

SHORT COMMUNICATIONS

**Photo-generation of Poly-functional Thiol and Thermal Curing
Reaction of Epoxy Resins Using the Thiol**

Tadatomi NISHIKUBO,* Atsushi KAMEYAMA, and Koutaro KASHIWAGI

*Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
Rokkakubashi, Kanagawa-ku, Yokohama 221, Japan*

(Received February 9, 1994)

KEY WORDS Poly-functional Thiol / Photo-generation / Thermal Curing
Reaction / Epoxy Resin /

Poly-functional thiol is a very useful reagent as well as poly-functional amine for thermal-crosslinking reaction of epoxy resins.¹ However, the storage stability of mixtures of epoxy resin with poly-functional thiol is insufficient at room temperature, since poly-functional thiol has high chemical reactivity. Therefore, the photo-generation of thiol from the blocked thiol group by UV-light irradiation and application to curative formulation of epoxy resins represent an important key technology in photopolymer chemistry.

The photo-generation of free amine from 2-nitrobenzyl carbamates² and formanilides³ has been reported as important for photocuring. The photo-generation of poly-functional hexane-1,6-diamine^{4,5} 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[[α -methyl-2-nitrobenzyl]oxy]carbonyl]hexane-1,6-diamine has also been carried out. Recently, the authors reported^{6,7} the photo-generation of various free diamines and application for thermal curing reaction of epoxy resins and polyurethane oligomers.

This communication reports the first photo-generation of poly-functional thiol and its

application for thermal curing reactions of epoxy resins.

EXPERIMENTAL

Apparatus

¹H NMR spectra were recorded on JEOL Models JNM EX-90 (90 MHz) and JNM FX-200 (200 MHz) instruments. Infrared (IR) spectra were obtained on a JASCO Model IR-700 spectrometer.

Synthesis of N-(2-Nitrobenzyloxycarbonyl)imidazole (NBCI)

The reaction of 10.7 g (70 mmol) of 2-nitrobenzyl alcohol with 11.4 g (70 mmol) of *N,N'*-carbonyldiimidazole was carried out in acetonitrile (280 ml) at room temperature for 24 h, and the solvent was evaporated *in vacuo*. The precipitated crude product was recrystallized from ethyl acetate. The yield of NBCI was 13.4 g (78%). mp 143–144°C. IR (KBr): 1751 (C=O), 1523 and 1342 (–NO₂), and 1179 cm^{–1} (C–O–C). ¹H NMR (90 MHz, CDCl₃, TMS): δ = 5.8 (s, 2H, CH₂), 7.1–7.2 (m, 1H, N=CH), 7.4–7.5 (m, 1H, N=CH), 7.5–7.8 (m, 3H, aromatic protons), and 8.1–8.2 ppm (m, 2H, aromatic proton, and

* To whom all correspondence should be addressed.

N=CH).

Synthesis of p-Xylenebis(2-nitrobenzyl- α -S-thio-carbonate) (XBBTC)

XBBTC was synthesized by reaction of 12.4 g (50 mmol) of NBCI with 4.3 g (25 mmol) of 1,4-bis(mercaptomethyl)benzene (BMMB) in DMF (250 ml) at 50°C for 30 min, and the crude product was recrystallized from ethyl acetate. The yield of XBBTC was 9.2 g (70%). mp 139–140°C. IR (KBr): 1709 (C=O), 1518 and 1338 (–NO₂), and 1136 cm⁻¹ (C–O–C). ¹H NMR (90 MHz, CDCl₃, TMS): δ =4.1 (s, 4H, S–CH₂), 5.7 (s, 4H, CH₂–O), 7.3 (s, 4H, aromatic protons), and 7.4–8.2 (m, 8H, aromatic protons).

Anal. Calcd for C₂₄H₂₀N₂O₈S₂: C, 54.54%; H, 3.81%; N, 5.30%. Found: C, 54.49%; H, 3.90%; N, 5.03%.

Photo-generation of Poly-functional Thiol in Solution

An XBBTC solution (0.03 mol·l⁻¹) in THF (30 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 the XBBTC was carried out using a 500-W, high-pressure mercury lamp (Ushio Electric Co., USH-500D) with thermal-ray cut filter (HA-50) under nitrogen atmosphere at 30°C for 6 h. During photo-irradiation, the intensity of the incident light was kept always at 1.92–1.98 mW·cm⁻² (at 310 nm), then the THF was evaporated *in vacuo*. The ¹H NMR spectrum (in CDCl₃) of the dried reaction mixture showed decrease (29%) of methylene protons at δ =4.1 and 5.7 ppm due to XBBTC molecules, and new appearance (15%) of methylene protons

(doublet) at δ =3.7 ppm and free thiol protons (triplet) at δ =1.8 ppm due to the BMMB.

