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THE INFLUENCE OF THE BACKBONE ON THE STRUCTURE OF SIDE-CHAIN LIQUID CRYSTAL POLYMERS

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Abstract Structural investigations using X-ray diffraction on four side-chain liquid crystal polymers with the same mesogenic units but different backbones are described. An S_C^* phase was identified in all of them. Three of the polymers exhibit an unusual phase with a superlattice structure below this S_C^* phase. A simple model of the packing in this phase is proposed to explain the formation of the superlattice. The effects of varying the polymer backbone on the stability of this phase are also discussed.

INTRODUCTION

Research into chiral side-chain liquid crystal polymers (SCLCP) remains vigorous since the first reported synthesis of a smectic C* polymer with a chiral centre in its side-chain by Shibaev *et al* in 1984[1]. In the search for new applications a combination of polymeric features with the properties of the liquid crystalline state, especially the ferroelectric S_C^* phase, remains an extremely desirable goal. For low molar mass liquid crystals it has been amply demonstrated how the physical properties of a system may be tailored by subtle variations on the molecular structure of the constituent molecules. Relatively few studies exist however concerning those aspects of molecular structure which favour the occurrence of chiral smectic phases in polymeric systems. Smectic C* phases have already

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been reported in SCLCP's having polyacrylate, poly-α-chloroacrylate, polymethacrylate, polymalonate and polysiloxane backbones[2]. To try and understand further the relationship between molecular structure and its effect on liquid crystalline phase behaviour we have investigated a new series of SCLCP's synthesised by one of us (M.V.). In this paper we report our X-ray structural studies on the effects of varying the backbone of a SCLCP with chirality in the terminal group of the side-chain mesogenic unit. The materials studied are shown in figure 1 below.

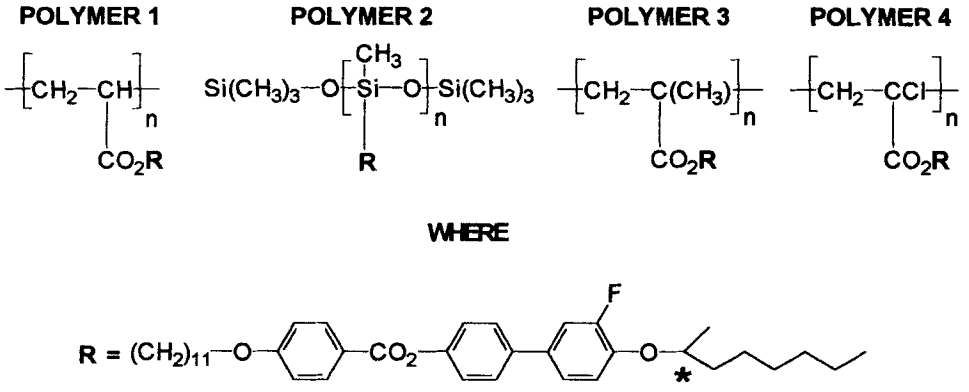

FIGURE 1 Chemical structures of the materials studied.

EXPERIMENTAL

A bulk sample of each polymer (0.75mm thick) was sandwiched between two polyimide sheets glued either side of a brass washer. This was cooled at approximately 1°C/min. from the isotropic phase to room temperature in a 9.4T magnetic field. The oriented sample was mounted in a home-made oven with a temperature stability ±0.2°C. Using collimated, CuKα radiation (λ=1.54Å, nickel filter with graphite monochromator) from a sealed-tube source, diffraction patterns were recorded electronically using a position sensitive two-dimensional ('area') detector[3].

Diffraction patterns were also recorded from shear aligned samples. In a specially built oven, heated to the temperature at which diffraction data were required, oriented drawn fibres were produced by raising a small, cylindrical metal rod whose flattened tip

was initially immersed in a "well" of the polymer. The oven was mounted on the diffractometer such that the vertical axis of the fibre lay perpendicular to the incident X-ray beam direction. Diffraction patterns were then recorded, as described for the magnetically oriented samples. The transition temperatures and possible phase sequences of the materials were determined by M.V. by optical and thermal analysis and are given in table 1 along with their number-average molecular weights ($\overline{M}_n$), polydispersity indices, ($\overline{M}_w/\overline{M}_n$) and degrees of polymerisation (DP).

