Paramagnetic resonance studies of the molecular motions of spin probes dissolved in polymers and polymer/plasticizer mixtures

James F. Morris and Edward Gelerinter*
Physics Department and Liquid Crystal Institute, Kent, OH 44242, USA
(Received 16 February 1988, accepted 17 June 1988)

Paramagnetic resonance was used to obtain rotational correlation times for spin probes dissolved in polymers and mixtures of polymer and plasticizer. The results were successfully matched to an assortment of literature models. Viscosity models generally gave more reasonable results than did rotational correlation time models. We also looked at some models associated with free volume calculations and present evidence that the free volume associated with the solvent might be a good indicator for the activation volume of the dissolved probe.

(Keywords: E.p.r., e.s.r., rotational correlation times, molecular motions, spin probes, polymers)

INTRODUCTION

Previously, we have studied the molecular motions of spin probes dissolved in glass forming isotropic liquids and liquid crystals[1-3]. The data were interpreted using a variety of viscosity models. There are many studies in the literature of viscous flow in glass forming materials[4-9]. Among the literature models that we wish to consider in this study is the classical energy activation model (EA) $\eta = \eta_0 \exp(E_A/RT)$, where E_A is the activation energy. A second model for the viscosity is the Vogel–Fulcher (VF) model[8,9] $\eta = \eta_0' \exp(B/(T - T_0))$, where T_0 is a theoretical glass temperature. Typically, but not always, T_0 is somewhat below the observed glass transition, T_g. The results of the VF model are in agreement with the excess entropy model of Gibbs and co-workers[7]. This latter model is based upon the concept that the configurational entropy decreases as the temperature is decreased making deformation more difficult.

Since one obtains the rotational correlation time, τ, from the electron paramagnetic (e.p.r.) data, it is necessary to convert the viscosity equations to correlation time equations using the Stokes–Einstein relation, $\tau = 4\pi a^2 \eta / 3kT = A(\eta/T)$. Here the probe is visualized as a sphere of radius a, tumbling in a viscous fluid. This relation applies to a 'normal' liquid, i.e. when the sample temperature is well above the glass transition, a condition that will be true throughout this study.

Another approach one might take is to interpret the data in terms of rotational correlation time models that are in the literature. The simplest is the assumption that τ, not η, follows the energy activation model, $\tau = \tau_0 \exp(E_A/kT)$. We will refer to this as EAL. This model, in the past, has led to unreasonably fast high temperature correlation times, τ_0, and some workers have proposed the use of a variable activation energy to deal with this problem[10]. It should be pointed out that the previously mentioned VF model for the viscosity can be viewed as a variable activation energy[3]. A second model that will be considered is the Williams, Landel, Ferry model (WLF).

$$\tau = \tau_g \exp[-c_1^g (T - T_g)/(c_2^g + T - T_g)]$$

This model has been used extensively to interpret the results of mechanical visco-elastic studies performed on polymers[6], and values for the mechanical constants have been tabulated for several systems[11].

Bullock, Cameron and Miles[12,13] have developed a model (BCM) for the temperature dependence of τ, based upon the free volume concept. This model, which assumes that the WLF mechanical constants are known, yields

$$\tau = \tau_\infty \exp f[2.303 c_1^g c_2^g/(T - T_g + c_2^g)]$$

where f is the activation volume of the probe/activation volume of the polymer segment.

In this work we report an extension of our studies of glass forming liquids to some polymers and mixtures of a polymer and plasticizer. There are several e.p.r. studies of polymers in the literature[14] but, to our knowledge, none of these take the approach reported here. If a relaxation map of a typical polymer is studied, one finds that there are relaxation modes that merge with the main glass to rubber transition at a temperature well above the glass transition temperature. At higher temperatures there appears to be only the main relaxation (cf. the relaxation map of Poly(vinyl acetate) (PVA) in ref. 13). In this work, data taken in the higher temperature regime will be studied.

EXPERIMENTAL

Samples consisted of Poly(ethyl methacrylate) (PEM), or PVA, or a solution of PVA and the plasticizer dibutyl phthalate (DB), and a spin probe. The probes used are 3-doxyl-5α-cholestane (COL) and 4-hydroxy-Tempo (TPL). The latter probe has alternately been referred to as

---

* Present address and to whom all correspondence should be addressed: Department of Isotope Research, The Weizmann Institute of Science, Rehovot, Israel.

