Novel Method of Thermal Epoxy Curing Based on Photogeneration of Polymeric Amines and Negative-Tone Image Formation

Alexander Mejiritski, Ananda M. Sarker, Bryan Wheaton,† and Douglas C. Neckers*

Center for Photochemical Sciences,[1] Bowling Green State University, Bowling Green, Ohio 43403

Received January 3, 1997⊗

Polymeric amines generated by UV-induced electron transfer in polymeric quaternized tetraalkylammonium borate salts are found suitable for the thermal cross-linking of epoxides where nucleophilic attack on the epoxy ring is favorable. A cross-linked polymer network insoluble in organic solvent becomes the basis of a negative-tone photoimaging system. Sensitivity and resolution parameters have been evaluated by atomic force microscopy (AFM). Addition of reagents containing hydroxyl moieties to a film containing both the polymeric amine precursor and epoxide improves sensitivity more than 3-fold manifesting chemical amplification due to the catalytic nature of the cross-linking process.

Introduction

Amines participate in thermo-cross-linking reactions of epoxidized materials and polyurethane oligomers to produce polymers used as adhesives, coatings, and thermosets.[2,3] Amines photogenerated from thermally stable precursors are especially important since they significantly alleviate the problems of storage stability of curable formulations which include epoxy resins and polyurethane oligomers. The search for such photoreactive precursors was initiated by Willson and Kutal,[4] who showed that cobalt−amine complexes yielded ammonia upon UV irradiation. Photolysis of these complexes in poly(glycidyl methacrylate-*co*-ethyl methacrylate) led to subsequent thermal cross-linking of this polymer which contains epoxy functionality. Further research in the field focused on UV-induced deblocking of protected amino groups. Efficient amine photoprecursors were designed from carbamates protected with the photolabile groups (α,α-dimethyl-3,5-dimethoxybenzyloxycarbonyl (Ddz),[5] 2-nitrobenzyloxycarbonyl,[6] and, most recently, 3′,5′-dimethoxybenzoinyloxycarbonyl[7]). These compounds were used for image reversal in an acid-catalyzed photo-cross-linkable resist as well as for curing and imaging of polyfunctional epoxy compounds based on thermal cross-linking.[8,9] Free amines have also been obtained by irradiation of *O*-acyloxyimines[10] as well as a result of photo-Fries type rearrangement.[11]

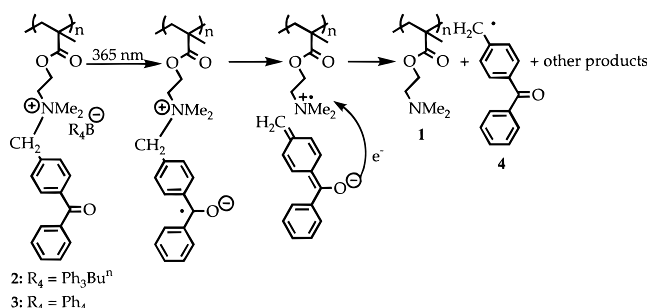


Figure 1. Mechanism of photogeneration of the polymeric amine.

Generally, photogenerated organic bases that are used as curing agents are produced by photolytic generation of low molecular weight aliphatic amines that induce the cross-linking of polymer matrixes containing appropriate reactive functionalities (for example, epoxidized resins or polyurethane oligomers).[12] On the contrary, there are few reports of utilizing photogenerated polymeric amines in this capacity.[13]

Recently, we have reported a new class of polymeric amine precursors. Polymeric amines, **1**, were obtained by UV irradiation of polymers **2** or **3** bearing pendant tetraalkylammonium borate salts in which one of the groups attached to the cationic center was a *p*-benzoylbenzyl group.[14] Photolysis (Figure 1) is believed to involve electron transfer from the borate (triphenyl-*n*-butyl or tetraphenyl) counter ions. The original polymer **2** or **3**, insoluble in aqueous acid, became acid sensitive

† Surface Characterization Laboratory, Corning, Inc., Corning, NY.
⊗ Abstract published in *Advance ACS Abstracts,* June 1, 1997.
(1) Contribution No. 303 from the Center for Photochemical Sciences.
(2) (a) Bauer, R. S. *Epoxy Resin Chemistry II*; ACS Symp. Ser. 221; American Chemical Society: Washington, DC, 1983. (b) Lee, H.; Neville, K. *Handbook of Epoxy Resins*; McGraw-Hill Book Co. New York, 1967.
(3) Buist, J. M.; Gudgeon, H. *Polyurethane Technology*; Maclaren and Sons Ltd.: London, 1968.
(4) Kutal, C.; Willson, C. G. *J. Electrochem. Soc.* **1987**, *134*, 2280.
(5) Cameron, J. F.; Frechet, J. M. J. *J. Org. Chem.* **1990**, *55*, 5919.
(6) Cameron, J. F.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4303.
(7) Cameron, J. F.; Willson, C. G.; Frechet, J. M. J. *APS Proc.* **1996**, 284.
(8) Matuszczak, S.; Cameron, J. F.; Frechet, J. M. J.; Willson, C. G. *J. Mater. Chem.* **1991**, *1*, 1045.
(9) Frechet, J. M. J. *Pure Appl. Chem.* **1992**, *64*, 1239.
(10) Song, K.-H.; Urano, A.; Tsunooka, M.; Tanaka, M. *J. Polym. Sci. C: Polym. Lett.* **1987**, *25*, 417.
(11) Tessier, T. G.; Frechet, J. M. J.; Willson, C. G.; Ito. H. *Materials for Microlithography*; ACS Symp. Ser. 266; American Chemical Society: Washington, DC, 1984; p 269.
(12) Nishikubo, T.; Takehara, E.; Kamayama, A. *J Polym. Sci. A: Polym. Chem.* **1993**, *31*, 3013.
(13) Beecher, J. E.; Cameron, J. F.; Frechet, J. M. J. *J. Mater. Chem.* **1992**, *2*, 811.
(14) Mejiritski, A.; Polykarpov, A. Y.; Sarker, A. M.; Neckers, D. C. *Chem. Mater.* **1996**, *8*, 1360.

