Nitroxide Spin Probe/Label Study of Hydrogen Bonding and Probe Size Effects in a Linear Epoxy Polymer

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ABSTRACT: An electron spin resonance (ESR) nitroxide spin probe/spin label study was performed on a linear diglycidyl ether Bisphenol A (DGEBA)−cyclohexylamine (CHA) epoxy polymer over a 30−200 °C temperature range. Measurements of correlation time and a T_{50G} parameter on two series of tetramethylpiperidyloxy-based spin probes occluded in an epoxy matrix and on the spin-labeled epoxy matrix itself have demonstrated the effects of probe size and hydrogen bonding. The probes in the series TEMPO, TEMPOL, and TAMINE (respectively, unsubstituted and 4-hydroxy- and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl) display large increases in hydrogen-bonded effects, as indicated by T_{50G} measurements, while the probe size remains small and nearly constant. These increases correlate with an increasing hydrogen bond acceptor strength. The enhanced hydrogen-bonded effect of TAMINE over TEMPO was directly observed for these probes in methanol and cyclohexane solvents where free volume and viscosity effects of the polymer matrix do not interfere. As the probe size becomes larger, as in the series of probes BZONO, PGETA, and CPGETA (respectively, 4-(benzoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl, 2:1 phenyl glycidyl ether:4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl, and 2:1 4-cumylphenyl glycidyl ether:4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl), the T_{50G} measurement gradually increases and approaches that of the spin-labeled epoxy matrix. These effects were analyzed using established theoretical relationships of T_{50G} to probe volume.

Introduction

In this study an epoxy polymer is characterized by nitroxide spin probe and spin label electron spin resonance (ESR) techniques for the purpose of eventual application of this polymer in fiber−resin interface studies. Of particular interest are the effects of hydrogen bonding and probe size. Hydrogen bonding in epoxy resins is very prevalent and is a primary contributor to adhesion at interfaces.[1] It also influences bulk polymer thermomechanical properties. Prerequisite to utilization of a spin-labeled polymer to probe adhesion at interfaces, a knowledge of the degree to which adhesive forces, such as hydrogen bonding, modulate polymer dynamics is important. The purpose of the work reported here is to examine hydrogen bonding between an epoxy polymer and spin probes of varying hydrogen bond acceptor strengths and, consequently, how the dynamics of the epoxy polymer are modulated by the hydrogen-bonded interaction. Utilization of the ESR technique is important because it has the sensitivity and capability of probing 10 Å coatings at the interfaces of heterogeneous systems. In the future, the spin-labeled epoxy prepolymer of this study will be used as a tool to study adhesion at the fiber−resin interface.

In this study, two series of spin probes and a spin label provide molecular level diagnostics of polymer segment mobility and its dependence on probe size and hydrogen bonding. Polymer segment mobility correlates with macroscopic properties such as glass transition temperature, thermal expansion, and mechanical deformation. However, the ESR experiment only reports information originating from the spin probe or spin label, and the correlation with macroscopic properties rests on the assumption that the probe or label mobility is correlated with polymer mobility. This correlation of mobility depends on a connectivity or a coupling between the spin center and polymer matrix. For spin labels, a covalent bond serves this function. For spin probes occluded in the epoxy matrix, this coupling occurs by a combination of dense molecular packing and secondary bonding forces such as hydrogen bonding which are sufficient to immobilize the probe in the matrix. Temperature elevation causes an increment in free volume and a weakening of secondary bonding. This promotes polymer segment and probe rotations. The degree of probe or label rotation detectable in the ESR spectrum is dependent on probe size, matrix rigidity, and strength of the hydrogen bonding.

The free volume dependence on temperature sharply increases at the polymer glass transition temperature, and a probe's onset of rapid motion may coincide with this temperature. However, the onset of rapid probe rotational motion is also dependent on the size of the probe and may occur below or above the T_g for very small or large probes. The correlations of T_g with probe size and its motional narrowing in the ESR spectrum have been studied.[2−4] For spin probes with a capability of hydrogen bonding to sites in the polymer matrix, the strength of this bonding should be a factor in addition to the free volume effect that determines the onset temperature for rapid probe rotational motion. This has only received passing comment in the literature,[5,6] but it is an important factor for adhesion studies and a central issue in this work. Here, using a linear amine−epoxy polymer, we examine hydrogen-bonding effects of small spin probes and of larger ones that mimic the polymer structure and compare them with the thermal response of the spin-labeled polymer itself. The structures of the spin probes and labeled and unlabeled polymers utilized in this study are presented in Figure 1. The objective of this work is to examine the extent to which hydrogen-bonded effects influence the mobility of spin probes and spin labels in an epoxy polymer as a function of temperature.

