CHEMISTRY LETTERS, pp. 1153-1156, 1992.

Photo-Initiated Amine-Formation in a Polymer Matrix and Its Application to Thermal Cross-Linking of Poly(Glycidyl Methacrylate) Films

Ken-ichi ITO,* Masamichi NISHIMURA, Minoru SASHIO, and Masahiro TSUNOOKA*
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, 1-1, Gakuen-cho, Sakai, Osaka 593

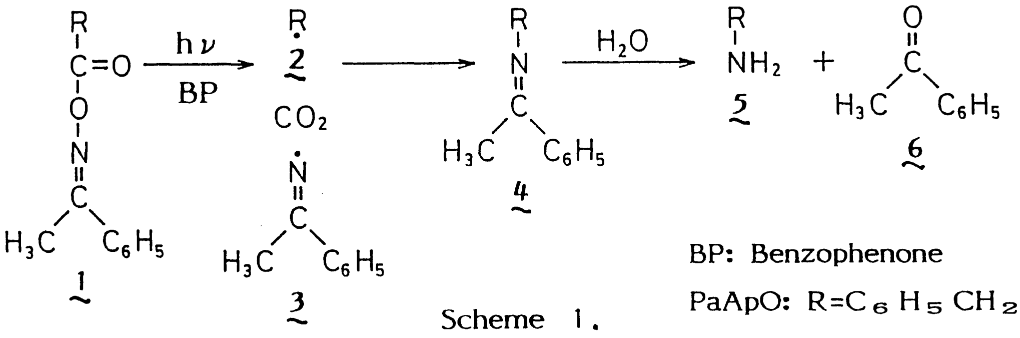
Photolysis of an *O*-acyloxime in a polymer solid was applied to thermal cross-linking of poly(glycidyl methacrylate) films.

Photo-initiated acid-formation is interesting from the view points of cationic polymerization of vinyl ethers or epoxides1) and catalytic behavior of the acids in the thermolysis of t-butoxycarbonyloxy groups in photoresists.2) Similarly, although photo-initiated base-formation is also thought to be very valuable in its application, only a few studies on the formation are reported. We reported that in the photolysis of copolymers of acryloyl acetophenone oxime (AAPO) with styrene (St) pendant acyloxyimino (AOI) groups led to pendant amino groups in a good yield3) and that the pendant amino groups were effective in cross-linking of the pendant epoxy groups in the same polymer.4) Willson et al. reported that photolysis of a cobalt-amine complex led to the formation of ammonia which induces the cross-linking of a 2,3-epoxypropyl acrylate - methyl methacrylate copolymer upon heating.5) Winkle et al. utilized an amine generated by photolysis of an o-nitrobenzyl carbamate in a positive photoresist.6) Fréchet et al. reported that photolysis of α,α-dimethyl-3,5-dimethoxybenzyl carbamates7) and o-nitrobenzyl carbamates8) led to the formation of amines and that resulting amines could be utilized as cross-linkers.

In the previous paper,4) although we reported that the pendant amino groups which were introduced by the photolysis of pendant AOI groups were utilized for the insolubilization of the copolymers bearing both AOI and epoxy groups, the area of their application was limited because both groups should be included in a same polymer. Furthermore, only their cross-linking behavior at room temperature was investigated. Recently, we have found that the photolysis of *O*-acyloximes in poly(glycidyl methacrylate) films followed by heating induces the effective cross-linking of pendant epoxy groups. In this paper, we report the formation of benzylamine (BA) by the photolysis of *O*-phenylacetyl acetophenone oxime (PaApO) in polystyrene (PSt) films and its application to thermal cross-linking of poly(glycidyl methacrylate) (PGMA) films.

PSt films ($\bar{M}n$=113000, ca. 45 µm) with 5 wt% PaApO and 10 wt% benzophenone (BP) as a sensitizer were prepared by casting a tetrahydrofuran (THF) solution of PSt and additives on a Petri dish. The films were irradiated with a high-pressure mercury lamp (Ushio UM102) at a distance of 10 cm at room temperature in air or N_2 for 1 h to photolyze PaApO completely. After H_2O-vapor treatment i.e. an exposure to saturated vapor of water (25 ℃, 10 min), the film (ca. 0.05 g) was dissolved in 2 ml of THF. Then 3,5-dinitrobenzoyl chloride (DNBC, ca. 0.02 g) was added to the solution and the solution was heated at 60 ℃ for 1 h. In this method BA was converted into *N*-(3,5-dinitrobenzoyl)benzylamine (DNBBA) quantitatively. After the PSt was precipitated by adding 10 ml of methanol to the solution and removed by centrifugation, the amount of DNBBA was determined on a high-pressure liquid chromatograph equipped with an UV detector (JASCO 870-UV).

