stiffness retention improves with increasing λ.

(3) The dynamic mechanical relaxation spectra of these films revealed that the low-temperature γ peak is very weak or absent.

(4) The β-relaxation peak diminishes in intensity and the peak position shifts to lower temperature with increasing draw ratio. Drawing increases the crystallinity of the specimens and thus causes a reduction of the interlamellar content which leads to a decreased peak intensity. It is proposed that the shift to lower temperature is associated with the relaxation of the stretching-induced residual strains of molecules located in the intercrystalline regions. The activation energy for the β-relaxation process for these solution-crystallized specimens is comparable to that of conventional melt-crystallized samples. This is due to physical constraints, such as increased orientation and tautness of tie molecules, imposed on the sample due to drawing.

(5) The α relaxation involves a single mechanism as evident from a sharp rise in tan δ with temperature and the presence of a single peak in the loss modulus (E'') curves. The average activation energy (53 kcal/mol) for this process is comparable to the values obtained for melt-crystallized PP. It is suggested that, although for undrawn and lightly drawn PP films lamellar reorientation may take place, for the highly drawn PP films the α process involves intracrystalline chain motions only.

Registry No. Polypropylene, 9003-07-0.

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Motional Behavior and Correlation Times of Nitroxide Spin Probes in Polymers above and below the Glass Transition

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ABSTRACT: The reorientational motions of nitroxide spin probes have been investigated in several polymers above and below the glass transition temperature, T_g. Three amine-cured epoxy resins having different cross-link densities and the thermoplastics bisphenol A polycarbonate and poly(dimethylphenylene oxide) were studied. At sub-T_g temperatures from 100 to 300 K the reorientational correlation times were the same for two small spherical probes and one large cylindrical probe in all the epoxy systems. Below T_g the activation energies for the nitroxide correlation times were typically ~11 kJ/mol, whereas above T_g the corresponding value was 24 kJ/mol after a correction for temperature-dependent changes in free volume. This result is explained in terms of differences in amplitudes of the motions (i.e., whether the motions involve restricted or unrestricted rotational diffusion) and differences in the coupling of the probe motions to the matrix motions below and above T_g.

Introduction

It is well-known that the mechanical, thermal, and transport properties of polymers change markedly in the region of the glass transition temperature, T_g. Such properties include the elastic moduli, the hardness, and the thermal expansion coefficients, as well as the translational diffusion coefficients for small molecules. These changes in polymer properties are related to the nature of the molecular motions above and below T_g.[1,2] For example, above T_g, where the motions of a polymer segment are rapid and correlated with the motions of surrounding segments, the polymer responds mechanically as a viscous liquid or a viscoelastic solid. On the other hand, below T_g, where the segmental motions are more localized and less cooperative,[1,3] the polymer exhibits the properties of a rigid glassy solid. At still lower temperatures, below the sub-T_g β transition, where even these noncooperative motions cease to be active at any significant rate, polymers tend to be even more brittle.

To understand this relationship between the macroscopic properties and the polymeric motions in more detail, we are exploring the dependence of molecular motion on temperature and fractional free-volume content[1,4] in polymers. In this paper we describe the results of some electron paramagnetic resonance (EPR) experiments which involve the measurement of another molecular parameter both below and above T_g, namely, the motional correlation time, τ_c, for the reorientational motions of small para-

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magnetic molecules that are dissolved in the polymer. In the present study, a series of amine-cured thermosetting epoxies and the two thermoplastics, bisphenol A polycarbonate and poly(dimethylphenylene oxide), were investigated. The approach taken employs the use of spin probes, where the nitroxide is unbound in the polymer, to provide information about the host polymer at the molecular level. This information can be determined from the temperature,[4] solvent,[5] pressure,[6,7] or probe size[8,9] dependences of the nitroxide motional correlation time.

The EPR line shapes of an unbounded nitroxide radical dissolved in a polymer show that even 150 K below T_g it undergoes reorientational motions. The nitroxide τ_c values can be determined accurately and reliably from the experimentally observed EPR line shapes over the two different ranges of values $5 \times 10^{-9} > \tau_c > 10^{-11}$ s and $10^{-5} > \tau_c > 10^{-7}$ s. In the former range, the motions are in the so-called fast-motional region and the τ_c values can be determined by using established theories[10] with or without some slight corrections for inhomogeneous line broadening.[11] Observation of the motionally collapsed spectrum verifies that the nitroxide samples all possible orientations in a time T_2, the electron spin–spin relaxation time; thus it is not surprising that the fast-motional region typically occurs at temperatures above the T_g of the host polymer. In the latter range, the slow-motional region, the τ_c values can be determined either analytically[12] or by computer simulation[13] of the line shapes. The line shape retains many of the features observed from a collection of randomly oriented, immobilized nitroxide molecules but in addition shows subtle changes in line widths and line positions as a result of the slow motions. It is difficult, however, to ascertain from the observed line shapes whether the nitroxide reorients by restricted or unrestricted rotational diffusion.[14] In this study the difficulty in determining the type of probe motion was addressed by employing nitroxides with different geometrical shapes and sizes in the different polymer matrices.