Experimental Section

Spin Probes and Spin Labels. The spin probes 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, Molecular Probes Inc.), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL, Al-

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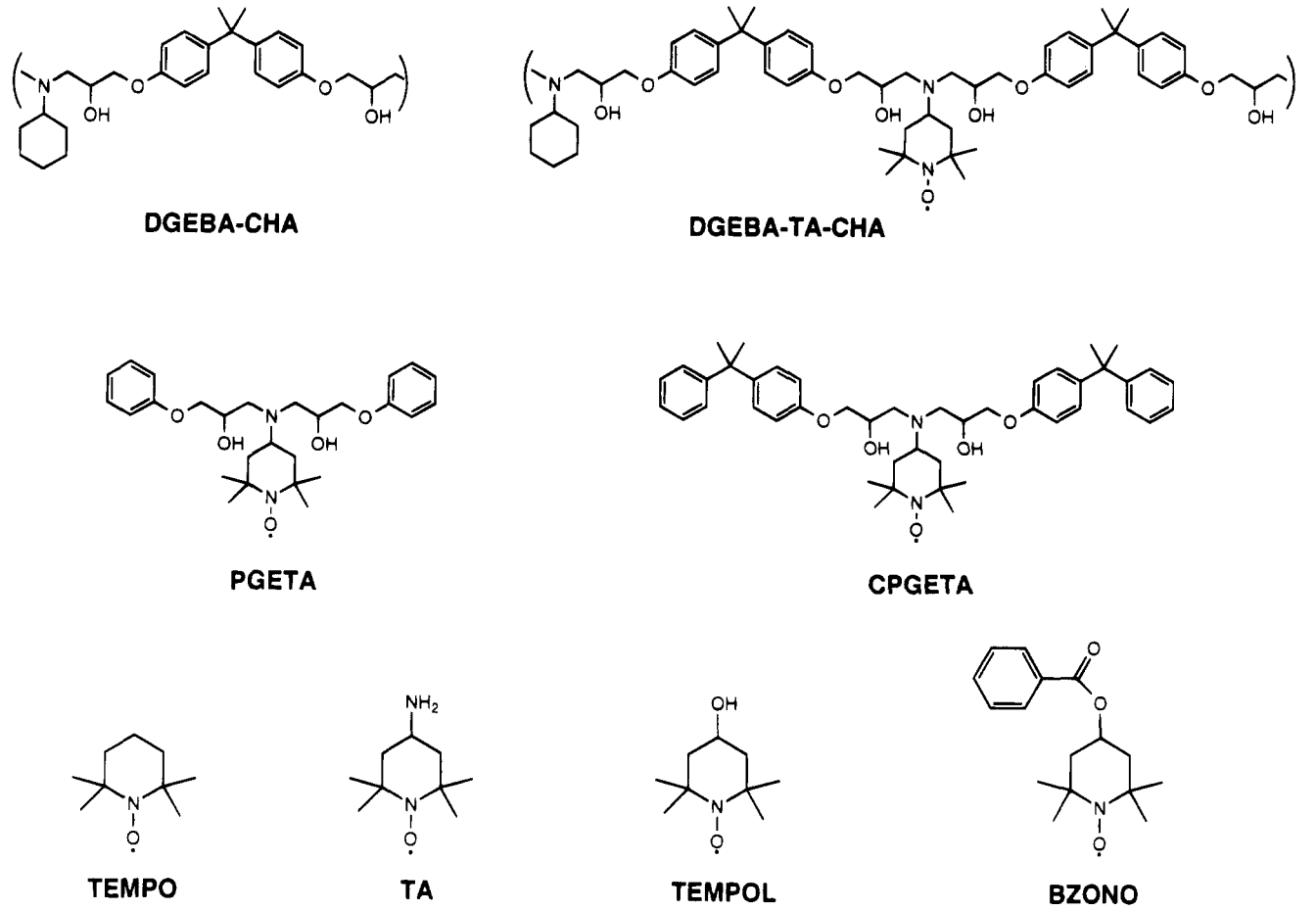

Figure 1. Chemical structures of the unlabeled (DGEBA–CHA) and spin-labeled (DGEBA–TA–CHA) linear amine–epoxy polymers, the epoxy-derived spin probes (CPGETA and PEGTA), and the small molecule spin probes (TEMPO, TAMINE, TEMPOL, and BZONO).

drich), and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (TAMINE, Aldrich) were purchased commercially and used as received.

4-Benzoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (BZONO) was synthesized by reaction of TEMPOL (0.250 g, 1.45 mmol) with benzoyl chloride (0.214 g, 1.53 mmol, freshly distilled) and triethylamine (0.154 g, 1.53 mmol) in a methylene chloride (6.0 mL) solution at 23 °C for 12 h. The reaction mixture was filtered, and the filtrate was extracted twice with 5% $NaHCO_3$, dried over Na_2SO_4, and chromatographed on a short alumina column (Woelm, activity 1, neutral, chloroform elution) which is necessary to separate residual TEMPOL. Yield: 60%.

