

# Characterization of the Cure of TGDDM/DDS Epoxy Resins by Chemiluminescence I. Spectral and Thermal Analysis

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## Synopsis

The emission of weak visible chemiluminescence (CL) during the cure of a tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM)-based epoxy resin, with three different concentrations of 4,4'-diaminodiphenylsulfone (DDS) has been studied at 135°C. Spectral analysis indicates that the CL originates from trace oxidation of the TGDDM resin and the emission intensity is sensitive to the viscosity changes during cure. From thermal analysis data, sharp discontinuities in CL intensity are shown to occur at the gel point. The temperature dependence of CL from a cured resin also shows a sharp discontinuity at  $T_g$ . These results indicate that CL provides a sensitive monitor of both the kinetics of gelation and the network formation in this epoxy resin.

## INTRODUCTION

The characterization of advanced composite materials requires detailed knowledge of the structure, extent of cure and thermal properties of the epoxy resin during the fabrication of the composite. While laboratory instrumental techniques such as FT-IR,<sup>1-4</sup> rheological analysis,<sup>3,5,6</sup> differential scanning calorimetry,<sup>5-8</sup> torsional braid,<sup>9,10</sup> and dynamic mechanical analysis<sup>11-13</sup> have brought a greater understanding of the process of network formation as well as the structure and degradation of the epoxy resin, these are not suitable for cure monitoring of the composite during fabrication. In commercial fabrication, the viscosity of the resin is monitored indirectly by measuring a dielectric property such as d.c. conductivity or a.c. phase lag as cure proceeds.<sup>14,15</sup> Recent advances in this area include the use of a charge-flow transistor as a microdielectric monitor.<sup>16,17</sup> Electrical methods suffer from problems of spurious noise in the industrial environment and attention has been paid to alternative optical methods for monitoring resin cure.<sup>18-20</sup>

Among the high performance epoxy resins used for carbon fiber-reinforced composites, tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) cured with 4,4'-diaminodiphenylsulfone (DDS) has been one of the most studied.<sup>1-8</sup> From studies of thermal and rheological properties of this resin, time-temperature-phase transformation curves have been generated to describe the cure process and the matrix properties to be expected from a particular cure cycle.<sup>5,6</sup> The cure of the resin takes place in the steps of gelation followed by vitrification.<sup>9</sup> Gelation of the epoxy resin is the formation of a well-developed

system of crosslinks that transforms the liquid to a rubber while vitrification represents further network formation leading to the glassy state. At this stage,  $T_g$ , the glass transition temperature becomes equal to the cure temperature.

Recently a technique has been described that monitors the change in the viscosity of an epoxy resin during cure by measuring the intensity of resin fluorescence.<sup>18</sup> The basis for this technique is the observation that some fluorescent molecules such as *p*-(*N,N* dialkylamino)benzylidene malonitrile have a quantum yield that depends on the solution viscosity.<sup>21,22</sup> At low viscosity, the molecules may lose excitation energy radiationlessly by intramolecular torsional or twisting motion of alkyl groups about the C—N bond to give a low quantum yield of fluorescence. As viscosity increases, the rate of radiationless decay decreases, and therefore, the quantum yield of fluorescence increases. The main structural unit of TGDDM is similar to molecules that show viscosity-dependent fluorescence quantum yields, and this has been exploited by Levy in studying the cure of TGDDM with DDS at 160°C.<sup>18</sup> The smooth increase in fluorescence intensity with time during the gelation phase of resin cure has led to the suggestion that this technique may provide an alternative to dielectric cure monitoring. The use of a reactive probe, *p,p'*-diamino azobenzene, to monitor the cure reaction of DDS with epoxy resins has also been reported.<sup>19</sup> The quantum yield of fluorescence increases when the probe reacts at a crosslink or branch point but is independent of the resin viscosity.

Among the other luminescence properties of epoxy resins that have been investigated, chemiluminescence is of particular interest. Chemiluminescence (CL) is the weak visible light emitted by many organic materials during thermal oxidation.<sup>23</sup> Studies of cured TGDDM/DDS epoxy resins have shown that they are moderately strong CL emitters<sup>24,25</sup> and it was therefore of interest to examine the CL properties of this resin system during cure, particularly in the critical gelation period.

In this paper, a commercial TGDDM resin, Ciba-Geigy MY720, cured with different concentrations of DDS has been studied to determine the spectral properties of the CL and the correlation between the changes in the CL intensity and the extent of cure as measured by differential thermal analysis (DTA).

