

Vapor Phase Photografting of Methyl Methacrylate on Polymer Films: Accelerating Effects of Solvent Mixed with Monomer

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Synopsis

The effects of solvent mixed with monomer on benzophenone-sensitized photografting of methyl methacrylate on polymer films were investigated in vapor phase at 60°C. The grafting on nylon 6 film was promoted by adding a pertinent quantity of solvent, such as phenol, *m*-cresol, benzyl alcohol, and formic acid, to the monomer. The similar effects accelerating the grafting on polyester film were observed for solvent, such as *m*-cresol, phenol, *o*-chlorophenol, and nitrobenzene. Such an accelerating function of the solvents is supposed to originate in the swelling of the film substrates due to solvents. On the other hand, solvents such as *n*-decane, decalin, and *p*-xylene retarded the grafting on low-density polyethylene and polypropylene films. The differences in the solvent effects by the types of film substrates are discussed in terms of photoinduced radicals on the substrates containing solvents.

INTRODUCTION

In previous papers^{1, 2} the authors investigated vapor phase photografting of vinyl monomers on various types of polymer films. The grafting on polyethylene (PE) and polypropylene (PP) films took place easily to yield a high percent grafting when methyl methacrylate (MMA) was used as the monomers. However, activities of nylon 6 (NY) and polyester (PET) films toward the grafting of MMA were very low. In this paper the effects of solvent added to monomer on the vapor phase photografting of MMA were investigated in order to enhance the graft copolymerizability of the latter films.

Solvent effects³⁻¹² in liquid phase grafting have been widely examined, but a few^{2, 13} have been reported on the effects in vapor phase grafting. The authors² investigated the effects of mixed solvent on the photografting of acrylic acid (AA) on polymer films, in which a mixture of AA and solvent was supplied in vapor phase. The grafting was largely promoted by adding a pertinent quantity of water among the solvents to AA. This paper deals with the effects of solvents other than water.

EXPERIMENTAL

Samples

Low-density PE, PP, NY, and PET, 30 μm thick, were used as film samples. Sensitizers, benzophenone (BP), anthraquinone (AQ), and benzoyl peroxide (BPO), were of all reagent grades and used without further purification. The

film samples were immersed in acetone or chloroform solution containing 0.1 wt % sensitizer and 0.3 wt % poly(vinyl acetate) ($\bar{M}_w = 100,000$) and dried to prepare sensitizer-coated films.

MMA, AA, styrene, and acrylonitrile were purified by distillation. Solvents were of all reagent grades and used without further purification.

Vapor Phase Photografting

Vapor phase photografting was carried out using a Pyrex glass tube.¹ The film sample (54 × 8 mm) fixed on a sample holder was kept at the center part of the tube and 2 mL of MMA or solution of 2 mL of MMA and a known volume of solvent was placed at the bottom part. The pressure of the system, after several freeze-thaw cycles, was adjusted to 1 mm Hg. 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 suitable solvents to remove homopolymers. Percent grafting was taken as the percentage of weight increase of the original film.

Adsorption of Solvent on Film Sample

The film sample (A-g) fixed on a sample holder was kept at the center part of the Pyrex glass tube described above and 1 ml of solvent was placed at the bottom part. The pressure of the system was adjusted to 1 mm Hg, and then the glass tube was kept at 60°C for 60 min without photoirradiation. After the

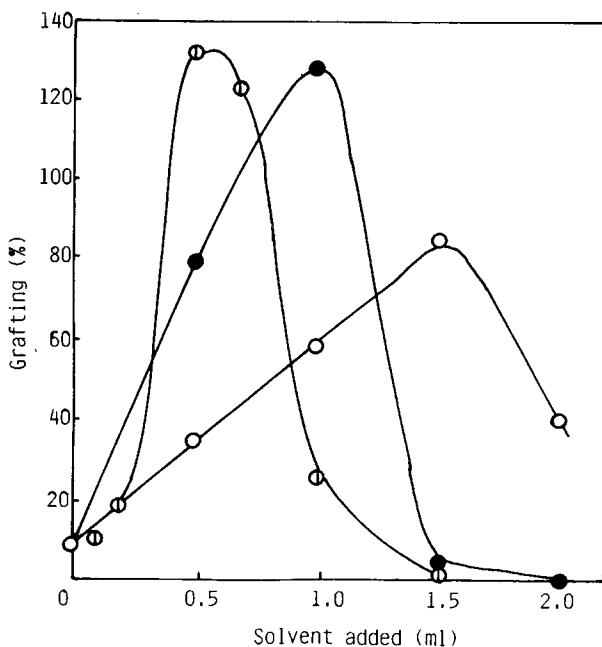


Fig. 1. Effect of solvents on photografting of MMA on NY film sensitized with BP. Concentration of BP 0.1 wt %; quantity of MMA 2 mL; irradiation 60°C, 60 min. (○) Benzyl alcohol; (⊙) phenol; (●) *m*-cresol.

