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Molecular dynamics and ordering of side chain liquid crystal polymers as studied by paramagnetic resonance

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Molecular dynamics of side chain liquid crystalline polymers (LCP) and their components were studied using the technique of paramagnetic resonance. A cigar shape spin probe (COL) and a nearly spherical spin probe (TPL) were used to study the motions and order of the LCPs. Computer simulations of the observed spectra were performed. Both rotational correlation times and order parameters were extracted from these simulations. We found that LCPs containing 30 per cent and 50 per cent of mesogenic side chains had about the same viscosity as indicated by nearly equal tumbling times at the same temperature. In addition, the LCPs motion is considerably slower than that of the monomeric liquid crystal indicating that the spacer couples the motions of the side chains to those of the main chain. Rotations about axes perpendicular to the side chain are slowed more than rotations about an axis parallel to the side chain. DSC measurements were employed to study the phase transitions. The 30 and 50 per cent LCPs displayed first order NS_A transitions, but the 50 per cent LCPs transition was much weaker, in agreement with McMillan's theory which predicts a first order transition for $T_{NS}/T_{NI} > 0{\cdot}87$ (observed ratios are 0·98, 0·90 and 0·86 for 30, 50 and 100 per cent LCPs, respectively). The 30 per cent LCP has a very short nematic range so that the nematic order, which is not saturated at the NS transition, can couple with the smectic order. This was indicated by a sharp change in slope of the order parameter versus temperature plot as the smectic is entered. The LCPs studied formed a highly ordered glass when cooled in a 1 T field. If one could find a LCP with similar ordering properties whose glass temperature is well above room temperature, then one would have a useful binder for the manufacture of haze-free polymer dispersed liquid crystal displays.

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1. Introduction

In this work we extend our previous studies of glass forming materials [1–8] to liquid crystalline polymers (LCP). Researchers have found two major difficulties when using paramagnetic resonance (EPR) to study LCPs. In many cases [9–13] their high viscosities made magnetic alignment (i.e. removal of mosaicity) of the director throughout the sample quite difficult. Fields far greater than the 3400 gauss used by X-band spectrometers are required, and these fields may need to be applied for long times [9]. In addition, the high viscosity restricted the tumbling time of the probe to a range not suitable for EPR studies, i.e. the probes appear to be standing still or nearly still on the EPR time-scale. Some workers [10, 11] have dealt with these problems by developing models which allowed them to simulate EPR line shapes in the slow-motion regime for samples whose macroscopic alignment is not complete. Such calculations have been applied to extract the macroscopic order of the probe molecules.

We have chosen a more 'friendly' LCP system to mitigate the problems described above. We use a siloxane co-polymer whose structure is indicated figure 1 (*a*) as a backbone. A 50-50 co-polymer is liquid at room temperature. The liquid crystalline monomer used is also shown in figure 1 (*c*), and the side chain or pendant LCP (see figure 1 (*b*)) is made by attaching this mesogenic unit to the polymer (see figure 1 (*a*)) via a $(CH_2)_6$ spacer which is quite flexible [14, 15]. An X-ray study of the corresponding 100 per cent side chain LCP has been reported [14]. The 100 per cent LCP reportedly displays both a nematic and a smectic C phase. In this work we present EPR data from COL (see figure 1 (*d*)) and TPL (see figure 1 (*e*)) spin probes dissolved in the pure liquid crystal, an approximately 50–50 co-polymer and three ($\simeq$30, $\simeq$50 and $\simeq$100 per cent liquid crystal) LCPs. Some of the characteristic temperatures associated with these materials appear in table 1. We will present evidence that the LCPs studied display both a nematic and smectic A phase. The order and molecular motions have

