Fluorescence monitoring of polarity change and gelation during epoxy cure

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The fluorescence spectrum of 1-(4-dimethylaminophenyl)-6-phenyl-1,3,5-hexatriene (DMA-DPH) dissolved in a stoichiometric mixture of diglycidyl ether of bisphenol A and diethylene triamine was measured as a function of cure time at various cure temperatures. The frequency of the fluorescence maximum for DMA-DPH increased during the curing reactions because of the change in the polarity of the epoxy resin. In an isothermal cure, the fluorescence frequency increased linearly with the cure time until the gelation occurred. The total change in fluorescence frequency that occurred from the beginning of the isothermal cure to the gelation time was 1000 cm^{-1} and was independent of the cure temperature, implying that the chemical structure of the infinite network at the gelation time was independent of the cure temperature. The rate constant, K_T, for the polarity change during an isothermal cure of the epoxy resin, defined as the rate constant for the linear increase in fluorescence frequency, was determined. The activation energy of K_T was estimated to be 60 kJ mol^{-1}.

(Keywords: cure monitoring; epoxy resins; fluorescence)

INTRODUCTION

The fluorescence spectra of many fluorophores are sensitive to the polarity of their environment because of the altered dipole moment of the excited fluorophores and the reorientation of the solvent molecules around the excited state dipole. For example, the fluorescence spectra of benzene derivatives, with an electron donor substituent and an electron acceptor substituent in *para* positions, are highly sensitive to solvent polarity because the localization of positive and negative charges on the donor and the acceptor, respectively, causes a large change in dipole moment upon excitation[1-4].

The interactions between the fluorophore and the solvent molecules affect the energy difference between the ground and the excited states. In the absence of specific chemical interactions between the fluorophore and the solvent molecules, such as hydrogen bonding and complexation, this energy difference (in cm^{-1}), called Stokes' shift, depends on the refractive index (n) and dielectric constant (ε) of the solvent. To a first approximation, the Stokes' shift is given by the Lippert equation[5]:

$$\nu_A - \nu_F = \frac{2}{hc}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right)\frac{(\mu^* - \mu)^2}{a^3} + \text{constant} \quad (1)$$

where h is Planck's constant, c is the speed of light, a is the radius of the cavity in which the fluorophore resides, μ^* and μ are the excited and ground state dipole moments of the fluorophore, and ν_A and ν_F are the peak frequencies (expressed in cm^{-1}) of the absorption and fluorescence, respectively.

For a polarity-sensitive fluorophore dissolved in a polymerizing system, the Lippert equation predicts a change in Stokes' shift as the polymerization proceeds, since the dielectric constant and the refractive index of the system change during the polymerization. By measuring the Stokes' shift of a polarity-sensitive fluorescent probe as a function of the cure time, an insight into the processes occurring in a polymerizing system can be obtained. This paper gives the results of such a study in which 1-(4-dimethylaminophenyl)-6-phenyl-1,3,5-hexatriene (DMA-DPH) was used as a polarity-sensitive fluorescent probe to investigate the cure of an epoxy resin.

EXPERIMENTAL

Materials

Diethylene triamine (DETA), diglycidyl ether of bisphenol A (DGEBA) and DMA-DPH were from commercial sources and were used without further purification. The DGEBA resin, with an epoxy equivalent weight of approximately 175, had fluorescence properties as described in ref. 6. DMA-DPH was dissolved in DGEBA at a concentration of 5×10^{-5} mol l^{-1}.

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Methods

The detailed description of the reaction cell has been given in ref. 6. The epoxy resin consisted of the same equivalents of DETA and DGEBA. In a typical experiment, 2 g of DGEBA containing the DMA-DPH probe was drawn into a syringe for weighing and then injected into a vial containing 0.236 g of DETA. The mixture was rapidly stirred for at least 5 min at room temperature under a nitrogen atmosphere until a clear solution was obtained. The mixed sample was injected into the reaction cell by using a syringe and was then heated immediately so that the sample reached the cure temperature within 2 min. The cure time was measured from the time when the mixing was completed. Uncorrected fluorescence spectra of the sample at an excitation wavelength of 420 nm were taken on a spectrofluorometer operating in the front surface illumination mode.