The PGETA and CPGETA model compound probes were synthesized as the 1:2 adducts of TAMINE with phenyl glycidyl ether and cumylphenyl glycidyl ether, respectively, as previously reported.[7] The spin-labeled linear amine–epoxy polymer (DGEBA–TA–CHA) was prepared by reacting an equivalence of amine (0.33 mol % TAMINE + 99.67 mol % cyclohexylamine (CHA)) with the Bisphenol A diglycidyl ether (Epon 828, Shell), and the unlabeled linear amine–epoxy polymer was prepared in an identical manner without the TAMINE, as previously described.[7]

Samples for the ESR experiment were prepared so that the spin probe concentration corresponded to that of the spin label in the linear epoxy (0.33 mol % of repeat units). Samples were prepared as rigid foams in 10 × 75 mm tubes which were previously silanized with Glassclad 6C for facile removal of the epoxy. Approximately 100 mg of unlabeled epoxy polymer was added to the tube followed by an analytical quantity (≈0.2 g) of spin label/chloroform stock solution (prepared such that the 0.2 g quantity of this solution contained the required amount of spin label). After dissolution, the tube was warmed for about 2 h at 50–60 °C, evaporating sufficient chloroform to leave a very viscous solution. The tube was connected to a vacuum and pumped at 1 Torr for 20 min. The bottom of the tube was then gently warmed with heated air, resulting in sudden formation of a rigid foam approximately 1 in. high in the tube. This was further pumped on for 12 h to ensure complete removal of residual chloroform. Approximately 50 mg quantities of the foam strips were compressed to the base of a 3 mm quartz cell with a close fitting inserted rod.

ESR Measurements. ESR spectra were recorded using a Bruker ER 200 spectrometer and a Bruker ER 300 spectrometer equipped respectively with Varian and Bruker temperature controllers. Spectra at variable temperatures were obtained in steps of 2 or 5 deg to a maximum of ca. 150 °C with 3–5 min of temperature equilibration allowed at each step. In this study, an empirical method was used to approximately measure the probe motional correlation times. This model estimates the correlation times on the basis of the theory of Kivelson and Lee.[5,8,9]

Results

In Figure 1 are presented the structures of the linear epoxy polymer (DGEBA–CHA), the spin-labeled linear epoxy copolymer (DGEBA–CHA–TA), and two series of spin probes which were occluded in the linear epoxy polymer matrix. The linear epoxy was prepared by reaction of the diglycidyl ether of Bisphenol A with an equivalence of cyclohexylamine.[7] This polymer has a glass transition temperature of 70 °C, as determined by DSC measurement.[10] The amine and hydroxyl functional groups serve as sites for hydrogen bonding. Model compound studies have shown that this epoxy resin structure has strong hydrogen bond donor and acceptor strengths.[1] The spin-labeled linear epoxy polymer was synthesized by substituting the amine-functionalized spin label TAMINE for 0.33 mol % of the cyclohexylamine in DGEBA–CHA. The series of spin probes which mimic the epoxy resin repeat unit struc-

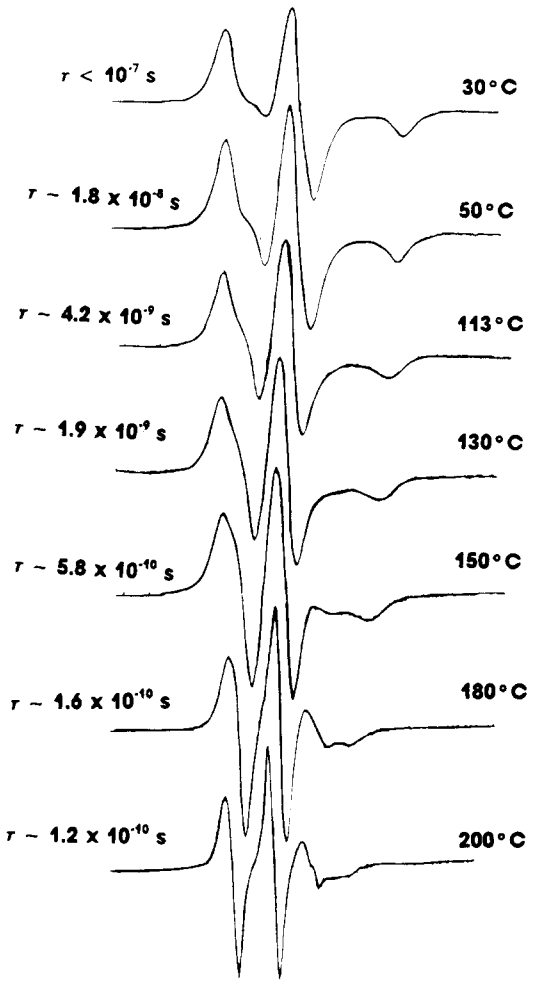

Figure 2. First-derivative ESR spectra of the spin-labeled DGEBA–TA–CHA polymer at various temperatures, showing the effect of spin label motion on the ESR line shapes. The correlation times were estimated on the basis of the equations described in the text. The immobile spin label spectrum at room temperature is shown in (a). For this spectrum g_X = 2.008, g_Y = 2.006, g_Z = 2.002 and A_{XX} = 0.6 mT, A_{YY} = 0.6 mT, A_{ZZ} = 2.8 mT.

