Use of Electron Beam in Pre-irradiation Grafting for Preparation of Ion Exchange Membrane and Application

Speaker: Jianhua Zu

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Shanghai Applied Radiation Institute, Shanghai University, Shanghai, 201800, China

- Applications for radiation processing of materials

- Introduction of radiation induced grafting and its application

- Our work on the preparation of cation exchange membrane by pre-irradiation method

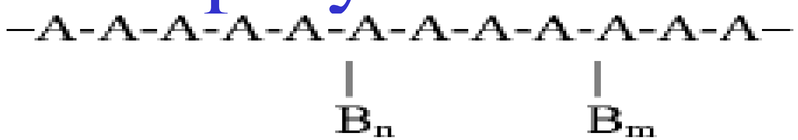
Applications for radiation processing of materials

- The physical and chemical properties of polymeric materials can be modified by treatment with ionizing radiation in the form of gamma rays, X-rays and electron beams

- Polymerizing (curing), grafting, crosslinking and chain scissioning reactions can be initiated by irradiation

Introduction of radiation induced grafting

- Graft copolymerization



- Radiation-induced graft polymerization
  - Simultaneous irradiation method
  - Pre-irradiation method

The pre-irradiation method has been given much attention because the homopolymer formation is little and the grafting can be carried out at any time.

Application of radiation induced grafting

- **Separation processes**

  Dialysis and electrodialysis
- **Energy conversion applications**

  Used as battery separator and solid polymer electrolytes
- **Solid-state applications**

  Sensors and ion selective electrodes
- **Biomedical and biological applications**

  Fixation of biological components
- **Environmental applications**

  Removal of heavy metals
- Miscellaneous applications

  Catalysis

Our work on the preparation of cation exchange membrane by pre-irradiation method

Introduction

- Many studies have been published on grafting of a weak acid onto polyemer membranes
- Only a few on the grafting of a strong acid such as sulphonic acid
- Ion-exchange membranes bearing sulphonic acid groups are prepared by two-step grafting method because of the incompatibility between the highly ionized sulphonic acid groups with its hydration sphere and the polymer backbone
- We used one step pre-irradiation grafting method to prepare cation-exchange membranes containing $–SO_3Na$ and $–COOH$ groups

Grafting procedure

- HDPE membranes were washed with acetone and dried in a vacuum oven at 50℃

- HDPE membranes were irradiated using electron beams from accelerator

- The reaction was carried out in the temperature-controlled bath

- grafted membranes were washed, dried and weighted

Measure of the overall grafting yield (G_t) and grafting yield of SSS onto HDPE (G_s)

$$G_t = (W_g - W_0) / W_0 \times 100\%$$

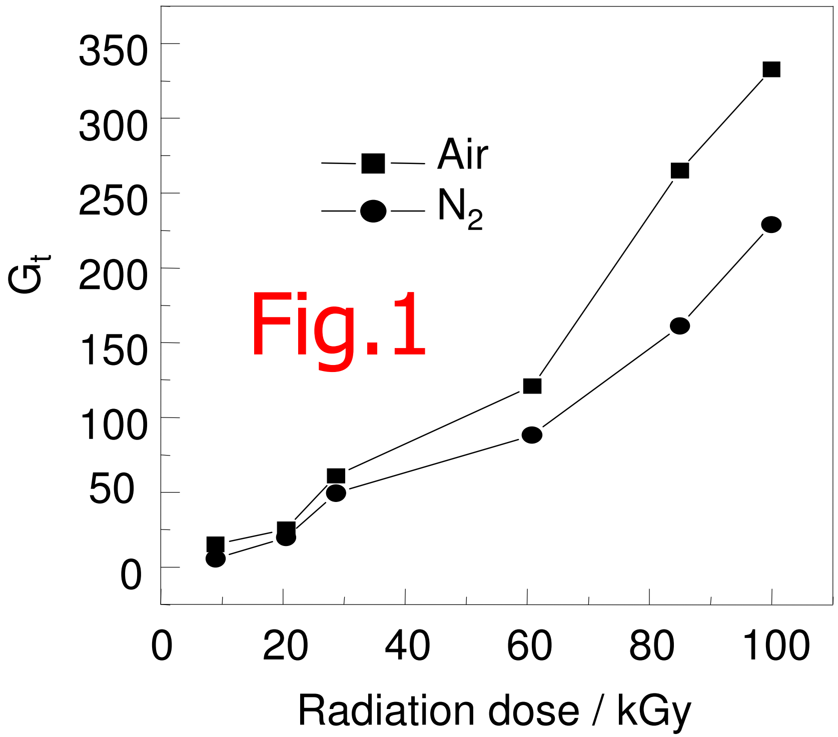
W_g : weight of grafted HDPE, W_o : weight of ungrafted HDPE

