is a high density of negative charge along the chains, radicals cannot recombine easily due to the repulsive coulombic forces. As a result they can have a lifetime of several minutes or even hours, which is a somewhat unusual feature for simple alkyl-type radicals in aqueous solution at RT. Certainly, these are very unsuitable conditions for cross-linking. Instead, strong degradation and other side reactions are observed.

On the other hand, it has been shown that at $\text{pH} < 3$, where the carboxylic groups are protonated, recombination of radicals becomes very fast, and therefore cross-linking dominates over scission, at least under the conditions of continuous gamma irradiation. Since solubility of PAA in water decreases at $\text{pH} < 1$, we have chosen to work at $\text{pH} = 2$. Under such conditions, where the PAA-derived radicals have a relatively short lifetime, slow side processes such as *e.g.* H-shift do not show up, and the list of possible reactions of these radicals is limited to recombination, disproportionation and chain scission (by β -fragmentation).

The ratio of the recombination to the disproportionation occurring when two radicals approach each other is a function of their chemical structure and cannot be easily influenced. It has been shown in a study on the radicals of a PAA model compound, 2,4-dimethylglutaric acid, that *ca.* 45 % of them decay by recombination, and this value sets the limit of the fraction of PAA radicals that will yield crosslinks, irrespective on the method of their generation. The rest is “lost”, at least at this stage of gel formation.

Recombination may occur either between two radicals localized on separate macromolecules or between two radicals within the same chain. The first of these processes leads to intermolecular cross-linking, increase in average molecular weight, and finally may result in the formation of macroscopic (“wall-to-wall”) gels. This reaction is the base of radiation technologies used to produce hydrogel materials on an industrial scale, mostly in the biomedical industry. Intramolecular recombination does not influence molecular weight but, by the formation of new C-C bonds between the formerly independent chain segments, yields nanogels.

As discussed above, high-dose pulse irradiation and low polymer concentration are the irradiation conditions that promote intramolecular cross-linking. In this work we have used PAA concentrations in the range of $10 \div 25$ mM of monomer units. This corresponds to approximately $3 \div 7 \times 10^{-6}$ M of polymer coils.

Product analysis

Figs. 28 and 29 illustrate the changes in weight-average molecular weight and radius of gyration of PAA subjected to pulse-irradiation in solutions of various concentrations, as a function of total absorbed dose.

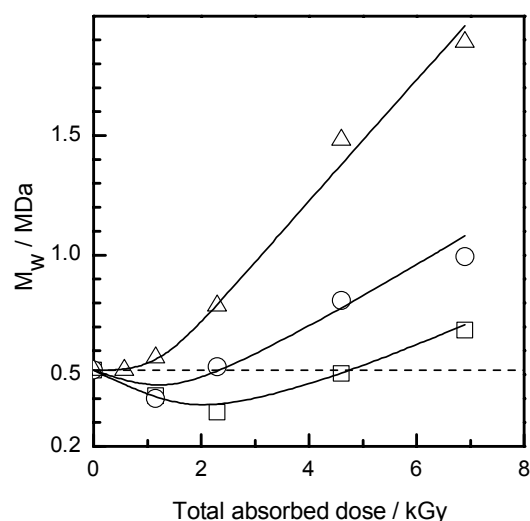


FIG. 28. Changes in the weight-average molecular weight of PAA molecules in the course of nanogel synthesis as a function of total absorbed dose (1.15 kGy corresponds to a single pulse), for samples of various PAA concentrations: \square - 10 mM, \circ - 17.5 mM, \triangle - 25 mM, irradiated in Ar-saturated aqueous solutions, pH 2.

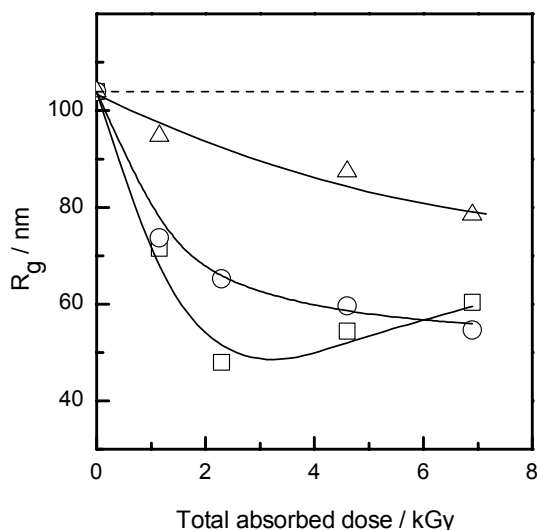


FIG. 29. Changes in the radius of gyration of PAA molecules in the course of nanogel synthesis as a function of total absorbed dose (1.15 kGy corresponds to a single pulse) for samples of various PAA concentrations: □ - 10 mM, ○ - 17.5 mM, △ - 25 mM, irradiated in Ar-saturated aqueous solutions, pH 2. Radii of gyration measured at 25.0 °C in aqueous 0.5 M NaClO₄, pH 10.

The data clearly indicate that, regardless of the polymer concentration, at high doses we obtain strongly internally cross-linked nanogels which, in comparison with the starting macromolecules, have higher molecular weight but at the same time significantly lower dimensions. While the main reason for the increase in molecular weight is the intermolecular cross-linking occurring in the system with very low yields (see below) in parallel to intramolecular recombination, the latter process is the dominant reason for the reduction in coil dimensions.

At the first stage of irradiation (first pulse corresponding to the dose of 1.15 kGy), for low PAA concentrations there is some decrease in the molecular weight – which is evidence of the fact that the balance between intermolecular cross-linking and chain scission is initially shifted towards the latter reaction. However, very soon this tendency is reversed. The most probable reason is that internal crosslinks that have been already formed make the structure less prone to losing fragments as a result of degradation. In other words, a chain segment of a nanogel is bound to other segments with more than one joint, thus if a chain break occurs in this segment, it does not cause its detachment from the rest of the molecule (see more detailed data and discussion below). Moreover, the nanogels, due to their reduced dimensions compared to the initial coils, have higher translational mobility, thus the rate of their mutual encounters leading to intermolecular cross-linking should increase (this effect is, however, counterbalanced to a certain extent by the reduced reaction radii, making the necessary diffusion distance longer).

The higher polymer concentration, the higher the yield of intermolecular cross-linking (due to the lower number of radicals per chain and closer distance between the coils), and therefore for 25 mM PAA there is no initial decrease in M_w . Finally, we obtain products of molecular weight higher than the molecular weight of the parent chains, but which have much smaller radii of gyration. Such a tight conformation, which is more densely packed than the starting coils of linear macromolecules, is a typical feature of internally cross-linked chains. Reduction in dimensions despite the increase in M_w is also evidenced by a pronounced decrease in intrinsic viscosity (Fig. 30).

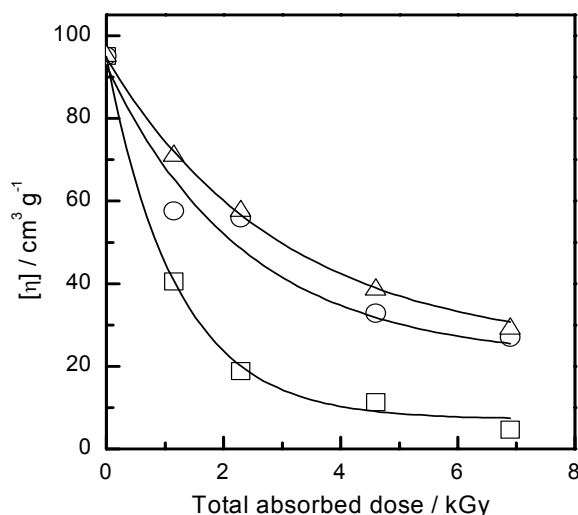


FIG. 30. Changes in intrinsic viscosity of PAA solutions in the course of nanogel synthesis as a function of total absorbed dose (1.15 kGy corresponds to a single pulse) for samples irradiated in Ar-saturated aqueous solutions, pH 2, at various PAA concentrations: \square - 10 mM, \circ - 17.5 mM, \triangle - 25 mM. Viscosity measured at 25.0 °C in aqueous 0.5 M NaClO₄, pH 10.

An important message from the data in Fig. 28 is that under these conditions intermolecular cross-linking is indeed a minor process compared to intramolecular recombination. Calculations lead to the intermolecular cross-linking yield of only $G(x, \text{inter}) = 1 \times 10^{-9} \text{ mol J}^{-1}$. This value should be compared with the total yield of recombination events in the system that can be estimated at $G(x, \text{total}) = 7 \times 10^{-8} \text{ mol J}^{-1}$. Since the yield of intermolecular cross-linking constitutes less than 2 % of the total recombination yield, over 98 % of the recombination events must have occurred in the intramolecular way.

In order to visualize the synthesized structures, AFM pictures were taken of dry films cast from solutions of linear PAA and nanogels (Fig. 32a and 32b, respectively). Despite the de-swelling and shrinking of the gels due to the loss of water, the spherical contours of individual nanogels particles can be clearly seen on the surface of the film, in contrast to the flat surface of the film cast from linear PAA.

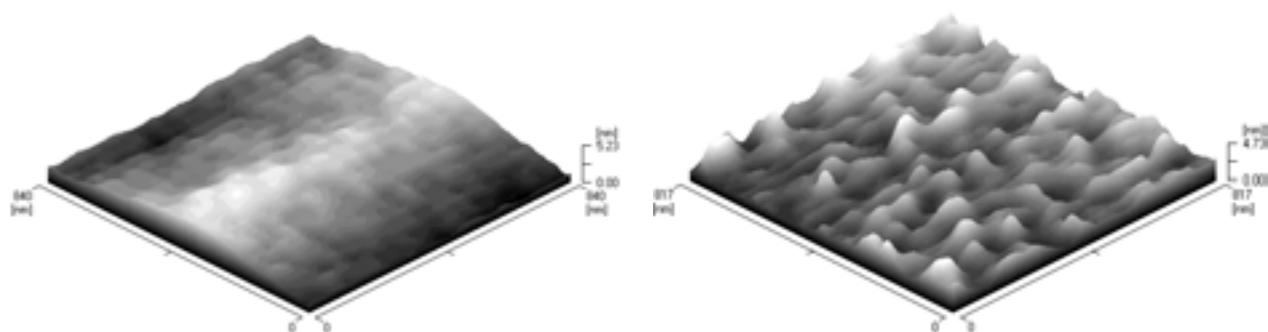


FIG. 31. Atomic force microscopy pictures of dry films cast from 10% (w/v) aqueous solution of: linear PAA (left side), and) nanogels of PAA (right side, obtained by irradiation of 17.5 mM PAA solution at pH 2 with a total dose of 2 kGy).

PAA nanogels bearing many carboxylic groups are expected to undergo expansion and contraction with changes in pH, albeit the magnitude of changes in their dimensions should be different than in the case of free linear chains. Such an effect is indeed observed. The data shown in Fig. 32 illustrate the pH-dependence of viscosity for the solutions of PAA molecules in the linear and nanogels forms, at identical concentrations. The viscosity of 5 mM nanogel solution at pH 2 was chosen as a relative unit in Figs. 32 and 33. At pH 2, the solution of linear PAA has a viscosity 1.8 times higher than the nanogel solution. The expansion of the linear PAA accompanying the change of conformation from a coil at low pH to a rod-like structure in the alkaline region results in a ca. 32-fold increase in the solution viscosity, while in the case of nanogels the expansion factor is only ca. 7. As a result, at the pH corresponding to the highest magnitude of electrostatic repulsive forces between the chain segments, the viscosity of a solution of the expanded linear chains is 8-folds higher than the viscosity of nanogels having the same average molecular weight.

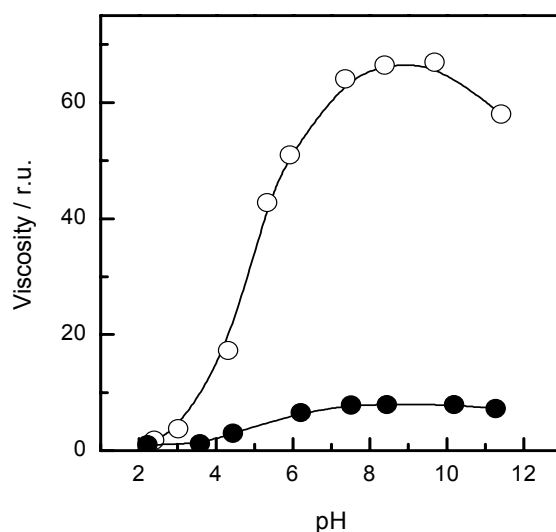


FIG. 32. Relative viscosity of 5 mM PAA solutions as a function of pH for \circ - linear chains and \bullet - nanogels of comparable weight-average molecular weight (ca. 5×10^5 Da). One unit corresponds to the viscosity of the salt-free nanogel solution at pH 2 (solution of linear chains at pH 2 has a viscosity of 1.8 units).

Fig. 33 illustrates the contraction behavior of both samples induced by adding a simple electrolyte at pH 10. Although the salt-concentration dependencies of viscosity have similar shapes for both linear and internally cross-linked chains, quantitative data indicate that nanogels are more susceptible to salt-induced collapse. Already at 0.3 M NaClO_4 the hydrodynamic dimensions of nanogels drop below the initial value corresponding to salt-free solution of pH 2 (*i.e.* below the viscosity of 1 relative unit, see above), while for linear chains even 1.2 M NaClO_4 is not enough to bring the viscosity back to the initial level. Similar differences in the swelling properties of linear and internally cross-linked macromolecules in response to changes in salt concentration have been reported for nanogels of a cationic polyelectrolyte, poly(allylamine).

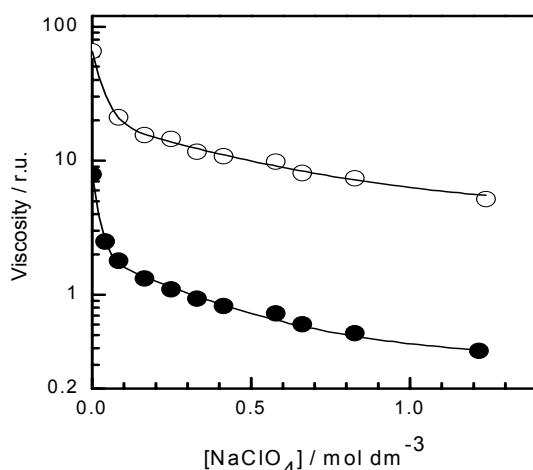


FIG. 33. Relative viscosity of 5 mM PAA solutions at pH 10 as a function of salt concentration, for ○ - linear chains and ● - nanogels of comparable weight-average molecular weight (ca. 5×10^5 Da). One unit corresponds to the viscosity of the salt-free nanogel solution at pH 2.

Degradation resistance

One of the most valuable properties of nanogels is their enhanced resistance against degradation. As a result of long-lasting stimulus inducing chain breakage a linear macromolecule is easily degraded to short fragments. The same number of chain breaks formed in a nanogel may cause no or very little fragmentation, since the chain segments are linked together in many points and will not fall apart as a result of a single chain break. In order to verify this assumption, aqueous solutions of linear chains and nanogels of PAA were subjected to the action of ionizing radiation in the presence of oxygen. Under such conditions, no cross-linking takes place in the system. However, the changes in molecular weight (Fig. 35) and in radius of gyration (Fig. 36) show striking differences. While linear PAA is easily degraded even at relatively low doses, which is clear from the parallel decrease in M_w and R_g , nanogels, within the same dose range, seem to remain intact.

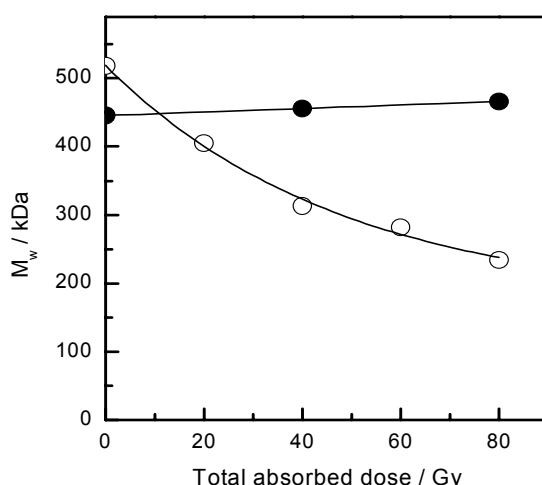


FIG. 34. Free-radical-induced degradation of PAA in O_2 -saturated aqueous solutions, pH 2, initiated by pulse-irradiation (pulse duration 17 ns, dose per pulse 20 Gy). ○ - linear chains, ● - nanogels (obtained by pulse-irradiation of Ar-saturated 10 mM PAA solution, pH 2, with a total dose of 4.4 kGy). Polymer concentration in both samples: 10 mM.

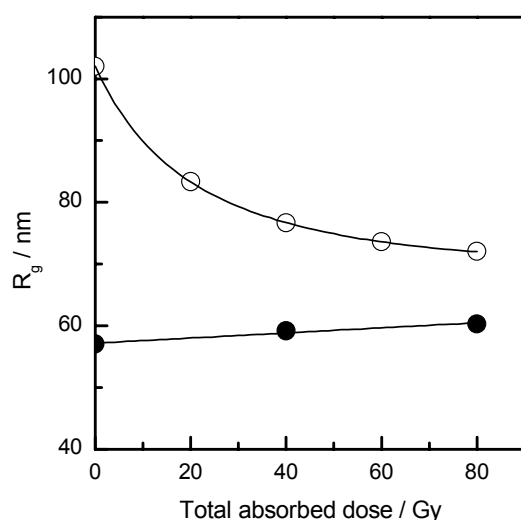


FIG. 35. Free-radical-induced degradation of PAA in O_2 -saturated aqueous solutions, pH 2, initiated by pulse-irradiation (pulse duration 17 ns, dose per pulse 20 Gy). Changes in the radius of gyration (determined in aqueous 0.5 M $NaClO_4$, pH 10) as a function of total absorbed dose. ○ - linear chains, ● - nanogels (obtained by pulse-irradiation of Ar-saturated 10 mM PAA solution, pH 2, with a total dose of 4.4 kGy). Polymer concentration in both samples: 10 mM.

Preliminary studies of ultrasound-induced degradation of linear and internally cross-linked polymer chains also clearly indicate that nanogel structures are characterized by a much higher resistance.

High degradation resistance shown by nanogels may be important for some potential medical applications. An example may be using polymer drugs to enhance the viscoelastic performance of malignant synovial fluid. These macromolecules are subjected to mechanochemical stress and abnormally high radical concentrations. It has been shown that under such conditions internally cross-linked macromolecules perform better than the corresponding linear ones.

Conclusions

- The example of poly(acrylic acid) has shown that subjecting linear polymer chains in solution to short, intense pulses of ionizing radiation is an efficient tool for inducing intramolecular cross-linking of individual macromolecules, leading to the formation of nanogels.
- When many carbon-centered radicals are generated simultaneously along each PAA chain in dilute solution, their recombination occurs mainly within a single chain, with only minor contributions of intermolecular recombination and chain scission.
- Average molecular weight and dimensions of the products may be controlled by changing the initial polymer concentration and the dose absorbed by the sample.
- The method allows synthesizing nanogels in a pure polymer-water system, eliminating the use of monomers, cross-linking agents or other auxiliary substances. Therefore it seems to be especially suitable for synthesizing polymeric nanogels for biomedical purposes.
- As expected, the pH- and ionic strength response of PAA nanogels is different than that of linear macromolecules. Constraints imposed by the intramolecular linkages hamper the expansion of nanogels with increasing deprotonation of carboxylic groups. By contrast, nanogels are more susceptible to the collapse caused by charge screening effects upon addition of salt.
- Nanogels of poly(acrylic acid) are much more resistant to free-radical-induced degradation than the parent linear macromolecules.

2.9. Formation and radiation-induced cross-linking of polyvinylpyrrolidone-poly(acrylic acid) complexes [14]

The possibility of synthesizing two- or multicomponent micro- and nanogels using interpolymer complexes as substrates was investigated. In our present work we deal with polyvinylpyrrolidone and oligomeric poly(acrylic acid) to investigate interpolymer complexation in their dilute solutions and we make an attempt to fix the obtained supramolecular structure into nanogels by means of radiation-induced cross-linking.

Experimental

Materials: Poly(acrylic acid) – PAA – (Aldrich) with weight-average molecular weight $M_w = 886$ Da, was dried at 50° C for 48 hours. PVP 90F (Kollidon, BASF), $M_w = 1.2 \times 10^6$ Da and $M_w / M_n = 3.65$ was used as received.

Complexes preparation: Stock solutions were used after 48 hours of stirring. Complexes were prepared by direct mixing of appropriate volume of PVP and PAA stock solutions passed through filters of 0.45 μm pore size (Sartorius) to obtain intended molar fraction of carboxylic groups expressed as $UM = [PAA] / ([PAA] + [PVP])$. All measurements were conducted at 25° C. There was no noticeable influence on samples behavior with regard to the way of preparation as proved on the basis of quasi-elastic light scattering measurements – it was not important if PAA solution was added to PVP solution or opposite, as reported for some other complexes.

Preparative pulse radiolysis: Pulse irradiation was conducted in a 1-liter, 3-necked glass reactor vessel equipped with argon saturation tool and stirrer. Mixed aqueous solutions containing PVP and PAA at appropriate ratios were irradiated during fast stirring with pulses of fast electrons generated by an ELU-6 linear accelerator (Eksma, Russia; pulse duration 2 μs , pulse frequency 5 Hz, energy of electrons 6 MeV). Doses of ionizing radiation during synthesis, averaged for the whole sample volume, were determined with ferrocyanide dosimeter.

UV-vis measurements: For measurements of critical pH, solutions were analyzed by transmittance changes at 500 nm with Perkin-Elmer Lambda 40 spectrophotometer directly after mixing and fixing appropriate value of pH.

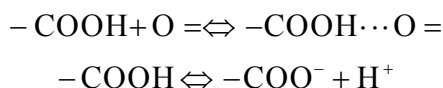
Viscometry: Measurements were conducted at 25.0 ± 0.1 °C using an AVS-350 setup (Schott Geraete) equipped with Ubbelohde viscometer. Solutions of complexes were measured after 24 hours from mixing. Irradiated solutions were analyzed directly after radiolysis.

