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Neutron scattering studies of terminally attached side chain liquid crystal polymers

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Three side chain liquid crystal polymers have been studied by neutron scattering methods. We have compared the three compounds, all with a polysiloxane backbone, a four-atom flexible spacer, $(CH_2)_3O$, and a benzoate ester mesogenic unit. However, the mesogenic unit was terminated by one of three different groups. The hexyloxy and cyano derivatives gave smectic A phases and the methoxy gave a nematic. Small angle neutron scattering measurements of mixtures of deuteriated and hydrogenous versions of the same polymer have been used to determine the dimensions and anisotropy of the backbone. The anisotropy was found to be similar in the smectic and nematic phases and suggested a tendency for the polymer backbone to be confined between the layers of mesogenic units. The SANS results show two different characteristic sizes. One is attributed to the size of a single polymer molecule. The other indicates density fluctuations on a scale larger than one polymer molecule. The local packing of the mesogenic units has been studied by comparison of neutron Bragg scattering from the smectic layers in materials with specific parts of the mesogenic units deuteriated. This has allowed the degree of interdigitation of mesogenic units in different layers to be deduced in the hexyloxy compound. It was found necessary to postulate a chain rich region midway between the polysiloxane backbones. This could only occur if the mesogenic units were significantly statistically tilted with respect to the smectic layer normal.

1. Introduction

X-ray diffraction is able to give information on repeat distances such as smectic layer spacings and on the degree of translational ordering in liquid crystal phases. Generally the information obtained is limited because only a few Bragg reflections can be measured in disordered materials. This paper reports an attempt to use neutron scattering with specifically deuterated materials to enhance our knowledge of the structure of polymeric mesophases. Three closely related side chain liquid crystal polymers were selected for this study and two different types of neutron scattering measurement have been made on them.

(i) Small angle neutron scattering (SANS) from a mixture of normal hydrogenous polymer and a partly deuteriated version has been used to determine the conformation and anisotropy of the polymer backbone in aligned samples.

(ii) Neutron Bragg scattering from smectic layers in materials with different sites deuteriated has been used to deduce information about the local packing of the mesogenic units.

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Both these methods take advantage of the fact that hydrogen and deuterium have very different scattering lengths for neutrons yet isotopic substitution is usually a negligible perturbation of the intermolecular interactions. Hydrogen has a negative scattering length ($-3{\cdot}73\times10^{-15}$ m) whereas deuterium has a positive one ($6{\cdot}64\times10^{-15}$ m), so deuteriation of an organic molecule makes a major change in the distribution of scattering length.

2. Experimental

2.1. *Materials*

The side chain liquid crystal polymers used were the polysiloxanes with the terminal group R = hexyloxy, cyano or methoxy as shown in figure 1. In all three cases, versions with all four hydrogen atoms of both rings replaced by deuterium were synthesized by standard procedures from deuteriated precursors. Two further labelled compounds were also made: for R = cyano, the version with only one ring deuteriated and for R = hexyloxy the version with only the hexyl group deuteriated. Their transition temperatures were determined by differential scanning calorimetry. No significant differences were observed between deuteriated and hydrogenous analogues. Their phases have been confirmed and the spacing (d) of the smectic layers determined by X-ray diffraction. These results are summarized in table 1 together with the distance (l) between the silicon of the polysiloxane backbone and the extremity of the mesogenic unit determined from model molecules, assuming an all-*trans* conformation of the spacer (and hexyloxy group). The degree of polymerization, n, was about 50 and the polydispersity index ($\gamma=\bar{M}_w/\bar{M}_n$) was about 2.

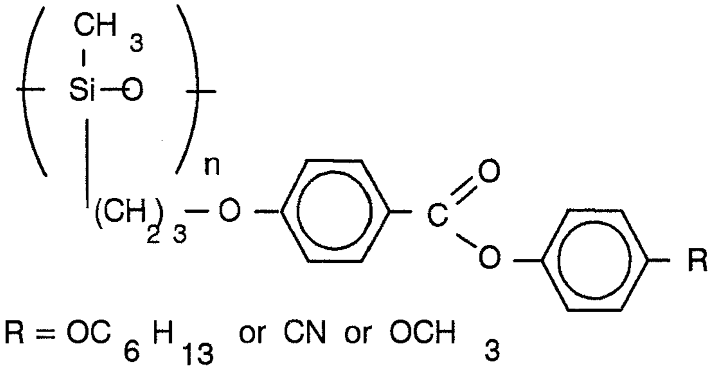


Figure 1. Structure of side chain polysiloxanes.

