

# Characteristics of Methacrylic Acid-Grafted Polyethylene Films Prepared by Photografting in the Presence of Polyfunctional Monomers

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**ABSTRACT:** Photografting of methacrylic acid (MAA) on low-density polyethylene film (thickness = 30  $\mu\text{m}$ ), on which xanthone photoinitiator was coated earlier, in the presence of polyfunctional monomers such as *N,N'*-methylenebisacrylamide, ethylene glycol dimethacrylate, and trimethylol propane triacrylate was examined at 60°C in water/acetone (3:1 v/v) mixture solvent. The photografting was retarded at the earlier stage of polymerization, and then accelerated when small amounts of the polyfunctional monomers (1–3 mol % of MAA monomer used) were added to the system. Addition of the polyfunctional monomers did not affect distribution of the grafted chains in the cross section of the resultant MAA-grafted PE film, which was measured by electron probe microanalysis. The MAA-

grafted samples were subjected to adsorption of cupric ions at 25°C for 24 h in the system of pH = 5. The adsorption was considerably suppressed for the grafted samples prepared at the earlier stage of polymerization in the system with the polyfunctional monomers. The phenomenon was discussed in terms of the formation of crosslinked and branched structures in the MAA-grafted chains depending on the polymerization stage in the system with polyfunctional monomers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1262–1268, 2006

**Key words:** photografting; methacrylic acid; low-density polyethylene film; polyfunctional monomers; adsorption of cupric ion

## INTRODUCTION

It has been reported that photografting of vinyl monomers on polyolefins<sup>1,2</sup> and cellulose<sup>3–5</sup> is considerably accelerated when small amounts of polyfunctional monomers such as triethylene glycol dimethacrylate, trimethylol propane triacrylate, trimethylol propane trimethacrylate, and divinylbenzene are added to the grafting systems. The effect of polyfunctional monomers has also been examined in high-energy radiation-induced grafting systems.<sup>6–9</sup> The authors<sup>10</sup> observed that photografting of acrylic acid (AA) on low-density polyethylene film is largely promoted by adding *N,N'*-methylenebisacrylamide (MBAAm) as a polyfunctional monomer to the grafting system. The MBAAm component was incorporated into polyethylene substrate and/or AA-grafted chains through the grafting reaction. Double bonds of the incorporated MBAAm residues seemed to act as a new site for the grafting initiation, leading to the promoted grafting. Peroxidation of the AA-grafted samples with hydrogen peroxide in the presence of methanesulfonic acid and thermal decomposition of the resultant polymeric

peroxides at 40°C were further examined. Both the peroxidation and the thermal decomposition were retarded for the grafted samples prepared in the system with MBAAm compared with those prepared in the system without MBAAm, suggesting the formation of a crosslinked structure in the AA-grafted chains of the former samples.

In the present study, photografting of methacrylic acid (MAA) on polyethylene film in the presence of polyfunctional monomers such as MBAAm, ethylene glycol dimethacrylate (EGDMA), and trimethylol propane triacrylate (TMPTA) was examined, and then adsorption reaction of cupric ion ( $\text{Cu}^{2+}$ ) with the resulting MAA-grafted polyethylene was also investigated to understand the characteristics of the grafted chains, such as reactivity and structure.

## EXPERIMENTAL

### Materials

Low-density polyethylene (PE) with 30  $\mu\text{m}$  thickness was used as a film sample. The film sample (3  $\times$  10 cm) was immersed at room temperature for 5 min in acetone solution containing 0.3 wt % xanthone and 0.5 wt % poly(vinyl acetate) ( $M_w = 100,000$ ), removed from the solution, and then dried under reduced pressure to prepare xanthone-coated film.<sup>11</sup> The quantity

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of xanthone on the film was too small to be determined gravimetrically. However, the existence of xanthone on the film surface was confirmed by attenuated total reflectance infrared measurement, where a specific absorption band due to aromatic ring of xanthone appeared at  $1608\text{ cm}^{-1}$ . Methacrylic acid (MAA) was purified by distillation under reduced pressure. Xanthone, *N,N'*-methylenebisacrylamide (MBAAm), ethylene glycol dimethacrylate (EGDMA), and trimethylol propane triacrylate (TMPTA) were all reagent grade and were used without further purification.

