

SHORT COMMUNICATIONS

Novel Thermal Curing Reactions of Epoxy Resin and Polyurethane Oligomers Using Photo-generated Poly-functional Amines

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Photo-generation of corresponding free amines by decomposition of 2-nitrobenzyl carbamates,¹ formanilides² as well as photo-Fries type rearrangement³ of acetanilide has been reported. Recently, Kutal and Willson reported⁴ the photo-generation of ammonia by UV irradiation of a cobalt-amine complex and thermo-crosslinking reaction of poly(glycidyl methacrylate-co-ethyl methacrylate) using the generated ammonia. This photoinduced thermo-crosslinking reaction pointed out a new photoresist technology. Tsunooka *et al.* also reported⁵ photo-generation of free amines from *O*-acyloxyamines in poly(glycidyl methacrylate) film and thermo-crosslinking reaction of the polymer film. Cameron and Frechet reported^{6,7} photo-generation of free hexane-1,6-diamine (HMDA) from *N,N'*-bis[[1-(3,5-dimethoxyphenyl)-1-methylethoxy]carbonyl]hexane-1,6-diamine, bis[[[(2-nitrobenzyl)oxy]carbonyl]hexane-1,6-diamine and bis[[$(\alpha$ -methyl-2-nitrobenzyl)oxy]carbonyl]hexane-1,6-diamine.

It is also well known that poly-functional amines are very important reagents for thermo-crosslinking reactions of epoxy resins and polyurethane oligomers with terminal isocyanate groups in adhesives, paints, coatings, composites, etc. However, the storage

stability of mixtures of epoxy resins and polyurethane oligomers with poly-functional amines, especially with aliphatic diamines, is not good enough at room temperature, since poly-functional amines have high chemical reactivity.

Therefore, the photo-generation of poly-functional free amines from the blocked amine groups by UV irradiation and applications for curative formulations of epoxy resins and polyurethane oligomers are very important and a new advanced concept in polymer chemistry. However, there has been no report on thermo-crosslinking reaction of the epoxy resins or the polyurethane oligomers with photo-generated poly-functional amines.

This communication reports on the photo-generation of free diamines and applications for thermal curing reaction of epoxy resins and polyurethane oligomers with terminal isocyanate groups.

EXPERIMENTAL

Typical Procedure for Synthesis of Blocked Diamine

Bis(4-formylaminophenyl)methane (FAPM) was synthesized by the reaction of 4,4'-methylenebis(benzeneisocyanate) (MBI) (10

mmol) with formic acid (22 mmol) in toluene (40 ml) at 80°C for 2 h. The yield of FAPM (mp 177–178°C) was 98%. The IR spectrum of FAPM (KBr) showed absorption peaks at 3200 (NH) and 1690 cm^{-1} (C=O). The UV spectra showed λ_{max} at 254 nm in dichloromethane. ^1H NMR spectrum (90 MHz, DMSO- d_6 , TMS) showed proton signals at $\delta=3.8$ ($-\text{CH}_2-$, s, 1H), 7.0–7.6 (ArH, m, 4H), 8.25 ($-\text{CHO}$, d, 1H), and 10.0 ppm ($-\text{NH}-$, s, 1H). *Anal.* Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2$: C, 70.85%, H, 5.55%, N, 11.02%. Found: C, 70.99%, H, 5.72%, N, 11.00%.

Bis(4-acetylaminophenyl)methane (AAPM)⁸ was prepared with 85% yield by reaction of MBI with acetic acid. mp 224–225°C. IR spectrum (KBr); 3230 (NH) and 1650 cm^{-1} (C=O). UV spectra (in CH_2Cl_2); $\lambda_{\text{max}}=253$ nm. ^1H NMR spectrum (90 MHz, DMSO- d_6 , TMS); 2.0 ($-\text{CH}_3$, s, 3H), 3.8 ($-\text{CH}_2-$, s, 1H), 7.0–7.6 (ArH, m, 4H), and 9.8 ppm ($-\text{NH}-$, s, 1H).

