

Effect of Water in Vapor-Phase Photografting of Vinyl Monomers on Polymer Films

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SYNOPSIS

The effect of water added to monomer being supplied in the vapor phase was investigated in photografting on sensitizer-coated polymer films at 60°C. A pertinent quantity of water accelerated sharply the photografting irrespective of the nature of monomer (acrylic acid, methacrylic acid, methyl acrylate, methyl methacrylate, and acrylonitrile), film substrate (low-density and high-density polyethylenes, polypropylene, nylon 6, and polyester), and sensitizer (benzophenone and anthraquinone). Water was found to increase the molecular weight of the grafts, which was studied on acrylonitrile-grafted nylon 6 film. It was confirmed that water exhibited an accelerating action on photoinduced solution polymerizations of acrylic acid and methyl methacrylate, resulting in an increased molecular weight of the both polymers. These results suggest that the accelerating action of water may result from the restriction of chain termination.

INTRODUCTION

Solvent effects in liquid-phase grafting have been observed in photoinduced systems¹⁻⁵ as well as in systems initiated by high-energy radiation.⁶⁻¹² However, the effects of coexisting solvent on the photografting with monomers being supplied in the vapor phase are not known. Needles and Alger¹³ studied vapor-phase photografting of methyl acrylate (MA) on nylon 6 (NY) and polyester fibers that were immersed in water-organic solvent mixtures beforehand. They reported that the percent grafting was enhanced for NY, whereas it was reduced for polyester by the mixtures present in the fiber tissue.

The authors¹⁴ examined the effect of solvent mixed with monomer on vapor-phase photografting of acrylic acid (AA) on polymer films. The grafting was markedly promoted by adding a pertinent quantity of water to AA among the solvents. This paper deals with the effect of water on photografting of vinyl monomers (AA as well as others) and on the molecular weight of the grafts. Moreover, the effect of water on photoinduced solution polymer-

izations of AA and methyl methacrylate (MMA) is also investigated.

EXPERIMENTAL

Samples

Benzophenone (BP), benzoyl peroxide (BPO), and anthraquinone (AQ) were used as sensitizer and all were of reagent grade. Low- and high-density polyethylenes (LDPE and HDPE, respectively), polypropylene (PP), NY, and poly(ethylene terephthalate) (PET) were used as polymer films (thickness = 30 μm). The polymer films were dipped in acetone or chloroform solution containing a known amount of sensitizer and 1.0 wt % poly(vinyl acetate) ($\bar{M}_w = 100,000$) and dried to prepare sensitizer-coated films. The amount of sensitizer on the film was indicated to be the concentration of acetone or chloroform solution offered for coating. AA, methacrylic acid (MAA), MA, MMA, and acrylonitrile (AN) were purified by distillation.

Photografting

Vapor-phase photografting, carried out using a Pyrex glass tube, was reported in a previous paper.¹⁵ The polymer film (54 \times 8 mm) fixed on a sample holder was set at the center part of the tube, and 2

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mL monomer or the solution of 2 mL monomer and a known volume of water was placed in the bottom part. The pressure of the system, after several freeze-thaw cycles, was adjusted to 1 mmHg. 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 Pyrex glass tubes were rotated. Polymerized film was extracted with a proper solvent to exclude homopolymers; namely, hot water was used for poly(AA) and poly(MAA). Acetone and *N,N*-dimethylformamide were chosen for poly(MA), poly(MMA), and poly(AN), respectively. Percent grafting was taken as the percentage of weight increase of the original film.

