

Effect of Hydroquinone on Location of Methacrylic Acid-Grafted Chains Introduced into Polyethylene Film by Photografting

HITOSHI KUBOTA^{1,*} and YASUO HATA²

¹Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan

²Central Research Laboratory, Idemitsu Kosan Co. Ltd., Kimitsu-Gun, Chiba 292-01, Japan

SYNOPSIS

Effect of hydroquinone (HQ) on photografting of methacrylic acid (MAA) on low-density polyethylene film (thickness = 30 μm) sensitized with xanthone was investigated at 60°C in water medium. Both the formation of grafted polymer and homopolymer were retarded by HQ. The contact angle of water on the MAA-grafted polyethylene films (sample with HQ) prepared in the system with HQ was larger than that of the grafted films (sample without HQ) prepared in the system without HQ. Based on electron probe microanalysis of the grafted films, it was found that distribution of grafted chains in the direction of film thickness is different between the both grafted films. Namely, the grafted chains of the sample with HQ distributed in the inside of the film compared with those of the sample without HQ. The difference in the distribution of grafted chains between the grafting systems with and without HQ was discussed in terms of effect of HQ on the photodecomposition of MAA-grafted chains and the subsequent initiation of polymerization by radicals due to the photodecomposition.

INTRODUCTION

In a previous paper,¹ effects of monomer concentration and polymerization temperature on liquid-phase photografting of methacrylic acid (MAA) on polyethylene film were investigated together with the relationship between the grafting conditions and the structure of grafted film. Benzophenone was used as a sensitizer by coating it on the film sample. It was found that the monomer concentration and the polymerization temperature 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 overcomes that of homopolymer, the grafted chains are distributed in the film inside. On the other hand, the grafted chains located on the film surface under grafting conditions where the formation of homopolymer is predominant. Thus, the formation ratio

of grafted polymer to homopolymer can be a factor to control the location of grafted chains in the film substrate.

In this paper, hydroquinone (HQ) was chosen in order to retard the formation of homopolymer in liquid-phase photografting of MAA on polyethylene film. It was observed that HQ retards the formation of grafted polymer as well as that of homopolymer. However, HQ was found to influence distribution of MAA-grafted chains in the film. This paper deals with effect of HQ on location of MAA-grafted chains introduced into polyethylene film by liquid-phase photografting.

EXPERIMENTAL

Samples

The film used was low-density polyethylene (PE) (thickness = 30 μm). The film (3 \times 10 cm) was immersed in acetone solution containing 0.1 wt % xanthone (XT) and 0.5 wt % poly(vinyl acetate)

* To whom correspondence should be addressed.

and dried to prepare sensitizer-coated film. Amount of XT on the film thus obtained by the treatment could be estimated by spectrophotometry as about 1.7×10^{-8} mol per apparent surface unit (cm^2) of the film surface. MAA was purified by distillation under reduced pressure.

Photografting

Liquid-phase photografting was carried out in a Pyrex glass tube containing the film sample and 20 mL of aqueous solution of known concentrations of MAA and HQ under nitrogen atmosphere. Irradiation with a high-pressure mercury lamp (400 W) was carried out at 60°C for 60 min 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. 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, similarly to the percent grafting.

The MAA-grafted film sample (first-step sample) prepared by the above procedure was coated with XT again to prepare the sample for second-step grafting. The second-step photografting of MAA was performed at 60°C for 20 min in the same system as that of the first-step grafting. The percent grafting of the second-step grafting was expressed as the percentage of weight increase of the first-step sample.

