Study of morphology in interpenetrating polymer networks using paramagnetic spin probes

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(Received 11 April 1988; accepted 2 June 1988)

The phase structure in a semi-interpenetrating polymer network (IPN) is studied using two nitroxide spin probes: the small probe 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and the elongated probe 12-doxylstearic acid. The semi-IPN studied consists of poly(vinyl chloride) (PVC) and a crosslinked polyurethane (PU) based on poly(caprolactone glycol) (PCL) and the aromatic isocyanate 4,4'-diphenylmethane diisocyanate (MDI). The IPN sample measured had a PU/PVC ratio of 60/40. The goal of these experiments was to compare the results obtained for the probes with those previously obtained for IPNs containing spin-labelled PVC. Electron spin resonance (e.s.r.) spectra of the probes were also studied in pure PVC, PCL and PU, in order to assess changes in the local environment of the probes. In PVC the probes are sensitive to the segmental motion above T_g. In PCL it seems that the long doxyl probe selectively intercalates in the crystalline domains and this location of the probe seems to persist in PU; TEMPO seems to be located in the amorphous regions of PCL. E.s.r. spectra of both probes in the semi-IPN consist of composite spectra, with fast and slow components. By contrast with results obtained from IPNs containing spin-labelled PVC, no distribution in the values of g_{iso} and A_{iso} of the probes was observed at 400 K. This is interpreted as further proof for the localization of the probes in specific regions of the polymer, differing in their morphology.

(Keywords: paramagnetic probes; electron spin resonance; poly(vinyl chloride); poly(caprolactone glycol); polyurethane; interpenetrating polymer networks)

INTRODUCTION

Stable nitroxide radicals have been extensively used for the study of motional processes and phase transitions in polymers and copolymers[1], in block polymers[2,3] and in polymer blends[4]. The principal values of the anisotropic molecular g-tensor and of the electron–nuclear hyperfine interaction tensor from the nitrogen nucleus ($I = 1$) are affected by temperature variations in a way that depends on the motion in the medium being probed. Changes in the lineshapes and in the separation between the outermost signals that appear in the electron spin resonance (e.s.r.) spectra of the probes are measured as a function of temperature. The temperature at which this separation is 50 G, or $T_{50\,G}$, has been correlated[1] with the glass transition temperature T_g. The difference between the values of T_g and $T_{50\,G}$ has been used[5,6] for deducing the ratio between the volumes of the probe and of the segment whose motion is responsible for the glass transition at T_g; this difference seems to depend on whether the nitroxide reporter molecule is mixed with the polymer (a 'probe') or covalently linked to the polymer (a 'label').

In some cases e.s.r. spectra of the probe and label can also reflect different environments in a given sample, with different rates of motion; 'fast' and 'slow' components are detected and they refer to the appearance of isotropic spectra due to fast motions and of anisotropic spectra for immobilized probes or for slower motions. The partition of the spin probes or labels and the detection of a composite e.s.r. spectrum indicate a heterogeneous medium; in polymer language this usually means a complex morphology and phase separation, both of which are common occurrences in polymer mixtures.

Interpenetrating polymer networks (IPNs) are polymer blends obtained by simultaneous crosslinking of two polymers. Semi-IPNs are obtained by crosslinking one type of chain in the presence of a linear polymer[7,8]. It is believed that these procedures increase the degree of mixing of the two components, or at least decrease the rate of phase separation. Measurement of T_g is a useful method for the study of morphologies in IPNs and semi-IPNs. The correlation between this macroscopic property and the phase structure on a molecular level is, however, at best uncertain. The major objective in our studies of polymer blends in general and more specifically of IPNs is to develop methods for the study of the degree of mixing in the system on a molecular scale.

