

# Radiation-Induced Grafting of Acrylic Acid and Sodium Styrene Sulfonate onto High-Density Polyethylene Membranes. I. Effect of Grafting Conditions

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**ABSTRACT:** Radiation-induced grafting of sodium styrene sulfonate and acrylic acid onto high-density polyethylene (HDPE) membranes was studied by the preirradiation technique. Grafting was carried out using an electronic beam from a 2-MeV accelerator at room temperature. The effects of the type of solvent, inhibitor concentration, preirradiation atmosphere, monomer concentration, and storage time of preirradiated HDPE membranes on the grafting yield were investigated. Easy control over the grafting yield was

achieved by proper selection of the reaction conditions. IR spectroscopy analysis of the grafted membrane confirmed the existence of sulfonate and carboxylic acid groups in the grafted membranes. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3401–3405, 2006

**Key words:** radiation-induced grafting; acrylic acid; sodium styrene sulfonate; high-density polyethylene

## INTRODUCTION

Radiation-induced grafting of hydrophilic monomers onto polyethylene (PE) has been frequently used to prepare ion-exchange membranes for various applications.<sup>1–3</sup> This technique has been found to be convenient because the grafting yield can be controlled by proper selection of grafting conditions. Furthermore, the grafting may be carried out onto commercially available polymeric membranes, which offers an advantage in terms of producing membranes without the problems associated with transforming the grafted matrix into a thin foil. Many studies have been published on grafting of a weak acid functionality such as acrylic acid (AA) onto PE membranes,<sup>4–7</sup> but only a few have appeared on the grafting of a strong acid such as sulfonic acid.

Shkolnik and Behar<sup>8</sup> reported difficulties in direct grafting of sodium styrene sulfonate (SSS) onto high-density PE (HDPE) membranes by radiation-induced grafting because of the incompatibility between the highly ionized sulfonic acid groups with its hydration

sphere and the polymer backbone. The two-step grafting method was used in the published article about the preparation of ion-exchange membranes bearing sulfonic acid groups. Styrene was grafted onto polymer membranes using the preirradiation method or the simultaneous radiation method, and the graft copolymer was subsequently sulfonated.<sup>9–11</sup>

In our studies, grafting of SSS and AA onto HDPE membranes was investigated using a one-step method. The effects of the grafting conditions, such as the irradiation dose, monomer concentration, and storage time, of preirradiated HDPE membranes on the grafting yield were investigated.

## EXPERIMENTAL

### Materials

HDPE membranes (15  $\mu\text{m}$ ) were supplied by Shanghai Shilong Scientific Co. Ltd., and SSS was procured from Zibo Longda Chemical Co. Ltd. AA was purchased from Gaoqiao Chemical Plant and purified by decompression distillation. Other chemicals were reagent grade and used as received.

### Grafting procedure

Rectangular HDPE membranes (13  $\times$  7 cm) were washed with acetone and dried in a vacuum oven at 50°C to constant weight. The HDPE membranes were packed in PE bags after the atmosphere was replaced by 99.99% pure nitrogen gas. The packed HDPE mem-

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TABLE I  
Effect of Type of Solvent on the Grafting Yield

Solvent	Water	Methanol–water (1:3)	Ethanol–water (1:3)	Propylalcohol–water (1:3)	Isopropylalcohol–water (1:3)
$G_t$ (%)	300.0	109.9	33.1	75.6	103.8
$G_s$ (%)	122.4	37.2	10.0	29.2	46.8

branes were irradiated by passing them under the electron beams of an accelerator with 1.8-MeV beam energy and 1.5-mA current. The irradiated membranes were put together with nonwoven polypropylene and rolled into a cylinder using glass sticks as axes. Then, they were immersed in the monomer solution that was prepared at a given concentration and deaerated by bubbling nitrogen. The reaction was carried out in a temperature-controlled bath. After reacting for a period of time, grafted membranes were taken out of the monomer solution in the glass tubes and washed thoroughly with 70°C distilled water. Subsequently, they were soaked in it overnight to extract the residual monomers and the homopolymer in the membranes. The membranes were weighed after being dried in a vacuum oven at 70°C until constant weight. The overall grafting yield ( $G_t$ ) was defined as

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

where  $W_g$  is the weight of grafted HDPE and  $W_0$  is the weight of ungrafted HDPE.