treatment an excess of solvent on the film surface was wiped by filter paper and followed by weighing the treated film ($B-g$). Amount of solvent adsorbed on the film sample was indicated as a weight increase, which is defined as follows:

$$\text{weight increase (\%)} = \frac{B - A}{A} \times 100$$

Measurement of ESR Spectrum

The quartz glass tube (5 mm internal diameter) containing the film sample was flushed with nitrogen gas and irradiated at -196°C for 30 min with light of $\lambda > 220$ nm. The light source was a Toshiba high-pressure mercury lamp H400-P (400 W) and the distance between the light source and the sample was set at 10 cm. ESR spectra were recorded with x-band and 100-kcps field modulation at -196°C with a JEOL JES-ME-X.

RESULTS

The effects of various solvents on vapor phase photografting on MMA on NY film are shown in Figure 1. The abscissa in the figure represents the quantity of solvent added to the 2 mL of MMA. The percent grafting in the system without solvent was about 10%. When the solvents such as phenol, *m*-cresol, and benzyl alcohol, which are known as a swelling reagent for NY,

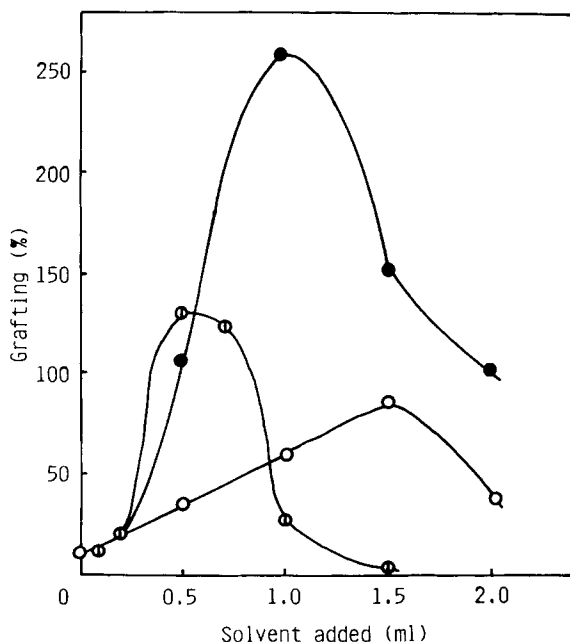


Fig. 2. Effect of solvent mixture on photografting of MMA on NY film sensitized with BP. Concentration of BP 0.1 wt %; quantity of MMA 2 mL; irradiation 60°C , 60 min. (○) Benzyl alcohol; (◇) phenol; (●) benzyl alcohol-phenol (1:1 v/v) mixture.

