

Photoinduced Grafting of Acrylamide onto Polyethylene Film by Means of Two-Step Method

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Synopsis

Benzophenone-coated low-density polyethylene (LDPE) was grafted with acrylic acid (AA), methacrylic acid (MA), acrylonitrile (AN), and methyl methacrylate (MMA) in an aqueous medium by photoirradiation. The first-step graft samples thus prepared with a grafting of about 50% were subjected to second-step photografting with acrylamide (AAm). On AA- and MA-grafted LDPE samples, the second-step grafting of AAm was very smooth, and a high level of grafting up to 800% was attained with ease. On the other hand, grafted LDPE samples employing hydrophobic monomers, AN and MMA, had a lower percent of grafting than those with hydrophilic monomers, AA and MA. By ESR study, a thermally stable radical was found in the first-step graft sample irradiated with light of $\lambda > 330$ nm. Mechanisms for the formation of such a radical in the first-step graft sample are proposed, and the contribution of the radical to the second-step grafting is discussed.

INTRODUCTION

In a previous article,¹ grafting of vinyl monomers such as acrylic acid (AA) and methacrylic acid (MA) on benzophenone (BP)-coated low-density polyethylene (LDPE) film, performed successfully under irradiation in an aqueous medium, was reported.

However, it was not easy to introduce the other hydrophilic monomer, acrylamide (AAm), by the same way in LDPE at a high level. On the other hand, AAm was smoothly introduced in nylon film² at a high level of grafting. This phenomenon seems to be closely related to the affinity between nylon substrate and AAm. Accordingly, the affinity between film substrate and monomer seems to be worth considering as an important factor for effective grafting.

In this study, the first-step graft samples were prepared from LDPE film with various monomers, which were then grafted again to perform the second-step photografting with AAm. The first-step graft samples were expected to have increased affinity for AAm by the proper choice of monomer employed in the first-step grafting.

EXPERIMENTAL

Samples

LDPE film, free from stabilizer and 30 μm thick, was immersed in an acetone solution including 0.3% benzophenone (BP) and 1.0% poly(vinyl acetate) (MW 100,000); it was then dried under reduced pressure to prepare BP-coated LDPE film. Acrylic acid (AA), methacrylic acid (MA), methyl methacrylate (MMA), and acrylonitrile (AN) were purified by distillation, and acrylamide (AAm) was recrystallized from benzene.

First-Step Grafting

Grafting was performed by irradiating 0.09 g BP-coated LDPE film (100 × 30 mm), 20 mL water, and 2 mL monomer contained in Pyrex glass under nitrogen gas at 60°C for 60 min. Polymerized film was extracted by a proper solvent to remove homopolymers, namely, hot water was used for poly(AA) and poly(MA). Acetone and *N,N*-dimethylformamide were chosen for poly(MMA) and poly(AN), respectively. The percent grafting of the first-step graft sample is as follows:

$$\text{Percent grafting (\%)} = \frac{\text{first-step graft film (g)} - \text{LDPE film (g)}}{\text{LDPE film (g)}} \times 100$$

Second-Step Grafting

The first-step graft sample was coated with BP again as above to prepare the sample for second-step grafting. A 0.1-g film sample, 20 ml water, and 2.0 g AAm were settled in the Pyrex glass tube, and the tube was then flushed with nitrogen gas and then irradiated at 60°C for 60 min to perform polymerization. Homopolymers were extracted with hot water, and the percent grafting of the second-step grafting was defined as follows:

$$\text{Percent grafting (\%)} = \frac{\text{second-step graft film(g)} - \text{first-step graft film (g)}}{\text{first-step graft film(g)}} \times 100$$

The light source used was a 400-W high-pressure mercury lamp which was set in a Riko Rotary Photochemical Reactor RH400-10W.

Grafting on Preirradiated Sample

Benzophenone-coated first-step graft sample, 0.1 g, was settled in a Pyrex glass tube under nitrogen gas, which was irradiated at room temperature for 60 min. The light source was a Toshiba high-pressure mercury lamp H400-P (400 W), which was set at 10 cm from the sample. After the irradiation, 20 ml aqueous solution of 1.4 mol/L AAm was injected into the tube, which was kept at 60°C for 60 min to perform grafting. The dissolved oxygen in the solvent was removed by the freeze-thaw method beforehand.

Measurement of ESR Spectrum

The quartz glass tube ($\phi = 5$ mm) containing the film sample was flushed with nitrogen gas and irradiated at -196°C . The light source was a superhigh-pressure mercury lamp (250 W) through a Pyrex lens ($\lambda > 330$ nm). ESR spectra were recorded with x-band and 100-kcps field modulation at -196°C with a Japan Electron Optics Laboratory JES-ME-X.