0032-3861/89/010165-05$03.00

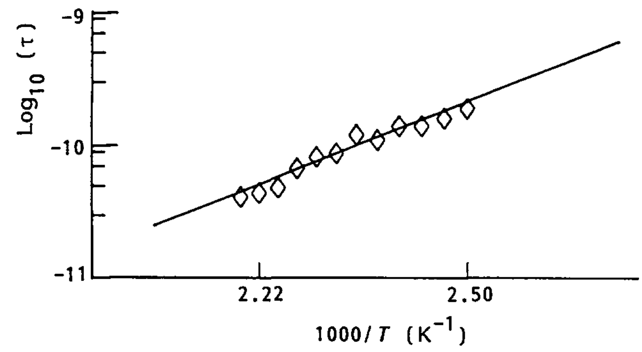

Figure 1 Match of the EAL model to τ from the PEM/TPL polymer/probe system

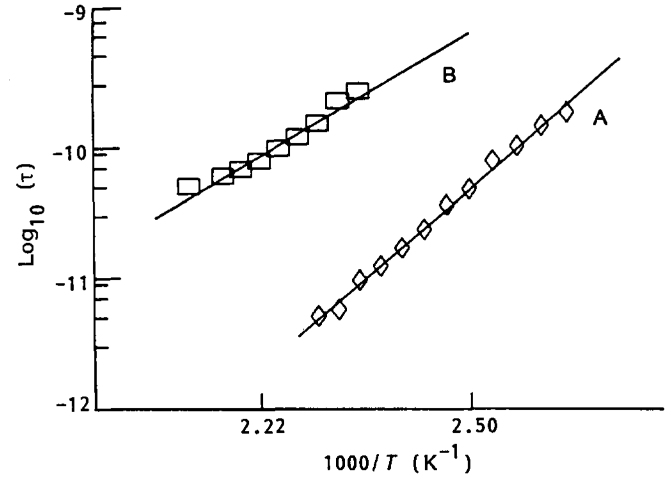

Figure 2 Match of the EAL model to τ from the PVA/TPL (curve A) and PVA/COL (curve B) polymer/probe systems

Tanol or Tempol in the literature. TPL is small and nearly spherical, but COL has a bulkier cigar shape. As a result, COL is expected to tumble more slowly than TPL under the same conditions, and it is usually required to go to higher temperatures, as compared to TPL, to get a well resolved three line spectrum. When studying PEM, which has a reported T_g of 335 K, we found that the high temperatures required caused COL to decompose, so that we do not report any studies of τ in PEM/COL.

The polymer and approximately 200 ppm probe (and in some cases DB) were dissolved in a solvent such as dichloro methane or chloroform, and, after mixing, the solvent was evaporated under vacuum. The samples were then sealed in 4 mm o.d. quartz tubes under approximately $\frac{1}{2}$ atmosphere of N_2. Data were obtained using an IBM 200D-SRC spectrometer with an ER 044 MRDH X-band microwave bridge. An IBM CS 9000 computer and the IBM EPR software package were used for spectrometer control, data acquisition and analysis. The temperature was controlled with an IBM ER 4111 VT temperature controller which has a precision of 1 K. The spectrometer frequency was measured using a Hewlett Packard 5351A microwave frequency counter, and the magnetic field was measured by the Hall probe of the spectrometer which had previously been calibrated near $g=2$ using an n.m.r. gaussmeter. These results were used to obtain g values and hyperfine constants used in our calculations of τ.

The values of τ were calculated from the e.p.r. spectral heights and widths using techniques described by Kivelson and others[15-17]. The matches of the EAL and BCM models to our data were done using a linear least squares fitting program[18], and the matches to all of the other models used a non-linear least squares fitting routine[19]. D.s.c. scans were performed using a Perkin Elmer DSC-S differential scanning calorimeter.