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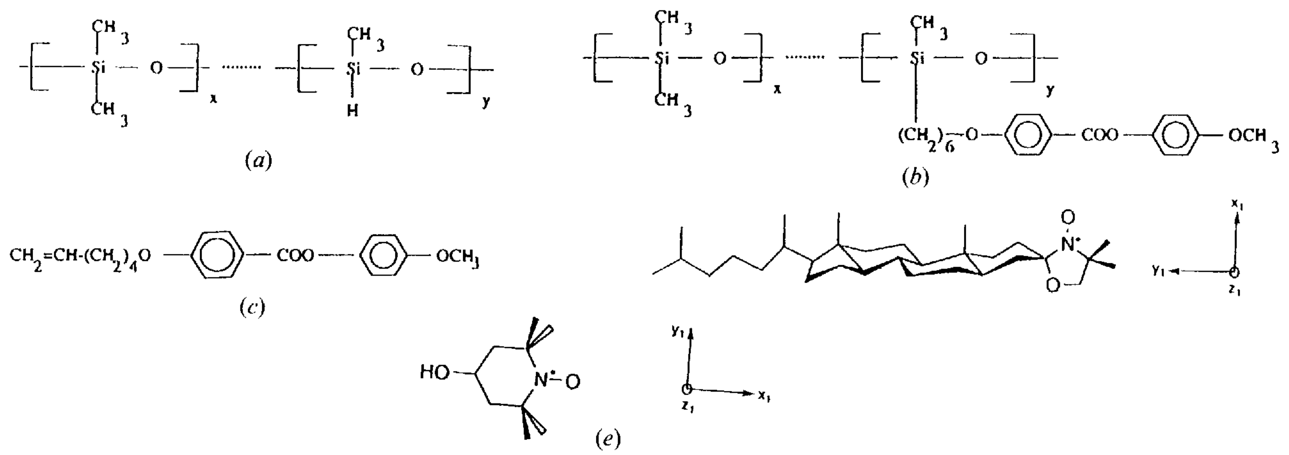

Figure 1. The polymers and liquid crystals used in this study. (*a*) The co-polymer, (*b*) The polymer liquid crystal (LCP), (*c*) The monomer used to form the LCP, (*d*) The COL spin probe, and (*e*) The TPL spin probe.

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been studied and the corresponding data will be presented. We also find that the LCPs form highly ordered glasses when cooled in the presence of a magnetic field. This may have some impact on haze-free polymer dispersed liquid crystal displays (PDLC) as will be observed in the discussion section.

2. Experimental

The paramagnetic resonance (EPR) spectrometer, temperature controller, spin probes and sample preparation were described earlier [5]. We found that we needed to be especially careful to pump off the solvent (dichloromethane) from the LCP samples to prevent extra spectral lines from appearing. The rotational correlation times, τ are extracted from diffusion constants used in spectral simulations. The simulation program originally written by Moro and Freed is based on the Lanczos algorithm [16, 17]. TPLs motion is characterized by a single diffusion constant, D since it has a nearly spherical shape, but COLs motion is characterized by $D_\parallel$ and $D_\perp$ with the parallel direction along the long molecular axis. COL has a geometrical aspect ratio of approximately 5, but we find that ratio of $D_\parallel/D_\perp$ required for the best fit to the data varies between 5 and 13. $\tau_{iso} = 1/6D$ 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 model is employed. The value of the order parameter of the probe is also obtained from the line shape simulations. In the very fast tumbling regime, $\tau < 10^{-10}$ s and the very slow regime $\tau > 10^{-7}$ s the simulations are not very sensitive to changes in τ or order. In the intermediate regime we find, by actual measurement, that the maximum error in the value of τ is less than 10 per cent and the maximum error in the order parameter is 4 per cent.

Table 1. Transition temperatures for the materials studied.

Material	T_{NI}K	$T/_{SN}$/K	T_gK
Co-polymer 50-50			143
LC	Monotropic 332 $T_{CI} = 332$‡	$T_{CN} = 322$‡	
30 per cent PLC	313	306	249
50 per cent PLC	331	299	263
100 per cent PLC†	363	311	281

† Values taken from [14].

‡ T_{CN} and T_{CI} are the crystal to nematic and crystal to isotropic transition temperatures respectively.

Arrhenius plots of the motional data are constructed and these plots are fitted to a straight line whose slope is the activation energy. The fits to the perpendicular data are shown, so that the reader can see the quality of the fit. Other fits are left off of the plots to prevent clutter.

The hyperfine interaction for COL is characterized by a nearly axial tensor with the symmetry molecular axis (z_1) perpendicular to the long direction of the molecular body and parallel to the nitrogen $2p\pi$ orbital. If the liquid crystal system is perfectly ordered, one finds that the observed spectrum takes on the x_1, y_1 hyperfine splitting (4-6 G). The z_1 hyperfine splitting is approximately 31-34 G. Similar effects are observed for TPL, but, since the molecule is so much smaller, the ordering is expected and observed to be considerably less than that observed for COL. The isotropic values of the g and hyperfine tensors are measured for the probe when the sample is in the isotropic phase and this is used to determine the parallel and perpendicular components of the corresponding tensor using the fitting program. It is well known that the actual value observed for hyperfine tensor depends both on the probe and the polarity of the solvent.

