# Electron Beam Processed Polyelectrolytes

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Abstract. Comparative results obtained by electron beam induced polymerization of water-soluble monomers at low and high absorbed dose level are presented. At high dose rate levels, the polymerization process is incomplete, monomer conversion decreases, polymer parameters become very sensitive to the chemical composition and variations in absorbed dose level. The effect of high-absorbed dose rate is reduced by the additional introduction of NaCl into acrylamide-acrylic acid aqueous solutions that under irradiation markedly increases conversion coefficient to nearly 100% and decreases residual monomer concentration under 0.01. The process has been demonstrated in a pilot-scale operation.

# 1. Introduction

Radiation induced polymerization is an envolving method which is environmentally friendly and which can produce a wide variety of water-soluble polyelectrolytes.

The *major advantages* of EB induced polymerization are:

*a)* Ease of manipulating the molecular weight from low to very high values by simple changing of the feed composition;

*b)* Precise control of charge density and of molecular weight distribution;

*c)* High production rate: from 500 to 2000 kg · $h^{-1}$ for each kW of electron beam power;

*d)* Mitigation of flammable and toxic solvents with no production of waste matter or evolution of obnoxious gases and no production of hazardous effluents;

*e)* The entire process is very clean and permits to obtain products with very low residual monomer contents that can also be used for potable water applications.

# 2. Methods and Apparatus

The characteristics of the acrylamide-acrylic acid copolymers are influenced by the following factors:

*a)* chemical composition of the solutions to be irradiated, absorbed dose level (D = energy quantity per unit mass in Gy or $J \cdot kg^{-1}$);

*b)* absorbed dose rate level (D* = energy quantity per unit mass and unit time in $Gy \cdot s^{-1}$ or $J \cdot kg^{-1} \cdot s^{-1}$).

Many years of investigations of polymeric material properties demonstrated that EB induced polymerization yields, under proper irradiation conditions and for fixed chemical composition of the monomer mixtures to be irradiated, higher conversion efficiency (near 100%) and lower residual monomer concentration (under 0.01%) than classical polymerization of the acrylamide-acrylic acid aqueous solutions.

The main function of the ionizing radiation in a radiation - initiated polymerization is limited to the primary events, the initiation step which leads to the production of free radicals and to a few specific secondary effects.

The subsequent steps of propagation, termination and chain transfer proceed as in a chemically catalyzed process.

Large dose rates (higher than 0.1 kGy · $s^{-1}$), lead to a decrease in efficiency of the polymerization process because of the dependence of free-radical reactions on the electron beam intensity.

Also, at large dose rates, the copolymer parameters become very sensitive to the chemical composition and variations in absorbed dose level.

Low-radiation doses are required for high process efficiency but high dose rates must be used to promote high production capacities.

Comparative studies at low, medium and high dose rates required three electron accelerators:

I. The *ALIN-10 electron accelerator* (Fig. 1) having 164 W maximum output power (for experiments at low dose rates)
II. The *ALID-7 electron accelerator* (Fig. 2 and Fig. 3) having 780 W maximum output power (for experiments at medium dose rates)
III. *The ILU-6M electron accelerator* (Fig. 4) having 10.8 kW maximum output power (for experiments at high dose rates).

EB irradiation with ALIN-10, ALID-7 and ILU-6M accelerators was performed at 50 Gy · $s^{-1}$, 100 Gy · $s^{-1}$ and 750 Gy · $s^{-1}$ absorbed dose rate, respectively.

