

# Photografting of Methacrylic Acid on Low-Density Polyethylene Film in Presence of Polyfunctional Monomers

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**ABSTRACT:** Photografting ( $\lambda > 300$  nm) of methacrylic acid (MAA) on low-density polyethylene (PE) film (thickness = 30 and 60  $\mu\text{m}$ ), on which xanthone photoinitiator was coated earlier, was investigated at 60°C in the presence of polyfunctional monomers such as *N,N'*-methylenebisacrylamide (MBAAm) and trimethylol propane triacrylate (TMPTA). Addition of the polyfunctional monomers (0.01 and 0.1 wt %) to the grafting system largely accelerated the photografting, and the magnitude of the enhancement was larger for TMPTA than MBAAm. MBAAm component was incorporated into PE substrate and/or MAA-grafted chains through the grafting reaction. Double bonds of the introduced polyfunctional component seemed to act as a new site for the grafting initiation, leading to the promoted grafting. The polyfunctional monomer did not affect distribution of the grafted chains in the cross section of the resultant MAA-grafted film, which was measured by electron probe microanalysis. Wettability of the MAA-grafted PE film was not influenced by the addition of MBAAm, but water absorbency was reduced by using a higher concentration of MBAAm. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1635–1641, 1997

**Key words:** photografting; methacrylic acid; low-density polyethylene; polyfunctional monomers

## INTRODUCTION

Grafting is known to be useful for the introduction of various functional groups into polymeric materials by selecting the type of monomer. We applied the photografting method to the functionalization of polyethylene (PE). In previous articles<sup>1–4</sup> photografting of methacrylic acid (MAA) on low-density PE film in vapor- and liquid-phase systems was investigated together with the relationship between the grafting conditions and the location of grafted chains. It was concluded that the distribution of the grafted chains in the cross section of the MAA-grafted PE film can be controlled by proper choice of polymerization system,<sup>1,2</sup> either vapor or liquid phases, additives,<sup>3</sup> and polymer-

ization conditions<sup>4</sup> including monomer concentration and polymerization temperature in the liquid-phase system. Moreover, functions of grafted PE films, such as wettability,<sup>1,2</sup> moisture permeability,<sup>1,5</sup> pH<sup>6</sup> and temperature<sup>7</sup> responsive characteristics, and catalytic activity<sup>8,9</sup> were greatly influenced by the location of grafted chains in the film substrate.

On the other hand, photografting of vinyl monomers on polyolefins<sup>10,11</sup> and cellulose<sup>12–14</sup> was considerably accelerated when small amounts of polyfunctional monomers such as triethylene glycol dimethacrylate, trimethylol propane triacrylate (TMPTA), trimethylol propane trimethacrylate, and divinylbenzene were added to the grafting systems. Ang et al.<sup>15,16</sup> reported on the effect of polyfunctional monomers for radiation-induced grafting of styrene on polyolefin films. Gineste et al.<sup>17,18</sup> examined grafting of acrylic acid on PE films in the presence of diethylene glycol

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dimethacrylate by the electron beam preirradiation method and influence of the polyfunctional monomer component on both the dissociation of the acrylic acid grafted chains and the permselectivity of the resultant grafted films. It seems that double bonds of polyfunctional components incorporated into the grafted chains act as a new initiation site for the grafting reaction. Thus, it is interesting to study the effect of the polyfunctional monomer on grafting reaction and location of grafted chains in the film substrate. This article deals with photografting of MAA on PE film in the presence of polyfunctional monomers such as *N,N'*-methylenebisacrylamide (MBAAm) and TMPTA in terms of the grafting behaviors and distribution of the grafted chains. Moreover, hydrophilic characteristics (wettability and water absorbency) of the resulting MAA-grafted PE film are also examined.