The co-polymers were purchased from HULS

America, Piscatway, NJ. The LCPs (see figure 1 (*b*)) were prepared by reacting the monomer (see figure 1 (*c*)) with the co-polymer in the presence of the platinum catalyst dicyclopentadienylplatinum (II) chloride [18] as described below.

A solution of the co-polymer and the liquid crystalline monomer (1·2 equivalents of the monomer to the Si-H bond in the polymer) in dry toluene was heated to reflux in an atmosphere of dry nitrogen. A few drops of a solution of the catalyst in dry methylene chloride (1 mg in 1 ml) was added and heated at reflux for 24 h. The cooled reaction mixture was diluted with excess methanol, and the precipated polymer was separated by centrifugation. The polymer was purified by precipitating it from a toluene solution with methanol. This process of purification was repeated until it was free of the monomer as monitored by thin layer chromatography. Finally, the polymer was dried under vacuum at 50°C for 4 h.

DSC measurements were made on a Perkin-Elmer DSC-7 calorimeter and a Perkin-Elmer DSC-4 calorimeter using pressurized liquid sample pans.

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3. Observations

3.1. *The pure liquid crystal*

This material displays a monotropic nematic at the temperatures indicated in table 1. The nematic director aligns in the 0·34 T field of the spectrometer. As the sample is rotated 90° in the field of the spectrometer, the 0·34 T field easily reorients the director. The glassy phase is obtained by quenching the liquid crystal from the isotropic phase to low temperature. If this quenching is done in the presence of 1 T field then the sample appears to be ordered. When cooling from the isotropic to room temperature or from the ordered nematic into the crystal phase the COL probe loses its order. This is consistent with the strong first order phase transition indicated by the DSC data.

In figure 2 we present Arrhenius plots for COL in the pure liquid crystal. One sees that the anisotropy in the tumbling time is much greater in the nematic phase than in the isotropic phase. $\tau_{\parallel}$ decreases rapidly and $\tau_{\perp}$ increases rapidly as the nematic phase is entered. The anisotropy is considerably greater than the aspect ratio of COL indicating that the anisotropy of the mesophase is also profoundly influencing the motion of COL. This is also indicated in figure 3 (*a*) where the plot of the order parameter versus temperature is presented. The order, obtained from spectral simulations, varies from ~0·3 to ~0·52, so that the liquid crystal orders the COL probe quite effectively. The liquid crystal also successfully ordered the nearly spherical (aspect ratio about 1·2) TPL. As seen in figure 4 (*a*) TPL has a maximum order parameter of approximately 0·22. An Arrhenius plot for TPL in the pure liquid crystal is shown in figure 5 (*a*) One observes that TPL tumbles quite rapidly in both the isotropic and nematic phases. Its motion is nearly an order of magnitude faster than than of COL.

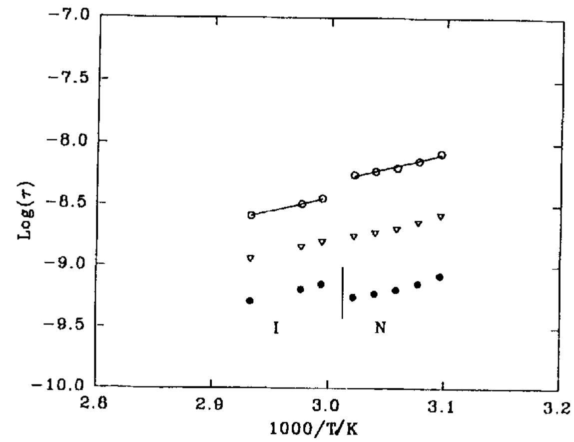

Figure 2. Arrhenius plots for COL in the pure liquid crystal. The vertical line indicates the NI phase transition: (○) $\tau_{\perp}$, (∇) τ_{iso}, (●) $\tau_{\parallel}$.

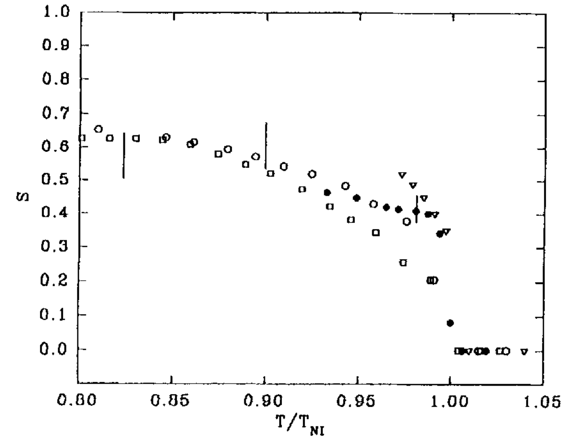

Figure 3. Order parameters of COL versus reduced temperature (T/T_{NI}). The vertical lines indicate the NS phase transitions. (*a*) Dissolved in the pure liquid crystal (∇), (*b*) dissolved in the 30 per cent LCP (●), (*c*) dissolved in the 50 per cent LCP (○), and (*d*) dissolved in the 100 per cent LCP (□).