RESULTS AND DISCUSSION

In *Figure 1* we show the fit of the EAL model to the PEM/TPL data. The parameters used in all of the reported cases are shown in *Table 1*. In the case of *Figure 1*, τ_0 is quite a bit faster than what one might reasonably expect. It is faster still in our matches to PVA/TPL and PVA/COL systems shown in curves A and B in *Figure 2*. This effect has also been observed by others. Furthermore, the activation energies obtained from the two PVA systems are quite different. This is a disturbing result for anyone who believes that the temperature dependent part of the probe's motion reflects the molecular motion of the solvent. These difficulties can be removed if we match the data to the corresponding viscosity model, EA. The matches are shown for PEM/TPL, PVA/TPL, and PVA/COL in *Figure 3* and curves A and B in *Figure 4*. Referring to *Table 1*, we see that the activation energies for the two PVA systems are equal, removing one of the previous difficulties. Further, one can calculate the value of τ_g from the EA model. Using $T_g = 335$ K for PEM, we get 8.6E–7 s for PEM/TPL,

Table 1 The parameters used to match the models described in the text to the data obtained in this study

EAL Model

Sample	Probe	τ_0 (s)	E_A (kcal/mole)
PEM	TPL	5.2E–16	10.3
PVA	TPL	2.2E–23	22.6
PVA	COL	2.6E–18	15.5

EA Model

Sample	Probe	$A\eta_0$ (s–K)	E_A (kcal/mole)
PEM	TPL	3.3E–13	9.9
PVA	TPL	2.0E–20	22
PVA	COL	8.6E–19	21.9

VF Model

Sample	Probe	$A\eta'_0$ (s–K)	B (K)	T_0 (K)
PEM	TPL	6.0E–9	249	300
PVA	TPL	9.6E–13	1027	302
PVA	COL	4.7E–11	994	299

WLF Model

Sample	Probe	τ_g (s)	c_1^g	c_2^g (K)	T_g (K)
PEM	TPL	3.7E–5	17	37.1	310.3
PVA	COL	1.4E–3	24	62.1	310.1
PVA	TPL	5.9E–5	23.8	61.7	310
75% PVA/25% DB	TPL	1.0E–5	21.1	60.7	269.9
50% PVA/50% DB	TPL	2.4E–5	20.9	58.9	223.4
DB	TPL	1.1E–5	20.1	53.1	189.4

BCM Model

Sample	Probe	f	τ_∞ (s)	r
PEM	TPL	0.256	1.1E–12	0.96
PVA	COL	0.82	6.4E–14	0.99
PVA	TPL	0.88	1.3E–15	0.99

WLFV Model

Sample	Probe	$A\eta_0$ (s–K)	$b/\Delta\alpha$	$f_g/\Delta\alpha$ (K)
PEM	TPL	2.4E–9	749	55.7
PVA	COL	2.6E–12	1893	55.5
PVA	TPL	7.9E–14	1883	57.4