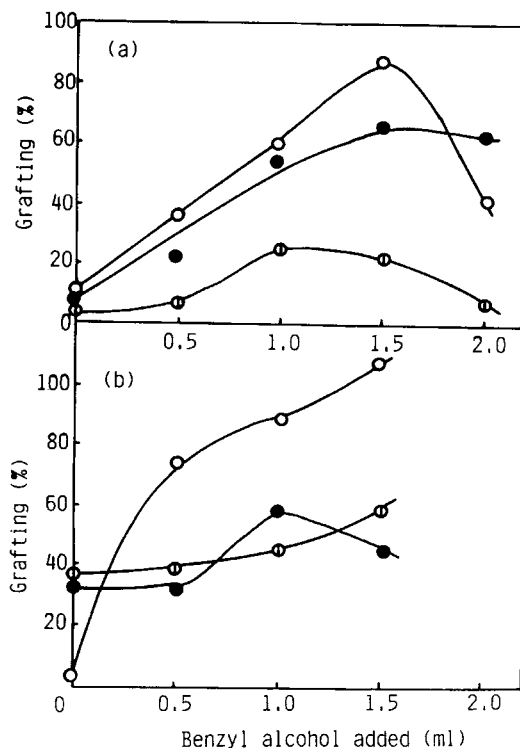


Fig. 3. Effect of benzyl alcohol on photografting on NY film. (a) Concentration of sensitizer 0.1 wt %; quantity of MMA 2 mL; irradiation 60°C, 60 min. (○) BP, (◇) AQ, (●) BPO. (b) Concentration of BP 0.1 wt %, quantity of monomer 2 mL, irradiation 60°C, 60 min. (○) Styrene; (◇) acrylonitrile; (●) acrylic acid.

were added to MMA, the percent graftings increased with increasing the quantity of the solvent, but they decreased gradually after passing a maximum value. Thus, it is clear that a pertinent quantity of solvent, such as phenol, *m*-cresol, and benzyl alcohol, mixed with MMA has a function to improve the activity of NY film toward the grafting. A part of the film was lost during the grafting due to dissolution in the system, to which 1.5 mL phenol or *m*-cresol was added, but such phenomenon was not observed for benzyl alcohol. The grafting was carried out using a solvent mixture of phenol and benzyl alcohol with a volume ratio of 1:1 in order to protect the dissolution of film due to solvent, and the result is shown in Figure 2. The use of the solvent mixture resulted in higher percent grafting than those of each solvent alone, showing no dissolving phenomenon of film.

The type of sensitizer and nature of monomer were examined using benzyl alcohol, and the results are presented in Figure 3. The effects of benzyl alcohol to accelerate the grafting were commonly observed for each sensitizer. The percent grafting decreased in the order BP > BPO > AQ. On the other hand, the solvent effects were also recorded for styrene, AA, and acrylonitrile besides MMA. Styrene was a special case where an extremely high improvement of the polymerizability is achieved. Thus, benzyl alcohol exhibited a function to

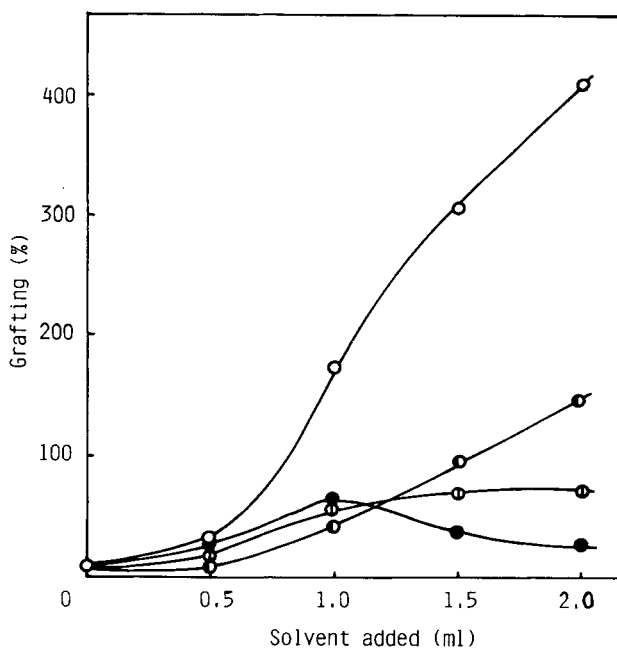


Fig. 4. Effect of various acids on photografting of MMA on NY film sensitized with BP. Concentration of BP 0.1 wt %; quantity of MMA 2 mL; irradiation 60°C, 60 min. (○) 40% Formic acid; (⊙) 40% acetic acid; (●) 40% propionic acid; (●) 5% hydrochloric acid.