Photodecomposition of MAA-Grafted Sample

Photodecomposition of XT-coated first-step sample (A g) was carried out at 60°C for 20 min in the same system as that of the second-step photografting without MAA. The irradiated sample (B g) was dried under reduced pressure and weighed. The amount of MAA-grafted chains decomposed was indicated as a weight decrease, which is defined as follows:

weight decrease (%)

$$= \frac{A - B}{\text{initial amount of grafted polymer}} \times 100$$

Measurement of ESR Spectrum

Quartz glass tube (5 mm internal diameter) containing MAA-grafted sample was flushed with nitrogen gas and irradiated at room temperature for

30 min with light of $\lambda > 300$ nm. A Toshiba high-pressure mercury lamp H400-P was used as the light source. ESR measurement was carried out at -196°C using an x-band spectrometer with 100 kc field modulation (JEOL JES-ME-X). Microwave power was about 2.0 mW.

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 of grafted film was measured with electron probe microanalyzer (EPM-810Q, Shimadzu Co. Ltd.).

RESULTS AND DISCUSSION

It is well known that cupric and ferrous salts are used to prevent the formation of homopolymer in radiation-induced grafting systems.²⁻⁸ Mohr's salt (ferrous ammonium sulfate) was observed to retard the formation of grafted polymer as well as that of homopolymer in radiation-induced grafting of acrylic acid on polyethylene film by preirradiation method.⁵ It was reported moreover that distribution of grafted poly(acrylic acid) in polyethylene film⁸ is controlled by the use of Mohr's salt.

We examined effect of Mohr's salt on photografting of MAA on PE film in water medium, but Mohr's salt accelerated the formation of homopolymer. So that, HQ, the inhibitor of polymerization, was chosen to prevent the formation of homopolymer, and the result is shown in Figure 1. The percent of homopolymer decreased with increasing the concentration of HQ. HQ was found to retard the formation of homopolymer, but at the same time it also prevented the formation of grafted polymer, showing that HQ has no effect on improvement of the graft efficiency, which is taken as the weight percent of grafted polymer relative to total conversion of monomer in a system.

Figure 2 shows contact angle of water on the MAA-grafted PE films. The contact angle decreased gradually with increasing the percent grafting, but the extent of the magnitude was different between the grafting systems with and without HQ. The contact angle of the grafted films (sample with HQ) prepared in the system with HQ was larger than that of the grafted films (sample without HQ) prepared in the system without HQ. Figure 3 presents X-ray image of potassium atom in the MAA-grafted film. The observation was done using the grafted

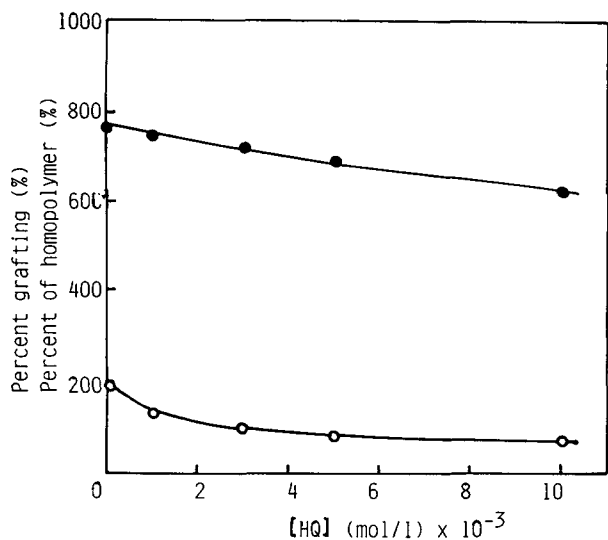


Figure 1 Effect of HQ on photografting of MAA on PE film sensitized with XT. Photografting was carried out at 60°C for 60 min: (○) percent grafting; (●) percent of homopolymer. [XT] = 0.1 wt %, [MAA] = 5.0 wt %.

samples treated with potassium hydroxide. Accordingly, the white part in the micrograph corresponds to potassium atoms, that is, the MAA-grafted chains. It was observed for the sample without HQ [Fig. 3(a)] that the ungrafted layer still remains at the inside of the film. For the sample with HQ [Fig. 3(b)], on the other hand, the grafted chains are likely to distribute in the film inside compared with

