E.s.r. and saturation transfer e.s.r. spectroscopy of spin-probed poly(vinyl acetate): A new spectral transition correlating with glass transition temperature

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From the temperature dependence of the rotational frequency of a nitroxide spin probe dispersed in poly(vinyl acetate) the size of the polymer segment involved in the glass to rubber relaxation can be estimated. The calculation is based on a free volume model which relates f, the ratio of the volumes of the spin probe and the polymer segment, to the rotational frequency of the probe. An increase in f with increasing size of the probe is demonstrated. Saturation transfer electron spin resonance spectra of two nitroxide probes are shown to undergo a rapid change with temperature at a temperature T_R which is characteristic of both the probe and its environment. T_R corresponds to a pseudo-isofrequency point and is analogous to, though at a lower characteristic frequency than, the widely-used parameter T_{50G}. For the systems examined, T_R correlates with the glass to rubber relaxation.

(Keywords: spin-probe; poly(vinyl acetate); e.s.r. spectroscopy; correlation times; segment size)

INTRODUCTION

From the electron spin resonance (e.s.r.) spectra of nitroxide radicals, details of their rotational motion may be obtained and information on the dynamics of their environment inferred. This is the basis of the spin-probe technique[1] which has been applied with some success in biological systems and, as in the present study, in the examination of relaxation processes in synthetic polymers[2]. The e.s.r. absorption spectrum is sensitive to changes in the correlation time, τ_R, for probe rotation over the range $10^{-11}\,s<\tau_R<10^{-6}$ s. This range may conveniently be divided into the motionally-narrowed region, $10^{-11}\,s<\tau_R<10^{-8}$ s, over which τ_R is calculated from the spectral linewidths, and the slow motion region $10^{-8}\,s<\tau_R<10^{-6}$ s, over which τ_R is measured via detailed spectral simulations. The separation of the spectral extrema decreases monotonically with decreasing τ_R and therefore with increasing temperature. In the motionally narrowed region the extrema separation is around 30 G while in the slow motion region it is 60–70 G, and it changes most rapidly in passing from one of these regimes to the other. An extrema separation of 50 G is generally taken as characteristic of the transition between the two regimes and the temperature associated with this separation, which depends on the particular probe/polymer system, is referred to as T_{50G}. Since the extrema separation for nitroxides is primarily determined by the anisotropy in the nitrogen hyperfine splitting tensor it changes most rapidly when the rotational frequency of the probe corresponds to this anisotropy. For nitroxide radicals this occurs at $\tau_R \sim 3\times10^{-9}$ s, that is near the middle of the frequency range accessible to τ_R measurements, and, in as much as the A tensor is similar for different nitroxides, T_{50G} approximates to an isofrequency point. The information provided by T_{50G} is more limited than that provided by τ_R measured over a range of temperatures, but it does have the advantage of being easily measured. It should be understood that T_{50G} (and τ_R) directly reflects the dynamic state of the probe not the host polymer. Nevertheless, it has been shown that probe motion is usually sensitive to the dynamic state of the host matrix and that T_{50G} for most nitroxide probe/polymer systems falls in the temperature range over which probe motion is determined by segmental reorientation. This leads to a correlation between T_{50G} and the glass transition temperature T_g and in such cases T_{50G} may be regarded as approximating to a high frequency ($\sim10^7$ Hz) glass transition temperature[3]. Provided that it is applied with discrimination and not assumed to be universally applicable, this concept is useful.

The frequency range of the spin-probe method has recently been extended by means of saturation transfer (ST) e.s.r. experiments[4]. In these, the microwave power is increased until the system is partially saturated. Such spectra are sensitive to motion which can provide a mechanism for diffusion of saturation between different parts of the spectrum. This process requires the motion to have a correlation time within the range $10^{-6}\leqslant\tau_R\leqslant10^{-3}$ s since the time constant, T_1, for relaxation of saturation generally lies in this range. Although in principle τ_R values may be obtained from ST experiments we confine ourselves here to the observation of a pseudo-isofrequency spectral transition occurring at a temperature T_R which is analogous to T_{50G}. In this paper

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we describe ST experiments with bulk poly(vinyl acetate) (PVA) and PVA plasticized with di-n-butyl phthalate (DBP) containing the spin probes 2,2-di-n-butyl-5,5-dimethyl-3-oxazolidinyl oxyl (DBOZ) and 2,2-di-n-nonyl-5,5-dimethyl-3-oxazolidinyl oxyl (DNOZ) (*Figure 1*). It is shown that, like T_{50G}, T_R correlates with the glass transition temperature in these systems.

