Radiation Grafting of Acrylic Acid onto Fluorine-Containing Polymers. I. Kinetic Study of Preirradiation Grafting onto Poly(tetrafluoroethylene)

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Synopsis

Preirradiation grafting of acrylic acid onto poly(tetrafluoroethylene) film was studied. The trapped radicals formed upon irradiation are able to induce graft polymerization under appropriate conditions. The influence of the grafting conditions were analyzed kinetically. The grafting reaction begins close to the film surface and proceeds into the center with progressive monomer diffusion through the grafted layer. The dependences of the grafting rate on preirradiation dose and monomer concentration were found to be 0.2 and 1.1 order, respectively. The overall activation energies for this grafting were calculated to be 15.2 and 4.8 kcal/mol below and above 35°C, respectively. The relationship between the grafting rate and film thickness gave a negative first-order dependence.

INTRODUCTION

Many studies have been carried out for the preparation of hydrophilic membranes by radiation grafting of various hydrophilic monomers onto poly(tetrafluoroethylene) (PTFE) film. By using simultaneous or preirradiation grafting techniques, PTFE was found to be grafted by vinyl acetate,[1] styrene,[2–6] *N*-vinylpyrrolidone,[7–9] acrylic acid,[10–12] 4-vinylpyridine,[7,11,13,14] and methyl methacrylate.[2] The grafting of PTFE by such monomers is of special interest since the grafting front gradually penetrates into the depth of the film under appropriate reaction conditions, despite the fact that PTFE scarcely swells in any monomers or solvents. The grafting is largely affected by the diffusion of monomer into the PTFE matrix. Dobo et al.[4] determined the penetration of grafted styrene into preirradiated PTFE by measuring the optical density across microsections of the grafted and colored films and found that grafting begins at the surface and then takes place in the polymer matrix with progressive diffusion of monomer.

Poly(acrylic acid) is insoluble in its monomer; hence, a solvent must be used in order to properly swell the grafted zone and make monomer diffusion possible. An aqueous medium was found to be suitable for this purpose. Ishigaki et al.[12] studied the grafting of acrylic acid onto PTFE by simultaneous grafting and found that the nongrafted layer remains in the middle part of the film at a lower grafting percent and then disappears as the grafting proceeds. They also reported that the lower the dose rate, the deeper the grafting proceeds. The γ

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ray-induced graft polymerization of vinyl acetate onto PTFE was studied by Restaino et al.[1] They found that the rate of grafting is proportional to 1.45 and 0.5 orders of the monomer concentration and dose rate, respectively. They also reported that the activation energy for the simultaneous grafting of vinyl acetate to PTFE is 4.78 kcal/mol. Chapiro et al., who have studied extensively the simultaneous grafting of acrylic acid[5,10,11] and 4-vinylpyridine[11,13] onto PTFE, reported that the activation energies for the grafting of acrylic acid onto PTFE are 15.0 and 5.1 kcal/mol below and above 33°C, respectively.

In the present study, the preirradiation graft polymerization of acrylic acid to PTFE was investigated kinetically for a wide range of grafting conditions, such as monomer concentration, preirradiation dose, reaction temperature, and film thickness. PTFE was chosen for this study because of its excellent mechanical and chemical properties, which are one of the essential factors, as well as electrochemical properties for the ion exchange membrane.

EXPERIMENTAL

Materials

PTFE film (specific gravity 2.2 g/cm^3, Nitto Co. Ltd.) was washed with acetone and dried at room temperature. Reagent-grade acrylic acid (Kishida Chemicals Co. Ltd.) stabilized with 200 ppm hydroquinone monomethyl ether was used as received. The other chemicals were reagent grade and were used without further purification.

Graft Polymerization

A glass ampoule containing strips of PTFE was evacuated for 3 h under reduced pressure less than 1×10^{-3} mm Hg. Then the glass ampoule was kept at −78°C and subjected to γ-ray irradiation from Co 60 at a dose rate ranging from 0.3 to 1 Mrad/h. Aqueous acrylic acid deaerated by bubbling nitrogen was then introduced into the preirradiated sample. Mohr's salt (0.25 wt %) were used to minimize the homopolymerization of the monomer. The polymerization was carried out in a nitrogen atmosphere and at a given temperature. The grafted film thus obtained was removed and washed thoroughly with hot distilled water and then soaked overnight in the water to extract the residual monomer and homopolymer contained in the film. The film was then dried in vacuo at 50–60°C for 24 h and weighed. The degree of grafting was determined by its percentage increase in weight.

