An e.p.r. spin probe study of the molecular motions of side and straight chain polymers and polymer/plasticizer mixtures

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E.p.r. studies of cholestane (COL) and tempol (TPL) spin probes dissolved in mixtures of two different side chain polymers and two different main chain polymers in the plasticizer dibutyl phthalate were performed. For each pair of polymers, one of the pair was considerably stiffer than the other due to its larger monomeric molecular weight. The studies demonstrated the existence of multiple relaxation times that were especially obvious at temperatures near T_{50}, i.e. the region intermediate between the fast and slow motion regimes. Arrhenius plots of relaxation times obtained from simulations of the observed spectra display many features previously reported for poly(vinyl acetate), including a gap or discontinuity in the COL data near T_{50}. In the present study, we showed that the spectra observed in the gap are sums of slow and fast spectra. Composite spectra, in which the fast portions of the observed spectra were subtracted out, were matched to spectral simulations. The relaxation times obtained in this way fell on the low temperature (slow motion) portion of the Arrhenius plots. Several features of the data appear to be associated with the stiffness of the samples and these features are examined.

(Keywords: e.p.r.; spin probes; molecular motions)

INTRODUCTION

Molecular motions in monomeric, polymeric and liquid crystal glass formers have been studied extensively using the e.p.r. technique[1-10]. In a recent study[7] of poly(vinyl acetate) (PVA) using the plasticizer dibutyl phthalate (DB) and the spin probes cholestane (COL) and tempol (TPL), we have shown that there are temperatures at which the observed spectra reflect the motions of multiple sites. This means that these spectra cannot be simulated using a single diffusion constant (D). The temperature at which this occurs appeared to be correlated with the temperature at which the overall spectral width was 50 G (T_{50})†. It also marks the boundary between the slow and fast motion regimes. Here the rotational relaxation time (τ) is $\sim 10^{-8}$ s. In this work we extended our studies to another side chain polymer, poly(butyl methacrylate) (PBM) and two other straight chain polymers, poly(ethylene succinate) (PES) and poly(ethylene oxide) (PEO). The same plasticizer and spin probes were used. Here we again saw a gap in the Arrhenius plots when the COL probe was used. In this region we could not simulate the spectra using a single τ or D. When TPL was used we could obtain usable simulations of the observed spectra near T_{50}. In both cases we could get very good to excellent simulations of the experimental spectra by assuming that they were sums of fast and slow spectra. The Arrhenius plots displayed some interesting features which will be detailed below.

EXPERIMENTAL

The e.p.r. spectrometer, temperature controller, spin probes, plasticizer and sample preparation have been described previously[5]. The τ values are extracted from diffusion constants used in spectral simulations. The program originally written by Moro and Freed is based on the Lanczos algorithm[11,12]. TPL's motion is characterized by a single diffusion constant (D) since it has a nearly spherical shape, but COL's motion is characterized by $D_{\parallel} = 5D_{\perp}$ since it has a geometrical aspect ratio of ~ 5. Strictly speaking, the anisotropy in D is not necessarily equal to the aspect ratio, but we find that the simulations are not very sensitive to moderate changes in this anisotropy. $\tau = 1/6D$ for TPL and $1/6(D_{\parallel}D_{\perp})^{1/2}$ for COL. The Brownian model of diffusion is used to simulate the spectra, and spot checks indicate only minor changes in the calculated diffusion constants when the free diffusion is employed. There are analytical[13-17] and phenomenological methods[18-22] in the literature for calculating relaxation times for the fast and slow motion regime, respectively. For this study it is necessary to actually simulate spectral line shapes and compare the results with the observed spectra to determine if one is observing single or multiple spectra. Occasionally extra structures appear in the spectra in the slow motion regime. This can mislead the experimenter into believing that the probe is responding to multiple relaxation times.

