

Photografting of Acrylonitrile and Methacrylic Acid on Polyethylene Film under Air Atmosphere

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SYNOPSIS

Photografting of acrylonitrile (AN) and methacrylic acid (MAA) on low-density polyethylene film (thickness 70 μm), on which benzophenone was coated earlier, was investigated at 60°C in water medium under air atmosphere. In the case of AN monomer, where grafted polymer was formed predominantly, oxygen in the system promoted the formation of both grafted polymer and homopolymer. With MAA monomer, in which homopolymer was formed preferentially compared to the formation of grafted polymer, the formation of homopolymer was accelerated by the presence of oxygen while suppressing that of grafted polymer. The formation of polyethylene peroxides by photoirradiation seemed to be a factor for the accelerated polymerization under air atmosphere. It was found that additives such as hydrazine and metallic ions (Fe^{2+} , Cu^{2+} , and Ni^{2+}) are useful for enhancing the photografting under air atmosphere. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In previous papers,^{1,2} photografting on polyolefin films was performed in the liquid phase using photoinitiators such as aromatic ketones and quinones, which were coated onto the film earlier. The photoinitiators enabled vinyl monomers such as acrylic acid, methacrylic acid (MAA), acrylonitrile (AN), and methyl methacrylate to graft easily with high yields. In the photografting, a deaerated system was employed to remove oxygen in the system, which generally inhibits the radical polymerization of vinyl monomers. The oxygen-removal process may be disadvantageous when the photografting is commercially utilized as a method for functionalization of polymer films on a large scale.

To exclude the necessity of inert atmosphere during the course of polymerization, Shukla et al.³⁻⁵ examined the grafting of methyl methacrylate onto wool in various redox initiation systems under air atmosphere. Photografting⁶ of acrylamide and hydroxyethyl methacrylate onto cellulose was successfully performed using an isopropyl thioxanthone photoinitiator in the presence of air. Recently, Uch-

ida et al.⁷ developed a new method of omitting oxygen-removal procedures for the photografting of acrylamide onto the surface of poly(ethylene terephthalate) film without a photoinitiator, to which an appropriate quantity of periodide was added. In this paper, photografting of AN and MAA onto polyethylene film under air atmosphere was investigated to determine the characteristics of polymerization behavior. Moreover, the effect of additives such as hydrazine and metallic ions on photografting under air atmosphere was also examined.

EXPERIMENTAL

Samples

The film used was low-density polyethylene (PE) (thickness 70 μm). The benzophenone (BP)-coated film was prepared by dipping the film into an acetone solution containing 0.3 wt % BP and 0.5 wt % poly(vinyl acetate) ($\bar{M}_w = 100,000$) and drying the treated film at room temperature under reduced pressure to remove the solvent. The quantity of BP on the film sample could be estimated by spectrophotometry to be about 5.1×10^{-8} mol per apparent unit surface (cm^2). AN and MAA were purified by distillation. $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$,

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ were all of reagent grade and were used without further purification.

Photografting

The film sample (3×10 cm) was placed in a Pyrex glass tube, to which 30 mL water, boiled beforehand to exclude dissolved oxygen, and 1.5 mL monomer were added. After introducing nitrogen gas into the system for 5 min, the system was closed and liquid-phase photografting (nitrogen system) was carried out at 60°C . Photografting under air atmosphere (air system) was performed using unboiled water in the system without introduction of nitrogen gas for 5 min. Irradiation with a high-pressure mercury lamp (400 W) was conducted in a Riko rotary photochemical reactor RH400-10W. Polymerized films were extracted for 24 h with hot water and *N,N'*-dimethylformamide to remove homopolymers of poly(MAA) and poly(AN), respectively. 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.

Formation of Peroxides

Photoinduced formation of peroxides on the film was carried out in the same system as that of the photografting without monomer. After irradiating the system at 60°C for a given duration, the film part was separated from the water. The amount of peroxide in each part was determined.

