Radiation Grafting of α, β, β-Trifluorostyrene onto Poly(Ethylene–Tetrafluoroethylene) Film by Preirradiation Method. I. Effects of Preirradiation Dose, Monomer Concentration, Reaction Temperature, and Film Thickness

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Synopsis

Preirradiation grafting of α, β, β-trifluorostyrene onto poly(ethylene–tetrafluoroethylene) film was studied. The trapped radicals formed upon irradiation were able to induce graft polymerization under appropriate conditions. The influences of the grafting conditions were analyzed kinetically. The grafting rate dependency on the preirradiation dose was found to be of order 0.3, and the monomer concentrations, 1.0. The overall activation energies for this grafting were calculated to be 6.2×10^4 and 9.3×10^3 J/mol below and above 50°C. The grafting rate was found to be independent of the film thickness, which ranged from 25 to 100 μm.

INTRODUCTION

Radiation-induced graft polymerization on fluorine-containing polymers has been frequently studied to meet requirements for chemical and heat resistant ion-exchange membranes for water electrolysis and caustic soda production.[1-8] However, the monomers used in this graft polymerization were mainly either low chemical resistant styrene or acrylic acid.

Omichi and Okamoto studied the grafting of methyl α, β, β-trifluoroacrylate onto polyethylene and fluorine-containing films by the simultaneous irradiation method using γ-rays from a ^{60}Co. They found that these membranes show good oxidation resistance.[9] The grafting of fluoro-containing monomers seems to be a useful way to make membranes with high chemical and heat resistance.

D'Agostino et al.[10-12] studied the grafting of α, β, β-trifluorostyrene (TFS) onto poly(tetrafluoroethylene–hexafluoropropylene) (FEP) film by the simultaneous irradiation method using γ-rays from a ^{60}Co. They found that membranes obtained by sulfonation of the grafted film can be used for various electrochemical cells such as chlor-alkali and fuel cells. Nevertheless, the

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radiation grafting of TFS by preirradiation, a more commercially available method,[13] has not yet been reported.

Our previous paper[14] reported our preliminary study of the grafting of TFS onto various polymer films, mainly fluorine-containing polymers. As a result of these investigations, we have concluded that the grafting of TFS by the preirradiation method is efficient and viable, especially for poly(ethylene–tetrafluoroethylene) (ETFE) film.

In this study, the grafting of TFS onto ETFE film by preirradiation method was attempted and analyzed kinetically to elucidate the influences of grafting conditions such as preirradiation dose, monomer concentration, grafting temperature, and film thickness.

EXPERIMENTAL

Materials

Commercially available ETFE (Asahi Glass Co., Ltd.) films of 25–100 μm thickness were used, and these films were washed with acetone and dried at room temperature. TFS was synthesized according to a method already reported in the literature.[15] Benzene to be used as the solvent was purified by passage through a column of activated Alumina (Gmb H, Alumina Woelm B).

Irradiation

The ETFE films were packed in polyethylene bags after the atmosphere was replaced by 99.999 pure nitrogen gas. The packed ETFE films were irradiated in a dry ice bath by passing them under the electron beams of a transformer type accelerator (EPS-750, Nissin-High Voltage., Ltd.) with a beam energy of 500 KV and a current of 3.95 mA. The dose rate was approximately 5.4×10^3 Gy/s.

Grafting Procedure

The irradiated films were immersed in a monomer solution at given TFS and benzene concentrations and degassed by several freeze–thaw cycles at 0.13 Pa. The reaction was carried out in a vacuum in a temperature-controlled bath. The grafted films were removed from the monomer solution in glass ampoules and soaked for 24 h in benzene, a good solvent of homopolymers, at room temperature to eliminate residual monomers and homopolymers. After 4 h drying in a vacuum at 60°C, the films were weighed. The degree of grafting was calculated using the following equation:

$$(W_g - W_0)/W_0 \times 100$$

where W_0 and W_g represent initial and grafted ETFE film weights, respectively.