## EXPERIMENTAL

### Materials

The formulations used in this study were prepared from the commercial tetraglycidyl 4,4-diaminodiphenyl methane (TGDDM)-based epoxy resin, MY720 (Ciba-Geigy) and 4,4'-diaminodiphenylsulfone (DDS, Ciba-Geigy). Some spectral studies were performed on TGDDM fractionated by high performance liquid chromatography (HPLC) to ~96% purity (compared to the usual TGDDM content of 60 to 68% in MY720).<sup>26</sup>

Three MY720 formulations containing 17%, 27%, and 37% by weight DDS were prepared. These values span the stoichiometric ratios for reaction of the epoxide with primary and secondary amine groups during cure.<sup>1</sup> The resin and hardener were weighed and preheated separately to 110°C. The hardener was

then progressively added, with stirring, to the resin over a space of five minutes at 110°C to 120°C to produce a clear mixture. The mixture was immediately cooled and stored in a freezer prior to the curing studies.

### Thermal Analysis

The gelation of each MY720/DDS formulation was studied by measuring the fractional heat evolved as a function of time during isothermal cure at 135°C by using a Rigaku Model M8075 DTA apparatus. Sample mass was 30 mg. The cure reaction was incomplete at this temperature and the residual heat of reaction,  $\Delta H_r$ , was obtained by carrying out a dynamic DTA scan from 100°C to 300°C at 10°C/min after cure at 135°C. The total heat of reaction,  $\Delta H_T$ , under these conditions was obtained by repeating the experiment on an uncured sample. The extent of reaction after isothermal cure is then  $(1 - \Delta H_r/\Delta H_T)$ . The fractional extent of reaction by DTA,  $\beta_t$ , may then be calculated at each point during the isothermal cure at 135°C.

### Luminescence Studies

The intensity of chemiluminescence (CL) was measured from 30 mg samples of the resin in DTA pans in a static air atmosphere using a photon-counting apparatus previously described.<sup>23</sup> The temperature was controlled to  $\pm 0.5^\circ\text{C}$ . The spectral distribution of the CL was measured by placing a series of Jena glass cut-off filters between the sample and the photomultiplier tube and measuring the difference in the photon count rate. The band edge of the filter cut-off was measured on a Varian DMS-100 spectrophotometer and approximated with a vertical line at the wavelength at which transmission was 50%. This enabled a broad spectral distribution curve to be constructed from 320 to 620 nm for each sample. The CL intensity was expressed as count rate per nm to compensate for the different bandwidths between the series of filters. The normal luminescence spectrum from thin films of cured or uncured MY720 was measured at 22°C using a Hitachi Model 204 spectrofluorometer equipped with a solid sampling accessory. The spectra were not corrected for the spectral response of the monochromator or photomultiplier.

## RESULTS AND DISCUSSION

### Changes in Chemiluminescence Intensity with Time of Heating

The total intensity of light emitted from the TGDDM epoxy resin when heated at  $135 \pm 0.5^\circ\text{C}$  in air was measured for both the neat resin and for the resin containing 17%, 27%, and 37% curing agent. As shown in Figure 1, the emission intensity from neat MY720 increases with time of heating, up to 120 minutes, after which it decreases. The increase in CL intensity with time of heating of an organic material in air corresponds to an increase in the rate of oxidation and is observed from most polymers during auto-oxidation.<sup>23</sup> When heated at lower temperatures, this emission intensity may be steady for long periods, enabling the measurement of the spectral distribution of the emitted light, as discussed below.