ture but vary in size were synthesized as 2:1 adducts of phenyl glycidyl ether:TAMINE (PGETA) and cumylphenyl glycidyl ether:TAMINE (CPGETA). A second series of small spin probes which vary in strength of hydrogen bonding but are nearly constant in size are TEMPO, TAMINE, and TEMPOL. The spin probe BZONO, while somewhat larger than the others of this group and weaker in strength of hydrogen bonding than TAMINE and TEMPOL, does have a large data base, particularly with non-hydrogen-bonding polymers.[3,11] The approach in studying probe size and hydrogen-bonding effects is to occlude these spin probes into the linear epoxy at the same concentration as the spin label and analyze temperature-activated molecular motion by the ESR spectral response.

The ESR spectral response to thermally activated molecular motion for the nitroxyl spin-labeled linear epoxy polymer is shown in Figure 2. At 30 °C, the three-line spectrum displays line broadening derived from hyperfine and **g**-tensor anisotropies characteristic of an immobilized nitroxyl spin center. This immobilization corresponds to spin label motion having a correlation time slower than detectable by continuous wave EPR ($\tau > 10^{-7}$ s). For randomly ordered immobilized spin labels in a rigid glass, the $m_I(^{14}N) = \pm 1$ lines of the spectrum are separated by the maximum value of $2A_{ZZ}$.[12] (A_{ZZ} is the maximum ^{14}N electron-nuclear hyperfine coupling component of the ^{14}N hyperfine tensor of the nitroxyl radical.) As the temperature is increased, the spin label motion becomes faster and the correlation time of the spin label becomes shorter, causing line narrowing and partial averaging of the ^{14}N hyperfine interaction. As a result, for rotational correlation times faster than 10^{-8} s, the value of $2A_{ZZ}$ noticeably decreases, and the highest and lowest field peaks of the ESR spectra, which are associated with the $m_I(^{14}N) = \pm 1$ lines, shift toward the center of the spectrum. This is shown in Figure 2 by the series of spectra of the spin-labeled epoxy recorded over a temperature range from 30 to 200 °C.

A temperature range exists where the spectra change from a broad asymmetric line shape characteristic of slow rotational motion on the ESR time scale to a narrow more symmetric line shape characteristic of rapid motion. This temperature range and its narrowness depend on the thermally activated conformational mobility of the matrix, the binding between the spin center and the matrix, and the void volume available to the spin center for rapid rotational motion. This temperature range may be detected by a rotational correlation time measurement from a line shape analysis or by a T_{50G} measurement from a $2A_{ZZ}$ vs temperature plot.

Methods for determining rotational correlation times from line shape analysis have been developed for these fast ($5 \times 10^{-9} > \tau > 10^{-11}$ s) and slow ($10^{-5} > \tau > 10^{-7}$ s) regions.[5] For fast motion the correlation time of spin probe or label motion can be calculated using the method of Brown and Sandreczki.[12]

$$\tau_c = 4\{\{Y(0)/Y(1)\}^{1/2} + \{Y(0)/Y(-1)\}^{1/2} - 2\}b^{-2}W(0)^{-1} \quad (1)$$

$$b = 4\pi/3\{A_{ZZ} - 1/2(A_{XX} + A_{YY})\} \quad (2)$$

where $Y(1)$, $Y(0)$, $Y(-1)$ are the peak-to-peak amplitudes of the m_I = 1, 0, −1 lines, respectively; A_{ZZ}, A_{XX}, A_{YY} are the principal components of the ^{14}N hfc tensor, and $W(0)$ is the line width of the center line. For example, for Figure 2f, $Y(0)/Y(1) = 0.72$, $Y(0)/Y(-1) = 1.0$, $W(0) = 2.7 \times 10^7$ s^{-1}, and $b = 9.17$ mT. Using these values gives a correlation time of *ca.* 1.6×10^{-10} s^{-1}. Correlation times calculated for the corresponding spectra are entered in Figure 2.