RESULTS AND DISCUSSION

Second-Step Grafting

Photoinduced graftings of AAm on first-step graft LDPE samples using monomers AA, MA, MMA, and AN were examined, which are shown in Figure

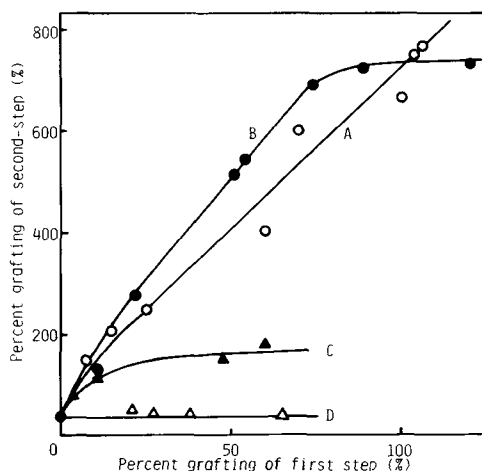


Fig. 1. Second-step photografting of AAm on first-step graft LDPE samples. A, B, C, and D represent AA-, MA-, AN-, and MMA-grafted LDPE samples, respectively. Second-step photografting was carried out at 60°C for 60 min.

1. The horizontal axis indicates the percent grafting of the first-step graft sample. On AA- and MA-grafted samples, the second-step grafting of AAm was very smooth, and a high level of grafting up to 800% was attained with ease. On the other hand, AN- and MMA-grafted samples employing hydrophobic monomers exhibited a lower percent grafting than those using hydrophilic monomers. It is believed that hydrophilic monomers used in the first-step grafting contribute to the elevation of hydrophilicity of the grafted LDPE, which contributes to the graft initiation of AAm, especially in second-step grafting.

Radicals on First-Step Graft Sample

First-step graft LDPE samples with 47–50% grafting were irradiated, and the ESR spectra are shown in Figure 2. Although conditions of irradiation and

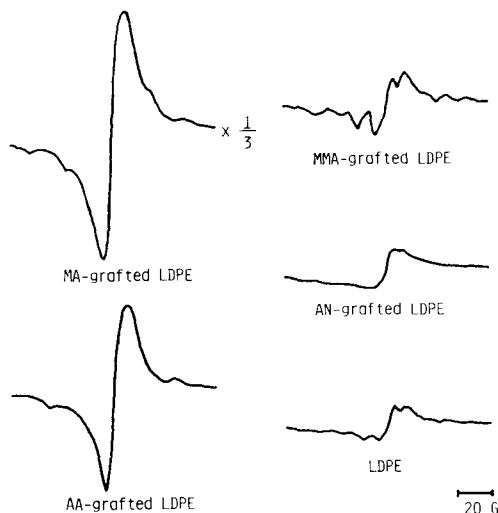


Fig. 2. ESR spectra of first-step graft LDPE samples with ca. 50% grafting irradiated with a light of $\lambda > 330$ nm at -196°C for 60 min. Concentration of BP, 0.3%.

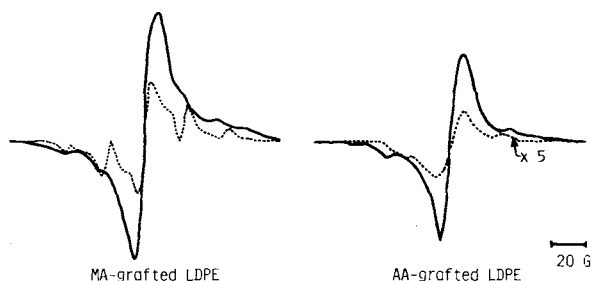


Fig. 3. ESR spectra of AA- and MA-grafted LDPE samples with ca. 50% grafting irradiated with light of $\lambda > 330$ nm at -196°C for 60 min. Concentration of BP, 0.3%. Dotted lines show spectra after warming to 20°C for 1 min.

measurement were controlled equally for each sample, the spectra of the AA- and MA-grafted samples indicated a markedly higher intensity than those of AN- and MMA-grafted samples. Thus, LDPE samples modified with hydrophilic monomers are more susceptible to formation of radicals as compared with those modified with hydrophobic monomers. This seems to be related closely to the activity of polymerization in the second-step grafting in Figure 1. That is, the grafted chain of first-step sample apparently contributes to the formation of radicals by irradiation.

Figure 3 shows the ESR spectra of irradiated samples after warming to 20°C for 1 min. Those of MA- and AA-grafted samples were five-line type (splitting constant 22.5 gauss) and three-line type (splitting constant 21 gauss), respectively, which are known to be stable thermally.