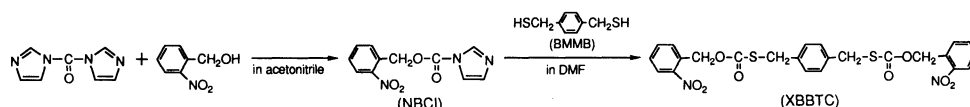
Measurement of the Rate of Thermal Curing Reaction of Epoxy Resin with Photo-generated Poly-functional Thiol

The rates of photolysis of XBBTC and thermal curing reaction of the epoxy resin were measured as follows. Epoxy resin (Epicoat 828 with epoxide equivalent: 190, M_w =380, M_w/M_n =1.1) (0.38 g; 1 mmol) and XBBTC (0.53 g; 1 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 250-W high-pressure mercury lamp (Ushio Electric Co., USH-250D) without a filter. The intensity of the incident light was kept at 0.45 mW cm⁻² (at 310 nm). Decreasing rates of the C=O group at 1709 cm⁻¹ due to the XBBTC and cyclic C–O–C group at 910 cm⁻¹ due to the epoxy resin 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 on heating at 120°C was also monitored.

RESULTS AND DISCUSSION

The reaction intermediate NBCI was prepared with 78% yield by the reaction of 2-nitrobenzyl alcohol with *N,N'*-carbonyldiimidazole in acetonitrile at room temperature for 24 h. The blocked dithiol XBBTC was synthesized in 70% yield by reaction of the intermediate NBCI with BMMB with free dithiol groups in DMF at 50°C 30 min.

Photolysis of XBBTC containing blocked dithiol groups was carried out in the THF solution in a cylindrical quartz reactor under UV-light irradiation using a 500-W high-pressure mercury lamp. As shown in Figure 1,



Scheme 1.

XBBTC was converted gradually to the corresponding dithiol compound BMMB under UV-irradiation. The reaction proceeded with 29% conversion after 6 h irradiation under nitrogen atmosphere. The ^1H NMR spectrum showed a new peak (15 mol%) of free thiol protons at $\delta=1.8$ ppm due to BMMB, when 29 mol% of methylene protons at $\delta=4.1$ and 5.7 ppm due to the XBBTC was decreased. This suggests that photo-deprotection of XBBTC to produce BMMB occurs very smoothly by UV-irradiation under nitrogen. However, the produced thiol groups in BMMB were partly used for subsequent side-reactions.

When the photochemical reaction of XBBTC was performed in a cylindrical Pyrex glass reactor under the same irradiation conditions, almost the same results in Figure 1 were

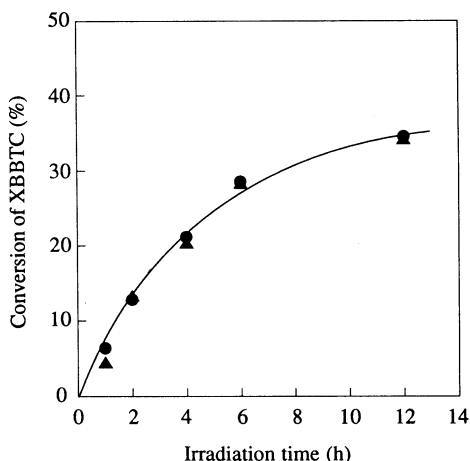


Figure 1. Rate of photolysis of XBBTC in THF solution. (●) in quartz reactor; (▲) in Pyrex reactor.

obtained.

The photolysis of XBBTC in bisphenol-A type epoxy resin (Epicoat 828) and thermal curing reaction of the epoxy resin were examined on a KBr plate. As shown in Figure 2, the degree of conversion of XBBTC to BMMB was determined from decrease of the absorption peak at 1709 cm^{-1} due to the $\text{C}=\text{O}$ stretching, and attained 67% after UV-irradiation for 1 h. A small decrease of the absorption peak at 910 cm^{-1} due to the epoxide group was also found. This shows that a small amount of the epoxide group reacted with the free thiol groups during UV-light irradiation.