RESULTS AND DISCUSSION

Figure 1 exhibits the fluorescence spectra at various cure times of the DMA-DPH probe in the DGEBA/DETA epoxy resin cured at 50°C. The spectrum at the top is for the cure time of 320 min. For the rest of the spectra, going from the bottom spectrum to the top, the cure time goes from 15 to 80 min with an increment of 5 min between successive spectra. As the cure time increased, the fluorescence intensity increased and the wavelength of the fluorescence maximum decreased. However, there was not a pronounced change in the shape of the fluorescence spectrum, indicating that there were no significant specific interactions of the fluorescent probe with the epoxy resin. The shift of the fluorescence spectrum to shorter wavelengths (higher wave numbers) is consistent with the prediction of the Lippert equation, since, for an epoxy resin, the refractive index usually increases with the extent of cure[7], while the dielectric constant decreases[8], leading to a decrease in the Stokes' shift.

Figure 1 also shows that the fluorescence intensity of the DMA-DPH probe increased with the cure time. This increase is consistent with the work of Loutfy and Arnold[9] which showed that environmental factors resisting the internal molecular rotation of donor–acceptor dyes led to a decrease in the non-radiative decay rate and, consequently, an increase in the fluorescence yield. Since the fluorescence intensity of the DMA-DPH probe and other donor–acceptor dyes is sensitive to the change in free volume, donor–acceptor dyes have been successfully used to monitor the cure of epoxy resins[6,10–12] and polymerization of monomers[13,14].

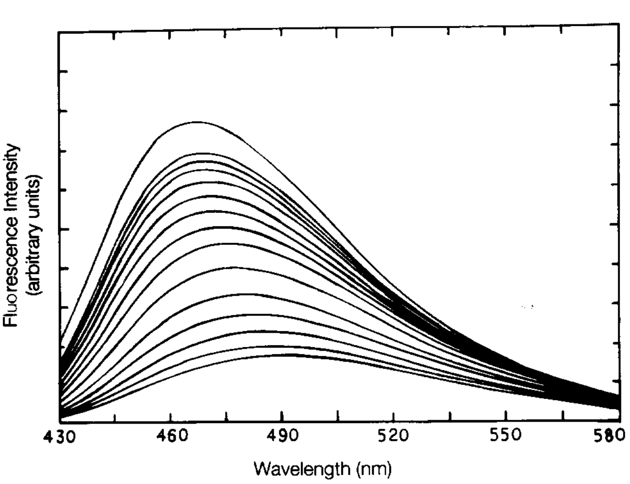

Figure 1 The emission spectra of the DMA-DPH probe dissolved in the DGEBA/DETA epoxy resin cured at 50°C for various cure times. The uppermost spectrum is for the cure time of 320 min. For the remaining spectra, going from the bottom spectrum to the top, the cure time goes from 15 to 80 min with an increment of 5 min between successive spectra

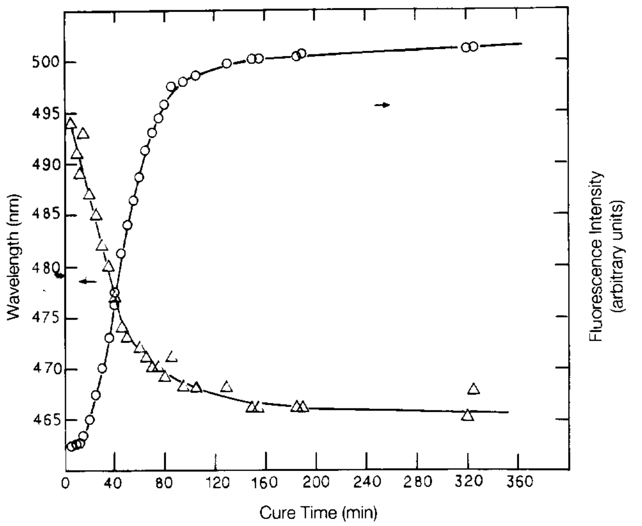

Figure 2 The wavelength (△) and the fluorescence intensity (○) at the maximum of the fluorescence spectrum are plotted as functions of the cure time for the DMA-DPH probe dissolved in the DGEBA/DETA epoxy resin cured at 50°C