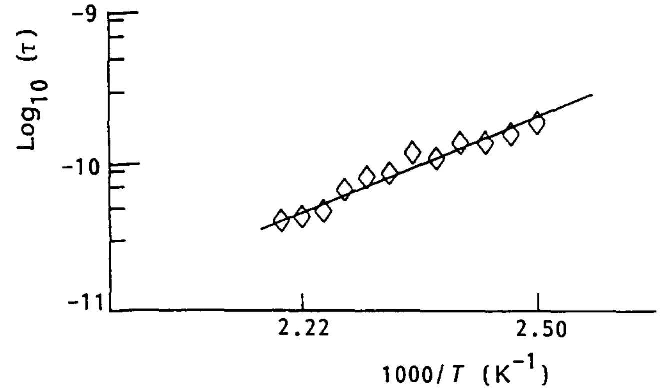

Figure 3 Match of the EA model to τ from the PEM/TPL polymer/probe system

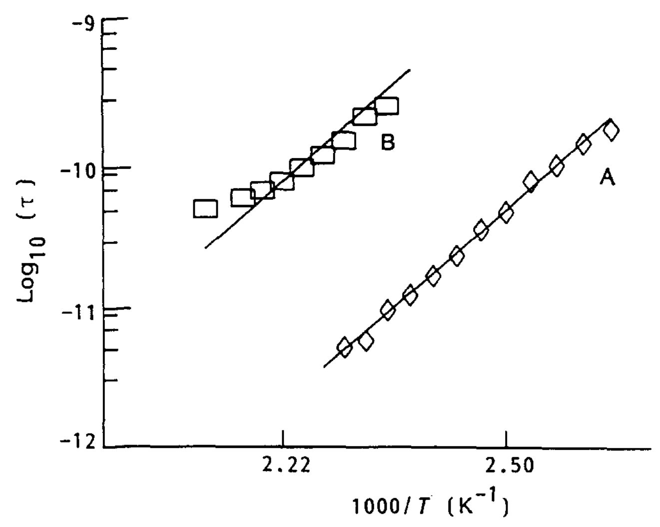

Figure 4 Match of the EA model to τ from the PVA/TPL (curve A) and PVA/COL (curve B) polymer/probe systems

and using $T_g = 307$ K for PVA, we get 2.6E–3 and 7.3E–5 s for the rotational correlation times of the spin probes (not the solvent molecules). These are not unreasonable and are, at least in the case of the PVA systems, comparable to the values obtained using the WLF model. In these cases the viscosity model appears to give much more reasonable results than the corresponding correlation time model.

The results for the VF model are shown in *Figures 5* and *6* for PEM/TPL, PVA/TPL and PVA/COL. The corresponding matching parameters are shown in *Table 1*. The results appear quite reasonable compared with those we have previously reported for pure DB. B for both PVA systems are quite close, and the effect of probe size can be seen by noting that COL tumbles considerably slower, at the same temperature, than TPL. TPL in PEM tumbles even more slowly, at the same temperature, indicating that PEM is more viscous than PVA at this temperature. This is easily understood because the reported T_g for PEM (335 K) is approximately 30 K higher than that for PVA (305–310 K), so at a given temperature PEM is considerably closer to its glass transition. These results can be noted in the EAL and EA model calculations. As pointed out previously, the VF model can be considered as a variable activation energy model with E_A (kcal/mole) $= (BR/1000)[T - T_0)]^2$. The EA model result is approximated for PVA at 440 K, and 386 K for PEM.

In *Figures 7* and *8* we show the matches of the WLF model to PEM/TPL, PVA/TPL and PVA/COL. In *Figure 9* we show the match of WLF to TPL dissolved into mixtures of PVA/DB of varying concentrations. The value of τ_g shown in *Table 1* for TPL dissolved in all of the polymers and polymer mixtures is approximately a few E–5. This is a reflection of the fact that the viscosity of all of the polymer mixtures at T_g is about the same. In fact, some authors define the onset of a glass in terms of the viscosity value. Since COL is considerably larger than TPL, it is not surprising to note that τ_g is considerably smaller for COL. Care should be taken in the interpretation of τ_g. It is the rotational correlation time of the probe molecule as predicted by the WLF model. It is not the rotational correlation time of the solvent molecules which would be expected to be quite a bit slower. (The relaxation map for PVA in ref. 13, predicts times of the order of 100 s.) It is also not the value which would be obtained actually measuring τ_g using e.p.r.. Miles and co-workers[13] have performed this measurement for PVA and find that $\tau_g \approx$ 1E–7 s and show that the data follows the γ transition. We have reported[1-3] a similar value for COL and Tempone (a small probe similar to TPL) dissolved in DB. We interpreted this in terms of the glass model put forth by Grest and Cohen in which there are liquid and solid-like sites[1-3,20-22]. In our

