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# A New Method To Characterize Curing of Epoxy with Aromatic Diamines by Azochromophore Labeling[†]

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ABSTRACT: When diepoxide is cured with aromatic diamine, primary amine reacts with the epoxide ring to form a secondary amine and eventually a tertiary amine. Due to the significant differences in the reactivities of primary and secondary amines, the major reaction products will be the four species $H_2NRNHR''$ (A), $R''HNRNHR''$ (B), $R''HNRNR''_2$ (C), and $R''_2NRNR''_2$ (D), where $R'' = CH_2CH(OH)\sim\!\sim$. In order to obtain the quantitative composition of these four species during cure, we used a very small amount of *p,p′*-diaminoazobenzene (DAA) as a label in the DGEBA–DDS epoxy (diglycidyl ether of bisphenol A–diaminodiphenyl sulfone). The reactivities of DDS and DAA appear to be similar so as to allow us to follow the curing as manifested by the UV–vis spectral changes of DAA. As epoxy is cured, $\lambda_{max}$ of the $\pi \rightarrow \pi^*$ transition corresponding to the azo bond of DAA shows bathochromic shifts in a way that provides spectral discrimination for the products A–D. On the basis of predicted $\lambda_{max}$ positions and with the assumption of equal extinction coefficients among the four products, deconvolution of the spectra shows increasing concentration of C and D (branch points and cross-links, respectively) after gelation and increasing concentration of cross-links after extensive curing.

The structure and properties of epoxies are known to strongly depend on the extent of cure and of physical aging which has taken place after the cure cycle is completed. A number of physicochemical techniques have been used or developed toward a better characterization of cure and physical aging phenomena in epoxies. Among them are such techniques as FT-IR spectroscopy,[1] thermal analyses,[2] GPC[3,4] (size exclusion chromatography), microdielectrometry,[5] torsional braid analyses,[6] $^{13}C$ solid-state NMR,[7] thermally stimulated current measurement,[8] fluorescence,[9] and ESR spectroscopy.[10] While these experimental techniques provide useful information on the extent of cure and on epoxy structure, there are certain limitations and disadvantages associated with each technique. For example, FT-IR fails to monitor later stages of cure when the epoxy peak disappears.[11] The use of GPC and of size exclusion chromatography is limited to the early stages of the curing reaction. Fluorescence and ESR techniques mainly measure decreasing mobilities of the label with increasing cure and viscosity but can shed some light on the reaction products. For example, when a nitroxide monoamine is reacted with epoxy, Brown and Sandreczki[12] recently observed different ESR spectra which may allow spectroscopic monitoring of the initial addition products, if the reactivity of the nitroxide is similar to that of a diamine.

$^{13}C$ MAS–CP (magic angle spinning–cross polarized)

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[†] This paper is dedicated to Professor W. H. Stockmayer on the occasion of his 70th birthday with admiration and gratitude.

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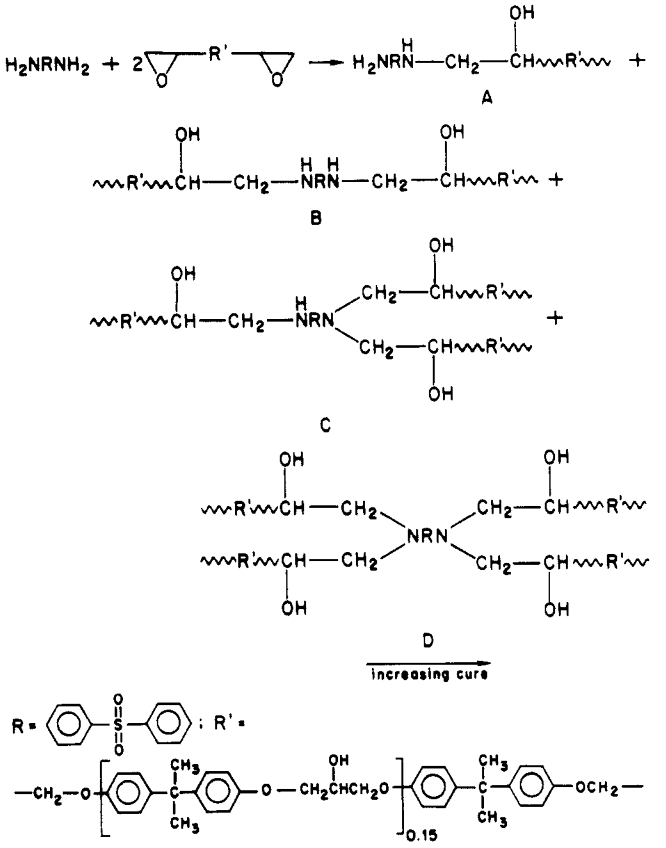
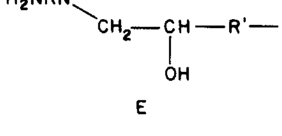
Scheme I[a]
Cure Products in the DGEBA-DDS Epoxy System