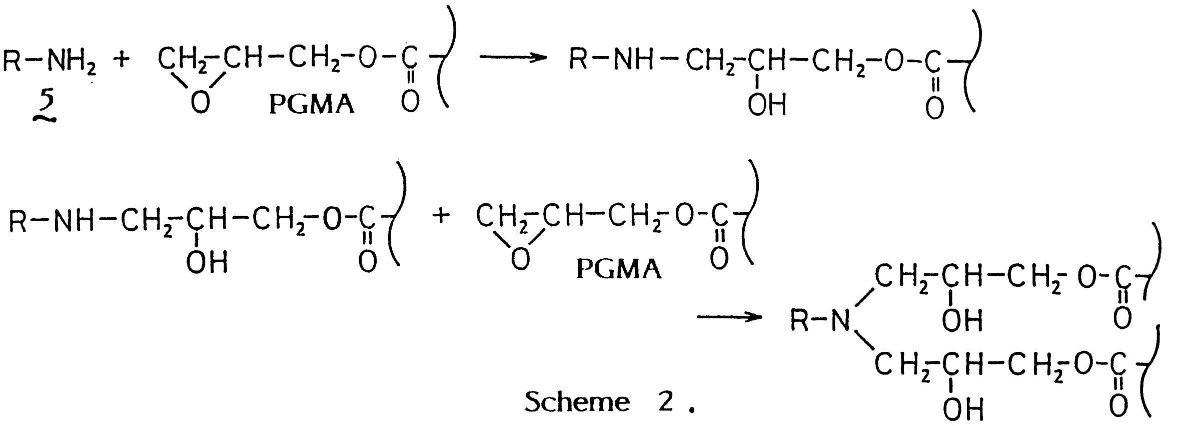
PGMA ($\bar{M}n$=117000) thin films (ca. 1 µm) on a quartz or thick films (ca. 35 µm) with 5 wt% PaApO and 10 wt% BP were prepared and irradiated in a similar manner as above. Post-treatment with H_2O-vapor and/or heating at 80 ℃ was carried out after irradiation. Then the thin or thick films were immersed in THF for 5 min or 1 d at room temperature, respectively. The insoluble fraction in the thin films was determined from the thickness of the films before and after dissolution measured using an interference microscope (Nikon OPTIPHOT). The insoluble fraction in the thick films was determined by weighing the dried insoluble polymer separated by centrifugation.



BP: Benzophenone

PaApO: R=$C_6H_5CH_2$

Scheme 1.



Scheme 2.

Scheme 1 shows that the photolysis of PaApO (**1**) leads to the formation of the alkyl radical (**2**), the imino radical(**3**), and carbon dioxide. Then the azomethine (**4**) is formed by the recombination of **2** and **3** , and finally BA (**5**) is generated by the hydrolysis of **4** . Scheme 2 shows that cross-linking of polymers occurs by reaction of amines with the epoxy groups in the polymer.9)

As shown in Table 1, the recombination yield i.e., the yield of BA in photolysis of PaApO in PSt films under N_2, was almost the same as that of the AAPO-St copolymer under air and $N_2$3) and higher than that of *O*-phenylacetyl benzophenone oxime in solution under N_2.10) This result shows that the recombination occurs more effectively in a polymer matrix than in solution. Since local segment motions of main-chains in PSt do not occur at room temperature, which is lower than the Tg of the PSt film containing PaApO and BP, 54 ℃, it is deduced that the movement of PaApO was restricted by the PSt-chains. Thus this result suggests the increase in the yield by the cage effect in the polymer matrix. The yield in the photolysis of PaApO under air was lower than that under N_2, which was very different from the result of a AAPO-St copolymer and it was apparent that O_2 in air trapped the radicals formed in the photolysis of PaApO.