Monomers MA and AA were irradiated at -196°C , and the spectra, which were recorded at the same temperature, are shown in Figure 4. They were assigned

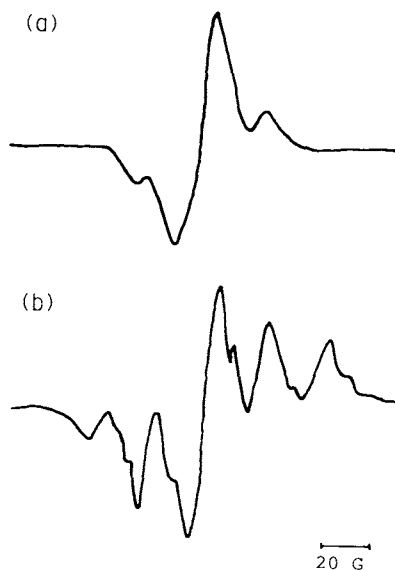


Fig. 4. ESR spectra of (a) AA and (b) MA monomers irradiated with a light of $\lambda > 330$ nm at -196°C for 60 min.

to radicals I and II, which correspond to the active ends of the growing chain,³ respectively:



As the spectra in Figure 3 coincide well with those in Figure 4 in the splitting constant, it is believed that the grafted chains in each sample undergo chain scission by the irradiation resulting in the formation of radical I or II.

Methacrylic acid-grafted LDPE in the absence of BP was irradiated and underwent the same warming as above; the spectrum is shown in Figure 5(a). The low intensity of the spectrum may suggest a poor formation of radicals for the sample without sensitizer. On the other hand, Figure 5(b) is the spectrum of irradiated sample with BP coating, and Figure 5(c) is the one employing naphthalene instead of BP, recorded after warming to 20°C for 1 min. Both spectra were regarded as five-line type, though their intensities were not so high. These spectra were analyzed to include a four-line component with a splitting constant

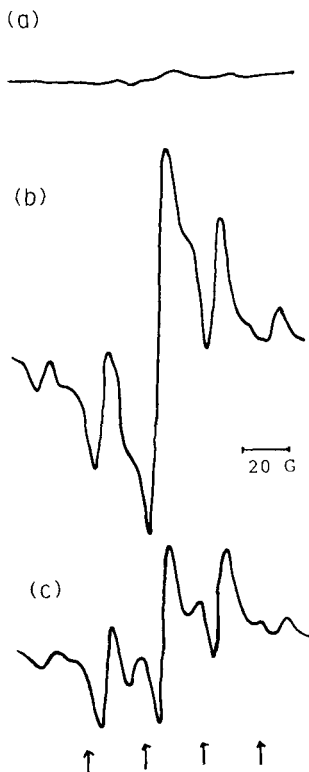
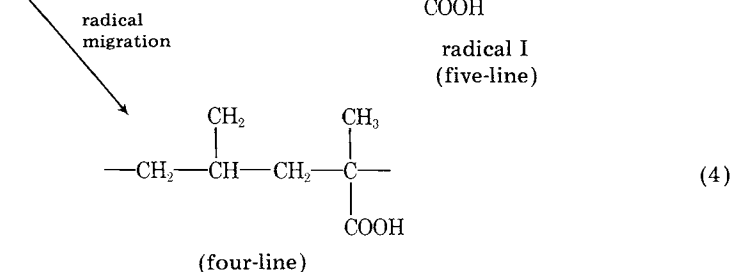
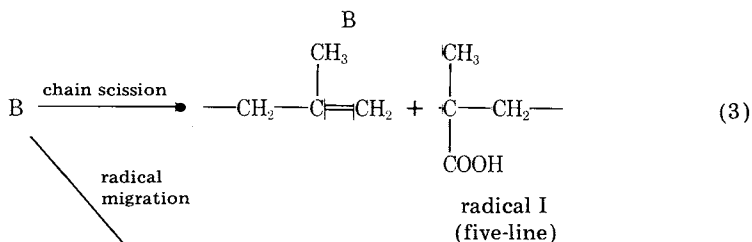
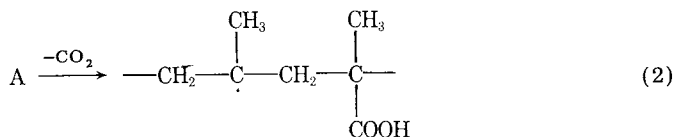
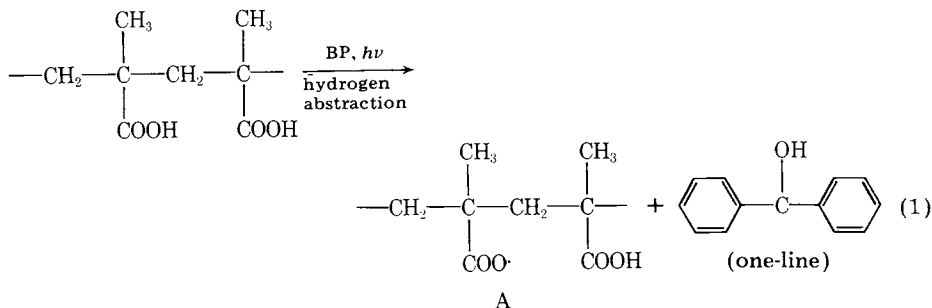


Fig. 5. ESR spectra of MA-grafted LDPE samples (58% grafting) (a) without sensitizer, (b) with BP (0.3%), and (c) with naphthalene (0.3%) after warming to 20°C for 1 min.

