Grafting of Poly(acrylic Acid) onto Polyethylene Filament and Its Distribution

KANAKO KAJI, *Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute, Mii-minami machi, Neyagawa, Osaka 572, Japan*

Synopsis

Radiation-induced simultaneous grafting of acrylic acid onto high density polyethylene filament is carried out with aqueous solution of acrylic acid in the absence and presence of ethylene dichloride. Distribution of grafted poly(acrylic acid) is studied by two methods. One is optical microscopic investigation of cross sections of dyed filament, and the other is electron probe microscopy of acrylic acid graft filament after conversion to calcium acrylate. Qualitative study with WAXS is also carried out. Grafting begins from the surface or periphery and proceeds, with sharp boundary, to the core. The reaction takes place only in the amorphous part of polyethylene. The percent graft in the grafted part is homogeneous and rather high from the beginning of the reaction; it is true that additional grafting to the already grafted part takes place, but it is not so noticeable.

INTRODUCTION

Grafting of acrylic acid onto polyethylene has been reported in a number of papers.[1-10] Most of these experiments were carried out under employment of polyethylene films. We were engaged in the study on the grafting of acrylic acid onto polyethylene filament for the modification of fiber properties such as thermal and fire resistance and affinity to water. The results were fairly good.[9,10] In the course of the study we were interested in the distribution of grafted poly(acrylic acid) in the fiber. Preliminary results concerning the distribution are to be reported in the present paper.

EXPERIMENTAL

Materials. Commercial high density polyethylene filament (340 d) was used. The density determined by density gradient tube method was 0.946 g/cm^3. Reagent grade acrylic acid monomer was purified by low pressure distillation. Ethylene dichloride (EDC) employed as swelling agent, and Mohr's salt as inhibitor of homopolymerization were reagent grade and used without further purification.

Procedure of Grafting. A typical grafting procedure is as follows. Polyethylene filaments (ca. 0.2 g) wound on a glass frame to avoid shrinkage during grafting and subsequent treatment were immersed in solution of acrylic acid–water (50/50 by vol) or acrylic acid–water–ethylene dichloride (50/25/25 by vol) to which Mohr's salt has been added up to an overall concentration of 4×10^{-3} mol/L to prevent homopolymerization outside the filaments. The samples were subjected to irradiation by γ-rays from a Co 60 source in ampoules sealed after

Journal of Applied Polymer Science, Vol. 28, 3767–3777 (1983)
 CCC 0021-8995/83/123767-11$02.10

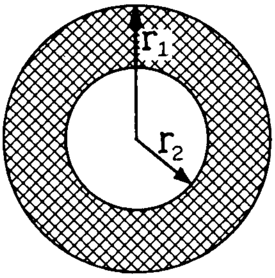


Fig. 1. Cross section of acrylic acid graft polyethylene filament: r_1 = radius of filament; r_2 = radius of unreacted core.

bubbling nitrogen gas for 2 min. The sealed ampoules were kept at room temperature at least for 16 h before the irradiation. The filaments after grafting were thoroughly washed with cold water and soaked in water at 50°C for several hours to remove homopolymer. Then they were weighed; the graft % G was calculated from the weight increase of the filaments with the following equation:

$$G = \frac{W - W_0}{W_0} \times 100 \tag{1}$$

where W_0 and W are weight (g) of a unit length, say 1 cm of polyethylene filament) before and after grafting, respectively. It is probable that the grafted polyethylene filaments contain, after the extraction with water, still a small amount of homopolymer of acrylic acid.[11] It is, however, not necessary for the discussion of the present experimental results to differentiate poly(acrylic acid) of which end is connected to polyethylene from that not connected to it at all.