To examine molecular weight of the grafts, AN-grafted NY film was prepared by vapor-phase photografting of AN on NY film (80 × 85 mm). The grafted sample was treated with 6*N* aqueous solution of hydrochloric acid at 100°C for 10–40 h, and the polyAN of the grafts was isolated. Number-average molecular weight of the polyAN was determined from the viscosity of the *N,N*-dimethylformamide solution¹⁶ at 25°C by using the following equation:

$$[\eta] = 3.92 \times 10^{-4} \bar{M}_n^{0.75}$$

Photoinduced Solution Polymerization

A Pyrex glass tube containing 8 mL tetrahydrofuran (THF) or methanol and 2 mL AA or MMA, in which 1×10^{-3} mol/L BPO was dissolved, was filled with nitrogen. Polymerization was then carried out by keeping the system at 60°C for a given duration under irradiation. The irradiation was conducted in the same reactor as described above. Conversion was determined gravimetrically. Weight-average molecular weights of poly(AA) and poly(MMA) were determined from the viscosities of the dioxane solution¹⁷ at 30°C and the acetone solution¹⁸ at 25°C, respectively, by using the following equations:

$$\text{Poly(AA)}: [\eta] = 7.4 \times 10^{-4} \bar{M}_w^{0.5}$$

$$\text{Poly(MMA)}: [\eta] = 0.659 \times 10^{-5} \bar{M}_w^{0.71}$$

RESULTS AND DISCUSSION

Table I shows the effect of water on vapor-phase photografting. The percent grafting of the AA-LDPE system, for example, increased with increas-

Table I Effect of Water on Vapor-phase Photografting^a of Vinyl Monomers on Polymer Films Sensitized with BP

| Monomer | Film | Grafting (%) | | | | |
|---------------------------|------|-------------------------------|------|------|------|-----|
| | | Water Added ^b (mL) | | | | |
| | | 0 | 0.5 | 1.0 | 1.5 | 2.0 |
| Acrylic acid (AA) | LDPE | 510 | 582 | 905 | 571 | 503 |
| | HDPE | 181 | 182 | 471 | 383 | 301 |
| | PP | 400 | 486 | 523 | — | 419 |
| | NY | 48 | 53 | 413 | 388 | 305 |
| | PET | 22 | 31 | 115 | 38 | 42 |
| Methacrylic acid (MAA) | LDPE | 103 | 263 | 368 | 330 | 321 |
| | HDPE | 71 | 85 | 80 | 76 | 51 |
| | PP | 70 | 86 | 118 | 103 | 42 |
| | NY | 11 | 51 | 40 | 33 | 35 |
| | PET | 3 | 5 | 9 | 4 | 4 |
| Methyl methacrylate (MMA) | LDPE | 610 | 608 | 615 | 608 | 625 |
| | HDPE | 425 | 661 | 702 | — | 588 |
| | NY | 7 | 11 | 12 | 18 | 14 |
| | PET | 5 | 6 | 5 | 8 | 7 |
| Methyl acrylate (MA) | LDPE | 753 | 1805 | 1057 | 801 | — |
| | NY | 105 | 1663 | 1758 | 1899 | — |
| Acrylonitrile (AN) | LDPE | 198 | 220 | 257 | 181 | 189 |
| | NY | 24 | 48 | 37 | 104 | 107 |

^a Irradiation was carried out at 60°C for 60 min. Concentration of BP is 0.3 wt %.

^b Quantity of water added to the 2 mL monomer.

ing the quantity of water added to AA, but it decreased gradually after passing a maximum value that was attained at about 1 mL water added. The same effect of water was recorded for HDPE, PP, NY, and PET. The accelerating effect of water was commonly observed for hydrophilic and hydrophobic monomers, MAA, MMA, MA, and AN, as well as for AA. However, the effect on the MMA-LDPE system was small. Thus, vapor-phase photografting was enhanced by adding a pertinent quantity of water to monomer, and the phenomena were commonly found irrespective of the kinds of film substrate and monomer.

Figure 1 shows vapor-phase photografting of AA on polymer films sensitized with AQ. The abscissa in the figure represents the quantity of water added to 2 mL AA. The effect of water was clearly recognized in the system sensitized with AQ. The same action of water was reported for the BPO-sensitized system.¹⁴ Thus, the accelerating action of water was commonly true irrespective of the types of sensitizer. These results suggest that water is unlikely to participate in the initiation process due to the interaction between film substrate and sensitizer. On the other hand, water is supposed not to have a swelling function for PE, PP, NY, and PET. Accordingly, the effect of water cannot be considered to relate directly to the swelling of film substrate. Egoyan et al.¹⁹ observed that the rate of grafting of *N,N*-dimethylaminoethyl methacrylate on ozonized poly(vinyl acetate) in methanol solution was in-