Static light scattering measurements: Multiangle static light scattering measurements of synthesized nanogels were performed on a BI-200SM goniometer (Brookhaven Instruments) with a Lexel 95E Ar ion laser ($\lambda = 514.5$ nm), at 25.0 ± 0.1 °C, in an aqueous solution of pH 10.0 (NaOH) containing 0.5 M NaClO₄. At this pH no complexation takes place, thus the one can selectively follow the permanent structural changes caused by irradiation. Data were analyzed according to Zimm algorithm to obtain z-average radius of gyration and apparent values of weight-average molecular weight of complexes. In the calculation of apparent M_w dn/dc value of $0.185 \text{ cm}^3 \text{ g}^{-1}$ was used, corresponding to pure PVP in water.

Results and discussion

Formation and properties of PVP-PAA complexes: One of the most important aims in investigations of hydrogen-bonding associates is evaluation of pH_{crit} as well as polymer stoichiometry in complex formation. As mentioned earlier, spontaneous formation of interpolymer complexes involving a polyacid can be observed only below a certain value of pH or in other words at a sufficient

protonation level of carboxyl groups of polyacid chains. Abe and Tsuchida showed that below and above $pH_{crit.}$ one has to distinguish two different states of equilibrium reaction:



Complex can be efficiently formed (equilibrium of the first reaction shifted to the right side) only below $pH_{crit.}$ value. Simultaneously, dissociation of carboxyl groups is strongly suppressed and accompanied by extraction of protons from solution to produce certain length of active sides on polyacid chain that are capable to form stable complex with proton acceptor. Above this pH value, equilibrium reaction dominates over spontaneous complexation process. Khutoryanskiy et al. treated discussed parameter as a criterion of the strength of interaction between polymers – the higher $pH_{crit.}$, the higher ability of a system to form intermolecular complexes.

In Fig. 36, changes in transmittance recorded at 500 nm are illustrated as a function of pH of $10^{-2} \text{ mol dm}^{-3}$ PAA solution mixed with $10^{-2} \text{ mol dm}^{-3}$ PVP solution at two COOH unit molar fractions: 0.5 (equimolar) and 0.8.

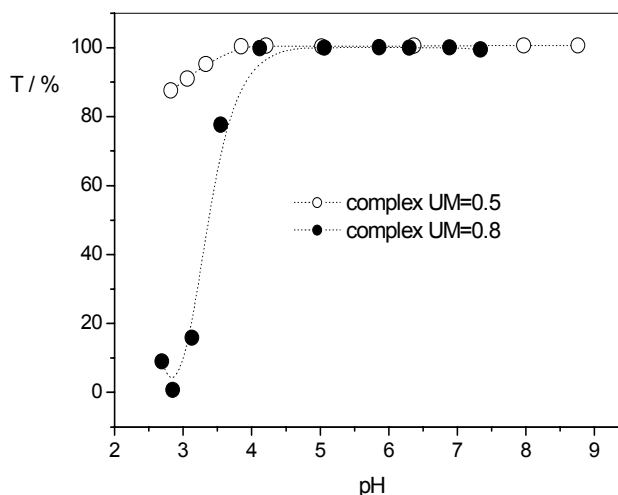


FIG. 36. Transmittance at 500 nm as a function of pH for aqueous solutions of PVP and PAA mixed at unit molar fractions of carboxylic groups equal 0.5 and 0.8. Concentrations of stock solutions are equal $10^{-2} \text{ mol dm}^{-3}$.

Value of critical pH is calculated as a crossing point of lines that come through experimental points before and after significant change of curves' slopes. In our case, stronger decrease in transmittance is observed for sample prepared at COOH molar fraction equal to 0.8 than for this mixed at equimolar stoichiometry. After applying the mentioned way of calculation, obtained pH critical values for UM = 0.8 and 0.5 are 4.03 and 3.68, respectively. In fact, both of them are somewhat lower than that obtained for PVP-PAA system investigated by Khutoryanskiy ($pH_{crit.} = 4.5$), however in that case polymers were of different molecular weight than in the current work. Moreover, one has to have in mind that in our study weight-average polymerization degree of poly(acrylic acid) is over 800 times lower than for polyvinylpyrrolidone. This disproportion in size is expected to have a significant influence on the complexation behavior of both polymers. One of the reasons for a difference in $pH_{crit.}$ may be a shift in the average pK_a towards higher values when going from oligomeric to polymeric PAA. For that reason, to obtain critical length of protonated carboxyl groups on shorter chain and in consequence to observe efficient complexation one has to significantly lower pH of the solution. It can be also concluded that a stronger complex was formed at stoichiometry that deviates from equimolar.

Results obtained by transmittance measurements are confirmed by preliminary viscosity data, where the maximum negative deviation from additivity law indicating strong complexation is observed at the AA molar fraction of *ca.* 0.8.

Measurements on the intensity of scattered light (data not shown) provide further proof of complex formation and aggregation. Similarly to viscometric results, also these data indicate that these effects are most pronounced for PAA molar fraction of *ca.* 0.8. Moreover, changes in intensity of light scattering with time indicate a dynamic behavior of association process at the timescale of minutes to hours. Because of that, the cross-linking experiments (see below) were performed 6 h after mixing the PAA and PVP solutions.

Radiation-induced intramolecular cross-linking of PVP-PAA interpolymers: Ionizing radiation in the form of γ -rays or electron beam interacts with dilute aqueous solutions of polymers in indirect manner causing water radiolysis. Unstable products of water radiolysis, mainly hydroxyl radicals and hydrogen atoms, react with macromolecules by hydrogen abstraction causing formation of polymer radicals. The latter undergo reactions typical for simple alkyl radicals, including recombination, disproportionation or fragmentation of chain. Detailed studies on radiation chemistry of hydrophilic polymers including PAA, PVP or PVAL have been published before.

Recombination reactions can proceed at various physical conditions leading to the formation of product in different size scale. By regulating concentration of polymer in solution and the dose rate one can change the average number of radicals present simultaneously on one chain, which is the main factor influencing mechanism of recombination (see preceding chapter).

When polymer coils overlap, *i.e.* above the critical hydrodynamic concentration c^* , irradiation at a low dose rate results in the average number of radicals per chain in the stationary state being lower than unity. At such conditions, intermolecular recombination is promoted which usually leads to the formation of macroscopic gels (“wall to wall”).

On the other hand, when dilute polymer solution is irradiated at a high dose rate (*e.g.* by pulses of fast electrons from an accelerator) the average number Z_{R0} of radicals generated simultaneously on one chain is higher than 1, favoring intramolecular recombination of radicals. This process does not change molecular weight of macromolecules, but presence of additional covalent bonds formed between polymer segments leads to a decrease in the radius of gyration of single chains.

Total concentration of mixed solution used in our experiments, $10^{-2} \text{ mol dm}^{-3}$, is convenient to follow interpolymers complex formation by means of viscometric or DLS methods and at the same time it is in appropriate range to produce nanogels by preparative pulse radiolysis via intramolecular (or, more precisely, intra-complex) radical recombination. In irradiated mixture of two different polymers that interact with each other by means of hydrogen bonds, intra- and intermolecular recombination of radicals can proceed simultaneously.

One of the techniques allowing to follow intramolecular cross-linking of PAA-PVP complex structures is viscometry. Changes in viscosity of the complex solutions as a function of absorbed dose are shown in Fig. 37. As mentioned earlier, complexation leads to more compact structure of interacting macromolecules. $\eta_{red.}$ of complex solutions prepared for different unit molar fractions is lower than for PVP. What is more, $\eta_{red.}$ for UM = 0.5 is higher than for UM = 0.7 due to stronger interactions between polymers at latter composition. This fact is in line with the already discussed deviation of interactions for investigated system from the 1:1 stoichiometry. Upon irradiation, viscosity decrease with increasing dose is observed in all cases. In parallel, static light scattering measurements were conducted to follow the changes in z-average radius of gyration during preparative pulse radiolysis process.

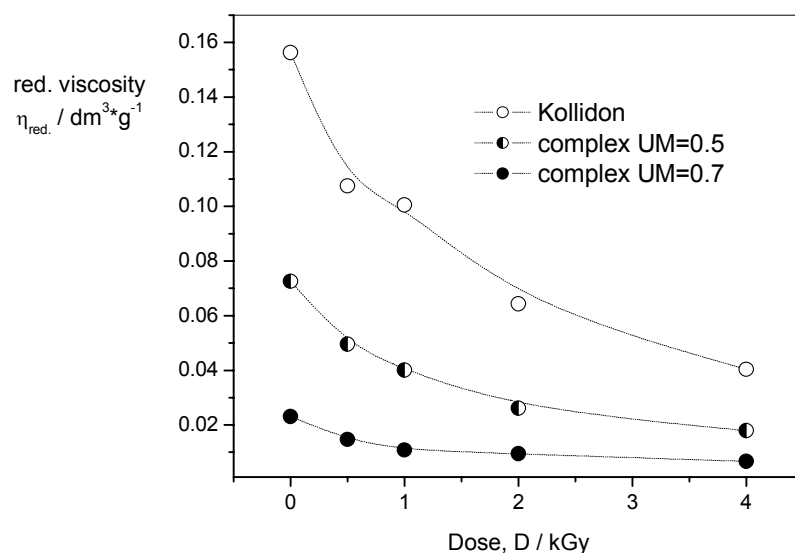


FIG. 37. Reduced viscosity as a function of total absorbed dose. Pulse irradiation of Ar-saturated aqueous solutions of PVP and PVP-PAA at different unit molar fractions of carboxylic groups. Concentrations of stock solutions: $10^{-2} \text{ mol dm}^{-3}$. Initial pH of PAA solution equal 3.4.

As shown in Fig. 38, R_g values, except for the lowest dose region, show a general tendency of decrease with increasing dose for all investigated systems, in agreement with viscosity results. A decrease in dimensions of a macromolecule is a typical feature of intramolecular cross-linking, no matter whether the latter reaction is induced chemically or by ionizing radiation. Formation of covalent bonds between the chain segments leads to the formation of more compact structures and limits the ability of segments to diffuse far away from the centre of macromolecule or particle.

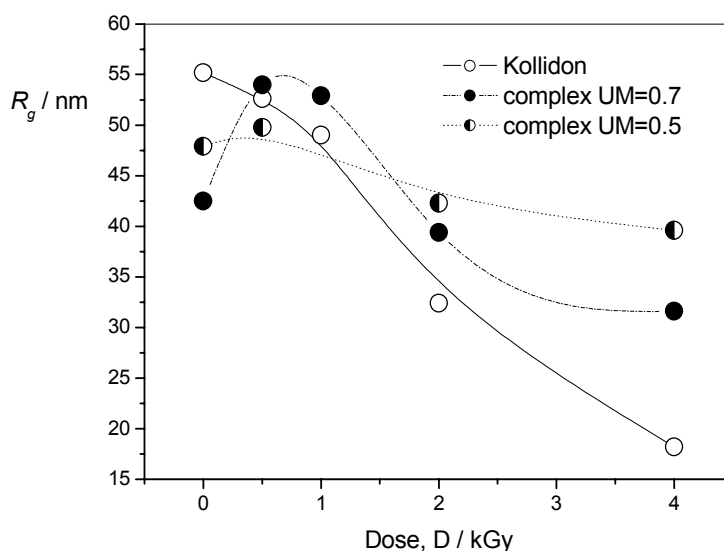


FIG. 38. Radius of gyration as a function of total absorbed dose. Pulse irradiation of Ar-saturated aqueous solutions of PVP and PVP-PAA at different unit molar fractions of carboxylic groups. Measurements conducted at pH = 10 after addition of 0.5 M NaClO₄ solution. Concentrations of stock solutions: $10^{-2} \text{ mol dm}^{-3}$.

The initial increase in R_g at low doses in the PAA-PVP systems can be explained by the fact that at the conditions of light scattering measurements ($\text{pH} = 10$) complexes, in contrast to cross-linked structures, do not show up. Thus the data points for zero dose reflect, in the most part, the R_g value of free PVP chains (free PAA chains are much smaller and only contribute to the slight decrease in the average R_g when compared with pure PVP sample at $D = 0$). Upon irradiation, PAA chains become permanently linked to PVP and at $\text{pH} 10$, due to dissociation of carboxylic groups and repulsive forces acting between the PVP-g-PAA chains, we observe initially an increase in the radius of gyration, before the internal cross-linking process starts to control the R_g changes at the later stages of irradiation.

Despite the irradiation conditions were set to promote intermolecular recombination of polymer radicals (understood here as radical recombination within a single complex “supramolecule”), intermolecular cross-linking (i.e. cross-linking between separate complex entities) could not be totally eliminated, as proved on the basis of changes in apparent weight-average molecular weight presented in Fig. 40. This is a typical effect accompanying the synthesis of nanogels of single polymers by preparative pulse radiolysis. One can estimate, however, that intermolecular cross-linking accounts only for up to a few percent of all recombination events. Average molecular weight during the synthesis may also be influenced by radical-induced degradation (chain breakage). This does not show up in the case of pure PVP at the studied concentration, but may be the cause of relatively weaker increase in molecular weight in the complexed systems. PAA-derived radicals have been shown to be much more prone to induce degradation than radicals of simple neutral polymers like PVP.

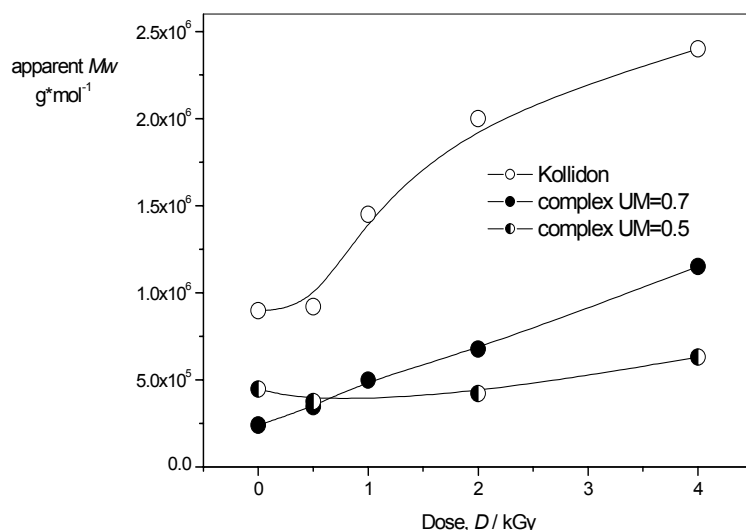


FIG. 39. Weight-average molecular weight as a function of total absorbed dose. Pulse irradiation of Ar-saturated aqueous solutions of PVP and PVP-PAA unit molar fractions of carboxylic groups. Measurements conducted at $\text{pH} = 10$ after addition of 0.5 M NaClO_4 solution. Concentrations of stock solutions: $10^{-2} \text{ mol dm}^{-3}$.

One should mention that the values plotted in Fig. 39 for PAA-PVP mixtures are apparent molecular weights and the fact that they appear to be lower than for pure PVP may be in part due to lower molecular weight of PAA (no complexes are present at the $\text{pH} = 10$ used for the light-scattering analysis) but also in part due to the difference in dn/dc values of the two components. In general, changes in R_g and M_w observed upon irradiation of PAA-PVP systems under our experimental conditions are similar to those typical for intramolecular cross-linking of pure, non-complexed polymers in solution, indicating that such complexes can be in fact internally cross-linked by pulsed ionizing radiation.

Conclusions

We have shown that polyvinylpyrrolidone forms complexes in dilute aqueous solution with oligomeric poly(acrylic acid). For this pair of polymers, critical pH value as well as stoichiometry of interaction equal 4.0 and ca. 0.8, respectively, were obtained by means of turbidimetry and viscometry. The complexes can be internally cross-linked by pulse-irradiation with fast electrons in deoxygenated aqueous solution. It seems that radiation technique may be a useful tool to obtain multi-component nanogels based on polymer complexes of hydrogen-bonding macromolecules.

3. STUDIES ON ABSORPTION- AND COMPLEX-FORMATION PROPERTIES INVOLVING STIMULI-SENSITIVE HYDROGEL-BASED POLYMERIC MATERIALS (IN CO-OPERATION WITH KAZAKHSTAN)

3.1. Complex formation of hydrogels based on MADQUAT and NIPAAm with potassium hexacyanoferrates (II, III). [10]

Water-soluble and cross-linked cationic polyelectrolytes, such as the MADQUAT-NIPAAm gels described above, have attracted considerable attention because of their ability to form polycomplexes with various large and small molecules. These complex formation reactions can be successfully utilized in purification of wastewater and enrichment technologies. Complexation of polymers with inorganic ions occurs due to two possible mechanisms—donor–acceptor bonding, and electrostatic interactions. The first kind of polycomplexes is formed between polymers having electron-donating groups and transition metal ions. The second kind of interactions is realized when the polyelectrolyte and inorganic ions are oppositely charged. In some cases, the binding of inorganic ions by polyelectrolytes occurs by two mechanisms simultaneously.

Some industrial processes involving application of iron–cyanide complexes have led to contamination of soil and ground water with wastes that are potentially hazardous, because they can be converted to extremely toxic free cyanides (CN^- , HCN) in the presence of UV-light. Different sorbents of inorganic and organic nature were suggested to remove these contaminations. The ability of hexacyanoferrates to form complexes with some polymers can be used for development of decontamination technologies.

Earlier, we synthesized water-soluble polymers and hydrogels by γ -radiation–induced homopolymerization of 2-(methacryloyloxy)ethyltrimethylammonium chloride (MADQUAT) in aqueous solutions and demonstrated the possibility of their complex formation with potassium hexacyanoferrates (II, III) through electrostatic interactions. It was shown that the composition of polycomplexes depends on the charge of low-molecular-weight coordination ion. The complexes were insoluble in water, stable to dilution, and destroyed at high ionic strength of solution.

In the present work, the temperature-responsive cationic polyelectrolytes were synthesized by copolymerization of MADQUAT with N-isopropylacrylamide (NIPAAm), and the water-soluble copolymers and hydrogels obtained were studied as complex-forming reagents with respect to potassium hexacyanoferrates (II, III).

3.2. Experimental

MADQUAT-NIPAAm polymers and gels were synthesized by radiation technique as described in the previous chapter. After synthesis, the hydrogels were washed with deionized water over a 2-week period. Viscometric measurements were performed using an Ubbelohde viscometer at 25.0 ± 0.1 °C.

Turbidimetric measurements were carried out with UV2401PC spectrophotometer (Shimadzu, Japan) at the wavelength $\lambda = 400$ nm. The temperature of solutions was regulated with the help of thermoelectrically temperature-controlled cell positioner CPS-240A (Shimadzu, Japan). The equilibrium swelling degree (DS) of hydrogels was determined gravimetrically and calculated using the following formula:

$$DS = (m - m_0)/m_0,$$

where m and m_0 are weights of gel in swollen and dry states, respectively.

The changes of linear dimensions of the hydrogels in the course of their complexation with inorganic salts were studied using a cathetometer V-630 (USSR) at 25 °C, and are expressed through the swelling ratio V/V_0 , where V is a volume of gel in swollen state and V_0 is a volume of gel swollen in monomer mixture immediately after synthesis.

The sorption capacity of the hydrogels with respect to the coordination compounds was studied spectrophotometrically using UV2401PC spectrophotometer (Shimadzu, Japan) at the wavelengths $\lambda = 450$ and $\lambda = 270$ nm for $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$, respectively. In sorption experiments the pieces of swollen gels were immersed into excessive amount of 0.001 M solutions of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$.

3.3. Results

Complex formation of linear MADQUAT–NIPAAm copolymers with potassium hexacyanoferrates (II, III) was studied in aqueous solutions by viscometric and turbidimetric methods. It can be seen from Fig. 40 that an addition of $K_3[Fe(CN)_6]$ solution to the solution of the copolymer is accompanied by drastic decrease in viscosity caused by compaction of macromolecules in the course of a complex formation reaction.

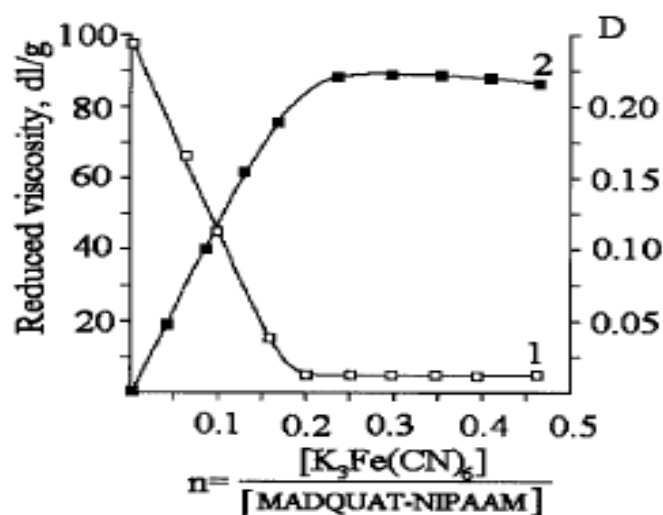


FIG. 40. Viscometric (1) and turbidimetric (2) titration curves of MADQUAT–NIPAAm (19:81 mol %) by aqueous solutions of $K_3[Fe(CN)_6]$. $C_{COPOLYMER} = C_{SALT} = 0.001$ (1), 0.01 M (2).

The same phenomenon is observed upon addition of $K_4[Fe(CN)_6]$ (data not shown). However, unlike the homopolymer PMADQUAT, the mixing of the copolymers with potassium hexacyanoferrates (II, III) in dilute solutions (0.001 M) is not accompanied by phase separation.

The appearance of the turbidity becomes seen in more concentrated solutions (0.01 M). Such difference between complexation behavior of PMADQUAT and the copolymers synthesized can be explained by the presence of NIPAAm units, which do not complex with $K_3[Fe(CN)_6]$ or $K_4[Fe(CN)_6]$ and provide higher solubility of polycomplexes in water. However, because the copolymers of MADQUAT and NIPAAm undergo separation upon heating, the polycomplexes can precipitate forming yellow sediments at higher temperatures.

The behavior of polycomplexes in solutions was studied in a wide temperature interval (Fig. 41). It can be seen from the figure that the polycomplexes aggregate and lose solubility at lower temperatures in comparison with the starting polymer. The aggregation of polycomplexes is due to the presence of NIPAAm in copolymer as well as additional hydrophobization caused by complexation. A decrease of turbidity observed in curves 2 and 3 at higher temperatures is caused by partial precipitation of aggregated polycomplex particles.

