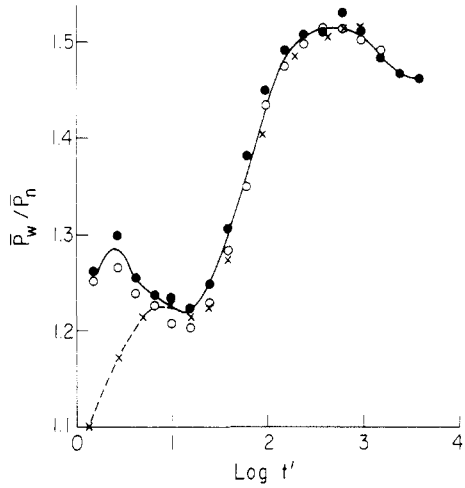

Figure 1. $\bar{P}_w/\bar{P}_n$ as a function of dimensionless time simulated by Monte Carlo on the Apple (○) and IBM (●) and by numerical solution of differential equations[1] (×).

longer times, so the same simulation was done on an IBM 4341, with the result also shown in Figure 1. It can be seen that the hump at low time was observed for all three simulations; it is most likely that the difference in time when the hump is observed in the Monte Carlo simulation compared to that in the numerical equation simulation is attributable to the difficulty in establishing equilibrium concentrations of the various propagating species. Nevertheless, the present observation of the hump sustains the contention[1] that it is not an artifact of the numerical differential equation solution; further, Figure 1 shows that the possible maximum in R observed by Szwarc and Zimm is truly a maximum but that the expected decline to $R = {}^4/_3$ (which they could not observe) occurs on a time scale so slow as to be unapproachable in real systems.

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Communications to the Editor

A Novel Fluorescence Technique for Monitoring Cure Reactions in Epoxy Networks

Properties of network polymers depend on the characteristics of network structure, namely, the number of cross-links and branch points. In order to correlate the structure with the properties of network polymers, it is therefore necessary to quantify such structural characteristics. To achieve this, we recently reported on a new technique for characterizing cure of epoxy by the azochromophore labeling method.[1a] In that technique, we use a small amount of *p,p'*-diaminoazobenzene (DAA) as a reactive label in a model epoxy consisting of the diglycidyl ether of bisphenol A and diaminodiphenyl sulfone (DGEBA–DDS). The reactivities of DDS and DAA are similar,[2] allowing us to follow the cure process as manifested by the UV–vis spectral changes of DAA occurring above 400 nm. As the epoxy is cured, the λ_{max} of the $\pi \rightarrow \pi^*$ transition corresponding to the azo bond of DAA shows red shifts allowing the spectral discrimination for four major cure products, namely, cross-links, branch points, linear chains, and chain ends. Deconvolution of the UV–vis spectra based on the band assignments of the model compounds[1b] representing cure products provides a quantitative estimate of the four cure products as a function of temperature or cure time. Our analyses showed the number of the branch points and the cross-links increasing near gelation, followed by leveling off after vitrification.[1] Such a leveling off is expected due to the difficulty in diffusion (or mobility) of the reactants (or reactive functional groups) after vitrificQtion and supported by IR spectroscopy on epoxy ring disappearance.[1]

We recently found that DAA-labeled epoxy (DGEBA–DDS) exhibits very sensitive changes in fluorescence intensity corresponding to the emission by the DAA label as a function of cure extent. This change in fluorescence behavior is not due to the viscosity or mobility changes as the polymerization proceeds, as exploited by many researchers.[3] Rather, it is attributed to the formation of DAA-labeled cure products which exhibit much greater fluorescence intensity as compared to DAA itself. This increase in fluorescence intensity is due to the overlap of the red-shifted $\pi \rightarrow \pi^*$ transition and the unshifted $n \rightarrow \pi^*$ transition in N-alkylated aminoazobenzene.[4] Pan and Morawetz used a fluorescing reagent which is converted to a nonfluorescent product for the kinetic analyses of acylation of aromatic amine residues attached to cross-linked polymers.[5] In this communication, we present data that demonstrate this novel fluorescence technique for monitoring cure reactions in an epoxy network.

