Cure monitoring of epoxy resins by excimer fluorescence

A. Stroeks, M. Shmorhun, A. M. Jamieson and R. Simha
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA
(Received 29 December 1986; revised 19 August 1987; accepted 5 September 1987)

Experimental studies are reported of the steady-state fluorescence of the excimer probe 1,3-bis-1-pyrene propane (BPP) during cure of Epon 828, a bis-diglycidylether epoxy, using 4,4'-methylene-bis-cyclohexylamine (MBCH) as hardener. We find that the ratio of excimer to monomer emission is of limited use for monitoring the viscosity increase that occurs during the cure reaction. However, the monomer emission of the excimer probe shows a substantial increase in intensity during the cure reaction which correlates quantitatively with the known change in viscoelastic properties of the Epon 828/MBCH system. Comparison with similar fluorescence enhancement of the probe 1,4-dimethylaminophenyl-6-phenyl-1,3,5-hexatriene (DMA–DPH) during cure of the Epon 828/MBCH epoxy suggests that the observed enhancement of the monomer intensity of BPP is also due to a decrease in non-radiative decay of singlets as the matrix viscosity increases.

(Keywords: fluorescence enhancement; epoxy cure; viscoelastic transitions; free volume)

INTRODUCTION

Recent reports have described the use of fluorescent probes to monitor changes in matrix viscosity during bulk polymerization reactions[1-3]. Several studies have focused on the crosslinking reaction of epoxies[4-6]. Three distinct classes of probes can be employed. One approach relies on the fluorescence enhancement that occurs in certain fluorophores when the matrix viscosity increases, because of a decrease in radiationless deactivation[1,4,6] of the excited state. A second technique[3] monitors the change in fluorescence depolarization which accompanies the slowing of rotational motion of the probe as the viscosity increases. A third method[2,6] utilizes an excimer-forming probe and follows the decrease in excimer-to-monomer emission that accompanies an increase in viscosity.

The present work was prompted by a recent study by Wang *et al.*[6], who employed two fluorescent probes to monitor the cure reaction of Epon 828, a bis-diglycidyl ether from epichlorohydrene and bisphenol A, using as hardener 4,4'-methylene-bis-cyclohexylamine (MBCH). One fluorophore, 1,4 dimethylaminophenyl-6-phenyl-1,3,5-hexatriene, (DMA–DPH), is expected to show fluorescence enhancement as the cure reaction proceeds, operating via the mechanism of a decrease in non-radiative decay described above. Wang *et al.* have indeed demonstrated that the emission intensity of DMA–DPH increases substantially during cure of Epon 828 by MBCH[6], and reaches an asymptotic value at times where gelation and/or vitrification may occur[7] (see below). A second fluorophore used by Wang *et al.*[6], viz. 1,3-bis-1-pyrene propane (BPP), is an intramolecular excimer-forming probe[8,9]. Two effects were observed: an initial decrease in the ratio of monomer-to-excimer emission F_M/F_D, associated with heating of the sample to the cure temperature, followed by a rapid increase in F_M/F_D as the viscosity rises in the subsequent course of the crosslinking reaction. The phase of rapid increase of F_M/F_D was followed by a sharp reduction in rate at cure times where the vitrification and/or gelation stage may be occurring[7]. It is noted here that previous work[9,10] has established that BPP is not a probe for absolute microviscosity since the excimer emission is influenced also by matrix polarity. However, for a fluid environment of specified polarity the ratio of monomer-to-excimer emission intensity, F_M/F_D, shows a strong correlation with the bulk viscosity and can therefore be used legitimately to measure changes in viscosity and/or changes in matrix free volume, which modify the rate of excimer formation.

The experiments of Wang *et al.*[6] raise the interesting question of whether the fluorescence probe methodology can serve to distinguish the different viscoelastic regimes in the polymerization–crosslinking reaction[7]. For this purpose, we have undertaken a more quantitative investigation of BPP and DMA–DPH fluorescence emission in the Epon 828/MBCH epoxy at several different cure temperatures, over extended cure times, and have further compared our fluorescence results with the viscoelastic data of Enns and Gillham[7] during cure of Epon 828/MBCH.

