Role of Additive HCl in the Radiation-Induced Grafting Copolymerization of Acrylic Acid and Sodium Styrene Sulfonate to High-Density Polyethylene

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ABSTRACT: Acrylic acid and sodium styrene sulfonate were grafted onto high-density polyethylene (HDPE) membrane by preirradiation, and we prepared a cation exchange membrane with strong acid and weak acid groups. The HCl was used as an additive to change the pH of grafting system, and the effect of pH on grafting yield was studied. In simultaneous radiation method, the overall grafting yield (G_t) and grafting yield of SSS onto HDPE (G_s) increased with decreasing of pH. In preirradiation method, G_t and G_s first increased with decreasing of pH, and the highest grafting yield was observed at pH = 2.80, then decreased if we further reduced the pH of the grafting system. Viscosity of grafting system was changed owing to the change of the ionization degree of polyacrylic acid in the presence of HCl, so that diffuse rate of monomers into matrix was affected. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2622–2626, 2007

Key words: additive; radiation; graft copolymer

INTRODUCTION

Generally the grafting yield increases with radiation dose for both simultaneous and preirradiation method. Hoffman et al.[1] thought that the rate of grafting also depends on the concentration of monomers inside the polymer substrate. To make the grafting reaction initiated by radicals faster and more effective, on one hand we should make the best use of the radicals formed by radiation, on the other hand additives should be used to increase the rate of diffusion of the monomers into the polymer substrate. The use of additive can also increase the grafting yield so that a particular level of grafting can be reached using a lower total radiation dose. This is of particular interest in the case where polymer substrate is affected by radiation.

In 1979, Garnett published a comprehensive review on the role of additive when grafting to polyvinyls and cellulose.[2] Since then some of the theories covering the mechanism were published. Metal salts are commonly used to suppress homopolymerization during grafting reactions.[3] The use of mineral acids as additives has been studied extensively for the grafting of vinylic monomers to polyethylene,[4–8] polypropylene,[4,9] and cellulose.[6–10] The mechanism of acid enhancement when grafting to polyolefins and cellulose was initially understood to be a purely radiolytic phenomenon where the irradiation of the solvent increased the hydrogen atom yield.[2,4,8] The hydrogen radicals can abstract hydrogen atoms from the polymer substrate and create additional sites for initiation of grafting.[2,4] In our grafting system, we found there were some discrepancies with this theory. The enhancement of grafting yield was also seen when the preirradiation method was adopted. In this situation there was no change in the yield of hydrogen radicals, because the solvent was not irradiated. In addition, Chappas and Silverman[2,5] found that when grafting styrene to polyethylene, the acid had no effect on the grafting yield below 100%. If the effect was due to the increase of initiating centers, then it would be expected that the acid would have an effect on all grafting yield.

By designing binary grafting system that includes acrylic acid (AA) and sodium styrene sulfonate (SSS), we prepared cation exchange membrane by one-step radiation grafting method. The author has in detail introduced the preparation procedure of cation exchange membrane in her previous article.[11] From the results in the previous research, we can see that the increasing of monomer concentration and radiation dose can improve the grafting yield to some extent. If the cost of the preparation of ion exchange membrane is taken into account,

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the method of changing monomer concentration and radiation dose is not advisable. In this article, aiming to promote the diffusion rate of monomers to the matrix, an effective method for preparation of cation exchange with high grafting yield was designed. We found that the use of HCl as an additive can enhance grafting yield obviously.

EXPERIMENTAL

Material

HDPE membranes of 15 μm thickness were supplied by Shanghai Dayu Plastic Membrane (Shanghai, China); AA was obtained from Shanghai Chemical Reagent; SSS was bought from Zibo Longda Chemical (Shandong Province, China). Other chemicals were of reagent grade and were used as received.

