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A Transition above T_g in Amorphous Polymers as Shown by the Spin-Probe Technique

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ABSTRACT: Samples of 50% plasticized polystyrene were studied at temperatures $>T_g$ by the nitroxide spin-probe BzONO (Tempol benzoate). Correlation times, τ_c, were calculated by line-width analyses. Arrhenius plots showed a break in slope and this break is considered to occur at the liquid–liquid transition, T_{ll}, observed by other methods (with due allowance for increased frequency of the spin-probe measurements). $T_{ll}/T_{50G} = 1.15 \pm 0.03$ (T_{50G} is the temperature at which the extreme separation is 50 G), and the ratio of the activation energies below and above the transition = 1.7 ± 0.2, in good agreement with previous data. The transition is observed in atactic polypropylene, but not in isotactic polybutene-1. The character of the spectra change on going above T_{ll} is much more liquid-like than below T_{ll}. The plot of log ($T\tau_c$) is linear in T^{-1} for polybutene-1 with an activation energy of 47 k J mol^{-1}.

The use of spin probes is proving a new and useful tool for the study of polymer relaxations. A stable free radical, normally of the nitroxide family, is added to the polymer matrix and the motion of the radical is studied by analysis of its electron spin resonance (ESR) spectrum. In particular, the broad-line solid-state ESR spectrum of a magnetically dilute nitroxide changes to the narrower three-line spectrum as the radical begins to move because of the motional averaging of the anisotropic hyperfine and g tensors; the temperature at which the extrema are separated by 50 G (T_{50G}) has been quantitatively related to the glass transition temperature (T_g) of the polymer.[1-3]

The present work reports an extension of the spin-probe technique to the study of those temperature regions above T_g where polymers exhibit rubbery or melt properties. There is considerable evidence for the existence of a transition in amorphous polymers in this region.

Relaxations have been found in plasticized anionic polystyrenes and in atactic polypropylene. The only known relaxation in amorphous polymers above T_g is the controversial T_{ll} relaxation which is thought to mark the change from limited ordering of the polymer chains to true liquid-like behavior.[4] Using automated Torsional Braid Analysis (TBA),[5] Gillham, Benci, and Boyer have studied the dependence of T_{ll} for mol wt 37 000 anionic PS on plasticizer content.[6] Variation of T_{ll} with molecular weight is discussed in ref 4. We have identified the ESR relaxation process with T_{ll} for reasons to be presented later, although such identification is not completely proven.

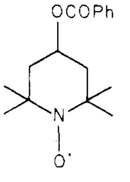
At temperatures $>T_g$, a spin probe is relatively fast moving, and it is possible to calculate the rotational correlation time τ_c for isotropic diffusion of the probe molecule by an analysis of the line widths of the ESR spectra.[7] The following experiments were undertaken to see if the motion of the probe was sensitive to transitions $>T_g$.

Experimental Section

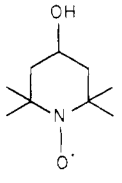
From the work of Gillham et al. on anionic polystyrene (PS), it was found that the T_{ll} occurs at 424 K for PS of mol wt 37 000 and T_g at 380 K.[6] However, spin probes are unstable at temperatures >430 K and, moreover, the increased frequency of the ESR measurements (~10^{10} Hz) above those used in TBA (~1 Hz) would also raise the expected value of T_{ll}. Plasticizing PS lowers the transitions: 50% plasticizer lowers T_{ll} by ~100 °C and T_g by ~90 °C for mol wt 37 000.[6] If it is assumed that a similar lowering would occur for other molecular weights, the temperature region around the expected T_{ll} could be studied comfortably by spin probes using plasticized PS. The plasticizer chosen was *m*-bis(*m*-phenoxyphenoxy)benzene, $(C_6H_5OC_6H_4O)_2C_6H_4$, obtained from Eastman Kodak Co., the same plasticizer as used in the TBA experiments.[6]

In addition to PS, a sample of low molecular weight atactic polypropylene (PP) was studied. This material had a below-ambient T_g (estimated as 211 K from T_{50G} vs. T_g correlation[2]) and was studied by two different probes. Isotactic PP is of course crystalline and spin-probe studies of isotactic PP show evidence of ordering in the polymer up to high temperatures (460 K) with the probe BzONO used in the present work.[8] To show the effect of crystallinity, a sample of commercial isotactic polybutene-1 (PB-1) was studied, because with PB-1 the ordering effect observed in PP was absent.

