

Further EPR Studies of Molecular Motions in Polymer/Plasticizer Mixtures

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SYNOPSIS

Molecular motions in mixtures of the side chain polymer—poly(vinyl acetate) and dibutyl phthalate were studied as a function of polymer concentration and temperature using the technique of paramagnetic resonance (EPR). When the small spherical probe tempol (TPL) was used, we were able to approximate the observed EPR spectrum with a simulation using a single rotational correlation time τ . The previously developed Grest–Cohen all-temperature model matched the Arrhenius plots. The EPR spectra from a cigar-shaped cholestane (COL) probe could not be adequately matched by a single τ simulation when the polymer was at temperatures somewhat above the glass to rubber transition temperature (T_g). Points corresponding to these temperatures were left off of the Arrhenius plot and a discontinuity was observed where the gap in the data occurred. As the concentration of plasticizer was increased, we found that the discontinuity became less steep, but the τ at which the gap occurs was always $\approx 10^{-8}$ s. The spectra observed at the temperature region of the gap were approximately 50–50 composites of experimental spectra observed at ± 10 K. In both the TPL and COL cases, there was evidence of the existence of multiple correlation times. Preliminary studies of other polymers, both with and without side chains, also indicated the existence of the gap when COL is used as the probe. © 1993 John Wiley & Sons, Inc.

Keywords: poly(vinyl acetate) • plasticizer • paramagnetic resonance • spin probes • molecular motions

INTRODUCTION

In this work we continue the study of glass-forming materials. Previous studies involved liquids, liquid crystals, polymers, and polymer/plasticizer mixtures.^{1–9} This study deals the molecular motions of polymer/plasticizer mixtures as a function of polymer concentration and temperature from well below to well above the glass transition. Previously we reported that the molecular motion of the nearly spherical spin-probe tempol (TPL) in pure poly(vinyl acetate) (PVA)⁶ and in pure dibutyl phthalate (DB)² could be approximately characterized by a single rotational correlation time τ , even though there was some evidence of motions at multiple τ 's, especially at temperatures just above the

glass transition. The motions of the large cylindrical probe cholestane (COL) dissolved in the pure plasticizer DB displayed similar results. The resulting Arrhenius plots were matched by the Grest–Cohen all-temperature model² (GCAT):

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

Here the high temperature data were matched by the Grest and Cohen^{10–12} expression (first term), and the low temperature data were matched by an activation energy model (second term).

More recently, Li and Gelerinter⁶ have shown that the results were somewhat different for COL

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dissolved in PVA. In this case the motion of the probe just above the T_g could not be adequately approximated by a single τ value. Points corresponding to these temperatures were not plotted on the Arrhenius plots, which then displayed a sharp discontinuity in the thermal region somewhat above the glass temperature T_g . In this work the discontinuity was observed for the COL probe as the concentration of polymer was varied. The steepness of the discontinuity decreased with decreasing polymer concentration, but the discontinuity always appeared at $\tau \approx 10^{-8}$ s.

EXPERIMENTAL

The paramagnetic resonance (EPR) spectrometer, temperature controller, and sample preparation have been described earlier.⁵ The τ values were extracted from diffusion constants used in spectral simulations. The program used was originally written by Moro and Freed and was based on the Lanczos algorithm.^{13,14} TPL's motion was characterized by a single diffusion constant D , since it has a nearly spherical shape, but COL's motion was characterized by $D_{\parallel} = 5D_{\perp}$ since it has a geometrical aspect ratio of approximately 5. Strictly speaking, the anisotropy in D is not necessarily equal to the aspect ratio, but we found that the simulations were not very sensitive to moderate changes in this anisotropy. $\tau = \frac{1}{6D}$ for TPL and $\frac{1}{6(D_{\parallel}D_{\perp})^{1/2}}$ for COL. The Brownian model of diffusion was used to simulate the spectra, and spot checks indicated only minor changes in the cal-



Figure 1. Experimental and calculated spectra from TPL dissolved in a mixture of 25% PVA with 75% DB by weight. The temperatures at which the spectra were observed are indicated in the center column.