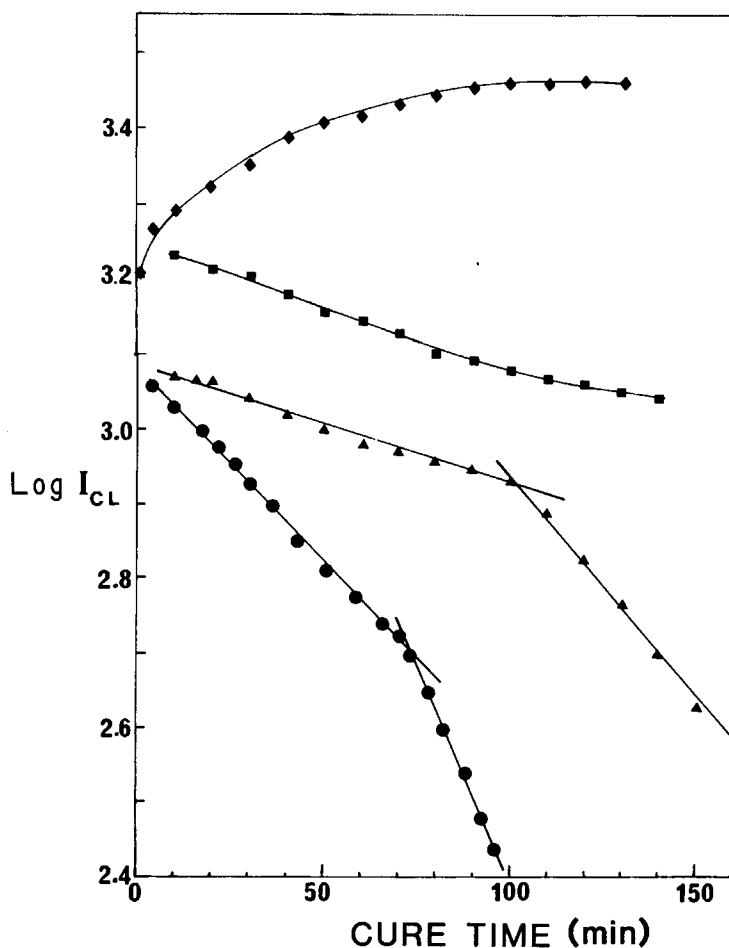


Fig. 1. The change in the intensity of chemiluminescence,  $I_{CL}$ , with time of heating at 135°C for: (◆) neat MY720; (■) MY720 + 17% DDS; (▲) MY720 + 27% DDS; (●) MY720 + 37% DDS.

In contrast, when the resin containing hardener is heated, there is an immediate decrease in the chemiluminescence intensity over the same time period (Fig. 1). Under the same conditions, the hardener DDS shows negligible luminescence intensity and it is concluded that the decrease in intensity results from the cross-linking reaction occurring during cure. It can also be seen from Figure 1 that there are sharp decreases in the CL intensity at 75 min for the sample containing 37% DDS and at 105 min for the sample containing 27% DDS. The sample containing 17% DDS does not apparently show a deflection over the time frame of the experiment. To determine the relationship between these clear changes in slope and the extent of cure of the resin, the fractional heats of reaction of the three resin/hardener mixes were measured during heating at 135°C.

#### Extent of cure of TGDDM/DDS During Heating at 135°C

The fractional extents of reaction,  $\beta_T$ , from thermal analysis of identical masses of resin to those studied by CL are shown in Figure 2. It has been

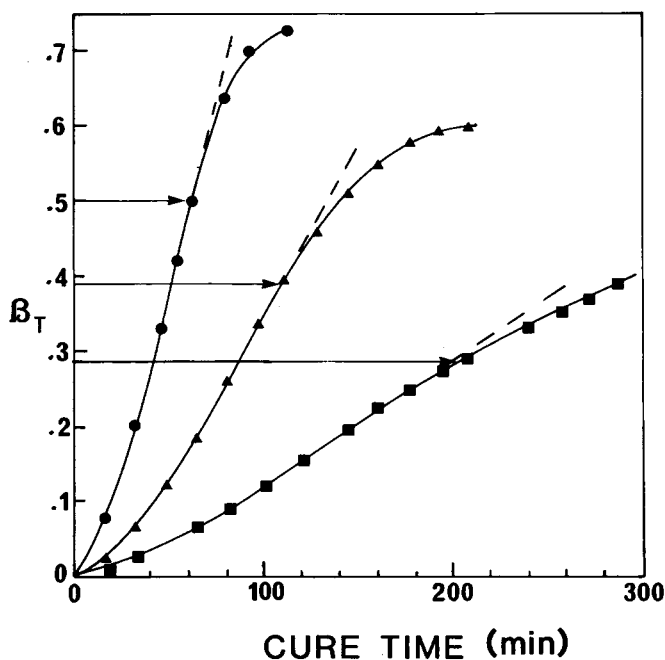


Fig. 2. Fractional extent of conversion  $\beta_T$ , measured by thermal analysis, as a function of time of heating at 135°C for: (■) MY720 + 17% DDS; (▲) MY720 + 27% DDS; (●) MY720 + 37% DDS. The value of  $\beta_T$  corresponding to gelation is marked in each case.

