Vol.16 No.1 NUCLEAR SCIENCE AND TECHNIQUES February 2005

Study of radiation-induced grafting of acrylic acid-sodium styrene sulfonate onto poly (tetrafluoroethylene–co-hexafluoropropylene) film

WANG Heng-Dong, YE Yin, ZHANG Xue-Bing, QIU Shi-Long

(Shanghai Institute of Applied Physics, the Chinese Academy of Sciences, Shanghai 201800)

Abstract Poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) films were immersed in aqueous solution of acrylic acid (AA) and sodium styrene sulfonate (SSS), then irradiated by ^{60}Co γ-rays at 25℃. The effects of reaction time，absorbed dose, dose-rate, inhibitor and monomer concentration on the grafting yield were studied. Grafting yields of both AA and SSS onto FEP, respectively, increase with irradiation dose, but some saturation will appear at high dose and monomer concentration. The grafting yield increases with reaction time and then levels off. The grafting of SSS onto FEP is more difficult than the grafting of AA. The analysis of grafted membranes using DSC and FT-IR have been done.

Keywords Poly(tetrafluoroethylene-co-hexafluoropropylene), Radiation-induced grafting, Sodium styrene sulfonate

CLC numbers O631.3$^+$4, O621.3$^+$92

1 Introduction

Graft copolymerization is a well-known method for modifying the chemical and physical properties of polymeric materials. It can be achieved by ionizing radiation, ultraviolet light or chemical initiators. Of these, radiation grafting is one of the most promising methods because of its deep penetration in polymer matrix and uniform formation of active sites for initiating grafting throughout the matrix, and the modification of polymers can be accomplished not only on the surface but also throughout the interior phase of polymers.

At present, radiation grafted sulfonic acid membranes have become an attractive material for electrochemical applications such as water electrolyte and polymer electrolyte fuel cells due to their potential to replace the highly expensive commercial membranes such as Nafion®.[1-3] This was also prompted by the low cost and the versatility of the radiation induced grafting method employed in their preparation.[4-5] These membranes are commonly prepared by radiation grafting of styrene or its derivatives onto various fluorinated polymer films followed by sulfonation.[6-9]

Functionalization of FEP grafted SSS can activate the grafted films chemically and convert them to ion conductive membranes. Scherer has used in particular commercially available films of FEP as the base polymer for the synthesis of sulfonated proton exchange membranes with very promising results[5]. But direct graft polymerization of the vinyl sulfonate onto FEP film is very difficult, because -SO_3^- groups of SSS with their hydration sphere are incompatible with hydrophobic FEP and can not diffuse into the FEP bulk. In this study, we introduce a binary mixture system, realizing the co-grafting of SSS and AA onto FEP. When AA was grafted onto FEP and the hydrophilicity of films increased, SSS could be grafted onto FEP. So the sulfonic groups were easily introduced onto FEP by a one-step method.

Supported partially by Exploration Project of Knowledge Innovation Program of the Chinese Academy of Sciences (No.55180219).

Received date: 2004-06-29

2 Experimental

2.1 Materials

The FEP films were supplied by Shanghai Institute of Plastic Research. The SSS was obtained from Zibo Zhongtian Chemical Co. LTD and used without any further purification. AA was provided by Gaoqiao Chemical Plant and purified by vacuum distillation.

2.2 Grafting procedure

FEP films were put together with polypropylene nonwoven cloth and rolled into cylinders using glass stick as axes, then immersed in the monomer solution which was prepared at the given concentration of monomers and inhibitor and deaerated by bubbling nitrogen. Then the sample was irradiated at 25℃ for a given time. After irradiation to a certain dose, grafted films were taken out from the glass tubes and washed thoroughly with hot distilled water, then soaked overnight to extract the residual monomers and the homopolymer in the films. After being dried in vacuum oven at 50℃ till a constant weight, the films were weighed. The overall grafting yield (G_t) was defined as:

$$G_t = \frac{W_g - W_0}{W_0} \times 100\%$$

where W_0 and W_g are the weights of FEP films before and after radiation-induced grafting, respectively.