The epoxy under study is the same as reported in ref 1, i.e., a stoichiometric mixture of DGEBA–DDS epoxy containing a small amount of DAA (0.1–0.3% by weight). Both DGEBA and DDS show strong fluorescence around 380 nm when excited at their absorption maxima, 330–340 nm. However, the fluorescence beyond 400 nm is negligible. The fluorescence intensity at 380 nm is independent of cure extent, which is consistent with the findings of Levy and Ames.[6]

When this DAA-containing epoxy is excited at 456 nm or near the red-shifted λ_{max} of the UV–vis spectra as cure proceeds, we observed sharply increasing fluorescence centered around 560 nm. Figure 1 illustrates such an s-shaped fluorescence intensity curve as a function of cure time at 160 °C. When the upper part of the curve is extrapolated, its intersection with a tangent to the inflection point of the curve defines a transition time t^*. At 160 °C, it turned out to be 50 min. Similar s-shaped curves were obtained at 180 °C as well as 140 °C, with t^* being 20 and 80 min, respectively (Figure 2). These time scales are very close to the gel time as reported by the T–T–T diagram of this epoxy.[7]

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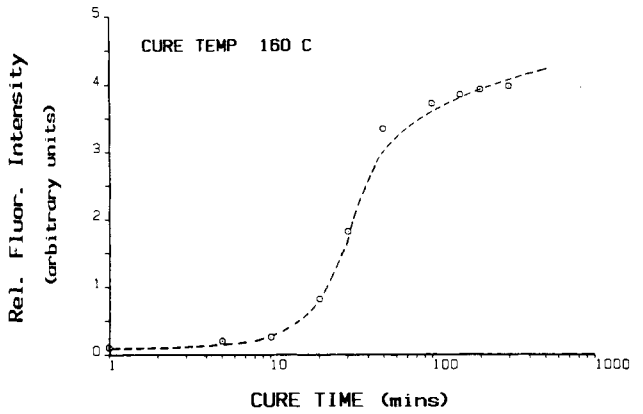

Figure 1. Relative fluorescence intensity changes at 565 nm as a function of cure time at 160 °C: (O) experimental data; (---) predicted by adding fluorescence from all the cure products.

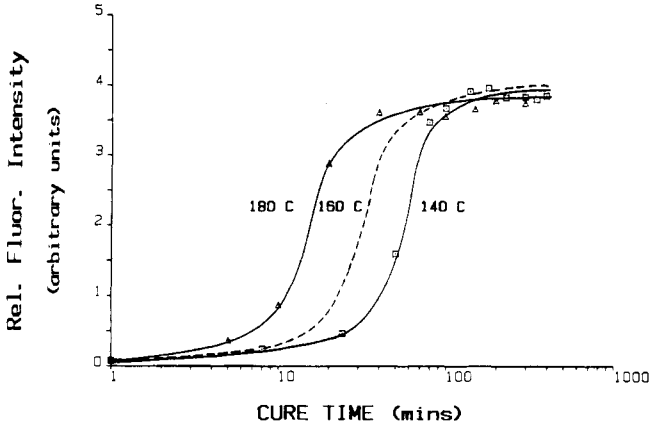

Figure 2. Relative fluorescence intensity changes at 565 nm as a function of cure at 180 and 140 °C. The dashed line corresponds to the data at 160 °C.

Azobenzene derivatives are generally known not to fluoresce.[8] *trans*-Azobenzene displays a fluorescence quantum yield less than 10^{-4} for excitation of both the $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transition.[9] However, Bisle et al. observed a weak fluorescence at low temperature in solutions of N-alkylated aminoazobenzenes and some diaminoazobenzenes. In these compounds as well as in DAA-labeled cure products in our epoxy system, the λ_{max} of the intense $\pi \rightarrow \pi^*$ transition has been shifted toward λ_{max} of the much weaker $n \rightarrow \pi^*$ transition which is independent of substituents.[8]

The actual observed emission intensity is given by the product of absorption and emission probabilities:

$$I_F = kI_0\epsilon(\lambda)\phi_F C \quad (1)$$

where I_0, $\epsilon(\lambda)$, ϕ_F, and C are the exciting beam intensity, the extinction coefficient at the exciting wavelength, the fluorescence quantum yield, and the concentration, respectively, and k is a constant taking care of experimental geometry. Therefore, one expects the actual observed fluorescence intensity to be increased due to the much greater absorption in these compounds, even if ϕ_F is not changed much.