Table 1. Properties of the polymers.

Polymer	R	Transition temperatures				d/Å	l/Å
I	$-OC_6H_{13}$	g 23°C	S_A	100°C	I	37	27
II	$-CN$	g †	S_A	133°C	I	27	20
III	$-OCH_3$	g †	N	86 to 90°C	I		20

Difficult to assign a precise glass transition temperature.

2.2. *Sample preparation and alignment*

The mixtures of hydrogeneous and deuteriated versions of the same polymer were prepared by evaporation of a solution of both polymers in an organic solvent. The samples were made up to contain either 10 wt% or 50 wt% of the normal hydrogenous polymer mixed with the version with the four hydrogen atoms on both the phenyl rings replaced by deuterium. All the samples were contained in 2 mm thick fused silica cells and they were aligned by cooling to room temperature from the isotropic phase in a 10 T magnetic field.

2.3. *Neutron scattering experiments*

The experiments to measure the SANS from the hydrogenous plus deuteriated mixtures were done on the D11 instrument at the Institute Laue Langevin (ILL), Grenoble. An incident wavelength of 4·5 Å and a sample to detector distance of 2·9 m were used to observe the SANS arising from the whole polymer molecule. A larger distance (10 m) was found to reveal SANS from some larger scale inhomogeneities in the materials, but this was observed for the pure compounds as well as for the mixture, so it does not apparently originate from the single molecule scattering.

The Bragg scattering measurements were done on the D17 instrument at ILL with a wavelength of 8 Å and a sample to detector distance of 0·82 m. The detector was off-set by 24° from the straight through position in order to see as many orders of Bragg reflections as possible.

3. Results

3.1. *Chain conformation*

The SANS from the pure polymer (with both rings deuteriated) showed a flat background from the incoherently scattering nuclei in the material. The mixtures with 10 wt% and 50 wt% hydrogenous material gave a strong scattering around the main beam. This is shown for the 50 wt% mixtures in figures 2 to 4. The scattering data have been corrected for background and detector efficiency. The direction of the aligning magnetic field is vertical. It can be seen that the anisotropy is modest, but the scattering is more extended in the vertical direction. This suggests that the backbones have a preference to extend perpendicular to the director. The data have been analysed by fitting the Debye [1] function to the two dimensional data sets. The Debye function describes the small angle scattering from a gaussian polymer chain and is

$$I(Q)=2(\exp(-x)+x-1)/x^2,$$

where x is the product of the scattering vector, $\mathbf{Q}$, and the radius of gyration, R_G. To account for the anisotropy, the radius of gyration has been made a function of the angle, θ, between $\mathbf{Q}$ and the director as follows:

$$R_G=R_\perp \sin^2\theta+R_\parallel \cos^2\theta.$$

The two radii, a scaling factor S and a flat background were allowed to vary during the fit. Although the above choice for the relationship between R_G and θ is arbitrary, the anisotropy of the data is not sufficient to justify a more detailed analysis. It can be seen from the fits to the 50 wt% mixtures (shown in figures 2 to 4) that this function provides an adequate description of the data. The discrepancy in the wings of the scattering is probably due to the fact that the labelled sites are not on the backbone but are on the rings of the mesogenic units. The results of the fits are given in table 2.