Determination of Peroxide

A flask containing the irradiated film and 20 mL isopropyl alcohol, to which 5 mL isopropyl alcohol solution with saturated sodium iodide and 2 mL glacial acetic acid was added, was refluxed at 85°C for 15 min. After being cooled to room temperature, the liberated iodine was titrated with 0.01*N* sodium thiosulfate solution.

RESULTS AND DISCUSSION

Figure 1 shows photografting of AN onto PE film. The percent grafting was much higher than the percent of homopolymer, showing a predominant formation of grafted polymer in this system. Both the percent grafting and the percent of homopolymer in the air system were higher than those in the nitrogen

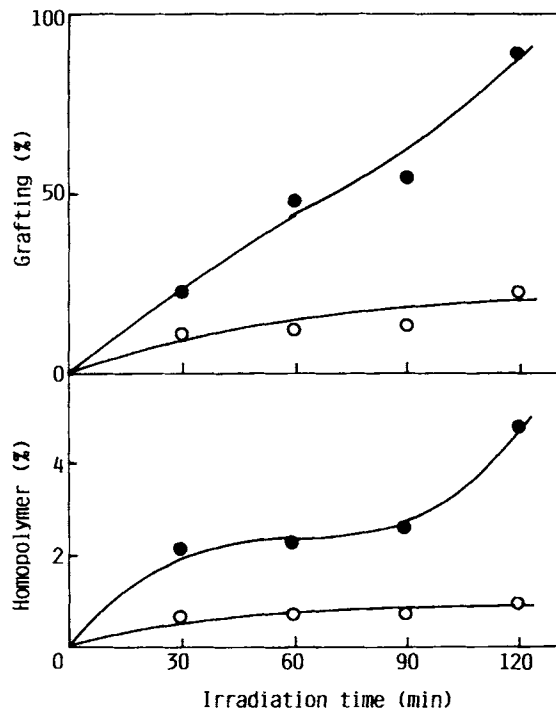


Figure 1 Photografting of AN onto PE film in (○) the nitrogen system and (●) the air system. Irradiation temperature: 60°C .

system, i.e., oxygen in the system was found to promote the grafting reaction of AN. Figure 2 presents the results of the MAA monomer. Contrary to the AN monomer, the photografting of MAA onto PE film was characterized by the predominant formation of homopolymer compared to the formation of grafted polymer. The percent grafting in the air system was lower than that of the nitrogen system, whereas the higher percent homopolymer was recorded for the air system. Photopolymerization of MAA was carried out at 60°C for 60 min in the same system as that of the photografting without film. The conversions were 42.9% and 13.7% in the air and nitrogen systems, respectively, which corresponded to about 80 and 90% of the yield of homopolymer formed in the both photografting systems. In the photografting of MAA in the air system, oxygen in the system is supposed to facilitate the formation of homopolymer, resulting in the decreased percent grafting. However, it is not clear why the photopolymerization of MAA is sharply promoted in the air system, though MAA is easily susceptible to the initiation of photopolymerization. It is well known that oxygen generally inhibits the radical polymerization of vinyl monomers. It has been reported, however, that oxygen promotes the rate of photopolymerization of styrene⁸ and *N*-vi-