The τ_R, T_{50G} and T_R data for these systems are interpreted in terms of our free volume model for rotation of a probe in a polymer matrix[5]. This model, which is based on the earlier work of Kusumoto[6] and of Bueche[7], relates the motion of spin-probe to its volume relative to that of a relaxing polymer segment.

EXPERIMENTAL

The probes DBOZ and DNOZ were synthesized from the corresponding n-alkyl ketones and 2-amino-2-methyl-propan-1-ol by the method of Keana[8]. The PVA (BDH, M.wt. 160 000) was purified by precipitation from toluene into n-hexane. The plasticizer DBP, (BDH), was used as supplied.

Bulk and plasticized PVA samples were doped with probe by freeze drying benzene solutions. For pure DBP the probe was dissolved directly in the plasticizer. The final concentration of probe was *ca.* 100 ppm for all samples. Spectra were obtained on a Varian E-109 ESR spectrometer with variable temperature accessory. Glass transition temperatures were measured with a Dupont differential thermal analyser at a heating rate of 10°C per minute.

ST experiments were carried out with the spectrometer in the out-of-phase, second harmonic absorption mode. The out-of-phase condition is obtained by adjusting the reference phase of the phase-sensitive detector in the absence of saturation, and the second harmonic by modulating the field at 50 kHz and detecting the signal component at 100 kHz. A modulation amplitude of 5 G and a microwave power of 60 mW were used.

RESULTS AND DISCUSSION

Values of τ_R for DBOZ in PVA were measured over a wide temperature range. At temperatures above T_{50G} this was done by analysis of the observed linewidths using the relationship derived by Freed *et al.*[9] Below T_{50G}, τ_R was obtained by comparison of observed spectra with spectra simulated using a program listed in the literature[2]. *Figure 2* compares a spectrum simulated in this manner with a typical experimental spectrum. In *Figure 3* our results are superimposed on a relaxation map for PVA. This map was redrawn from a more detailed diagram[10] which was based on data obtained by a variety of techniques by various authors. At low temperatures our e.s.r. data lie close to the curve for the γ-transition, suggesting that in this range DBOZ may be responding to the γ-relaxation of PVA. At higher temperatures, the probe appears to respond to the glass to rubber relaxation (or to a merged relaxation) of PVA, and in this regime a free volume model[5] predicts that the correlation time, τ_R, of probe tumbling will follow the relationship of equation (1).

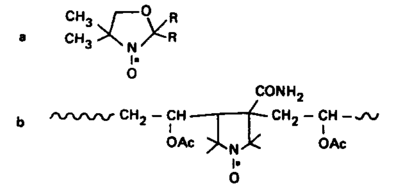

Figure 1 (a) Nitroxide spin probes. DBOZ, R = n-butyl; DNOZ, R = n-nonyl; TMOZ, R = methyl. (b) Spin-labelled PVA

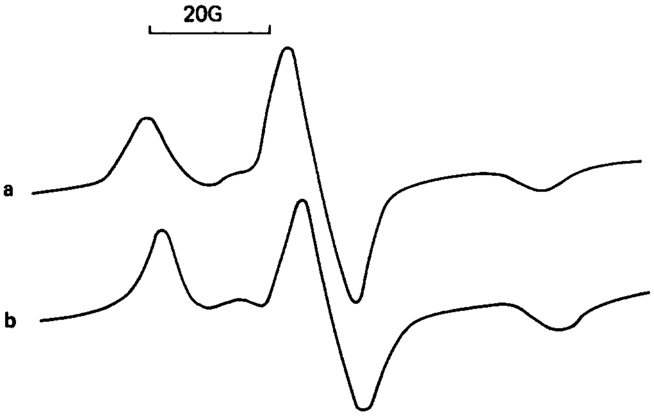

Figure 2 (a) Observed spectrum of DBOZ in DBP at 151 K. (b) Spectral simulation with $N = 1.7$, $\tau_R = 7.6 \times 10^{-8}$ s

