

Graft Polymerization of Acrylic Acid onto Polyethylene Film by Preirradiation Method. I. Effects of Preirradiation Dose, Monomer Concentration, Reaction Temperature, and Film Thickness

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Synopsis

Low- and high-density polyethylenes were irradiated by electron beams with dose of 2–50 Mrad and then immersed in aqueous solution of acrylic acid (monomer concentration from 30 to 100 wt %) for 10 min–5 h at a temperature of 25–40°C. The degree of grafting increases with time and levels off. High density polyethylene shows lower grafting rate and higher final % grafting in compared with low-density polyethylene. Both grafting rate and final % grafting increase with total dose of preirradiation, but show some saturation at high doses. The highest grafting rate was observed at 60 wt % of monomer concentration where the grafted polyethylene swells to the largest extent in the monomer mixture. Apparent activation energies for the grafting are 19.6 and 27.3 kcal/mol for low- and high-density polyethylenes, respectively, reflecting the process of monomer diffusion in the film. Grafting rate decreases with increasing film thickness. Graft polymerization starts on the surface of the film and proceeds to the inner part with monomer diffusion through the grafted layer.

INTRODUCTION

Graft polymerization is a well-known method for modification of the chemical and physical properties of polymeric materials, and is of particular interest for achieving specifically desired membrane properties as well as excellent mechanical properties, since various commercial polymers can be used as the grafting substrate.

Graft polymerization can be achieved by ionizing radiation, ultraviolet light, or chemical initiators. Of these, radiation grafting is one of the most promising methods because of its large penetration in polymer matrix, rapid and uniform formation of active sites for initiating grafting throughout the matrix. Under an appropriate experimental conditions for homogeneous diffusion in the polymer, modification of polymer properties can be accomplished not only at the surface but also throughout the internal phase of polymer.

Several papers have been reported on the radiation grafting of acrylic acid onto polyethylene.^{1–6} These involve both the direct method and the preirradiation method. Rieke et al.,^{1,2} studying mainly the properties of the polymer grafted by preirradiation method, found that most properties closely parallel those of the backbone polymer and that the adhesion of the graft polymer is greatly im-

proved over that of unmodified polyethylene surface. Hamil et al.³ studied the direct grafting method and found that the grafting step is diffusion-controlled and the properties are a linear function of the amount of poly(acrylic acid) in the graft polymer.

Aly et al.⁴ and Lawler and Charlesby⁶ studied the effects of grafting conditions on the direct grafting by using the aqueous monomer solution containing redox system. The former found that the best graft/homopolymer ratios are obtained at radiation doses between 2 and 3 Mrad, at acrylic acid concentrations of 40–60%, and at $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentrations of 0.25–0.5% by weight. The latter used a specially designed apparatus which enabled monomer to be confined to one side of the film and reported that the grafting proceeds into the polyethylene with monomer diffusion through the fissures.

In these papers, only Hamil et al.³ measured the ion exchange capacity of the grafted films and suggested that essentially all the carboxyl groups in the film are available for ion exchange. In recent years, however, the acrylic acid-grafted polyethylene film is recognized as one of the most useful battery separators, especially for the battery in which alkaline solution is used as electrolyte.^{7,8} Ostler and Rogers⁹ investigated further modification of the polyethylene-graft-poly(potassium acrylate) in order to enhance its permselectivity and degradation resistance and found it can be achieved by subsequent grafting of styrene to the membrane.

The major role of separator membranes is to isolate physically the two half-cells of the battery in order to prevent contact or contamination of the active materials. In the silver oxide–zinc battery, silver hydroxide formed by dissolution of positive active material, Ag_2O , in highly concentrated alkaline solution¹⁰ can migrate through the separator membrane to the zinc electrode, causing the internal short-circuiting (self-discharge) and lowering the cell performance. Therefore, the separator must be capable of suppressing the migration of the silver hydroxide.

An another problem is the oxidizing effects of silver hydroxide in the concentrated alkaline solution against the membrane separators. The penetration of silver hydroxide into membrane lead to its chemical degradation, accompanied with deposition of metallic silver in the membrane.

Membranes made from regenerated cellulose, e.g., cellophane, have long been used as a separator in the alkaline batteries, such as silver oxide–zinc primary cell. However, it has poor durability due to the oxidative breakdown during operation or storing.