$$G_S = \frac{C_{NaOH} \cdot V_{NaOH} \cdot 206}{1000 \cdot W_0} \times 100\%$$

- C_{NaOH}: the concentration of NaOH (mol/L) V_{NaOH}: the volume of NaOH (ml)

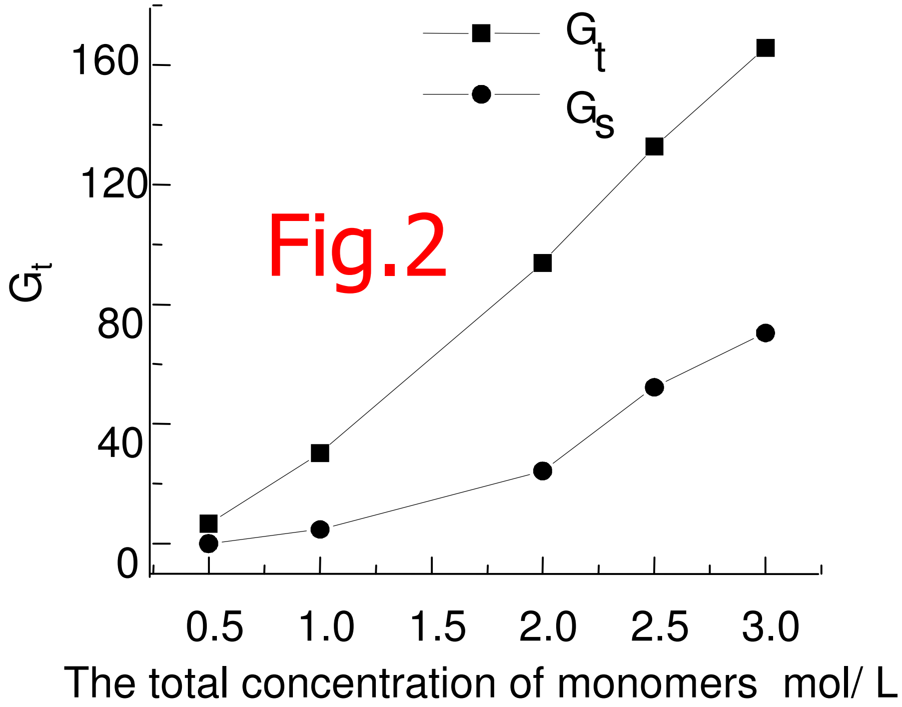
Results and discussion

➢Effect of radiation dose on grafting yield at different irradiation atmosphere



Total concentration: 3mol·L^{-1}, Grafting time: 15h, Molar ratio of SSS:AA: 1:2, Grafting temperature: 70℃

Effect of monomers concentration on the grafting yield



Total concentration: 2mol·L^{-1}, Molar ratio of SSS: AA: 1:2, Grafting temperature: 40ºC, Grafting time: 10h