The spin probe chosen for most of this work was 2,2,6,6-tetramethyl-4-hydroxypiperidinyl-1-oxy benzoate, BzONO, which has been widely used in spin-probe studies (especially in the T_{50G} vs. T_g work[2]). A smaller probe, 2,2,6,6-tetramethyl-4-hydroxypiperidinyl-1-oxy, Tempol, was also used in PP.



BzONO



Tempol

0024-9297/79/2212-0061$01.00/0

Table I

T_{ll} and T_g Values by ESR Spin-Probe BzONO and TBA (Temperatures in K, Activation Energies in kJ mol^{-1})[d]

		ESR			TBA			ESR		
polymer	% plasticized	T_{ll}	T_{50G}	T_{ll}/T_{50G}	T_{ll}[a]	T_g[a]	T_{ll}/T_g	$E_1 <$ T_{ll}[b]	$E_2 >$ T_{ll}[b]	E_1/E_2
PS 110 000	50	377	323	1.17	333	290	1.15	57	38	1.5
PS 17 000	50	381	327	1.17	324	288	1.14	65	38	1.7
PS 4000	50	363	328	1.11	301	269	1.12	67	39	1.7
PS 4000	30	398	338	1.18	334	302	1.11	67	36	1.9
PP atactic	0	325	289	1.12	298[c]	265[c]	1.12	61	28	2.2
PB-1 isotactic	0		300					55		

[a] Estimated from ref 6. [b] Maximum error ±4 kJ mol^{-1}. [c] Reference 11. [d] Colborne (*J. Macromol. Sci., Phys.*, 1, 517 (1967)) observed melt viscosities by the falling ball method for PS, $\bar{M}_n$ = 97 000, $\bar{M}_w$ = 212 000 with 70 and 50% di(2-ethylhexyl) phthalate. Activation energies in each case were 125.4 kJ below and 62.7 below T_{ll} or a ratio of 2.00. These are bulk viscosities whereas the probe is subjected to a local viscosity.

Details of the preparations of the samples follow. To avoid spin-exchange effects, the concentration of probe was kept <0.01% by weight incorporation in all cases.

Polystyrene. Anionic polystyrenes of $\bar{M}_n$ = 4000, 17 500, and 110 000 were obtained from Pressure Chemical Co., Pittsburgh. Sufficient plasticizer was added to give a 1-g sample of 30 or 50% plasticized polymer. The polymer was then dissolved in 5 mL of chloroform containing 5×10^{-5} g of BzONO, the solvent was evaporated, and the polymer was dried in vacuo at 320 K for at least 1 day.

Polypropylene, atactic, from ICI Ltd, England, had $\bar{M}_n$ = 1400 and M_w/M_n = 6.3. It was 96% soluble in boiling heptane. The probe BzONO was added, in chloroform solution, to the molten polymer at 330 K to give <0.01% probe, and the solvent was evaporated as with PS. Tempol was added to the molten polymer as crystals, with rapid stirring.

Polybutene-1 (Witron 0100) was estimated to be 64% crystalline by comparison of its density (as received 0.914 g mL^{-1}) with known values.[9] Crystalline BzONO was added to the molten polymer at 410 K with rapid mixing and cooling.

All samples were prepared for ESR in evacuated Pyrex tubes and ESR spectra were recorded on a Varian 4502 spectrometer, using a Digitec 5900-T digital thermometer accurate to ±0.7 K. A spectrum was normally obtained at liquid nitrogen temperature, and then the specimen was heated. Spectra were recorded at 5 K intervals starting about 50 K below T_{50G} in order to obtain T_{50G} and hence an estimate of T_g[2] and 10 K intervals above T_g. The upper temperature reached was determined by either decomposition of the probe (~420 K) or too-fast rotation of the probe ($\tau_c < 5 \times 10^{-11}$ s). Line intensities and center line widths were obtained as the mean from at least three spectra.