Experimental Section

The epoxy samples were made from the diglycidyl ether of bisphenol A (DGEBA) obtained from Dow Chemical Co. (DER332) and the aliphatic amine curing agents *N,N'*-dimethyl-1,6-diaminohexane (DDH) and 1,4-diaminobutane (DAB) obtained from Aldrich Chemical Co. These curing agents are difunctional and tetrafunctional, respectively, and were used separately and in a 1:1 ratio, by equivalents, to produce cured samples having different cross-link densities. Thus, the samples had the following equivalent ratios of DAB/DDH/DGEBA: 2:0:2, 1:1:2, and 0:2:2. Their T_g values, as measured by using a Du Pont 942 dilatometer, were 303, 335, and 396 K, respectively. A fourth epoxy sample was prepared by mixing equivalent amounts of DGEBA and the curing agent diethylenetriamine (DETA) obtained from Eastman Kodak Co. The samples were typically cured overnight at room temperature in closed containers and were then postcured at 368 K for 1 h. This postcuring was above T_g for the 0:2:2 and 1:1:2 samples but below T_g for the 2:0:2 and DETA/DGEBA samples, which were therefore subsequently postcured another 15 min at 413 K (T_g + 18 K) and 418 K (T_g + 17 K), respectively.

Bisphenol A polycarbonate (polycarbonate; Aldrich) was prepared for investigation by heating to 553 K (above the crystalline melting point) for 6 min and cooling to below T_g (418 K) over a 2-min period. The material was an amorphous glass following this treatment.

The spin probes employed (see Figure 1) were 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl-d_{17} (TANOLD), 2,2,6,6-tetramethyl-1,2,3,6-tetrahydropyridine-1-oxyl-d_{16} (TEMPENED), DOXYL cholestane (DOC), and di-*tert*-butyl nitroxide (DBNO). TANOLD was obtained from Merck Sharp and Dohme, TEMPENED and DOC were obtained from Molecular Probes, and DBNO was obtained from Eastman Kodak Co. TANOLD, TEMPENED, and DOC were used in the epoxy samples and were introduced by dissolution in the DGEBA resin prior to curing. Concentrations of 0.1–0.2 wt % nitroxide were used for the sub-T_g experiments, and concentrations of 0.03 to 0.08 wt % were used above T_g. DBNO was used in the polycarbonate matrix. In this case, approximately 0.2-μm-thick shavings of polycarbonate were sealed in a vial along with 0.1–0.2 wt % DBNO and heated to 433 K (i.e., T_g + 15 K) to vaporize the DBNO and force it to diffuse into the polycarbonate. The average concentration of DBNO in the polycarbonate was <0.1 wt % by following this procedure.

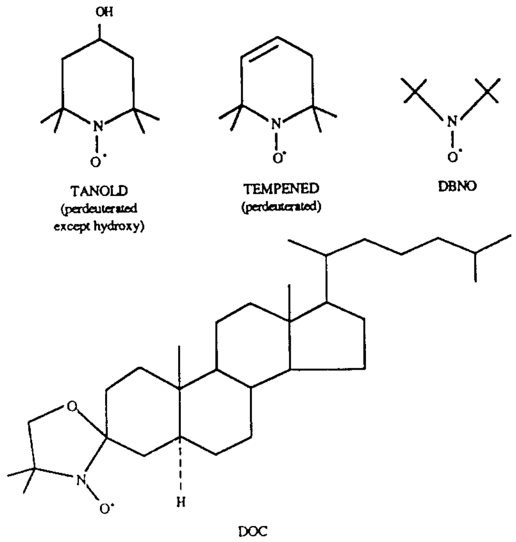

Figure 1. Spin probes used in this work.

A glassy sample of poly(dimethylphenylene oxide) (PDMPO; Scientific Polymer Products) containing approximately 0.2 wt % TANOLD was also prepared. The PDMPO and TANOLD were dissolved together in chloroform, which was then allowed to evaporate. The resulting polycrystalline material was heated to 543 K in a nitrogen atmosphere for 4 min and then cooled to ambient temperature over a 2-min period. (The resulting glassy sample gave a decreased EPR signal due to partial TANOLD decomposition during the procedure.)

EPR data were collected with an IBM Instruments ER/200D EPR spectrometer interfaced with an IBM-9001 computer. Data acquisition and analysis were performed by use of an accompanying EPR software package. Spectra recorded above T_g and most spectra recorded below T_g were first-derivative spectra obtained as a result of 100-kHz magnetic field modulation. Second-derivative spectra generated from first-derivative spectra with computer software facilitated measurement of sub-T_g spectral line widths. Some second-derivative spectra had poor signal-to-noise; so in a few cases, line widths of second-derivative spectra were analyzed on a VAX 780 computer by fitting polynomial curves to sections surrounding the maxima and minima of the individual spectral lines. Absolute line positions, corrected for changes in spectrometer frequency, were determined with the ER-035M NMR gaussmeter from IBM Instruments and the Model 575 Microwave Counter from EIP Microwave, Inc. Magnetic fields were measured to 10^{-3} mT, and frequency was measured to within 10 kHz in these experiments.