The ratio of the scaling factor for the 50 wt% to the 10 wt% mixtures should be given by (0·5 × 0·5)/(0·1 × 0·9) which is 2·78. It can be seen that polymers I and III agree quite

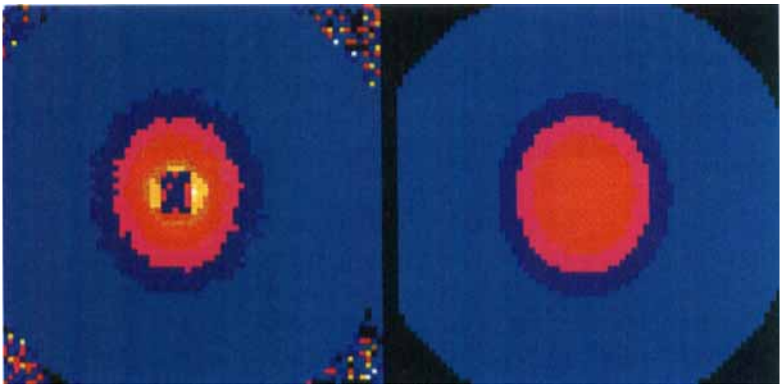


Figure 2. SANS data (left) and fit (right) for hexyloxy polymer.

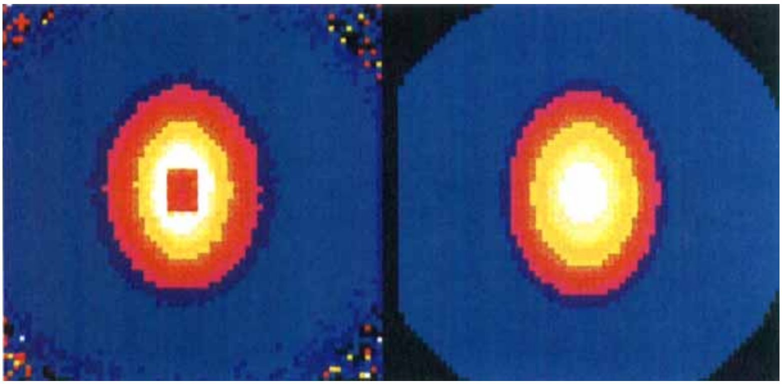


Figure 3. SANS data (left) and fit (right) for cyano polymer.

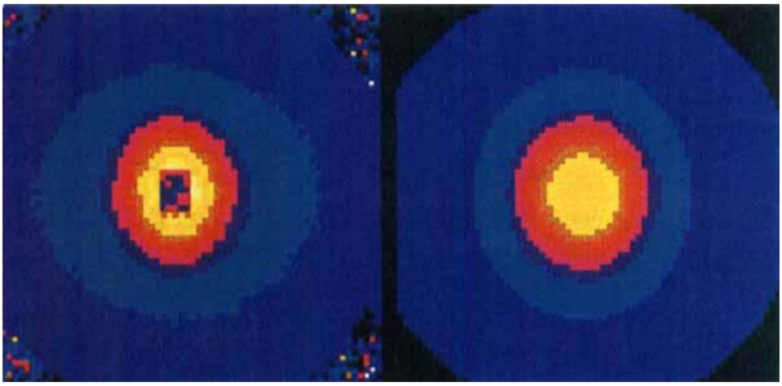


Figure 4. SANS data (left) and fit (right) for methoxy polymer.

Table 2. Results of the 10 wt% and 50 wt% mixtures.

	10 wt% mixture			50 wt% mixture			
Polymer	$S10$	$R_{\perp}$/Å	$R_{\parallel}$/Å	$S50$	$R_{\perp}$/Å	$R_{\parallel}$/Å	$S50:S10$
I	0·5	40	33	1·5	38	32	2·9
II	3·2	47	33	4·5	46	34	1·4
III	1·9	43	37	4·9	42	36	2·6

well with this, but polymer II does not. One explanation for this is that the mixtures of polymer II (the cyano derivative) may not be random because of the possibility that a small amount of cross-linking involving the cyano group occurred during the Pd-catalysed hydrosilylation reaction of the cyano substituted ω-alkene. The results in the table do however confirm that the polymer molecules are more extended in a direction perpendicular to the director. The real local anisotropy is probably much greater than indicated by these results because the samples were not very well-aligned. The reasons for this are discussed further in the next section.

