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Sub-Glass Transition Motions in Linear and Cross-Linked Bisphenol-Type Epoxy Resins by Deuterium Line Shape NMR

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ABSTRACT: Deuterium solid-state echo delay line shapes are used to establish the local motions occurring in linear and cross-linked epoxy systems based on Bisphenol A. Four isotopically labeled samples were prepared: linear and cross-linked resins with deuterated methylene units, and linear and cross-linked resins with deuterated phenylene units. Two local motions are observed in all four samples: trans−gauche isomerization of the methylene units and π flips of the phenylene units. The solid-state echo delay line shapes were simulated to obtain the rates of motion, the amplitudes of motion, and apparent distribution of rates, and the apparent temperature dependence of the rates. The two jump motions differ by about an order of magnitude in rate, with the π flip process being the faster of the two. Both have similar distributions of relaxation times given by a stretched exponential correlation function with an exponent of 0.6−0.7. The apparent activation energy for the π flip process is 50 kJ/mol and for the trans−gauche isomerization, 57 kJ/mol. For a given frequency, the breadth and temperature of the shear loss peak can be calculated from the information determined from the NMR data. Both motional processes lie in the envelope of relaxation referred to as the β process, with the π flips occurring on the lower temperature side of the envelope and the trans−gauche isomerization occurring on the higher temperature side. These two motions do not appear to account for all of the relaxations contributing to the β peak.

Introduction

Epoxy resins containing the Bisphenol A unit are among the most commonly employed cross-linked or network polymer systems. These materials display significant relaxations below the glass transition. These sub-glass transition relaxations of Bisphenol A based epoxide resins have been widely studied by dynamic mechanical response,[1−16] dielectric response,[17−18] and solid-state NMR.[19−22] In both the mechanical and dielectric studies, the principal low-temperature loss peak (the β peak) is quite broad and lies between −80 and −40 °C at a frequency of 1 Hz. The effects of cross-link density and changes in chemical structure on the β peak have been studied.

The interpretation of the main loss peak in terms of a molecular-level motion remains unclear. One group of investigators,[6,7,23] has attributed this loss to motion of the diphenylpropane unit, specifically phenylene group rotation.[19] Others attribute the relaxation to motion of the hydroxy ether groups,[3,4,8−12,22,24] while some of the more recent mechanical studies suggest the β peak is a composite of motions of both of these units.[8,13−17] According to this latter interpretation, the low-temperature side (−110 to −80 °C) of the β peak arises from motion of the phenylene groups in the diphenylpropane and the high-temperature side of the β peaks arises from the motion of the hydroxy ether groups (−70 to −55 °C). To the current authors, the literature is not definitive on the molecular sources of the sub-glass transition motion. It is difficult to establish the molecular origin of a mechanical loss by observing changes in mechanical loss produced by structural variations. It is the purpose of this contribution to use solid-state deuterium echo line shapes to more clearly identify the structural source, geometry, time scale, and temperature dependence of the molecular motions present and to associate them with the mechanical response of the Bisphenol epoxide resin.

Deuterium[25−27] and carbon-13[28] line shape studies have been established as a definitive technique for the characterization of motion in solid polymers and for establishing the relationship between molecular motions and the bulk mechanical response of the solid material. To apply these techniques most directly, isotopically labeled samples must be prepared. For the current study, the obvious sites to label with deuterium in separate samples are the phenylene rings of the diphenylpropane portion and the methylene groups of the hydroxy ether portion. This will allow for detailed, direct monitoring of motion in each of the two key regions of the material separately. To test the effects of cross-linking or curing, the dynamics of a cured, cross-linked material will be compared with those of a linear material.

