A paramagnetic resonance study of the molecular motions of spin probes dissolved in poly(vinyl acetate)

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The molecular motions of two spin nitroxide probes of vastly different geometries dissolved in poly(vinyl acetate) have been studied over a large temperature range. The smaller spherical probe's motion follows the main glass relaxation at higher temperatures and the γ transition at lower temperatures. Its small size allows it to occupy multiple sites as indicated by the observed spectra. The larger probe appears to occupy a single type of site. Its motion follows the main relaxation at higher temperatures and appears to abruptly jump to the β relaxation at ~ 330 K.

(Keywords: poly(vinyl acetate); paramagnetic resonance; spin probes)

INTRODUCTION

In this work we continue our study of the molecular motions of spin probes dissolved in glass forming isotropic liquids, liquid crystals and polymer/plasticizer mixtures[1–4]. In a recent paper[4], we studied the molecular motions of spin probes dissolved in poly(vinyl acetate) (PVA) at temperatures well above the glass transition. Here we extend our studies to lower temperature in order to study the glass transition ($T_g \sim 305$–310 K) of PVA. The rotational correlation times (τ) are obtained from spectral simulations of the e.p.r. data[5,6]. The values of τ, at high temperature, are matched to a variety of models[4,7–14] namely, relaxation time (EAL): $\tau = \tau_0 \exp(E_A/RT)$; viscosity (EA) using the Stokes–Einstein relation $\tau = 4\pi a^2\eta/3kT$: $\tau = (A\tau_0/T)\exp(E_A/RT)$; Vogel–Fulcher (VF): $\tau = (A\tau_0/T)\exp[B/(T - T_0)]$; Williams–Landel–Ferry (WLF):

$$\tau = \tau_g \exp[-C_1^g(T - T_g)/(C_2^g + T - T_g)],$$

where C_1^g and C_2^g are mechanical constants; WLF viscosity models (WLFV):

$$\tau = (A\tau_0/T)\exp[(b/\Delta\alpha)/(fg/\Delta\alpha + (T - T_g))];$$

and Bullock–Cameron–Miles (BCM):

$$\tau = \tau_\infty \exp f[(2.303C_1^g C_2^g)/(T - T_g + C_2^g)],$$

using $C_1^g = 15.6$, $C_2^g = 46.8$ K and $T_g = 305$ K. These models have been previously discussed by us in reference 4, so the discussion will not be repeated here. In addition to these models we will also use an all temperature model (GCAT) we have previously developed[2]. We use the percolation model of Grest and Cohen[15–17] at higher temperatures coupled with an activation energy model at lower temperatures with the result:

$$\tau^{-1} =$$

$$\left[\frac{\tau_{01}}{T} \times \exp\left\{-\gamma v_m \frac{1}{(T - T_g) + [(T - T_g)^2 + \beta T]^{1/2}}\right\}\right]^{-1} + \left[\frac{\tau_{02}}{T}\exp(\Delta E/RT)\right]^{-1}$$

The literature contains many interesting e.p.r. studies of spin probes dissolved in polymers[4,18–20]. PVA, the side chain polymer we have chosen to study (*Figure 1*), undergoes a variety of motions that are illustrated by the abbreviated relaxation map presented in the work of Miles *et al.*[19]. At higher temperatures there appears to be only the main glass to rubber transition. At lower temperatures, one observes a γ relaxation which may be associated with the motions of the methyl group at the end of the side chain. The frequency varies in the neighbourhood of 10–100 MHz. One also notes a β relaxation which may be associated with the side chain motions. The relaxation frequency of the β relaxation varies with temperature reaching a value of ~ 1 MHz at ~ 270 K. Two different types of probes were used in the current studies (*Figure 1*); a bulky cigar-shaped cholestane molecule (COL) and a small, nearly spherical, tempol (TPL) molecule. We take advantage of the differences in their size and shape to study different motions of the probe and polymer.

