rigid-rod regime. Neither of the data by the previous authors satisfy these two requirements. This is why an independent estimate of α and Φ has not been attempted for their data. Finally, we find no theoretical justification for the experimental Φ removed from unity and diversity of α among different polymers. The need for further theoretical study is indicated.

Acknowledgment. We acknowledge gratefully the partial support of Idemitsu Kosan Co., Ltd. through a research grant.

Registry No. Schizophyllan, 9050-67-3.

References and Notes

(1) Robinson, C. *Trans. Faraday Soc.* **1956**, *52*, 571.
(2) Robinson, C.; Ward, J. C.; Beevers, R. B. *Discuss. Faraday Soc.* **1958**, *25*, 29.
(3) Hermans, J., Jr. *J. Colloid Sci.* **1962**, *17*, 638.
(4) Papkov, S. P.; Kulichikhin, V. G.; Kalmykova, V. D.; Malkin, A. Ya. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1753.
(5) Chu, S. G.; Venkatraman, S.; Berry, G. C.; Einaga, Y. *Macromolecules* **1981**, *14*, 939.
(6) Baird, D. G.; Ballman, R. L. *J. Rheol. (N.Y.)* **1979**, *23*, 505.
(7) Asada, T.; Yanase, H.; Onogi, S. *Polym. Prepr. Jpn.* **1982**, *31*, 1893.
(8) Morgan, P. W. *Macromolecules* **1977**, *10*, 1381.
(9) Kwolek, S. L.; Morgan, P. W.; Schaefgen, J. R.; Gulrich, L. W. *Macromolecules* **1977**, *10*, 1390.
(10) Aharoni, S. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1439.
(11) Doi, M. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, 607.
(12) Doi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 229.
(13) Berry, G. C. *J. Polym. Sci., Polym. Symp.* **1980**, *No. 34*, 43.
(14) Enomoto, H.; Einaga, Y.; Teramoto, A. *Macromolecules* **1984**, *17*, 1573.
(15) Yanaki, T.; Norisuye, T.; Fujita, H. *Macromolecules* **1980**, *13*, 1462.
(16) Norisuye, T.; Yanaki, T.; Fujita, H. *J. Polym. Sci. Polym. Phys. Ed.* **1980**, *18*, 547.
(17) Itou, T.; Van, K.; Teramoto, A. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1985**, *41*, 35.
(18) Van, K.; Norisuye, T.; Teramoto, A. *Mol. Cryst. Liq. Cryst.* **1981**, *78*, 123.
(19) Van, K.; Teramoto, A. *Polym. J. (Tokyo)* **1982**, *14*, 999.
(20) Einaga, Y.; Miyaki, Y.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2103.
(21) Einaga, Y.; Miyaki, Y.; Fujita, H. *J. Soc. Rheol., Jpn.* **1977**, *5*, 188.
(22) Kashiwagi, Y.; Norisuye, T.; Fujita, H. *Macromolecules* **1981**, *14*, 1220.
(23) These η_0 values may be regarded as those in the plateau regions, although no plateau region is seen in the actual data because of the limited range of torque available.
(24) Matheson, R. R., Jr. *Macromolecules* **1980**, *13*, 643.
(25) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980; Chapter 10.
(26) These K and β values have been determined by the least-squares method so as to minimize the mean square of relative difference from the theoretical values. They are different from those reported in our previous paper.[14] This is because the analysis was made on the whole data, including those for samples R-4 and H-23 together with a d value different from the previous one.
(27) Valiev, K. A.; Ivanov, E. N., *Sov. Phys.-Usp. (Engl. Transl.)* **1973**, *16*, 1.
(28) Ferry, J. D., ref 25, Chapter 17.
(29) Berry, G. C.; Venkatraman, S.; Einaga, Y. *Proc. IUPAC, I. U.P.A.C. Macromol. Symp., 28th* **1982**, 790.
(30) Teramoto, A.; Fujita, H. *Adv. Polym. Sci.* **1975**, *18*, 65.
(31) Itou, S.; Nishioka, N.; Norisuye, T.; Teramoto, A. *Macromolecules* **1981**, *14*, 904.
(32) Yang, J. T. *J. Am. Chem. Soc.* **1958**, *80*, 1783.
(33) Metzger, P. Ph.D. Thesis, Carnegie-Mellon University, Pittsburgh, PA, 1979.
(34) In the present analysis, d is taken to be 1.67 nm, the value calculated from the partial specific volume of schizophyllan in water,[16] because α and d may be regarded as the thermodynamic parameters determining the spatial distribution of rodlike molecules in solution. Use of the hydrodynamic diameter 2.6 nm gives $\alpha = 12.8 \pm 1$ and $\Phi = 0.05$.

Motional Correlation Times of Nitroxide Spin Labels and Spin Probes in an Amine-Cured Epoxy Resin: Solvent Dependence

I. M. Brown* and T. C. Sandreczki

McDonnell Douglas Research Laboratories, St. Louis, Missouri 63166.
Received December 17, 1984

ABSTRACT: Nitroxide spin labels and spin probes have been used to investigate the microstructure in the polymer network of an amine-cured epoxy resin. The behavior of the electron paramagnetic resonance (EPR) line shapes of the nitroxides was studied as a function of solvent plasticizer content. At low solvent contents ($\lesssim$5 wt %) the line shape was a slow-phase spectrum that differed little from that in the dry sample, whereas at high solvent contents ($\gtrsim$30 wt %) the line shape was a fast-phase spectrum similar to the typical motionally narrowed spectrum. Over a range of intermediate solvent contents, the line shape was a superposition of a slow-phase and a fast-phase spectrum where the motional correlation times characterizing these spectra differed by more than 1.5 orders of magnitude. The slow phase is identified with nitroxides located in regions of high cross-link density, whereas the fast phase is attributed to nitroxides in regions of lower cross-link density that have been selectively plasticized by the solvent. The mobile fraction of the spin labels, evaluated from the areas under the fast- and slow-phase absorption spectrum, is a crude measure of the distribution of cross-link density in the epoxy network.

Introduction

Epoxy resin polymers are used as matrix materials for composite structural components in the aerospace industry. At present there is considerable evidence to suggest that the polymer network in cured epoxy resins contains regions of nonuniform cross-link density.[1-7] These network inhomogeneities consist of regions of high cross-link density, variously referred to as globules,[2] nodules,[3] or domains,[7] embedded in and bound to regions of lower cross-link density. It is important to characterize these network inhomogeneities because of the consequences of network morphology on mechanical properties such as yield strength and toughness.