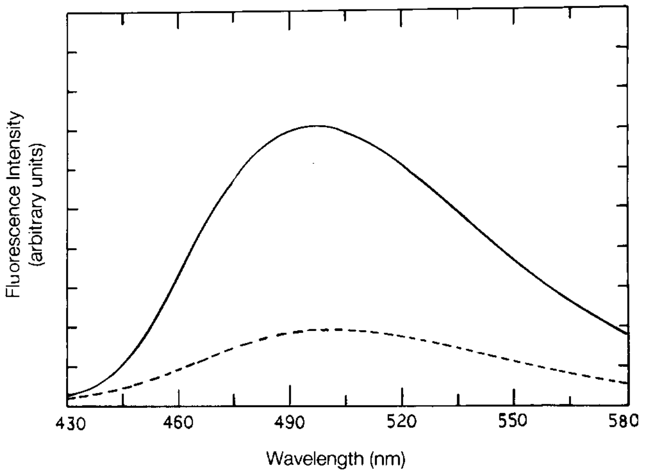

Figure 3 The emission spectra of the DMA-DPH probe dissolved in the DGEBA monomer measured at 25°C (——) and 72°C (– – –)

Figure 2 shows how the wavelength and the fluorescence intensity changed with the cure time when the epoxy resin was cured at 50°C. The wavelength at the maximum of the fluorescence spectrum decreased rapidly and then decreased slowly after the cure time of 50 min. The wavelength remained practically unchanged after the cure time of 160 min. Similarly, the fluorescence intensity at the maximum of the fluorescence spectrum increased rapidly and then increased slowly after the cure time of 80 min.

Figure 3 gives the fluorescence spectra of the DMA-DPH probe in the DGEBA resin at 25°C (solid curve) and at 72°C (broken curve). The fluorescence intensity was lower at the higher temperature because the decrease in the viscosity of DGEBA led to an increase in the non-radiative decay rate. However, the decrease in the viscosity at the higher temperature increased the peak fluorescence wavelength by only 0.6%, indicating that the reorientation of the dipoles of DGEBA at these temperatures was essentially complete prior to fluorescence. According to the Debye equation[15], the dielectric relaxation time for spherical molecules in a liquid is given by:

$$\tau = 4\pi\eta a^3/kT \qquad (2)$$

where η is the viscosity of the liquid, a is the molecular radius, k is the Boltzmann constant and T is the absolute temperature. Using the data from ref. 16 for the viscosity of DGEBA at 30°C, we obtained an estimated value of 10^{-6} s for the dielectric relaxation time of DGEBA molecules in the DGEBA resin. Since this relaxation time is much longer than the lifetime of the excited DMA-DPH, the whole molecular rotation of DGEBA did not contribute to the Stokes' shift resulting from the solvent reorientation. The major dipole group that contributes to the dielectric relaxation of DGEBA molecules has been reported to be the C–O–C moiety in the epoxy group[17]. Therefore, the reorientation of the dipoles of DGEBA which led to the Stokes' shift was probably primarily due to the rotation of single bonds in the Ep–CH_2–O– group, where Ep represents the epoxy ring.