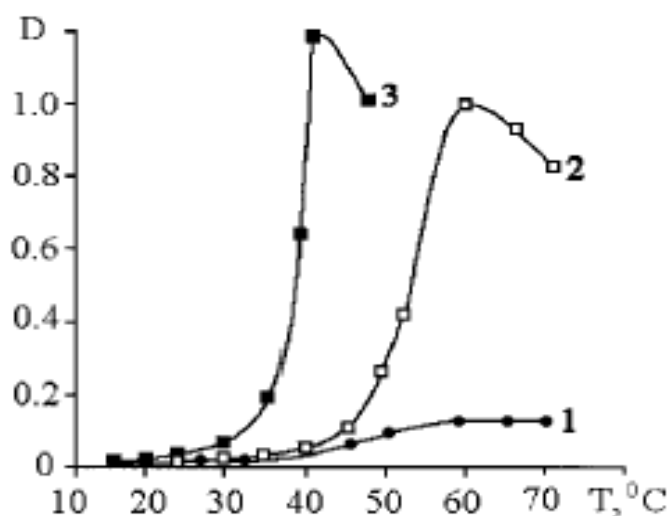


FIG. 41. Effect of temperature on the optical density of 0.01 M MADQUAT–NIPAAm (12:88 mol %) solution (1) and its polycomplexes with $K_3[Fe(CN)_6]$ (2) and $K_4[Fe(CN)_6]$ (3).

The hydrogels MADQUAT–NIPAAm were synthesized and characterized in our previous work (see above). Here we study the complexation of these hydrogels with potassium hexacyanoferrates (II, III). It can be seen that the volume ratio V/V_0 of the starting hydrogels depends strongly on the composition of copolymers [Fig. 42 (a) and (b)]. An increase in MADQUAT content increases the swelling ability of the samples due to ionic contribution to the total swelling pressure. The gel samples immersed in aqueous solutions of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ undergo contraction and acquire green-yellow color, which is caused by complexation. The amplitude of contraction depends on MADQUAT content in copolymers, and is maximal for hydrogels with the highest MADQUAT content.

The dependence of equilibrium swelling degree of hydrogels on the relative concentration of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ in solution is plotted in Fig. 43 (a) and (b). The contraction curves of the samples also depend on the NIPAAm content in the copolymers. The higher the NIPAAm content, the higher the final DS of the hydrogels saturated by potassium hexacyanoferrates (II, III) because NIPAAm does not participate in complexation and remains relatively hydrophilic after the process. In addition, an increase in NIPAAm content in the hydrogels shifts the saturation point to the lower relative concentration of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$. The limiting saturation points, that is the concentration ratio starting from which the curve comes to a plateau, were also observed earlier for PMADQUAT hydrogels. In the case of PMADQUAT hydrogels, they were equal to 0.3 and 0.25 for $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$, respectively.

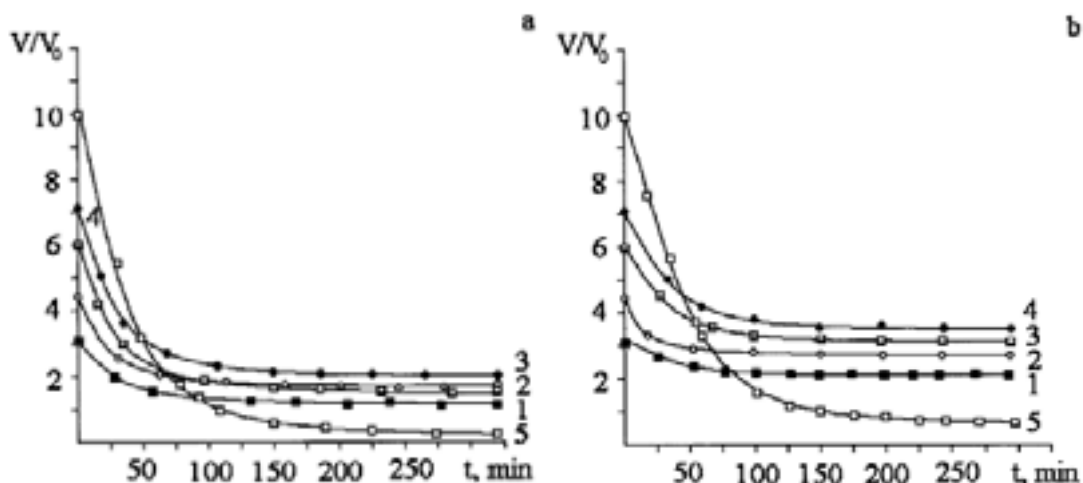


FIG. 42. Kinetics of contraction of MADQUAT-NIPAAm hydrogels in aqueous solutions of $K_3[Fe(CN)_6]$ (a) and $K_4[Fe(CN)_6]$ (b). $[MADQUAT]:[NIPAAm] = 7:93$ (1), $12:88$ (2), $19:81$ (3), $26:74$ (4), $35:65$ mol % (5). $CSALT = 0.001$ M.

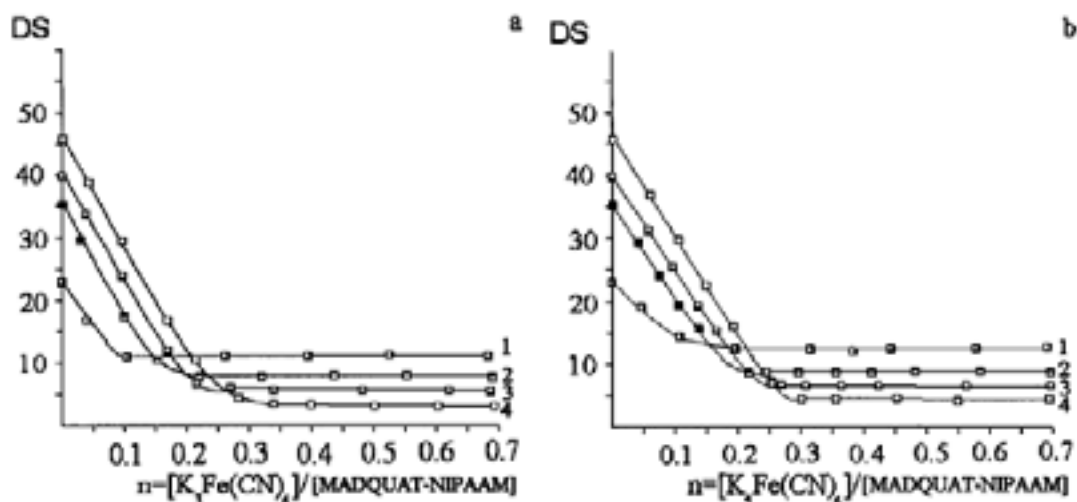


FIG. 43. Swelling of MADQUAT-NIPAAm hydrogels in aqueous solutions of $K_3[Fe(CN)_6]$ (a) and $K_4[Fe(CN)_6]$ (b). $[MADQUAT]:[NIPAAm]$, mol % $7:93$ (1); $12:88$ (2); $26:74$ (3); $35:65$ mol % (4).

The sorption ability of copolymeric hydrogels was evaluated by a spectrophotometric method, and the data are summarized in Table 4. We listed the data on the weight of absorbed salt per 1 g of dry gels, and also indicated the results in mol of the salt per mol of MADQUAT unit in the network in parentheses. The hydrogels bind more amount of $K_3[Fe(CN)_6]$ than $K_4[Fe(CN)_6]$ because every coordination ion $[Fe(CN)_6]^{3-}$ interacts with three units of MADQUAT, but the ion $[Fe(CN)_6]^{4-}$ requires four MADQUAT units for binding. It can be seen that the higher MADQUAT content in copolymers leads to a greater sorption ability. Also, the amount of the salt absorbed by hydrogel containing 1 mol of MADQUAT units is not constant and depends on the composition of copolymers.

TABLE IV. UPTAKE OF INORGANIC COORDINATION COMPOUNDS BY MADQUAT-NIPAAm HYDROGELS

[MADQUAT]:[NIPAAm] Copolymer Composition, mol %	Uptake of $K_3[Fe(CN)_6]$, g/g (mol/mol)	Uptake of $K_4[Fe(CN)_6]$, g/g (mol/mol)
7:93	0.088 (0.055)	0.05 (0.009)
11:89	0.15 (0.095)	0.105 (0.059)
19:81	0.21 (0.128)	0.114 (0.062)
24:76	0.24 (0.159)	0.154 (0.091)
35:65	0.27 (0.172)	0.18 (0.102)

Conclusions

Temperature-responsive complex forming linear polyelectrolytes of high molecular weight and their hydrogels were synthesized by γ -irradiation copolymerization of MADQUAT and NIPAAm. It was shown that the linear copolymers are able to form polycomplexes with potassium hexacyanoferrates (II, III), which solubility greatly depends on concentration of the reagents and temperature.

Using the temperature-sensitivity of the copolymers it is possible to regulate the solubility of polycomplexes. The hydrogels of copolymers absorb potassium hexacyanoferrates (II, III) and undergo contraction. The sorption ability of hydrogels depends on MADQUAT content in copolymers, and is higher with respect to $K_3[Fe(CN)_6]$ than to $K_4[Fe(CN)_6]$.

3.4. Polyelectrolyte complexes of MADQUAT-NIPAAm hydrogels with poly(acrylic acid) [13]

Specific interactions between unlike macromolecules result in formation of interpolymer complexes, which represent new compounds with properties completely different from initial components (IPC). Depending the nature of interaction the complexes of different categories can be formed. There are polyelectrolyte complexes, hydrogen-bonded complexes, stereocomplexes and charge-transfer complexes. The first and second group of polycomplexes are mostly studied because there are a lot of polymers, which form these IPC. A variety of possible applications including biomedical field and separation technologies attract considerable attention of different researchers to these kinds of interaction.

In the present work we have studied complexation between linear copolymers and hydrogels based on copolymers of 2-[(methacryloyloxy)ethyl]-trimethylammonium chloride with N-isopropylacrylamide (MADQUAT:NIPAAm) and poly(acrylic acid).

Experimental

MADQUAT-NIPAAm polymers and gels were synthesized by radiation technique and characterized as described in previous chapters. PAA with weight-average molecular weights 2, 250, 450, 750 kDa was purchased from Aldrich and used without further purification.

Results and discussion

An interesting feature of the copolymers of MADQUAT and NIPAAm is the possibility to participate in different interactions. From the one hand the units of MADQUAT bearing positively charged quaternized nitrogen atoms could form polyelectrolyte complexes with anionic polymers.

From the other hand the units of NIPAAm can participate in hydrogen-bonding with unionized carboxylic groups of poly(carboxylic acids) and there are several papers published on complexation between homopolymer PNIPAAm and poly(acrylic acid) as well as poly(methacrylic acid). However, the hydrogen bonding is very sensitive to environmental pH because unionized COOH-groups exist in acidic or in weakly acidic media only. In this connection if the complexation takes place in the media with higher pH the NIPAAm units will not form hydrogen bonds and can be considered as a structure defects disturbing complexation. In acidic media the possible hydrogen bonding will additionally stabilize the structure of polycomplexes but the electrostatic attraction will be weakened because of suppression of carboxylic groups ionization.

The mixing of aqueous solutions of PAA and MADQUAT-NIPAAm is accompanied by appearance of turbidity, which is a result of formation of hydrophobic particles of polycomplexes and their further aggregation. This process can be followed by turbidimetric titration and measurements of viscosity. The changes of turbidity and viscosity of mixed solutions are plotted in Fig. 44 for copolymers with different content of MADQUAT. It can be seen from the figure that the position of maximum on turbidimetric curve coincides well with the position of minimum on viscometric curve and indicate the composition of PEC. This composition is significantly affected by the content of MADQUAT in copolymer. Indeed, the higher the MADQUAT content in copolymer the lower amount of copolymer is necessary to add to PAA solution in order to reach saturation. The copolymers enriched by NIPAAm units form complexes, which composition is more close to stoichiometric 1:1.

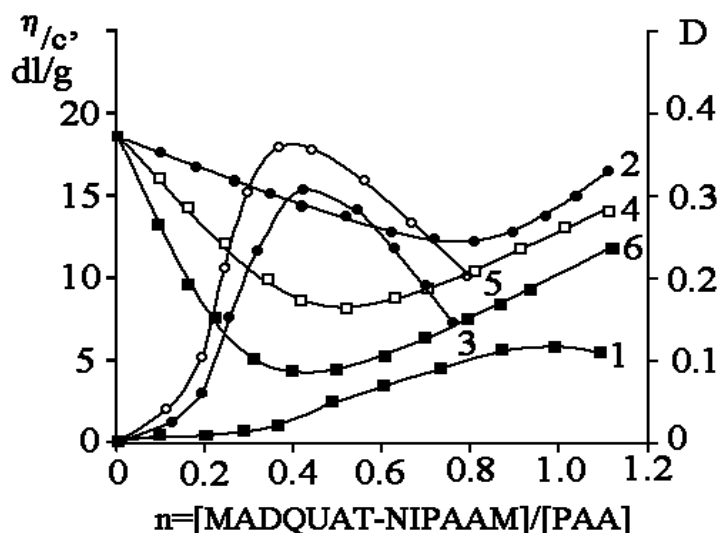


FIG. 44. Viscometric (1, 3, 5) and turbidimetric (2, 4, 6) titration curves of PAA by MADQUAT-NIPAAm. $C_{POLYMERS} = 0.01$ M; $M_w(PAA) = 250$ kDa; $[MADQUAT]:[NIPAAm] = 12:88$ (1, 2); 26:74 (3, 4); 35:65 mol.% (5, 6).

The interaction between weak polyacid and strong polybase is always accompanied by change in pH. Therefore, the potentiometric titration is a helpful tool to study complexation. An addition of MADQUAT-NIPAAm copolymers to PAA solutions leads to significant decrease in pH until the certain stoichiometry is achieved (Fig. 45) and then pH stays practically constant or increases slightly. The potentiometric results are in good agreement with turbidimetric and viscometric data and confirm strong effect of copolymer composition on complexation.

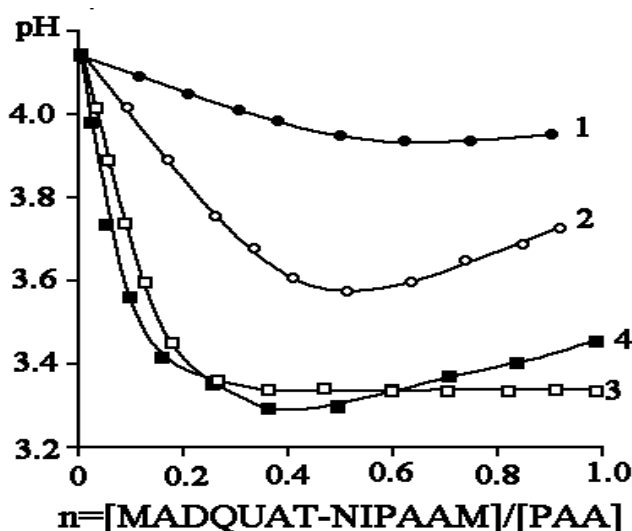


FIG. 45. Potentiometric titration curves of PAA by MADQUAT-NIPAAm. $C_{\text{POLYMERS}} = 0.001 \text{ M}$; $M_w(\text{PAA}) = 250 \text{ kDa}$; $[\text{MADQUAT}]:[\text{NIPAAm}] = 12:88$ (1); $26:74$ (2); $35:65 \text{ mol.}\%$ (3).

It is well known that the molecular weight of polymers affects the complexation processes significantly. In this connection we have studied the complexation using PAA with different molecular weights. Fig. 46 (a, b) shows turbidimetric data on complexation for PAA with molecular weight 2 and 450 kDa. It can be seen that even PAA with low molecular weight forms polycomplexes but the absolute values of turbidity are different from complexes formed by higher molecular weight polyacid. It is likely that this is related to different colloidal stability of polycomplexes formed by PAA with different molecular weight.

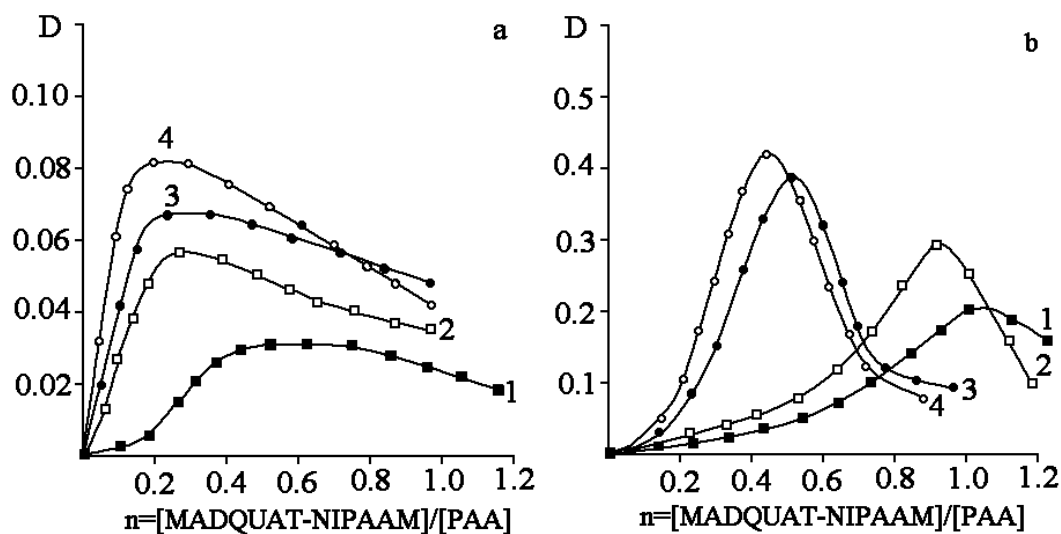


FIG. 46. Turbidimetric titration curves of PAA by MADQUAT-NIPAAm. $C_{\text{POLYMERS}} = 0.001 \text{ M}$; $M_w(\text{PAA}) = 2 \text{ Da}$ (a), 450 kDa (b); $[\text{MADQUAT}]:[\text{NIPAAm}] = 12:88$ (1); $26:74$ (2); $35:65 \text{ mol.}\%$ (3).

Poly(acrylic acid) is a weak polyelectrolyte and its ionization strongly depends on pH, which might affect its complexation ability. Fig. 47 (a, b) shows the turbidimetric results obtained for solutions with certain pH (1.86 and 6.86), which was maintained using buffer solutions. The formation of polycomplexes is observed in both cases.

However in acidic medium (pH 1.86) an increase in MADQUAT content in copolymers leads to higher values of turbidity. For copolymer containing 12 mol.% MADQUAT the increase of turbidity is not very significant and after achievement of stoichiometric ratio the turbidity is practically not changed, which indicates sedimental stability of polycomplexes. It is likely that in these conditions the complex is mainly stabilized by hydrogen bonds between NIPAAm units and unionized carboxylic groups. The MADQUAT units in this case are remained free and maintain the sedimental stability of the aggregates. The situation is completely changes upon passing to pH 6.86. In these conditions the higher the content of MADQUAT the lower the maximal turbidity because relatively hydrophilic NIPAAm units, which do not participate in interaction, but disturb the aggregation process.

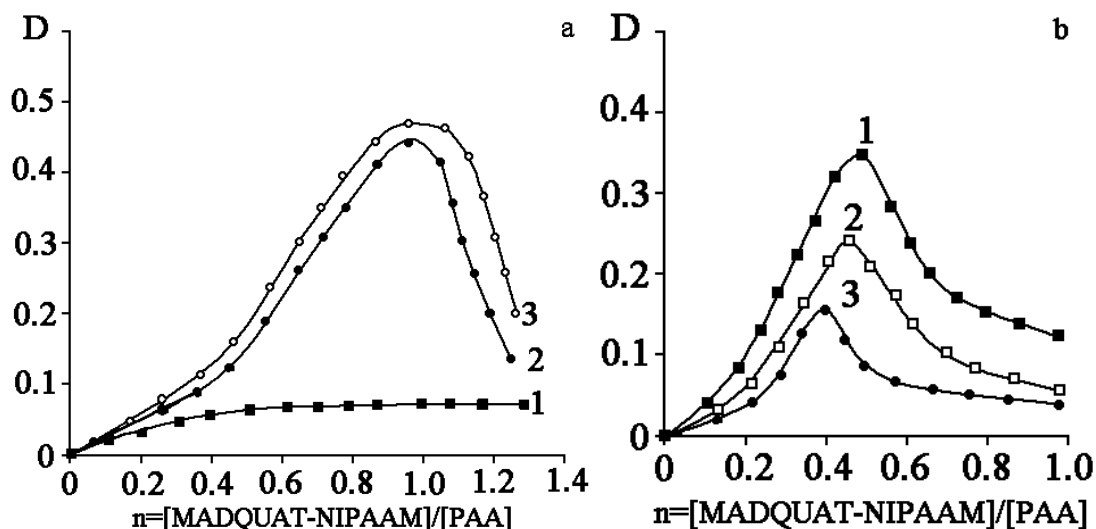


FIG. 47. Turbidimetric titration curves of PAA by MADQUAT-NIPAAm. $C_{POLYMERS} = 0.001$ M; $M_w(PAA) = 250$ kDa; pH = 1.86 (a), 6.86 (b); $[MADQUAT]:[NIPAAm] = 12:88$ (1); 26:74 (2); 35:65 mol.% (3).

Weakly cross-linked macromolecules of hydrophilic polymers loss the ability to dissolve in water but are able to swell and form soft and elastic materials or so-called hydrogels. Hydrogels have very high sorption ability with respect to small molecules and macromolecules. The interactions between oppositely charged polyelectrolyte hydrogels and linear macromolecules were thoroughly studied by Kabanov, Zezin and co-workers. They found that the reactions proceed as a frontal process and follow by strong (three orders of magnitude) contraction of the gel sample. It was shown that the kinetics of linear polyions absorption by polyelectrolyte network strongly depends on the nature of interacting polymers, temperature, presence of inorganic salts and pH of solution. The “relay-race” mechanism of linear macromolecules transport through the network has been established.

In our earlier works we have studied different interacting systems including oppositely charged weakly cross-linked weak and strong polyelectrolytes. It was found that in certain conditions the first stage of the interaction between linear macromolecules and gel is characterized by slight increase in the network volume. Then in the following stage the network undergo contraction and losses its transparency.

