

Factors Influencing Vapor-Phase Photografting of Styrene/Acrylonitrile Monomer Mixtures on Polymer Films

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SYNOPSIS

An accelerating effect due to a styrene (St)/acrylonitrile (AN) monomer mixture was investigated in vapor-phase photografting on polymer films, on which a photoinitiator was coated. A maximum percent grafting was observed at a certain St concentration of monomer feed irrespective of the nature of photoinitiator, such as benzoyl peroxide, benzophenone, and α,α' -azobisisobutyronitrile, and the type of polymer film, such as low- and high-density polyethylene, polypropylene, and nylon 6. The same effect due to the monomer mixture was recorded for liquid-phase photografting in a water-ethanol mixture solvent. With photoinduced copolymerization of the St/AN mixture using benzoyl peroxide, conversion of AN was sharply reduced by the addition of St to the AN system using DMF, DMSO, methanol, and ethyl acetate solvents. In case of saturated hydrocarbon solvents such as *n*-hexane, cyclohexane, *n*-octane, and *n*-decane, on the other hand, a maximum conversion was observed at a certain St concentration of monomer feed. The accelerating effect due to the St/AN mixture was discussed in terms of copolymerizability of monomers and a gel effect.

INTRODUCTION

In a previous paper,¹ the authors observed that vapor-phase photografting on low-density polyethylene (LDPE) was markedly accelerated by the combination of two kinds of monomers, which is rich in an alternative copolymerizability, showing a maximum percent grafting at a certain monomer ratio of monomer feed. Such monomer combinations were styrene (St)/acrylonitrile (AN), St/acrylic acid, St/methacrylic acid, St/glycidyl methacrylate, and *N*-vinylpyrrolidone/AN. The purpose of this study was to determine the factors causing the accelerating effect due to the monomer mixtures. Thus, grafting conditions such as the nature of photoinitiator, the type of polymer film, irradiation time, and temperature, comparison between vapor- and liquid-phase photografting, and characteristics of photoinduced copolymerization were investigated using the St/AN monomer mixture.

EXPERIMENTAL

Samples

Benzophenone (BP), α,α' -azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), and anthraquinone (AQ) were used as the photoinitiator and all were reagent grade. LDPE, high-density polyethylene (HDPE), polypropylene (PP), and nylon 6 were used as films (thickness = 30 μm). The photoinitiator-coated films were prepared according to a previous paper,¹ namely, the film samples were dipped in acetone solution containing 0.3 wt % photoinitiator and 1.0 wt % poly(vinyl acetate) ($\bar{M}_w = 100,000$) and dried to prepare the photoinitiator-coated films. St and AN were purified by distillation.

Photografting

Vapor-phase photografting was carried out using a Pyrex glass tube, which was reported in previous papers.^{1,2} The film (54 \times 8 mm) fixed on a sample holder was set at the center part of the tube, and 2 mL of monomer or monomer mixture was placed in

the bottom part. The pressure of the system was adjusted to 1 mmHg after several freeze-thaw cycles.

Liquid-phase photografting was carried out in a Pyrex glass tube containing film (100 × 30 mm), 2 mL of monomer or monomer mixture, and 20 mL of water-ethanol (1 : 1 vol %) mixture under nitrogen at 60°C.

Irradiation with a high-pressure mercury lamp (400 W) was carried out using a Riko rotary photochemical reactor RH400-10W, around which Pyrex glass tubes were rotated. Polymerized film was extracted with hot DMF for 24 h to exclude homopolymers. Percent grafting was taken as the percentage of weight increase of the original.

Photoinduced Copolymerization

A Pyrex glass tube containing 2 mL of monomer or monomer mixture and 2 mL of solvent, in which a known quantity of BPO was dissolved, was filled with nitrogen. Then, copolymerization was carried out by keeping the system at 40°C for a given duration under irradiation. The irradiation was conducted with the same reactor as mentioned above. Conversion was determined gravimetrically.

