

Synthesis of Functional Polymers by Radiation-Induced Grafting of Acrolein onto Polyethylene Film

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Synopsis

Acrolein was grafted onto polyethylene film with radiation energy in order to make functional polymers containing hydrazone, oxime, and oxyacid. The kinetic analysis of the grafting reaction revealed that the irradiation dose affected not only the initiation but also the propagation and termination steps. The activation energies were 12.5 kcal/mol for propagation and 23.3 kcal/mol for termination, respectively. All the introduced aldehyde groups, free, hydrolyzed, and used for ring formation, participated in the reaction with phenylhydrazine. The conversions of aldehyde group to hydrazone, oxime, and oxyacid were small when the grafting yield of acrolein was high.

INTRODUCTION

The radiation-induced grafting has been tried to make such functional polymers as ion-exchange membranes, adsorbents for heavy metal ions, etc., because this is a convenient method for introducing functional groups into polymeric substrates. In order to obtain various kinds of functional polymers, grafting of monomers containing different types of functional group or those which are easily modified to functional groups should be tried. Acrolein is one of these monomers. When it is polymerized, the aldehyde groups of polyacrolein are easily changed to oximes, hydrazones, carboxylic acids, alcohols, etc.¹⁻⁹

Concerning the grafting of acrolein, Henglein et al.⁴ briefly indicated that a graft copolymer of acrolein onto poly(methyl methacrylate) film was obtained. Miyauchi grafted acrolein onto polystyrene and discussed about the effect of solvent on the reaction.¹⁰ Kabanov et al. reported the increase in the yield by the ionic grafting of acrolein onto polyethylene.¹¹ However, there is little detailed works about the kinetics of the grafting and about the conversion reaction of acrolein groups in graft copolymers to such functional groups as mentioned above. In the present paper, the kinetic analysis of the radiation-induced grafting of acrolein onto a commonly available polyethylene film and the following conversion of aldehyde groups of graft chains to hydrazone, oxime, and oxyacid groups were studied.

EXPERIMENTAL

A commercially available polyethylene (PE) film (Asahi Kasei, Japan) of 0.05 mm thick was washed with acetone and dried in a vacuum oven at room temperature for 16 h. Acrolein was purified by the usual distillation method.

The film (3×3 cm) in a PE bag containing N_2 gas was irradiated at -78°C with an electron beam accelerator, Dynamitron (Radiation Dynamics, Model IEA 3000-25-2) operating at a beam energy of 1.5 MeV and a current of 1 mA. The irradiated film was evacuated for 5 min in a glass ampule kept at -78°C and contacted with monomer solution. The grafting was carried out at 10 – 35°C under N_2 atmosphere. The grafting yield was obtained from the increase in weight of the film. The grafted film was immersed in a 1% ethanol solution of phenylhydrazine at 50°C to convert aldehyde group to hydrazone. In order to promote the reaction two to three drops of neat acetic acid were added to the solution. Oximes were obtained by heating the grafted film in a methanol–water 1:1 solution of 3% hydroxylamine hydrochloric acid salt at 80°C . The conversion of aldehyde group to oxyacid was carried out by boiling the grafted film in a 40 wt % methanol solution of potassium hydroxide. Infrared absorption spectra and ultraviolet absorption spectra of the films were obtained with a JASCO IR photometer, Model A-302, and a Shimadzu UV photometer, Model UV-265, respectively.

RESULTS AND DISCUSSION

Grafting of Acrolein onto PE Films

Figure 1 shows the effect of the preirradiation dose on the grafting yield of acrolein onto PE film. The initial rapid increase in the grafting yield was followed by leveling off after 5 h reaction. The final grafting yield reached 20–90%, depending on the irradiation dose.