Experimental Section

Four deuterium-labeled materials were prepared for this study. First linear poly(diglycidyl ether of Bisphenol A) (poly(DGEBA)) was prepared with deuterated methylene units in the hydroxy ether portion. A second sample of the same linear polymer was prepared with deuterated phenylene units in the diphenylpropane portion. The third labeled sample is made by curing the methylene-labeled DGEBA with 4,4′-methylenedianiline (MDA) to produce a model one-to-one network. A similar network sample is prepared by curing the phenylene-labeled DGEBA with MDA. The cross-linked resins were synthesized by the addition of 1 equiv of MDA to 4 equiv of DGEBA. They were then cured by heating for 16 h at 55 °C followed by 2 h at 125 °C and 2 h at 175 °C. The linear polymers were made by addition of Bisphenol A and DGEBA (1:1) followed by the same cure conditions. The structures of the four labeled systems are shown in Figure 1.

The deuterium NMR experiments were carried out with a Bruker MSL-300 spectrometer operating at a deuterium

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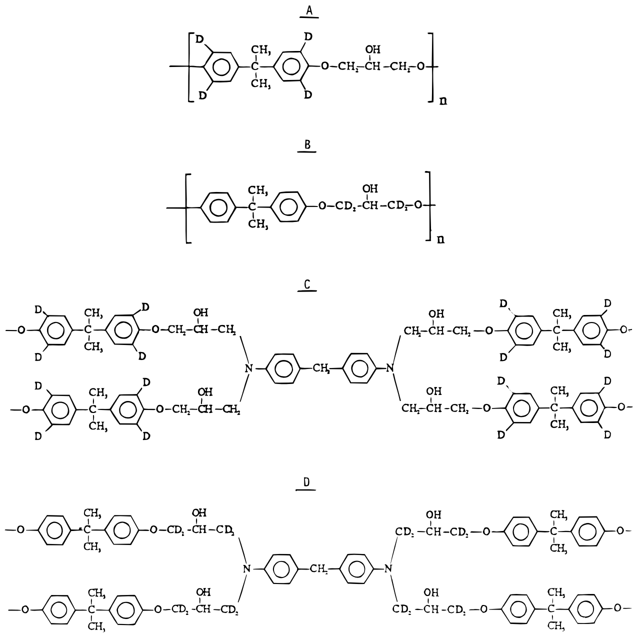

Figure 1. Chemical structures of the four deuterium-labeled epoxy systems.

resonance frequency of 46.07 MHz. Temperature was regulated with a Bruker VT-1000 control unit. The deuterium spectra were obtained using a quadrupole echo pulse sequence with echo delay times of 15, 30, 50, 80, and 120 μs. The 90° pulse width was 2.5 μs, and the recycle time of the experiment was 5−20 s, depending on the sample and the temperature.

Results

Representative examples of the 104 solid echo spectra on the four samples as a function of echo time and temperature over the range of about −100 to +100 °C are shown in Figure 2. At the lowest temperatures (−80 °C), Pake patterns are observed corresponding to nearly rigid specimens. The quadrupole coupling constant for the methylene-labeled systems is 170 kHz; and for the phenylene-labeled systems, 180 kHz. As temperature is raised, the methylene-labeled systems partially collapse to a line shape corresponding to an asymmetric tensor which has generally been associated with the onset of trans−gauche isomerization plus rapid libration.[26,27] The phenylene-labeled systems partially collapse as temperature is raised and show a splitting at high temperatures, which is indicative of π flips plus rapid libration.[25] Both methylene- and phenylene-labeled systems show line shape changes as a function of echo delay time at certain temperatures, which verifies the presence of motions on time scales comparable to the selection of echo delay times. Also the spectra show significant intensity reductions with increasing echo delay time at these same temperatures, further identifying the time scale of motion as comparable to the echo delay times.[25]

Interpretation

To quantitatively determine the rates and amplitudes of motion, the deuterium line shapes are simulated according to the procedures described by Wittebort[29] and Mehring.[30] Simulation calculations were performed on a DEC UNIX workstation, and the simulated spectra include the effects of finite pulse width. Because of the complexities of molecular dynamics in polymeric glasses, several additions to these procedures must be made. The first is that motion in a glass cannot be characterized by a single rate but rather the motion is heterogeneous and must be described by a distribution of rates.[19,31] In this regard, one of the more successful functions for describing relaxation in polymers is the stretched exponential or Kohlrausch−Williams−Watts function[19,32−32]

