The Study on Radiation Grafting of Acrylic Acid onto Fluorine-Containing Polymers. III. Kinetic Study of Preirradiation Grafting onto Poly(tetrafluoroethylene–Hexafluoropropylene)

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Synopsis

A kinetic study has been made on the preirradiation grafting of acrylic acid (AAc) onto poly(tetrafluoroethylene–hexafluoropropylene) (FEP) film. The effect of grafting conditions was investigated. The dependencies of the grafting rate on preirradiation dose and monomer concentration were found to be 0.58 and 1.25 order, respectively. The overall activation energy for the graft polymerization was 7.4 kcal/mol. The final degree of grafting increased with preirradiation dose and monomer concentration and slightly decreased as the grafting temperature was elevated. The relationship between the grafting rate and film thickness gave a negative first-order dependency, which is in agreement with that obtained for polytetrafluoroethylene—AAc grafting system. It was reasonably concluded that this grafting proceeds from the surface to the center of film with progressive monomer diffusion through the grafted layer which swells in the monomer solution.

INTRODUCTION

Recently, much work has been devoted to study on radiation-induced grafting on fluorine-containing polymers.[1–5] Membranes obtained by grafting of hydrophilic monomers onto hydrophobic polymers seem to meet all the requirements due to the fact that such grafting can induce hydrophilicity as well as good electrochemical properties. As mentioned in the previous papers,[6,7] grafting of acrylic acid onto poly(tetrafluoroethylene) (PTFE) film shows a promising way for the practical application as a cation exchange membrane. Grafting onto the FEP copolymer was found to proceed, under appropriate conditions, with a higher degree of grafting than that for the PTFE polymer.

The grafting of FEP as trunk polymer for membrane preparation has not been studied in detail. In the present study, the preirradiation grafting of acrylic acid onto FEP film was studied and analyzed kinetically to elucidate the influence of grafting conditions such as preirradiation dose, monomer concentration, grafting temperature, and film thickness. FEP film was chosen due to its excellent mechanical properties, thermal, chemical stability, and considerably higher radiation resistance than PTFE ones, and also it can be irradiated without extensive degradation.[8]

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EXPERIMENTAL

Materials and Grafting Method

Poly(tetrafluoroethylene–hexafluoropropylene) (FEP) film (Mitsui Fluoro Chemical Co., Ltd.) was washed with acetone and dried at room temperature. Reagent grade acrylic acid (AAc) (Kishida Chemical Co., Ltd.), and the other reagent grade chemicals were used without further purification.

The preirradiation method was used as a grafting technique. The irradiation was carried out using Co-60 γ-rays at a dose rate ranging from 0.3 to 1 Mrad/h and the film was kept at $-78°C$. Mohr's salt (ammonium ferrous sulfate), 0.25 wt %, was added to the aqueous AAc solution to minimize the homopolymerization. Details of the grafting procedures have been described in the previous paper.[6]

The grafted film was washed with hot distilled water and soaked in water overnight for the extraction of homopolymer which may be occluded in the film. The grafted film, thus obtained, was dried under vacuum at 60–80°C until the constant weight was reached. The degree of grafting was calculated using the following equation:

$$\text{degree of grafting (\%)} = (w_g - w_0)/w_0 \times 100$$

where w_0 and w_g represent the weights of initial and grafted FEP films, respectively.

Swelling measurement was carried out by the same method used in the previous study.[6]

RESULTS AND DISCUSSION

Effect of Preirradiation Dose and Dose Rate

Figure 1 shows the degree of grafting-time curves for the grafting of AAc onto FEP film at various preirradiation doses. It can be seen that, for all the preirradiation doses, the degree of grafting increases with time until 8 h and then levels off. The initial grafting rate and final degree of grafting are proportional to preirradiation dose. Figure 2 shows the logarithmic plots of grafting rate and final degree of grafting against preirradiation dose. The dependence of grafting rate on preirradiation dose was calculated to be 0.58 order. It is suggested that this grafting proceeds by radical mechanism with bimolecular termination of growing chain radicals. In the previous study[6] on the grafting of AAc onto PTFE film, it was found that the dependence of grafting rate on the preirradiation dose is 0.2 order at the same range of preirradiation dose. Also, the final degree of grafting on PTFE film was not remarkably affected by the preirradiation dose, and its value is approximately one-third of that for FEP film under the same grafting conditions. It is obvious that the final degree of grafting on FEP film remarkably increases with preirradiation dose.

