Radiation Grafting of α,β,β-Trifluoroethylenesulfonyl Fluoride onto Low-Density Polyethylene Film by Simultaneous Irradiation Method. I. Kinetic Study of Simultaneous-Irradiation Grafting

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Synopsis

α,β,β-Trifluoroethylenesulfonyl fluoride (TFESF) was grafted onto polyethylene (PE) film by a simultaneous-irradiation method. The influences of the grafting conditions were analyzed kinetically. The dependencies of the grafting rate on the dose rates and monomer concentrations ranging from 10 to 75% were found to be of 1 and 0 order, respectively. The overall activation energy for the graft polymerization was 2.05×10^4 J/mol. The grafting rate was found to be independent of the film thicknesses ranging from 25 to 100 μm.

INTRODUCTION

Radiation-induced graft polymerization is a convenient means of preparing ion-exchange membranes, and many studies of the grafting of various hydrophilic monomers onto polyethylene (PE) film have been made. For example, the use of simultaneous or preirradiation grafting techniques in the grafting of styrene or acrylic acid onto PE film has been extensively studied.[1-5] Acrylic-acid-grafted polyethylene film was found to be especially useful as a separator in alkaline batteries and the membrane has been put into industrial production.[6]

Recently the syntheses of fluorine-containing ion-exchange membrane by radiation grafting have been attempted to meet requirements for a chemical and heat resistant ion-exchange membrane for water electrolysis and caustic soda production. An example is the grafting of acrylic acid onto polytetrafluoropropylene or poly(tetrafluoroethylene–hexafluoropropylene) film as a fluoro-containing trunk polymer, which has been studied in particular detail.[7-9] However, there has been little report of the grafting of fluorine monomers containing fluorine onto trunk polymers except for α,β,β-trifluoro acrylate grafting.[10,11]

In the course of this study, the radiation-induced graft polymerization of α,β,β-trifluoroethylenesulfonyl fluoride (TFESF) onto low-density polyethyl-

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ene (LDPE) was attempted and analyzed kinetically to elucidate the influences of grafting conditions such as dose rate, monomer concentration, grafting temperature, and film thickness.

EXPERIMENTAL

Materials

Commercially available LDPE (Asahi-Dow Ltd.) films of 25–100 μm thickness were used, and these films were washed in acetone and dried at room temperature.

TFESF was prepared according to the procedure developed by Banks et al.[12]

n-Hexane to be used as the solvent was purified by passage through a column of activated Alumina (GmbH, Alumina Woelm B).

Graft Polymerization

LDPE films and a mixture of TFESF and hexane in a glass ampoule were degassed by several freeze-thaw cycles at 1.33×10^{-3} Pa and then the ampoule was sealed. After standing at room temperature for 24 h, the sample was subjected to γ-ray irradiation by Co-60 at dose rates ranging from 1×10^{3} to 1×10^{4} Gy/h and temperatures ranging from 20 to 60°C. After irradiation, the grafted films were removed and soaked in acetone for 24 h to eliminate the residual monomers and homopolymers. After drying for 4 h in a vacuum at 60°C, the films were weighed.

The grafting percentage was calculated as

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

where W_i and W_g represent the weight of the initial and grafted film, respectively.

Measurement of Swelling

The degree of swelling was determined by immersing 50-μm-thick LDPE film in a monomer solution at 25°C for 12 h. Upon removal the film was quickly blotted with absorbent paper to remove the surface liquid and immediately weighed. The degree of swelling was calculated as

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

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

Grafting Distribution

The distribution of graft chains in the grafted film was investigated by X-ray microanalyzer (JXA-Super Prove 773, Japan Electron Optics Laboratory Co., Ltd.). The grafted film, pretreated in 20 wt % KOH DMSO/water 1 : 2 solution for 24 h at temperatures ranging from 90 to 100°C was cut perpendicularly to its surface at liquid nitrogen temperature, and its cross section was observed.