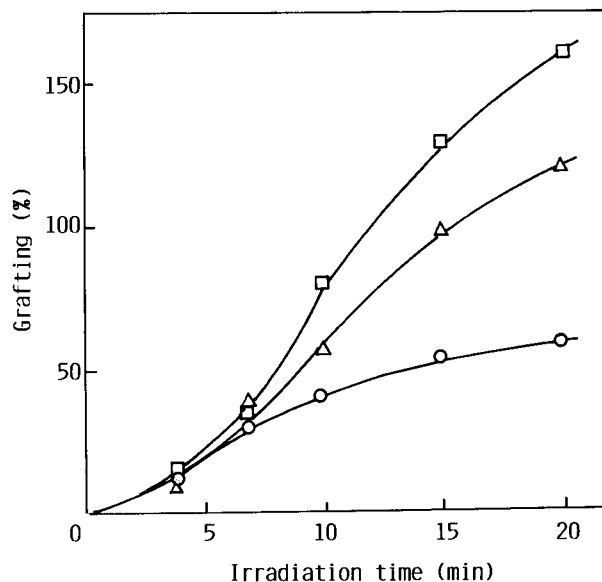
## EXPERIMENTAL

### Materials

PE films, 30 and 60  $\mu\text{m}$  thick, were used as a film sample. The film sample was immersed in acetone solution containing 0.3 wt % xanthone and 0.5 wt % poly(vinyl acetate) ( $\bar{M}_w$  100,000), removed from the solution, and then dried under reduced pressure to prepare xanthone-coated film. The quantity of xanthone on the film was too small to determine gravimetrically. MAA was purified by distillation under reduced pressure. Xanthone, MBAAm, and 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 ( $3 \times 10$  cm), 1.5 mL MAA, and 30 mL water or organic solvent-water (7/23 v/v) solution in which known quantities of MBAAm or TMPTA, respectively, were dissolved under nitrogen atmosphere. Irradiation with a high-pressure mercury lamp (400 W) was carried out at 60°C using a Riko rotary photochemical reactor (RH400-10W). Polymerized films were extracted for 24 h with hot water to remove the homopolymer of polyMAA. The extraction<sup>2</sup> is known to be almost sufficient for removing the homopolymer in the film. The percent grafting was taken as the percentage of weight increase of the original film.



**Figure 1** Photografting of MAA on PE film (30- $\mu\text{m}$  thickness) in the presence of MBAAm at 60°C. MBAAm concentration (wt %): (○) 0, (△) 0.01, (□) 0.1.

### Electron Probe Microanalysis (EPMA)

MAA-grafted film was immersed in an aqueous solution of 1.0 wt % potassium hydroxide at 25°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-8000) of Shimadzu Co. Ltd.

### Measurements of Contact Angle and Water Absorbency

Contact angle measurement was made with a contact angle meter (type CA-P, Kyowa Kaimenkagaku Co.) at ambient humidity and temperature. Grafted film ( $W_0$ , in grams) was immersed in water at 25°C for 24 h. After immersion, any excess water on the film surface was wiped by filter paper, and then the weight ( $W_s$ , in grams) of the treated film was measured. Water absorbency was defined as follows:

$$\text{water absorbency (\%)} = \frac{W_s - W_0}{W_0} \times 100$$

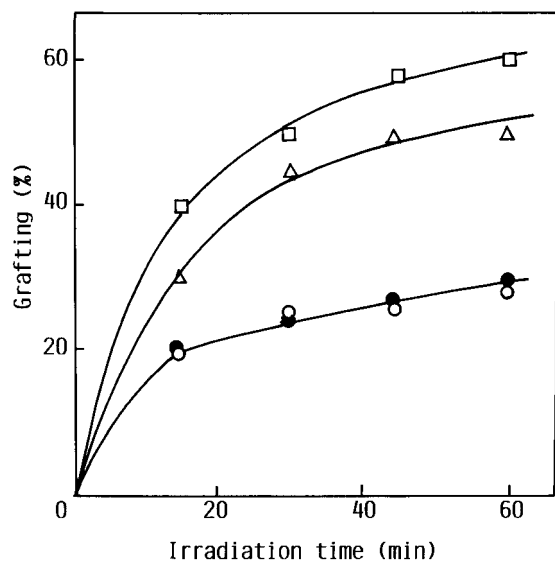
## RESULTS AND DISCUSSION

### Grafting Behavior

Figure 1 shows the effect of MBAAm on photografting of MAA on PE film. The photografting

in the absence of MBAAm proceeded easily, and the percent grafting increased with the irradiation time. Addition of MBAAm to the grafting system caused a marked increase in the percent grafting, which increased with the MBAAm concentration, showing that MBAAm accelerates the photografting. The same effect of MBAAm was observed for the grafting of MAA on PE film of 60- $\mu\text{m}$  thickness (Fig. 2), although 0.001 wt % MBAAm concentration did not exhibit the effect. The graft efficiencies in the 60- $\mu\text{m}$  thickness, which are expressed as the weight percent of grafted polymer relative to total conversion of monomer, were less than 10%, showing a predominant formation of homopolymer. The values of the systems without and with MBAAm (0.1 wt %) were 4.8 and 7.5%, respectively, under the irradiation time of 60 min.