Relationship between grafting yield and storage time

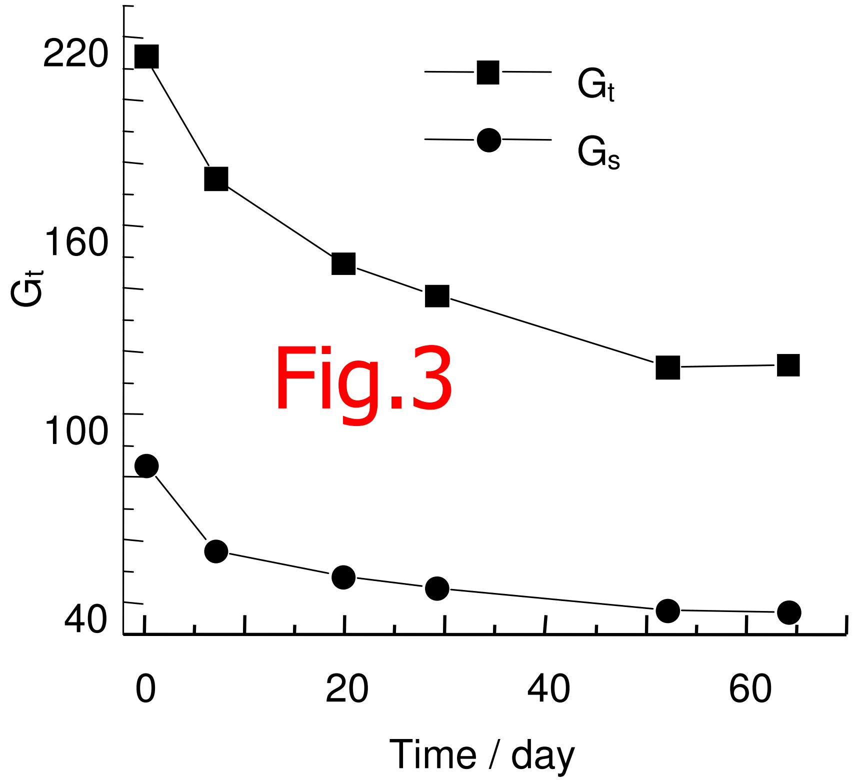
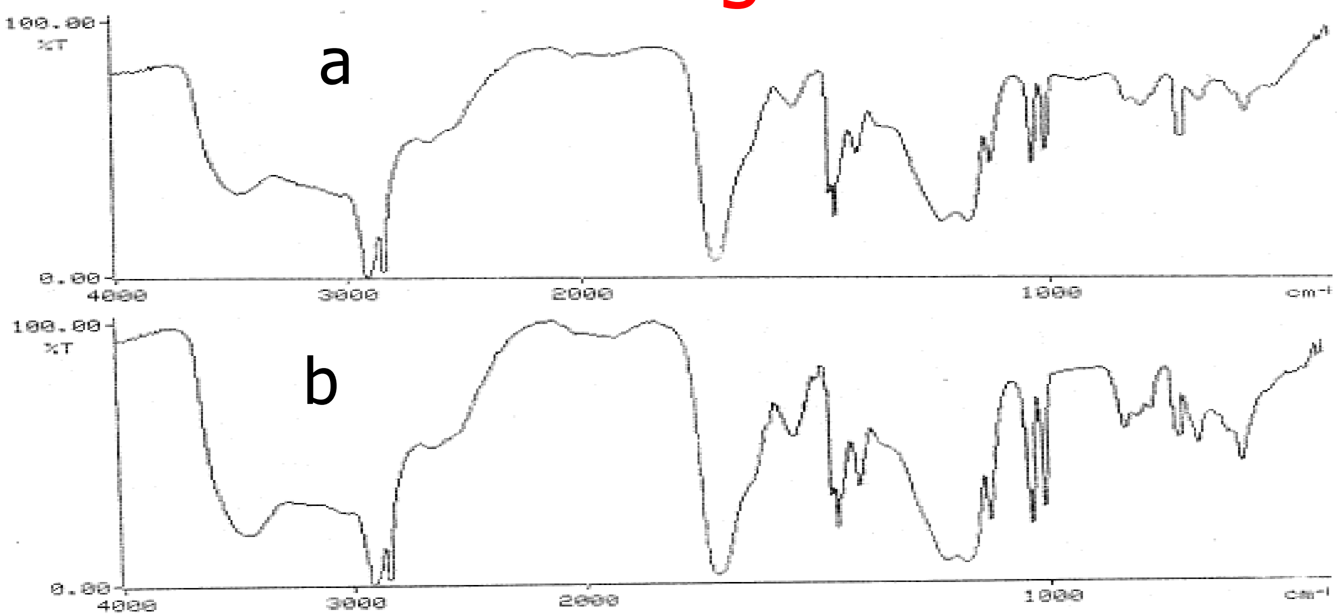


