

Radiation Grafting of α,β,β -Trifluorostyrene onto Various Polymer Films by Preirradiation Method

TAKASHI MOMOSE, KAZUO TOMIIE, ISAO ISHIGAKI* and
JIRO OKAMOTO,* *Chlorine Engineers Corp., Ltd.,
2-1-1 Toranomon, Minato-ku, Tokyo, Japan*

INTRODUCTION

There are very few reports relating to radiation grafting of α,β,β -trifluorostyrene (TFS) onto various polymer films. In general, two radiation-grafting techniques are employed: simultaneous irradiation method, in which a polymer film is immersed in a monomer or monomer solution and the entire mixture is irradiated; and preirradiation method, in which a polymer film is activated by irradiation and subsequently allowed to react with a monomer.

D'Agostino et al.¹⁻³ studied the grafting of TFS onto poly(tetrafluoroethylene-hexafluoropropylene) (FEP) film by simultaneous irradiation using γ rays from a ⁶⁰Co. They found that the membrane obtained by sulfonation of the grafted film can be used for various electrochemical cells such as chloralkali and fuel cells. Nevertheless, the radiation grafting of TFS by preirradiation, which is known as a more commercially available way compared with simultaneous irradiation⁴ has not been reported.

In this communication, the preliminary study on the radiation grafting of TFS onto various polymer films, mainly fluorine-containing polymers, by preirradiation is reported.

EXPERIMENTAL

The TFS was synthesized according to the method reported in the literature.⁵ Films of low-density polyethylene (LDPE; Asahi-Dow Co., Ltd.; 100 μm), poly(ethylene-tetrafluoroethylene) (ETFE; Asahi Glass Co., Ltd.; 100 μm), poly(tetrafluoroethylene-perfluorovinylether) (PFA; du Pont Co., Ltd.; 130 μm), poly(tetrafluoroethylene-tetrafluoropropylene) (FEP; du Pont Co., Ltd., 130 μm), and polytetrafluoroethylene (PTFE; Nitto Denko Co., Ltd.; 100 μm) were used as base polymers.

The films were irradiated by being passed under the electron beams of a transformer type accelerator (EPS-750, Nissin-High Voltage, Co., Ltd.) operating at beam energy of 500 KV and with a current of 3.95 mA. The dose rate was approximately 5.4×10^3 Gy/s, and preirradiation dose was 1×10^5 Gy.

The irradiated films were immersed in a monomer solution and degassed by several freeze-thaw cycles at 0.13-Pa. The reaction was carried out at 25°C

*Present address: Takasaki Radiation Chemistry Research Establishment, Takasaki Gunma, 370-12 Japan.

TABLE I
Swelling Properties of Polymer Films in Pure TFS

Polymer	Sorbed TFS ^a (wt.%)	Solubility parameters ((cal/cm ³) ^{1/2})
LDPE	5.4	8.0 ^b
ETFE	4.1	6.7 ^c
PFA	0.8	—
FEP	0.4	—
PTFE	0.2	6.2 ^b

^aSwelling conditions: temp., 25°C; swelling time, 24h; polymer substrate, PE(100 μm), ETFE(100 μm), PFA(130 μm), FEP(130 μm), PTFE(100 μm).

^bFrom ref. 7.

^cCalculated by means of ref. 6.

for a maximum of 4 days. The degree of swelling was determined by immersing polymer films in a monomer at 25°C for 24 h. Analysis by infrared spectroscopy was carried out by ATR method (IR-435, Shimadzu Seisakusho Co., Ltd.). The distribution of graft chains in the grafted film was investigated with an x-ray microanalyzer (X-560, Hitachi Co., Ltd.) after sulfonation of the grafted films by chlorosulfonic acid, followed by hydrolysis of the sulfonated films by KOH solution.

RESULTS AND DISCUSSION

Table I shows the degree of polymer film swelling in pure TFS and the solubility parameters of LDPE, ETFE, and PTFE. Among the five polymer films, the highest is LDPE film and the lowest is PTFE film. It is known that the sorption of liquid in polymer depends on the affinity between the liquid and the polymer. The solubility parameter of TFS was calculated to 8.0 (cal/cm³)^{1/2} according to the method reported by Hoy.⁶ By comparing the results in Table I and the solubility parameter of TFS, it is clear that the smaller the difference in solubility parameter between polymer and TFS, the greater the polymer film swelling.

Figure 1 shows the graft yield-time curves of TFS onto various polymer films. For all the polymer films, the degree of grafting increased at first and leveled off at a given limiting value which is called the final percent grafting in this report. Among these five polymer films, both the grafting rates and final percent graftings are relatively high for the LDPE and ETFE films. As shown in Table I, the degree of swelling of LDPE and ETFE are also high among the five polymer films; therefore, it is clear that the higher the degree of polymer film swelling, the higher the grafting rate and final percent grafting in this grafting system.