Swelling Measurement

The degree of swelling was determined as follows: the 200-μm-thick PTFE film was immersed in the monomer solution for four days at 25°C. Then, the film was removed, blotted quickly with absorbent paper to remove the liquid attached on its surface, and weighed quickly. Swelling measurements were done on 200-μm-thick films due to the higher accuracy attainable with thicker sample.[15]

RESULTS AND DISCUSSION

Effect of Preirradiation Dose

Figure 1 shows the graft yield–time curves at various preirradiation doses. The degree of grafting at first increases rapidly with time and then levels off at a given limiting value which is called the final percent grafting in this report. Both the rate of grafting and final percent grafting increase with preirradiation dose. The logarithmic plots of these values vs. preirradiation dose are shown in Figure 2. The dose exponent of the grafting rate was found to be approximately 0.2, which is very small compared with the calculated theoretically for the free radical polymerization (0.5).

Generally, the grafting rate and final percent grafting are largely dependent on the concentration of radicals. The amount of radicals formed by irradiation at first increases linearly with dose and then usually reaches a certain limiting values at a higher dose due to the recombination of themselves. It is also known

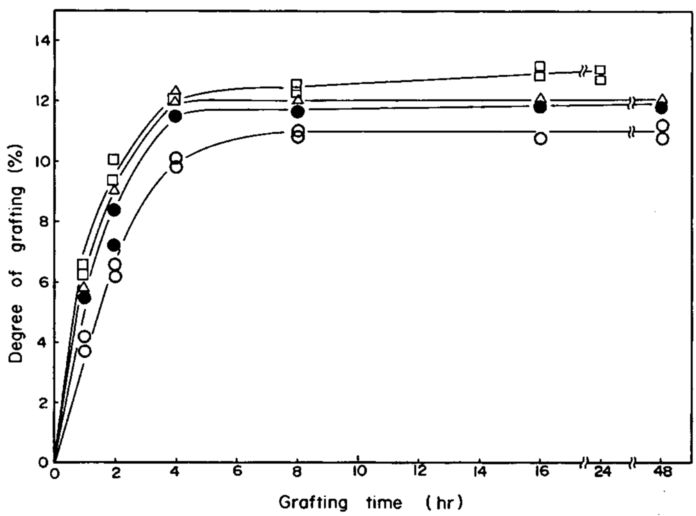

Fig. 1. Graft yield vs. time at various preirradiation doses. Monomer conc., 40 wt %; Mohr's salt, 0.25 wt %; grafting temp., 35°C; film thickness, 80 μm. (O) 1 Mrad; (●) 3 Mrad; (△) 5 Mrad; (□) 10 Mrad.

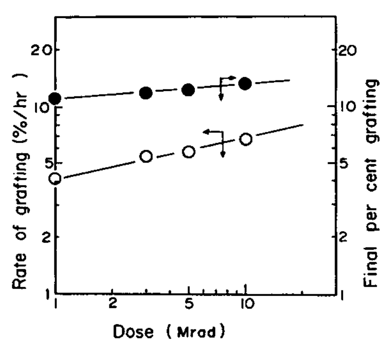

Fig. 2. Logarithmic plots of grafting rate and final percent grafting vs. preirradiation dose. Grafting conditions same as in Fig. 1.

that crystallinity of PTFE increases upon irradiation of ionizing radiation.[16–18] Since PTFE is easily degraded by irradiation, the degraded PTFE with lower molecular weight in the amorphous phase rearranges to crystallize. The diffusion rate of monomer through the irradiated PTFE seems to decrease with increasing preirradiation dose due to the increase in crystallinity. Therefore, the lower dependences of rate and final percent grafting found for this grafting system can be attributed not only to the decrease in efficiency of radicals initiating the graft reaction at a higher dose but also to the decrease in diffusion rate of monomer into polymer matrix.

Effect of dose rate on this grafting has been also investigated by using films irradiated up to 5 Mrad at dose rates of 0.31, 1.0, and 1.7 Mrad/h. The rate of grafting and final percent grafting were not influenced by dose rate.

Effect of Monomer Concentration

The effects of monomer concentration on grafting are shown in Figure 3. The rate of grafting increases with monomer concentration and the final percent grafting is almost constant at a monomer concentration less than 60% and then increases at a higher monomer concentration.