In recent publications[9,10] we have described the first application of the spin-*label* method for the study of phase morphology in semi-IPNs in which the linear component was spin-labelled poly(vinyl chloride) (PVC) and the crosslinked component was a polyurethane (PU) prepared from an aromatic isocyanate and poly(caprolactone glycol) (PCL). The corresponding linear blends were also studied, for comparison. In these studies we have observed the changes in the e.s.r. spectra of spin-labelled PVC incorporated in IPNs and linear blends of various compositions. The results obtained indicate that the temperature variation of the e.s.r. spectra can be used to detect phase separation in systems where macroscopic properties such as glass transition temperatures T_g indicate the presence of one phase only. We have also deduced that the segmental motion of PVC involves about 5–10 monomeric units.

Comparison of e.s.r. results obtained from labels and

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0032-3861/89/010011-06$03.00
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probes in polymeric systems has been discussed at length in many papers[1,3]; it seems that the advantage of the *probe* is the ease of preparation, while the advantage of using a *label* is that labels are expected to reflect the polymer motion more closely. The size of both probe and label are also important considerations.

In light of this discussion and our results obtained from spin labels, we thought it relevant to study spin probes in IPNs and to compare the results with the spin-labelled case. We chose to study e.s.r. spectra of two probes, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 12-doxylstearic acid (DSA). .The first probe is small and has no reactive groups. The second is a large probe containing a chain of 18 carbon atoms and is approximately the size of the PVC fragment involved in segmental motion above T_g; the reporter group is situated approximately in the centre of the long chain.

Several reasons determined our choice of the components in the semi-IPN studied. First, the morphologies of the major constituent polymers, PVC and PCL, are fairly well understood. The melting point of crystalline PVC is 480 ± 5 K and the glass transition temperature is 356 ± 10 K, depending upon the method of polymerization; a broad transition below T_g has also been detected[11,12]. PCL has a glass transition temperature of 202 K in the amorphous material and 218 K in the semicrystalline polymer[13,14]; its melting range is 218–328 K. Blends of PVC and PCL have been extensively studied using a variety of methods[15–19]. The results obtained indicate that compatible blends are obtained for compositions that include up to 60 wt% PVC. There is evidence that enrichment of the blend in PVC reduces the degree of crystallinity of PCL and a recent nuclear magnetic resonance (n.m.r.) study has specifically focused on blends containing 70 wt% or more of PVC, in order to avoid contributions from the crystalline phase of PCL[18].

The phase structures in bulk hard-segment polyurethanes based on aromatic isocyanates and in segmented PU containing PCL have also been studied, using n.m.r.[19], dielectric relaxation[20], differential scanning calorimetry (d.s.c.)[21], Fourier-transform infrared (*FT*i.r.) spectroscopy[22] and small-angle X-ray diffraction[23]. The phase structure in blends of PCL-based PU with PVC has been studied by X-ray diffraction and electron microscopy[24]; the results indicate that in these blends the compatibility is reduced, compared with that in PVC/PCL blends, due to the presence of the aromatic isocyanates. Finally, the macroscopic phase structure in the semi-IPN investigated in this report has also been studied by dynamic mechanical methods[25].

EXPERIMENTAL

Preparation of PU and semi-IPNs

The prepolymer in tetrahydrofuran (THF) was prepared by the usual methods from 4,4′-diphenylmethane diisocyanate (MDI, from Mobay) and PCL (Union Carbide, *MW* 2000) in a molar ratio of 3/2. To prepare the IPN, a 10% solution of PVC in THF was added, together with triethanolamine (TEA, from Matheson) as the crosslinking agent and several drops of dibutyltin dilaurate (T-12, from M & T Chemicals) as the catalyst. The amount of TEA was 1.8 wt% of the combined weights of PCL and MDI. The curing was done at 343 K in vacuum for 24 h. To prepare the PU, the PVC was omitted and curing was done at 333 K for 1 h. Additional experimental details have been published[26].

Spin-probed PVC

PVC containing the spin probe 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, from Aldrich) was prepared by mixing solutions of PVC and TEMPO in THF, stirring for 15 min and evaporation of the solvent. DSA (from Aldrich) was used for doping the PVC using a similar procedure.