TABLE I Number-average molecular weights ($\overline{M}_n$), polydispersity indices, ($\overline{M}_w/\overline{M}_n$), degrees of polymerisation (DP) and phase transitions of the polymers.

POLYMER	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	DP	Transition temperatures / °C
1	9,610	1.31	14	S? 53 S_C 130 S_A 147 I
2	9,230	1.39	14	g 12 S? 22 S_C 152 I
3	12,300	1.67	18	g 29 S? 65 S_C 144 I
4	19,500	1.66	28	g 45 S_C 134 S_C 151 I

where g stands for glassy state; I for isotropic liquid and S? for unknown smectic mesophase.

RESULTS AND DISCUSSION

POLYMER 1

Figure 2(i) shows the X-ray diffraction pattern obtained from the magnetically aligned sample at 30°C. Many reflections are seen at smaller scattering angles, positioned along and either side of the meridian (direction of the applied magnetic field). These indicate that the side-chain mesogenic units have arranged themselves in layers perpendicular to the aligning field direction with some in-plane modulation of the layers. These diffraction features index as the (±1,0,±1), (±1,0,±3), (±1,0,±5), (00±2) and (00±4) Bragg reflections

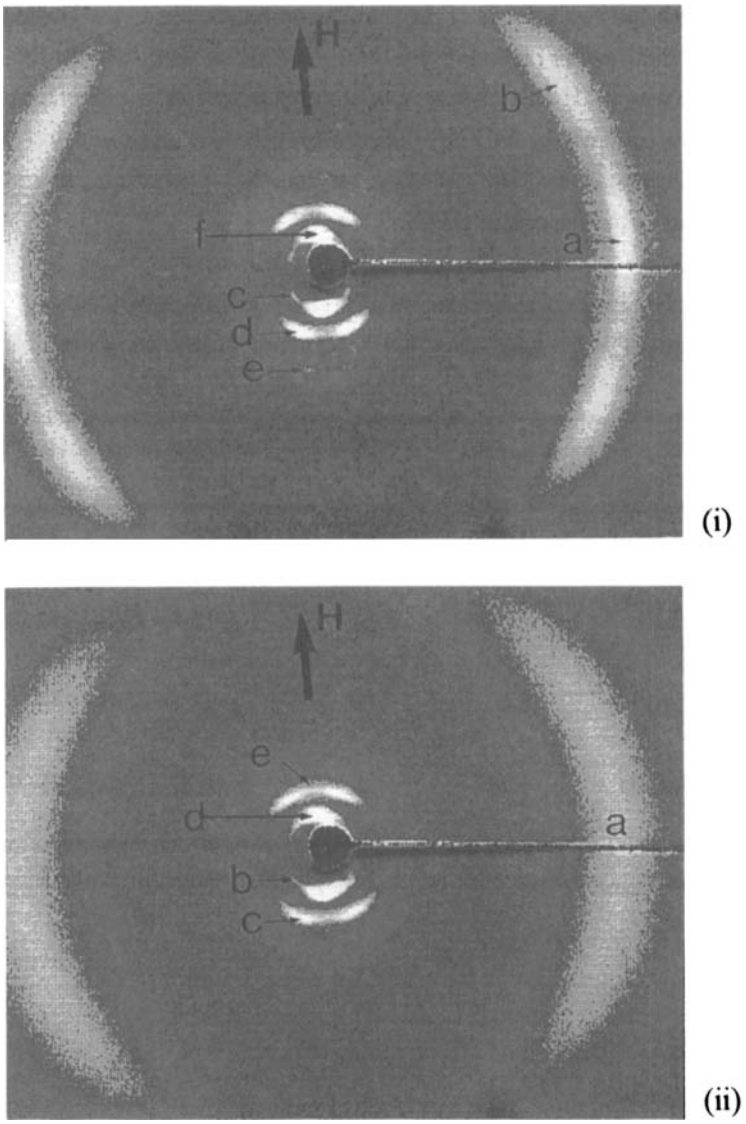

FIGURE 2 X-ray diffraction patterns obtained from a magnetically aligned bulk sample of Polymer 1. (i) at 30°C, (a) (020) reflection, (b) (110) reflection, (c) $(\bar{1}0\bar{1})$ reflection, (d) $(\bar{1}0\bar{3})$ reflection, (e) $(\bar{1}0\bar{5})$ reflection and (f) (002) reflection. (ii) at 60°C, (a) wide-angle diffuse crescent, (b) $(\bar{1}0\bar{1})$ reflection, (c) $(\bar{1}0\bar{3})$ reflection, (d) (002) reflection and (e) (004) reflection. H is the direction along which the magnetic field had been applied (meridian). See Color Plate X.