### Photografting

Photografting was carried out in a Pyrex glass tube containing the film sample ( $3 \times 10\text{ cm}$ ) and 30 mL water/acetone (3:1 v/v) mixture solvent, in which known quantities of MAA and polyfunctional monomers were dissolved, under nitrogen atmosphere. The mixture solvent was used to dissolve EGDMA and TMPTA in water solvent. Irradiation with a high-pressure mercury lamp (400 W) was carried out at  $60^\circ\text{C}$  using a Riko rotary photochemical reactor (RH400–10W). Polymerized films were extracted for 24 h with hot water to remove homopolymer of poly-MAA. The percentage of grafting was taken as the percentage of weight increase of the original film.

### Photopolymerization

Photopolymerization was performed in a 5-mm i.d. Pyrex glass tube containing *n*-hexane solution of MAA, in which known concentrations of xanthone and MBAAm were dissolved, under nitrogen atmosphere. Irradiation was carried out at  $60^\circ\text{C}$  using the same reactor as the one described in the previous section. After polymerization, the polymerized products were poured into a large excess of methanol, filtered, and then extracted with hot methanol. Crosslinked polymer yield was defined as follows:

Crosslinked polymer yield (%)

$$= \frac{\text{weight of methanol-insoluble fraction}}{\text{weight of feed monomer}} \times 100$$

### Electron probe microanalysis

MAA-grafted film was immersed in an aqueous solution of 1.0 wt % potassium hydroxide at  $25^\circ\text{C}$  for 24 h and then washed with water. The distribution profile of potassium atoms in the cross section of the grafted film was measured by an electron probe microanalyzer model EPM-810 of Shimadzu.

### Adsorption of $\text{Cu}^{2+}$

A known amount of grafted film was added to 50 mL of 0.01 mol/L aqueous  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  solution, whose

pH was adjusted by Clark-Lubs buffer solution, and then adsorption reaction was carried out at  $25^\circ\text{C}$  for 24 h. After the reaction, the reaction mixture was filtered off, and the concentration of  $\text{Cu}^{2+}$  in the filtrate was determined by chelate titration<sup>12</sup>, using EDTA standard solution to calculate the amount of  $\text{Cu}^{2+}$  adsorbed.

### Measurement of water absorbency

Grafted film ( $W_0$ , in grams) was immersed in water at  $25^\circ\text{C}$  for 24 h. After immersion, any excess water on the film surface was wiped with filter paper, and then the weight ( $W_s$ , in grams) of the treated film was measured. Water absorbency was defined as follows:

$$\text{Water absorbency (\%)} = 100 \times (W_s - W_0) / W_0$$

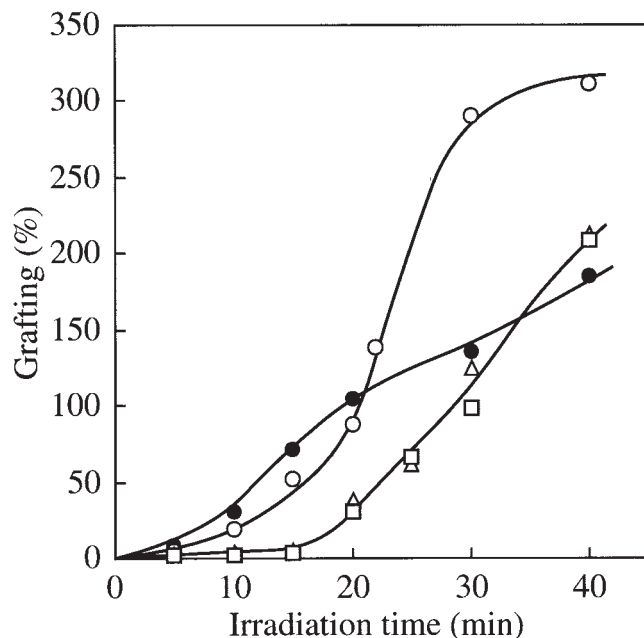
### Crosslinking treatment of MAA-grafted film

Crosslinking treatment was carried out in a Pyrex glass tube containing grafted film and 30 mL of an aqueous  $\text{H}_2\text{O}_2$  solution (5 mmol/L), in which known quantities of MBAAm were dissolved, under nitrogen atmosphere. Irradiation was carried out at  $25^\circ\text{C}$  for 20 min, using the same reactor as the one described in the earlier section.