RESULTS AND DISCUSSION

Photoinitiator and Polymer Film

Figure 1 shows vapor-phase photografting of the St/AN monomer mixture on LDPE film using various photoinitiators. There were large differences in the percent grafting among the photoinitiators, decreasing in the order of BPO > BP > AIBN. BPO^{3,4} and AIBN⁵ may decompose by photoirradiation to produce fragment radicals of photoinitiator that contribute to the extraction of the hydrogen atom from the film substrate. On the other hand, BP^{6,7} is excited to a triplet state, which might extract the hydrogen atom from the film substrate to yield polymer radicals capable of initiating grafting. A maximum percent grafting was recorded for each system at an St concentration of 10–20 mol % in the monomer feed. Homopolymers were also formed on the film surface, and the maximum yield was observed at the same St concentration as that of the maximum percent grafting. Graft efficiencies, which were taken as the weight percent of grafted polymer relative to total conversion of monomer in a system, were 80–85% in each system irrespective of the component of the monomer feed.

Figure 2 shows the results of vapor-phase pho-

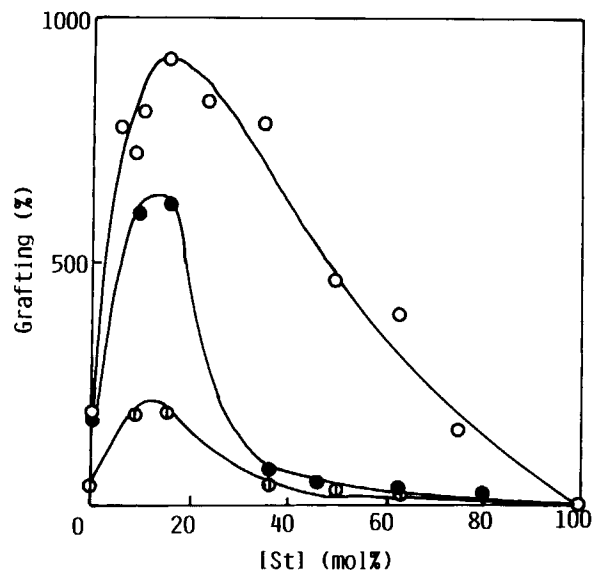


Figure 1 Vapor-phase photografting of St/AN mixture on LDPE film: (○) BPO; (●) BP; (⊙) AIBN. Quantity of monomer, 2 mL; irradiation, 60°C, 60 min; concentration of photoinitiator, 0.3 wt %.

tografting on various polymer films. The activities of HDPE and nylon 6 toward the photografting were lower than those of LDPE and PP. Especially, the percent grafting of nylon 6 was very low level, indicating the different activity of the film toward the photografting. However, the St concentration resulting in maximum percent grafting was commonly recorded for each polymer film.

Irradiation Time and Temperature

Figure 3 shows the effect of irradiation time on vapor-phase photografting. As shown in Figure 3(a), almost no change in the St concentration resulting in maximum percent grafting was observed for each irradiation system. Figure 3(b) presents the relationship between percent grafting at a fixed composition of the St/AN mixture and irradiation time. A sharp increase in percent grafting was recorded over the irradiation time of 30–60 min for each system, showing an S-shape curve between both systems. Yamamoto et al.⁸ reported a similar phenomenon in γ -ray induced grafting of methyl acrylate on polyethylene in the vapor-phase system and observed the presence of an autoacceleration region in the grafted monomer amount-irradiation time curve.

Figure 4 shows the effect of irradiation temperature on photografting. Higher percent grafting was exhibited for the system with higher temperature.