In this study we have used electron paramagnetic resonance (EPR) spectroscopy to obtain information about this network microstructure. Since the epoxy resins are diamagnetic, nitroxide free radicals[8] were used as paramagnetic probes of their dynamic local environments in the polymers. The nitroxide was employed either as a spin label, where it was covalently bound at a known site in the

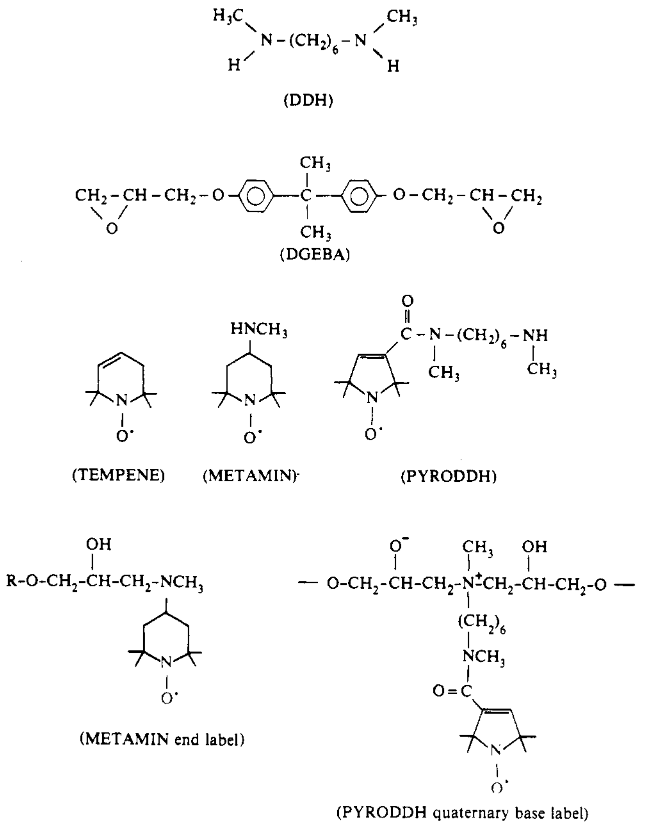


Figure 1. Materials studied.

polymer, or as a spin probe, where it was randomly distributed throughout the polymer.[8]

The epoxy studied was the diglycidyl ether of bisphenol A (DGEBA) cured with stoichiometric amounts of the amine curing agent *N*,*N'*-dimethyl-1,6-diaminohexane (DDH). Both structures are shown in Figure 1. Although both the epoxy and amine curing agent are primarily bifunctional, the cured sample is lightly cross-linked through the formation of trifunctional quaternary base groups[9,10] so that it is a thermosetting polymer with a glass transition temperature T_g of 305 K. The low cross-linking is apparent since these cured samples can be extensively swelled with solvents.

The spin labels studied were attached at the oxirane ring following ring opening by the nitroxide amines 4-(methylamino)-2,2,6,6-tetramethylpiperidine-1-oxyl (METAMIN) or 3-[*N*-methyl-*N*-(6-(methylamino)hexyl)carbamoyl]-2,2,5,5-tetramethylpyrroline-1-oxyl (PYRODDH). The labels were a neutral species consisting of one molecule of DGEBA bound to one molecule of METAMIN to form an end label, and a zwitterion species where two molecules of DGEBA were bound to one molecule of PYRODDH.[10] The spin probe used was 2,2,6,6-tetramethyl-1,2,3,6-tetrahydropyridine-1-oxyl (TEMPENE). The molecular structures of the nitroxides are shown in Figure 1.

Sample Preparation

The EPR spectrum of a mixture of METAMIN (≈0.05 wt %) in DGEBA was monitored at intervals as the spin-labeling reaction proceeded in the uncured resin at 300 K. After 48 h, when the spectrum indicated no detectable METAMIN spin probe, i.e., 100% end-label formation, the reaction was terminated by cooling quickly to 250 K. The sample was later warmed to 300 K and cured with a stoichiometric amount of DDH. In the preparation of a typical cured epoxy sample, the following procedure was used. After the appropriate amount of curing agent was added, the mixture was thoroughly mixed by hand (≈20 min), heated to 320 K, and degassed in a vacuum oven until all air bubbling ceased. The mixture was then poured into either flexible silicone rubber molds (G.E. Type RTV 664 silicone compound was found satisfactory) or 5-mL glass vials, where it was allowed to cure at 300 K for at least 24 h.

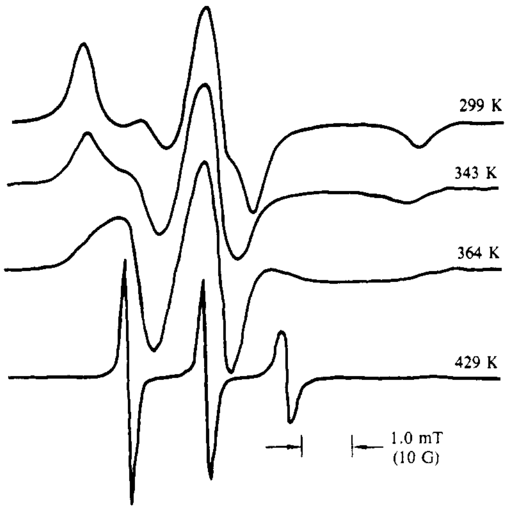


Figure 2. Spectra of the end-labeled DGEBA in a sample of DGEBA cured with DDH recorded at the temperatures shown.

In the spin labeling of DGEBA with PYRODDH the reaction was allowed to go to completion to form a spin-labeled quaternary base[9,10] before curing at 300 K with a stoichiometric amount of DDH.

Results

The temperature dependence of the EPR line shapes for the spin probe TEMPENE and both spin labels dissolved in DGEBA samples cured with DDH was studied from 293 to 400 K. With increasing temperature the spectra of all three nitroxides exhibited the typical features indicating the onset of motional collapse and line narrowing. The temperature ranges over which the motional narrowing took place indicated that in order of increasing rotational mobility the sequence was the PYRODDH spin label, the METAMIN end label, and the spin probe TEMPENE. Thus, the same spectrum (i.e., with the same relative intensities) was observed from the PYRODDH label at 385 K, from the METAMIN end label at 370 K, and from TEMPENE at 350 K. The important point to note is that at all temperatures the line shapes for both spin labels and the spin probe can be characterized by essentially one value of the motional correlation time τ_c or at most a narrow distribution of correlation times. The observed set of line shapes for the end label is shown in Figure 2. This temperature dependence is in marked contrast to the spectral behavior observed from all three nitroxides at a fixed temperature (295 K) on increasing the solvent content. For example, as shown in Figure 3, at low solvent contents (<10 wt % methylene chloride) the spectrum of the end label corresponds to that of a slow nitroxide phase with $\tau_c \gtrsim 30$ ns. This spectrum is only slightly modified from that of the dry sample by the presence of the solvent. At high solvent contents (>35% methylene chloride), a motionally narrowed three-line spectrum was observed that corresponds to that of a fast nitroxide phase with $\tau_c < 3$ ns. At intermediate solvent contents (10–35 wt % methylene chloride) the observed line shape appears to be a superposition of a slow phase and a fast phase that can be characterized by a bimodal distribution of motional correlation times whose principal values differ by more than 1.5 orders of magnitude.