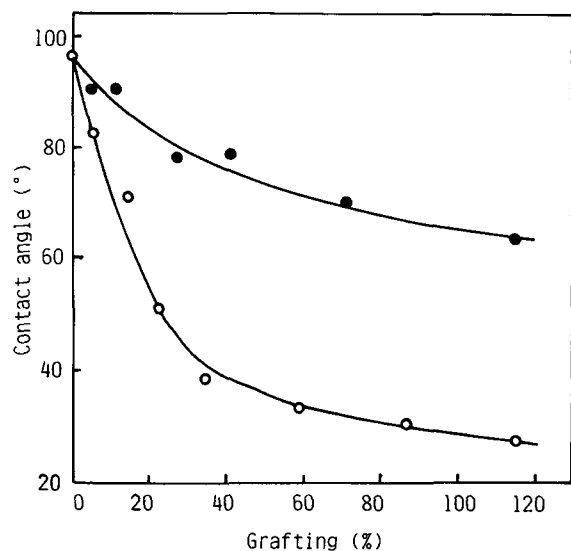


Figure 2 Contact angle of MAA-grafted PE films: (○) sample prepared in the system without HQ; (●) sample prepared in the system with HQ. [HQ] = 1.0 × 10⁻² mol/L.

those of the sample without HQ. It is supposed that the grafted chains of the sample with HQ tend to step in the inside of the film, resulting in larger contact angle than the sample without HQ.

The difference in distribution of the grafted chains between the samples with and without HQ

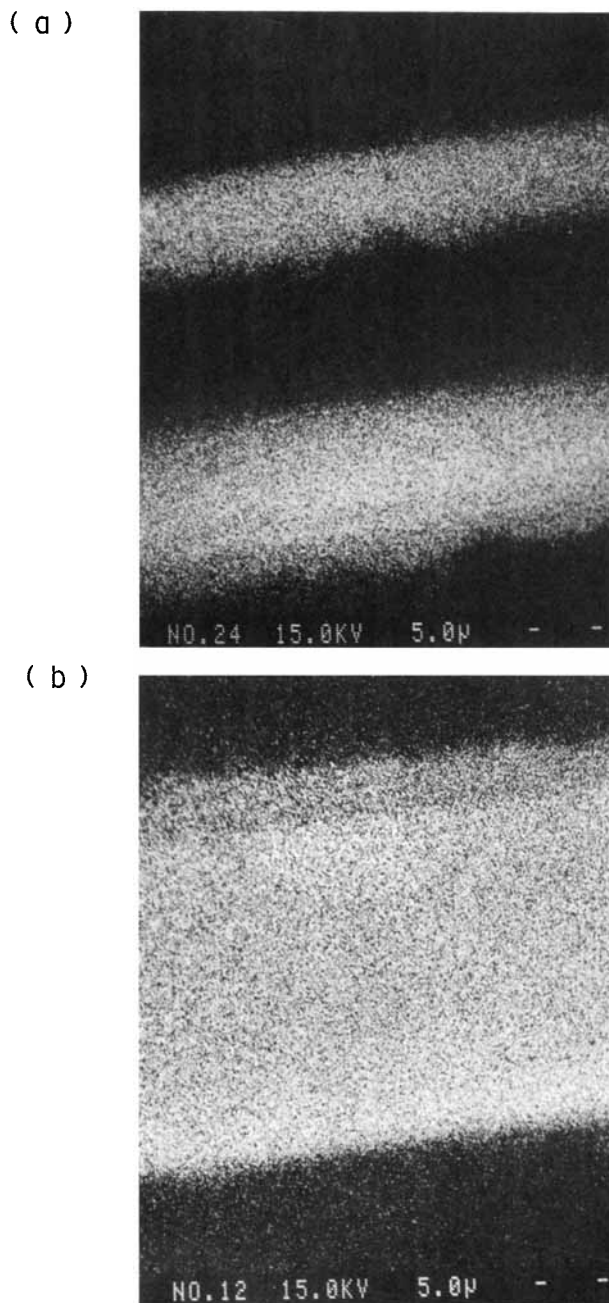
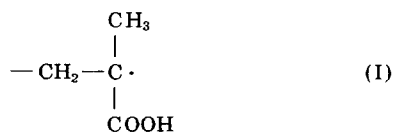