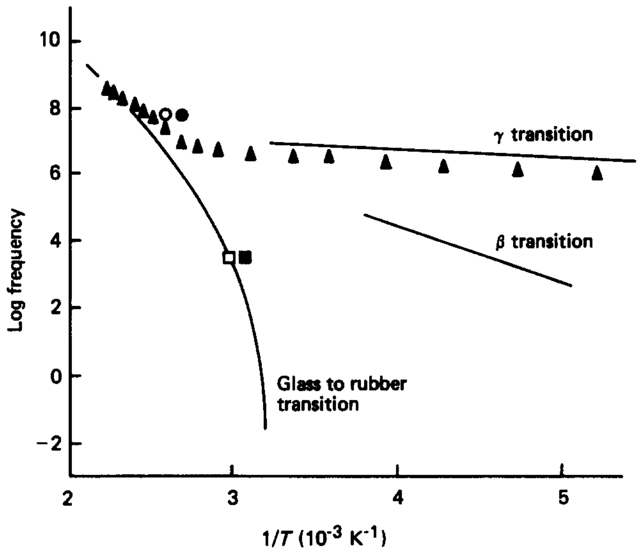

Figure 3 Relaxation map of PVA: (▲), from τ_R for PVA with spin-probe DBOZ; (○), from T_{50G} with DNOZ; (●), from T_{50G} with DBOZ; (□), from T_R with DNOZ; (■), from T_R with DBOZ. Solid curves correspond to literature data based on n.m.r., e.s.r., dielectric, and mechanical measurements[10]

$$\ln\tau_R = \ln\tau_\infty + f\left[\frac{2.303\, C_{1g}C_{2g}}{T - T_g + C_{2g}}\right] \qquad (1)$$

where τ_∞ = high temperature limit of τ_R

C_{1g} and C_{2g} = constants for a given polymer as defined[11] by Williams *et al.*

= 15.6 and 46.8 respectively for PVA[12]

f = activation volume of probe/activation volume of polymer segment ≈ volume of probe/volume of polymer segment

T_g = low frequency glass transition temperature = 307 K for PVA as measured by d.s.c.

T = temperature.

A plot of $\ln\tau_R$ *versus* $\dfrac{2.303\, C_{1g}C_{2g}}{T - T_g + C_{2g}}$ is thus predicted to be a straight line of slope f and intercept $\ln\tau_\infty$. *Figure 4* is such a plot for DBOZ in PVA using only those data from the

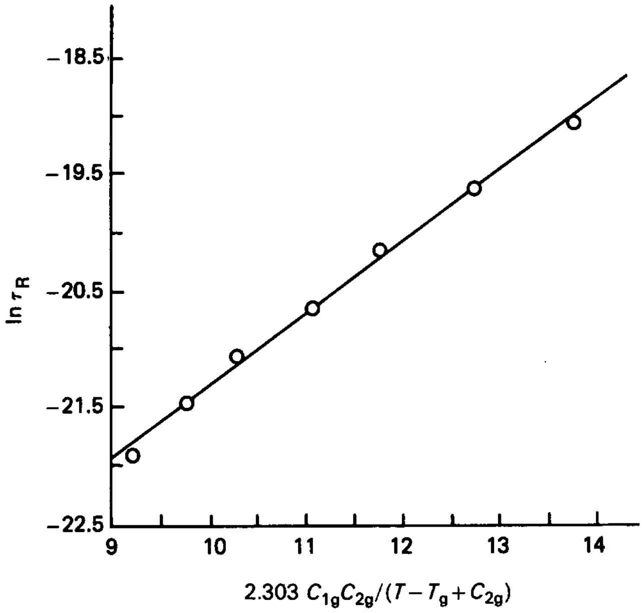

Figure 4 Correlation times τ_R for DBOZ in PVA plotted according to equation (1)

temperature range in which the probe responds to the glass to rubber relaxation. The data lie on a straight line the intercept of which yields $\ln\tau_\infty = -27.5$, i.e. $\tau_\infty \approx 1.1 \times 10^{-12}$ s. This is in good agreement with an extrapolation of the published data[10] on PVA's glass to rubber transition to infinitely high temperature. It is more physically reasonable than the value of $\tau_\infty = 8 \times 10^{-18}$ s obtained for τ_∞ from an Arrhenius plot of the same data.