Table I presents MBAAm content of the resultant MAA-grafted PE films, which was determined by nitrogen analysis and represented as millimoles per unit film surface ( $\text{cm}^2$ ). The MBAAm content increased with increased percent grafting and higher content was afforded for the grafted films prepared in the system with higher MBAAm concentration. The MBAAm component seemed to be incorporated into the MAA-grafted chains. Photoirradiation was carried out at 60°C in a Pyrex glass tube containing xanthone-coated PE film and 30 mL of water, in which 0.1 wt % MBAAm was dissolved under a nitrogen atmosphere. MBAAm contents of the irra-



**Figure 2** Photografting of MAA on PE film (60- $\mu\text{m}$  thickness) in the presence of MBAAm at 60°C. MBAAm concentration (wt %): (○) 0, (●) 0.001, (△) 0.01, (□) 0.1.

**Table I** MBAAm Content of MAA-Grafted PE Film

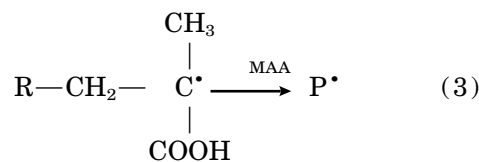
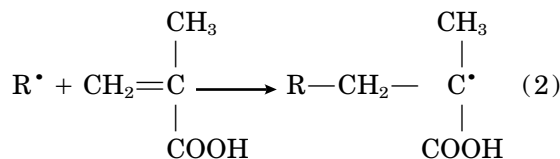
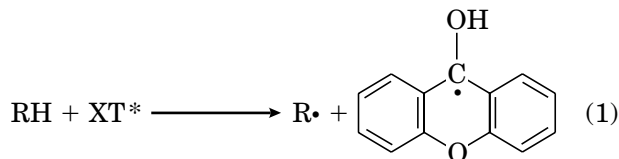
Irradiation Time (min)	MBAAm Concentration (wt %)	Grafting (%)	MBAAm Content ( $\text{mmol}/\text{cm}^2$ ) $\times 10^4$
4	0.01	11.8	0.45
7	0.01	39.2	3.71
10	0.01	55.9	3.98
20	0.01	120.8	6.03
4	0.1	12.4	1.24
7	0.1	31.7	5.14
10	0.1	81.3	5.20
20	0.1	161.8	6.77
4	0.1	—	0.41 <sup>a</sup>
10	0.1	—	4.07 <sup>a</sup>
15	0.1	—	4.83 <sup>a</sup>
20	0.1	—	5.50 <sup>a</sup>

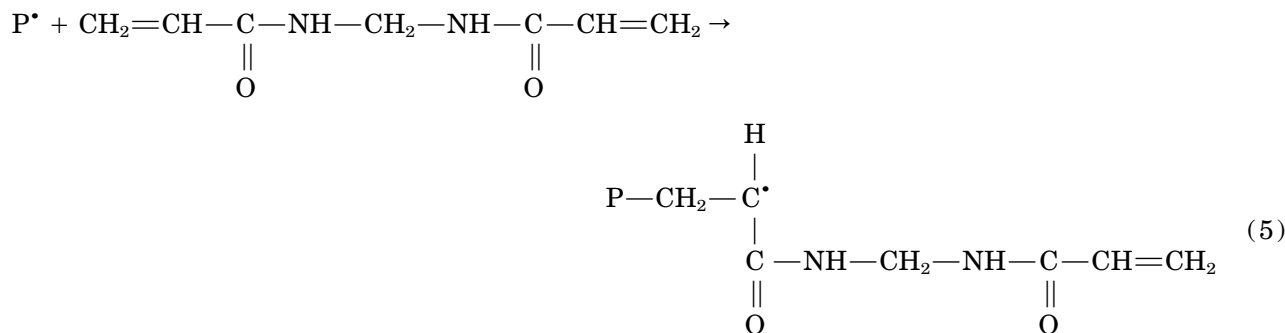
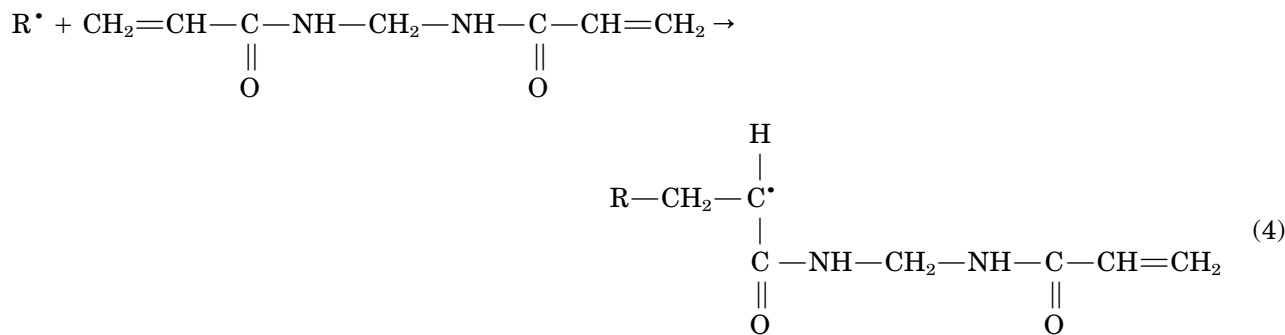
Photografting of MAA on PE film of 30- $\mu\text{m}$  thickness was carried out at 60°C for given times.

