Cure characterization of an epoxy network by fluorescence behaviour of *trans*-diaminostilbene

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A small amount of *trans*-diaminostilbene (DAS) was used as a reactive label to probe cure reactions in an epoxy, a stoichiometric mixture of the diglycidyl ether of butanediol (DGEB) and methylene dianiline (MDA). DAS was found to mimic the reactivities of MDA. Bathochromic shifts of about 20 nm are found in ultra-violet spectra due to the conversion of primary amine groups to tertiary amine groups in DAS. The fluorescence spectra show similar bathochromic shifts with enhanced emission (about a factor of 3), especially after gelation. Comparison of the fluorescence intensity of DAS with the fully substituted DAS (tt-DAS) as a function of cure of the matrix indicates that the chemical reaction as well as the medium viscosity effect contribute to the emission enhancement, particularly at later stages of cure. A calibration curve relating emission intensity with the extent of epoxide reaction by the infra-red method has been established to estimate cure extent from emission measurement. Lastly, the fluorescence behaviour of DAS and tt-DAS as a function of medium viscosity is discussed assuming similar photochemical and photophysical mechanisms as in *trans*-stilbene.

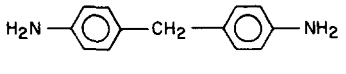
(Keywords: cure characterization; epoxy network; fluorescence reactive label; bathochromic shifts; *trans*-diaminostilbene)

INTRODUCTION

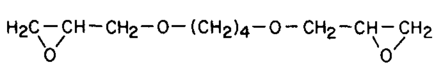
One of the challenging problems in polymer science remains the characterization of crosslinking in thermoset polymers. The development of new methods to probe cure reactions has been one of the major research efforts in our laboratory in recent years. We took an approach based on labelling with reactive dyes to mimic the reactivities of the curing agent. The photochemical and photophysical behaviour of the reactive label provides information on the curing process.

For example, we used a reactive label, *p,p'*-diaminoazobenzene (DAA), to monitor cure reactions in two epoxy–diamine resins. As cure proceeds, λ_{max} of the $\pi \rightarrow \pi^*$ transition corresponding to the azo bond of DAA shows red shifts (about 60 nm) in the visible spectra in a way that provides spectral discrimination for the cure products[1]. Furthermore, the fluorescence intensity of the DAA label at 560 nm increases sharply (more than 100 times), because the fluorescence quantum yield of DAA increases more than a thousand-fold when the amine groups of DAA become tertiary amines[2]. Since the effect of the viscosity change as cure proceeds was negligible when monitored at 20°C, the fluorescence intensity has been used to follow cure reactions in a quantitative way, especially in the later stages of cure (after gelation). By analysing visible and fluorescence spectra, we were able to obtain parameters characteristic of cure kinetics and mechanisms such as cure product composition, the reactivity ratio of primary and secondary amine, initial rate constants and an activation energy of amine–epoxy reaction[3,4]. Furthermore, our experimental results were compared with the theoretical predictions on the weight-average molecular weight and the soluble fractions[4]. In these epoxy resins, DAA was used to mimic the reactivity of the curing agent, diaminodiphenylsulphone (DDS). Careful studies show that DAA reacts slightly faster than DDS, requiring a correction for such differences through calibration.

In this study, we have used *trans-p,p'*-diaminostilbene (DAS) as a reactive label for another important epoxy–amine resin (DGEB–MDA resin) because DAS is expected to have reactivities similar to methylene dianiline (MDA) according to the Hammet constant[5]. DGEB (diglycidyl ether of butanediol) was chosen rather than DGEBA (diglycidyl ether of bisphenol A) since the cure reaction can progress much further at cure temperatures above 80°C due to the absence of vitrification. DAS is of interest for two reasons. First, unlike DAA, DAS is fluorescent even when the amine groups are primary, providing a greater sensitivity at early stages of cure. Secondly, the photophysical behaviour of *trans*-stilbene and some of its derivatives are known to be sensitive to environmental viscosity[6–8]. Thus, we may expect to see the effects on photophysical behaviour from both the increasing viscosity and the chemical reaction as cure proceeds.