The four polymers studied here were obtained from Aldrich Chemicals and used without further purification: PBM (high molecular weight, M_w, and glass transition temperature, $T_g = 300$ K), PVA (medium M_w and

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† $1\ \mathrm{G} = 1 \times 10^{-4}$ T

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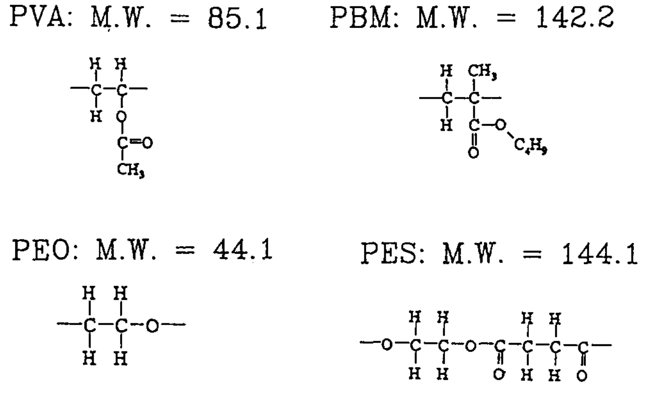

Figure 1 Structures and monomeric molecular weights of the polymers used

$T_g = 305$ K), PES (high M_w and $T_g = 272$ K) and PEO ($M_w = 100\,000$, $T_g = 203$ K). The molecular structures and the monomeric molecular weights are shown in *Figure 1*. Note that PBM and PVA are side chain polymers, and PES and PEO are straight chain polymers. This study does not attempt to account for the average number of monomer units in the polymer, but it is generally thought that increasing the M_w increases the stiffness of the polymer.

RESULTS

We show, by the simulation of composite spectra, that some of the observed spectra reflect the motions of different sites. We have previously used a similar technique[1] to illustrate the presence of multiple relaxation times when studying the liquid crystal MBBA. The technique is illustrated in *Figure 2*. *Figure 2a* shows the spectrum observed, at 310 K, from a COL probe dissolved in a mixture of 75% PVA/25% DB. *Figure 2b* shows a composite spectrum where some observed faster spectrum has been subtracted out. Specifically, for the case illustrated, it consists of 1.70 × the 310 K spectrum minus 0.70 × the 330 K spectrum. *Figure 2c* shows a calculated spectrum which is our best match of the composite shown in *Figure 2b*. Note the very good agreement between the two spectra illustrating that the observed spectrum is the sum of at least two spectra reflecting different relaxation times. The data used to obtain the result discussed above are shown in *Table 1*. The first column indicates the weight per cent polymer in the polymer/DB mixture. The second column indicates the composition of the composite spectrum and the third column indicates the value of the rotational relaxation time obtained by matching a simulated spectrum to the composite spectrum. Note that all of the entries are a few times 10^{-8}. All of the cases studied are summarized in *Table 1*. The results will now be discussed in more detail.

PVA

We have studied PVA extensively[5-8], but this is our first report of the simulation of composite spectra for this side chain polymer. *Figure 3* shows the Arrhenius plots for 75, 50 and 25% mixtures of PVA in DB, using the COL probe. We observe the previously reported gap. In the 75% plot three activation energies are observed: one in the fast motion regime (10^{-10}–10^{-9} s), one in the intermediate motion regime (a few times 10^{-9} s) and one in the slow motion regime (10^{-7} s). The intermediate motion activation energy approaches the fast motion activation energy as the concentration of PVA is decreased. The closed symbols represent the data obtained

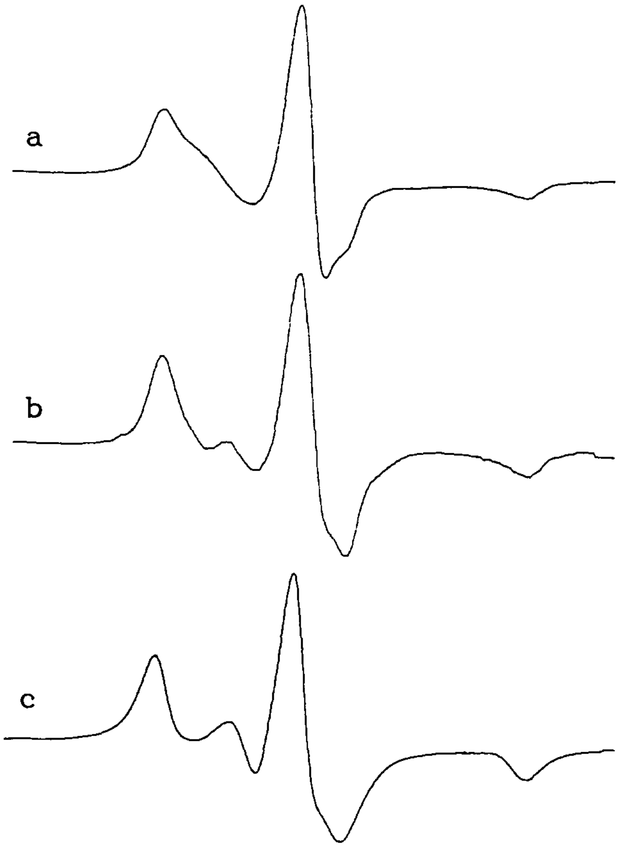

Figure 2 (a) Spectrum obtained from COL dissolved in 75% PVA/25% DB at 310 K. (b) Composite spectrum consisting of 1.70 × the 310 K spectrum minus 0.70 × the 330 K spectrum. (c) Simulation of the composite spectrum