MATERIALS AND METHODS

Shell Epon 828 epoxy resin and Aldrich Chemicals 4,4-methylene-bis-cyclohexylamine (MBCH) hardener were used in this study. No important differences were observed between experiments performed with these chemicals as received and those with the vacuum-distilled hardener.

Since we wished to compare our fluorescence data with the viscoelastic data of Enns and Gillham[7] it was necessary to verify that the cure kinetics of our Epon 828/MBCH epoxy were similar to that used in the study of Enns and Gillham[7]. Therefore, infra-red spectra of the

0032-3861/88/030467-04$03.00

epoxy/hardener system were collected on a Digilab model FTS-14 Fourier transform infra-red spectrometer. A drop of Epon 828/MBCH was placed between NaCl discs, then mounted in a spectrometer maintained at 24°C and continuously purged with nitrogen. Spectra were measured in the range 400 to 4000 cm^{-1} and were averaged over sixty scans with a 4 cm^{-1} resolution. A series of spectra were taken over a 5 h period to monitor the epoxy cure. Spectral data were initially stored in the Digilab computer memory and then transferred to a VAX-11/780 having subroutines for spectral peak integration.

Extent of conversion (x) is proportional to the area under the epoxide peak (916 cm^{-1}) at any time divided by the initial area of that peak. To correct for errors such as sample slippage, the area under the epoxide peak was normalized by dividing it by the area of the 1184 cm^{-1} C–C stretch reference peak, as in the method described by Enns and Gillham[7]. A first-order conversion rate constant k is determined from the slope of the linear portion in a plot of $\ln(1-x)$ vs. time and has been calculated as $k=0.00205\ min^{-1}$. In order to compare with the data of Enns and Gillham it was necessary to extrapolate their data to a 24°C cure temperature. Using an Arrhenius plot of $\ln k$ vs. $1/T$, the data of ref. 7 would predict a rate constant at 24°C of $k=0.00217\ min^{-1}$. Thus there is a difference of only 5.5% between the two rate constants, or sufficiently good agreement to make reasonable kinetic comparisons between our study and that of Enns and Gillham[7].

Fluorophoric probes used were 1,3-bis-1-pyrene propane (BPP) and 1-(4-dimethylaminophenyl)-6-phenyl-1,3,5-hexatriene (DMA/DPH) obtained from Molecular Probes Inc. (Junction City, OR, USA), and pyrene from Aldrich Chemical Co. (Milwaukee, WI, USA). The probes were mixed with resin by stirring overnight at 60°C at a concentration of $5\times10^{-5}\ mol\ l^{-1}$. The hardener and doped resin were mixed in stoichiometric amounts with a mechanical stirrer at the cure temperature immediately prior to injection into the thermostatically controlled sample cell, which had been preheated to the cure temperature. Cure times were measured from the time of initial contact of resin and hardener.

The possibility of fluorescence quenching of emission by the amine hardener was investigated by dissolving probe and hardener into low and high viscosity solvents, cyclohexane and glycerol respectively. If quenching occurs then the fluorescence emission will decrease with increasing quencher concentration and will be evident in Stern–Volmer plots[8] of the intensity as a function of quencher concentration. Our results indicate that quenching by the amine does not occur for both solvents and can therefore be ignored in interpreting the fluorescence enhancement that occurs during epoxy cure. The Epon 828 resin showed a weak emission at 405 nm when excited at 343 nm, as reported by Wang *et al.*[6] This emission comprises only 20% of the BPP monomer emission at 380 nm. During the cure reaction, under intermittent illumination, the peak intensity increased by 25% and the peak maximum moved to 415 nm. The result was a 12% increase at 308 nm, at which the BPP monomer emission was monitored.