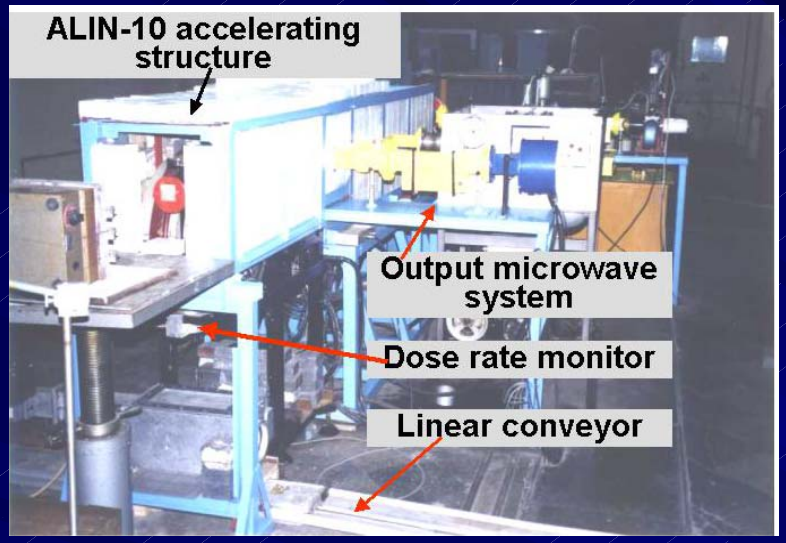



*Fig. 1: ALIN-10 accelerating structure (travelling wave) and microwave system*

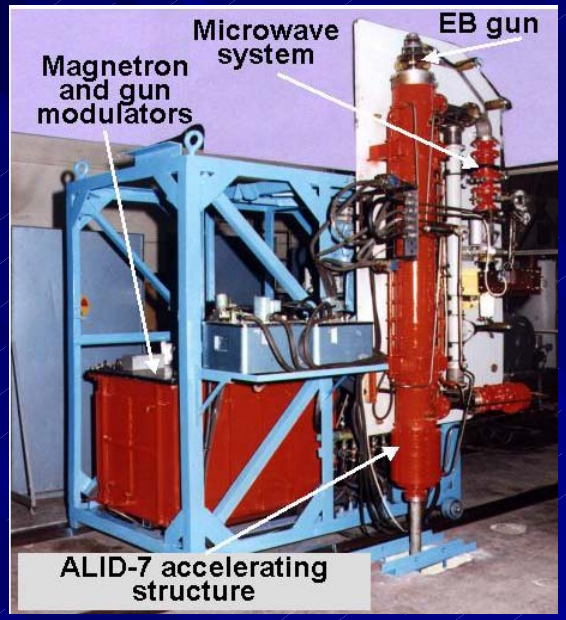
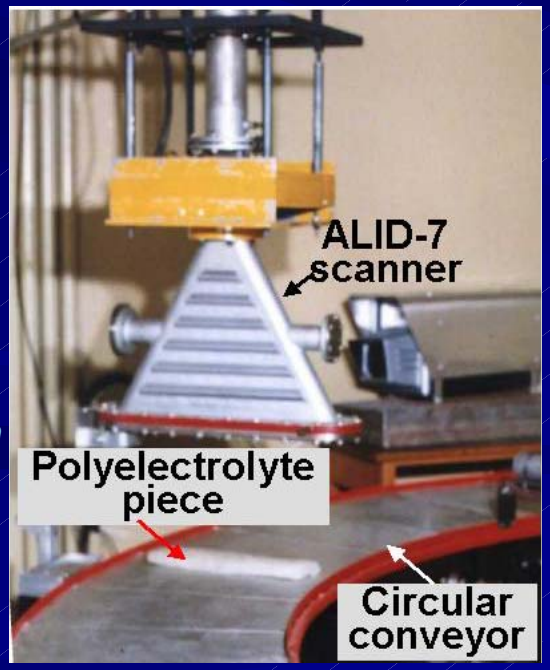



*Fig. 2: ALID-7 accelerating structure (travelling wave), microwave system, gun and modulators*

*Fig. 3: ALID-7 scanner and circular conveyor (325 cm average diameter, 50 cm width)*



