Molecular dynamics in bulk and plasticized poly(vinyl acetate): a spin-probe study

G. Gordon Cameron*, Isabel S. Miles† and Anthony T. Bullock‡
Department of Chemistry, University of Aberdeen, Aberdeen, Scotland AB9 2UE, UK
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Poly(vinyl acetate) (PVA) in bulk and plasticized with di-*n*-butyl phthalate (DBP) over a wide composition range was spin-probed with the nitroxide radicals 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). The correlation times, τ_c, for rotational diffusion of the probes over the temperature range 130–370 K were calculated from their electron spin resonance (e.s.r.) spectra by standard methods. Arrhenius plots of τ_c for all samples except pure DBP showed three distinct regimes: a high-temperature region of relatively high activation energy (E_a) in which E_a^{-1} decreased linearly with increasing PVA content, a low temperature region of very low E_a in the range 0–3 kJ mol^{-1}, and an intermediate region of E_a *ca.* 7 kJ mol^{-1} independent of composition. It was concluded that in the high-temperature region the probe responds to the glass-to-rubber relaxation of PVA and in the intermediate region to the γ or merged β, γ relaxation. In the low-temperature region it seems likely that a proportion of the probes can rotate freely in 'holes' or voids in the polymer, the remainder being immobilized within the glassy matrix. The values of E_a for rotation of DBOZ and DNOZ in pure bulk PVA were 69 and 56 kJ mol^{-1}, respectively. It is tentatively suggested that this reversal of the order expected from the relative molecular volume of the two probes, is due to local plasticization by the long alkyl chains on DNOZ.

(Keywords: plasticized poly(vinyl acetate); di-*n*-butyl phthalate; spin-probe study; molecular dynamics)

INTRODUCTION

The electron spin resonance (e.s.r.) spectrum of a nitroxide radical is sensitive to its rotational mobility over the frequency range 10^5–10^{10} Hz[1]. The rotational correlation time, τ_c, can be calculated from the dependence of spectral linewidth on the nitrogen nuclear quantum number, M_N, provided the spectrum is motionally narrowed ($\tau_c < 10^{-9}$ s). For longer correlation times, when slow motion spectra are observed, τ_c can be evaluated by comparison of spectra with detailed spectral simulations.

The rotational freedom of a nitroxide radical is sensitive to the mobility of its environment. Therefore, the motional state of a medium can be explored indirectly by introducing a nitroxide radical and analysing its e.s.r. spectrum. When the nitroxide is attached by a covalent bond to the material under investigation it is known as a 'spin label'. If it is simply dispersed physically in the medium it is called a spin probe. Spin-probe and spin-label experiments have been carried out on bulk polymer systems[2]. The temperature dependence of nitroxide rotational frequency is commonly found to parallel the relaxation behaviour of the host polymer as determined by direct methods such as nuclear magnetic resonance (n.m.r.) or mechanical characterization[3]. It thus appears that probe rotation depends on and corresponds closely in frequency to polymer dynamics. Detailed information on nitroxide mobility is directly accessible by e.s.r. with relative ease and high sensitivity. The technique therefore provides an attractive approach to studies of polymer dynamics. However, the route is indirect and the properties of the polymer can only be inferred from those of the associated nitroxide radical. Furthermore, as with all 'reporter group' experiments, the possibility always exists that the nitroxide may significantly perturb the motions of the medium it is intended to reflect. Extreme caution must therefore be exercised when interpreting the results of spin-label or spin-probe experiments on polymers.

For many polymers the temperature dependencies of the various relaxation processes have been studied in detail, and hence the interpretation of e.s.r. data can be tested directly by comparison with those from other techniques. Addition of plasticizer to polymer has a major impact on the glass-to-rubber transition. Secondary polymer relaxations on the other hand are generally insensitive to the presence of plasticizer[4,5]. Thus, the effect of plasticizer concentration on nitroxide rotation will depend on the type of polymer relaxation, if any, to which the probe responds. An extensive study of the effect of temperature (in the range 130–370 K) and plasticizer concentration on the mobility of a nitroxide probe in poly(vinyl acetate) (PVA) is reported in this paper. The data are used to test the hypothesis that spin probes can yield information on the glass-to-rubber transition, the β relaxation and the γ relaxation in this polymer.

