

## Reversible Isomerization and Cure Monitoring of Epoxy Azobenzene Resins

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**ABSTRACT:** The photoresponsive behavior of the glycidyoxyazobenzene (GOAB) monomer, synthesized using an improved method, is examined by UV/Vis spectroscopy. The monomer is cured with diethylenetriamine (DETA), forming a new epoxy resin. Proton NMR spectroscopy is used to monitor the completion of the curing reactions. Kinetics for reversible trans and cis isomerization in the cured system and also in the epoxy monomer are identified by UV/Vis spectroscopy during *in situ* irradiation with appropriate wavelengths (290–320 nm for UV and 400–500 nm for visible). The rates of recovery of the monomer from cis to trans forms are also obtained by heating and storing in the dark. Furthermore, the reactivity of the monofunctional GOAB monomer with a common amine, DETA, as a curing agent, is investigated using isothermal and dynamic heating scans in a DSC pan and by simultaneously monitoring the near-FTIR spectra. The modified epoxy azobenzene proved to be reactive enough with DETA to form a network that can sustain temperatures of up to 200°C. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40770.

**KEYWORDS:** crosslinking; irradiation; properties and characterization

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### INTRODUCTION

The ability of azobenzene chromophores to change the structure of the whole matrix in which they are incorporated either by light or temperature as a stimulus, is attributed to the photomechanical effect.<sup>1–5</sup> The definition of the photomechanical effect is the reversible change in shape induced in some molecules by the absorption of light, which results in a significant macroscopic mechanical deformation of the host material.<sup>6</sup> More significantly, azobenzene and its derivatives have two geometric isomers, the thermodynamically more stable trans form and the less stable cis form, which interconvert upon irradiation with light of appropriate wavelength or with the application of heat, resulting in changes of mechanical, optical, and flow properties.<sup>1</sup>

Azobenzene polymers irradiated with UV light have the potential to modify the viscosity of a material. The viscosity of copolymer solutions of methacryloyloxyazobenzene and methylmethacrylate in DMSO was found to be reduced by the dipole–dipole interaction caused by photoisomerization of the azobenzene chromophore.<sup>5</sup> Various studies have been conducted in thermoplastic and acrylic-based azobenzene polymers for photoviscosity effects,<sup>7,8</sup> stiffness changes,<sup>8,9</sup> and elongation–contraction cycles.<sup>10–12</sup> This study will be the first research related to the cure monitoring of azobenzene-based epoxy thermosettings.

Epoxy resins are classified as thermosetting materials and have been widely used as coatings and composite matrices for various military and civilian applications.<sup>13,14</sup> Epoxy thermosets with highly cross-linked density often face the problem of brittleness.<sup>7,13</sup> Reactive modifiers, like phenyl glycidyl ether (PGE) or butyl glycidyl ether (BGE) are included into the epoxy mixture for the adjustment of the cross-link density and the enhancement of impact resistance.<sup>14</sup>

Thermosetting polymers are formed by the chemical reaction of epoxy monomers with di- or multifunctional amines.<sup>15</sup> Thus, the reactivity of new modified azobenzene epoxies is a vital criterion for the process conditions as well as for the investigation of photomechanical changes. The epoxy curing process can be generally characterized by spectroscopic and/or thermal analysis techniques such as mid- and near-IR and DSC.<sup>16,17</sup> Poisson et al.<sup>18</sup> demonstrated that near-IR spectroscopy is the most suitable and quantitative analytical technique for monitoring the degree of curing of epoxy/amine systems, since its wavenumber ranges corresponding to amine and epoxy peaks are well defined.

Polymers are generally sensitive to UV light which can lead to undesired degradation with increased brittleness and reduced fatigue strength. Preventing such degradation is of continuous interest to material scientists. Previous researchers demonstrated that acrylic-based azobenzene polymers show improved mechanical properties

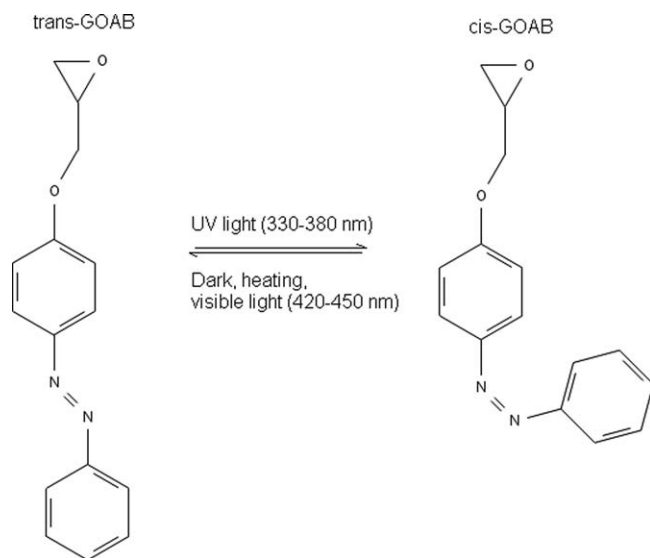


Figure 1. Reversible trans/cis isomerization of GOAB.

when they are exposed to UV radiation.<sup>8</sup> The introduction of an epoxy azobenzene as a reactive modifier into a resin is thought to have a great potential in improving the mechanical properties of composite structures that are frequently exposed to UV radiation. Before introducing this class of resins into composites their ability to react with common hardeners such as amines, as well as their reaction kinetics and photoresponsive behavior have to be fully understood.

In this article, we report on the synthesis and the photoresponsive behavior of a new azobenzene-based system (GOAB/DETA). The kinetics of the reversible trans/cis isomerization for the GOAB were investigated by photo treatment (UV and Vis), heating and storage in the dark. The degree of curing of the epoxy/amine system, assessed by <sup>1</sup>H-NMR and near-FTIR/DSC techniques is discussed.

## EXPERIMENTAL

### Materials

4-Phenylazophenol, epichlorohydrin and dichloromethane were purchased from Alfa Aesar and used without further purification. Benzyltriethylammonium chloride was obtained from Sigma Aldrich and used as received. Silica gel for flash chromatography and magnesium sulphate were obtained from Fluka.

### Synthesis of 4-Glycidyoxyazobenzene (GOAB)

Glycidyoxyazobenzene with both isomeric forms illustrated in Figure 1, was synthesized using an improved procedure by Peris et al.<sup>19</sup> 4-Phenylazophenol (5.0 g, 24.7 mmol), epichlorohydrin (20.2 mL, 247.2 mmol) and benzyltriethylammonium chloride (236.4 mg, 1.2 mmol), with molar ratio 1 : 10 : 0.05, respectively, were taken in a 100-mL two-necked round bottom flask equipped with a condenser and a magnetic stirrer. The reaction mixture was refluxed at 120°C under continuous stirring. The progress of the reaction was monitored by thin layer chromatography (TLC). <sup>1</sup>H-NMR spectroscopy was used to confirm the authenticity of the end product that was assumed to be 4-glycidyoxyazobenzene by TLC. The phenylazophenol was

found to have completely reacted after 2.5 h. The excess of epichlorohydrin was removed under reduced pressure using a rotary evaporator and subsequently high vacuum. The crude product was then dissolved in dichloromethane (DCM, 20 mL) and extracted three times with water (3 × 20 mL). The organic phase was left overnight on anhydrous magnesium sulphate, filtered, and the solvent evaporated using a rotary evaporator. The crude product was recrystallized from DCM/petroleum ether. It was further purified by column chromatography to yield an orange product with 81% yield.