From the slope of the plot we obtain $f = 0.62$. The physical significance of this figure is that it predicts the volume of a PVA segment, relaxing in the glass transition, to be around 1.6 times that of DBOZ. Calculations based on molecular models of DBOZ indicate an effective volume between 80 and 160 Å^3 depending on the conformation of the butyl chains[13]. The segmental volume of PVA is therefore predicted to lie between 130 and 260 Å^3. For an approximately spherical segment this corresponds to between 4 and 7 monomer units per segment. Similar estimates of segmental size have been obtained by other techniques in other systems[14,15]. In PVA, an activation volume of 560 Å^3 for segmental reorientation has been obtained[16] by the method of Eby[17] and is of the same order as our calculated volume.

Thus, both the intercept and the slope obtained from *Figure 4* are physically reasonable. Further support is given to our basic premise that, over a limited temperature range, probe motion is controlled by the availability of free volume, by a study of 23 nitroxides in natural rubber[18]. This study demonstrated that it is the volume of the probe rather than its molecular weight that determines mobility.

For DBOZ in PVA/DBP mixtures of various compositions and in the pure components, and also for DNOZ in PVA, T_{50G} was measured. A typical plot of extrema separation *versus* temperature is shown in *Figure 5*. ST experiments were carried out on the same systems. In *Figure 6* a representative spectrum is given and the spectral intensities L, L'', H and H'' are defined. The ratios L''/L and H''/H have been shown to vary smoothly with τ_R.[4] Simulations of saturation transfer spectra over the range 10^{-7} s $< \tau_R < 3 \times 10^{-2}$ s were carried out using a program described in the literature[19]. In addition to the spectrometer settings, input parameters to the program included the g and A tensors, which are assumed to be axially symmetric, the relaxation times T_1 and T_2, the number of possible orientations of the probe with respect to the field, and the number of increments in the 100 G spectrum. The two latter were set at the maximum values, 90 and 131 respectively, allowed by the program. Because of the large computer requirements only one set of simulations was carried out. This is justified by the similarities of g, A, T_1 and T_2 for the systems studied. Thus, $A_\parallel = 33.8$ G and $A_\perp = 4.9$ G for both DBOZ and DNOZ, while the corresponding values for the g tensor for DBOZ and DNOZ respectively are 2.0022 and 2.0019 for $g_\parallel$, and 2.0078 and 2.0077 for $g_\perp$[13]. The data for DBOZ were used for all simulations. An effective transverse relaxation time T_2^* and spin lattice relaxation time T_1 were estimated for DBOZ in pure DBP at −80°C and 120°C and for DBOZ in 40% PVA/60% DBP at −100°C from the observed linewidths and the saturation behaviour of the systems[13]. The values obtained were 2.2×10^{-8} s and 6×10^{-5} s for T_2^* and T_1 respectively. Using these data the simulated spectra in *Figure 7* were produced. Comparison of *Figures 6* and *7* demonstrates that agreement between the observed and simulated spectra is at best qualitative. This is borne out by *Figure 8* in which the ratios L''/L and H''/H are plotted against temperature for a typical set of experimental spectra, and against $\log \tau_R$ for the simulated spectra. The overall shapes of the plots are qualitatively similar but the spectral ratios derived from the simulations do not cover the range of values observed experimentally. Considering the assumptions inherent in the simulations the lack of detailed agreement is not surprising. In particular, the simulation program assumes isotropic rotational diffusion whereas we demonstrate elsewhere[20] that in these systems rotational diffusion is anisotropic. All systems showed a smooth, sigmoidal variation of L''/L and H''/H with temperature. For a given