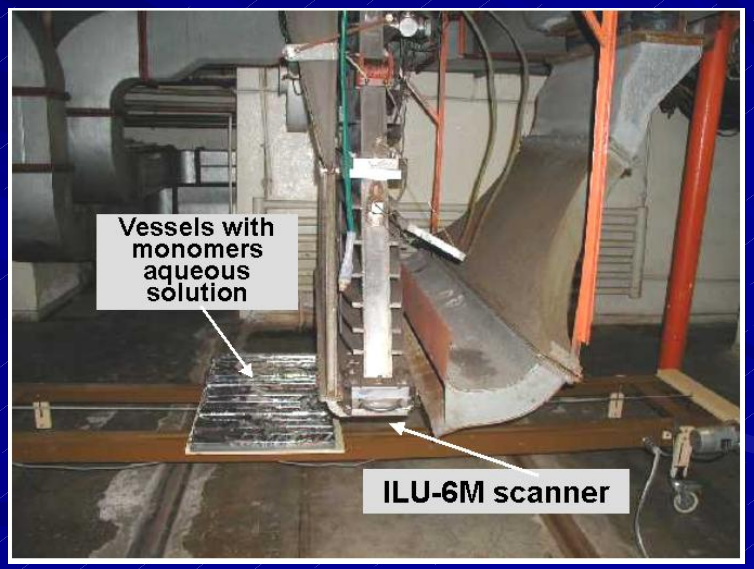




*Fig. 4: The irradiation facility for EB processed polyelectrolytes at pilot -scale. Lateral view of the ILU-6M scanner (1.1 m beam width) and conveyor (surface of the platform: 0.5 m2 to 3 m2)*

# 3. Results

Preparation of polyelectrolytes is based on co-polymerization by EB irradiation of the aqueous solutions containing appropriate mixtures of acrylamide (AMD) and acrylic acid (AA) monomers and certain agents, such as complexing agents (CA) for impurity inhibition, chain transfer agents (CTA) to mitigate cross-linking of the polymer structure, and initiators (I) to optimize the monomer conversion process.

The typical chemical composition of aqueous solutions that were irradiated to produce acrylamide-acrylic acid copolymers is presented in Table 1.

TABLE 1: TYPICAL CHEMICAL COMPOSITION OF THE AQUEOUS SOLUTIONS

| Chemical composition | Characteristics |
|---|---|
| Total monomer concentration, TMC | 30% - 40% |
| Monomer Ratio, AMD/AA | 4/1 - 9/1 |
| Chain transfer agent, CTA (10% solution of sodium formate) concentration | 0.05% - 0.25% |
| Initiator, I (2% solution sodium formate) concentration | 0 -1% |
| Complexing agent, CA (5% solution ethylene diamine tetra acetic acid) conc. | 0.02% - 0.2% |
| NaCl concentration | 0 -8% |

The thickness of the irradiated samples (monomer aqueous solutions) was 23 mm, 20 mm and 6 mm for the experiments with ALIN-10, ALID-7 and ILU-6M, respectively.

*Our interest was focused on the basic optimization of the characteristics involved in waste water treatment, such as conversion coefficient (CC), residual monomer concentration ($M_r$), intrinsic viscosity ($\eta_{intr}$) or average $M_w$ (molecular weight) and a linearity coefficient given by the Huggins' constant ($k_H$).*

The analysis of the experimental results shows that for each chemical composition there is an "optimum" EB absorbed dose ($D_0$) which strongly depends on the absorbed dose rate (D*) level.

- At high dose rate levels the results can be bad: the polymerisation process is incomplete under irradiation and continues after irradiation for an uncontrollable time period.
- At a low value of absorbed dose rate D* of 50 Gy · $s^{-1}$, CC and $\eta_{intr}$ exhibit high values even for a low value, of 600 Gy, of the absorbed dose level. Our experiments demonstrated that only the change of the chemical composition of the monomer aqueous solutions is able to solve this problem. Thus, NaCl addition to the monomer aqueous solutions much improved the polyelectrolyte parameters.