Spin-probed PU and IPNs

PU containing TEMPO and DSA as spin probes was prepared by swelling a film of PU prepared as described above in ethanol for 12 h and addition of the probes to the solution; the PU sample was removed after stirring for ~30 min, washed repeatedly with ethanol and allowed to dry for 2 days. A similar procedure was used for the

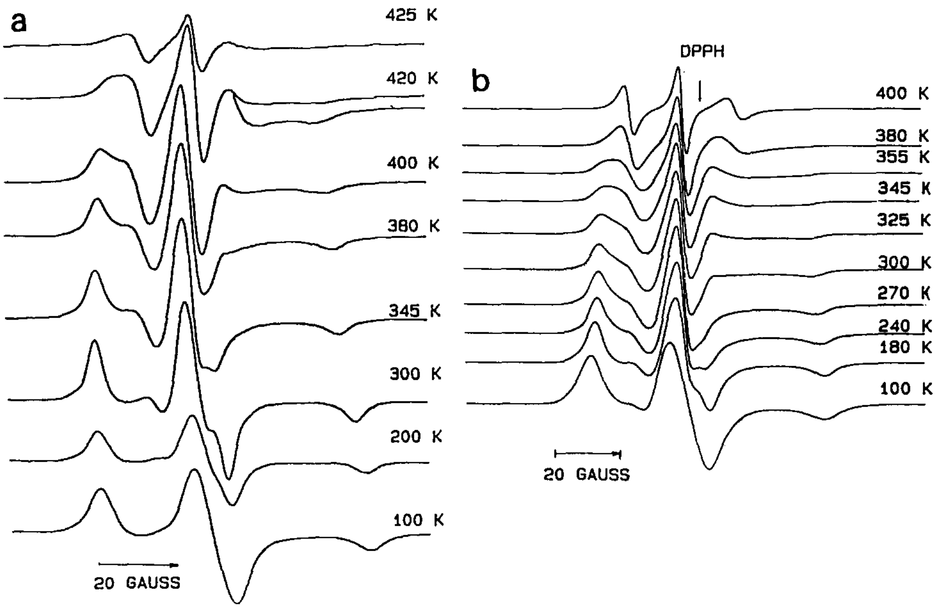

Figure 1 X-band e.s.r. spectra of (a) 12-doxylstearic acid and (b) TEMPO in PVC at indicated temperatures

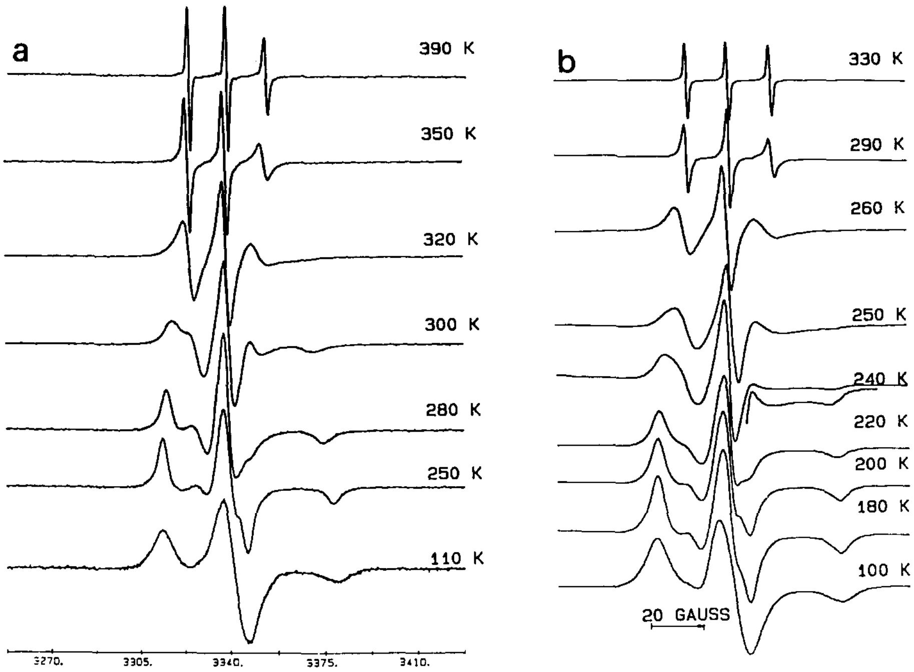

Figure 2 X-band e.s.r. spectra of (a) 12-doxylstearic acid and (b) TEMPO in PCL at indicated temperatures

preparation of spin-probed semi-IPN containing a PU/PVC ratio of 60/40 by weight.