EXPERIMENTAL

The PVA (BDH Ltd, $M_w = 160000$) was purified by precipitation from toluene into *n*-hexane. The plasticizer di-*n*-butylphthalate (DBP, BDH Ltd) was used as supplied. The spin probes 2,2-di-*n*-butyl-5,5-dimethyl-3-

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* To whom correspondence should be addressed
† Present address: ICI plc, Wilton Materials Centre, PO Box 90, Wilton, Middlesbrough, Cleveland, England TS6 86E, UK
‡ Present address: 'Aldan', Schoolhill, Ellon, Aberdeenshire, Scotland AB4 9AJ, UK

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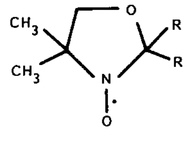

Figure 1 Oxazolidinyl spin probes. DBOZ, R = n-butyl; DNOZ, R = nonyl

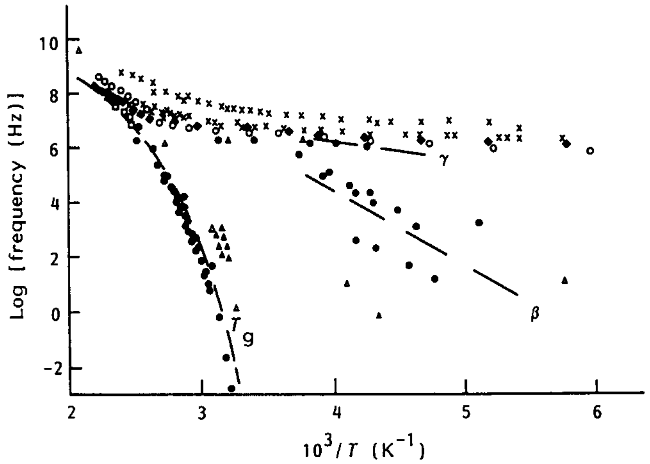

Figure 2 Relaxation map of PVA including data for DBOZ and DNOZ. Data from the literature: ●, dielectric; △, mechanical; □, n.m.r.; ×, e.s.r. Present work: ◆, DNOZ; ○, DBOZ

oxazolidinyl oxyl (DBOZ) and 2,2-di-*n*-nonyl-5,5-dimethyl-3-oxazolidinyl oxyl (DNOZ) were synthesized by Keana's method from the corresponding *n*-alkyl ketones and 2-amino-2-methyl propan-1-ol[6]. The structures of these nitroxides are given in *Figure 1*.

Bulk PVA was doped with DBOZ or DNOZ and plasticized PVA was doped with DBOZ by freeze-drying from solution in benzene. DBOZ in pure DBP was prepared by direct dissolution. All samples contained around 100 ppm of probe. Spectra were recorded on a Varian E-109 e.s.r. spectrometer with variable temperature accessory. Values of τ_c were calculated from motionally narrowed spectra by the treatment of Freed *et al.*[7] and in the slow-motion regime by comparison of observed and simulated spectra using a program listed in the literature[8].

RESULTS AND DISCUSSION

Figure 2 is a relaxation map for unplasticized PVA taken from the literature[3]. Our results for DBOZ and DNOZ, which have been added to this map, are consistent with other e.s.r. data in the literature and with data obtained by other techniques. The broken lines indicate the regions on the map associated with the glass-to-rubber transition, the β relaxation and the γ relaxation. On a molecular level these are attributed to segmental motion of the polymer chain, motion of the whole acetate side group and motion of the methyl group, respectively. It has been suggested[3] that spin probes in PVA respond to and yield information on all three relaxation processes depending on the temperature range investigated. Our data for DBOZ and DNOZ in *Figure 2* appear to be consistent with this interpretation, but a more stringent test of this hypothesis comes from the investigation on PVA plasticized with DBP and probed with DBOZ, as discussed below.