#### Measure of grafting yield of SSS onto HDPE

The grafted membranes were immersed in 1 mol/L HCl solution, and  $-\text{SO}_3\text{Na}$  was simultaneously transformed into  $-\text{SO}_3\text{H}$ . After being taken out and washed with distilled water until pH equaled 7.0, the membranes were immersed in 5% NaCl solution for 24 h with stirring. The replaced HCl was titrated with NaOH solution. The grafting yield of SSS onto HDPE ( $G_s$ ) can be calculated according to the following equation:

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

where  $C_{\text{NaOH}}$  is the concentration of NaOH (mol/L) and  $V_{\text{NaOH}}$  is the volume of NaOH (mL).

The ionization of  $-\text{COOH}$  in 5% NaCl solution can be ignored. Because  $-\text{SO}_3\text{H}$  is a strong acid, the  $\text{H}^+$  that comes from its ionization can restrain the ionization of  $-\text{COOH}$ .

## RESULTS AND DISCUSSION

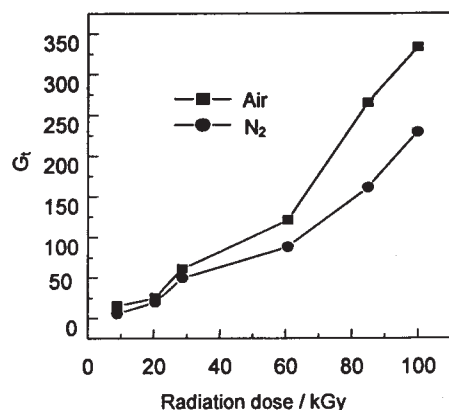
### Effect of type of solvent on grafting yield

The effect of the type of solvent on the grafting yield is shown in Table I. The solvents were deionized water, methanol-deionized water, ethanol-deionized water, propyl alcohol deionized water, and isopropyl alcohol deionized water. No inhibitor was added. It was found that dilution of AA and SSS with deionized water causes a great increase of  $G_t$  and  $G_s$  compared to that obtained upon dilution with a mixed solution of alcohol and deionized water. The results can be explained by the nature of the solvents. The polarity of water is stronger than alcohol. When hydrophilic monomers such as AA or SSS were grafted onto HDPE, the swell rate of the grafted layer in deionized water was higher than in the alcohol and deionized water mixture solution. As a result, more monomers were accessible at the grafting sites, leading to the higher initial rate of grafting when using deionized water as the solvent. On the contrary, when the grafted reaction was carried out in mixed solutions of alcohol and deionized water, the low swelling rate of the grafted layers led to the slower diffusion rate of the monomers compared to selecting deionized water as the solvent. Dilution of AA and SSS with alcoholic solvent, which has a high chain transfer constant and is an electron donor, caused a rapid termination in growing chains, which also resulted in the decrease of the grafting yield when alcohol was used as the solvent.

### Preirradiation atmosphere

It can be seen from Figure 1 that the grafting yield increases gradually with increases of the irradiation dose within the limits of the studied values (10–100 kGy). This behavior can be attributed to the increase in the number of radicals formed in the grafting system. Figure 1 also shows that the grafting yield for HDPE membranes was higher when they were preirradiated in air rather than in nitrogen. This might be interpreted in the following way:

1. Monomer can diffuse more easily in a polymer preirradiated in air than in a polymer preirradiated in nitrogen because the gel fraction of



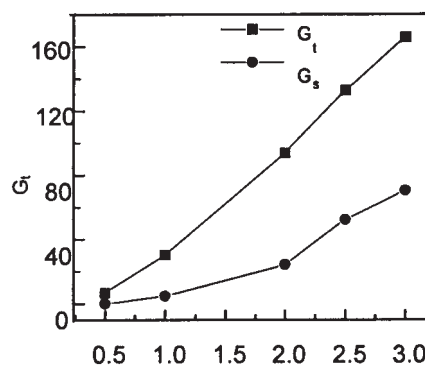
**Figure 1** The effect of the radiation dose on the grafting yield with different irradiation atmospheres; total concentration = 3 mol L<sup>-1</sup>, grafting time = 15 h, SSS/AA molar ratio = 1:2, grafting temperature = 70°C.

HDPE irradiated in nitrogen is markedly larger than that of HDPE irradiated in air. These results indicate that HDPE chains crosslink in nitrogen but do so only rarely in air, and consequently the diffusion of monomer in the polymer matrix appears to be higher in HDPE preirradiated in air.