Figure 4 gives the fluorescence spectra of the DMA-DPH probe in the cured DGEBA/DETA epoxy resin at 32°C (solid curve) and at 138°C (broken curve). The fluorescence intensity was lower at the higher temperature, because the increase in the free volume of the cured epoxy resin led to an increase in the non-radiative decay rate[13,14]. However, the increase in temperature and free volume increased the peak fluorescence wavelength by only 0.4%, indicating that, at these temperatures, the reorientation of the dipoles of the cured epoxy resin was essentially complete prior to emission. As DGEBA reacts with an amine hardener, the Ep–CH_2–O– group is converted to a –CH_2–CH(OH)–CH_2–O– group. A mechanism of dielectric relaxation that has been suggested[18] is the crank-shaft type rotation hindered by the pendant hydroxyl group. The reorientation of the dipoles in the DGEBA/DETA epoxy resin which led to the Stokes' shift was presumably due to the rotation of the hydroxyl group and the crank-shaft type rotation.

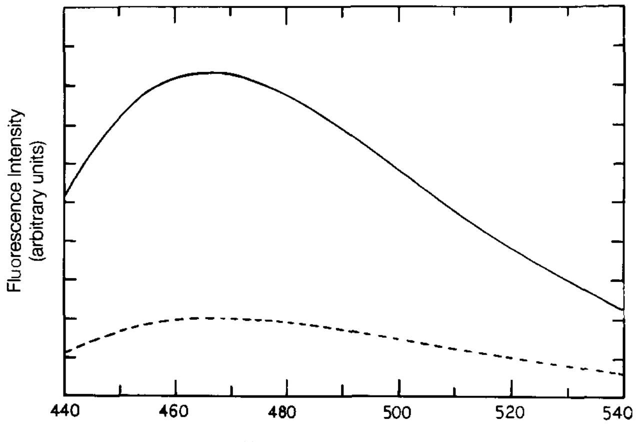

Figure 4 The emission spectra of the DMA-DPH probe in the fully cured DGEBA/DETA epoxy resin measured at 32°C (——) and 138°C (– – –)

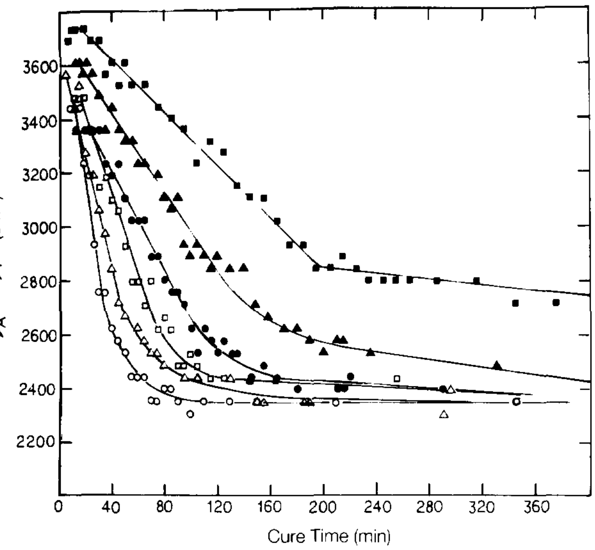

Figure 5 The Stokes' shift of the emission spectrum of the DMA-DPH probe in the DGEBA/DETA epoxy resin, measured at the cure temperature, as a function of the cure time: ■, 29.5°C; ▲, 35°C; ●, 40°C; □, 45°C; △, 50°C; ○, 55°C

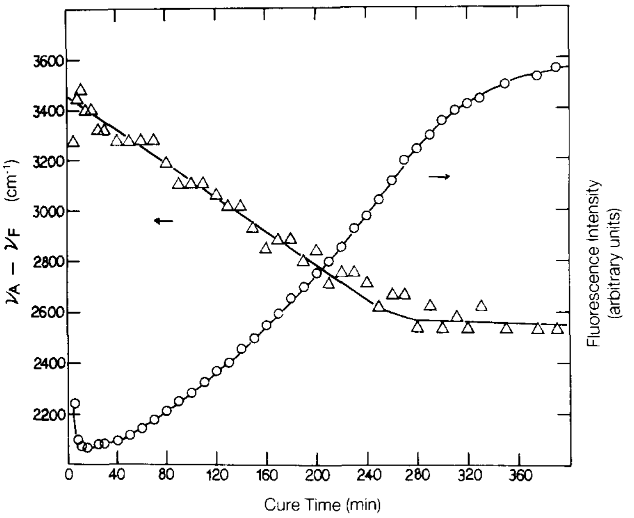

Figure 6 The Stokes' shift (△) and the fluorescence intensity (○) of the DMA-DPH probe in the DGEBA/DETA epoxy resin as a function of the cure time at 25°C