The product was characterized by FTIR and <sup>1</sup>H-NMR spectroscopy for purity. The melting point was determined by DSC and found to be 85°C, which is in agreement with the literature value.<sup>19,20</sup>

<sup>1</sup>H-NMR (250 MHz, DMSO-*d*<sub>6</sub>, δ): 7.86–7.97 (t, 4H, Ar H), 7.43–7.53 (m, 3H, Ar H), 7.02–7.05 (d, 2H, Ar H), 4.29–4.34 (d, 1H, –OCH<sub>2</sub>–), 4.00–4.07 (q, 1H, –OCH<sub>2</sub>–), 3.50 (1H, –CH–), 2.98 (m, 1H, –CH<sub>2</sub>–), 2.92 (m, 1H, –CH<sub>2</sub>–).

IR (KBr): (–C–H–) aromatic rings; 3053 cm<sup>–1</sup>, alkanes; 2927 cm<sup>–1</sup>, (–C=C–) aromatic rings; 1500 cm<sup>–1</sup>, 1600 cm<sup>–1</sup>, (–N=N–) diazo; 1581 cm<sup>–1</sup>, (–C–N–) amine; 1224–1256 cm<sup>–1</sup>, (–C–O–) ether; 1070–1144 cm<sup>–1</sup>.

### Sample Preparation for Curing Reaction

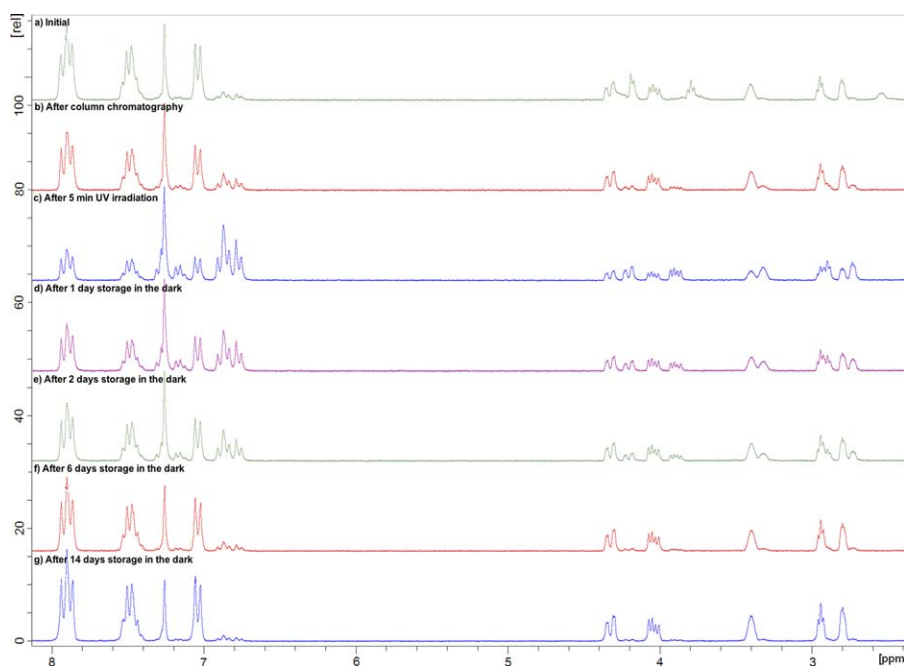
The reaction mixture was prepared for curing by adding 1.71 μL or 2.85 μL of DETA to 20 mg of GOAB in a DSC pan at room temperature. GOAB was thought to be a potential candidate for curing as it contains an epoxy group which is able to react with hardeners such as amines and the azobenzene chromophore contributes to the photoresponsive behavior of the material. DETA has five reactive sites; one secondary and two primary amines. The molar ratios of GOAB and DETA were chosen to be 5 : 1 in order to maintain the stoichiometry and 3 : 1 based on an assumption that the two secondary amines that will be formed from the two primary amines may not be very reactive to undergo complete reaction due to steric hindrance.

### Characterization

The <sup>1</sup>H-NMR spectra were recorded on a Bruker 400 MHz spectrometer using tetramethylsilane (TMS) as an internal reference. Deuterated chloroform (CDCl<sub>3</sub>) and dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) were used as solvents.

Differential Scanning Calorimetry (DSC) experiments were conducted using a METTLER TOLEDO DSC with STAR<sub>c</sub> Software, Version 9.10 under nitrogen with a flow rate of 80 mL/min. The calibration of the instrument was performed using indium (In) as a pure metal for reference at 156.6°C. The weights of the samples were between 6 and 9 mg. The melting point (*T*<sub>m</sub>) was determined using two heating and cooling cycles within the 25–200°C temperature range at a heating rate of 2°C min<sup>–1</sup>.

For the collection of the near-FTIR spectra within 4 cm<sup>–1</sup> resolution, a Nexus Nicolet instrument, equipped with a non-contact probe was used. The sample was taken in an aluminum pan with a glass cover which allowed external data recording. The noncontact probe was placed above the glass cover at a distance of 1 mm from the sample. The background spectrum was



**Figure 2.**  $^1\text{H-NMR}$  spectra of GOAB in  $\text{CDCl}_3$  at room temperature as (a) unirradiated, (b) after purification, (c) after UV irradiation and after storage in the dark (d–g). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

obtained using an empty aluminum DSC pan with a glass cover in an aerobic atmosphere. The temperature of the DSC was set to  $30^\circ\text{C}$  for a minute and then dynamic scans were performed between 30 and  $180^\circ\text{C}$  at a rate of  $5^\circ\text{C min}^{-1}$ . The molar ratio of 3 : 1 (GOAB/DETA) was chosen for all the DSC/FTIR experiments.

The UV–visible spectra were recorded over 260–600 nm wavelength range using a UV–visible spectrometer (Zeiss, MCS 522 UV–Vis) equipped with a xenon flash lamp (Zeiss, BLX 500/4). The epoxy azobenzene monomer (15 mg) was dissolved in 25 mL DMSO and used as stock solution. Each sample solution was diluted further in order to achieve smooth and clear absorbance spectra. The required concentration of the solutions used for carrying out the UV/Vis spectroscopy measurements was  $10^{-3}$  M in DMSO. Spectra were recorded in a quartz cuvette with all sides transparent. The sample holder was modified to have better access for the irradiation of samples.