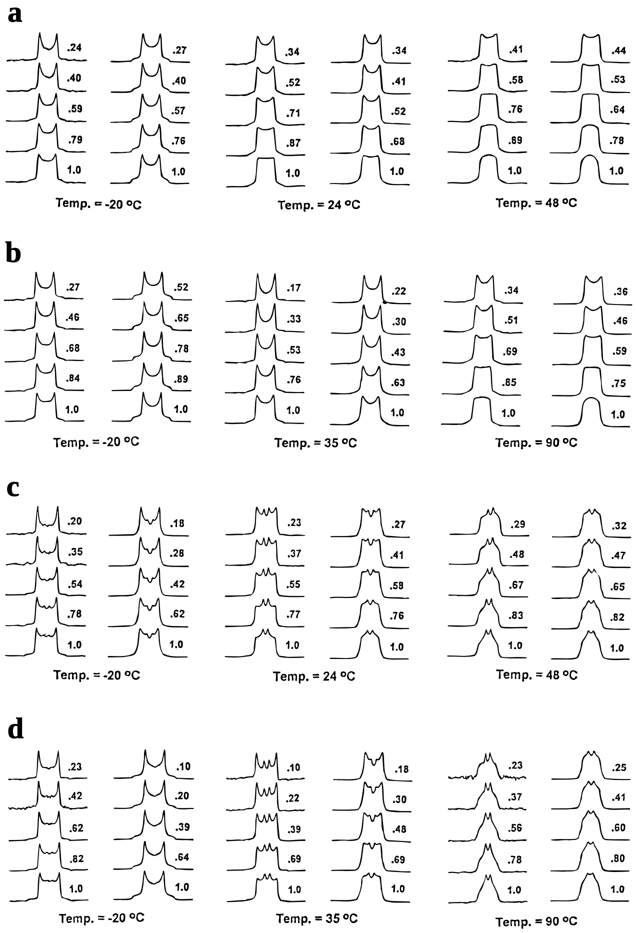

Figure 2. ^{2}H experimental (left) and simulated (right) line shapes for (a) chain-labeled linear epoxy, (b) chain-labeled cross-linked epoxy, (c) ring-labeled linear epoxy, and (d) ring-labeled cross-linked epoxy as a function of echo delay times: 15, 30, 50, 80, and 120 μs from bottom to top. Reduction factors are listed at the right.

$$\phi(t) = \exp[-(t/\tau_p)^{\alpha}] \qquad (1)$$

which can be written as a sum of exponentials.[33] The fractional exponent α controls the breadth of the distribution, and the characteristic time τ_p controls the time scale. Accordingly, these two parameters will be quoted when summarizing the rates or time scales of motion.

Two jump motions are considered in the interpretation: trans−gauche isomerization for the methylene units and π flips for the phenylene units. However, in disordered glasses, a distribution of jump angles is required for both of these motions, and following English[26,27] et al., a Gaussian distribution of jump angles centered around the conformational minimum will be used. The usual Gaussian breadth parameter σ is reported to characterize this aspect of the dynamics.

The last dynamic influence on the line shape spectra comes from the presence of librational motion, which is relatively rapid on the line shape collapse time scale. To include the effect of this motion, the quadrupole tensor is preaveraged before the line shape collapse

Table 1. Simulation Parameters for the Chain (Methylene) Motion for the Linear Epoxy

T (°C)	τ_p (s)	α	libration (deg)	σ (deg)	T_2 (ms)
70	6.6×10^{-6}	0.6	85	18	1.5
48	1.6×10^{-5}	0.6	80	18	1.5
35	2.5×10^{-5}	0.6	76	18	1.5
24	4.5×10^{-5}	0.6	71	18	1.5
0	1.5×10^{-4}	0.6	61	18	1.5
−20	5.0×10^{-4}	0.6	52	18	1.5

Table 2. Simulation Parameters for the Chain (Methylene) Motion for the Cross-Linked Epoxy