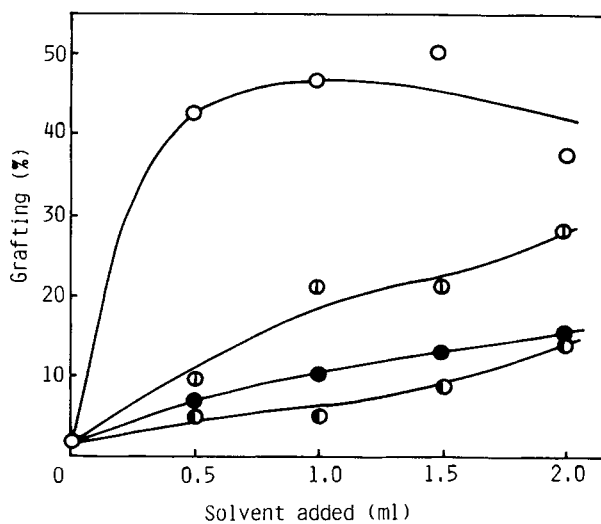


Fig. 5. Effect of solvents on photografting of MMA on PET film sensitized with BP. Concentration of BP 0.1 wt %, quantity of MMA 2 mL; irradiation 60°C, 60 min. (○) *m*-Cresol; (⊙) phenol; (●) nitrobenzene; (●) *o*-chlorophenol.

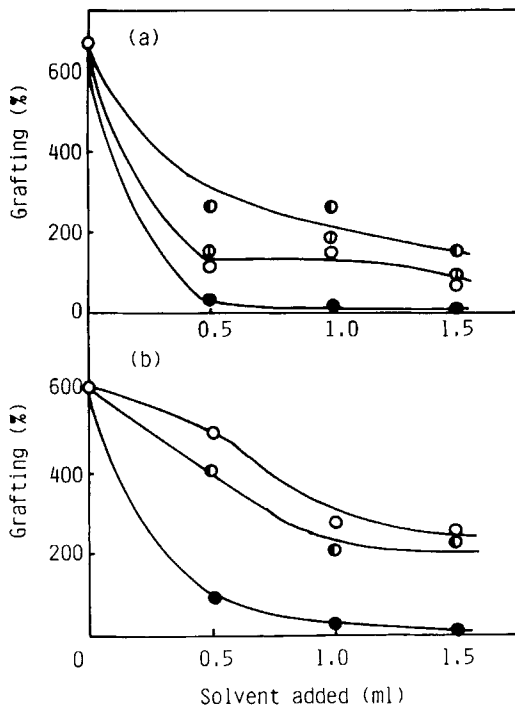


Fig. 6. Effect of solvents on photografting of MMA on polyolefin films sensitized with BP. Concentration of BP 0.1 wt %; quantity of MMA 2 mL; irradiation 60°C, 60 min. (a) PE film: (○) decalin; (⊙) *p*-xylene; (●) *n*-decane; (●) benzyl alcohol. (b) PP film: (○) decalin; (⊙) *n*-decane; (●) benzyl alcohol.

promote vapor phase photografting irrespective of the type of sensitizer and nature of monomer.

The effects of organic and inorganic acids as a solvent for NY were studied, and the results are shown in Figure 4. Each acid was used as its aqueous solution. The function accelerating the grafting was observed for hydrochloric acid additional to organic acids. The function of formic acid was remarkable among the solvents, giving about 400% grafting in the 2-mL-added system. It has been observed in radiation- and UV-induced graftings¹⁴⁻²² on cellulose and polyolefins in liquid phase that acids accelerate the polymerization and formic acid¹⁶ sensitizes the photografting. The marked enhancement of photografting by formic acid in this study may also be ascribed to the sensitization effect of formic acid besides swelling function of NY substrate by acids described later.

Figure 5 shows the solvent effects on photografting of MMA on PET film. The percent grafting in the system without solvent was about 5%. The percent grafting was risen by adding *m*-cresol, phenol, *o*-chlorophenol, and nitrobenzene to the polymerization system, indicating a function of the solvents to accelerate the grafting. However, the percent grafting was lower than that of NY film.

Figure 6 presents the solvent effects on photografting on polyolefin films. The grafting on PE and PP films took place easily, resulting in about 600% grafting in the system without solvent. The percent graftings of PE and PP