Arrhenius plots for DBOZ in PVA/DBP mixtures spanning the entire composition range are given in *Figure 3*. For the sample in pure PVA there are three linear regions which, in order of decreasing temperature and activation energy, may be interpreted as corresponding to the glass-to-rubber transition, the β relaxation and the γ relaxation. For each of the three regimes this premise can be tested by consideration of the absolute values of activation energy (E_a) and by the dependence of behaviour on composition.

In the high temperature region, DBOZ rotates in PVA with an activation energy of 69 kJ mol^{-1}. This is significantly lower than the literature value of 184 kJ mol^{-1} (ref. 9) for the glass-to-rubber relaxation of PVA. However, as *Figure 2* demonstrates, this transition does not follow an Arrhenius relationship over a wide temperature range but shows pronounced curvature, behaviour which is more accurately described by the well known WLF relationship[10]:

$$\ln \nu(T) = 2.303\, C_{1g}(T - T_g)/(C_{2g} + (T - T_g)) \qquad (1)$$

where $\nu(T)$ = frequency of segmental relaxation at temperature T, T_g = glass transition temperature at 1 Hz and C_{1g}, C_{2g} = constants for a given polymer.

Equation (1) predicts that the apparent activation energy, $E_{a_{app}}$, measured over a limited temperature range will depend on the position of that range relative to T_g. E.s.r. spectroscopy, being a relatively high frequency technique, is expected to yield a relatively low value of E_a. When equation (1) is followed, the apparent value of $E_{a_{app}}$ for relaxation at a specific temperature may be obtained by differentiating equation (1) with respect to inverse temperature, since, from the Arrhenius relationship $E_a = -R\dfrac{\partial \ln\nu}{\partial(1/T)}$. Thus, from equation (1) we obtain:

$$E_{a_{app}} = -R\frac{\partial \ln\nu}{\partial(1/T)} = \frac{RT^2 2.303\, C_{1g}C_{2g}}{(C_{2g} + T - T_g)^2} \qquad (2)$$

Substituting T_g = 307 K, and the literature values of C_{1g} and C_{2g}[11], and taking T = 400 K, which is close to the midpoint of the high temperature region of our spin-

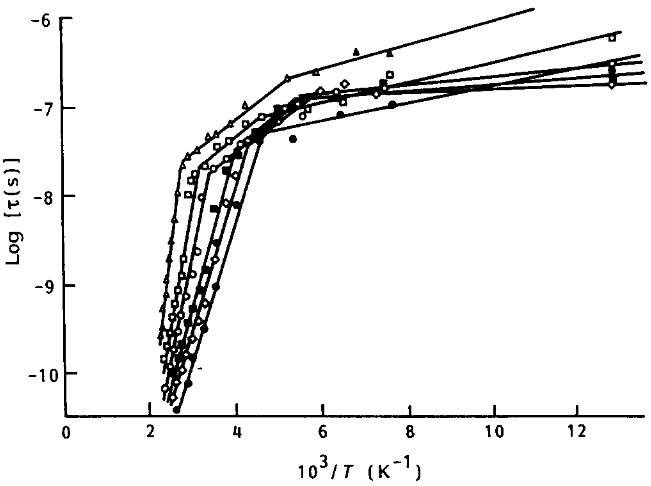

Figure 3 Arrhenius plots for rotation of DBOZ in various PVA–DBP compositions (w/w). ●, Pure DBP; ◇, 20% PVA; ■, 41% PVA; ○, 57% PVA; □, 80% PVA; △, pure PVA