Grafting procedure

HDPE membranes were washed with acetone for 24 h and dried in a vacuum oven at 50°C to constant weight. The washed membranes were put together with nonwoven polypropylene and rolled into cylinder using glass sticks as axes, then immersed in the monomer solution, which was prepared at the given concentration, and deaerated by bubbling nitrogen. Deionized water was used as solvent for the grafting reaction. The reaction was carried out in the temperature-controlled bath, which was placed beside a ^{60}Co γ-ray radiation source when simultaneous radiation method was used. After reacting for a period of time, grafted membranes were taken out from the monomer solution and washed thoroughly with 70°C distilled water, then soaked into it overnight to remove the residual monomers and the homopolymer from the grafted membranes. After being dried in vacuum oven at 70°C until a constant weight, the membranes were weighed. As far as preirradiation method was concerned, the HDPE membranes were put into polyethylene bags and thereafter atmosphere in the bag was replaced by 99.99% nitrogen gas. After the polyethylene bags were made airproof, they were irradiated at dose of 100 kGy using ^{60}Co γ-ray radiation source. After radiation, the grafting reaction was carried out in a temperature-controlled bath. The operating processes were the same as described in simultaneous radiation method. When AA and SSS were grafted onto HDPE, the overall grafting yield (G_t) was defined as

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

where W_g = weight of grafted HDPE and W_o = weight of ungrafted HDPE. When AA was grafted onto HDPE, the grafting yield of AA (G_a) was defined as

$$G_a = \frac{W_g - W_o}{W_o} \times 100\%$$

Measurement of grafting yield of SSS onto HDPE (G_s)

The grafted membranes 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 membranes were immersed in 5% NaCl solution and stirred for 24 h. After the grafted membrane was taken out, the replaced H^+, which came from ionization of —SO_3H, was titrated with NaOH solution. G_s can be calculated according to the following equation:

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

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

The ionization of —COOH in 5% NaCl solution can be ignored. Because —SO_3H is a strong acid, the H^+ that come from its ionization can restrain the ionization of —COOH.

As far as AA and SSS grafted onto HDPE system was concerned, G_a could be calculated by the following equation: $G_a = G_t - G_s$.

RESULTS AND DISCUSSION

The effect of additive HCl on grafting yield when AA and SSS were grafted onto HDPE using simultaneous radiation method

When the total concentration of SSS and AA was 2 mol/L and the mole ratio of AA to SSS was 1 : 1, and the pH value of the system was 3.38, the total grafting yield (G_t) was 70.03%, and the grafting yield of SSS (G_t) was 15.71%. The result is shown in Figure 1. By adding HCl to grafting system and changing the pH to 1.58, G_t is 1.2 times to that without adjusting pH (pH = 3.22), and G_s is two times to that at the same grafting conditions.

The effect of additive HCl on grafting yield when SSS were graft onto HDPE-*g*-AA membrane using simultaneous radiation method

In grafting system including AA and SSS, firstly AA is grafted onto HDPE membranes and the hydrophilicity of membranes is increased, thus SSS and AA compete the radical in HDPE matrix or grafting chains, which is propagating, so the —SO_3Na and —COOH groups are introduced onto HDPE by a one-step method. To study the influence of variation of pH value on G_s, two-step grafting method is adopted. Firstly, AA is grafted onto HDPE by simul-