Since the data of *Figures 3* and *4* show that the peak fluorescence wavelength (and therefore the Stokes' shift) of the DMA-DPH probe in uncured and cured DGEBA remained the same with an increase in temperature, the reorientation of dipoles in the curing DGEBA/DETA epoxy resin was essentially complete prior to fluorescence. Furthermore, the blue shift to shorter wavelengths shown in *Figure 1* was caused by the change in polarity due to chemical reactions and not by the change in viscosity or free volume due to chemical reactions. Therefore, by measuring the blue shift of the fluorescence spectrum of DMA-DPH probe, we can monitor the curing reactions of epoxy resins.

Figure 5 shows the Stokes' shift of the DMA-DPH probe for various temperatures as a function of the cure time when the probe was dissolved in an epoxy resin made of the same equivalents of DETA and DGEBA. *Figure 6* gives the Stokes' shift and the fluorescence intensity of the DMA-DPH probe as functions of the cure time when the probe was dissolved in the same epoxy resin as for *Figure 5* but at 25°C. In *Figure 5*, the small decrease in the initial Stokes' shift at higher temperatures was due to the thermal degradation of the DMA-DPH probe in a stock solution of the probe in DGEBA. The thermal degradation occurred because the stock solution was heated to reduce its viscosity each time it was used to prepare the epoxy resin samples. Since the epoxy resin cured at higher temperatures was made from the stock solution that had been heated more often, its initial wavelength shift was smaller. The data measured at 55°C, shown in *Figure 5*, and the data measured at 25°C, shown in *Figure 6*, were obtained from the cure of samples from the same stock solution. For these data, the initial frequency shift of the DMA-DPH probe for the resin cured at 25°C was similar to that for the resin cured at 55°C. Therefore, the change in the isothermal cure temperature apparently had no effect on the initial frequency shift of the DMA-DPH probe, as long as the effect of the thermal degradation was eliminated.

In *Figures 5* and *6*, the Stokes' shift decreased linearly with the cure time, then deviated from the linear behaviour, and finally levelled off. Moreover, the deviation from the linear behaviour and the subsequent transition to a plateau value occurred more rapidly at lower temperatures than at higher temperatures. At 25 and 29.5°C, in particular, the transition to a plateau-like region occurred abruptly. While the transition to the plateau-like region of the Stokes' shift occurred more abruptly with a decrease in temperature, the rate of change in fluorescence intensity increased with an increase in temperature. This difference in temperature dependence can be seen when *Figures 2* and *6* are compared. The vitrification of the curing epoxy resin occurs only when the cure temperature is lower than the glass transition temperature of the epoxy resin at its highest degree of cure. (For the epoxy resin of this investigation, the maximum glass transition temperature was determined to be 117°C by fluorescence spectroscopy[19]. For the DMA-DPH probe dissolved in DGEBA and 4,4'-methylene-bis-cyclohexylamine, Stroeks *et al.*[10] reported that the fluorescence intensity of the DMA-DPH probe reached a plateau value when the vitrification of the epoxy resin occurred. The experimental result, that the fluorescence intensity reached a plateau value more rapidly at higher temperatures, was an indication that the epoxy resin vitrified more rapidly at higher temperatures.