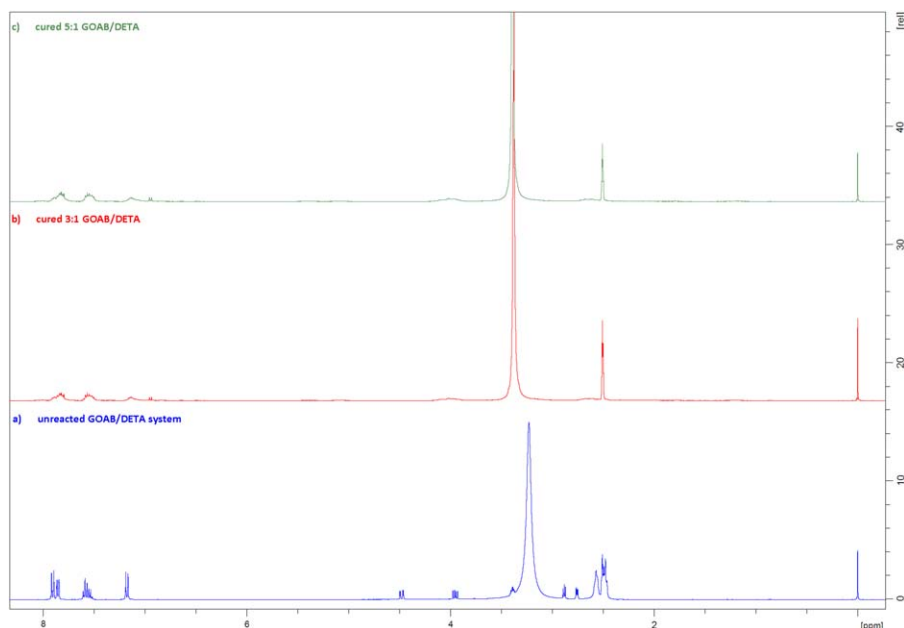
The samples were illuminated *in situ* by a M2100 Novacure light source, using filters with 320–390 nm for UV and 400–500 nm for visible light. The intensities of  $500\text{ mW cm}^{-2}$  for UV light and  $2800\text{ mW cm}^{-2}$  for visible light were used. A liquid light guide was used to deliver the light to the sample. The distance between the cuvette and light guide was chosen to 12 mm in order to achieve maximum irradiation of the materials under investigation.

## RESULTS AND DISCUSSION

### $^1\text{H-NMR}$ Spectroscopy Study to Identify Isomers in GOAB

The  $^1\text{H-NMR}$  spectra of the purified GOAB were recorded in  $\text{CDCl}_3$  at room temperature and characteristic chemical shifts are presented in Figure 2.

The spectrum in Figure 2(a) indicated the characteristic chemical shifts of GOAB at  $\delta$  7.86–7.97 (aromatic, t, 4H),  $\delta$  7.43–7.53 (aromatic, m, 3H),  $\delta$  7.02–7.05 (aromatic, d, 2H),  $\delta$  4.29–4.34 ( $-\text{OCH}_2-$ , d, 1H),  $\delta$  4.00–4.07 ( $-\text{OCH}_2-$ , q, 1H),  $\delta$  3.50 ( $-\text{CH}-$ , 1H),  $\delta$  2.98 ( $-\text{CH}_2-$ , m, 1H) and  $\delta$  2.92 ( $-\text{CH}_2-$ , m, 1H). These chemical shifts were assigned to the trans conformation of GOAB monomer. However, the appearance of additional signals at  $\delta$  7.15–7.31 (m, 3H),  $\delta$  6.87–6.90 (t, 4H),  $\delta$  6.75–6.87 (d, 2H),  $\delta$  4.17–4.22 (d, 1H),  $\delta$  2.89 (s, 1H) and  $\delta$  3.38–3.90 (q, 1H) in the NMR spectrum [Figure 2(a)] were assumed to be due to the presence of an impurity. The impurity in question was 18 mol %. To remove the impurity silica column chromatography was carried out and  $^1\text{H-NMR}$  analysis was repeated [Figure 2(b)], but the spectrum looked similar to Figure 2(a), suggesting that the additional chemical shifts may not be due to an impurity. To verify this further, a solution was prepared using the pure product from column chromatography and irradiated with UV light for 5 min. The NMR spectrum, shown in Figure 2(c), was recorded. The signals at  $\delta$  7.15–7.31 (m, 3H),  $\delta$  6.87–6.90 (t, 4H) and  $\delta$  6.75–6.87 (d, 2H) corresponding to trans azo-aromatic protons moved downfield upon UV irradiation, suggesting isomerization to the cis form. The methylene protons ( $\text{CH}_2$ ) of oxirane in the cis-GOAB were resonated at  $\delta$  4.17–4.22 (d, 1H) and  $\delta$  3.38–3.90 (q, 1H) and the CH proton singlet was at 2.89 ppm. The signals of the methylene group between the epoxy and the ether bond in the trans-GOAB shifted upfield, creating a broader multiplet at  $\delta$  2.92–2.96 and another signal at  $\delta$  2.87–2.89. To confirm the cis conformation further, the irradiated solution was stored in the dark and NMR spectra were recorded after 1, 2, 6, and 14 days; the spectra are shown in Figure 2(d–g), respectively. Comparison of the spectra in Figure 2 shows that the intensity



**Figure 3.**  $^1\text{H-NMR}$  spectra of GOAB/DETA at room temperature as (a) unreacted system, (b) cured with 3 : 1 molar ratio system, and (c) cured with 5 : 1 molar ratio system. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of the additional proton signals increased by UV irradiation and decreased after storage in the dark, confirming that the so called impurity was the cis isomer of GOAB.<sup>19</sup> The trans/cis isomerization of azobenzene-based acrylic monomer and polymers has been reported elsewhere.<sup>21,22</sup> The results suggest that about 18% of GOAB was the cis isomer formed by the influence of natural light in the laboratory during the synthesis and purification procedures. Note that after 5 min UV irradiation the intensity of the trans peaks decreased with a 60% increase of the cis isomer. After keeping the sample in the dark for 1 day a reversible behavior was noticed by NMR analysis. A 20% increase of trans molecules was observed after the first day in the dark, while subsequent storage in the dark and NMR analysis showed full recovery of the cis isomer to the trans conformation within 14 days.

#### Curing Analysis by $^1\text{H-NMR}$

$^1\text{H-NMR}$  spectra of unreacted and reacted GOAB/DETA systems are presented in Figure 3. The chemical shifts for a mixture of GOAB with DETA in  $\text{DMSO-d}_6$  are illustrated in the spectrum [Figure 3(a)]. The spectra for the cured samples (3 : 1 and 5 : 1 molar ratio) of GOAB/DETA are presented in Figure 3(b,c), respectively.