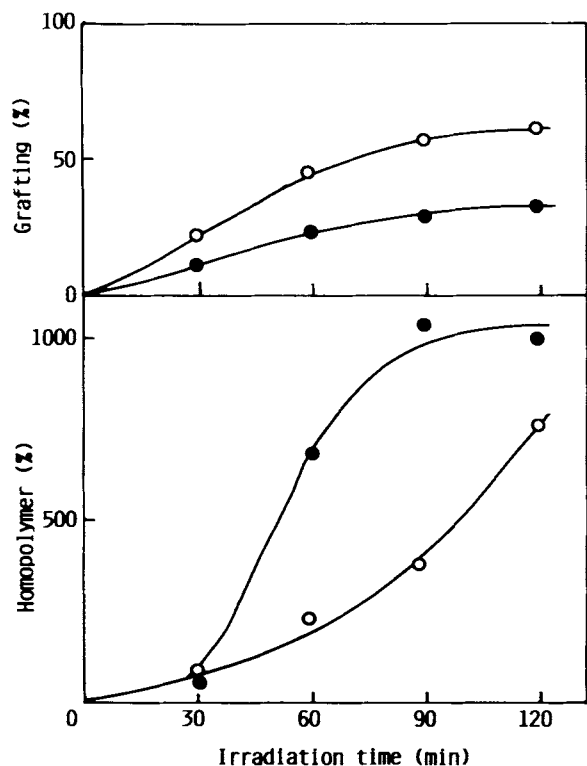


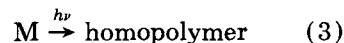
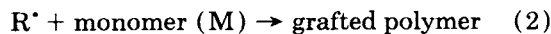
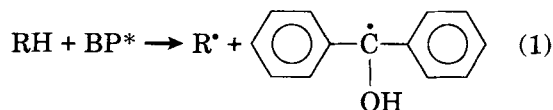
Figure 2 Photografting of MAA onto PE film in (○) the nitrogen system and (●) the air system. Irradiation temperature: 60°C.

nylpyrrolidone.⁹ Ishibashi¹⁰ examined photografting of styrene onto nylon 6 fiber without a photoinitiator and observed that the rate of grafting is higher in the presence of air than in the vacuum system when irradiated with light of $\lambda > 300$ nm.

To determine the function of oxygen on the photografting under air atmosphere, the photoinduced formation of peroxides onto PE film was examined, and the result is shown in Figure 3. Peroxides were formed on the PE film and in water medium by photoirradiation under air atmosphere. The amount of peroxides formed on the PE film decreased beyond a certain irradiation time, whereas that formed in water medium increased with irradiation time. It is supposed that the reaction sites to form the peroxides on PE film are reduced as the photoirradiation proceeds. Accordingly, the decomposition of peroxide by photoirradiation overcomes the formation of peroxide, resulting in the maximum amount of peroxide at a certain irradiation time. The formation of peroxide on PE film and in water medium by photoirradiation seems to be a factor for the accelerated polymerization shown in Figures 1 and 2. Uyama and Ikada¹¹ studied grafting of acrylamide onto films of polypropylene, nylon 6, and ethylene-vinyl ace-

tate copolymer that had been UV-preirradiated in air atmosphere. They concluded that the species initiating the grafting would be peroxides that had been generated upon UV-irradiation in air.

It is conceivable that photografting of AN and MAA onto PE film in the nitrogen system proceeds according to eqs. (1)–(3), where RH and R^{*} denote PE and its radicals, respectively. Equation (1) is the formation of PE radicals due to hydrogen-abstrating reaction by photoexcited BP. Equation (2) leads to the formation of grafted polymer, whereas eq. (3) is the formation of homopolymer:



With photografting in the air system, PE radicals, yielded by the formation of PE peroxides by eq. (5) and its decomposition by eq. (6), participate in the initiation of the grafting reaction according to eq.

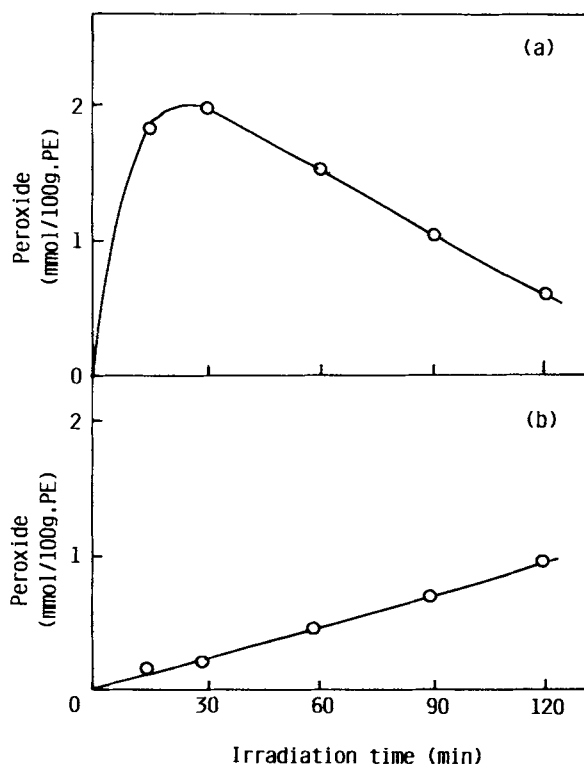


Figure 3 Photoinduced formation of peroxides (a) onto PE film and (b) in water medium under air atmosphere. Irradiation temperature: 60°C.