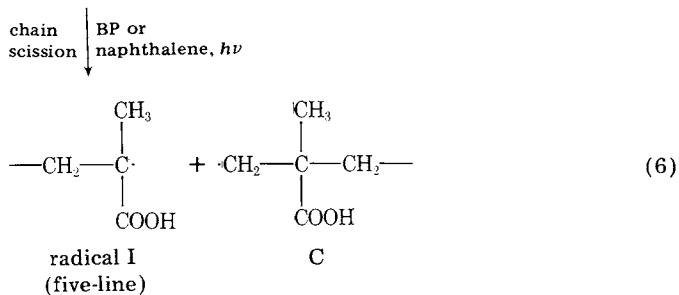
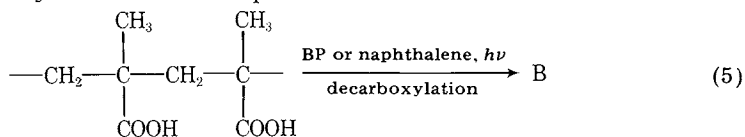
of 23 gauss, which is indicated with arrows. Thus, the formation of five-line radical I was proved on samples with sensitizers of BP as well as naphthalene.

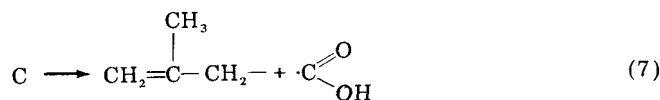
Based on the above investigations, the mechanisms forming radical I in MA-grafted LDPE were estimated as follows:

Hydrogen abstraction by excited BP:



Energy transfer by excited BP or naphthalene:





The photodegradation⁴ of poly(AA) and poly(MA) is known to proceed through a decarboxylation or chain scission process. The formation of radical I due to hydrogen abstraction from poly(MA) by BP can be described by eqs. (1) to (4). The ketyl radical was confirmed experimentally using irradiated BP as a singlet spectrum with a line width of 12 gauss and a *g* value of 2.002. The spectrum intensity decreased sharply by warming the sample to room temperature. Therefore, it is conceivable that the spectrum of irradiated MA-grafted LDPE originates from two radicals, one the stable radical I and the other the thermally unstable ketyl radical.

Naphthalene contributed to the formation of the radical I despite the inability of abstracting hydrogen atom. It is believed that radical I can also be introduced by way of the energy transfer from excited BP or naphthalene according to eq. (5) or (6). The four-line component observed in Figure 5(c) was assigned as the radical appearing in eq. (4), which is known to indicate a four-line spectrum in the ESR studies of polypropylene.⁵⁻⁸

Referring to AA-grafted LDPE, the same mechanisms as above seem applicable to yield radical II.

Grafting on Preirradiated Sample

The preirradiated AA-grafted sample was observed to initiate grafting of AAm on it, shown in Figure 6. The irradiated sample may contain mostly radical II, because the ketyl radical based on BP is thermally unstable and cannot exist at room temperature. Thus, one may appreciate the ability of radical II to initiate grafting reaction, by which AAm is possibly introduced in a block chain type. Omichi and Araki⁹ studied the radiation-induced two-step grafting of styrene and MMA on PE using the ESR method and reported that the polymerization proceeds as block type.

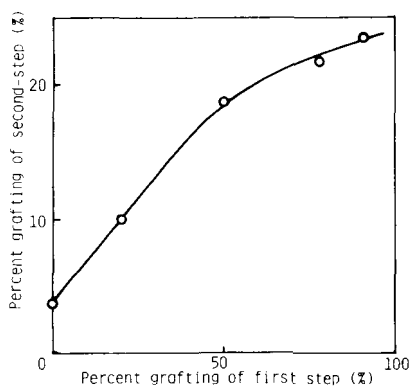


Fig. 6. Grafting of AAm on AA-grafted LDPE sample with BP (0.3%) preirradiated at room temperature for 60 min in Pyrex glass tube. Grafting of AAm was carried out at 60°C for 60 min in water medium.

As discussed above, the two-step grafting was characterized by the introduction of AAm with a high yield, in which an elevated affinity of the first-step graft sample with AAm monomer seems to contribute to make the second-step grafting effective. Another factor for the successful grafting should be the thermally stable radical from the grafted chain of first-step graft sample, which was confirmed using the ESR method.

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