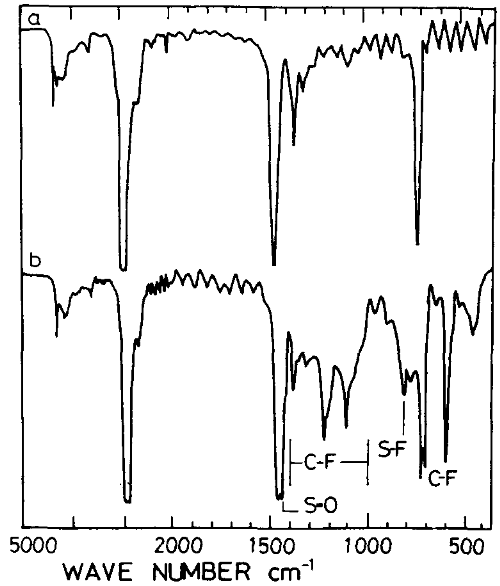

Fig. 1. Infrared spectra of the films: (a) LDPE, film thickness 25 μm; (b) the grafted LDPE, degree of grafting 16.1%.

RESULTS AND DISCUSSION

Grafted Film Identification

Figure 1 shows the infrared spectra of LDPE film and grafted film with a 16.1% grafting yield. The absorption spectra of the grafted polymer were between 600 and 1440 cm^{-1}. The function of sulfonyl fluoride was established by the S=O stretching vibration at 1440 cm^{-1}, the S—F stretching vibration at 820 cm^{-1}, and the C—S stretching vibration at 600 cm^{-1}. The 1000–1400 cm^{-1} bands were assigned to CF and CF_2 stretching. C=C

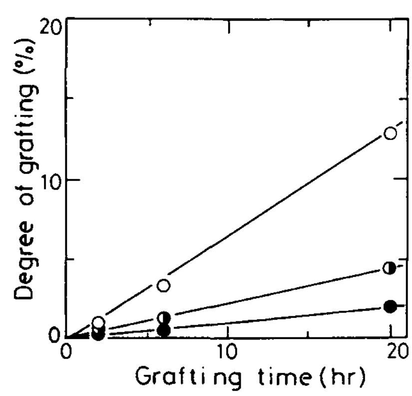

Fig. 2. Degree of grafting–time curves at various simultaneous-irradiation dose rates (Gy/h): (○) 1×10^4; (◑) 4×10^3; (●) 2×10^3. Grafting conditions: monomer concn, 25%; grafting temp, 20°C; film thickness, 50 μm.

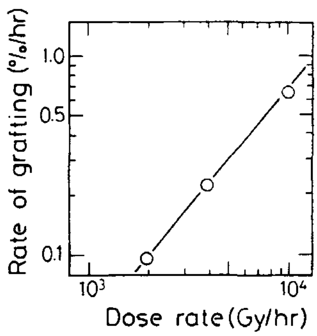

Fig. 3. Logarithmic plots of grafting rates vs. simultaneous-irradiation dose rates. Grafting conditions are the same as in Figure 2.

stretching vibration due to α,β,β-trifluoroethylene was not observed. These features confirm that TFESF was grafted onto the LDPE film.

Effect of Dose Rate

Figure 2 shows the grafting percentage as a function of the irradiation time at various dose rates. Under experimental conditions the grafting percentage increased linearly with the irradiation time. The initial rate of grafting at a dose rate of 1×10^4 Gy/h was 0.64%/h, considerably lower than the graft polymerization rate of styrene onto polyethylene[3] (11.2%/hr at a dose rate of 2.13×10^3 Gy/h). Moreover, homopolymers were scarcely observed.

The initial rates of grafting determined from the grafting–time curves in Figure 2 were plotted against the dose rates as shown in Figure 3, and found to be approximately proportional to a 1 power of dose rate. The dose exponent of the grafting rate is twice that of graft polymerization of styrene onto polyethylene in which the polymerization is terminated by the usual bimolecular coupling.[3] It may be considered that the graft polymerization of TFESF was terminated by some other reactions, such as the chain transfer of the propagation radicals to the solvent.

