

# Distribution of Methacrylic Acid-Grafted Chains Introduced into Polyethylene Film by Photografting

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## INTRODUCTION

Photografting is known to be a useful means for introduction of various functional groups into polymeric substrates. The technique has been applied for wide fields such as surface modification<sup>1-3</sup> of polymers, immobilization of enzyme,<sup>4</sup> photostabilization<sup>5</sup> of polypropylene, and syntheses of insoluble polymeric ligand<sup>6</sup> for adsorption of metallic ions and polymer for humidity sensor,<sup>7</sup> where liquid- and vapor-phase processes are utilized as the polymerization system.

In previous papers<sup>8,9</sup> photografting on polyolefin films was performed in liquid and vapor phases using sensitizers such as aromatic ketones and quinones, which were coated on the film earlier. The sensitizers enabled vinyl monomers such as methyl methacrylate, acrylic acid, and methacrylic acid (MAA) to graft easily with high yields. From the viewpoint of utilizing the photografting as a method for functionalization of polymer films, it is important to investigate the location of grafted chains in the film substrates. Thus, this article deals with a comparative study on distribution of MAA-grafted chains introduced into polyethylene film by liquid- and vapor-phase photograftings.

## EXPERIMENTAL

### Materials

The film used was low-density polyethylene (PE) (thickness = 70  $\mu\text{m}$ ). Thioxanthone (TX) and 2-chloro-anthraquinone (AQ) were used as sensitizers, which were all of reagent grade and used without further purification. The films (40  $\times$  75 mm) were immersed in acetone or chloroform solution containing 0.3 wt % TX or AQ and 0.5 wt % poly(vinyl acetate) and dried under reduced pressure at room temperature to prepare sensitizer-coated films. The quantities of TX and AQ in the film thus obtained by the treatment were  $4.7 \times 10^{-8}$  and  $4.2 \times 10^{-8}$  mol/apparent surface unit ( $\text{cm}^2$ ), respectively, which were deter-

mined spectrophotometrically. MAA was purified by distillation under reduced pressure.

### Photografting

Photograftings in vapor and liquid phases, carried out using a Pyrex glass (Fig. 1), were reported in previous studies.<sup>8,9</sup> Using the liquid phase, 30 mL of water and 1.5 mL of MAA were used, while 1.5 mL of MAA was used for the vapor phase. Irradiation with a high-pressure mercury lamp (400 W) was carried out at 60°C for given durations using a Riko rotary photochemical reactor (RH400-10W), around which the Pyrex glass tubes were rotated. After the reaction, the film was extracted for 24 h with hot water to remove homopolymer of poly(MAA). The extraction<sup>10</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. The percent of homopolymer was expressed as the percentage of homopolymer formed based on the original film, similar to the percent grafting.

### Electron Probe Microanalysis (EPMA)

Grafted poly(MAA) was converted to potassium salts by immersing the grafted film in aqueous solution of 1% potassium hydroxide at room temperature for 24 h. Distribution profile of potassium atom in grafted film was measured with electron probe microanalyzer model EPM-800Q of Shimadzu Co. Ltd.

## RESULTS AND DISCUSSION

Figure 2 refers to photografting of MAA on PE films sensitized with TX and AQ in liquid- and vapor-phase systems. The percent grafting was higher

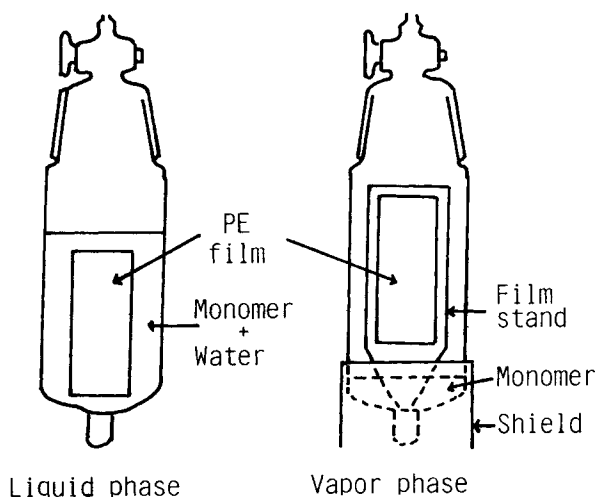


Fig. 1. Photografting apparatus.