We now deal with the observation that the deviation from the linear behaviour of the Stokes' shift and the subsequent transition to a plateau value occurred more abruptly at lower temperatures than at higher temperatures. We first identify the cure time, t_D, when the change in Stokes' shift began to deviate from the linear behaviour as the gelation time, when the epoxy resin became an infinite network. In a similar manner, Stroeks *et al.*[10] indicated that the pregel viscoelastic transition occurred near the cure time when the time derivative of the fluorescence intensity reached the maximum. At t_D, the deviation from the linear decrease in the Stokes' shift occurred because the curing reactions slowed down when the diffusion of the reactive groups became highly restricted upon the formation of an infinite network. Riccardi *et al.*[20] also observed a significant decrease in the curing rate of a similar epoxy resin after the gelation, and attributed the decrease to the restriction on the diffusion of the reactive groups. According to the time–temperature–transformation (TTT) isothermal cure diagram developed by Gillham[21], the logarithmic difference between the cure times to reach the gelation and the vitrification is larger at higher cure temperatures than at lower cure temperatures. This prediction holds unless the cure temperatures are higher than the

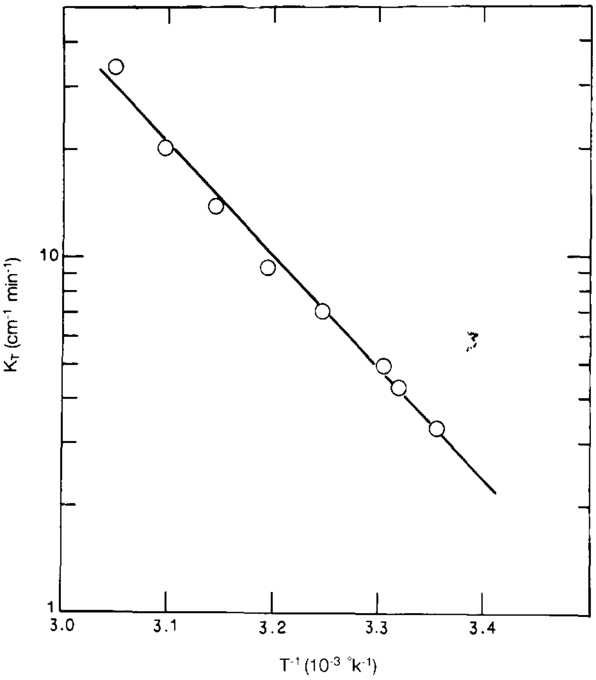

Figure 7 Arrhenius plot of K_T *versus* $1/T$, where K_T is the rate constant of the polarity change and T is the absolute temperature

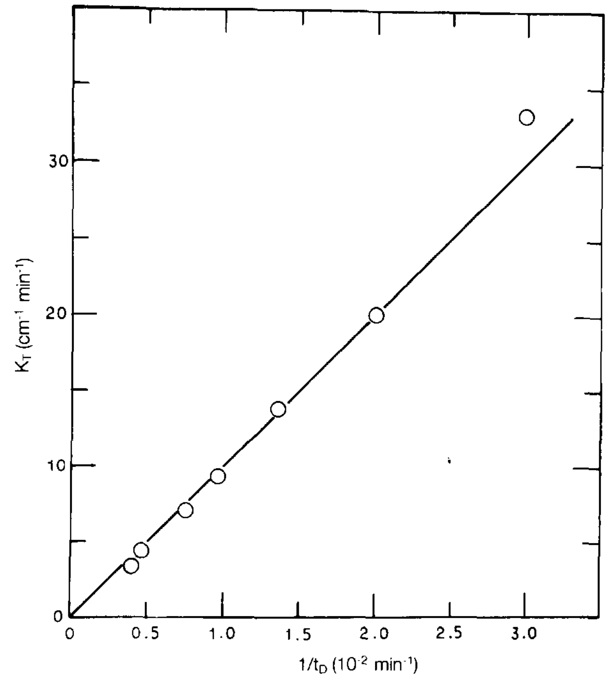

Figure 8 Plot of K_T *versus* $1/t_D$, where K_T is the rate constant of the polarity change and t_D is the cure time at which the Stokes' shift began to deviate from linear behaviour

maximum glass transition temperature for the epoxy resin. At higher temperatures, the transition to a plateau value of the Stokes' shift occurred less abruptly than at lower temperatures, because the diffusion of reactive groups (though restricted after the gelation) was faster than at lower temperatures and because, at higher temperatures, there was a longer period of time for the curing reactions before they were inhibited by the vitrification transition, according to the TTT isothermal cure diagram. Furthermore, the plateau value of the Stokes' shift was lower at higher temperatures because of the faster diffusion, and the longer reaction period between the gelation and the vitrification transition.