S0897-4756(97)00003-3 CCC: $14.00 © 1997 American Chemical Society

after irradiation. The irradiated polymer film was degraded and partially removed when exposed to aqueous HCl. If followed by additional water and ethanol washes, the irradiated areas could be completely removed, allowing us to design a positive-tone photoimaging system based on these polymers. This system yielded images of 3−5 μm resolution; however, it was of relatively low speed.

Knowing that amines have been used as commercial curing agents for epoxidized resins,[2b] we have tested polymeric amines produced in our process as catalysts for thermally driven epoxy cross-linking. If this process were to take place to yield a matrix insoluble in organic solvents, we would have a basis for a negative-tone image formation. Thus, our photoimaging system could act in both tones. There are very few such dual-tone systems.[15] Besides, since polymerization and cross-linking of polyepoxides is catalytic in nature, we would expect to achieve chemical amplification in the negative-tone mode, thus increasing the speed of the photoimage formation.

Experimental Section

General. Melting point determinations were made using a Thomas-Hoover capillary melting point apparatus; all temperatures are uncorrected. All new compounds were characterized by NMR, IR, and elemental analysis (Atlantic Microlab, Inc., Georgia). ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on Gemini GEM-200 (200 MHz). Chemical shifts are reported in parts per million (ppm) relative to TMS at 0.0 ppm on the δ scale. ^{11}B NMR spectra were recorded on Varian Unity+ 400 (128 MHz) with $B(OMe)_3$ as the external standard. Infrared (IR) spectroscopy was performed with a Galaxy series Mattson Instruments spectrometer, Model 6020. Atomic force microscopy (AFM) was performed with a Burleigh Metris 2000 microscope in contact mode with Si tip (spring constant 0.1 N/m) with reference force set at 5.0 V. The incident dose was measured by appropriately positioned PMT power meter Scientech 365.

All reagents and solvents were obtained from Aldrich Chemical Co. and used as received, except epoxides which were a gift from Spectra Group Limited, Inc. (Maumee, OH).

***N,N*-Dimethyl-*N*-(*p*-benzoyl)benzyl-*N*-ethyl Methacrylate Ammonium Bromide (5).** To a solution of 1.50 g (5.45 mmol) of 4-(bromomethyl)benzophenone[16] in 12 mL of a toluene−acetone mixture (5:1) was added 0.75 g (4.77 mmol) of 2-(dimethylamino)ethyl methacrylate dropwise with stirring at room temperature (Figure 2a). A white precipitate formed almost immediately. The solution was stirred for another 30 min. The precipitate was separated by filtration and washed thoroughly with acetone. After drying under vacuum, 1.70 g (72% yield by weight) of **5** was obtained as white crystals, mp 155−156 °C. ^{1}H NMR (CD_3CN) δ 7.79 (m, 6H), 7.68 (m, 1H), 7.55 (m, 2H), 6.14 (s, 1H), 5.70 (s, 1H), 4.82 (s, 2H), 4.64 (m, 2H), 3.85 (t, J = 4.7 Hz, 2H), 3.15 (s, 6H), 1.93 (s, 3H). Anal. Calcd for $C_{22}H_{26}BrNO_3$: C, 61.14; H, 6.02; N, 3.24. Found: C, 60.90; H, 6.05; N, 3.23.

***N,N*-Dimethyl-*N*-(*p*-benzoyl)benzyl-*N*-ethyl Methacrylate Ammonium Tetraphenyl Borate (6).** **5** {1.90 g (4.40 mmol)} was dissolved in 100 mL of a water−ethanol mixture (4:1). Undissolved dust materials, if present, were filtered. The sodium salt of tetraphenyl borate {1.50 g (4.39 mmol)} in 5 mL of water was added dropwise into the mixture with stirring at room temperature. After 30 min, 250 mL of water was added and the reaction stirred for 1 h. The precipitate formed was filtered. After recrystallization from an ethanol−acetone mixture, 2.15 g (72% yield by weight) of desired product was obtained as white powder, mp 178−180 °C. ^{1}H NMR (CD_3CN) δ 7.80 (m, 4H, ortho to carbonyl), 7.60 (m, 5H, meta and para to carbonyl), 7.26 (m, 8H, ortho to B), 6.98 (t, J = 7.0 Hz, 8H, meta to B), 6.81 (t, J = 7.0 Hz, 4H, para to B), 6.15 (s, 1H), 5.73 (s, 1H), 4.82 (s, 2H), 4.64 (m, 2H), 3.85 (t, J = 4.7 Hz, 2H), 3.16 (s, 6H), 1.95 (s, 3H). ^{11}B NMR (DMSO) δ −28.52. Anal. Calcd for $C_{46}H_{46}BNO_3$: C, 82.30; H, 6.85; N, 2.09. Found: C, 82.21; H, 6.85; N, 2.10.