Results

Representative spectra for BzONO in PS are shown in Figure 1. Correlation times for the rotation of the probe were calculated from the equation[7,26]

$$\tau_c = A\Delta\nu(R_+ + R_- - 2) \times 10^{-10} \text{ s}$$

where $\Delta\nu$ is the center line width in MHz, and $R_+ = (I_0/I_{+1})^{1/2}$, $R_- = (I_0/I_{-1})^{1/2}$ with $I_{0,+1,-1}$ the intensities of the center, low-field, and high-field lines, respectively. The parameter A represents the anisotropy of the hyperfine tensor, $(b^2/4\pi(3^{1/2}))^{-1}$, where $b = 2\pi(A_{zz} - a_N)$. A_{zz} is the z component of the hyperfine tensor (the z direction is parallel to the magnetic field), found from the extrema separation ($2A_{zz}$) of the ESR spectrum in the motionally frozen limit (see Figure 1). The isotropic hyperfine splitting a_N can be measured from the motionally narrowed spectrum. For BzONO, A_{zz} = 98 ± 2 MHz at 77 K, a_N = 42.6 ± 0.5 MHz for all samples, giving A = 1.80; whereas Tempol had A_{zz} = 93 ± 1 MHz at 120 K and a_N = 45 ± 1 MHz, giving A = 2.42.

The calculated correlation times were not corrected for the line-broadening effects of the β protons of the radical.[7] This effect was considered negligible in the present work when the radicals were moving in a highly viscous medium (the molten polymer) and the central line width was, at its narrowest, 1.4 G (3.9 MHz), and was usually much broader than this.[10]

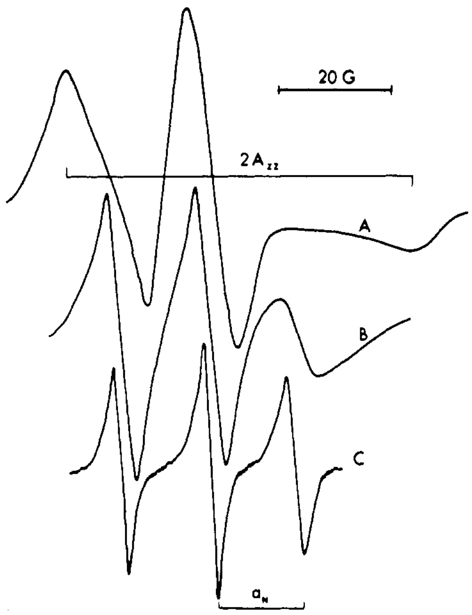


Figure 1. Representative ESR spectra for BzONO in polystyrene $\bar{M}_n$ = 4000 containing 50% plasticizer by weight: A, $T < T_{50G}$; B, $T_{50G} < T < T_{ll}$; C, $T > T_{ll}$. The actual temperatures for A to C are 296, 366, and 402 K. The correlation times, τ_c, are $>3 \times 10^{-9}$, 5.4×10^{-10}, and 2.1×10^{-10} s, respectively. $2A_{zz}$ illustrates the extreme separation for spectrum A. a_N is defined in the text.

Figure 2 shows a least-squares Arrhenius plot for the PS samples, with Figure 3 a similar plot for the PP and PB-1 polymers. Two activation energies can be calculated above and below the break points of Figures 2 and 3. These break points are considered to indicate the temperature of an activated process at the ESR frequencies employed. This activated process is taken to be T_{ll}. Data for the various transitions and activation energies are given in Table I.

Discussion

In Table I, values for T_{ll} and T_g for polystyrene by TBA are given, by estimation from the values of Gillham et al.,[4] for pure PS and the known effect of plasticizer on T_g and T_{ll} from ref 6. It is seen that the transition observed by the spin probe is about 50 K above T_{ll} by TBA, analogous to the raising of the T_{50G} transition 30–40 K above T_g. This raising of the transition temperature can be accounted for by the difference in frequencies of the measurements which are ~10^{10} Hz for ESR and ~10^0 Hz for TBA. No quantitative estimation of this frequency factor is possible for T_{ll} since data for the enthalapy of the T_{ll} transition are