In the present work we have studied the interaction between hydrogels of MADQUAT-NIPAAm (26:74 mol.%) and linear PAA with different molecular weights (2, 250, 450, 750 kDa). Fig. 48 shows the dependence of the relative volume of the gel samples immersed in aqueous solutions of PAA on time. It can be seen that the hydrogel sample immersed into solution of PAA with lowest molecular weight (2 kDa) undergo contraction with the highest rate. The sample reaches the equilibrium for 40-60 mins. The gel samples immersed into PAA solutions with 250 and 450 kDa also reduce their volume gradually but their final equilibrium swelling is much higher.

The PAA with the highest molecular weight 750 kDa also causes the volume changes of the gel sample. However in the first stage of interaction (first ten minutes) the gel sample increases its swelling degree slightly. Then the gel begins to contract reaching the equilibrium during 60-70 mins. In summary, the molecular weight of linear PAA strongly affects the interaction. The higher the molecular weight of PAA the lower the amplitude of hydrogel contraction as a result of interpolyelectrolyte interaction. This trend can be explained by decrease in penetration ability of linear macromolecules through the network. A slight increase in the first 10 mins of interaction observed for PAA with 750 kDa can be explained by temporary increase in the hydrogel surface charge density caused by local contraction of the surface. After the macromolecules penetrate deeper they neutralize the inner part of the gel charge, forming additional cross-physical links and the sample undergo contraction. Similar trend was observed in our earlier work for hydrogel of homopolymer PMADQUAT immersed into solution of PAA with the same molecular weight (750 kDa).

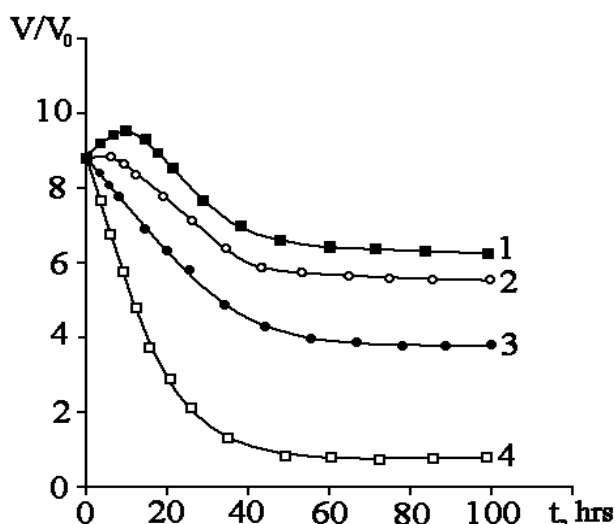


FIG. 48. Swelling behavior of MADQUAT-NIPAAm hydrogels in PAA aqueous solutions. $C_{PAA}=0.01M$; $[MADQUAT]:[NIPAAm]=26:74$ mol.%; $M_w=750$ (1); 450 (2); 250 (3) 2 kDa (4).

The effect of polymer concentration on the kinetics of hydrogel contraction was studied for PAA with the lowest molecular weight 2 kDa (Fig. 49). It can be seen that if the concentration of PAA is very low (0.001 M) the contraction of the gel sample is slower. However there is practically no difference in contraction kinetics for 0.01 M and 0.1 M solutions of PAA. It is likely that above 0.01 M concentration there is saturation, *i.e.* there is more than enough macromolecules of PAA in solution, which can interact with the sample.

The effect of environmental pH at constant ionic strength (μ) on the gel contraction kinetics as a result of interpolyelectrolyte reaction is shown in Fig. 50. An increase in solution pH accelerates the contraction process. Such a trend can be explained by dissociation of carboxylic groups of PAA. At low pH value (pH 2.8) the dissociation of carboxylic groups of PAA is completely suppressed, hence the linear polymer interacts with NIPAAm units of hydrogel mainly through hydrogen bonding. In these conditions the MADQUAT units are remained charged, which leads to a relatively higher swelling degree of the sample. At higher pH (pH 6.7 and 8.4) the ionization of carboxylic groups is very high and they are able to interact with MADQUAT units of hydrogel and reduce the gel volume very efficiently.

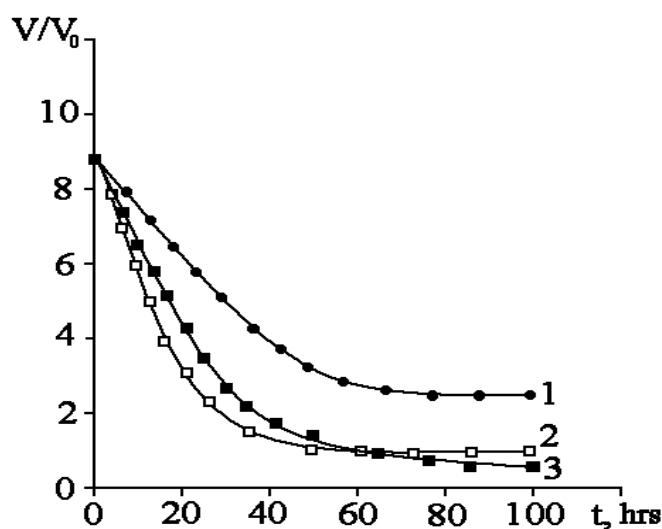


FIG. 49. Swelling behavior of MADQUAT-NIPAAm hydrogels in PAA aqueous solutions. $M_w(\text{PAA}) = 2 \text{ kDa}$; $[\text{MADQUAT}]:[\text{NIPAAm}] = 26:74 \text{ mol.}\%$; $C_{\text{PAA}}=0.001$ (1); 0.01 (2); 0.1 M (3).

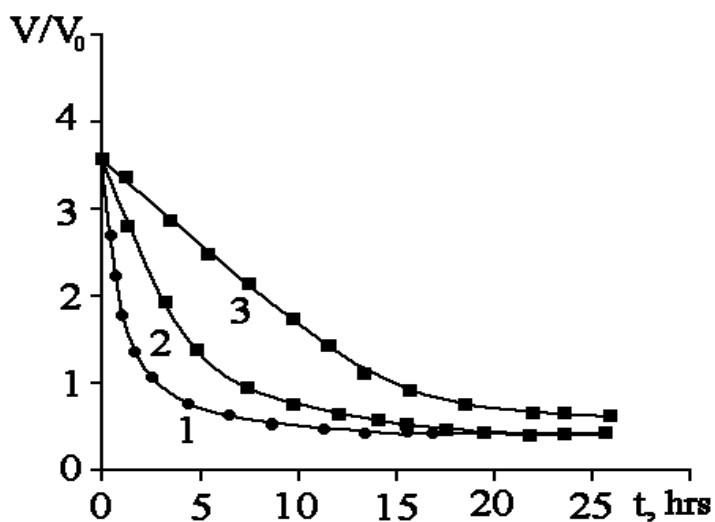


FIG. 50. Swelling behavior of MADQUAT-NIPAAm hydrogels in PAA aqueous solutions. $M_w(\text{PAA})=2 \text{ kDa}$; $[\text{MADQUAT}]:[\text{NIPAAm}] = 26:74 \text{ mol.}\%$; $C_{\text{PAA}}=0.01 \text{ M}$; $\mu=0.01$; $\text{pH} = 8.4$ (1); 6.7 (2); 2.8 (3)

Conclusion

Water-soluble copolymers as well as hydrogels based on MADQUAT and NIPAAm are able to interact with linear PAA and form polycomplexes. The nature of interaction is different at different pH. In acidic media the polycomplexes are stabilized by hydrogen bonds but at higher pH the electrostatic forces play the major role. The molecular weight of PAA as well as the composition of copolymers affects the aggregation stability of polycomplexes and their composition.

4. FINAL REMARKS

The activity of our research group within the framework of the Co-ordinated Research Programme “Radiation Synthesis of Stimuli-responsive Membranes, Adsorbents and Hydrogels for Separation Purposes” was focused on basic and practical aspects of the radiation-assisted formation and properties of stimuli-responsive hydrogels

The main achievements of our group within the programme were:

- Contribution to understanding the radiation-induced processes in a thermo-sensitive polymer PVME (alternative to PNIPAAm) and the radiation formation of thermo-sensitive PVME hydrogels
- Elaboration of new products: two types of composite thermo-sensitive membranes based on PVME
- Elaboration of a new, monomer-free, radiation-based method for synthesis of microgels and nanogels of stimuli-sensitive polymers (including the option using interpolymer complexes as substrates)
- Modification of this technique allowing to synthesize nanogels of independently chosen molecular weight and dimensions (tailored internal density)
- Elaboration of new, stimuli-sensitive hydrogels based on p(MADQUAT-co-NIPAAm) and detailed characterization of their properties
- Contribution to understanding the polymer-polymer interactions in aqueous solutions (may be useful for example for binding biological macromolecules by polymer gels)
- Ideas of two new products based on the knowledge gained during the realization of the project (synovial fluid supplement and fat-binding diet additive)

Both basic and application-oriented research on stimuli-responsive hydrogels for separation purposes described in this report were understood as steps towards future application of radiation technologies in modern self-regulating /controllable /reversible separation/ binding/ filtration processes, especially in the biomedical field.

A considerable part of the presented work results from a close co-operation within the CRP with the research group of Kazakhstan. Moreover, many ideas that were helpful in the realization of our research tasks originate from the very stimulating and open discussions between all the participating partners at the CRP Meetings.

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RADIATION SYNTHESIS OF STIMULI RESPONSIVE HYDROGELS AND THEIR USE FOR THE SEPARATION AND ENRICHMENT OF WATER POLLUTANTS

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Abstract

In the framework of the CRP, the radiation synthesis, characterization of swelling behavior and network structure of poly (n,n-dimethylaminoethyl methacrylate)(p(dmaema)), and poly (n,n-dimethyl aminoethyl methacrylate-co-n-vinyl 2-pyrrolidone)(p(dmaema-co-vp)) hydrogels have been studied. The influence of irradiation dose in cross-linking agent was investigated. The effect of pH and temperature on the swelling behavior of hydrogels has also been examined. Hydrogels showed typical pH and temperature responses, such as low pH and temperature swelling and high pH and temperature deswelling. Polymer-solvent interaction parameter (χ) and enthalpy and entropy changes appearing in the χ parameter for the p(dmaema-co-vp)-water system were determined by using flory-rehner theory of swelling equilibrium. The negative values for Δh and Δs indicate that prepared pure p(dmaema) and p(dmaema-co-vp) hydrogels have lower critical solution temperature and flory-rehner theory of swelling equilibrium provides a satisfactory agreement to the experimental swelling data of the hydrogels. Removal of nitrite ions from aqueous solutions was investigated by using protonated P(DMAEMA) hydrogels. We have shown that poly-cationic and pendant secondary amine group containing P(DMAEMA) hydrogels is very efficient and highly selective for the removal of nitrite ions from aqueous solutions at even in very high concentrations. Adsorption studies have shown that pH of the nitrite solution influence on the nitrite ion uptake capacity of P(DMAEMA) hydrogels. The adsorption capacity of hydrogels had been increased upto 3100 mg NO₂-1 /g dry gel, by changing pH of the solution. As a result of FTIR studies it has been found that nitrite binding onto hydrogels occurs through formation a N-nitroso groups and these hydrogels can be regenerate by concentrated acid solutions and can be reuse for removing of nitrite ions from aqueous solutions.

1. OBJECTIVE OF THE RESEARCH

The objectives of proposed research contract were first to obtain environmental sensitive hydrogels by radiation induced polymerization and cross-link of some hydrophilic monomers in aqueous media or solute state. The monomers to be selected for this purpose are the controlling factors the behavior of hydrogels. By preparing hydrogels from a mixture of monomers or polymer it will be possible to synthesis copolymeric building blocks. Incorporation of cationic or anionic moieties in the gels will import different levels of pH and temperature sensitivity of these gels. Homopolymer of N, N, dimethylamino ethyl methacrylate and copolymer of this monomers with N-vinyl 2-pyrrolidone monomer are planned to be prepared for the synthesis of such hydrogels in this project.

The second objective was to investigate the effect of external stimuli such as pH, temperature, ionic strength and electric signal on the their swelling-deswelling behaviour and identification of environmental sensitive conditions of hydrogels. Investigation of adsorption of heavy metal ions and noble metal ions such as Cu, Zn, Co, Pb, Ni, Cd, Fe, Se, Tl, Hg, Au, Pd and anions such as NO₂⁻, NO₃⁻, PO₄⁻² onto these hydrogel systems and cleaning of polluted waters and enrichment of these metals and anions was another objective.

Heavy metals are quite toxic and drinking water standards for these metals allow only a low level. During the last decades it has been witnessed a substantial growth in interest and uses of cheating sorbents in the field of waste water treatment and pollution control. Due to this trend, there has been an interest in the use of radiation induced polymerization, copolymerization and grafting of functional monomers for cheating sorbent material. The research project conducted in the frame of the CRP was focus on the preparation of new and environmentally sensitive poly-electrolyte hydrogels and modification for the adsorption and enrichment of heavy metal ions and anions simultaneously from water and waste water.

2. INTRODUCTION

In recent years, the increase of heavy metal ions and anions pollution in drinkable water and waste water is one of the biggest problem of all of the world. Heavy metals are quite toxic and drinking water standards for these metals allow only a low level. During the last decades it have been witnessed a substantial growth in interest and uses of cheating sorbents in the field of waste water treatment and pollution control. Environmental problems have generated needs for new materials that can be used as adsorption and separation and enrichment of different heavy metal ions and anions simultaneously. Due to this trend, recently there has been substantial grown in interest in the use of radiation induced polymerization copolymerization and grafting of functional monomers for cheating sorbent material. In this project preparation of new and environmentally sensitive poly-electrolyte hydrogels and modification for the adsorption and enrichment of heavy metal ions and anions simultaneously from water and west water are planned.

During the last decade pH, temperature and signal sensitive gels have been suggested in a variety of novel applications including drug delivery systems, biosensors and separation processes such as separation membranes separation of heavy metal ions, uranyl ions and dyes. Recently Tamada synthesized alkaline and asitic polymer networks containing sulpha and tertiary amine pendants groups by radiation induced graft polymerization for the recovering of odors and heavy metal ions from sea water[1]. They investigated the effect of external stimuli pH on the adsorption capacity of hydrogels and they observed 130 g Pb adsorption per 1 kg adsorbent at pH 4 and proposed that these hydrogels applicable to the recovering of Pb from acidic waste water from catalyst industry.

Hegazy and his research group show that modified poly(ethylene-g-styrene/maleic anhydride) membranes are also suitable polymeric systems for the recovering of various kind of metal ions such as Cu, Cd, Fe, Ni, Co, and Pb from waste water[2]. In the last decade the research studies of Karadağ et al[3-5]. and Saraydın et. al [6-7] show that maleic and itaconic acid containing hyrogels are also applicable environmental sensitive hydrogels for the adsorption of uranyl and heavy metal ions.

Not only cations also anions like as nitrite represents important wide spread contaminants of aqueous environment and serve as significant indicators of natural water quality. The increasing level of nitrite in waters results mainly from agricultural application of fertilisers as well as from many industrial processes[8]. Determination and speciation of nitrite and nitrate in waters and foodstuffs has increasing attention in recent years because of their potential harmful impact on human health. NO₂⁻ is highly toxic to certain species of fish. NO₂⁻ enters the bloodstream through the gill by mechanism that normally transport chloride [9]. After entering the bloodstream NO₂⁻ oxidized the iron in the hemoglobin molecule from ferrous state (Fe²⁺) to the ferric state (Fe³⁺).

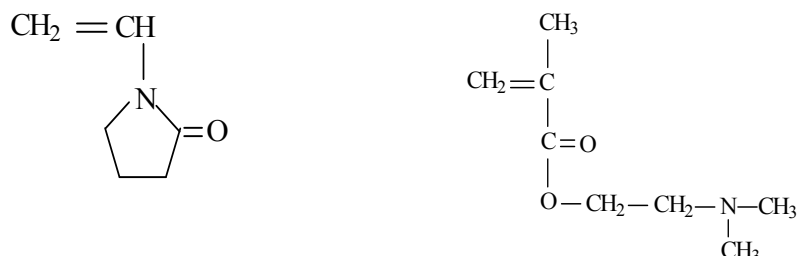
The resultant product, called methemoglobin, is incapable of reversibly binding with oxygen, so exposure to NO₂⁻ causes respiratory distress because of the loss in blood oxygen-carrying capacity. It has been also reported that nitrite can react in vivo with secondary or tertiary amines to form N-nitroso compounds, some of which are known to be carcinogenic, teratogenic and mutagenic[10]. Kioussis et al. were developed poly(allyl amine hydrochloride) polymer hydrogels, that efficient remove nitrate, nitrite and orthophosphate nutrient anions from aquaculture wastewater [11]. Biçak and Şenkal were prepared epoxy-amine resins contains secondary amino groups for removal of nitrite ions from aqueous solutions[12]. They found that, nitrile loading capacity of the resin was 11.7 mmol/g of HCl-free sample.

Not only these research groups indicated above but also many research groups interests to the preparation of new and functional external stimuli polymers for the purification and separation purposes of different kind of materials from aqueous solutions, such as Japan, China, USA, Egypt and Turkey.

3. MATERIALS AND METHODS

3.1. Chemicals

The two monomers used in this study, namely N,N-dimethylaminoethyl methacrylate (DMAEMA), N-vinyl 2-pyrrolidone were obtained from Aldrich. Ethylene glycol dimethacrylate (EGDMA) use as cross-linking agent obtained from BDH. The chemical structures of used monomers is as follows:



3.2. Radiation synthesis of P(DMAEMA) and P(DMAEMA/VP) hydrogels

The N,N-dimethylaminoethyl methacrylate is selected as a first monomer and N-vinyl-2 pyrrolidone co-monomer at the beginning of this project and for the preparation of homo and copolymeric hydrogels firstly N,N-dimethylaminoethyl methacrylate solutions have been irradiated with γ -rays at different doses.

The P(DMAEMA) hydrogels that were synthesized had poor mechanical stability, low % gelation even high doses such as 70 kGy. Therefore, both in order to reach good mechanical stability, and hydrophilicity N-vinyl 2 pyrrolidone(VP) has been added in the initial solutions and DMAEMA /VP solutions at various compositions have been prepared. After that ethylene glycol dimethacrylate (EGDMA) has been added to form more stable hydrogels and to provide more cross-linking and percentage gelation at even low doses. Finally, water was also added to the ternary mixture of DMAEMA/VP/EGDMA to prevent the formation of heterogeneous polymerization. Then DMAEMA/VP/EGDMA/water solutions that contain 0, 10, 30 % VP and 0.1, 0.25, 0.5, 1.0, and 2.0 % EGDMA were irradiated upto 14 kGy with gamma rays at 0.160 kGy/h dose rate. A series of hydrogel system were synthesised by using these initial mixtures according to these values. At the end of the preliminary irradiations approximately 95 % gelation was observed for all mixtures at 4 kGy irradiation. On the other hand slight decrease in the % gelation was observed may be due to chain scission of system above 4 kGy. For this reason, monomer solutions were irradiated at low doses , 0-2.5 kGy, in order to obtain complete dose-conversion curves.

The hydrogel systems prepared from 100 % DMAEMA, 90 % DMAEMA+10 %VP, 70% DMAEMA + 30 % VP and 2.0 % EGDMA added initial mixtures rapidly loss mechanical stability and disintegrated into small parts during swelling. So these hydrogel systems could not be investigated in this study. As a result of all these preliminary studies, % gelation, monomer conversation experiments were followed with 10 % DMAEMA, 90%DMAEMA+10 % VP, and 70 % DMAEMA+30 % VP and and 0.1, 0.25, 0.5, and 1.0 EGDMA added initial mixtures. All prepared initial mixtures and abbrevitions used for these mixtures are given in Table I

These solutions were placed in PVC straws of 3 mm diameter and irradiated at different doses in air at ambient temperature in a 60Co Gammacell 220 type γ irradiator. Hydrogels obtained in long cylindrical shapes were cut into pieces of 2-3 mm long. Hydrogels were dried in vacuum oven at 315 K to constant weight and subjected to soxhlet extraction with water as solvent. Uncrosslinked polymer and/or residual monomer were removed with this extraction from the gel structure.

Extracted gels were dried again in vacuum oven at 315 K to constant weight. Percentage gelation i.e. percentage conversion of monomers into insoluble network was based on the total weight of the DMAEMA, VP and EGDMA in the initial mixture. The amount of uncrosslinked DMAEMA was determined by titration of extract against HCl (0.1M or 0.02M) to phenolphthalein and point.

TABLE I. ALL PREPARED INITIAL MIXTURES AND ABBREVIATIONS USED FOR THESE MIXTURES

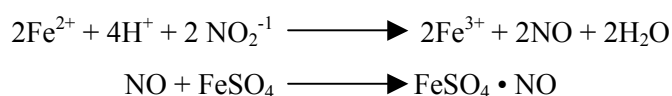
Gel Name		DMAEMA mL; (%)	VP mL; (%)	EGDMA mL; (%)
100 DMAEA	0.1 EGDMA	10; (100)	0; (0)	0.01; (0.1)
	0.25 EGDMA	10; (100)	0; (0)	0.025; (0.25)
	0.5 EGDMA	10; (100)	0; (0)	0.05; (0.5)
	1.0 EGDMA	10; (100)	0; (0)	0.1; (1.0)
	2.0 EGDMA	10; (100)	0; (0)	0.2; (2.0)
90 DMAEMA 10 VP	0.1 EGDMA	10; (90)	1.0; (10)	0.011; (0.1)
	0.25 EGDMA	10; (90)	1.0; (10)	0.028; (0.25)
	0.5 EGDMA	10; (90)	1.0; (10)	0.055; (0.5)
	1.0 EGDMA	10; (90)	1.0; (10)	0.11; (1.0)
	2.0 EGDMA	10; (90)	1.0; (10)	0.22; (2.0)
70 DMAEMA 30 VP	0.1 EGDMA	10; (70)	4.0; (30)	0.014; (0.1)
	0.25 EGDMA	10; (70)	4.0; (30)	0.035; (0.25)
	0.5 EGDMA	10; (70)	4.0; (30)	0.07; (0.5)
	1.0 EGDMA	10; (70)	4.0; (30)	0.14; (1.0)
	2.0 EGDMA	10; (70)	4.0; (30)	0.28; (2.0)

3.3. Metal ion adsorption

The selectivity of hydrogels towards Pb(II), Cd(II), Ni(II), Zn(II), Cu(II) and Co(II) ions were determined via batch equilibrium technique, that is, approximately 0.05 gram P(DMAEMA) hydrogels transferred into salt solutions of metals having various concentrations ranging from 50 ppm to 2000 ppm, and stirred for 48 hours. Equilibrium concentration of Cu(II) was determined by Philips PU 8715 UV-Vis spectrophotometer. And equilibrium concentrations of the other metal ions were determined by titration against EDTA using Xylenol Orange indicator for Co(II), Cd(II), Pb(II) and Eriochrome Black –T indicator for Zn(II) and Ni(II).