Determination of T_{50G} is a simpler and somewhat empirical measurement but is historically widely used for comparison of motional effects observed in ESR probe spectra.[3] Measurements of $2A_{ZZ}$ as a function of temperature for a spin label or probe incorporated into a polymer matrix have shown that a relatively narrow temperature range exists where a narrowing of $2A_{ZZ}$ from 65 to 35 G occurs. At the midpoint of this narrowing, the parameter T_{50G} (temperature where $2A_{ZZ}$ has a value of 50 G or 5.0 mT) has been defined. Studies indicate that, in general, T_{50G} corresponds to the temperature at which the reorientational correlation time of the spin probe is *ca.* 3.0×10^{-8} s.[13] The data for determination of this parameter are presented in Figure 3, and the T_{50G} values for the label and probes in the epoxy matrix work are presented in Table 1. These values range from 20 to 150 °C. Depending on size and hydrogen-bonding characteristics of the particular probe, the corresponding T_{50G} may be significantly above and below the 70 °C T_g of the epoxy matrix.

The series of sigmoidal curves in Figure 3 displays a variation in maximum and minimum values of $2A_{ZZ}$ and

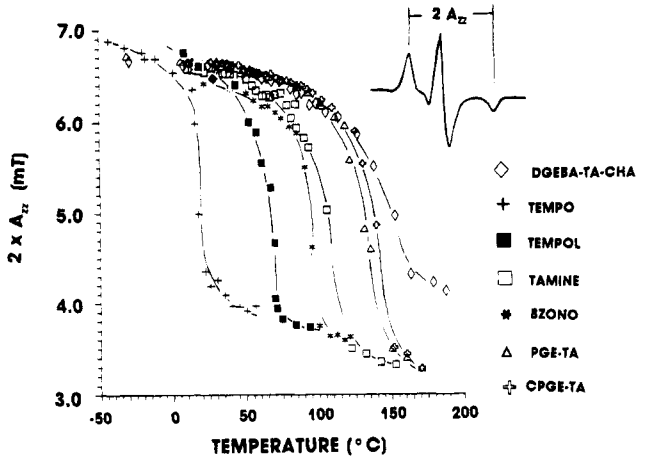

Figure 3. Plots of temperature versus the separation of the low- and high-field extrema ($2A_{ZZ}$) in the ESR spectra of the probes in the unlabeled DGEBA polymer and of the spin-labeled DGEBA–TA–CHA polymer.

Table 1. T_{50G}, Molecular Volume, and Representative α- and β-Scale Hydrogen Bond Donor and Acceptor Strengths of Spin Probes

spin probe	T_{50G} (°C)	V (Å^3)[a]	α^b	β^b
TEMPO	20	171	0	0
TEMPOL	67	177	0.30	0.51
TAMINE	110	182	0	0.72
BZONO	93	274	0	0.41
PGETA	136	483	0.44	0.51
CPGETA	145	757	0.44	0.51
DGEBA–TA–CHA	150			

[a] References 14 and 15. [b] References 1 and 16.

in steepness of the vertical portion of the curve at the T_{50G} values. The maximum and minimum $2A_{ZZ}$ values reflect the frequency of the spin center's orientational motion on the ESR time scale. In the glassy state this orientational motion is related to the efficiency of matrix packing, and in the rubbery state it is related to the fluidity or viscosity of the medium. Since the spin label is covalently bound to the polymer matrix, in a fluid medium, it never attains orientational freedom comparable to that of a spin probe or the corresponding $2A_{ZZ}$ minimum. The steepness of the curve reflects a breadth in distribution of thermally activated volume increments sufficient for rapid spin center motion.

Discussion

The T_{50G} results for the low molecular weight probes occluded in the linear epoxy polymer display wide temperature variations with varying hydrogen-bonding capabilities and molecular sizes. As the probes become larger in size and similar in hydrogen-bonding characteristics to that of the repeat unit of the epoxy polymer, the T_{50G} values approach that of the spin label. This is exemplified by the progression of PGETA and CPGETA spin probes toward the spin-labeled epoxy polymer in the results of Figure 3 and Table 1.

As a size parameter for the spin probes, a Kitaigorodskii molecular volume calculated from substructure volume increments may be utilized.[14,15] The calculated volumes are entered into Table 1. For the spin probe series TEMPO, TEMPOL, and TAMINE, there is little variation in size but a large variation in T_{50G}. This is an effect of hydrogen bonding to the epoxy polymer with the T_{50G} variation arising from the TAMINE ($-NH_2$), TEMPOL ($-OH$), and TEMPO (CH_2, control) functionalities, as depicted in Figure 1. Using TEMPO as a non-hydrogen-bonding control, substitution of the hydroxyl group causes a 47 deg increment in T_{50G}, and substitution of the amine group causes a 97 deg increment in T_{50G}.