Results

Sub-T_g Results. In the slow-motion region, the effects of probe reorientational motions were investigated by measuring the dynamic shifts and line widths of the EPR spectra. These shifts were determined by measuring the magnetic field positions of the parallel-edge lines of the powder-pattern spectra after a correction was made for the temperature-dependent frequency shift of the cavity containing the sample. As shown in Figure 2, these shifts are defined as the differences between these field values and the corresponding values obtained in the rigid limit, i.e., when there is no reorientational motion of the nitroxide. The definitions of the widths also shown in Figure 2 are

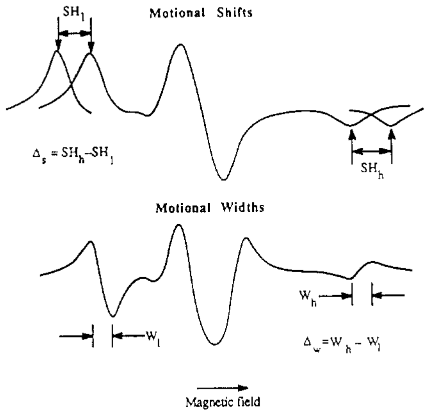

Figure 2. Definitions of spectral shifts and line widths.

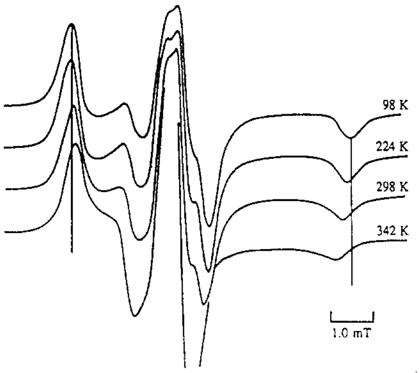

Figure 3. Sub-T_g spectra from TANOLD in 0:2:2 DAB/DDH/DGEBA.

the peak-to-peak widths of the second-derivative line shapes of the parallel-edge lines.

The exact expressions used to evaluate τ_c were taken from the theory of Kivelson and Lee[12] and are of the form

$$\Delta_s = A[(|B + C|^{1/2} - |B - C|^{1/2})]\tau_c^{-1/2} \qquad (1)$$

with

$$A = h^{1/2}/(200^{1/4}\pi^{1/2}g_{\parallel}\beta) \qquad (1a)$$

$$B = h\nu(g^2_{\perp} - g^2_{\parallel})/g^2_{\parallel} \qquad (1b)$$

and

$$C = (A^2_{\perp} - A^2_{\parallel})/A_{\parallel} \qquad (1c)$$

where $g_{\parallel}$ and $g_{\perp}$ and $A_{\parallel}$ and $A_{\perp}$ are the principal components of the g-tensor and the nitrogen hyperfine tensor, respectively.

The EPR line shapes of TANOLD in the three amine-cured epoxy samples with DAB/DDH/DGEBA having the values 0:2:2, 1:1:2, and 2:0:2 were studied from 77 to 345 K. As is shown in Figure 3 for a typical series of spectra, when the temperature is increased above ~100 K, the low-field and the high-field parallel-edge lines move inward from their rigid-limit field values. Over the temperature range from 100 to >300 K, the Δ_s values for TANOLD in the 0:2:2, 1:1:2, and 2:0:2 epoxy samples typically increased from initial values of <0.01 mT to final values of >0.07 mT.

If it is assumed that τ_c has an Arrhenius temperature dependence, then because of eq 1, Δ_s has a temperature dependence of the form

$$\Delta_s = \Delta_0 \exp(-E_b/2RT) + \Delta_1 \qquad (2)$$

where E_b is the activation energy for probe reorientational motion below T_g, Δ_0 is the preexponential factor, and Δ_1 is a constant offset to account for the uncertainty in the rigid-limit values of the high- and low-field peak positions.