2.3 Calculation of grafting yield of SSS onto FEP (G_s)

The grafted films were immersed in 1 mol/L HCl solution, at the same time $-SO_3Na$ was transformed into $-SO_3H$. After being taken out and washed with distilled water until a pH of 7.0, the films were immersed in 5% NaCl solution for 24 hours. The replaced H^+ was titrated with standard NaOH solution. G_s can be calculated according to the equation:

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

where C_{NaOH} is the concentration of NaOH (mol/L), V_{NaOH} is the volume of NaOH (mL).

In this process, the ionization of —COOH can be ignored. Because AA is a mild acid, the H^+ coming from the strong acid group $-SO_3H$ can restrain the ionization of —COOH.

2.4 DSC and IR analysis

The grafted membranes were tested by an FTIR spectrometer (Thermo Nicolet, AVATAR 370 FT-IR). The spectra were analyzed using commercial software (Omnic 6.1a, Thermo Nicolet Corporation 1992-2001). Differential scanning calorimetry (DSC) was performed on membranes having various degrees of grafting as well as the original FEP film sample. And DSC runs were carried out with a typical sample weight of about 10 mg using DSC822^e (Produced by METTLER TOLEDO) in a temperature range of -100～350℃ at a constant heating rate of 20℃/min and under nitrogen atmosphere.

3 Results and discussion

3.1 Effect of inhibitor concentration on grafting yield

In the process of radiation grafting copolymerization, inhibitor is added into the reaction system for restraining the copolymerization of monomers and increasing the using percentage of monomers. In this experiment, $Cu(CH_3COO)_2$ was used as inhibitor. Fig.1 shows the effect of inhibitor concentration on the grafting yield. It is obvious that the grafting yield decreases with the increasing of $Cu(CH_3COO)_2$ concentration under the same reaction condition. Subsequently the grafting yield can reach a lower levels when the concentration of $Cu(CH_3COO)_2$ is more than 0.5%.

The decrease of grafting yield with an increasing of $Cu(CH_3COO)_2$ concentration can be explained by the reaction:

$$Cu^{2+} + -R^{\bullet} \rightarrow -R^{+} + Cu^{+}$$

where $-R^{\bullet}$ is the growing chain radical.

This reaction suggests that a part of the growing chain radicals ($-R^{\bullet}$) was deactivated by reacting with Cu^{2+}. And at the same time, Cu^{2+} can also make the monomer radicals and active particles to be deactivated, for example, $Cu^{2+} + H^{\bullet} \rightarrow H^{+} + Cu^{+}$. The amount of active particles and free radicals determined the amount of reaction product. So introducing

$Cu(CH_3COO)_2$ can decrease the grafting yields and the homo-polymerization of the monomers.

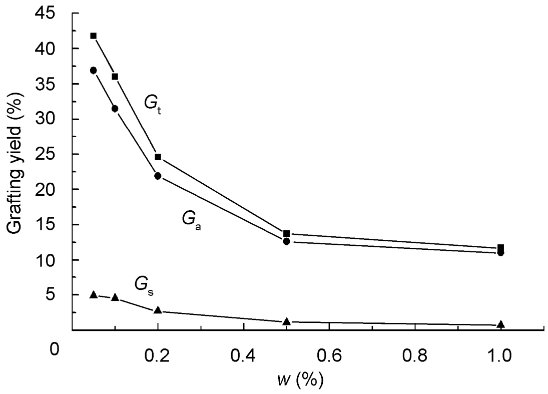

Fig.1 Effect of $Cu(CH_3COO)_2$ concentration *w* on grafting yield (G_t: overall grafting yield; G_s: grafting yield of SSS onto FEP; G_a: grafting yield of AA onto FEP; G_t=G_s+G_a).
Absorbed dose: 20kGy; AA concentration: 3.0 mol/L; SSS concentration: 1.5 mol/L; Inhibitor: $Cu(CH_3COO)_2$; Reaction time: 16.5 h.