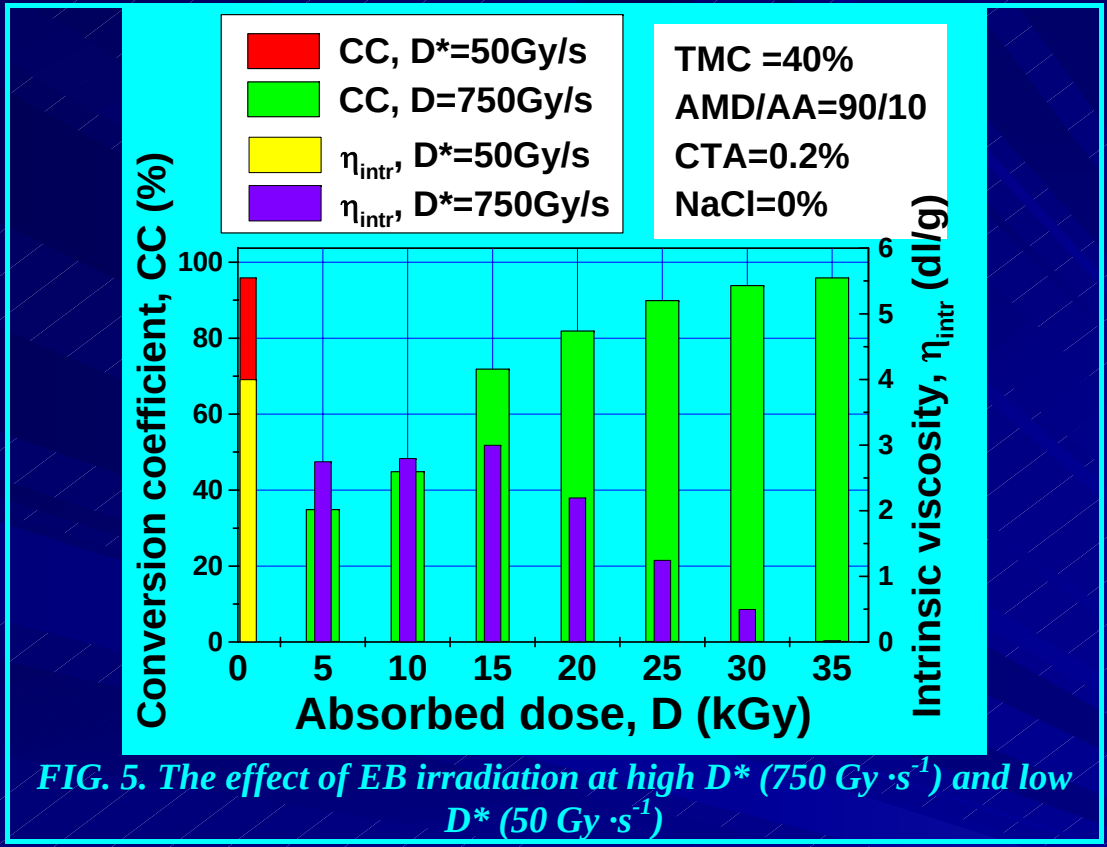



*FIG. 5. The effect of EB irradiation at high D* (750 Gy ·$s^{-1}$) and low D* (50 Gy ·$s^{-1}$)*

At high absorbed dose rate D* of 750 Gy · $s^{-1}$, the conversion coefficient CC obtains high values, over 95%, only for a high absorbed dose level (over 35 kGy), but $\eta_{intr}$ decrease rapidly as a function of absorbed dose D.

Our experiments demonstrated that only the change of the chemical composition of the monomer aqueous solutions is able to solve this problem. Thus, NaCl addition to the monomer aqueous solutions much improved the polyelectrolyte parameters.

Thus, for the increase of NaCl concentration from 4% to 6%, CC rapidly increases (Fig. 6) and $M_r$ rapidly decreases (Fig. 7). At higher NaCl concentrations they vary slowly with NaCl concentration.

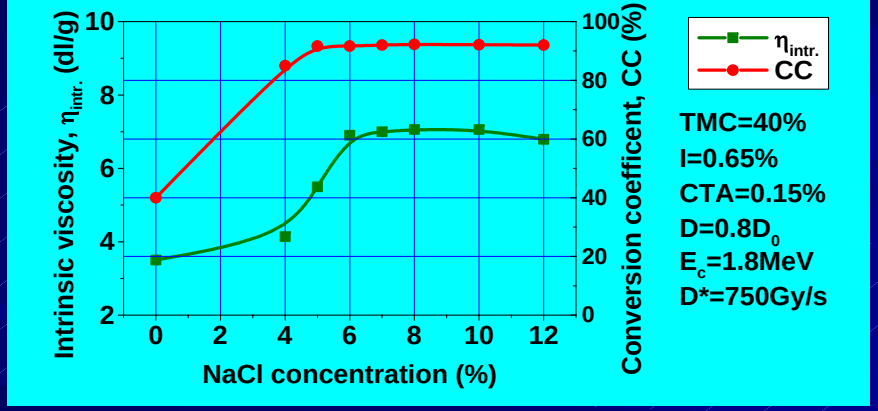



*FIG 6. EB irradiation at high D* (750 Gy ·s$^{-1}$). The effect of NaCl on $\eta_{intr}$ and CC*