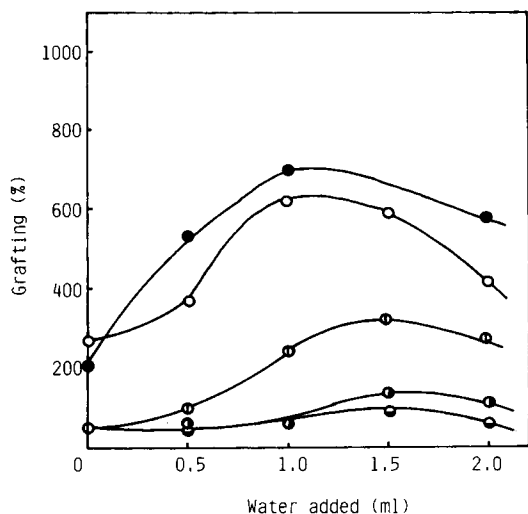


Figure 1 Effect of water on vapor-phase photografting of AA on AQ-sensitized polymer films. Irradiation was carried out at 60°C for 60 min. Concentration of AQ was 0.1 wt %. (●) LDPE; (○) HDPE; (○) PP; (●) PET; (●) NY.

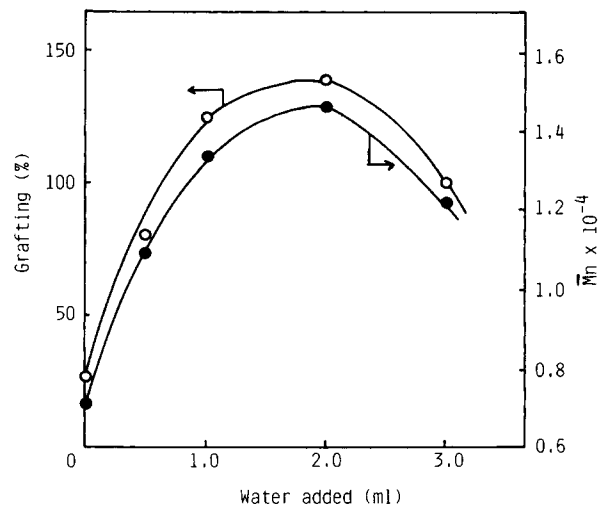


Figure 2 Effect of water on the molecular weight of polyAN grafts introduced into NY film. Photografting of AN on NY film sensitized with BP was carried out at 60°C for 60 min. Concentration of BP was 0.3 wt %.

creased by water present in the system due to the inhibition of chain termination.

In liquid-phase grafting, the solvent effect has often been understood as a gel effect and the phenomenon has been explained in terms of polymer chain entanglement.^{4,20} The effect of water on molecular weight of the grafts was investigated to determine whether the phenomenon originated from the gel effect. To examine it, AN-grafted NY film was chosen due to a relatively easy isolation of the grafts by acid hydrolysis. Figure 2 presents percent grafting of the grafted samples prepared. The molecular weight of polyAN grafts is also included in the figure. The abscissa in the figure represents the quantity of water added to 2 mL AN. The molecular weight of the grafts increased with increasing the quantity of water added, but it decreased beyond a certain quantity of water. Thus, it was confirmed that water added to monomer in vapor-phase photografting contributes to the increase of the molecular weight of the grafts.

The effect of water on photoinduced solution polymerization was further examined. Figure 3 shows the effect of water on photopolymerization of AA in THF solvent. The abscissa in the figure represents the vol % of water in THF-water mixture solvent. The conversion increased with increasing the water content in the system, and then it reached a maximum value at about 20 vol % of the water content. The phenomenon is similar to the relationship between percent grafting and quantity of water added as shown in Figure 1. The molecular weight of