Precautions were taken to eliminate the effects of nonequilibrium sorption of the solvent on the observed line shapes. This nonequilibrium sorption would occur in situations where plasticization had taken place only in the

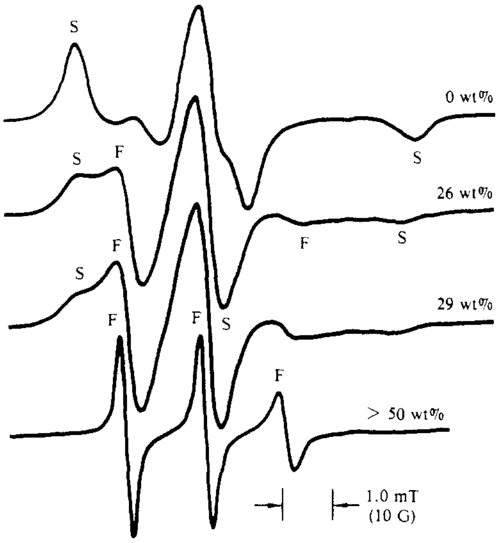


Figure 3. Spectra of the end-labeled DGEBA in a sample of DGEBA cured with DDH containing the amounts of the solvent plasticizer shown. The peaks belonging to the slow- and fast-phase spectra are denoted by S and F, respectively.

outside layers of the sample since the solvent had not penetrated into the interior. Our weight-gain measurements show that sorption equilibration of methylene chloride by DGEBA/DDH samples is a fast process (few minutes). However, to verify that sorption nonequilibrium was not a problem, measurements were made on (a) powdered samples (particle sizes $\lesssim 10^{-9}$ m^3) and (b) samples in sealed tubes that had experienced long exposures to the solvent ($\approx$48 h). The data on all plasticized samples were consistent in that all showed the same composite line shape over the same range of solvent contents.

All EPR spectra were digitized and stored on magnetic tape with a data acquisition system (Varian E-900). The spectra could be scaled, field-shifted, added, subtracted from one another, or integrated with the available software. The line shape for the fast-phase component in the composite spectrum was determined by removing the contribution of the slow-phase spectrum. This procedure was carried out by subtracting a scaled version of the dry-sample spectrum from the composite spectrum. The best criterion for the amount to be subtracted, i.e., the scaling factor to be used, was found by displaying the resulting difference spectrum and obtaining the line shape that appeared to be the best fit to a fast-phase spectrum. This difference spectrum and the composite spectrum were integrated, and the ratio of the areas under the integrals, i.e., the areas under the absorption spectra, was taken as the fractional amount of fast phase present. Typical examples of the composite spectrum, the rigid-phase spectrum (i.e., the dry-sample spectrum), and the resulting difference spectrum for the fast phase are shown in Figure 4.

The spectra in Figure 3 for samples of DGEBA cured with DDH containing the end label and different amounts of solvent show two notable features: (a) the fast-phase spectrum narrows with increasing solvent content (i.e., the motional correlation time for the fast phase decreases with increasing solvent content), and (b) the amount of fast phase increases with increasing solvent content.

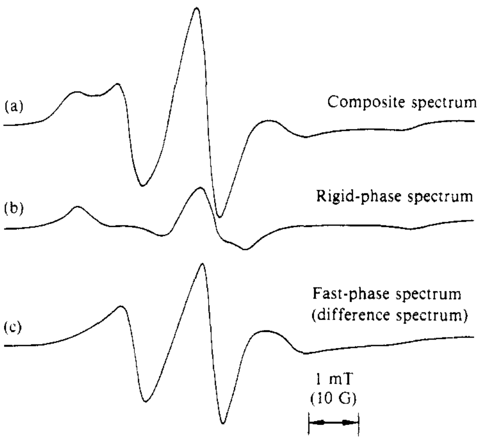


Figure 4. Typical examples of (a) the composite spectrum, (b) the rigid-phase spectrum, and (c) the resulting difference spectrum, which is that of the fast phase.

We have adopted the arguments of Veksli and Miller[11,12] to fit our motional correlation time data in the fast phase to a modified form of the Fujita–Doolittle equation.[13,14] The rationale for this approach is as follows. When a polymer is uniformly plasticized with a low molecular weight solvent that is molecularly dispersed (i.e., no clustering), the monomeric friction coefficients and hence the viscoelastic relaxation times are reduced.[13] The dependence of these relaxation times on the amount of solvent in the polymer is usually given by the Fujita–Doolittle equation, which can be written in the form[13,14]

$$\ln \alpha_c = -\frac{v_1 - v_1^0}{(f_0/B)((f_0/\beta) + v_1 - v_1^0)} \tag{1}$$

with

$$\alpha_c = [\tau]_c/[\tau]_{cr} \tag{2}$$

where $[\tau]_c$ is the viscoelastic relaxation time for the sample containing the solvent fraction v_1, $[\tau]_{cr}$ and v_1^0 are the corresponding values for the reference state, B is an empirical parameter in the Doolittle equation,[15] and f_0 and β are constants for a given polymer/solvent system corresponding to the free volume fraction in the reference state and the proportionality constant for the dependence of the total fractional free volume f_c on the solvent volume fraction, respectively; i.e., $f_c = \beta(v_1 - v_1^0) + f_0$.

Equation 1 is applicable not only to the diffusion of monomeric polymer units but also to the translational diffusion of small molecules dissolved in the polymer.[13] We assume the applicability of this equation also extends to the rotational diffusion of small molecules. Thus, the rotational diffusion coefficient for the spin probe (or spin label) bears the same relationship to the free volume as does the monomeric translational diffusion coefficient in the polymer,[13] i.e.

$$\alpha_c' = \tau_c/\tau_{cr} = D_{rr}/D_{rc} \tag{3}$$

whereas

$$\alpha_c = [\tau]_c/[\tau]_{cr} = D_{tr}/D_{tc} \tag{4}$$

where τ_c is the motional correlation time obtained from the EPR line shapes, D_t and D_r are the diffusion coefficients for translational diffusion of the monomer unit and rotational diffusion for the nitroxide, respectively, the subscripts c and r refer to the values at solvent volume fractions v_1 and a reference v_1^0, respectively, and the rest of the symbols are as defined in eq 2.