Figure 2 shows the infrared spectra of LDPE film and the grafted film with 16.6% grafting yield. The presence of an aromatic ring is established by the skeletal C=C in-plane-stretching vibrations at 1500 and 1600 cm⁻¹. Mono-substitution of the ring is confirmed by the aromatic CH deformation bands at 690 and 760 cm⁻¹. The stretching vibrations of CF₂ and CF are observed from 1000 to 1400 cm⁻¹. Stretching vibrations of C=C at 1750 cm⁻¹ due to

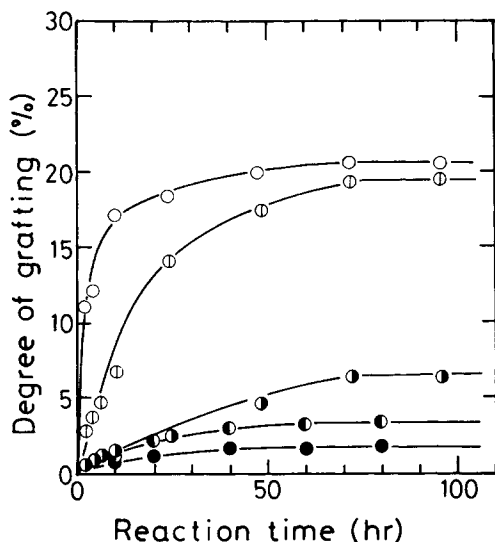


Fig. 1. Graft yield-time curves of TFS onto various polymer films: (○) LDPE; (◻) ETFE; (◻) PFA; (◻) FEP; (●) PTFE. Grafting conditions: preirradiation dose, 1×10^9 Gy; monomer conc., 100%; grafting temp., 25°C.

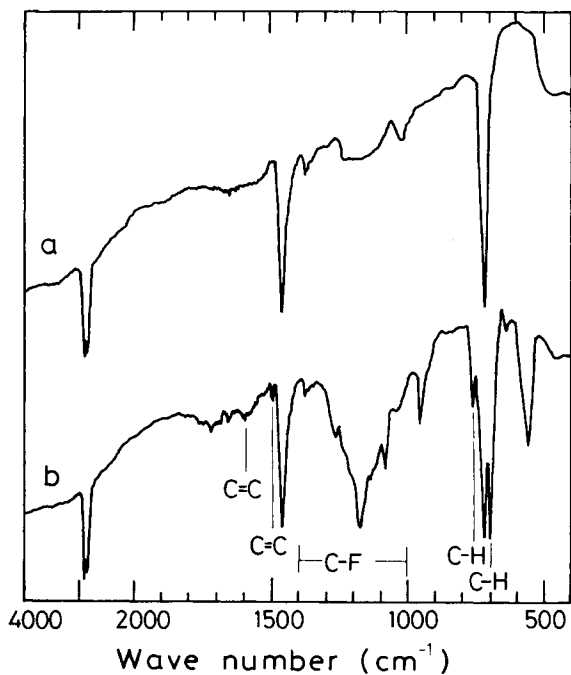


Fig. 2. Infrared spectra of the films: (a) LDPE; (b) the grafted LDPE with a 16.6% grafting yield.

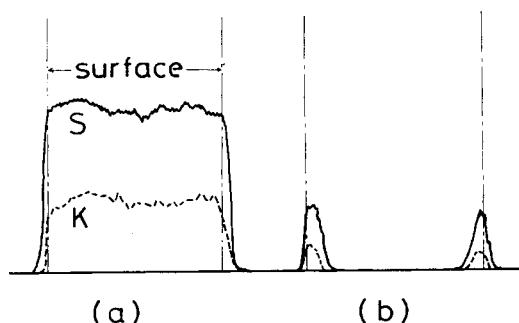


Fig. 3. Distribution of graft chain in the grafted films (XMA profile). Grafting conditions are the same as in Figure 1. (a) Grafted ETFE film: reaction time, 96 h; grafting yield, 19.4%. (b) Grafted PTFE film: reaction time, 80 h; grafting yield, 1.7%.

TFS was not observed. These features confirm that TFS was grafted onto the LDPE film.

Figure 3 shows the transversal distribution curves of graft chains in the grafted films obtained from line profiles of potassium and sulfur located in the graft chains with an electron-probe x-ray microanalyzer. Both the grafted films have final percent of grafting at the experimental conditions previously mentioned. The graft chain distribution of the grafted ETFE film is largely constant over the range of film thickness. On the other hand, the graft chain distribution of the grafted PTFE film has two peaks located $\sim 10 \mu\text{m}$ inside the film surface. These results suggest a higher monomer diffusibility in the ETFE film but not in the PTFE film.

Investigation of further details is in progress and will be reported elsewhere.

References

1. V. F. D'Agostino, J. Y. Lee, and E. H. Cook Jr., U.S. Patent 4,012,303 (1977).
2. V. F. D'Agostino, J. Y. Lee, and E. H. Cook Jr., U.S. Patent 4,107,005 (1978).
3. V. F. D'Agostino, J. Y. Lee, and E. H. Cook Jr., U.S. Patent 4,113,922 (1978).
4. T. Momose et al., U.S. Patent 4,605,685 (1986).
5. R. B. Hodgdon, Jr., *J. Polym. Sci., Part A-1*, **6**, 171 (1968).
6. K. L. Hoy, *J. Paint Technol.*, **42**, 76 (1970).
7. H. Omichi and J. Okamoto, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1559 (1982).

Received November 18, 1987

Accepted March 30, 1988