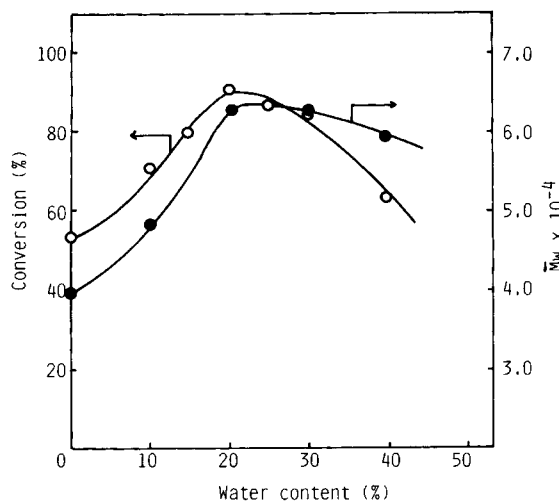


Figure 3 Photopolymerization of AA in THF-water mixture solvent. Irradiation was carried out at 60°C for 30 min. Concentrations of BPO and AA were 1×10^{-3} mol/L and 2.7×10^{-2} mol/L, respectively.

poly(AA) increased with the water content, which is also shown in Figure 3. Figure 4 shows the effect of water on photopolymerization of MMA in methanol solvent. The same relation as that observed in Figure 3 was indicated for both conversion and molecular weight of poly(MMA). Changes of conversion with irradiation time are shown in Figure 5. A higher conversion was shown for the system in the presence of water as compared to the system without water over the whole irradiation time, and the con-

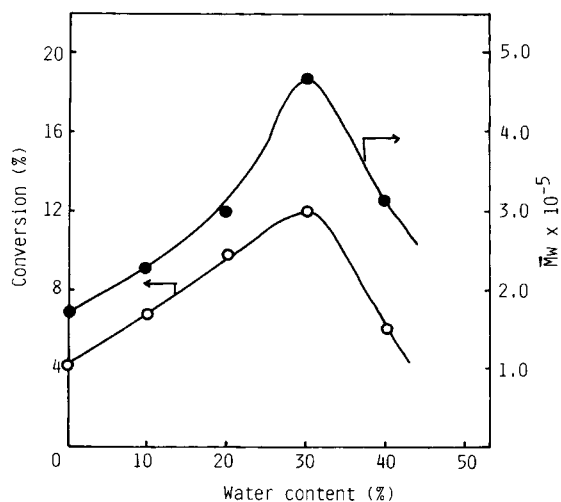


Figure 4 Photopolymerization of MMA in methanol-water mixture solvent. Irradiation was carried out at 60°C for 30 min. Concentrations of BPO and MMA were 1×10^{-3} mol/L and 1.95×10^{-2} mol/L, respectively.

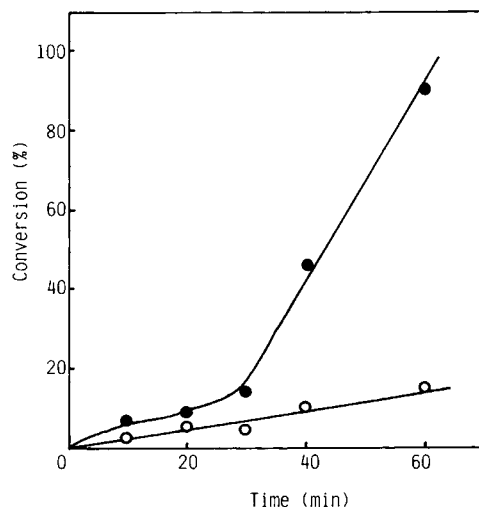


Figure 5 Photopolymerization of MMA in methanol-water mixture solvent. Irradiation was carried out at 60°C. Concentrations of BPO and MMA were 1×10^{-3} mol/L and 1.95×10^{-2} mol/L, respectively. (○) methanol-solvent; (●) methanol-water (7 : 3 v/v) mixture solvent.

version sharply rose after passing a certain period. Thus, water was found to have a function of facilitating the photoinduced solution polymerizations of AA and MMA.

Based on the above investigations, it was confirmed that polymerization was accelerated by using a pertinent quantity of water being mixed with monomer, which was commonly observed for vapor-phase photografting and photoinduced solution polymerization, resulting in an increased molecular weight of the polymers produced in each system. These facts suggest that the effect of water may result from the suppression of chain termination induced by the gel effect.

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