As mentioned above, the acrylic acid-grafted polyethylene was found to be useful as a separator membrane and have an excellent durability. In order to prepare such an excellent separator membrane, one must utilize the carefully and specially controlled grafting techniques. To develop this grafting technique, we have extensively investigated the preirradiation grafting of acrylic acid onto polyethylene film not only in a beaker scale but also using a pilot plant which was designed on the basis of the results by a beaker scale experiment. We have elucidated the effects of various factors on this grafting system and the various properties of the products, and discussed the grafting mechanism.

The interesting results will be reported successively in a series of papers. In this paper, the grafting behaviors found in the beaker scale experiments will be presented and discussed in detail.

EXPERIMENTAL

Materials

Commercially available low- and high-density polyethylene (low-density polyethylene, Asahi-Dow, Ltd.; high-density polyethylene, Asahi Chemicals Co., Ltd.) films of 25–150 μm thickness were used.

Technical grade acrylic acid (Kishida Chemicals Co., Ltd.), containing 200 ppm hydroquinone monomethyl ether as a stabilizer, was used without further purification. No significant difference was observed in the grafting results between monomers with and without purification by distillation so long as the grafting was carried out in the presence of 0.25 wt % Mohr's salt.

Mohr's salt was reagent grade (Kishida Chemicals Co., Ltd.).

Irradiation

The films were irradiated by being passed under the electron beams of a cascade type accelerator (Dynamitron IEA 3000-25-2, Radiation Dynamics, Ltd.) operating at beam energy of 2 MeV and with a current of 1 mA. The dose rate was approximately 10^5 rad/s. Unless otherwise indicated, the irradiations were carried out under nitrogen.

Grafting Procedure

The irradiated films were immersed in the monomer solution which was prepared at given concentrations of acrylic acid and Mohr's salt and deaerated by bubbling nitrogen. The reaction was carried out under nitrogen in the temperature-controlled bath. Grafted films were taken out from the monomer solution in glass ampoules and washed with water, followed by soaking in a distilled water overnight. The films were then dried *in vacuo* until a constant weight was reached and weighed. The grafting yield was determined by the percent increase of weight based on the initial film weight.

RESULTS AND DISCUSSION

Preirradiation Dose

Figure 1 shows the typical curves plotted degree of grafting vs. reaction time for low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The degree of grafting increases with reaction time and then levels off at a certain value, which is called as a final percent grafting. It can be seen that LDPE has a higher rate of grafting but a lower final percent grafting as compared with those of HDPE. This result may be explained by a higher diffusion rate of monomer and a lower concentration of the trapped radicals due to the lower crystallinity and smaller crystallites in LDPE. In fact, the crystallinities were measured to be 57% and 77% for LDPE and HDPE, respectively, by wide-angle X-ray scattering.

The logarithmic plots of the rate of grafting and final percent grafting against preirradiation dose are shown in Figure 2. Both the rate of grafting and final percent grafting increase with dose and then tend to level off at a higher dose.

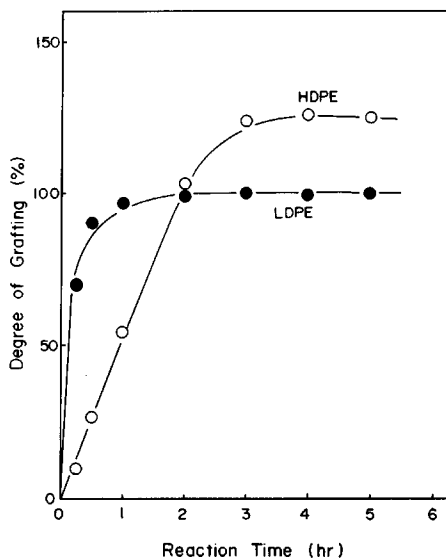


Fig. 1. Preirradiation grafting of acrylic acid onto polyethylene film. Preirradiation dose, 30 Mrad; monomer concn, 50 wt %; Mohr's salt, 0.25 wt %; grafting temp, 25°C; film thickness, 25 μ m.

The leveling of grafting rate in high dose region is explained by assuming that the rate depends largely on monomer diffusion as well as on radical concentration. The dose exponent (0.3–0.4) less than 1/2 even below 20 Mrad for the final percent grafting is not consistent with the bimolecular termination of growing radicals. The observed deviation from this law is due to the mutual recombination of primary radicals before initiating grafting.