## RESULTS AND DISCUSSION

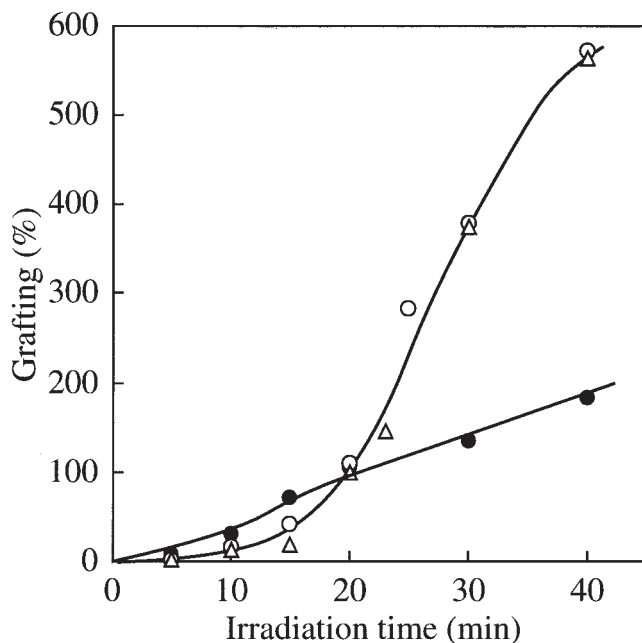
### Grafting behavior

Figure 1 shows the effect of MBAAm on photografting of MAA on PE film. It was observed that addition of MBAAm, the amounts of which correspond to 1–3 mol % of MAA monomer used, to the grafting system causes a marked decrease in the percentage of grafting at the earlier stage of polymerization. The extent of the decrease increased with the MBAAm concentration. However, after the retarded grafting at the earlier stage of polymerization, the percentage of grafting of the system with MBAAm became higher than that of the system without MBAAm, showing that the addition of MBAAm results in the accelerated grafting. Figure 2 shows the effect of EGDMA and TMPTA on photografting of MAA on PE film. Again, addition of the polyfunctional monomers to the grafting system resulted in the decreased percentage of grafting at the earlier stage of polymerization and then the increased percentage of grafting after the retarded grafting. Thus, photografting of MAA on PE film in the presence of polyfunctional monomers was characterized by retarded grafting at the earlier stage of polymerization and subsequent accelerated grafting at the later stage of polymerization. Figure 3 presents MBAAm content of the resultant MAA-grafted PE films, which was determined by nitrogen analysis, and represented

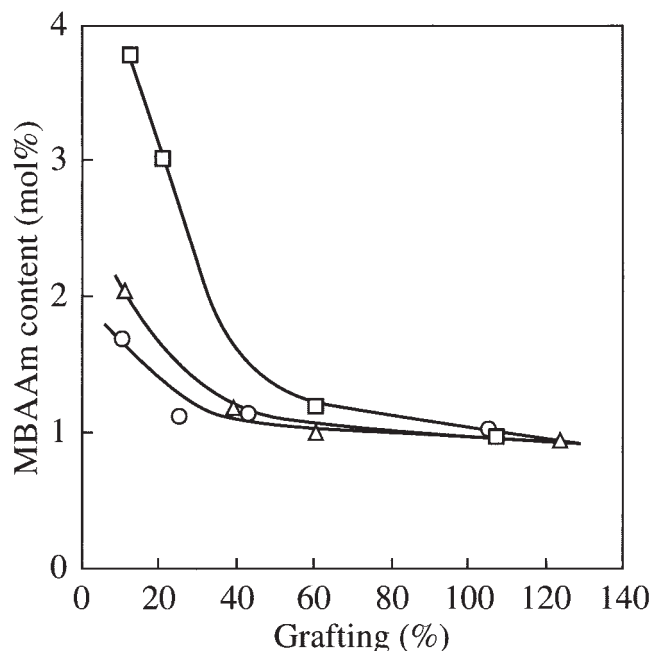


**Figure 1** Photografting of MAA on PE film in the presence of MBAAm at 60°C. [MAA] = 0.79 mol/L, [MBAAm] (mmol/L): (●) 0, (○) 7.9, (△) 11.8, (□) 23.7.