The dependence of the grafting rate on the monomer concentration was calculated to be 1.1 order. In the preirradiation grafting, generally, the initial rate should be largely dependent on the diffusibility of monomer into the polymer matrix. Figure 4 shows the relationship between the degree of swelling and acrylic acid concentration determined for the original PTFE film. It is well known that PTFE scarcely swells in any solvent or monomer. The degree of swelling, however, was found to increase linearly with the acrylic acid concentration ranging from 10 to 80%, and then the value at 100% acrylic acid deviated from the straight line, although the absolute value of swelling was very small. The slope of the straight line was also found to be in fair agreement with that obtained for the rate of grafting. Therefore, the rate of grafting in this system is mainly dependent on the swelling properties of polymer substrate.

On the other hand, the final percent grafting was found to be independent of the acrylic acid concentration in the range of 10 to 60%. These results suggest

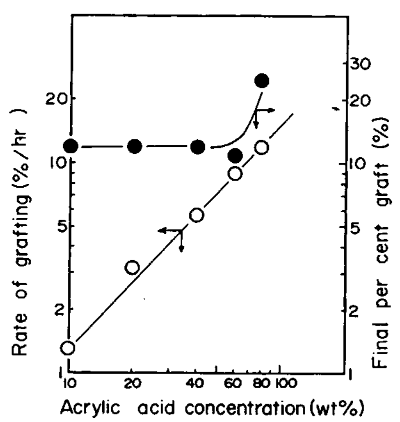

Fig. 3. Logarithmic plots of grafting rate and final percent grafting vs. acrylic acid concentration. Preirradiation dose, 5 Mrad; Mohr's salt, 0.25 wt %; grafting temp., 35°C; film thickness, 80 μm.

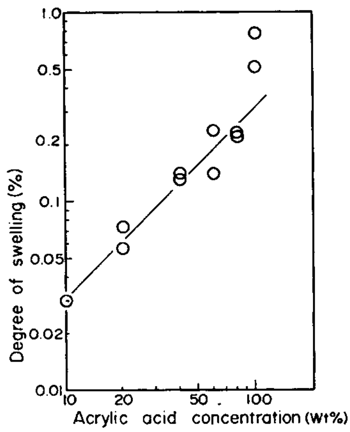

Fig. 4. Logarithmic plots of percent swelling vs. acrylic acid concentration. Swelling temp., 25°C; swelling time, four days; film thickness, 200 μm.

that the degree of grafting is dependent only on the amount of radicals; i.e., trapped radicals in PTFE seem to be stable enough to survive and react with monomer which diffuses into polymer matrix at the temperature examined here.

The higher value at 80% seems to indicate that the termination reaction of growing chain is depressed at a higher monomer concentration, since poly(acrylic acid) is insoluble in its monomer, i.e., the mobility of growing chains decreases with increasing monomer concentration. Also, the amount of Mohr's salt, which works to lower the graft reaction as well as to inhibit the homopolymerization, may not be enough to work effectively until the grafting is completed. During grafting at a higher monomer concentration such as 80%, in fact, part of Mohr's salt precipitated in the reaction medium, and a marked increase in viscosity of the reaction medium was observed as the grafting proceeded.

Effect of Temperature

Figure 5 shows the graft yield–time curves obtained at temperatures in the range of 15 to 60°C. The initial rate of grafting increases with temperature and the final percent grafting has a certain maximum value. Since the decay of trapped radicals is enhanced at a higher temperature, the grafting reaches the final percent grafting faster. The final percent grafting is dependent not only on the grafting temperature but also on the reaction time at which the grafting levels off, because the amount of trapped radicals decreases gradually with increasing time even at a lower temperature. Therefore, the final percent grafting has an optimum value.

The temperature dependence of the initial rate of grafting can be reasonably understood by the diffusibility of monomer into polymer matrix and the reactivity of trapped radicals. Figure 6 shows Arrhenius plots for this grafting which show a breaking point at ca. 35°C. The overall activation energy was calculated to be 15.2 and 4.8 kcal/mol below and above 35°C, respectively. These values were found to be in close agreement with those obtained for the simultaneous grafting of acrylic acid onto PTFE by Chapiro et al.[11] It was also reported that PTFE crystal undergoes a series of transitions and that there is a higher internal