3.2. *Mesogenic unit packing*

For the cyano derivative, only a single first order Bragg reflection was obtained from the smectic layers of all the hydrogenous and deuteriated versions. The appearance of the peak was similar to that in figure 6 (*b*) but even more spread into an arc indicating that the polymeric liquid crystal was not well-aligned. It was not possible to obtain reliable intensities, but it was observed that the sample with both rings deuteriated gave very much stronger diffraction than the other two versions. The integrated intensities from the two ring deuteriated, one ring deuteriated and normal hydrogenous versions were found to be in the approximate ratio 25:2:1. Without higher order reflections, only very limited conclusions can be drawn from these data.

In order to make some useful interpretation of these data, we have assumed that the internal structure of the smectic layer can be described as a series of strata each with a different scattering length density (ρ). The disordered nature of the material means that the scattering length density will vary smoothly across the layer. However the simple picture of strata can help to identify the strongest Fourier components in the variation of ρ across the layer. It is possible to make realistic estimates of the scattering length density of these strata from the values calculated for bulk phases containing predominantly the same chemical groups and isotopic content. For instance, the region around the polysiloxane backbone and flexible spacer would be expected to have ρ close to 0·0 (in units of $10^{15}\,\mathrm{m}^2$), because polydimethylsiloxane has $\rho = -0{\cdot}01 \times 10^{15}\,\mathrm{m}^2$ and hexane has $\rho = -0{\cdot}06 \times 10^{15}\,\mathrm{m}^2$. The core region of the mesogenic units contains two benzene rings and so would be expected to have a scattering length density similar to those of liquid benzene: $0{\cdot}12 \times 10^{15}\,\mathrm{m}^2$ for hydrogenous and $0{\cdot}54 \times 10^{15}\,\mathrm{m}^2$ for deuteriated. The hexyl tail would have ρ about $-0{\cdot}06 \times 10^{15}\,\mathrm{m}^2$, but much higher at about $0{\cdot}62 \times 10^{15}\,\mathrm{m}^2$ when deuteriated.

The intensities from the different isotopically labelled versions of the cyano derivative are qualitatively consistent with a model of overlapping cores between the polysiloxane backbones as shown in figure 5. In the normal hydrogenous version of the polymer the backbone region will have ρ near to 0, and the overlapping cores will have ρ approximately equal to 0·12 in the units used above. There will be a strong Fourier

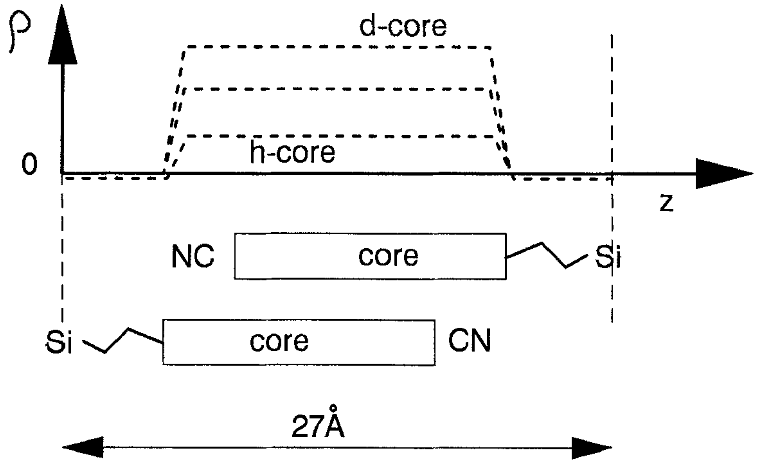


Figure 5. Schematic diagram of overlapping cores model for the cyano polymer with the scattering length density for the three isotropic versions. The backbones extend perpendicular to the page.