3.2. *The co-polymer*

For purposes of comparison an approximately 50–50 co-polymer was studied in some detail. It is interesting to note that this polymer is liquid at room temperature. In figure 6 we show Arrhenius plots for COL dissolved in

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this co-polymer. One observes two regions in the plot of τ_{iso}. The activation energies in each of these two regions are quite different (see table 2(*a*)) since the probe samples different motions of the polymer. This is a result that has been observed for many polymers in the literature [7, 8, 19]. Typically the higher activation energy occurs at higher temperature. One usually associates the higher activation energy with the α relaxation of the polymer backbone and the lower activation energy with the γ relaxation of the methyl groups. It is interesting to note that the anisotropy in the rotational correlation times is about 5 at very high and very low temperatures and closer to 10 in the region of 180–206 K. $T_g = 143$ K, $T_{50} = 188$ K and the temperature at which the observed signal cannot be simulated as a single spectrum is (T_{gap}) is 175–180 K. Here, as in most cases, T_{gap} is slightly lower than T_{50}. The significance of these temperatures has been discussed in earlier papers [7, 8], so we will not repeat the discussion here except to remind the reader that they depend upon the probe used as well as the solvent. Generally the gap will occur when $\tau \sim 10^{-8}$ s, so that T_{gap} will be smaller for smaller probes. This point will be illustrated when we discuss the TPL results below.

In figure 5(*b*) the Arrhenius plot for TPL is shown. Here again we observe two activation energies as discussed above (see table 2(*b*)). Over most of the thermal range the TPL probe is observed to move considerably faster than the COL probe. This is to be expected since the TPL probe is considerably smaller than the COL probe. For the TPL case $T_{50} = 163$ K and $T_{gap} = 155$ K. As expected, these temperatures are quite a bit lower than those for COL.

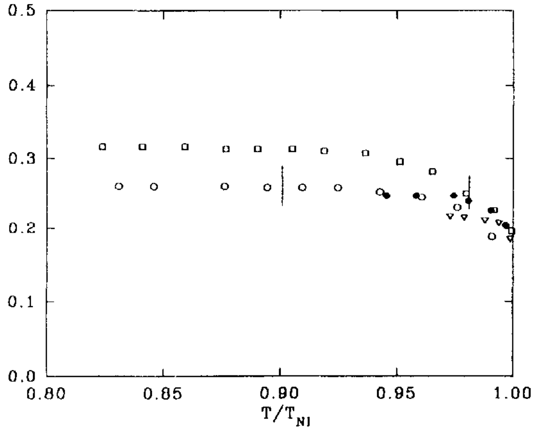

Figure 4. Order parameters of TPL versus reduced temperature (T/T_{NI}). The vertical lines indicate the NS phase transitions. (*a*) Dissolved in the pure liquid crystal (∇), (*b*) dissolved in the 30 per cent LCP (●), (*c*) dissolved in the 50 per cent LCP (○), and (*d*) dissolved in the 100 LCP (□).

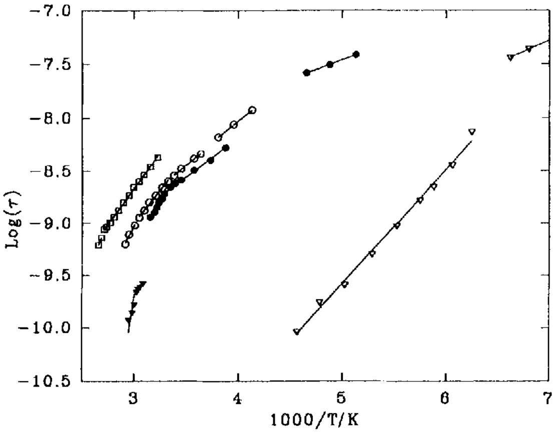

Figure 5. Arrhenius plots for TPL dissolved in the (*a*) pure liquid crystal (▼), (*b*) 50–50 polymer (∇), (*c*) 30 per cent LCP (●), (*d*) 50 per cent LCP (○) and (*d*) dissolved in the 100 per cent LCP (□).