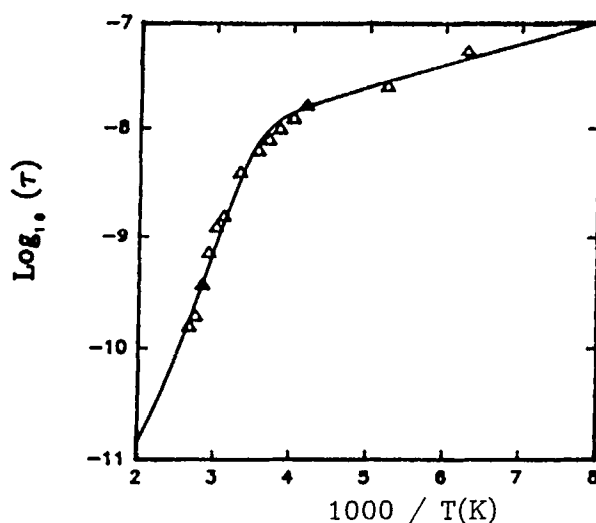


Figure 2. A plot of the \log_{10} of the rotational correlation time of the TPL probe dissolved in a mixture of 75% PVA with 25% DB by weight.

culated diffusion constants when the free diffusion was employed. The matches of the GCAT model to the TPL data were done using a nonlinear least squares fitting routine.¹⁵ First the high temperature data were fit to the Grest-Cohen model and then, using the fitting parameters thus obtained, all of the data were fit to the GCAT model.

RESULTS AND DISCUSSION

We have studied mixtures of the side-chain polymer PVA in DB using both TPL and COL spin probes. In Figure 1 we present some of the TPL data from a 25% mixture of PVA in DB, along with the spectral simulations. The data obtained, with the sample at 250 K, displays the low field structure previously reported for pure PVA,⁶ indicating that some of the probes are sensing motions at τ values different from that used in the simulation. One possible explanation is that this is due to TPL being squeezed out of the region between the main chains as T_g is approached. Similar effects have been reported by us and others when studying liquid crystals.^{16,17} A second possible explanation is that as T_g is approached from above, the polymer has sites that are liquid-like and solid-like, and the observed EPR spectra are composites of signals from probes in these sites. We have preliminary evidence that these spectra can be matched by a sum of a motionally narrowed spectrum and a motionally broadened spectrum. This observation favors the second possibility.

Table I. Parameters Used in Matching the GCAT Model to the TPL Data

| PVA | τ_{01} (s K) | τ_{02} (s K) | $-\gamma\nu_m$ (K) | β (K) | $\Delta E/R$ (K) | T_g (K) |
|-----|----------------------|----------------------|-----------------------|----------------|---------------------|--------------|
| 100 | 0.28E-10 | 1.7E-06 | 2110 | 57 | 86 | 305 |
| 75 | 0.27E-09 | 0.97E-06 | 1783 | 100 | 320 | 270 |
| 50 | 0.26E-09 | 1.5E-06 | 1776 | 91 | 185 | 223 |
| 25 | 0.19E-09 | 2.8E-06 | 1776 | 93 | 69 | 205 |
| 0 | 0.09E-09 | 10E-06 | 1849 | 91 | 64 | 185 |

In Figure 2 we show a typical Arrhenius plot for TPL dissolved in a mixture of 75% PVA and 25% DB by weight. The solid line is a match of the GCAT model to the data. T_g was obtained from literature sources.^{6,8} The matching parameters appear in Table I. The data for pure PVA⁶ have been previously reported by Li and Gelerinter. We expect the data for the 100% case to be different from the mixtures since here the motions of the side chains need to be coupled because of the crowding. In Table I, we note

that the activation energy ($\Delta E/R$) for the mixtures monotonically decreases as the glass temperature is reduced, indicating that barrier to reorientation is reduced with decreasing concentration of PVA. Also, the monotonically decreasing value of τ_{01} indicates that the Grest-Cohen portion of the plots moves to lower temperature as the concentration of PVA is reduced.

When COL was used to probe the PVA/DB mixtures, the situation was quite different. A disconti-