<sup>a</sup> MBAAm content of PE film of 30- $\mu\text{m}$  thickness irradiated at 60°C in the same system as that of photografting in the absence of MAA monomer.

diated PE film are also included in the table. MBAAm residues were proven to be incorporated into PE film substrate by the photoirradiation. These results suggest that the MBAAm component was introduced into MAA-grafted chains and/or PE substrate through 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 XT, RH, R<sup>•</sup>, and P<sup>•</sup> denote xanthone, PE and its radicals, and growing grafted polymer radicals, respectively.





Equation (1) is the formation of PE radicals due to the hydrogen-abstracting reaction by photoexcited XT. Equations (2) and (3) lead to the formation of grafted polymer. The MBAAm component seemed to be incorporated into the PE substrate and/or grafted chains according to eqs. (4) and (5), respectively. It is plausible that the resultant MBAAm radicals add further MAA monomer to yield grafted polymers. On the other hand, double bonds in the MBAAm residues of eqs. (4) and (5) may act as a new site for grafting initiation, resulting in an increased percent grafting as shown in Figures 1 and 2. Table II shows the effect of TMPTA having three double bond units in the molecule, where organic solvent-water solutions were used as a polymerization solvent because TMPTA did not dissolve in water. TMPTA was proven to accelerate the grafting, and the magnitude of the increased percent grafting was larger than MBAAm. This may support the contribution of double bond units in the polyfunctional monomer component, which was introduced into the PE substrate and/or the MAA-grafted chains, to the accelerated grafting.

#### Distribution of MAA-Grafted Chains

Figure 3 shows the distribution profile of potassium atoms in the cross section of MAA-grafted

PE films prepared in the presence and absence of MBAAm. The total thickness of the film and the thickness of the ungrafted layer were measured, and the results are shown in Figure 4 as a function of the amount of grafts. The dotted line represents the thickness of the original film. The total thickness increased with an increasing amount of grafts. On the other hand, the thickness of the ungrafted layer decreased with the amount of grafts, and the extent of the magnitude was almost the same between the grafted films prepared in the presence and absence of MBAAm. The phenomenon was commonly observed for the grafted films prepared using PE films of 30- and 60- $\mu\text{m}$  thickness. This means that addition of MBAAm to the grafting system does not affect the distribution of grafted chains in the cross section of the resultant grafted films. The same tendency was recorded for the TMPTA-added system (Fig. 5).

#### Hydrophilic Characteristics of MAA-Grafted PE Film

Figure 6 presents the contact angles of water on the MAA-grafted PE films. The contact angles decreased with an increased amount of grafts, and the extent of the magnitude was nearly equal

**Table II** Photografting of MAA on PE Film of 30- $\mu\text{m}$  Thickness in Presence of Polyfunctional Monomers

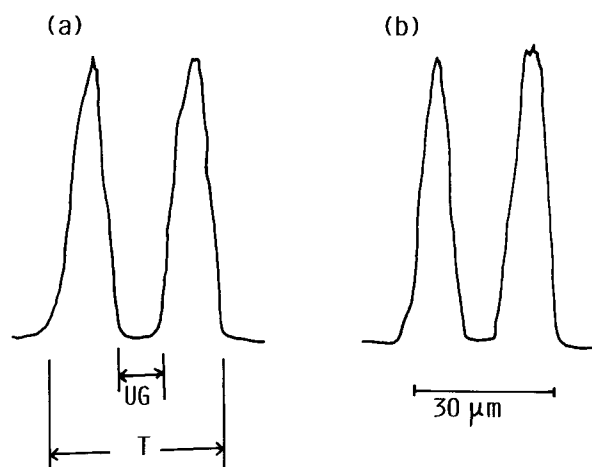
Solvent	Irradiation Time (min)	Grafting (%)		
		None	MBAAm	TMPTA
Water-acetone	20	177.3	193.5	267.1
	40	328.0	515.3	625.9
Water-ethanol	20	158.6	167.2	201.0
	40	270.8	522.5	643.8
Water-dioxane	20	128.7	150.4	167.3
	40	213.9	408.1	495.2