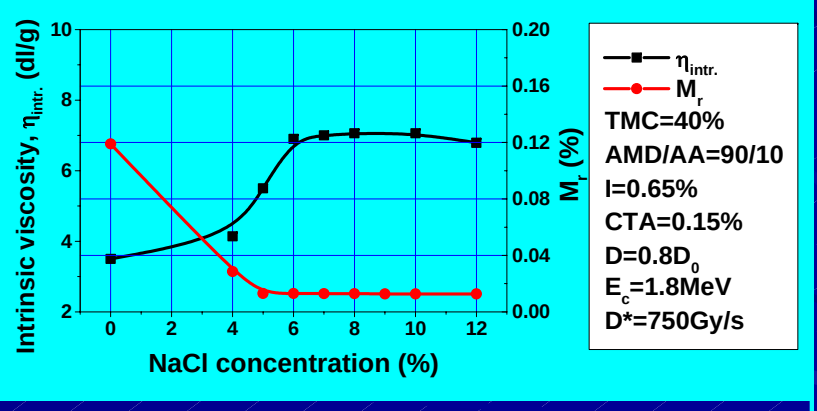



*FIG 7. EB irradiation at high D* (750 Gy ·s$^{-1}$). The effect of NaCl on $\eta_{intr}$ and $M_r$*

For EB irradiation at a low dose rate of 50 Gy · $s^{-1}$, CC and $M_r$ exhibit acceptable values even for zero NaCl concentration, but the additional use of NaCl in the range of 8-10% increases the CC near 99%, decreases $M_r$ under 0.01% and increases the $\eta_{intr}$ level (Figs. 8 and 9).

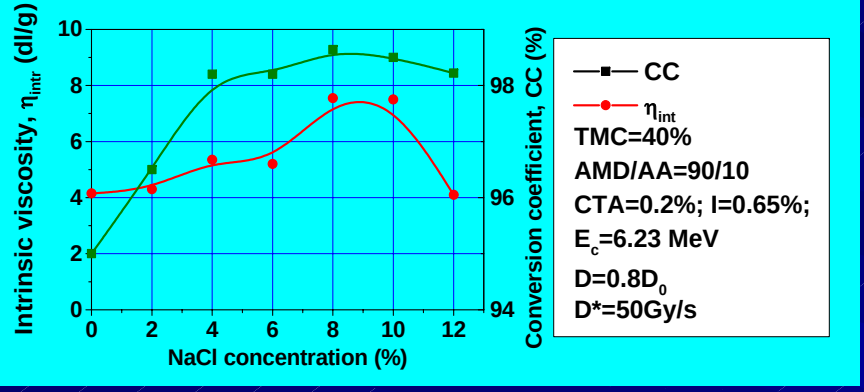



*FIG. 8. EB irradiation at low D* (50 Gy ·$s^{-1}$). The effect of NaCl on $\eta_{intr}$ and CC*

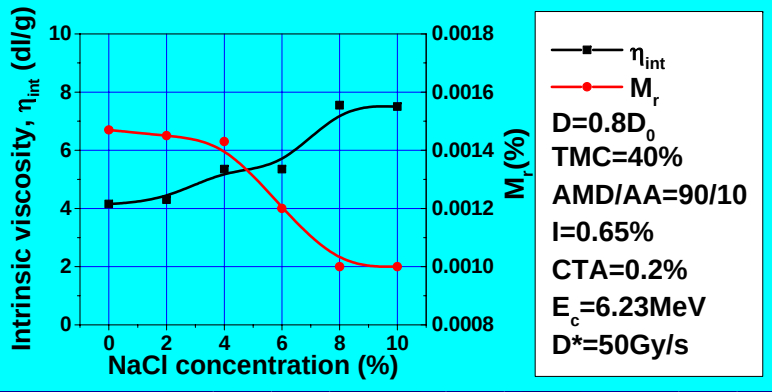



*FIG. 9. EB irradiation at low D* (50 Gy ·$s^{-1}$). The effect of NaCl on $\eta_{intr}$ and $M_r$*

In the final chemical composition, we kept NaCl concentration at 8%.

Besides NaCl, another critical parameters that lead to an increase of CC and a decrease of $M_r$ are: absorbed dose level and initiator concentration.