Although the degree of conversion of the

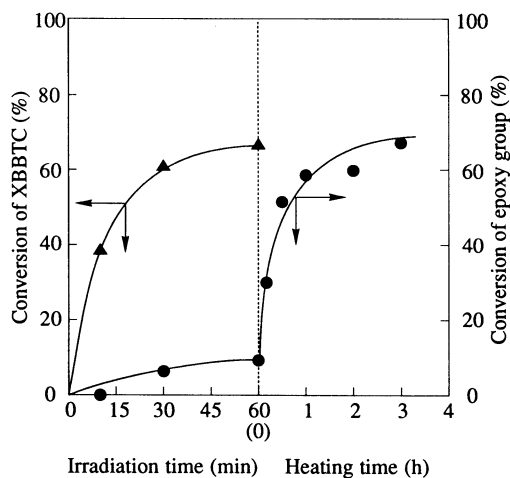
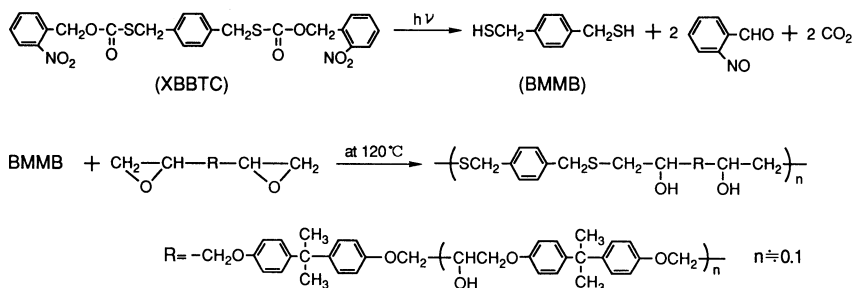


Figure 2. Rates of photochemical reaction of XBBTC in epoxy resin (Epicoat 828) and addition reaction of epoxy groups with photo-generated BMMB. (▲) conversion of $\text{C}=\text{O}$ at 1709 cm^{-1} ; (●) conversion of cyclic $\text{C}-\text{O}-\text{C}$ at 910 cm^{-1} .



Scheme 2.

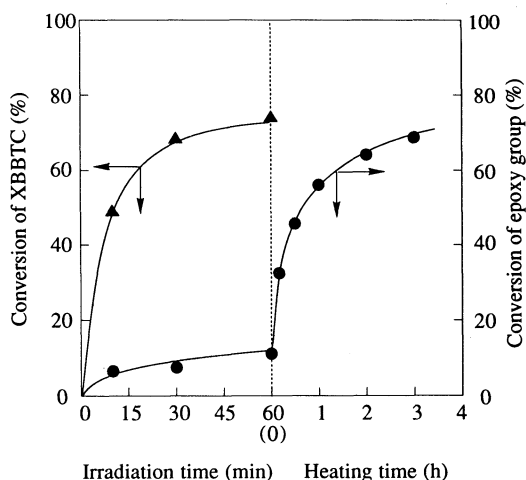
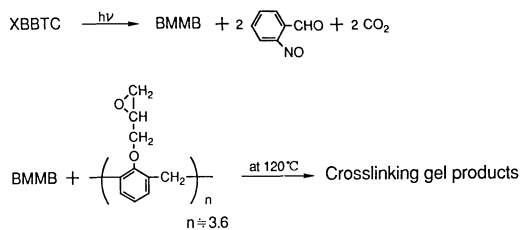


Figure 3. Rates of photochemical reaction of XBBTC in epoxy resin (Epicoat XXX) and addition reaction of epoxy groups with photo-generated BMMB. (▲) conversion of C=O at 1709 cm^{-1} ; (●) conversion of cyclic C-O-C at 910 cm^{-1} .

absorption peak at 910 cm^{-1} was only 9% after UV irradiation for 1 h, the degree of conversion of cyclic ether increased very rapidly by heating at 120°C , and conversion reached 67% for 3 h. A new absorption peak due to a hydroxy group appeared at 3300 cm^{-1} . This means that the most of photo-generated thiol group in BMMB reacted with the same amount of the epoxy group in the resin.

The above reaction products of the bisphenol-A type epoxy resin (Epicoat 828) with XBBTC was soluble in chloroform after UV-light irradiation for 1 h, followed by heating at 120°C for 3 h. This suggests that the reaction of the epoxy resin with the photo-generated BMMB produces linear polymers or oligomers as shown in Scheme 2, where n is the degree of polymerization.

Accordingly, the photochemical reaction of novolac type epoxy resin (DEN 438) containing three or more epoxy groups in the molecule



Scheme 3.

with XBBTC was performed under the same conditions. As shown in Figure 3, the degree of conversion of XBBTC to BMMB was 74% after UV-irradiation for 1 h. The degree of conversion of the epoxy group in the resin was only 11%. However, the degree of conversion increased very rapidly by heating at 120°C , and reached 69% after thermal treatment for 3 h. A mixture of the novolac-type epoxy resin with XBBTX became insoluble in THF after UV-irradiation for 1 h, followed by heating at 120°C for 3 h. Present results indicate that thermal curing reaction of novolac type epoxy resin with the photo-generated BMMB occurs very smoothly under the above conditions as shown in Scheme 3, where n is the degree of polymerization.

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