Irradiation temperature, 60°C; [MBAAm] = [TMPTA] =  $5.8 \times 10^{-4}$  mol/L; organic solvent/water = 7/23 v/v.

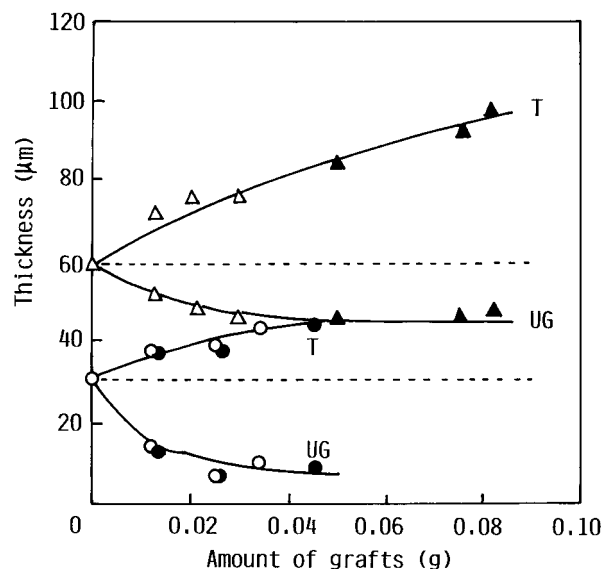
among each grafted film. Thus, the wettability of the MAA-grafted PE film was not influenced by the addition of MBAAm to the grafting system. Figure 7 shows the water absorbency of the MAA-grafted PE films. The water absorbency of the grafted film prepared in the system of 0.01 wt % MBAAm concentration was similar to that prepared in the absence of MBAAm. However, the value of the grafted film prepared in the 0.1 wt % MBAAm concentration was lower compared to the 0.01 wt % MBAAm concentration. The same phenomenon was observed for the grafted PE films

that were treated by 1.0 wt % aqueous sodium hydroxide solution at 25°C for 24 h. It is supposed that addition of high concentration MBAAm to the grafting system caused a reduction of water absorbency due to the contribution of MBAAm to crosslinking of the grafted chains.

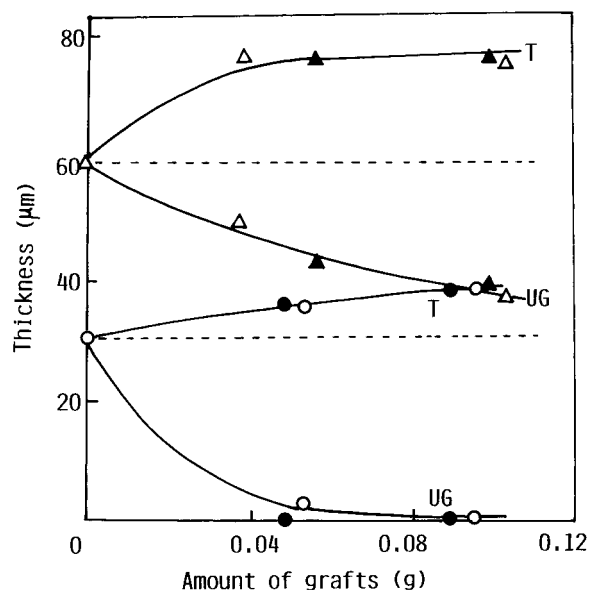
Based on the above investigations, it was concluded that addition of about 0.01 wt % MBAAm concentration to the photografting system of MAA on PE film is useful for enhancing the rate of



**Figure 3** Distribution profile of potassium atoms in the cross section of MAA-grafted PE film measured by EPMA. (a) grafted film (34.3 grafting %) prepared in the absence of MBAAm, (b) grafted film (34.4 grafting %) prepared in the system of 0.1 wt % MBAAm concentration.  $T$  and  $UG$  denote total thickness and thickness of the ungrafted layer of the grafted film, respectively.