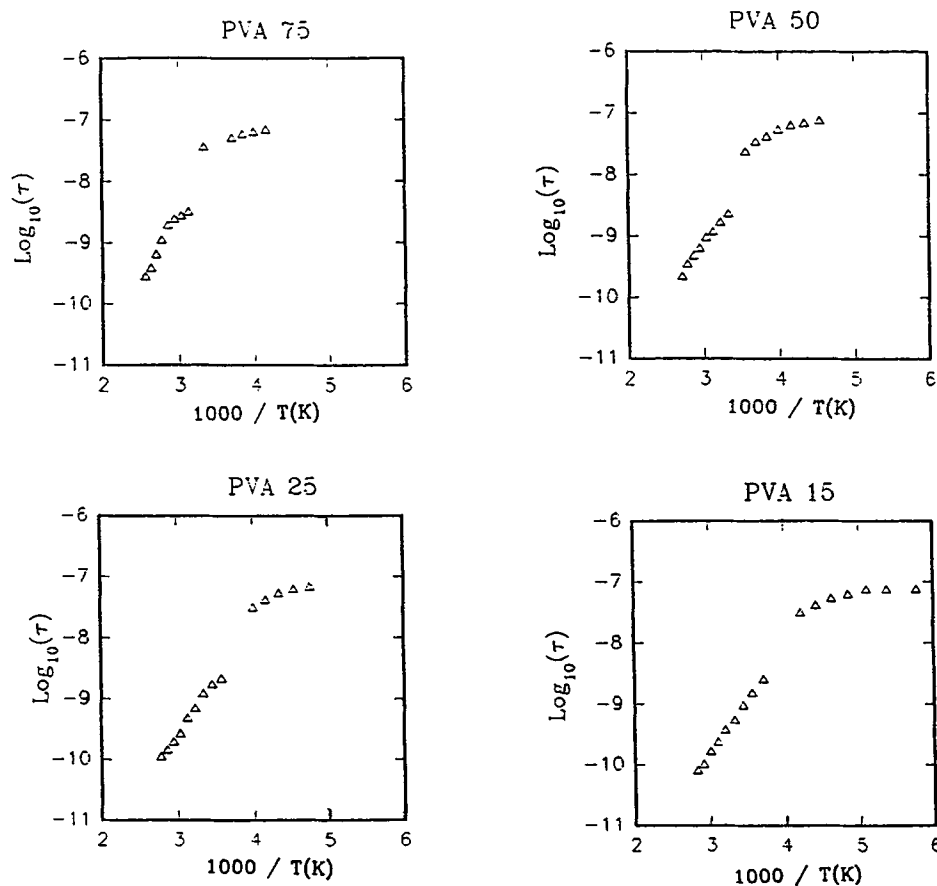


Figure 3. Plots of the \log_{10} of the rotational correlation time of the COL probe dissolved in mixtures of various concentrations of PVA with DB. The PVA concentrations are indicated.

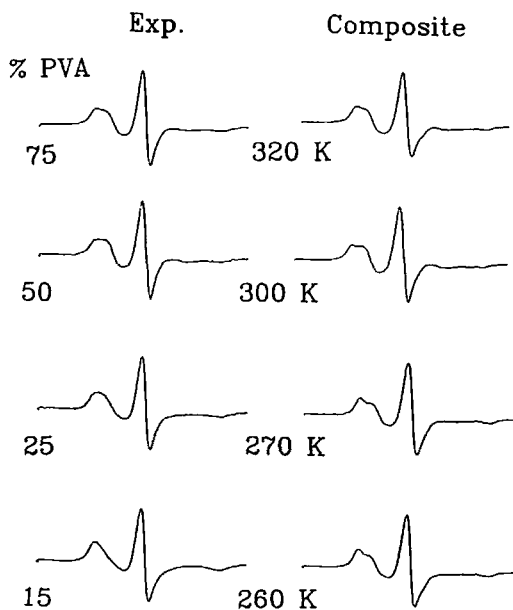


Figure 4. COL spectra observed at gap temperatures and their simulations as composite spectra. The gap temperatures are indicated.

nity or gap in the Arrhenius plots was observed (Figure 3). The gap persisted until the PVA concentration was reduced to 10% by weight, but the steepness of the jump decreased with decreasing concentration of PVA. We were unable to simulate spectra observed in the gap as a single spectral line, but the observed spectra were approximately matched by a sum of a higher and a lower temper-

Table II. Parameters Used to Construct the Composite Spectra

| % PVA | T_{gap} (K) | %-Temperature (K) | %-Temperature (K) |
|-------|----------------------|-------------------|-------------------|
| 75 | 320 | 50-330 | 50-310 |
| 50 | 300 | 50-310 | 50-290 |
| 25 | 270 | 50-280 | 50-260 |
| 15 | 260 | 55-270 | 45-250 |

ature spectrum (Figure 4), indicating a continuous variation in the τ 's. The details of the fits appear in Table II, where we can note that the composites are 50-50 mixtures of spectra just above and below the observed spectra. Here again, preliminary work indicates that these spectra can also be fit by a sum of a motionally broadened and a motionally narrowed spectrum, indicating the existence of at least two types of sites.

