

Vapor Phase Photografting on Low-Density Polyethylene Film in Binary Monomer Systems

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Synopsis

Vapor phase photografting of monomer mixtures on low-density polyethylene film, on which benzoyl peroxide is coated, was investigated at 60°C using various vinyl, allyl, and solid monomers. Styrene (St) itself was difficult to graft on the film substrate, but the combinations of St with vinyl monomers such as acrylonitrile (AN), glycidyl methacrylate (GMA), acrylic acid, and methacrylic acid led to the accelerated grafting, affording a maximum percent grafting at an certain monomer ratio. The same combination effect was observed for AN-*N*-vinyl pyrrolidone and -GMA monomer mixtures. The monomer combinations such as allyl aldehyde-St and allyl alcohol-maleic anhydride were useful for performing the grafting of allyl monomers effectively. Maleic anhydride and maleimide as solid monomers were also possible to introduce into the film substrate by means of the monomer combination, where St, *N*-vinyl pyrrolidone, vinyl ethers, and benzyl methacrylate were available as comonomers. Thus, the monomer combinations affording an accelerating effect on grafting may be monomer pairs rich in an alternative copolymerizability, suggesting that monomer reactivity ratio controls a major factor for the combination effect. It was confirmed from IR study on grafted films that both monomer components are introduced in the film substrate as the grafted chain component.

INTRODUCTION

In a previous paper¹ the authors observed that various vinyl monomers are successfully introduced in polymer film substrate when photografting is carried out in vapor and liquid phases using the film on which sensitizers such as benzophenone and anthraquinone are coated. The photografting supplying monomers in their gaseous state is thought to have the following advantages: (1) There is less formation of homopolymer and (2) various monomers are applicable since it is not necessary to consider monomer solubility in polymerization solvent. In such a vapor phase system, grafting of styrene (St) did not initiate under the irradiation condition at 60°C for 60 min, while methyl methacrylate (MMA), acrylonitrile (AN), and acrylic acid (AA) were possible to introduce into polyolefin substrates easily under the same irradiation, remaining a big problem on applicable range of monomers.

On the other hand, attempts on grafting²⁻¹³ using mixtures of two or more kinds of monomer have been extensively made for various initiation systems, monomers, and polymer substrates. The advantage of this grafting method is that the proper combination of monomers makes possible the polymerization of monomers whose abilities to initiate the polymerization singly are very low. This study aimed at the grafting by monomer mixtures as a method to

introduce monomer into polyolefin films, onto which the monomer itself is hard to graft. Thus, the combination effect was examined for various vinyl, allyl, and solid monomers in vapor phase photografting.

EXPERIMENTAL

Samples

Low-density polyethylene (PE) film, which was prepared with a thickness of 30 μm , was dipped in acetone solution containing 0.3% benzoyl peroxide (BPO) and 1.0% poly(vinyl acetate) ($\bar{M}_w = 100,000$) and dried to prepare BPO-sensitized film. The amount of BPO in the film sample was determined iodometrically to be 3.2×10^{-8} mole per apparent film surface unit (mol/cm^2). AA, methacrylic acid (MAA), benzyl methacrylate (BMA), glycidyl methacrylate (GMA), AN, *N*-vinyl pyrrolidone (VP), St, MMA, ethyl vinyl ether (EVE), and *n*-butyl vinyl ether (BVE) as vinyl monomers, allyl alcohol (AAL) and acrolein (AL) as allyl monomers, and maleic anhydride (MAH) and maleimide (MI) as solid monomers were purified by distillation or recrystallization.

Photografting

Vapor phase photografting, carried out using a Pyrex glass tube, was reported in previous articles.^{1,14} The PE film (54 \times 8 mm) fixed on a sample holder was set at the center part of the tube, and 2 mL of monomer mixture or the solution of 2 mL of monomer and a known quantity of solid monomer was placed in the bottom part. The pressure of the system was adjusted to 1 mm Hg after several freeze-thaw cycles. 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 proper solvents to remove homopolymers. Percent grafting was taken as the percentage of weight increase of the original film.