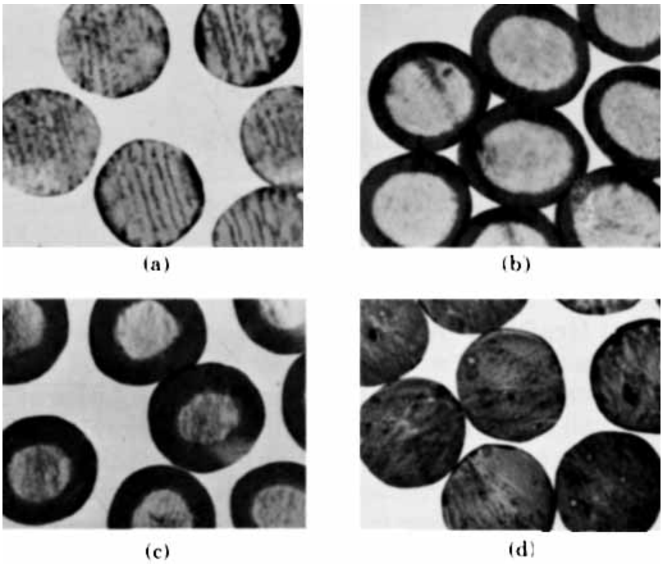


Fig. 2. Micrographs of cross sections of acrylic-acid-*g*-polyethylene filament: (a) starting polyethylene; (b) G = 9.7%; (c) G = 20.5%; (d) G = 38.4%.

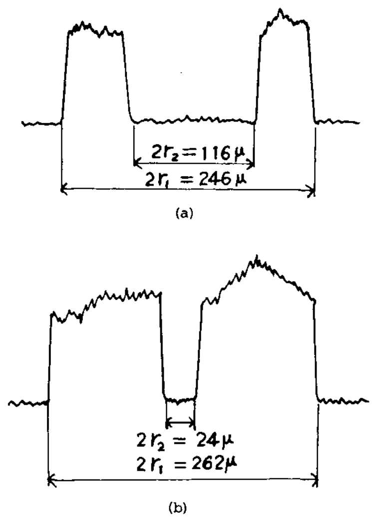


Fig. 3. Electron probe microanalysis of acrylic-acid-*g*-polyethylene filament: (a) $G = 14.3\%$; (b) $G = 34.4\%$.

Hereafter the term poly(acrylic acid) is often used instead of "apparently grafted poly(acrylic acid)" to call poly(acrylic acid) in the matrix of polyethylene.

Optical Microscopic Observation. It was expected that the presence of

TABLE I
Radiation Induced Grafting of Acrylic Acid onto Polyethylene Filament at 80°C and 50°C in the Absence (−) and Presence (+) of Ethylene Dichloride

Time (h)	Graft (%)		Radii of cross section r_1 (10^{-2} cm)	r_2 (10^{-2} cm)
		80°C, EDC −		
0.5	3.6		1.20	1.09
1.0	9.7		1.20	0.86
2.0	20.3		1.23	0.46
5.0	33.3		1.29	0.09
		80°C, EDC +		
0.5	7.1		1.23	0.94
1.0	14.3		1.23	0.57
2.0	23.6		1.26	0.14
5.0	30.1		1.26	0
		50°C, EDC −		
3.0	5.1		1.20	1.09
5.0	9.0		1.20	1.03
8.0	14.1		1.23	0.91
16.0	29.1		1.26	0.63
		50°C, EDC +		
2.0	4.4		1.20	1.03
3.0	7.7		1.20	0.91
5.0	13.3		1.23	0.77
8.0	20.0		1.23	0.60
16.0	34.4		1.31	0.14

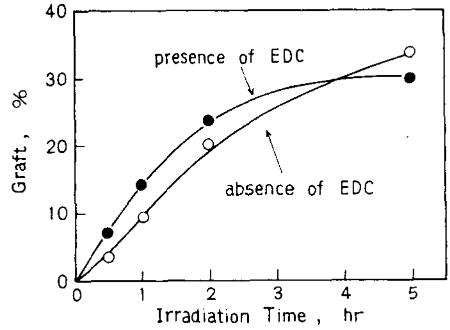


Fig. 4. Radiation induced grafting of acrylic acid onto polyethylene filaments at 80°C.

poly(acrylic acid) is detectable by microscopic observation of the cross section of the dyed filaments because poly(acrylic acid) is smoothly dyed with cationic dyes, whereas pure polyethylene is highly hydrophobic and is not dyed with the dye. The grafted filaments were dyed with cationic dye (Sevron Brilliant Red B), the dyed filaments were fixed in wax, and then cut perpendicularly to the direction of the filament axis with a microtome. The cross sections were observed with an optical microscope and photographed. The radial thickness of the dyed part was measured by enlarging the micrographs.