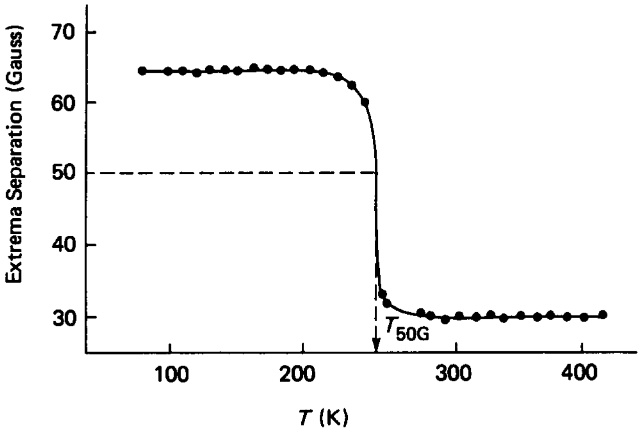

Figure 5 Plot of extrema separation vs. temperature of the e.s.r. spectra of DBOZ in 20% PVA/80% DBP

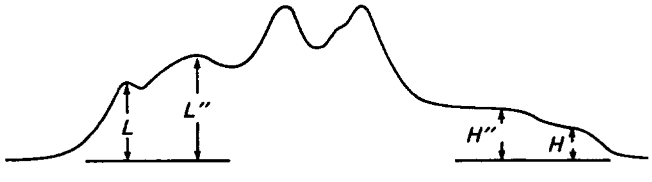

Figure 6 Saturation transfer e.s.r. spectrum of DBOZ in PVA at 253 K showing the parameters L, L', H'' and H

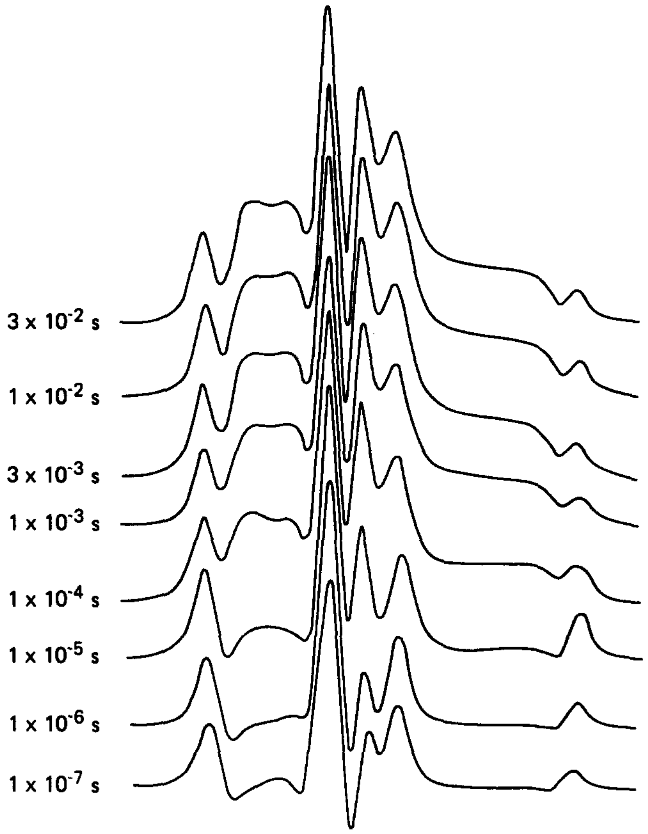

Figure 7 Saturation transfer e.s.r. spectra simulated according to ref. 4 showing input correlation times

system, the gradients of these curves went through a maximum at the same temperature which we define as T_R (see *Figure 8a*). T_R was observed to depend on both the probe and the matrix, but was unaffected by cycling the temperature.