Methylene dianiline (MDA)



Diglycidyl ether of butanediol (DGEB)

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EXPERIMENTAL

DGEB (98% purity) was purchased from Aldrich and used without further purification, and MDA was recrystallized from toluene. DAS dihydrochloride from Aldrich was neutralized with sodium carbonate and recrystallized from methanol to obtain the free amine.

A stoichiometric mixture of DGEB and MDA was used with 0.1% DAS as a label. The sample preparation method was the same as in ref. 2. Perkin–Elmer u.v.-vis. diode array (model 3840) and fluorescence spectrometer (MPF-66) were used to record the spectra with a model 7500 data station. U.v.-vis. and fluorescence spectra were obtained after cooling the sample to room temperature following cure in an oven for a specific time. Fluorescence usually was measured with a 0.3 nm wide excitation slit and a 5 nm wide emission slit, after exciting at 372 nm. Fully substituted DAS (tt-DAS) was synthesized by reacting DAS with a large excess of mono-epoxide (phenyl glycidyl ether, PGE) at 140°C for 12 h followed by removal of excess PGE under vacuum. A u.v.-vis. absorption at 372 nm confirms the structure of tt-DAS as reported in the literature[9]. The fluorescence quantum yield (ϕ_f) of DAS in PGE and tt-DAS in PGE was measured in comparison with 9,10-diphenylanthracene whose fluorescence quantum yield was assumed to be unity.

The extent of the reaction (ξ_b) was estimated by monitoring the epoxy ring i.r. absorption at 915 cm^{-1}, after correcting with an absorption at 1610 cm^{-1} due to MDA, according to the following equation:

$$\xi_b = 1 - \frac{A_{915\,\mathrm{cm}^{-1}(t)}}{A_{1610\,\mathrm{cm}^{-1}(t)}} \times \frac{A_{1610\,\mathrm{cm}^{-1}(0)}}{A_{915\,\mathrm{cm}^{-1}(0)}} \qquad (1)$$

Differential scanning calorimetry (Omnitherm model 900) was used to obtain the glass transition temperatures of epoxy resin as well as for the dynamic cure run of the stoichiometric mixtures of DGEB–MDA and DGEB–DAS at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Model reactions

In order to see how u.v.-vis. spectra and fluorescence spectra of DAS change as a function of reaction with the epoxy, a mono-epoxide, phenyl glycidyl ether (PGE), in large excess was reacted with DAS. *Figure* 1 (trace A), corresponding to DAS before any reaction took place, shows two absorption peaks at 327 and 352 nm. These spectral positions are in agreement with the spectra of DAS in ethanol reported by Bernstein[9], who provided spectroscopic evidence for the existence of multiple transitions in the $\pi \rightarrow \pi^*$ transition region of di-*para*-substituted *trans*-stilbenes.