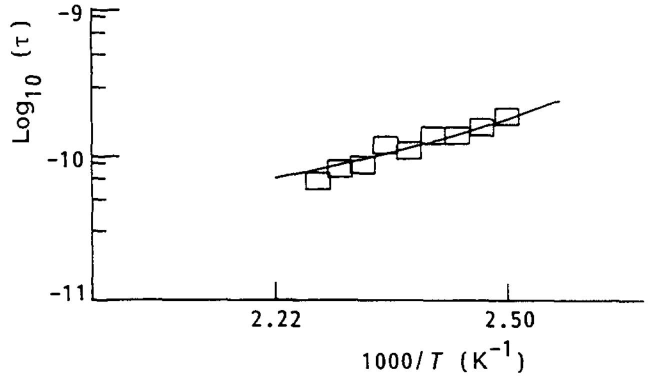

Figure 5 Match of the VF model to τ from the PEM/TPL polymer/probe system

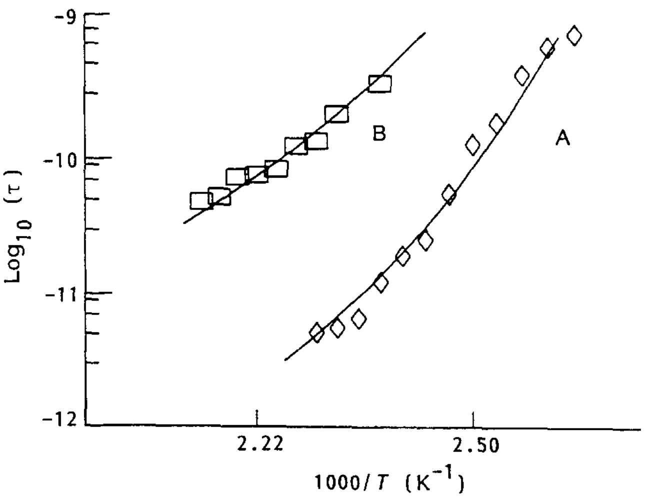

Figure 6 Match of the VF model to τ from the PVA/TPL (curve A) and PVA/COL (curve B) polymer/probe systems

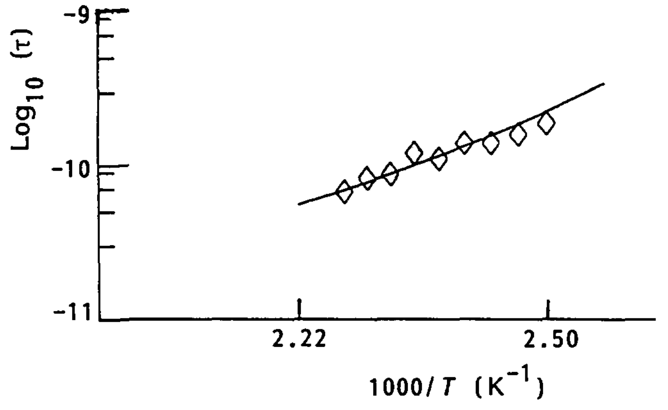

Figure 7 Match of the WLF model to τ from the PEM/TPL polymer/probe system

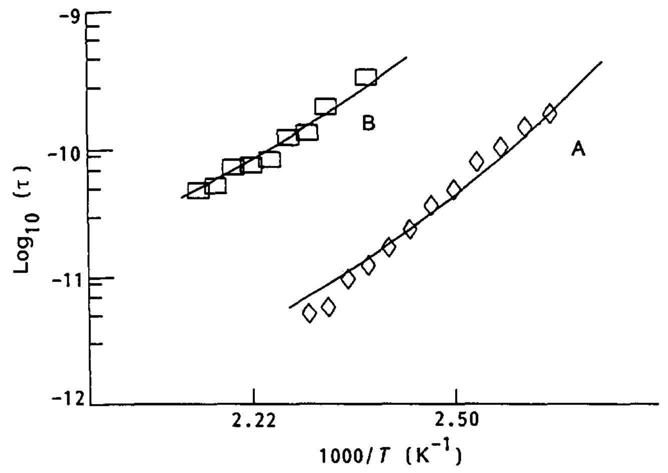

Figure 8 Match of the WLF model to τ from the PVA/TPL (curve A) and PVA/COL (curve B) polymer/probe systems

view, this is because the e.p.r. spectra came from probes in the liquid-like sites, and the probes in the solid-like sites would have rotational correlation times too slow to be detected by conventional e.p.r.. The work of Miles and cooworkers provide support for this view. Their low temperature measurements of τ using saturation transfer e.s.r. spectroscopy result in values that fall on the main glass to rubber transition, i.e. these values are the order of 0.001 s. The saturation transfer technique is sensitive to rotational correlation times from 10^{-3} to 10^{-6} s, so that it detects the motions of the probe molecules in the more rigid (solid-like) sites.

