

Benzil-Sensitized Photografting of Methacrylic Acid on Low-Density Polyethylene Film

INTRODUCTION

It is well known that aromatic ketones act as photoinitiator for photopolymerization^{1,2} of vinyl monomers and their function is classified into two types: hydrogen abstracting and photofragmenting. Benzophenone (BP) is typical of the former type and benzoin and its derivatives are involved in the latter type. Benzil (BZ), aromatic diketone, has been reported to act as hydrogen-abstracting initiator³⁻⁸ for photopolymerization of vinyl monomers. Recently, Allen et al.⁹ studied photopolymerization of *n*-butyl methacrylate sensitized with eight kinds of aromatic ketones. They observed that BZ-sensitized polymerization is accelerated in a large extent than BP- and benzoin ethyl ether (BEE)-sensitized systems by adding diethylmethylamine to the system, in which BZ primarily acts as photofragmenting initiator.

Aromatic ketones such as BP and BEE also are useful photoinitiators for photografting¹⁰⁻¹⁴ of vinyl monomers. This paper deals with comparative examinations of photografting behaviors sensitized with BZ, BP, and BEE in order to clarify the characteristics of BZ-sensitized photografting.

EXPERIMENTAL

Materials

BZ, BP, and BEE were all of reagent grade and used without further purification. The film used was low-density polyethylene (PE) (thickness = 30 μm). The photoinitiator-coated films were prepared by dipping the films into an acetone solution containing known quantities of photoinitiator and 0.5 wt % of poly(vinyl acetate) ($M_w = 100,000$) and by drying the treated films at room temperature under reduced pressure to remove solvent. The quantities of photoinitiator and poly(vinyl acetate) coated by this procedure were too small to analyze gravimetrically. Accordingly, the amount of photoinitiator in the film was represented as the concentrations in the acetone solution used for doping. However, the quantities of BZ, BP, and BEE on the film sample could be estimated by spectrophotometry as about 4.7×10^{-8} , 4.9×10^{-8} , and 4.1×10^{-8} mole per apparent unit surface (cm^2) of the film sample for the concentration of 0.3 wt % used for doping, respectively. The quantities slightly decreased by immersing the initiator-coated film samples in 20 mL water containing 1 mL methacrylic acid (MAA) at 60°C for 60 min without photoirradiation. The magnitude of the decrease was less than about 1% of the initial quantity and nearly equal among the three photoinitiators. MAA was purified by distillation under reduced pressure.

Photografting

The film sample (3×10 cm, 0.05 g) was placed in a Pyrex glass tube; 20 mL water, boiled beforehand to exclude dissolved oxygen, and 1 mL (1.02 g) of MAA were added. After introducing nitrogen gas into the system for 5 min, the system was closed and liquid phase photografting was carried out at 60°C. 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 to remove homopolymer of poly(MAA). The extraction¹⁵ is known to be effective for removing the homopolymer in the film. 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.

Electron Probe Microanalysis (EPMA)

Grafted poly(MAA) was converted to potassium salts by immersing the grafted film in aqueous solution of 1% potassium hydroxide at room temperature for 24 h. Distribution profile of potassium

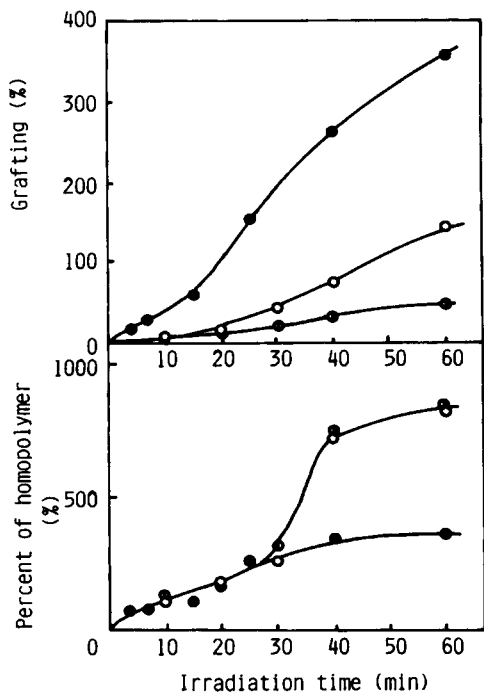


Fig. 1. Photografting of MAA on PE films sensitized with (○) BZ, (●) BP, and (○) BEE. Concentration of photoinitiator is 0.3 wt %. Irradiation was carried out at 60°C.