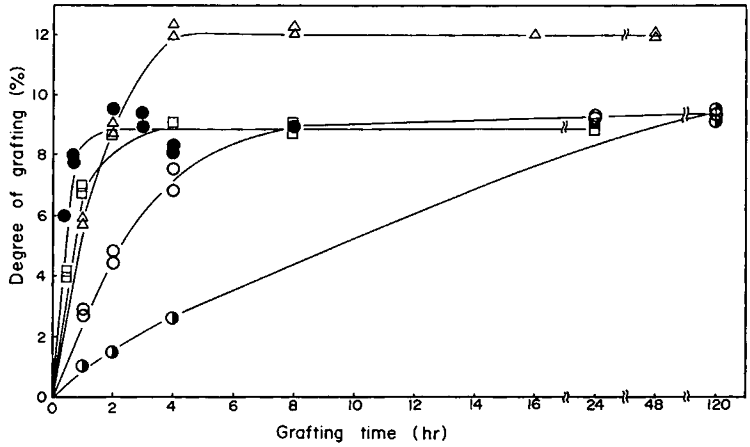

Fig. 5. Graft yield vs. time at various grafting temperatures. Preirradiation dose, 5 Mrad; monomer conc., 40 wt %; Mohr's salt, 0.25 wt %; film thickness, 80 μm. (◑) 15°C; (○) 25°C; △ 35°C; (□) 45°C; (●) 60°C.

friction in the range of 200 to 290 K.[19] Therefore, it is concluded that the increase in diffusibility of monomer into PTFE matrix results in the lowering of the activation energy in the temperature ranging from 35 to 60°C.

Effect of Film Thickness

Figure 7 shows the graft yield-time curves for the film with various thicknesses. The degrees of grafting level off at the values ranging from 10 to 12%, and the grafting rate decreases with increasing film thickness. The logarithmic plots of the grafting rate as a function of film thickness, as shown in Figure 8, gave a straight line with a slope of −1.1. This negative first-order dependence coincides with that found in the grafting of 4-vinylpyridine onto polyethylene.[15,20]

The results shown in Figure 7 were analyzed by taking account of weight increase per unit surface area of the film as shown in Figure 9. The initial rate of weight increase per unit surface area was found to be constant, irrespective of film thickness. The final weight of grafted poly(acrylic acid) per unit surface area is linearly proportional to the thickness, and its dependence indicates a good first-order plot.

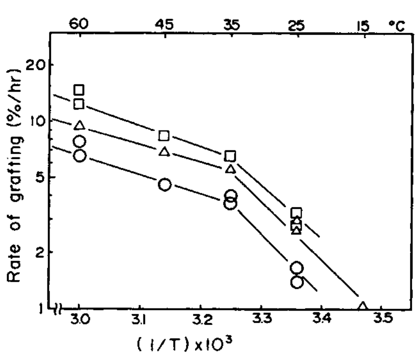

Fig. 6. Arrhenius plots of grafting rate. Grafting conditions same as in Fig. 5. (○) 1 Mrad; (△) 5 Mrad; (□) 10 Mrad.

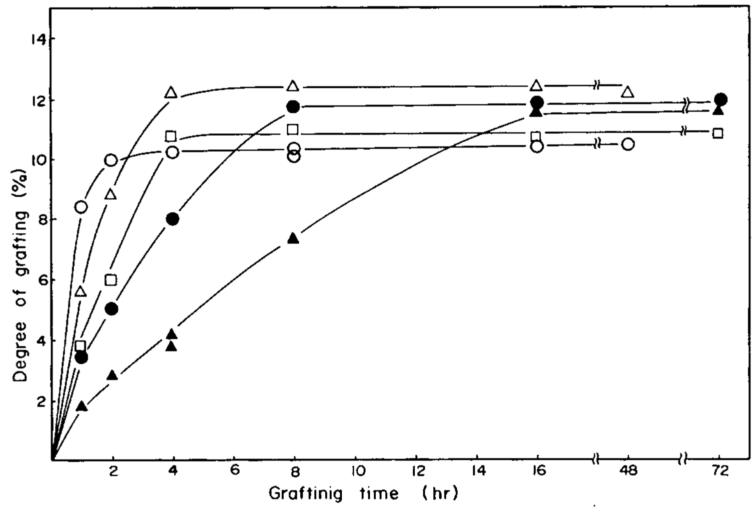

Fig. 7. Graft yield vs. time at various film thicknesses. Preirradiation dose, 5 Mrad; monomer conc., 40 wt %; Mohr's salt, 0.25 wt %; grafting temp., 35°C. (○) 50 μm; (△) 80 μm; (□) 100 μm; (●) 130 μm; (▲) 200 μm.

These results suggest that, in this grafting system, the reaction begins at the part close to the surface and then proceeds gradually into the center of the film with progressive diffusion of monomer through the surface and the grafted layer, so that the grafting is mainly controlled by the monomer diffusion.

