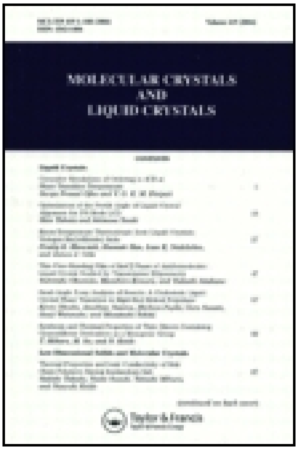

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A Small Angle Neutron Scattering Study of the Effect of Molecular Weight on the Conformation of Side Chain Liquid Crystal Polymers in a Smectic Phase

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A Small Angle Neutron Scattering Study of the Effect of Molecular Weight on the Conformation of Side Chain Liquid Crystal Polymers in a Smectic Phase

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The Small Angle Neutron Scattering (SANS) from specifically deuterated samples of side-chain liquid crystal polymers has been used to determine the dimensions of the backbone both parallel and perpendicular to the director as well as the degree of polymerisation. It has been possible to determine the effect of molecular weight on the chain dimensions in the smectic phase. There is strong anisotropy of the backbone conformation and it becomes stronger as the molecular weight increases. This means that the tendency for the chains to be confined between the smectic layers is stronger for larger molecular weight polymers.

Keywords: Small angle neutron scattering; side-chain liquid crystal polymers; backbone conformation; molecular weight

INTRODUCTION

Side chain liquid crystal (LC) polymers have been extensively studied over the last 20 years because of their potential applications and their fundamental interest[1]. In this paper we investigate the competition between the backbone which would form a random coil in the melt (with no side groups) and the mesogenic side groups which form a smectic phase. Small angle neutron scattering (SANS) from a mixture of the normal and deuterated liquid crystal polymers has been used extensively[2] to measure the conformation of the backbone. In this work we have used the technique to investigate the effect of a chain's length on its anisotropy by measuring SANS from four LC polymers with different molecular weights. It is well established experimentally that the backbone tends to be confined to lie parallel to the smectic layers but that it can "hop" between layers. This has been interpreted theoretically as a thermally activated crossing of a barrier imposed by the ordered mesogenic units. If this barrier were the only contribution to the potential confining the chains the anisotropy would be expected to be independent of the molecular weight [3,4]. The motivation for this study is to measure such anisotropies and determine whether they are independent of molecular weight.

SANS THEORY

For a mixture of normal and deuterium labelled polymer chains it is reasonable to assume random mixing provided the degree of polymerisation and the level of deuteration are not too high. For the materials studied in this work, the neglect of interactions between the normal and deuterated versions is justified because less than 20% of the proton sites in each segment are labelled. For a flexible polymer with negligible interactions, the labelled chains will have a gaussian segment density distribution and the small angle neutron scattering for a monodisperse polymer is given by the Debye formula[5].

$$I(Q) = I(0)\frac{2(\exp(-x) + x - 1)}{x^2} \qquad 1$$

where $x = Q^2 R_G^2$, R_G is the radius of gyration of the chain and Q is the scattering vector. The intensity at zero Q depends upon the number density of polymer molecules, N, the volume fraction of labelled molecules, φ, the degree of polymerisation, z, the number of labelled sites in each segment, s, and the difference, Δb, in the scattering length of hydrogen and deuterium atoms.

$$I(0) = N\,\varphi\,(1-\varphi)\left(z\,s\,\Delta b\right)^2 \qquad 2$$

If the degree of polymerisation of the normal and hydrogenous versions of the polymer are not the same (i.e. $z_H \neq z_D$) then corrections must be introduced to these equations[6]. However in this work the molecular weight of the two fractions were approximately equal and the volume fractions of the two version were equal so were have use a simple mean value (i.e. $z = (z_H + z_D)/2$). Although number density may be determined from the mass density, we found it more convenient to estimate it from the transmission to neutrons, Tr, since the cell thickness, l, is known accurately and the measurement is made in-situ so any air bubbles are compensated.

$$N = \frac{-\ln(Tr)}{l\sigma z} \qquad 3$$

where σ is the total (absorption plus scattering) cross section per segment averaged over the values for the hydrogenous and deuterated segments.