3.2 Effect of absorbed dose and dose-rate on grafting yield

Number and length of the grafted branches formed in the direct grafting method are determined respectively by dose and by dose-rate. In this study, though the system of monomers is a binary mixture one, the influence of absorbed dose in this grafting reaction is just like in a common grafting reaction.

The influence of absorbed dose in the grafting reaction is illustrated in Fig.2. It shows that all the grafting yields including G_t, G_s and G_a are almost linear with absorbed dose at the beginning, because the rate of grafting reaction is controlled by the number of "active sites" in polymer created by irradiation. Then the reaction becomes controlled by the rate of diffusion of monomers into polymer when the rate of the graft copolymerization is comparable to or exceeds the rate of diffusion of monomers. Finally the grafting yield does not change obviously with the absorbed dose due to high viscosity of the reaction system caused by homo-polymerization of the monomers. Compared with SSS, the grafting yield of AA is higher and easy to be affected by the change of absorbed dose. Because the monomer SSS has a strong hydrophilic group and bigger size than AA, the appetency for "active sites" in hydrophobic polymer FEP of SSS is weaker than AA.

The dose-rate, which determines the rate of initiation of the polymerization of monomers, may further affect the yield of grafting. The dose-rate will necessarily affect the kinetic chain length and consequently the length of the grafted branches, provided the latter is not controlled by other factors such as, chain transfer. Consequently, an increase in the dose-rate may favour the grafting process with respect to homo-polymerization and thus increase the grafting yield. Fig.3 shows the effect of dose-rate on grafting yields. It illustrates that the grafting yields including G_t, G_s and G_a decrease with the increase of dose-rate.

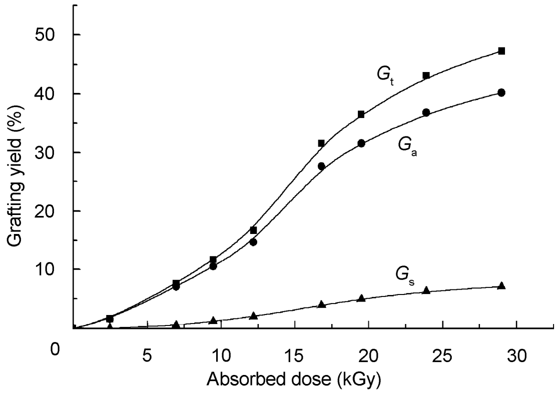

Fig.2 Effect of absorbed dose on grafting yield.
AA concentration: 3.0 mol/L; SSS concentration: 1.0 mol/L; $Cu(CH_3COO)_2$ concentration *w*: 0.1%; Dose-rate: 0.43 kGy/h.

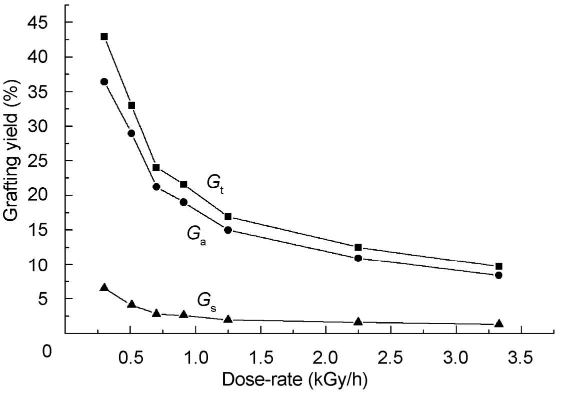

Fig.3 Effect of dose-rate on grafting yield.
Absorbed dose: 20kGy; AA concentration: 3.0mol/L; SSS concentration: 1.0mol/L; $Cu(CH_3COO)_2$ concentration *w*: 0.1%.