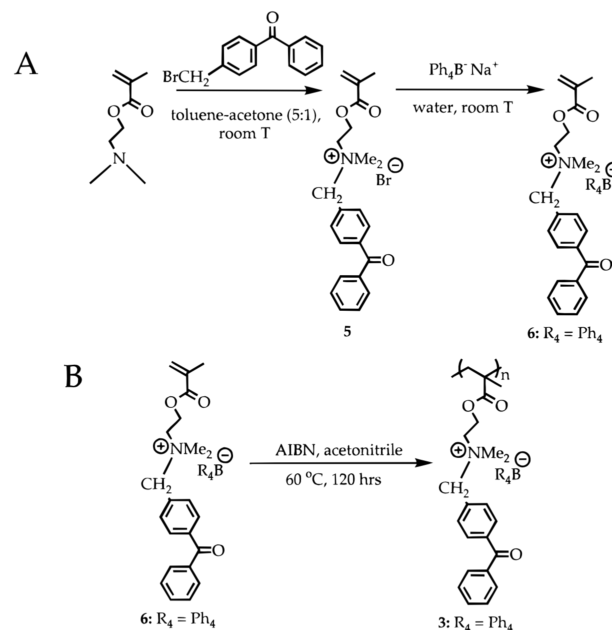


Figure 2. Synthetic procedure for: (A) monomeric quaternized tetraalkylammonium tetraphenyl borate salt **6** and (B) polymer **3**.

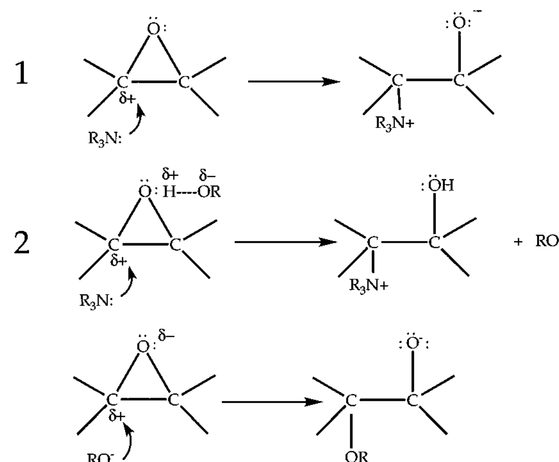
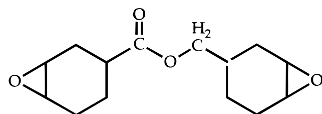


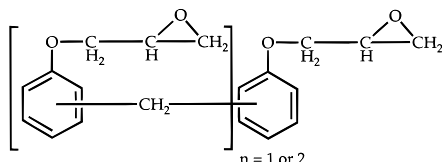
Figure 3. Mechanism of anionic polymerization of epoxides with tertiary amines as initiators.

Poly[*N,N*-dimethyl-*N*-(*p*-benzoyl)benzyl-*N*-ethyl methacrylate ammonium tetraphenyl borate] (3). A solution of 1.20 g (1.78 mmol) of **6** and 16 mg (0.09 mmol) of 2,2′-azobisisobutyronitrile (AIBN) in 10 mL of dry acetonitrile was charged into an oven-dried polymerization tube. The polymerization tube was subjected to four freeze−pump−thaw cycles, sealed, and heated at 60 °C for 120 h (Figure 2b). Insoluble materials were filtered, and the filtrate was poured into 250 mL of methanol. The precipitate was collected by filtration and purified by repricipitation from acetonitrile in methanol. After drying in vacuo overnight 0.70 g (60% yield by weight) of polymer was obtained as white powder. ^{1}H NMR (CD_3CN) δ 7.40−7.80 (br m, 9H, benzophenone moiety), 7.28 (m, 8H, ortho to B), 6.98 (m, 8H, meta to B), 6.79 (m, 4H, para to B), 4.46 (br s, 2H, Ph-CH_2), 3.37 (m, 2H, O−CH_2), 2.82 (br, 2H, CH_2−N), 2.19 (s, 6H, N−CH_3), 1.95 (M, 3H, α-methyl), 1.25

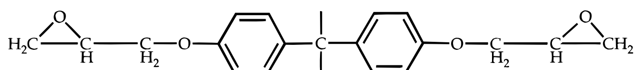
(15) MacDonald, S. A.; Willson, C. G.; Frechet, J. M. J. *Acc. Chem. Res.* **1994**, *27*, 151.
(16) Itoh, T.; Hall, H. K. *Macromolecules* **1990**, *23*, 4879.