shown that thermal analysis underestimates the fractional conversion of epoxy resins during cure.<sup>5</sup> The fraction  $\beta_g$ , of epoxide groups reacting up to the gel point can be calculated from the formula of Flory:<sup>5</sup>

$$\beta_g = \sqrt{\frac{1}{(1-f)(1-g)r}}$$

where  $f$  and  $g$  are the functionalities of the resin and hardener, respectively, and  $r$  is the ratio of the number of amine groups in the hardener to the epoxide groups in the resin. Thus  $\beta_g$  depends on the hardener concentration and in these mixtures is calculated as 0.40 (37% DDS); 0.32 (27% DDS); and 0.24 (17% DDS). When this is corrected for the discrepancy between fractional epoxide consumption and fractional heat of conversion,<sup>5</sup> the values of  $\beta_T$  corresponding to the gel point are, respectively 0.50, 0.39, and 0.29. From Figure 2 this gives the times for gelation at 135°C of 64 min, 108 min, and 206 min, respectively. It is noted that these times correspond to the points at which the plots of  $\beta_T$  against cure time deviate from linearity, indicating a decrease in reaction rate at the onset of gelation of the resin.

It is of interest to compare the gelation times measured here for the MY720/DDS system with those from other authors. Dusi et al.<sup>6</sup> have presented a time-temperature-phase transformation diagram for this system indicating a gel time of around 110 minutes at 135°C. While the stoichiometry of their reaction mixture is not mentioned, the reported value of  $\beta_T$  of 0.33 to 0.36 suggests a value close to the 27% DDS system studied here. Our 27%

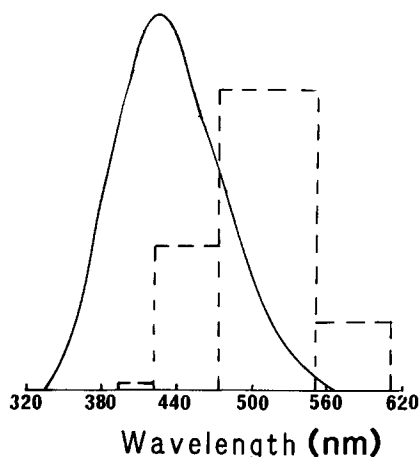


Fig. 3. Luminescence spectra from neat MY720 resin: (—) fluorescence at 22°C in air.  $\lambda_{\text{ex}}$  350 nm; (---) chemiluminescence at 115°C in air.

DDS sample gave a gel time of 108 minutes, in very close agreement with their reported value.

These gelation times may now be compared with the times at which the sharp decrease in CL intensity in Figure 1 occurred. These values are summarized along with the thermal analysis data in Table I and it can be seen that, particularly for the 27% DDS system, there is close agreement suggesting that gelation of the resin leads to the decrease in the intensity of CL. The reasons for this depend on an understanding of the origin of the CL from the TGDDM/DDS system.

### Origin of CL from Epoxy Resins

Chemiluminescence during oxidation of organic compounds or "oxyluminescence" is a widespread phenomenon.<sup>23-25</sup> Although the detailed mechanism of light emission may vary with the chemical composition of the material, the usually accepted mechanism involves the free radical oxidation of the substrate as shown in Table II, with chemiluminescence resulting from the exothermic termination reaction of the primary or secondary alkyl peroxyradicals. This reaction [(5) in Table II] results in the formation of an alcohol, oxygen, and a ketone in an excited state. The CL emission spectrum should thus correspond to the luminescence spectrum of this ketone and this

TABLE I  
Comparison of Gel Times ( $t_{\text{gel}}$ ) and Glass Transition Temperature ( $T_g$ ) from Thermal Analysis with Discontinuity Points in Chemiluminescence Curves,  $t_{\text{disc}}$  (CL) and  $T_{\text{disc}}$  (CL); MY720 Cured with Different Concentrations of DDS

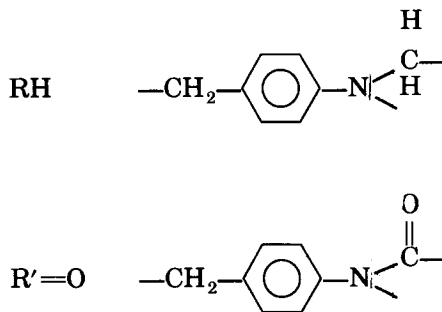
Wt% DDS	17%	27%	37%
$t_{\text{gel}}$ (DTA) min	206	108	64
$t_{\text{disc}}$ (CL) min	> 200	105	73
$T_g$ (DTA)°C	93	125	—
$T_{\text{disc}}$ (CL)°C	95	135	—