Figure 1 shows schematically the cross section; r_1 and r_2 are radii of the grafted polyethylene filament and unreacted core, respectively. Pictures taken in a series of experiment of grafting are shown in Figures 2(a)–(d). It may be seen that the reaction begins at the periphery and proceeds with sharp boundary to the center.

If acrylic acid has penetrated into the filament during the immersion in the grafting mixture, it is expected that more or less indication of the presence of poly(acrylic acid) is to be observed in the cross section at the early stage of the irradiation. But it is not the case.

Electron Probe Microanalysis. For electron probe microanalysis, grafted poly(acrylic acid) was converted to calcium salt by immersing the filament in aqueous solution of 1% calcium acetate at 50°C for 24 h. The electron probe microanalysis was carried out with an Electron Microprobe X-ray Analyzer/JXA-733 of JEOL Co., Ltd.

Figures 3(a) and (b) show spectra of the microanalysis on cross sections in the

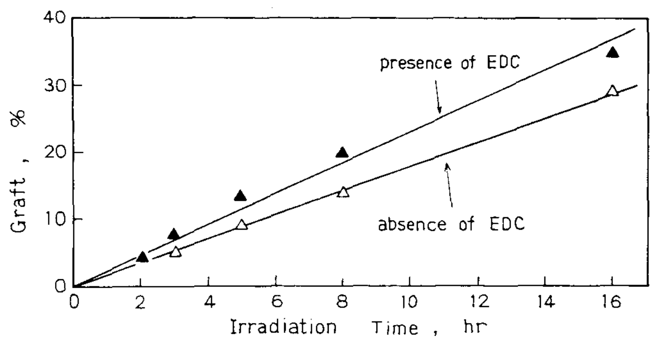


Fig. 5. Radiation induced grafting of acrylic acid onto polyethylene filaments at 50°C.

TABLE II
Initial Rate of Grafting of Acrylic Acid onto Polyethylene Filament under Various Conditions (%/h)

	Temperature (°C)			
	80		50	
Presence (+) or absence (−) of EDC	−	+	−	+
Rate of grafting (%/h)	9.5	14	1.8	2.5

direction of the diameter of graft polyethylene filaments with graft percent of 14.3% and 34.4%, respectively. The ordinate shows the concentration of calcium in the filament in arbitrary unit. It is seen that the height at the center of the cross section is the same as that outside the filament, showing that the center does not contain polyacrylic acid. Further, it is able to measure r_1 and r_2 in the figure. The height of the curve of the grafted part are not quite flat and irregularities are observed. It may, however, be regarded that the concentration of poly(acrylic acid) in the grafted part is practically constant.

RESULTS AND DISCUSSION

Rate of Grafting. Radiation induced simultaneous grafting of acrylic acid onto polyethylene filament was carried out with aqueous solution of acrylic acid, either in the absence or presence of ethylene dichloride, at 80°C or 50°C. The progress of the grafting was followed analytically and the results are summarized in Table I.

Figures 4 and 5 show graphically the results at 80°C and 50°C, respectively. It is seen that the influence of an addition of ethylene dichloride on the grafting is small, though that of the temperature is large; when the temperature of grafting is dropped from 80°C to 50°C, the graft percent is reduced to 20%.

It is noteworthy that the graft percent increases almost linearly at 80°C up

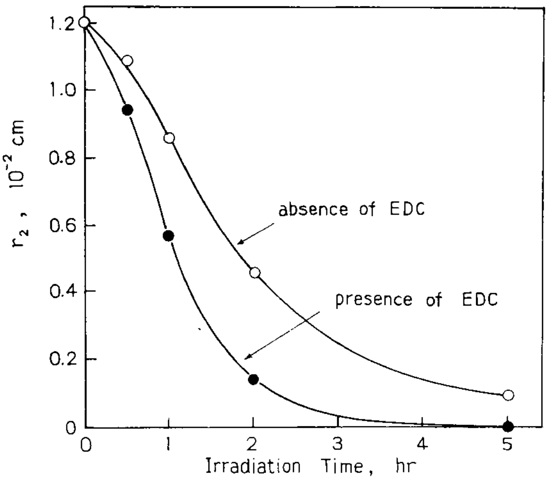


Fig. 6. Penetration of acrylic acid into polyethylene filament in the course of grafting reaction at 80°C.