The degree of swelling was determined by immersing 100-μm-thick ETFE film in a monomer solution at 50°C for 24 h. The films were then removed and the excess solution on the surface was quickly removed with blotting paper.

These films were weighed, and the degree of swelling was calculated as

$$(W_s - W_g)/W_g \times 100$$

where W_g and W_s represent the dry and swollen film weights, respectively.

Graft Distribution

The grafted film was sulfonated by immersion for 40 min at 135°C in a solution consisting of 30 parts chlorosulfonic acid and 70 parts 1,1,2,2-tetrachloroethane and subsequently hydrolyzed by immersion for 2 h at 90°C in a 2*N* KOH solution. The film thus obtained was cut perpendicularly at liquid nitrogen temperature, and its cross section was observed. The line profile of potassium salts in the grafted chains was then measured with an X-ray microanalyzer (Hitachi X-560).

RESULTS AND DISCUSSION

Grafted Film Identification

Figure 1 shows the infrared spectra of ETFE film and grafted film with a 32.0% grafting yield. The presence of an aromatic ring is established by the =C—H stretching vibration at 3050 cm^{-1} and the skeletal C=C in-plate stretching vibrations at 1500 and 1600 cm^{-1}. Monosubstitution of the ring is confirmed by the aromatic CH deformation bands at 690 and 760 cm^{-1}. The stretching vibrations of CF and CF2 are supposed to overlap with those of ETFE film. Stretching vibration of C=C at 1750 cm^{-1} due to TFS was not observed. These features confirm that TFS was grafted onto the ETFE film.

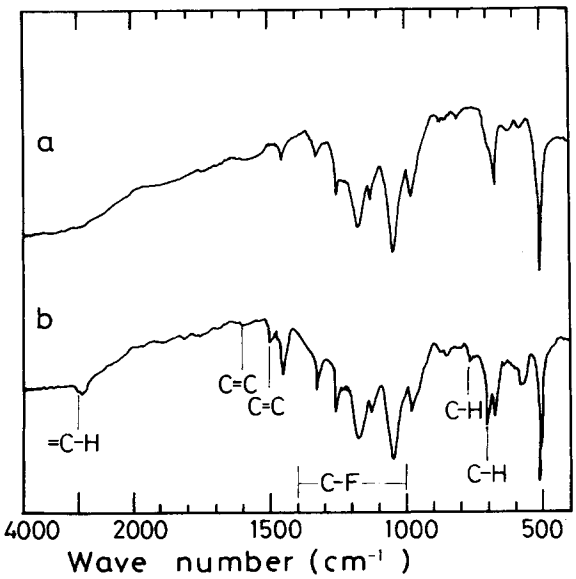

Fig. 1. Infrared spectra of the films: (a) ETFE; (b) the grafted ETFE with a 32.0% grafting yield.

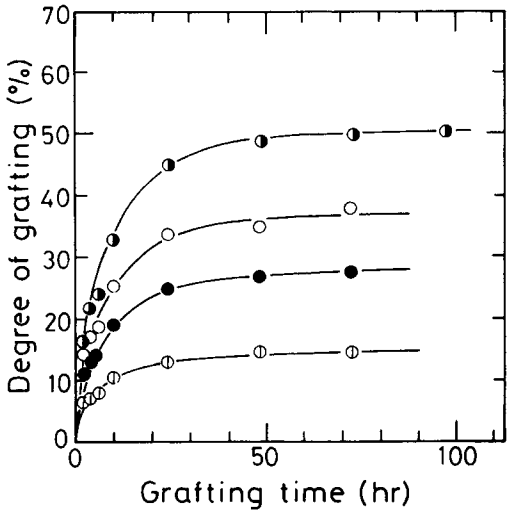

Fig. 2. Graft yield vs. time at various preirradiation doses: (Ⓓ) 1×10^4 Gy; (●) 3×10^4 Gy; (○) 5×10^4 Gy; (◑) 1×10^5 Gy. Grafting conditions: monomer conc, 100%; grafting temp, 50°C; film thickness, 100 μm.