The infrared (IR) spectrum was recorded with a Nippon Bunko IR spectrophotometer A-100.

RESULTS AND DISCUSSION

Vinyl Monomers

Vapor phase photografting was carried out using the combinations of St and various vinyl monomers, and the results are shown in Figure 1. St itself showed almost no initiation under the present irradiation conditions, but percent grafting was clearly increased by using the combinations of St and monomers such as AN, GMA, AA, and MAA. The percent grafting exhibited a maximum value at a certain monomer ratio, indicating that the mol % of St making the value depends on the kind of comonomers. Figure 2 shows the combination of AN and comonomers such as VP and GMA. A maximum percent grafting was recorded at a certain mol % of AN in each system though AN itself gave about 180% grafting. Table I presents monomer reactivity

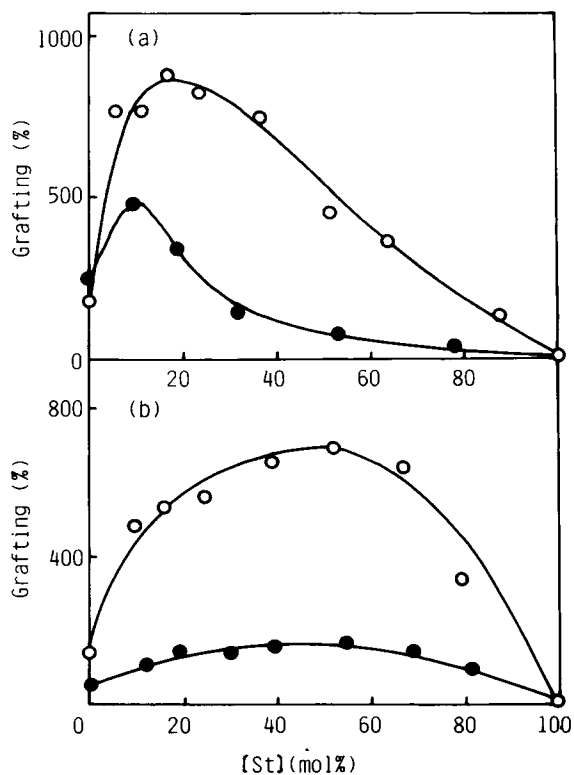


Fig. 1. Vapor phase photografting of monomer mixtures of St with AN, GMA, AA, and MAA on PE film sensitized with BPO: (a) (○) St-AN; (●) St-GMA; (b) (○) St-AA, (●) St-MAA. Quantity of monomer, 2 mL; irradiation, 60°C, 60 min.

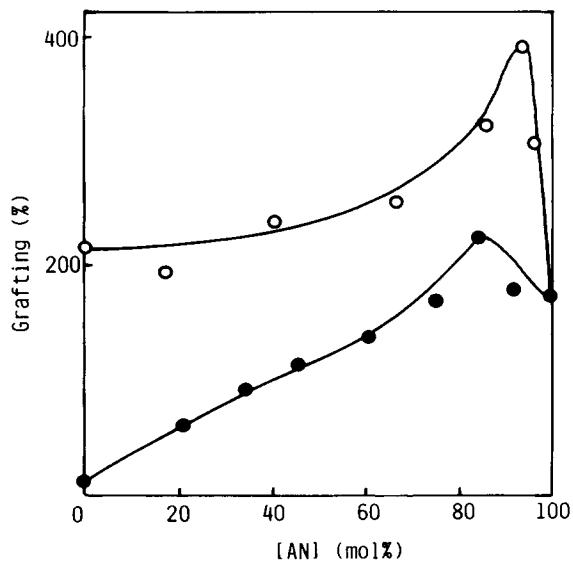


Fig. 2. Vapor phase photografting of monomer mixtures of AN with GMA and VP on PE film sensitized with BPO: (○) AN-GMA; (●) AN-VP. Quantity of monomer, 2 mL; irradiation, 60°C, 60 min.