Increasing the irradiation dose affects the number of radicals which may be applicable to the initiation of grafting. The results in Figure 1 indicate a possibility that propagation and termination are also affected by the irradiation dose. A kinetic treatment was applied to the reaction in order to clarify how the irradiation dose affected the elementary steps of grafting. Each step of the graft polymerization by the preirradiation method is represented as

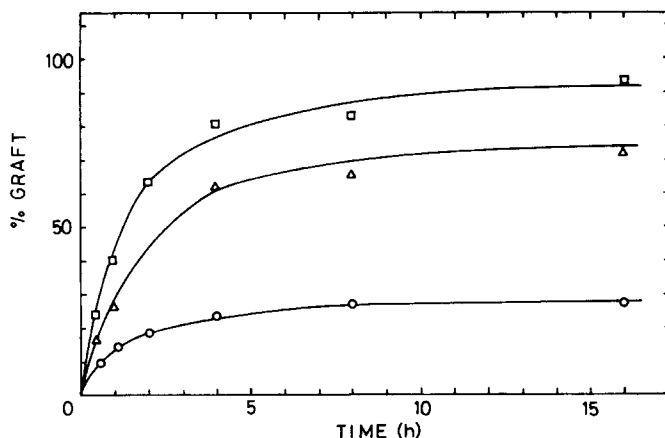
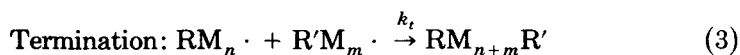
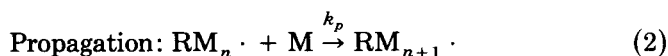


Fig. 1. Effect of irradiation dose (kGy) on grafting yield of acrolein onto PE film: (○) 50; (△) 100; (□) 200.

follows:



where $R \cdot$, $RM_n \cdot$, and M denote polymeric radicals produced in PE, growing radicals of acrolein, and monomer, respectively. The rates of propagation and termination are given by

$$R_p = k_p [RM_n \cdot] [M] \quad (4)$$

$$R_t = k_t [RM_n \cdot]^2 \quad (5)$$

When the reaction proceeds in a steady state, the next equation is applicable:

$$R_p = k_p [M] (R_i/k_t)^{1/2} \quad (6)$$

In a nonsteady state, however, this assumption is not applicable. The change in $[RM_n \cdot]$ from the start of the reaction till time t should be considered.¹² Then, $[RM_n \cdot]$ is given as

$$[RM_n \cdot] = \int_0^t R_i dt - \int_0^t R_t dt \quad (7)$$

The combination of eqs. (4), (5), and (7) gives the next equation:

$$R_p / \int_0^t R_p^2 dt = k_p [M] \int_0^t R_i dt / \int_0^t R_p^2 dt - k_t/k_p [M] \quad (8)$$

Figure 2 shows the plots between $U = R_p / \int_0^t R_p^2 dt$ and $V = 1 / \int_0^t R_p^2 dt$, which were calculated from the results in Figure 1. Judging from the straight lines in this figure, it is clear that the application of this kinetic treatment to the present grafting reaction is reasonable. The slope and intercept at $V = 0$ provide $p = k_p [M] \int_0^t R_i dt$ and $q = -k_t/k_p [M]$, respectively. Figure 3 shows the relation between p , q , and the irradiation dose D as

$$p = k_p [M] \int_0^t R_i dt \propto D^{0.5} \quad (9)$$

$$q = k_p [M] / k_t \propto D^{1.1} \quad (10)$$

Because the uptake of monomer $[M]$ with PE film is independent of the preirradiation dose, the relations in eqs. (9) and (10) are reduced to the dependencies of $k_p \int_0^t R_i dt$ and k_p/k_t on D . The value $\int_0^t R_i dt$ is the amount of radicals which are used for the initiation until time is equal to t . When all the radicals produced are used to initiate the grafting, this amount may be