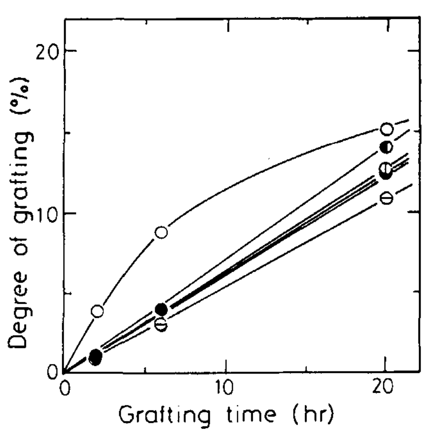

Fig. 4. Degree of grafting–time curves at various monomer concentrations: (●) 100%; (⊖) 75%; (⦶) 50%; (◑) 25%; (◐) 20%; (○) 10%. Grafting conditions: dose rate, 1×10^4 Gy/h; grafting temp, 25°C; film thickness, 50 μm.

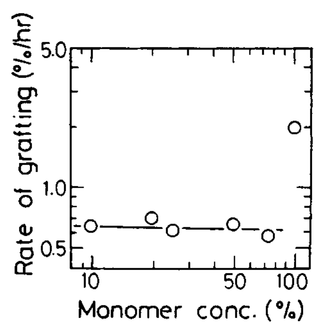

Fig. 5. Logarithmic plots of grafting rate vs. monomer concentration. Grafting conditions are the same as in Figure 4.

Effect of Monomer Concentration

Figure 4 shows the grafting percentage as a function of irradiation time in various monomer concentrations. The grafting percentage increases linearly with irradiation time in monomer concentrations ranging from 10 to 75%. On the other hand, the grafting percentage increases more rapidly and then levels off in 100% monomer concentration.

The initial rates of grafting determined from the grafting–time curves shown in Figure 4 were plotted against the monomer concentration percentages in Figure 5. The rates of grafting in the monomer concentrations in the range of 10–75% are constant. Figure 6 shows the relationship between the degree of swelling and monomer concentration. Swelling was found to decrease as monomer concentration increased. The curve was also found not to be in agreement with that obtained for the grafting rate. Therefore, the grafting rate in this system is independent of polymer substrate swelling.

These results suggest that the grafting rate is independent of the monomer diffusibility into the LDPE matrix.

Effect of Temperature

Figure 7 shows the grafting percentage as a function of the irradiation time at temperatures ranging from 20 to 60°C. The initial rate of grafting increases

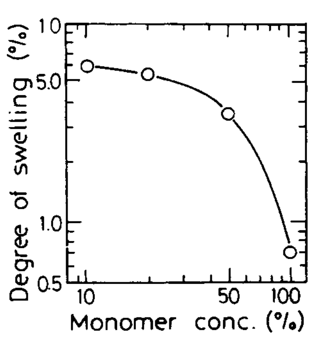

Fig. 6. Logarithmic plots of swelling percentage vs. monomer concentration. Swelling temp, about 25°C; swelling time, 1 day; film thickness, 50 μm.

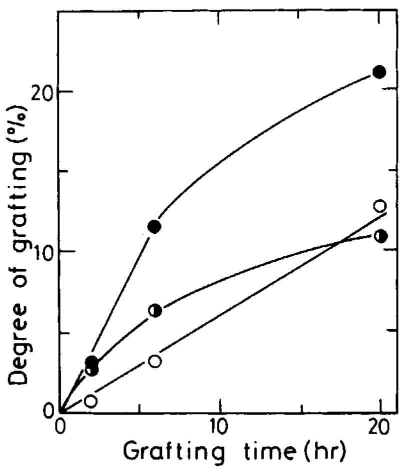

Fig. 7. Degree of grafting–time curves at various grafting temp: (○) 20°C; (◑) 40°C; (●) 60°C. Grafting conditions: dose rate 1×10^4 Gy/h; monomer concn, 25%; film thickness, 50 μm.

with temperature, but the grafting percentage has a tendency to level off at 40 and 60°C.

Figure 8 shows Arrhenius plots for this grafting. The overall activation energy was calculated to be 2.05×10^4 J/mol. This value was found to be in close agreement with that obtained for the preirradiation grafting of acrylic acid onto PTFE above 35°C, where there is a high monomer diffusibility into the PTFE matrix,[7] suggesting such a high diffusibility in this system.

Effect of Film Thickness

Figure 9 shows the grafting percentage as a function of irradiation time for films of various thickness. Under the experimental conditions, the grafting percentage increased linearly with irradiation time.