It is well known that the preirradiation grafting largely depends on the amount and efficiency of trapped radicals formed upon irradiation. Since the decay of free radicals in the amorphous structure is much larger than that in the crystalline regions, the preirradiation grafting is well performed for the crystalline or semicrystalline polymers. According to this phenomenon and the results ob-

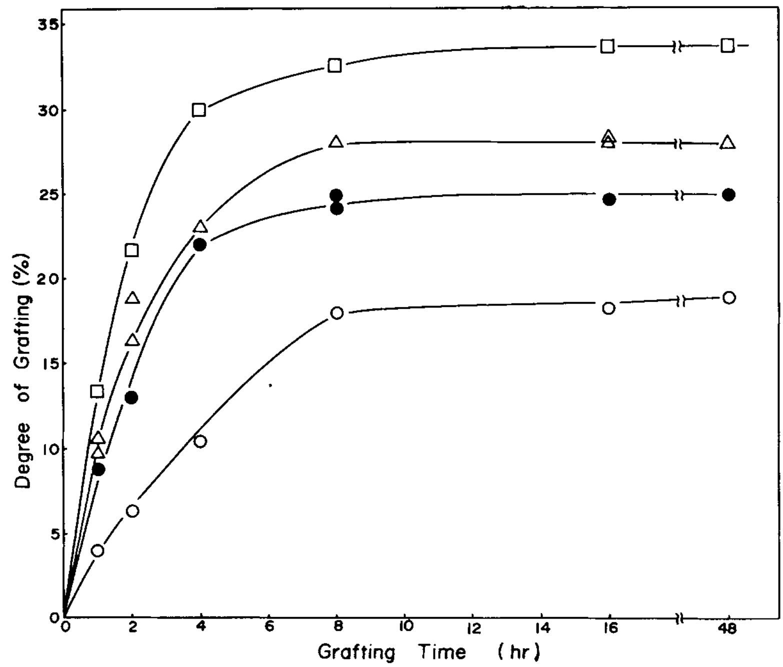

Fig. 1. Degree of grafting-time curves at various preirradiation doses (Mrad): (○) 1; (●) 3; (△) 5; (□) 10. Grafting conditions: AAc conc, 40 wt %; Mohr's salt, 0.25 wt %; grafting temp, 35°C; film thickness, 80 μm.

tained for FEP film, it can be suggested that the free radicals formed in FEP are more stable and are used more effectively than those in PTFE film.

As can be expected, no effect of dose rate (0.3–1 Mrad/h) on the grafting onto FEP film was observed. This result coincide with that obtained on the grafting onto PTFE film.[6]

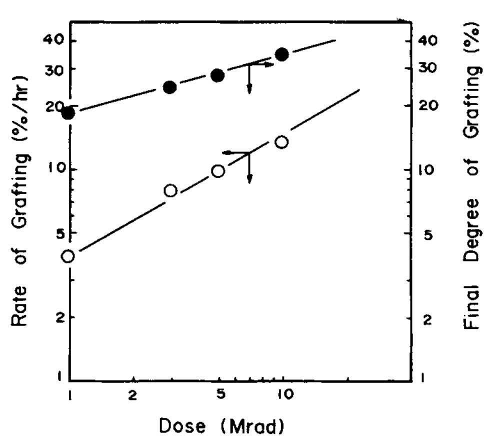

Fig. 2. Logarithmic plots of grafting rate and final degree of grafting vs. preirradiation dose. (○) Rate of grafting, (●) final degree of grafting. Grafting conditions are the same as in Figure 1.

Effect of Monomer Concentration

The swelling properties of original FEP film were investigated at various AAc concentrations and shown in Figure 3. The degree of swelling increases with AAc concentration, although its absolute value is very small. Figure 4 shows the degree of grafting-time curves obtained at various aqueous AAc concentrations. It is obvious that both the initial rate and final degree of grafting increase with monomer concentration. The degree of grafting levels off at a certain value. The higher the monomer concentration, the faster and the higher the degree of grafting reaches. The grafting rate and final degree of grafting were determined from Figure 4 and plotted logarithmically in Figure 5. The dependence of the grafting rate on the monomer concentration was found to be 1.25 order.