[a] The presence of A and B has been experimentally confirmed by chromatographic separation by Hagnauer.[24]

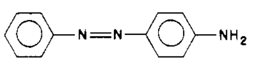
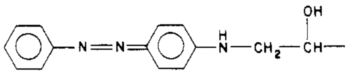
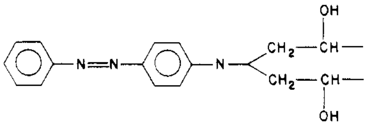
solid-state NMR is a powerful technique for the characterization of polymeric solids.[12] As Garroway et al.[7] demonstrated, it can provide information on certain molecular motions in epoxy. It may not be easy, however, to obtain quantitative compositional information on the reaction products by $^{13}C$ NMR in cross-linked polymers due to such complications as line broadening[13a] and spinning side bands. The fact that the peak intensity is not generally representative of the concentration in cross-polarization experiments is another problem.[13b] $^{15}N$ NMR, in principle, may be more useful, but its sensitivity is poor because of its low natural abundance.[13b]

Epoxies formed with aromatic diamines such as DGEBA-DDS (diglycidyl ether of bisphenol A-diaminodiphenyl sulfone) are important networks for high-temperature applications. In this system (DGEBA-DDS), at the stoichiometric ratio, four species, A-D as shown in Scheme I, will be the major products as the cure proceeds. This is due to the well-known fact that the amine groups are major reactive species, and the hydroxyl groups do not initiate epoxypolymerization in uncatalyzed epoxy cured with aromatic diamines at the stoichiometric ratio.[14b] The reactivities of primary vs. secondary amine groups are significantly different in aromatic amines so that the following species E is considered to be negligible.[14]



E

Table I
**Positions of $\lambda_{max}$ for $\pi \rightarrow \pi^*$ Transition of *trans*-AA* in DGEBA-DDS Epoxy**

| species | $\lambda_{max}$, nm | $\Delta\lambda$, nm |
|---|---|---|
|  | 395 | 0 |
|  | 405 | 10 |
|  | 418 | 23 |

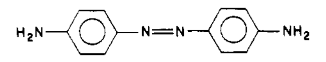
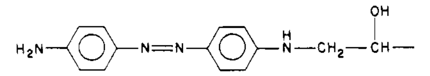
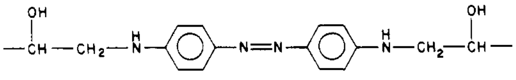
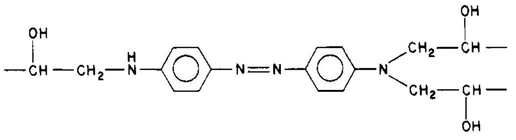
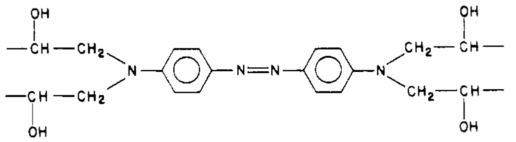
[a] *p*-Aminoazobenzene.