3.3. *The 30 per cent LCP*

The first LCP studied consists of a polymer backbone with the mesogenic groups attached to approximately 30 per cent of the co-polymers ($Y \approx 30$ per cent in figure 1(*b*)). The transition temperatures of interest are indicated in table 1. We found that 0·9 T was required to get adequate alignment of the nematic phase. It is no surprise that the motions of the COL probe were quite sluggish compared with those of TPL. In figure 7 we show the Arrhenius plots for COL in 30 per cent LCP. As expected, we observe changes in the slope at the transition temperatures and $\tau_{\|}$ gets much faster as the nematic is entered from the isotropic phase. In figure 5(*c*) the Arrhenius plot for TPL in 30 per cent LCP is shown. First note that in the nematic phase typical values of τ_{iso} for COL are about 10^{-8} s compared with approximately $1{\cdot}6 \times 10^{-9}$ s for TPL. Also note that for TPL the motion

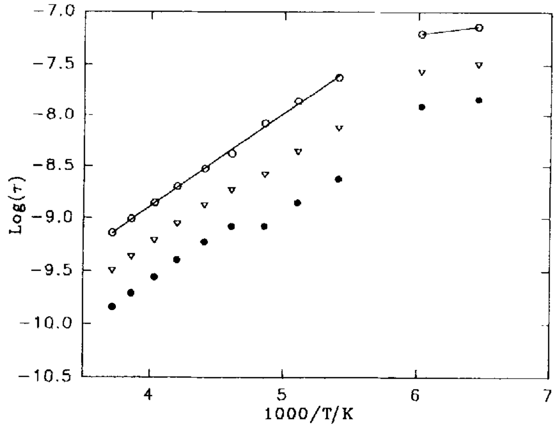

Figure 6. Arrhenius plots for COL in the 50–50 polymer backbone: (○) $\tau_{\perp}$, (∇) τ_{iso}, and (●) $\tau_{\|}$.

Table 2. Activation energies (kJ mol^{-1}) obtained from fits to the arrhenius plots and their standard deviation for (*a*) COL and (*b*) TPL dissolved in the materials studied.

(*a*)

Material	Isotropic	Nematic	Smectic	Glass
LC	43·6±1·0	44·8±4·0		
Co-polymer	17·4±0·3			3·1±0·0
30 per cent LCP	23·1±4·8	40·3±1·6	9·5±1·2	
50 per cent LCP	24·1±1·2	23·8±1·2	14·4±1·0	
100 per cent LCP	38·2±9·8	22·6±0·8		

(*b*)

Material	Isotropic	Nematic	Smectic	Glass
LC	128±10·8	24·4±2·3		
Co-polymer	21·0±0·6			7·9±0·3
30 per cent LCP	22·5±0·0	29·3±6·0	14·4±0·6	6·6±0·2
50 per cent LCP	38·6±6·0	24·0±1·0	15·3±0·5	14·6±0·3
100 per cent LCP	49·0±0·0	26·3±0·3		

in the smectic phase is still much more rapid compared with the comparable motions for COL. The 30 per cent LCP effectively orders both probes (see figures 3 (*b*) and 4 (*b*)). One observes that the order parameter increases rapidly with decreasing temperature in the nematic phase and then increases more slowly at lower temperatures. We observe the order to be nearly constant in the smectic phase. The COL order parameter in the smectic phase is observed to be ~0·47 which, not surprisingly, is considerably greater than the ~0·25 observed for TPL.

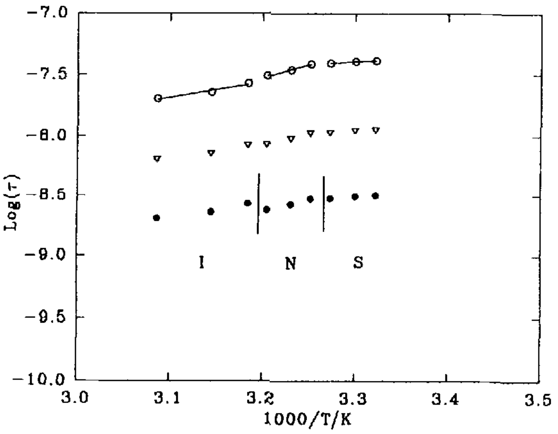

Figure 7. Arrhenius plots for COL in the 30 per cent LCP. The vertical lines indicate the NS and NI phase transitions: (○) $\tau_{\perp}$, (▽) τ_{iso}, and (●) $\tau_{\parallel}$.