Spin-probed PCL

This was obtained by addition of the probes to the molten polymer at 340K. Some samples were obtained by first preparing a solution of the probes in acetone and mixing of this solution with the molten PCL. No noticeable differences in the e.s.r. spectra of samples prepared by the two methods were detected.

The amount of spin probe in each sample was carefully controlled, in order to avoid line broadening due to magnetic dipole–dipole interactions.

Glass transition temperatures T_g based on the loss factor were obtained with a Rheovibron Dynamic Viscoelastometer (Model DDV-II-c, Toyo Baldwin Co., Tokyo).

E.s.r. spectra were measured at X-band with a Bruker 200D SRC spectrometer operating at 9.7 GHz and 100 kHz modulation. Data acquisition and manipulation is based on an IBM PC, using the software EPRDAS (Mega Systems Solutions Inc., Rochester, NY). Spectra were measured in the temperature range 100–425 K using the Bruker Variable Temperature Unit ER 4111 VT. E.s.r. spectra at 77 K were measured in a finger Dewar inserted in the e.s.r. cavity. The absolute value of the magnetic field was measured using the Bruker ER 035M NMR Gaussmeter. Calibration of g-values is based on 2,2-diphenyl-1-picrylhydrazyl (DPPH) ($g = 2.0036$) and Cr(III) in a single crystal of MgO ($g = 1.9800$).

RESULTS AND DISCUSSION

E.s.r. spectra of PVC, PCL, PU and IPN containing the TEMPO and DSA probes as a function of temperature were measured in the range 100–425 K at intervals of 10 K or less. Selected spectra are shown in *Figures 1–4*.

E.s.r. spectra of the two probes in PVC (*Figure 1*) have a very different temperature dependence, most likely due to probe size. Because the PVC used in this study is predominantly amorphous, we expect that both probes reflect the amorphous phase. For the small probe TEMPO $T_{50G} = 355$ K, within the range of the glass transition temperature. In contrast, for the doxyl probe the low- and high-field lines corresponding to the parallel transition are clearly detected even at 420 K, with $2A'_{zz} = 52 \pm 3$ G; T_{50G} is 422 ± 2 K. Based on the free-volume treatment of Bueche, it was suggested that the ratio f between the volume of the probe and that of the segment involved in segmental motion above T_g can be calculated from the difference $T_{50G} - T_g$, as shown below[5]:

$$T_{50G} - T_g = 52[2.9f(1 - \ln f) - 1] \qquad (1)$$

When $T_g = T_{50G}$, as in the case of the TEMPO probe in PVC, we obtain $f = 0.1$. The volume of the label is 170 Å^3 (ref. 5). The value of f indicates that the volume of the motional segment is ~1700 Å^3. The volume of one monomer unit of PVC is ~160 Å^3, based on tabulated bond lengths, bond angles and van der Waals radii[27]; therefore we can conclude that about 10 monomer units are involved in the segmental motion above T_g. This result is identical to that we obtained for PVC spin-labelled with 4-hydroxy-TEMPO[10].

For the doxyl probe in PVC, $T_{50G} - T_g = 60$ K and $f = 0.4$. In this case it is not easy to define the molar volume of the probe because of its elongated shape. The effective volume of the probe seems to be four times greater than for TEMPO, or ~700 Å^3.