T (°C)	τ_p (s)	α	libration (deg)	σ (deg)	T_2 (ms)
90	1.0×10^{-5}	0.7	75	18	0.8
70	1.5×10^{-5}	0.7	72	18	0.8
48	3.5×10^{-5}	0.7	65	18	0.8
35	6.0×10^{-5}	0.7	60	18	0.8
24	1.4×10^{-4}	0.7	56	18	0.8
0	6.0×10^{-4}	0.7	47	18	0.8
−20	2.8×10^{-3}	0.7	39	18	0.8

Table 3. Simulation Parameters for the Ring Motion for the Linear Epoxy

T (°C)	τ_p (s)	α	libration (deg)	σ (deg)	T_2 (ms)
70	2.4×10^{-7}	0.6	50	25	0.28
48	6.5×10^{-7}	0.6	47	25	0.28
35	1.4×10^{-6}	0.6	44	25	0.28
24	2.8×10^{-6}	0.6	41	25	0.28
0	1.5×10^{-5}	0.6	35	25	0.28
−20	4.0×10^{-5}	0.6	30	25	0.28

calculation is made.[25−28] Again a distribution of librational amplitudes is often required in glasses,[26,27] but to simplify the calculations and reduce the time required on the computer, a single librational amplitude was employed. Improved fits could be achieved if a distribution of librational amplitudes was employed, but the essential aspects of the dynamics are captured without a distribution for this influence on the line shape. The amplitude of libration is temperature dependent in the modeling presented here and is allowed to increase with temperature. Improved simulations could also be produced if the librational motion was given an actual rate and not simply assumed to be fast on the NMR time scale. Again this simplification is made to limit the simulation to reasonable times on a workstation.

To properly calculate the changes in amplitude with increasing echo delay times, the spin−spin relaxation time, T_2, must be included, and it can be estimated from the low-temperature spectra or the high-temperature spectra where the reduction of intensity associated with dynamics is minimal.

The calculated line shapes and reduction factors (the integrated intensity of the solid echo relative to the free induction decay) are compared with the experimental results in Figure 2a for the linear poly(DGEBA) with methylene deuterated hydroxy ether units. The simulation parameters are summarized in Table 1. The analogous comparisons of experiment and simulation for the cross-linked methylene-deuterated hydroxy ether system are shown in Figure 2b, and the associated simulation patterns are given in Table 2. Figure 2c contains the comparison of experiment and simulation for the phenylene-labeled linear poly(DGEBA), and the simulation parameters are contained in Table 3. The last set of simulations for the phenylene-labeled cross-linked system is compared with experiment in Figure 2d, and the parameters are listed in Table 4. Note that the libration amplitude quoted here is the overall width of the libration and not the deviation from the mean position.

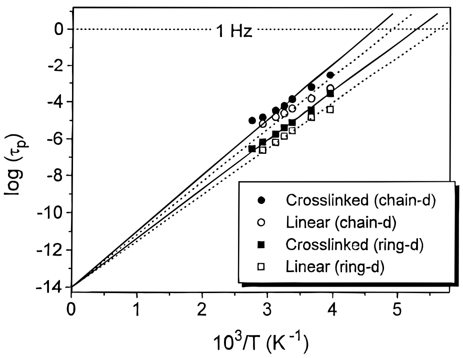

Figure 3. Arrhenius plot for both the chain and ring motion in the epoxy systems studied. The rate for comparison with the mechanical relaxation (1 Hz) is shown as a dotted line.

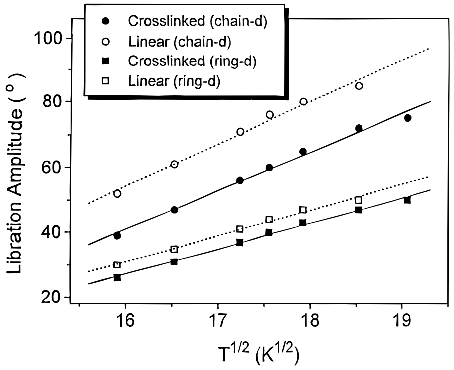

Figure 4. Temperature dependence of the amplitude of the librational motion of the chain methylenes and the phenylene rings.