All spectra were recorded using an Aminco–Bowman spectrofluorometer with a xenon lamp as excitation source. A reference phototube continuously monitored the excitation radiation to correct spectra for xenon arc fluctuations. Three sample configurations were explored: (a) 1 cm × 1 cm rectangular acrylic cells; (b) 5.5 mm int. diam. cylindrical glass tubes; (c) sandwich cells formed from parallel glass flats, 2 mm apart. Results were reproducible in all three configurations; however, in (b) and (c) photobleaching of the probes was observed in the later stages of the cure and hence F_M and F_D values had to be determined during 10 s of illumination followed by 2 min in the dark. Evidently Beer's Law attenuation of the incident beam is sufficient to prevent photobleaching in the 1 cm path length acrylic cells.

RESULTS AND DISCUSSION

In *Figure 1* we show BPP fluorescence spectra, following excitation at 343 nm, during cure of the Epon 828/MBCH epoxy in 1 cm × 1 cm acrylic cells at a nominal temperature of 44°C. The high initial viscosity of the Epon 828/MBCH system is immediately seen in the first spectrum, recorded 5 min after mixing, as evidenced by the low intensity of the excimer peak at 480 nm relative to the monomer peaks at 380 and 400 nm. Following Wang *et al.*[6], we measured monomer intensities, F_M, at 380 nm and excimer intensities, F_D, at 480 nm. In *Figure 2* we plot F_M, F_D and F_M/F_D and the sample temperature for Epon 828/MBCH at a nominal cure temperature of 46°C in 1 cm × 1 cm rectangular acrylic cells. Similar experiments performed in 5.5 mm diameter cylindrical cells gave comparable results in the initial stages of cure. However, at later times an anomalous decrease in F_M and hence in F_M/F_D was observed which was due to photobleaching of the BPP at high viscosities. This effect can be avoided by irradiating the sample intermittently. F_M values, measured during 10 s illumination periods, the sample remaining in the dark at other times, showed no evidence of photobleaching.

From *Figure 2* it is clear that the ratio F_M/F_D reaches an asymptotic value at cure times much earlier than those where the individual value of F_M and F_D level off. We suggest, therefore, that the F_M/F_D ratio does not represent

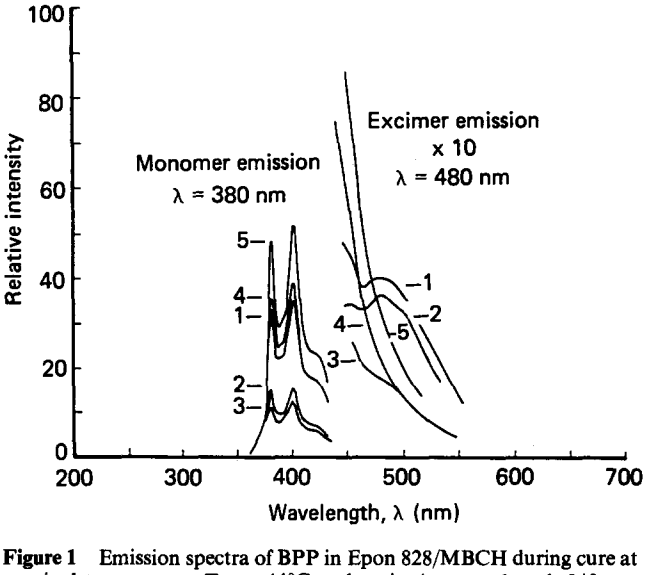

Figure 1 Emission spectra of BPP in Epon 828/MBCH during cure at nominal temperature $T_{nom}=44$°C and excitation wavelength 343 nm. Cure time: 1, 5 min; 2, 14 min; 3, 20 min; 4, 33 min; 5, 360 min