Bis[(2-nitrobenzyl)oxy]carbonyl]hexane-1,6-diamine (NBHA) was obtained with 92% yield by the reaction of hexamethylene diisocyanate (5 mmol) with 2-nitrobenzyl alcohol (10.1 mmol) catalyzed by a small amount of dibutyltin dilaurate in toluene (30 ml) at 80°C for 3 h as reported previously⁷. IR spectrum (KBr); 3330 (NH) and 1700 cm^{-1} (C=O). ^1H NMR spectrum (90 MHz, DMSO- d_6 , TMS); 1.3 [$-(\text{CH}_2)_4-$, s, 8H], 3.0 ($\text{N}-\text{CH}_2$, d, 4H), 5.35 ($\text{O}-\text{CH}_2$, s, 4H), 7.3–7.9 (ArH, 8H), and 8.1 ppm ($-\text{NH}-$, s, 2H).

Typical Procedure for Photo-generation of Poly-functional Free Amine in Solution

An FAPM solution (0.01 mol l^{-1}) in tetrahydrofuran (THF) (40 ml) was charged into a small cylindrical quartz reactor with a water jacket and thermometer. Nitrogen gas was bubbled through the solution for 30 min before UV irradiation. Photolysis of FAPM was carried out using a 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D) without filter under nitrogen atmosphere at

30°C for 5 h, in which the intensity of the incident light was always kept at 10 mW cm^{-2} (at 254 nm), then the THF was evaporated *in vacuo*. The ^1H NMR spectrum (in DMSO- d_6) of the dried reaction mixture showed a decrease of methylene protons at $\delta=3.8$ ppm and aromatic protons at $\delta=7.0$ –7.6 ppm due to the FAPM molecule, and a new appearance of methylene protons at $\delta=3.55$ ppm and of aromatic protons at $\delta=6.1$ –6.95 ppm due to 4,4'-methylenedianiline (MDA) molecule. The degree of conversion of FAPM to MDA, calculated from the integration ratio of the ^1H NMR spectrum, was 80%.

Measurement of the Rate of Thermal Curing of Epoxy Resin and Polyurethane Oligomer by Photo-generated Poly-functional Free Amine

The rate of photolysis of the blocked amine and rate of thermal curing of the epoxy resin were measured as follows. Commercial epoxy resin (Epicoat-828 with epoxide equivalent: 190) (1.52 g; 8 mequiv.) and FAPM (0.51 g; 2 mmol) were mixed in an agate mortar, and the mixture was cast on a KBr plate. The mixture on the plate was irradiated by a high-pressure mercury lamp without a filter, in which the intensity of the incident light was kept always at 5 mW cm^{-2} (at 254 nm). The rates of decrease of the C=O group at 1690 cm^{-1} and cyclic C–O–C group at 910 cm^{-1} were measured by IR spectroscopy. The rate of decrease of the epoxide group at 910 cm^{-1} in the mixture on the same KBr plate upon heating at 140°C was monitored in the same way.

Commercial polyurethane oligomer prepared by reaction of tolylene diisocyanate with poly(tetramethylene glycol) (isocyanate equivalent: 652) (2.61 g; 4 mequiv.) and FAPM (0.25 g; 1 mmol) were mixed in an agate mortar. The mixture was cast on a KBr plate, and irradiated under the same conditions as above.

RESULTS AND DISCUSSION

Photolysis of FAPM containing blocked amino groups was carried out under UV irradiation in THF solution. The reaction proceeded with 80% conversion to produce MDA with free amino groups after 5 h under nitrogen atmosphere. The degrees of conversion of AAPM and bis(4-benzoylaminophenyl)-methane (BAPM) from the corresponding bis(3-acetyl-4-aminophenyl)methane and bis-(3-benzoyl-4-aminophenyl)methane were only 32 and 38%, respectively, under the same irradiation conditions. This means that although the rate of photo-generation of MDA by the reaction of FAPM is rather slow, the rate of photolysis of FAPM was clearly higher than the rates of photo-Fries type rearrangement of AAPM and BAPM.

The photolysis of FAPM, AAPM and BAPM in the epoxy resin followed by the thermal curing reaction of the epoxy resin was carried out using a KBr plate. As shown in Figure 1, the degree of conversion of FAPM was 73% under UV irradiation after 4 h. However, the degrees of conversion of AAPM and BAPM were only 2-4% under the same irradiation conditions.