3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate, Union Carbide resin UVR 6110



Epoxy novolac resin from Dow, DEN 438



Diglycidyl ether of bisphenol A, Shell resin EPON 828

Figure 4. Epoxides resins employed in the study.

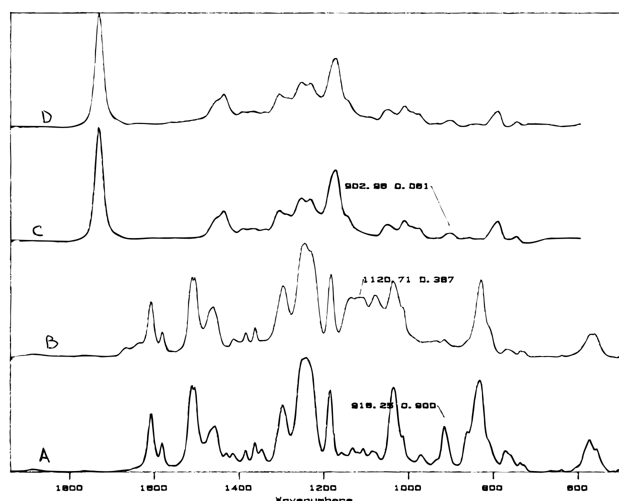


Figure 5. Transmission IR spectra of mixtures between NaCl plates for (A) EPON 828 and DMBA at room temperature, (B) EPON 828 and DMBA after thermal exposure at 80 °C for 30 min, (C) UVR 6110 and DMBA at room temperature, and (D) UVR 6110 and DMBA after thermal exposure at 80 °C for 30 min.

(m, 2H, polym chain). Anal. Calcd for $C_{46}H_{46}BNO_3$: C, 82.30; H, 6.85; N, 2.09. Found: C, 81.86; H, 6.90; N, 2.16.

The polymer molecular weight was estimated using an Ubelhode viscometer with measurements conducted in acetonitrile at 30 °C ± 1. The obtained value for the intrinsic viscosity was $[\eta] = 1.16$ dL g^{-1}. The polymer molecular weight was then estimated at 80 000−90 000 after comparison with appropriate model polymer−solvent system.[17]

Sample Preparation and Imaging Experiments. Films were prepared from solutions of polymer **3** and epoxy resin in *N,N*-dimethylformamide with overall solids constituting 20 wt % via spin-coating onto 13 × 13 mm silicon wafers with a Headway Research spinner in air at room temperature by spinning at 6000 rpm for 30 s. Prebake at 80 °C for 30 min was done where indicated.

UV exposures were performed with a custom-made irradiation setup with 200 W high-pressure mercury arc lamp as the irradiation source. The irradiation was filtered through a 365 nm filter (bandwidth ca. 40 nm). The distance between irradiated substrate and the lamp remained fixed at 11 cm.

(17) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons, Inc.: New York, 1989.

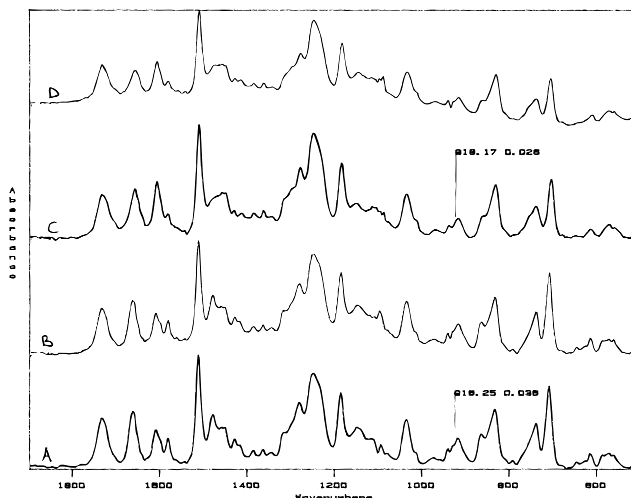


Figure 6. Transmission IR spectra of spin-coated film including polymeric amine precursor **3** and EPON 828 resin: (A) before prebake; (B) after prebake at 80 °C for 30 min; (C) after prebake and UV irradiation for an accumulated dose of 4500 mJ cm^{-2}; (D) after prebake,irradiation and postbake at 80 °C for 30 min.

Table 1. Sensitivity Parameters for Mixtures Containing the Polymeric Amine Photoprecursor and Epoxides in Different Compositions

mixture	molar ratio amine/epoxy/OH (where present)	sensitivity parameters (mJ cm^{-2})
(**A**) UVR 6110 + **3**	1:2	no image
(**B**) EPON 828 + **3**	1:2	$D_o = 1600$
		$D_c = 3800$
(**C**) DEN 438 + **3**	1:2.5	$D_o = 600$
		$D_c = 3200$
(**D**) DEN 438 + **3** + glycerol (prebake)	1:2.5:5	$D_o = 600$
		$D_c = 3200$
(**E**) DEN 438 + **3** + glycerol (no prebake)	1:2.5:5	$D_o < 200$
		$D_c = 1050$

All imaging experiments were performed with samples in soft contact mode utilizing Model T-2000 (bar size 5 μm, pitch size 12 μm) copper foil TEM (transmission electron microscopy) grids as masks purchased from Electron Microscopy Sciences (Fort Washington, PA). Postbaking was done at 80 °C for 30 min. Development was achieved by dipping wafers in acetonitrile for 10 s, which is enough for unexposed areas to dissolve and the film to be removed.