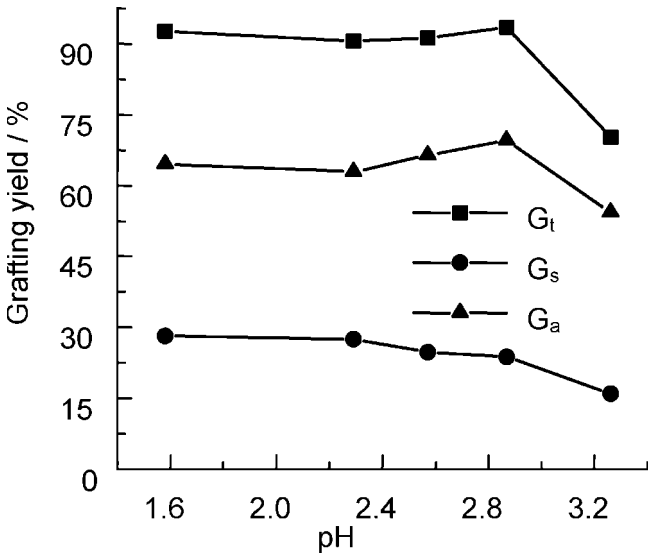

Figure 1 The effect of pH on grafting yield when AA and SSS were grafted onto HDPE using simultaneous radiation method. Grafting temperature: 28°C, Total concentration: 3 mol L^{-1}, Molar ratio of SSS to AA: 1 : 2, Grafting time: 17 h, Radiation dose: 30 kGy.

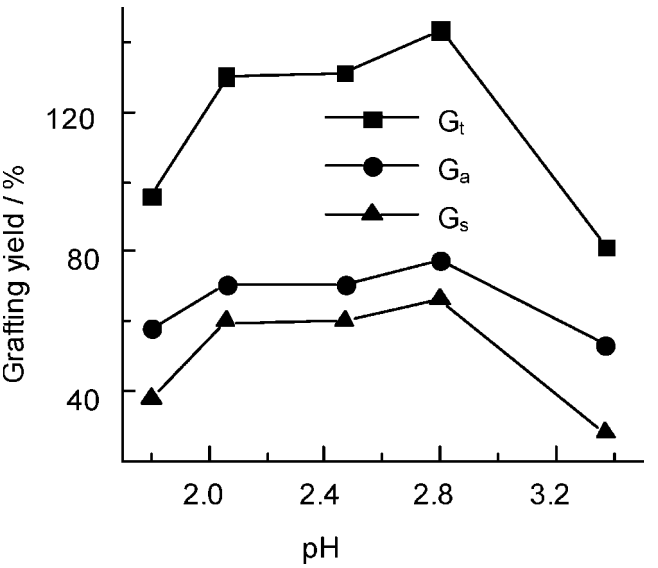

Figure 3 The effect of pH on grafting yield when AA and SSS were grafted onto HDPE using preirradiation method. Total concentration: 2 mol L^{-1}, Molar ratio of SSS to AA: 1 : 1, Grafting temperature: 35°C, Grafting time: 20.5 h, Radiation dose: 100 kGy.

taneous radiation method, then SSS is grafted onto HDPE-*g*-AA membrane using the same method. From Figure 2, we can see that, at pH 1.43, G_s is three times to that without changing of pH value. Because G_a (the grafting yield of AA onto HDPE) of HDPE-*g*-AA membrane, which is used in two-step grafting method, is low (G_a = 45%), the hydrophilicity of HDPE-*g*-AA membrane is so weak that limits the further increase of G_s. Comparing Figure 1 with Figure 2, we can conclude that G_s or G_t is high at low pH value, because the viscosity of grafting system is small at low pH value, which benefit the increase of monomer diffusion rate into HDPE matrix. On the contrary, the viscosity of grafting system is high when no HCl is added. The radicals of matrix is generated at any time when the grafting is continued in simultaneous radiation method, so there is a lot of radicals in the neighborhood of grafting chains. If the viscosity of the system is high, then a lot of grafting chains, which is propagating, become deactivated by reacting with radicals in matrix before monomers diffuse into the matrix. The method of regulating pH of grafting system is not only simple and convenient, but also can reduce the costs that are need for the preparation of ion exchange membrane.