From *Figure 2* we deduce for TEMPO in PCL that $T_{50G} = 258$ K, higher than the glass transition of 218 K. The higher T_g is often obtained in semicrystalline polymers[28]. Using equation (1), we obtain $f = 0.27$, which corresponds to a segmental volume of 630 Å^3. The monomer volume of PCL is ~170 Å^3 (ref. 27); the implication is that the segmental motion in PCL involves about four monomeric units or 24 backbone atoms. This value is in the range of the segmental size of 10–50 chain atoms determined by measuring the effect of the molecular weight between crosslinks on the value of T_g (ref. 29).

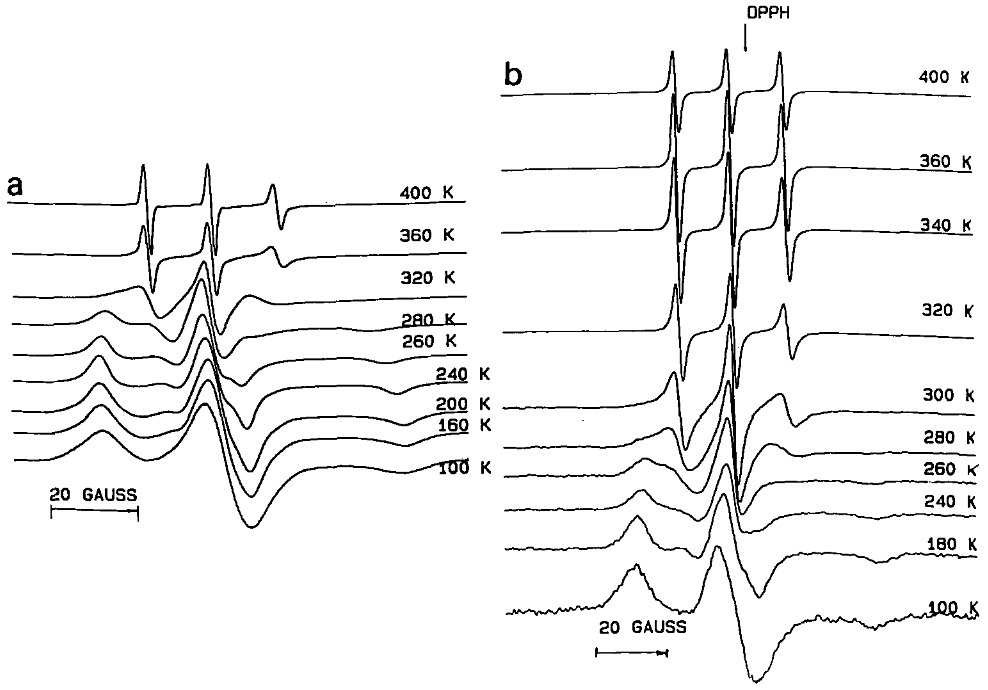

Figure 3 X-band e.s.r. spectra of (a) 12-doxylstearic acid and (b) TEMPO in PU at indicated temperatures

From e.s.r. spectra of the doxyl probe in PCL (*Figure 2a*) we observe that $T_{50\,\mathrm{G}} = 306$ K; an isotropic spectrum appears at 320 K, very close to the melting range of the PCL used, 318–328 K. We suggest that this probe intercalates preferentially in the *crystalline* phase of PCL. Additional support for this assignment is provided in the e.s.r. spectra of the doxyl probe in PU (*Figure 3a*), where the same $T_{50\,\mathrm{G}}$ value and the same temperature for the appearance of the isotropic spectrum are measured. It has been suggested that in PU the aromatic isocyanate is part of the amorphous phase of PCL while crystalline PCL is unchanged[24]. Our recent results on spin-labelled PU[10] support this conclusion and also the assumption that the doxyl probe is located in crystalline PCL. Additional support is provided by the observation that, while we detected *two* components in spin-labelled PU[10], only one is observed in the PU doped with DSA.

In most studies of probes and labels in polymers the emphasis has been on the correlation between the temperature variation of the e.s.r. spectra and the glass transition temperature[30]. Our suggestion above, that the long doxyl probe intercalates in the *crystalline* domains, presents the exciting possibility of *selective* examination of the amorphous and crystalline domains, provided the polymer is doped with morphology-sensitive probes. We will now verify this assumption by a motional model for the DSA probe.