As discussed above, the grafting reaction is controlled by the rate of diffusion of monomers for a high dose of 20 kGy. The long irradiation time or lower dose-rate make that the rate of polymerization of monomers is not too high with respect to the rate of diffusion of monomers, more monomers will diffuse through the superficially grafted layer during the irradiation treatment and thus to be grafted onto a deeper, ungrafted polymer zone. That is to say, the decrease in the dose-rate and the increase in the irradiation time favour the increase of grafting yield under the same absorbed dose.

3.3 Effect of film thickness on grafting yield

According to the definition of grafting yield, we know that grafting yield is determined by weight of the original FEP film. The weight is mainly determined by thickness, area and density of the film. Fig.4 shows the effect of the film thickness on grafting yield. It is obvious that the grafting yields decrease with the increasing of the thickness of FEP film. All the grafted films have the same area and density before grafting. So the weight of the film is determined by the thickness only. With the increasing of thickness of the FEP film, the grafting yields decrease.

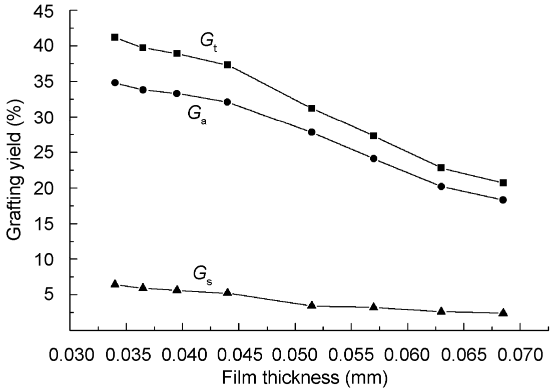

Fig.4 Effect of the film thickness on grafting yield.
Absorbed dose: 20kGy; AA concentration: 3.0mol/L; SSS concentration: 1.0mol/L; $Cu(CH_3COO)_2$ concentration *w*: 0.1%; Reaction time: 16.5h; Film area: 90cm^2.

But results of the grafting experiment also indicate that the grafting quantities onto FEP film are hardly affected by thickness of FEP film. Under the same reaction condition, all grafted films with the same area have approximate grafting quantities. This means that the quantities of grafted copolymer per unit area are nearly equal because the grafting reaction is mainly controlled by monomer diffusion rate and the diffusion of monomers mainly depends on monomer concentration, reaction temperature and area of the original film. So the film with the same area should have approximate grafting quantities under the same reaction condition.

3.4 Effect of monomer concentration on grafting yield

On the basis of the mechanism of radiation grafting copolymerization, any factor which can increase the rate of diffusion of the monomer with respect to the rate of polymerization will favour homogeneous grafting. Monomer concentration is one of the most important factors to affect the grafting yield, especially for a binary mixture monomer system. Fig.5 shows the effect of total monomer concentration on grafting yield. It is easy to see that the grafting yields increase with the increase of total monomer concentration. At the beginning of reaction, the grafting yield of SSS is very low because of its weaker appetency for “active sites” in hydrophobic polymer than AA. When total monomer concentration increases, grafting yields including G_t, G_s and G_a increase with a similarly linear relation.

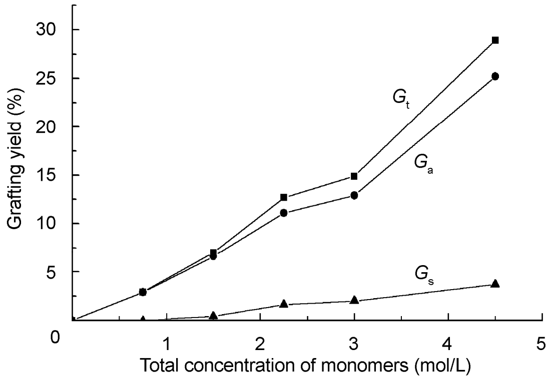

Fig.5 Effect of total nonomer concentration on grafting yield.
Molar ratio of SSS:AA=1:2; Reaction time: 16.5h; $Cu(CH_3COO)_2$ concentration *w*: 0.1%; Absorbed dose: 20kGy.