Substituting eq 3 into eq 1, one obtains

$$-\frac{1}{\ln(\tau_c/\tau_{cr})} = \frac{f_0^2}{B\beta(v_1 - v_1^0)} + \frac{f_0}{B} \tag{5}$$

or, alternatively

$$-\frac{v_1 - v_1^0}{\ln(\tau_c/\tau_{cr})} = \frac{f_0}{B}(v_1 - v_1^0) + \frac{f_0^2}{B\beta} \tag{6}$$

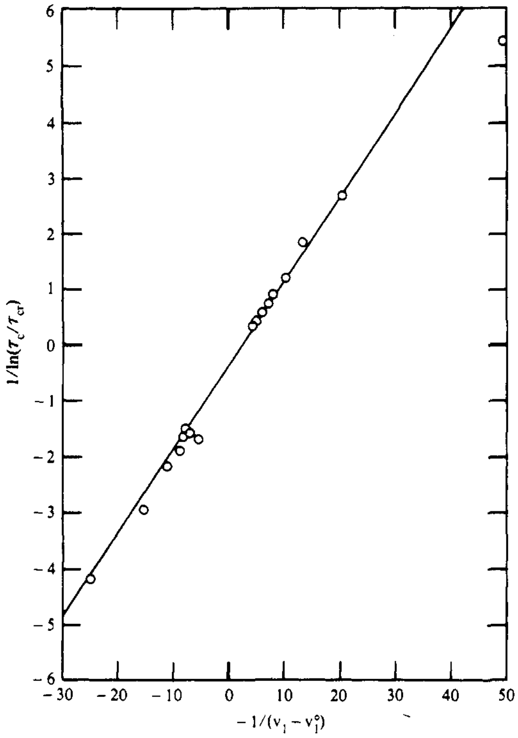


Figure 5. Fujita–Doolittle plot for the end-labeled DGEBA in DGEBA cured with DDH and plasticized with methylene chloride.

Thus, a plot of the left-hand side of eq 5 against $1/(v_1 - v_1{}^0)$ and also the left-hand side of eq 6 against $(v_1 - v_1{}^0)$ provides a critical test[13] for the applicability of the modified Fujita–Doolittle equation to the solvent dependence of the motional correlation time for the nitroxides.

Motional correlation times in the range $\tau_c \leqslant 3$ ns were evaluated from the EPR line shapes of the fast-phase spectra with the theory of Kivelson.[16] The equation used is

$$\tau_c = 4[(Y(0)/Y(1))^{1/2} + (Y(0)/Y(-1))^{1/2} - 2]b^{-2}[T_2(0)]^{-1} \tag{7}$$

with

$$b = (4\pi/3)[A_{zz} - \tfrac{1}{2}(A_{xx} + A_{yy})] \tag{8}$$

where $Y(1)$, $Y(0)$, and $Y(-1)$ are the peak-to-peak intensities of the low-, middle-, and high-field lines, A_{xx}, A_{yy}, and A_{zz} are the principal values of the nitrogen hyperfine interaction tensor, and $[T_2(0)]^{-1}$ is the line width of the center line.

The values of τ_c and v_1 were plotted in the forms shown in eq 5 and 6, and the results are illustrated in Figures 5 and 6. The linearity of the plots in both Figures 5 and 6 is strong evidence that the solvent-dependent data obey the modified form of the Fujita–Doolittle equation shown in eq 5.

The EPR line shapes for the PYRODDH label and the spin probe TEMPENE in DGEBA/DDH samples were also investigated as functions of the methylene chloride content. Both nitroxides in these systems exhibited the same behavior as the end label: at intermediate solvent contents the observed spectra appear to be composed of a superposition of a fast phase and a slow phase. The corresponding plots for τ_c for these nitroxides in the fast phase and v_1 are shown in Figures 7 and 8. The linearity of these plots indicates that the modified form of the Fujita–Doolittle equation shown in eq 5 fits the experimental data.

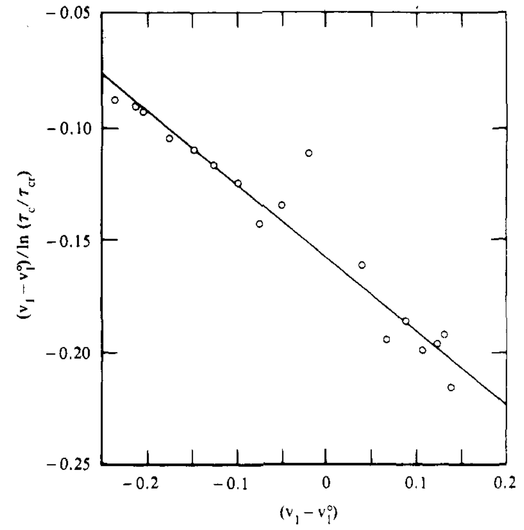


Figure 6. Alternative form for the Fujita–Doolittle plot for end-labeled DGEBA in DGEBA cured with DDH and plasticized with methylene chloride.

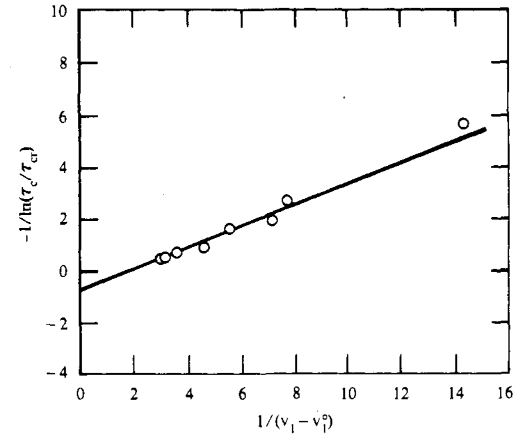


Figure 7. Fujita–Doolittle plot for samples of DGEBA cured with DDH containing the spin label PYRODDH and the solvent methylene chloride.

