Fluorescence Polarization Study of the Curing Process of Epoxide with Aminimide

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Synopsis

The curing process of epoxide (Epikote 828, EK) with aminimide (trimethylamine valerimide, TMAV) was studied by a fluorescence polarization method. Two types of probe molecules were used: One was perylene (PE), which was just physically incorporated into the curing mixture and termed as the "extrinsic" probe, and the other was fluorescent product(s) formed during curing of EK with TMAV, which was termed as the "intrinsic" probe. Extraction experiments revealed that the "intrinsic" probe was covalently incorporated into the crosslinked matrix. No emission was observed for the "intrinsic" probe before heating, but its intensity increased with curing at 150°C. Fluorescence anisotropy (r) of both EK/TMAV/PE and EK/TMAV systems increased monotonically with curing time at the initial stage and then remained nearly constant. This means that at the early stage of curing the network becomes rigid enough to restrict rotational diffusion of the probe molecules. Calculated r values for the "extrinsic" probe alone were lower than observed r values of the "intrinsic" probe, which was well explained in terms of the mode of incorporation of the two types of the probe molecules into the matrix.

INTRODUCTION

Fluorescence polarization is one of the most frequently used methods to evaluate rotational diffusion of fluorescent molecules attached or embedded in molecular aggregates. Large dependence of the rotational diffusion upon restriction imposed on the fluorophores by their adjacent environments has made this technique quite valuable to estimate rigidity or fluidity of the environments. In fact, numerous applications have been reported in biological[1-4] and polymer research.[5-8]

In fluorescence polarization methods, the choice of a probe molecule is crucial. Essential properties which the probe molecules should be provided with are high fluorescence quantum yield, fluorescence lifetime comparable to rotational correlation time, and definite direction of absorption and emission dipoles. Among fluorophores, perylene and 1,6-diphenylhexatriene have been used most popularly because both molecules satisfy the above requirements.[9]

Recently we developed a new type of one-part epoxy resin using aminimides as latent curing agents which are activated above 130°C.[10] Aminimides are thermolyzed to produce isocyanates and tertiary amines.[11,12] The application of aminimides as precursors of isocyanates has been extensively studied by Culbertson et al.,[13-15] and the amine product can initiate the ring-opening polymerization of the epoxides.[16,17] Participation of the simultaneously gener-

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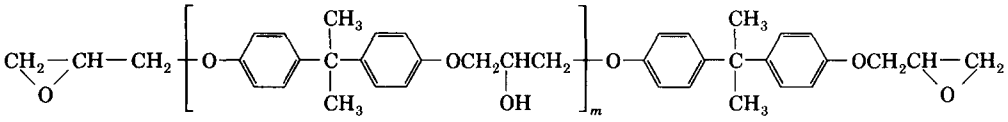
ated isocyanate into the cured resin matrix through chemical reaction (e.g., urethane bond formation) provides the cured resin with special mechanical properties such as high fracture energy, high elongation, and good adhesion.[10,18]

In this paper, we report on the fluorescence polarization study of the curing process of epoxide with aminimides. The study was initiated to try and determine how the cured resin becomes rigid with curing time. For this purpose, we chose perylene as an external probe and unidentified fluorescent product(s) formed during curing as an internal probe. Choice of perylene was based on its chemical stability against heating and against reactions with the thermolyzed products derived from aminimides.

EXPERIMENTAL

Materials

Trimethylamine valerimide (TMAV) was synthesized and purified as reported previously.[16] Perylene (PE) (Aldrich, gold label) was used as received. Epikote 828 (EK) (Yuka Shell Epoxy) was used as an epoxy prepolymer. Its composition determined by gel permeation chromatography (eluent, chloroform) was $m = 0$ (86%) and $m = 1$ (14%):



All solvents used were of spectroscopic grade.

METHODS

Samples were prepared from EK and TMAV (20 : 1 mole ratio), and, for those containing PE as an external probe, PE was added to the sample so as to obtain the final concentration of PE of $4 \times 10^{-5}M$ in EK. The samples were then transferred to a JASCO HTV-1 cell in which thickness of the sample solution was adjusted to 1 mm. With this cell, all spectroscopic measurements were performed in the presence of air.