Because the monomer system used in this study is a binary mixture system, somewhat different from the common unitary system in the radiation reaction, it is obvious that the effect of molar ratio of AA to SSS on grafting yield cannot be ignored. All our experiments show that the AA concentration is a key factor influencing the grafting yield of SSS.

For example, Fig.6 indicates that when the SSS concentration is constant, the grafting yields including G_t, G_s and G_a increase with the increase of the AA concentration. Particularly the grafting yield of SSS is zero at low concentration of AA. And when the AA concentration is constant, the grafting yields including G_t, G_s and G_a do not increase with the increase of the SSS concentration. The increase of SSS concentration does not advance the improvement of SSS grafted onto FEP. On the contrary, when the SSS concentration is high, AA and SSS easily copolymerize and lead to the increase of viscosity of the reaction system. This is disadvantageous to the diffusion and grafting of monomers onto films. Thus the grafting yield of SSS drops to zero at very high concentration of SSS. When the total concentration of monomers is constant, the grafting yields including G_t, G_s and G_a also decrease when the SSS concentration is increased.

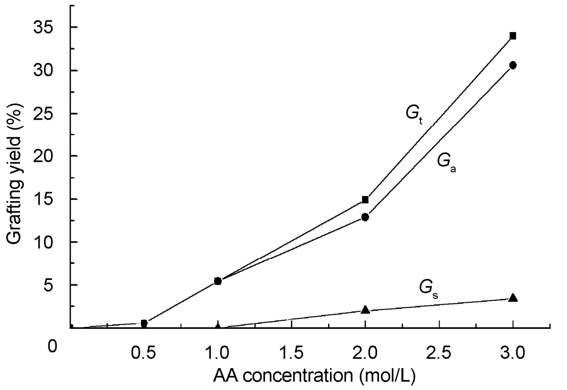

Fig.6 Effect of the molar ratio of AA to SSS on grafting yield. Concentration of SSS: 1.0 mol/L; $Cu(CH_3COO)_2$ concentration *w*: 0.1%; Reaction time: 16.5h; Absorbed dose: 20kGy.

All the results indicate that the increase of the molar ratio of AA to SSS helps improve the grafting of SSS onto FEP. The existence of AA in the reaction system is the key of SSS grafted onto FEP directly, because the grafted AA will improve the hydrophilicity of the FEP film and make the SSS easier to diffuse and grafted onto the FEP film. And the diffusion of SSS is slow for its big molecule size and strong hydrophilicity. So the SSS concentration does not affect strongly the grafting of SSS onto FEP films. On the contrary, high SSS concentration will advance the homo-polymerization of monomers and increase viscosity of the reaction system, thus decrease the grafting yields including G_t, G_s and G_a.

3.5 Analysis of grafted membrane using DSC and IR

Fig.7 show typical DSC thermogram of original FEP film and grafted FEP films with various grafting yield of AA and SSS. These figures show clearly that the melting temperature (T_m) is hardly changed for all samples. This is because the grafting polymerization does not cause obvious decrease in the crystallinity of FEP films. But by contrast with original FEP film, a peak appears in the region of 100～200℃ due to the melting of grafting copolymer, and the temperature corresponding to the peak increases with the increase of grafted SSS, for thermal stability of SSS is better than AA.