Table 4. Simulation Parameters for the Ring Motion for the Cross-Linked Epoxy

T (°C)	τ_p (s)	α	libration (deg)	σ (deg)	T_2 (ms)
90	2.9×10^{-7}	0.7	50	25	0.20
70	6.7×10^{-7}	0.7	47	25	0.20
48	1.8×10^{-6}	0.7	43	25	0.20
35	4.1×10^{-6}	0.7	40	25	0.20
24	7.8×10^{-6}	0.7	37	25	0.20
0	3.7×10^{-5}	0.7	31	25	0.20
−20	2.8×10^{-4}	0.7	26	25	0.20

Table 5. Activation Parameters for Linear and Cross-Linked Epoxies

	E_a (kJ/mol)	temp at 1 Hz °C
linear, chain motion	54.6	−70
cross-linked, chain motion	57.9	−57
linear, ring motion	47.7	−95
cross-linked, ring motion	50.7	−84

Apparent activation energies are calculated from a fit of the simulation values of τ_p according to the Arrhenius equation

$$\tau_p = \tau_\infty \exp(E_a/RT) \qquad (2)$$

which are shown in Figure 3. Since the time scales of motion are all rather similar, a fixed value of the prefactor of 10^{-14} s is used in all fits. Table 5 gives a summary of the apparent activation energies obtained for the motion in each system.

The amplitude of libration as a function of temperature is shown in Figure 4. Actually, the libration amplitude has a nearly linear dependence on the square root of temperature as has been observed in other systems, so Figure 4 is plotted accordingly.

Discussion

The most rapid motion observed in the four systems studied is for π flips of the phenylene group in the linear poly(DGEBA), and the second most rapid motion is for π flips of the phenylene groups in the cross-linked network. The effect of cross-linking on phenylene group motion is about equivalent to a shift of time scale corresponding to a temperature change of 5 or 10 deg. The breadth parameter determining the distribution of correlation times, α, of 0.6 for the linear system and 0.7 for the cross-linked network. This corresponds to a fairly narrow distribution of correlation times, and a prediction of the temperature of the maximum of the mechanical loss peak can be obtained by extrapolating the fit of the NMR data to a time scale of 1 Hz. The 1 Hz line is indicated in Figure 3, and the corresponding temperature is −95 °C for the linear resin as listed in Table 5. The position of the mechanical loss peak predicted from the NMR data for the cross-linked network is 11 deg higher. The positions of these predicted mechanical loss peaks place them on the low-temperature side of the β peak but part of the overall envelope of loss associated with the β peak. This is consistent with the views of some of the mechanical investigators,[8,13−17] though mechanical data are so featureless that changes produced by structure variation leave considerable uncertainty as to the position of the peak to be associated with phenylene group motion. The absolute uncertainty of the NMR estimate of the temperature of the loss peak is between 5 and 10 deg, though the error in the relative difference of 11 deg between linear and cross-linked is closer to 2 deg.

The activation energy of 48−51 kJ/mol for the π flip motion is typical of those found for phenylene groups in the backbones of polymers. For instance, the apparent activation energy for the same motion in linear polycarbonate is 40−50 kJ/mol.[28,31] In Garroway's NMR study,[19] a value of 60 kJ/mol is obtained for phenylene group motion in a cross-linked epoxy.