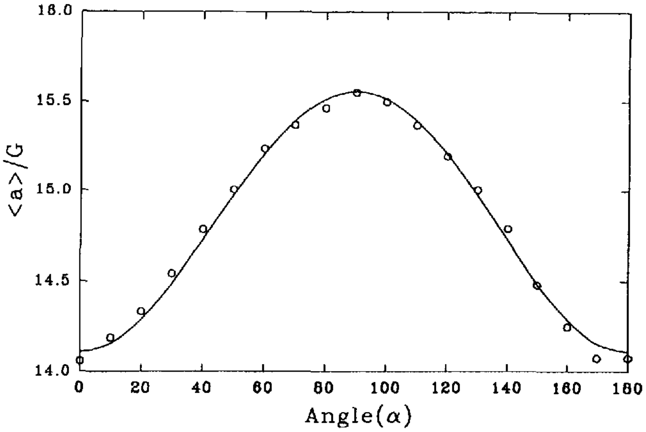

Figure 8. Line splitting versus α, the angle between the director and the magnetic field, for TPL in 30 per cent LCP.

The smectic phase of 30 per cent LCP was investigated by observing the line splitting as a function of the angle between the director and the magnetic field and the results are shown in figure 8. The solid line is a fit of the equation $<a> = [A_1^2 + (A_2^2 - A_1^2)\cos^2\alpha]^{1/2}$ with the fitting parameters $A_1 = 15{\cdot}6$ and $A_2 = 14{\cdot}1$ gauss. There is no evidence of the director reorientation usually associated [20–24] with a smectic C phase, so that we conclude that a smectic A phase is being observed.

When the 30 per cent LCP containing the COL probe is quenched from the ordered nematic to the glass in the presence of a 1 T magnetic field, a highly ordered glass spectrum is observed. In figure 9 (*a*) we show this spectrum. Notice the small line separations corresponding to high order. In figure 9 (*b*) we show the simulated spectrum from which we get the order parameter ≈0·8. When the ordered glass sample is rotated 90°, one expects to observe spectral contributions from probes of all orientations resulting in a broad glassy spectrum of width $2A_z$. This is what is observed as indicated in figure 9 (*c*). When the 30 per cent LCP containing the TPL probe is quenched from the nematic to the glass in a 1 T magnetic field, the results are quite different. Here a glass spectrum reflecting little or no order is observed. Possibly, this is a reflection of the lower order observed for TPL in the nematic phase. An alternate explanation is that liquid like sites [20] or voids [21] exist whose free volume is greater than that of TPL.

3.4. *The 50 per cent LCP*

The other LCP studied consists of a polymer backbone with the mesogenic groups attached to approximately

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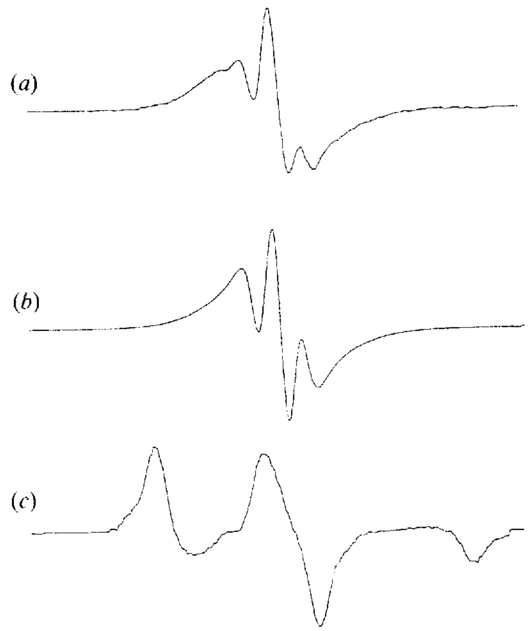

Figure 9. Observed and calculated spectra from COL dissolved in 30 per cent LCP. (*a*) Observed spectrum at 130 K when the director and the magnetic field are parallel. (*b*) Calculated spectrum at 130 K when the director and the magnetic field are perpendicular.