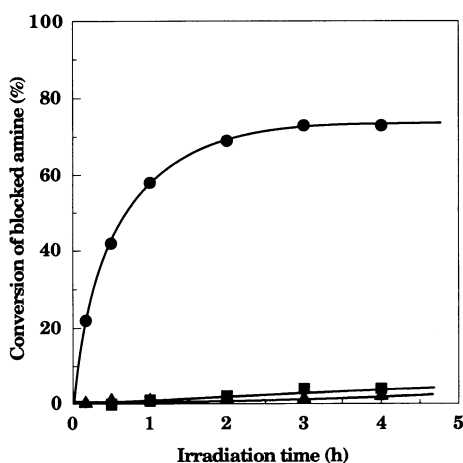


Figure 1. Rate of photochemical reaction of the blocked poly-functional amine: (●) FAPM; (▲) AAPM; (■) BAPM.

The degrees of conversion of the epoxy group under UV irradiation followed by heating at 140°C are summarized in Figure 2. The reaction rate of the epoxy group in the mixture with the irradiated FAPM was higher than with AAPM and BAPM. However, the degrees of conversion of the epoxy group with irradiated FAPM, AAPM and BAPM were about 20% under UV irradiation at 4 h, respectively. The degree of conversion of the epoxy group without any additives was about 15% under the same conditions. This suggests that although the addition reaction of the epoxy groups with the produced free amine MDA occurred, some side reactions between the epoxy groups and hydroxyl groups in the resin and amide groups in the blocked amine compounds were also promoted by photo-irradiation.

As shown in Figure 2, the degree of conversion of the epoxy group in the mixture with converted MDA was 75%, and the viscous mixture became an insoluble cured film on the KBr plate upon heating at 140°C for 2 h. On the other hand, the degrees of conversion of the epoxy groups in the mixture with AAPM and BAPM were about 37%, respectively, and the degree of conversion of the epoxy group in

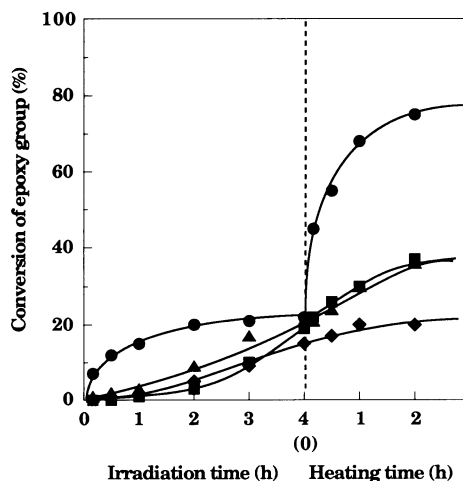
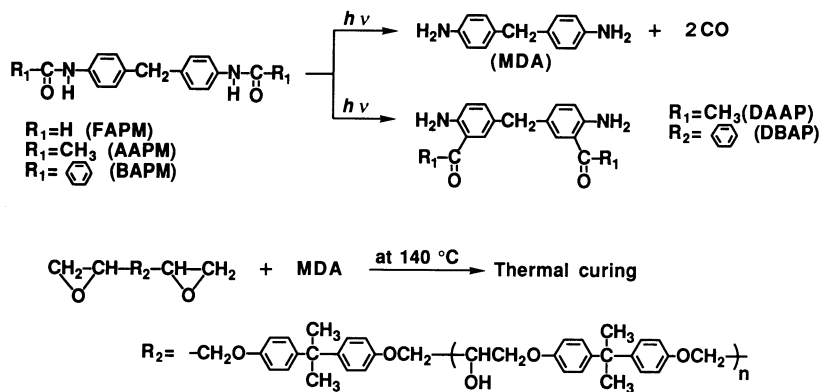


Figure 2. Rate of the reaction of the epoxy group in the mixture of epoxy resin with the blocked poly-functional amine: (●) with FAPM; (▲) with AAPM; (■) with BAPM; (◆) without any additive.



Scheme 1.

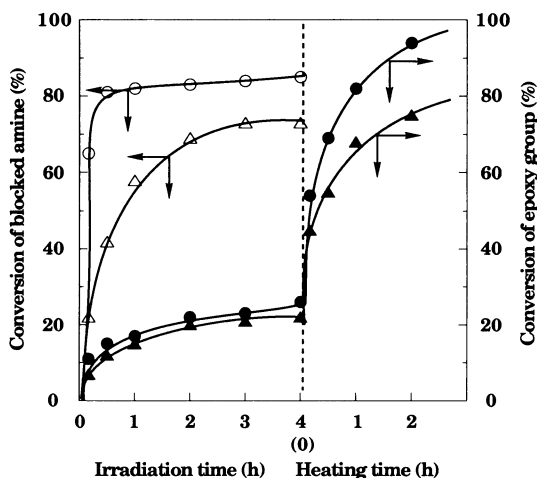


Figure 3. Rate of photochemical reaction of the NBHA in the epoxy resin and rate of addition reaction of the epoxy group with the produced HMDA: (○) NBHA; (△) FAPM; (●) epoxy group with NBHA; (▲) epoxy group with FAPM.

the resin without any additive was 20% under the same conditions. The thermal curing reaction of the epoxy resin with the converted MDA containing free amino groups is thus enhanced strongly by heating at 140°C.