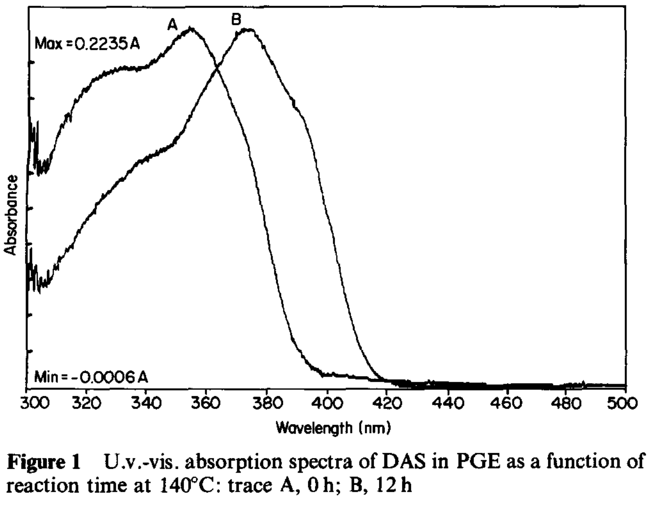
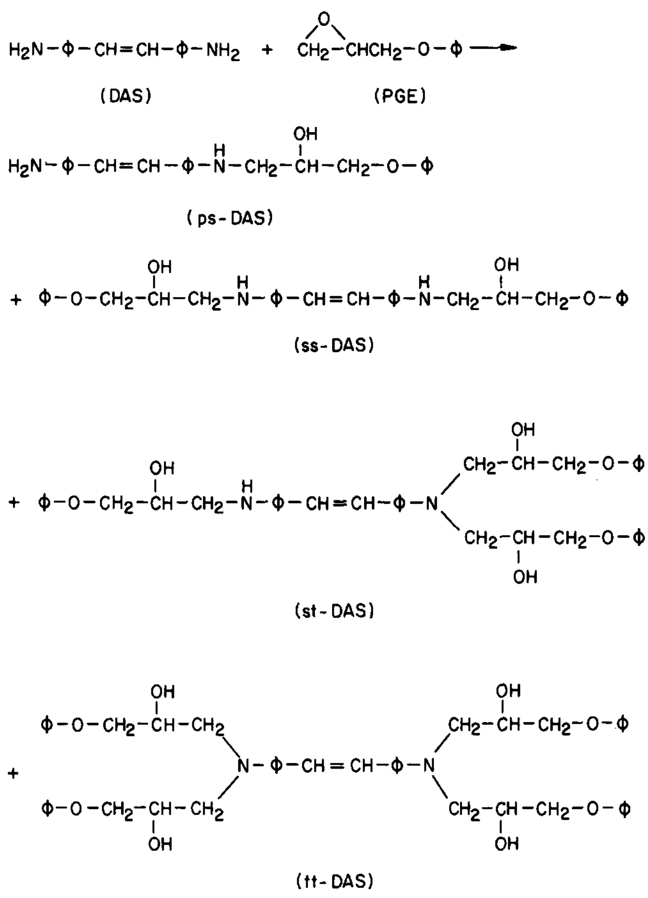


Figure 1 U.v.-vis. absorption spectra of DAS in PGE as a function of reaction time at 140°C: trace A, 0 h; B, 12 h



Scheme I Various reaction products from DAS and PGE

Table 1 Photophysical parameters for DAS and tt-DAS according to equations (3) and (5)

	tt-DAS (before epoxy cure or in PGE)	tt-DAS (in 75% cured epoxy)	DAS (in PGE)
ϕ_f	0.29	0.87	0.12
k_f (s^{-1})	5.98×10^8	5.98×10^8	5.98×10^8
A (s^{-1})	3.98×10^{12}	2.0×10^{16}	3.98×10^{12}
ΔE^* (kcal mol^{-1})	4.6	11.1	4.0
k_{tw} (s^{-1})	1.5×10^9	0.1×10^9	4.4×10^9

As the reaction between PGE and DAS proceeds, we would expect to obtain intermediate reaction products as shown in *Scheme I*. Basically, the amine groups in DAS change from primary to secondary to tertiary as the reaction progresses. Secondary and tertiary amines are more electron-donating toward the central CH=CH bond in DAS than are primary amines. Thus, bathochromic shifts should be expected as a function of the progress of reaction. This is what we observed in *Figure 1* (trace B), which shows the red shifts of both absorption peaks in u.v.-vis. spectra when both amines in DAS have become tertiary. We will designate this model compound as tt-DAS, which shows absorption maxima at 340 and 372 nm. The overall red shift for the 352 nm peak is thus 20 nm from DAS to tt-DAS, which agrees with the finding of Bernstein in ethanol[9]. This degree of red shift is much smaller than in the case of DAA, and is due to the fact that it requires greater energy to produce the same shifts in the u.v. region where DAS absorption occurs as compared to the visible region of DAA absorption. These small shifts in DAS make it difficult to deconvolute the absorption spectra into various intermediate model cure products.