Effect of Preirradiation Dose

Figure 2 shows the graft yield-time curves at various preirradiation doses. The degree of grafting at first increases rapidly and levels off at a given limiting value, which is called the final percent grafting in this report. Both the grafting rate and final percent grafting increase with preirradiation dose. The logarithmic plots of these values vs. preirradiation dose are shown in Figure 3. The dose exponent of the grafting rate was found to be approximately 0.3, lower than the theoretical value for free radical polymerization (0.5).

Generally, the low dependence of the grafting rate on the preirradiation dose can be ascribed to one or more of at least four factors: (1) decay of trapped radicals by temperature increases during irradiation; (2) decay of trapped radicals during irradiated polymer substrate storage; (3) decay

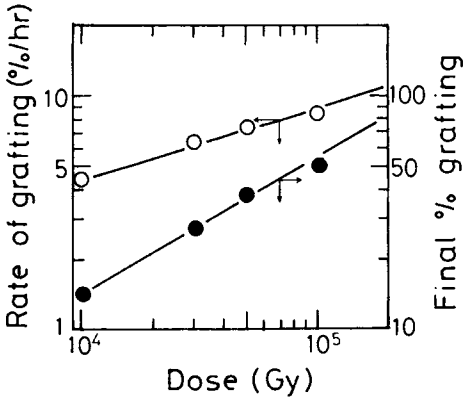

Fig. 3. Logarithmic plots of grafting rate and final percent grafting vs. preirradiation dose. Grafting conditions are the same as in Figure 1.

of trapped radicals by their own recombination; (4) inefficient monomer diffusion in the irradiated polymer substrate.

To counter the first factor, the irradiation of the ETFE film was carried out in a dry ice bath to avoid a rapid temperature increase; there was hardly any decay of trapped radicals during the irradiation. The irradiated film storage time of 4 h also took place in a dry ice bath; there was, once again, almost no decay during this period. For example, irradiated ETFE film which was kept for 72 h at 0°C had 50% final grafting percentage, almost the same as the irradiated ETFE film kept for only 4 h (51%). The third factor is based on Hegazy's et al.[5] observation of the recombination of trapped radicals at a dose rate of 3×10^3 Gy/s in the graft polymerization of acrylic acid onto polytetrafluoroethylene (PTFE) by the preirradiation method. In our grafting system, the dose rate was 5.4×10^3 Gy/s, more than that of Hegazy's experiment. There is a possibility, therefore, that the decay of the trapped radicals took place by their own recombination. The fourth possibility was discounted, due to the fact that in this grafting system the monomer diffusibility in the irradiated ETFE film is high. This will be discussed in a later section.

In consideration of these aspects, it was concluded that an efficiency decrease of radicals initiating the graft reaction due to their recombination could be the major cause of the lower dependence of grafting rate on the preirradiation dose.

Effect of Monomer Concentration

Figure 4 shows the graft yield–time curves at various monomer concentrations. Both the initial rate and final percent grafting increase with monomer concentration. The degree of grafting levels off at approximately 50 h.

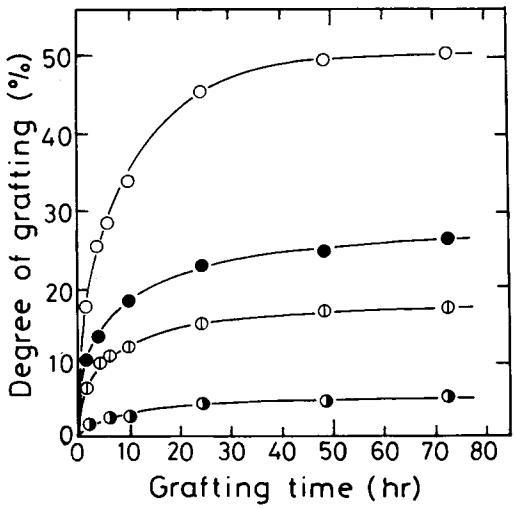

Fig. 4. Graft yield vs. time at various monomer concentrations: (◑) 10%; (◐) 30%; (●) 50%; (○) 100%. Grafting conditions: preirradiation dose, 1×10^5 Gy; grafting temp, 50°C; film thickness, 100 μm.