TABLE I
 Copolymerization Reactivity Ratios

M_1 (e value)	M_2	r_1	r_2	e value (M_2)
St (-0.80)	AN	0.40 ± 0.05	0.04 ± 0.04	1.20
	GMA	0.63 ± 0.1	0.34 ± 0.05	0.10
	AA	0.15 ± 0.01	0.25 ± 0.02	0.77
	MAA	0.15	0.37	0.65
AN (1.20)	MMA	0.52 ± 0.02	0.46 ± 0.02	0.40
	VP	—	—	-1.14
	GMA	0.04 ± 0.01	1.32 ± 0.03	0.40

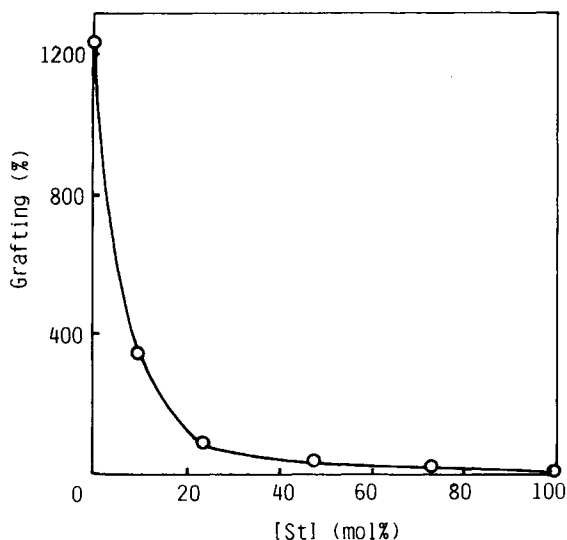


Fig. 3. Vapor phase photografting of St-MMA monomer mixture on PE film sensitized with BPO. Quantity of monomer, 2 mL; irradiation, 60°C, 60 min.

ratios^{15,16} r_1 and r_2 of each system. The monomer combinations affording an accelerating effect on grafting are supposed to be monomer pairs rich in an alternative copolymerizability because the r_1 and r_2 in each system are less than unity. That is, the combination of two monomers having a large interaction between the both is inferred to be one of factors for the increased percent grafting.

Figure 3 shows the result of St-MMA monomer mixture, to which an accelerating effect on grafting is expected from their monomer reactivity ratios of Table I. However, decreased percent grafting was recorded when St was added to MMA. Such phenomenon is conceivable to relate to the concept of cross-termination which is well known in general copolymerization system.¹⁷ That is, the rate of cross-termination is greater than that of termination of either monomer alone. It is plausible therefore that such characteristic of copolymerization is reflected to the grafting of St-MMA monomer mixture.

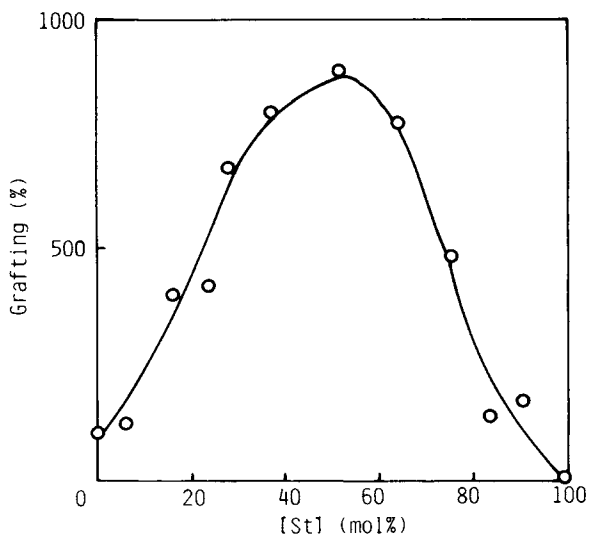


Fig. 4. Vapor phase photografting of St-AL monomer mixture on PE film sensitized with BPO. Quantity of monomer, 2 mL; irradiation, 60°C, 60 min.

Thus, complex factors, which cannot be sufficiently explained with monomer reactivity ratio, are supposed to participate in generation of the accelerating effect on grafting by monomer mixtures.