Hydrogen bond donor and acceptor strength parameters for these functional group sites have been characterized by respective solvatochromic hydrogen bond acidity (α) scales and hydrogen bond basicity (β) scales which range from 0 (very weak) to 1 (very strong).[16] Representative values based on analogues with the respective amine, alcohol, methylene, and ester functionalities (cyclohexylamine for TAMINE, 2-propanol for TEMPOL, cyclohexane for TEMPO, ethyl benzoate for BZONO)[16] and on an epoxy resin model compound (2:1 CPGE:CHA adduct for PGETA and CPGETA[1]) are presented in Table 1. Assigning these surrogate α- and β-scale values to spin probes in this study ignores any contribution of the nitroxyl functional group. While α- and β-scale measurements on the nitroxyl group incorporated in a non-hydrogen-bonding molecule such as di-*tert*-butyl nitroxide or TEMPO were not found in the literature, there is good indication that it is of weak basicity.[17] The data of Figure 3 indicate its behavior is dominated by the amine and hydroxyl functional groups in the respective TAMINE and TEMPOL compounds. For the TEMPO, TEMPOL, and TAMINE series where the probe size is nearly constant, there is a correlation between hydrogen bond donor strength (β-scale parameter) and T_{50G}. The stronger the hydrogen bond between the probe and the polymer, the higher the temperature necessary for thermally activated rapid probe motion on the ESR time scale.

The hydrogen-bonding character of the nitroxide functional group may be observed directly and separately from that of the amine or hydroxyl functional group on the TAMINE or TEMPOL molecule in a low-viscosity medium. In this case the electronic structure of the nitroxide is perturbed toward the more ionic resonance form by hydrogen bonding with a consequent increase in the isotropic ^{14}N hyperfine splitting constant, A_N. The amine or hydroxyl hydrogen-bonding character is manifested by the rotational correlation time increment when a hydrogen complex is formed. This correlation time increment is enhanced at lower temperatures. The data in Table 2 for TEMPO and TAMINE in methylcyclohexane and methanol demonstrate the above effects. Both the TEMPO and TAMINE A_N increase by 1.2 G as the solvent polarity increases from that of methylcyclohexane to methanol. For TAMINE, this effect has been well studied and correlated with solvent hydrogen bond acidity.[21] By doing the variable temperature experiment, we are able to observe an increased rotational correlation time resulting from hydrogen bond complex formation of the methanol solvent with the TAMINE amine group. The control experiments in the non-hydrogen-bonding methylcyclohexane solvent and with the TEMPO spin probe do not show this enhanced correlation time effect. Thus, while A_N indicates comparable hydrogen bonding between the nitroxide group and solvent, the correlation time shows enhanced hydrogen bonding through the TAMINE amine functional group. This parallels what is observed in the epoxy matrix. For the situation of the spin probe in the polymer, it would be very useful to obtain the hydrogen-bonding information from the magnitude A_N, but the polymer is a viscous solid in which such hyperfine splitting is obscured by unaveraged anisotropy.

The BZONO probe is a significant increase in size from that of the TEMPO, TEMPOL, and TAMINE series, and the benzoate functionality is a weaker base

Table 2. TEMPO and TAMINE Nitrogen Hyperfine Coupling Constants and Correlation Times in Methylcyclohexane and Methanol at +30, −50 and −120 °C

A_N/τ	TEMPO/$CH_3C_6H_{11}$	TAMINE/$CH_3C_6H_{11}$	TEMPO/CH_3OH	TAMINE/CH_3OH
A_N(30 °C) (G)	15.4	15.2	16.6	16.4
A_N(−120 °C) (G)	15.7	15.5	16.9	16.7
τ(30 °C) (s)	10^{-11}	10^{-11}	10^{-11}	10^{-10}
τ(−50 °C) (s)	10^{-11}	10^{-11}	10^{-11}	10^{-10}
τ(−120 °C) (s)	10^{-10}	10^{-10}	10^{-10}	10^{-9}

than the amine or hydroxyl functional groups. This probe in the epoxy matrix has a T_{50G} intermediate to that of TEMPOL and TAMINE, reflecting the larger size and weaker hydrogen bonding. BZONO is a particularly important spin probe because there is a data base for a significant number of polymers.[2,11] The epoxy polymer T_g (70 °C) *vs* BZONO T_{50G} (93 °C) correlation is in excellent agreement with the T_g−T_{50G} correlation plot of ref 11 which includes a total of 19 polymers.