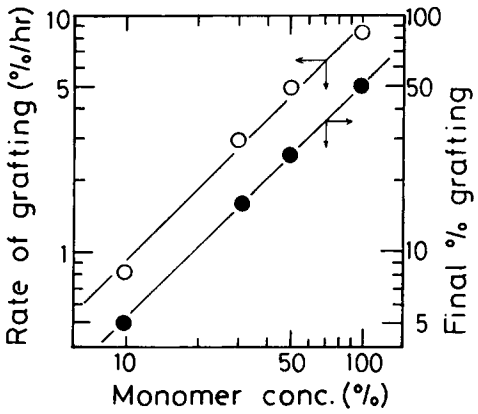

Fig. 5. Logarithmic plots of grafting rate and final percent grafting vs. monomer concentration. Grafting conditions are the same as in Figure 4.

The grafting rate and final percent grafting were determined from Figure 4 and plotted logarithmically in Figure 5. The dependence of grafting rate and final percent grafting on the monomer concentration were both calculated to be of order 1.0.

In preirradiation grafting, generally, the initial rate has a tendency to be largely dependent on the monomer diffusibility into the polymer matrix. Figure 6 shows the relation between the degree of swelling and the monomer concentration as determined for the original ETFE film; the degree of swelling ranged from 3.8 to 4.2%, relatively high for a fluorine-containing substrate in a solvent or monomer. As a comparison, the degree of swelling of PTFE in TFS at 50°C was only 0.3%. The effect of benzene was observed on the swelling of the grafted ETFE film; for example, the degrees of swelling of the grafted film (grafting yield, 40%) in benzene and TFS at 50°C were 8.0 and 5.0%, respectively. However, almost no effect of benzene on the initial rate or the final percent grafting was observed, except for the dilution of the monomer. It seems, therefore, that the initial rate was not largely dependent on the

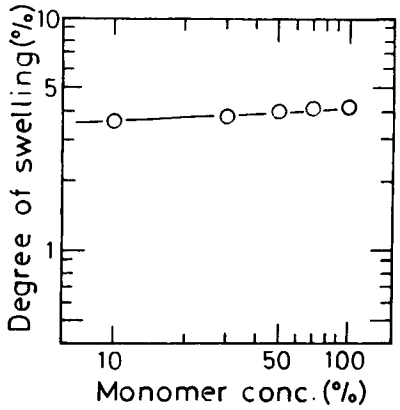

Fig. 6. Degree of swelling vs. monomer concentration. Swelling conditions: solvent, benzene; swelling temp, 50°C; film thickness, 100 μm.

diffusibility of TFS into the ETFE film because of the high swelling of the ETFE film in TFS.

High swelling of grafted ETFE film in benzene can be understood by comparing solubility parameters of each material. The solubility parameter of the graft chain, which is the homopolymer of TFS,[15] is 19.1 $(J/cm^3)^{1/2}$, closer to benzene,[16] 18.8 $(J/cm^3)^{1/2}$, than to TFS,[14], 16.4 $(J/cm^3)^{1/2}$.

Effect of Temperature

Figure 7 shows the graft yield–time curves at temperatures ranging from 25 to 70°C. The initial rate of grafting increases with temperature, and final percent grafting has a maximum value at 50°C. In general, trapped radicals in the interior of the film partially decay before grafting due to mutual recombination. The decayed radical fraction increases at higher temperatures, causing the decrease in the final percent grafting at elevated temperatures. The chain segment mobility also increases at higher temperature, enhancing the bimolecular termination of growing radicals. In this grafting system, the final percent grafting at 70°C is lower than that at 50°C, seemingly caused by the mutual recombination of the trapped radicals and/or the bimolecular termination of growing radicals.