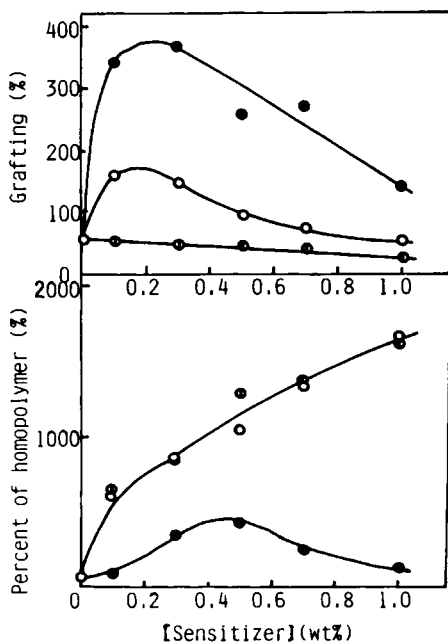


Fig. 2. Effect of photoinitiator concentration on photografting of MAA on PE films sensitized with (○) BZ, (●) BP, and (○) BEE. Irradiation was carried out at 60°C for 60 min.

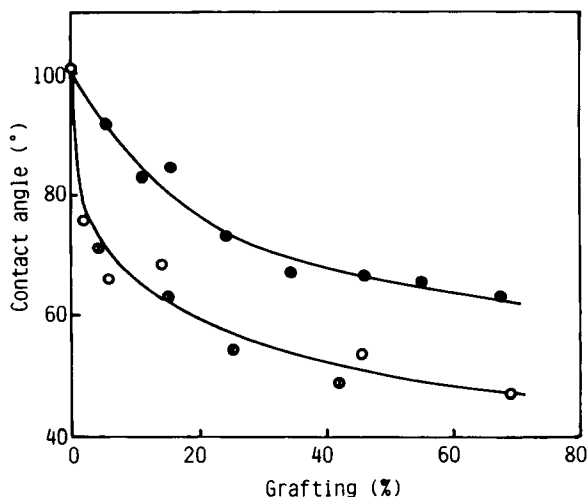


Fig. 3. Contact angle with water of MAA-grafted PE films prepared by using photoinitiator, such as (○) BZ, (●) BP, and (◐) BEE. Grafting was carried out at 60°C using 0.3 wt % photoinitiator.

atom of grafted film was measured with electron probe microanalyzer model EPM-810Q of Shimadzu Co., Ltd.

RESULTS AND DISCUSSION

Ultraviolet spectra of BZ, BP, and BEE in dichloromethane recorded absorption maxima at 370, 340, and 330 nm and their extinction coefficients were 71, 132, and 209, respectively. Each absorption maximum shifted at lower wavelengths, 365, 328, and 323 nm, respectively, in methanol which is more polar solvent than dichloromethane. This suggests that the absorptions are originated in the $n-\pi^*$ transition of the ketone. The Pyrex glass tube used in this study transmits light with $\lambda > 290$ nm. Thus, the photoinitiators absorb sufficiently the light irradiated in the present polymerization system, though the extinction coefficients are considerably different among the three.

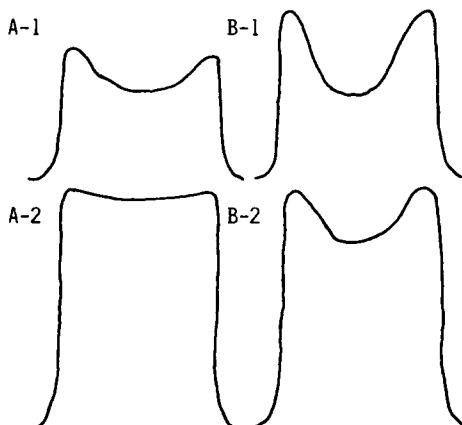


Fig. 4. Concentration distribution of potassium atom in MAA-grafted PE film obtained by EPMA. A and B represent samples prepared by using BP and BZ photoinitiators, respectively. Grafting (%): (A-1) 34.4; (A-2) 68.1; (B-1) 45.3; (B-2) 69.4.

Figure 1 shows the results of photografting sensitized with BZ, BP, and BEE. The percent graftings of each sensitized system increased with the irradiation time and the extent of magnitude decreased in the order BP > BZ > BEE. On the other hand, the percent of homopolymer was found to be almost same between the three systems up to 30 min of irradiation time. In the irradiation time beyond 30 min, however, the formation of homopolymer became very active in BZ- and BEE-sensitized systems, showing about twice as much as BP-sensitized system. Figure 2 presents the effect of the concentration of photoinitiator on photografting. The percent grafting and the percent of homopolymer in the system sensitized with BP showed maxima at a certain concentration, resulting in suppressed polymerization at a high concentration of BP. The percent grafting of BEE-sensitized system decreased with increasing the concentration of BEE while increasing the percent of homopolymer. Thus, the formation of homopolymer was sharply promoted in the BEE-sensitized system, so that low levels of percent grafting resulted. It was observed in BZ-sensitized system, on the other hand, that the percent grafting gives a curve similar to the BP-sensitized system, while the percent of homopolymer increased with the concentration of BZ. BZ showed polymerization behaviors close to those of BEE in that the formation of homopolymer proceeds favorably.