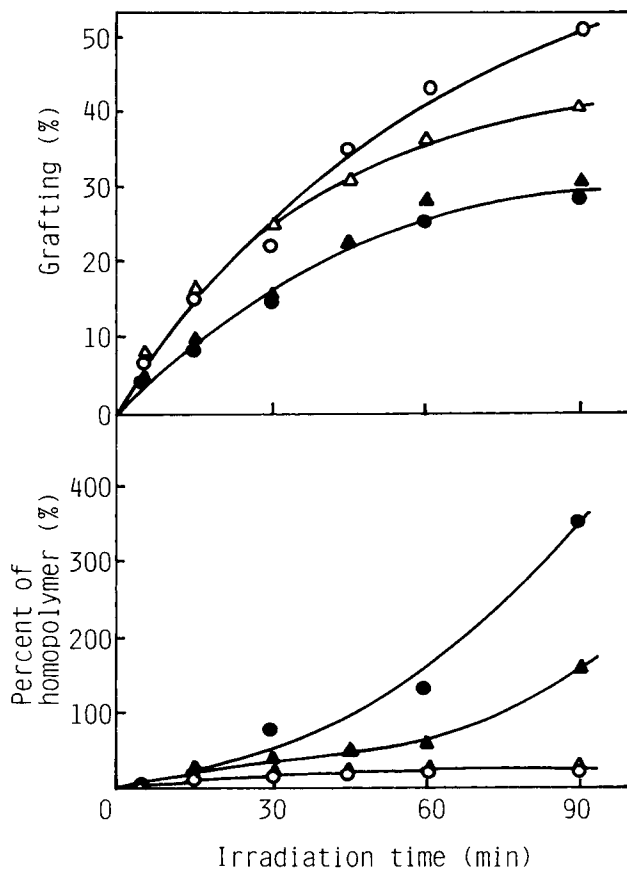


Fig. 2. Photografting of MAA on PE film in liquid- and vapor-phase systems. Liquid-phase system: (●) TX, (▲) AQ. Vapor-phase system: (○) TX, (△) AQ. Irradiation was carried out at 60°C.

in the vapor-phase system than that of the liquid-phase system, while the percent of homopolymer was considerably higher in the liquid-phase system, which was commonly observed for the TX- and AQ-sensitized systems. With com-

TABLE I  
TX-Sensitized Photografting of MAA on PE Films with and without PVAc

Grafting system	Grafting (%) <sup>a</sup>		Grafting (%) <sup>b</sup>	
	With PVAc	Without PVAc	With PVAc	Without PVAc
Liquid-phase	24.3	25.6	22.9	24.8
Vapor-phase	42.5	40.7	41.1	40.2

<sup>a</sup> Percent graftings obtained by the first extraction with hot water for 24 h.

<sup>b</sup> Percent graftings obtained by the second extraction with methanol for 24 h.

Photografting was carried out at 60°C for 60 min.