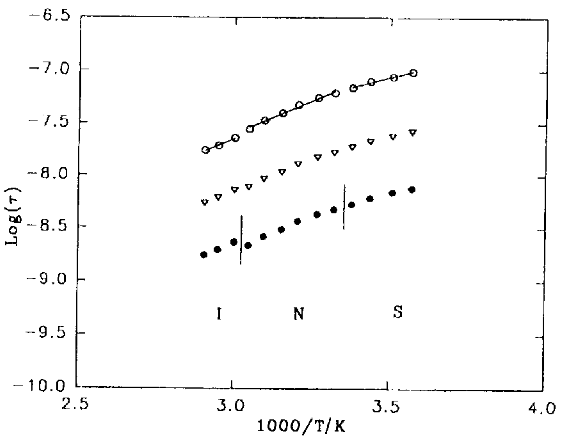

Figure 10. Arrhenius plots for COL in the 50 per cent LCP. The vertical lines indicate the NS and NI phase: (O) $\tau_{\perp}$, (V) τ_{iso}, and (●) $\tau_{\parallel}$.

50 per cent of the co-polymers (Y= 50 per cent in figure 1 (*b*)). The transition temperatures of interest are indicated in table 1. We found that 0·5 T was required to get adequate alignment of the nematic phase at 301 K, but 0·8 T was required to align the nematic phase at 322 K. Qualitatively it appeared that the 50 per cent LCP kept its alignment longer than the 30 per cent LCP. Again we observed that the motions of the COL probe were quite sluggish compared with those of TPL. In figure 10 we show the Arrhenius plots for COL in 50 per cent LCP. As expected, we again observe changes in the slope at the NI and NS transition temperatures (see table 2). The parallel motion rapidly increases as the nematic phase is entered from the isotropic. In figure 5 (*d*) the Arrhenius plot for TPL in 50 per cent LCP is shown. Typical values of τ_{iso} for COL, with the sample in the nematic phase, are about 10^{-8} s compared with approximately $1{\cdot}6\times10^{-9}$ s for TPL. Also the TPLs motion in the smectic phase is much more rapid compared with that of COL. The 50 per cent LCP effectively orders both probes (see figures 3 (*c*) and 4 (*c*)). One observes that the order parameter increases rapidly with decreasing temperature in the nematic phase and then it continues to increase, albeit more slowly, as the temperature is reduced. The COL order parameter at a reduced temperature of approximately 0·93 is about 0·53 which, not surprisingly, is considerably greater than the 0·26 observed for TPL.

The smectic phase of 50 per cent LCP was investigated by observing the line splitting as a function of the angle between the director and the magnetic field and the results are quite similar to those shown in figure 8. The fit of the equation $<a> = [A_1^2+(A_2^2-A_1^2)\cos^2\alpha]^{1/2}$ to the 50 per cent LCP data yields the parameters $A_1 = 14{\cdot}8$ and $A_2 = 12{\cdot}4$ gauss. Again there is no evidence of the director reorientation usually associated [22–26] with a smectic C phase, so that we conclude that a smectic A phase is being observed for both the 30 per cent and 50 per cent LCPs.

When the 50 per cent LCP containing the COL probe is quenched from the ordered nematic to the glass in the presence of a 1 T magnetic field, it behaves in manner similar to the 30 per cent LCP. The order parameter obtained from our simulation is ~0·81.

3.5. *The 100 per cent LCP*

In this case all of the co-polymer sites have mesogenic groups attached (y = 100 per cent in figure 1 (*b*)). This sample has the longst nematic range (see table 1). The order parameter for both COL (see figure 3) and TPL (see figure 4) dissolved in the 100 per cent LCP grows gently in this long nematic range and saturates before the smectic range is reached. The arrhenius for TPL in 100 per cent LCP is shown in figure 5 and the activation energies appear in table 2. Preliminary rotation experiments show no sign of a smectic C phase.

4. Discussion

The EPR technique is a powerful non-destructive tool for gathering information concerning the molecular motions and ordering of LCPs. The arrhenius plots (see figure 6) for COL dissolved in the polymer indicate that the anistropy in τ is different in different thermal regimes.

At the low and high end of the temperature scale the anistropy is approximately 5 which is quite similar to the aspect ratio of the probe (4·8). In the intermediate region it is closer to 10 indicating that it may be sensing anisotropic motion. There is no clear site for hydrogen bonding, so this is currently ruled out as a cause of anisotropy.