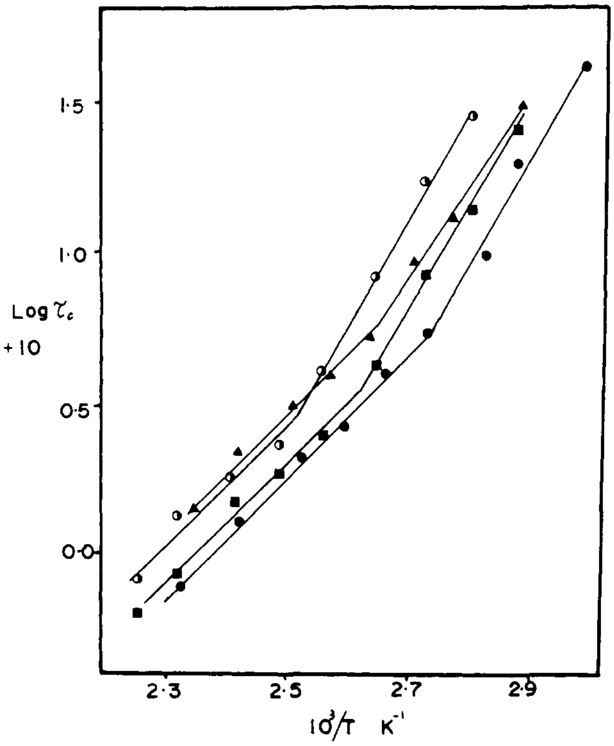


Figure 2. Arrhenius plots for BzONO in plasticized polystyrene: ●, PS 4000 + 50% plasticizer; ■, PS 17 500 + 50% plasticizer; ▲, PS 110 000 + 50% plasticizer; and ◑, PS 4000 + 30% plasticizer.

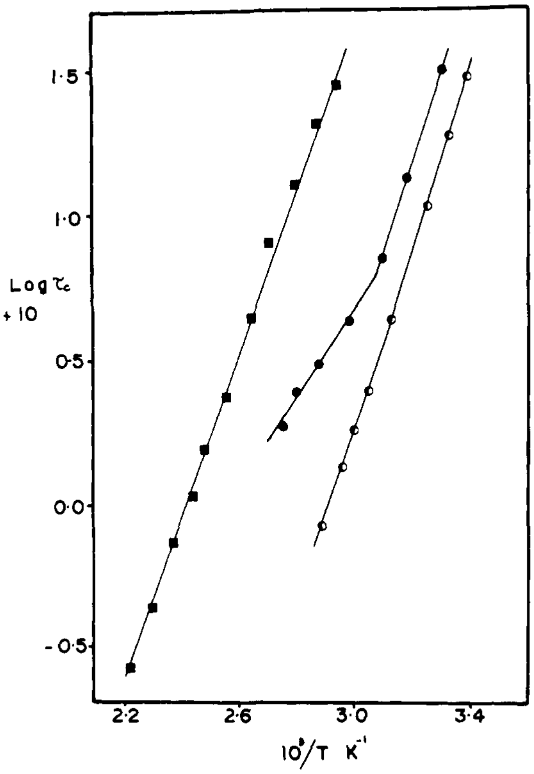


Figure 3. Arrhenius plots for polypropylene and polybutene-1: ●, PP + BzONO; ◐, PP + Tempol; and ■, PB-1 + BzONO.

not available at these high frequencies.

More revealing, perhaps, is the T_{ll}/T_g ratio, which, from previous studies at low frequencies (10^{-2}–10^0 Hz), is found to be 1.2 (see ref 4, Figure 24). Values for PS with mol wt from 600 to 36 000 are in the range of 1.05 to 1.11,[12] and differential scanning calorimetry (DSC) data give the ratio of 1.15 for pure PS.[4] T_{ll} has a lower activation energy than does T_g (see Figure 12 of ref 4) which means that the ratio T_{ll}/T_g should increase with increasing frequency. At the same time, the presence of plasticizer will decrease the activation energy of T_g.[13] That for T_{ll} is likely also lowered but to a different extent. Thus it is difficult to predict a value of the ratio. The ESR data given in Table I show $T_{ll(ESR)}/T_{50G} = 1.15 \pm 0.03$ which is very reasonable but cannot be judged rigorously until activation maps are available for the specific systems studied up to frequencies approaching 10^{10} Hz. However, it is reasonable to conclude that the transition above T_g observed by spin probes is the same transition as shown by TBA and DSC, that is, T_{ll}.

It is noted that in the present work, T_{50G} is independent of molecular weight, contrary to previous results for pure PS.[14] The present observation is attributed to high plasticizer content and experimental error.