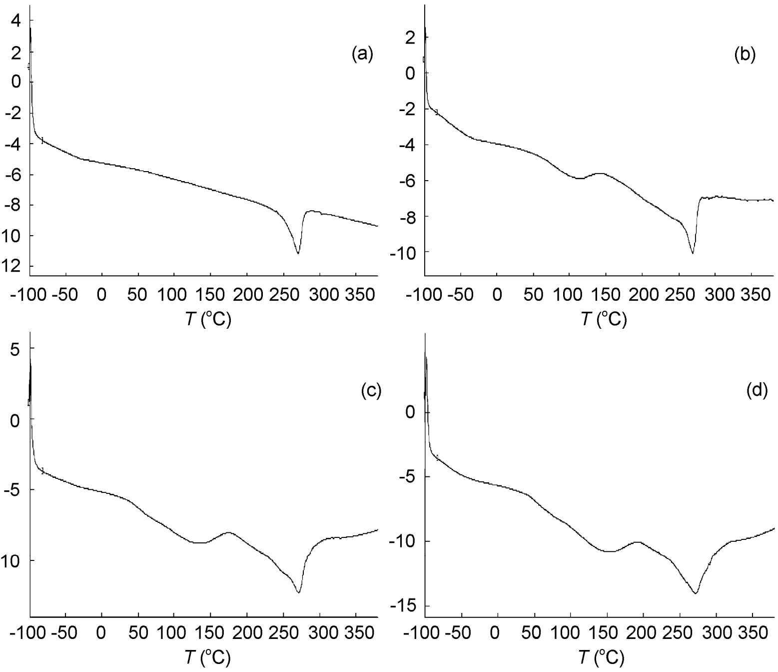

Fig.7 DSC thermogram of original FEP film and grafted FEP films with various grafting yields of AA and SSS.
(a) Original FEP film; (b) Grafted FEP film (G_t: 7.5%, G_s: 0%, G_a: 7.5%); (c) Grafted FEP film (G_t: 22.8%, G_s: 2.4%, G_a: 20.4%); (d) Grafted FEP film (G_t: 47.3%, G_s: 7.1%, G_a: 40.2%).

Fig.8 are the FT-IR spectra of original FEP and grafted FEP with various grafting yields of AA and SSS. By contrast with original FEP, the FT-IR spectrum of AA grafted FEP (Fig.(b)) includes some new characteristic peaks in the regions of 3450～2650 cm^{-1} (due to O—H stretching vibrations), 1717 cm^{-1} (due to C=O stretching vibrations) and 1461, 1411 cm^{-1} (due to aromatic C=C stretching vibrations). And in the FT-IR spectrum of binary grafted FEP (Fig.(c)) some new characteristic peaks in 1009 cm^{-1} (due to S=O stretching vibrations) appear. The result shows that both AA and SSS have been grafted onto FEP film.