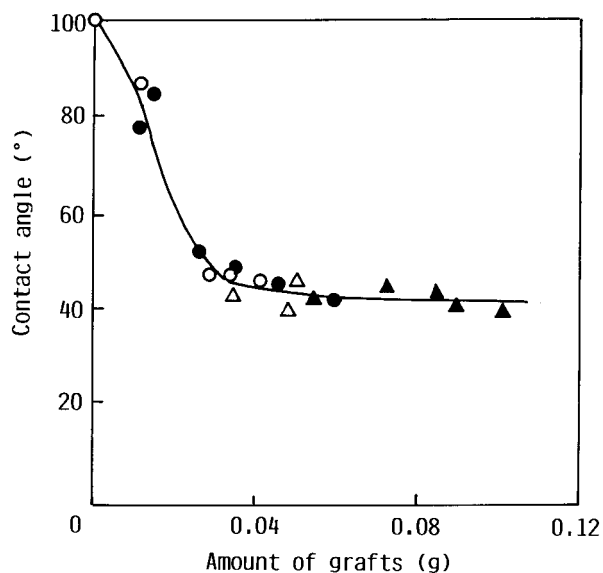


**Figure 4** Relationship between total thickness ( $T$ ) of the film and thickness of the ungrafted layer ( $UG$ ) and amount of grafts. Thickness of PE film, 30  $\mu\text{m}$ : (○) without MBAAm, (●) with 0.1 wt % MBAAm; 60  $\mu\text{m}$ : (Δ) without MBAAm, (▲) with 0.1 wt % MBAAm.

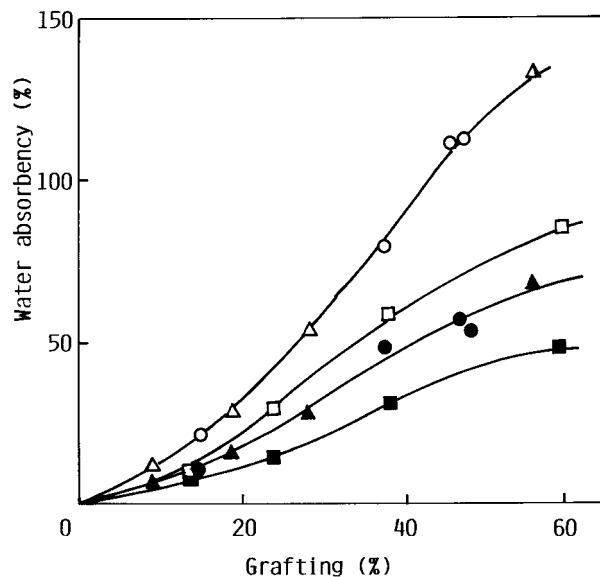


**Figure 5** Relationship between total thickness ( $T$ ) of the film and thickness of the ungrafted layer ( $UG$ ) and amount of grafts. Thickness of PE film,  $30\ \mu\text{m}$ : ( $\circ$ ) without TMPPTA, ( $\bullet$ ) with 0.02 wt % TMPPTA;  $60\ \mu\text{m}$ : ( $\Delta$ ) without TMPPTA, ( $\blacktriangle$ ) with 0.02 wt % TMPPTA.

grafting without large modification in distribution of the grafted chains and hydrophilic characteristics of the grafted film. Studies on the pH-respon-



**Figure 6** Contact angles of water on MAA-grafted PE films. Thickness of PE film,  $30\ \mu\text{m}$ : ( $\circ$ ) without MBAAM, ( $\bullet$ ) with 0.1 wt % MBAAM;  $60\ \mu\text{m}$ : ( $\Delta$ ) without MBAAM, ( $\blacktriangle$ ) with 0.1 wt % MBAAM.



**Figure 7** Water absorbency of MAA-grafted PE films prepared using PE film of  $30\text{-}\mu\text{m}$  thickness. The grafted films (H type) were treated by 1.0 wt % aqueous sodium hydroxide solution at  $25^\circ\text{C}$  for 24 h to yield their sodium salt (Na type). H type: MBAAM concentration (wt %), ( $\bullet$ ) 0, ( $\blacktriangle$ ) 0.01, ( $\blacksquare$ ) 0.1; Na type: MBAAM concentration (wt %), ( $\circ$ ) 0, ( $\Delta$ ) 0.01, ( $\square$ ) 0.1.

sive character of MAA-grafted PE films prepared by photografting in the presence of MBAAM are in progress in this laboratory to understand the characteristics of the grafting method for the functionalization of PE.

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