We also see that WLF gives reasonable values for T_g. The reported T_g for PEM[11] is 335 K, and our match gives a slightly lower value. The value obtained for PVA is consistent with the literature values[11,13] of 305–307 K, and our d.s.c. measurements of 303–305 K. Note that the results using TPL and COL are consistent. We measure T_g for the 75% PVA/25% DB as ≈ 285 K using d.s.c. and 260 K can be estimated from *Figure 9* in ref. 13. These values straddle the WLF result. At 50% PVA/DB we estimate T_g to be 215 K from ref. 13. This is in good agreement with the WLF result. We have measured T_g for DB using a variety of methods and find values of 180–184 K, which are fairly close to the WLF result.

The WLF results for the mechanical constants are somewhat different from those obtained from mechanical measurements. The previously reported values for c_1^g and c_2^g are 17.6 and 65.6 for PEM and 15.6 and 46.8 for PVA[11]. Perhaps one should not really be surprised at this discrepancy because the mechanical experiments measure the motions of the solvent molecules, not those of the solute probe. Nevertheless, we note that COL and TPL both give the same results for the mechanical constants. Furthermore, as the ratio of PVA to DB in the mixtures decreases, the constants monotonically decrease toward the pure DB values. These two observations along with those concerning the WLF results for τ_g and T_g contribute to the idea that the WLF parameters we report are reflective of the properties of the solvent. The goodness of fit parameters and the plots indicate that the WLF model is a good fit to the data.

The BCM model has been successfully applied to obtain values for f that agree with those from other sources[13] when f is approximated by the probe volume/polymer segment volume. We have also matched this model to our data and the results are shown in *Table 1*. We also include a column showing the value of the correlation coefficient, r. $r=1$ indicates a perfect fit. The PVA data is fitted somewhat better than the PEM data. The values for f and τ_∞ are reasonable, but it is hard to understand why the results for PVA/COL and PVA/TPL are so close, given the different probe sizes. Perhaps it is a reflection of the fact that the probe's activation volume is determined by the free volume available to it, rather than its physical volume. This might also account for the f value for PEM/TPL being about one third of that for the PVA samples.

There is another interesting observation to be made. WLF also report[6] a form for the viscosity near T_g,

$$\eta=\eta_0 \exp[b/(f_g+\Delta\alpha(T-T_g))]$$

where typical values for b, f_g and $\Delta\alpha$ are 1.0, 2.5E–2 and 5E–4, respectively. If the numerator and denominator of the exponent are divided by $\Delta\alpha$ a form that looks just like the BCM exponent results. It appears that this model is to the BCM model as EA is to EAL. Further, if the typical values are used $2.303c_1^g c_2^g \to b/\Delta\alpha \approx 2000$ and $c_2^g \to f_g/\Delta\alpha \approx 50$. The corresponding results using the published mechanical constants and $f=0.85$ for PVA are 1430 and 46.8. Using $f=0.26$ and the published mechanical

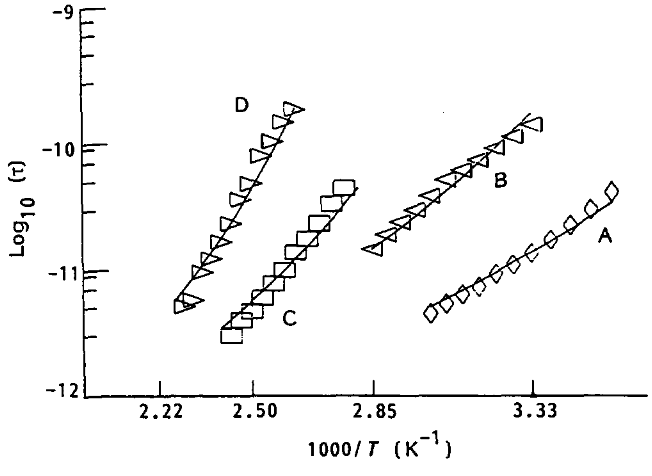

Figure 9 Match of the WLF model to τ from mixtures of PVA/DB/TPL. Curve A, pure DB, curve B, 50% PVA/50% DB, curve C, 75% PVA/25% DB and curve D, pure PVA

constants for PEM, we arrive at 690 and 65.5 for these results. Alternately, the observed values of τ can be matched to this equation for η using the Stokes–Einstein relation to find the values shown in *Table 1* under the heading WLFV Model. Here we used the published values for T_g, 305 for PVA and 335 for PEM. $f_g/\Delta\alpha$ is directly affected by the choice of T_g because they are summed in the denominator of the exponent. We note that the matching parameters $b/\Delta\alpha$ and $f_g/\Delta\alpha$ from the PVA data are nearly independent of the probe, giving credence to our assertion that the activation volume of the probe is probably determined by the free volume of the polymer. Also, we note that the 749 we report for $b/\Delta\alpha$ is close to value of 690 calculated above.