scattered from a two-dimensional face-centred rectangular lattice. Using the reciprocal lattice vectors, **c*** and **a***, directed along and perpendicular to the meridian respectively, the dimensions of this lattice were measured from the diffraction pattern. At 30°C, c = 71.1Å and a = 54.0Å.

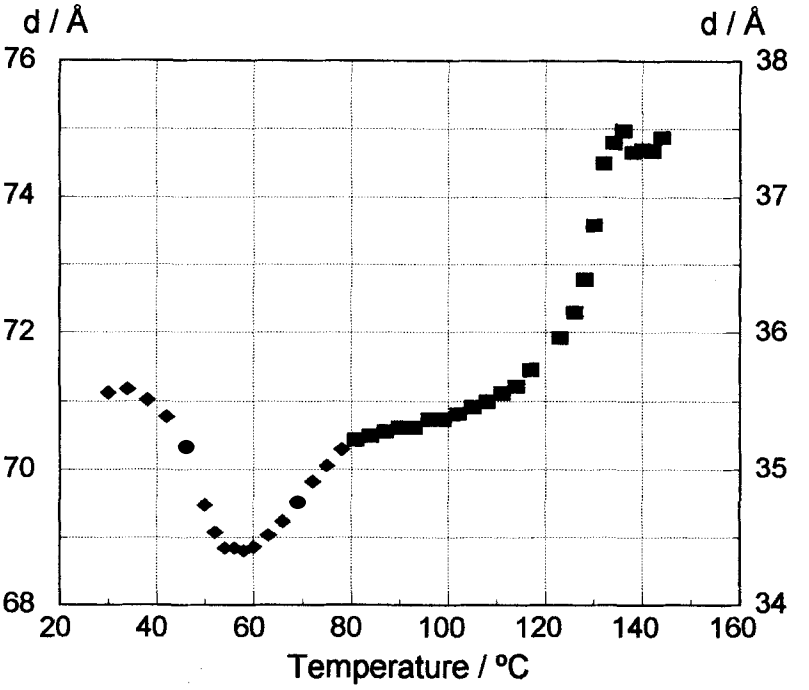

FIGURE 3 Temperature dependence of polymer 1 smectic periodicity, d; ■ correspond to a monolayer structure and the 34-38Å scale, ◆ correspond to a bilayer structure and the 68-76Å scale.

The measured smectic periodicity (see figure 3) decreased with increasing temperature from 71.1Å at 30°C to a minimum of 68.4Å at 54°C. Using CPK models, the fully extended length of a side-chain mesogenic unit plus a backbone segment was estimated at L_{ext} = 44±2Å for all of the polymers investigated. The magnitude of the smectic layer spacing alone therefore indicates that the phase has bilayer character with either tilted side-chain mesogenic units or an interdigitated arrangement of overlapping anti-parallel side-chains giving a smectic A type structure. Six diffraction maxima in the shape of diffuse bars elongated along the meridian were observed at wide angles. Their centres of scattering occur at the (±1,±1,0) and (0,±2,0) nodes of another reciprocal lattice. The