In order to quantify the contribution of each cure product on fluorescence, we made model compounds representing major cure products by reacting DAA with phenyl glycidyl ether, followed by purification and fractionation.[10] The observed fluorescence intensities per mole of the model compounds (in the concentration range of 10^{-7}–10^{-6} M in epoxy) are in the following ratios when excited at 456 nm: cross-linker, 1400; branch point, 1100;[11] linear chain, 18, chain end, 9; DAA, 1. This large increase observed with cross-linkers and branch points is in part due to greater absorption at this excitation wavelength as compared to linear chains or chain ends. In view of the fact that absorption does not increase 100-fold at 456 nm when going from secondary amines to tertiary amines, we have to invoke the possibility of a higher fluorescence quantum yield for cross-linkers and branch points to account for the observed fluorescence.

One may also ask whether the increase in viscosity as cure proceeds contributes at all to the increased fluorescence. When the model compound representing the cross-linker was added in the epoxy, there was no change in fluorescence intensity during the cure. If the fluorescence originates entirely from the cure products alone, the total fluorescence intensity in DAA-labeled epoxy can be written as $I_F = \sum K_i C_i$, where K_i is the fluorescence intensity ratio obtained for each cure product under the same experimental conditions and C_i is their concentration. Using the concentration values obtained by deconvolution of UV–vis spectra[1] and the observed fluorescence intensity ratios, one can plot I_F as a function of cure time, for example at 160 °C. Figure 2 shows such a plot as a dashed line, which compares well with the experimental points.

In summary, fluorescence intensity increases with the formation of cure products in DAA-labeled epoxy. Gelation can be identified with a sharp increase in fluorescence. The fluorescence levels off after gelation as shown in Figures 1 and 2, and this must be due to the vitrification which occurs shortly after gelation in this epoxy system. If cure proceeds at a rubbery temperature, we would expect a further increase in fluorescence. The advantage of this fluorescence technique in comparison to the UV–vis technique[1] is a greater sensitivity and the capability for monitoring epoxy on metallic substrates in situ by using front-face illumination. However, it does not provide a complete composition analyses of the cure products, which is possible by the UV–vis technique.[1] Since N,N′-dialkylated diaminoazobenzenes are strongly fluorescent, one may be able to synthesize star polymers using long alkyl chains, which can be used to measure diffusion constants by forced Rayleigh scattering or by fluorescence after photobleaching.

Experimental Details. In a typical run, recrystallized DGEBA (5.0 g), DDS (1.825 g), and DAA (20 mg) were mixed by heating them with a magnetic stirrer at 120 °C. For cure monitoring, two circular quartz plates were clamped together with two thin Mylar films (1.5 mil) on the edges, leaving a center space for the sample. Epoxy was introduced by capillary action by dipping the clamped quartz plates with Mylar spacers into epoxy heated to 100 °C. Fluorescence was measured after curing in an oven for a specific time and cooling the sample to room temperature. Fluorescence was measured with a 1-nm-wide excitation slit and a 10-nm-wide emission slit using a Perkin-Elmer MPF-66 spectrometer with a 7500 data station. UV–vis spectra were obtained with a Perkin-Elmer diode array system (Model 3840) with a 7500 data station. The area under the UV–vis peak for DAA was used to calibrate for concentration and thickness changes during cure to obtain the relative fluorescence intensity.

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(12) Present address: IBM, Est Fishkill, Hopewell Junction, NY 12533.