SUMMARY

We have obtained rotational correlation times for the polymers PEM and PVA, and mixtures of PVA with DB. These results were matched to a variety of models for the temperature dependence of both τ and η with some success. The mechanical parameters obtained from matching the data to the WLF model allowed us to find the mechanical constants of the probe rotating in the given solvent. We have also successfully matched the data to the BCM and WLFV models.The results of these matches provide evidence that the tumbling of the probe may be influenced by the available free volume because the parameters obtained are much more dependent upon the polymer than the probe.

ACKNOWLEDGEMENTS

The authors would like to thank Dr M. Neubert of the Liquid Crystal Institute and her student D. Leonhardt for assistance in preparing the samples. The students, S. Bucey, G. Crawford, S. Joseph and D. Paterson helped by recording data and performing matches.

REFERENCES

1 Spielberg, J. I. and Gelerinter, E. *Phys. Rev. A* 1985, **32**, 3647

2 Spielberg, J. I. and Gelerinter, E. *Phys. Rev. B* 1984, **30**, 2319

3 Spielberg, J. I. and Gelerinter, E. *J. Chem. Phys.* 1982, **77**, 2159

4 Angell, C. A., Clarke, J. H. R. and Woodcock, L. V. *Adv. Chem. Phys.* 1981, **48**, 397

5 Wong, J. and Angell, C. A. 'Glass Structure by Spectroscopy', Dekker, New York, 1976

6 William, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701

7 D. Marzio, E. A. and Gibbs, J. W. *J. Chem. Phys.* 1958, **28**, 807; *J. Polym. Sci.* 1963, **A1**, 1417; *J. Polym. Sci.* 1959, **40**, 121

8 Vogel, H. *Phys. Z.* 1921, **22**, 645

9 Fulcher, G. S. *J. Amer. Ceram. Soc.* 1925, **6**, 339

10 Buchachenko, A. L., Kovarskii, A. L. and Vasserman, A. M. 'Advances in Polymer Sciences', (Ed. Z. A. Rogovin), Wiley, New York, 1947, p. 26

11 Ferry, J. D. 'Viscoelastic Properties of Polymers', Wiley, New York, 1970

12 Bullock, A. T., Cameron, G. G. and Miles, I. S. *Polymer* 1982, **23**, 1536

13 Miles, I. S., Cameron, G. G. and Bullock, A. T. *Polymer* 1986, **27**, 190

14 Törmälä, P. *J. Macromol. Sci. Rev. Macromol. Chem.* 1979, **C17**, 297

15 Kivelson, D. *J. Chem. Phys.* 1960, **33**, 1094

16 Stone, T. J., Buckman, T., Nordio, P. L. and McConnell, H. M. *Proc. N.A.S.* 1965, **54**, 1010

17 Fried, J. H., 'Spin Labeling Theory and Applications', (Ed., L. J. Berliner), Academic Press, New York, 1976

18 Bevington, P. R. 'Data Reduction and Error Analysis for the Physical Sciences', McGraw Hill, New York, 1969

19 Hubin, W. N. 'Basic Programming for Scientists and Engineers', Prentice Hall, Englewood Cliffs, NJ, 1978

20 Grest, G. R. and Cohen, M. H. 'Advances in Chemical Physics' (Eds, I. Prigogine and S. A. Rice), Wiley, New York, 1981

21 Cohen, M. H. and Grest, G. S. *Phys. Rev. B* 1979, **20**, 107; *Phys. Rev. Lett.* 1980, **45**, 1271

22 Grest, G. R. and Cohen, M. H. *Phys. Rev. B* 1980, **21**, 411