Absorption, corrected fluorescence spectra and fluorescence lifetimes were measured on a Hitachi UV-300 spectrometer, a Hitachi F-4000 fluorometer, and a PRA system 3000 single-photon counting apparatus, respectively. Steady-state fluorescence polarization was measured with an apparatus constructed by Japan Spectroscopic Co. Ltd. (JASCO) in the course of a joint research scheme on construction and application of a simple and reliable apparatus for fluorescence polarization measurements (see Ref. 19 for details). For the present work, some modification was made: In place of a 500-W xenon lamp and a Jobin Yvon H-20 monochromator, a combination of 20-W tungsten lamp and Toshiba glass filters was employed for excitation of the

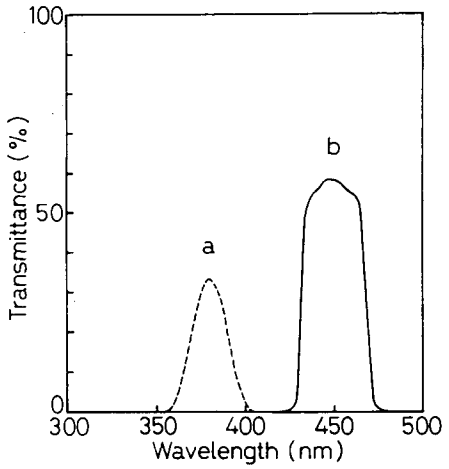


Fig. 1. Transmission characteristics of filters: (a) excitation site; (b) emission site.

samples. Transmission characteristics of the filters placed in excitation and emission sites are shown in Figure 1. In fluorescence spectra, lifetime and polarization measurements, the HTV-1 was placed in such a way that the incident angle of the excitation beam was 60° and the emitted light from the front face of the cell was observed at a right angle to the incident beam.

Curing of EK was performed in the HTV-1 cell by quickly raising the temperature of the sample to 150°C. After an appropriate time, the samples were cooled down to room temperature and subjected to the spectroscopic measurements.

RESULTS

Emission Spectroscopy

Figures 2 and 3 show the fluorescence spectra in the presence and absence of PE, respectively, at various curing times. Before heating, no fluorescence was observed in the absence of PE on excitation with λ_{ex} = 350–410 nm. As curing proceeded, emission intensity increased with simultaneous red shift of the emission maximum as shown in Figure 3. At the same time, the sample became slightly yellow-colored and absorbance at 390 nm increased. In the presence of PE, clear vibrational structure of PE fluorescence initially observed became broadened with curing time (Fig. 2). It was expected that fluorescence spectra in the presence of PE were made by the superposition of PE fluorescence and that of thermolyzed products. In order to confirm this interpretation, cured resins were subjected to Soxhlet extraction. A EK/TMAV mixture (20 : 1 mol/mol, 2.54 g), containing $4 \times 10^{-5} M$ PE in EK, was heated in a hot press for 5 h at 150°C, and the resulting cured resin was extracted with benzene for 30 h. Before extraction, the fluorescence spectrum of the cured film clearly showed vibrational structure corresponding to that of PE, whereas after extraction the residual film showed only broad emission as shown in Figure 4. The emission spectrum differences clearly show that the extracted fluorescent component is PE [Fig. 4(c)]. It was also

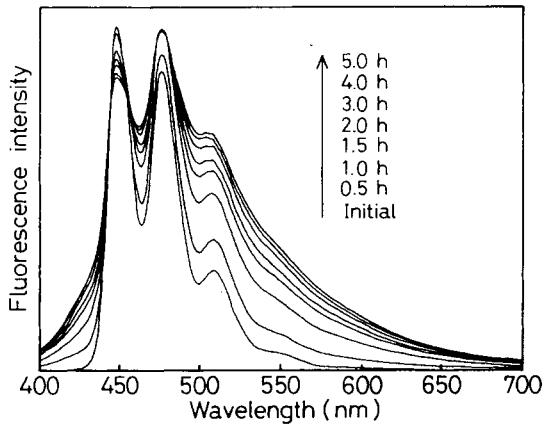


Fig. 2. Change in fluorescence spectra of EK/TMAV/PE during the curing reaction at 150°C. EK/TMAV (20/1 mole ratio); PE, $4 \times 10^{-5}M$ in EK. $\lambda_{ex} = 390$ nm.

confirmed, by absorption spectroscopy, that PE doped in the EK/TMAV mixture before curing was nearly quantitatively recovered after curing by the extraction procedure. This means that under the present curing condition the size of the networks is large enough for PE molecules to escape from the matrix and thermal reaction of PE leading to chemical inclusion of the PE molecules into the matrix is, if any, negligible. As a control experiment, EK/TMAV mixture was heated under the same condition, and the fluorescence spectra before and after extraction with benzene for 30 h were compared. These two spectra were identical within an experimental error, indicating that the fluorescent compound(s) produced on curing is covalently incorporated into the crosslinked matrix. The extraction experiments demonstrate the property of our two types of fluorescence probes. PE, termed as the "extrinsic" probe, reflects constraint imposed on rotational diffusion through space by the networks, while the fluorescent product(s) which can be termed as the "intrinsic" probe monitor through-bond constraint on motion.