Table 1. Recombination Yields of Imino Radicals and Alkyl Radicals

Compound	Condition	Atmosphere	Yield/%
PaApO	PSt Film	Air	35
		N_2	72
AAPO(26.3)-St Copolymer	Film	Air, N_2	70 3)
O-phenylacetyl benzophenone oxime	Benzene Solution	N_2	51 10)

Figures 1 and 2 show that the insoluble fraction in the irradiated films increased with irradiation time without post-treatment in both films. Judging from the formation of amines in Table 1, it is deduced that the cross-linking of PGMA proceeds by the reaction of amines with the epoxy groups. The facts that THF was good solvents for PaApO and PGMA and that the results in Figs. 1 and 2 were reproducible suggest that the PaApO dispersed homogeneously in the films. Since only H_2O-vapor treatment had no influence on the insoluble fraction in both films, most of the azomethines in the films are considered to be hydrolyzed by the water vapor in air during irradiation even in the thick films, resulting in the formation of the amines. Heating or the combination of H_2O-vapor treatment and heating accelerated the insolublization in both films. These results suggest the further hydrolysis of the residual azomethines and/or the acceleration of the reaction of the amines with the epoxy groups. It can be seen from these results that the photolysis of PaApO and the subsequent cross-linking can occur in thick films as well as in the thin films, although it is unknown to what extent the thickness affects the reactions. Further details are now under investigation.

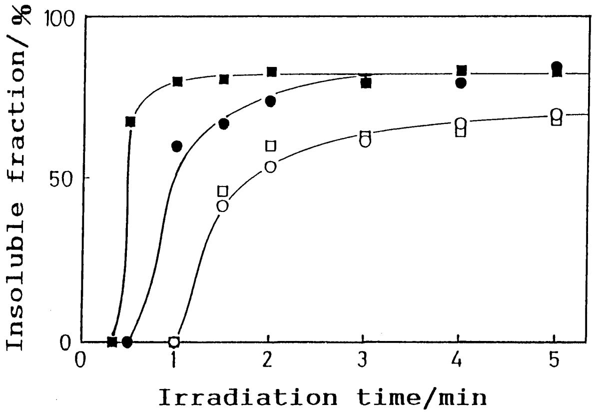


Fig. 1. Relationship between irradiation time and insoluble fraction of PGMA thin films (ca. 1 μm) containing PaApO in air.
(○)no treatment,
(□)H_2O-vapor treatment for 10 min,
(●)heating at 80 ℃ for 10 min,
(■)H_2O-vapor treatment for 10 min and heating at 80 ℃ for 10 min.

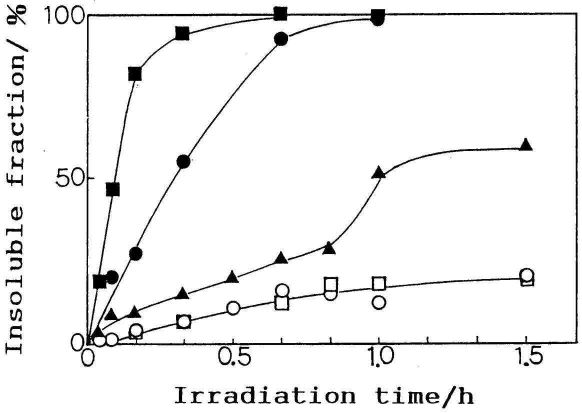


Fig. 2. Relationship between irradiation time and insoluble fraction of PGMA thick films (ca. 35 μm) containing PaApO in air.
(○)no treatment,
(□)H_2O-vapor treatment for 10 min,
(▲)heating at 80 ℃ for 10 min,
(●)heating at 80 ℃ for 1 h,
(■)H_2O-vapor treatment for 10 min and heating at 80 ℃ for 1 h.

References

1) J. V. Crivello, CHEMTECH, 1980, 624.
2) H. Ito and M. Ueda, J. Photopolym. Sci. Technol., 2, 1 (1989).
3) K. H. Song, M. Tsunooka, and M. Tanaka, J. Photochem. Photobiol., A, 44, 197 (1988).
4) K. H. Song, A. Urano, M. Tsunooka, and M. Tanaka, J. Polym. Sci., Part C, Polym. Lett., 25, 417 (1987).
5) C. Kutal and C. G. Willson, J. Electrochem. Soc., 134, 2280 (1987).
6) M. R. Winkle and K. A. Graziano, J. Photopolym. Sci. Technol., 3, 419 (1990).
7) J. F. Cameron and J. M. J. Fréchet, J. Photochem. Photobiol., A, 59, 105 (1991).
8) J. F. Cameron and J. M. J. Fréchet, J. Am. Chem. Soc., 113, 4303 (1991).
9) S. Muroi and S. Ishimura, "Nyuumon Epoxy Zyushi," Koubunshi Kankoukai, Kyoto (1988), p.140.
10) H. Sakuragi, S. Ishikawa, T. Nishimura, M. Yoshida, N. Inamoto, and K. Tokumaru, Bull. Chem. Soc. Jpn., 49, 1949 (1976).

(Received March 30, 1992)