Allyl Monomers

It is generally known that an effective initiation could not be expected in radical polymerization of allyl compounds because of the reduced activity of allyl radicals toward the initiation due to a large resonance stabilization of the

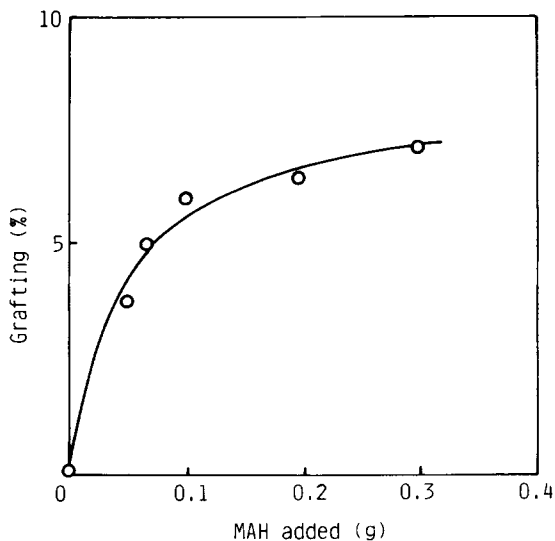


Fig. 5. Vapor phase photografting of MAH-AAL monomer mixture on PE film sensitized with BPO. Quantity of AAL, 2 mL; irradiation, 60°C, 60 min.

radicals. AL itself showed about 90% grafting. However, the grafting was sharply promoted by the addition of St to AL, affording a maximum percent grafting at about 50 mol % of St (Fig. 4). Ouchi and Ohiwa¹⁸ observed in copolymerization of AL (M_1) and St (M_2) initiated by AIBN that r_1 and r_2 are 0.22 and 0.33, respectively, and the rate of copolymerization is maximized at about 0.4 mol fraction of St. It is conceivable that such a characteristic of the copolymerization is directly reflected in the present grafting system. No initiation of grafting was recorded for AAL itself, but the polymerization took place by the addition of MAH to AAL, indicating an increased percent grafting with increasing quantity of MAH added, though the values are considerably low (Fig. 5). Further investigations were performed for allyl amine, allyl cinnamate, allyl thiocyanate, and allyl bromide. These monomers did not initiate the polymerization singly and the combination of monomers of generating the accelerating effect on the grafting could not be found out.

Solid Monomers

Figure 6 presents the results of photografting, which is carried out using the combination of MAH and various vinyl monomers. No grafting was recorded for St, VP, EVE, BVE, and BMA in the system without the combination with MAH. However, the grafting was initiated by adding MAH to these comonomers, showing that percent grafting increases with increasing the quantity of MAH added. Umezawa and Hirota¹⁹ observed an increased percent grafting due to addition of MAH to the liquid phase grafting of St on polypropylene fiber preirradiated in air with high-energy radiation. MAH is known to copolymerize easily with monomers such as St,²⁰ vinyl ethers,²¹ and

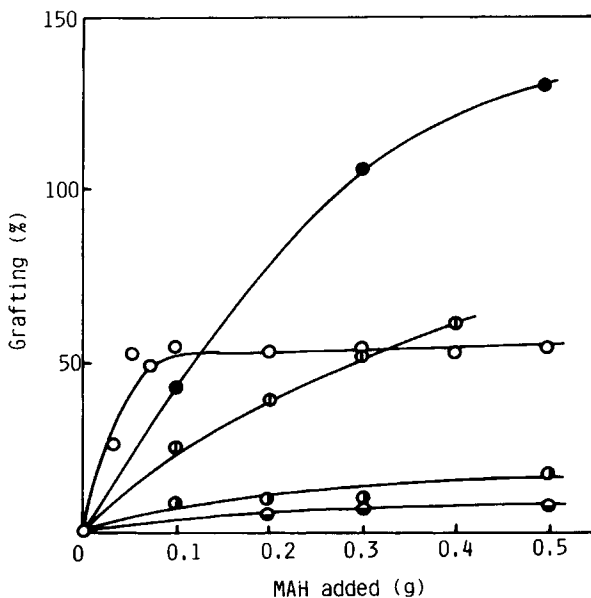


Fig. 6. Vapor phase photografting of monomer mixtures of MAH with comonomers on PE film sensitized with BPO. Quantity of comonomer, 2 mL; irradiation, 60°C, 60 min. (○) MAH-St; (●) MAH-BMA; (⊙) MAH-EVE (40°C); (⊚) MAH-BVE; (⊖) MAH-VP.