The ratio of activation energies of the probe in PS above and below T_{ll} is 1.7 ± 0.2 (Table I). Previous estimates of the activation energies for bulk PS near T_{ll} have been based on diffusion of *n*-pentane and zero shear melt viscosities. The former method gave values of 184 and 53 kJ mol^{-1} below and above T_{ll} which is a ratio of 3.5,[15] while the latter gave 242 and 125 kJ mol^{-1} which is a ratio of 1.93.[16] Spencer and Dillon have shown that the presence of diluent content up to 60% plasticizer lowers the activation energies for viscous flow linearly with plasticizer content.[17] These data are based on zero shear melt viscosities at $T \geq T_{ll}$. We suggest that the activation energies reported in this work by ESR are consistent with prior data in the T_{ll} region of PS obtained by classical methods. (See also a later discussion of activation enthalpies.)

A transition, designated T_{ll}', has been observed some 30–50 K above T_{ll} in plasticized polystyrenes by Gillham et al.[6] Enns et al. have also found a T_{ll}' by DSC for pure PS and for a variety of polymers having bulky side groups.[18] The present work has not investigated this temperature region.

T_{50G} for pure PS increases from 116 to 122 °C as mol wt increases from 17 500 to 110 000.[14] This difference would be even less for a 50% plasticized polymer. Likewise T_{ll} by ESR is essentially constant for these two molecular weights, indicative of a measuring technique which involves only a local viscosity as in DSC and not a macroscopic viscosity as in TBA. This point requires further study, i.e., will T_{ll} at mol wt 2×10^6 be the same as for 110 000?

The results for atactic PP confirm the above discussion of the PS results. The activation energy plot (Figure 3) of the probe BzONO shows a break where T_{ll} would be expected (see data, Table I). This illustrates that the ESR transition is not a feature of the pendant phenyl ring of the PS. Although data for the motion of the probe Tempol in PP are not given in Table I (but see Figure 3), computer analysis of the data shows that there is a break in the activation energy plot although the change in slope is small; thus $E_1 < T_{ll} = 63 \pm 2$ kJ mol^{-1} and $E_2 > T_{ll} = 58 \pm 2$ kJ mol^{-1}. The break in the slope occurs at 314 K which is reasonably close to the value found using BzONO (325 K). T_{50G} for Tempol is 250 K. The explanation of these results is that the probe Tempol is less sensitive than BzONO to the transitions occurring in the polymer. It is smaller (mol wt 172 as compared to 276 for BzONO) and is rotating at least twice as fast as BzONO at the same temperature.

The effects of the molecular size of the spin probe on the correlation times and activation energies of probes in natural rubber have been quantitatively discussed by Törmälä and Weber.[19]

The T_{50G} behavior of Tempol in PS has been reported,[20] with $T_{50G} = 250$ K as compared to $T_{50G} = 390$ K for

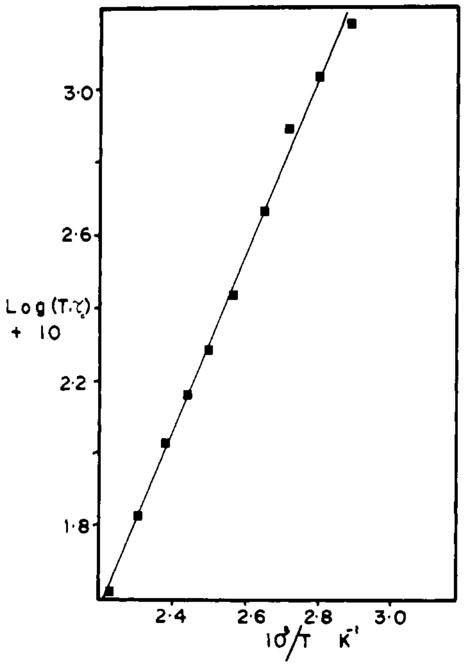


Figure 4. Plot of log ($T\tau_c$) vs. $10^3/T$ for PB-1 + BzONO.

BzONO in pure PS. Tempol may be "seeing" a subglass transition or it may be responding to a larger available volume as a result of thermal expansion in the glassy state. It is the relative size of the probe with respect to the relaxing polymer segments which determines the rotational mobility of the probe. The fact that $T_{\rm ll}$ for Tempol in PP is approximately the same as the $T_{\rm ll}$ shown by BzONO is significant; there is a real transition in the polymer occurring in this region which is "seen" by both probes (although more so by BzONO).