CONCLUSIONS

The grafting of acrylic acid onto poly(tetrafluoroethylene) film has been studied by using a preirradiation technique. From the experimental results discussed above, it can be concluded that:

(1) The dependences of the grafting rate on preirradiation dose and monomer concentration were found to be 0.2 and 1.1 order, respectively, although those of the final percent grafting were not remarkable.

(2) The overall activation energies for this grafting system were calculated to be 15.2 and 4.8 kcal/mol below and above 35°C, respectively.

(3) The relationship between the grafting rate and film thickness was found to give a negative first-order dependence.

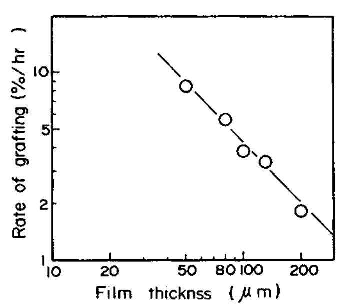

Fig. 8. Logarithmic plots of grafting rate vs. film thickness. Grafting conditions same as in Fig. 7.

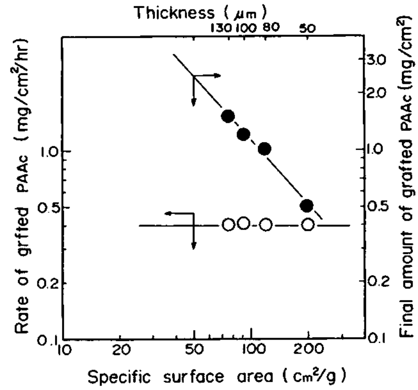

Fig. 9. Logarithmic plots of rate of grafted poly(acrylic acid) and final weight increase per unit surface area vs. specific surface area of film. Grafting conditions same as in Fig. 7.

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References

1. A. J. Restaino and W. N. Reed, *J. Polym. Sci.*, **36**, 499 (1959).
2. A. Chapiro, *J. Polym. Sci.*, **34**, 481 (1959).
3. A. Chapiro and A. Matsumoto, *J. Polym. Sci.*, **57**, 743 (1962).
4. J. Dobo, A. Somogyi, and T. Czvikovszky, *J. Polym. Sci., Part C*, **4**, 1173 (1964).
5. A. Chapiro, G. Derai, and A.-M. Jendrychowska-Bonamour, *Eur. Polym. J.*, **7**, 1595 (1971).
6. S. Munari, F. Vigo, M. Nicchia, and P. Canepa, *J. Appl. Polym. Sci.*, **20**, 243 (1976).
7. P. Aptel, J. Cuny, J. Jozefowicz, G. Morel, and J. Neel, *J. Appl. Polym. Sci.*, **16**, 1061 (1972).
8. P. Aptel, J. Cuny, J. Jozefowicz, G. Morel, and J. Neel, *Eur. Polym. J.*, **9**, 877 (1973).
9. A. Chapiro, A.-M. Jendrychowska-Bonamour, G. Morel, and R. Oppelt, *Eur. Polym. J.*, **9**, 847 (1973).
10. A. Chapiro and P. Seidler, *Eur. Polym. J.*, **1**, 189 (1965).
11. A. Chapiro, G. Bex, A.-M. Jendrychowska-Bonamour, and T. Oneill, *Adv. Chem. Ser.*, **91**, 560 (1969).
12. I. Ishigaki, N. Kamiya, T. Sugo, and S. Machi, *Polym. J.*, **10**, 513 (1978).
13. A. Chapiro, E. Gordon, and A.-M. Jendrychowska-Bonamour, *Eur. Polym. J.*, **9**, 975 (1973).
14. G. Canepa, S. Munari, C. Rossi, and F. Vigo, *Desalination*, **13**, 159 (1973).
15. A. M. Rabie, M. I. Aly, S. A. Hegazy, and N. I. El-Awady, *Polym. J.*, **11**, 359 (1979).
16. A. Nishioka, M. Tojima, and M. Owaki, *J. Polym. Sci.*, **28**, 617 (1958).
17. D. E. Kleine and J. A. Sauer, *J. Polym. Sci.*, *A*, **1**, 1621 (1963).
18. M. Tsuchiya and K. Yamamoto, *Oyo Butsuri*, **34**, 424 (1965); *ibid.*, **37**, 718 (1968).
19. N. G. McCrum, *J. Polym. Sci.*, **34**, 355 (1959).
20. G. Odian, A. Derman, and K. Imre, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 737 (1980).

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