It can be observed from the spectrum [Figure 3(a)] that there are three strong multiplets at  $\delta$  7.91–7.84 (m, 4H),  $\delta$  7.61–7.53 (t, 3H), and  $\delta$  7.19–7.17 (d, 2H) corresponding to the benzene rings of the GOAB. These resonance signals became broader and shifted downfield compared with the uncured GOAB/DETA sample, indicating its polymeric character. Two sharp signals at  $\delta$  4.50–4.46 (d, 1H) and  $\delta$  3.97–3.93 (q, 1H) corresponding to the methylene of the epoxy disappeared and instead a broad multiplet appeared at 4.08–3.96 ppm, showing that the epoxy ring has been opened. The other two sharp signals at  $\delta$  2.89–2.87 (m, 1H) and 2.77–2.75 (m, 1H) corresponding to the methylene

group next to the ether linkage and the broader ones at 2.57–2.46 ppm disappeared completely. For the cured solutions the NMR spectra indicated a new weak multiplet peak in the middle at 2.67–2.50 ppm, confirming the formation of a new amino bond with the opened epoxy ring.

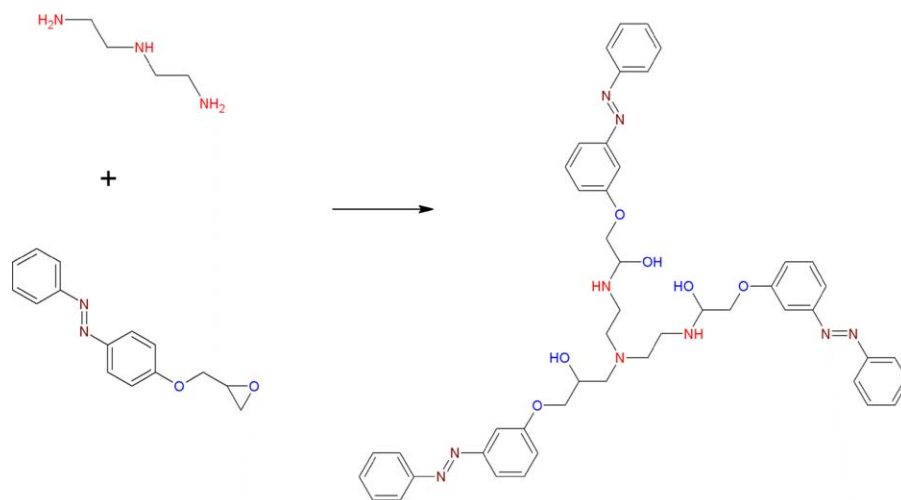
Moreover, the rate of the reaction was calculated by quantitative analysis of the integrals corresponding to the reacted amines. It was found that for the 3 : 1 system, about 2.76 molecules ( $\sim 3$ ) GOAB reacted with each DETA molecule. Similarly, 3.07 molecules of GOAB were attached to each DETA molecule in the 5 : 1 (GOAB/DETA) system. It is clear that even though the DETA has five functional protons, only a maximum of three molecules of GOAB can react with it. Once three GOAB molecules are attached to a DETA molecule the cured system becomes too crowded to accommodate more GOAB molecules. The reactivity decreases due to steric hindrance and, most probably the positions of the amines that reacted with the GOAB are one secondary, in the middle and two primary amines, at each side of the DETA. Two newly formed secondary amines ( $-\text{NH}$ ) from the two primary amines ( $-\text{NH}_2$ ) after reaction are thought to be sterically less favorable for addition of any further GOAB molecule as can be seen in Figure 4. Other authors reported that electron density and steric hindrance affect the reactivity of amines as curing agents.<sup>23,24</sup>

The  $^1\text{H-NMR}$  studies confirmed that the reaction had occurred from the disappearance of the oxirane group and the amine protons.

#### UV/Vis Spectroscopy Analysis of GOAB Monomer

Reversible photo-isomerization of GOAB monomer in DMSO, studied by UV/Vis spectroscopy analysis, is shown in Figures 5 and 6.

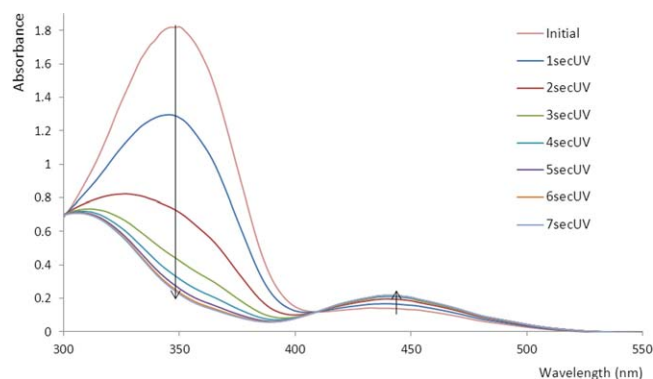
The unirradiated solution exhibited two absorption bands at 378 nm and at 440 nm (Figure 5). The absorption band at 378



**Figure 4.** Proposed GOAB/DETA reaction scheme. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

nm is attributed to the  $\pi-\pi^*$  transition of electrons of the trans azobenzene molecules and 440 nm is due to the forbidden  $n-\pi^*$  transition of the cis isomer.<sup>25</sup> Upon UV irradiation for 1 s, the intensity of the peak at 378 nm decreased and subsequently disappeared after 7 s. Similarly the intensity of the absorbance peak at 440 nm corresponding to the cis configuration increased suggesting that all the trans isomers were converted to their cis conformation.

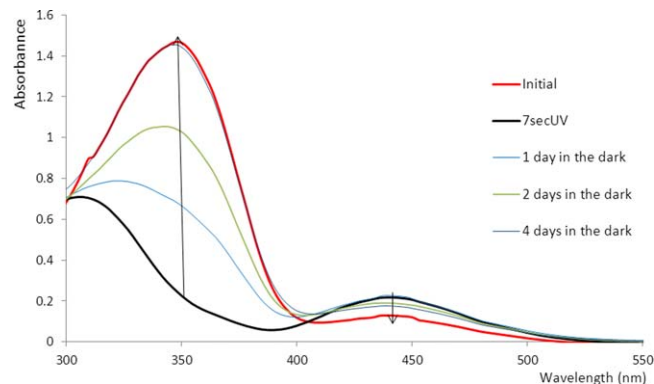
The rates of cis to trans isomerization by visible light, thermal treatment, and in the dark were monitored using UV/Vis spectroscopy analysis. The absorbance-wavelength plot is illustrated in Figure 6. The pretreated sample showed two absorption bands at 360 and 440 nm, which corresponds to the trans isomers of GOAB. Immediately after 7 s of UV irradiation the intensity of the trans absorbance band decreased dramatically, while the intensity of the band corresponding to the cis isomers indicated a significant hyperchromic shift. Upon storage in the dark for 1 day, the intensity of the absorbance band at 375 nm increased and simultaneously the band at 440 nm decreased. Further storage in the dark for 4 days showed a complete recovery of the cis isomer to the trans form as can be noticed in Figure 6.