In DSA probes the direction of the 2p orbital of the unpaired electron is along the molecular long axis z[31]. From the extreme separation in PCL we measured at low temperature (100 K) we obtain $A_{zz} = 33.5$ G. For a rotation about the long axis which is fast on the e.s.r. timescale, the values of A_{xx} and A_{yy} are averaged; this average value is 5.0 G, based on the isotropic value of 14.5 G we measured at 400 K. For a rotation about the molecular axis the extreme separation should be 67.0 G. Experimentally, a decrease of the extreme separation is observed on raising the temperature. These changes can be explained by assuming that, in addition to a rotation about the long axis, there is a restricted random 'wobbling' motion of the axis of rotation on the surface of a sphere[31]. The motion is shown in the inset of *Figure 5*; the angle θ between the axis of rotation and the molecular axis can change from 0 to γ; the value of γ specifies the extent of the wobbling motion and is temperature-dependent.

The maximum hyperfine A'_{zz} measured depends on θ as:

$$A'_{zz} = A_{xx} + (A_{zz} - A_{xx})\langle\cos^2\theta\rangle \qquad (2)$$

In equation (2), $\langle\cos^2\theta\rangle$ is the average value defined in*:

$$\langle\cos^2\theta\rangle = \int_{\theta=0}^{\gamma}\cos^2\theta\sin\theta\,\mathrm{d}\theta \Big/ \int_{\theta=0}^{\gamma}\sin\theta\,\mathrm{d}\theta$$
$$= \tfrac{1}{3}(\cos^2\gamma + \cos\gamma + 1) \qquad (3)$$

The angle of wobbling can be calculated from the measured extreme separation as a function of temperature. The volume spanned by the rotating probe scales as the solid angle defined by γ, divided by the solid angle of a sphere. We obtain

$$V(\gamma) \propto (1 - \cos\gamma)/2 \qquad (4)$$

In *Figure 5* we plotted $V(\gamma)$ vs. T; the increase in $V(\gamma)$ correlates with the melting range of the polymer, and reflects the large increase in volume on melting.

In *Figure 3b* we observe that for TEMPO in PU we obtain $T_{50\,\mathrm{G}} = 296$ K and an averaged spectrum is detected at 300 K. The increase in the value of $T_{50\,\mathrm{G}}$ for TEMPO in PU, compared to pure PCL, is most likely due to inclusion of the isocyanate segments in amorphous PCL on formation of PU. The assignments above are reasonable and explain the fact that only one component is detected in spin-probed PU, while two components have been detected in spin-labelled PU[10].

The e.s.r. spectra of DSA and TEMPO in the IPNs

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* In ref. 31, the expression for calculating $\langle\cos^2\theta\rangle$ seems to include several typographical errors. The final expression is, however, identical to that given in equation (3) in this study

