Factors Affecting Photografting of Methacrylic Acid on Polyethylene Film in Liquid Phase System

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Synopsis

Factors affecting photografting ($\lambda > 300$ nm) of methacrylic acid on low-density polyethylene film were investigated in liquid-phase system with water. Benzophenone was used as a sensitizer by coating it on the film surface. Factors examined were monomer concentration (1.3 wt% to 10.0 wt%), polymerization temperature (30°C to 70°C), and film thickness (30 μm and 80 μm). It was found that grafted polymer is formed preferentially as compared with homopolymer under conditions such as monomer concentration higher than 6.0 wt%, polymerization temperature higher than 50°C, and film thickness of 30 μm. The structure of the grafted samples obtained in the above systems was characterized by the grafted chains distributing over the film and the flat appearance of film surface. In the grafting systems using the monomer concentration lower than 6.0 wt%, the polymerization temperature lower than 50°C, and the film thickness of 80 μm, homopolymer was formed predominantly. The resultant grafted chains localized mainly on the film surface, which appeared to be grainy.

INTRODUCTION

In a previous article,[1] it was observed that the surface appearance and the distribution of grafted chains in methacrylic acid (MAA)-grafted polyolefin films prepared by photografting are greatly influenced by the polymerization system, either liquid or vapor phase. Regarding the grafted samples prepared by using the liquid-phase system, the grafted chains located mainly on the film surface, which contributes to the formation of grainy surface. By using the vapor phase system, on the other hand, the grafted chains were distributed to the inside of the film, resulting in the formation of flat surface.

With comparison of polymerization behaviors between the liquid- and vapor-phase systems under the same irradiation conditions, the grafting efficiencies of the latter system were 70% to 80% depending on the grafting conditions, which were about twice higher than those of the former system. Thus, the vapor-phase system was characterized by the predominant formation of grafted polymer compared with the liquid-phase system. This may be one of reasons why the vapor-phase system results in the grafted film with a homogeneous distribution of the grafted chains. In this paper, effects of monomer concentration, polymerization temperature, and film thickness on liquid-phase photografting were investigated together with the relationship between the grafting conditions and the structure of grafted film in order to

prepare the grafted film in which the grafted chains locate homogeneously in the film substrate.

EXPERIMENTAL

The film used was low-density polyethylene (PE) (thickness = 30 μm and 80 μm). The film (45 × 74 mm) was immersed in acetone solution containing 0.3 wt% benzophenone and 1.0 wt% poly(vinyl acetate) and dried to prepare sensitizer-coated film. Amount of benzophenone on the film thus obtained by the treatment was 5.4 × 10^{-8} mole per apparent surface unit (cm^2), which was determined spectrophotometrically. MAA was purified by distillation under reduced pressure.

Liquid-phase photografting was carried out in a Pyrex glass tube containing the film sample and 40 mL of aqueous solution of MAA under nitrogen atmosphere. Irradiation with a high-pressure mercury lamp (400 W) was
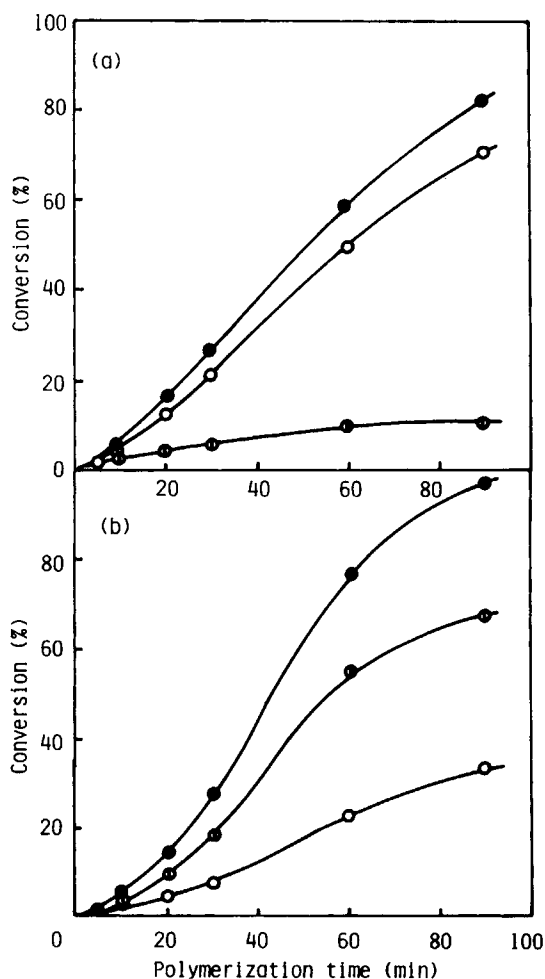