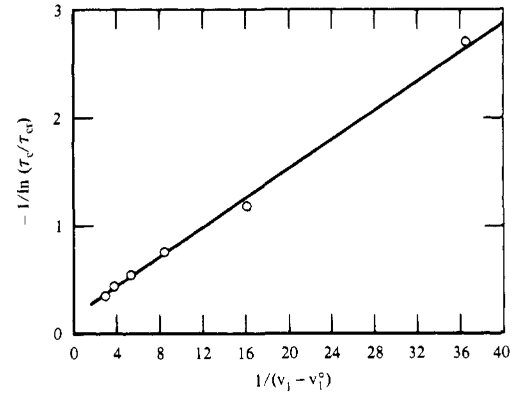


Figure 8. Fujita–Doolittle plot for TEMPENE in DGEBA cured with DDH plasticized with methylene chloride. Reference solvent volume fraction is 0.18.

The fractional amount of fast phase present (the mobile fraction) was determined as a function of methylene chloride content for both spin labels and the spin probe by measuring the areas under the fast-phase absorption spectrum and the total absorption spectrum. The results for the three nitroxides in the DGEBA/DDH system are shown in Figure 9.

For a given solvent content (e.g., a solvent volume fraction of 0.38) the motional correlation time for the spin

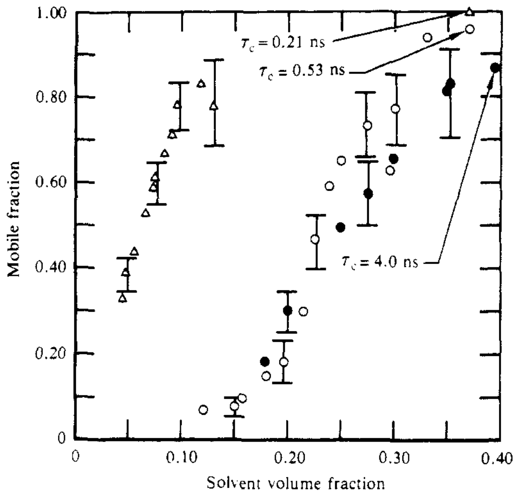


Figure 9. Mobile fraction as a function of solvent (methylene chloride) content for sample of DGEBA cured with DDH containing the end label (○), the bridging group label (●), and the spin probe TEMPENE (△).

probe TEMPENE (0.21 ns) is less than that for either spin label (0.53 and 4.0 ns). It is therefore not surprising that TEMPENE is more sensitive at low solvent contents to the plasticization of the DGEBA/DDH epoxy than the spin labels. For example, at a solvent volume fraction of 0.12 TEMPENE shows a mobile fraction of 0.8 whereas both labels show a 0 value.

We have studied nitroxides in epoxy polymers other than those described here. From all the results we have drawn the general conclusion that when a fast-phase spectrum characterized by $\tau_c \leq 3$ ns is observed, the nitroxide is located in a region that is above its macroscopic T_g value.

Discussion

According to the theory of Cohen and Turnbull,[17] the WLF equation[13] can be derived by assuming that molecular translational diffusion depends only on the free volume fluctuations adjacent to the diffusing molecule. Free volume added to the polymer by way of a plasticizing solvent should therefore affect the viscoelastic properties in the same manner as free volume added by way of an increase in temperature.[14] The corresponding relationship for samples containing plasticizing solvents, which is derived by assuming free volume changes only, is the Fujita–Doolittle equation (eq 1).

As described in the previous section, the motional correlation times for the two spin labels and the spin probe in DGEBA/DDH samples plasticized with methylene chloride show excellent agreement with the modified form of the Fujita–Doolittle equation shown in eq 5. We conclude that the agreement of the nitroxide data in the dry polymers with the modified WLF equation[18] and the agreement of the nitroxide data in the plasticized polymer with the modified Fujita–Doolittle equation indicate that the rotational motions of the nitroxides in polymers above T_g are sensitive to the free volume in the polymer. The question to be answered is why only one spectrum is present at each temperature in the dry sample but two spectra are present over a range of solvent contents in the plasticized polymers.

Our results can be reformulated in the following manner: the onset of the motional narrowing of the EPR line shapes can be crudely characterized by a temperature range δ_T and a critical temperature T_C. These parameters are defined in Figure 10a, where the solid line qualitatively depicts the typical form of the temperature dependence of the extrema splitting for a set of spin probes in identical environments in the polymer. Thus the value of δ_T is determined by the range of temperatures over which the motional narrowing occurs, whereas the value of T_C is determined by the temperature above which the motional correlation time is in the fast-motional regime; i.e., $\tau_c \lesssim 3$ ns. Although T_C may not correspond to T_g, the two are usually related because the spin probe motion is sensitive to changes in free volume and hence to the onset of the segmental motions.[18-21] A distribution in cross-link density implies that the spin probes in regions with different rigidities exhibit different values of T_C, e.g., T_{C1} and T_{C2} in Figure 10. Thus, a distribution in cross-link density results in a distribution in T_C values that can be characterized by a half-width Δ_T.

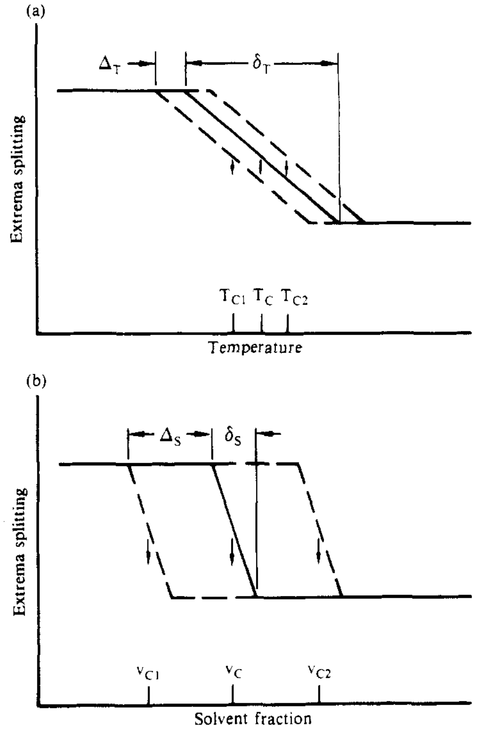


Figure 10. (a) Idealized temperature dependence of the extrema splitting with a distribution of critical temperatures T_{C1}, ..., T_{C2} with a half-width Δ_T, and (b) idealized solvent dependence of the extrema splitting with a distribution of critical solvent fractions v_{C1}, ..., v_{C2} with a half-width Δ_S.