as mol % in MAA-grafted chains. The MBAAm content considerably decreased in the range of low percentage of graftings, within about 50%, and then gradually reduced with the percentage of grafting. This suggests that MBAAm component in the system is



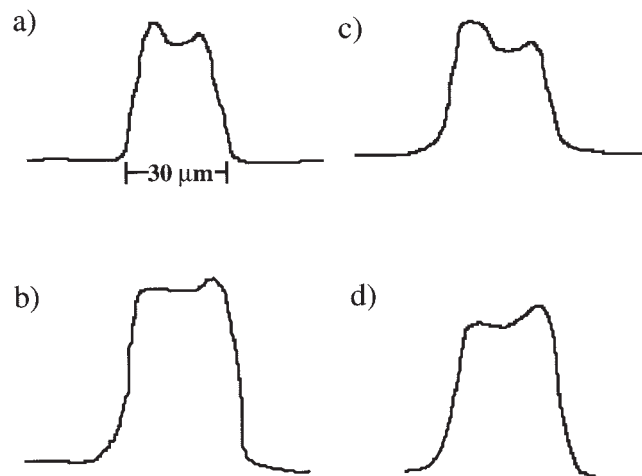
**Figure 2** Photografting of MAA on PE film in the presence of polyfunctional monomers at 60°C. [MAA] = 0.79 mol/L, [polyfunctional monomer] (mmol/L): (●) 0, (○) [EGDMA] = 7.9, (△) [TMPTA] = 7.9.



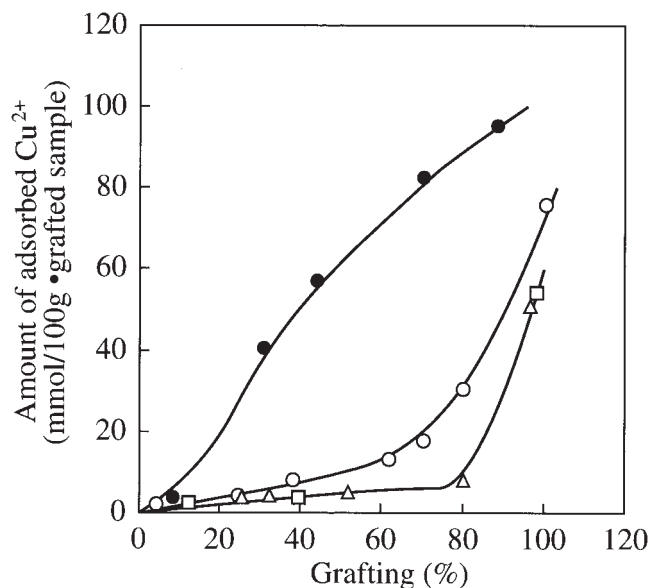
**Figure 3** MBAAm content in MAA-grafted PE films prepared in the system with MBAAm. [MBAAm] (mmol/L): (○) 7.9, (△) 11.8, (□) 23.7.

incorporated into MAA-grafted films at the earlier stage of the photografting reaction. Higher MBAAm content was afforded for the grafted films prepared in the system with higher MBAAm concentration.

The distribution profile of potassium atoms in the cross section of MAA-grafted PE film was recorded by EPMA, and the results are shown in Figure 4. The MAA-grafted chains distributed the film inside, even



**Figure 4** Distribution profiles of potassium atom in the cross section of MAA-grafted PE film measured by EPMA. The grafted films were prepared in the systems without and with polyfunctional monomers (7.9 mmol/L). Grafting (%): (a) without polyfunctional monomer, 45.3, (b) with MBAAm, 52.7, (c) with EGDMA, 47.6, (d) with TMPTA, 47.0.