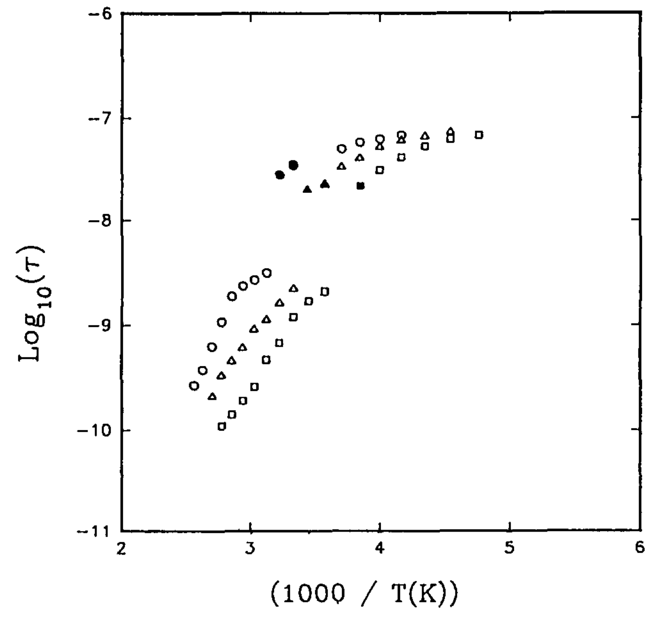

Figure 3 Arrhenius plots for COL dissolved in PVA/DB mixtures. The open symbols represent data from observed spectra and the closed symbols represent data from composite spectra (*Table 1*): (○) 75% PVA; (△) 50% PVA; (□) 25% PVA

Table 1 Composite spectra and relaxation times obtained from their simulation

Wt% of polymer	Composite	τ ($\times 10^{-8}$ s)
PVA/COL		
100	1.28×345 K − 0.28×380 K	2.14
75	1.70×310 K − 0.70×330 K	2.76
	1.20×300 K − 0.20×330 K	3.39
50	1.60×290 K − 0.60×310 K	2.00
	1.25×280 K − 0.25×310 K	2.24
25	1.25×260 K − 0.25×280 K	2.14
PVA/TPL		
100	1.35×248 K − 0.35×312 K	2.40
	1.30×227 K − 0.30×312 K	2.45
75	1.35×250 K − 0.35×300 K	2.40
	1.30×240 K − 0.30×300 K	2.51
50	1.30×240 K − 0.30×270 K	2.40
	1.17×230 K − 0.17×270 K	2.57
25	1.30×230 K − 0.30×230 K	2.18
	1.17×220 K − 0.17×230 K	2.24
PBM/COL		
50	1.60×281 K − 0.60×301 K	1.55
25	1.25×260 K − 0.25×281 K	1.66
10	1.30×247 K − 0.30×268 K	1.35
PBM/TPL		
100	1.40×236 K − 0.40×300 K	3.72
	1.30×225 K − 0.30×300 K	4.07
75	1.35×237 K − 0.35×275 K	2.75
50	1.50×228 K − 0.50×248 K	2.09
PEO/COL		
100	1.50×280 K − 0.50×300 K	2.14
50	1.28×248 K − 0.28×268 K	1.55
PEO/TPL		
100	1.30×235 K − 0.30×256 K	2.45
50	1.25×216 K − 0.25×226 K	2.19
PES/COL		
100	1.60×333 K − 0.60×340 K	1.55
	1.20×322 K − 0.20×340 K	2.69
PES/TPL		
100	1.50×281 K − 0.50×301 K	2.52

from simulating the composite spectra. They follow the slow motion data since the faster part of the observed spectrum has been subtracted out. It is comforting to see these data appear as an extension of our slow motion curves. *Figure 4* shows the corresponding Arrhenius plots obtained using the TPL probe. The curves are continuous since we were able to get approximate matches to the observed spectra even in the region of T_{50}. The intermediate activation energy is clearly seen in the 75% plot but not in the lower concentration plots. The closed symbols are the results of matching the composite spectra and occur at smaller τ values since the faster parts of the spectra have been subtracted out.