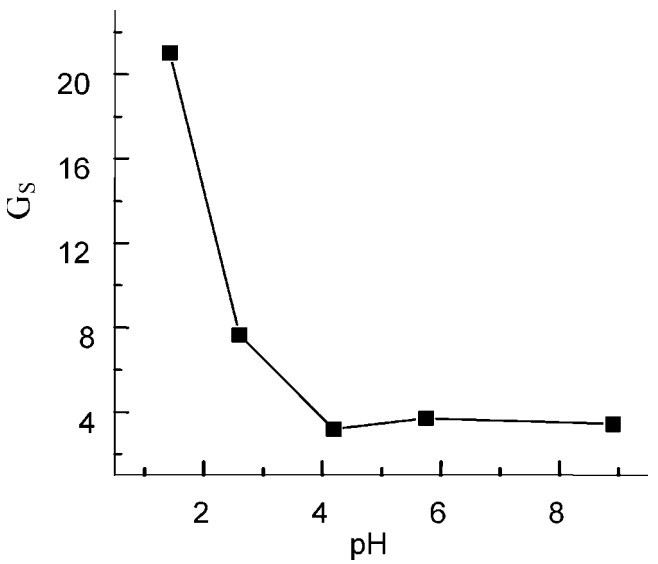

Figure 2 The effect of pH on G_S when SSS were grafted onto HDPE-*g*-AA membrane using simultaneous radiation method. SSS concentration: 1 mol L^{-1}, Grafting temperature: 28°C, Grafting time: 17 h, G_a: 45%, Radiation dose: 30 kGy.

The effect of additive HCl on grafting yield when AA and SSS were grafted onto HDPE using preirradiation method

From Figure 3, we can see that the grafting yield first increases, then decreases with the decrease of pH value. G_t and G_s reach maximum when the pH value is 2.80. At the point of pH = 2.80, the viscosity of the grafting system is lower than that without addition of HCl, but higher than the lowest pH value. The movement of grafting chains that have great molecular weight is inhibited, which hinders the termination by combination with other growing chains, but does not appreciably disturb diffusion of monomers. The rate of the chain propagation is

faster than chain termination, so the grafting yield increases obviously. During this period, Trommsdorff phenomenon[12] come into being. When grafting styrene to polyolefins[4] and cellulose,[13] Trommsdorff phenomenon was observed. In preirradiation method, the quantity of radicals in the matrix is decided by radiation dose. Lower is the pH value, smaller is the viscosity of grafting system. Because of low viscosity, a lot of propagating chains can move freely and react with radicals in the matrix, which lead to shorter grafted chains, so grafting yield decreases when pH value is very low. Without addition of HCl, the viscosity of system is so high that diffusion rate of monomers into the matrix decrease distinctly. Under such conditions, the rate of monomer reaction with the growing chain may be considerably lowered, so grafting yield decreases without addition of HCl.

The effect of the comonomer composition on grafting yield with the addition of HCl

Figure 4 shows the effect of comonomer composition on grafting yield at point of pH = 2.08. G_s, G_a, and G_t increase with increasing the content of SSS. G_s and G_t reach 41.90 and 119.20% respectively, when molar ratio of SSS to AA is 7:8. Under the same reaction condition, if no HCl is added, G_s is 22.3% when G_t is 123.3%.[14] The influence of SSS/AA mixture composition on G_s/G_a is shown in Figure 5 G_s/G_a also increases with the increasing of molar ratio of SSS to AA. By regulating the pH value of grafting system, we have successfully solved the difficulty that G_s can not be further improved when AA and SSS were grafted onto HDPE using simultaneous or preirradiation method.