Figure 3 shows the logarithmic plots of the final percent grafting against the relative concentration of trapped radicals determined by ESR. It can be seen that the final percent grafting is predominantly proportional to the concentration of trapped radicals regardless of the density of polyethylene.

Seguchi et al.,^{11–13} studying the preirradiation grafting of methyl methacrylate and 1,3-butadiene onto polyethylene, found that, though both alkyl and allyl radicals can initiate grafting reactions, the alkyl radicals play a main role in the

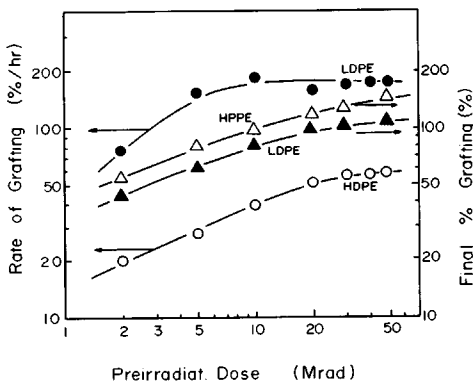


Fig. 2. Logarithmic plots of rate and final % grafting vs. preirradiation dose. Monomer concn, 50 wt %; Mohr's salt, 0.25 wt %; grafting temp, 25°C; film thickness, 25 μ m.

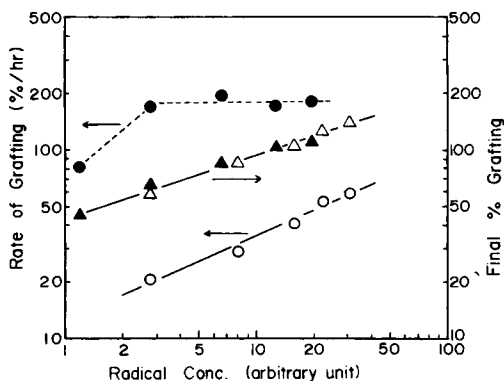


Fig. 3. Logarithmic plots of rate and final % grafting vs. radical concentration. Grafting conditions and the symbols are the same as in Figure 2.

initiation of grafting when the monomer is adequately supplied to amorphous region of polyethylene, while the allyl radicals are a main initiating species of grafting when the monomer content in the polymer matrix is very low.

Regardless of the type of initiating radicals, it is suggested that the grafting reaction initiates mainly at the surface of crystallites and proceeds in the amorphous region, since monomer cannot penetrate into the crystalline region. The grafting, rate and degree of grafting, therefore, is mainly governed by the factors such as (1) concentration of radicals trapped at the surface of crystallites; (2) migration rate of radicals in the crystalline region; and (3) diffusion rate of monomer in the amorphous region.

In the grafting of acrylic acid onto polyethylene film, the higher rate of grafting for LDPE than HDPE is presumably attributable to both higher concentration of radicals at the surface of crystallites and higher diffusion rate of monomer into polyethylene film, because LDPE has smaller crystallite size and lower crystallinity than those of HDPE. On the other hand, the rate of grafting for HDPE seems to depend not only these two factors but also on the migration rate of alkyl radicals in the crystalline region, since the rate of reaction with the monomer at the surface of the crystallite is much faster than the rate of radical migration. The fact that the final percent grafting depends only on the total amount of the trapped radicals, in spite of a large difference in the rate of grafting for LDPE and HDPE, may be explained by assuming that the molecular mobilities of growing radicals in the amorphous region of polyethylene is restricted to depress their recombination even at a higher radical concentration.

Monomer Concentration

The grafting is controlled by monomer concentration and free radical concentration in the polymer substrate. The effects of monomer concentration on the grafting rate and the final percent grafting are shown in Figure 4. The rates of grafting for both HDPE and LDPE are maximal around monomer concentration of 60%. The final percent graftings increase with monomer concentration up to 75% and fall markedly at 100%.