For an anisotropic polymer such as an aligned liquid crystal, the radius of gyration is not sufficient to describe the shape of the chain. If it is assumed that there is a Gaussian distribution of segments at every angle to the director but that the width of the distribution varies with angle, then the Debye formula will apply to the scattering with Q at any angle to the director. There are several reasonable ways to model the angular variation of the chain dimensions but we have chosen the simplest which replaces x in equation 1 by a quantity dependent on the chain dimension parallel and perpendicular to the director.

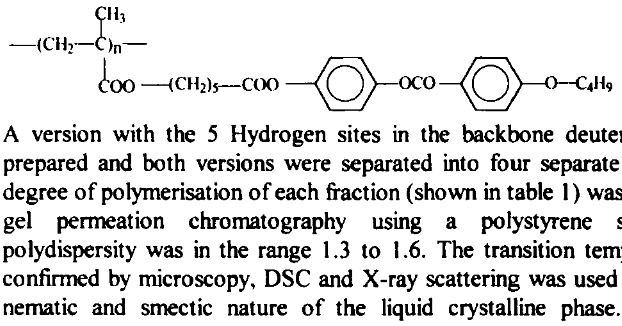
$$x = Q^2 (R_{//}^2 \cos^2 \beta + R_{\perp}^2 \sin^2 \beta) \qquad 4$$

where β is the angle between Q and the director

EXPERIMENTAL

Sample Preparation

The molecular formula of the polymers was the following:



A version with the 5 Hydrogen sites in the backbone deuterated was also prepared and both versions were separated into four separate fractions. The degree of polymerisation of each fraction (shown in table 1) was determined by gel permeation chromatography using a polystyrene standard. The polydispersity was in the range 1.3 to 1.6. The transition temperatures were confirmed by microscopy, DSC and X-ray scattering was used to confirm the nematic and smectic nature of the liquid crystalline phase. The polymer samples showed the nematic, SmA and SmX (preliminary data suggest this phase is $\mathrm{Sm}\tilde{C}$) phases. For SANS, they were then made up into 50:50 mixtures of the normal and D-labelled version of each fraction by evaporation from a common solvent. They were then prepared for the neutron scattering experiment by placing the mixture in a fused silica cell with path length 2mm and aligning by cooling from the isotropic phase in a 9.4T magnetic field. They generally looked optically clear which indicated that the mesogenic units were well aligned. Fraction 1 was not clear which suggested incomplete alignment. A random copolymer of the normal and D-labelled monomers was also prepared for use as a background sample.

Table 1. Phase behaviour and degree of polymerization z (GPC) of fractions of LC polymers.

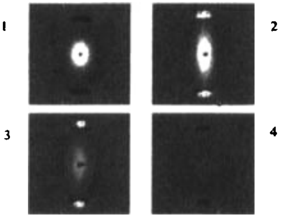
Fraction	Hydrogenous		Deuterated	
	z	Phase transitions / °C	z	Phase transitions / °C
1	526	g 40 SmX 83 SmA 137 N 139 I	538	g 40 SmX 81 SmA138 N 140 I
2	196	g 40 SmX 78 SmA 135 N 137 I	192	g 40 SmX 79 SmA135 N 137 I
3	78	g 40 SmX 77 SmA 133 N 135 I	79	g 40 SmX 78 SmA133 N 135 I
4	28	g 40 SmX 72 SmA 128 N 130 I	28	g 40 SmX 72 SmA126 N 128 I

Small Angle Neutron Scattering

The small angle neutron scattering measurements were carried out on the LOQ diffractometer which is situated at the ISIS[7] pulsed neutron source. It has an area detector that measures the scattering from a the sample over a wavelength band from 2 to 10Å and uses the time-of flight to determine the scattering vector of each detected neutron. The instrument covers a Q range of 0.01 to 0.21$Å^{-1}$. The samples were placed in the instrument with their alignment axis vertical so that scattering both parallel and perpendicular to the director was recorded on the detector. The scattering is corrected for sample transmission and detector efficiency using standard procedures[8]. A background measured from a random copolymer of the normal and D-labelled monomers was subtracted to correct for scattering from inhomogeneities. The intensity is put on an absolute scale by comparison with the scattering from a standard copolymer. The accuracy of the absolute intensity is expected to be about 20% because of inelastic and multiple scattering effects.