The solvent dependence of the EPR line shapes can be characterized in an analogous manner; i.e., the motional correlation time is in the fast-motional regime for samples with solvent contents above a critical value v_C. Moreover, low cross-link density regions will be plasticized at low solvent contents so that the value of v_C in those regions (e.g., v_{C1} in Figure 10b) is less than that in a higher cross-link density region (v_{C2} in Figure 10b). In other words, a distribution in cross-link density produces a distribution in v_C values with half-width Δ_S. If one assumes that (a) T_C depends on only the free volume, (b) the free volume above T_g depends linearly on the temperature and the solvent content, and (c) the sorbed solvent is distributed homogeneously throughout the polymer, then it is not difficult to show that

$$\Delta_S/\delta_S = \Delta_T/\delta_T \qquad (9)$$

However, our experimental EPR data from the amine-cured epoxies are not consistent with this relation. The temperature dependences of the EPR line shapes indicate only a narrow distribution of motional correlation times at a given temperature. Our results imply that the relation

$\Delta_T/\delta_T < 1$ holds. On the other hand, the solvent dependence of the EPR line shapes indicates a distribution of motional correlation times that is more than 1.5 orders of magnitude wide for some solvent contents. This result implies that the relation $\Delta_S/\delta_S > 1$ holds.

Equation 9 can be reconciled with the above conclusions drawn from the experimental results in the following manner. In deriving eq 9 it was assumed that the solvent was dispersed uniformly and the plasticization was nonuniform only in as much as the rigid regions (more dense cross-linking) become rubbery at higher solvent contents than the less rigid regions. The EPR results indicate that the temperature-dependent and solvent-dependent results are different in nature. We therefore conclude that the solvent preferentially partitions into the low cross-linked regions. As a result, the lowest cross-link density regions, which have the greatest free volume in the dry polymer, have even greater free volume content relative to the rest of the polymer following the addition of solvent. The overall effect of the solvent plasticizer is to enhance the differences in rigidity and hence nitroxide mobility in the polymers so that microstructural features not observable on varying the temperature are apparent on varying the solvent plasticizer content. The solvent partitioning therefore produces an increase in Δ_S so that $\Delta_S/\delta_S \gtrsim 1$. Such a partitioning of solvent among the different microstructural regions is not surprising since it is known that polymers having high average cross-link densities are swelled by solvents to a lesser extent than chemically similar polymers with lower cross-link density.[22]

Measurements on samples of DGEBA/DDH using differential scanning calorimetry show that the T_g can be reduced to room temperature with $\lesssim 5$ wt % methylene chloride. The motional correlation times for both spin labels in the fast phase were plotted as a function of solvent content, and the results were extrapolated to 5 wt % solvent content. In both cases the motional correlation times are estimated to be ≈ 10 ns. This value is 8 orders of magnitude smaller than the correlation time associated with the main-chain segmental motions at the glass transition. We conclude that the motions of the end label and the bridging labels in the fast phase are determined mainly by a solvent-dependent local mode[11,23] located in the polymer network only a few bonds away from the attached nitroxide. Such a local mode has already been identified in amine-cured epoxy networks from dynamic mechanical data. In this study[23] the β-relaxation transition was attributed to a solvent-dependent crankshaft motion of the glycidyl group.

An inspection of the line shapes for the end label in the dry cured epoxy (Figure 2) shows that at 429 K the intensity of the low-field line is $\approx 20\%$ greater than that of the center line. This feature is usually the result of anisotropy in the nitroxide motions;[24] i.e., the rotational rate about one axis is different from that about a perpendicular axis. On the other hand, as shown in Figure 3, at all solvent contents the low-field line is always less intense than the middle line. Thus, the nitroxide motion is more isotropic in the plasticized sample than in the dry sample. It seems reasonable to expect that a localized mode would result in isotropic motion of a nearby spin label.

The original motivation for using the PYRODDH bridging label was that a nitroxide at the end of a flexible chain might prove to be more sensitive to plasticization effects than a label like the METAMIN quaternary base label,[9,10] which is bound more tightly to the polymer network. It is possible, however, that the carbonyl group is hydrogen bonded either to the intramolecular hydroxyl group or to a hydroxyl group located on a neighboring epoxy chain. In either case, the mobility of the nitroxide group is reduced and the effects of a local mode on this flexible chain are suppressed. Evidence for the hydrogen bonding is also contained in the motional anisotropy. In the uncured resin at 365 K the intensity of the low-field line for the spin label is $\approx 7\%$ larger than the center line. Moreover, as shown in Figure 9, despite the flexible chain the PYRODDH bridging label is less mobile ($\tau_c = 4.0$ ns at 37% solvent content) than the end label ($\tau_c = 0.53$ ns at 36% solvent content).

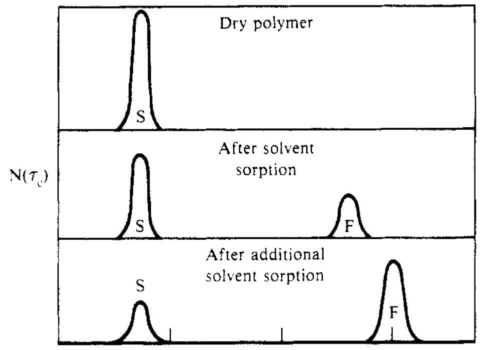
The motional correlation time for TEMPENE in the DGEBA/DDH system containing ≈ 5 wt % methylene chloride is also ≈ 10 ns. However, because of the lack of covalent bonding to the polymer network, there are fewer constraints on the motion of the spin probe, and the motional correlation time for the spin probe need not equal that of the polymer. We can only conclude that the rotational motion of the spin probe in the fast phase is determined by free volume in areas associated with segmental motions of the polymer network and/or local mode motions.