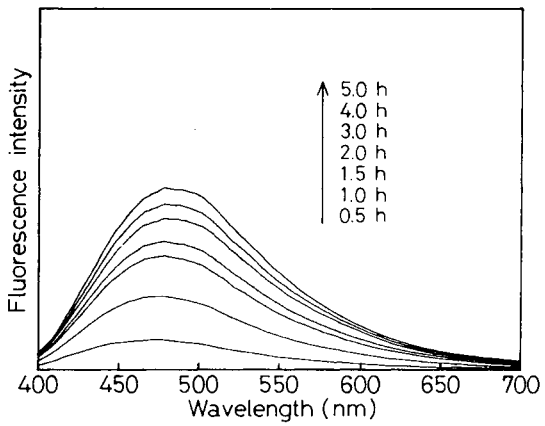


Fig. 3. Change in fluorescence spectra of EK/TMAV during the curing reaction at 150°C. EK/TMAV (20/1 mole ratio). $\lambda_{ex} = 390$ nm.

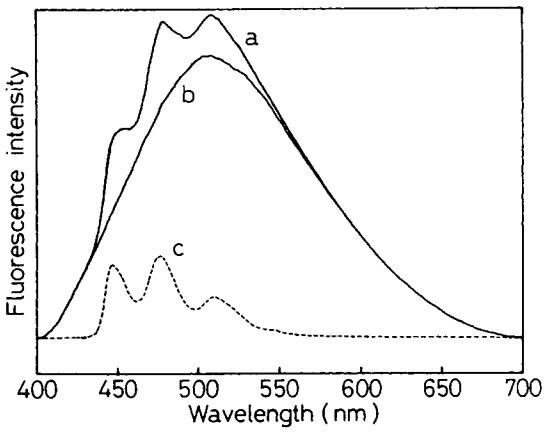


Fig. 4. Fluorescence spectra of cured film (EK/TMAV/PE) before and after extraction. EK/TMAV (20/1 mole ratio); PE, $4 \times 10^{-4}M$ in EK; cured at 150°C for 5 h. (a) Before extraction; (b) after extraction with benzene for 30 h; (c) difference spectrum (a − b). λ_{ex} = 390 nm.

Model Reactions

In order to explore the structure of the "intrinsic" probe, the following model reactions were performed. Our previous work revealed that TMAV is thermolyzed to produce *n*-butylisocyanate (BI) and trimethylamine[16]:

$$C_4H_9C(=O)-N^- - N^+(CH_3)_3 \xrightarrow{\Delta} C_4H_9-N=C=O + N(CH_3)_3$$

The latter acts as an initiator for ring-opening polymerization of EK and the former contributes to provide the cured resin with superior mechanical properties. We used BI and triethylamine (TEA) as the model compounds for the thermolyzed products of TMAV.

When EK alone was heated for 5 h at 150°C, no emission was observed on excitation with λ_{ex} = 350–410 nm. Furthermore, a mixture of EK and BI (EK/BI = 10/1 mol/mol) was heated at the same temperature for 5 h; no emission was observed as well. In Figure 5 are shown fluorescence spectra observed for EK/TEA/BI (10/1/1 mole ratio) (a) and EK/TEA (10/1 mole ratio) (b) in comparison with that of EK/TMAV (c). All the samples were cured at 150°C for 5 h. It can be seen that the fluorescence spectrum of the EK/TEA/BI mixture is very similar to that of EK/TMAV, while the emission of the EK/TEA mixture is blue-shifted compared with that of (a) or (c). This fact indicates that the "intrinsic" probe is produced by thermal reactions in the mixture of EK, TEA, and BI. We tried to isolate the fluorescent product from the EK/TEA/BI mixture by extraction, but as in the case of EK/TMAV, no product was extracted. Although chemical structure of our "intrinsic" probe is unknown at the present stage of study, it will be sufficient to know its photophysical properties such as emission spectra and lifetimes for pursuing the curing process by the fluorescence polarization method.