**Figure 5** Adsorption of  $\text{Cu}^{2+}$  with MAA-grafted PE films. The grafted films were prepared in the systems without and with MBAAm (mmol/L): (●) 0, (○) 7.9, (△) 11.8, (□) 23.7.  $[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}] = 0.01$  mmol/L, pH = 5.0, 25°C, 24 h.

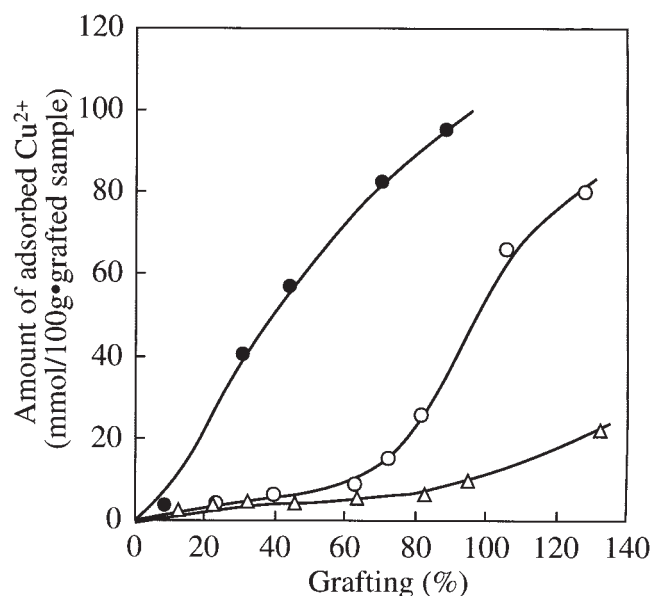
in the grafted films with relatively low percentage of graftings, which was commonly observed for the grafted samples (samples without and with polyfunctional monomer) prepared in the systems without and with polyfunctional monomers, respectively. It was found accordingly that addition of polyfunctional monomers to the grafting system does not affect the distribution of grafted chains in the cross section of the resultant grafted films.

#### Adsorption of $\text{Cu}^{2+}$

Figure 5 shows the adsorption of  $\text{Cu}^{2+}$  with the grafted samples without and with MBAAm. The amount of adsorbed  $\text{Cu}^{2+}$  in the sample without MBAAm increased with increase in the percentage of grafting. However, the amount of the sample with MBAAm was lower than that of the sample without MBAAm, indicating a suppressed adsorption of  $\text{Cu}^{2+}$ . Especially, the adsorption of  $\text{Cu}^{2+}$  by the samples with MBAAm was extremely low in the range of low percentage of graftings, which correspond to those of the grafted samples formed during the retarded grafting at the earlier stage of polymerization in Figure 1. Moreover, it was observed that the amount of the samples with MBAAm, which are prepared at the later stage of polymerization, markedly increased beyond a certain percentage of grafting though the amount is still lower than that of the sample without MBAAm. Figure 6 presents the results of adsorption of  $\text{Cu}^{2+}$  with MAA-grafted PE films prepared in the systems with EGDMA and TMPTA. Again, markedly

retarded adsorption of  $\text{Cu}^{2+}$  was recorded for the sample with polyfunctional monomer in the range of low percentage of graftings. Thus, the sample with polyfunctional monomer was characterized by a suppressed adsorption of  $\text{Cu}^{2+}$ , which was specially emphasized for the samples with low percentage of graftings prepared at the earlier stage of polymerization. Figure 7 shows the water absorbency of the MAA-grafted PE films. The water absorbency of the sample with polyfunctional monomer was lower compared with that of the sample without polyfunctional monomer. The addition of the polyfunctional monomer to the grafting system may result in a reduction of water absorbency due to the contribution of the polyfunctional monomer component to crosslinking of the grafted chains. Therefore, it is considered that the suppressed adsorption of  $\text{Cu}^{2+}$  with the sample with polyfunctional monomer originates in the limited permeation of reagents into the grafted chains with a crosslinked structure.