PBM

PBM is a side chain polymer with a T_g that is not too different from that of PVA. For the pure material we find that we need to go to a much higher temperature, compared with PVA, before fast motion is observed. This effect is exacerbated when the large COL probe is used. This stiffness is probably due to PBM's larger side chain and higher monomeric molecular weight (142 compared with 85 for PVA). The methacrylate group reacts with the probes at elevated temperature causing them to lose their paramagnetic properties. This precluded studies of COL in 100 and 75% PBM/DB mixtures. We have reported similar results when studying another methacrylate polymer[5]. *Figure 5* shows the Arrhenius plots for COL in PBM/DB mixtures. Here again we see a gap that is similar to that observed for the PVA case, but unlike the PVA case[7], the gap is still quite dramatic for the mixture containing 10% polymer. In the 50% plot the three activation energies are quite apparent. In all three cases the closed symbols, which again come from the match to the composite spectra, are associated with the slow motion regime. *Figure 6* shows the Arrhenius plots for TPL in mixtures of PBM/DB. For the 100% mixture the most dramatic observation is the steep rise in the relaxation time near τ equal to a few times 10^{-8} s. Curves are shown for two different quenchings to illustrate the small effects of thermal history. The 75% data show a hint of the remnant of the steep rise observed for the 100% data. This would probably not be noticed

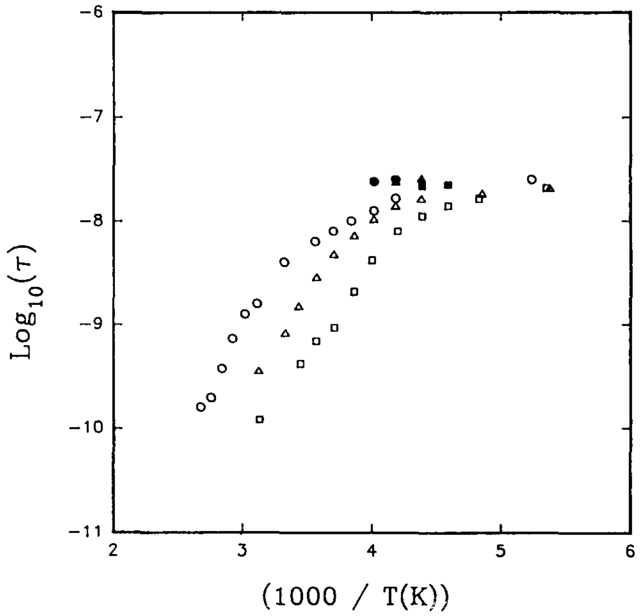

Figure 4 Arrhenius plots for TPL dissolved in PVA/DB mixtures. The open symbols represent data from observed spectra and the closed symbols represent data from composite spectra (*Table 1*): (○) 75% PVA; (△) 50% PVA; (□) 25% PVA

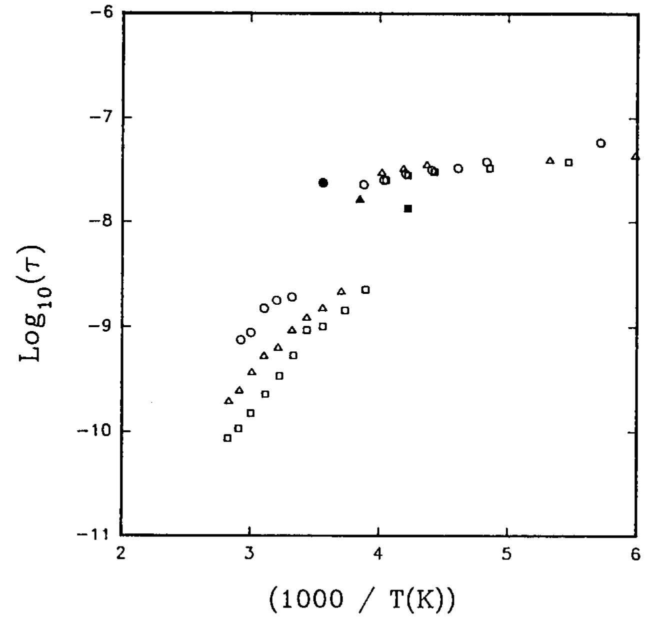

Figure 5 Arrhenius plots for COL dissolved in PBM/DB mixtures. The open symbols represent data from observed spectra and the closed symbols represent data from composite spectra (*Table 1*): (○) 50% PBM; (△) 25% PBM; (□) 10% PBM