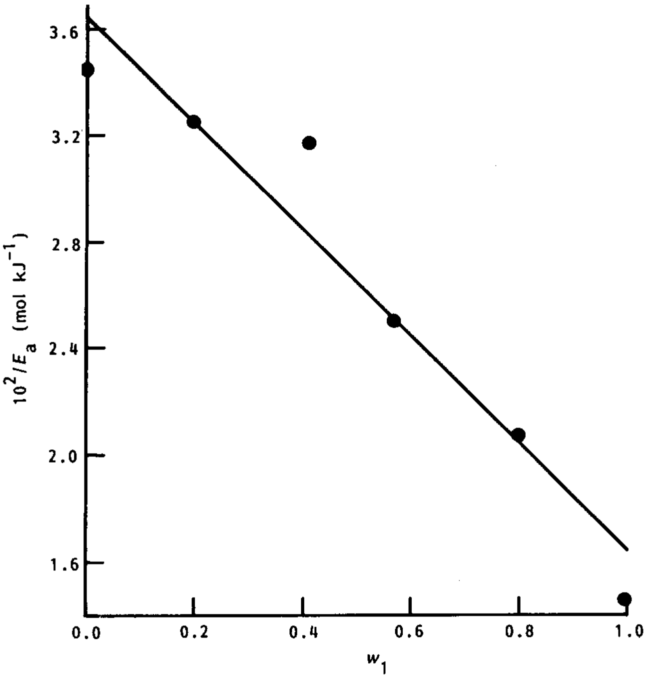

Figure 4 Inverse activation energy for rotation of DBOZ in high temperature range *versus* weight fraction of PVA, w_1, in PVA–DBP compositions

probe experiments, gives $E_{a_{app}} = 114\,\mathrm{kJ\,mol^{-1}}$ for the E_a of the glass-to-rubber transition. This figure is closer to, and much more appropriate to compare with, the value of 69 kJ mol^{-1} from rotation of DBOZ in PVA in the high temperature region. However, free volume treatment[12,13] suggests that the E_a for rotation of a nitroxide probe whose motion is entirely governed by segmental motion within the matrix, will not generally be identical to that for segmental reorientation. This is because there is generally a difference between the molecular volume of the nitroxide and that of the relaxing polymer segment. Changes in the free volume with temperature, which according to free volume theory determine E_a, should therefore have different effects on the probe and the polymer segments. In a previous publication[13], we have presented a free volume equation for the dependence of nitroxide rotational frequency on temperature in a polymer matrix

$$\ln \tau_c = \ln \tau_\infty + f\frac{2.303\,C_{1g}C_{2g}}{T - T_g + C_{2g}} \tag{3}$$

where τ_∞ = high temperature limit of τ_c, and f = activation volume of probe/activation volume of polymer segments.

By *assuming* that DBOZ in PVA responds to the glass-to-rubber transition at high temperatures, we calculated[14] that the ratio of the probe volume to the segmental volume of PVA is 0.62, which is physically quite reasonable.

Equation (3) predicts that the energy of activation for probe motion will differ from that for segmental motion by the same factor f. The self-consistency of this treatment is underlined by the fact that the ratio of our observed value of E_a for probe motion to that calculated from equation (2) for segmental motion at 400 K is very close to 0.62.

A more stringent test of the nature of the probe's response to polymer dynamics is the dependence of its motion on composition. In many two-component, homogeneous systems, including DBP/PVA, the glass transition temperature at a given frequency varies with composition as[14,15]:

$$\frac{1}{T(\nu)} = \frac{T_2(\nu) - T_1(\nu)}{T_1(\nu)T_2(\nu)}w_1 + \frac{1}{T_2(\nu)} \tag{4}$$

where $T(\nu)$ = the temperature of the glass to rubber transition at frequency ν, w_1 = weight fraction of component 1, and $T_i(\nu)$ = the temperature at frequency ν of the glass-to-rubber transition in pure component i.

Thus, at any given frequency the reciprocal of the glass transition temperature is linear in composition. Consequently, the change in reciprocal temperature required to move from one given frequency to another is also linear in composition. Assuming that the temperature-dependence of frequency follows Arrhenius behaviour (a reasonable approximation over a restricted temperature range), this change in reciprocal temperature is inversely proportional to the activation energy.