For all PVA/DBP compositions a single glass transition temperature was detected by d.s.c., indicating complete miscibility of the two components. Also, T_g was a monotonic function of composition. Likewise in the same systems when doped with DBOZ, single, composition-dependent values of T_{50G} and T_R were observed. In homogeneous systems $1/T_g$ is frequently a linear function of composition[21]; *Figure 9* shows that $1/T_g$, $1/T_R$ and $1/T_{50G}$ all vary in this manner. This leads us to conclude that at both T_{50G} and T_R, DBOZ in PVA/DBP compositions is responding to the glass to rubber relaxation. At T_{50G}, $\tau_R \sim 3 \times 10^{-9}$ s so that T_{50G} refers to a much higher frequency measurement than does T_g. At T_R the value of τ_R may be estimated from the region where the spectral ratios for simulated spectra fall off most rapidly. From *Figure 8* we obtain values of 8×10^{-5} s and 3×10^{-5} s from H''/H and L''/L respectively. These values are close to that of the time constant T_1 (*ca.* 6×10^{-5} s) associated with ST spectra. Thus, T_R is an approximate iso-frequency point in much the same way as T_{50G} though variations in spin-lattice relaxation time in the former case and in the anisotropy of the A tensor in the latter prevent either from being a true iso-frequency point. Since the characteristic frequency at T_R is intermediate between that at T_g and that at T_{50G}, T_R data should lie between T_g and T_{50G} data and this is indeed the case as shown in *Figure 9*.

Values of T_{50G} and T_R for DBOZ in bulk PVA are 370 K and 323 K respectively while the corresponding values for DNOZ are 392 K and 340 K respectively. These data are included in the relaxation map, *Figure 3*. Clearly both probes respond to the glass to rubber relaxation at both T_R and T_{50G}, and the points are in reasonable agreement with data from other sources. As in the case of T_{50G}, values of T_R can be obtained with much greater ease than absolute values of τ_R. However, again as for T_{50G}, caution must be exercised in drawing conclusions from T_R. Although T_R correlates with T_g in the systems under discussion this may not always be the case. It should be noted that a collapse in the spectral ratios L''/L and H''/H is expected for $\tau_R \sim T_1$ even in situations where there is no glass to rubber transition. Nevertheless, we believe that the observation of T_R in nitroxide-doped polymers is a useful addition to the range of techniques available for studying polymer dynamics.

Both T_{50G} and T_R are higher for the larger probe DNOZ. This, together with their correlation with T_g, suggests that equation (1) should hold at both temperatures. Setting τ_∞ at 1.1×10^{-12} s, and assuming that $\tau_R = 1 \times 10^{-8}$ s at T_{50G} and $\tau_R = 6 \times 10^{-5}$ s at T_R, we can rearrange equation (1) to obtain

$$T_{50G} - T_g = C_{2g}\left[\frac{2.303\, C_{1g} f}{9.1} - 1\right] \qquad (2)$$

$$T_R - T_g C_{2g}\left[\frac{2.303\, C_{1g} f}{17.8} - 1\right] \qquad (3)$$

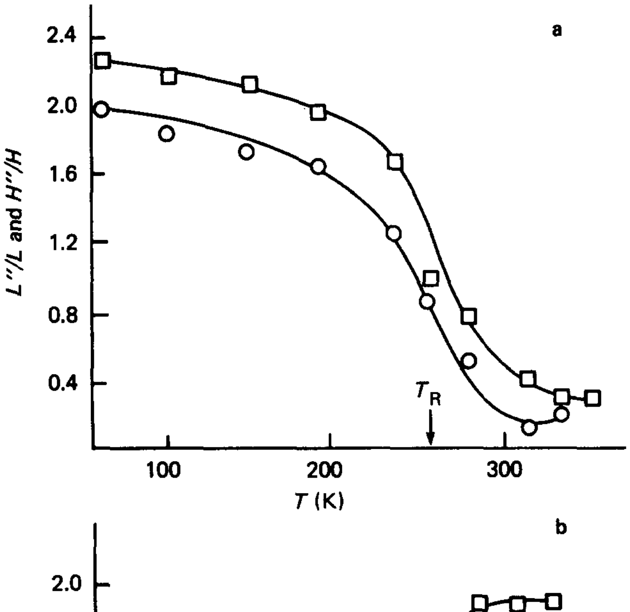

Figure 8 (a) Ratios L''/L (○) and H''/H (□) vs. temperature from saturation transfer e.s.r. spectra of DBOZ in 40% PVA/60% DBP. (b) Ratios L''/L and H''/H vs. $\log \tau_R$ from simulated saturation transfer e.s.r. spectra

