Radiation-Induced Grafting of *N,N*-Dimethylacrylamide onto Polytetrafluoroethylene

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Synopsis

Grafting of *N,N*-dimethylacrylamide (DMAA) onto polytetrafluoroethylene (PTFE) has been carried out by using gamma rays from a ^{60}Co source. Degree of grafting was affected by grafting conditions. Especially, solvent for the grafting was found to be a very significant parameter to obtain a higher grafting yield. When ethylacetate or acetone was used as the solvent, grafting yield greater than 5% was obtainable while the graftcopolymerization scarcely occurred in the presence of other kinds of solvent such as ethanol or water.

Apparent activation energy of the grafting in ethylacetate was calculated to be 7.90 Kcal/mol, and initial grafting rate of it was proportional to 0.55 power of dose rate.

INTRODUCTION

To enhance the antithrombogenicity of a fluoropolymer such as an alternating copolymer of ethylene and tetrafluoroethylene (AFLON), a hydrophilic monomer was grafted onto it. Monomer employed for the grafting was *N,N*-dimethylacrylamide (DMAA) and it had been grafted under various grafting conditions. After grafting, antithrombogenicity of DMAA-g-AFLON was found to be improved at certain grafting conditions.[1]

In the present work, grafting of DMAA onto polyteterafluoroethylene (PTFE) has been carried out as a series of our work related to improvement of blood compatibility of fluoropolymers by grafting. Selection of PTFE as a fluoropolymer for the grafting was made because PTFE has the best blood compatibility among all commercial fluoropolymers. Hence, it may be expected that antithrombogenicity of DMAA-g-PTFE is better than that of DMAA-g-AFLON.

It is, however, generally difficult for PTFE to graft hydrophilic monomers onto it.[2] Therefore, we have studied here effect of grafting parameters such as solvent, dose rate, or temperature on the grafting of DMAA onto PTFE.

The present paper which is the first report concerned with such grafting describes aspects of the grafting behavior of DMAA onto PTFE.

EXPERIMENTAL

Materials

Polytetrafluoroethylene (PTFE) film (50 μm thickness; specific gravity 2.2 g/cm^{-3}) was purchased from Japan Baluka Industry Co. Ltd. The film was

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washed using detergent and rinsed with ethanol and distilled water, it was then dried in vacuo for two hours at room temperature.

N,N-dimethylacrylamide (DMAA) was supplied by Kohjin Co. Ltd., and this monomer was used as received.

Other chemicals were reagent grade and used without further purification.

Procedure

Sample preparation. A weighed sheet of PTFE film (35 × 35 mm) was placed in a glass ampoule connected to a removable valve. A certain volume of DMAA monomer with a solvent was filled into the ampoule. The ampoule was then attached to a vacuum line and degassed four times by alternate freezing and thawing technique. After the fifth degassing the removable valve of the ampoule was closed at the vacuum degree of 10^{-4} Torr. The ampoule was then warmed up to room temperature to melt the contents.

Irradiation. The grafting was carried out by irradiating the ampoule with gamma rays from a ^{60}Co source at constant conditions of dose rate and temperature.

Grafting yield. After irradiation, PTFE film was removed, washed, and soaked overnight in distilled water. It was boiled for five hours to extract monomer and homopolymer involved in the film. The film was then dried under vacuum for 24 h at room temperature and, weighed.

The percent of grafting was calculated as follows.

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

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

RESULTS AND DISCUSSION

To obtain a high grafting efficiency, particularly in the simultaneous irradiation, the monomer must present as close as possible near the active center created in the polymer backbone.[3] This may be attainable when the monomer can be diffused into the polymer. For grafting monomers onto PTFE, however, it may not attained since diffusion of monomers into PTFE is very difficult. Therefore, an appropriate solvent which makes it possible for the monomer to diffuse into PTFE is often used.[4]

In the grafting of DMAA onto PTFE, such appropriate solvents have been surveyed first. Table I shows degree of grafting obtained in the presence of various solvents. In all solvents examined here, ethylacetate (EtAc) and acetone were found to be good solvents for the grafting. Degree of the grafting in the both solvents is more than 6%, while that in other solvents is less than 1%. The same two solvents are also appropriate ones for the grafting of DMAA onto AFLON.