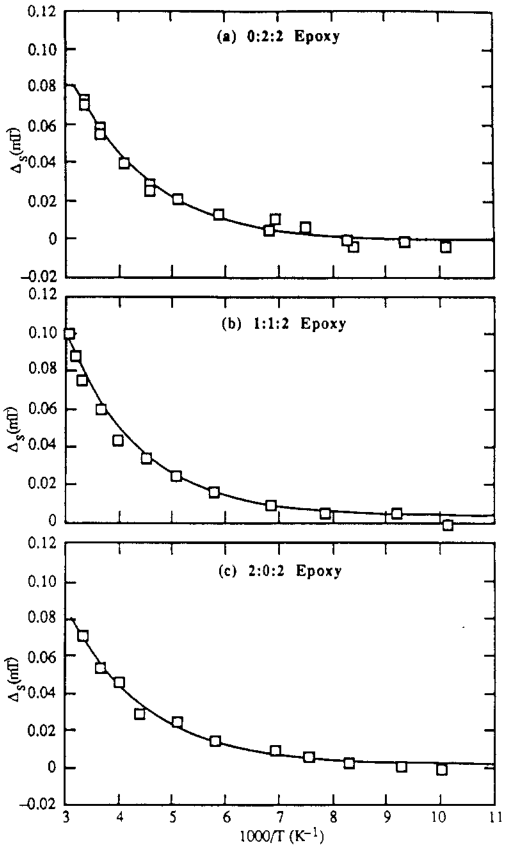

Figure 4. Δ_s versus $1000/T$ for TANOLD in DAB/DDH/DGEBA samples: (a) 0:2:2; (b) 1:1:2; (c) 2:0:2.

Table I
Activation Energies for Spin Probes in Epoxy Samples

spin probe	polymer	ΔE_b,[a] kJ/mol	ΔE_a,[b] kJ/mol	ΔE_a,[c] kJ/mol
TANOLD	0:2:2	11.5	67	24
	1:1:2	11.5	76	24
	2:0:2	11.5	94	24
TEMPENED	2:0:2	10		
DOC	DETA/ DGEBA	10.5		

[a] Below T_g. [b] Above T_g, corrected for inhomogeneous broadening. [c] Above T_g, corrected for changes in free volume; single average calculated for all TANOLD samples.

Plots of the temperature dependence of Δ_s in the three samples are shown in Figure 4. Equation 2 was fit to the data by use of variable parameters for Δ_0, Δ_1, and E_b. The values of E_b evaluated from the data are listed in Table I where it can be seen that the three values for the TANOLD spin probe are 11.5 ± 1.5 kJ/mol. This value is somewhat higher than those values determined by Kovarskii et al.[15] for similar spin probes in polymers at temperatures below T_g (3.8–8.8 kJ/mol). This disagreement may in part arise because Kovarskii et al. used a calibration plot derived from a jump diffusion model, whereas eq 1 was derived by assuming Brownian diffusion.[12] According to Goldman et al.[16] the consequence of assuming other than Brownian diffusion is the introduction of an exponent less than $-^1/_2$ for τ_c in eq 1, resulting in a correspondingly lower value for E_b. The important point in the present work is that E_b is no larger than ~11.5 kJ/mol.

The same measurements were also made by using the spin probe TEMPENED in the 2:0:2 epoxy sample. Analysis of these data (Figure 5a) yields a value E_b = 10

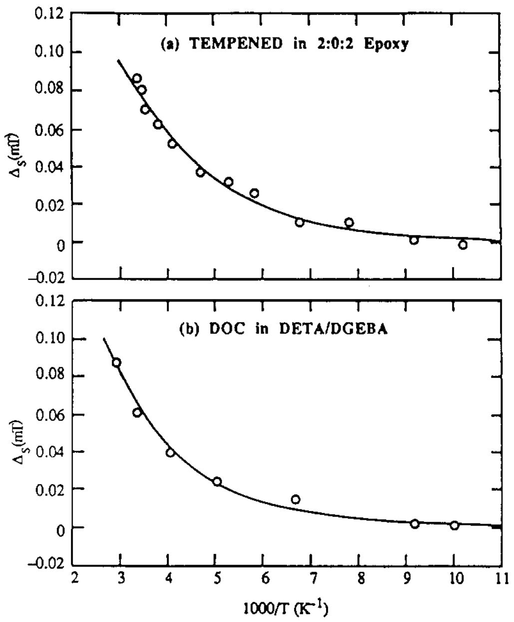

Figure 5. Δ_s versus $1000/T$ for (a) TEMPENED in 2:0:2 sample and (b) DOC in DETA/DGEBA.

± 1.5 kJ/mol. Since this probe lacks the hydroxyl group which is a potential hydrogen-bonding site, it might be expected to have an activation energy for reorientational motion somewhat less than that for TANOLD.

Samples of DGEBA cured with stoichiometric amounts of DETA containing the spin probe DOXYL cholestane (DOC) were also investigated. Since DOC is a cylindrical molecule with a length-to-diameter aspect ratio of approximately 3, its rotational motion about an axis perpendicular to the cylindrical axis will be restricted when it is in a highly cross-linked polymer like DGEBA/DETA below T_g. The reorientational motions will preferentially average the A and g tensors in one plane and might be expected to produce a different sequence of spectral collapse from that shown in Figure 3 for TANOLD. (Spin-labeled poly(benzyl glutamate) is an example of a nitroxide undergoing extremely anisotropic rotational motions that are evident from the temperature dependence of the EPR line shapes.[17]) However, the observed spectral collapse for DOC was essentially the same as that shown by the smaller, nearly spherical probes TEMPENED and TANOLD. The corresponding line-shift data plotted in Figure 5b yield a value of E_b = 10.5 ± 1.5 kJ/mol.