TABLE II  
Simplified Reaction Scheme for Oxidation of TGDDM  
Leading to Chemiluminescence

Reaction		Rate
(1) RH	$\rightarrow R \cdot$	$r_i$
(2) $R \cdot + O_2$	$\xrightarrow{k_2} RO_2 \cdot$	$k_2[R \cdot][O_2]$
(3) $RO_2 \cdot + RH$	$\xrightarrow{k_3} ROOH + R \cdot$	$k_3[RO_2 \cdot][RH]$
(4) $R \cdot + R \cdot$	$\xrightarrow{k_4} R-R$	$k_4[R \cdot]^2$
(5) $RO_2 \cdot + RO_2 \cdot$	$\xrightarrow{k_5} R'=O + ROH + O_2$	$k_5[RO_2 \cdot]^2$

has generally been observed from studies of both low molecular weight hydrocarbons and polymers.<sup>23</sup>

If this mechanism also applies to the oxidation of TGDDM, alkyl peroxy radicals should occur preferentially in a position  $\alpha$  to the tertiary nitrogen atom so that the species RH and  $R'=O$  in Table II are as follows:



The termination reaction (5) of Table II will lead to the formation of the amide group  $R'=O$  in the first excited triplet state. The chemiluminescence spectrum should therefore be equivalent to the phosphorescence spectrum of an aromatic amide. Bellenger and Verdu<sup>27</sup> have identified aromatic amide formation as a major product of both thermal and photochemical oxidation of amine-cured epoxy resins consistent with the above mechanism. The same authors<sup>28</sup> showed that little amide formation occurred during the oxidation of DDS-cured bisphenol-A epoxy and this was attributed to a lower electron density at the nitrogen atom in DDS compared to DDM. This suggests that in the DDS-cured TGDDM the chemiluminescence intensity should arise from oxidation at the TGDDM site above and not at the amine site from the DDS.

The observed ultraviolet-excited luminescence and chemiluminescence spectrum of TGDDM before and after curing with DDS can be examined with reference to the above. Figure 3 shows the measured broad-band chemiluminescence spectral distribution from neat MY720 resin oxidizing at 115°C in air. This spectral distribution was identical to that obtained when highly

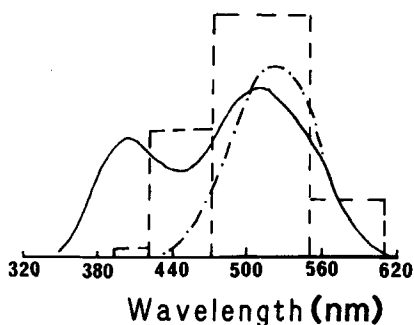


Fig. 4. Luminescence spectra from MY720 cured with 17% DDS: (—) luminescence  $\lambda_{\text{ex}}$  350 nm; (---) luminescence  $\lambda_{\text{ex}}$  430 nm; (.....) chemiluminescence at 135°C in air.

purified TGDDM<sup>26</sup> was studied under the same conditions. Also shown is the luminescence spectrum from a film of the resin in air at room temperature when excited at 350 nm. It can be seen that the chemiluminescence is of different spectral origin to the fluorescence. The fluorescence is sensitive to excitation wavelength, consistent with the results of Levy and Ames.<sup>29</sup> They report the spectrum of 96% TGDDM to be a broad band from 400 to 600 nm with a maximum at 463 nm. They also reported the maximum in the excitation spectrum for this emission wavelength to be 390 nm. In this investigation, the film of commercial MY720 when excited with 390 nm radiation also showed a maximum at  $\sim$  460 nm. The shift in emission spectrum with excitation wavelength suggests several species are responsible for the observed fluorescence. Levy and Ames also reported that during cure the emission spectrum shifted to longer wavelength but a spectrum was not presented.<sup>29</sup> The luminescence spectrum from a sample of MY720 cured with 17% DDS is shown in Figure 4. The emission is now bimodal with a component similar to the fluorescence from the neat MY720 resin and a more intense, broad-band centered on 520 nm. This broad band has an excitation spectrum maximum at 430 nm and, as shown in Figure 4, when emission is excited at 430 nm the luminescence is now identical to the spectral distribution of chemiluminescence from the cured resin.