It is interesting that the combination of a polymer that is liquid at room temperature and a monotropic liquid crystalline material that is solid at room temperature form a LCP that displays both a nematic and a smectic A phase. The NI and NS_A phase transitions for the liquid crystal and the LCPs are clearly indicated in the respective Arrhenius plots, and the anisotropy of COLs motion appears to be considerably greater in the liquid crystal phases than in the isotropic phase. At 323 K (i.e. the nematic phase) we observe $\tau_\parallel$ to be 0·83 ns for the liquid crystal compared with 2·4 ns for the 50 per cent LCP. We also find that $\tau_\perp$ for the liquid crystal 8·3 ns compared with 34 ns for the 50 per cent LCP. In the LCP the parallel motion is slowed by a factor of 2·9 and the perpendicular motion is slowed by a factor of 4·1. This may indicate that the main chain slows the motion of the side chain via the flexible spacer. Further, the perpendicular motion is slowed considerably more than the parallel motion.

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The 30 and 50 per cent LCPs both have about the same viscosity as indicated by the fact that the probes tumble at approximately the same rate in both. For example, $\tau_\parallel$ at 306 K is 3·0 and 4·3 ns for the 30 per cent and 50 per cent LCP, respectively. In addition the plots of observed order parameter versus the reduced temperature are not very different for the 30 and 50 per cent LCP. A closer inspection of figure 3 reveals some interesting differences however. First note that the nematic range of 30 per cent LCP is much smaller than that of the 50 per cent LCP, and the order rises rapidly in this range of the 30 per cent sample. For the 30 per cent LCP there is a sharp decrease of slope of the order curve as the smectic A phase is entered. For the 50 per cent sample, the order rises sharply in the high temperature region of the nematic range but converts to a more gentle slope well before the smectic A phase is reached. The 100 per cent LCP data reveal almost no change in slope asd the smectic A phase is entered. There is an interesting feature in the DSC curves for these samples. The 30 per cent LCP displays a strong first order NS transition ($\sim 2.5\,J_g^{-1}$) while the 50 per cent LCP displays a considerably weaker first order transition ($\sim 0{\cdot}31\,J_g^{-1}$). Microscopic theory for liquid crystal indicates that one should expect first order behaviour for $T_{NS}/T_{NI} > 0{\cdot}87$. This arises from the observation that for a narrow nematic range (as observed for the 30 per cent LCP), the nematic order is not yet saturated, allowing for a coupling between the nematic and smectic order resulting in a first order phase transition. We observe T_{NS}/T_{ni} $\sim 0{\cdot}98$ for the 30 per cent LCP and $\sim 0{\cdot}90$ for the 50 per cent LCP. These ratios are consistent with all of the observations described above. A LCP containing slightly more than 50 per cent liquid crystal site, should display a second order NS transition, possibly to a S_C phase which would be consistent with the literature report of a smectic C in the 100 per cent LCP ($T_{NS}/T_{NI} = 0{\cdot}86$) as described above.

The activation energy is a measure of the rate of change of the correlation time with temperature. In a simple isotropic fluid this is a measure of how fast the viscosity changes. In an isotropic polymer at high temperature the probe most likely follows the motions of the main chain, i.e. the α relaxation, so here the activation energy is indicative of the slope of the frequency versus temperature curve for the α relaxation. The data in tables 2 (*a*) and (*b*) show a definite trend. For both probes the activation energies in the isotropic phase increases with increasing LC concentration indicating that the slope of the α relaxation increases with increasing LC content. In the nematic phase, the rate of change of the order parameter is probably the most important consideration—more so for the COL probe which, due to its size and shape, is more ordered by the nematic. The 30 per cent LCP has a very short nematic temperature range during which the order rises rapidly but does not even get to saturate (see paragraph above) before reaching the smectic phase. Here we expect a large activation energy in the nematic phase. At the other end the 100 per cent LCP has a long nematic range in which the order rises much more gently and saturates before the smectic phase is reached. In this case we expect a lower activation energy. As expected the activation energy (see table 2 (*a*) for COL goes from 40·3 to 22·6 as the LC content goes from 30 to 100 per cent. The effect is also present in the TPL data (see table 2 (*b*)) with the activation energy going from 29·3 to 26·3. The effect is much smaller for TPL as is expected.

Doane [28] has indicated that a polymer dispersed liquid crystal display (PDLC) that uses an ordered LCP as the binder will be haze-free. Our study of the 30 and 50 per cent LCPs indicate that they form a highly ordered glass when cooled in a 1 T field, and that they do not lose their order if they are kept below their glass transition temperature. These properties are the sort required by the haze-free PDLC. Unfortunately, the materials studied do not have a high enough glass temperature to be practical, but we have illustrated how the EPR studies of molecular motions could be used to determine the properties of other LCPs that have T_gs above room temperature.

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