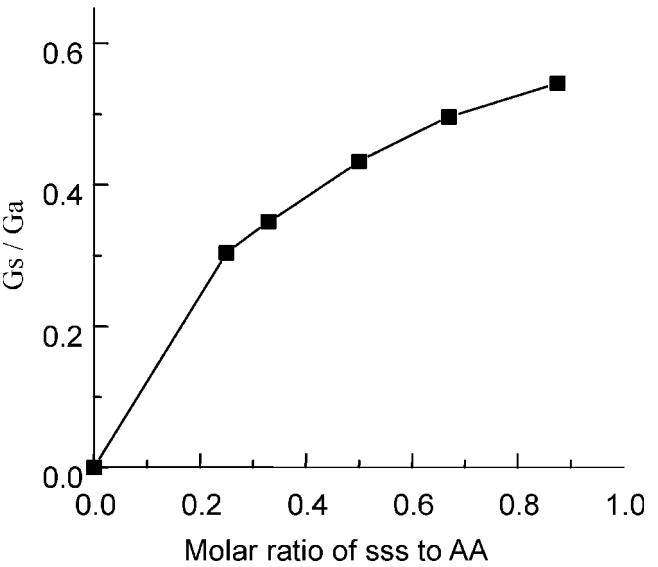

Figure 5 The Effect of comonomer composition on G_s/G_a.

The same research results were obtained in preirradiation method. Figures 6 and 7 show that G_s, G_t, G_a, and G_s/G_a increase with increasing the content of SSS. G_s/G_a is 1:1 when molar ratio of SSS to AA is 1:2. G_s is higher than G_a if molar ratio of SSS to AA is bigger than 1:2. G_t is 142.30% when SSS does not

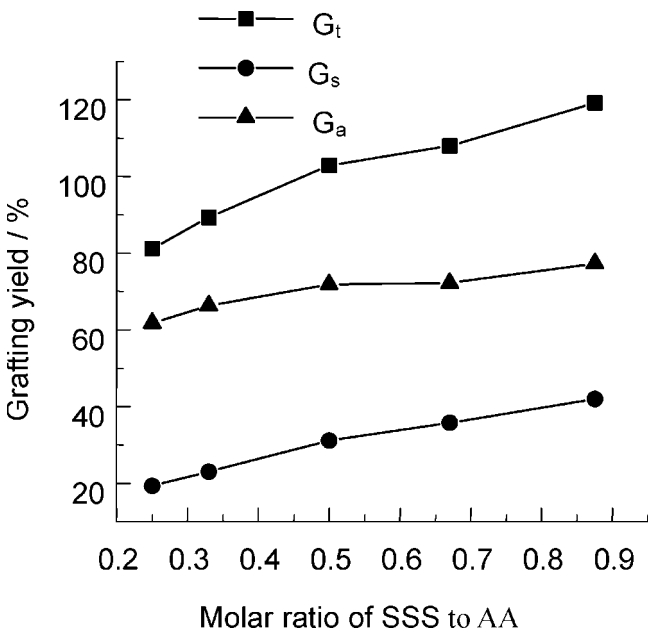

Figure 4 The effect of comonomer composition on grafting yield when AA and SSS were grafted onto HDPE using simultaneous method. Total concentration: 3 mol L^{-1}, Grafting time: 17 h, pH: 2.08, Grafting temperature: 28°C, Radiation dose: 30 kGy.

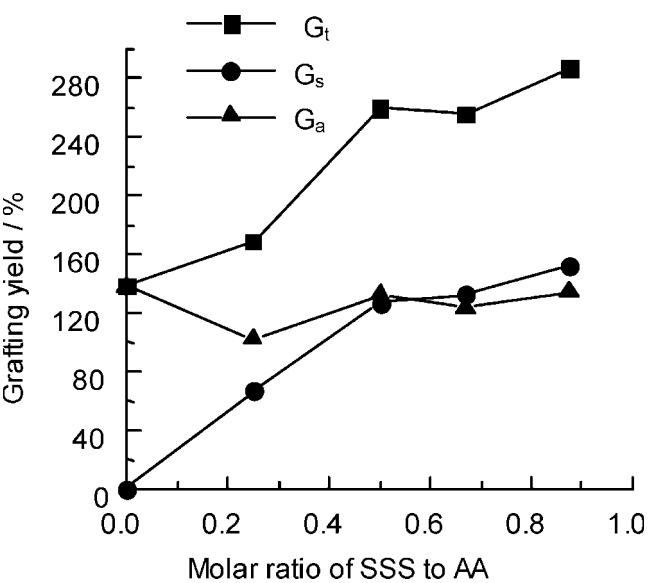

Figure 6 The Effect of comonomer composition on grafting yield when AA and SSS were grafted onto HDPE using preirradiation method. Total concentration: 3 mol L^{-1}, Grafting time: 17 h, pH: 2.08, Grafting temperature: 35°C, Radiation dose: 100 kGy.