Figure 8 shows Arrhenius plots for this grafting, showing a breaking point at 50°C. The overall activation energy was calculated to be 6.2×10^4 and 9.3×10^3 J/mol below and above 50°C, respectively. The breaking point in the Arrhenius plots was also observed during the preirradiation grafting of acrylic acid onto PTFE film,[5] in which the lowering of the activation energy above 35°C was caused by the increase of monomer diffusibility into the PTFE matrix accompanied by the glass transition of PTFE. As mentioned above, the low dependencies of temperature on grafting rate above 50°C seems to be due to the decay of the trapped radicals rather than the glass transition

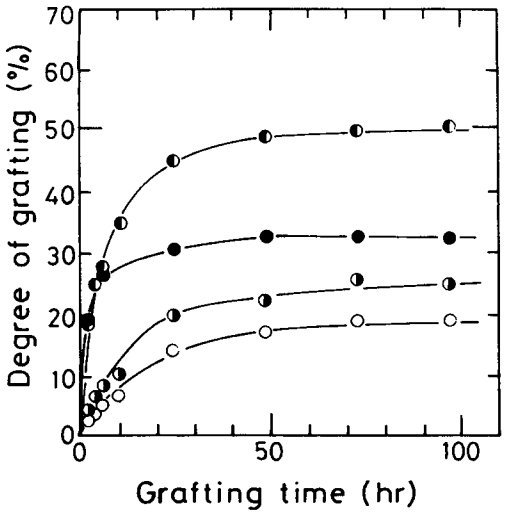

Fig. 7. Graft yield vs. time at various grafting temperatures: (○) 25°C; (◑) 35°C; (◐) 50°C; (●) 70°C. Grafting conditions: preirradiation dose, 1×10^5 Gy; monomer conc, 100%; film thickness, 100 μm.

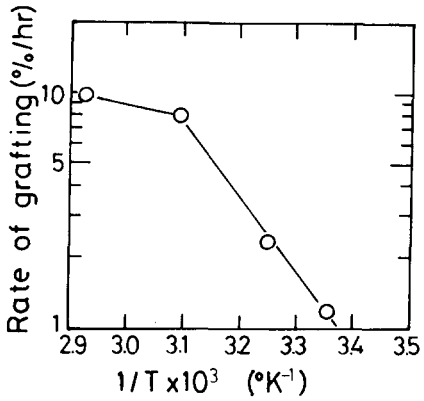

Fig. 8. Arrhenius plots of grafting rate. Grafting conditions are the same as in Figure 7.

of ETFE. Further investigation will be necessary to make certain the cause of the change in the apparent energy at 50°C, especially for the glass transition of ETFE.

Effect of Film Thickness

Figure 9 shows the graft yield–time curves for films of various thicknesses. The degree of grafting levels off at almost the same values, irrespective of film thickness.

The grafting rates and final percent grafting were determined from Figure 9 and plotted logarithmically in Figure 10. The grafting rates were found to be of similar value, irrespective of film thickness.

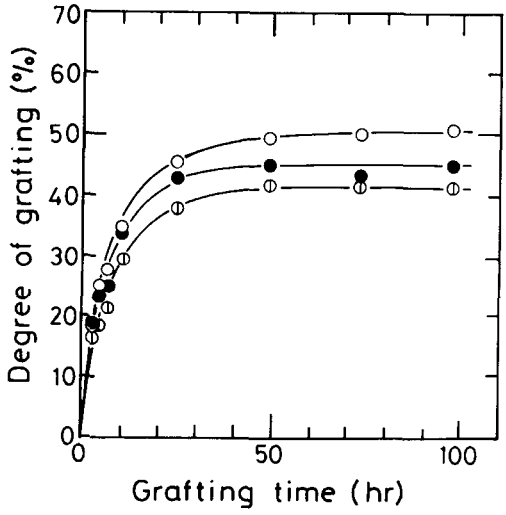

Fig. 9. Graft yield vs. time at various film thickness: (Φ) 25 μm; (●) 50 μm; (○) 100 μm. Grafting conditions: preirradiation dose, 1×10^5 Gy; monomer conc, 100%; grafting temp, 50°C.