EXPERIMENTAL

The samples, their preparation and the experimental equipment have been previously described in the litera-

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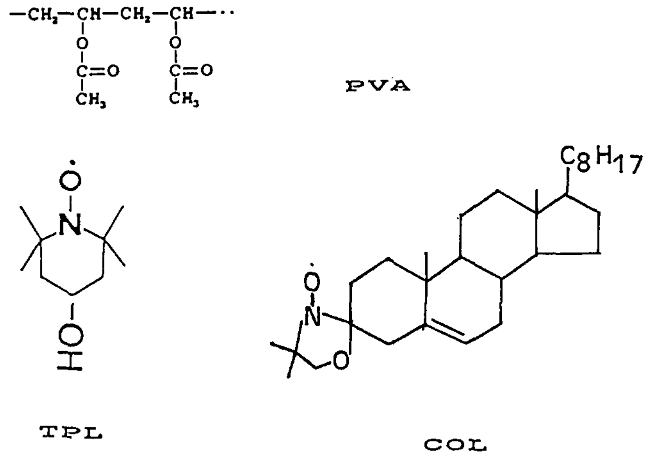

Figure 1 The polymer and spin probes used

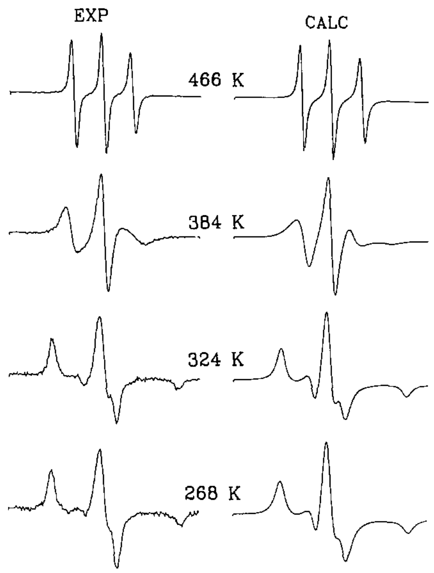

Figure 2 Representative experimental and simulated spectra from COL in PVA. A full sweep is 100 G

ture[4]. The τ values were extracted from spectral simulations. The TPL probe was assumed to tumble isotropically, but the COL probe was assumed to rotate five times faster around its long axis than around a perpendicular axis since the geometrical aspect ratio of COL is approximately five. The EAL and BCM models were matched to τ using a linear least square fitting[21] program while the other models were fit with a non-linear least squares match using either SigmaPlot 4.0* or a BASIC program from the literature[22].

RESULTS AND DISCUSSION

In *Figure 2* we show some representative spectra from COL along with the corresponding simulations. The spectra below 280 K take the nearly unchanging form (illustrated by the 268 K spectrum of *Figure 2*) one would expect from a stationary distribution of probes, i.e. the probe motion is too slow to be detected by e.p.r. In contrast the 280 K spectrum from TPL (*Figure 3*) and those obtained at lower temperatures (not shown) have shapes corresponding to a probe tumbling at tens of megahertz, a temporal region where e.p.r. is still sensitive to changes in τ. Also, note the structure that appears on the low field line in a range of temperatures near the glass transition. TPL apparently occupies more than one site here. Presumably, as the backbones crowd together when the main glass transition is approached the TPL is forced out of this area and probably resides between the side chains. Similar effects have been reported by others in the e.p.r. studies of a similar probe in a smectic liquid crystal[23], and by us in the e.p.r. study of a nematic liquid crystal[24]. The larger COL probe does not display this effect.

In *Figure 4* we plot the log of the geometrical mean of the rotational correlation time for COL *versus* $1000/T$. Note the gap in the region of $1000/T = 3$ which is slightly above T_g. One possible interpretation is that the

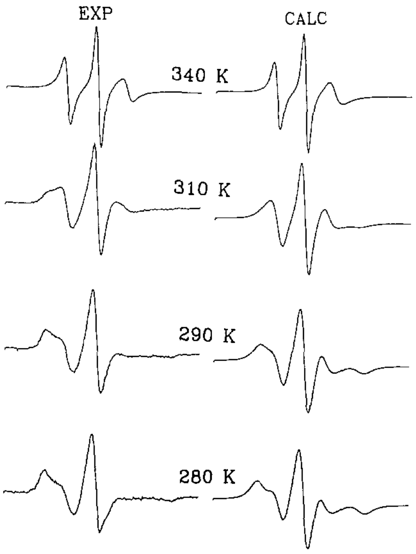

Figure 3 Representative experimental and simulated spectra from TPL in PVA. A full sweep is 100 G