symmetry[4] of this reciprocal lattice demonstrates pseudo-hexagonal packing within the smectic layers of the phase. Each side-chain mesogenic unit is tilted with respect to the layer normal, the unique tilt direction being towards the apex of a two-dimensional hexagonal net. This gives rise to a local, centred monoclinic structure, i.e., there is a smectic I type ordering of the side-chains within this phase. Since the wide angle peaks are diffuse and elongated along the meridian it can be concluded that there is negligible positional correlation of the side-chains between layers. The monoclinic unit cell can be identified with the tilt angle of the side-chain mesogenic units, with respect to the layer normal. This can therefore be determined from the azimuthal angle, ϕ, between the (110) and (020) peaks using the following equation

$$\text{tilt angle}, \theta_t = \sin^{-1}(\pm(\sqrt{3}/2)\sin\phi) \qquad (1).$$

At 30°C, the calculated tilt angle was 26±2°. Using the reciprocal lattice vectors, $\underline{\mathbf{b}}_h^*$ and $\underline{\mathbf{a}}_h^*$ (the subscript h is used solely to differentiate between the two separate 2-dimensional lattices characterising the phase and refers to the lattice with pseudo-hexagonal packing described by the mesogenic units), the dimensions of the unit cell were measured from the diffraction pattern. At 30°C, the unit cell parameters for this pseudo-hexagonal lattice were b_h = 8.8Å and a_h = 5.6Å.

In the absence of the observed (*h*0*l*) reflections the diffraction pattern shown in figure 2(i) would be characteristic of those obtained from oriented liquid crystals with the X-ray beam parallel to the smectic layers and the phase could be assigned as $S_{I_2}^*$. Similar additional small angle reflections have also been observed by Davidson *et al.* in their 'U2' phase[5]. A simple model to explain the formation of a face-centred lattice is that there is a discrepancy in the packing volume required by the backbone and the mesogenic units. The strain is relieved by the layers breaking up into ribbons, as illustrated in figure 4. This can also be visualised as defect walls in the bc plane. The diffraction data obtained from polymer 1 between 30°C and 54°C are consistent with such a structural description, an additional feature being that the side-chains are pseudo-hexagonally packed within each of the layers.

On heating the sample above 54°C, the small angle peaks still index as the (±1,0,±1), (±1,0,±3), (±1,0,±5), (00±2) and (00±4) Bragg reflections from a two-dimensional face centred rectangular lattice (at 60°C, the measured lattice parameters were c = 68.9Å and a = 52.0Å). The six wide-angle diffraction maxima observed at lower temperatures are replaced by two more diffuse wide angle scattering crescents (figure 2(ii), (a)) centred on

the equator. This indicates a transition to a less ordered phase, which has only short range liquid-like order rather than the hexatic order within its smectic layers.

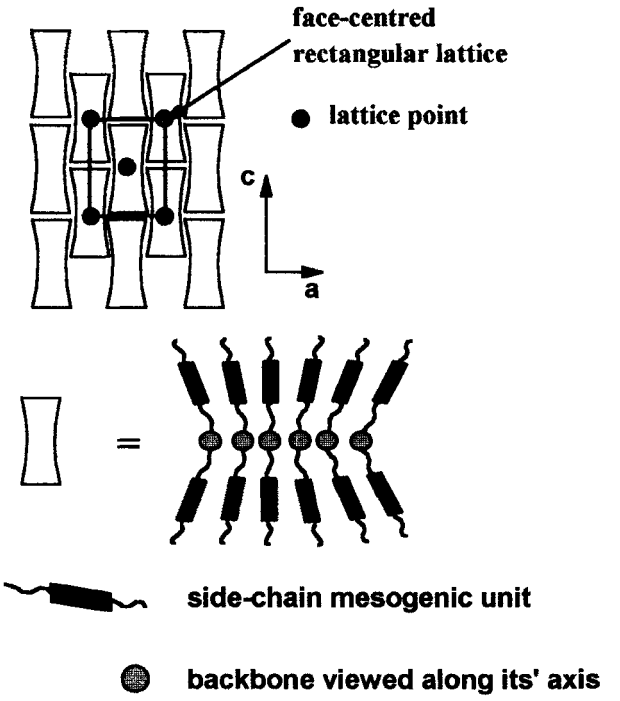

FIGURE 4 Simple model of the structural arrangement of the polymer which would lead to a face-centred lattice as observed with polymer 1.