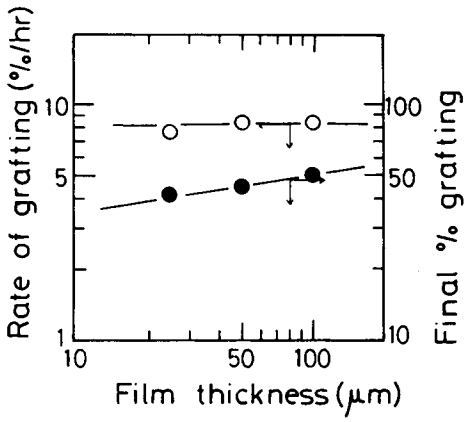

Fig. 10. Logarithmic plots of grafting rate vs. film thickness. Grafting conditions are the same as in Figure 9.

Figure 11 shows the graft chain distribution in grafted films with grafting yield ranging from 18 to 45% obtained by grafting of TFS onto 100-μm-thick ETFE film. In this figure, the graft chain distribution are largely constant for the grafted films with grafting yield ranging from 18 to 45%.

Generally, grafting proceeds from both surfaces of the film into the interior in preirradiation grafting. At a lower degree of grafting, an ungrafted layer still remains in the film interior, and then disappears as grafting proceeds, to produce a homogeneous graft chain distribution. In this grafting system, the swelling of ETFE film in TFS is as high as a fluorine-containing substrate as mentioned before, and the swelling rate is 0.4%/min just after the 100-μm-thick ETFE is immersed in TFS at 50°C. From this, the TFS seems to be supplied smoothly to the inner part of the ETFE film because the initial grafting is approximately 0.13%/min, lower than the swelling rate. Therefore, a homogeneous graft chain distribution can be obtained at only a lower degree of grafting in this grafting system. These results suggest that the grafting is mainly controlled by the amount of trapped radicals, rather than the monomer diffusion into the ETFE matrix.

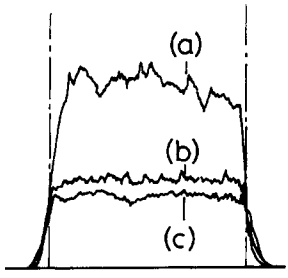

Fig. 11. Distribution of graft chains in the grafted film (XMA profile). Grafting conditions: preirradiation dose, 1×10^5 Gy; monomer conc, 100%; grafting temp, 50°C; film thickness, 100 μm. (a) Reaction time, 24 h; grafting yield, 45%. (b) Reaction time, 10 h; grafting yield, 34%. (c) Reaction time, 2 h; grafting yield, 18%.

CONCLUSION

Preirradiation grafting of α, β, β-trifluorostyrene onto poly(ethylene–tetrafluoroethylene) film was studied to elucidate the effects of grafting conditions. The results obtained and discussed above can be summarized as follows:

1. The dependences of the grafting rate on the preirradiation dose and monomer concentration were found to be of 0.3 and 1.0 order, respectively, and the final degree of grafting also depended on the preirradiation dose and monomer concentration.

2. The overall activation energies for this grafting system were calculated to be 6.2×10^4 and 9.3×10^3 J/mol below and above 50°C, respectively.

3. The grafting rate was found to be independent of film thicknesses ranging from 25 to 100 μm.

4. In this grafting system, graft polymerization was found to be controlled by the amount of trapped radicals, rather than the monomer diffusion into the poly(ethylene–tetrafluoroethylene) matrix.

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