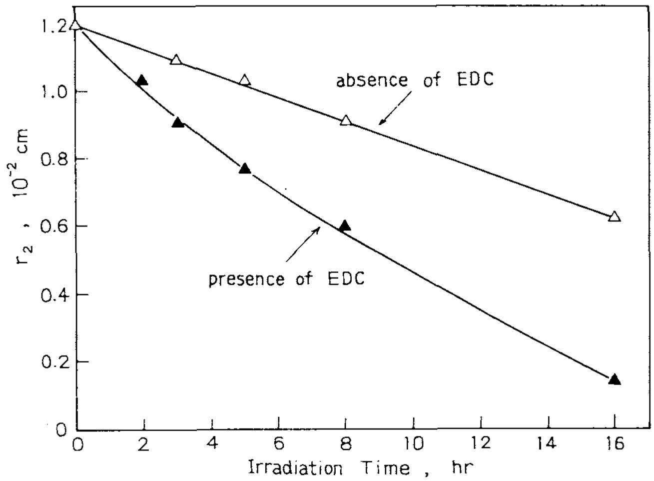


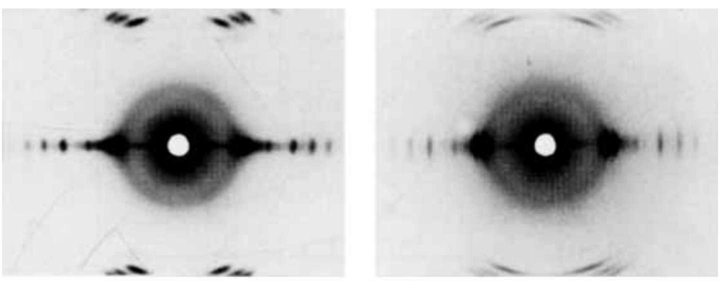
Fig. 7. Penetration of acrylic acid into polyethylene filament in the course of grafting reaction at 50°C.

to 20% graft and at 50°C up to 30% graft. The linearity means nothing other than that the amount of poly(acrylic acid) penetrated into and grafted to polyethylene per unit time is practically constant. The numerical values of the grafting rate calculated from the linearity of curves in Figures 4 and 5 are shown in Table II.

Grafted and Ungrafted Volume. It is seen in Figure 1 that the total and ungrafted areas of the cross section are πr_1^2 and πr_2^2, respectively, and hence the grafted area is $\pi(r_1^2 - r_2^2)$. Values of r_1 and r_2 obtained in a series of grafting carried out at 80°C and 50°C in the absence and presence of ethylene dichloride are shown along with graft percent in Table I.

It is clear from Table I that the change of r_1 which is due to the volume increase of the filament by grafting is very small whereas the decrease of r_2 which is due to the penetration and grafting of acrylic acid is large. It seems that the volume of the graft polyethylene filament is not equal to the simple addition of volumes of the starting polyethylene filament and that of poly(acrylic acid) formed in the filament, but we will not go further in this problem in the present paper.

Changes of r_2 were plotted against time of grafting reaction in Figures 6 and



(a) (b)

Fig. 8. WAXS photographs of polyethylene filament: (a) starting polyethylene; (b) 31.5% graft.