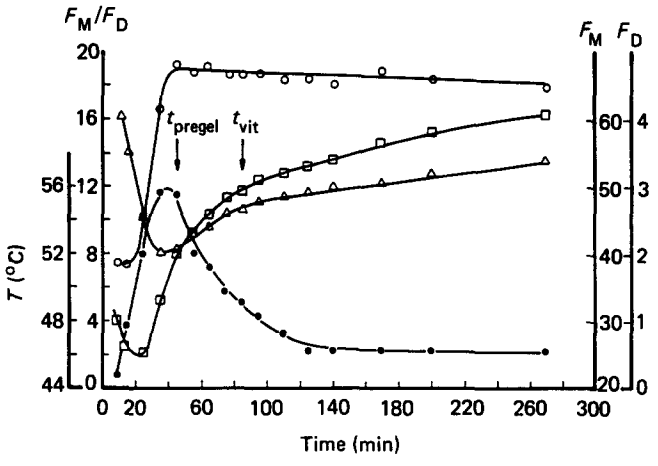

Figure 2 Plot of BPP monomer emission (F_M, □), excimer emission (F_D, △), F_M/F_D (○) and temperature profile (●) during Epon 828/MBCH cure at $T_{nom}=46°C$ in 1 cm rectangular cells. Average sample temperatures at t_{vit} and t_{gel} are estimated to be 51°C

a simple measure of the viscosity effect. The reason for this may be seen by inspection of *Figure 1*. Note that the scale for the spectrum in the region of excimer emission has been increased by a factor of 10. Comparing spectral records nos. 4 and 5, corresponding to cure times of 33 and 360 min respectively, during which the viscosity rises sharply, it is apparent that the spectral wing of the monomer emission dominates any contribution from the excimer at wavelengths where F_D is measured. Thus, even at early stages of cure, one is to a large extent measuring ratios of intensities at different points on the envelope of the monomer emission. Also, since the fluorescence intensity in the vicinity of the excimer emission is a small number, varying rapidly with wavelength (*Figure 1*), values of the F_M/F_D ratio at longer cure times are prone to large systematic and random errors. The large increase in emission at 380 nm must originate from sources other than a decrease in excimer formation. A negligible contribution (<5%) comes from an increase in the background matrix fluorescence emission. The remainder (>95%) derives from a large enhancement, about twofold, of the BPP monomer peak. The probable source of this enhancement, discussed below, is a decrease in the non-radiative decay rate, because the increased rigidity of the microenvironment interferes with non-radiative decay of excited monomer singlets.

It thus appears from our experiment that a more pertinent measure of the progress of the reaction using the BPP probe is obtained from the monomer intensity. It is interesting to note that in all of our cure experiments to date, the increase of the monomer intensity encompasses the range of cure times where the gelation and vitrification transitions are known to occur[7]. Thus in *Figure 2* we have indicated by arrows the cure times at which we estimate the Epon 828/MBCH epoxy will cross, respectively, the 'pregel', gelation and vitrification transitions, based on the time–temperature transition (TTT) diagram of Enns and Gillham. In this calculation, we have computed an average cure temperature from the thermocouple readings. Clearly, the F_M/F_D values reach an asymptotic value at times significantly shorter than t_{vit}, where the cure reaction stops. As is evident in *Figure 2* for a large sample, the profile of the intensity curve may be influenced by the temperature profiles of the sample. However, in thin samples, where thermal equilibration is rapid, it is clear, as seen in *Figure 3*, that similar behaviour of the F_M curve is observed. It appears, therefore, that in the highly viscous epoxy resin, the BPP operates as a probe for viscosity or free volume, mainly via changes in non-radiative decay processes. This conclusion is supported by our observation that the fluorescence enhancement of the DMA–DPH probe, as shown earlier by Wang *et al.*[6], exhibits a qualitatively similar profile during cure to that of the monomer emission of BPP.

In an effort to be more quantitative with regard to the enhancement of probe fluorescence as the cure reaction proceeds, we have carried out a series of experiments in which the fluorescence intensity was monitored at closely spaced intervals in 5.5 mm diameter cylindrical samples, in which rapid thermal equilibration can be achieved. Typical results are shown in *Figures 3* and *4*, which plot, respectively, the time evolution of the monomer emission, F_M, of BPP and the fluorescence intensity, F, of DMA–