BP and BEE on the film surface are seen to exhibit well known photochemical reactions. Namely, BP^{16,17} is excited to a triplet state, which might extract the hydrogen atom from PE substrate to yield PE radicals capable of initiating grafting. On the other hand, BEE^{2,18} may decompose by photoirradiation to produce fragment radicals of photoinitiator, which is sure to contribute to the extraction of the hydrogen atom from PE substrate. The fragment radicals in the latter may also react with monomer to yield homopolymer. This should be a main cause for higher percent of homopolymer in BEE-sensitized system than BP-sensitized one. As mentioned above, BZ gave almost the same percent of homopolymer as that of BEE. At the present time, it is not clear why BZ behaves like BEE with respect to the formation of homopolymer, though BZ seems to act as photofragmenting initiator.

Figure 3 shows the contact angle of water on the MAA-grafted PE film. The contact angles of each grafted sample decreased gradually with the percent grafting, showing hydrophilization of the surface of PE film by means of photografting of MAA. The contact angle of the sample prepared by BZ-sensitized system (BZ sample) was lower than that of the sample prepared by BP-sensitized system (BP sample), but it was equal to that of the sample prepared by using BEE. This is supposed to mean that the grafted chains of the BZ sample locate mainly on the film surface. Figure 4 shows the distribution profile of the potassium atom in the grafted film. It was observed that the grafted chains tend to distribute in the inside of the film with increasing the percent grafting, but the grafted chains of the BZ sample are liable to locate on the surface as compared with the BP sample. Such difference in the distribution of grafted chains between the both samples seems to reflect directly on wettability of the MAA-grafted PE film.

Based on the above investigations, it was found that BZ-sensitized photografting of MAA on PE film is characterized by the polymerization behaviors similar to BEE rather than BP and by the distribution of grafted chains on the film surface. In BZ-sensitized photografting, the formation of homopolymer overcomes that of grafted polymer and this causes the distribution of grafted chains different from the BP sample.

References

1. G. Oster and N. L. Yang, *Chem. Rev.*, **68**, 125 (1968).
2. S. P. Pappas, *Radiat. Curing*, **28** (1981).
3. D. L. Bunbury and C. T. Wang, *Can. J. Chem.*, **46**, 1473 (1968).
4. D. L. Bunbury and C. T. Wang, *Can. J. Chem.*, **47**, 2045 (1969).
5. A. Ledwith, P. J. Russel, and L. H. Sutcliffe, *J. Chem. Soc. Perkin Trans. II*, 1925 (1972).
6. J. Hutchinson and A. Ledwith, *Polymer*, **14**, 405 (1973).
7. P. K. Sengupta and S. K. Modak, *J. Macromol. Sci. Chem.*, **A20**, 789 (1983).
8. M. V. Encinas, E. Lissi, L. Gargallo, D. Radic, and R. Sigdman, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 2469 (1984).
9. N. S. Allen, F. Catalina, P. N. Green, and W. A. Green, *Eur. Polym. J.*, **22**, 49 (1986).
10. N. Geacintov, V. Stannett, E. W. Abrahamson, and J. J. Hermans, *J. Appl. Polym. Sci.*, **3**, 54 (1960).
11. S. Tazuke and H. Kimura, *Makromol. Chem.*, **179**, 2603 (1978).
12. C. H. Ang, J. L. Garnett, R. Levot, M. A. Long, and N. T. Yen, *J. Polym. Sci. Polym. Lett. Ed.*, **18**, 471 (1980).

13. Y. Ogiwara, M. Kanda, M. Takumi, and H. Kubota, *J. Polym. Sci. Polym. Lett. Ed.*, **19**, 457 (1981).
14. H. Kubota, K. Kobayashi, and Y. Ogiwara, *Polym. Photochem.*, **7**, 379 (1986).
15. Y. Ogiwara, K. Kobayashi, and H. Kubota, *J. Polym. Sci. Polym. Lett. Ed.*, **24**, 511 (1986).
16. G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).
17. N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, California, 1978, p. 261.
18. A. Merlin and J. P. Fouassier, *Makromol. Chem.*, **181**, 1307 (1980).

HITOSHI KUBOTA

Department of Chemistry
Faculty of Engineering
Gunma University
Kiryu, Gunma 376, Japan

YASUO HATA

Central Research Laboratory
Idemitsu Kosan Co. Ltd.
Kimitsu-Gun, Chiba 292-01, Japan

Received November 8, 1988

Accepted June 9, 1989