Figures 10-12 (high D* = 750 kGy/s) and figures 13-15 (low D* = 50 Gy/s) show the effect of the initiator (I) concentration upon $\eta_{intr}$, CC, $M_r$ and $k_H$.

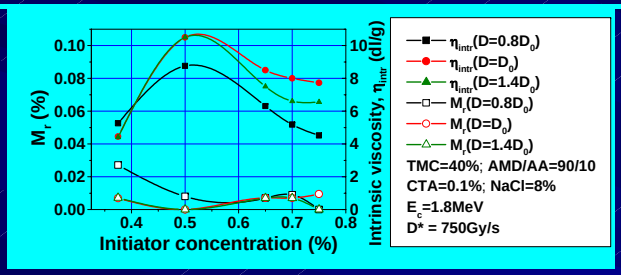



*FIG. 10. Initiator effect on $M_r$ and $\eta_{intr}$ at high D* (750 Gy ·$s^{-1}$)*

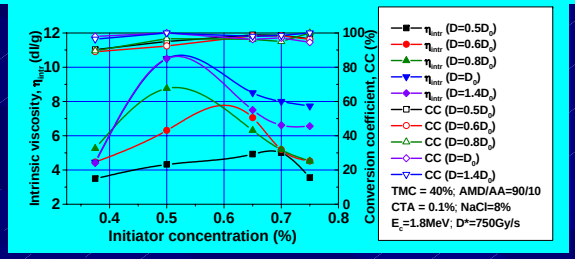



*FIG. 11. Initiator effect on $\eta_{intr}$ and CC at high D* (750 Gy ·$s^{-1}$)*

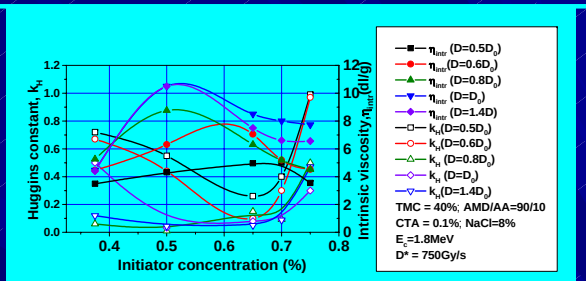



*FIG. 12. Initiator effect on $k_H$ and $\eta_{intr}$ at high D* (750 Gy ·$s^{-1}$)*

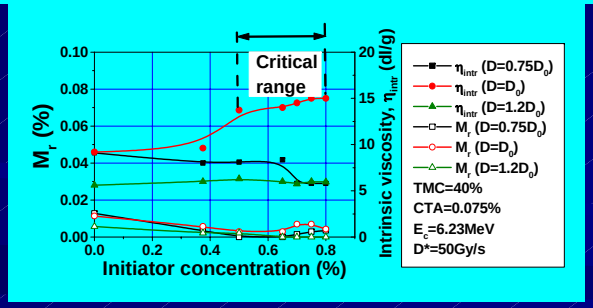



*FIG. 13. Initiator effect on $M_r$ and $\eta_{intr}$ at low D* (50 Gy ·$s^{-1}$)*

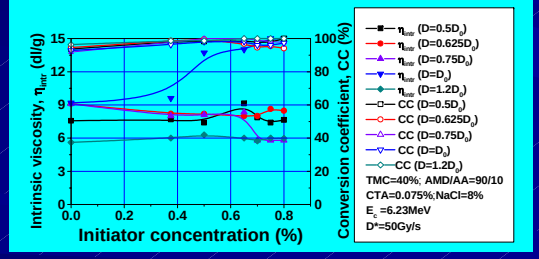



*FIG. 14. Initiator effect on $\eta_{intr}$ and CC at low D* (50 Gy ·$s^{-1}$)*

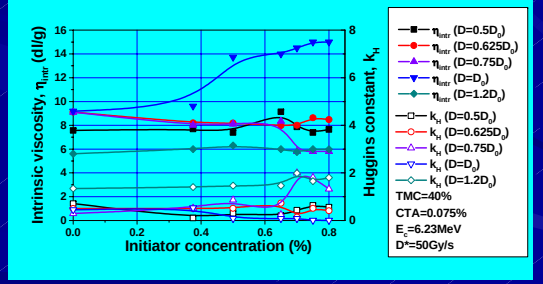



*FIG. 15. Initiator effect on $\eta_{intr}$ and $k_H$ at low D* (50 Gy ·$s^{-1}$)*

Irradiation over the level of the optimum absorbed dose $D_0$ leads to a cross-linked structure in the final product, which becomes water-insoluble ($k_H$ >0.5), and to lower values for $\eta_{intr}$ (Fig. 10 and Fig. 13).