Results and Discussion

The proposed mechanism of photolysis of quaternized polymer **3** (Figure 1) implies that polymeric product **1** should be a tertiary amine. However, until now this has not been demonstrated. The behavior of the product in effecting polymerization of epoxides proves to be consistent with the hypothesis.

Organic bases, such as tertiary amines (R_3N:), function as curing agents for epoxides in what is believed to be a two-stage process. The first, or initiating, step involves nucleophilic attack of an amine on carbon which leads to the epoxy ring opening. The chain reaction that follows leads to a cross-linked product in case of the polyfunctional epoxides. Tertiary amines, as sole curing agents, are not normally employed since they are also good chain terminators. Most often the presence of hydroxyl group (in the form of polyol) is required for the first step. Transfer of the proton to the oxygen of the epoxy substrate produces an alkoxide and quaternary ammonium ions. Chain propagation then

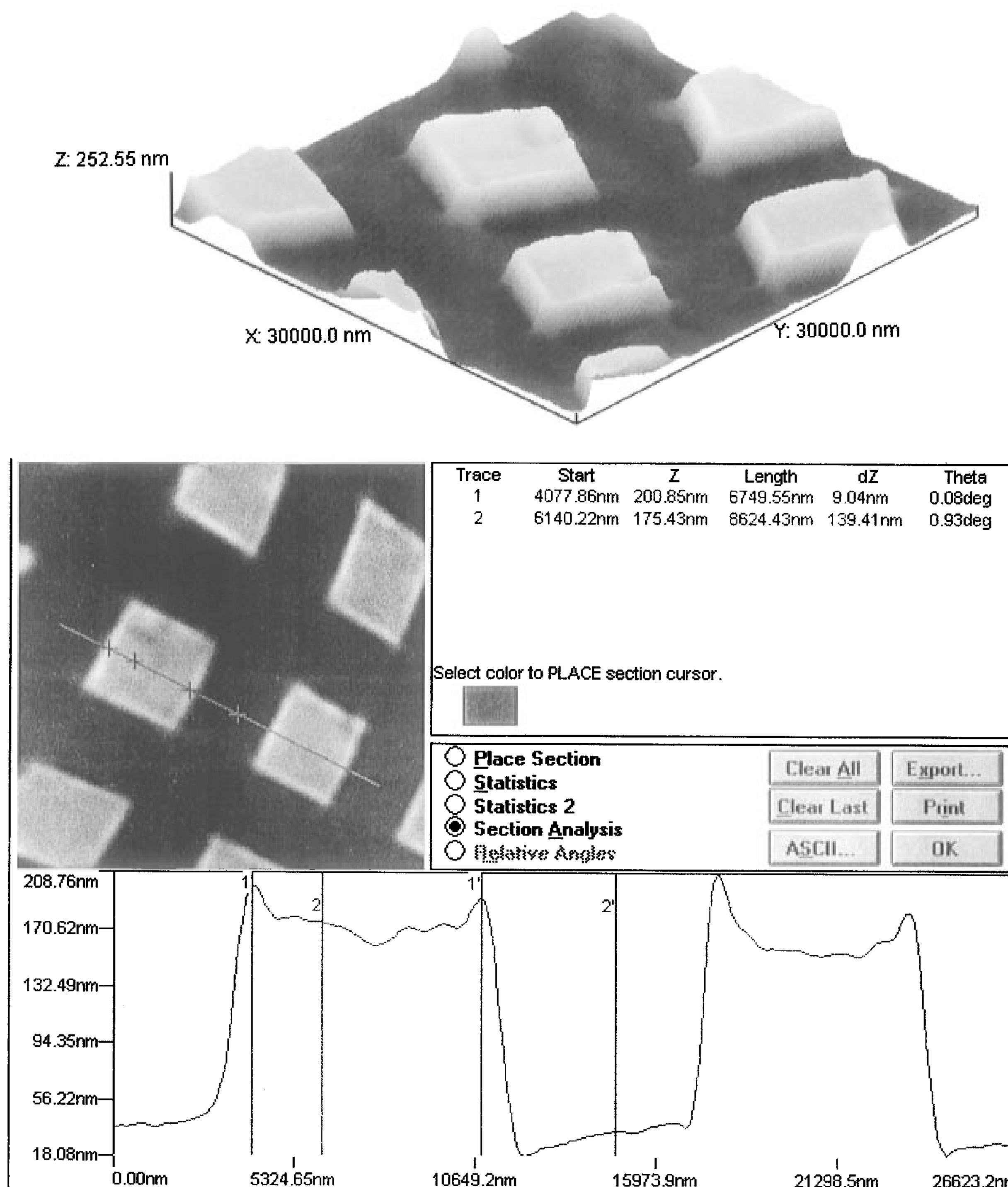


Figure 7. AFM micrograph of negative-tone relief image obtained in the film polymeric amine precursor **3**–epoxy resin EPON 828 after prebake at 80 °C for 30 min, UV irradiation for an accumulated dose of 3800 mJ cm^{-2}, postbake at 80 °C for 30 min and development in acetonitrile: (A) three-dimensional view; (B) crossection view and film thickness measurements.

involves repeated attack of alkoxide ions on available epoxides (Figure 3).[2b]

An important implication of the mechanism is that nucleophilic attack on the epoxide in the initiating step should be sensitive to steric hindrance. Consequently, only substrates with terminal epoxides are subject to catalytic polymerization by tertiary amines, since the relatively unhindered CH_2 group is available for nucleophilic attack in this case.