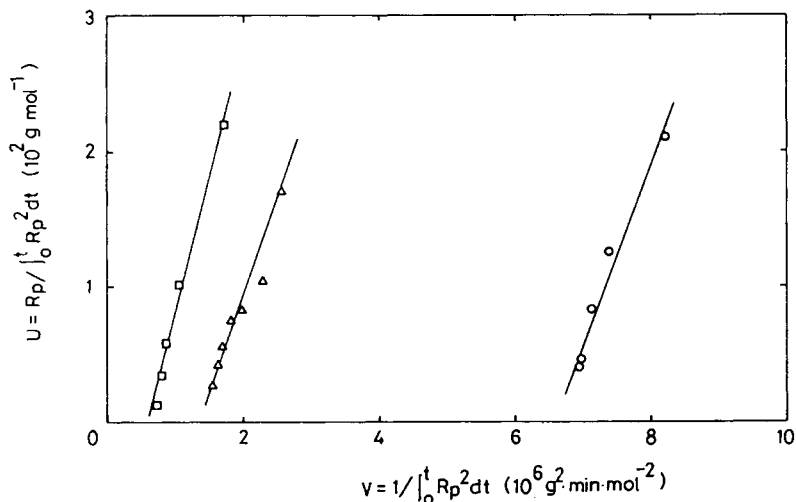


Fig. 2. Plots of $R_p / \int_0^t R_p^2 dt$ against $1 / \int_0^t R_p^2 dt$ for the grafting of acrolein onto the preirradiated PE film. Symbols are the same as shown in Figure 1.

proportional to D . However, the amount of radicals which are practically used for the initiation is quite small when compared with the total amount of radicals produced. For example, it was estimated that the amount of initiating radicals was only 1/3–1/10 that of the total radicals in the case of grafting styrene onto poly(ethylene oxide) and poly(isobutylene oxide).¹² Therefore, it is not probable that the value of $\int_0^t R_i dt$ is a simple first-order relation of D . In any case, it is not possible to extract the effects of D on k_p and k_p/k_t only from the present results.

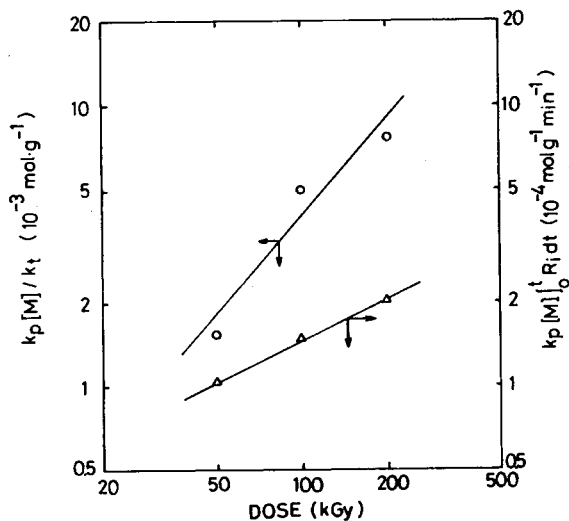


Fig. 3. Plots of $k_p[M]/k_t$ (O) and $k_p[M] \int_0^t R_i dt$ (Δ) against irradiation dose D for the grafting of acrolein onto PE film.

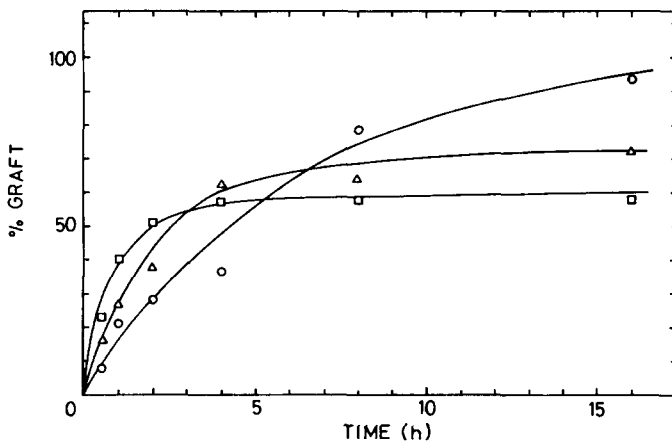


Fig. 4. Effect of temperature ($^{\circ}\text{C}$) on grafting yield of acrolein onto the preirradiated PE film: (O) 10; (Δ) 20; (\square) 35.

Figure 4 shows the effect of temperature on the grafting yield of acrolein onto PE film. Under the present reaction condition, no induction period was observed even at 10°C . The increase in temperature raised the initial grafting rate, while the grafting yield obtained at 16 h was in the order: $10^{\circ}\text{C} > 20^{\circ}\text{C} > 35^{\circ}\text{C}$.