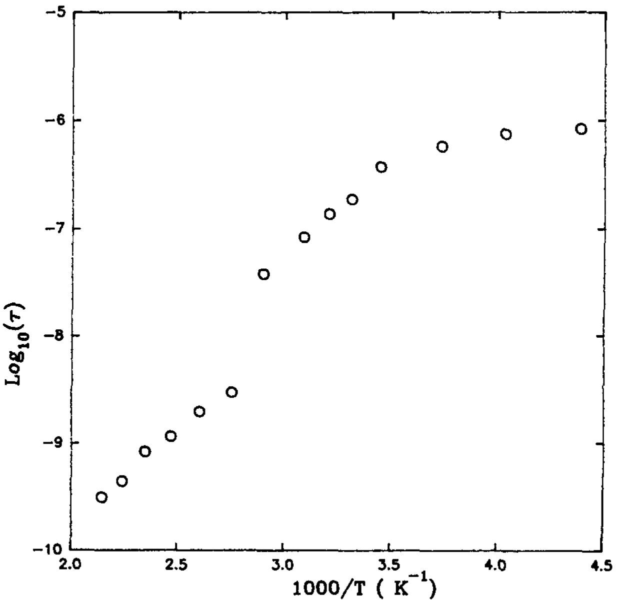

Figure 4 Plot of the log of the geometric mean of the parallel and perpendicular rotational correlation times *versus* inverse temperature for COL in PVA

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* SigmaPlot 4.0 (Jandel Scientific) is a plotting program with modules that allow fitting to data using a variety of techniques

motion of COL was following the main relaxation at higher temperature and then abruptly started to follow the β relaxation as the main glass transition was approached. Both straight line portions have activation energies of $\sim 17\,\mathrm{kJ\,mol^{-1}}$. The curve flattens in the region of 1 μs where the e.p.r. spectrum is insensitive to further reductions in relaxation time. If the COL is following the β relaxation, then it is slowing down with decreasing temperature, but this is not detectable by conventional e.p.r.

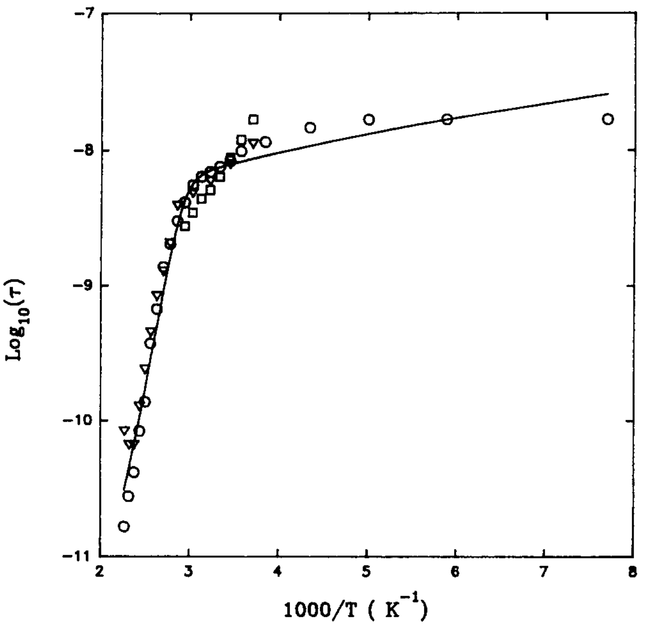

Figure 5 Plot of the log of the rotational correlation time *versus* inverse temperature for TPL in PVA. The different symbols indicate data obtained on different days. The solid line is a GCAT match to the data

A plot of log τ *versus* $1000/T$ for TPL (*Figure 5*) has quite a different appearance. The continuous curve bends and flattens at $\tau \sim 10^{-7}$ s or less. Here the e.p.r. spectrum is still responding to a variation in τ. The TPL appears to be following the γ relaxation. The curve connecting the points is the GCAT fit, and the fitting parameters are given in *Table 1*. We have also fit the high temperature portion of the curve to the various models indicated in the introduction. The fits do not look very different to those shown in reference 4 and so they are not shown. The fitting parameters are listed in *Table 1* with the corresponding values obtained in our previous work[4] in parentheses where appropriate. The values of τ in reference 4 were obtained from analytical calculations valid at higher temperatures where the three hyperfine lines were well separated. In spite of this we find generally good agreement between the two sets of fits.