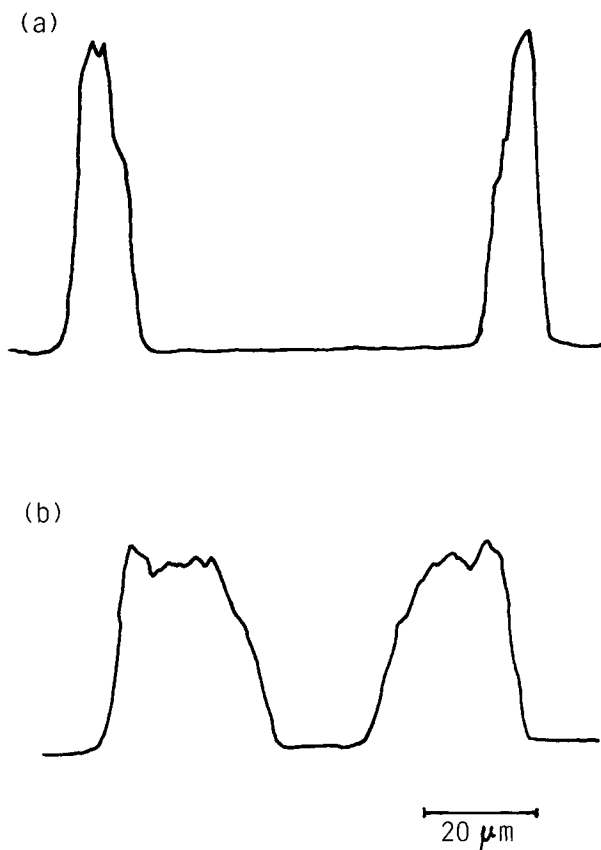


Fig. 3. Distribution profile of potassium atom in the cross section of MAA-grafted PE film measured by EPMA: (a) liquid-phase sample (grafting = 31.6%), (b) vapor-phase sample (grafting = 32.6%). Grafted samples were prepared by using TX sensitizer.

parison of the graft efficiencies between the liquid- and vapor-phase systems, which were taken as the weight percent of grafted polymer relative to total conversion of monomer in a system, the graft efficiency of the former system was less than 40%, while that of the latter system was 60% to 80%. Thus, the liquid-phase system was characterized by the predominant formation of homopolymer compared to the vapor-phase system. The formation of homopolymer in the liquid-phase system occurs mainly in the monomer solution, while that in the vapor-phase system proceeds on the film surface. This may lead to the higher formation of homopolymer in the former system compared to the latter system.

In this study, poly(vinyl acetate) (PVAc), the polymeric carrier of sensitizer, was used to hold the sensitizer homogeneously and tightly on the film surface. The different polymerization behaviors between the two systems observed in Figure 2 may be originated in the PVAc carrier. Photografting of MAA on TX-sensitized PE film without PVAc was carried out in order to examine the contribution of PVAc to the grafting initiation, and the results are presented in

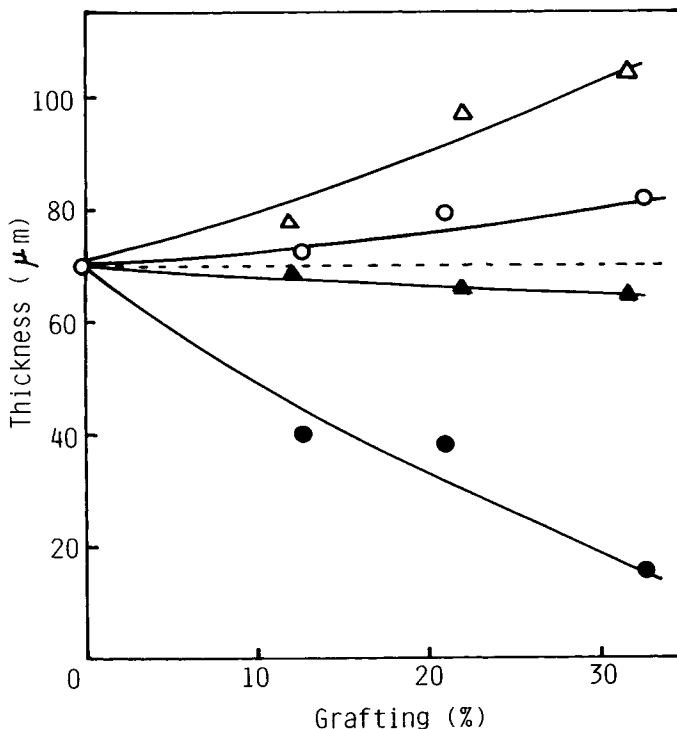


Fig. 4. Relationship between total thickness of the film and thickness of ungrafted layer and percent grafting. Liquid-phase sample: ( $\Delta$ ) total thickness, ( $\blacktriangle$ ) thickness of ungrafted layer. Vapor-phase sample: ( $\circ$ ) total thickness, ( $\bullet$ ) thickness of ungrafted layer. Grafted samples were prepared by using TX sensitizer.

Table I. Percent graftings of the system with PVAc were nearly equal to those of the system without PVAc, which was commonly observed for the liquid- and vapor-phases. Moreover, the grafted samples were extracted further for 24 h with methanol, which is a solvent of both PVAc and polyMAA. The percent graftings recorded after the second extraction indicated only a slight decrease due to the extraction (Table I). This suggests that the grafted polyMAA is linked directly to the PE substrate, not to the PVAc carrier. It is conceivable, therefore, that the PE substrate radicals might contribute mainly to the grafting initiation observed in Figure 2.