To relate T_{50G} to T_g and quantify the probe size effect, Kusumoto has derived an equation based on polymer segmental diffusion above its glass transition temperature.[22-24]

$$T - T_g = \left[\frac{[\beta^* + \ln(v_n/v_p)]v_p^* v_{fg} v_m^*}{v_{fg} v_m^* \ln(\phi_0/\phi) - (v_{fg} v_n^* v_p)/v_m} - v_{fg}\right]\frac{1}{v_{mg}\Delta\alpha} \quad (3)$$

where v_p and v_m are the respective volumes of the probe and polymer segment associated with a conformational jump, v_f is the size of a packet of free volume, v_{fg} and v_{mg} are the respective free volume and polymer segment volume at T_g, v_p^* and v_m^* are the respective minimum volumes into which a probe or segment can jump, $\Delta\alpha$ is the different in volume thermal expansion coefficient above and below T_g, ϕ is a hole jumping frequency, ϕ_0 is its Arrhenius preexponential factor, and β^* is a term defined by Bueche[25] as $\beta^* \equiv \ln(v_p^*/v_f) - 1$. Kusumoto reduced eq 3 to eq 4 by employing the approximations[25] $\beta^* v_m^*/v_{fg} = 40$, $v_{fg}/(v_{mg}\Delta\alpha) = 52$, $\beta^* = 1$, $\ln(\phi_0/\phi) = \ln(10^{14}/10^8) = 13.8 \gg f$ where $f = v_p/v_m = v_p^*/v_m^*$.

$$T_{50G} - T_g = 52[2.9f\{\ln(1/f) + 1\} - 1] \quad (4)$$

This equation is based on Bueche's theory for free molecule and polymer segment motion at and above the glass transition temperature in amorphous polymers, and a critical assumption in its derivation is that a function defined as β^* approximates a value of 1, where $\beta^* \equiv \ln(v_p^*/v_f) - 1$. Bullock has modified Kusumoto's approach by defining a β^* function for both the probe molecule, $\beta_p^* \equiv \ln(v_p^*/v_f) - 1$, and the polymer segment, $\beta_m^* \equiv \ln(v_m^*/v_f) - 1$, which are then combined to a single expression for β_p^*, $\beta_p^* = \beta_m^* + \ln(v_p^*/v_m)$, and by incorporating the WLF parameters, C_{1g} and C_{2g}, to obtain eq 5 which reduces to eq 6 when the "universal" values of C_{1g} (17) and C_{2g} (52) are used.[26]

$$T_{50G} - T_g = C_{2g}[(2.303C_{1g}f/13.8) - 1] \quad (5)$$

$$T_{50G} - T_g = 52[2.9f - 1] \quad (6)$$

This modification changes the relationship between T_{50G} and f from nonlinear to linear. As Bullock points out, eq 4 has the shortcoming that T_{50G} passes through a maximum at $f = 1$ and then declines with increasing probe size. On the other hand, eq 5 predicts a continuously increasing T_{50G} with increasing probe size past $f = 1$. When f is unity, eqs 4 and 6 predict $T_{50G} - T_g$ is 98.8 °C. For flexible chain polymers and compatible probes of similar structure, the case of $f = 1$ might be considered that when the probe size approaches that of a spin label. For the epoxy matrix of this study the calculated T_{50G} at $f = 1$ is 169 °C, which is a reasonable prediction but somewhat greater than the experimental 150 °C.

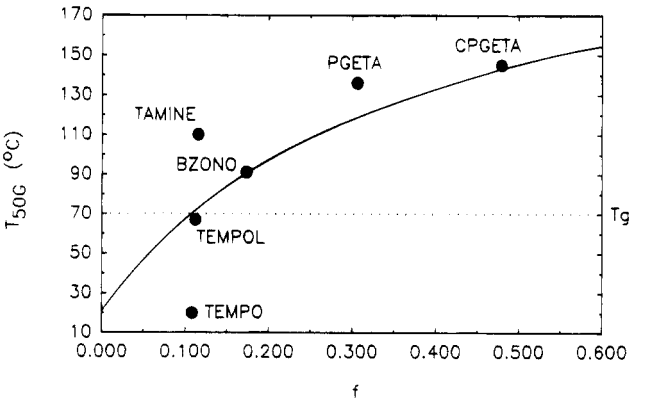

Figure 4. Plot of T_{50G} versus f according to eq 4 for the spin probes of this study occluded in the linear epoxy matrix. The solid line is the theoretical behavior which has been normalized by the BZONO data point. The dotted line is the T_g of the linear epoxy matrix.

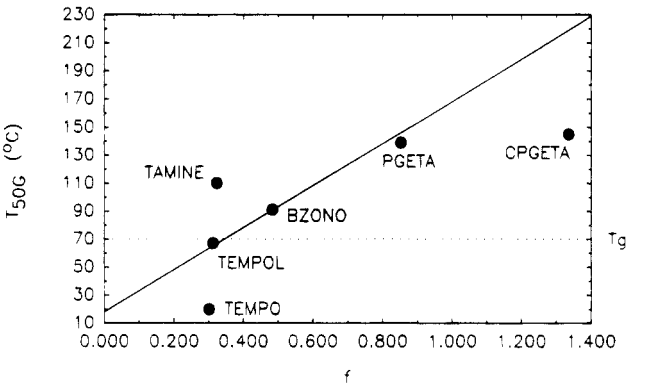

Figure 5. Plot of T_{50G} versus f according to eq 6 for the spin probes of this study occluded in the linear epoxy matrix. The solid line is the theoretical behavior which has been normalized by the BZONO data point. The dotted line is the T_g of the linear epoxy matrix.