The measured smectic periodicity increases slightly from 68.8Å at 56°C to 70.3Å at 78°C. Such magnitudes of the layer spacing are consistent with a tilted bilayer structure in which the tilt of the side-chain mesogenic units with respect to the layer normal decreases with increasing temperature i.e., classical smectic C phase behaviour. Again, in the absence of the observed (*h*0*l*) reflections, the diffraction pattern shown in figure 2(ii) would be entirely consistent with those expected from S^{*}_{C2} systems having either an inherent helical superstructure or a uniaxial distribution of unwound domains.

Above 78°C, the (*h*0*l*) reflections disappear. Previously assigned (00±2) and (00±4) diffraction peaks now represent the first and second order (00±1) and (00±2) Bragg peaks (see figure 5(i), (b) and (c) respectively) from the smectic layers in a phase which has only one-dimensional quasi long range order. The two diffuse crescents (see figure 5(i),

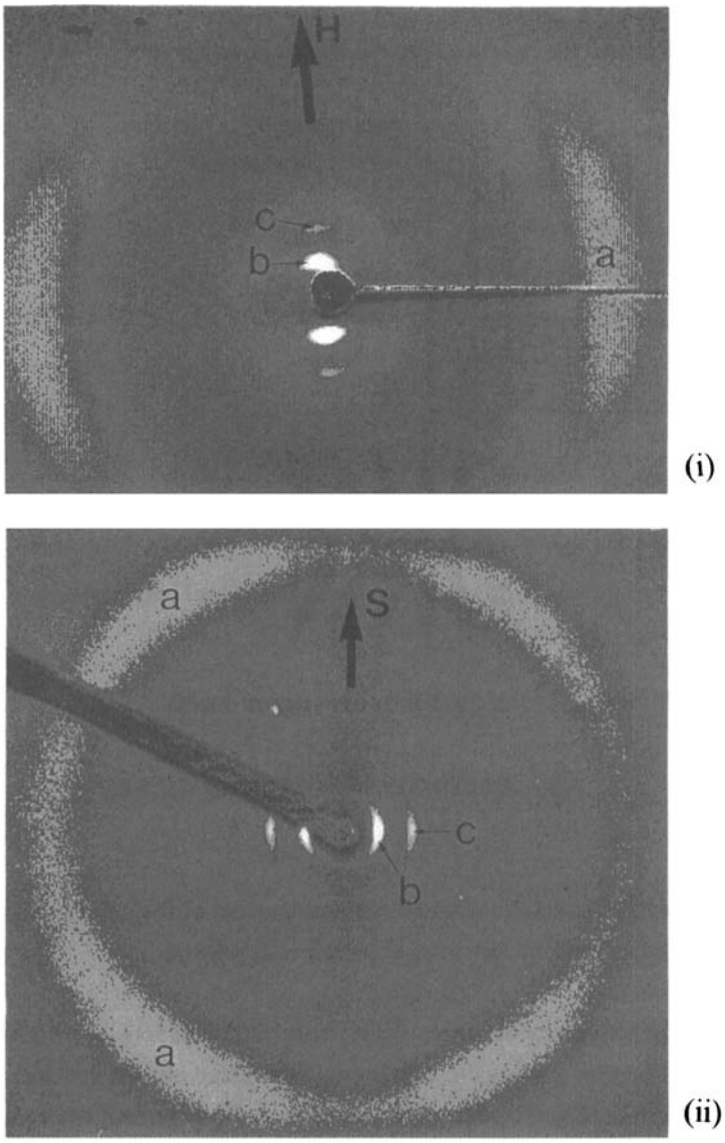

FIGURE 5 (i) X-ray diffraction pattern obtained from a magnetically aligned bulk sample of Polymer 1 at 90°C; (a) wide angle diffuse crescent; (b) (001) reflection; (c) (002) reflection; H is the direction along which the magnetic field had been applied (meridian). (ii) X-ray diffraction pattern obtained from a stretched oriented fibre of polymer 2 at 75°C, (a) intensity maxima in wide-angle diffuse ring, (b) (001) reflection and (c) (002) reflection. S is the stretching direction (meridian). See Color Plate XI.