3.4. Determination of the nitrite ion concentration

For the determination of nitrite ion concentration ferrous sulfate method was used. In an acidic medium ferrous sulfate reduces nitrogen in nitrite (NO_2^{-1}) to form nitrous oxide (NO). Ferrous ions combine with the nitrous oxide to form a brown-colored complex ion, the color intensity of which is in direct proportion to the nitrite present in the water sample [13].



Concentration of brown-colored complex ion was determined at 333 nm by using Philips 8710 UV-Vis spectrometer.

4. RESULTS AND DISCUSSION

4.1. Composition of Hydrogels

After syntheses of hydrogels, percentage gelation of initial monomer solutions and percentage conversion of the DMAEMA and (VP+EGDMA) into insoluble network were investigated. The effect of irradiation dose on the percentage gelation of P(DMAEMA/VP) hydrogels prepared from 100 % DMAEMA and 0.1, 0.5 and 1.0 % EGDMA containing initial mixtures are given in Fig. 1(a). The effect of irradiation dose on the percentage gelation of P(DMAEMA/VP) hydrogels prepared from 90 % DMAEMA + 10 % VP and 70 % DMAEMA + 30 % VP and 0.1, 0.5 and 1.0 % EGDMA added initial mixtures are given Fig. 1(b). and 1(c). As can be easily seen from Fig.1 the percentage gelation increases with the increase of irradiation dose. After 4 kGy, percentage gelation remains almost constant. As mentioned above slightly decrease was observed in the % conversion for all initial mixtures after 4 kGy. This can be attributed to chain scission of system in the presence of oxygen. Fig. 1 also indicates that the percentage gelation increases with increasing of the cross-linking agent, EGDMA, content and comonomer, VP, content. The effects of EGDMA and VP content on the % gelation are certainly observed at low irradiation doses. At high doses, these changes have completely disappeared.

The variation of the percentage gelation depends on the VP content at constant EGDMA which is easily seen in Fig. 2. As can be shown clearly from Fig. 2, VP promotes % gelation in the presence of EGDMA. Fig. 3 shows the effect of irradiation dose on the percentage conversion of DMAEMA in the 100 % DMAEMA, 90 % DMAEMA+10 % VP, 70 % DMAEMA+30 % VP initial mixtures containing 0.1, 0.5 and 1.0 % EGDMA respectively. Effect of VP content is also seen in the figures. As can be shown from figures the effect of VP is more predominant especially at low dose values and after 2.5 kGy % DMAEMA conversion is independent of the amount of EGDMA and VP content. By using the percentage DMAEMA conversion and percentage gelation data the weight percentage of DMAEMA in the gel was also calculated, Fig.3. Variation of weight percentage of DMAEMA in the hydrogel prepared at 4 and 8 kGy irradiation is given in Table 2. As can be seen from Table 2 percentage weight content of DMAEMA in the initial mixture is almost the same as the percentage content of DMAEMA in the hydrogel. This is due to almost 100 % conversion of initial mixtures at those irradiation doses. The percentage conversion of total VP+EGDMA was calculated by using the total percentage gelation and DMAEMA conversion data. Effect of irradiation dose on the percentage conversion of (VP/EGDMA) is given in Fig. 4. Percentage conversion of (VP/EGDMA) was not significantly changed with VP content of initial solutions but it increased with irradiation dose as expected.

TABLE II. PERCENTAGE DMAEMA COMPOSITION OF DRY GELS PREPARED AT 4 AND 8 KGY

Initial composition of mixture EGDMA %		%DMAEMA in gels (weight/weight) at 4 kGy	%DMAEMA in gels (weight/weight) at 8 kGy
100 % DMAEMA	0.1	100	99.85
	0.5	99.48	100
	1.0	99.92	99.13
90 % DMAEMA + % 10VP	0.1	89.12	91.41
	0.5	91.18	89.47
	1.0	90.59	89.79
70 % DMAEMA + % 30VP	0.1	71.81	70.13
	0.5	71.10	69.82
	1.0	72.45	71.21

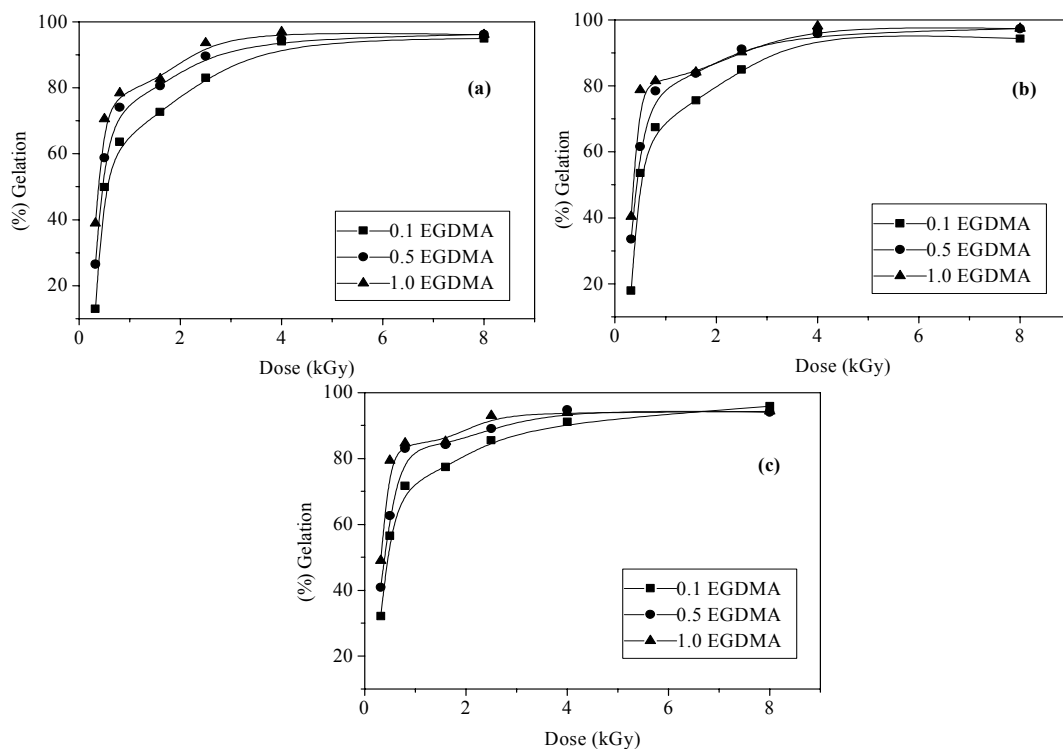


FIG. 1. Effect of irradiation dose on percentage gelation of (a) 100 % DMAEMA (b) 90 % DMAEMA+ 10 % VP and (c) 70 % DMAEMA+ 30 % VP containing mixtures.

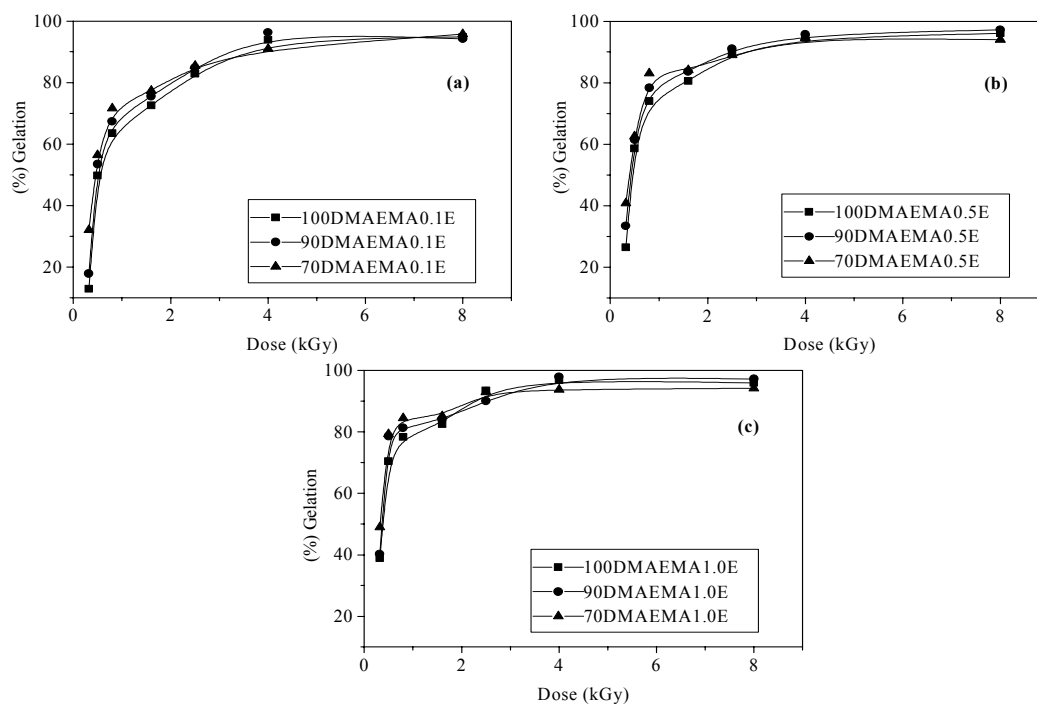


FIG. 2. Effect of irradiation dose on gelation of 100 % DMAEMA (100DMAEMA), 90 % DMAEMA+ 10 % VP (90DMAEMA10VP), 70 % DMAEMA+ 30 % VP (70DMAEMA30VP) containing initial mixtures

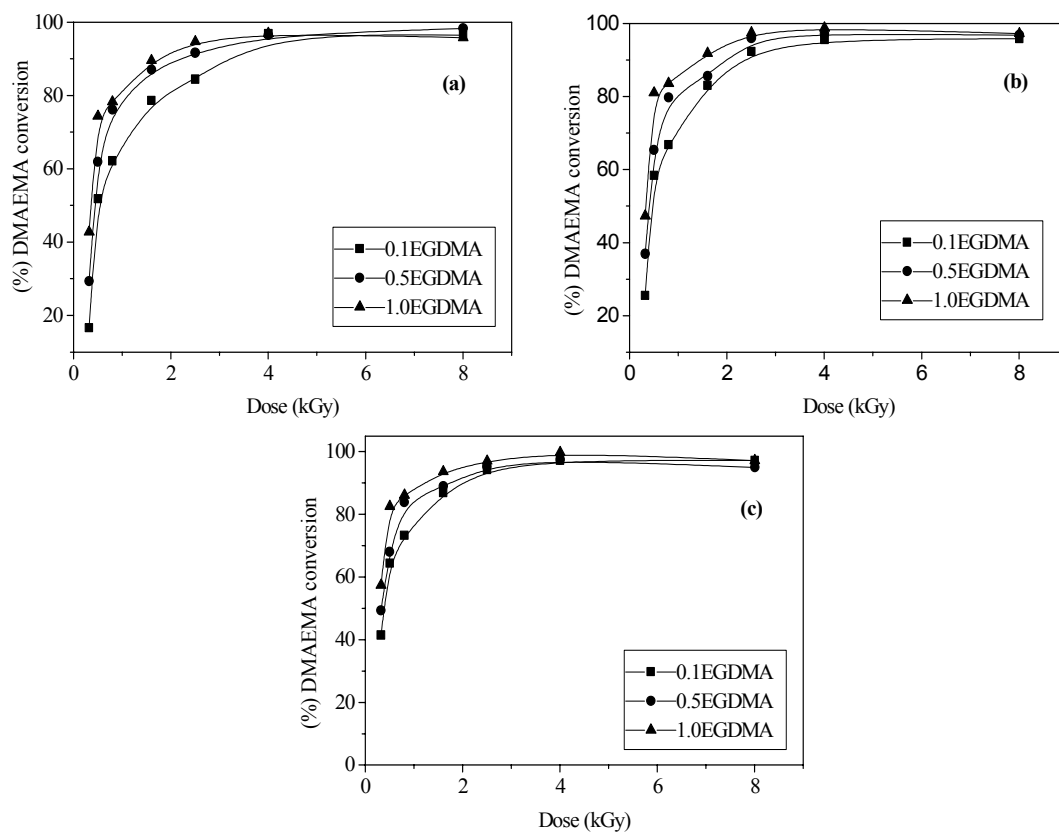


FIG. 3. Effect of irradiation dose on the % conversion of DMAEMA into insoluble network in the (a) 100 % DMAEMA (b) 90 % DMAEMA+ 10 % VP and (c) 70 % DMAEMA+ 30 % VP containing mixtures. EGDMA content in all mixtures is 0.1, 0.5 and 1.0 %.

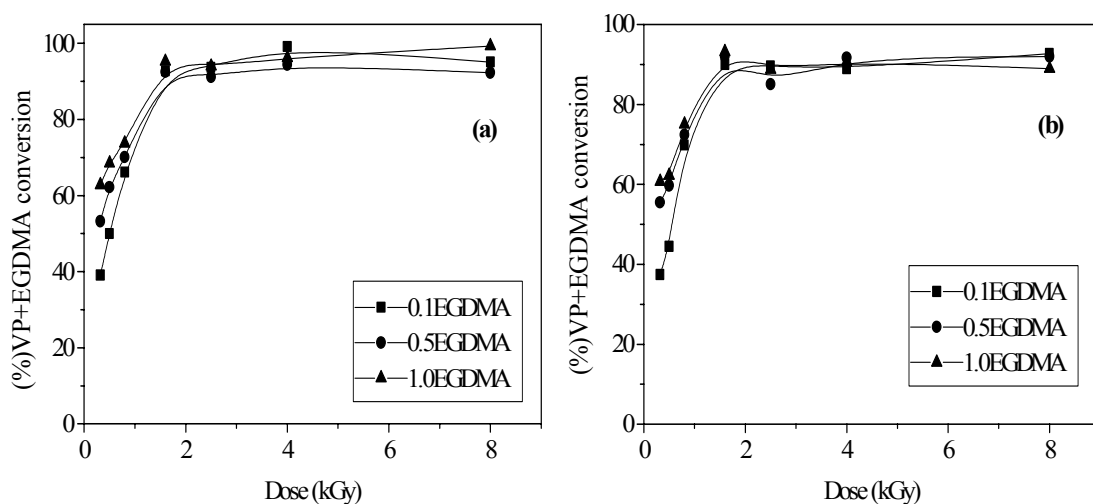


FIG. 4. Effect of irradiation dose on the % conversion of VP+EGDMA in the (a) 90 % DMAEMA + 10 % VP, (b) 70 % DMAEMA + 30 % VP and 0.1, 0.5, 1.0 % EGDMA containing initial mixtures.

4.2. Effect of external stimuli on the swelling behavior of hydrogels

Effect of pH

For the characterization of network structure of P(DMAEMA/EGDMA) and P(DMAEMA/VP/EGDMA) hydrogels initially pH responsive characteristics were investigated. In order to follow the pH response of the hydrogels, dry samples were weighed and allowed to swell to equilibrium in phosphate buffer of varying pH at fixed ionic strength (0.1 M) and temperature (25 °C). Swollen gels taken from water were dried superficially with filter paper, weighed and placed in the same bath. The measurements were continued until a constant weight was reached for each sample. Every data point shows on the EDS values-pH figures are the average of tripled measurements. The swollen and dry weight and the density of the gels were used to calculate equilibrium degree of swelling (EDS) , Q, and the volume fraction, v_{2m} , of given gel samples. The equation used for the calculation of Q and v_{2m} values are given below[14].

$$v_{2m} = V_d / V_s = 1 - [1 + \rho_{gel} / \rho_w (1/w - 1)] \quad (1)$$

Here, V_d is the volume of dry polymer sample and V_s is the gel sample volume fraction after equilibrium swelling, ρ_{gel} and ρ_w are the densities of dry gel and water respectively. Density of water is taken as 1 gr/ cm³. The densities of gels irradiated at 4 and 8 kGy are given Table 3. Slight increase was obtained in the density values with increasing both VP and EGDMA content but densities of hydrogels decreased with increasing irradiation dose from 4 kGy to 8 kGy. This behavior can be explained by the slight degradation of hydrogel systems at high doses. w is the volume fraction of polymer in swollen gel and can be defined as; w = weight of dry gel/weight of swollen gel. The equilibrium degree of swelling (EDS) ,Q, was defined as;

$$Q = 1 / v_{2m} = V_s / V_d \quad (2)$$

TABLE III. THE DENSITIES OF PREPARED HYDROGELS

Initial composition of mixtures EGDMA %		Densities in 4 kGy, (g/cm ³)	Densities in 8 kGy, (g/cm ³)
100 DMAEMA	0.1	1.0817	1.0798
	0.5	1.0932	1.0873
	1.0	1.0985	1.0918
90 % DMAEMA + 10 %VP	0.1	1.1082	1.1049
	0.5	1.1127	1.1085
	1.0	1.1183	1.1126
70 % DMAEMA + 30 %VP	0.1	1.1200	1.1143
	0.5	1.1251	1.1188
	1.0	1.1453	1.1246

The effect of pH on the equilibrium degree of swelling (EDS), Q, of P(DMAEMA/EGDMA) and P(DMAEMA/VP/EGDMA) hydrogels prepared at 4 and 8 kGy are given in Fig. 5-7 Consistent with poly-electrolyte behavior swelling of hydrogels was found to decrease with pH. At all compositions, maximum extent of swelling was reached at pH 2, being due to the sample dissociation of amine groups of DMAEMA at this pH value. Cross-linked copolymer gels based on n-alkyl esters of methacrylic acid, including methyl methacrylate (MMA), ethyl methacrylate (EMA), propyl methacrylate (PMA), butyl methacrylate (BMA) copolymerized with N,N-dimethylaminoethyl methacrylate (DMAEMA) display aqueous equilibrium swelling properties that depend strongly on the pH and ion composition of the solution and on gel structure [15].

These gels generally undergo a sharp pH-induced swelling transition from a collapsed, hydrophobic state to a swollen ionized hydrophilic state as solution pH is reduced into the acidic range. Such swelling behavior has been attributed to alterations in the internal osmotic balance of the gel brought about by changes in the ionic composition of the external solution. The inherent hydrophobicity of these gels, which dominates at high pH and favors the exclusion of water, is opposed by the development of an internal ion osmotic pressure at lower pH, as a result of protonation of the gel amine groups, which induces water imbibition and gel swelling. Thus, their hydrophobicity was dominant at pH values above 6.6. and as the pH was lowered, the tertiary amine side chains on the N,N-dimethylaminoethyl methacrylate (DMAEMA) became protonated causing an increase in the charge density of the network. This resulted in electrostatic repulsion between these groups and swelling of the network ensued [15-16]. As can be shown from figures, the value of the equilibrium degree of swelling of hydrogel systems very much depends on the concentration of cross-linking agent in the network. Increase in the EGDMA content in the network reduced swelling degree dramatically at all pH values especially where the concentration of EGDMA is relatively high.

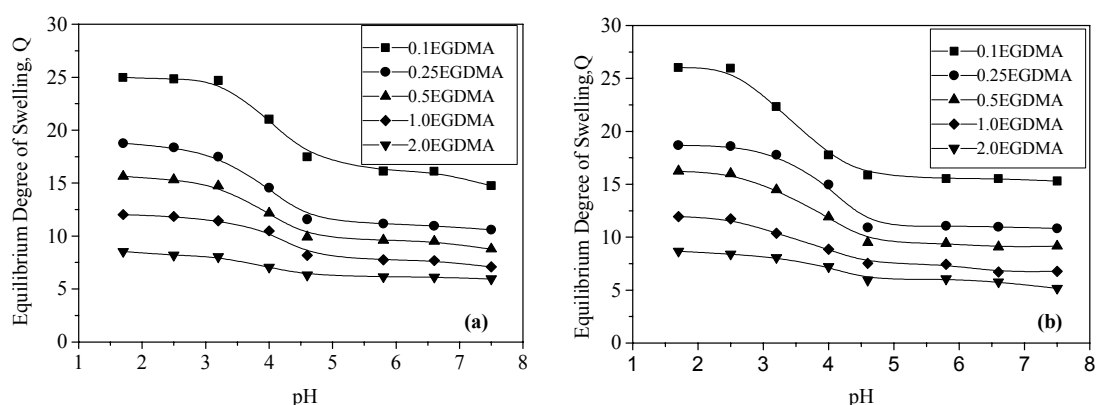


FIG. 5. Effect of pH on the EDS values of *P*(DMAEMA/EGDMA) hydrogels prepared from 100 % DMAEMA and 0.1, 0.25, 0.5, 1.0, 2.0 % EGDMA containing initial mixtures. Total dose given (a) 4 (b) 8 kGy.

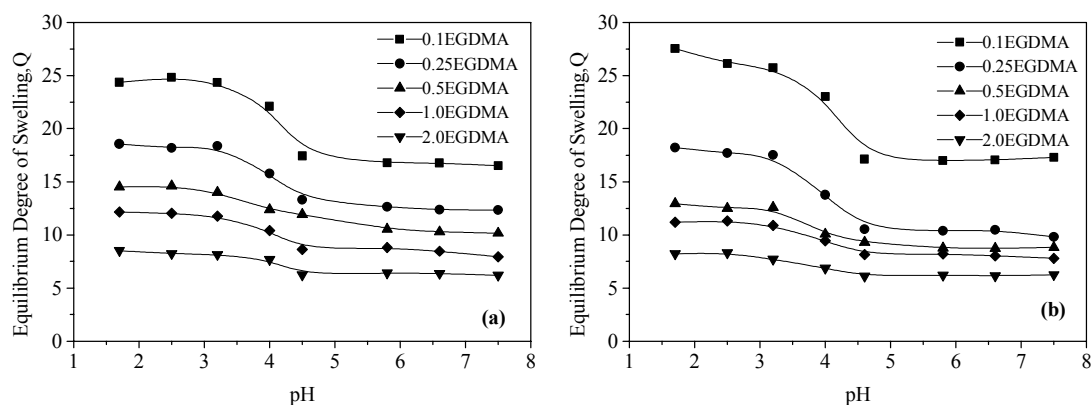


FIG. 6. Effect of pH on the EDS values of *P*(DMAEMA/VP/EGDMA) hydrogels prepared from 90 % DMAEMA+ 10 % VP and 0.1, 0.25, 0.5, 1.0, 2.0 % EGDMA containing initial mixtures. Total dose given (a) 4 (b) 8 kGy.