In Figure 5 we show a plot of the overall spectral width for both TPL and COL in 100% PVA. Such plots for the rest of the concentrations studied are quite similar, but they shift toward lower temperature as the concentration of PVA is decreased. At the high temperature end, the value of the splitting is $2A_{\text{iso}}$ i.e., twice the isotropic splitting, while at the low temperature end, the splitting is $2A_{\text{ZZ}}$, which is the largest possible splitting for a stationary distribution of probes of random orientations. We also note that the curve for TPL occurs at a lower temperature than that for Col, and the TPL curve ap-

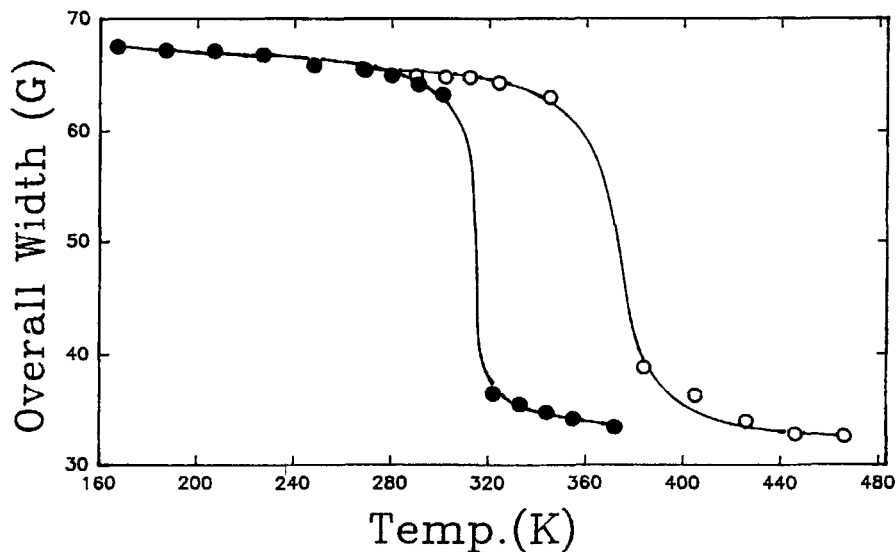


Figure 5. A plot of the overall spectral width for TPL (solid circles) and COL (open circles) dissolved in pure PVA.

Table III. Summary of the Data Obtained from the COL Probe

| % PVA (by Wt.) | T_g^a (K) | T_{gap} (K) | T_{50} (K) | T_{min} (K) |
|-------------------|----------------|-------------------------|-----------------|-------------------------|
| 100 | 305 | 333 | 366 | 348 |
| 75 | 270 | 320 | 333 | 309 |
| 50 | 225 | 300 | 302 | 280 |
| 25 | 205 | 270 | 282 | 269 |
| 15 | 200 | 260 | 267 | 248 |
| 0 | 185 | — | 256 | |

^a These are literature values.

pears steeper. One can find the parameter T_{50} , the temperature at which the splitting is 50 gauss. This is often used as an indicator of the type of molecular motions, but one should note that T_{50} depends both on the solvent and the probe. Hence, when using T_{50} to compare the motions of molecules in samples with different polymer concentrations, one must use the same probe. T_{50} is the approximate temperature of transition from fast to slow motion of the probe. At T_{50} one would expect to detect motions from probes in both stiff and fluid regions of the polymer.

In Table III we show a table for COL in which we compare T_g , the glass temperature, T_{gap} , the temperature at which the gap appears, and T_{50} , the temperature that indicates the intermediate region between the slow and fast motion regimes. We see that they appear to be following the same trends. Note the good correlation between T_{50} and T_{gap} . This is to be expected since the gaps occur in the thermal region where there are sites of differing fluidity, i.e., the thermal region where the glass is approached. The data in the last column, T_{min} , will be discussed below.

In Table IV we show the same data for the TPL probe. There is no gap per se, but the observed spectra at certain temperatures have extra structure that

Table IV. Summary of the Data Obtained from the TPL Probe

| % PVA (by Weight) | T_g^a (K) | T_{gap} (K) | T_{50} (K) |
|----------------------|----------------|-------------------------|-----------------|
| 100 | 305 | 290 | 315 |
| 75 | 270 | 270 | 281 |
| 50 | 225 | 260 | 261 |
| 25 | 205 | 240 | 244 |
| 0 | 185 | — | 231 |

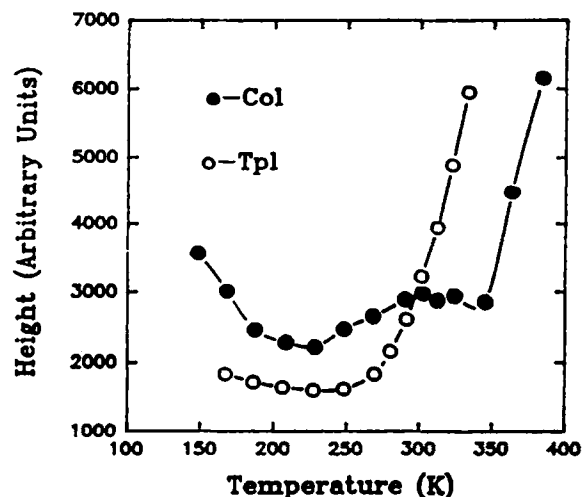
^a These are literature values.

indicates that the TPL is occupying more than one site. In analogy with the COL observations, we call this the gap temperature. Here again T_{50} and T_{gap} are well correlated, as one would expect for the reasons outlined above.