In comparison between EtAc and acetone, EtAc has been found to be more suitable for the grafting than acetone since the grafting yield in EtAc is higher than that in acetone as Table I shows. This superiority of EtAc has been confirmed in more detail at various grafting conditions. Figures 1 and 2 show the comparison of graftability of DMAA in EtAc with that in acetone. Figure 1 shows the relation between irradiation time and graft level obtained in both

TABLE I
Effect of Solvent on Graft Copolymerization of DMAA onto PTFE by Simultaneous Irradiation Technique[a]

Run No.	Solvent	Total dose (KGy)	Percent grafting (%)
GPT 1–1	H_2O	3	0.685
GPT 1–2	MeOH	3	0.436
GPT 1–3	EtOH	3	0.439
GPT 1–4	MEK[b]	3	0.764
GPT 1–5	EtAc[c]	3	9.860
GPT 1–6	CCl_4	3	0.340
GPT 2–8	Acetone	3	6.600

[a] Dose rate 1.5 KGy/h, Irrad. temp. 27°C DMAA/solvent compositions 23.1 vol%.
[b] Methyl ethyl ketone.
[c] Ethylacetate.

solvents at a dose rate of 1.5 KGy/h, monomer volume percent of 23.1 and room temperature. In both solvents, degree of grafting is increased similarly with irradiation time, and it seems to be saturated at a certain graft level. However, at any irradiation time, degree of grafting is proved to be higher in EtAc than in acetone. In the former solvent it may be about 11% while it may be about 9% in the latter.

The difference in the graft level obtained at various concentrations of DMAA in both solvents is shown in Figure 2. The grafting of DMAA onto PTFE was carried out at a dose rate of 1.5 KGy/h and at room temperature.

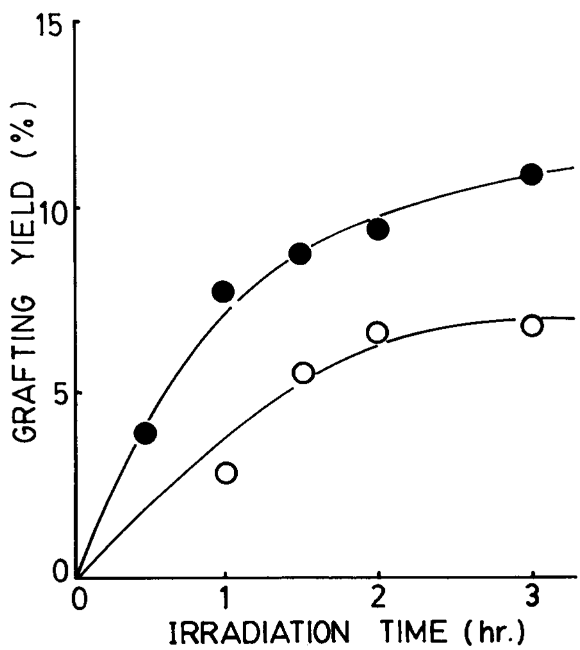

Fig. 1. Grafting yield vs. irradiation time on the grafting of DMAA onto PTFE in ethylacetate and acetone. Dose rate 1.5 KGy/h, irradiation temperature 27°C., and DMAA concentration 23.1 vol%. ● = in ethylacetate. ○ = in acetone.

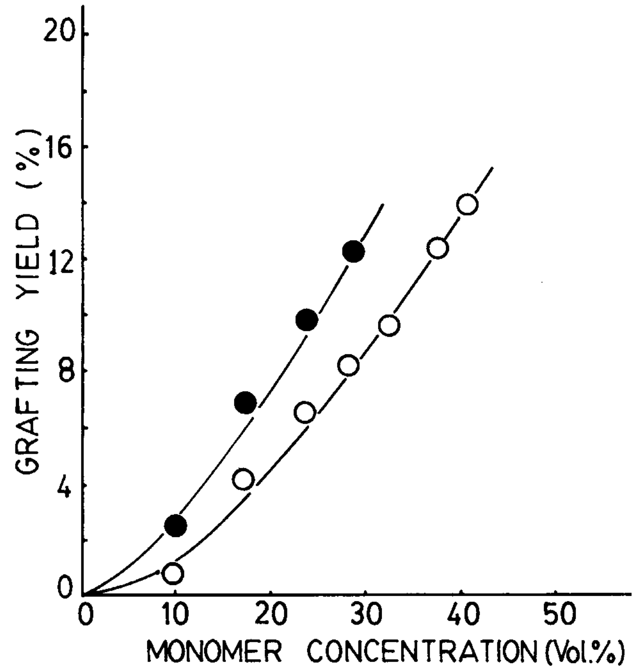

Fig. 2. Effect of monomer concentration on the grafting of DMAA onto PTFE. Dose rate 1.5 KGy/h, irradiation temperature 27°C and total dose of 3.0 KGy. ● = in ethylacetate. ○ = in acetone.

Degree of grafting in both solvents is increased similarly with monomer concentration, but it is slightly larger in EtAc than in acetone at monomer concentration from 10 to 40 vol%.