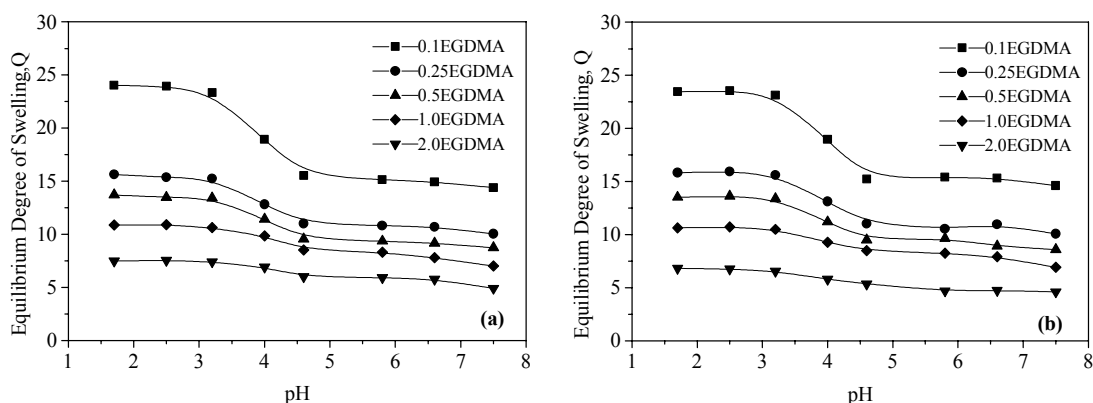


FIG. 7. Effect of pH on the EDS values of P(DMAEMA/VP/EGDMA) hydrogels prepared from 70 % DMAEMA+ 30 % VP g and 0.1, 0.25, 0.5, 1.0, 2.0 % EGDMA containing initial mixtures. Total dose given (a) 4 (b) 8 kGy.

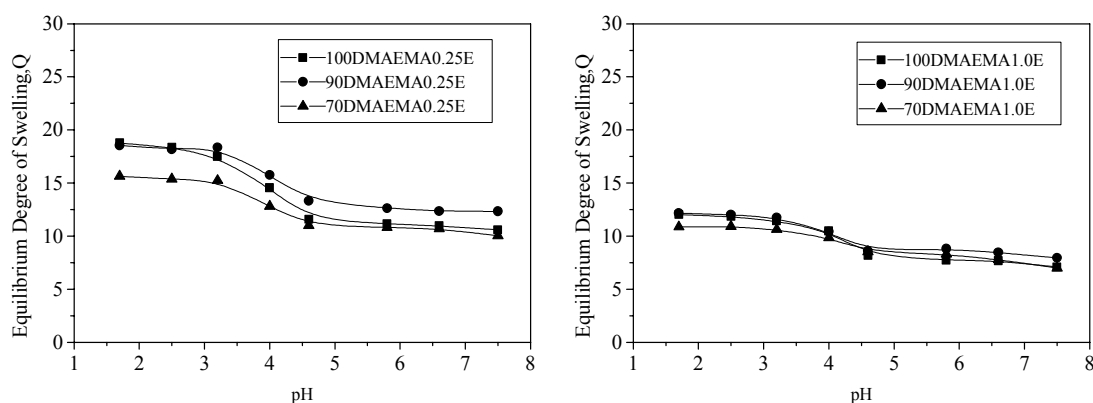


FIG. 8. Effect of pH on the EDS values of P(DMAEMA/EGDMA) and P(DMAEMA/VP/EGDMA) hydrogels prepared from 100 % DMAEMA, 90 % DMAEMA+ 10 % VP, 70 % DMAEMA+ 30 % VP and (a) 0.25 (b) 1.0 % EGDMA containing initial mixtures. Total dose given 4 kGy.

The value of the EDS of anionic network also depends very much on the concentration of ionizable groups in the network.[17] Şen et al. studied the cross-linked poly(N-vinyl 2-pyrrolidone/ itaconic acid) poly-electrolyte hydrogels. The effect of pH on the EDS value was investigated at various pH values. It was found that the addition of only minute amount of itaconic acid comonomer (0.2 mol %) radically changes the swelling behaviour of the hydrogel system.

However, in this study any significant change on the EDS values was not observed with the variation of DMAEMA weight percent in the gel system as shown in Fig. 8. This can be attributed to constant ionizable amine group/ total amine group ratio. It is quite well known that increase of acid or base concentration in the system decreases the % of ionizable groups and at high acid or base concentration the % of ionizable acid or base concentration remains almost constant.

The variation of hydrophilicity/hydrophobicity ratio with variations of composition may be another reason for this behaviour, although decrease of ionizable groups with decreasing DMAEMA content, increases hydrophilicity or swelling with VP content increases % swelling of hydrogel systems. Consequently, the same EDS values could be obtained for different DMAEMA/VP ratios.

Effect of temperature

The effects of temperature on the equilibrium degree of swelling of hydrogels was explained in this chapter. The measurements were carried out in water at 4, 25, 30, 35, 41, 46 °C. In order to investigate the temperature response of the hydrogels, dry samples were weighed and allowed to swell to equilibrium. Swollen gels were removed from water, dried superficially with filter paper, weighed and placed in the same bath. The measurements were continued until a constant weight was reached for each sample. These weight values were used to calculate volume fraction of polymer, v_{2m} , and equilibrium volume swelling ratio, (V/V_0) (volume of swollen gel/volume of dry gel) or equilibrium degree of swelling of the gel in a given gel sample swollen to equilibrium in aqueous solution.

Fig. 9 represent the influence of temperature on the equilibrium volume swelling ratio of PDMAEMA and P(DMAEMA-co-VP) hydrogels in water. As can be seen from figure, slightly cross-linked DMAEMA hydrogels exhibit sharp changes in water content as a function of temperature. The curve of the swelling ratio against the temperature becomes continuous volume transition for each hydrogel composition as the EGDMA content in the gel increased. Water content changes are due to volume collapse upon warming. It has been shown that a number of hydrogels demonstrate sharp or nearly continuous volume transition and associated phase transition from a low temperature, highly swollen gel network to a collapsed, high temperature phase near their critical points. For the poly PDMAEMA hydrogels, the hydrophilic group (amino $-NH(CH_3)_2$) in the hydrogel structure forms an intermolecular hydrogen bond with the surrounding water at low temperatures (under the gel transition temperature, $\sim 30^\circ\text{C}$) [18]. However, this behavior changes when the temperature is greater than the gel transition temperature.

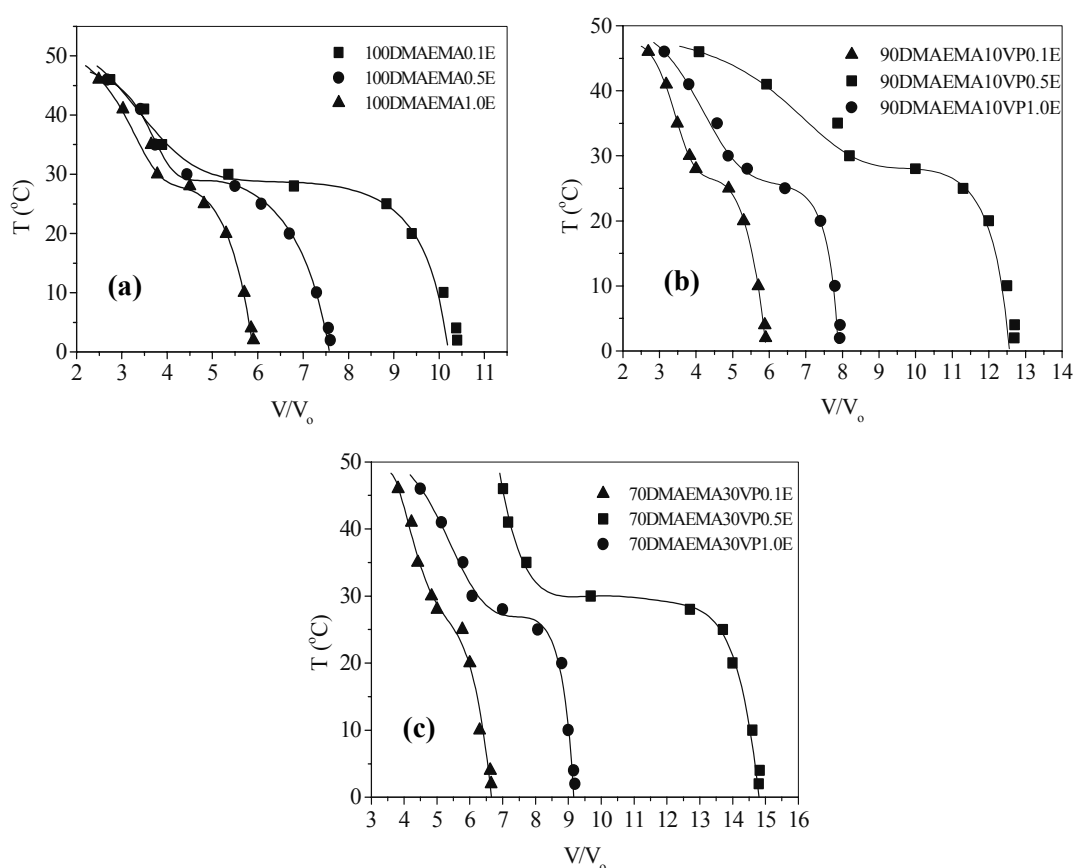


FIG. 9. The effect of temperature on the equilibrium volume swelling ratio of (a) 100DMAEMA (b) 90DMAEMA10VP (c) 70DMAEMA30VP, hydrogels

The phase transition is analogous though fundamental distinct from the lower critical solution phase transition (LCST). The phase transition is analogous through fundamentally distinct from the lower critical solution phase transition (LCST). Güner and Ataman [19] have found that un-crosslinked PVP exhibits a LCST between 35 and 40 °C, dependently on the salt type in the aqueous solution. Recently, Siegel et al. [15, 20] synthesized DMAEMA and DMAEMA/ methyl methacrylate copolymers. They observed similar phase transitions between 25-35°C temperature range. Cho et al. [21] have found that PDMAEMA has a LCST around 50 °C in water and with the formation of the gel network it exhibits transition temperature around 40 °C and shifts to the lower temperatures with the increasing cross-linking density. It is known that the LCST decreases with increasing hydrophobicity of the polymer. With the increase of cross-linker content in the gel network, the cross-linking density increases result in the decrease of swelling and the increase of hydrophobicity of the gel network.

The transition temperature of P(DMAEMA) and P(DMAEMA-co-VP) hydrogels were determined from the first derivative of the temperature versus V/V₀ curves in Fig. 9 and the results are given in Table IV. Table IV indicates that the transition temperature is independent from DMAEMA or VP content in the gel and also the cross-link density of the network structure. This behavior may be attributed to the higher degree of cross-linking of the hydrogel structure as a result of radiation induced and chemical cross-linking during preparation.

TABLE IV. THE TRANSITION TEMPERATURES OF HYDROGELS.

Gel name	Transition Temperature (°C)
100DMAEMA0.1E	28.3
100DMAEMA0.5E	27.4
100DMAEMA1.0E	27.3
90DMAEMA10VPE0.1	27.9
90DMAEMA10VPE0.5	25.4
90DMAEMA10VPE1.0	26.8
70DMAEMA30VPE0.1	30.0
70DMAEMA30VPE0.5	26.7
70DMAEMA30VPE1.0	27.8

4.3. Enhancement and control of crosslinking of DMAEMA

One of the basic parameters that describes the structure of a hydrogel network is the molecular weight between cross-links or cross-link density for highly swollen network. Several theories have been proposed to calculate the average molecular weight between cross-links. In the highly swollen state, the constrained junction theory indicates that a real network exhibits properties closer to those of the phantom network model. The following derived equation using the phantom network model is valid for natural or non-ionic structures [22, 23].

$$M_c = - \frac{(1 - 2/\phi) V_l v_{2r}^{2/3} v_{2m}^{1/3}}{V (\ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2)} \quad (3)$$

Here, \overline{M}_c is the average molecular weight of network chains, v_{2m} is the polymer volume fraction of cross-linked polymer in equilibrium with swollen gel, V_l is the molar volume of the swelling agent, χ is the polymer-solvent interaction parameter, ϕ is the functionality, \bar{v} is the specific volume of the polymer, and v_{2r} is the polymer volume fraction in the relaxed state, i.e. after cross-link but before swelling.

In recent years rubberlike elasticity and uniaxial deformation experiments have been used for the characterization of various types of polymeric systems by many researchers. For uniaxial deformation, the statistical theories of rubber elasticity yield eq. 4 for gaussian chains.

$$f = G(\lambda - \lambda^{-2}) \quad (4)$$

where, f is the force acting per unit cross-sectional area of the undeformed gel specimen, G is the elastic modulus of the sample, and λ is the deformation ratio (deformed length/initial length). For a homogenous network of gaussian chains, the elastic modulus of gel swollen to equilibrium, G , is related to the network cross-link density by eq. 5 [24].

$$G = A \frac{\rho}{M_c} RT v_{2r}^{2/3} v_{2m}^{1/3} \quad (5)$$

where ρ is the polymer density. The prefactor A , equals 1 for an affine network and $(1-2/\phi)$ for a phantom network.

The effective cross-link density, v_e , of a cross-linked structure can be obtained from the results of compressive strain measurements using eqs. 4, 5 and 6:

$$\overline{M}_c = \frac{\rho}{v_e} \quad (6)$$

In our recent studies, we observed that pure N,N-dimethylaminoethyl methacrylate (DMAEMA) monomer and its aqueous solutions shows very low tendency to cross-linking when irradiated with gamma rays at low dose rates. However, when this monomer is irradiated in the presence of a chemical cross-linker, ethyleneglycol dimethacrylate (EGDMA), in very low concentrations, the percentage gelation increases abruptly and gelation reaches 100 % even at very low irradiation doses [25, 26]. In the part of the work ternary systems composed of DMAEMA/water/EGDMA were prepared at varying compositions and irradiated with gamma rays up to 4 kGy. The hydrogels thus prepared were characterized with respect to their swelling properties, network structures and mechanical properties by compression tests. By using theoretically and experimentally calculated cross-link densities, the cross-linking enhancement efficiency of EGDMA was calculated.

For the characterization of the network structure and determination of effective cross-link density of prepared hydrogels, the swelling properties at pH 7 were first investigated. Some information about the structural properties of hydrogels necessary for the determination of \overline{M}_c and v_e are collected in Table V. The other relevant experimental parameters to be used with eq. 4 are as follows: molar volume of the solvent $V_l = 18.0 \text{ cm}^3/\text{mol}$ and the number of branches originating from a cross-link site, $\phi = 3.0$. The χ parameters of hydrogels were calculated by using eq. 7 [27]:

$$\chi \cong 1/2 + v_{2m}/3 \quad (7)$$

By using these relevant experimental parameters $\overline{M}_c(\overline{M}_{c(s)})$ and $v_e(v_{e(s)})$ are calculated and collected in Table V. To account for calculations of these parameters from swelling experiments, the subscript “s” was used in abbreviations. The effect of EGDMA concentration on the cross-link density of DMAEMA hydrogels is clearly seen from these results.

TABLE V. STRUCTURAL PROPERTIES OF PDMAEMA AND P(DMAEMA-CO-VP) HYDROGELS

Gel name	v_{2m}	v_{2r}	ρ	G	\overline{M}_c	χ
100D0.1E	0.2584	0.703	0.9244	42.05	31570	0.595
100D0.5E	0.3124	0.718	0.9147	73.78	19651	0.663
100D1.0E	0.5322	0.734	0.9103	111.4	15848	0.677
90D10VPE0.1	0.1551	0.717	0.9023	17.94	64700	0.544
90D10VPE0.5	0.2938	0.723	0.8987	68.84	21084	0.578
90D10VPE1.0	0.3122	0.741	0.8942	111.7	11495	0.686
70D30VPE0.1	0.1078	0.711	0.8928	15.25	67880	0.536
70D30VPE0.5	0.1860	0.734	0.8888	61.70	20626	0.585
70D30VPE1.0	0.2647	0.741	0.8731	99.39	14755	0.746

For the investigation of the effect of EGDMA on the mechanical properties of hydrogels and for the determination of \overline{M}_c ($\overline{M}_{c(m)}$) and v_e ($v_{e(m)}$), uniaxial compression was applied using the Universal Testing Instrument. Due to calculation of these parameters from mechanical experiments the subscript “m” was used in abbreviations. Typical stress-strain curves of hydrogels are given in Fig. 10. As can be seen from the figure, the magnitude of % strain at maximum deformation decreased with increasing EGDMA content and % stress increased. Shear modulus values of hydrogels were calculated by using elastic deformation theory and eq. 4 [24]. When the equation is applied to the initial stages of deformation, plots of f vs. $\lambda - \lambda^{-2}$ yield straight lines, Fig 11. Where, λ is deformation ratio and equal to L/L_o . L_o and L are the length of the undeformed and deformed hydrogels during compression, respectively. The G value was calculated from the slope of lines and listed in Table V. By using G values and other relevant experimental parameters, \overline{M}_c and v_e were calculated and collected in Table VI. As can be seen from Table VI the magnitudes of \overline{M}_c and v_e calculated from mechanical properties are close to the calculated values obtained by using swelling experiments. Slight differences can be attributed to the uncertainty on the determination of the χ parameter made in the theoretical deviations.

For the determination of cross-linking efficiency of gamma rays on the preparation of P(DMAEMA/EGDMA) hydrogels, the theoretical \overline{M}_c and v_t values were first calculated. The theoretical cross-link density v_t is given as follows, in terms of mole content of EGDMA(n_{EGDMA}) and DMAEMA(n_{DMAEMA}) and the average molecular weight of the repeating unit, M_r .

$$v_t = \frac{\rho}{\overline{M}_c} = \frac{1}{2} \frac{n_{DMAEMA}}{n_{EGDMA}} M_r \quad (8)$$

As shown in Table VI, the theoretical cross-link density of P(DMAEMA) hydrogel increased from 6.20×10^{-6} to 2.46×10^{-4} with increasing amount of EGDMA, ranging from 0.05 % to 2.0 %. The large differences observed between the experimentally calculated and theoretical cross-link densities are assumed to be due to non-consideration of cross-linking efficiency of gamma rays in the theoretical calculation. The experimentally found cross-link density of P(DMAEMA)-1 hydrogel is 8 times higher its theoretically calculated counterpart. This value decreased to 5.5 and 2.3 when 0.5 and 2.0 % EGDMA was used in the gel preparation, respectively.

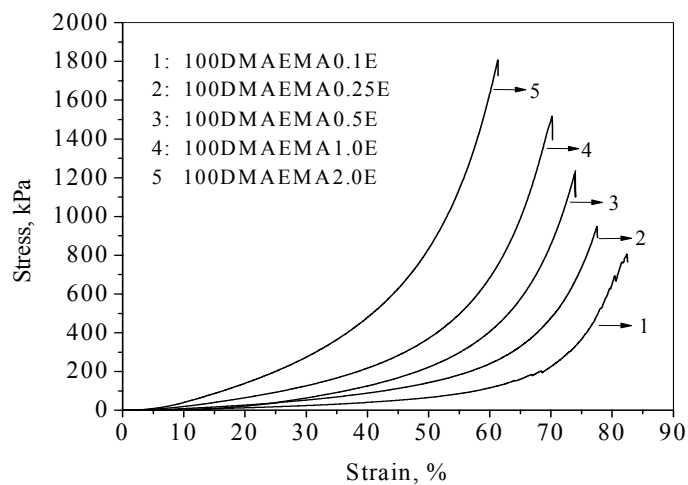


FIG. 10. Strain versus stress curves of *P*(DMAEMA) hydrogels

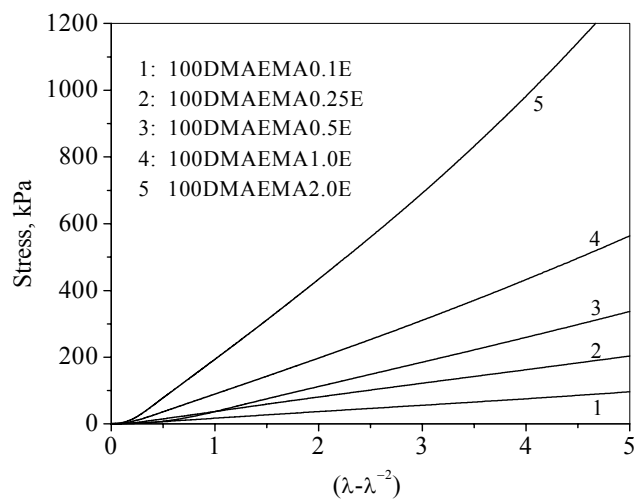


FIG. 11. $\lambda - \lambda^{-2}$ versus stress curves of *P*(DMAEMA) hydrogels

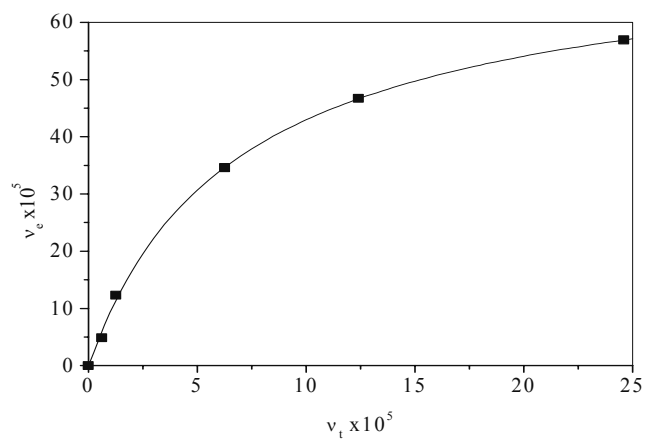


FIG. 12. v_e versus v_t curve of *P*(DMAEMA) hydrogels

From the plot of ν_e versus ν_l (Fig. 12) it has been observed that, there is no linear relation between these two parameter unlike the expected. The exponential increase may be due to changing of cross-link efficiency of EGDMA and gamma rays at higher EGDMA concentrations. For the lower EGDMA content or initial region of the ν_e versus ν_l curve, the α and β values were calculated as 3.8×10^{-5} and 4.9 respectively. Similarly, an unusual β value was also observed by Davis and Huglin [28]. The inverse of the α value, which is equivalent to 26300 relates to, \overline{M}_c , for DMAEMA cross-linked by gamma rays to 4 kGy dose in the in the absence of EGDMA. The lower \overline{M}_c values obtained in this study indicate that EGDMA is facilitating the cross-linking reaction effectively during irradiation, and that is improves the cross-link efficiency of gamma rays depending on its concentration.