Table I presents the results of adsorption of  $\text{Cu}^{2+}$  with MAA-grafted PE films, which were treated beforehand with MBAAm to introduce a crosslinked structure into the grafted films. The amount of adsorbed  $\text{Cu}^{2+}$  decreased with the increase of the MBAAm content in the grafted films. It was confirmed that the introduction of the crosslinked structure into the MAA-grafted PE film causes a retarded adsorption of  $\text{Cu}^{2+}$  with the grafted film.



**Figure 6** Adsorption of  $\text{Cu}^{2+}$  with MAA-grafted PE films. The grafted films were prepared in the systems without and with polyfunctional monomer of 7.9 mmol/L. (●) without polyfunctional monomer, (○) with EGDMA, (△) with TMPTA.  $[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}] = 0.01$  mmol/L, pH = 5.0, 25°C, 24 h.

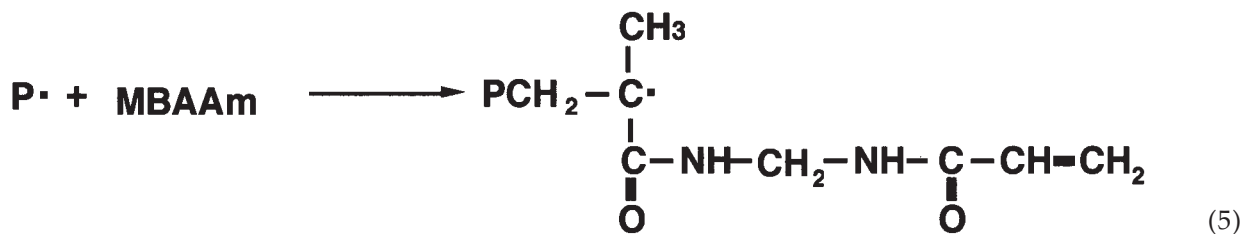
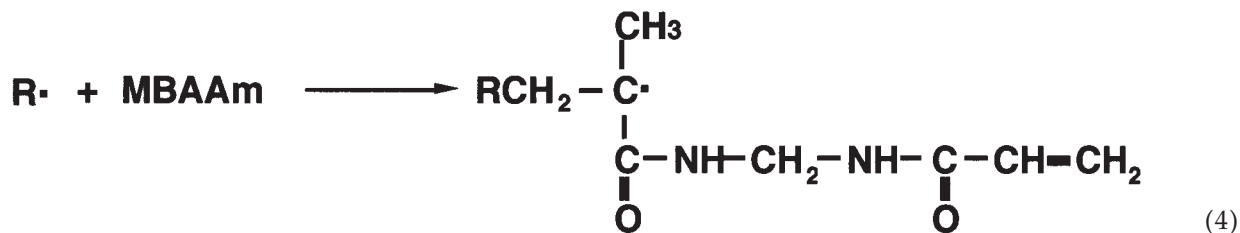
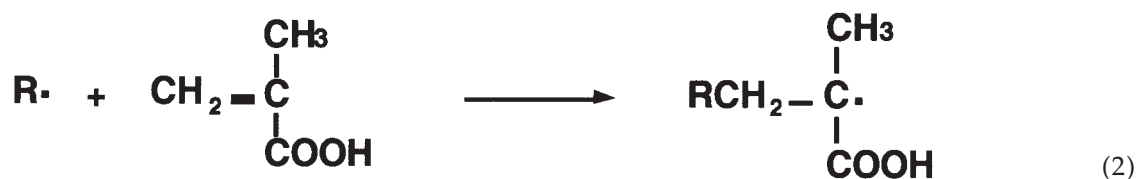
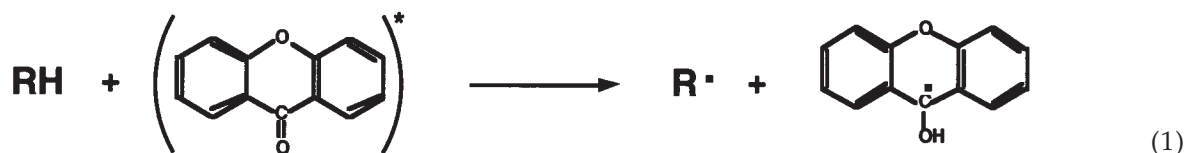
### Photopolymerization