Figure 2 (traces A and B) shows the fluorescence spectra of DAS and tt-DAS, respectively, when excited at 372 nm. In the DAS fluorescence spectra, *Figure 2* (trace A), we see two emission maxima, one at 418 nm and the other around 403 nm. In the tt-DAS fluorescence spectra, *Figure 2* (trace B), both peaks have been red-shifted, appearing at 430 and 418 nm. Also, tt-DAS is inherently more fluorescent than DAS, since its emission quantum yield is about 2.4 times greater in dilute PGE solution.

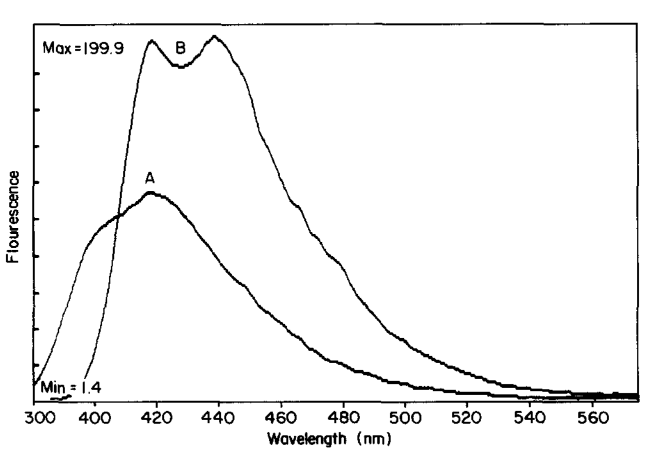


Figure 2 Fluorescence spectra of DAS in PGE as a function of reaction time at 140°C: trace A, 0 h; B, 12 h

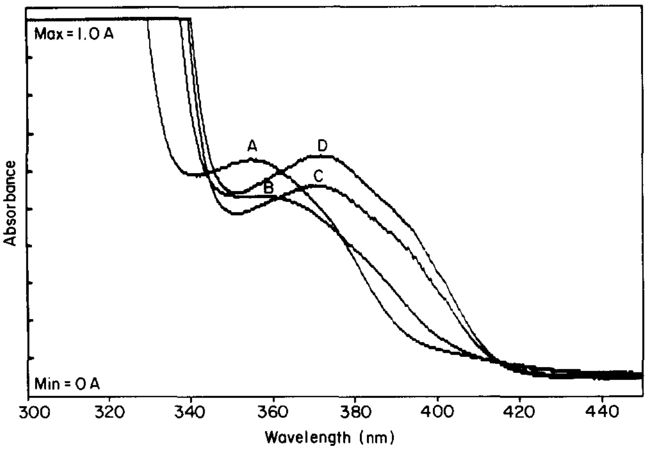


Figure 3 U.v.-vis. absorption spectra of DAS in DGEB–MDA epoxy as a function of cure time at 140°C: trace A, 0 min; B, 15 min; C, 45 min; D, 250 min

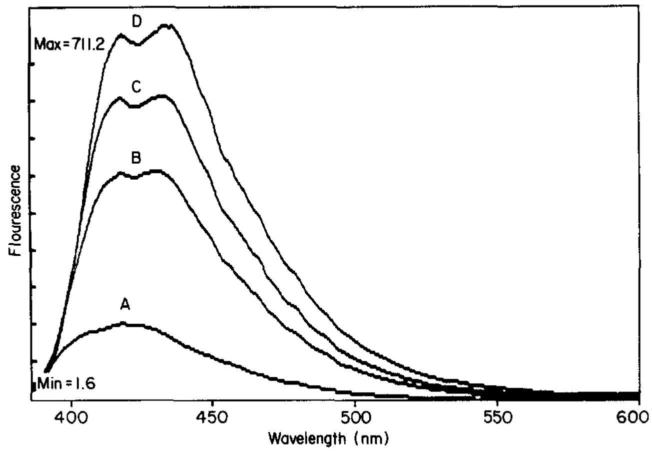


Figure 4 Fluorescence spectra of DAS in DGEB–MDA epoxy as a function of cure time at 140°C: trace A, 0 min; B, 15 min; C, 25 min; D, 250 min