- Free radicals formed in the amorphous regions and some of those that migrated from the crystalline region on its surface may react with oxygen to form peroxides such as diperoxides (R—O—O—R) and hydroperoxides (R—O—O—H), which can initiate the grafting reaction in the presence of monomers at the elevated temperature (70°C) used in our grafting system. As a result, the grafting yield for air-irradiated HDPE is always more than those for N<sub>2</sub>-irradiated ones.

### Monomer concentration

Figure 2 shows the variation of the grafting yield with the monomer concentration. The grafting yield is found to increase dramatically with the increase of the total concentration of monomers in a range of 0.5–3 mol/L. Because the grafting depends largely on the monomer's availability to the radicals sites within the membrane, at higher monomer concentration the AA and SSS availability into membranes increases. One of the important requirements for the monomer's diffusion into the bulk of the membranes is its high swelling in the grafting medium. If the dilution of monomers has an impact on the swelling of the grafted matrix, the monomer diffusion rate will be influenced accordingly. Fortunately, grafted copolymer chains swell in deionized water, which was used in the dilution of the monomers. As a result, this also benefits the increase of the grafting yield.



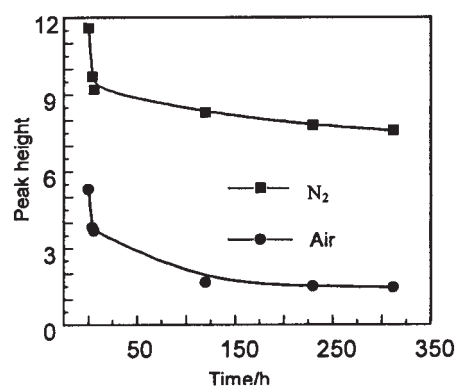
**Figure 2** The effect of the monomer concentration on the grafting yield; total concentration = 2 mol L<sup>-1</sup>, SSS/AA molar ratio = 1:2, grafting temperature = 40°C, grafting time = 10 h.

### Storage after preirradiation

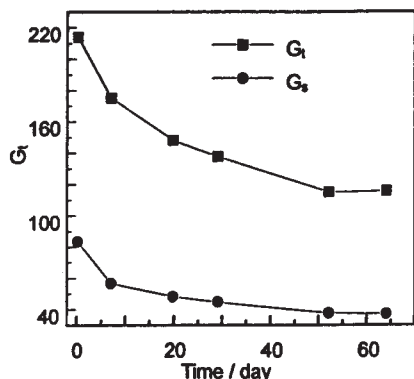
It is well known that the grafting activity of preirradiated polymers is decreased with storage of the irradiated HDPE because of the decay of radicals and that the higher the storage temperature is, the larger the decreasing rate. The decay characteristics of trapped radicals in HDPE are provided in Figure 3. The plot of the grafting yield versus the storage time at -4°C is shown in Figure 4. At first  $G_t$  and  $G_s$  decrease remarkably with time, and then they remain almost constant through the duration of storage. The  $G_t$  value declines 30% during 2 months. This shows that the radicals formed by preirradiation of HDPE are stable at -4°C, which is the advantage of the preirradiation grafting technique compared to the simultaneous technique. Therefore, bulk HDPE membranes may be irradiated once and stored at low temperature before carrying out grafting. Another advantage of preirradiation grafting is low homopolymer yield.

### Inhibitor concentration

When HDPE membranes were irradiated in air, free radicals formed in the amorphous regions and a part



**Figure 3** The variation of the maximal electron spin resonance peak height at -4°C.

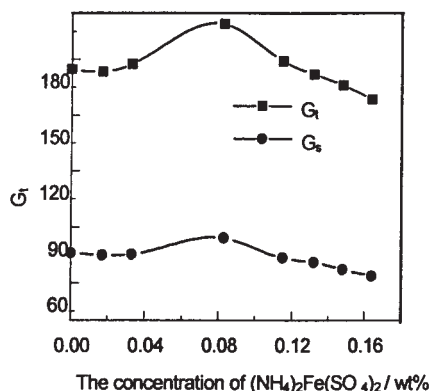


**Figure 4** The relationship between the grafting yield and storage time; total concentration =  $3 \text{ mol L}^{-1}$ , grafting time = 30 h, SSS/AA molar ratio = 1:2, grafting temperature =  $25^\circ\text{C}$ , HDPE stored temperature =  $-4^\circ\text{C}$ .