(7), rather than by the initiation according to eq. (2). This causes a promoted grafting reaction. On the other hand, hydroxyl radicals formed by eq. (6) may contribute to the formation of peroxides in water medium according to eq. (8) and to the formation of homopolymer by eq. (9):

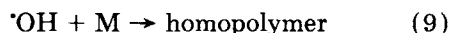
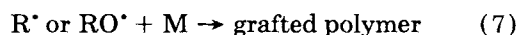
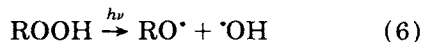
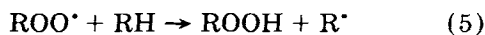
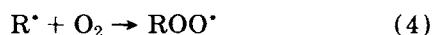


Figure 4 shows the effect of hydrazine on photografting of AN and MAA onto PE film in the air system. Hydrazine is known to be a strong reducing agent. It was observed that the percent graftings of AN and MAA were increased by adding a pertinent quantity of hydrazine to the system. Das and Palit¹² studied aqueous polymerization of methyl methacrylate initiated by hydrazine hydrate and observed that oxygen in the system acts as a cocatalyst for the hydrazine-initiated system. Figure 5 presents the effect of hydrazine on the decomposition of peroxides onto PE film. The amount of peroxides decomposed increased with increasing hydrazine concentration, indicating that hydrazine accelerates the decomposition of PE peroxides irrespective of pho-

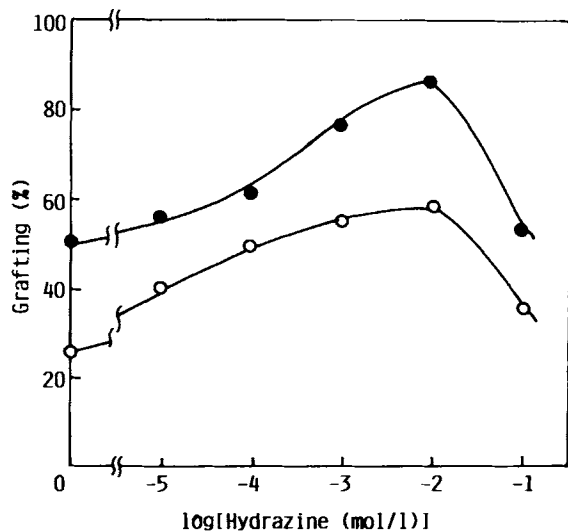


Figure 4 Effect of hydrazine on photografting of (○) MAA and (●) AN onto PE film under air atmosphere. Irradiation: 60°C, 60 min.

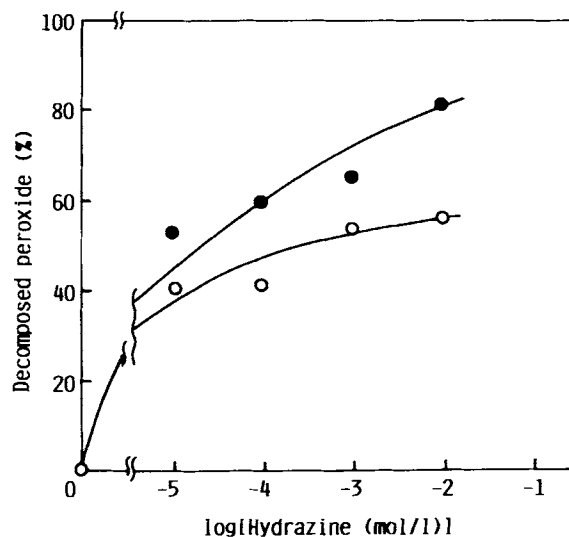
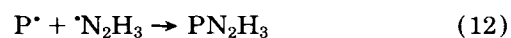
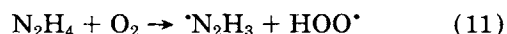
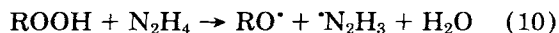