Spectroscopic observations in the epoxy matrix

Figure 3 shows u.v.-vis. spectra of DGEB–MDA–DAS (0.1%) following cure at 140°C. Before cure, the DAS absorption maximum occurs at 352 nm. DAS in DGEB shows another absorption peak at 327 nm, which is hidden under the MDA absorption in the DGEB–MDA epoxy. As cure proceeds, we observe red shifts of the peak at 352 nm. After 300 min of cure at 140°C the DAS absorption peak is shifted to 371 nm. Further curing even at high temperatures does not shift this absorption beyond 372 nm, which is consistent with the model reactions. *Figure 4* shows fluorescence spectra as a function of cure time at 140°C. At zero cure time, the emission spectrum is broad with a maximum near 418 nm. As cure increases, enhancement of emission as well as splitting into two emission peaks at 418 and 430 nm are noted. This splitting is due to the red-shifted emission of tertiary-amine-containing DAS as a result of cure reactions (compare with *Figure 2*). When emission intensity at 418 nm is plotted as a function of cure time at two cure temperatures, 140 and 120°C, we obtain S-shaped curves as illustrated in *Figure 5*. At these cure temperatures, the gelation for DGEBA–MDA epoxy is known to take place after 8 min and 16 min respectively, as shown by two arrows[10]. We may assume that the gelation takes place at similar times in DGEB–MDA epoxy. We note in *Figure 5* that, after gelation, fluorescence emission increases sharply at the respective cure temperature. Also, it is noted that the overall increase in emission intensity is about 3.5 times greater at longer cure times, as compared to zero cure time.

In order to delineate the effect of viscosity on the fluorescence intensity, we cured DGEB–MDA epoxy containing a small amount of tt-DAS as a probe molecule. In this experiment, any fluorescence change is due to the viscosity effect of the medium since tt-DAS can no longer react in the matrix. *Figure 6* compares the emission intensity of DAS with tt-DAS in the DGEB–MDA matrix as a function of cure time at 140°C. Emission intensity in *Figure 6* is calibrated to reflect emission per mole of DAS or tt-DAS. At zero cure time, the emission from tt-DAS is 2.4 times greater than DAS as mentioned earlier. While DAS shows an increase in emission after gelation, the emission from tt-DAS is constant well past gelation up to the cure time of 100 min. At this cure time, about 75% of the epoxide in the matrix has reacted, as determined by i.r. spectra. After 100 min the emission from tt-DAS increases sharply, at least 3 times. From these trends, we may conclude that the emission enhancement of DAS near gelation is due to chemical reactions, whereas it includes the medium viscosity effect at later stages. Even though we cannot separate in a quantitative way the contributions from chemical reactions and the medium viscosity effect at a given cure time when DAS was used, a