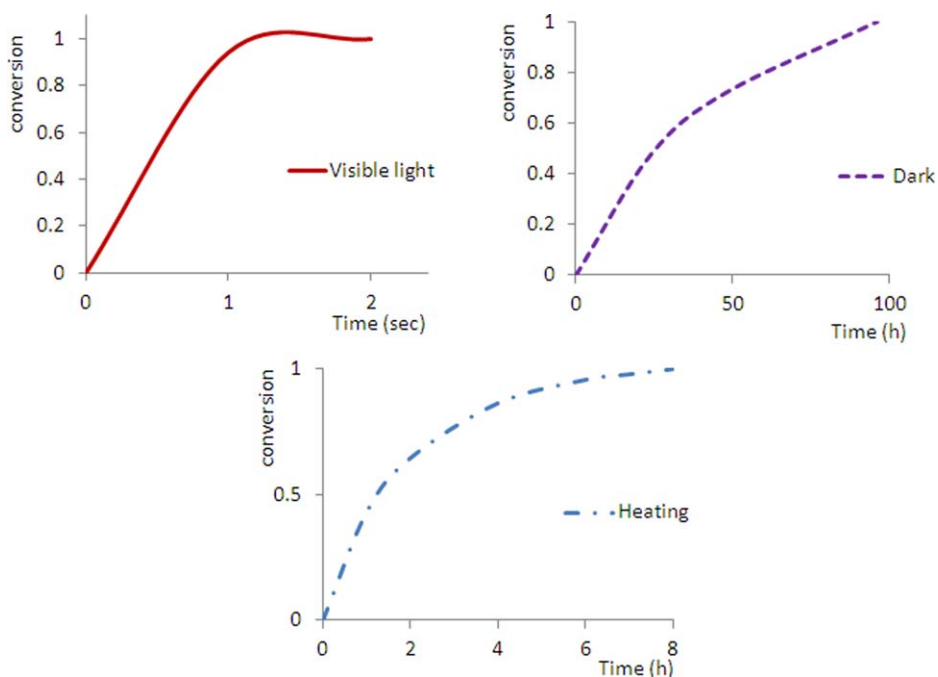
**Figure 5.** UV/Vis absorption spectrum of GOAB monomer in DMSO solution before and after 7 s of UV irradiation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Figure 7 shows the conversion of cis isomers to their trans counterparts against treatment time. The cis isomers of the GOAB converted to trans after heating the solution at 50 °C for 8 h. Consequently, it took 2 s to revert the cis form back to the trans isomers by visible light. Thermal isomerization and relaxation in the dark are two established processes used by other researchers to convert azo molecules from cis to trans isomer.<sup>1</sup>

Figure 8 shows the comparison of energy values required to convert cis isomer to the trans form by three different methods that were applied. For visible irradiation, the intensity was converted to energy while for heating the temperature change  $\Delta T$  was converted to energy and the time for each experiment was taken into consideration. It is obvious that the rate of cis to trans isomerization by visible light is faster than that of the thermal treatment. But as it has been demonstrated the azobenzene can efficiently return to its more thermodynamically stable trans state even without the need of energy; by simply storing the solution in the dark.<sup>1</sup> The obtained results suggest that visible light is the optimum method to reverse the cis isomer of the epoxy azobenzene to the trans form, not only from a time



**Figure 6.** UV/Vis absorption spectrum of GOAB monomer in DMSO solution in the dark. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7.** Cis to trans isomerization of azobenzene against time upon (a) visible light, (b) storing in the dark, and (c) heating at 50°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

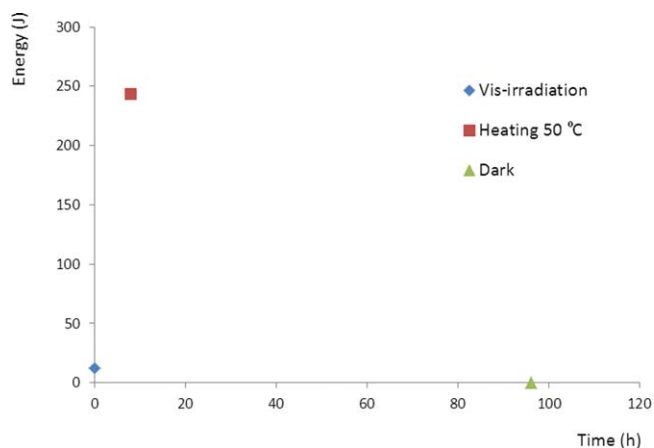
perspective, but also for the requirement of smaller amount of energy.

#### UV/Vis Spectroscopy of the Cured System (GOAB/DETA)

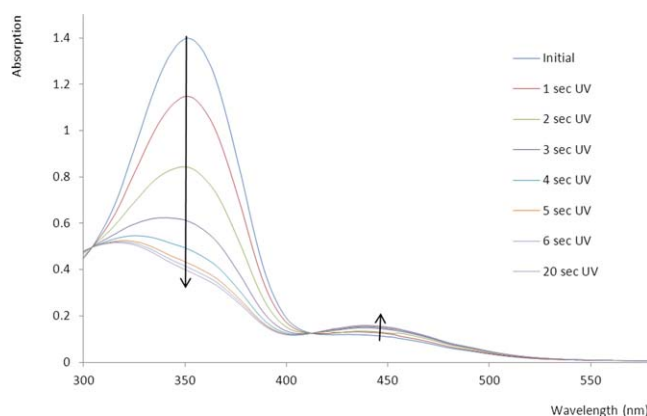
The isomerization of the cured system was investigated by UV/Vis spectroscopy in order to compare the required time to interconvert cis and trans isomers. Figure 9 shows the UV/Vis spectra of the cured system (GOAB/DETA) in DMSO solution against the UV irradiation time. It can be observed from Figure 9 that the absorbance band at 350 nm for trans isomer ( $\pi-\pi^*$ ) decreased gradually with irradiation time and after 5 s the decrease slowed down. Irradiation spectrum for 20 s showed complete conversion of trans isomer to the cis form. This can also be confirmed by the increase in the intensity of the second

absorption band at 440 nm corresponding to the forbidden  $n-\pi^*$  electronic transition.