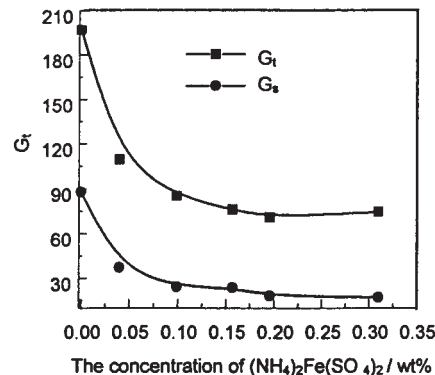
of the radicals formed in the crystalline regions. Some radicals may react with oxygen to form peroxydides such as diperoxides ( $\text{R}-\text{O}-\text{O}-\text{R}$ ) and hydroperoxides ( $\text{R}-\text{O}-\text{O}-\text{H}$ ), which can initiate a graft reaction in the presence of monomer only at high temperature.<sup>12</sup> Comparing Figure 5 to Figures 6 and 7, we find the grafting yield increases with the increase of the reaction temperature without the addition of Mohr's salt because of the higher temperature, the faster rate of monomer diffusion, and peroxydide decomposition. When Mohr's salt is added, the change of the grafting yield is different for a different reaction temperature. In an air atmosphere preirradiation system, the reaction stimulated by the decomposition of peroxides and ferrous ions induces this decomposition of hydroperoxides by a redox process. The thermal decomposition of hydroperoxides



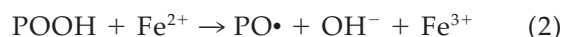
is then replaced by



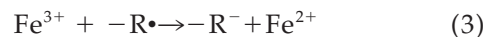
**Figure 5** The effect of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  quantities on the grafting yield when HDPE is preirradiated in air; grafting temperature =  $35^\circ\text{C}$ , grafting time = 24 h.



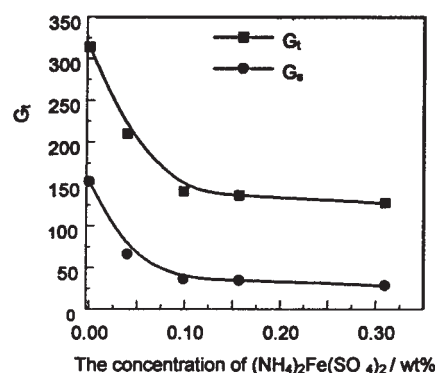
**Figure 6** The effect of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  quantities on the grafting yield when HDPE is preirradiated in air; grafting temperature =  $50^\circ\text{C}$ , grafting time = 24 h.



Reaction (2) indicates that ferrous ions increase the rate of initiation via the redox process. At the same time, ferrous ions also increase the rate of chain termination via reaction (3):



The net result of the addition of ferrous ions in the reaction medium is the reduction of the grafting yield by enhanced chain termination at higher temperature ( $50$  and  $70^\circ\text{C}$ ). When the reaction is carried out at  $35^\circ\text{C}$ , the grafting yield increases with the Mohr's salt concentration, then decreases beyond  $0.083 \text{ wt } \%$ . As indicated in reaction (2), in the presence of Mohr's salt, diperoxides and hydroperoxides may decompose even at a lower temperature to form radicals that can initiate grafting.<sup>12</sup> As indicated in reaction (3), the decay rate of the matrix and growing chain radical is lower at  $35$  than  $50$  or  $70^\circ\text{C}$ , which works against the increase of the grafting yield. As a result, at lower



**Figure 7** The effect of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  quantities on the grafting yield when HDPE is preirradiated in air; grafting temperature =  $70^\circ\text{C}$ , grafting time = 24 h.