In the previous paper[6] on the grafting of AAc onto PTFE film, it was found that the dependence of grafting rate on monomer concentration is 1.1 order. However, the final degree of grafting was found to be independent of the AAc concentration in the range of 10–60%. In the present study on FEP film, the final degree of grafting increases remarkably with increasing the monomer concentration.

These results suggest that the degree of grafting is dependent not only on the amount of trapped radicals but also on the diffusibility of monomer into the polymer matrix. The diffusibility of AAc through the grafted layer of FEP film seems to be enhanced at higher monomer concentrations which lead to the increase of final degree of grafting as well as the rate of grafting. This behavior is reasonable with that obtained for the swelling properties of the original FEP film.

Effect of Temperature

Figure 6 shows the degree of grafting-time curves at various grafting temperatures ranging from 15°C to 60°C. It is obvious that the graft polymerization is largely affected by the reaction temperature, and that the higher the temperature the higher the grafting rate and the faster the grafting levels off at a lower degree. Generally, the increase in temperature facilitates the monomer

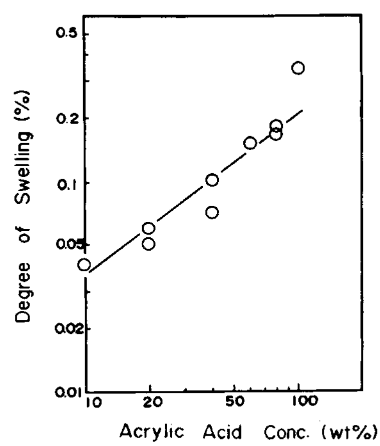

Fig. 3. Logarithmic plots of degree of swelling vs. acrylic acid concentration. Swelling temp, 25°C; swelling time, 4 days; film thickness, 190 μm.

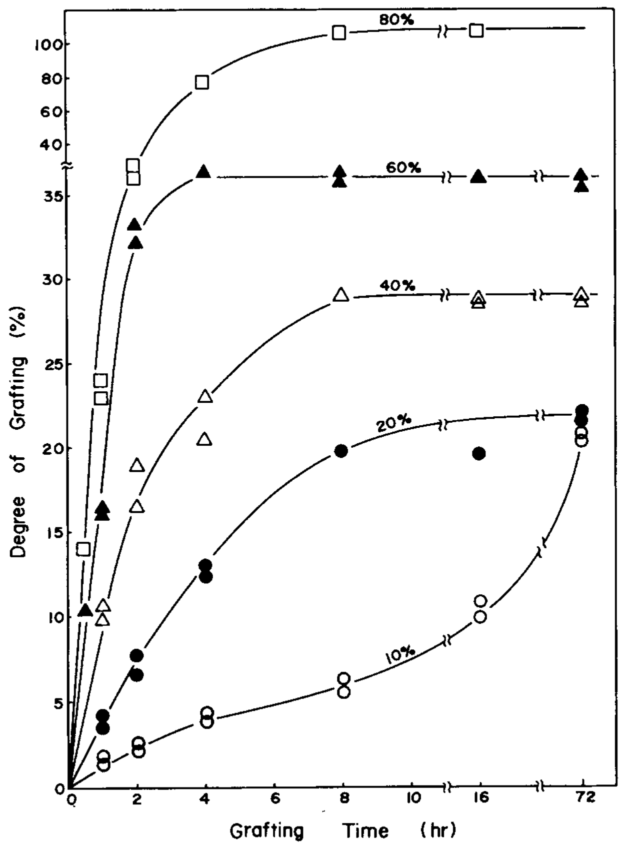

Fig. 4. Degree of grafting-time curves at various acrylic acid concentrations. Grafting conditions: preirradiation dose, 5 Mrad; Mohr's salt, 0.25 wt %; grafting temp, 35°C; film thickness, 80 μm.

diffusibility as well as the mobility of chain segment. Therefore, increasing monomer diffusibility causes the increase in a initial grafting rate. However, the increase in chain segment mobility favors the bimolecular termination of primary and growing chain radicals. Consequently, the final degree of grafting

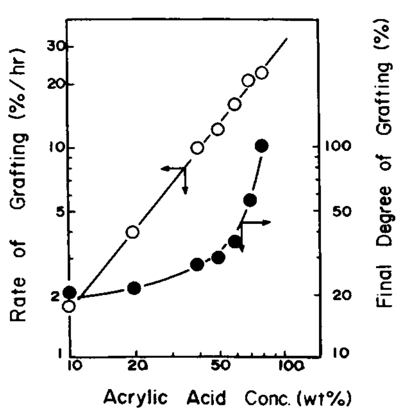

Fig. 5. Logarithmic plots of grafting rate and final degree of grafting vs. acrylic acid concentration. Grafting conditions are the same as in Figure 4.