Fig. 1. Effect of monomer concentration on photografting of MAA to PE film. Polymerization temperature 60°C; film thickness 30 μm. (a) [MAA] = 2.5 wt%; (b) [MAA] = 10.0 wt%. (●) total conversion; (◐) grafted polymer conversion; (○) homopolymer conversion.

conducted in a Riko rotary photochemical reactor RH400–10 W, around which Pyrex glass tubes were rotated. Polymerized film was extracted for 24 h with hot water to exclude homopolymer of poly(MAA). The extraction[2] is known to be almost sufficient for removing the homopolymer in the film. Grafted polymer and homopolymer conversions were expressed as percentage of weights of grafted polymer and homopolymer to weight of monomer employed, respectively.

The surface of the grafted film was observed by a scanning electron microscope (JEOL JEM-100C). The grafted film was immersed in 0.1 wt% aqueous solution of methylene blue at room temperature for 2 h and then dried to prepare methylene blue-dyed sample. Observation of the distribution of MAA-grafted chains in the direction of film thickness was made by an optical microscope using the dyed sample.

RESULTS AND DISCUSSION

Factors Affecting Photografting

Figure 1(a) shows the irradiation time-conversion curve in the system of 2.5 wt% monomer concentration. Total conversion is the sum of grafted polymer and homopolymer conversions. The grafted polymer conversion was extremely lower than the homopolymer conversion, showing a predominant formation of homopolymer in the system. On the contrary, higher formation ratio of grafted polymer to homopolymer was observed for the system of 10.0 wt% monomer concentration [Fig. 1(b)]. Figure 2 shows relationship between the grafted polymer conversion and the monomer concentration at 50% total conversion in the irradiation time-conversion curve given in Figure 1. The figure also includes the homopolymer conversion for reference, which is represented by a dotted line. The grafted polymer conversion increased with
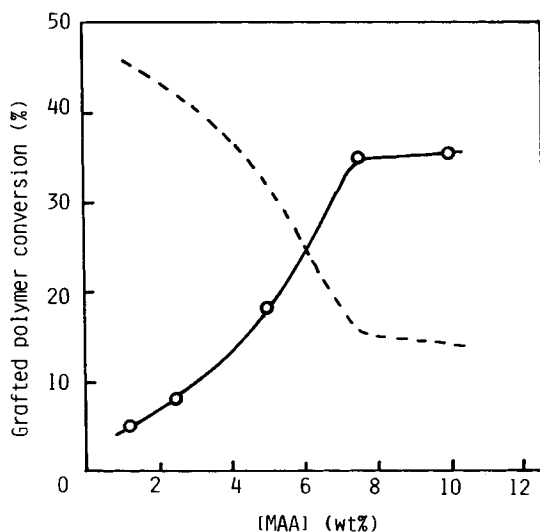

Fig. 2. Relationship between grafted polymer conversion and monomer concentration at 50% total conversion. Polymerization temperature 60°C; film thickness 30 μm. A dotted line represents the homopolymer conversion at 50% total conversion.

increasing the monomer concentration and got ahead of the homopolymer conversion in the monomer concentrations beyond 6.0 wt%. Thus, the formation ratio of grafted polymer to homopolymer seems to change according to the monomer concentration.