It is known from previous work[25,26] that the rate for translational diffusion of nitroxide spin probes in rubbery regions is fast. Furthermore, if the rate for translational diffusion across the interphase between the rubbery and rigid regions is also fast, the spin probes partition between the two regions. The temperature-dependent equilibrium involving the numbers of spin probes present in the rubbery and rigid regions determines the EPR line shapes. In particular, the mobile fraction evaluated from the relative areas under the fast-phase and slow-phase absorption spectrum is then determined by the heat of solution of the spin probe in the rigid and rubbery regions.[25]

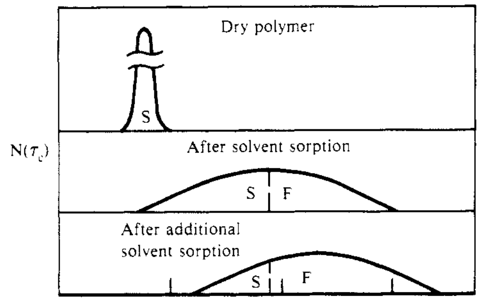
In the case of the spin probes, the possibility of translational diffusion from the plasticized rubbery regions to the rigid regions cannot be ruled out completely. The rate for this translational diffusion probably depends on the amount of solvent in the rigid region. It is clear, however, that the two spin labels studied are prevented from undergoing large-scale translational diffusion because of the constraints imposed by the covalent binding. As more solvent is absorbed the spin label goes from the slow to the fast phase when the frequency of the local mode is $\approx 2 \times 10^8$ s^{-1}. This frequency should depend on the total solvent uptake, the solvent partitioning, the size of the side groups close to the local mode (including the spin label), and the chain rigidity in the region of the local mode. This chain rigidity should depend on cross-link density, and the solvent should partition preferentially into the regions with lowest cross-link density. Hence, as the solvent uptake increases, the spin labels in the regions with increasing cross-link density progressively become part of the fast phase. Therefore, for a given spin label and a given solvent content, the value of the mobile fraction represents the relative amount of material with a cross-link density less than a certain value that has become plasticized by the solvent. The mobile fraction is thus a crude measure of the distribution of cross-link density in the network.

In the three-dimensional random network associated with the cured epoxy system, one can expect to find regions with a distribution of cross-link densities. Consequently, we might expect to observe a distribution of motional correlation times for nitroxide spin labels and spin probes in either dry or plasticized epoxies. Two points should be made concerning our results. First, the temperature dependence of the nitroxide line shapes in the dry samples indicates that the distribution of motional correlation times

(a) Bimodal distribution



(b) Monomodal distribution



(c) Bimodal-like distribution

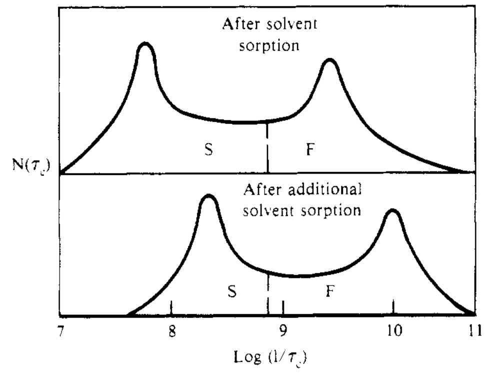


Figure 11. Assumed solvent dependence of the distribution function $N(\tau_c)$ for the nitroxide motional correlation time τ_c assuming (a) a bimodal distribution, (b) a wide monomodal distribution, and (c) a bimodal-like distribution. The total areas under each distribution function remain constant after solvent sorption. The areas designated S and F represent the amount of nitroxide in the slow and fast phases, respectively.

is not wide enough to show up in these line shapes. Second, the exact form of the distribution function for the nitroxide motional correlation times in the plasticized epoxies depends on the details of the solvent partitioning process. The two extreme cases considered are illustrated in Figure 11a,b: (a) a bimodal distribution and (b) a broad monomodal distribution.

The bimodal distribution (Figure 11a) implies that the solvent is initially selectively absorbed into the low cross-linked regions with no solvent sorption in the more extensively cross-linked regions. As the solvent uptake increases, the plasticized regions absorb more solvent to become more mobile and the fast-phase nitroxides move to higher frequencies in accordance with the modified form of the Fujita–Doolittle equation. At the same time, some of the more extensively cross-linked regions become plasticized and the nitroxides located there become part of the fast phase. No solvent uptake in the rigid regions implies no shift in the motional correlation time for the spin labels in the slow phase. This solvent uptake process by the sample proceeds until all regions are plasticized and all nitroxides are in the fast phase.

The broad monomodal distribution shown in Figure 11b is probably a more realistic behavior. The solvent absorption by the sample occurs in all regions but to different extents depending on the cross-link density. As the solvent uptake increases, the amount of solvent in every region increases and the distribution of motional correlation times moves to higher frequencies. The amount of nitroxide in the slow (S) and fast phases (F) is given by the areas under the distribution function designated S and F in Figure 11b, i.e., the nitroxides with motional frequencies less than or greater than 2×10^8 s^{-1}. The observed line shapes are given by the weighted sum of all contributions represented by the distribution function, but to a good approximation the observed line shape can be characterized by the superposition of a slow-phase and a fast-phase spectrum.[27,28]

There may be polymer systems that exhibit either of the above extreme types of plasticization behavior. Moreover, the distribution function may change shape with increasing solvent content and at some values may show the bimodal-like shape shown in Figure 11c. To date, we have insufficient evidence to identify confidently the exact form of the distribution function for the nitroxide motional correlation times in the amine-cured epoxies.

In their treatment of motional correlation time distributions in polymers, Kaplan and Garroway[29] have distinguished between two types of distribution functions, viz., "inhomogeneous" and "homogeneous", that arise in two fundamentally different ways. In the inhomogeneous distribution there is a spatial distribution of sites such that at each site the motion can be characterized by a single value of the motional correlation time (i.e., an exponentially decaying autocorrelation function), but this value can vary from site to site. On the other hand, in the homogeneous distribution the autocorrelation function at each site is the same, but it is nonexponential and hence can also be described by a distribution of exponential autocorrelation functions. Computer simulations of the NMR line shapes for spins undergoing chemical exchange show that the type of distribution can be identified from details in the line shape behavior with increasing exchange rates. The main distinctive feature produced by the inhomogeneous distribution is the superposition of a motionally narrowed central peak arising from spins at sites that have fast correlation times and the broader peaks associated with spins located at sites with slower correlation times. We have considered only inhomogeneous distributions in explaining the nitroxide EPR line shapes reported here. The fact that to a good approximation the line shapes of the nitroxides in the plasticized samples can be considered as the superposition of a fast-phase and a slow-phase spectrum would seem to justify this approach.

Conclusions

We have interpreted the composite nature of the EPR spectrum observed in cured epoxy samples containing either spin labels or spin probes and certain solvent plasticizer contents as indicating the presence of regions with different cross-link densities. The fast-phase spectrum is attributed to nitroxides in regions of low cross-link density, whereas the slow-phase spectrum is assigned to nitroxides in regions of higher cross-link density. The differences in nitroxide mobility are enhanced by a selective plasticization of the low cross-linked regions. Any or all of the following factors could be responsible for the observed inhomogeneous nature of the polymer network: (a) insufficient mixing of the epoxy and amine components necessary to provide uniform concentrations at a molecular level, (b) phase separation of the uncured components from the gel network, and (c) sterically imposed incompleteness of the curing reactions so that either unreacted epoxy or unreacted amine groups are trapped in the cured epoxy network.