The results described above, therefore, indicate certainly that EtAc is more suitable for grafting than acetone, from the point of grafting yield.

The solvent effect on the grafting would be explained by the magnitude of swelling of DMAA into PTFE. In fact, swelling of PFTE by DMAA and each solvent which is shown in Table II has demonstrated the difference. By the table, swelling percent of PTFE by DMAA and EtAc is larger than that of DMAA and acetone at volume percents of DMAA from 10 to 100. It is, therefore, expected that swelling by DMAA itself of PTFE film is also larger in the presence of EtAc than that of acetone. On the other hand, by the same table in the both combinations of DMAA-EtAc and DMAA-acetone, degree of swelling is shown to be dependent on monomer concentration. The swelling degree by DMAA and EtAc or DMAA and acetone seems to become maximum at a certain monomer concentration below than 50%. This may suggest that there is a maximum in the grafting yield.

Effect of other grafting parameters, such as dose rate and temperature, on the grafting yield has been examined next. In this case, only ethylacetate has been used as the solvent since it is the most suitable solvent for the grafting in all solvents examined here.

Figure 3 shows dose rate dependency of the grafting of DMAA onto PTFE which was carried out in a 23 vol% concentration of DMAA at 27°C. In a region of dose rate from 0.1 to 3.26 KGy/h, there is a similar relation between

TABLE II
Swelling Ability of PTFE in Various Composition of DMAA Monomer in the Presence of Ethylacetate and Acetone[a]

DMAA/solvent (vol%)	Swelling ability (%)[b]	
	Ethylacetate	Acetone
10	0.576	0.388
30	0.771	0.475
50	0.571	0.291
70	0.388	0.196
90	0.190	0.097
100	0.190	0.092

[a]Swelling conditions:
[b]Swelling time 24 h, temperature 27°C.

Swelling ability of PTFE film was measured as follows. The film was immersed into the solution of DMAA-acetone or DMAA-ethylacetate for 24 h at 10^{-4} torr. Then, the film was taken out and excess of the monomer and the solvent attached on the surface of it was removed by a piece of blotting paper, and the film was weighed quickly. Swelling ability was determined by the following equation.

$$\text{Swelling ability (\%)} = (W_s - W_g)/W_g \times 100$$

where W_g and W_s represent the weights of dry PTFE film and that of wet PTFE film, respectively.

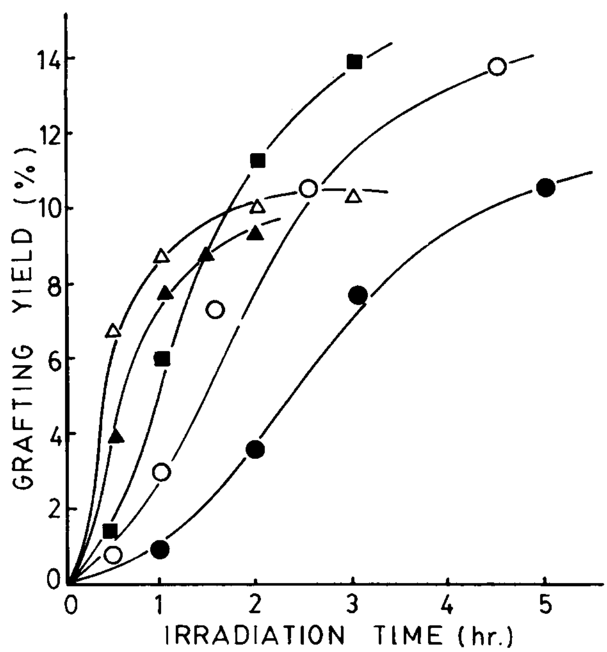

Fig. 3. Effect of dose rate on the grafting of DMAA onto PTFE in ethylacetate. DMAA/Et.Ac = 23.1 vol%, Irradiation temperature 27°C. △ = 3.26 KGy/h, ▲ = 1.5 KGy/h, ■ = 0.60 KGy/h, ○ = 0.33 KGy/h, ● = 0.10 Kgy/h.