Figure 8 shows the xanthone-sensitized photopolymerization of MAA in the presence of MBAAm. *n*-Hexane was used as a polymerization solvent in the present system. It is conceivable accordingly that photoexcited xanthone abstracts hydrogen atoms from the solvent to yield hexane radicals capable of initiating the polymerization of MAA. No formation of polyMAA gel was observed for the system without MBAAm, but the polymer gel was formed in the system with MBAAm. Thus, it was found that MBAAm component in the polymerization system contributes

to the formation of polyMAA with a crosslinked structure. This result supports the formation of MAA-grafted chains with a crosslinked structure during photografting of MAA on PE film in the presence of MBAAm.

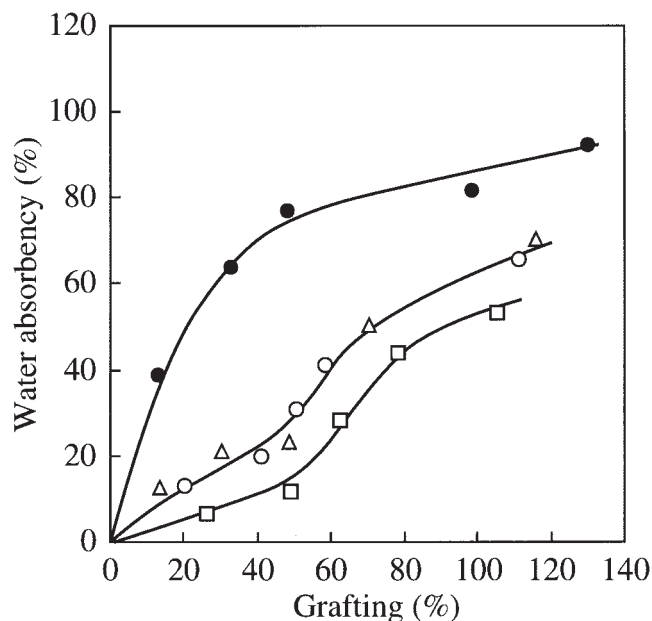
### Photografting in the presence of MBAAm

It is conceivable that photografting of MAA on PE film in the presence of MBAAm proceeds according to eqs. (1)–(5) where RH, R $\cdot$  and P $\cdot$  denote PE and its radicals and growing polymer radicals, respectively.



Equation (1) is the formation of PE radicals due to hydrogen-abstracting reaction by photoexcited xanthone. Equations (2) and (3) lead to the formation of the grafted polymer. The MBAAm component is incorporated into the PE substrate and/or MAA-grafted

chains according to eqs. (4) and (5), respectively. The addition of MAA monomer to radicals on the MBAAm residues, incorporated by eqs. (4) and (5) may lead to further performance of grafting. However, MBAAm component preferentially adds to rad-



**Figure 7** Relationship between water absorbency and percentage of grafting in MAA-grafted PE films. The grafted films were prepared in the systems without and with polyfunctional monomers of 7.9 mmol/L (●) without polyfunctional monomer, (○) with MBAAm, (△) with EGDMA, (□) with TMPTA.