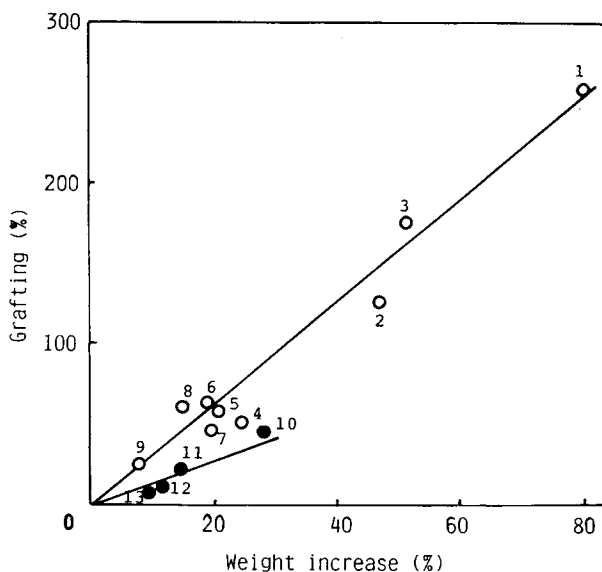


Fig. 7. Relationship between percent grafting and weight increase of solvent. (○) NY film: (1) benzyl alcohol-phenol (1:1) mixture; (2) *m*-cresol; (3) 40% formic acid; (4) 40% acetic acid; (5) 20% formic acid; (6) 40% propionic acid; (7) 5% hydrochloric acid; (8) benzyl alcohol; (9) phenol. (●) PET film: (10) *m*-cresol; (11) phenol; (12) *o*-chlorophenol; (13) nitrobenzene.

decreased with increasing the quantity of solvent added when *n*-decane and *p*-xylene, which are known as a swelling reagent for PE and PP, were mixed with MMA. Benzyl alcohol effective for NY film was found not to have the effects for polyolefins. Thus, the effects of solvent on vapor phase photografting differ by the kind of film substrates, where the accelerating effects are indicated for NY and PET, while the retarding effects for polyolefins.

DISCUSSION

Vapor phase photografting of MMA on NY and PET films was sharply facilitated by adding a pertinent quantity of solvent for each substrate to monomer (Figs. 1, 3, and 4). These solvents are phenol, *m*-cresol, benzyl alcohol, *o*-chlorophenol, and nitrobenzene, which are supplied together with monomer to film sample in vapor phase. Various solvent gases were exposed at 60°C for 60 min to NY and PET films, and the amount of solvent adsorbed on the film was measured, which is represented as weight increase. Figure 7 shows relationship between the weight increase and percent grafting of MMA recorded in the system, to which 1 mL solvent is added. Higher percent grafting was indicated for the sample with higher amount of solvent adsorbed in common with NY and PET films. This fact suggests that the solvents contribute to swelling of the film substrates, resulting in the accelerated grafting.

Vapor phase photografting on polyolefin films was suppressed by adding solvent, *n*-decane and *p*-xylene, to monomer (Fig. 6). Namely, the solvent effects observed for NY and PET are not indicated for the solvents, though they have swelling function for polyolefin substrates. The effect of solvent on

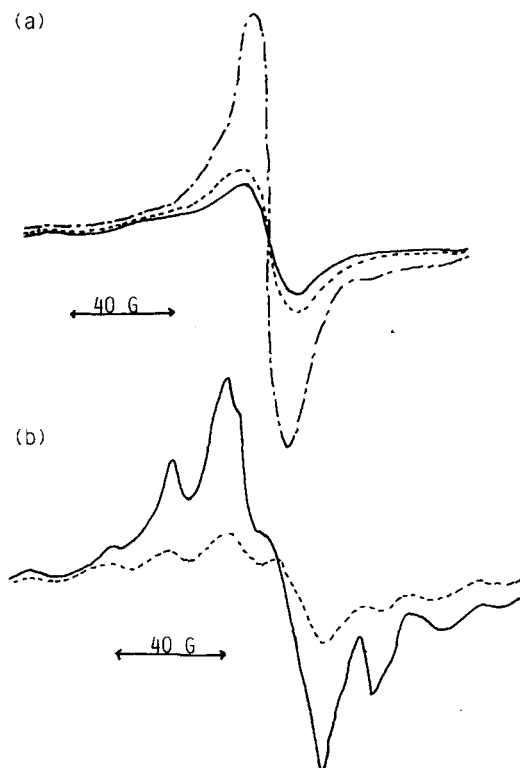


Fig. 8. ESR spectra of NY and PET films irradiated with light of $\lambda > 220$ nm at -196°C for 30 min. (a) NY film: (—) untreated film; (---) film treated with 20% formic acid; (- - -) film treated with 40% formic acid. (b) PE film: (—) untreated film; (---) film treated with *n*-decane.

photoinduced radicals on NY and PE was investigated. The film samples were immersed in solvent at 60°C for 60 min to prepare a solvent-containing film sample. ESR spectra of irradiated samples are shown in Figure 8. Higher spectrum intensity was given for NY treated with an aqueous solution of formic acid with higher concentration, indicating the accelerated radical formation on NY substrate due to formic acid. The swelling of NY substrate due to formic acid is supposed to be a factor leading to the facilitated radical formation on the substrate and the advantageous grafting. The authors observed in previous papers^{23,24} that swelling treatment for fibrous polymers, poly(vinyl alcohol), NY, PET, and cellulose, promotes the formation of their radicals by photoirradiation, resulting in an effective initiation of liquid phase photografting.