The values of the motional correlation times were determined from the Δ_s values using eq 1 and the results for all five nitroxide/epoxy polymer systems are plotted in Figure 6. At any given temperature the values of τ_c for all five systems are the same within experimental error. These values appear to be slightly longer than those reported for TANOLD in bisphenol A polycarbonate where E_b was found to be 8.5 kJ/mol.[18] The difference in these E_b values is consistent with results obtained by using positron annihilation spectroscopy where unusually long lifetimes for trapped ortho positronium indicate that there is more free volume in the polycarbonate than in the epoxies.[19,20] It seems reasonable to argue that larger free volumes, and, hence larger average hole sizes, should result in lower values for the barrier to reorientational motions for the spin probe.

The motional correlation times were also evaluated from the differences in the widths of the parallel-edge lines in the second-derivative spectra. The expression used was[12]

$$\Delta_w = (50/27)^{1/2}\Delta_s \qquad (3)$$

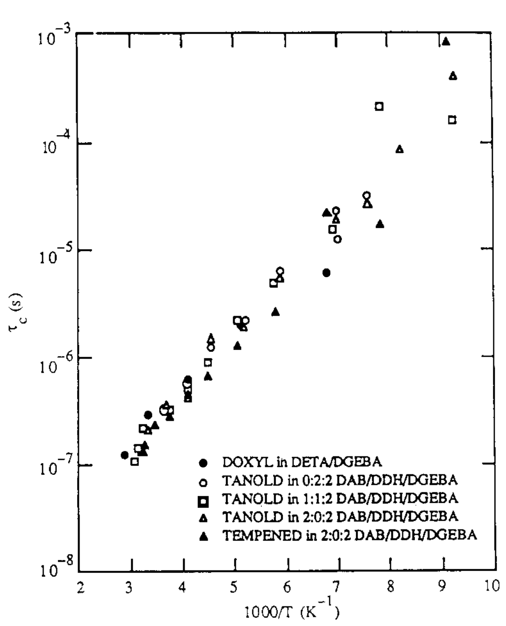

Figure 6. Arrhenius plots of τ_c for spin probes in sub-T_g epoxies.

In this equation, $\Delta_w = W_h - W_l$, where W_h and W_l are the peak-to-peak second-derivative line widths shown in Figure 2 and Δ_s is defined by eq 1. These widths were measured as a function of temperature in three nitroxide/epoxy samples: TANOLD in 0:2:2, TEMPENE in 0:2:2, and TANOLD in 2:0:2. In each case, at temperatures near 300 K, the τ_c values were smaller than those evaluated from the differences in the dynamic line shifts. Moreover, at 77 K where the line shifts indicated that the probes were immobile, there remained a residual difference between the widths of the low-field and high-field parallel-edge lines contrary to the theoretical predictions.[12] Although the exact reason for these anomalous widths is not known conclusively, they can be understood in terms of a distribution in the polarities of the probe environments. Environmental polarity can affect the nitroxide **g** and **A** tensors[21,22] in such a way that contributions from $g_\parallel$ and $A_\parallel$ to the parallel-edge lines can be additive on the high-field line but cancel on the low-field line to produce a residual difference in widths at low temperatures. This difference, observed when the nitroxide is known to be immobile, can be considered a measure of the distribution in polarities of the nitroxide environments in the polymer.

As the results in Figure 6 and Table I show, in the epoxy samples at sub-T_g temperatures, the motional correlation times and the barriers to reorientation for the three spin probes TANOLD, TEMPENED, and DOC all have values that are nearly independent of the actual spin probe and host matrix studied. This independence exists despite the differences in shape and size of these nitroxide molecules and despite the differences in cross-link density in the host polymers. We believe that the explanation for this surprising result may lie in the exact nature of the reorientational motions.

We have considered the experimental evidence indicating whether a spin probe is undergoing either unrestricted or restricted rotational diffusion[14] in a polymer below T_g. Unfortunately, it is not possible to distinguish between these two types of motion solely from the slow-motion EPR spectrum.[23] Other evidence must be considered. Phosphorescence depolarization results[24] indicate that the reorientation times of small molecules such as naphthalene in a polymer matrix below T_g are $\sim 10^5$ times longer than our values of τ_c for the spin probes with comparable sizes in epoxies. Furthermore, the reorientational

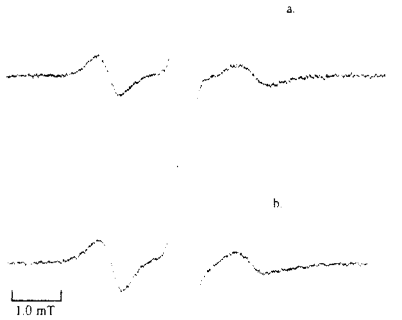

Figure 7. Spectra of (a) DNBO in polycarbonate at $T_g - 5$ K and (b) TANOLD in PDMPO at $T_g - 11$ K.