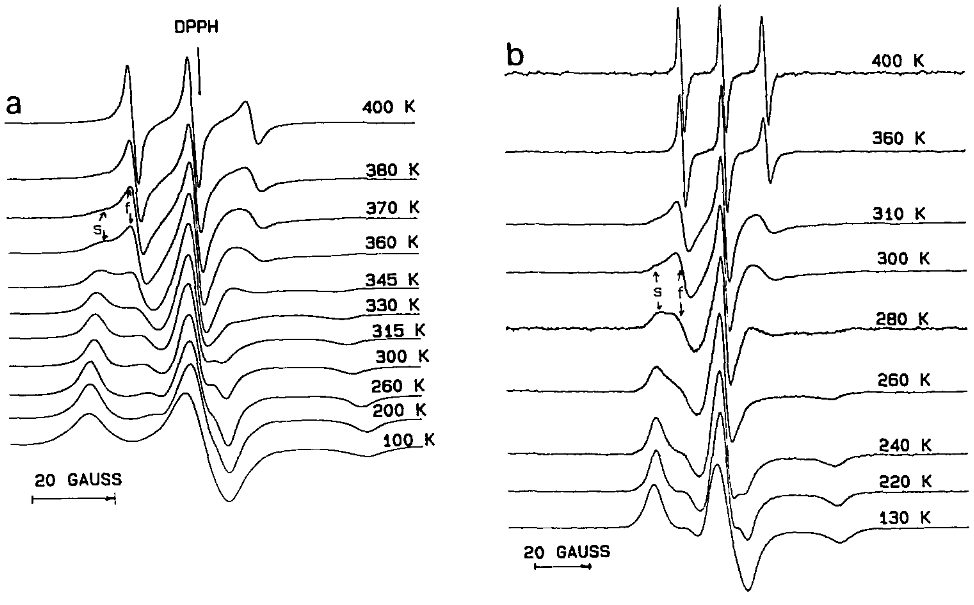

Figure 4 X-band e.s.r. spectra of (a) 12-doxylstearic acid and (b) TEMPO in IPN at indicated temperatures. The IPN composition is 60/40 PU/PVC by weight. 'Slow' and 'fast' components are indicated at some temperatures by 's' and 'f', respectively

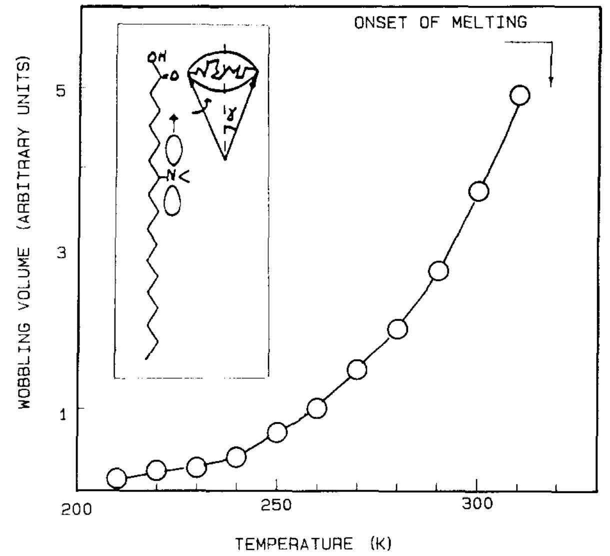

Figure 5 The 'wobbling' volume, calculated according to equation (3) *versus* $T(K)$. The inset shows the rotation axis and the wobbling of this axis between 0 and γ. Data is for DSA in PCL

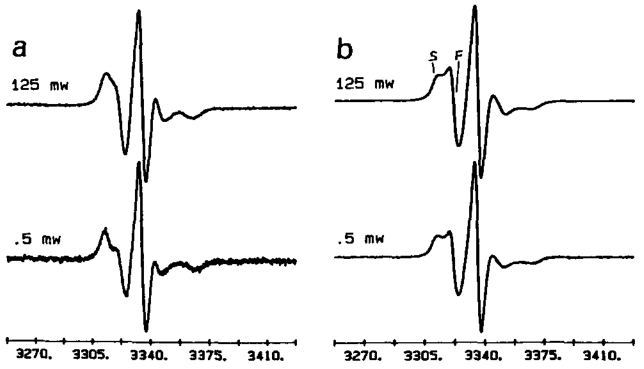

Figure 6 X-band e.s.r. spectra of 12-doxylstearic acid in (a) PCL at 300 K and (b) IPN at 350 K, at two microwave power levels

(*Figure 4*) indicate clear partition of the probes in two environments. DSA in IPN shows two components in the range 345–370 K; the slow component resolved at 370 K has an extreme separation of ~56 G and the isotropic component is visible at 345 K. TEMPO has two well resolved components in the temperature range 280–310 K and the isotropic component is visible at ~280 K. In general, we found it difficult to follow separately the temperature dependence of each component because at high temperatures the 'slow' component is 'buried' under the strong contribution of the fast component. This is evident in the e.s.r. spectrum of DSA in IPN at 370 K: the isotropic triplet dominates and the slow component is detected only at high gain and a modulation amplitude that broadens to some extent the 'fast' component.