In order to obtain a quantitative relation between temperature and grafting rate, the above-mentioned kinetic treatment was carried out. The values U and V , which were calculated from the results in Figure 4, were plotted against temperature as shown in Figure 5. These straight lines again assure that the application of the kinetic treatment for this reaction is reasonable. The values $p = k_p[M] \int_0^t R_i dt$ and $p \times q = k_t \int_0^t R_i dt$ were calculated from the slopes and intercepts of Figure 5 at various temperatures. Figure 6 shows the plots of $k_p[M] \int_0^t R_i dt$ vs. $1/T$ and $k_t \int_0^t R_i dt$ vs. $1/T$.

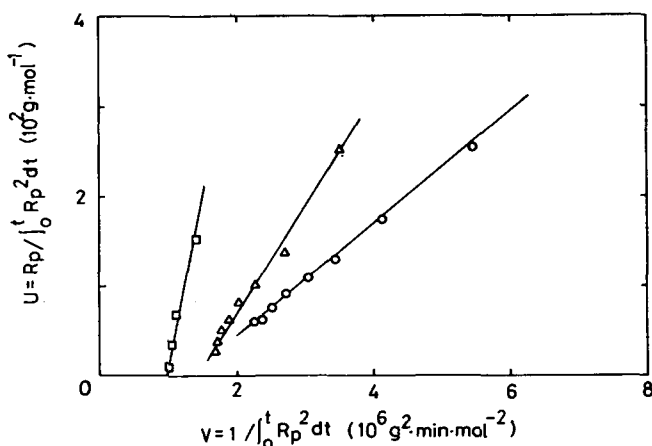


Fig. 5. Plots of $R_p / \int_0^t R_p^2 dt$ against $1 / \int_0^t R_p^2 dt$ for the grafting of acrolein onto the preirradiated PE film. Symbols are the same as shown in Figure 4.

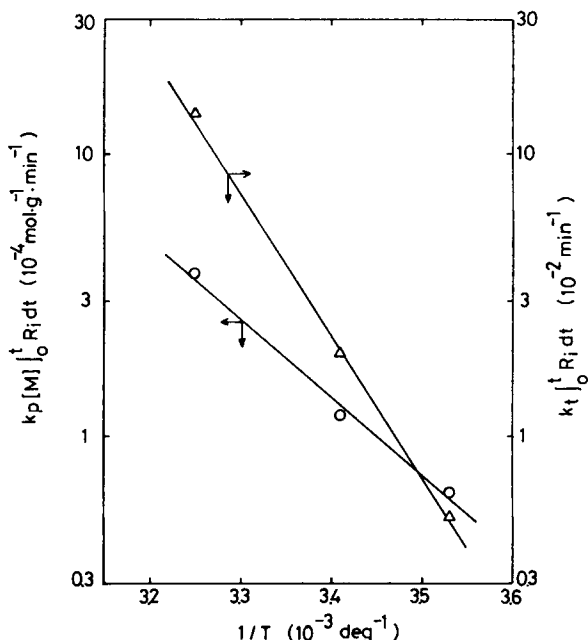


Fig. 6. Plots of $k_p[M] \int_0^t R_i dt$ (O) and $k_t \int_0^t R_i dt$ (Δ) against $1/T$ for the grafting of acrolein onto PE film.

If it is considered that the grafting starts virtually instantaneously when the preirradiated polymer is contacted with a monomer solution,¹² it is quite probable that the effect of temperature on the very initial stage is much smaller than those on the long periods of the following propagation and termination. Then, the change in $\int_0^t R_i dt$ with temperature is almost negligible when compared with those of k_p and k_t . Because acrolein was supplied in a form of dilute aqueous solution (less than 20 wt %) under the present condition, it is possible to assume that $[M]$ which appears in $k_p[M] \int_0^t R_i dt$ is represented by the uptake of water with PE. It was observed that the uptake of water with PE film was less than 1 wt % and was little affected by the temperature in the range 10–35°C. This consideration indicates that the change in $[M]$ with temperature is virtually negligible. Consequently, the changes in $k_p[M] \int_0^t R_i dt$ and $k_t \int_0^t R_i dt$ with temperature are reduced to the changes in k_p and k_t with $1/T$. The slopes of the straight lines give activation energies 12.5 kcal/mol for propagation and 23.3 kcal/mol for termination, respectively.