In order to understand cure mechanism, kinetics, and structure/property correlations, it will be important to know the relative concentrations of the primary reaction products (A-D) during the course of the curing process. While FT-IR may be used in epoxy curing studies to follow the decrease in the primary amine concentration and the increase in the secondary amine concentration,[10,15] spectral discrimination between species A-D is not possible. To the best of our knowledge, none of the techniques used so far has provided such specific compositional information.

In this study, we introduce a new technique which can provide quantitative compositional and site-specific mobility information during the curing process. Our technique is based on azobenzene chromophore labeling with UV-vis spectroscopy. Azobenzene can exist either as a trans isomer or as a cis isomer. The trans form is more stable and shows intense absorption around 317 nm due to the $\pi \rightarrow \pi^*$ transition of the azo bond and a weak absorption around 444 nm due to the $n \rightarrow \pi^*$ transition.[16] The $\pi \rightarrow \pi^*$ transition for the cis isomer occurs at a much shorter wavelength, due to the lack of coplanarity. As expected, electron-donating substituents such as an amine group in the para position of azobenzene lower the energy for the $\pi \rightarrow \pi^*$ transition so that the wavelength of maximum absorption is shifted to a longer wavelength (bathochromic effect).[17] Of particular interest to us is a *p*-aminoazobenzene (AA), which shows $\lambda_{max}$ at 385 nm in 95% ethanol. When the primary amine in AA becomes the secondary amine or the tertiary amine, as in *p*-(ethylamino)azobenzene or *p*-(diethylamino)azobenzene, $\lambda_{max}$ in the same solvent is further shifted to 405 or 415 nm, respectively, but the extinction coefficients remain unchanged.[17a] These bathochromic shifts are due to the increasing electron-donating ability of the tertiary and secondary amines compared to that of the primary amine. The solvent is known to influence the position of $\lambda_{max}$ but similar bathochromic shifts are observed even in different solvents.[18]

In order to confirm that such bathochromic shifts do occur in epoxy matrices, we added a very small amount (0.33%) of *p*-aminoazobenzene (AA) to our epoxy system. Figure 1 shows the UV-vis spectra of such a system as the epoxy cures. In this spectral range (above 350 nm), the epoxy matrix has no absorption. Figure 1a shows the spectrum for AA just dissolved; spectra b and c show the results after 20 and 1290 min of curing at 160 °C, respectively. From Figure 1, it is clearly observed that the $\lambda_{max}$ of the azochromophore is shifted to longer wavelenghts as expected and assigned in Table I. The intensity decrease in Figure 1b,c is due to decreasing thickness and not due to the changes in extinction coefficients. Bathochromic shifts of 10 and 23 nm were observed when the primary amine group became secondary and tertiary amine

**Table II**
**Predicted Positions of $\lambda_{max}$ for $\pi \rightarrow \pi^*$ Transition of *trans*-DAA[a] in DGEBA-DDS Epoxy**

| species | $\lambda_{max}$, nm | $\Delta\lambda$, nm |
|---|---|---|
|  1' | 410 | 0 |
|  2' | 420 | 10 |
|  3' | 430 | 20 |
|  4' | 443 | 33 |
|  5' | 456 | 46 |

[a] *p,p'*-Diaminoazobenzene.

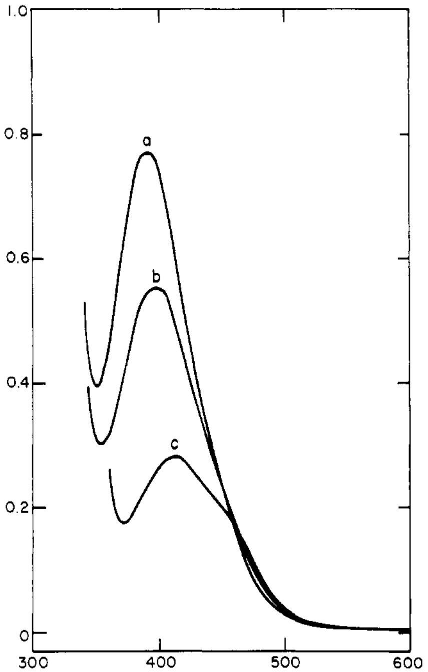


**Figure 1.** UV-vis spectra of *p*-aminoazobenzene (AA) in stoichiometric DGEBA-DDS expoxy: (a) when AA is dissolved in DGEBA (by heating for 5 min at 120 °C); (b) after cure at 160 °C for 20 min; (c) after cure at 160 °C for 1290 min (thickness of the sample placed between two quartz plates is decreased with cure extent).