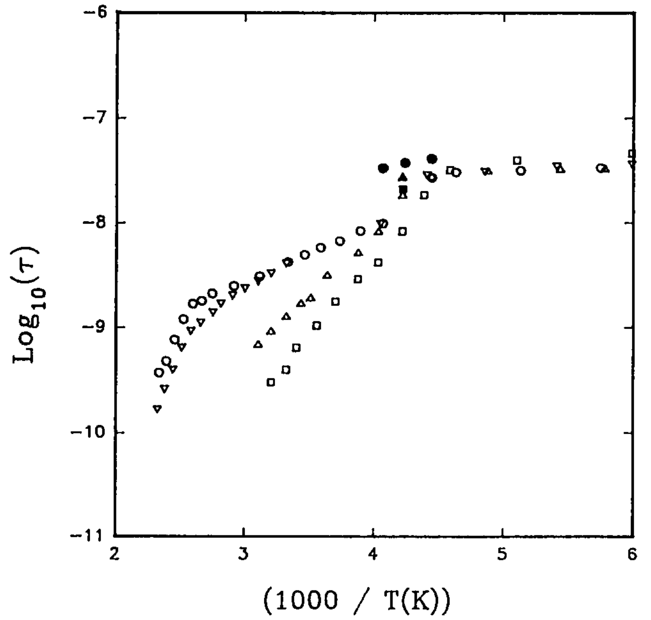

Figure 6 Arrhenius plots for TPL dissolved in PBM/DB mixtures. The open symbols represent data from observed spectra and the closed symbols represent data from composite spectra (*Table 1*): (○) 100% PBM, quenched from a temperature slightly above T_g; (▽) 100% PBM, quenched from a temperature above the softening point; (△) 75% PBM; (□) 50% PBM

if one did not have the 100% data. A similar comment could be made for the 50% data. In all three cases the closed symbols are the results obtained from the simulations of the composite spectra and, as expected, they lie above the simulations of the observed spectra.

PEO and PES

PEO and PES are the straight chain polymers that were also studied. The monomeric M_w of PEO (44) is considerably less than that of PES (144), and, in this regard, the pair is analogous to the PVA–PBM pair. The data indicate that PES is stiffer than PEO, at the same temperature. *Figure 7* shows Arrhenius plots for COL in PEO/DB mixtures, and also shows the corresponding data for 100% PES. All three plots show the characteristic gap at τ equal to a few times 10^{-8} s that appears to be associated with the COL probe. The closed symbols, corresponding to data from the composite spectra, again fall above the open symbols, corresponding to data from the observed spectra. *Figure 8* shows Arrhenius plots for TPL in PEO/DB mixtures and 100% PES. The appearance of a steep rise in the relaxation time near τ equal to a few times 10^{-8} s is seen in the PES data, but is not seen in the PEO data. Also one sees evidence of the three

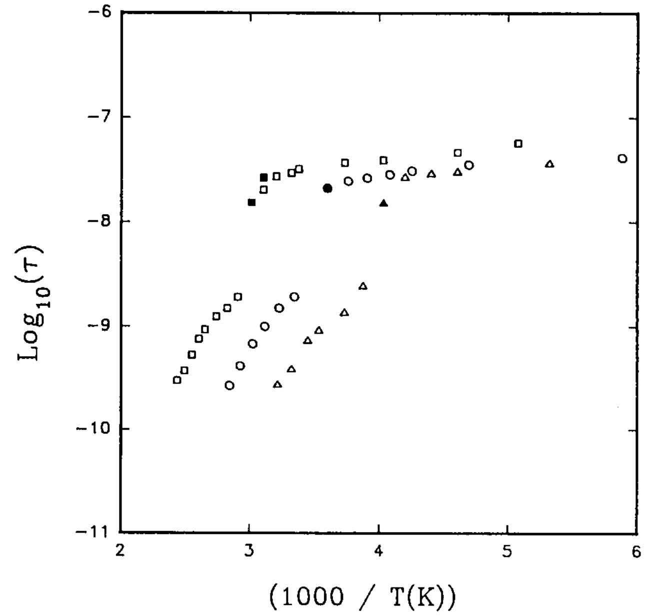

Figure 7 Arrhenius plots for COL dissolved in PEO/DB mixtures and 100% PES. The open symbols represent data from observed spectra and the closed symbols represent data from composite spectra (*Table 1*): (○) 100% PEO; (△) 50% PEO; (□) 100% PES