We performed certain model studies in order to evaluate the possibility of selected epoxides curing by a tertiary amine. *N,N*-Dimethyl-*n*-butylamine (DMBA), a close analogue of the 2-(*N,N*-dimethylamino)ethyl groups in polymer **1**, was used as the model compound. Portions of mixtures of DMBA with commercial epoxides UVR 6110, EPON 828, and DEN 438 (Figure 4) (molar ratio epoxy/amine = 8:1) were spread between NaCl rectangular plates and heated at 80 °C. Curing was observed visually and measured quantitatively by recording transmission IR spectra of all mixtures. Portions of mixtures of DMBA with EPON 828 and DEN 438 were cured in 30 min to the point that NaCl plates could not be separated. There was also a significant decrease in intensity of an IR band at 916 cm^{-1} assigned to the closed epoxide rings and a significant increase in intensity of an IR band at 1120–1145 cm^{-1} assigned to

ether linkages formed by ring opening (Figure 5) (assignments were made in accordances with refs 18a,b). Further thermal exposure of these mixtures led to no changes in the IR. At the same time no curing was observed in the mixture with UVR 6110, a cycloaliphatic epoxide; no changes in the IR spectrum were observed even after 2 h of thermal exposure (Figure 5). The addition of glycerol (a polyol) did not influence the curing behavior or changes in IR spectrum for either of the three mixtures. The results clearly show that tertiary amines of the kind outlined above are suitable only for thermal curing of polyfunctional epoxides with terminal epoxy groups.

Single-crystalline Si wafers are transparent in the fingerprint region of the IR spectrum.[19] Therefore, they offer a good choice of substrate for monitoring the polymerization of epoxides initiated by our polymeric photobases by the means of IR spectroscopy. For spin-coated films containing the polymeric quaternary salt and epoxides in different compositions (Table 1) the molar ratio of photoactive pendants to epoxy moieties was chosen to be 1:2 (1:2.5 in the case of DEN 438). This is a lower ratio than that used in the work of Beecher et al.[13] in which the mole ratio was biased in favor of the amine precursor.

Prebaking of films containing both epoxides and quaternized polymer at 80 °C for 30 min does not induce curing. No changes in IR spectrum were observed (Figure 6), and films of all compositions were completely soluble in acetonitrile.

Parts of films were then exposed through a 365 nm filter (bandwidth ~ 40 nm) to different doses of defocused UV irradiation. No changes in the epoxy region (902−916 cm^{-1}) of the IR spectrum for irradiated areas were observed for any of the compositions even for doses yielding ca. 75% conversion to polymeric amine (earlier results).[20] However, the changes in the carbonyl region of the spectrum noted previously[14] during irradiations of films of polymer **3** alone were again observed. We infer, therefore, that photochemical processes leading to the formation of polymeric amine proceeded uninhibited in the epoxy matrix. Films of all compositions were then exposed to the doses (4500 mJ cm^{-2}) which have been shown to be adequate to render the film **3** completely removable by our acid development procedure.[20] All areas of the films were completely soluble in acetonitrile regardless of whether they were irradiated or not. This comes as no surprise since it is known that the anionic polymerization of epoxides is thermally driven.[2b] As a result, UV exposure was followed by a subsequent heating step during which the whole film was heated to 80 °C for 30 min. This temperature was chosen to be below T_g for polymer **3**. The decrease in intensity for IR band at 916 cm^{-1} in the irradiated portions of the films of compositions **B** and **C** is indicative of epoxy ring opening (Figure 6). However, no changes in this region of IR spectrum were observed for films containing **A**. Immersion of irradiated films containing **B** or **C** in acetonitrile leads to the immediate dissolution of nonirradiated areas with film retention in the irradiated portions. Apparently, sufficient epoxide polymerization had occurred forming an insoluble network.[4] It is likely that complete consumption of the epoxides was inhibited because of the low mobility of the polymers, both amine and epoxy, in the cross-linked matrix. Film containing **A** is completely dissolved upon immersion even though polymeric amine was formed. The results are entirely consistent with the view that photolysis produces polymeric tertiary amines which can initiate polymerization of epoxides. However, only those epoxides which contain terminal epoxy groups are cross-linked.