TABLE II
 Copolymerization Reactivity Ratios

M_1 (e value)	M_2	r_1	r_2	e value (M_2)
MAH (2.25)	St	0	0.04 ± 0.01	-0.80
	BVE	0.045	0	-1.20
	BMA	0.188 ± 0.035	0.003 ± 0.005	0.42
MI (1.35)	St	0.01	0.01	-0.80
	BMA	—	—	0.42
	VP	—	—	-1.14
	EVE	—	—	-1.17

BMA,²² though MAH itself is difficult to homopolymerize. Copolymerization reactivity ratios^{15,16,22} of MAH and other monomers, r_1 and r_2 , are shown in Table II. These combinations are suggested to be monomer pairs rich in an alternative copolymerizability.

Figure 7 presents the combination of MI and various vinyl monomers such as St, BMA, VP, and EVE, which are effective comonomers for MAH. It was found that percent graftings in each system increased with increasing the quantity of MI added, though MI itself did not initiate the grafting. Thus, the combination of MI and these monomers are available for the introduction of MI into PE substrate. Monomer reactivity ratios (Table II) of these monomer pairs (except St) are not available in literatures. However, e values suggest that MI easily interacts with these comonomers. This may be a factor for the increased percent grafting. As above, it was observed that MAH and MI as a

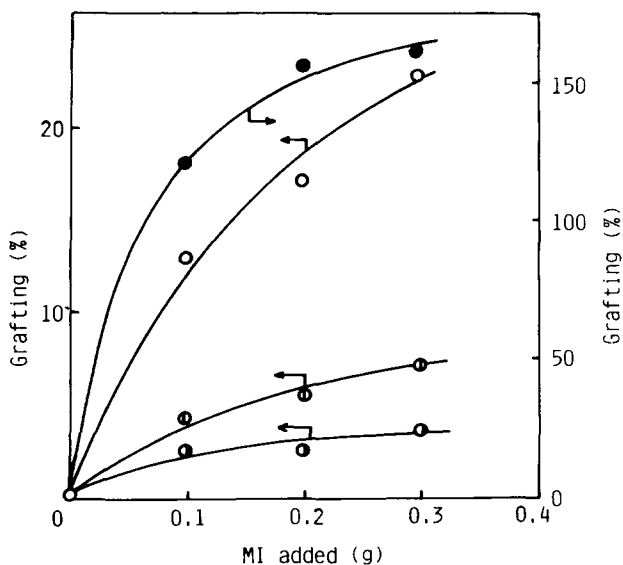


Fig. 7. Vapor phase photografting of monomer mixtures of MI with comonomers on PE film sensitized with BPO. Quantity of comonomer, 2 mL; irradiation, 60°C, 60 min. (○) MI-St; (●) MI-BMA; (⊙) MI-VP; (⊖) MI-EVE (40°C).

solid monomer in vapor phase photografting are supplied in their gaseous state with comonomer to the film substrate and participate in the grafting reaction.

IR Spectra of Grafted Films

Characteristic bands of IR spectra of typical grafted films are summarized in Table III. It was confirmed that both characteristic bands of St and comonomer are observed in IR spectra of the grafted films prepared in the system in which an accelerating effect on grafting is exhibited. The same results were obtained for AN-VP and AN-GMA monomer mixtures. On the other hand, it was found in St-MMA system that both monomer components are introduced as the grafted chain component, though the system does not exhibit the acceleration effect. With the combination of MAH with comonomers, both monomer components were also confirmed to constitute the grafted chains. Thus, it was clarified that both monomer components are contained in the grafted films prepared by using the monomer combinations.