TABLE III
Total Volume of the Grafted Part and Weight of Polyacrylic Acid in a 1-cm Length of the Polyethylene Filament and Its Concentration in the Grafted Part

Graft percent of PAA (%)	Total volume of grafted part, V_g (10^{-4} cm^3)	Weight of PAA, W_g (10^{-4} g)	Concn of PAA, W_g/V_g (g/cm^3)
	80°C, EDC −		
3.6	0.79	0.15	0.20
9.7	2.20	0.41	0.19
20.3	4.08	0.87	0.20
33.3	5.18	1.42	0.28
	80°C, EDC +		
7.1	1.98	0.30	0.15
14.3	3.74	0.61	0.16
23.6	4.36	1.01	0.23
30.1	4.99	1.29	0.26
	50°C, EDC −		
5.1	0.78	0.22	0.28
9.0	1.19	0.39	0.32
14.1	2.14	0.60	0.28
29.1	3.74	1.25	0.33
	50°C, EDC +		
4.4	1.19	0.19	0.16
7.7	1.91	0.33	0.17
13.3	2.89	0.57	0.20
20.0	3.61	0.86	0.24
34.4	5.34	1.47	0.28

7. It is seen from Figure 6 for the grafting at 80°C that the presence of ethylene dichloride in the grafting mixture has not so great an influence on the penetration of acrylic acid into the filament. This is quite similar to the case of the rate of grafting. On the other hand, the presence of ethylene dichloride shows great influence at 50°C (see Fig. 7) on the penetration of acrylic acid, though the influence on the rate of grafting is not essentially different from other cases. The influence of slow penetration for the grafting in the absence of ethylene dichloride at 50°C is to be discussed later again.

The graft volume of 1 cm length is given by the following equation:

$$V_g = \pi(r_1^2 - r_2^2) \qquad (2)$$

Further, the weight of polyacrylic acid in the filament of 1 cm length, W_g is calculated by the following equation:

$$W_g = \frac{GW_0}{100} = \frac{G}{100}\pi r_0^2 \rho \qquad (3)$$

where r_0 and ρ are the radius and density of the starting polyethylene filament; the numerical values are 1.2×10^{-2} cm and 0.946 g/cm^3, respectively.

In this equation it is assumed that the polyethylene content in g per unit length of filament is independent of the grafting, because the reaction is carried out under inhibition of the change of the filament length. W_0 in eq. (3) is the same symbol as used in eq. (1); it is the weight (g) of polyethylene of 1 cm length, and the value is 4.28×10^{-4} g.

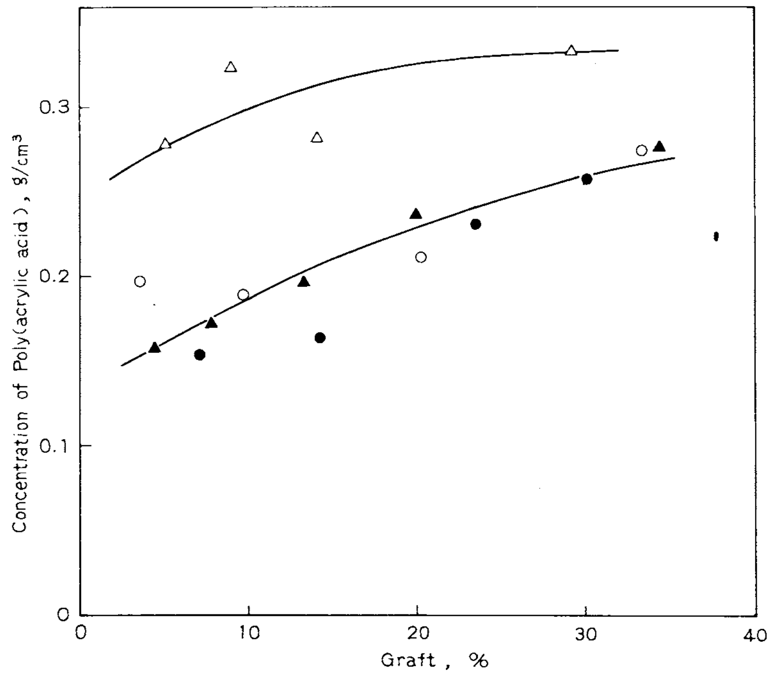


Fig. 9. Relation between concentration (C) of poly(acrylic acid) in the grafted part and graft % (G): (○,△) absence of EDC; (●,▲) presence of EDC.