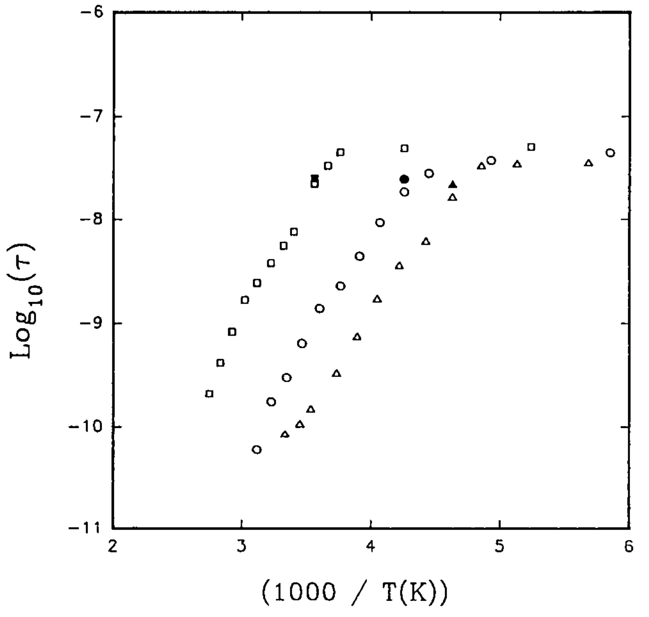

Figure 8 Arrhenius plots for TPL dissolved in PEO/DB mixtures and 100% PES. The open symbols represent data from observed spectra and the closed symbols represent data from composite spectra (*Table 1*): (○) 100% PEO; (△) 50% PEO; (□) 100% PES

activation energies in the data from the stiffer PES polymer. As before, the closed symbols represent data obtained from simulations of the composite spectra.

DISCUSSION

We have demonstrated that spectra taken where τ is approximately a few times 10^{-8} s (at T_{50}) can be simulated as composite spectra reflecting *at least* two different relaxations. This is not as surprising as the ability to simulate data, taken at other temperatures, with a single relaxation time. This can be explained as follows. One notes that the overall spectral width changes rapidly in the region of T_{50}, which is the boundary between fast and slow motion. In this region probes tumbling at somewhat different τ values would yield very different spectra. At higher or lower temperature, the spectral width changes much more slowly with changing temperature, so that the differences in spectra from probes tumbling at somewhat different τ values would be much less apparent allowing one to obtain very good simulations of the observed spectra.

Some of the observations are clearly related to the size of the probe and/or the stiffness of the polymer. The latter correlates with the monomeric molecular weight. In all cases presented here, when the large probe COL is used, one observes a steep, discontinuous rise in τ. This is even true in the Arrhenius plot for 10% PBM. Contrast this with the previously presented data[6,7] from the less stiff polymer PVA that show the disappearance of the gap at ~15% polymer concentration. For COL in 75% PVA there are three activation energies observed. The intermediate slope seems to be associated with the stiffness of the sample. Upon increasing the amount of plasticizer, it gradually goes away. The three activation energies are also seen for TPL in 75% PVA, but not for lower polymer concentrations. The intermediate activation energy is clearly seen for COL in 50% PBM and for COL in 100% PES. The latter is considerably stiffer than PEO, the other straight chain polymer studied here. For TPL in 100% PBM there is a dramatic rise in the Arrhenius plot in the region of $T = 236$ K which is not present in the less stiff samples. There is an indication of a similar rise in the Arrhenius plot for TPL in PES, but it is not nearly as dramatic. These effects are clearly associated with the size of the probe and stiffness of the solvent. Unfortunately, the detailed mechanism leading to their origin remains unexplained. It may have to do with the flexibility of the spacers in the main chain (note that PVA is considerably more flexible than PBM).

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