motions that result in phosphorescence depolarization cease below the β transition, whereas the spin probe motions can be detected from the slow-motion spectra at temperatures (~100 K) well below the epoxy β-transition temperatures (~225 K). To rationalize the EPR results so that they are consistent with the phosphorescent depolarization data, we conclude that the spin probe motions responsible for the dynamic shifts and widths in the slow-motion spectra are within a restricted cone of angles and do not result in complete orientational randomization, even on a time scale orders of magnitude longer than T_2.

Further complicating the issue is evidence that at some temperatures below T_g a spin probe the size of TEMPENED (or TANOLD) can undergo rotational diffusion in some polymers such that it can sample all angles within a time T_2. Such motion can be verified directly by the observation of the three-line, motionally narrowed, and collapsed spectrum characteristic of the fast-motion region ($\tau_c < T_2 < 5 \times 10^{-9}$ s). One optimum system chosen for this study was DBNO in polycarbonate, since this spin probe is nearly the smallest nitroxide available and polycarbonate has a high free-volume content below T_g.[19] Figure 7a shows the spectrum observed at 413 K [i.e., (T_g - 5 K)]. The motionally collapsed nature of this spectrum clearly indicates that DBNO can undergo large angular displacements in a time T_2. Another system investigated in the same manner was TANOLD in PDMPO.[8] This polymer was selected since it has a high T_g (484 K) which means that the nitroxide will have a large kinetic energy at (T_g - 11 K). The spectrum observed at 473 K is shown in Figure 7b. The motionally collapsed nature of this spectrum indicates that even a nitroxide capable of hydrogen bonding can undergo end-over-end tumbling at temperatures below T_g. Our conclusion from these two experiments is that small probes comparable in size to DBNO, TEMPENE, or TANOL can undergo rotational diffusion in some polymers at some temperatures below T_g. However, since these experiments were both conducted above 400 K, it is likely that these nitroxides will undergo only restricted rotational diffusion at lower temperatures (i.e., below 300 K).

Since the τ_c values and activation energy evaluated from the slow-motion spectra of the spin probe DOC are the same as those for the small spin probes, it is reasonable to conclude that the motions of DOC are also limited to angles within a restricted cone. (Furthermore, the 3:1 aspect ratio of the DOC molecule suggests that the restricted motions are primarily about the long axis.)[21,25] The size of DOC prevents it from producing a fast-motion spectrum in any polymer below T_g.

If the τ_c values measured from the slow-motion spectra of spin probes correspond to restricted rotational diffusion, we would expect the barrier heights for these motions to be lower than the barrier heights for rotation out of the restricted cone. The fact that the observed activation energies (~11.5 kJ/mol) for reorientation of the spin probes are much smaller than the smallest activation energies (≥40 kJ/mol)[24] for reorientation of the phosphorescent probes supports the conclusion that spin probes in the slow-motion region reorient by restricted rotational diffusion.

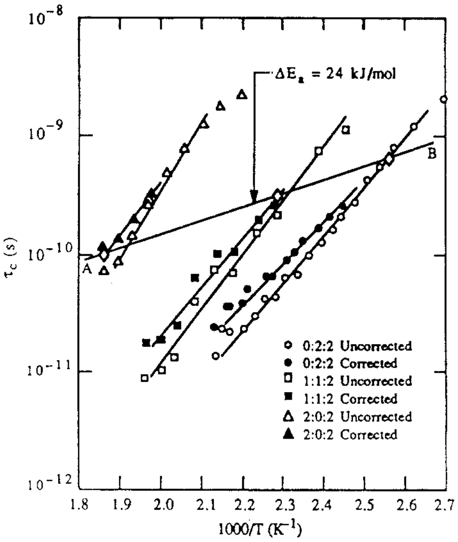

Figure 8. Arrhenius plots of τ_c from TANOLD in above-T_g DAB/DDH/DGEBA samples.

Comparison of Data above and below T_g. The correlation times and activation energies measured below T_g were compared with the corresponding parameters measured for the same probe in the same epoxy sample above T_g. Spectra for TANOLD in epoxy samples 0:2:2, 1:1:2, and 2:0:2 were obtained at several temperatures above T_g. Previously,[4] in a similar study on TANOL and TEMPENE in amine-cured epoxies above T_g, we used expressions derived by Kivelson[10] to obtain the τ_c values. In the present analysis, we have used the Kivelson theory but we have also included a correction for inhomogeneous broadening to allow for any deviations from Lorentzian line shapes.[11,26] The temperature dependence of the values of τ_c calculated both with and without this additional correction is shown in Figure 8. For values of $\tau_c > 5 \times 10^{-10}$ s the correction changed the value only ~10%, but for $\tau_c < 5 \times 10^{-11}$ s this correction amounted to ~50%. The correction lowered the activation energies by 15%. The corrected values for these activation energies are listed in Table I.