Role of Amorphous Part of Polyethylene. If we wish to discuss the grafting reaction from the standpoint of the fine structure of polyethylene, it is clear that grafting takes place only in the amorphous part of the polyethylene filament. Crystal part plays a role of strong knot in the network of the two-phase structure. As in the case of swelling, the degree of grafting is also limited by the knots. In the present case neither acrylic acid nor ethylene dichloride is a good swelling agent of polyethylene, and hence the grafting is suppressed to a rather low level, as will be discussed later. Poly(acrylic acid) grafted onto polyethylene may serve to introduce acrylic acid rapidly into the structure, but it has no effect on the network.

Figures 8(a) and 8(b) show WAXS photographs of the starting and graft (G = 31.5%) polyethylene filament, and it may be seen that the intensity of the crystal diffration is not changed by the grafting.

Concentration of Poly(acrylic Acid) in the Grafted Part. By use of eqs. (2) and (3) we can calculate the concentration C of polyacrylic acid in the grafted part (g/cm^3):

$$C = \frac{W_g}{V_g} = \frac{G r_0^2 \rho}{100(r_1^2 - r_2^2)}$$

$$= \text{const} \frac{G}{r_1^2 - r_2^2} \qquad (4)$$

The calculated results of C are summarized in Table III and graphical representation of the relation between C and G is shown in Figure 9. Results of the

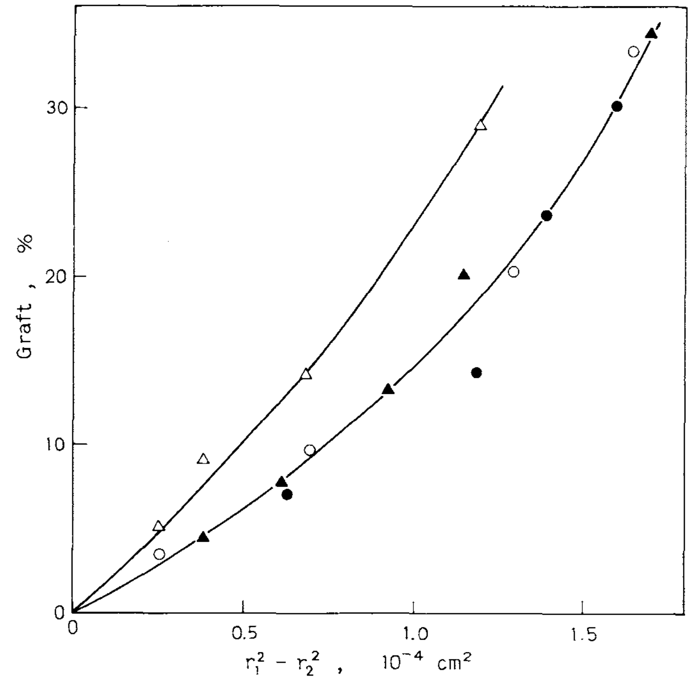


Fig. 10. Relation between graft % (G) and ($r_1^2 - r_2^2$). See caption of Figure 9 for symbols.

four series of the grafting seems to be divided into two groups. When we denote the absence and presence of ethylene dichloride in the reaction mixture with − and + signs, respectively, and add to the reaction temperature, then it is found that 80− and 80+, 50+ belong to the first group, whereas 50− is assigned to the other.

It is interesting that the relation between graft percent and concentration of polyacrylic acid of group 1 are expressed with a single curve independent of the reaction conditions.

It is noteworthy that the extrapolation of the two curves in Figure 9 suggests that the concentration of poly(acrylic acid) at graft percent 0 is not zero but have a rather large definite value. It is likely that grafting reaction begins at the front of the diffusion of acrylic acid very rapidly to a rather large extent by radiation. Additional grafting to the already grafted part occurs only to a small extent; it seems that the concentration approaches a definite value even when the graft percent increases.

Two Groups in the Behavior of Grafting. Next percent graft G is plotted against $r_1^2 - r_2^2$, which is proportional to the volume of the grafted part in Figure 10, it is seen, in this case also, that two curves are suitable to plot the relation as in the case of Figure 9. When the graft percent is compared at the same graft volume, group 2 shows higher graft percent. In other words group 2 shows smaller volume at the same graft percent.