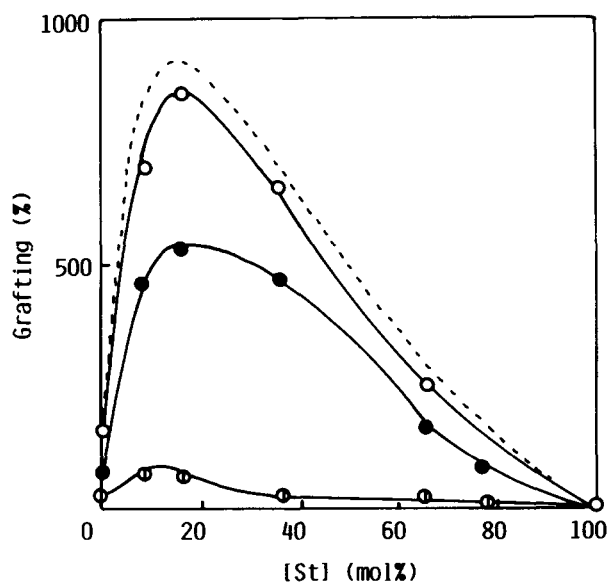


Figure 2 Vapor-phase photografting of St/AN mixture on polymer films using BPO: (○) PP; (●) HDPE; (⊙) nylon 6. Quantity of monomer, 2 mL; irradiation, 60°C, 60 min; concentration of BPO, 0.3 wt %. Dotted line represents the result of the LDPE film.

The St concentration resulting in maximum percent grafting was nearly equal in each system.

Liquid-Phase Photografting

Figure 5 presents liquid-phase photografting of the St/AN mixture on LDPE film in a water-ethanol medium. The percent grafting of the liquid-phase system was much lower compared to that of the vapor-phase system. However, the St concentration affording maximum percent grafting was present in each system and the value roughly agreed with the result of the vapor-phase system. Accordingly, it was confirmed that the accelerating effect due to the St/AN mixture is a common phenomenon for both vapor and liquid phases.

Photoinduced Copolymerization

Based on the above investigations of vapor-phase photografting of the St/AN mixture, it was found that the St concentration resulting in maximum percent grafting is hardly influenced by grafting conditions such as the nature of photoinitiator, the type of polymer film, irradiation time and temperature, and polymerization system, either the vapor

or liquid phase. This fact suggests that the accelerating effect closely relates to the copolymerization characteristics of the monomer mixture.

Figure 6 shows photoinduced copolymerization of the St/AN mixture in bulk and various solvents. The polymerization of AN alone was markedly suppressed by the addition of St to the system, the homogeneity of which was kept during the polymerization in DMF and DMSO solvents, but which was not in the methanol solvent. The same conversion curve was recorded for 1,4-dioxane and ethyl acetate solvents. Such polymerization phenomenon⁹ is known to take place in the case in which termination between the different types of monomer radicals is preferential to that between the same type of monomer radicals. In general, the rate of copolymerization¹⁰ of the M_1/M_2 monomer mixture is expressed by the following equation:

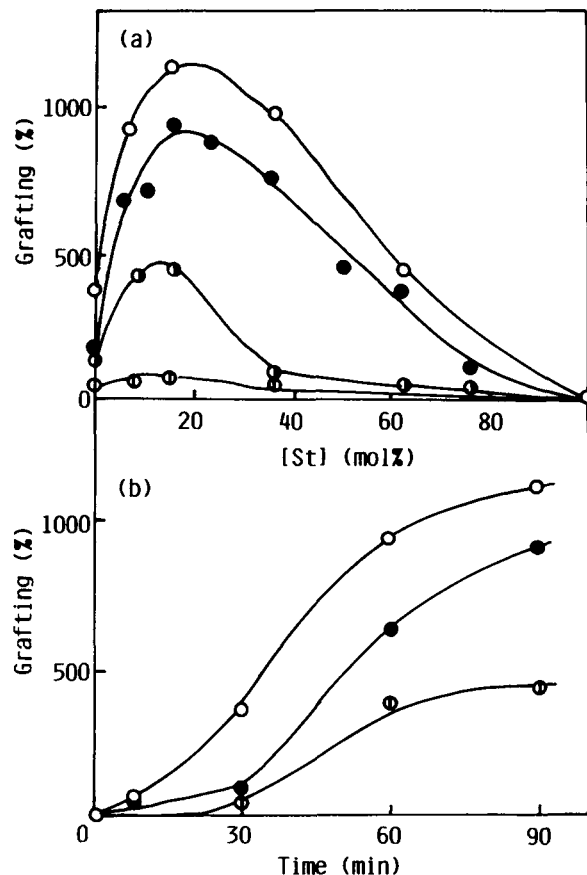


Figure 3 Vapor-phase photografting of St/AN mixture on LDPE film using BPO. Quantity of monomer, 2 mL; irradiation, 60°C; concentration of BPO, 0.3 wt %. (a) Irradiation time (min): (○) 10; (●) 30; (●) 60; (○) 90. (b) St concentration of monomer feed (mol %): (○) 16; (●) 36; (○) 63.