Conversion of Aldehyde Groups in Grafted PE Films

Schulz reported that a UV absorption peak was observed at 283–290 nm in the copolymer of acrolein with acrylonitrile.⁶ In the present case of the acrolein-grafted PE film, two UV absorption peaks, one at ca. 200 nm (peak I) and the other at 260 nm (peak II), were observed as shown in Figure 7. These two peaks are due to $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transition, respectively. With the increase in grafting yield, the peak I slightly shifts to a higher

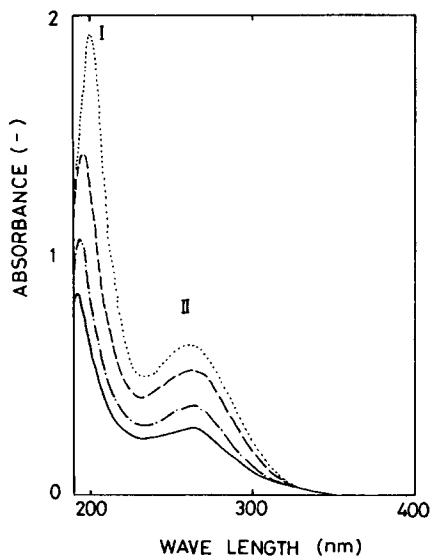


Fig. 7. UV absorption spectra of PE film grafted with acrolein. Reaction times: (—) 0.5 h; (·····) 1; (---) 2; (-·-·-) 4.

wavelength while the position of the peak II is unchanged. As shown in Figure 8, the increases in absorbance of both peak I and peak II are not in proportion to the weight fraction of graft chains, $G/(100 + G)$, where G denotes grafting yield, but to its square root. This result indicates that a portion of aldehyde groups are changed to other groups which do not have UV absorption in these regions. In other words, the higher the grafting yield, the smaller the portion of the remaining free aldehyde group.

IR absorption spectrum of the grafted PE film is shown in Figure 9(a). The absorption at 1720 cm^{-1} is due to the aldehyde group of polyacrolein graft

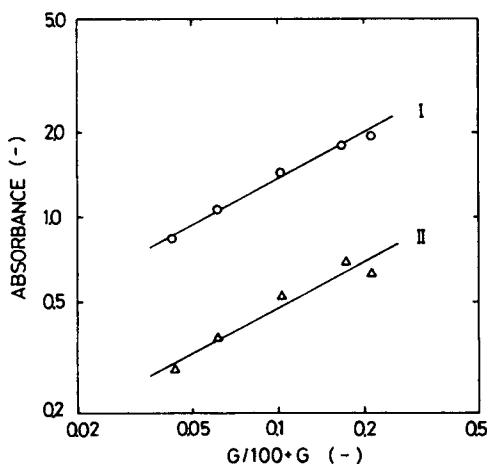


Fig. 8. Increases in absorbance of peak I and peak II with the weight fraction of polyacrolein graft chains, $G/(100 + G)$.