TABLE VI. MECHANICAL PROPERTIES AND THEORETICALLY CALCULATED CROSS-LINK DENSITY OF P(DMAEMA) HYDROGELS

Gel Name	$\overline{M}_{c(m)}$	$\nu_{e(m)}$	$\overline{M}_{c(t)}$	$\nu_{e(t)}$
100DMAEMA0.1E	22400	4.87×10^{-5}	176000	6.20×10^{-6}
100DMAEMA0.25E	8970	1.23×10^{-4}	88000	1.26×10^{-5}
100DMAEMA0.5E	3200	3.46×10^{-4}	17690	6.26×10^{-5}
100DMAEMA1.0E	2370	4.67×10^{-4}	8900	1.24×10^{-4}
100DMAEMA2.0E	1950	5.69×10^{-4}	4500	2.46×10^{-4}

It has been found that small amount of EGDMA can facilitate the cross-linking of DMAEMA effectively during low dose rate gamma irradiation and improves the cross-linking efficiency approximately 8 fold when used only about 0.05 % concentration in the initial monomer mixture. Furthermore, the experimental results clearly showed that simple compression analyses and equations derived from Phantom network theory can be used for the determination of effective cross-link density of hydrogels without needing some polymer-solvent based parameters. As can be seen from Table 5 the molecular weight between crosslink of PDMAEMA and P(DMAEMA-co-VP) hydrogels increases with increasing amount of EGDMA, ranging from 0.1 % to 1.0 % but not changes significantly with changing of VP content in the gel system.

4.4. Thermodynamic properties of P(DMAEMA) and P(DMAEMA/VP) hydrogels

The polymer solvent interaction parameter, χ , is the one of the important factor effecting the swelling of gels. In poor solvents $\chi \geq 0.7$ and the equilibrium degree of swelling is not effected at all with variations in pH and temperature. In such solutions one can hardly expect any swelling [21, 22]. For good solvents $\chi \leq 0.5$ however, because of increasing polymer solvent interactions, equilibrium swelling is shifted to higher values at every pH.

For the determination of polymer-solvent interaction parameter of P(DMAEMA) and P(DMAEMA-co-VP)-water system at pH 7, the temperature sensitive swelling behavior of hydrogels was analyzed by using Flory-Rehner theory of swelling equilibrium. According to the Flory-Rehner theory, there are two contributions to the osmotic pressure π of a non-ionic and unionized polyelectrolyte gel:

$$\pi = \pi_{mix} + \pi_{el} \quad (9)$$

where, mixing (π_{mix}) and elastic-retractive(π_{el}) contribution are the osmotic pressure due to polymer solvent mixing and due to deformation of network chains to a more elongated state respectively.

The first term in the right hand side of equation, for the mixing of polymer chains with the solvent can be given in terms of the Flory-Huggins relationship:

$$\pi_{mix} = -\frac{RT}{V_1}(\ln(1-v_{2m}) + v_{2m} + \chi v_{2m}^2) \quad (10)$$

where, V_1 is the molar volume of the solvent and v_{2m} is the polymer volume fraction and χ is the Flory polymer-solvent interaction parameter. Polymer-solvent interaction parameter χ is expressed as a series expansion in powers of the cross-linked polymer volume fraction v_{2m} i.e.:

$$\chi = \chi_1 + \chi_2 v_{2m} + \chi_3 v_{2m}^2 + \dots \quad (11)$$

where, the coefficients χ_1 , χ_2 , and χ_3 are the functions of temperature and the molecular characteristics of the polymer-solvent system.

In the slightly swollen state, the constrained junction theory indicates that a real network exhibits properties closer to those of the Affine network model consequently eq. 12 is more realistic representation for π_{el} .

$$\pi_{el} = -RT \frac{\rho}{M_c} V_1 \left((v_{2m})^{1/3} (v_{2r})^{2/3} - v_{2m}/2 \right) \quad (12)$$

Using eq. 10 and 12 and putting $\pi = 0$, one obtains the following well-known equation.

$$(\ln(1-v_{2m}) + v_{2m} + \chi v_{2m}^2) + \frac{\rho}{M_c} V_1 \left((v_{2m})^{1/3} (v_{2r})^{2/3} - v_{2m}/2 \right) = 0 \quad (13)$$

Here, v_{2r} is the polymer volume fraction in the relaxed state i.e. after cross-linking but before swelling, ρ is the density of polymer, V_1 is the molar volume of the swelling agent and \overline{M}_c is the average molecular weight between consecutive cross-links.

For large swelling ratio, we can neglect v_{2m} dependence of χ defined by eq. 4. In this case χ reduces to χ_1 and the following equation can be obtained for it.

$$\chi_1 = \frac{\Delta G}{RT} = \frac{\Delta H - T\Delta S}{RT} \quad (14)$$

Where, ΔG , ΔH and ΔS are the changes in the free energy, enthalpy and entropy during the swelling of cross-linked polymer in a solvent respectively. By using experimentally determined equilibrium volume swelling ratios of the hydrogels in water and \overline{M}_c values were found from uniaxial compression experiments (Table 7).

The variation of χ parameter for P(DMAEMA) and P(DMAEMA-co-VP) hydrogels with temperature and polymer volume fraction are given in Fig. 13 and Fig. 14 respectively. As can be seen from the Figures, at low temperatures or high swelling ratios, χ parameter is almost independent from temperature changes. This indicates that the enthalpy and the entropy contribution to Flory interaction parameter are constant and χ equals to χ_1 in this swelling ratio and temperature [29].

ΔH and ΔS values appearing in the χ_1 parameter were calculated from the slope and intercept of these lines. ΔH and ΔS values of all prepared hydrogels are given in Table VII. As can be seen from table, the signs of the both quantities are negative for all prepared hydrogels. The negative values for ΔH and ΔS indicate that P(DMAEMA) and P(DMAEMA-co-VP) hydrogels shows LCSTs in water.

Almost constant ΔS value and increasing ΔH value with increasing EGDMA and VP content indicate that formation of polymer-solvent interactions are mainly controlled by enthalpy factor. However, with the comparison of the ΔH and ΔS values of P(DMAEMA) and P(DMAEMA-co-VP) hydrogels compared with ΔH and ΔS values of PNIPA and poly(TBA-co-AAm) copolymers, it has been observed that the temperature dependence of the present hydrogels is weaker than that hydrogels. Almost constant ΔG value indicates that temperature sensitivity of the P(DMAEMA) and P(DMAEMA-co-VP) hydrogels are independent from cross-link density and comonomer VP content in the hydrogel systems.

ΔH and ΔS concentration dependent parameters, by using non-linear regression analyses of the data, χ , v_{2m} and T in Fig. 13 and 14 simultaneously for all prepared hydrogels represented in the following equation were obtained for the dependence of χ on v_{2m} and temperature (T):

$$\chi = \chi_1 + \left(a - \frac{b}{T}\right)v_{2m} + \left(c - \frac{d}{T}\right)v_{2m}^2 \quad (15)$$

In order to control of the Affine network theory and validity of χ parameters of hydrogels, the theoretical swelling ratios (V/V_0) were calculated by using eq. 13 and 15. The solid curves in Fig. 9 represent the theoretical swelling ratio of hydrogel as a function of the temperature. It is clearly seen that, after taking into account the sensitive dependence of the χ parameter on both temperature and polymer concentration, the prediction of the Flory-Rehner theory provides a satisfactory agreement to the experimental swelling data.

In this study, radiation synthesis of P(DMAEMA) and P(DMAEMA-co-VP) hydrogels have been investigated. Swelling studies show that pH and temperature are the basic parameters affecting the equilibrium volume swelling of hydrogels. Also, it is a notable fact that addition of 10 or 30 % VP in P(DMAEMA) hydrogels does not change the swelling behaviour and transition temperature of P(DMAEMA) and P(DMAEMA-co-VP) hydrogels. The experimental results clearly show that simple compression analyses at nonionized state and Flory–Rehner theory can be used for the determination of polymer-solvent interaction parameter, enthalpy and entropy changes appearing in the χ parameter and the dependence of χ on the polymer volume fraction and temperature.

TABLE VII. ENTHALPY, ENTROPY AND FREE ENERGY CHANGES APPEARING IN THE χ PARAMETER FOR THE P(DMAEMA) AND P(DMAEMA-CO-VP) HYDROGELS IN WATER

Gel Name	$\Delta H(\text{J/mol})$	$\Delta S(\text{J/mol K})$	$\Delta G(\text{J/mol})$
100DMAEMA0.1E	-187 ± 36	-4.9 ± 0.1	-1273 ± 36.1
100DMAEMA0.5E	-307 ± 43	-5.5 ± 0.2	-1332 ± 43.2
100DMAEMA1.0E	-295 ± 8	-5.6 ± 0.1	-1373 ± 8.1
90DMAEMA10VP0.1E	-73 ± 22	-4.5 ± 0.1	-1268 ± 22.1
90DMAEMA10VP0.5E	-119 ± 36	-4.8 ± 0.1	-1311 ± 36.1
90DMAEMA10VP1.0E	-322 ± 50	-5.7 ± 0.2	-1376 ± 50.2
70DMAEMA30VP0.1E	-72 ± 27	-4.7 ± 0.1	-1328 ± 27.1
70DMAEMA30VP0.5E	-168 ± 14	-4.9 ± 0.1	-1292 ± 14.1
70DMAEMA30VP1.0E	-485 ± 88	-6.2 ± 0.3	-1362 ± 88.1

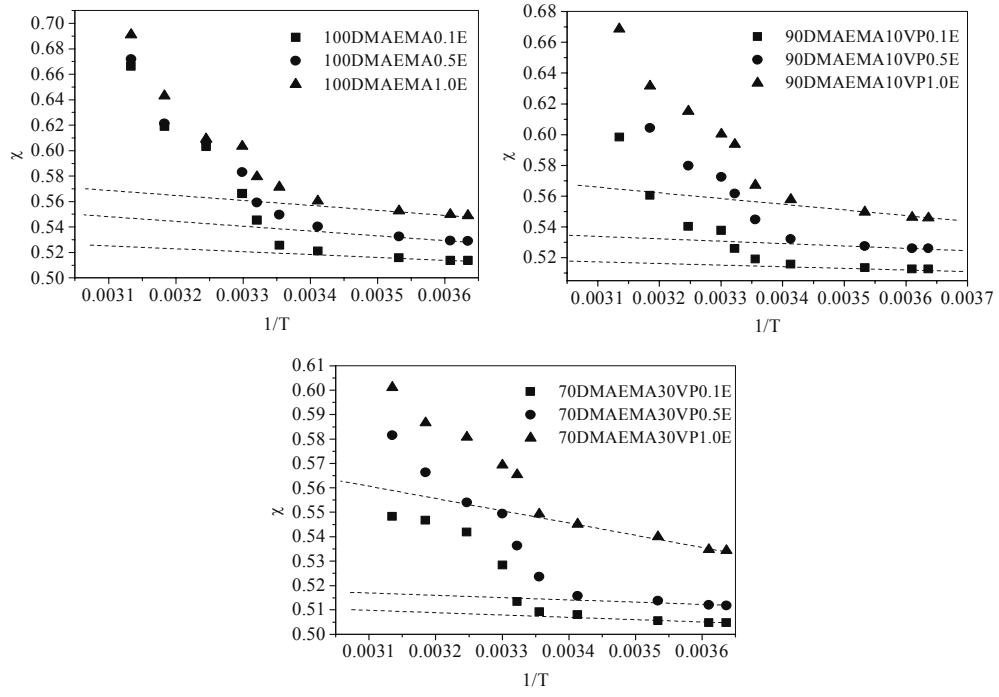


FIG. 13. Variation of polymer-solvent interaction parameter χ for $P(\text{DMAEMA})$ and $P(\text{DMAEMA-co-VP})$ hydrogels-water system as a function of inverse temperature. (a) 100DMAEMA, (b) 90DMAEMA10VP, (c) 70DMAEMA30VP hydrogels.

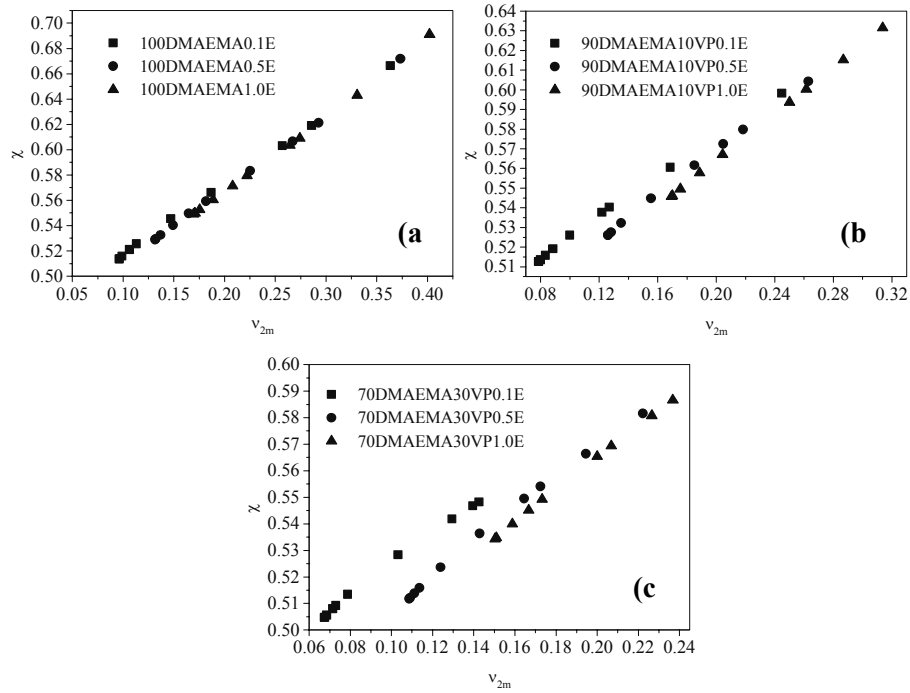


FIG. 14. Variation of polymer-solvent interaction parameter χ for $P(\text{DMAEMA})$ and $P(\text{DMAEMA-co-VP})$ hydrogels-water system as a function of polymer volume fraction. (a) 100DMAEMA, (b) 90DMAEMA10VP, (c) 70DMAEMA30VP hydrogels.

4.5. Adsorption of heavy metal ions onto P(DMAEMA/EGDMA) hydrogels

For the investigation of heavy metal ions adsorption capacities of DMAEMA based hydrogels firstly P(DMAEMA/EGDMA) hydrogels were used in the adsorption studies. In the first year of this project the metal ion adsorption capacities of hydrogels were investigated with Cu^{2+} , Zn^{2+} , Pb^{2+} . For the adsorption of metal ions dry polymer discs (2 mm thickness, 4 mm diameter) hydrogels were immersion into aqueous solution of metal ions at ambient temperature at pH 7 for 2 days.

Adsorption of ions into hydrogel matrices was measured by using a Philips 8715 spectrophotometer and specific cheating agents for each metal ion. The effect of metal ion concentration and the metal ion adsorption capacities of hydrogels are given in Fig. 15-17. As can be seen from figures the amount of adsorbed metal ion increased rapidly with increasing metal ion concentration. In order to investigate the effect of cross-linking density on the adsorption capacities of DMAEMA hydrogels 0.1, 0.5 and 1.0 % EGDMA containing hydrogels were used in the adsorption studies. As can be seen all adsorption figures the cross-linking density of hyrogels is not a parameter controlling the adsorption capacities of hydrogels. Very similar adsorption isotherms were obtained for all hydrogel systems.

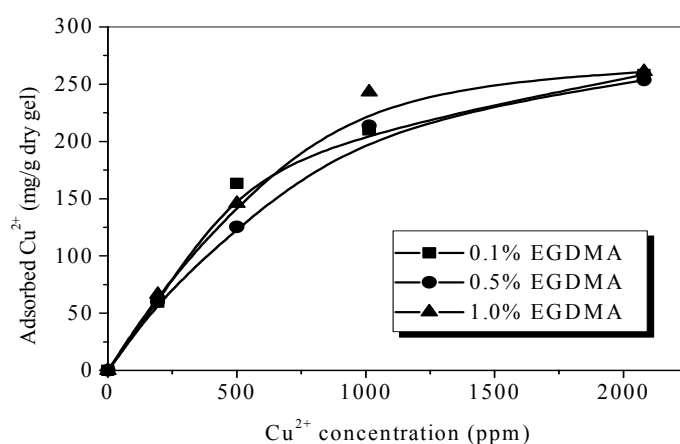


FIG. 15. Effect of Cu^{2+} concentration on the adsorption capacity of P(DMAEMA) hydrogels

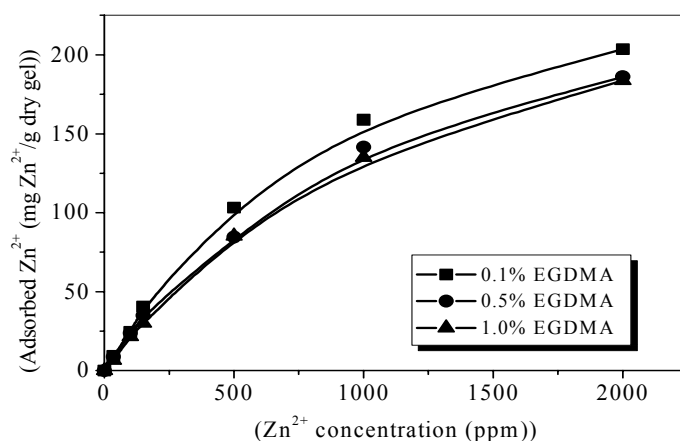


FIG. 16. Effect of Zn^{2+} concentration on the adsorption capacity of P(DMAEMA) hydrogels

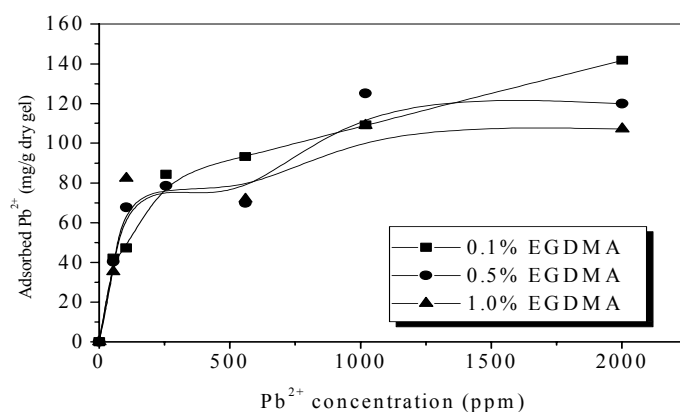


FIG. 17. Effect of Pb^{2+} concentration on the adsorption capacity of $P(DMAEMA)$ hydrogels

The effect of metal ion adsorption on the swelling of hydrogels are given for Cu^{2+} and Zn^{2+} in Fig. 18 and 19. The equilibrium degree of swelling abruptly increase with metal ion adsorption. This increase was attributed strong electrostatic repulsion between metal ions in gel matrix.

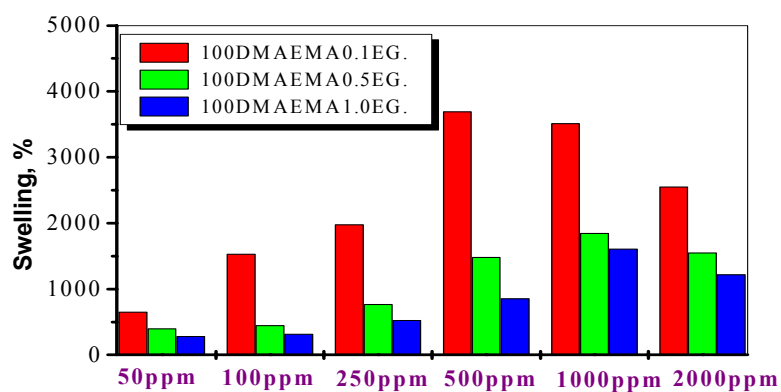


FIG. 18. Effect of Cu^{2+} concentration on the % swelling of $P(DMAEMA)$ hydrogels

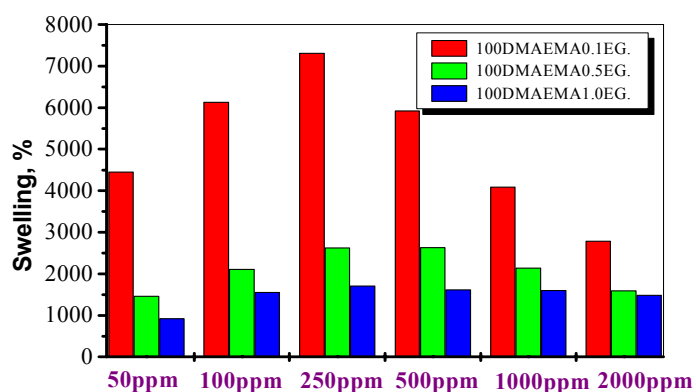


FIG. 19. Effect of Zn^{2+} concentration on the % swelling of $P(DMAEMA)$ hydrogels

In the second year of this project the metal ion adsorption capacities of hydrogels were investigated with Cd^{2+} , Ni^{2+} , Co^{2+} . For the adsorption of metal ions dry polymer discs (2 mm thickness, 4 mm diameter) hydrogels were immersion into aqueous solution of metal ions at ambient temperature at pH 7 for 2 days.