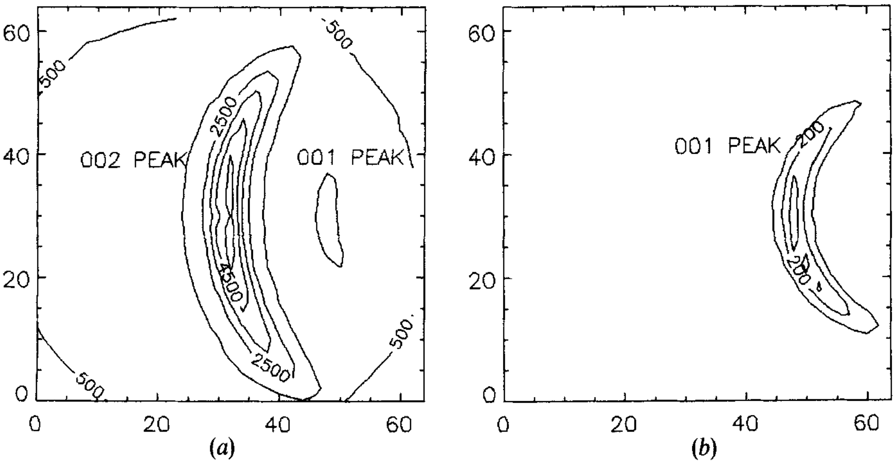
component in the scattering length density variation along the layer normal with the same period as the spacing between the backbones, and so the first order peak will be strong. As deuterium is introduced into the core region, its scattering length density will increase to about 0·62. This increases the amplitude of the Fourier component and hence gives the observed increase in the intensity of the first order peak on progressing along the series: hydrogenous, one ring deuteriated, two rings deuteriated.

The hexyloxy derivative gave both first and second order Bragg reflections from the smectic layers as shown in figure 6 (*a*), but third or higher orders could not be seen. It appeared to be rather better aligned than the cyano derivative and the integrated intensities (shown in table 3 below) were determined by summing peak minus background as before. The integration was done over the detector, but not while scanning the sample angle through the Bragg condition. Since the degree of alignment of the three samples was very similar, the neutron scattering intensities from the samples should be on the same scale at least to an accuracy of 10 per cent. The X-ray equivalent intensities have been included for comparison, but they will be on a different absolute scale. The intensities of the second order peak have been doubled to compensate for the Lorentz factor.

The main feature of these data is that both the two rings deuteriated and hydrogenous compounds have very strong second order peaks. This can be seen by comparing the scattering data shown in figures 6 (*a*) and (*b*). The smectic layer may be modelled as two overlapping mesogenic units from adjacent polysiloxane backbones. For a strong second order peak in the hydrogenous compound, there must be a Fourier component of the scattering length density with a wavelength of half the smectic layer spacing (i.e. $d/2$). This can be achieved with this model if the aromatic cores ($\rho = 0{\cdot}12$) are located near $z = 1/4$ and $z = 3/4$, where z is the fractional distance across the smectic layer from backbone to the other. This would leave a hydrocarbon rich region around $z = 1/2$ with low scattering length density as shown in figure 7. Since the scattering length density is also near zero around the backbones, there would be a strong Fourier component with a wavelength of $d/2$. This scheme explains why deuteriation of the core enhances the second order still further, since the amplitude of the $d/2$ Fourier

Table 3. Intensities from hexyloxy derivative.

Version	First order	Second order
Two rings deuteriated	1·6	82
Hydrogenous	3·8	15
Terminal chain deuteriated	46	<1
X-ray	37	44



(*a*) (*b*)

Figure 6. Neutron Bragg scattering from hexyloxy polymer. (*a*) The version with deuteriated rings in the core of the mesogenic unit and (*b*) the deuteriated hexyl tail version. The axes are in detector pixels.