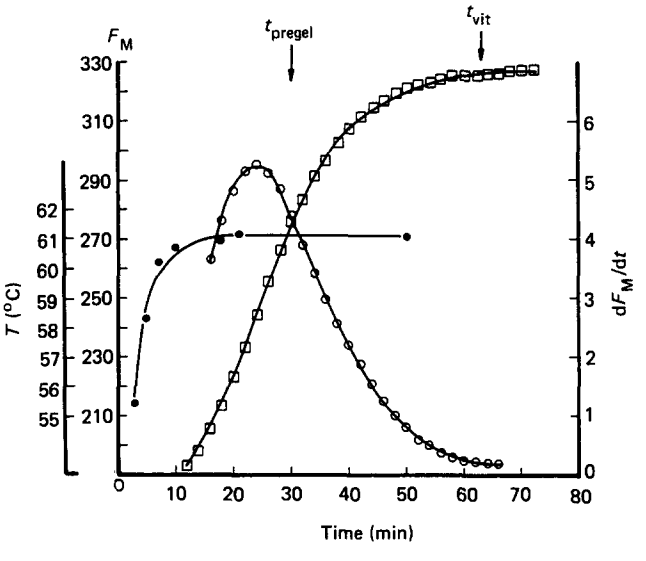

Figure 3 F_M (□), dF_M/dt (○) and temperature profile (●) of BPP fluorescence during Epon 828/MBCH cure in a cylindrical cell at $T_{nom}=61°C$

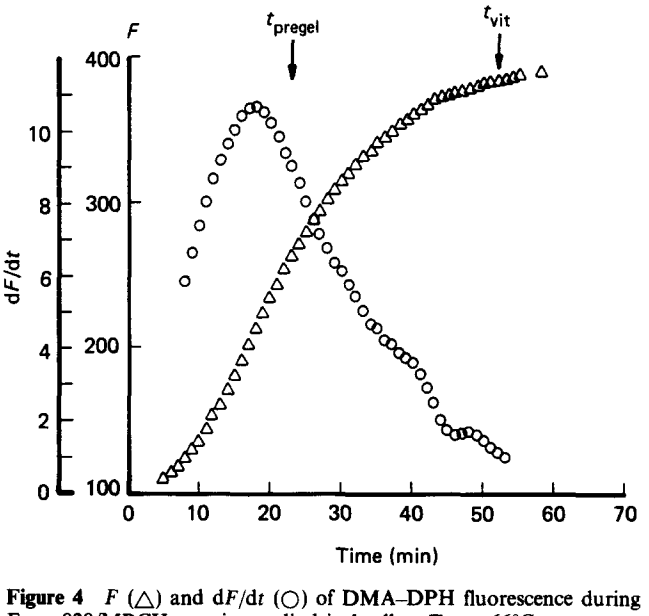

Figure 4 F (△) and dF/dt (○) of DMA–DPH fluorescence during Epon 828/MBCH cure in a cylindrical cell at $T_{nom}=66°C$

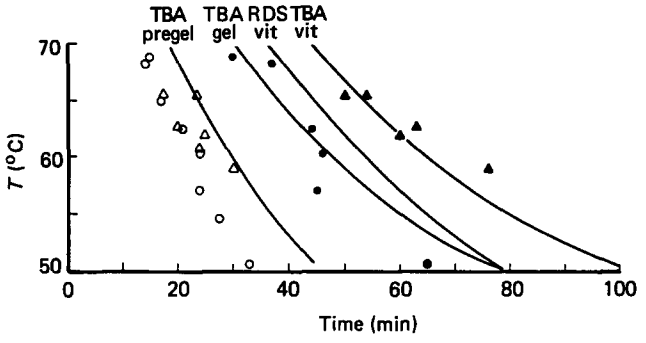

Figure 5 Temperature–time cure diagram for Epon 828/MBCH. Full lines are transitions determined from viscoelastic measurements: TBA = log decrement by torsional braid analysis; RDS = shear modulus by rheometrics dynamic mechanical spectrometer. Open symbols indicate maximum in slope of fluorescence intensity vs. time data (dF/dt) for: △, DMA–DPH; ○, BPP probes. Full symbols are values of asymptotic slopes for: ●, BPP; ▲, DMA–DPH

DPH during cure of Epon 828/MBCH at 66°C. Moreover, we show the time derivatives dF_M/dt_{cure} and dF/dt_{cure}, calculated by the moving arc method based on a least-squares fit to a seven-point parabola[11]. We indicate with arrows in these diagrams the location of the pregel and vitrification viscoelastic transitions. Evidently, the maximum in dF_M/dt and dF/dt occurs near t_{pregel}, while the onset of the long-time asymptote in F_M and F corresponds to the range of cure times where vitrification occurs, as monitored by different mechanical techniques[7].