It follows that the inverse of the E_a should be linear in composition. Hence, for a probe which responds to the glass-to-rubber transition over a given frequency range, E_a^{-1} for probe rotation should yield a straight line when plotted against composition. *Figure 4* is such a plot for PVA/DBP spin-probed qith DBOZ. Each data point on *Figure 4* is derived from the slope of the high temperature region of one of the plots in *Figure 3*. This necessarily leads to significant errors in the values of E_a, and the fit of *Figure 4* to a straight line is therefore remarkably good. The evidence thus strongly suggests that at high temperatures the motion of DBOZ in PVA plasticized with DBP is governed by, and reflects, the glass-to-rubber transition of the matrix.

In the central of three linear regions in the plots in *Figure 3*, the hypothesis to be tested is that the probe responds the β relaxation. As can be seen from *Figure 3*, all samples which contain PVA give rise to three linear regions and the central linear regions are more or less parallel. Thus, the E_a values governing probe tumbling in these regions are approximately equal. This insensitivity to the presence of plasticizer is consistent with a response to a secondary relaxation, since it is well known that such relaxations, unlike the glass-to-rubber relaxation, are not shifted significantly by the addition of plasticizer[4]. Furthermore, there are only two linear regions in the Arrhenius plot for DBOZ in pure DBP and neither yields a value of E_a that corresponds to the central region in the polymer-containing samples. Secondary relaxations originate from local motion of part of a polymer molecule and as such would not be expected to occur in the pure plasticizer. These observations support the premise that at intermediate temperatures DBOZ in pure and plasticized PVA responds to a secondary relaxation. In all polymer-containing samples the activation energy in this regime lies in the range $7 \pm 2\,\mathrm{kJ\,mol^{-1}}$. Published values of E_a for the β and γ relaxations of PVA are 40 kJ mol^{-1} (ref. 16) and 4–12 kJ mol^{-1} (ref. 17), respectively. The latter value is an estimate based on the barrier to methyl group rotation in low molecular weight compounds. The observed value of E_a suggests that the probe in this region probably responds to the γ relaxation or to a merged β, γ relaxation. Clearly the value of E_a is too low to be consistent with the postulated response to the β relaxation.

At the lowest temperatures examined, activation energy varies with composition as shown in *Figure 5*.

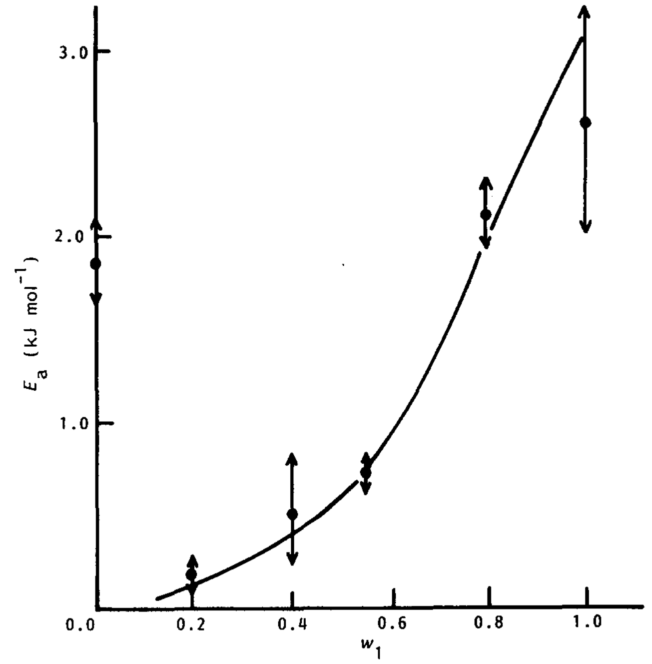

Figure 5 Energy of activation, E_a, for rotation of DBOZ at low temperatures as a function of weight fraction of PVA, w_1, in PVA–DBP compositions

There are two important respects in which these data are inconsistent with the hypothesis that DBOZ in PVA in this temperature region responds to the γ relaxation. The first is that there is a clear dependence of E_a on composition. The second is that all the activation energies are very low indeed and fall below the lowest estimate for methyl group rotation[17].