That there is no transition observed by BzONO in the semicrystalline PB-1 is consistent with observations that $T_{\rm ll}$ is suppressed by crystallinity; that is, $T_{\rm ll}$ is a transition in amorphous polymers only.[18] From DSC measurements of the PB-1 used in the present work, $T_g = 228$ K and $T_m = 394$ K. $T_{50G} = 300$ K by ESR, that is, 72 K above T_g (these two values fit the T_{50G} vs. T_g curve of ref 2). No transition is observed by the spin probe at the melting of the polymer at 394 K (see Figure 3). The probe is presumably rotating in the amorphous regions of the polymer both below and above T_m and so is relatively insensitive to this transition; there may still be sufficient ordering of the molten polymer just above T_m to have little effect on the probe rotating at ESR frequencies.

The activation energy for viscous flow of PB-1 is given as 46 and 50 kJ mol^{-1} by various authors,[21,22] for temperatures >100 K above T_g, in which region log η vs. $1/T$ is linear.

The value for the rotational diffusion activation energy for BzONO in PB-1 is 55 kJ mol^{-1}. The Debye model for rotational diffusion gives a relationship between the correlation time and the viscosity of the medium,

$$\tau_c = 4\pi\eta r^3/3kT$$

where r is the radius of the rotating sphere. If this relationship holds for the probe in the molten polymer, then a plot of log ($T\tau_c$) vs. $1/T$ should have the activation energy of the viscous flow of the polymer. Figure 4 shows such a plot, which is indeed linear, with an activation energy of 47 ± 1 kJ mol^{-1}, in excellent agreement with the literature values.

A similar analysis for polystyrene (using the data for PS 4000 + 50% plasticizer) gives $E_\eta = 28 \pm 2$ kJ mol^{-1}, slightly lower than an $E_\eta = 36$ kJ mol^{-1} estimated for the viscous flow of PS + 50% plasticizer from the data of Spencer and Dillon.[17]

Activation Energies for Viscous Flow of Polystyrene

One of the reviewers considered it desirable to cite available independent evidence for activation enthalpies of plasticized polystyrene in the region above T_g. Colborne[23] has provided such information using a falling ball viscosimeter on several PS's at several levels of plasticizer. Most pertinent data were for 70 and 50% by weight of di(2-ethylhexyl)phthalate in a heterogeneous PS of $\overline{M}_n = 97\,000$ and $\overline{M}_w = 212\,000$. Activation enthalpies at both levels of plasticizer were 125.4 kJ mol^{-1} below and 62.7 kJ mol^{-1} above $T_{\rm ll}$, for a ratio of exactly 2.0.

These values of E_1 and E_2 are approximately twice the values shown in Table I for the several plasticized PS's. The falling ball method was obviously measuring a macroscopic melt viscosity including the effect of chain entanglements. The probe was responding to a local viscosity free from entanglement effects. That this is so is seen by comparing E_1 and E_2 values for the 4000 and 17 000 specimens, both below the entanglement molecular weight, with the corresponding value for $\overline{M}_n = 110\,000$ which is still entangled even at 50% plasticizer level.

Colborne's $T_{\rm ll}$ value for 50% plasticizer is 342 K which is close to the value for $\overline{M}_n = 110\,000$ at 50% diluent. This similarity in $T_{\rm ll}$ values by ESR at $\sim 10^{10}$ Hz and falling ball viscosimetry in the Newtonian range (say 10^{-4} Hz) is probably a consequence of the fact that a dynamic method such as falling ball viscometry is responding to the very high $\overline{M}_w$ value for the Colborne specimen, thereby raising $T_{\rm ll}$, just as TBA does above M_c.[12]

Note on Figures 2 and 3

In response to a reviewers query, Figures 2 and 3 represent hand drawings and hand fitting. However, all straight-line segments were verified by linear least-squares regression analysis and the reported activation energies were calculated from the slopes of the regression lines. One can clearly rule out continuous curvature over this narrow temperature region. Straight-line segments on either side of $T_{\rm ll}$ by zero shear melt viscosity appear in Figure 8, p 357 of ref 16, and in ref 24.

Conclusion

The transition observed by spin probes above T_g in amorphous polymers can be confidently identified with the $T_{\rm ll}$ observed at lower temperatures (because of the frequency factor) by torsional braid analysis and differential scanning colorimetry. The activation energies also fit the expected pattern.