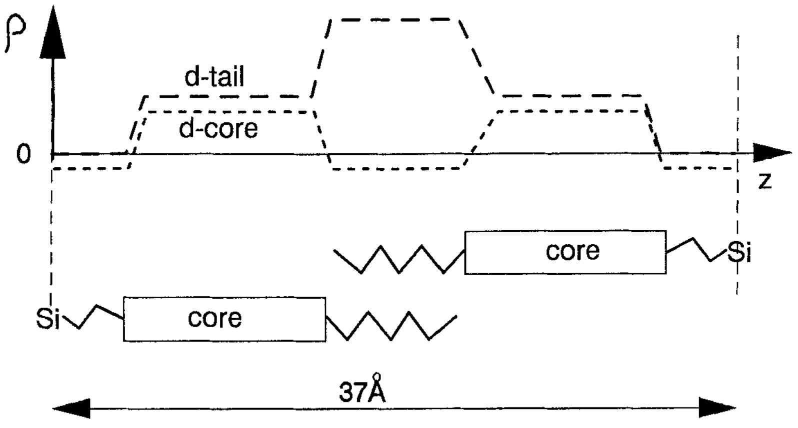


Figure 7. Schematic diagram of hexyloxy polymer mesogenic units in a smectic layer. The units are arranged to give a hydrocarbon rich layer in the middle.

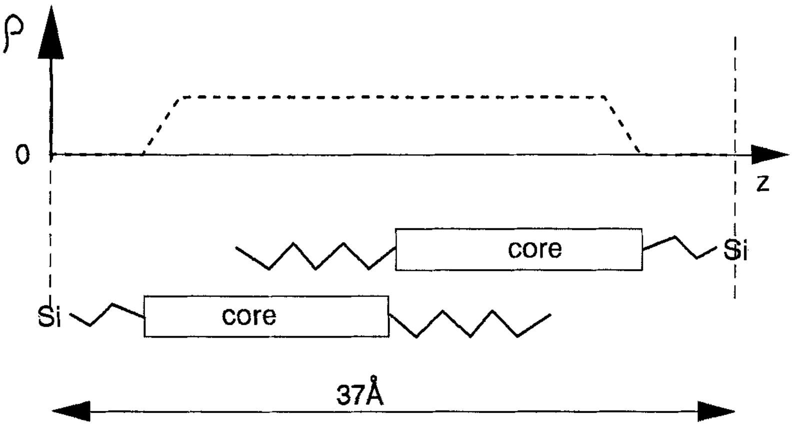


Figure 8. Schematic diagram of hexyloxy polymer with mesogenic units stretched perpendicular to the backbone. Only one maximum occurs in the scattering length density distribution.

component would be increased. It can also explain why deuteriation of the hexyloxy tails reverses the intensities giving a strong first order peak and a second order peak too weak to be observed. With deuteriated tails, the dominant feature of the scattering length density distribution across the layer is a maximum at $z=1/2$, with a monotonic decrease towards $z=0$ or $z=d$. This will give a strong first order peak. This hypothetical model seems to fit the available observations very well. However, to obtain a hexyl tail rich region in the middle of the smectic layer the mesogenic units must tilt with respect to the layer normal. If they were stretched perpendicular to the backbone, the two core regions would overlap and there would be no low ρ region around $z=1/2$ as indicated in figure 7. A tilt of about 30° would be sufficient to provide a chain rich region of roughly 6 Å thickness.

4. Conclusion

This work has shown that the polysiloxane backbone tends to extend in the direction perpendicular to the director in the smectic A or nematic phase of these terminally attached side chain liquid crystal polymers. Similar results [2–7] have been found by other workers for smectic A phases. For the nematic phase, both this result and the opposite have been observed [7].

The information deduced from the neutron Bragg reflections has been limited by the fact that only one or two orders were visible. For simple rigid rod low molecular weight liquid crystals, only a few parameters (an orientational order parameter being the most important) are necessary to define the local packing. Some progress has been made in determining these parameters from neutron Bragg scattering intensities from such simple systems [8]. However more parameters are needed to describe a complex structure such as a side chain liquid crystal polymer and so more observatiosn are needed. In future, better aligned samples should be achieved by using mesogenic units with longer flexible spacers. This will enable higher order peaks to be distinguished above the incoherent background, because the Bragg scattering is concentrated at one point. With more observations it should be possible to determine these structural parameters with a much greater degree of certainty.

However, even the qualitative analysis undertaken here has confirmed the overlapping core packing for the cyano derivative and suggested that for the hydroxy derivative tilted mesogenic units exist with a hydrocarbon rich stratum in the middle of the smectic layer. This would not have been foreseen from a simple comparison of the length of the mesogenic units with the layer spacing.

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