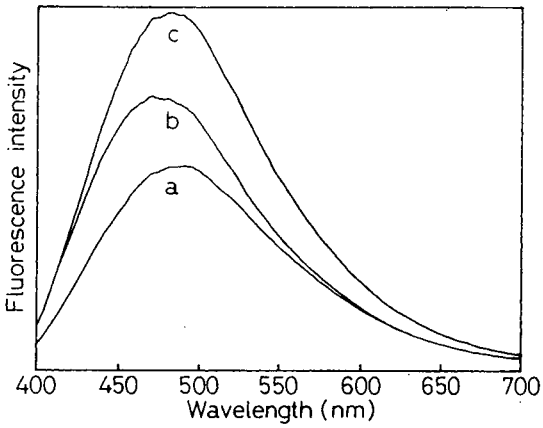


Fig. 5. Fluorescence spectra for model reactions: (a) EK/TEA/BI (10/1/1); (b) EK/TEA (10/1); (c) EK/TMAV (20/1) mole ratio; cured at 150°C for 5 h. λ_{ex} = 390 nm.

Lifetime Measurements

Fluorescence decays of EK/TMAV and EK/TMAV/PE were measured by means of a single photon counting method. Excitation wavelength was selected with a monochromator and emission was observed through an interference filter whose optical characteristics are shown in Figure 1. The decay profiles were analyzed by a multiexponential function up to three exponential terms. Validity of the analysis was judged by residuals, autocorrelation function, reduced chi-square (χ^2) and Durbin–Watson (DW) parameters. The results of the decay analysis are summarized in Table I, in which the preexponential factor A_i, lifetime τ_i, χ^2,and DW parameters are listed.

TABLE I
Lifetime Measurements

150°C	A_1	τ_1	A_2	τ_2	A_3	τ_3	χ^2	DW
			EK/TMAV/PE (λ_{ex} = 390 nm)					
Initial	0.54	4.8 (100)					1.154	1.668
1 h	0.52	5.0 (100)					2.013	1.354
2 h	0.29	1.2 (14)	0.38	4.3 (68)	0.05	9.8 (18)	0.883	1.732
3 h	0.29	1.2 (15)	0.36	3.7 (55)	0.09	8.4 (30)	1.062	2.032
4 h	0.36	1.3 (20)	0.32	4.5 (66)	0.03	12.1 (14)	0.936	2.078
5 h	0.29	1.3 (18)	0.33	4.0 (61)	0.05	9.6 (21)	1.077	2.076
			EK/TMAV (λ_{ex} = 390 nm)					
1 h	0.44	1.1 (25)	0.30	3.3 (52)	0.04	10.0 (23)	1.060	1.988
5 h	0.70	1.1 (37)	0.29	3.5 (48)	0.03	10.0 (15)	1.168	1.903

For EK/TMAV/PE system, three-exponential analysis was required to obtain good fitting as judged by χ^2 and DW parameters after 2 h heating. Before heating, no "intrinsic" probe was produced; thus emission from PE alone could be analyzed by a single exponential function. At 1 h, all of the analysis (from single to triple exponential analysis) gave poor fitting. This may be because the amount of the "intrinsic" probe produced was not so large after 1 h reaction, and this small amount of the fluorescent component interfered with the analysis. The values listed in the table ($A_1 = 0.52$, $\tau_1 = 5.0$) were the best ones obtained after many analyses, suggesting that at this stage of the thermal reaction the fluorescence decay can be expressed essentially with a single exponential term.

After 2 h, the decays are composed of three exponential terms; ~ 1, ~ 4, and ~ 10 ns. Comparison with EK/TMAV system suggests that both short (~ 1 ns) and long (~ 10 ns) lifetime components in EK/TMAV/PE system arise from the "intrinsic" probe and the component with $\tau = \sim 4$ ns results from the superposition of PE (~ 5 ns) and one of the "intrinsic" probe (~ 3.5 ns). With our present analysis system, it is impossible to separate these two components.