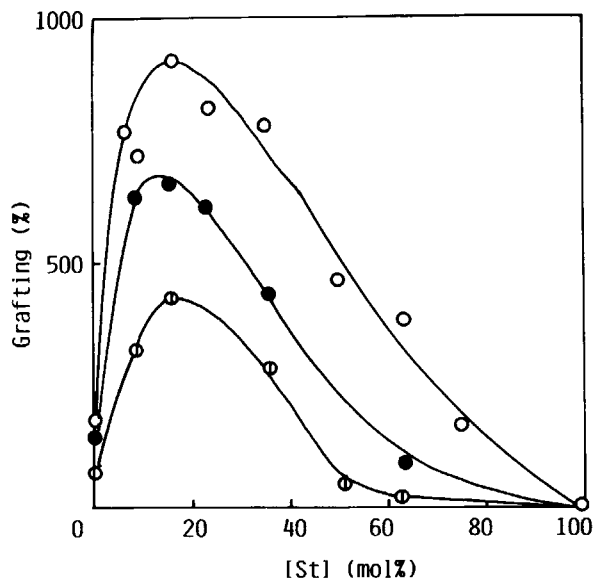


Figure 4 Vapor-phase photografting of St/AN mixture on LDPE film using BPO. Irradiation temperature ($^{\circ}\text{C}$): (\circ) 40; (\bullet) 50; (\circ) 60. Irradiation time, 60 min; quantity of monomer, 2 mL; concentration of BPO, 0.3 wt %.

$$R_p = \frac{(I^{1/2}/\delta_1) \cdot (r_1 \cdot [M_1]^2 + 2[M_1] \times [M_2] + r_2 \cdot [M_2]^2)}{\{r_1^2 \cdot [M_1]^2 + 2(\phi \cdot r_1 \cdot r_2 \cdot \delta_2/\delta_1)[M_1] \times [M_2] + (r_2^2 \cdot \delta_2^2/\delta_1^2) \cdot [M_2]^2\}^{1/2}} \quad (1)$$

where $\delta_1 = (k_{t11}/k_{11}^2)^{1/2}$, $\delta_2 = (k_{t22}/k_{22}^2)^{1/2}$, and $\phi = k_{t12}/(k_{t11} \cdot k_{t22})^{1/2}$. I , k_{11} , and k_{22} denote the rate

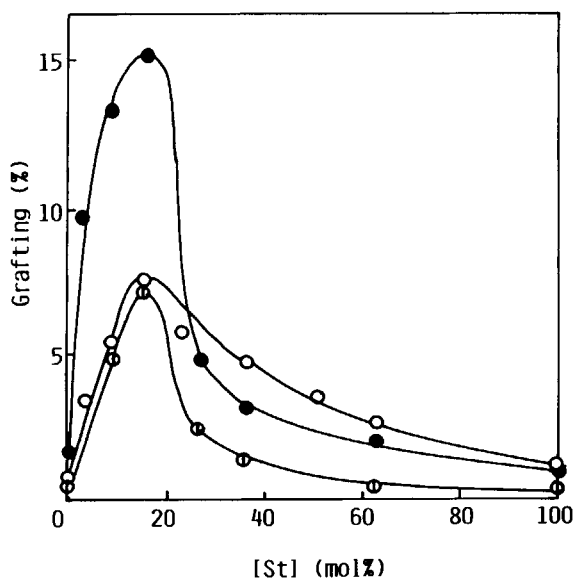


Figure 5 Liquid-phase photografting of St/AN mixture on LDPE film: (\circ) BPO; (\circ) AQ; (\bullet) BP. Irradiation, 60°C , 60 min; quantity of monomer, 2 mL; concentration of photoinitiator, 0.3 wt %; solvent, ethanol/water (1:1).