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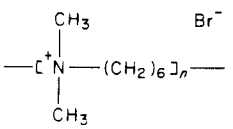
Observation of an Interdigitated Gel Phase in Dipalmitoylphosphatidylglycerol Bilayers Treated with Ionene-6,6

We have been interested for some time in modification of phospholipid bilayers by synthetic polymers.[1-3] With molecular dimensions comparable to or greater than the thickness of the lipid bilayer and many times the intermolecular spacing in the bilayer plane, synthetic polymers might be expected to serve as potent modifiers of bilayer structure and function. We have reported recently that synthetic poly(carboxylic acids) behave as "molecular switches" in phosphatidylcholine bilayers, triggering the release of bilayer-entrapped substances in response to small changes in ambient pH.[1,2] We describe herein the observation of an interdigitated gel phase in dipalmitoylphosphatidylglycerol (DPPG) bilayers treated with ionene-6,6 (1).



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Dispersion of DPPG in 50 mM sodium phosphate buffer, pH 7.4, provides a turbid suspension which melts sharply at 39.8 °C, with a smaller pretransition at 32 °C (Microcal MC-1 scanning calorimeter, heating rate 10 °C/h, [DPPG] = 1 mg/mL). These results are in good agreement with those of previous workers.[4-6] In contrast, hydration of the lipid in phosphate buffer which contains 1 mg/mL of ionene-6,6 produces an aggregated suspension which melts at 43.6 °C, with no pretransition. Identical results are obtained if the polymer is added subsequent to the lipid hydration step.

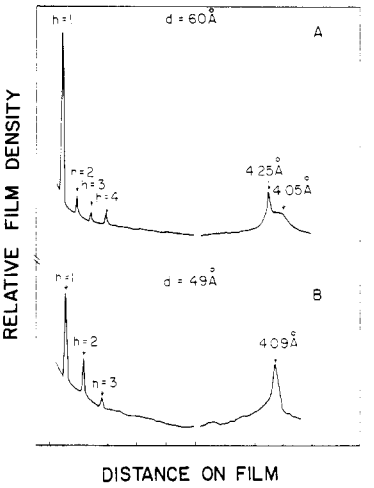

Figure 1. Densitometer traces of X-ray diffraction patterns of DPPG hydrated at a concentration of 1 mg/mL in 50 mM sodium phosphate buffer, pH 7.4 (A), or in similar buffer containing 1 mg/mL of ionene-6,6 (B). In trace A there are four orders of a lamellar repeat period of 60 Å and a double wide-angle reflection at 4.25 and 4.05 Å. In trace B there are three orders of a lamellar repeat period of 49 Å and a single wide-angle reflection at 4.09 Å.

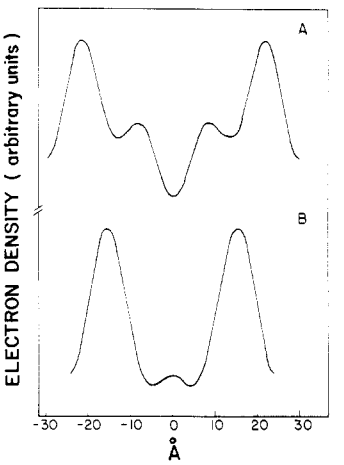

Figure 2. Electron density profiles generated from the diffraction patterns of Figure 1 and the same phase angles as in ref 12 and 13: (A) DPPG; (B) DPPG/ionene-6,6.

Figure 1 shows densitometer traces of X-ray diffraction patterns recorded at room temperature from DPPG suspensions prepared in phosphate buffer (A) and in the same buffer to which ionene-6,6 was added at a concentration of 1 mg/mL (B). The pattern in Figure 1A is in good agreement with that reported by Watts et al.[7] and reveals a lamellar repeat period of 60 Å. The double wide-angle reflection at 4.25 and 4.05 Å is characteristic of the $L_{\beta'}$ phase, in which the hydrocarbon tails of the lipid are tilted by approximately 30° from the bilayer normal.[7] Addition of ionene-6,6 produces the pattern shown in Figure 1B, with a lamellar repeat period of 49 Å and a single wide-

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