Based on the above investigations, it is concluded that vapor phase photografting aiming at the effect of mixed monomer is a useful method for introducing monomers in PE substrate. In this system, the monomer reactivity ratio is supposed to be one of a measure of generating the accelerating effect on grafting due to the monomer combination. However, more detailed

TABLE III
IR Data of Grafted PE Films^a

Grafter sample	Wave number (cm ⁻¹)	Probable assignment
St-AN	756, 1495, 1603 2230	Benzene ring — CN group
St-GMA	756, 1495, 1603 1720	Benzene ring Ester Bond
St-AA	1250, 3050 756, 1495, 1603	Epoxy ring Benzene ring
	1710	C=O group of COOH group
	3400	—OH group of COOH group
St-MMA	756, 1495, 1603 1720	Benzene ring Ester Bond
MAH-St	1779, 1850 756, 1495, 1603	C=O group of anhydride Benzene ring
MAH-BMA	1779, 1850 756, 1495, 1603	C=O group of anhydride Benzene ring
MAH-VP	1779, 1850 1670	C=O group of anhydride C=O group of pyrrolidone ring
MAH-EVE	1779, 1850 1090	C=O group of anhydride Ether bond

^a Percent graftings range from 10 to 50.

studies including grafting conditions and copolymerization characteristics of combined monomers are in progress in this laboratory to provide insight into the effect of mixed monomer.

References

1. Y. Ogiwara, M. Kanda, M. Takumi, and H. Kubota, *J. Polym. Sci. Polym. Lett. Ed.*, **19**, 457 (1981).
2. N. Geacintov, V. Stannett, E. W. Abrahamson, and J. J. Hermans, *J. Appl. Polym. Sci.*, **7**, 54 (1960).
3. G. Odian, T. Acher, A. Rossi, and E. Ratchik, *J. Polym. Sci.*, **57**, 661 (1962).
4. W. H. Rapson and E. Kvasnicka, *Tappi*, **46**, 662 (1963).
5. I. Sakurada, T. Okada, S. Hatakeyama, and F. Kimura, *J. Polym. Sci. C*, **4**, 1233 (1963).
6. J. A. Harris and J. C. Arthur, Jr., *J. Appl. Polym. Sci.*, **14**, 3113 (1970).
7. K. Matsuzaki, S. Nakamura, and S. Shindo, *J. Appl. Polym. Sci.*, **16**, 1339 (1972).
8. T. Takahashi, T. Yasukawa, K. Murakami, H. Omichi, T. Sasuga, and K. Araki, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 1687 (1977).
9. J. L. Garnett, R. S. Kenyon, and J. D. Leeder, *J. Polym. Sci. Polym. Lett. Ed.*, **15**, 93 (1977).
10. S. N. Bhattacharyya and D. Malpas, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 939 (1982).
11. A. Hebeish, S. Shalaby, and A. Bayazeed, *J. Appl. Polym. Sci.*, **27**, 197 (1982).
12. M. D. Teli, H. T. Lokhanode, K. N. Rao, and M. H. Rao, *J. Appl. Polym. Sci.*, **29**, 1843 (1984).
13. M. H. Rao, K. N. Rao, H. T. Lokhande, and M. D. Teli, *J. Appl. Polym. Sci.*, **33**, 2707 (1987).
14. H. Kubota, N. Yoshino, and Y. Ogiwara, *J. Polym. Sci. Polym. Lett. Ed.*, **21**, 367 (1983).
15. G. E. Ham, Ed., *Copolymerization*, Wiley-Interscience, New York, 1964, p. 695.
16. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Wiley-Interscience, New York, 1975, p. II-105.
17. G. E. Ham, Ed., *Copolymerization*, Wiley-Interscience, New York, 1964, pp. 459, 655.
18. T. Ouchi and M. Ohiwa, *Kogyo Kagaku Zasshi*, **72**, 1587 (1969).
19. M. Umezawa and K. Hirota, *Kobunshi Kagaku*, **21**, 352 (1964).
20. J. Barton and I. Capek, *Makromol. Chem.*, **181**, 241 (1980).
21. D. Fles, R. Vukovic, V. Kuresevic, and R. Radicevic, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 35 (1981).
22. H. Boudevska and S. Platchkova, *Makromol. Chem.*, **182**, 1119 (1981).

Received January 30, 1989

Accepted February 7, 1989