Figure 3 shows the distribution profile of the potassium atom in the cross section of MAA-grafted PE film measured by EPMA. The grafted chains of the sample prepared by using the liquid-phase system (liquid-phase sample) seem to appear at the film surface compared with those of the sample prepared by using the vapor-phase system (vapor-phase sample). The total thickness of the film and the thickness of ungrafted layer were measured, and the results are shown in Figure 4 as a function of percent grafting. The dotted line represents the thickness of the original film. The liquid-phase sample exhibited a larger increase in the total thickness with increasing the percent grafting than that of the vapor-phase sample. The thickness of ungrafted layer decreased

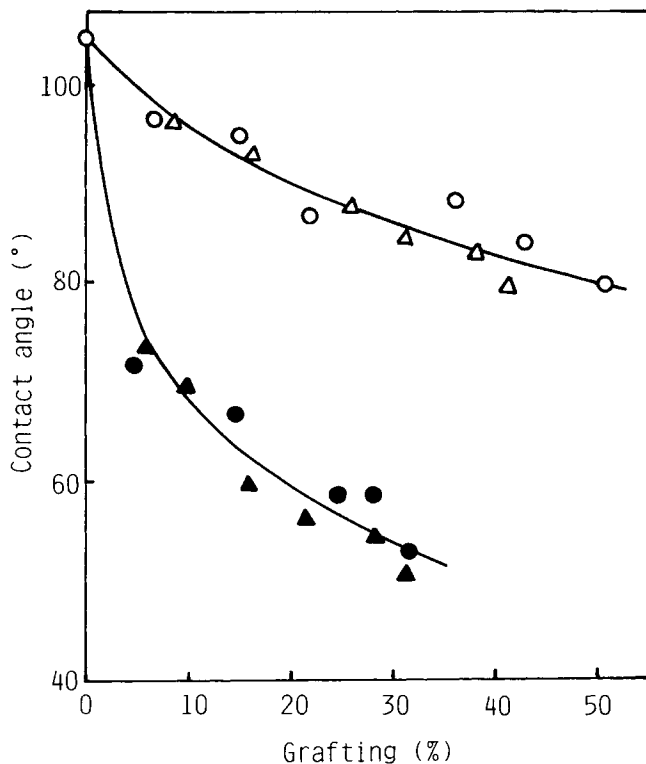


Fig. 5. Contact angle with water of MAA-grafted PE films. Liquid-phase sample: (●) TX, (▲) AQ. Vapor-phase sample: (○) TX, (△) AQ.

with increasing the percent grafting and the extent of the magnitude was extremely small in the liquid-phase sample. It was observed, thus, that the grafted chains of the liquid-phase sample are likely to locate on the film surface, while those of the vapor-phase sample distribute in the inside of the film. As shown in Figure 2, the formation of homopolymer was predominant in the liquid-phase system. This may be a main reason why the liquid-phase system results in the grafted film with a localized distribution of the grafted chains.

Figure 5 shows the contact angle of water on the MAA-grafted PE films. The contact angle of the liquid-phase sample was lower than that of the vapor-phase sample in the wide range of percent graftings. This means that the grafted chains of the former sample distribute on the film surface rather than in the inside of the film. It was found that wettability of the MAA-grafted PE film is remarkably influenced by distribution of the grafted chains.

Based on the above investigations, it is clear that the distribution of grafted chains is quite different depending on the polymerization system such as the liquid- and vapor-phase processes. This phenomenon is supposed to be originated in different polymerization behaviors between the both systems. That is, with the liquid-phase system where the formation of homopolymer is predominant, the grafted chains locate mainly on the film surface. In the system where the formation of grafted polymer proceeds favorably, on the other hand,

the grafted chains distribute in the film inside. This is true for the vapor-phase system. Accordingly, the formation ratio of grafted polymer to homopolymer in the system can be an important factor for distribution of MAA-grafted chains introduced into PE film substrate by means of photografting.

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