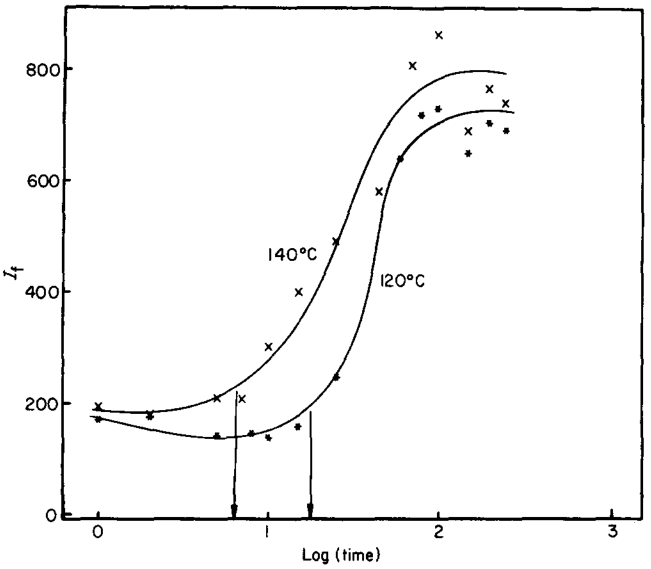


Figure 5 Fluorescence intensity at 418 nm as a function of cure time at 140°C and 120°C, respectively, in DAS (0.1%) labelled DGEB–MDA epoxy

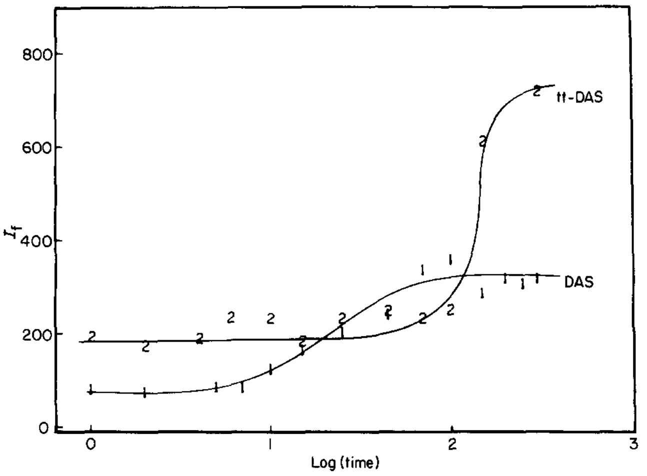


Figure 6 Fluorescence intensity at 418 nm as a function of cure time at 140°C, comparing DAS and tt-DAS in DGEB–MDA epoxy

plot of emission intensity in DAS-labelled epoxy as a function of the overall extent of epoxide reaction can be established to estimate epoxy cure extent. Such a plot is shown in *Figure 7*, for a cure at 140°C, where a sharp increase in emission is shown after gelation.

In order to confirm that the reactivity of DAS is similar to that of MDA, we compared a d.s.c. thermogram of the stoichiometric mixtures of DGEB–MDA and DGEB–DAS, which is shown in *Figure 8*. The heat generated, as indicated by the area under the curves, is about the same. The peak temperature for DGEB–MDA is about 7°C lower than that for DGEB–DAS. From these observations we may assume that DAS will mimic the reactivity of MDA.

The effects of substitution and medium viscosity on the fluorescence of DAS

In this section, we attempt to explain the observed fluorescence enhancement of tt-DAS in comparison to DAS, as well as the medium viscosity effects based on photophysical and photochemical considerations.

Stilbene and its derivatives have been under intense investigation for their solution photophysics and photochemistry[6]. Direct absorption of light on *trans*-stilbene excites the molecule to the excited singlet state, which reaches a twisted singlet excited state of geometry after passing over a small thermal barrier of $\sim 4.0\,\mathrm{kcal\,mol^{-1}}$. Overwhelming experimental evidence[7] has shown that the fluorescence is the only major process competing with this twisting mechanism; in other words, non-radiative decays such as intersystem crossing are negligible. Therefore, the fluorescence quantum yield ϕ_f can be expressed as:

$$\phi_f = \frac{k_f}{k_f + k_{tw}} \quad . \qquad (2)$$

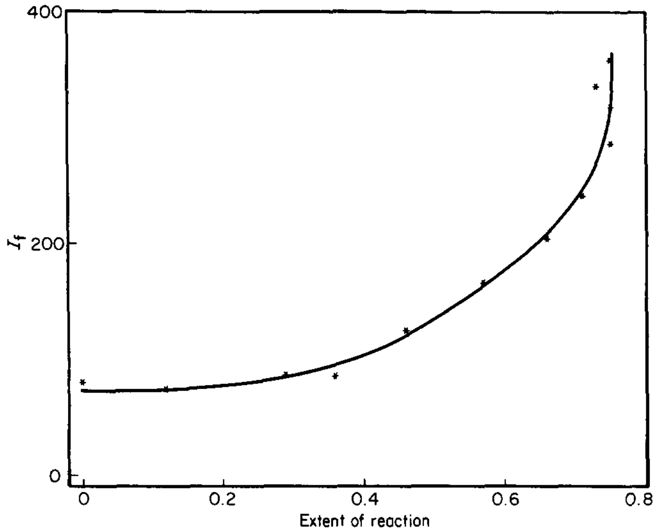


Figure 7 Correlation of fluorescence intensity at 418 nm with the extent of epoxy reaction (ξ_b) by i.r. method at 140°C cure

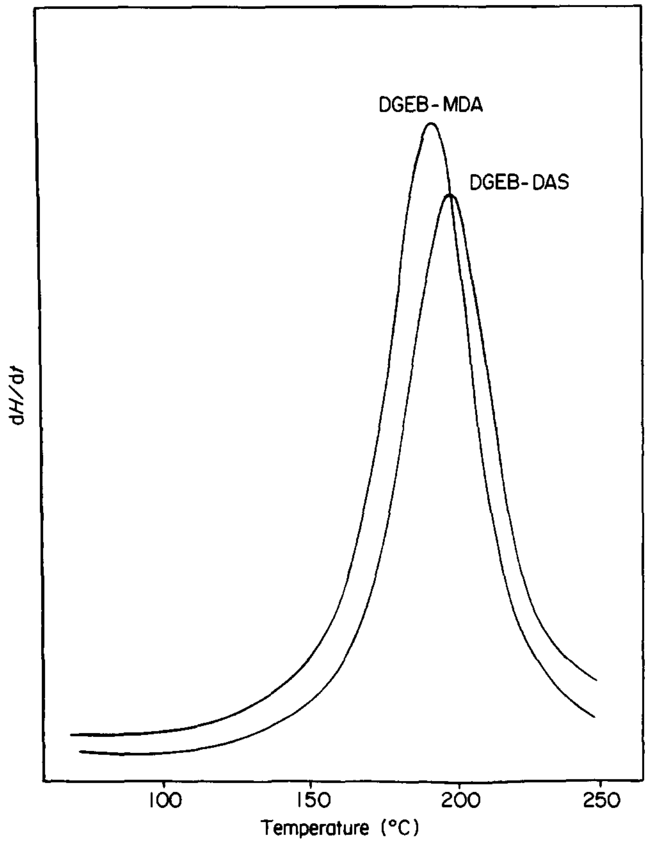


Figure 8 Differential scanning thermogram for stoichiometric mixtures of DGEB–MDA and DGEB–DAS at a heating rate of $10°\mathrm{C\,min^{-1}}$

where k_f and k_{tw} are the rate constants of fluorescence and twisting. Of the two, only the value of k_{tw} is known to be sensitive to temperature and medium viscosity, according to the following equation:

$$k_{tw} = A\exp(-\Delta E^*/RT) \qquad (3)$$

By substituting (3) into (2), we can obtain:

$$\phi_f = \frac{k_f}{k_f + A\exp(-\Delta E^*/RT)} \qquad (4)$$

The value of k_f for *trans*-stilbene is known to be $5.8\times10^8\ s^{-1}$ (ref. 6). The activation energy and the pre-exponential factor are 3.53 kcal mol^{-1} and $4\times10^{12}\ s^{-1}$ for a low-viscosity solvent[6]. Therefore, equation (4) predicts an increase in ϕ_f with lower temperature or with higher viscosity (equivalent to a greater ΔE^*). Experimental data on the temperature dependence agree well with the prediction of equation (4)[6].