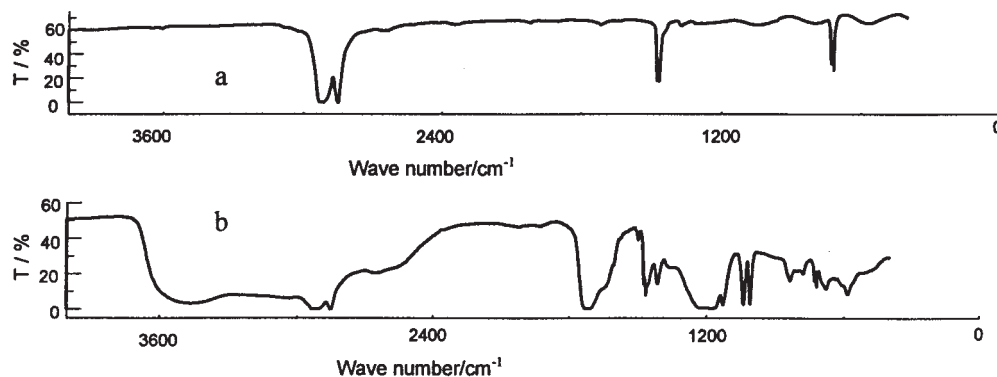


Figure 8 IR spectra of ungrafted HDPE and HDPE-g-AA-SS membrane ( $G_t = 58.54\%$ ,  $G_s = 15.9\%$ ).

temperature (35°C) the grafting yield is higher with the addition of ferrous ions (under 0.107 wt %) than without ferrous ions, because at the 35°C reaction temperature reaction (3) occurs at a slower speed than at 50 or 70°C.

#### Grafted membrane identification

The IR spectra of HDPE and ion-exchange membranes modified with the sulfonate ( $-\text{SO}_3\text{Na}$ ) and carboxylic acid ( $-\text{COOH}$ ) groups are shown in Figure 8. When the IR spectra of Figure 8(a,b) are compared, some new absorptions appear in the spectrum of Figure 8(b), one at  $1715\text{ cm}^{-1}$  that due to the absorption of  $\text{C}=\text{O}$ , and one at  $1128$  and  $1037\text{ cm}^{-1}$  that is due to  $\nu_s\text{S}=\text{O}$  and  $\nu_{as}\text{S}=\text{O}$ . A strong peak at  $836\text{ cm}^{-1}$  compared with the small peak at  $778\text{ cm}^{-1}$  indicated that the monomer added to HDPE is *para*-styrene sulfonate.

#### CONCLUSIONS

We investigated the radiation-induced grafting of SSS and AA onto HDPE using the preirradiation method. The effect of the type of solvent on the grafting yield showed that the best solvent was deionized water. The grafting yield increased with the increase of the total concentration of monomers in a range of 0.5–3 mol/L. The radicals formed by preirradiation of HDPE were stable at temperatures below  $-4^\circ\text{C}$ , so bulk HDPE membranes could be irradiated once and stored at low

temperature before carrying out grafting. A high temperature was suitable for obtaining high grafting yield when HDPE was irradiated in an air atmosphere. At high temperature the grafting yield decreased with the Mohr's salt concentration, but it increased at low temperature in some ranges of Mohr's salt concentration. This can be explained by the fact that, in the presence of  $\text{Fe}^{2+}$ , hydroperoxides may decompose at low temperature to form radicals that can initiate the grafting reaction.

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#### References

1. Ghosh, P.; Chattopadhyay, B.; Sen, A. K. *Polymer* 1998, 39, 193.
2. Aydinli, B.; Tinçer, T. *Radiat Phys Chem* 2001, 60, 237.
3. Taher, N. H.; Dessuoki, A. M.; El-Arnaouty, M. B. *Radiat Phys Chem* 1998, 53, 437.
4. Kaur, I.; Chauhan, G. S.; Misra, B. *Desalination* 1997, 110, 129.
5. Hegazy, E.-S. A.; Kamal, H.; Maziad, N.; Dessuoki, A. M. *Nucl Instrum Methods Phys Res B* 1999, 151, 386.
6. Ishigaki, I.; Sugo, T.; Senoo, K. *J Appl Polym Sci* 1982, 27, 1033.
7. Ishigaki, I.; Sugo, T.; Senoo, K. *J Appl Polym Sci* 1982, 27, 1043.
8. Shkolnik, S.; Behar, D. *J Appl Polym Sci* 1982, 27, 2189.
9. Sara, D.; Robert, C. *Solid State Ionics* 1997, 97, 299.
10. Nasef, M. M. *Polym Degrad Stab* 2000, 70, 497.
11. Gupta, B.; Scherer, G.; Chapiro, A. *J Membr Sci* 1996, 118, 231.
12. Chapiro, A. *High Polymers: Radiation Chemistry of Polymer Systems*; Interscience: New York, 1962; Vol. XV.