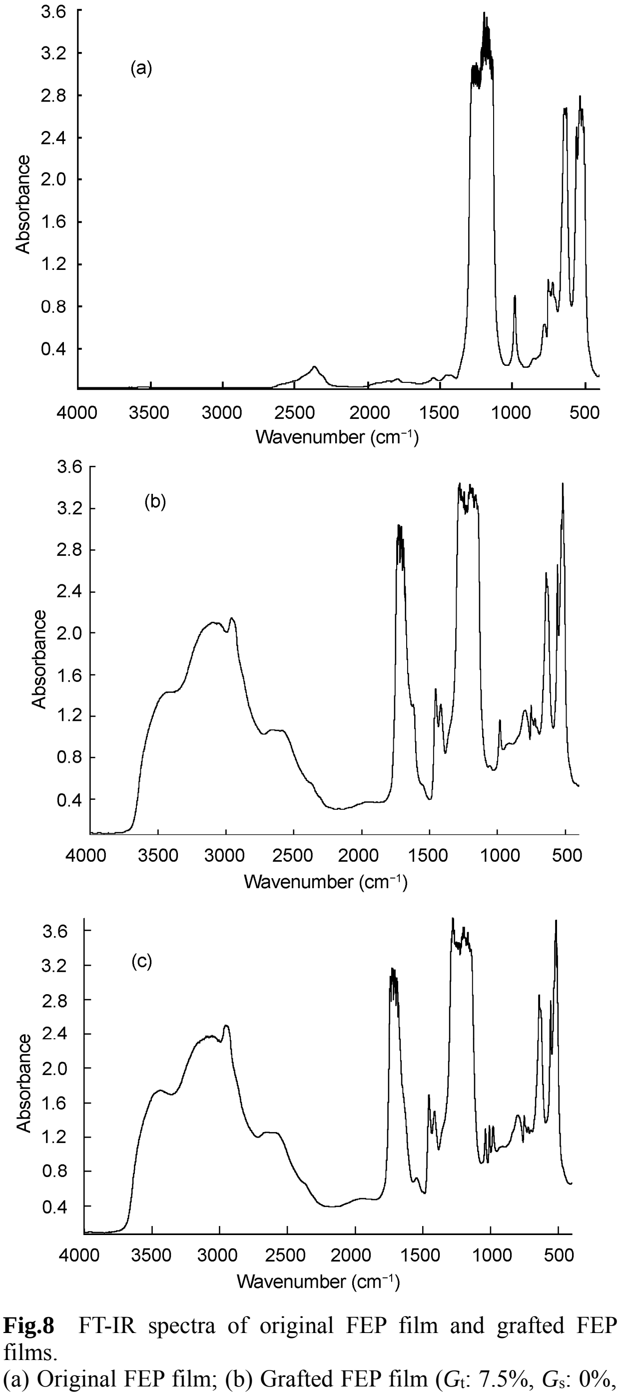

Fig.8 FT-IR spectra of original FEP film and grafted FEP films.
(a) Original FEP film; (b) Grafted FEP film (G_t: 7.5%, G_s: 0%, G_a: 7.5%); (c) Grafted FEP film (G_t: 47.3%, G_s: 7.1%, G_a: 40.2%).

4 Conclusion

By introducing AA to the reaction system, sulfonation of FEP can be accomplished easily. Grafting yields of both AA and SSS onto FEP film respectively increase with total concentration of monomers. The AA concentration is the important factor to affect the grafting yield. High AA concentration, low dose-rate and long reaction time favor the grafting of SSS onto FEP film. The inhibitor can effectively decrease the copolymerization and homopolymerization of monomers, but also affect the grafting yields. As a result of compromise, the amount of inhibitor should be in the range of 0.05% to 0.2%.

Acknowledgements

The authors wish to thank Shanghai Shilong Technology Co. Ltd for providing the ^{60}Co γ-ray irradiation. Thanks are also to the Radiation Research Centre of Shanghai Institute of Applied Physics for the analysis of grafted membrane using DSC and IR.

References

1 Buchi F N, Gupta B, Haas O *et al*. Electrochem Acta, 1995, **40**(3): 345-353.

2 Guzman-Garcia A G, Pintauro P N, Verbrugge M W *et al*. J Appl Electrochem, 1992, **22**(3): 204-214.

3 Wang H, Capuano G A. J Electrochem Soc, 1998, **145**(3): 780-784.

4 Chapiro A. Radiation chemistry of polymeric systems. New York: Wiley-Interscience, 1962: 598-619

5 Scherer G G, Momose T, Tomiie K. J Electrochem Soc, 1988, **135**(12): 3071-3073.

6 Munari S, Vigo F, Tealdo G *et al*. J Appl Polym Sci, 1967, **11**: 1563-1570.

7 Rouilly M V, Kōtz E R, Haas O *et al*. J Membr Sci, 1993, **81**: 89-95.

8 Momose T, Yoshioka H, Ishigaki O. J Appl Polym Sci, 1989, **38**(11): 2091-2101.

9 XU Zhi-li, WANG Geng-hua, WANG Han-ying *et al*. Radiat Phys Chem, 1983, **22**(5): 939-945.