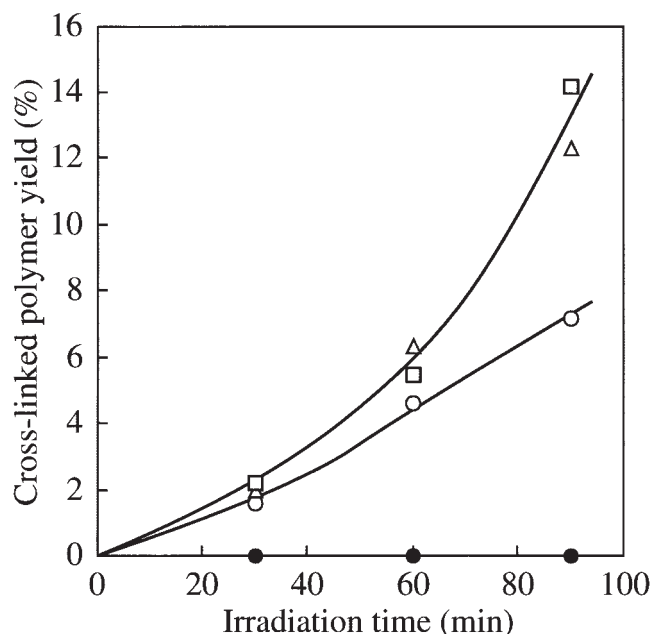
icals on the MBAAm residues rather than MAA monomer, since MBAAm component is mainly incorporated into the grafted film during the retarded grafting at the earlier stage of polymerization, which is shown in Figure 3. Photografting of MAA and MBAAm binary monomers (total monomer concentration = 0.20 mol/L) on PE film sensitized with xanthone was carried out at 60°C for 30 min with changing of the ratio of both monomer components in the system, and MBAAm content in the resulting MAA-grafted chains was measured. Based on the data, monomer reactivity ratios of MAA ( $r_1$ ) and MBAAm ( $r_2$ ) were calculated to be 0.79 and 5.47, respectively, using the Fineman–Ross method. These values support the above consideration. Therefore, radicals on the MBAAm residues introduced by eqs. (4) and (5) preferentially add to

**TABLE I**  
Adsorption<sup>a</sup> of Cu<sup>2+</sup> with Crosslinked MAA-Grafted PE Film<sup>b</sup>

MBAAm content (mmol/100 g grafted film)	Amount of adsorbed Cu <sup>2+</sup> (mmol/100 g grafted film)
0	128.4
2.4	122.5
5.5	116.7
9.0	94.1
16.1	82.3

<sup>a</sup> [CuCl<sub>2</sub> · 2H<sub>2</sub>O] = 0.01 mol/L, pH = 5.0, 25°C, 24 h.

<sup>b</sup> Grafting, 137.5%.



**Figure 8** Relationship between crosslinked polymer yield and irradiation time in photopolymerization of MAA in the presence of MBAAm. [MAA] = 0.97 mol/L, [xanthone] = 5 mmol/L, [MBAAm] (mmol/L): (●) 0, (△) 6.5, (○) 19.5, (□) 32.4.

MBAAm component in the system, including pendant double bonds of the MBAAm residues. The reaction with the pendant double bonds leads to the formation of a crosslinked structure in the MAA-grafted chains. Such reaction is considered to proceed mainly at the earlier stage of polymerization, resulting in the retarded grafting. On the other hand, addition of unreacted MAA monomer, which is in a large excess in the system, to radicals yielded by eqs. (1)–(5), and new grafting initiation due to the pendant double bonds proceed with the progress of polymerization to promote the grafting. The accelerated grafting reaction leads to the formation of a branched structure in MAA-grafted chains. Arriola et al.<sup>13</sup> monitored copolymerization of <sup>13</sup>C-labeled TMPTA and AA by <sup>13</sup>C NMR and reported the monomer reactivity ratios of AA (0.49) and TMPTA (3.60). They proposed the polymerization mechanism in which TMPTA component is incorporated into poly(AA) chains to participate in the formation of crosslinked gels at the earlier stage of polymerization, and then AA monomer adds to radicals formed on the resulting crosslinked gels, resulting in the progress of grafting reaction.

## CONCLUSIONS

Based on the above investigations, it is concluded that photografting of MAA on PE film in the presence of polyfunctional monomers is characterized by retarded grafting at the earlier stage of polymerization and

subsequent accelerated grafting at the later stage of polymerization, resulting in the MAA-grafted chains with crosslinked and branched structures, respectively, depending on each polymerization stage. Adsorption reaction of  $\text{Cu}^{2+}$  with the resultant MAA-grafted PE films was largely influenced by the structures of grafted chains. Photografting in the presence of polyfunctional monomers is conceived to be useful for introduction of grafted chains with crosslinked and/or branched structures into polymeric materials.

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