(a)), centred on the equator, at wide angles still show that there is only liquid-like ordering within the layers. An initial steady increase of the measured smectic periodicity with increasing temperature is followed by a considerably more rapid increase after approximately 126°C reaching a maximum of 37.5Å, at 134°C. The diffraction patterns obtained and the magnitude of the measured smectic periodicity are certainly consistent with a tilted monolayer structure between 78°C and approximately 134°C, an $S^*_{C_1}$ phase is therefore suggested.

Results from optical microscopy and DSC studies infer the onset of a S_A phase at approximately 130°C. The measured layer spacing remains essentially constant at approximately 37.4Å above 134°C until the clearing temperature at 146°C. This is generally characteristic of a S_A rather than S_C phase. Such a rapid increase in the smectic periodicity, at approximately 126°C, suggests that a first order $S^*_{C_1}$ to S_{A_1} phase transition takes place.

The measured layer spacing above 126°C is considerably shorter than that estimated assuming a fully extended side-chain length. This is often found to be the case in the S_A phase of low molar mass liquid crystals consisting of a rigid central core and one or two terminal aliphatic chains. It can be accounted for by liquid-like (i.e., deviating from an all-*trans* conformation) alkyl chains and/or randomly tilted central cores, which can lead to values of the effective molecular length, determined from X-ray data, as low as 80% of that estimated assuming a fully extended conformation. Random, uncorrelated tilting of the side-chains and/or spacer/terminal alkyl chain deformation would lead to an overall orthogonal alignment of the mesogenic units with respect to the smectic layer normal and could therefore account for the magnitude of the smectic periodicity observed. The diffraction data are therefore consistent with assigning the phase between 126°C and 146°C as S_{A_1}.

POLYMER 2

Attempts to align this sample by cooling in a magnetic field as previously described proved unsuccessful. Diffraction patterns obtained from a powder sample throughout the entire temperature range 30-150°C were similar and characteristic of a smectic phase with disordered layers. A diffuse outer ring in the where Q ($=4\pi\sin\theta/\lambda$) range 1.3-1.4Å^{-1} indicates a lack of any long range lateral order between the mesogenic groups. A well-defined inner ring, corresponding to a repeat spacing of 35.3-32.5Å (see figure 6), is interpreted as a first order reflection from the smectic layers. A second order ring is also seen. The magnitude of the observed smectic layer spacing is less than L_{ext} which implies

that the phase has monolayer character with tilted side-chain mesogenic units, i.e., $S^*_{C_1}$. Support for this interpretation is obtained on examination of the diffraction pattern from a stretched oriented fibre of the polymer (see figure 5,(ii)).