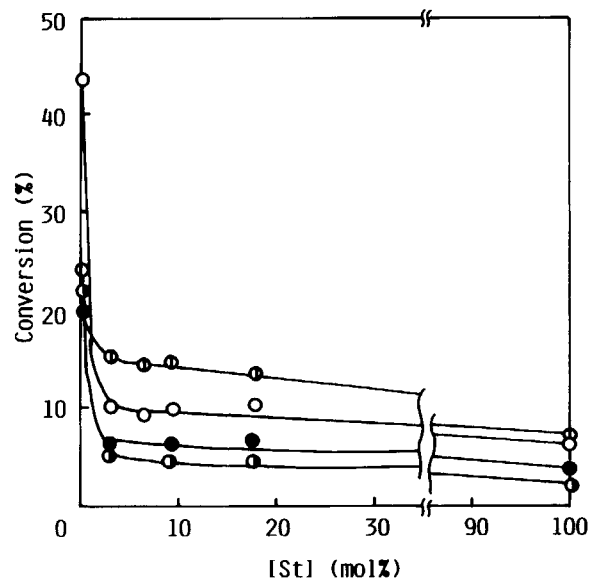


Figure 6 Photoinduced copolymerization of St/AN mixture in various solvents: (\circ) bulk; (\bullet) methanol; (\circ) DMF, (\bullet) DMSO. Quantity of monomer, 2 mL; irradiation, 40°C , 60 min; concentration of BPO, 0.01 mol/L.

of initiation and rate constants of propagation between the same type of monomers, respectively, and k_{t11} , k_{t22} , and k_{t12} are rate constants of termination that are shown in eqs. (2)–(4), respectively:

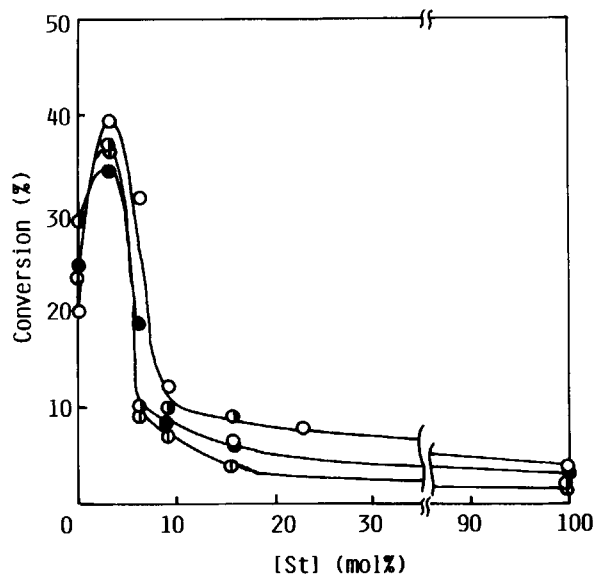
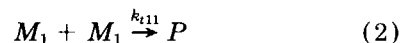
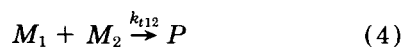


Figure 7 Photoinduced copolymerization of St/AN mixture in various solvents: (\circ) *n*-hexane; (\bullet) cyclohexane; (\circ) *n*-octane; (\bullet) *n*-decane. Quantity of monomer, 2 mL; irradiation, 40°C , 60 min; concentration of BPO, 0.01 mol/L.



ϕ is a measure of expressing the extent of termination of eq. (4) compared to those of eqs. (2) and (3); it is also called the rate constant of cross-termination. Suzuki et al.¹¹ observed in photoinduced copolymerization of St/AN using AIBN that the average value of ϕ is 80, implying a very high frequency of cross-termination in the system.

On the other hand, the accelerating phenomenon by the addition of St was observed in saturated hydrocarbon solvents such as *n*-hexane, cyclohexane, *n*-octane, and *n*-decane, in which the polymerization proceeds heterogeneously (Fig. 7). It is presumed that the cross-termination of eq. (4) is restricted in these systems, resulting in the increased conversion. Thus, the copolymerization behavior of the St/AN mixture was found to be largely influenced by the nature of polymerization solvents.