The decrease in both rate of grafting and final percent grafting above 60–70% monomer concentration is due to the decrease in monomer concentration and

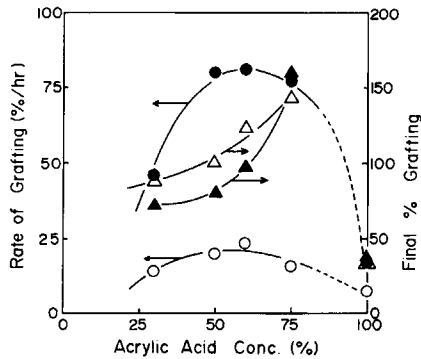


Figure 4. Effects of monomer concentration on rate and final % grafting. Preirradiation dose, 10 Mrad; Mohr's salt, 0.25 wt %; grafting temp, 25°C; polymer substrate: (○, Δ) 50 μm HDPE; (●, ▲) 50 μm LDPE.

diffusion rate in the grafted layer which is most swollen at 50% monomer concentration, as clearly shown in Figure 5.

Grafting Temperature

The reaction temperature is one of the important factors to control the grafting. As shown in Figure 6, the initial rate of grafting increases with temperature, but the final percent grafting decreases.

The logarithmic plots of the rate of grafting against the reciprocal temperature are shown in Figure 7. From the slopes of Arrhenius plots, the overall activation energy of the grafting was determined to be approximately 19.6 and 27.3 kcal/mol for LDPE and HDPE, respectively. These values are apparently too high for a reaction of free radical with vinyl monomers. The graft reaction is heterogeneous, and, as will be described later, occurs from the surface to the interior of the polymer matrix. Therefore, the high apparent activation energy is mainly due to that of the monomer diffusion process. The higher activation energy for HDPE than LDPE is due to higher crystallinity of HDPE.

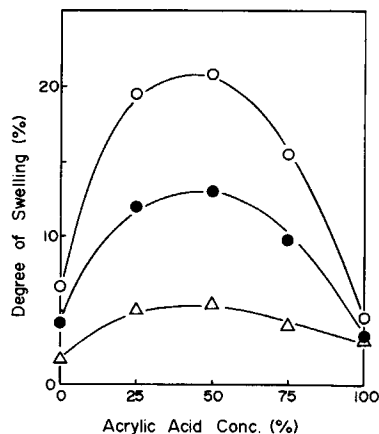


Fig. 5. Swelling of grafted film in aqueous solution of acrylic acid. Swelling temp, 25°C; swelling time, 24 h; degree of grafting: (○) 80%; (●) 50%; (Δ) 20%; polymer substrate, 25 μm HDPE.

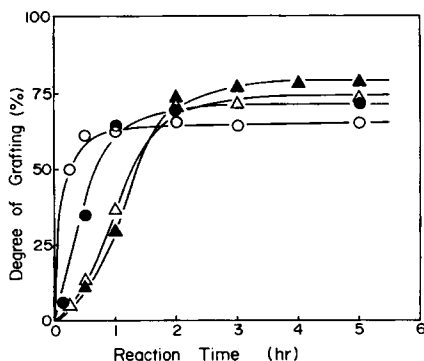


Fig. 6. Grafting curves at various grafting temperatures. Preirradiation dose, 10 Mrad; monomer concn, 30 wt %; Mohr's salt, 0.25 wt %; grafting temp; (O) 40°C; (●) 35°C; (Δ) 30°C; (▲) 25°C, polymer substrate, 25 μm HDPE.

It is observed that the higher grafting temperature gives the lower final percent grafting. In the inner part of the film, the trapped radicals partially decay before the grafting due to the mutual recombination and/or reaction with dissolved oxygen. The fraction of decayed radicals is increased at higher temperature; this causes the decrease in the final percent grafting at elevated temperature. And, also, the molecular weight of the poly(acrylic acid) grafted at a higher temperature should be lower in comparison with that obtained at a lower temperature, so that the final percent grafting decreases with increasing temperature, even if the number of radicals would not decrease. Shinohara and Tomioka¹⁴ studying the preirradiation grafting of *N*-vinyl pyrrolidone onto polyethylene, reported that the lower limiting value at a higher temperature is attributable to the shortness of the grafted chains, since in free radical polymerizations of vinyl monomers in homogeneous systems the molecular weight of polymer is generally small at elevated temperatures.

Film Thickness

Figure 8 shows the grafting curves for the films with different thicknesses. The rate of grafting decreases with increasing film thickness. The final percent grafting, however, was found to be of similar value, irrespective of the thickness.