Fluorescence Polarization Measurements

We evaluate the contribution of PE and the "intrinsic" probe to the observed anisotropy individually by the following procedure. The polarization (P) and the anisotropy (r) are defined by

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}, \qquad r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \tag{1}$$

where $I_{\parallel}$ and $I_{\perp}$ are the fluorescence intensities observed with parallel and perpendicular orientation of the polarizer to the direction of the vertically polarized excitation light, respectively. Since our steady-state fluorescence polarimeter gives P values directly, we calculated r values by

$$r = \frac{2P}{3 - P} \tag{2}$$

With this parameter, the average anisotropy observed in a mixture of fluorophores, each with anisotropy r_i and a fractional fluorescence intensity f_i, is given by

$$r = \sum_i f_i r_i \tag{3}$$

When the fluorescence polarization measurements were carried out, fluorescence was always monitored through an interference filter whose optical characteristics are shown in Figure 1. The fractional fluorescence intensities of

PE alone (f_1) and of the "intrinsic" probe (f_2) can thus be calculated by

$$f_1 = \frac{I_1}{I_1 + I_2}, \qquad f_2 = \frac{I_2}{I_1 + I_2} \tag{4}$$

where I_1 and I_2 are integrated fluorescence intensities of PE alone and "intrinsic" probe, respectively, evaluated by

$$I_1 + I_2 = \int_{\nu_1}^{\nu_2} F_{12}(\nu)\, d\nu \tag{5}$$

$$I_2 = \int_{\nu_1}^{\nu_2} F_2(\nu)\, d\nu \tag{6}$$

Here, $F_{12}(\nu)$ and $F_2(\nu)$ are observed fluorescence intensities in EK/TMAV/PE and EK/TMAV, respectively, and integration was performed with respect to wavenumber from ν_1 (21270 cm^{-1} = 470 nm) to ν_2 (23250 cm^{-1} = 430 nm). Applying eq. (3), we obtain

$$r_{12} = r_1 f_1 + r_2 f_2 \tag{7}$$

where r_{12} and r_2 stand for anisotropies observed for EK/TMAV/PE and EK/TMAV, respectively, and r_1 is an expected anisotropy for PE in the EK/TMAV/PE mixture.

Figure 6 shows the observed values of r_{12} and r_2 and the calculated value of r_1 as a function of curing time. Because of the nature of the "intrinsic" probe, reliable values for r_2 were only obtained after 30 min. Before that, contribution of r_2 to r_{12} was negligibly small ($f_2 \sim 0$); thus it is reasonably assumed that $r_1 = r_{12}$. Figure 6 clearly indicates how the epoxy resin becomes rigid on curing with TMAV. During the initial 1.5 h, r_1, r_2, and r_{12} increase monotonically with curing time; thereafter, they remain nearly constant. This means that under the present curing condition, curing for 1.5 h produces networks rigid enough to restrict rotational diffusion of the probe molecules. Another

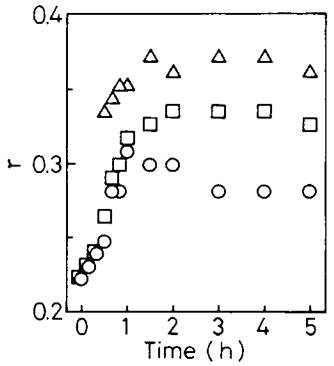


Fig. 6. Change in anisotropy (r) during the curing reaction of epoxide with aminimide at 150°C. (○) r_1 (calculated values for PE); (△) r_2 (EK/TMAV (20/1 mole ratio)); (□) r_{12} (EK/TMAV/PE [EK/TMAV, 20/1 mole ratio; PE, $4 \times 10^{-5} M$ in EK]).

interesting point seen in the figure is that r_2 is higher than r_1. This is easily explained in terms of location sites of the probe molecules. As was demonstrated by the extraction experiments, the "intrinsic" probe is covalently bonded to the matrix; thus the restriction imposed on the rotational diffusion of the probe molecules must be larger than that for physically incorporated PE molecules. Effect of fluorescence lifetime heterogeneity on anisotropy will be discussed in the following section.

DISCUSSION

The present study clearly demonstrates the usefulness of the fluorescence polarization method to pursue the curing process of epoxide. With curing time, the network becomes rigid, which is well reflected in fluorescence anisotropy of the two types of probes.