RESULTS

Figures 1 shows the corrected SANS from the butyl polymers sample at 25°C that was measured on LOQ. The quality of the alignment can be assessed from the sharp Bragg peaks from the smectic layers. These would be smeared into arcs if the alignment were poor. The strong anisotropy of the small angle scattering reflects the anisotropic shape of the labelled backbone. Since the extent of the scattering is inversely proportional to the dimensions of the chain, it is clear that the backbone is confined to lie between the smectic planes to some extent. We have made a quantitative analysis of these data by fitting an anisotropic form of the anisotropic Debye formula (equations 1 and 4) together with a flat background to the SANS from these polymers. This is a full fit over the whole two-dimensional array but the quality of the fit is easier to judge by inspecting the fit over two perpendicular sections of the data as shown in figure 2. The results are given in table 3 below.



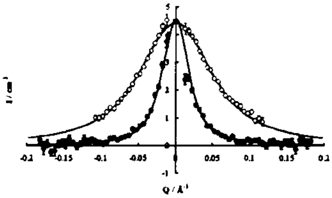


Figure 1 (left) Showing SANS from fractions 1 to 4 of the LC polymer. The alignment field was vertical and a background from a random copolymer has been subtracted so the Bragg peaks appear to be negative in places.

Figure 2 (right) Fits of the anisotropic Debye formula to orthogonal sections of the SANS from fraction 2 of the polymer. Filled circles are for scattering vector parallel to the director and open circles for perpendicular.

(See Color Plate III at the back of this issue)

Table 3

fraction	T / °C	$I(0)$ / cm^{-1}	$R_{\|\|}$ / Å	$R_{\perp}$ / Å
1*	78	10.9 ± 0.4	102 ± 3	76 ± 2
2	37	4.6 ± 0.1	76 ± 1	28 ± 1
2	78	4.4 ± 0.1	77 ± 1	27 ± 1
3	37	1.5 ● 0.0	39 ● 1	17 ± 1
3	78	1.4 ± 0.0	39 ± 1	16 ± 1
4	37	0.5 ± 0.0	19 ± 2	15 ± 2
4	78	0.5 ± 0.0	21 ± 2	13 ± 2

* This high MW sample was not transparent after alignment

DISCUSSION

The Degree of Polymerisation

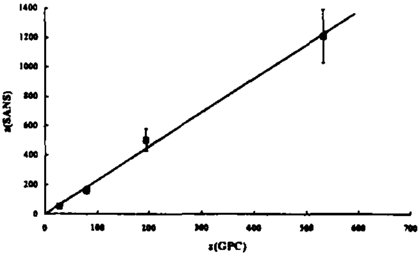


Figure 3 showing a comparison between the degree of polymerisation determined by GPC and SANS. The line shows that they are directly proportional but that the SANS values are on average 2.3 times higher than the GPC.

The degree of polymerisation, z, has been calculated from the values of I(0) by combining equations 1 and 2 to obtain the following equation.

$$z = \frac{I(0).\sigma.l}{(-\ln Tr).s^2.\varphi(1-\varphi).\Delta b^2} \quad 5$$

The results from equations 5 above are compared with the degree of polymerisation determined by GPC (z(gpc)) in figure 3. The value of z(neutrons) is proportional to that of z(gpc) but it seems the GPC technique underestimates the degree of polymerisation. This probably results from the difference between the calibration standard for GPC and the LC polymers.