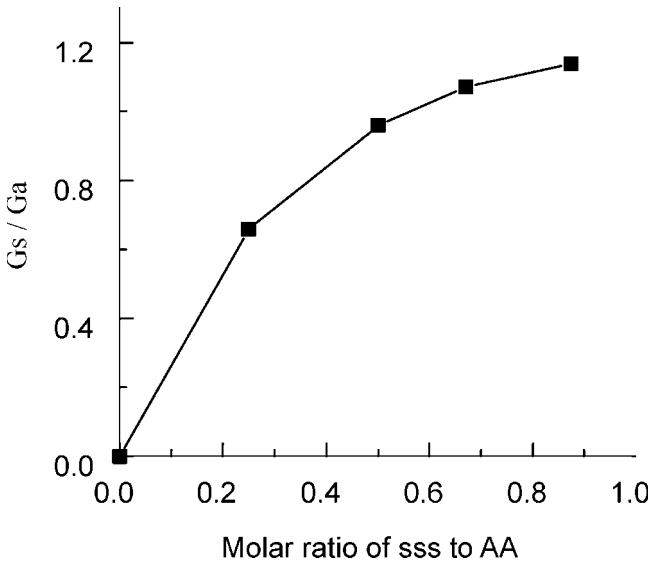

Figure 7 The Effect of comonomer composition on G_s/G_a.

exist in grafting system, however, at same total monomers concentration, G_t is 285.20% when molar ratio of SSS to AA is 7:8, which indicates that the existence of SSS can promote the increasing of G_t. The results can be explained by the reactivity ratios of monomers, which give a good indication about their interaction with each other as well as their capability of reacting with the free radical in the matrix. The reactivity ratios in copolymerization reaction of AA and SSS can be defined as r_1 and r_2 respectively ($r_1 = k_a{:}k_{as} = 0.1$, and $r_2 = k_s{:}k_{as} = 1$). k_a is the rate constant of AA homopolymerization, k_{as} is the rate constant of AA and SSS copolymerization, and k_s is the rate constant of SSS homopolymerization.[15] The value of r_1 (0.1) suggests that AA reacts with SSS almost ten times as fast as its own molecules; similarly, the value of r_2 (1) indicates that SSS reacts with AA one time as fast as its own molecules. The reactivity ratios of AA and SSS clearly suggest that SSS not only prefer to homopolymerize but also tend to copolymerize with AA. So the presence of SSS enhanced G_s to a considerable extent.

CONCLUSIONS

The use of HCl as additive has been studied extensively for the grafting of AA and SSS onto HDPE using different radiation methods. We can conclude that the addition of HCl is an effective method for the enhancement of G_s and G_t. An illustration of the enhancing effect of HCl in grafting solution attributes to two factors. On one hand, the ionization of polyacrylic acid is restrained in the existence of HCl, as a result, the repulsion force between chains of pAA is weak. Some of polyacrylic acid chains change from straight state into curly state, which lead to low viscosity of grafting system and is beneficial for the diffusion of monomer into the matrix. On the other hand, solubility of SSS in water at low pH value increases, so G_t and G_s enhance. The research results indicate that at the point of pH = 2.08, G_t is twice to that without the introduction of HCl when preirradiation method is used. The role of HCl is important in radiation grafting process, since the radiation dose or monomers concentration required to achieve some degree of grafting yield can be lowered in the presence of HCl. It is predicted that the results will become an effective and economical method to improve the grafting yield at lower expense.

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