We have previously shown that a plot of the height of the central line in the low temperature spectra *versus* temperature has a minimum which is associated with the glass transition[1-3,24]. For an isotropic liquid the minimum occurs at the glass transition. For a nematic liquid crystal the situation is more complicated[1,24]. A small spherical probe detected a single glass transition while a longer flexible probe detected the main glass transition, at a higher temperature than the small probe. The larger probe also detected a lower temperature transition which can be associated with chain melting[25,26]. Similar results were reported earlier by a group using the Mossbauer technique[27]. In *Figure 6* we plot the height of the central line *versus* temperature for the two probes in PVA. The line is a cubic spline fit to the points obtained, using SigmaPlot 4.0. TPL displays a broad minimum at a

Table 1 Parameters used when fitting the various models presented in the text to the rotational correlation time data for TPL

GCAT	τ_{01} (s K) 0.28×10^{-10}	τ_{02} (s K) 1.7×10^{-6}	$-\gamma v_m$ (K) 2110	β 57	$\Delta E/R$ (cal mol^{-1}) 86
EAL	τ_0 (s) 2.5×10^{-20} (2.2×10^{-23})	E_A/R (kcal mol^{-1}) 9.2 (22.6)			
EA	$A\tau_0$ (s K) 1.8×10^{-17} (2.0×10^{-20})	E_A/R (kcal mol^{-1}) 8.8 (22)			
VF	$A\tau_0$ (s K) 1.5×10^{-10} (9.6×10^{-13})	B (K) 836 (1027)	T_0 (K) 262 (302)		
WLF	τ_g (s) 0.48×10^{-3} (0.59×10^{-3})	C_1^g 23.7 (23.8)	C_2^g (K) 62 (61.7)	T_g (K) 294 (310)	
WLFV	$A\tau_0$ (s K) 0.62×10^{-11} (0.79×10^{-13})	$b/\Delta\alpha$ (K) 1618 (1883)	$fg/\Delta\alpha$ (K) 81.4 (57.4)		
BCM	τ_r (s) 2.24×10^{-14} (1.3×10^{-15})	f 0.75 (0.88)			

The values of the corresponding fitting parameters from reference 4 are in parentheses

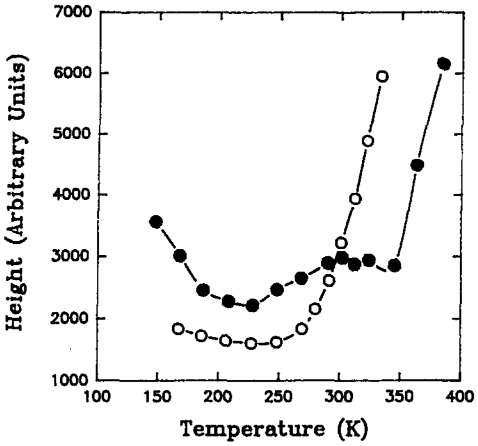

Figure 6 Plot of the central line height from the low temperature spectra of both COL (●) and TLP (○) *versus* temperature. The lines are cubic spline fits to the data

temperature below the main glass transition. The e.p.r. spectra presented indicate that TPL is forced out of the region between the main chains so we do not observe a sharp minimum at the main glass transition. Instead, we observe the broad minimum over the range of temperatures where a variety of motions 'freeze' out. The COL curve shows two minima. The first occurs at a temperature just above the reported glass transition where the relaxation time is reduced due to the rapidly increasing viscosity and the bulkiness of the probe. The low temperature minimum occurs at 200–225 K. At this temperature the γ relaxation is $\sim$1 MHz, i.e. the rate where motion 'freezes' out as far as the e.p.r. data are concerned. We associate the lower minimum in the COL plot with the 'freezing' of the methyl chain motions. It is interesting to note that even though the main features of the spectra from COL are essentially unchanging at these temperatures, there are still some minor features that respond to the γ relaxation.

CONCLUSIONS

We have extracted rotational correlation times from e.p.r. spectra of spin probes dissolved in PVA over a wide range of temperatures by performing theoretical simulations of the spectra. The use of different sized and shaped probes allows us to obtain a wide variety of results. The bulky COL probe does not appear to occupy multiple sites. Its motions follow the main glass to rubber relaxation at higher temperatures and appear to follow the β relaxation at lower temperatures. The low temperature spectra also have some sensitivity to the γ relaxation as evidenced by the apparent detection of the 'freezing' of the motions of the methyl group. TPL, the smaller probe, clearly occupies multiple sites. At higher temperatures its motions also follow the main glass to rubber relaxation, but at lower temperatures its motions follow the γ relaxation. The rotational correlation time data are well fitted by the GCAT model which we have developed previously. In addition, the high temperature data can be fit to a variety of viscosity and tumbling time models as we have previously done using the analytically calculated data. We find reasonably good agreement between the simulations and the analytical data.

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