As discussed earlier, the decrease in the Stokes' shift shown in *Figures 5* and *6* was due to the polarity change of the epoxy resin which resulted from the curing reactions. From the linear portion of the plot of the Stokes' shift *versus* the cure time, we determined the slope K_T and defined K_T as the rate constant of the polarity change for the epoxy resin at a cure temperature T. *Figure 7* is an Arrhenius plot giving the logarithm of K_T *versus* the reciprocal of the cure temperature. The linear relationship shown in *Figure 7* can be fitted to an Arrhenius equation with an activation energy of 60 kJ mol^{-1} and a pre-exponential factor of 1.02×10^{11} cm^{-1} mol^{-1}. The activation energy for the polarity change is attributed to the energy barrier to the curing reactions that led to the change in the polarity and the Stokes' shift of the epoxy resin. This value of the activation energy is in close agreement with a value of 59 kJ mol^{-1} determined by Riccardi *et al.*[20] for the isothermal cure of DGEBA and ethylene diamine.

Stokes' shift began to deviate from the linear behaviour, decreased with an increase in the cure temperature, while the slope, K_T, of the linear portion increased. *Figure 8* gives a plot of K_T *versus* the reciprocal of t_D. The data are well fitted to a straight line which passes through the origin and has a slope of 1000 cm^{-1}. Thus, the product of K_T and t_D, i.e. the total change in the Stokes' shift that occurred from the beginning of the cure to the gelation time, had a constant value of 1000 cm^{-1} in the temperature range investigated. Since the change in Stokes' shift was due to the curing reactions, the constant of the total Stokes' shift implied that the chemical structure of the infinite network at the gelation time was independent of the temperature. The same chemical structure of the infinite network at the gelation is not unexpected because the extent of cure, α_c, at the gelation depends only on the functionality, f_E, of the epoxy resin and the functionality, f_A, of the amine hardener, if the reactivities of the primary and secondary amines of DETA are assumed to be equal. (This assumption is supported by the report that the primary and the secondary amines of similar aliphatic amines, such as ethylene diamine, have the same reactivity[20].) For the epoxy resin of this study, α_c was 0.5, as determined by the equation[22]:

$$\alpha_c^2 = \frac{1}{(f_E - 1)(f_A - 1)} \qquad (3)$$

The observed temperature independence of the total Stokes' shift at the gelation time is also consistent with the afore-mentioned conclusion that the reorientation of dipoles in the curing epoxy resin was essentially complete prior to fluorescence.

CONCLUSIONS

The Stokes' shift of 1-(4-dimethylaminophenyl)-6-phenyl-1,3,5-hexatriene (DMA-DPH), which was dissolved in a stoichiometric mixture of diglycidyl ether of bisphenol A (DGEBA) and diethylene triamine (DETA), decreased during the curing reactions because of the change in the polarity of the epoxy resin. In an isothermal cure, the Stokes' shift decreased linearly with the cure time until the gelation occurred. The total change in the Stokes' shift that occurred from the beginning of the isothermal cure to the gelation time was 1000 cm^{-1} and was independent of the cure temperature, implying that the chemical structure of the infinite network at the gelation time was independent of the cure temperature. The rate constant, K_T, for the polarity change during an isothermal cure of the epoxy resin was defined as the rate constant for the linear decrease of the Stokes' shift before the gelation time. The activation energy of K_T was estimated to be 60 kJ mol^{-1} and represented the energy barrier to the curing reactions which led to the polarity change of the epoxy resin.

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