It has been observed that changing of cross-link density of P(DMAEMA) hydrogels not change their adsorption capacity so the adsorption studies with Cd^{2+} , Ni^{2+} , Co^{2+} ions followed with 100 % P(DMAEMA) and 0.1 % EGDMA containing hydrogel (100DMAEMA0.1EG.) system. The details of adsorption studies achieved with Cd^{2+} , Ni^{2+} , Co^{2+} ions are given below. The adsorption characteristics of P(DMAEMA) hydrogels for the Cu^{2+} , Zn^{2+} and Pb^{2+} ions are also given with these ions for comparison.

0.05 gram of P(DMAEMA) hydrogel prepared by using 0.1 % EGDMA was put into different concentrations (100-2000 ppm) of metal ion solutions until they reach adsorption equilibrium. The binding properties of these metal ions i.e. Zn(II), Pb(II), Cu(II), Co(II), Ni(II) and Cd(II) with P(DMAEMA) hydrogel determined in different concentration of aqueous metal solution is given in Fig 20. The adsorption values were given as adsorbed M^{2+} (mg M^{2+} /g of gel) versus equilibrium M^{2+} concentration.

The new hydrogel exhibited higher affinity for Cu(II) ion, the highest value was found to be 258 mg Cu(II) ion/ g dry gel from 2000 ppm solution. The adsorption amount of Zn(II), Co(II) and Pb(II) ions were lower adsorption capacities compared to copper ion. It was found that the adsorption capacity of P(DMAEMA) hydrogel for Zn(II), Co(II), Pb(II) and Ni(II) ions for 2000 ppm initial concentration was 204, 199, 142 mg metal ion / g dry polymer, respectively. The adsorption behavior of Ni(II) (95 mg/g dry gel) and Cd(II) (93 mg/g dry gel) ions which have lowest adsorption capacities compared to copper ion show similar adsorption isotherms with Co(II) ion. The order of adsorption affinity based on the amount of metal ion uptake (mg metal ion/g dry gel) is as follows: $\text{Cu(II)} > \text{Zn(II)} \cong \text{Co(II)} > \text{Pb(II)} \gg \text{Ni(II)} > \text{Cd(II)}$. This order was almost in agreement with the stability constants for amine complexes such as ethylene diamine-metal complexes [30]. Metal adsorption studies achieved with 0.5 and 1.0 % EGDMA containing hydrogels any changes in the adsorption affinity was not observed and almost same degree metal ion adsorption per gram dry gel was found.

During the course of adsorption of metal ions on P(DMAEMA) hydrogels colour changes were observed. The colours of the P(DMAEMA) hydrogels metal complexes are similar to those of ammine complexes. For example Cu(II), Co(II) and Ni(II) complex were light blue, light pink and light yellow, respectively. The other colourless metal ions (Zn(II), Pb(II), Cd(II)) complexes were observed as opaque. This colour change of the polymer shows that functional groups containing nitrogen atoms were interacted with metal ions. Moreover applying the data of Cu(II), Zn(II), Co(II) and Pb(II) ions adsorption kinetics to different equations, adsorption isotherms constructed for P(DMAEMA) hydrogel.

Adsorption isotherms of P(DMAEMA) were analyzed according to the linear form of the Langmuir isotherms for Cu(II), Zn(II), Co(II) and Pb(II) ions, using the following expression,

$$\frac{C_e}{q_e} = (1/K_L q_{mon}) + (1/q_{mon})C_e$$

where C_e is the equilibrium concentration of hydrogel in solution, q_e represents the adsorbed metal ions per unit mass of adsorbent at equilibrium. q_{mon} denotes the amount of adsorption corresponding to complete monolayer coverage. K_L is the Langmuir constant. A plot of C_e/q_e versus C_e would give K_L and q_{mon}

The plots of isotherms are shown in Fig. 21 and seen to be linear over the whole concentration range studied. K_L and q_{mon} values calculated from Langmuir equation are given in Table VIII.

The constant, K_L , contains enthalpic interaction of the binding of metal ions with polymer, and can be found from the intercept of the lines given in Fig. 21. q_{mon} is a quantity representing adsorption capacity, also known as monolayer coverage of the surface. q_{mon} values of P(DMAEMA) hydrogel from the Langmuir equation for Cu(II), Zn(II), Co(II) and Pb(II) ions were found to be 322, 285, 294 and 156 mg/g, respectively. This is in good accordance with previous results.

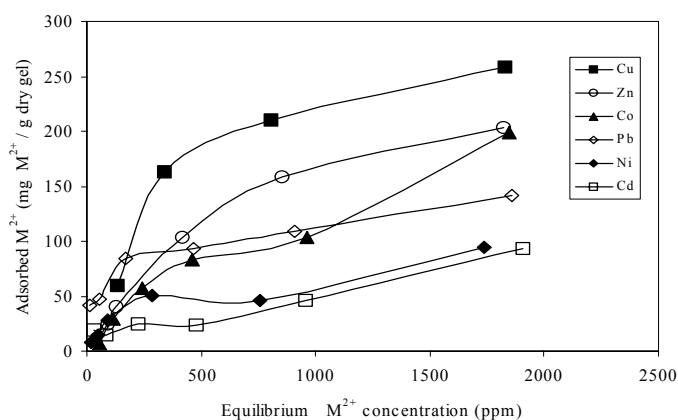


FIG. 20. Dependence of metal ion uptake on the equilibrium concentrations of metal ions for polyDMAEMA hydrogel.

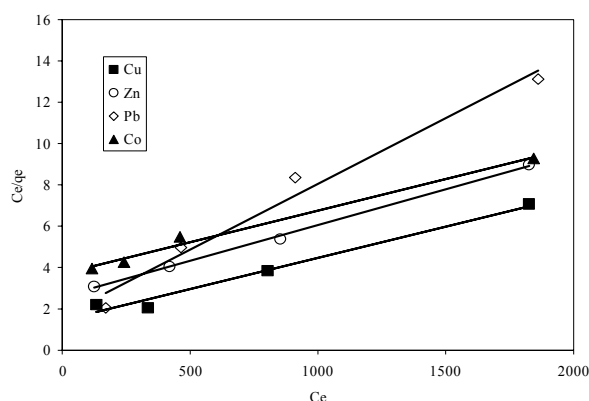


FIG. 21. Langmuir isotherms for Cu(II), Zn(II), Co(II) and Pb(II) ions adsorption on poly DMAEMA hydrogel.

TABLE VIII. K_L AND Q_{MON} VALUES FOR ADSORPTION OF CU(II), ZN(II), CO(II) AND PB(II) IONS

Adsorbed Ion	K_L	q_{mon}
Cu(II)	2.17×10^{-3}	322
Zn(II)	1.14×10^{-3}	285
Co(II)	8.45×10^{-4}	294
Pb(II)	3.78×10^{-3}	156

For the investigation of swelling behavior of P(DMAEMA) hydrogels in metal ion solution, hydrogels swelled in various metal ion solutions. The effect of the metal ion concentrations on the mass swelling value of hydrogels are given Fig. 22.

As can be shown from Fig. 22, for all metal ions except relatively low adsorbed cadmium ion, mass swelling of hydrogel generally increased with increasing concentration of metal ion and after reached a maximum value decreased continuously. This increase was attributed to the electrostatic repulsions between metal ions in hydrogel structure and expansion of the chains. The decrease of mass swelling after a maximum probably due to osmotic pressure of metal ions onto hydrogel.

In order to determine the effect of pH on the adsorption characteristic of hydrogels, adsorption studies were conducted in phosphate buffer solutions, pH 5-3. As can be seen from Fig. 23 metal ion adsorption property changes strongly depend on the pH of the adsorption solution. Rapidly decrease of adsorption because of the protonization of tertiary amine groups and exclusion of the metal ions from gel structure. The adsorption data in phosphate buffer solutions compared with adsorption isotherm of polyDMAEMA hydrogels given in Fig. 20. It has been observed that co-ions in adsorption medium .also effects adsorption properties of P(DMAEMA) hydrogels.

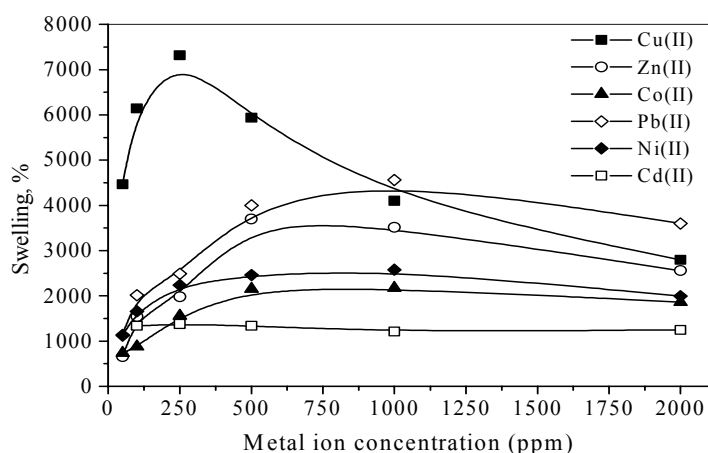


FIG. 22. Effect of metal ion concentration on the mass swelling of hydrogels.

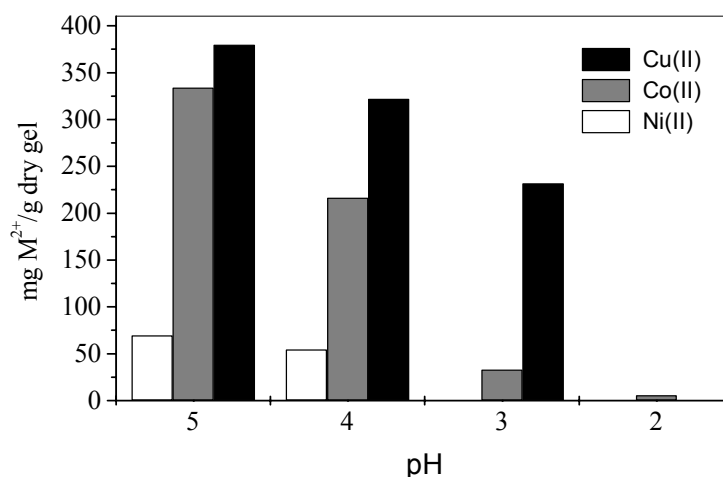


FIG. 23. Effect of pH on the metal ion adsorption.

As a conclusion, the adsorption studies clearly showed that external stimuli, pH, and ionic species in the adsorption medium play an important role on the adsorption behaviour of P(DMAEMA) hydrogels. It seems also that these hydrogels may be consider as potential sorbent for the removal of heavy metal ions from wastewater and aqueous effluents. At the beginning of this project the adsorption and removing of anionic water pollutants such as NO_2^- , NO_3^- , PO_4^{2-} ions by using DMAEMA are also planned. The details of experimental studies for the adsorption and removing of NO_2^- ions from aqueous solutions are given below.

5. ADSORPTION OF NO_2^- IONS ONTO P(DMAEMA/EGDMA) HYDROGELS

5.1. Determination of the nitrite adsorption capacity and adsorption kinetics

In order to estimate maximum nitrite loading capacity of the P(DMAEMA) hydrogel, 0.05 gram 100DMAEMA0.1E hydrogel was placed in contact with 50 ml of 1 M HCl solution and left over night. The swollen polymer was decanted and washed with water. Then it was transferred into 100 ml of 0-2000 ppm NaNO_2 solutions. The hydrogels stirred for 24 h at room temperature. The remaining nitrite ion concentration in the solution was determanid by using ferrous sulfate method.

Kinetics of nitrite sorption was investigated by simple batch experiment as follows: 0.05 g hydrogel was soaked in 100 ml of 1000 NaNO_2 solution. While string gently at room temperature at certain intervals, 100 μL aliquots were removed from solution for the determination of concentration of NO_2^- ion. The adsorbed amount was calculated as the difference between the nitrite contents of the initial and final solutions Fig. 24 shows the adsorption curve of nitrite onto P(DMAEMA) hydrogels. The adsorption values are given as adsorbed nitrite, mg/g dry gel. High adsorption rates were observed within 20 min for nitrite ions and after one hour the plateau value was reached. Approximately 82.5 % removal of nitrite ions was achieved within 1 hour from 500 ppm nitrite solution.

The binding of nitrite ion onto P(DMAEMA) hydrogels was confirmed by FTIR analyses. The FTIR spectra of P(DMAEMA), original, protonated and nitrite ion adsorbed forms, were given in Fig. 25. After protonation of P(DMAEMA), a broad stretching bond was observed in the 2704 cm^{-1} region which was characteristic for NR_3H^+ . For the spectrum of nitrite ion adsorbed form, the N-O stretching bands appeared at 1381 cm^{-1} and 982 cm^{-1} as given in literature[12].

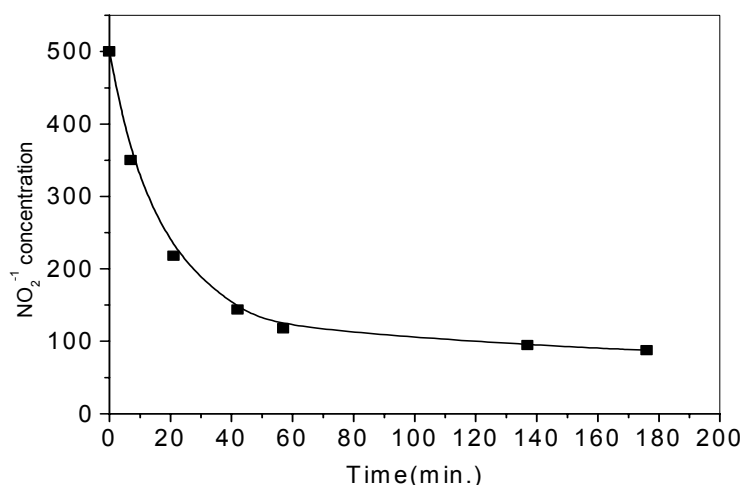


FIG. 24. Adsorption kinetics of nitrite ions from 500 ppm NO_2^- solution.

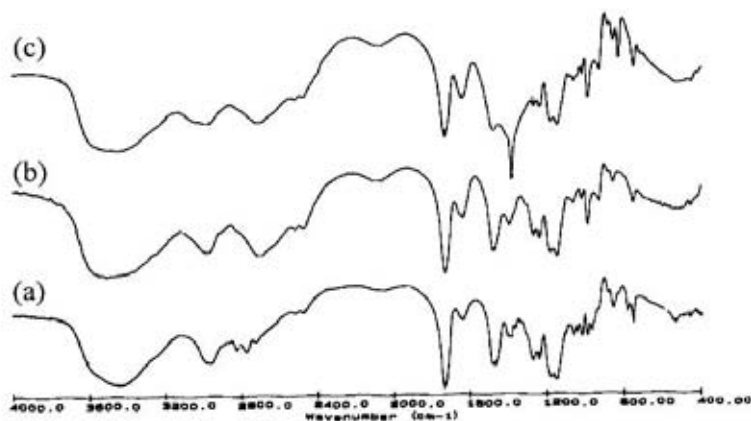


FIG. 25. FTIR spectra of P(DMAEMA) a) unprotonated, b) protonated, c) nitrite ion adsorbed

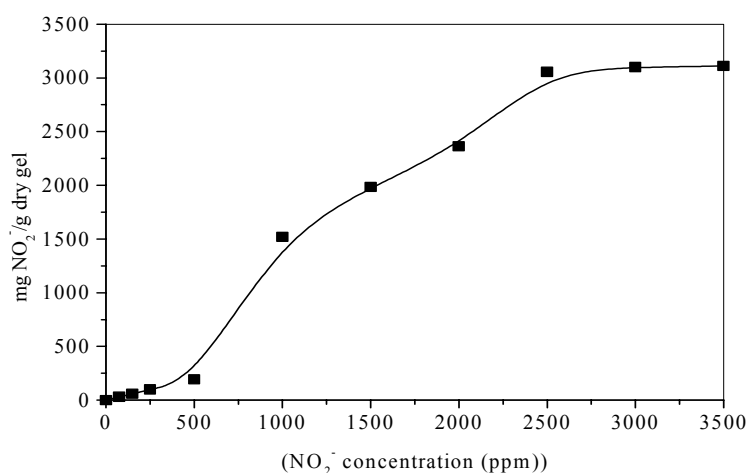


FIG. 26. Dependence of nitrite ion uptake on the initial concentration of nitrite ions

The effect of the initial concentration of nitrite ions on the adsorption behaviour of protonated P(DMAEMA) hydrogel (0.05 g) was determined in 24 h contact times for NO_2^- ion for ten different. NO_2^- ion concentrations (75, 150, 200, 250, 500, 1000, 1500, 2000, 2500 3000 and 3500 ppm) and given in Fig. 26. Figure shows that adsorption of nitrite ions increased continuously with increasing initial NO_2^- concentration. Adsorption of NO_2^- ion reached equilibrium after 3000 ppm initial concentration.

Nitrite adsorption isotherm of P(DMAEMA) were analyzed according to the linear form of the Langmuir using the following expression,

$$\frac{C_e}{q_e} = (1/K_L q_{mon}) + (1/q_{mon})C_e$$

where C_e is the equilibrium concentration of hydrogel in solution, q_e represents the adsorbed nitrite ion per unit mass of adsorbent at equilibrium. q_{mon} denotes the amount of adsorption corresponding to complete monolayer coverage. K_L is the Langmuir constant. A plot of C_e/q_e versus C_e would give K_L and q_{mon}

The plot of isotherm is shown in Fig. 27 and seen to be linear over the high concentration range (>500 ppm) studied. K_L and q_{mon} values calculated from Langmuir equation are 2.86×10^{-3} and 3333, respectively.

5.2. Effect of pH on the nitrite adsorption

In order to determine the effect of pH on the adsorption characteristic of hydrogels, adsorption studies were conducted in various concentration HCl solutions, pH 2-7. As can be seen from Fig. 28 NO_2^- ion adsorption property changes strongly depend on the pH of the adsorption solution. Rapidly decrease of adsorption because of the deprotonization of tertiary amine groups and decrease of specific interactions between quarternized amine groups and nitrite ions.

As a conclusion, these results show that P (DMAEMA) hydrogels may be consider as potential adsorbent for the removal of nitrite ions from wastewater and aqueous effluents.

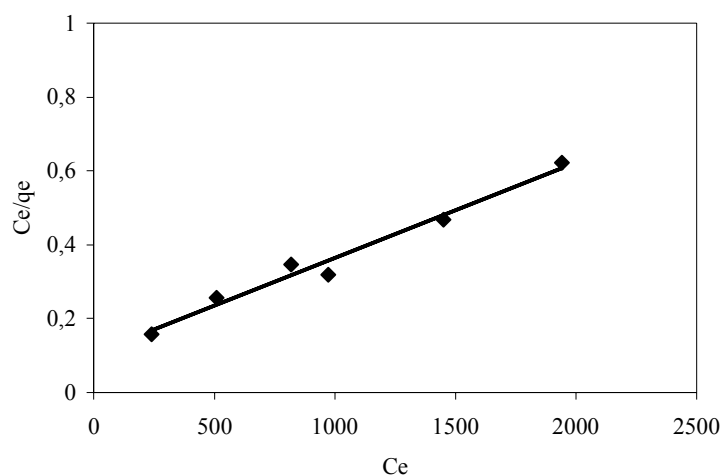


FIG. 27. Langmuir isotherm for nitrite ion adsorption on P(DMAEMA)

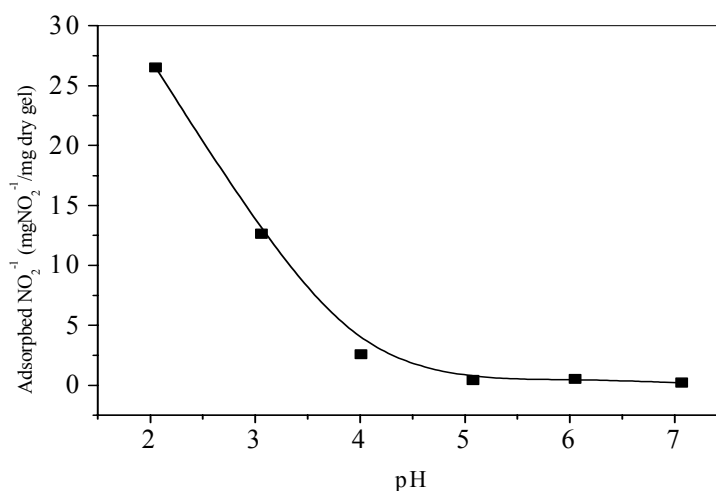


FIG. 28. Effect of pH on nitrite ion adsorption

6. CONCLUSION

In this project, radiation synthesis, characterization of swelling behavior and network structure of poly(N,N-dimethylaminoethyl methacrylate)(P(DMAEMA)), and Poly(N, N-dimethyl aminoethyl methacrylate-co-n-vinyl 2-pyrrolidone)(P(DMAEMA-co-VP)), hydrogels and their use for the separation and enrichment of water pollutants have been investigated.

The influence of irradiation dose, comonomer, VP, and cross-linking agent, EGDMA, content on the total percentage gelation and monomer conversion and the effect of pH and temperature on the swelling behavior of hydrogels have been examined. Hydrogels showed typical pH response and temperature responses, such as low-pH and low temperature swelling and high-pH and high temperature deswelling. Polymer-solvent interaction parameter (χ) and enthalpy and entropy changes appearing in the χ parameter for the P(DMAEMA-co-VP)-water system were determined by using Flory-Rehner theory of swelling equilibrium. The negative values for ΔH and ΔS indicate that prepared pure P(DMAEMA) and P(DMAEMA-co-VP) hydrogels have lower critical solution temperature(LCST) and Flory-Rehner theory of swelling equilibrium provides a satisfactory agreement to the experimental swelling data of the hydrogels.

It was found that the metal ion uptake by P(DMAEMA) hydrogel gradually increased with increasing initial metal ion concentrations and not reaching adsorption equilibria even at 2000 ppm metal ion concentration. The order of adsorption affinity based on the amount of metal ion uptake (mg metal ion/g dry gel) is as follows: Cu(II) > Zn(II) \cong Co(II) > Pb(II) >> Ni(II) > Cd(II). For the removal of nitrite ions from aqueous solutions was investigated by using protonated P(DMAEMA) hydrogels. We have shown that poly-cationic and pendant secondary amine group containing P(DMAEMA) hydrogels is very efficient and highly selective for the removal of nitrite ions from aqueous solutions at even in very high concentrations.

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