There have been many methods employed so far for the investigation of curing process of epoxides: absorption,[20] fluorescence,[21,22] ^{13}C solid-state NMR,[23] torsional braid analysis (TBA),[24] thermal analysis,[18] and ESR.[25] Each method monitors different physical properties of the cured resin. Among them, it is solid-state NMR, TBA, and ESR that can reflect the rigidity of the formed networks. In fact, both the solid-state NMR and ESR can provide useful information on molecular motion in the resin, but it is not easy to obtain quantitative data due to line broadening. TBA can give direct information on the rigidity of the cured resin. However, it has a serious disadvantage that it is only applicable to the initial stage of the curing process where torsional motion of sample specimen is still possible.[26] On the other hand, the fluorescence polarization method can provide information on rigidity in the whole range of the curing process.

Along a similar line of work, Loutfy and Arnold studied the fluorescence behavior of "molecular rotors" extensively.[27] This principle lies in the fact that certain fluorophores reduce their fluorescence quantum yield very much when a part of molecule is twisted, and thus the fluorescence intensity is quite sensitive to media viscosity. Loutfy and Arnold successfully applied the probes to evaluate the viscosity change in polymerization process of various vinyl monomers.[28] Unfortunately, most of these fluorophores possess the dialkyl-amino moiety in the molecule which is an efficient initiator of ring-opening polymerization of epoxides. This makes the use of such probes in the study of curing process of epoxides quite difficult.

In the emission, lifetime and polarization measurements, the excitation wavelengths for PE were chosen so as to correspond to $S_0 \rightarrow S_1$ (^1L_a) transition in which the absorption and emission dipoles are oriented parallel.[9] In such a case, theoretical maximum anisotropy (r_0) is 0.4 for random distribution of the chromophores.[9] In fact, r values as high as 0.35 have been measured for PE in dilute vitrified solutions where depolarization processes such as rotational diffusion and energy migration are negligible.[29] In the case of the "intrinsic" probe, the lifetime measurements showed that there exist three species in the excited states, each decaying with a different lifetime. It is not clear at the moment whether they may arise from three fluorophores or from a single fluorophore in three different environments or so on. No matter what the nature of the fluorophores, it may be reasonably assumed that the

transition involved is $S_0 \rightarrow S_1$ transition in view of the fact that excitation wavelengths for the "intrinsic" probe are near the red edge of its absorption and the observed anisotropies for prolonged cure are very close to the limiting value of 0.4.

When rotational diffusion of fluorophores is a dominant factor of fluorescence depolarization as in the present study, anisotropy is related to the fluorescence lifetime (τ) and the rotational correlation time (ϕ) by the Perrin equation[9,30]

$$r = \frac{r_0}{1 + (\tau/\phi)} \tag{8}$$

This equation predicts that $r \rightarrow r_0$ when $\tau \ll \phi$ and $r \rightarrow 0$ when $\tau \gg \phi$. In a case where the fluorescence decay does not obey a single exponential function, the steady-state anisotropy can be described by

$$r = \frac{\int_0^\infty I(t)r(t)\,dt}{\int_0^\infty I(t)\,dt} \tag{9}$$

where $I(t)$ is a time-resolved decay of the total fluorescence intensity and $r(t)$ is that of anisotropy.[9] It seems reasonable to assume that the rotational correlation time for three species of the "intrinsic" probe be identical since this parameter is only governed by viscosity (η) of the medium, temperature (T), and rotating volume (V) of the fluorophore as expressed by the equation[9]

$$\phi = \frac{\eta V}{RT} \tag{10}$$

Then, for the "intrinsic" probe, the anisotropy can be expressed by

$$r = \left(r_0 \sum_i \frac{A_i\tau_i}{\tau_i/\phi + 1}\right)\left(\sum_i A_i\tau_i\right)^{-1} \tag{11}$$

where $I(t) = \Sigma_i A_i e^{-t/\tau_i}$ and $r(t) = r_0 e^{-t/\phi}$.

Using the values of A_i and τ_i for the "intrinsic" probe listed in Table I and the observed r values, ϕ is estimated as $\sim$ 40 ns. As ϕ is much larger than the τ_i's, heterogeneity in the lifetimes becomes less significant, since $\tau_i/\phi \rightarrow 0$ results in $r \sim r_0$.

In the EK/TMAV/PE system, a large increase in anisotropy was observed at the initial stage of the curing, namely from 0 to 1 h. At this stage, emission is mainly from PE and its decay can be approximated by a single exponential function (Table I). Thus, the increase in anisotropy at this stage corresponds satisfactorily to the increase in ϕ as judged by eq. (8), which means that rotational diffusion of PE molecules becomes restricted with curing time.

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