Figure 8 presents the relationship between conversion and irradiation time at a fixed composition of the St/AN mixture. A sharply increased conversion was observed in the range of 20–60 min for the conversion curve of the system using an St concentration of 3 mol %, at which a maximum conversion is given for the *n*-hexane solvent. The phenomenon

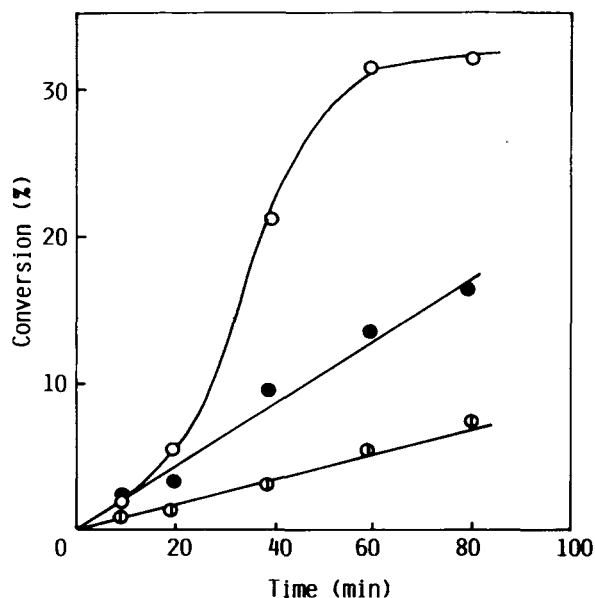


Figure 8 Photoinduced copolymerization of St/AN mixture. St concentration of monomer feed (mol %): (O) 3, *n*-hexane; (D) 16; *n*-hexane; (●) 3, DMF. Irradiation, 40°C; quantity of monomer, 2 mL; concentration of BPO, 0.01 mol/L.

Table I Copolymer Compositions for Photoinduced Copolymerization of the St/AN Monomer Mixture

AN in Monomer Mixture (mol %)	Conversion (%)		AN in Copolymer (mol %)	
	Bulk	<i>n</i> -Hexane	Bulk	<i>n</i> -Hexane
37	6.3	3.4	32.6	38.3 (42.8)
84	8.5	6.0	54.5	57.0 (75.5)
94	10.0	26.0	68.7	83.2 (87.1)
97	10.8	36.0	83.2	94.3

Copolymerization of the St/AN mixture was carried out at 40°C for 60 min. Values in parentheses were the results of grafted copolymers prepared with vapor-phase photografting of the St/AN mixture on LDPE film.

is supposed to be due to a gel effect. On the other hand, such a phenomenon was not observed for the DMF solvent system using an St concentration of 3 mol % and for the *n*-hexane system using an St concentration of 16 mol %. The gel effect was found to easily take place at the monomer composition at which a maximum conversion is afforded.

Table I shows composition of copolymers prepared with bulk and *n*-hexane systems. In the former system, the polymerization of AN alone was restricted by the addition of St, but a maximum conversion was recorded for the latter system. The copolymer compositions were determined by elementary analysis. AN content of copolymers prepared with the *n*-hexane system was higher than that of copolymers prepared with the bulk system, showing a remarkable difference in the values around the monomer composition that resulted a maximum conversion. Table I also includes the composition of grafted copolymers prepared by vapor-phase photografting on LDPE film using BPO. The composition was characterized by an AN content higher than that of the *n*-hexane system. It is an outstanding characteristic that copolymer with higher AN content is produced in the system where an accelerated polymerization due to the St/AN mixture is observed. It was reported in the copolymerization¹² of St/*n*-butyl acrylate that the content of the polar monomer component, *n*-butyl acrylate, in the copolymer increases with decreasing ϕ .

As above, it was found that copolymerization of the St/AN mixture is promoted in the system where the termination between the different types of monomer radicals is restricted and the phenomenon is characterized by a gel effect. In general, grafting on polymer substrates is carried out in a heteroge-

neous system, in which autoacceleration phenomenon of polymerization (gel effect) is observed for vapor^{8,13} and liquid¹⁴⁻¹⁷-phase systems. In the present vapor-phase system, Figure 3(b) showed a percent grafting-irradiation time curve peculiar to the gel effect. Consideration of the essential copolymerizability of the St/AN mixture would suggest that an accelerating effect is not predicted because of a preferable cross-termination. It is conceivable, accordingly, that the accelerating effect due to the St/AN mixture is generated in the polymerization system where a gel effect easily occurs.

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