The photolysis of NBHA in the epoxy resin and thermal curing reaction of the epoxy resin with produced free amine HMDA were carried out on a KBr plate. As shown in Figure 3, about 80% of the NBHA was changed to HMDA under UV irradiation after 30 min, and the thermal curing reaction of epoxy resin with

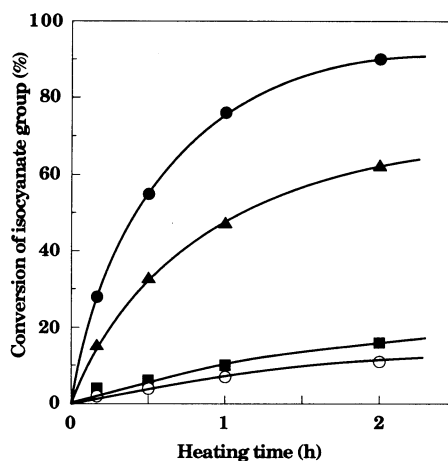
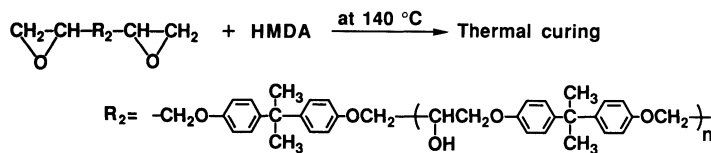
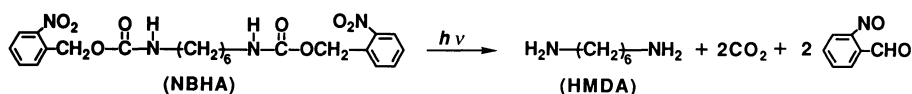


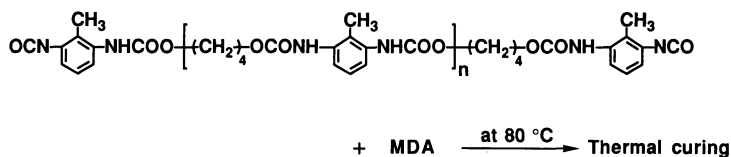
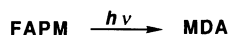
Figure 4. Rate of the addition reaction of the isocyanate group with the converted MDA in the mixture of polyurethane oligomer: (○) before irradiation; (■) irradiated at 0.5 h; (△) irradiated at 2 h; (●) irradiated at 4 h.

the produced free amino group in the HMDA proceeded very smoothly upon heating at 140°C for 2 h. This suggests that NBHA has higher photochemical reactivity than FAPM under the same irradiation conditions.

Since the degree of photo-generation of MDA from FAPM in the mixture with polyurethane oligomer containing terminal isocyanate groups could not be confirmed from the decrease of C=O groups by IR spectrometry, the degree of conversion of N=C=O group at 2270 cm⁻¹ in each mixture of the polyurethane oligomer with FAPM was



Scheme 2.



Scheme 3.

measured by IR spectrometry. As shown in Figure 4, although the degree of conversion of the N=C=O group in the mixture before irradiation was only 11% upon heating at 80°C for 2 h, the degree of conversion of the N=C=O group increased gradually with increase in the irradiation time. That is, the degree of conversion of the N=C=O group in the irradiated mixture after 4 h was 90%, and the viscous mixture became insoluble cured film on the KBr plate upon heating at 80°C for 2 h. This suggests that the thermal curing reaction of polyurethane oligomer by using photo-generated MDA proceeds very smoothly at 80°C.

From the above results, it is concluded that thermal curing reactions of the epoxy resin and the polyurethane oligomer can be conducted using photo-generated poly-functional amines. The comparative rates of photo-generation of

poly-functional free amine were as follows: NBHA > FAPM > AAPM, BAPM.

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