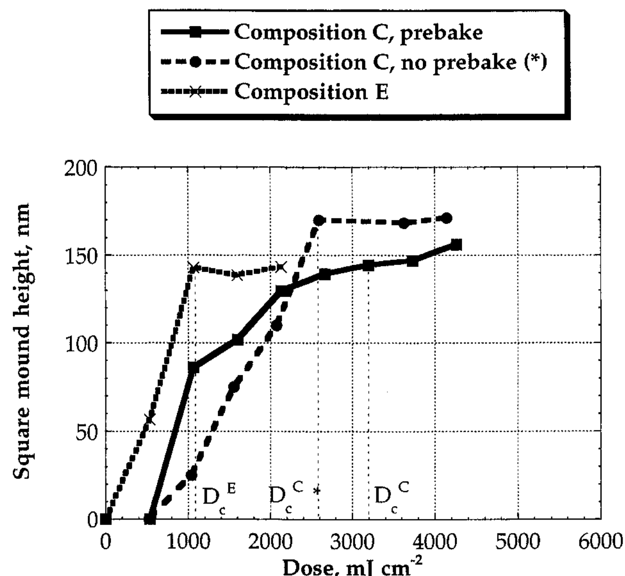


Figure 8. Sensitivity graphs for negative-tone image formation for compositions **C** (prebaked and not prebaked) and **E** (see Table 1).

Since the irradiated and the unexposed areas evidence differential solubility in the developing solvent (exposed areas are rendered less soluble), the formation of negative photoimages is possible.[21] We have decided, therefore, to determine both resolution and sensitivity parameters for this system.

A number of films of all compositions were exposed to different doses of UV light imagewise through soft-contact Cu foil grids. After the postbake and development procedures described above, the three-dimensional relief images of the mask (ca. 7 × 7 μm square mounds) were formed in the case of all compositions except **A** (Figure 7a). Atomic force microscopy (AFM) was utilized to determine the thickness of the remaining film portions as well as its surface structure. The thickness of the film remaining after development (dZ parameter in Figure 7b) was plotted versus the exposure dose in order to obtain a sensitivity curve for each composition (the examples for compositions **C** and **E** are shown in Figure 8). Sensitivity parameters D_c and D_0 can be determined from the corresponding sensitivity curve and are shown in Table 1. D_0 is defined as the minimum exposure dose required to start insolubilization of the matrix leading to the thinnest detectable films under the conditions of exposure, prebake, and

(18) (a) Watt, W. R. *Epoxy Resin Chemistry*; ACS Symp. Ser. 114; American Chemical Society: Washington, DC, 1979; p 17. (b) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley & Sons, Inc.: New York, 1991.

(19) Lee, E. J.; Bitner, T. W.; Ha, J. S.; Shane, M. J.; Sailor, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 5375.

(20) Mejiritski, A.; Polykarpov, A. Y.; Sarker, A. M.; Neckers, D. C. *J. Photochem. Photobiol. A: Chem.*, in press.

(21) Thompson, L. F.; Willson, C. G.; Bowden, M. J. *Introduction to Microlithography*, 2nd ed.; ACS Professional Reference Book; American Chemical Society: Washington, DC, 1994.

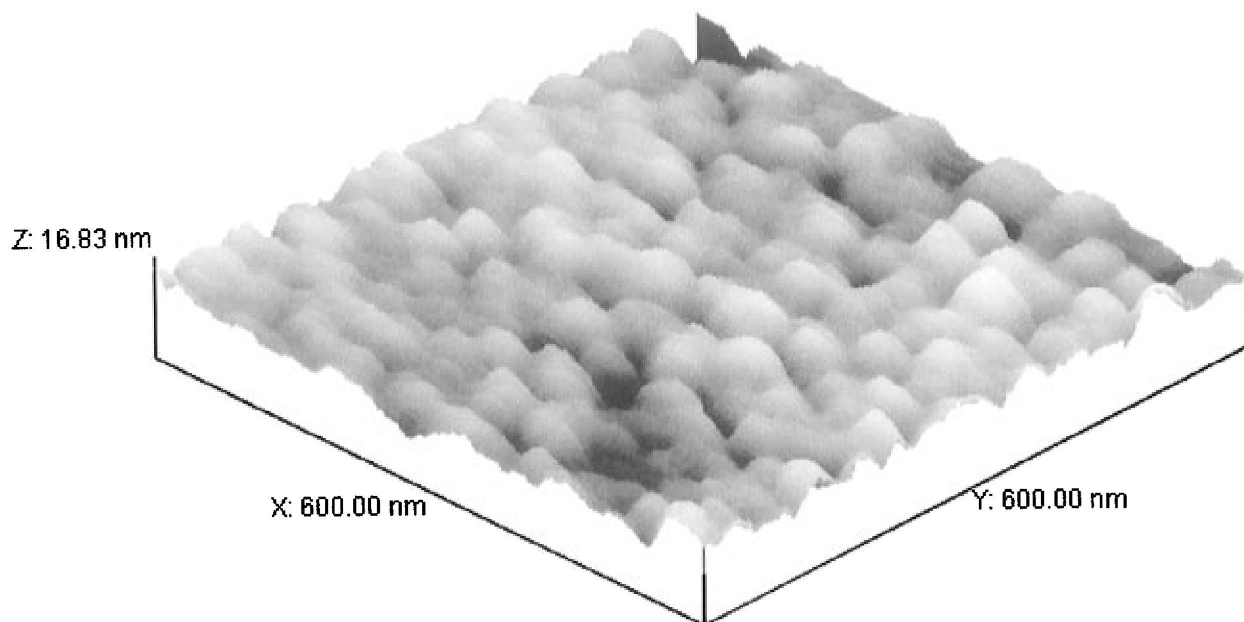


Figure 9. AFM micrograph showing surface morphology of film of epoxidized resin cross-linked with polymeric amine generated by UV photolysis of polymer **3**.