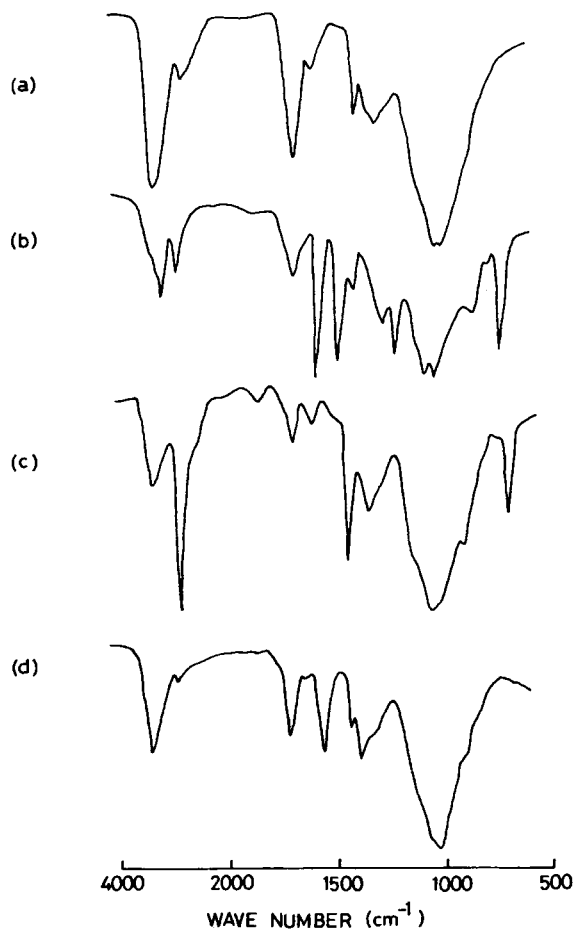


Fig. 9. IR absorption spectra of PE film: (a) PE grafted with acrolein; (b) acrolein-grafted PE after the reaction with phenylhydrazine; (c) acrolein grafted PE after the reaction with hydroxylamine; (d) acrolein-grafted PE after the reaction with potassium hydroxide.

chains. Two other strong absorptions at 3400 and $900\text{--}1100\text{ cm}^{-1}$ are due to the aldehyde groups which are hydrolyzed and those used for the ring formation among the adjacent hydrolyzed groups, respectively.¹ Although the degree of hydrolysis and ring formation depends on the content of water uptaken from the air with the grafted film, the presence of absorption at 1720 cm^{-1} indicates that the water content of the grafted film is not more than 25 wt %.¹³ The small absorption at 1630 cm^{-1} is due to the presence of the free water or the loosely absorbed water.

A new absorption of phenyl group was observed at 1603 cm^{-1} when the acrolein-grafted PE film was contacted with phenylhydrazine as shown in Figure 9(b). The decreases in absorption at 1720 , 3400 , and $900\text{--}1000\text{ cm}^{-1}$ along with the reaction indicate that not only the free aldehyde group but also the hydrolyzed and ring-forming aldehyde groups participated in the reaction with hydrazine. Probably, the hydrolyzed and ring forming aldehyde groups easily released water and returned to free aldehyde groups when the

TABLE I
Conversion^a of Aldehyde to Hydrazone

Time (h)	Grafting yield (%)		
	14.5	27.5	36.0
1	47	42	40
2	48	44	39
5	50	44	39

$$^a[\text{Hydrazone}]/[\text{aldehyde}]_{\text{orig}} \times 100.$$

TABLE II
Conversion^a of Aldehyde to Oxime

Time (h)	Grafting yield (%)		
	8.5	23.0	39.0
20	31	25	22
45	39	30	26
90	40	31	26

$$^a[\text{Oxime}]/[\text{aldehyde}]_{\text{orig}} \times 100.$$

TABLE III
Conversion^a of Aldehyde to Oxyacid

Time (h)	Grafting yield (%)		
	14.0	23.5	27.0
5	1.5	0.9	0.8
15	4.5	2.6	2.5
40	14.8	4.9	5.1

$$^a[\text{Carboxyl}]/[\text{aldehyde}]_{\text{orig}} \times 100.$$

reaction started. Figure 9(c) is the IR spectrum of the acrolein-grafted PE film after the reaction with hydroxylamine. The absorption peaks at 940, 1650, and 3200–3400 cm^{-1} are due to $=\text{N}-\text{O}-$, $> \text{C}=\text{N}-$, and $-\text{OH}$, respectively. The absorption at 1560 cm^{-1} in Figure 9(d) is based on the formation of oxyacid from the reaction of the grafted PE film with potassium hydroxide.

Table I shows the conversions of aldehyde group to hydrazone in the PE film of different grafting yields. Under the present condition, the reaction rapidly proceeded and the conversion leveled off in less than 5 h. The conversion of the sample with a higher grafting yield was lower than that of the sample with a lower grafting yield. Similar tendencies were observed in the conversions from aldehyde to oxime and to oxyacid as shown in Tables II and III, respectively.

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