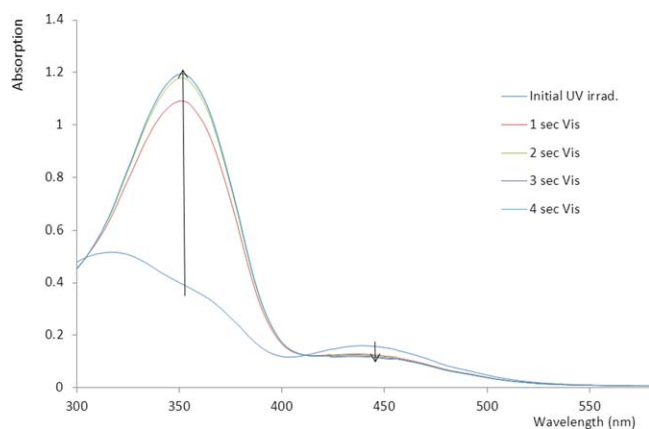
Absorption spectra of the cured cis-GOAB/DETA by irradiation with visible light are illustrated in Figure 10. Almost 91% of the cis isomers reverted back to the trans form within 1 s by the drastic increase of the absorption peak at 440 nm. After 2 and 3 s of irradiation with visible light, 98 and 99% of the cis form were converted to trans isomer, respectively. It took about 4 s for the cured system to be completely transferred to its trans form by visible irradiation. The results suggest that the isomerization of azobenzene can be triggered by UV light even when it is in its cross-linked form. However, the conformational change from trans to cis isomer in the cured system was three times



**Figure 8.** Required energy for reversible isomerization of GOAB against time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9.** UV/Vis absorption spectra of GOAB/DETA in DMSO solution before and after 20 s of UV. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

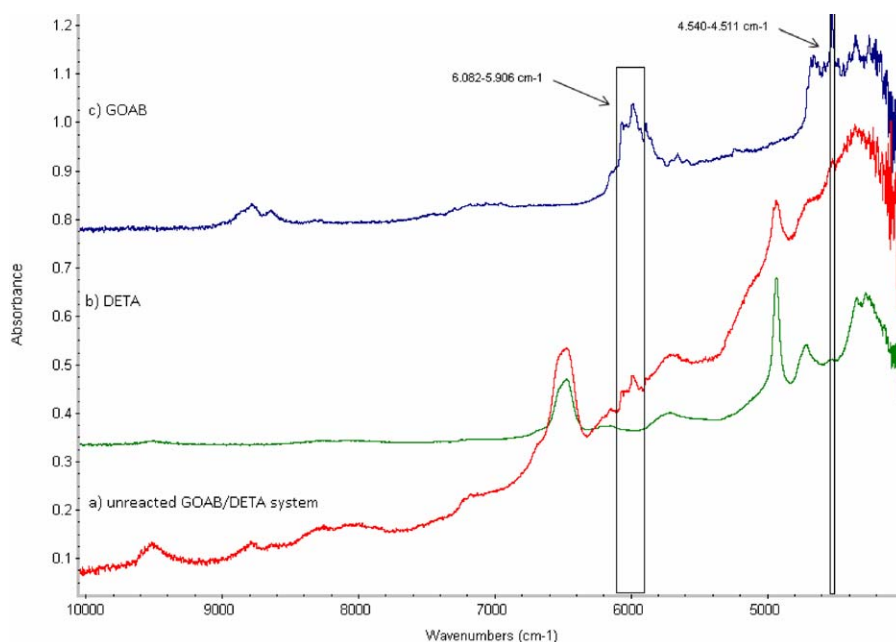


**Figure 10.** UV/Vis absorption spectrum of GOAB/DETA in DMSO solution irradiated with UV and visible light. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

slower than that in the GOAB monomer. Moreover, the *cis* conformation of the cured GOAB/DETA system reverted back to the *trans* form by visible irradiation twice slower compared to its monomeric counterpart (GOAB). The differences in the isomerization times between the monomer and cured system were expected due to the formation of new bonds between amine and epoxide. The new bonds restricted the movement of the azo-molecules, since the isomerization occurs by rotation or inversion between the two nitrogen atoms.<sup>1</sup>

#### Cure Monitoring of GOAB/DETA by Near-FTIR

The reaction kinetic was investigated between 30 and 180 °C by *in situ* near-FTIR monitoring. The near-infrared spectra of GOAB, DETA, and that of the unreacted GOAB/DETA system are illustrated in Figure 11.



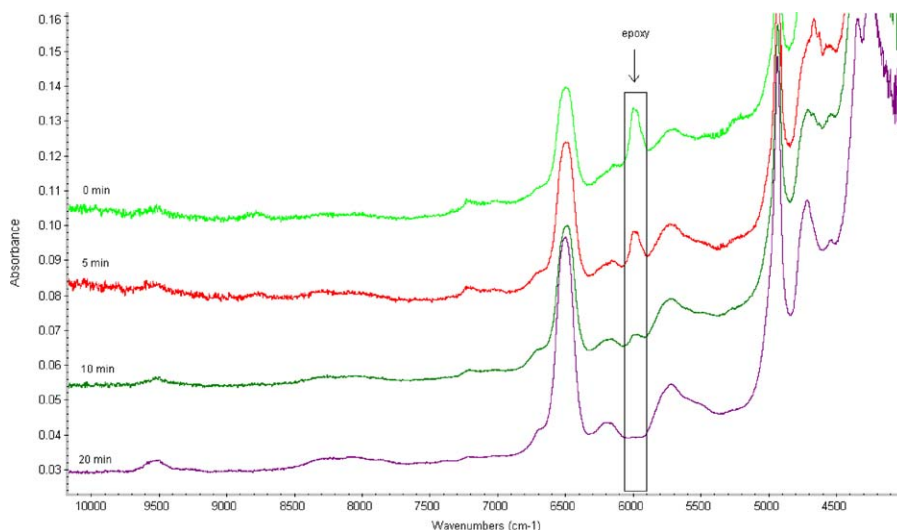
**Figure 11.** Near-IR spectra of (a) unreacted GOAB/DETA system, (b) DETA and (c) GOAB. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The peaks at 6475 and 5046  $\text{cm}^{-1}$  appeared due to the existence of  $-\text{NH}$  group, in DETA, while the peaks at 5993 and 4528  $\text{cm}^{-1}$  are characteristics of the oxirane ring of the GOAB.<sup>18</sup> Structural changes in the unreacted system were observed during curing process as shown in Figures 11 and 12. Selected absorption peaks whose intensities changed during the reaction are listed in Table I.

In Figure 12 the absorption peaks in the 4400 to 4000  $\text{cm}^{-1}$  region are attributed to the aromatic  $-\text{CH}$  and  $-\text{CH}_2$  combination bands.<sup>18</sup> Primary amines ( $-\text{NH}_2$ ) show two intense stretching first overtone bands (symmetric and anti-symmetric) between 6897  $\text{cm}^{-1}$  and 6452  $\text{cm}^{-1}$ , which overlap with the single band for secondary amines ( $-\text{NH}$ ); hence the peaks at 6475  $\text{cm}^{-1}$  for secondary amines could not be used for quantitative calculations.