In a study of the phosphorescence from cured and uncured epoxy resins, Allen has reported triplet excimer emission centred on 460 nm to be the dominant spectral feature.<sup>30</sup> This is not seen in the spectrum of cured MY720 and the longer wavelength emission observed here is thus not intrinsic to the MY720 structural unit but is considered to arise from oxidation of the resin during cure. As discussed before, the oxidation of the TGDDM repeat unit  $\alpha$  to the nitrogen will produce an aromatic amide or possibly an *N*-acyl amide if both sites are oxidized. The phosphorescence spectra from analogous systems—aromatic dicarbonyl polymers—have been reported as broad spectra at room temperature centred on 550 nm.<sup>31</sup> Phosphorescence from polyamides in air at room temperature can be observed because of the low diffusion coefficient of the quenching molecule, oxygen, in the solid polymer.<sup>34</sup> It is therefore possible that triplet emission from the amide site in the cured epoxy resin can be observed under these experimental conditions. In the more fluid system of the uncured resin at 135°C the quantum yield of the phosphorescence will be



greatly reduced. The spectral similarity of the CL to the room temperature phosphorescence supports a CL mechanism of bimolecular termination of alkyl peroxy radicals to produce an excited triplet state aromatic amide group or, at higher extents of oxidation, an *N*-acyl amide as shown in Table II. This excited amide then emits phosphorescence. The impure nature of the commercial TGDDM resin<sup>26,32</sup> and the possible secondary oxidation of the oxirane residue after ring opening probably ensures a more complex sequence of reactions is occurring. For example in the thermal decomposition of DDS-cured TGDDM at temperatures above 125°C, carbonyl compounds such as propanal, ethanal, propenal, and methyl pentenal were detected by G.C.-M.S.<sup>33</sup> All of the aldehydes except propenal were believed to be trace oxidation products formed during cure, consistent with the above.

The effect of heating time on the emission intensity can now be understood. The intensity of CL emission depends on the rate of the termination reaction (5)

$$I_{\text{CL}} = \phi k_5 [\text{RO}_2]^2 = \phi r_i$$

where  $\phi$  is the quantum yield of chemiluminescence and  $r_i$  is the rate of initiation of the oxidation [reaction (1)]. The change in any of these parameters during cure will lead to a change in  $I_{\text{CL}}$ . As oxidation proceeds, the alkyl peroxy radical concentration will increase to a steady-state value with an increase in  $I_{\text{CL}}$ . This is observed in the heating of the MY720 resin. The quantum yield,  $\phi$ , is the product of a chemical yield and a photophysical efficiency term and represents the fraction of carbonyl molecules produced in reaction (5) that ultimately emit phosphorescence. This is typically  $10^{-9}$ , and in the course of the cure reaction might be expected to increase as the viscosity of the resin increases. This results from an increase in the triplet yield with the decrease in bimolecular deactivation reactions as the resin gels. However, competing with this effect will be the dramatic decrease in the termination rate constant  $k_5$ . Since termination is diffusion controlled, the increase in viscosity of  $> 10^3$  at the gel point will result in a similar decrease in  $k_5$ . This will be the dominant factor, so that the sudden decrease in  $I_{\text{CL}}$  at the gel point in Figure 1 results from the drop in the termination rate of alkyl peroxy radicals on the MY720 backbone.

The slight decrease in the emission intensity from the neat MY720 resin on prolonged heating most probably arises from the increase in viscosity that results from the homopolymerization reaction of TGDDM. This is reported to have a high activation energy and is only a minor reaction at the cure temperature used here.<sup>5</sup>

### Temperature Dependence of Chemiluminescence

The intensity of chemiluminescence from the uncured MY720 resin increases exponentially with temperature. An Arrhenius plot of this emission intensity over the temperature range from 50°C to 135°C is shown in Figure 5 and it can be seen that a single straight line can describe the temperature dependence. When the luminescence intensity from cured samples with 17% and 27% DDS are plotted, there is a change in slope of the lines at tempera-