Acknowledgment. This research was conducted in part under Naval Air Systems Command Contract N00019-79-C-0414 and in part under the McDonnell Douglas Independent Research and Development program.

Registry No. DGEBA (homopolymer), 25085-99-8; DDH, 13093-04-4; METAMIN, 42585-33-1; PYRODDH, 87655-74-1; TEMPENE, 2564-83-2.

References and Notes

(1) Kenyon, A. S.; Nielsen, L. E. *J. Macromol. Sci.* **1976**, *A3*, 275.
(2) Cuthrell, R. E. *J. Appl. Polym. Sci.* **1967**, *11*, 949.
(3) Racich, J. L.; Koutsky, J. A. *J. Appl. Polym. Sci.* **1976**, *20*, 2111.
(4) Mijovic, J. S.; Koutsky, J. A. *J. Appl. Polym. Sci.* **1979**, *23*, 1037.
(5) Mijovic, J.; Koutsky, J. A. *Polymer* **1979**, *20*, 1095.
(6) Maty, R. J.; Uhlmann, D. R.; Koutsky, J. A. *J. Polym. Sci.* **1980**, *18*, 1053.
(7) Morgan, R. J.; O'Neal, J. E. *J. Mater. Sci.* **1977**, *12*, 1966.
(8) Berliner, L. J., Ed. "Spin Labeling: Theory and Applications"; Academic Press: New York, 1976.
(9) Brown, I. M.; Sandreczki, T. C. *Chem. Phys. Lett.* **1979**, *64*, 85.
(10) Brown, I. M.; Sandreczki, T. C. *Macromolecules* **1983**, *16*, 1890.
(11) Veksli, Z.; Miller, W. G. *Macromolecules* **1977**, *10*, 686.
(12) Veksli, Z.; Miller, W. G. *Macromolecules* **1977**, *10*, 1245.
(13) Ferry, J. D. "Viscoelastic Properties of Polymers"; Wiley: New York, 1980.
(14) Fujita, H.; Kishimoto, A. *J. Chem. Phys.* **1961**, *34*, 393.
(15) Doolittle, A. K.; Doolittle, D. B. *J. Appl. Phys.* **1957**, *28*, 901.
(16) Kivelson, D. *J. Chem. Phys.* **1960**, *33*, 1094.
(17) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164.
(18) Sandreczki, T. C.; Brown, I. M. *Macromolecules* **1984**, *17*, 1789.
(19) Rabold, G. P. *J. Polym. Sci., Part A-1* **1969**, *7*, 1203.
(20) Kumler, P. L.; Boyer, R. F. *Macromolecules* **1976**, *9*, 903.
(21) Buchachenko, A. L.; Kovarskii, A. L.; Wasserman, A. M. "Advances in Polymer Science"; Rogovin, Z. A., Ed.; Halsted Press: New York, 1976.
(22) Flory, P. J.; Rehner, J. *J. Chem. Phys.* **1943**, *11*, 521.
(23) Keenan, J. D.; Seferis, J. C.; Quinlivan, J. T. *J. Appl. Polym. Sci.* **1979**, *24*, 2375.
(24) Miller, W. G. "Spin Labeling"; Berliner, L., Ed.; Academic Press: New York, 1980; Vol. II.
(25) Brown, I. M. *Macromolecules* **1981**, *14*, 801.
(26) Lee, S.; Brown, I. M. *Macromolecules* **1979**, *12*, 1235.
(27) Resing, H. A. *J. Chem. Phys.* **1965**, *43*, 669.
(28) Miller, W. G., private communication.
(29) Kaplan, J. I.; Garroway, A. N. *J. Magn. Reson.* **1982**, *49*, 464.

NMR Study of Nematic Order of Semiflexible Thermotropic Polymers

Sergio Bruckner,[†] J. Campbell Scott, and Do Y. Yoon*

IBM Research Laboratory, San Jose, California 95193

Anselm C. Griffin

Department of Chemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406. *Received March 4, 1985*

ABSTRACT: Chain conformations and orientational order parameters in the nematic state of the deuterium-labeled thermotropic polyester $(C_{10}D_{20}OC_6H_4COOC_6H_4OC_{10}D_{20}OC_6H_4OOCC_6H_4O)_x$ are determined by deuterium (D) NMR and H NMR methods. The D NMR spectra show one quadrupole splitting in the nematic state, indicating that only a specific set of chain conformations are admitted for $C_{10}D_{20}$ spacer groups. They are found to comprise those conformers that place every second bond starting from the OCD_2 attached to the rigid (phenylene) unit almost exclusively in the trans state. From the magnitudes of quadrupole splittings, the orientational order parameters of chain segments, the alignment axis of which virtually coincides with the axis of rigid (phenylene) units for these conformers, are found to fall around 0.8 and extrapolate to ca. 0.75 at the nematic–isotropic transition. Separate determination of orientational order parameters of the rigid aromatic units from H NMR dipolar splittings yields the order parameters in excellent agreement with those derived from D NMR results, and thus validates our interpretation of D NMR spectra in terms of the specific conformational order. The conformational order thus elucidated by NMR study therefore supports the previous conclusion of Yoon and Bruckner, who proposed that the poly(methylene) spacers assume highly extended configurations in the nematic state upon considering the enthalpies and the entropies of isotropic–nematic transitions of thermotropic polymers comprising rigid groups connected by poly(methylenes).

Introduction

The molecular order in the liquid crystalline state of polymers has been the subject of a considerable number of publications in recent years.[1–7] For polymer liquid crystals the specific questions are concerned not only with the orientational order parameter, which is well studied for monomer liquid crystals, but more importantly with the ordering, or selection, of chain conformations for the flexible sequences in the liquid crystalline state.[20]

A number of experimental results point to rather high degree of conformational and orientational order in polymeric nematogens, compared to those of their monomeric counterparts. For example, polymeric nematogens comprising poly(methylene) spacers exhibit much larger enthalpy and entropy changes at isotropic–nematic transitions as well as greater oscillations in clearing temperatures with the even–odd alternation of the number of methylene units of the spacers.[4,8,9] In a recent paper[1] (which will be designated as I hereafter) Yoon and Bruckner, upon comparing the isotropic–nematic transition characteristics with the distribution of chain sequence extension, concluded that the stability of the nematic state and the concomitant

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[†] IBM World Trade Postdoctoral Fellow. Permanent address: Dipartimento di Chimica, Politecnico di Milano, Milan, Italy.