The trans−gauche isomerization of the methylene groups in the hydroxy ether portion is a slower motion than π flips in either the cross-linked or linear systems, though the two geometries of motion are only separated by about a decade in time of frequency. The effect of cross-linking is to slow the isomerization motion slightly relative to the linear system. The slowing corresponds to a temperature shift of about 5 deg. The apparent activation energy obtained for this motion is 55−58 kJ/mol, which leads to a slightly larger temperature separation at the time scale of 1 Hz corresponding to mechanical measurements. Since the distributions of correlation times are again relatively narrow, the relaxation map of Figure 3 leads to a predicted temperature for mechanical loss of −70 °C for the linear system and −57 °C for the cross-linked system. This difference between linear systems and cross-linked systems seems reasonable relative to mechanical data on similar systems.[16] These temperatures fall on the high side of the envelope of mechanical loss associated with the β peak. Thus in both the linear and cross-linked systems, the two motions, π flips and trans−gauche isomerization, would likely overlap in a mechanical experiment and contribute to the overall mechanical peak described as the β peak. This coincidence between the mechanical experiment and the prediction based on the interpretation of the NMR line shape data can be further visualized when a calculated[31] loss peak is plotted and compared with the experimental loss data[22] (Figure 5).

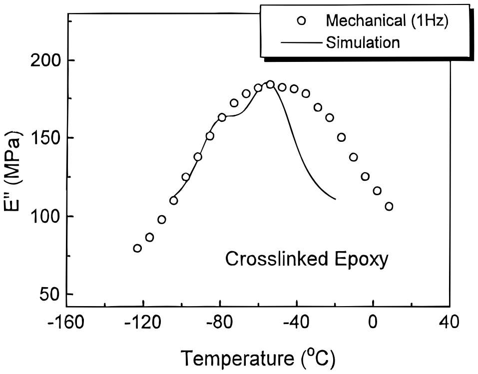

Figure 5. Comparison of the experimental mechanical response[22] (circles) with the prediction (line) based on the ring and chain dynamics obtained from the NMR analysis.

The equation[31] used to calculate the shear loss from the rate and temperature dependence established from the interpretation of the NMR data is

$$G(\omega)^{\mathrm{loss}} = \frac{\langle \sigma(0)^2 \rangle}{kT}\int_0^{\infty} \sin(\omega t)[-\phi'(t)]\, \mathrm{d}t \qquad (3)$$

The calculation provides information on the breadth of the loss peak and the position in frequency and temperature but not on the amplitude of the loss peak. An amplitude is assumed which matches experimental observation. The calculated loss peak includes the low-temperature (fast) ring motion and the slower, higher temperature chain motion, and these can be discerned in the calculated line. It is clear from the comparison that the β relaxation contains contributions from further slower motions not detected in our NMR study which contribute to loss at the high-temperature side of the mechanical relaxation. There are two potential sources for this slower motion in the cross-linked system. One is motion associated with the cross-linking agent itself, MDA. Since a sample with deuterium-labeled MDA is not available, we are unable to observe directly any local motion of the MDA moiety in the resin. The cross-linked epoxy might also exhibit an additional slow-motion component associated with the presence of the cross-linker at one side of the methylene units relative to the more symmetric linear system. This could explain the slightly lower quality of the simulations for the cross-linked system (Figure 2b,d). The fit could obviously be improved by the inclusion of more parameters to account for this, but this does not seem justified in view of the inherent information content of the line shapes and since the general interpretation is not enhanced.

The apparent activation energy of ca. 57 kJ/mol is high relative to other observed trans−gauche isomerization energies for methylene units. For instance, the value obtained by English et al. on the methylene groups in nylon is 33 kJ/mol. The higher value may reflect the presence of the hydroxyl groups on this portion of the network which can participate in hydrogen bonding.

Conclusion

Deuterium line shape data and the subsequent analysis identify the role of π flips of the Bisphenol A unit and trans−gauche isomerization of the methylene units in the mechanical response of epoxy networks. Both motions contribute to the main sub-glass transition relaxation process, the β process, with the π flips occurring at lower temperatures and the trans−gauche isomerization at higher temperatures but with overlap of the two relaxations. The activation energy of the trans−gauche isomerization is about 7 kJ/mol higher than the π flip process. The effect of cross-linking is a shift of either relaxation process about 10 deg at the typical frequency of a mechanical experiment of 1 Hz. Cross-linking may produce some subtle changes in the distribution of relaxation times, but it was not necessary to include these to produce reasonable simulations.

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