Fig.3

Total concentration: 3mol·L^{-1}, Grafting time: 30h, Molar ratio of SSS:AA: 1:2, Grafting temperature: 25℃, HDPE stored temperature: -4℃

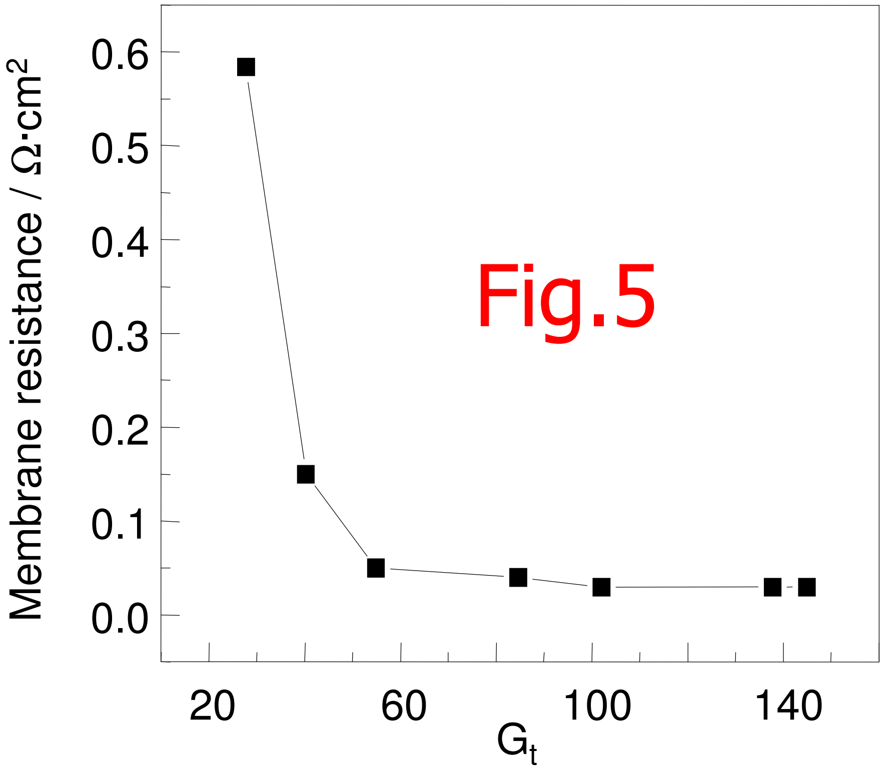
Grafted membrane Identification

Fig.4



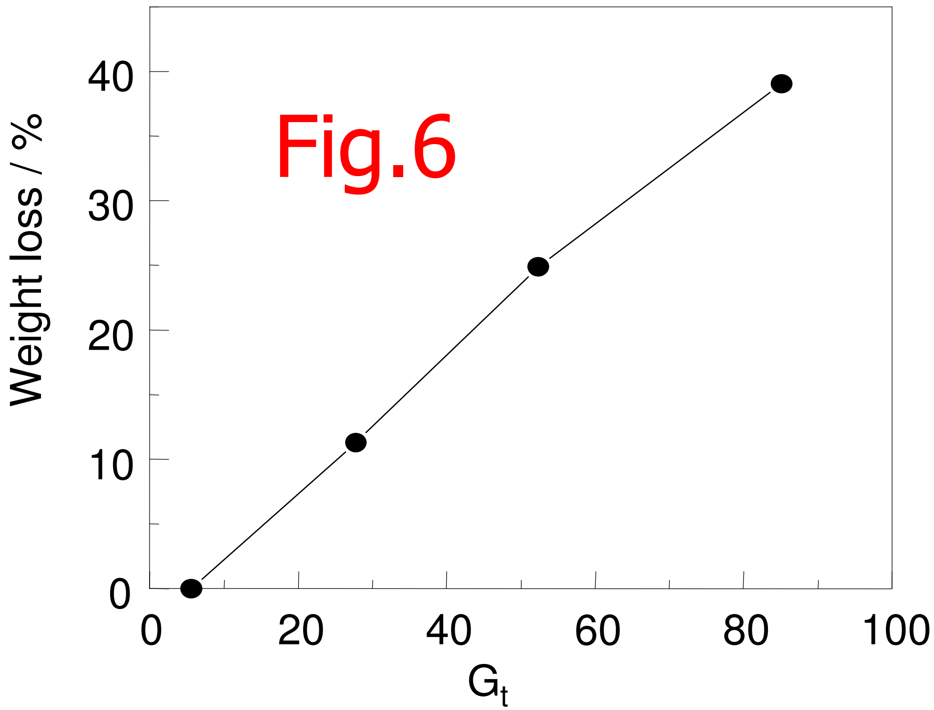
IR spectra of (a) without grafting HDPE; (b) grafted membrane, G_t=27.8%, G_s=4.5 %