As concerned with the higher concentration of poly(acrylic acid) of group 2, the following is noteworthy. When r_2's are compared at the same percent graft, it is seen in Figure 11 that r_2's of group 2 are much greater than those of group

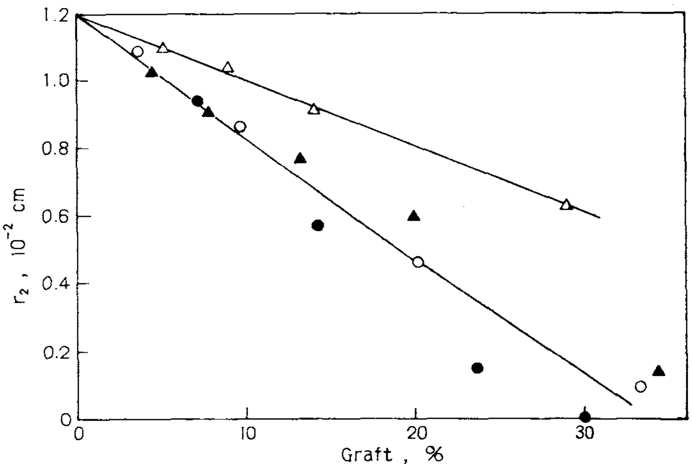


Fig. 11. Relation between r_2 and graft % (G). See caption of Figure 9 for symbols.

1, and hence it is calculated that the same weight of poly(acrylic acid) is contained in the case of group 2 in smaller volume than in the case of group 1. It seems that the structure of polyethylene filament at 50°C is much tighter than that at 80°C and less volume is available to poly(acrylic acid). When ethylene dichloride is added to the reaction mixture, the tightness is reduced to the same extent as in the case of experiments at 80°C.

The Extent of Grafting. Further it is noteworthy that two curves in Figure 11 are straight lines, and the extrapolation is formally easy. The extrapolation of the lower line (group 1) intercepts the abscissa at a value of 33 graft % whereas the intercept of the upper line (group 2) is estimated to be near 65%. At the abscissa, r_2 is zero, which means that no more ungrafted vacant volume is available. Probably we may conclude that the grafting which has been discussed comes to end at the point. For further grafting, it seems to be necessary that the crystal lattice be destroyed to allow further expansion of a new amorphous part. Further experiments are in preparation.

The author wishes to express here sincere thanks to Professor Emeritus Ichiro Sakurada of Kyoto University for his critical reading and invaluable efforts to improve this paper. We wish to thank Dr. I. Kuriyama, Head of the Osaka Laboratory for Radiation Chemistry, the Japan Atomic Energy Research Institute, and Professor T. Okada of Oita University for their encouragement.

References

1. H. F. Hamil, L. M. Adams, W. W. Harlowe, Jr., and E. C. Martin, *J. Polym. Sci., A-1*, **9**, 363 (1971).

2. M. I. Aly, K. Singer, N. A. Ghanem, and M. A. El-Azmirly, *Eur. Polym. J.*, **14**, 545 (1978).

3. S. H. Tabaddor, F. Fazilat, and R. Gouloubandi, *J. Macromol. Sci., Chem.*, **A13**, 1213 (1979).

4. J. P. Lawler and Charlesby, *Radiat. Phys. Chem.*, **15**, 595 (1981).

5. I. Ishigaki, T. Sugo, K. Senoo, T. Okada, J. Okamoto, and S. Machi, *J. Appl. Polym. Sci.*, **27**, 1033 (1982).

6. I. Ishigaki, T. Sugo, T. Takayama, T. Okada, J. Okamoto, and S. Machi, *J. Appl. Polym. Sci.*, **27**, 1043 (1982).

7. J. K. Rieke and G. M. Hart, *J. Polym. Sci., Part C*, **1**, 117 (1963).
8. J. K. Rieke, G. M. Hart, and F. L. Saunders, *J. Polym. Sci., Part C*, **4**, 549 (1964).
9. K. Kaji, T. Okada, and I. Sakurada, *Radiat. Phys. Chem.*, **18**, 503 (1981).
10. K. Kaji, thesis, Kyoto University, 1981.
11. I. Sakurada, Y. Ikada, and F. Horii, *Makromol. Chem.*, **139**, 171 (1970).

Received April 11, 1983
Accepted July 8, 1983