Under irradiation conditions below the $D_0$ level and for solutions containing increased I content, the $M_r$ value decreases (Fig. 10 and Fig. 13) but $k_H$ increases (Fig. 12 and Fig. 15) and leads to the cross-linking effect.

At an optimum absorbed dose $D_0$, as demonstrated in Fig. 10 and Fig. 11, $M_r$ is under 0.01% and CC is near 100%.

$\eta_{intr}$ gradually increases with I concentration in the range of 0.375-0.5%, reaches a maximum for I concentration in the range of 0.5-0.55% and afterwards, decreases with I concentration increase above 0.55%.

At the optimum dose level, the required initiator concentration is greatly diminished and $\eta_{intr}$ is less sensitive to I, as is shown in Fig. 10.

The main conclusion of the above experimental results is: irradiation over the level of the optimum absorbed dose leads to a cross-linking structure of the final product (polyelectrolytes become water insoluble) and irradiation below the level of optimum absorbed dose leads to an unacceptable residual monomer concentration.

Also, the features of an electron accelerator used to produce polyelectrolytes are of special importance to permit efficient power utilisation:

- enough operating mode flexibility and reproducibility;
- adequate beam sweeping over the monomer aqueous solution under irradiation (in order to reduce the dose rate effect as small is possible), optimised operating regime;
- automatic control of the required dose and dose rate;
- automatic control of the conveyor velocity; adequate auxiliary systems for maximum processing rates.

The optimum absorbed dose for the AMD-AA aqueous solution polymerization, established by optimization of chemical composition and EB irradiation conditions, is rather small, of about 1 kGy. This makes the use of electron beam processing very economically attractive in this type of application. Thus, if all auxiliary systems are suitable adapted and automated, the estimation of processing rate for an electron accelerator of 1 kW output power is up to 1800 kg · $h^{-1}$ for an EB utilization factor of 0.5 and absorbed dose D of 1 kGy.

For industrial waste water treatment, the acrylamide - acrylic acid copolymers are used in the range of:

- 4 to 8 g per 1 $m^3$ of waste water;
- 0.1 to 0.2 g per 1 $m^3$ of potable water.

A vegetable oil plant, which processes 100,000,000 kg per year of sunflower oil, produces about 1,260,000 $m^3$ per year waste water. The required quantity of polyelectrolytes for remediation of waste water in this plant is in the range of 5,040-10,080 kg per year.

This quantity can by achieved using this technology in a very short time, from 2.8 h to 5.6 h.

Also, in Romania the required quantity of potable water is 10,000,000 $m^3$ per day that need a polyelectrolyte amount of 1000 to 2000 kg per day.

In many cases, $P_n$ type polyelectrolytes obtained by EB irradiation are used as coagulation aids together with electrolytes $E_m$ ($Al_2(SO_4)_3$, $FeSO_4$ and $Ca(OH)_2$).

In order to provide measurable improvements in water quality we have studied the effects of different classical treatments with electrolytes and the effects of various combined treatments with electrolytes + polyelectrolytes ($E_m$+$P_n$ treatment type).

Also, many polyelectrolytes of $P_n$ type with various characteristics were used. For real waste water treatment the interest was focused upon the following quality indicators established by the Romanian Standard NPTA-002/2002 concerning the conditions for waste water evacuation in the urban sewerage system:

- Total Suspended Solids (TSS in $mg \cdot dm^{-3}$);
- Fatty Matter (FM in $mg \cdot dm^{-3}$);
- Chemical Oxygen Demand (COD in $mgO_2 \cdot dm^{-3}$).

Table II presents the comparative results obtained by classical treatment ($E_m$) and combined treatment ($E_m + P_n$) with waste water samples, which ranged from relatively clean to extremely contaminated, taken from a vegetable oil plant (VOP) and from a slaughter house (SH).