The models for the derivation of eqs 3 and 4 are based only on probe volume and have no factor for a hydrogen-bonded contribution. As such, deviations from these models may be an index for hydrogen-bonded effects. The data of Table 1 are plotted in Figures 4 and 5 according to eqs 4 and 6, respectively, by using BZONO to determine the polymer segment volume for calculation of f for the other probes. The solid line is the theoretical curve normalized to the BZONO data point. In Figure 4 this line is curved with an enhanced dependence on the smaller probes ($f \ll 1$) as a consequence of the $\{\ln(1/f) + 1\}$ term in eq 4. The dotted line is the T_g of the epoxy matrix below which the assumption of polymer segmental motion is invalid. Both TEMPO and TEMPOL fall in this category, but TAMINE displays a distinct hydrogen-bonded enhancement of T_{50G} over what is predicted for a probe of its size.

In Figure 4, PGETA also displays a hydrogen-bonded enhancement, and CPGETA correlates well with the theoretical curve. The amine–hydroxyl adduct structure common to these probes has been characterized as both a strong hydrogen donor and acceptor,[1] and it is expected that the smaller of the two probes would show the greater enhancement. While CPGETA does not appear to show any hydrogen-bonded enhancement in Figure 4, the BZONO probe used to normalize the theoretical curve may not be the best selection. As indicated in Table 1, BZONO is a hydrogen bond acceptor, and factoring in its effect if it could be quantified would have the effect of displacing the theoretical curve to a lower temperature.

In Figure 5 the situation with PGETA and CPGETA is quite different. In particular, CPGETA shows a large negative deviation from the theoretical line as well as an f parameter considerably greater than 1. This occurs because of the linearity of eq 6 and the selection of BZONO to normalize the theoretical curve. While the linearity of eq 6 permits $T_{50G} - T_g$ values greater than 98.8 °C as f becomes greater than 1, these values become unreasonably high at f parameters significantly greater than 1. The selection of BZONO to normalize the theoretical curve has the effect of forcing the epoxy matrix to have a smaller motional segment volume when using eq 6 (567 Å^3) as opposed to eq 4 (1581 Å^3). This occurs because the BZONO $T_{50G} - T_g$ value (93–70 °C) generates the smaller f parameter from eq 4.

Equation 4 provides the most logical fit for the data of this work. However, the approximation of β^* or β_p^* to unity is a very difficult one to check because of uncertainties in assessments of free volumes and of activation volumes for molecular movement in the polymer matrix. If β^* is not approximated to unity, eq 4 takes the form of eq 7. For a ±10% variation in β^*

$$T_{50G} - T_g = 52[2.9f\{\ln(1/f) + \beta^*\} - 1] \qquad (7)$$

from unity (i.e. 0.9, 1.0, 1.1) at $f = 1$, the corresponding variation in the $T_{50G} - T_g$ maximum is significant (i.e. 83.7, 99.8, and 113.9 °C, respectively).

Summary

Measurements of correlation time and T_{50G} on two series of tetramethylpiperidyloxy-based spin probes occluded in an epoxy matrix and on the spin-labeled epoxy matrix have demonstrated the effects of hydrogen bonding and probe size. The TEMPO, TEMPOL, and TAMINE probe series displays large increases in hydrogen-bonded effects, as indicated by T_{50G} measurements, while the probe size is small and nearly constant. Comparative hydrogen-bonded interactions of TAMINE and TEMPO in low-viscosity hydrogen-bonding and non-hydrogen-bonding solvents at low temperatures show a parallel enhancement for TAMINE. As the probe size becomes larger in the series BZONO, PGETA, and CPGETA, the T_{50G} measurement gradually increases and approaches that of the spin label. These effects were analyzed using established theoretical relationships of T_{50G} to probe volume.

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References and Notes

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(9) Using the equations, Brown and Sandreczki have determined correlation times for $\tau_c > 10^{-8}$ s, which we use to calculate some of the correlation times in Figures 4 and 5. For convenience, we give the relevant eqs from ref 5.

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

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

$$B = h\nu(g_\perp^2 - g_{||}^2)/g_{||}^2$$

$$C = (A_\perp^2 - A_{||}^2)/A_{||}$$

where Δ_s is the shift factor, h is Planck's constant, ν is the microwave frequency, and $g_{||}$, $g_\perp$ and $A_{||}$, $A_\perp$ are components of the **g** tensor and nitrogen hyperfine tensor, respectively.

(10) Previous work in ref 7 reported a T_g of 66 °C, which was determined at the onset of the step in the DSC thermogram. The 70 °C T_g value corresponds to the midpoint of the step transition in the thermogram.

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