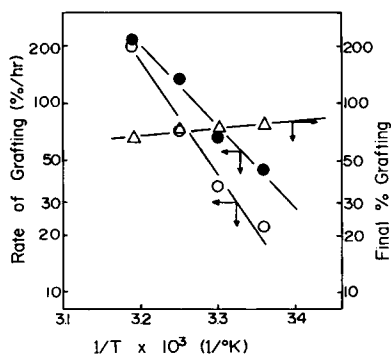


Fig. 7. Logarithmic plots of rate and final % grafting vs. reciprocal of grafting temperature. Grafting conditions are the same as in Figure 6. Polymer substrate: (O, Δ) 25 μm HDPE; (●) 25 μm LDPE.

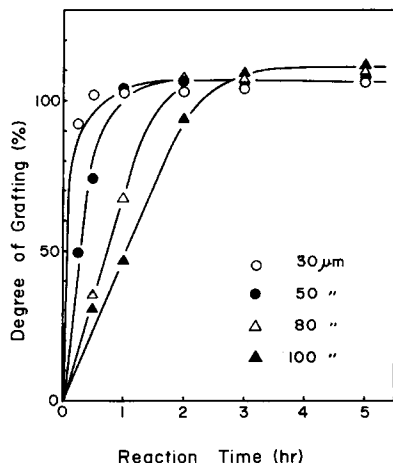


Fig. 8. Grafting curves for various film thicknesses. Preirradiation dose, 30 Mrad; monomer concn, 50 wt %; Mohr's salt, 0.25 wt %; grafting temp, 25°C; polymer substrate, LDPE. (○) 30 μm; (●) 50 μm; (Δ) 80 μm; (▲) 100 μm.

This result is also replotted in the relation between the amount of grafted poly(acrylic acid) per unit surface area of the film and reaction time, in Figure 9. The initial rate of weight increase per unit surface area was found to be independent of the thickness.

The thickness exponents of them, as shown in Figure 10, were found to be approximately -1.0 and 1.0 for the rate of grafting and final amount of grafted poly(acrylic acid), respectively. The negative first-order dependency of grafting rate, as well known, indicates that the monomer diffusion in the film is a rate controlling step of the grafting.

Lawler and Charlesby⁶ studied the simultaneous grafting of acrylic acid onto polyethylene and found that the water uptake of the grafted film is zero at the graft level less than 15%. Therefore, they deduced that the fissures which may be caused to appear in the surface graft can allow fresh monomer to reach the polyethylene surface again, and thus it is possible for grafting to proceed into

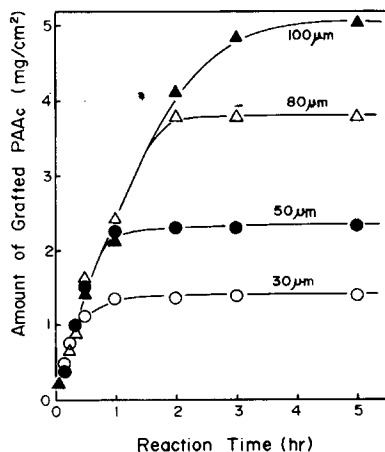


Fig. 9. Relationships between amount of grafted poly(acrylic acid) and reaction time. Grafting conditions are the same as in Figure 8.

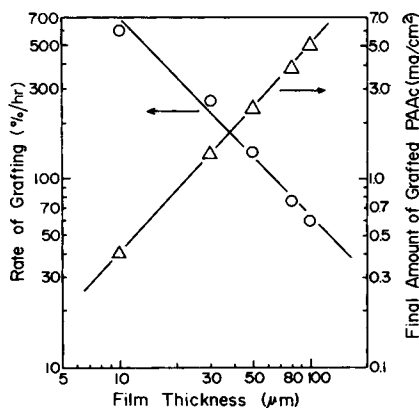


Fig. 10. Logarithmic plots of grafting rate and final amount of grafted poly(acrylic acid) vs. film thickness. Grafting conditions are the same as in Figure 8.

the polyethylene, since the poly(acrylic acid) surface graft away from the polyethylene interface is impervious to water due to the hydrogen-bonded, high-molecular polymer.

On the contrary, the grafted film obtained in this preirradiation method is wettable and swollen in water even at the degree of grafting lower than 10%. The water uptake of the grafted film was found to be linearly proportional to the degree of grafting in the range of 0–150% grafting. It is reasonably concluded that the grafting begins at the part close to the surface and then proceeds into polymer matrix by gradual diffusion of acrylic acid through the grafted layers, which can swell in the reaction medium.

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