**Table III**
**Compositional Analyses of DGEBA-DDS Epoxy by the DAA Labeling Technique as a Function of Curing Time at 160 °C**

| | % compn of species[a] | | | | |
|---|---|---|---|---|---|
| curing time, min | 1' | 2' | 3' | 4' | 5' |
| 0[b] | 75 | 25 | 0 | 0 | 0 |
| 20 | 24 | 22 | 44 | 10 | 0 |
| 50 | 12 | 21 | 22 | 28 | 17 |
| 150 | 9 | 21 | 18 | 26 | 26 |
| 1140 | 6 | 20 | 13 | 20 | 41 |

[a] Species are defined in Table II. [b] Heated to 120 °C for 5 min to mix the reactants prior to curing.

groups, respectively, as shown in Table 1.

For *p,p'*-diaminoazobenzene (DDA), $\lambda_{max}$ appears at a longer wavelength (by about 15–25 nm) in comparison with *p*-aminoazobenzene, due to the additive effect of the electron-donating nature of two amino groups in the *p,p'* positions. As expected, it has been observed that $\lambda_{max}$ of *p,p'*-bis(dialkylamino)azobenzene is further shifted to longer wavelengths as the amino groups become secondary and tertiary amines.[17a] In fact, Bridgeman and Peters reported that $\lambda_{max}$ can shift by as much as 100 nm when different substituents are introduced on the two nitrogens on DAA.[18b]

We can take advantage of these large bathochromic shifts in $\lambda_{max}$ of DAA as the epoxy is cured with diamine. Our label, DAA, can be added to the DGEBA-DDS system in a very small amount (<1%). Provided that the reactivities of the label are similar to those of DDS, we may then interpret the results as representing the cure system. Fortunately, their reactivities seem reasonably close, as suggested by their similar Hammett $\sigma$ parameters.[19] Figure 2 shows the UV-vis spectra when a very small amount (0.14%) of DAA was added to a stoichiometric mixture of DGEBA and DDS. Again, the decrease in intensity is due to the decrease in thickness rather than to changes in extinction coefficients. Figure 2a represents the spectrum when DAA was dissolved in DGEBA, while spectra b–e are the spectra after cure at 160 °C for 20, 50, 150, and 1140 min, respectively. On the basis of the previous studies on the substituent effects[17,18] and the data in Table I, we may predict the positions of $\lambda_{max}$ for the four reaction products as listed in Table II. It is noted that $\lambda_{max}$ may be shifted by about 50 nm when both nitrogens become tertiary. It is important to point out that we may discriminate between symmetrically and asymmetrically substituted diamines (e.g., 2' vs. 3' or 4' vs. 5').

Assuming that the positions $\lambda_{max}$ for the reaction products are approximately the same as in Table II and as-