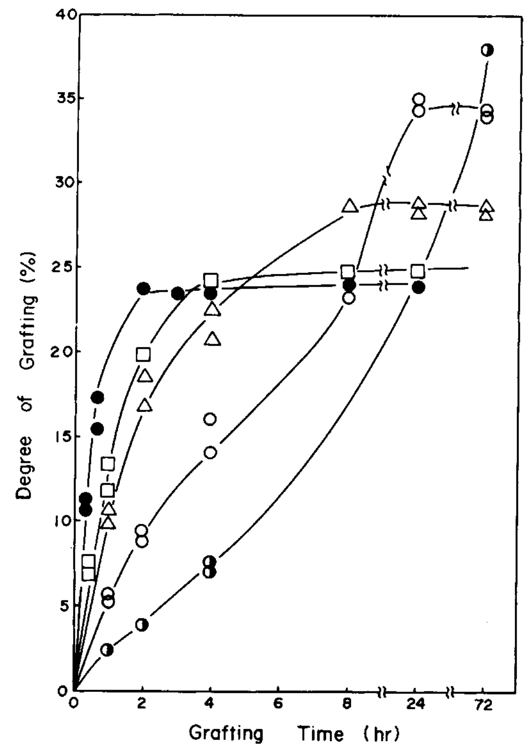

Fig. 6. Degree of grafting-time curves at various grafting temperatures (°C): (◑) 15; (○) 25; (△) 35; (□) 45; (●) 60. Grafting conditions, except preirradiation dose (5 Mrad), are the same as in Figure 1.

must decrease with increasing the temperature and reaches faster to a lower limiting value. Result also indicates that the lifetime of trapped radicals at a lower temperature is long enough to give the higher final degree of grafting.

Arrhenius plots for this graft polymerization are shown in Figure 7. The

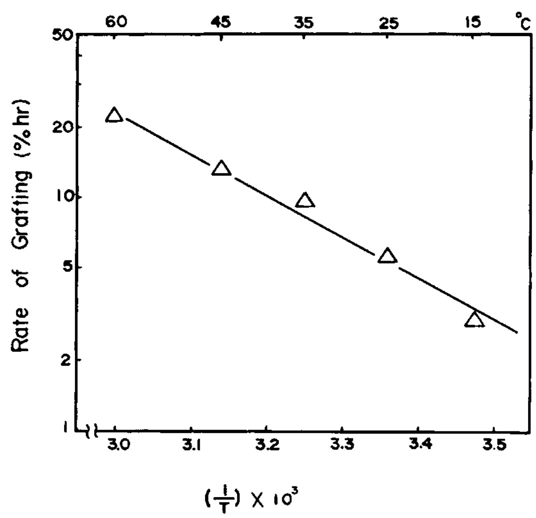

Fig. 7. Arrhenius plots of grafting rate. Grafting conditions are the same as in Figure 6.

overall activation energy was calculated to be 7.4 kcal/mol. In the previous studies on the grafting of AAc onto PTFE by direct[9] and preirradiation[6] methods, a break point was observed in the Arrhenius plots around the glass transition of PTFE. In the present study, however, no such break point was observed. From this result, it may be predicted that there is no glass transition for FEP film in the range of temperatures examined here.