Some substituted stilbenes are known to follow the same photochemical and photophysical mechanisms as *trans*-stilbene. These include substituents whose steric effect does not cause deviations from planarity of *trans*-stilbene. Examples are *p*-methoxystilbene[6], *p*-alkylstilbene, *p,p'*-dialkylstilbene[11] and *p'*-dimethylaminostilbene[12]. It is expected that DAS and tt-DAS will behave like the above substituted stilbenes[13]. Therefore, we attempt to explain the fluorescence behaviour of DAS and tt-DAS based on equation (4). We will first address the medium effect we observed with tt-DAS, a probe molecule in DGEB-MDA matrix, whose fluorescence increased after about 100 min of cure at 140°C corresponding to 75% of cure (see *Figure 6*). In comparison to the fluorescence quantum yield of unity for 9,10-diphenylanthracene in PGE, the fluorescence quantum yields of DAS in PGE, of tt-DAS in PGE, and of tt-DAS in cured epoxy were determined to be 0.12, 0.29 and 0.87 respectively. Assuming the same k_f for tt-DAS and *trans*-stilbene, we can estimate an activation energy by rearranging (4) as follows:

$$\Delta E^* = -RT\ln\left(\frac{k_f}{\phi_f A}(1-\phi_f)\right) \qquad (5)$$

Uncured epoxy of DGEB-DDS at room temperature has low viscosity, unlike that based on diglycidyl ether of bisphenol A (DGEBA). So we used the value of A ($3.98\times10^{12}\ s^{-1}$) for uncured epoxy, which is the reported value of *trans*-stilbene in a non-viscous solvent. For cured epoxy, we used a value of $2\times10^{16}\ s^{-1}$, reported for *trans*-stilbene in glycerol including the temperature range when glycerol is a rigid glass[14]. In the first two columns of *Table 1*, we list the activation energies estimated from (5) and k_{tw} from (3) for tt-DAS before and after cure of the epoxy matrix. From *Table 1*, it becomes obvious that the activation energy of tt-DAS in the cured epoxy is much greater than that in uncured epoxy. This trend leads to a smaller k_{tw} (twisting rate constant) in the cured epoxy as compared with the uncured epoxy. The activation energy (11.1 kcal mol^{-1}) of cured epoxy is higher than the activation energy (9.7 kcal mol^{-1}) of *trans*-stilbene in glycerol[6]. Given the assumptions noted above, this means that tt-DAS experiences a slightly greater impediment to twisting around the CH=CH bond in cured epoxy than in glycerol. Since the T_g of the cured epoxy after 100 min of cure at 140°C is above 40°C, the matrix was in the glassy state when fluorescence was measured at 20°C. In the glassy state, bulky tertiary amine groups in tt-DAS make the twisting around the CH=CH bond more difficult than in *trans*-stilbene. We can also explain why ϕ_f of tt-DAS did not increase on gelation of the epoxy matrix (see *Figure 6*); its gelation point is about −30°C, so that this matrix was in the rubbery state when fluorescence was measured at 25°C. Thus, even though the gelled matrix has an infinite macroscopic viscosity, the tt-DAS molecule has enough free volume for rotation around its centre bond. This trend is consistent with the behaviour of various photochemical isomerizations in bulk polymers[15,16].

In order to compare DAS and tt-DAS in a low-viscosity solvent, PGE, we also estimated ΔE^* and k_{tw} for DAS, using equations (5) and (3) as listed in the last column of *Table 1*. Comparing column 1 with column 3 shows that the activation energy for DAS is smaller than for tt-DAS. This difference is manifested in a greater k_{tw} (4.4×10^9) for DAS as compared to tt-DAS (1.5×10^9). Thus, under the assumption that DAS and tt-DAS behave similarly to *trans*-stilbene, the increase in fluorescence of tt-DAS can be explained by kinetics: it is due to an effective increase in an activation barrier to the rotation, which is the main competing process to fluorescence.

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