Membrane resistance



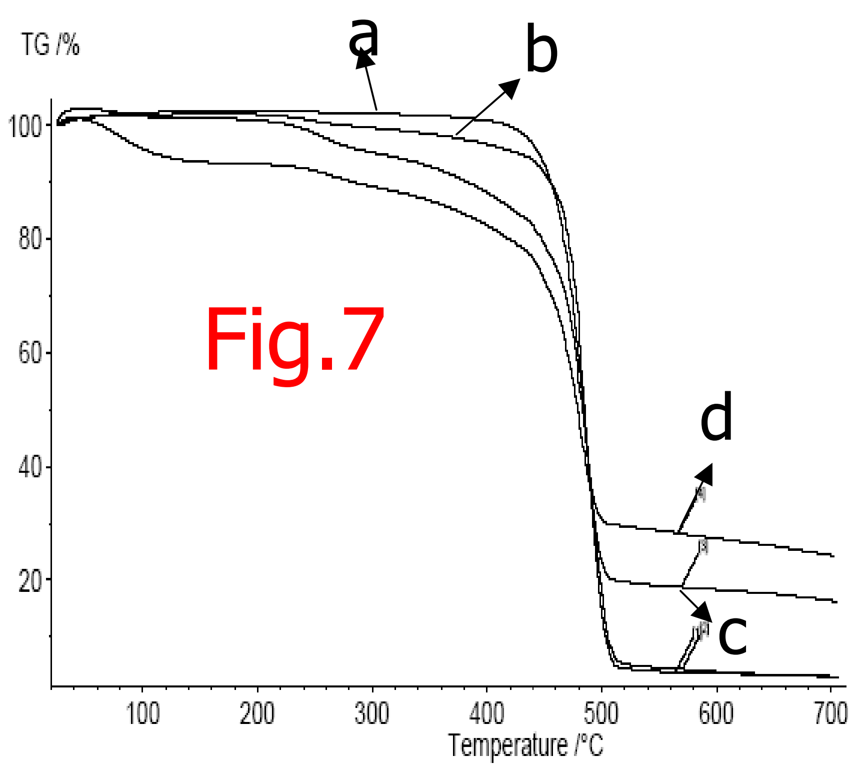
Electric resistance vs. G_t

Chemical Stability of grafted membranes



The grafted membrane were dipped in 3% H_2O_2 solution (Fe^{2+}, 4ppm) at 70 ℃ for 5h

Thermogravimetric Analysis of grafted membrane



TGA thermograms of ungraftd HDPE and grafted HDPE with different grafting yield

a: ungraftd HDPE; b: G_t =12.5%, G_s= 1.3%; c: G_t =72.8%, G_s= 17.8%; d: G_t =155.1%, G_s= 60.7%