TABLE II: COMPARATIVE RESULTS OBTAINED BY CLASSICAL TREATMENT ($E_M$) AND COMBINED TREATMENT ($E_M+P_M$)

| Treatment type per $dm^3$ of water | Polyelectrolyte characteristics | | | Quality indicator | | |
|---|---|---|---|---|---|---|
| | $M_r$ (%) | $(\eta_{intr})$ (dl/g) | $k_H$ - | TSS ($mg.dm^{-3}$) | FM ($mg.dm^{-3}$) | COD ($mgO_2.dm^{-3}$) |
| Allowed value | - | - | - | 350 | 30 | 300 |
| Raw water: VOP-1 | - | - | - | 2554 | *1816* | 1519 |
| $E_9$: 0.8g $FeSO_4$ + 1g $Ca(OH)_2$ | - | - | - | 46 | *216* | 107 |
| $E_9$+8mg$P_1$ | 0.010 | 4.36 | 0.02 | 32 | *26* | 102 |
| Raw water: VOP-2 | - | - | - | 1214 | *418* | 480 |
| $E_{29}$: 0.5g $Al_2(SO_4)_3$ + 0.5g$Ca(OH)_2$ | - | - | - | 320 | *172* | 101 |
| $E_{29}$+8mg$P_1$ | 0.010 | 4.36 | 0.02 | 12 | *26* | 60 |
| $E_{29}$+8mg$P_2$ | 0.078 | 9.22 | 0.28 | 39 | *30* | 69 |
| Raw water: SH -1 | - | - | - | 920 | *6117* | 256 |
| $E_{10}$: 0.1g $Al_2(SO_4)_3$ + 0.1g$Ca(OH)_2$ | - | - | - | 836 | *5708* | 75 |
| $E_{15}$: 0.1g $FeSO_4$ + 0.1g $Ca(OH)_2$ | - | - | - | 144 | *3196* | 70 |
| $E_{10}$+6mg$P_3$ | 0.010 | 8.91 | 0.27 | 68 | *16* | 33 |
| $E_{10}$+6mg$P_4$ | 0.010 | 9.74 | 0.08 | 58 | *28* | 31 |
| $E_{10}$+6mg$P_5$ | 0.008 | 11.64 | 0.2 | 88 | *18* | 30 |
| $E_{10}$+6mg$P_6$ | 0.006 | 10.24 | 0.11 | 36 | *20* | 29 |
| $E_{15}$+6mg$P_3$ | 0.010 | 8.91 | 0.27 | 68 | *16* | 28 |
| $E_{15}$+6mg$P_4$ | 0.010 | 9.74 | 0.08 | 64 | *12* | 30 |
| $E_{15}$+6mg$P_5$ | 0.008 | 11.64 | 0.2 | 48 | *32* | 26 |
| $E_{15}$+6mg$P_6$ | 0.006 | 10.24 | 0.11 | 60 | *28* | 39 |

The most important conclusion is the following: for each waste water type there is a certain combined treatment, based upon a certain polyelectrolyte $P_n$, which leads to a considerable decreasing of the "fatty matter" indicator as compared with classical treatments. There are no classical treatments that have the ability to reduce the fatty matter under the level of 30 mg · $dm^{-3}$, established by Romanian Standard NTPA-002/2002. Also, there are many combined treatments, as are shown in Table II, which give smaller values for the TSS and COD indicators than the classical treatments.

# 4. Conclusions

The EB absorbed dose rate level is very important. At high dose rate levels, the polymerization process is incomplete, monomer conversion decreases, polymer parameters become very sensitive to the chemical composition and variations in absorbed dose level. The effect of high-absorbed dose rate is reduced by the additional introduction of NaCl into acrylamide-acrylic acid aqueous solutions that under irradiation markedly increases conversion coefficient to nearly 100% and decreases residual monomer concentration under 0.01%. Because the optimum absorbed dose for the acrylamide-acrylic acid aqueous solution polymerization is rather small, about 1 kGy, the use of electron accelerators is economically attractive for commercial production of the polyelectrolytes, if all auxiliary systems are made and suitably adapted. The estimation of processing rate is up to 1800 kg · $h^{-1}$ for an electron beam power of 1 kW and for an EB power utilization factor of 0.5.

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