Figure 5 shows the time–temperature cure diagram for Epon 828/MBCH established by Enns and Gillham[7], on which we have plotted the locations of the maxima in dF_M/dt_{cure} for BPP and dF/dt_{cure} for DMA–DPH, as well as the cure times where F_M for BPP and F for DMA–DPH reach their asymptotic slopes, i.e. the time at which dF_M/dt_{cure} reaches a constant value, within experimental uncertainty. The maxima in dF/dt_{cure} for BPP and for DMA–DPH coincide closely with the location of the 'pregel' transition. Also, the DMA–DPH fluorescence intensity, F, reaches its asymptote near the vitrification transition times, as observed in the torsional braid experiments of Enns and Gillham[7]. However, the corresponding points for F_M of BPP occur at earlier times and correlate quite well with either the gel times as deduced from torsional braid measurements or vitrification times as measured by the shear modulus[7].

These observations can be interpreted qualitatively using a discussion by Loutfy[1] which argues that changes in rotation-dependent, non-radiative decay couple the excited-state conformation of the probe to the rigidity of the matrix. The internal molecular motion becomes controlled by the microscopic free volume of the polymer matrix. It is therefore possible to relate the fluorescence enhancement to the van der Waals volume V_m of the probe, and the matrix free volume, V_f, viz.[1]:

$$F_M/F_M^0 = \exp\left(\frac{V_m}{bV_f}\right) = F/F^0 \qquad (1)$$

where F_M^0 and F^0 are the corresponding fluorescence intensities in the absence of hindered rotation. The earlier approach to the long time asymptote of the monomer emission of BPP, compared to the fluorescence emission of DMA–DPH suggests that BPP has a larger van der Waals volume. It is interesting to note that the van der Waals volume of BPP and DMA–DPH are estimated to be 249 and 179 $cm^3\ mol^{-1}$, respectively, using methods of Bondi[12].

ACKNOWLEDGEMENT

We are grateful to the Center for Adhesives, Sealants and Coatings of Case Western Reserve University for support of this research. Partial support was also received from National Science Foundation Grant DMR 85-04372, Polymers Program.

REFERENCES

1 Loutfy, R. O. *Macromolecules* 1980, **14**, 270
2 Wang, F. W., Lowry, R. E. and Grant, W. H. *Polymer* 1984, **25**, 690
3 Scarlata, S. F. and Ors, J. A. *Polym. Commun.* 1986, **27**, 41
4 Levy, R. L. *Polym. Mater. Sci. Eng.* 1984, **50**, 124
5 Sung, C. S. P., Chin, I. J. and Yu, W. C. *Macromolecules* 1985, **18**, 1510
6 Wang, F. W., Lowry, R. E. and Fanconi, B. M. *Polym. Mater. Sci. Eng.* 1985, **53**, 180
7 Enns, J. B. and Gillham, J. K. *J. Appl. Polym. Sci.* 1983, **28**, 2567
8 Birks, J. B. 'Photophysics of Aromatic Molecules', Wiley-Interscience, New York, 1970
9 Zachariasse, K. A., Duveneck, G. and Busse, R. *J. Am. Chem. Soc.* 1984, **106**, 1045
10 Zachariasse, K. A. *Chem. Phys. Lett.* 1978, **57**, 429
11 Zakin, J. L., Simha, R. and Hershey, H. C. *J. Appl. Polym. Sci.* 1966, **10**, 1455
12 Bondi, A. *J. Phys. Chem.* 1964, **68**, 441