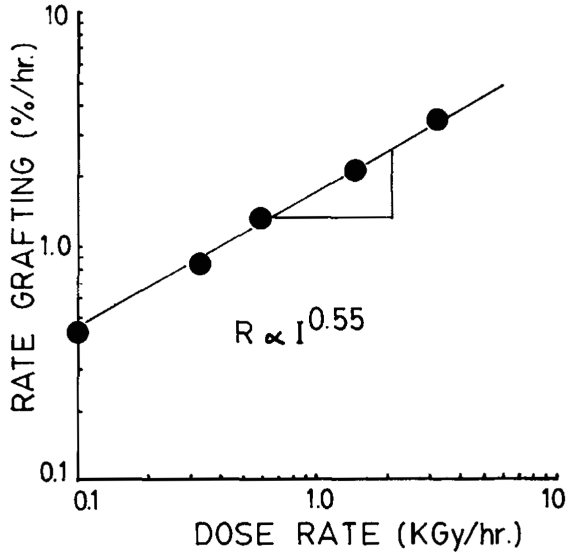

Fig. 4. Dose rate dependency on the grafting of DMAA onto PTFE in ethylacetate. DMAA concentration 23 vol% and irradiation temperature 27°C.

graft level and irradiation time. As all curves in Figure 3 show, grafting percent is increased with irradiation time and levels off at a certain graft level. The difference, however, which comes from dose rate is also observed in the curves. Degree of acceleration in the grafting yield and saturated graft level are dependent on dose rate. The former is increased with dose rate, and the

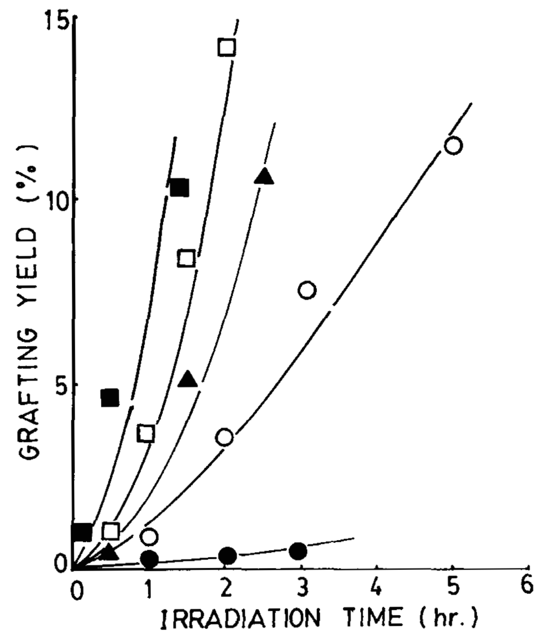

Fig. 5. Effect of temperature on the grafting of DMAA onto PTFE in ethylacetate. Dose rate 0.1 KGy/h, and DMAA conc. 23 vol%. ■ = 74°C., □ = 48°C., ▲ = 35°C., ○ = 27°C., ● = 0°C.

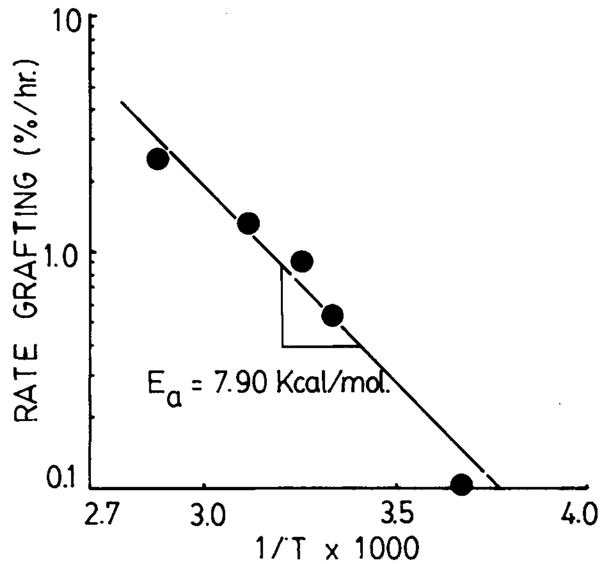

Fig. 6. Arrhenius plot of temperature dependency on the grafting of DMAA onto PTFE in ethylacetate. Reaction conditions are the same with Fig. 5.

latter is contrarily decreased with it. According to these results, it may be said that lower dose rate is more effective to obtain higher graft level. In generally, the same tendency would be expected in the simultaneous irradiation method because for higher dose rate the rate of homopolymerization becomes higher, and because of this, saturated graft level would be decreased.

Figure 4 shows dose rate dependency of the initial grafting rate which has been calculated from Figure 3. Initial grafting rate in log plot is found to be proportional to logarithmic dose rate, and the relation between them is represented by the equation of $R \propto I^{0.55}$, where I and R are dose rate and initial grafting rate, respectively. The value of 0.55 suggests that termination of the graft copolymerization proceeds via bimolecular process.

Temperature dependency of graft copolymerization is shown in Figure 5. The graft level at different temperature is increased similarly with irradiation time and the initial grafting rate is dependent on temperature. From the Arrhenius plot which is shown in Figure 6, apparent activation energy for the grafting was determined to be 7.90 kcal/mol.

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