There remain many points of interest for future study. For example, the ESR spectra show a qualitative change of shape near $T_{\rm ll}$ (see Figure 1). There is no discontinuity in volume or in melt viscosity at $T_{\rm ll}$[4] and yet the BzONO probe behaves as if it were in a different environment above $T_{\rm ll}$ than below $T_{\rm ll}$. This phenomenon will be treated in a separate paper where it will be shown to be the result of anisotropic rotation.[25] The sensitivity of different probes to transitions in a wider range of polymer systems is being investigated in on-going experiments in this laboratory.

Acknowledgment. We are indebted to Professor George Eastland, Chairman of the Chemistry Department, Saginaw Valley State College, University Center, MI 48710, for the use of the Varian ESR spectrometer on which the

described experiments were conducted.

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(26) This equation assumes isotropic rotation of the probe. Analysis of the data in terms of anisotropic rotation reveals that the T_{ll} transition occurs at the same temperature as discussed here (see Conclusion and ref 25).

Intrinsic Viscosities and Huggins' Constant for Ethylene–Propylene Copolymers. 1. Effect of the Correlations of Orientations in the Pure Components or in the Solutions on the Solvent Quality. Viscosities in Linear Alkanes and Three Highly Branched Alkanes

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Received August 3, 1978

ABSTRACT: Intrinsic viscosities of three ethylene–propylene copolymers (33, 63, 75%, mole percent of ethylene) have been measured at 25 °C in the series of linear alkanes and three branched alkanes 2,2,4-trimethylpentane, 2,2,4,6,6-pentamethylheptane, and 2,2,4,4,6,8,8-heptamethylnonane. Intrinsic viscosities are lower in branched alkanes than in linear alkanes for the 63 and 75% samples. The 33% sample is, on the contrary, more expanded in branched alkanes. Intrinsic viscosities depend very little on chain length for the branched alkanes for the three samples while they do in linear alkanes particularly for the 33% sample. Results are interpreted in terms of correlations of orientations between the alkanes and the ethylene sequences of the polymer. Correlations of orientations are possible without regard to the solvent chain length in the 75% sample which has a distribution of ethylene sequences of different lengths. On the other hand, the short ethylene sequences of the 33% sample correlate more easily with the short alkanes. The presence of a low free-volume component in the solution makes correlations of orientations possible even with short-chain molecules. The Huggins' constant k' seems to be higher for ethylene-rich copolymers in linear alkanes than in the other systems. Correlations of orientations between solvent and polymer increase the solvent quality.

Intrinsic viscosity measurements[1] of copolymers of ethylene and propylene have shown that branched hexadecane was a better solvent than linear hexadecane for copolymers rich in propylene and that linear hexadecane was a better solvent for copolymers rich in ethylene. The difference in intrinsic viscosity in the two alkanes was found to be a linear function of the ethylene content so that these measurements could be used as a method of ethylene content determination. Intrinsic viscosities of the same copolymers in *n*-octane and in a branched octane had indicated that these two alkanes were not as suitable as the longer ones for composition determination. Consequently, it was thought worthwhile to make more extensive intrinsic viscosity measurements in order to establish more clearly the effect of solvent size and shape on the solubility of these copolymers.

EP copolymers are used commercially as additives to oils. They act as viscosity improvers or as agents to lower the pouring points of oils and these properties depend rather critically on the amount of ethylene present in the copolymer. From this, one could expect some different behavior particularly at low temperatures of the samples of dissimilar composition. The Huggins' constant k' has been obtained in the present work as a first step to predict the effect of the solvent shape on the viscosities at moderate concentrations (2%) used in the oil mixtures.

Correlations of Orientations in Long Chains. A way to approach the understanding of the behavior of the EP copolymers is to recognize their likeness to linear and branched alkanes. Extensive thermodynamic studies of linear and branched alkanes (or alkane-like molecules) have shown that the heats are very sensitive to the shape of the molecule mixed.[2–6] The results were interpreted in terms of the presence of orientational order between the molecules in the liquid state, e.q., linear alkanes and mixtures of linear alkanes, and the lack of this order in liquids of globular, isotropic molecules. Long linear alkanes such as *n*-hexadecane lose most of their correlations of orientations at room temperature when mixed with globular molecules. These results have been confirmed by

0024-9297/79/2212-0065$01.00/0