On the other hand, the spectrum intensity of the irradiated PE was largely decreased by treating it with *n*-decane. Namely, the treatment of PE with *n*-decane led to the retarded radical formation on PE. The solvent effect is supposed to be reflected on the vapor phase grafting, resulting in the decreased percent grafting in the *n*-decane-added system. However, it is not clear how the solvent affects to the PE substrate followed by depressing the photoinduced radicals.

Based on the above investigations, it is confirmed that the use of a mixture of monomer and solvent having a swelling function for polymer substrates is a useful method to enhance their abilities to initiate vapor phase photografting. This is true for the grafting on NY and PET films. However, the method is not always available for polyolefin films, suggesting a complexity of the solvent effects on the grafting.

References

1. Y. Ogiwara, M. Kanda, M. Takumi, and H. Kubota, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 457 (1981).
2. Y. Ogiwara, K. Torikoshi, and H. Kubota, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 17 (1982).
3. G. G. Daian, A. Rossi, and E. N. Trachtenberg, *J. Polym. Sci.*, **42**, 575 (1960).
4. G. Odian, M. Sobel, A. Rossi, and R. Klein, *J. Polym. Sci.*, **55**, 663 (1961).
5. M. Tsunooka, M. Tanaka, and I. Murata, *Kobunshi Kagaku*, **22**, 107 (1965).
6. H. Ishibashi, *Kobunshi Kagaku*, **25**, 481 (1968).
7. S. Machida, I. Kamel, and I. Silverman, *J. Polym. Sci., A-1*, **8**, 3329 (1970).
8. H. Kubota, Y. Murata, and Y. Ogiwara, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 485 (1973).
9. N. P. Davis, J. L. Garnett, and R. Urquhart, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 537 (1976).
10. J. A. Harris, J. C. Arthur, Jr., and J. H. Carra, *J. Appl. Polym. Sci.*, **22**, 905 (1978).
11. P. J. Burchill, D. M. Pinkerton, and R. H. Stacewicz, *J. Macromol. Sci. Chem.*, **A14**, 79 (1980).
12. S. N. Bhattacharyya and D. Maldas, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 939 (1982).
13. H. L. Needles and K. W. Alger, *J. Appl. Polym. Sci.*, **22**, 3405 (1978).
14. S. Dilli, J. L. Garnett, and D. H. Phuoc, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 711 (1973).
15. J. L. Garnett and N. T. Yen, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 225 (1974).
16. N. P. Davis and J. L. Garnett, in *Modified Cellulose*s, R. M. Rowell and R. A. Young, Eds., Academic, New York, 1978, p. 197.
17. J. L. Garnett, *Radiat. Phys. Chem.*, **14**, 79 (1979).
18. J. L. Garnett, R. S. Kenyon, R. Levat, M. A. Long, and N. T. Yen, *J. Macromol. Sci. Chem.*, **A14**, 87 (1980).
19. J. L. Garnett and S. V. Jankiewicz, *Radiat. Phys. Chem.*, **18**, 469 (1981).
20. J. L. Garnett, S. V. Jankiewicz, and D. F. Sangster, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 171 (1982).
21. C. H. Ang, J. L. Garnett, S. V. Jankiewicz, and D. F. Sangster, *Graft Copolymerization of Lignocellulosic Fibers*, ACS Symposium Series No. 187, N. S. Hon, Ed., Am. Chem. Soc., New York, 1982, p. 141.
22. P. Dorwianyn and J. L. Garnett, *Polym. Mat. Sci. Eng.*, **57**, 278 (1987).
23. H. Kubota, Y. Ogiwara, and K. Matsuzaki, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2809 (1974).
24. Y. Ogiwara, H. Kubota, and T. Yasunaga, *J. Appl. Polym. Sci.*, **19**, 887 (1975).

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