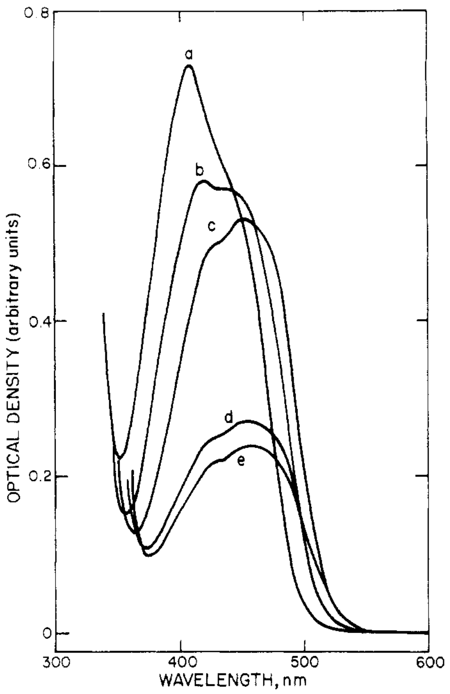


**Figure 2.** UV-vis spectra of *p,p'*-diaminoazobenzene (DAA) in stoichiometric DGEBA-DDS epoxy: (a) when DAA is dissolved in DGEBA (by heating for 5 min at 120 °C); (b-e) after cure at 160 °C for (b) 20, (c) 50, (d) 150, and (e) 1140 min (thickness of the sample placed between two quartz plates is decreased with cure extent).

suming equal extinction coefficients for the products, we made an attempt to deconvolute Figure 2 with a computer program. The program is written to fit Figure 2 as a sum of various species, assuming a Gaussian distribution curve for each species in Table II. Table III summarizes the results obtained. In Table III, the trend of increasing concentration of species 2', 3', 4', and 5' is noted as the cure proceeds. According to Enns and Gillham,[20] the gel time at 160 °C for this epoxy system is about 50 min. Therefore, the composition after 50-min curing is expected to show increasing concentration of species 4' and 5' (branch point and cross-link points, respectively). This is indeed the case as shown in Table III, thus supporting our assumption of similar reactivities of DAA and DDS. Additional curing at this temperature (e.g., 7 days) produces few changes in composition. This behavior is expected because this epoxy vitrifies after about 200 min.[6] After vitrification, further chemical reaction is believed to be limited. Such a limited reaction is supported by IR spectroscopy. The extent of reaction as monitored by epoxy ring ($A_{915\text{cm}^{-1}}/A_{1184\text{cm}^{-1}}$) shows only about 60% after 1140 min of reaction at 160 °C, which, at least indirectly, supports the presence of unreacted primary and/or secondary amine. There appears some indication for the presence of unreacted primary (1630 $\text{cm}^{-1}$) and secondary amine (3410 $\text{cm}^{-1}$) in the IR spectra. However, due to strongly overlapping peaks near the amine peaks, quantitative analyses by IR spectroscopy are very difficult.

We are now in the process of making and separating model compounds as reaction products of DAA and monoepoxy compound for a better estimation of their $\lambda_{\max}$ positions and extinction coefficients, which will lead us to more accurate estimations of the composition. Once we can identify the exact position(s) of $\lambda_{\max}$ for each species, we can also study the mobility or free volume environment in the vicinity of each species by following the trans $\rightleftharpoons$ cis photoisomerization behavior of azo labels as volume-sensitive label since it provides useful insights for understanding the molecular structure of the polymer.[21]

We believe that this study with DAA provides unique opportunities to follow mechanism, kinetics, and mobility in epoxy systems and to test theories of network formation.[22,23] When other aromatic curing agents are used, DAA can be modified to match its reactivities with those of the curing agents. Also, our technique is not limited to epoxy systems. In fact, it can be applied in any polymerization system using aromatic diamines.

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(25) **Note Added in Proof**: Compositions estimated in Table III were based on $\lambda_{max}$ values close to those of model compounds, namely 420, 445, 460, and 470 nm for species **2′**, **3′**, **4′**, and **5′**, respectively.

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# Block Copolymers near the Microphase Separation Transition. 2. Linear Dynamic Mechanical Properties

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ABSTRACT: Three 1,4-polybutadiene–1,2-polybutadiene diblock copolymers near the microphase separation transition (MST) have been examined rheologically. The low-frequency linear dynamic shear moduli are shown to be strongly dependent on the phase state of these samples, which exhibit an upper critical temperature. Heating a microphase-separated (ordered) sample containing 38% 1,4-polybutadiene through the MST produces a discontinuity in both the elastic modulus and dynamic viscosity at a temperature $T_m$, corresponding to the first-order melt transition from the ordered to the disordered (homogeneous) state. Cooling from the disordered state produces no discontinuity in the moduli at $T_m$; instead, the polymer melt exhibits metastable behavior down to the stability limit in temperature, $T_s < T_m$. Below $T_s$, the viscoelastic response is characteristic of microphase-separated block copolymer, regardless of thermal history. These findings quantitatively verify the predicted phase behavior for diblock copolymers characterized by an upper critical temperature.