Figure 3 shows the effect of polymerization temperature on photografting. The grafted polymer conversion was very low as compared with the homopolymer conversion in the system at 30°C [Fig. 3(a)], while the reverse tendency was recorded for the system at 70°C [Fig. 3(b)]. Figure 4 presents the relationship between the grafted polymer conversion and the polymerization temperature at 50% total conversion in the same manner as Figure 2. Again, there exists a certain polymerization temperature, at which the formation ratio of grafted polymer to homopolymer inverses, and the temperature corresponds to about 50°C. It was found, as above, that the monomer concentration and the polymerization temperature greatly influence on photo-
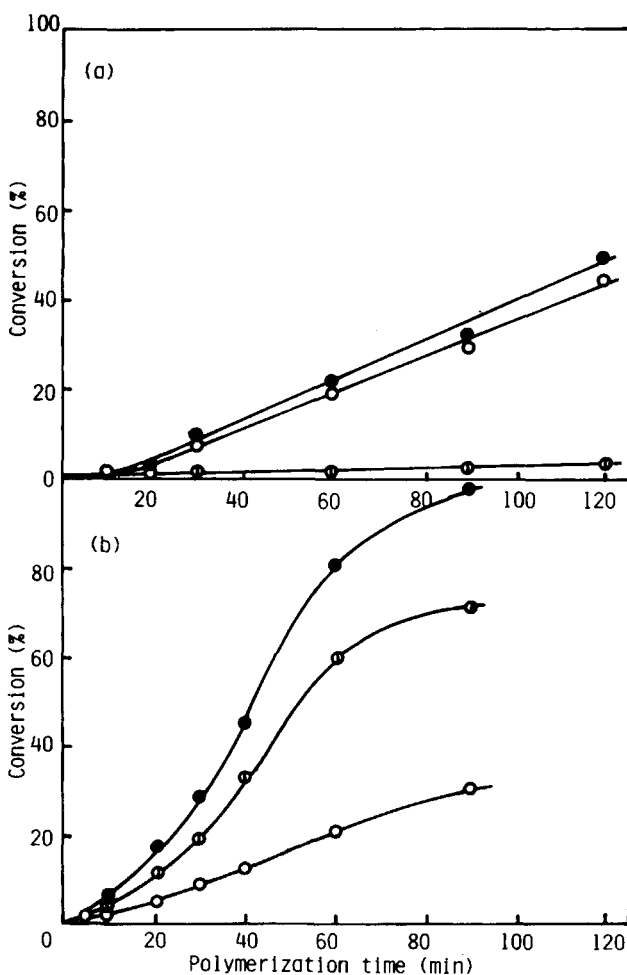

Fig. 3. Effect of polymerization temperature on photografting of MAA to PE film. Monomer concentration 10.0 wt%; film thickness 30 μm. (a) 30°C; (b) 70°C. (●) total conversion; (◐) grafted polymer conversion; (○) homopolymer conversion.
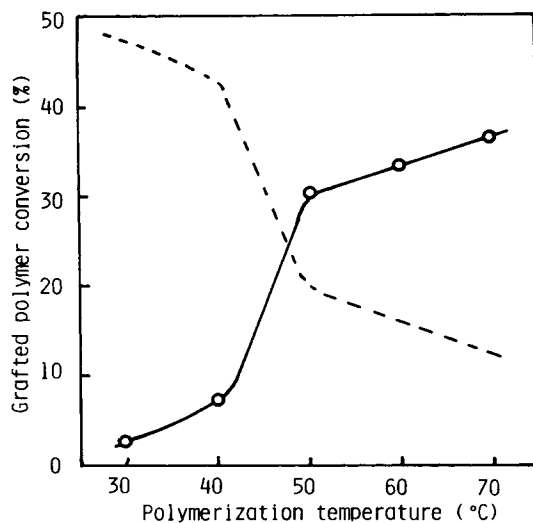
Fig. 4. Relationship between grafted polymer conversion and polymerization temperature at 50% total conversion. Monomer concentration 10.0 wt%; film thickness 30 μm. A dotted line represents the homopolymer conversion at 50% total conversion.
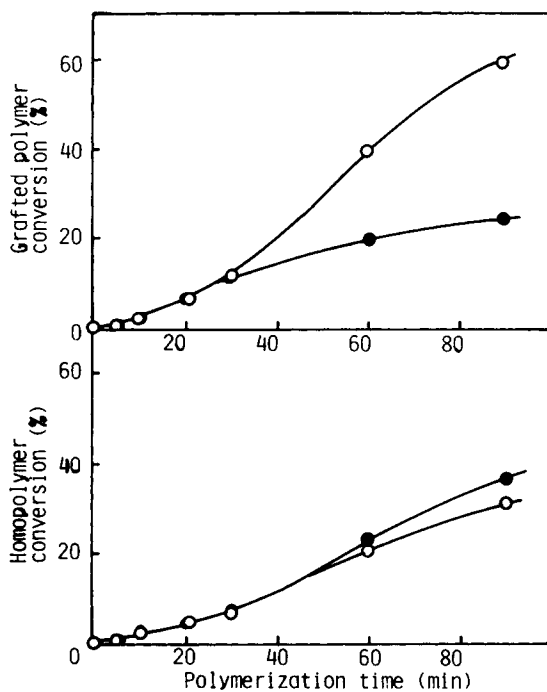