Nevertheless, the DBOZ probe is relatively mobile though it appears not to be associated with the dynamics of the polymer which is in the glassy state at these low temperatures. This phenomenon has been observed previously in a range of spin-probed polymers in the glassy state and was ascribed to the existence in the polymer of 'holes' or structural defects within which relatively rapid, unhindered rotation of the probe can occur[18]. Other independent evidence for the existence of such voids is found in the transport properties of gases in glassy polymers. Gas solubility in polymer glasses is best described in terms of a dual-mode sorption[19], in which the gas molecules are divided into two distinct populations. The first comprises conventionally dissolved gas molecules obeying Henry's law, while the second population is located in regions of locally high free volume or 'holes'. Behaviour in the latter case is described by a Langmuir isotherm relationship, so that the overall dependence on pressure of the concentration of gas is given by a combination of Henry's law and the Langmuir isotherm.

There may be also a dual population of nitroxides in spin-probed glassy polymers. Saturation transfer e.s.r. spectroscopy[14] has shown that DBOZ in PVA tumbles with a correlation time of *ca.* 10^{-4} s at temperatures at which conventional e.s.r. spectroscopy indicates much more rapid rotation. Thus, there is either an improbably wide distribution of correlation times or there are two distinct populations of spin probes with widely different correlation times. In the latter case, those probes in voids can rotate with a rather low E_a at relatively high frequencies, while the remainder are locked in an essentially immobile state in the glassy matrix.

Apart from specialized techniques, such as saturation transfer e.s.r. spectroscopy, the e.s.r. spectrum of a nitroxide is insensitive to changes in rotational frequency, for values of τ_c greater than 10^{-6} s. The dependence of the e.s.r. spectrum on temperature is therefore of necessity determined by the activation energy for rotation of those probes whose correlation times are below 10^{-6} s. At low temperatures the number of such probes may be relatively small and variable. Care must therefore be exercised in interpreting data obtained in this regime since apparent activation energies will be influenced by any temperature dependence of the relative numbers of 'frozen' and mobile spin probes.

Figure 5 indicates that activation energy is a smooth function of composition at low temperatures. This is consistent with the above model since the energy of activation for probe rotation within voids could reasonably be expected to depend on the average magnitude of, and distribution in, the size of these voids. These parameters would be expected to depend on composition.

All the data presented above indicate that the mobility of DBOZ is sensitive to its environment. At the lowest temperatures it is insensitive to the dynamics, but not to the structure, of the matrix in which it is dissolved. More detailed analysis of spin-probe data could yield potentially valuable information on the variation of structure in glassy polymers at the local level. However, this would necessitate extracting detailed information on the distribution of correlation times. At intermediate temperatures the behaviour of DBOZ can be interpreted as a response to the γ relaxation of PVA or to a merged β,γ relaxation, with a fair degree of confidence. At the highest temperatures encountered there is an unambiguous response of DBOZ to the glass-to-rubber transition.

However, these conclusions have only been reached after a detailed study of the effect of plasticization and probe dynamics, and on a careful comparison with data from other techniques. A superficial examination of the data for DBOZ in PVA in *Figure 2* could have led all too easily to an assignment of three linear regions to the glass-to-rubber transition, the β relaxation and the γ relaxation. This highlights the need for caution in the use of the spin-probe technique. It must be emphasized that it is information on the dynamics of the spin-probe which is extracted directly from the e.s.r. spectrum. It should never

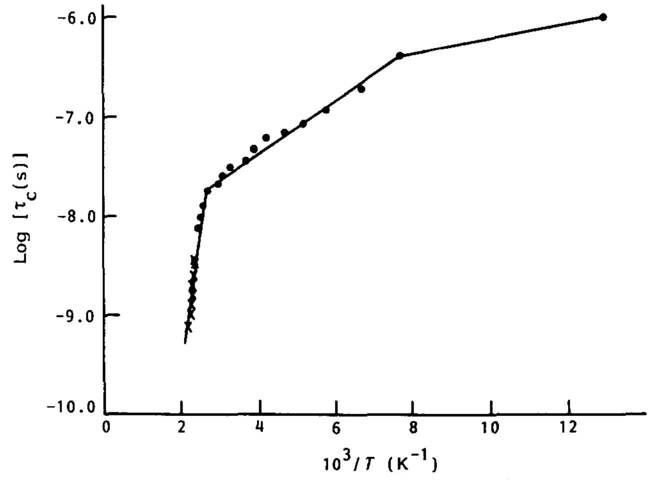

Figure 6 Arrhenius plot for rotation of probe DNOZ in pure PVA. ×, From linewidth analysis; ●, from spectral simulation