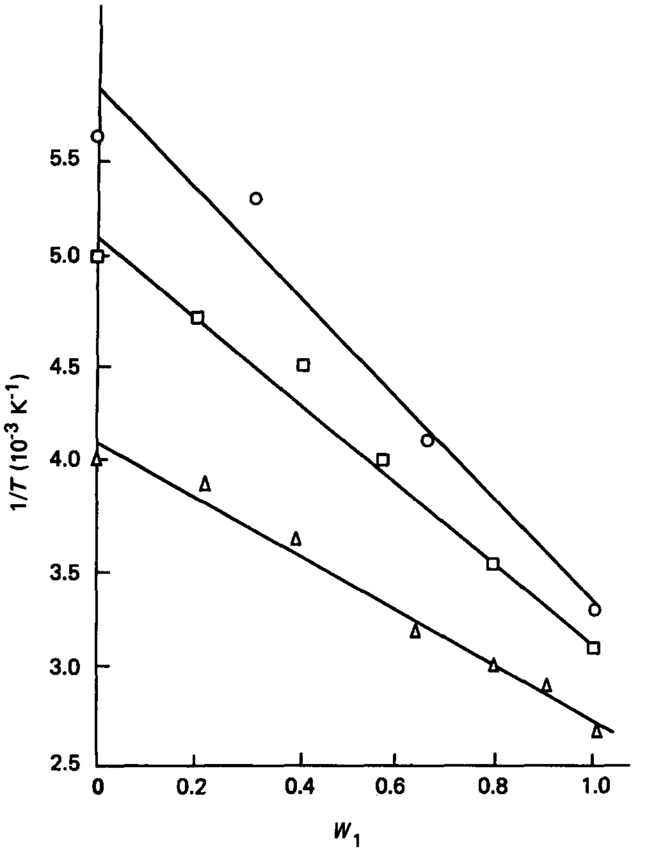

Figure 9 Reciprocal temperatures T_g, T_R and T_{50G} vs. weight fraction w_1 of PVA in PVA/DBP systems with spin-probe DBOZ. (○) T_g; (□) T_R; (△) T_{50G}

Table 1 Values of the parameter f from T_{50G} and T_R for various spin probes in bulk PVA and for spin-labelled PVA

Spin probe	TMOZ	DBOZ	DNOZ	Spin labelled PVA
T_{50G} (K)	311	370	392	434
f from T_{50G}[a]	0.28	0.59	0.71	0.94
T_R (K)	–	323	340	–
f from T_R[b]	–	0.66	0.84	–

[a] From equation (2)
[b] From equation (3)

The values of the parameter f for DBOZ and DNOZ in PVA, calculated from equations (2) and (3) are shown in *Table 1*. Values of T_{50G} (311 K and 434 K respectively) were also available for the spin-probe 2,2,5,5-tetramethyl-3-oxazolidinyl-1-oxyl (TMOZ, see *Figure 1*) in PVA[22] and for PVA carrying the spin-label shown in *Figure 1b* (*ca.* 1 spin per 20000 monomer units)[23]. Values of f for these systems were calculated from equation (2) and are included in *Table 1*. The values of f for DBOZ in PVA calculated from T_{50G} and T_R agree quite well with each other and with the value 0.62 obtained from equation (1) and the τ_R data. For DNOZ in PVA the values of f obtained from T_R and T_{50G} are also in reasonable agreement. When comparing values of f calculated from T_R and T_{50G}, it should be remembered that there is a difference in effective frequency of three orders of magnitude involved. It is also possible that the size of the relaxing polymer segment is temperature-dependent, and if this is so, then the comparative values of f from T_R and T_{50G} suggest that as the temperature decreases the average size of the relaxing polymer segment decreases.

The volumes of the probes increase in the order TMOZ<DBOZ<DNOZ and in accord with the basic premises of the theory, f increases in the same order. The estimated value of f for spin-labelled PVA is close to unity as expected if the effective volume of a labelled segment is similar to that of an unlabelled segment. In an earlier publication[5] is was demonstrated that for a specific nitroxide probe f increased as the T_g of the polymer in which it was dispersed decreased and therefore, presumably, as the segmental volume decreased. In the present work we have shown that for a series of nitroxides in a single polymer f increases with increasing probe size. The observed behaviour is therefore consistent with equation (1) in both cases.

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