Figure 5 Effect of hydrazine on decomposition of PE peroxides: (○) without irradiation; (●) with irradiation at 60°C for 10 min. Initial amount of PE peroxides is 1.9 mmol/100 g PE.

toirradiation according to eq. (10). It is inferred, accordingly, that the addition of hydrazine to the air system leads to an accelerated decomposition of PE peroxides, resulting in an increased percent grafting. Nitrogen analysis was performed for the MAA-grafted PE films prepared in the air system with hydrazine concentrations of 10^{-4} , 10^{-2} , and 10^{-1} mol/L. The nitrogen contents were 0.13, 0.17, and 0.21% for the samples prepared with hydrazine concentrations of 10^{-4} , 10^{-2} , and 10^{-1} mol/L, respectively. This means that hydrazine radicals, which are yielded by eqs. (10) and (11), may participate in the termination of growing polymer radicals (P^*). It is plausible that a maximum percent grafting could be generated by a balance between eqs. (10) and (12):



Based on the above result of hydrazine, it is expected that the photografting in the air system may be promoted by adding a pertinent quantity of reducing agent toward peroxides. Figure 6 shows photografting of AN onto PE film in the air system, to which various metallic ions were added as the reducing agent. A maximum percent grafting was observed for each metallic ion at a certain concentration of metallic ion. Thus, a pertinent quantity of

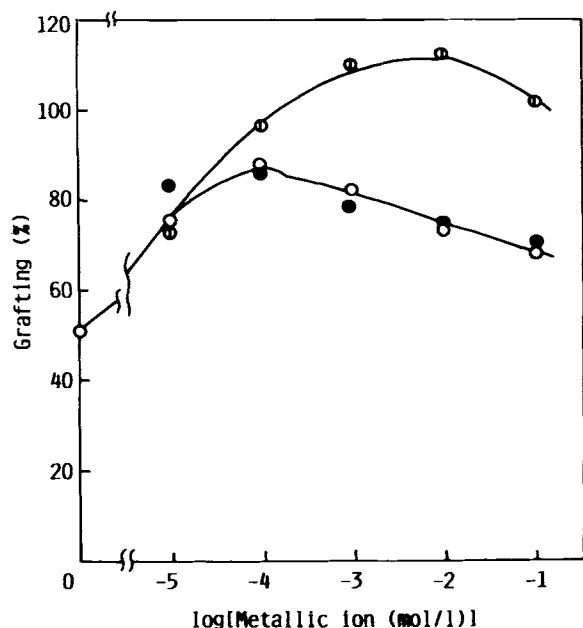
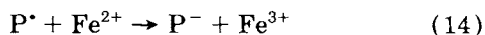
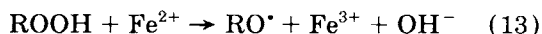


Figure 6 Effect of metallic ions on photografting of AN onto PE film under air atmosphere: (○) Ni²⁺; (◐) Cu²⁺; (●) Fe²⁺. Irradiation: 60°C, 60 min.

metallic ion accelerated the photografting in the air system. Fe²⁺ is known to decompose peroxides according to eq. (13), which leads to the promoted decomposition of the peroxides:



On the other hand, it was reported in the grafting¹³ of acrylic acid onto PE film by a preirradiation method that Fe²⁺ contributes to the termination of

growing polymer radicals by eq. (14). The maximum percent grafting is supposed to be originated in the balance between the two reactions of eqs. (13) and (14). It is concluded that use of a pertinent quantity of hydrazine as well as of metallic ions is useful for promoting photografting on PE film in the air system.

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