In some cases the e.s.r. spectra of some nitroxide probes can be interpreted either in terms of anisotropic motion or by assuming superposition of two components[30]. Anisotropic motion is expected for probes whose structure is conducive to motion around a specific molecular axis; in the doxyl case it is clear that rotation around the long axis will occur at lower temperatures with lower free-volume requirements than motion around the other two axes.

In this study e.s.r. spectra of DSA in PCL and in IPN have been assigned to one component and to two components, respectively, on the basis of the temperature variation of the spectra shown in *Figures 2a* and *4a*. At some temperatures, where two components are assumed to exist in IPN, the spectra are very similar to those detected in PCL, where one component is assumed. In order to verify our assignment, we followed the change in e.s.r. spectra as a function of the microwave power. Some results are presented in *Figure 6*, where e.s.r. spectra of DSA in PCL at 300 K (*Figure 6a*) are compared with DSA in IPN at 350 K (*Figure 6b*). Increase in the microwave power from 0.5 mW to 125 mW leads to some broadening of *all* the lines in PCL. By contrast, in IPN the spectrum assigned to the 'fast' component is enhanced, most likely due to a shorter electronic spin–lattice relaxation time. It seems that the saturation method can

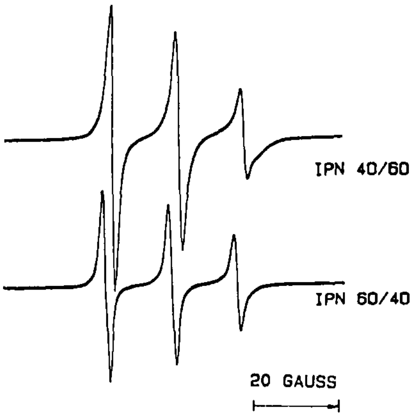

Figure 7 X-band e.s.r. spectra of two semi-IPNs containing spin-labelled PVC[10], at 400 K

be used to help in the interpretation of complex spectra.

In our study of IPNs containing spin-labelled PVC[10] we have detected at high temperatures, around 400 K, an unusual dependence of the linewidth as a function of the nuclear spin value m_I, which was assigned to a distribution in the values of g_{iso} and A_{iso}. Typical spectra for two IPN compositions are shown in *Figure 7*. The distribution was thought to arise from the location of the probe in domains with different polarities. Such an effect was not detected in this study. We believe that this is due to the fact that the probes used in this study scan a narrow range of environments. This result is supportive of our suggestion that in PCL the doxyl probe is located in the crystalline domains and TEMPO is located in the amorphous domains. The environments detected in the IPN might be predominantly crystalline PCL and amorphous PVC for the doxyl probe, and predominantly amorphous PCL (which includes the MDI) and amorphous PVC for the TEMPO probe.

CONCLUSIONS

TEMPO in PVC is sensitive to the glass transition temperature and its spatial sensitivity is of the order of 10 monomeric units.

The long 12-doxylstearic acid probe intercalates preferentially in the crystalline domains of PCL. The small TEMPO probe is located in the amorphous regions.

In PU the small TEMPO probe reflects the increase in the glass transition temperature of PCL due to the incorporation of the aromatic isocyanate groups. The crystalline regions consist of pure PCL.

Two components differing in their dynamics are detected for both probes in IPN. The assumption that two components are present is supported by the saturation behaviour of the e.s.r. spectra.

This study opens the exciting possibility that the crystalline and amorphous regions of polymers with complex morphologies can be selectively studied by morphology-sensitive probes.

ACKNOWLEDGEMENTS

This study was supported by the Army Research Office through a Graduate Fellowship to R.D.H. Acquisition of the e.s.r. spectrometer was possible through an NSF Instrumentation Grant DMR-8501312. We thank M. Omoto, J. Kusters and D. Klempner for their help in the preparation of the IPN sample and for numerous helpful discussions.

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