The characteristic peak at 4530  $\text{cm}^{-1}$  for the oxirane ring is generally used for estimating the progress of the curing reaction.<sup>16,18,26</sup> As can be observed from the spectra in Figure 12, the 5993  $\text{cm}^{-1}$  peak intensity decreased with curing time and thus it was chosen for the quantitative analysis of curing reaction. Figure 12 clearly shows that the intensity of the absorbance was decreasing with time and after 20 min of curing the peak at 5993  $\text{cm}^{-1}$  completely disappeared suggesting the completion of curing reaction.

The stretching vibrations of the epoxy group at 5993  $\text{cm}^{-1}$  as shown in the spectra of GOAB and the unreacted system (Figure 11) were used for the kinetic studies. The disappearance of this peak indicated that the reaction was completed (20 min). The conversion  $\chi$  was calculated using eq. (1), where  $A_0$  and  $A_t$  are the area at time 0 and  $t$ , respectively, of the peaks of the epoxy group.



**Figure 12.** Near-IR spectra of GOAB/DETA system during dynamic heating at 0, 5, 10, and 20 min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$$\chi = 1 - \frac{A_t}{A_0} \quad (1)$$

The progress of the reaction over time is plotted in Figure 13. It is a typical S-shape graph for epoxy/amine systems, signifying an “autocatalytic” character of the epoxy resin.<sup>26</sup> The first value of the epoxy conversion was  $\chi = 0.2$  which became 0 after 5 min. At this point (5 min) the curing appears to begin and within 11 min the degree of epoxy conversion increased rapidly. Between 15 and 20 min the conversion values were higher than 1. These anomalies can be attributed to the fact that the sample surface was not smooth at the beginning of the experiment. The near-IR data were collected from the sample surface, not from within the sample.

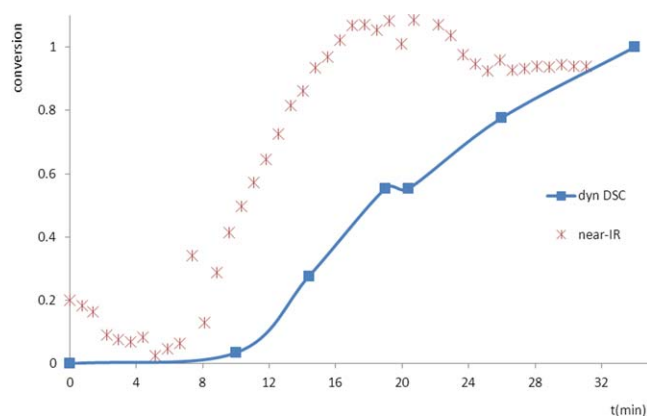
### Thermal studies

The curing reaction of GOAB and DETA mixture in a stoichiometric ratio of 3 : 1 was studied by DSC using a dynamic heating rate of 5°C/min and the result is presented Figure 14. The first exothermic peak at 75°C corresponds to the curing reaction of GOAB/DETA system. The melting peak of GOAB at 85°C

did not appear in the thermograph, probably due to its overlap with the curing peak. The broad peak with onset at 100°C is attributed to the post-curing reaction. It is assumed that the post-curing peak appeared once the melting of GOAB was accomplished. At around 200°C a strong peak resulted from the thermal decomposition of the cured network.

Dynamic DSC scans of GOAB/DETA system were performed at three different heating rates, for identification of curing and post-curing peaks, as can be seen in Figure 15. The thermographs indicated that the curing reaction in the GOAB/DETA (3 : 1) mixture started after 42°C and was completed within 15, 21, and 45 min at 5, 3, and 1°C min<sup>-1</sup> heating rates, respectively. The curing time of this system depends on the heating rate; shorter curing time was required at a faster heating rate. The peaks of the thermal traces shifted to higher temperature as the heating rate increased by 2°C min<sup>-1</sup>; this was expected.<sup>27</sup>

The temperature of the onset and peak obtained from the dynamic DSC scans with respect to the three different heating



**Figure 13.** Conversion of azobenzene epoxy resins with time by near-IR and dynamic DSC analyses. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table I.** Near-FTIR Wavenumbers and Assignments of GOAB/DETA System

Wavenumber (cm <sup>-1</sup> )	Assignment
9550	—NH <sub>2</sub> stretching vibrations (2 <sup>nd</sup> Overtone)
8802	—CH Combination of symmetric and asymmetric stretching vibrations (1 <sup>st</sup> Overtone)
7188	—CH 1 <sup>st</sup> Overtone, Combinations
6475	—NH <sub>2</sub> stretching vibrations (1 <sup>st</sup> Overtone)
5993	—CH—O—CH <sub>2</sub> (epoxy group) stretching vibrations (1 <sup>st</sup> Overtone)
5230	—OH stretching vibrations
5046	—NH <sub>2</sub> Combination of stretching and bending vibrations



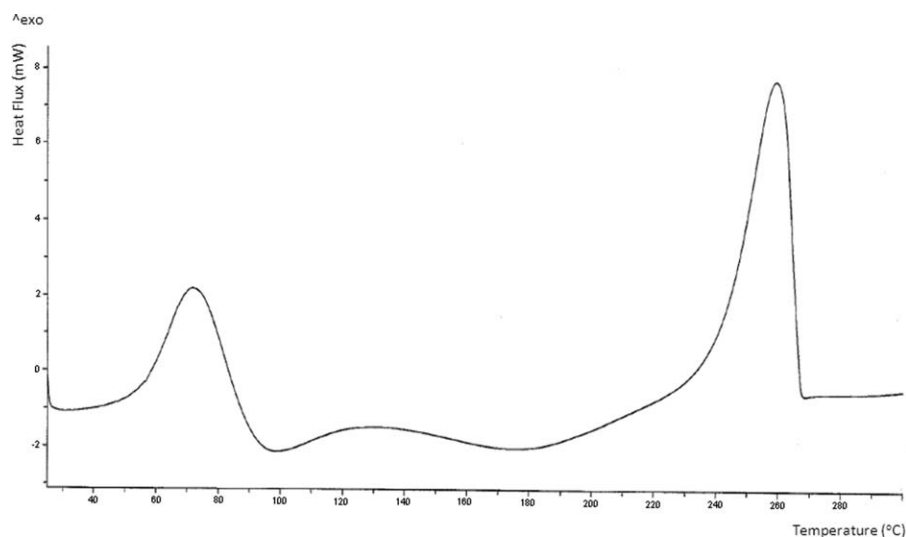


Figure 14. Dynamic scan for GOAB/DETA system.

rates are listed in Table II. As already discussed, the peak temperature increases with the heating rate. However, no correlation with the heating rate was noticed for the onset temperature of the curing peaks. It should be mentioned that no post cure peak was observed at 1 and  $3^{\circ}\text{C min}^{-1}$  heating rates. These data suggest the completion of curing at lower heating rates. Moreover the differences at heat release from the exothermic peaks deserve some comments. The samples heated at 1 and  $3^{\circ}\text{C min}^{-1}$  obtained higher values than the one at  $5^{\circ}\text{C min}^{-1}$ ; therefore, the latter sample exhibited a second post-curing peak after achieving completeness of reaction.