## Introduction

Over the past several decades, researchers have reported extensively on the viscoelastic properties of block copolymers. Yet, with few exceptions, these investigations have dealt exclusively with microphase-separated systems. As a result, the rheological properties of block copolymers near the microphase separation transition (MST) are not well understood. This situation is a natural consequence of the difficulty of preparing bulk block copolymers near the phase boundary. As demonstrated by Leibler,[1] the critical point in a block copolymer phase diagram scales as $(\chi N)_c = 10.5$, where $N$ is the degree of polymerization and $\chi$ is the Flory segment–segment interaction parameter. This prediction is based upon an upper critical temperature, often referred to as an upper critical solution temperature (UCST), for which $\chi > 0$. Therefore, the MST can be approached from the microphase-separated (ordered) state by decreasing either $\chi$ or $N$. In practice, $N$ must be adjusted so as to bring $\chi N$ close to the phase boundary; varying temperature ($\chi \sim T^{-1}$) then provides the means of probing the sample rheology through the MST. Since most polymer pairs are characterized by a relatively large interaction parameter, high molecular weight diblock copolymers ($N > 100$) near the critical point are correspondingly rare. Until present, the rheology of block copolymers near the MST has been studied in only a few samples.[2-4]

Chung et al.[2] and Gouinlock and Porter[3] have both examined the dynamic mechanical properties of a styrene–butadiene–styrene triblock copolymer (7S–43B–7S) at elevated temperatures and have reported similar results. These authors found that upon raising the temperature, the low-frequency dynamic elastic modulus and dynamic viscosity decreased dramatically between 140 and 150 °C. Above this transition temperature the rheological behavior was Newtonian, while below 140 °C it was highly non-Newtonian. Both groups related these findings to the block copolymer microphase separation transition. Widmaier and Meyer[4] subsequently examined the rheological properties of a styrene–isoprene–styrene triblock copolymer (14S–17I–14S) and concluded that a structural transition occurred in that sample at 225 °C.

**Table I**
**Molecular Characterization**

| sample | $N_n \times 10^{-2}$ [a] | $N_w/N_n$ [b] | $\Phi$ [c] |
|---|---|---|---|
| BB2 | 10.6 | 1.03 | 0.46 |
| BB6 | 13.3 | 1.05 | 0.38 |
| BB7 | 15.5 | 1.05 | 0.48 |

[a] Number-average degree of polymerization. [b] Polydispersity index as determined by high-pressure size exclusion chromatography. [c] $\Phi = N_{1,4}/(N_{1,4} + N_{1,2})$ as determined by $^{13}$C NMR.

In the first of this series of articles,[5] we reported on the preparation and physical characterization of a model set of 1,4-polybutadiene–1,2-polybutadiene diblock copolymers near the MST. In that report, the phase state of the polymers was identified by qualitatively examining the flow behavior of each sample. In another recent article,[6a] the structure of the homogeneous melt state was determined by small-angle neutron scattering (SANS); this provided a direct measurement of the segment–segment interaction parameter, which determines the location of the MST. The present text describes the quantitative linear dynamic mechanical analysis of three of these diblock copolymers, lying near the phase boundary. These results, while consistent with those described above, further provide a detailed description of the thermodynamic behavior of block copolymers near the microphase separation (order-to-disorder) transition, including the identification of the equilibrium and stability limits between the microphase-separated and homogeneous melt states. These findings, together with the SANS results, quantitatively confirm the mean-field predictions of Leibler[1] concerning the microphase separation transition in diblock copolymers.

## Experimental Section

Synthesis and characterization of the diblock copolymers have been previously reported.[5] Characterization data for the three presently discussed samples are listed in Table I. The 1,4-polybutadiene block microstructure is 89% 1,4 (cis and trans) and 11% 1,2, while that of the 1,2-polybutadiene block is >98% 1,2.

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