development. D_c is the minimum exposure dose after which thickness of the remaining film reaches saturation. For compositions **B** and **C** D_c is equal to ca. 3200–3800 mJ cm^{-2}, which corresponds to the ca. 70% of precursor conversion to polymeric amine.[20] This value quantitatively corresponds to the conversion necessary for positive-tone photoimaging in polymeric systems **2** and **3**. Thus, no significant chemical amplification is achieved from expected catalytic chain mechanism of epoxide curing by polymeric tertiary amine. Another possible reason for low sensitivity is low optical density (less than 5%) of the film in the irradiation range (340–380 nm). This leads to inefficient light absorption by the amine generating chromophores. Low optical density at the irradiation wavelength is the direct result of the low extinction coefficient of the benzophenone chromophore (~200 L mol^{-1} cm^{-1}). The search for other chromophores capable of participation in the similar amine-photogenerating photolysis is under way.

The appearance of the surface of the developed, cross-linked matrix undergoes significant transformation as the irradiation dose, followed by postbake, is gradually increased. While the film appears to be an ensemble of polymer islands only slightly fused together at doses equal D_0, it becomes a unified solid with island tops comprising surface "waves" at doses equal to D_c (Figure 9).

Highly sensitive photoresists are sought in modern microlithography because of their effective utilization of low-brightness sources. Since quantum yields of most photochemical transformations are less than 1.0, thermal catalytic processes are investigated to enhance the photochemical effect in the phenomenon known as chemical amplification.[15,22] We expected to achieve amplification by adding glycerol [$CH_2(OH)CH(OH)CH_2$-(OH)] to the film containing **C** with the OH/epoxy molar ratio chosen to be 2:1. A series of spincoated films of composition **D** on Si wafers were prebaked, imagewise exposed, postbaked, and developed according to the procedure described above. This resulted in very little amplification still requiring ca. 70% of precursor conversion to reach D_c. It has been noticed that the intense glycerol IR stretch corresponding to a hydroxyl group at ca. 3450 cm^{-1} disappears as the film is prebaked at 80 °C for 30 min. We thus decided to omit the prebake step for the next series of spin-coated films of composition **E**. After exposure, postbake, development, and remaining film thickness AFM analysis, this series yielded sensitivity parameters of D_0 and D_c equal to 200 and 1050 mJ cm^{-2}, respectively (Figure 8). This corresponds to only 20% conversion to polymeric amine in order to reach D_c, the point of maximum possible film thickness. In accordance with the above mechanism for epoxide cross-linking (Figure 3) the presence of hydroxyl functionality significantly promotes the process. If allowed to remain in the film (no prebake in the case of glycerol or use of completely nonvolatile polymeric alcohols), hydroxyl-containing reagents lead to more than 3-fold increase in sensitivity.

An increased mobility of the photogenerated catalyst may occur when the prebaking step of the processing sequence is omitted. Such a mobility increase would originate from plasticization of the films by residual casting solvent and glycerol. No characteristic carbonyl stretch at 1676 cm^{-1} for *N,N*-dimethylformamide was observed when the transmission IR spectrum was recorded for a spin-coated film of composition **C** before prebake. This indicated that less than 5% (IR sensitivity limits) of the residual casting solvent remained in the film. To elucidate the influence of the residual casting solvent on the sensitivity, the nonprebaked batch of films of composition **C** was subjected to the imaging and AFM evaluation described above. Only a slight improvement was provided by not prebaking the films (Figure 8). This eliminates residual *N,N*-dimethylformamide as the plasticizer. However, some plasticization of the films by glycerol may be as important in the observed sensitivity increase as the proposed amplification mechanism.

(22) Reichmanis, E.; Houlihan, F. M.; Nalamasu, O.; Neenan, T. X. *Chem. Mater.* **1991**, *3*, 394.

Conclusion

We have shown that photogenerated polymeric amines can be used as curing agents for epoxidized substrates. Since a tertiary amine is formed, monomeric epoxides in which epoxy groups are terminal are especially suitable. To reach the maximum possible thickness of film remaining after exposure, postbake, and development in acetonitrile doses on the order of ca. 3200−3800 mJ cm^{-2} are required. When hydroxyl moieties are introduced and retained in the film, the bulk catalytic nature of the thermal cross-linking process leads to more than 3-fold improvent in sensitivity.

Acknowledgment. The work has been supported by grants from the National Science Foundation (NSF 9013109), the Office of Naval Research (N00014-91-J-1921) and DARPA (DAAH 04-95-1-0053). We are sincerely grateful for the support of these agencies. We are indebted to the McMaster Endowment for financial support, to Professors George S. Hammond and Thomas H. Kinstle for extremely valuable discussions, and to Adrian Lungu for his help with polymer molecular weight determination.

CM970003J