The activation energies are significantly larger above T_g than below T_g. The main reason for this lies in the fact that above T_g the nitroxide mobility depends on the free-volume content in the polymer as well as on the temperature. Previously we took this into account with the following expression for τ_c:[4]

$$\ln\left(\frac{\tau_c}{\tau_{cr}}\right) = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right) + B\left(\frac{1}{f} - \frac{1}{f_r}\right) \qquad (4)$$

where τ_c is the rotational correlation time at temperature T and fractional free-volume f; τ_{cr} is the corresponding value of τ_c at T_r and f_r, the reference temperature and fractional free-volume, respectively; and E_a is the activation energy in the Arrhenius term. The WLF definition of free volume was used, viz.,[1]

$$f(T) = f(T_g) + \alpha(T - T_g) \qquad (5)$$

where $f(T)$ is the fractional free volume at temperature T, $f(T_g)$ is the corresponding value at $T = T_g$ and is assumed here to have a value of 0.025, and α is the difference in thermal expansion coefficients above and below T_g.

In the current work we have used the same expressions and have evaluated E_a from the slope of line AB in Figure 8 which is a line drawn through "iso-free-volume" points. The temperature corresponding to a fractional free volume of $f = 0.065$ in each of the epoxy samples 0:2:2, 1:1:2, and 2:0:2 was calculated from eq 5 by using the measured values of α (4.6×10^{-4}, 4.0×10^{-4}, and 2.9×10^{-4} K^{-1}, respectively) and T_g. The temperatures were found to be 389, 436, and 535 K, respectively. At these temperatures, the τ_c values are 7.3×10^{-10} s, 3.3×10^{-10} s, and 1.0×10^{-10} s in the three samples and are plotted as diamonds in Figure 8 to define line AB.

The slope of the line AB corresponds to an activation energy of $E_a = 24$ kJ/mol which is much smaller than the values (>65 kJ/mol) obtained from the slopes of the individual data sets above T_g shown in Figure 8. On the other hand, the value $E_a = 24$ kJ/mol is significantly larger than $E_b = 11.5$ kJ/mol, the comparable value below T_g.

In making this comparison it should be kept in mind that the situations below and above T_g differ in several respects. In the first place, the free-volume contents in the samples were different below and above T_g; E_b and E_a were evaluated for $f = 0.025$ and 0.065, respectively. Even so, if the activation energies were dependent on the free volume, then one would expect $E_b > E_a$ since the average hole size would be expected to increase as f increases. Second, E_b is probably the barrier height to sub-T_g restricted rotational diffusion, whereas E_a is the barrier to above-T_g unrestricted rotational diffusion. Finally, regardless of whether the nitroxide reorients by unrestricted or restricted rotational motions, E_b is the average barrier height to reorientation for the nitroxide molecules located in holes of fixed dimensions,[27] whereas E_a is the average barrier height for the nitroxide in an environment that has fluctuating boundaries because of the polymer chain segmental motions. It has been shown in positron annihilation studies[20] that at $T_g + 100$ K the correlation time for reorientation of a polymer segmental unit, or the lifetime of a free-volume hole, is on the order of 10^{-9} s. Thus, the segmental correlation time is on the same time scale as the probe reorientational time. The probe motions can be coupled to the high-frequency motions of the matrix, so that if the activation energy for matrix segmental motions, even after correcting for free-volume changes, is higher than the sub-T_g activation energy of the probe molecule, then this higher activation energy will be reported by the probe.

Summary

The temperature-dependent EPR line shapes of nitroxide spin probes with different shapes and sizes have been studied in several polymers both below and above T_g. Several features of the spin probe motion below T_g have been considered. We conclude that the τ_c values obtained from the dynamic shifts and widths exhibited in the slow-motion EPR spectra are correlation times for rotational motions of the nitroxide within a restricted cone of angles. Furthermore, for small spherical nitroxides in some polymers, these restricted motions change to unrestricted rotational diffusion at temperatures above the slow-motion region ($\tau_c < 10^{-7}$ s) but below T_g. One the other hand, for the large cylindrically shaped molecule DOC, in all the polymers studied there was no evidence from the line shapes to suggest that the motions were other than restricted rotational diffusion below T_g.

The activation energies for the τ_c values for TANOLD, measured at constant volume above T_g, are larger than the corresponding values below T_g. This difference is related to the dynamical nature of the probe environments above T_g. Consequently, we conclude that below T_g the barrier height to the restricted rotational motions is determined by nitroxide–polymer interactions, whereas above T_g the barrier height to the unrestricted rotational diffusion is determined by polymer–polymer interactions.