In previous work^{1,2,6} we demonstrated that a minimum in the height of the central line vs temperature was associated with the glass transition. In fact, it appeared to be a good indicator of the glass temperature for isotropic glass formers. In the work of Li and Gelerinter⁶ we observed such a plot, which is reproduced here (Figure 6). We noted a sharp minimum in the COL data and a broad minimum in the TPL data. These plots provided additional support for our explanations of the observed data. We have made plots for the other polymer concentrations with similar results. The temperatures at which the minima occur in the COL plots were entered in Table III under the heading T_{min} , and the values also correlated loosely with the rest of the data presented. Since the observed minima in the TPL data were quite broad, we chose not to enter the corresponding values in Table IV.

Summary

It appears that both TPL and COL behave in a manner that is qualitatively similar. They both occupy multiple sites as the temperature of the mixtures is reduced toward T_g . The large COL probe's EPR spectra cannot be satisfactorily simulated with a single τ in the thermal region corresponding to $\tau \approx 10^{-8}$ s. There is also a sharp change in τ as one crosses this thermal region, which results in a gap


Figure 6. A plot of the height of the central line vs temperature for both TPL and COL.

in the Arrhenius plot. The gap gradually disappears as the isotropic liquid is approached. TPL, on the other hand, is quite small. The effect of occupying multiple sites appears to be present, but the sharp change in τ , observed in the COL data, is not observed for TPL. Satisfactory approximate simulations of the TPL data is possible in this case.

We have also performed preliminary studies of COL and TPL dissolved in mixtures of DB with poly(butyl methacrylate), a side-chain polymer, and DB with poly(ethylene oxide), a polymer with no side chain. In both cases the COL data showed a gap similar to that observed with PVA. No gap appeared in any studies of pure DB. One concludes from this that some polymer is required to see the described effects, but it need not be a side-chain polymer.

REFERENCES AND NOTES

1. J. I. Spielberg and E. Gelerinter, *Phys. Rev. A*, **32**, 3647 (1985).
2. J. I. Spielberg and E. Gelerinter, *Phys. Rev. B*, **30**, 2319 (1984).
3. J. I. Spielberg and E. Gelerinter, *J. Chem. Phys.*, **77**, 2159 (1982).
4. J. I. Spielberg and E. Gelerinter, *Chem. Phys. Lett.*, **92**, 184 (1982).
5. J. F. Morris and E. Gelerinter, *Polymer*, **30**, 165 (1989).
6. J. Li and E. Gelerinter, *Polymer*, **33**, 963 (1992).
7. A. T. Bullock, G. G. Cameron, and I. S. Miles, *Polymer*, **23**, 1536 (1982).
8. I. S. Miles, G. G. Cameron, and A. T. Bullock, *Polymer*, **27**, 190 (1986).
9. P. Törmälä, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C17**, 297 (1979).
10. G. R. Grest and M. H. Cohen, in *Advances in Chemical Physics*, I. Prigogine and S. A. Rice, (eds.), Wiley, New York, 1981.
11. M. H. Cohen and G. S. Grest, *Phys. Rev. B*, **20**, 107 (1979); *Phys. Rev. Lett.* **45**, 1271 (1980).
12. G. R. Grest and M. H. Cohen, *Phys. Rev. B*, **21**, 411 (1980).
13. G. Moro, Cornell University Report (1980) unpublished.
14. G. Moro and J. H. Freed, *J. Phys. Chem.*, **84**, 2837 (1980). Dr. E. Meirovich, formerly of the Weizmann Institute of Science, was kind enough to provide a version of the simulation program suitable for the IBM mainframe computer.
15. W. N. Hubin, *Basic Programming for Scientists and Engineers*, Prentice-Hall, Englewood Cliffs, NJ, 1978.
16. W. J. Lin and J. H. Freed, *J. Phys. Chem.*, **83**, 379 (1979).
17. J. I. Spielberg and E. Gelerinter, *Chem. Phys. Lett.*, **92**, 184 (1982).

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