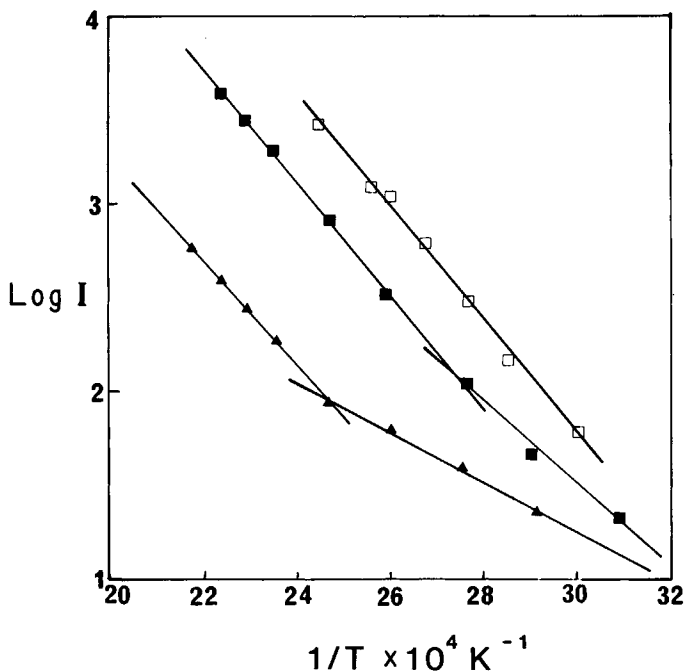


Fig. 5. Arrhenius plots of the temperature dependence of the chemiluminescence intensity,  $I_{CL}$ , for: (□) neat MY720 resin; (■) MY720 + 17% DDS; (▲) MY720 + 27% DDS.

tures of 95°C and 135°C, respectively. Above these temperatures the slope is the same as that of the uncured resin whereas below these temperatures the slope is lower. This discontinuity is consistent with the reported glass transition temperature for this resin system which is sensitive to the DDS concentration<sup>11</sup> and time of cure.<sup>12</sup>

The apparent glass transition temperatures measured by the changes in the CL plots of Figure 5 are compared in Table I with values calculated from data of Apicella et al. for  $T_g$  as a function of epoxy conversion<sup>5</sup> and using our thermal analysis data for these resins. The identification of the point of discontinuity of the CL curve as  $T_g$  for the resin is also supported by the observed effect of postcuring the 27% DDS sample for one hour at 170°C. The discontinuity increases from 135°C to 166°C consistent with the known increase in  $T_g$  on postcure at a higher temperature.<sup>11</sup>

The close similarity of the slopes of the CL curves for the uncured MY720 and the cured resin above  $T_g$  supports a common oxidation reaction for both systems as discussed earlier. This slope gives an activation energy of  $56 \pm 2$  kJ mol<sup>-1</sup> for the oxidation reaction. Monaco and Richardson<sup>25</sup> have reported a single activation energy for CL over the range 25°C to 190°C of 42 kJ mol<sup>-1</sup> for a TGDDM sample cured with 23% DDS at 120°C and postcured at 170°C. However, careful examination of their data shows a discontinuity in their Arrhenius plot at 143°C with an activation energy above this temperature of 54 kJ mol<sup>-1</sup>. This is then consistent with the results reported here.

The discontinuity on the CL curve at  $T_g$  represents either a change in the CL quantum yield,  $\phi$ , that will occur with a change in the free volume of the

resin or a change in the termination rate constant  $k_5$  which, being diffusion controlled, will be greater in the rubbery region.

### CONCLUSIONS

The chemiluminescence (CL) from a TGDDM-based epoxy resin, MY720, cured with different concentrations of DDS, has been studied throughout the process of network formation of the resin at 135°C. From a comparison of the CL curves with thermal analysis data, it has been shown that the gel point of the resin can be identified by a sharp discontinuity in a plot of  $\log I_{CL}$  against cure time. From spectral analysis of both the CL and ultraviolet-excited luminescence from uncured and cured resins, the CL is considered to originate from bimolecular termination of alkyl peroxy radicals formed  $\alpha$  to the nitrogen on the TGDDM backbone, producing an excited aromatic amide group as the emitting species. The emission intensity, being sensitive to the rate of termination of these radicals, will decrease as the viscosity of the resin increases during cure. Similarly, if the CL from cured MY720/DDS resins are studied as a function of temperature, the change in free volume at  $T_g$  results in a sharp increase in the CL intensity.

These results suggest that chemiluminescence is a viable noncontact optical technique for monitoring both the kinetics of gel formation in TGDDM/DDS epoxy resins and also the extent of network formation as given by  $T_g$ .

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