Figure 3 X-ray image of potassium atom in the direction of thickness of MAA-grafted PE film obtained by EPMA: (a) sample prepared in the system without HQ, grafting (%) = 35.2; (b) sample prepared in the system with HQ, grafting (%) = 36.1.

may be considered together with grafting behaviors as follows: Photografting of MAA on PE film can be initiated by PE radicals. As the grafting reaction proceeds, however, it is plausible that MAA-grafted chains undergo photodecomposition yielding radicals which can initiate polymerization and contribute to the formation of subsequent grafted chains. The polymerization proceeds through repetition of such reactions. It is conceivable in the grafting system without HQ that polymerization induced by radicals due to the photodecomposition of grafted chains proceeds preferentially during the grafting reaction. This may lead to the distribution of grafted chains localized at the film surface. In the grafting system with HQ, on the other hand, the photodecomposition of grafted chains and the subsequent initiation of polymerization by radicals on grafted chains are retarded by HQ, resulting in the distribution of grafted chains to the film inside.

In order to clarify the relationship between grafting behaviors and distribution of grafted chains described above, effect of HQ on photodecomposition of MAA-grafted chains and second-step photografting of MAA on first-step sample was investigated. Figure 4 shows ESR spectrum of the MAA-grafted PE film irradiated at room temperature for 30 min and recorded at -196°C . MAA-grafted sample exhibited five-line signal with splitting constant of 23 gauss. The spectrum seems to be attributed to radical of the type,



formed by the scission of grafted poly(MAA).⁹ The mechanism forming radical I in MAA-grafted PE film was estimated as follows:



Figure 4 ESR spectrum of MAA-grafted PE film irradiated at room temperature for 30 min and recorded at -196°C . [XT] = 0.1 wt %, grafting (%) = 56.0.

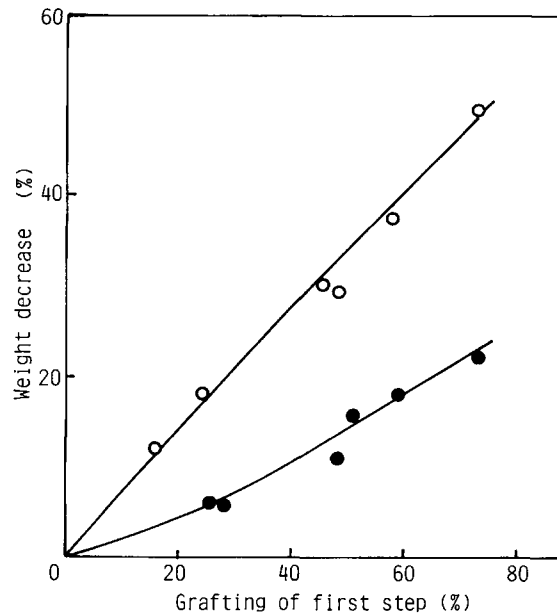
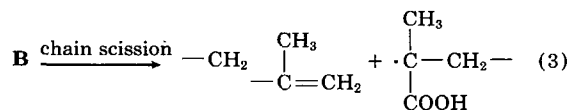
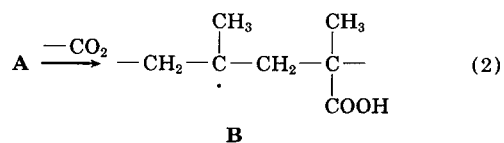
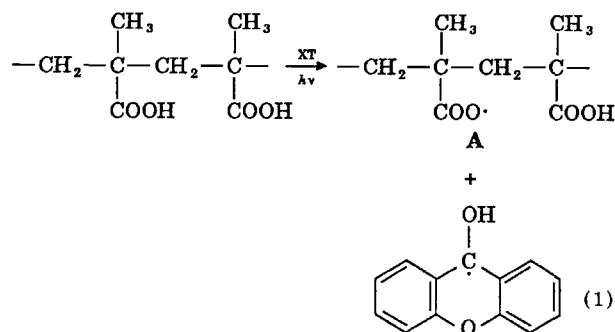