be assumed *a priori* that these dynamics are governed by a particular relaxation of the surrounding matrix. Notwithstanding these reservations, there is a large body of experimental evidence which demonstrates the value of the spin-probe technique in studies of polymer dynamics[2], and in particular that at temperatures at which τ_c for probe tumbling is less than *ca.* 10^{-8} s, the probe is responding to the glass-to-rubber transition[20].

The behaviour of the probe DNOZ in bulk PVA provides an interesting test as to the generality of the response observed when DBOZ was probe. In the Arrhenius plot for DNOZ in PVA (*Figure 6*) three linear regimes may again be distinguished. At high temperatures the E_a is 56 kJ mol^{-1}, which is consistent with a response to the glass-to-rubber transition. At intermediate temperatures the E_a of 5 kJ mol^{-1} coincides within experimental error with the corresponding data for DBOZ in PVA and is consistent with a response to the γ relaxation. The region of low E_a at very low temperatures is not clearly defined since it rests on a single data point obtained at liquid N_2 temperature where the spectrum is very similar to the rigid limit spectrum yielding a value close to 10^{-6} s for τ_c. At this point the uncertainty in τ_c is necessarily large. In order to define the very low temperature range in *Figure 6* with more confidence, it would be necessary to obtain data points within the range between the two lowest temperatures. Unfortunately, this temperature range is not accessible with our existing temperature control system. Assuming for the moment that there is a distinct regime at very low temperatures the associated E_a is 1.3 kJ mol^{-1}. Like the corresponding values of DBOZ, this is anomalously low and is consistent with rotation within voids in the polymer matrix.

Thus, the behaviour of DNOZ in PVA is broadly similar to that of DBOZ, but closer examination reveals significant differences. For example, the apparent response of DNOZ to the γ relaxation persists to much lower temperatures than is the case for DBOZ. Also, the E_a values for DNOZ in PVA in the highest and lowest temperature regimes (56 and 1.3 kJ mol^{-1}, respectively) are lower than the corresponding values for DBOZ (69 and 2.6 kJ mol^{-1}). The difference between the low E_a values is probably not significant, but that between the higher E_a values is significant. On the basis of equation (3), the larger probe would be predicted to have a *higher* E_a in its response to the glass-to-rubber transition. The fact that DNOZ has the lower E_a indicates that the two probes, despite their structural similarity, do not respond to this transition in precisely the same way. The only structural difference between the probes DBOZ and DNOZ is the length of the alkyl chains attached to the oxazolidine ring (*Figure 1*). The flexibility of these chains means that they and the oxazolidine ring have a certain degree of motional independence, an effect which will increase with increasing alkyl chain length. As this chain length increases the activation volume and E_a of probe motion in a polymeric matrix will increase, rapidly at first, then more slowly as motion of the nitroxide moiety and the chain extremities becomes progressively more decoupled. Eventually the activation volume and E_a will level off becoming independent of alkyl chain length. By this mechanism it is possible to envisage the two probes having the same energy of activation for motion in PVA, but not the observed situation where E_a for DNOZ is less than that for DBOZ. It is possible that this is an example of a probe perturbing the motions of the surrounding matrix. This could occur if the alkyl chains of the probe exert a plasticizing effect on neighbouring PVA segments, since, as has been demonstrated in *Figure 4*, plasticization leads to a decrease in E_a for probe motion in the high temperature region. Clearly, this is a highly speculative explanation which could be substantiated or disproved only after extensive additional investigations. This is also a fitting point at which to recall the complications and ambiguities that can arise in any 'reporter group' experiment as a consequence of the subtleties in the interactions between the probe molecule and the host.

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