Anisotropy of backbone conformation

Figure 4 shows the $R_{//}$ and $R_{\perp}$ values as a function of the degree of polymerisation derived from the SANS results. Since very little temperature dependence was found below 70°C the values have been obtained by averaging over temperatures. The results fall on a straight line on this logarithmic plot. It can be seen that the anisotropy becomes more marked as the degree of polymerisation increases. The highest points in the two series are anomalous because the alignment procedure did not work completely giving an optically opaque sample. The lines are the best fits to the data (omitting the highest points) are give by the equations:

$$\ln(R_\perp) = (0.59 \pm 0.06)\ln z + (0.78 \pm 0.04)$$
$$\ln(R_{//}) = (0.30 \pm 0.08)\ln z + (1.5 \pm 0.4)$$

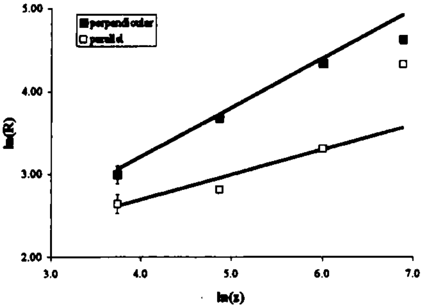


Figure 4 showing log-log plot of the radii vs. the degree of polymerisation. The straight-line fits were only made to the first three points of each set because the highest molecular weight sample did not align completely.

For a simple flexible linear polymer in a melt the exponent is expected to be 0.5. Theories of liquid crystal polymers also suggest that the exponent in both the parallel and perpendicular directions is also expected to be 0.5. These experimental results show that the larger chains are more strongly confined to lie between the smectic layers than the short ones so that the exponent for $R_{//}$ is less than 0.5 and for $R_\perp$ is greater than 0.5. This suggests that the potential that opposes layer hopping by the backbone is not only imposed by the smectic order since this would affect all molecular weights equally. There are two possible explanations:

(i) The end sections of the chains are able to cross layers more easily than the middle sections because they are less tangled with other chains.
(ii) The ends produce gap defects which allow other chains to hop between layers with a lower energy penalty.

We are only aware of one other molecular weight dependant measurements on smectic side chain liquid crystal polymers[9]. In this paper by Noirez et al it was found that $R_{//}$ increased more rapidly with molecular weight than $R_\perp$ and gave an exponent of 0.83±0.03. This is very different to our result. There are several possible reasons for this. For instance they have used the "model free" Zimm approximation at low Q to determine the radii whereas we have modelled our data with an anisotropic Debye formula over a wide Q range. Another difference could arise from the different magnetic field strengths used to align the samples (1.4T in reference 9, 9.4T here). However we have not identified any convincing difference so we believe that the contradiction can only be resolved by further experiments on a range of samples using different Q ranges and alignment fields.

CONCLUSION

We have shown that GPC and SANS methods of determining the degree of polymerisation give proportional results but they differ by a factor of 2.3 for the material studied. The exponents for molecular weight dependence of the chain dimensions in a smectic liquid crystal polymer are 0.3 parallel to the director and 0.6 for perpendicular. This suggests that the larger chains are more strongly confined to lie between the smectic layers than the short ones and suggests that chain ends are important in facilitating the layer hopping process.

Acknowledgements
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References

[1] Shibaev, V.P., Freidzon, Ya.S., and Kostromin S.G., Liquid Crystalline and Mesomorphic polymers (eds. Shibaev, V.P., and Lui Lam), Springer-Verlag, New York, 77–120 (1994)
[2] Cotton, J.P. and Hardouin, F. Prog. in Poly. Sci. **22,** 795–827. (1997)
[3] Renz, W. and Warner, M., Phys. Rev. Lett., **56,** 1268–1271. (1986)
[4] Rieger, J., J.Phys.France **49,** 1615–1625. (1988)
[5] Debye, P. Beuche, A.M., J. Appl. Phys. **20,** 518. (1949)
[6] Cotton, J.P., Decker, D., Benoit, H., Farnoux, J., Higgins, J., Jannink, G., des Cloizeaux, J., Ober, R., & Picot, C., Macromolecules, **7,** 863(1974)
[7] Boland, B. and Whapham, S. (eds.), User Guide to Experimental Facilities at ISIS. Rutherford Appleton Laboratory. (1992). RAL 92–041.
[8] King, S.M. R.K. Heenan. The LOQ Instrument Handbook. (1996). RAL-TR-96–036
[9] Noirez, L., Boeffel C. and Daoud-Aladine, A., Phys. Rev. Lett., **80,** 1453–11456, (1998)