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Registry No. (DAB)(DGEBA) (copolymer), 69777-26-0; (DAB)(DDH)(DGEBA) (copolymer), 99037-53-3; (DDH)(DGEBA) (copolymer), 31832-83-4; DETA, 134-62-3; PDMPO (homopolymer), 25134-01-4; PDMPO (SRU), 24938-67-8; TANOLD, 100326-46-3; TEMPENED, 111616-38-7; DOC, 18353-76-9; DBNO, 2406-25-9; bisphenol A polycarbonate (copolymer), 25037-45-0; bisphenol A polycarbonate (SRU), 24936-68-3.

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On the Crystallization of High Molecular Weight Normal Hydrocarbons

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ABSTRACT: It is pointed out in this paper that the chain lengths at which low molecular weight polyethylene fractions and the recently synthesized high molecular weight *n*-alkanes no longer form extended-chain crystallites are very close to one another for crystallization from either the pure melt or dilute solution. On the basis of this observation, a nucleation theory, utilizing the Flory free energy of fusion function, which is inherent in chain molecules, has been applied to the problem. This treatment gives a natural explanation for the molecular weight at which the demarcation in crystallite form occurs. No restraints are placed on the thickness of the mature crystallite that develops.

Introduction

There have been several recent reports which describe the synthesis and properties of *n*-alkanes whose chain lengths are much higher than have been available for study heretofore.[1-3] The results of Lee and Wegner[1,2] and of Ungar et al.[3] have shown that for these compounds, depending on the crystallization mode, there is a molecular weight below which extended-chain crystallites are always formed. (It has been established that for the lower molecular weight *n*-alkanes, where all the molecules are of exactly the same size, molecular crystals are formed.) Above this molecular weight some type of folded-chain crystallite is formed. (We use the concept of folded-chain crystallites to convey the idea that the crystallite thickness is not comparable to the extended chain length. There is no implication in this phraseology as to the nature of the interfacial structure of the basal plane.) In the latter case the crystallite thickness is substantially less than that of the extended chain. Ungar et al. have concluded that the crystallite thicknesses are an integral fraction of the extended chain length, in analogy to previous reports for low molecular weight poly(ethylene oxide) fractions.[4,5] Lee and Wegner,[1,2] on the other hand, concluded that when chain folding occurs the crystal thicknesses are not exactly integral values of the extended chain length. The different conclusions are based on very similar experimental methods, namely, Raman LAM and small-angle X-ray scattering (SAXS). In one case the comparison of the Raman and SAXS results indicates a substantial, 10–15 Å, disordered overlayer for crystals formed in dilute solution.[1] In the other study it was found for similar crystallite thicknesses, involving similar techniques, that there was no disordered overlayer.[3] These differences in interpretation with undoubtedly be settled in due time by those involved. They do not directly concern us in the present work. For present purposes it is important that both schools of investigators agree as to the molecular weight range in which some type of folding occurs.

Wegner and Lee[1] report that for crystallization from the pure melt a nonextended-type crystallite is formed when the carbon number *n* is greater than 168. When crystallized from dilute solution the molecular weight range for the formation of a folded-chain type crystallite is reduced to $n = 168$ ($M = 2352$).[1] For this *n*-alkane, depending on the crystallization temperature, the ratio of crystallite thickness to extended chain length was in the range 0.55–0.67. Ungar et al.[3] found that for bulk crystallization a folded-type crystallite could be developed at $n = 246$ ($M = 3466$); while for crystallization from dilute solution a similar result is found for $n = 150$ ($M = 2102$). Thus, both studies are in substantial agreement with respect to the molecular weight at which folding occurs, for either mode of crystallization.

Recent studies have shown that low molecular weight linear polyethylene fractions display a very strong similarity to the *n*-alkanes.[6-8] Although the low molecular weight polymers are well fractionated, molecular crystals cannot be formed since all the molecules are not exactly the same chain length. For crystallization from the pure melt a fraction, $M_n = 1586$ and $M_w = 2221$, formed crystallites under all crystalline conditions with thicknesses comparable to the extended chain length.[6] However, when the molecular weight is slightly increased to $M_n = 3769$, crystallites having a thickness smaller than the extended molecular length are formed at the lower crystallization temperature. However, with only a small, 2–3 °C, increase in the crystallization temperature, thicknesses comparable to extended chain length were found. For $M_n = 5600$ the ratio of crystallite thickness to extended chain length ranged from 0.37 to 0.99. It has been quantitatively shown that the crystallite thicknesses of this fraction are *not* integral fractions of the extended chain length. For molecular weights 8000 and greater, extended-type chain crystals could not be formed. There is, therefore, almost quantitative agreement between the *n*-alkanes and polyethylene fractions with respect to the molecular weight at which nonextended crystallite structures can be developed in bulk crystallization.

Similar results are obtained with respect to crystallization from dilute solution. We have found that for polyethylene fractions with $M_n = 1586$ either folded- or extended-type crystals are formed.[7] The exact type observed

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