Effect of Film Thickness

Figure 8 shows the degree of grafting-time curves obtained with various film thicknesses. The degree of grafting levels off at almost the same value irrespective of film thickness, but the initial grafting rate is reversely proportional to the film thickness. As shown in Figure 9, the logarithmic plots of the initial

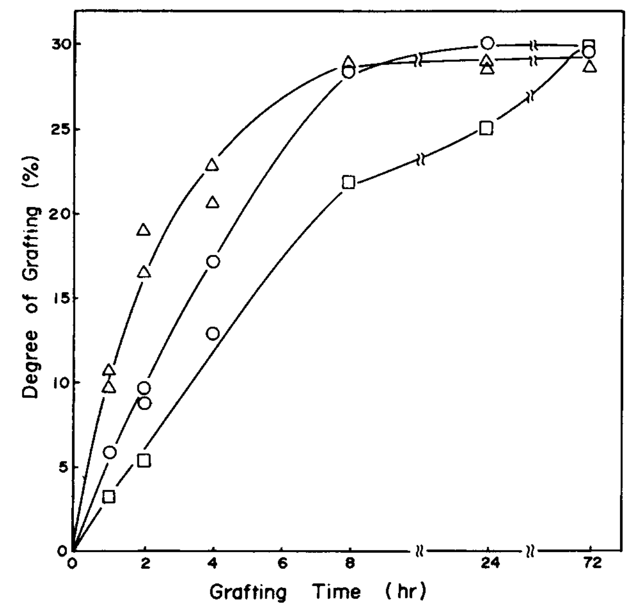

Fig. 8. Degree of grafting-time curves at various film thicknesses (μm): (△) 80; (○) 130; (□) 190. Grafting conditions, except preirradiation dose (5 Mrad), are the same as in Figure 1.

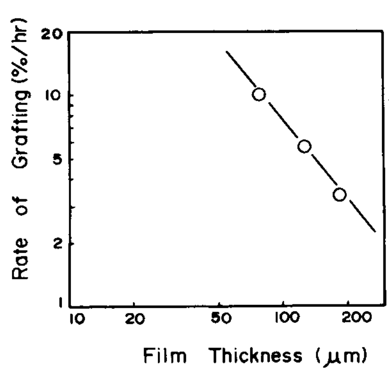

Fig. 9. Logarithmic plots of grafting rate vs. film thickness.

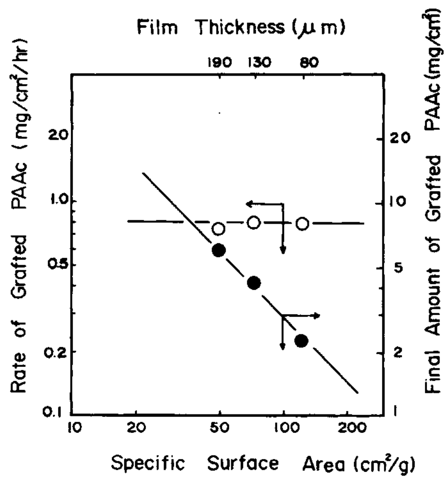

Fig. 10. Logarithmic plots of rate of grafted poly(acrylic acid) and final weight increase per unit surface area vs. specific surface area of film. Grafting conditions are the same as in Figure 8.

grafting rate against film thickness give a straight line with a slope of −1.1, i.e., a negative first-order dependence on the film thickness. This result is in good agreement with that obtained for PTFE film.[6]

On the basis of the result obtained in Figure 8, the amount of grafted poly(acrylic acid) per unit surface area were plotted as a function of the specific surface area of film and are shown in Figure 10. It is obvious that the rate of weight increase per unit surface area is constant regardless of the specific surface area of the film. However, the final amount of grafted poly(acrylic acid) per unit surface area increases with decreasing the specific surface area and shows a good negative first-order dependency.

It can be assumed that this graft polymerization is a diffusion-controlled one, i.e., the grafted layer formed initially at the film surface may swell in the monomer solution and the grafted zone gradually moves inwards into the film until it eventually reaches the whole bulk of the polymer. This means that at first the monomer diffuses through the grafted layer, followed by graft polymerization onto the polymer while it diffuses.

CONCLUSION

The preirradiation grafting of acrylic acid onto poly (tetrafluoroethylene–hexafluoropropylene) film has been studied to elucidate the effect of grafting conditions. The results obtained and discussed above can be summarized as follows:

1. The dependencies of grafting rate on preirradiation dose and monomer concentration were found to be 0.58 and 1.25 order, respectively, and the final degree of grafting was also dependent on the preirradiation dose and monomer concentration.

2. The overall activation energy for the graft polymerization was found to be 7.4 kcal/mol.

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

4. The graft polymerization is a diffusion-controlled one, and the grafting begins at the part close to the film surface and then proceeds through the grafted layer, which swells in the reaction medium, to reach finally the center part with progressive monomer diffusion.

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