Fig. 5. Effect of film thickness on photografting of MAA on PE film. Monomer concentration 10.0 wt%; polymerization temperature 60°C; film thickness (○) 30 μm, (●) 80 μm.

grafting reaction and can be factors to control the formation ratio of grafted polymer to homopolymer.

Figure 5 shows the effect of film thickness on photografting. The formation of grafted polymer was predominant in the system with film thickness of 30 μm (30 μm film). For the film sample of 80 μm thick (80 μm film), however, the conversion became lower than that of homopolymer. Moreover, the 80 μm film showed lower grafted conversion than those of the 30 μm film in the range beyond the irradiation time of 30 min. This phenomenon differs from the results reported by Inagaki et al.[4] They observed in grafting of acrylic acid on polyethylene (PE) film by preirradiation method that the initial formation rate of grafted polymer per unit surface area is independent of the film thickness, but the final amount of grafted polymer increases with increasing thickness. Our result may suggest that there are some differences in the structure between the two films. Unfortunately, we have not had a clue to them yet. However, the polymerization behavior of Figure 5 may be considered as described below. The grafted polymer conversion was found to be almost same between both films up to 30 min of irradiation time. From microscopic observations of graded films, as mentioned later, the grafted chains in the 30 μm film were confirmed to distribute in the film inside, while they located mainly on the film surface in the 80 μm film. Accordingly, it is supposed that the grafted chains in the 30 μm film reach the center of the film at a certain stage of irradiation earlier than those in the 80 μm film. It is plausible in such a system that the film texture is loosened to increase the volume capable of accepting the reaction, leading to reaction conditions favorable to the further formation of grafted polymer. It was found in a previous paper[5] on two-step photografting that poly(MAA) chains grafted on PE film are easily susceptible to decomposition by irradiation with light of $\lambda > 300$ nm in the presence of benzophenone and the resultant poly(MAA) radicals participate in the initiation of acrylamide grafting. On the other hand, the grafted chains of the 80 μm film were observed not to reach to the center of the film even at the irradiation time of 90 min.

Structure of Grafted Film

Figure 6 shows typical electron micrographs of the surface appearance of grafted film. The surface appearance[6,7] was roughly classified into two types, that is, grainy [Fig. 6(a)] and flat [Fig. 6(b)]. Micrographs of the cross-section of the grafted films with the structure of above surface are shown in Figure 7. The part dyed in blue corresponds to the MAA-grafted chains. For the grafted film with grainy surface [Fig. 7(a)], only the film surface was dyed in blue and the inside was not dyed. On the other hand, the grafted film with the flat surface [Fig. 7(b)] was dyed through whole film thickness. It was confirmed, thus, that the grafted chains of the former sample locate mostly on the film surface, but they distribute homogeneously through film inside of the latter sample.