Finally, Figure 16 illustrates a typical isothermal DSC trace of GOAB/DETA at  $95^{\circ}\text{C}$ . Curing is the only thermal phenomenon that occurred and it was completed within 8 min. The curing reaction of the azobenzene epoxy resin began immediately after

the heating was started and it reached to an optimum value within 2 min. At that point, the heat release, which is proportional to the reaction rate, began to decrease, and the decrease was complete within 8 min. After the isothermal heating, a dynamic cycle was followed where only the degradation peak appeared without any sign of post-curing.

The curing progress at  $5^{\circ}\text{C min}^{-1}$  heating rate is shown in Figure 13. The dynamic DSC results did not completely agree with the near-FTIR data. According to near-FTIR, the reaction of epoxies started after 5 min and was completed within 20 min as proved by the disappearance of the oxirane ring. On the other hand, the dynamic DSC scans showed that the curing reaction started approximately after 8 min and was completed within 34 min. These differences in curing time are assumed to be due to the use of different techniques which have different

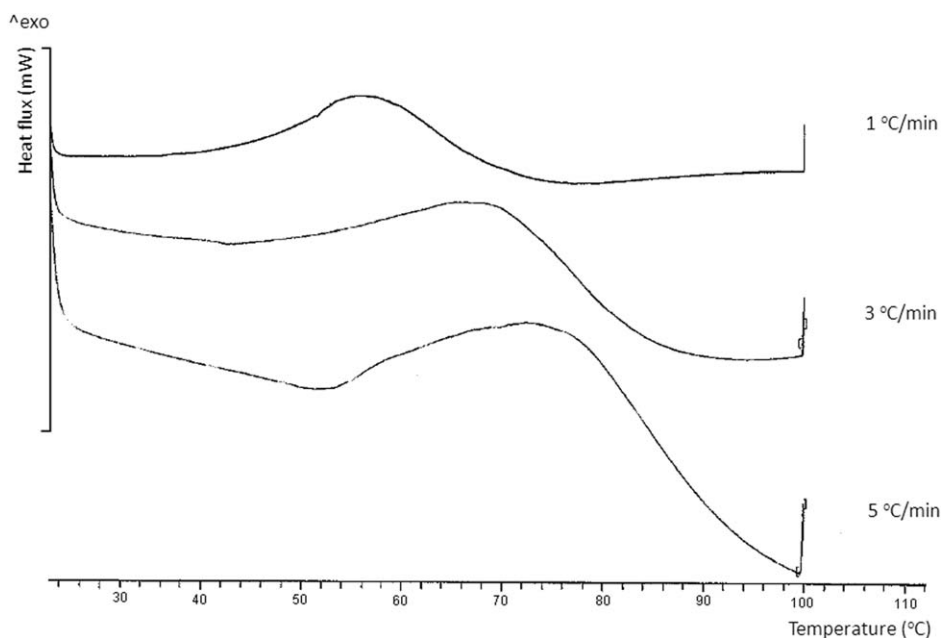
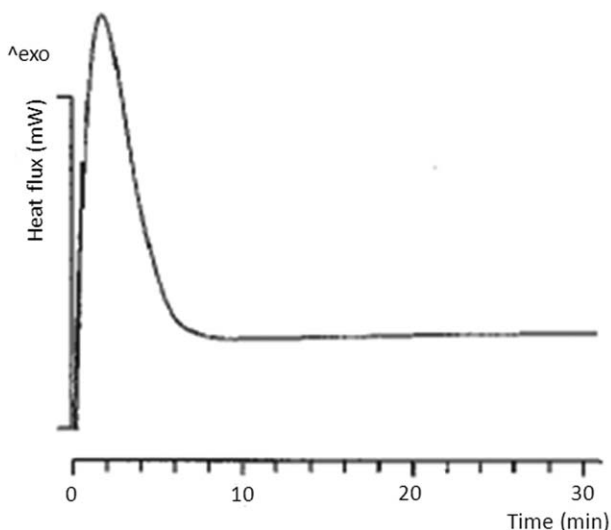


Figure 15. Dynamic scans for GOAB/DETA at 1, 3, and  $5^{\circ}\text{C min}^{-1}$  heating rates.

**Table II.** Thermal Data Corresponding to Different Heating Rates of Dynamic DSC Scan

Heating rate (°C/min)	Onset temperature (°C)	Peak temperature (°C)	Exothermic heat (J g <sup>-1</sup> )
1	50	56	130.16
3	42	69	66.97
5	70	76	57.27

**Figure 16.** Isothermal DSC thermograph of GOAB/DETA at 95°C.

resolutions. Other factors, such as the film smoothness for near-FTIR analysis, where noncontact probes were used, and heating rates for DSC scans might have contributed to the different curing times.

## CONCLUSIONS

An epoxy azobenzene was synthesized by modifying the existing synthetic route in order to investigate its response to light and its curing behavior with diethylenetriamine. The rates of trans/cis isomerization in the GOAB and GOAB/DETA systems by visible light, thermal treatment and storage in the dark were studied using UV/Vis spectroscopy. The conformational changes in the two systems are influenced by the chemical structures of both systems and also by the method employed to trigger the isomerization. The rate of cis to trans isomerization in GOAB is faster by visible light than by heat or dark storage although visible irradiation involved smaller amount of energy compared with the heat energy. Conversely, the rate of reversible trans/cis isomerization is slower in the cured system (GOAB/DETA) than in the individual monomer (GOAB). The curing of the azobenzene epoxy resin was successfully accomplished for the first time and was confirmed by <sup>1</sup>H-NMR, near-FTIR spectroscopy, and dynamic DSC analyses. It was found that only three molecules of GOAB can react with one molecule of DETA although each DETA molecule possesses five reactive protons. Isothermal DSC

scans of 3 : 1 epoxy/amine system at 95°C demonstrated that curing completed within 8 min. On the other hand, the data obtained from the dynamic DSC scans, indicated the completion of the curing reaction within 45, 21, and 15 min at 1, 3, and 5°C min<sup>-1</sup> heating rates respectively. Finally, at the 5°C min<sup>-1</sup> heating rate a post curing reaction occurred due to the formation of the azobenzene network. Azobenzene-based epoxy resins could be incorporated into the matrix of composites, which will enhance the matrix-dominated mechanical properties of the composites when exposed to UV radiation. However, to fully exploit the benefits of these photoresponsive polymers, further work related to their photomechanical and thermal properties is required and will be reported in the future.

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