Differential scanning calorimetry analysis

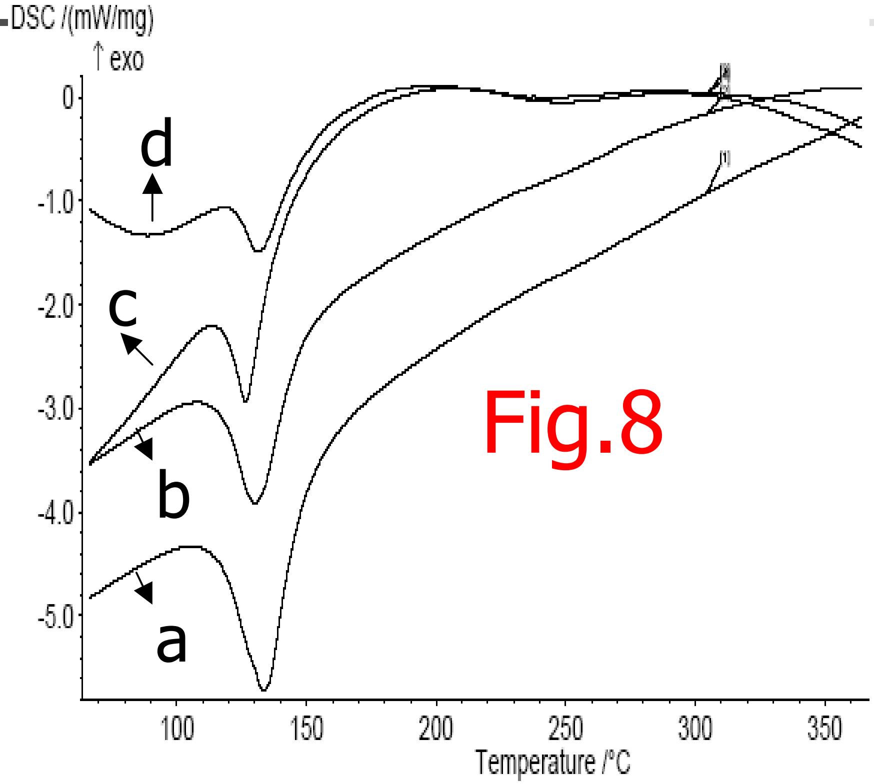


Fig.8

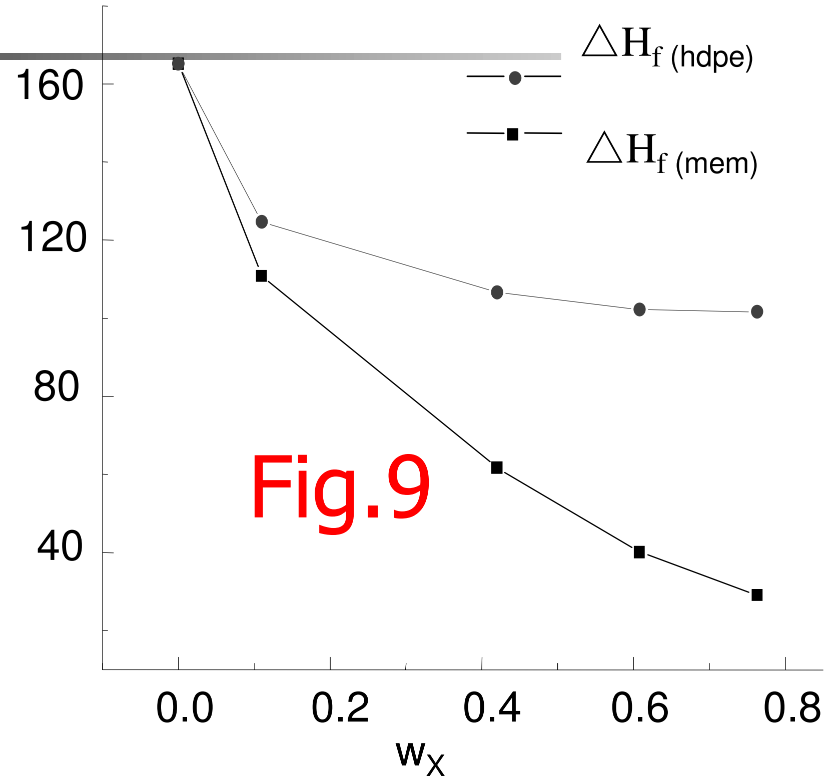
a: ungraftd HDPE

b: G_t =12.5%

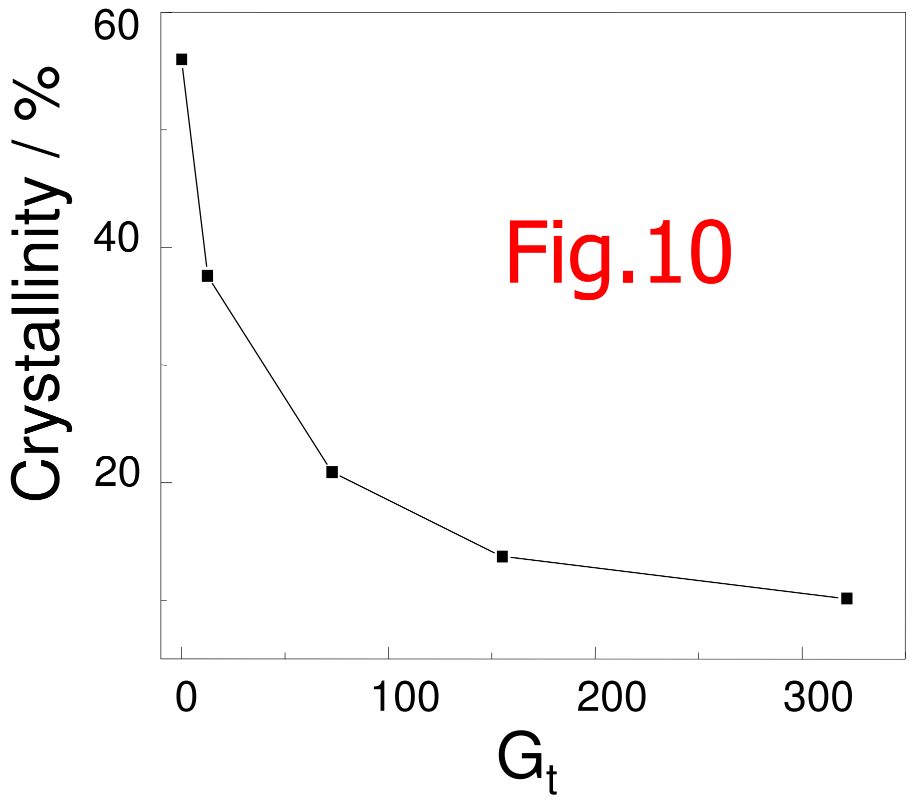
c: G_t =72.8%

d: G_t =155.1%

DSC thermograms of ungraftd HDPE and grafted HDPE with different grafting yield



Variation of heat of fusion with W_x in membranes



Variation of crystallinity with G_t

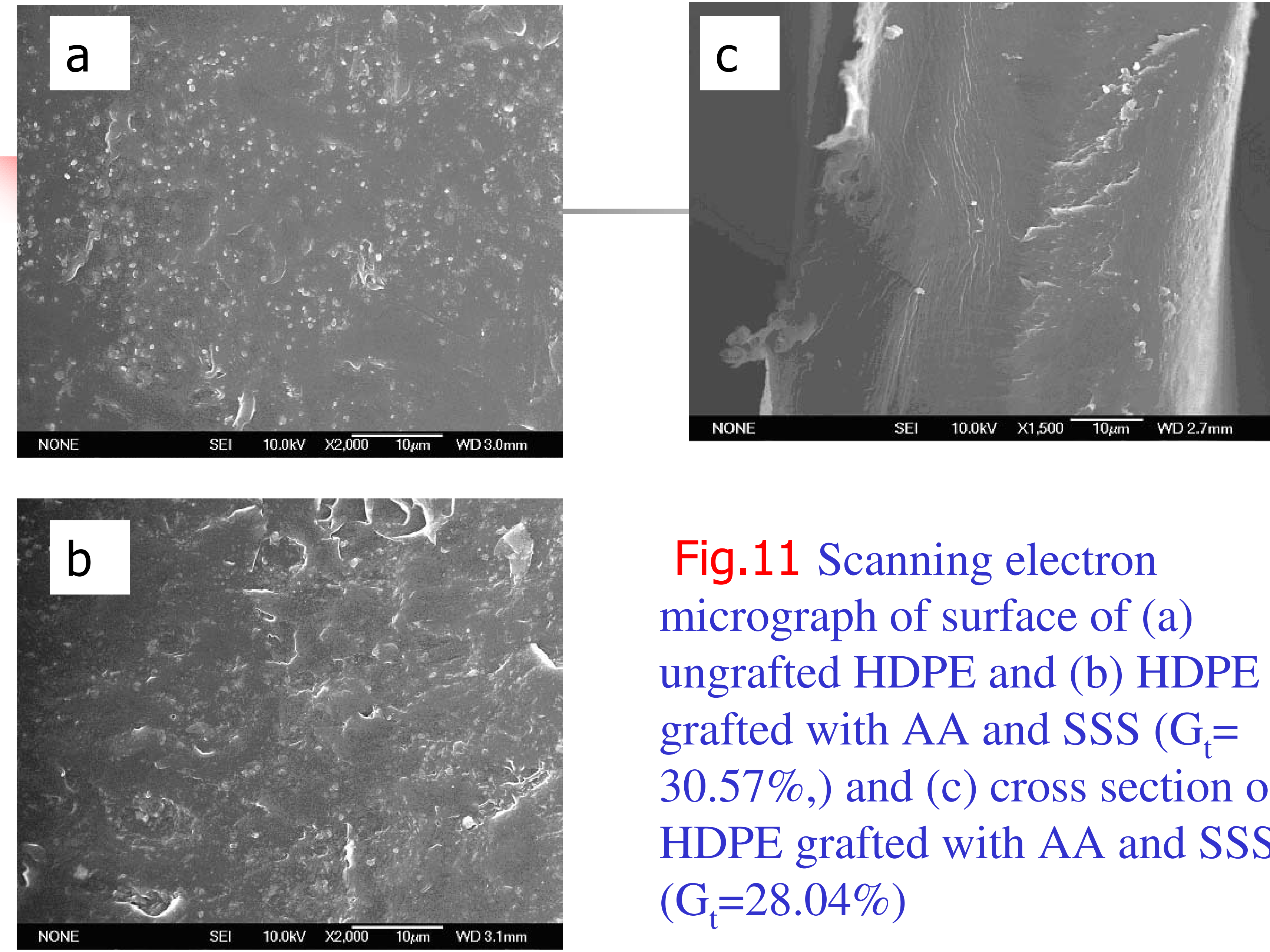


Fig.11 Scanning electron micrograph of surface of (a) ungrafted HDPE and (b) HDPE grafted with AA and SSS (G_t= 30.57%,) and (c) cross section of HDPE grafted with AA and SSS (G_t=28.04%)

Conclusion

- We have investigated the radiation-induced grafting of sodium styrene sulfonate and acrylic acid into the HDPE using the pre-irradiation method. The grafting yield increases with the increase of total concentration of monomers at a range of 0.5-3mol/L. Radicals formed by pre-irradiation of HDPE is stable at temperature below -4℃, so we can once irradiate a bulk of HDPE membranes and stored them at low temperature before carrying out grafting. High temperature is suitable for obtaining high grafting yield When HDPE irradiated at air atmosphere.