Figure 5 Photodecomposition of MAA-grafted PE film sensitized with XT: (O) without HQ; (●) with HQ. [XT] = 1.0×10^{-2} mol/L. Photoirradiation was carried out at 60°C for 20 min.



The photodegradation of poly(MAA)¹⁰ is known to proceed through a decarboxylation or chain scission process. The formation of radical I due to hydrogen abstraction from poly(MAA) by XT can be described by eqs. (1)–(3). Figure 5 shows effect of HQ on photodecomposition of MAA-grafted PE film, which was performed in the system consisting the first-step sample and water. The percent of

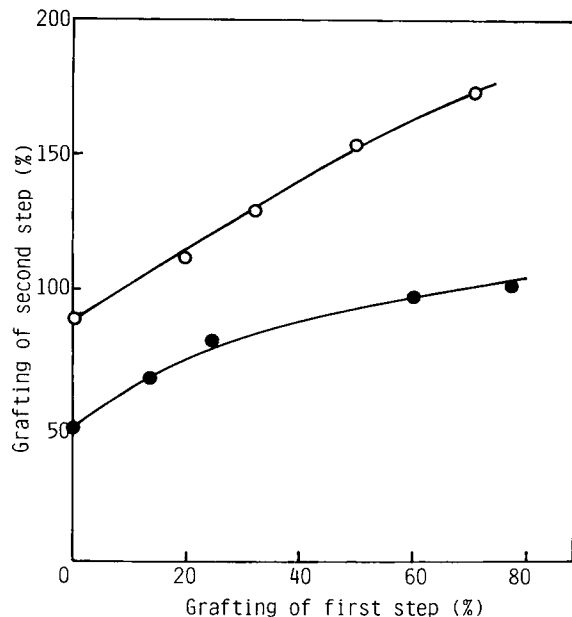


Figure 6 Second-step photografting of MAA on first-step sample sensitized with XT: (○) without HQ; (●) with HQ. $[HQ] = 1.0 \times 10^{-2}$ mol/L, $[MAA] = 5.0$ wt %, $[XT] = 0.1$ wt %. Second-step photografting was carried out at 60°C for 20 min.

weight decrease increased with increasing the percent grafting, but the extent of the increase in the sample with HQ was smaller than that of the sample without HQ. It was found thus that HQ prevents the photodecomposition of MAA-grafted chains. Figure 6 presents the result of second-step photografting of MAA on first-step sample. The horizontal axis indicates the percent grafting of the first-step sample. In the system without HQ, the percent grafting of second-step sample increased with the percent grafting of first-step sample, indicating that grafted chains of the first-step sample participate in the initiation of the second-step photografting. The same tendency was observed for the system with

HQ, but the increase of the percent grafting of second-step sample was smaller compared with the system without HQ. It was confirmed that HQ retards photodecomposition of MAA-grafted chains and second-step photografting of MAA.

Based on the above investigations, it is clear that HQ influences distribution of MAA-grafted chains in PE film, though it has no effect on improvement of the graft efficiency in a system. It is characterized that the grafted chains of the sample without HQ appear at the film surface, while those of the sample with HQ tend to distribute in the inside of the film. Such action of HQ is supposed to be based on prevention of the photodecomposition of MAA-grafted chains, which is shown in eqs. (1)–(3), and of the subsequent initiation of polymerization by radicals due to the photodecomposition.

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