It was reported in radiation-induced grafting that distribution of grafted chains can vary depending on the polymerization system[8] (vapor and liquid phases), the absence or presence of solvent,[9] the use of monomer mixture,[10] the one- or multistep grafting,[11] the use of Mohr's salt,[12] the reaction
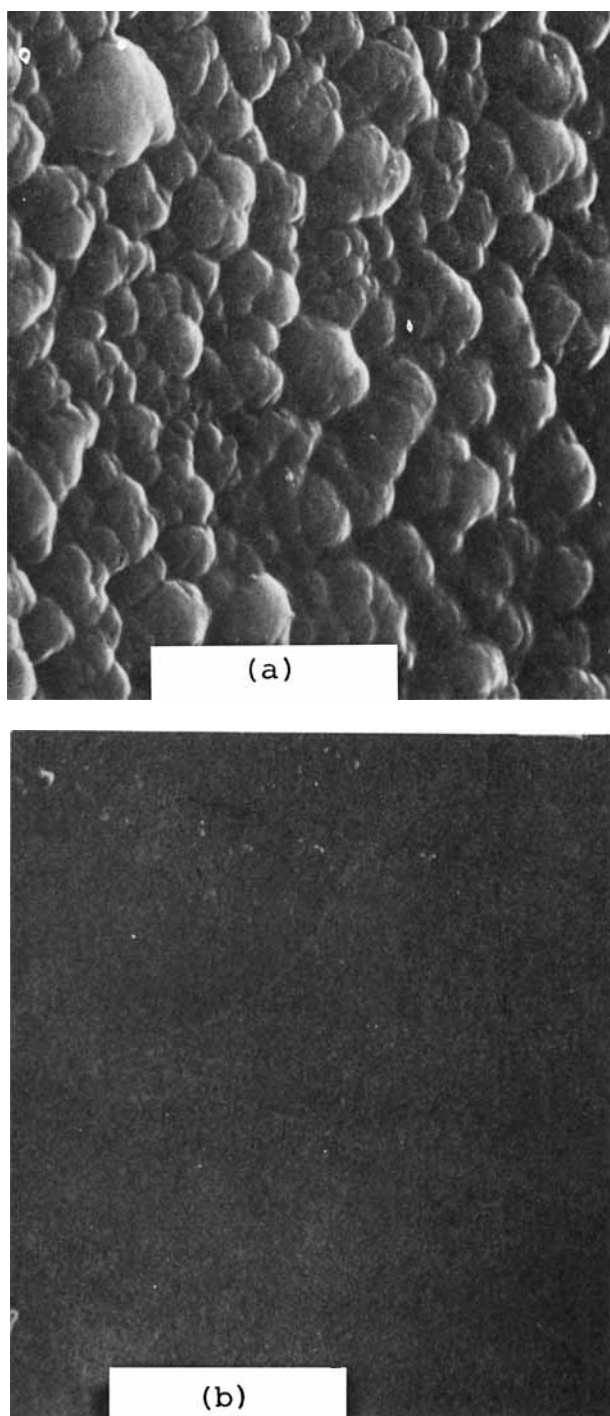
Fig. 6. Electron micrographs of the surface of MAA-grafted PE film. (a) grafted polymer conversion 11.0 %; grafting conditions: [MAA] = 2.5 wt%; temperature = 60°C; film thickness = 30 μm. (b) Grafted polymer conversion 17.5%; grafting conditions: [MAA] = 10.0 wt%; temperature = 60°C; film thickness = 30 μm.
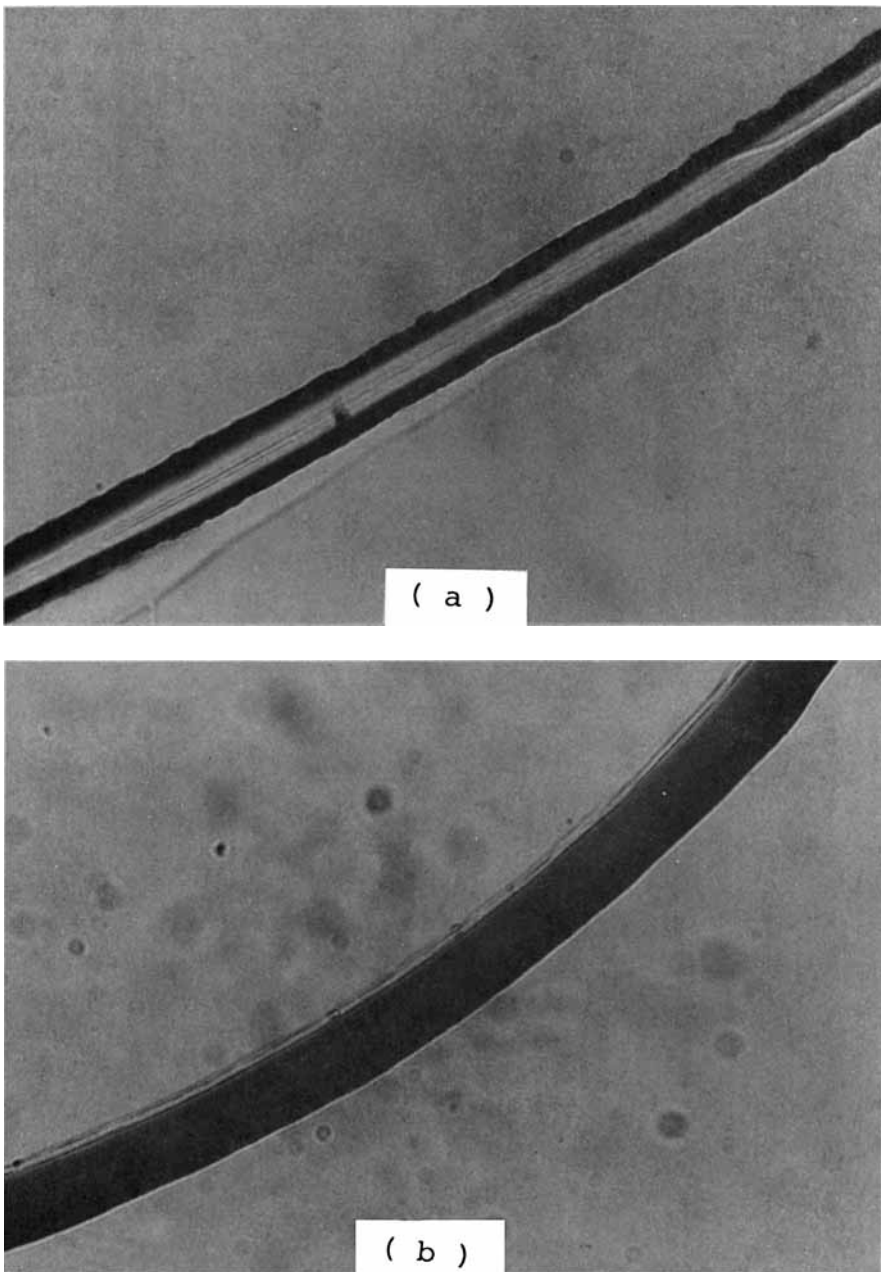
Fig. 7. Micrographs of cross-section of MAA-grafted PE film treated with methylene blue. Grafted samples of (a) and (b) used for the observation are the same as those of Figure 6.