- The resistance of the grafting membranes decrease with the increase of grafting yields, then reach stable to the value 0.03-0.04 $\Omega \cdot cm^2$. This low value is favorable for using as battery separator to discharge at large current.

- The anti-oxidation property of the ion-exchange membranes increase after the introduction of sulfonate groups. Anti-oxidation property as well as low resistance is of importance. Due to the particular environment of membranes in fuel cell, membranes must have high oxidative stability.

Current status of radiation grafted ion membranes

- The contribution of membranes made by radiation graft copolymerization techniques to main production of membranes prepared by conventional techniques is relatively small. This may be attributed to general reasons such as:

A. limited access of irradiation facilities among membrane workers due to their ownership by governmental institutions in most countries.

B. captivity of irradiation facilities to com-mercial routine work.

C. high cost of irradiation facilities required for mass production and lack of knowledge on radiation graft copolymerization among membrane researchers and manufacturers.

- Today there is a number of commercial companies that produces radiation grafted ion exchange mem-branes of different types for various applications

Pall-RAI (USA), Asahi ; Chlorine Engineers (Japan) De Morgan (France)

- Since 1990 HDPE-g-acrylic acid membranes have produced in Shanghai Applied Physics institute where I mainly occupied on the preparation of membrane containing –SO_3H during 1996-2002.

HDPE-g-acrylic acid membranes which are used as battery separator have produced in Shanghai Applied Physics institute since 1990

High-frequency and high-voltage electron accelerator in our institute

Control system

Steel canister

Beam energy 2.0Mev; Max. beam power 20kW; Beam current 10mA

The equipment for radiation of wire and cable

Thanks for your attention