Figure 10 shows the relationship between the initial rate of grafting and film thickness. The initial rate of grafting was found to be independent of film thicknesses ranging from 25 to 100 μm.

Figure 11 shows the graft chain distribution in grafted films having almost the same grafting percentage and different thicknesses. In this figure, the graft

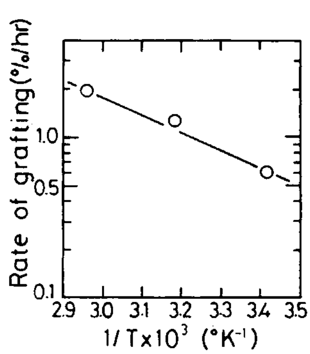

Fig. 8. Arrhenius plots of grafting rate. Grafting conditions are the same as in Figure 7.

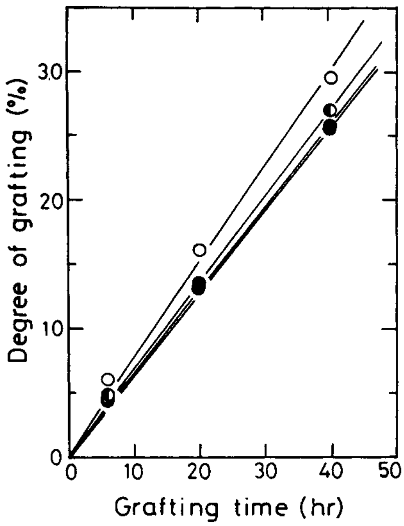

Fig. 9. Degree of grafting–time curves at various film thickness: (○) 25 μm; (◑) 50 μm; (◐) 75 μm; (●) 100 μm. Grafting conditions: dose rate, 1 × 10^4 Gy/h; monomer conc, 25%; grafting temp, 20°C.

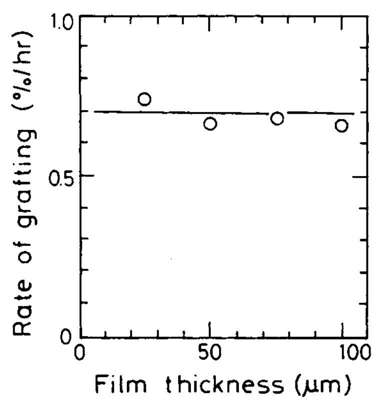

Fig. 10. Grafting rate vs. film thickness. Grafting conditions are the same as in Figure 9.

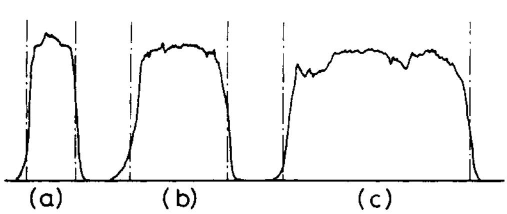

Fig. 11. Distribution of graft chain in the membrane (XMA profile). Grafting conditions: dose rate, 1 × 10^4 Gy/h; dose, 4 × 10^5 Gy/h; monomer concn, 25%; grafting temp, 25°C. (a) Film thickness = 25 μm; grafting percentage = 29.6%; (b) film thickness = 50 μm; grafting percentage = 26.2%; (c) film thickness = 100 μm; grafting percentage = 26.2%.

chain distribution is largely constant over the range of film thicknesses. These results suggest a high monomer diffusibility in the LDPE matrix. Therefore, in this grafting system, grafting is mainly controlled by the amount of trapped radicals, rather than monomer diffusion into the LDPE matrix.

CONCLUSIONS

Simultaneous irradiation was used to study the grafting of α,β,β-trifluoroethylenesulfonyl fluoride onto low-density polyethylene film. From the experimental results that we have discussed it can be concluded that:

1. The grafting rate dependence on dose rates was found to be in the order of 1.
2. The grafting rate dependence on monomer concentrations was found to be in the order of 0 in monomer concentrations ranging from 10 to 75%.
3. The overall activation energy for this grafting system was calculated to be 2.05×10^4 J/mol.
4. The grafting rate was found to be independent of the film thicknesses ranging from 25 to 100 μm.
5. In this grafting system, grafting was found to be controlled by the amount of trapped radicals, but not by monomer diffusion into the low-density polyethylene matrix.

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