

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*

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Poly-functional thiol is a very useful reagent as well as poly-functional amine for thermal-crosslinking reaction of epoxy resins.<sup>1</sup> 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 carbamates<sup>2</sup> and formanilides<sup>3</sup> has been reported as important for photocuring. The photo-generation of poly-functional hexane-1,6-diamine<sup>4,5</sup> 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 has also been carried out. Recently, the authors reported<sup>6,7</sup> 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*

<sup>1</sup>H 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 (–NO<sub>2</sub>), and 1179 cm<sup>-1</sup> (C–O–C). <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 5.8 (s, 2H, CH<sub>2</sub>), 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- $\alpha$ -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 (–NO<sub>2</sub>), and 1136 cm<sup>-1</sup> (C–O–C). <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>, TMS):  $\delta$ =4.1 (s, 4H, S–CH<sub>2</sub>), 5.7 (s, 4H, CH<sub>2</sub>–O), 7.3 (s, 4H, aromatic protons), and 7.4–8.2 (m, 8H, aromatic protons).

*Anal.* Calcd for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>: 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<sup>-1</sup>) 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<sup>-2</sup> (at 310 nm), then the THF was evaporated *in vacuo*. The <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of the dried reaction mixture showed decrease (29%) of methylene protons at  $\delta$ =4.1 and 5.7 ppm due to XBBTC molecules, and new appearance (15%) of methylene protons

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

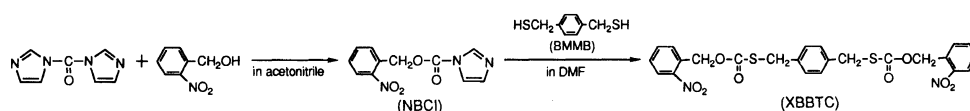
*Measurement of the Rate of Thermal Curing Reaction of Epoxy Resin with Photo-generated Poly-functional Thiol*

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<sup>-2</sup> (at 310 nm). Decreasing rates of the C=O group at 1709 cm<sup>-1</sup> due to the XBBTC and cyclic C–O–C group at 910 cm<sup>-1</sup> due to the epoxy resin were measured by IR spectroscopy. The rate of decrease of the epoxide group at 910 cm<sup>-1</sup> 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.

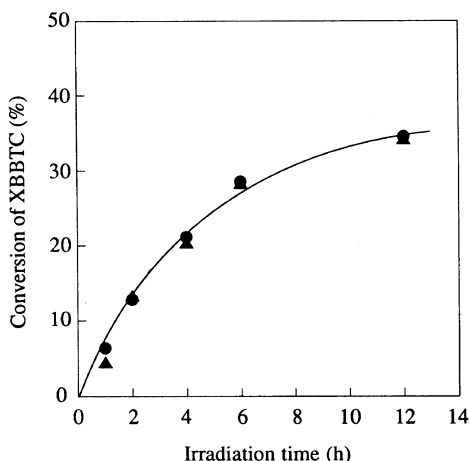
Photolysis of XBBTC containing blocked dithiol groups was carried out in the THF solution in a cylindrical quartz reactor under UV-light irradiation using a 500-W high-pressure mercury lamp. As shown in Figure 1,



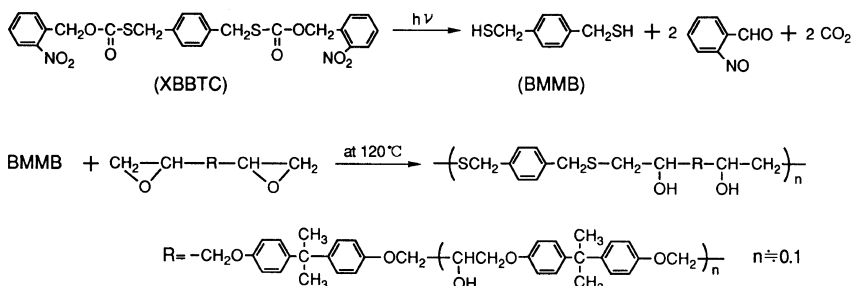
Scheme 1.

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  $^1\text{H}$  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.

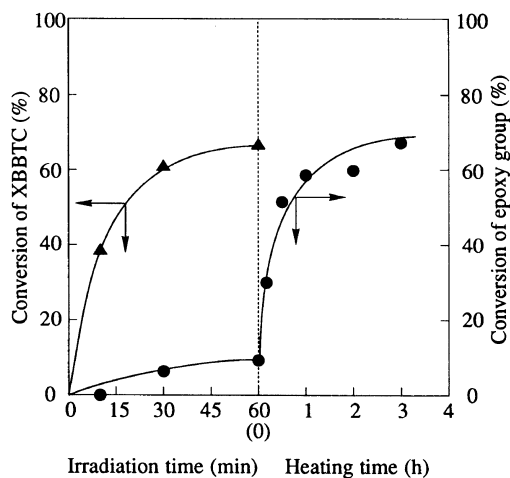


**Scheme 2.**

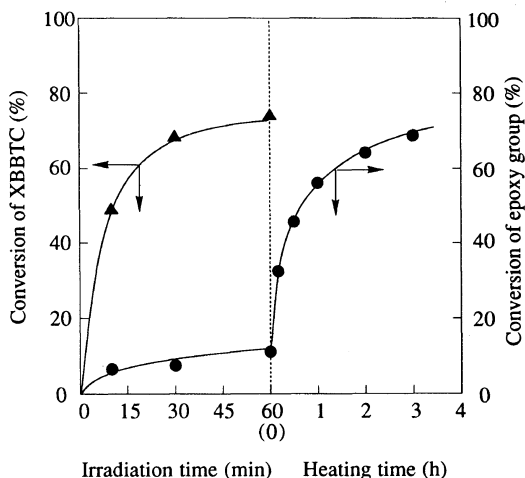
obtained.

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  $1709\text{ cm}^{-1}$  due to the C=O stretching, and attained 67% after UV-irradiation for 1 h. A small decrease of the absorption peak at  $910\text{ cm}^{-1}$  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 C=O at  $1709\text{ cm}^{-1}$ ; (●) conversion of cyclic C-O-C at  $910\text{ cm}^{-1}$ .

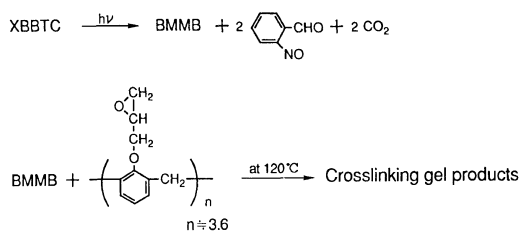


**Figure 3.** Rates of photochemical reaction of XBBTC in epoxy resin (Epicoat XXX) and addition reaction of epoxy groups with photo-generated BMMB. (▲) conversion of C=O at  $1709\text{ cm}^{-1}$ ; (●) conversion of cyclic C-O-C at  $910\text{ cm}^{-1}$ .

absorption peak at  $910\text{ cm}^{-1}$  was only 9% after UV irradiation for 1 h, the degree of conversion of cyclic ether increased very rapidly by heating at  $120^\circ\text{C}$ , and conversion reached 67% for 3 h. A new absorption peak due to a hydroxy group appeared at  $3300\text{ cm}^{-1}$ . 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  $120^\circ\text{C}$  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  $120^\circ\text{C}$ , 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  $120^\circ\text{C}$  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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