temperature,[13] and the swelling agent.[13] Regarding the effect of monomer concentration on the structure of grafted film, the grafted chains were observed in this study to locate on the film surface with the use of monomer concentration lower than 6.0 wt%, resulting in the grainy surface. With the systems with the higher monomer concentration than 6.0 wt%, however, the grafted chains were distributed homogeneously in the film, and flat surface

was formed. With respect to the polymerization temperature, the grainy and flat surfaces were given for the systems at lower and higher temperatures than 50°C, respectively. It was confirmed that the grafted chains distributing in the film inside contribute to the formation of flat surface. Such grafting conditions correspond to higher monomer concentration and polymerization temperature, with which the formation of grafted polymer overcomes that of homopolymer. Moreover, the 30 μm film formed grafted polymer predominantly, which is shown in Figure 5, and the resultant grafted chains distributed in the film inside, resulting in the flat surface appearance. On the other hand, the grafted chains in the 80 μm film located mostly on the film surface, the appearance of which is grainy.

It was clarified, as above, that factors such as the monomer concentration, the polymerization temperature, and the film thickness greatly influence both the grafting reaction and the structure of grafted film in the following manner. Under grafting conditions where the formation of grafted polymer proceeds favorably, the grafted chains distribute in the film inside and the flat surface can be generated. By the proper choice of monomer concentration, polymerization temperature, and film thickness, accordingly, it is concluded that the grafted film with a homogeneous distribution of the grafted chains can also be prepared in the liquid-phase photografting.

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