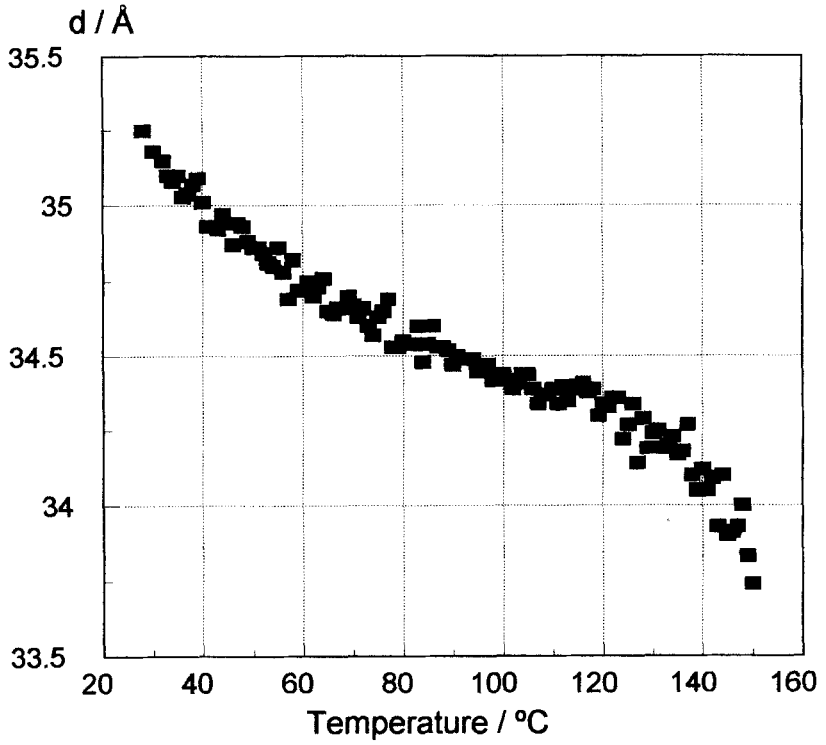

FIGURE 6 Temperature dependence of Polymer 2 smectic periodicity, d.

Four small angle Bragg peaks, corresponding to the first two orders of reflection from the smectic layers are located on the equator, which indicates that the smectic layers and consequently the polymer backbones are parallel to the fibre axis. At large scattering angles the diffuse ring confirms the liquid-like order between the side-chains. The ring is modulated in intensity and shows four scattering maxima (see figure 7). These are split either side of the meridian thereby confirming that the phase has side-chain mesogenic units which are tilted with respect to the layer planes. The diffraction data are therefore consistent with assigning the phase between 30°C and 150°C as $S^*_{C_1}$. Clearly, the introduction of a polysiloxane backbone has had a remarkable effect when these results are compared to those from the acrylate polymer 1. The modulation of the smectic layers has been removed and there is no evidence for a higher ordered smectic phase over the same

temperature range. These changes are presumably a consequence of the introduction of a more flexible backbone.

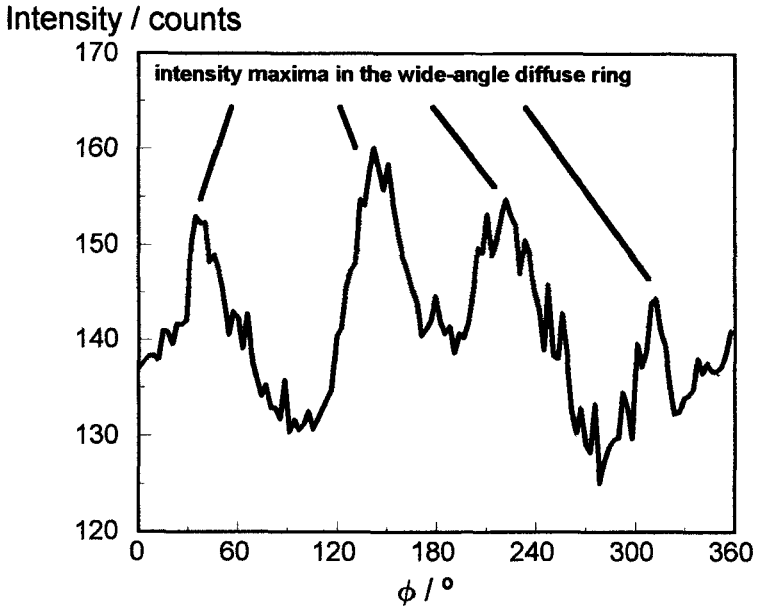

FIGURE 7 Plot of intensity versus azimuthal angle, ϕ, at $|Q| \approx 1.4 Å^{-1}$ for Polymer 2 at 75°C obtained from a stretched oriented fibre.

POLYMER 3

Figure 8(i) shows the X-ray diffraction pattern obtained from the magnetically aligned methacrylate polymer at 30°C. Two diffuse scattering crescents characteristic of liquid-like order are observed at wide angles. These are centred on the equator indicating that the long axes of the side-chains have oriented on average parallel to the direction of the magnetic field. Many reflections are observed at smaller scattering angles. As with polymer 1 these features can also be indexed as the (±1,0,±1), (±1,0,±3), (±1,0,±5), (00±2) and (00±4) peaks scattered from a two-dimensional face-centred rectangular lattice which characterises the modulation of the smectic layers. The (00±2) and (00±4) peaks are split either side of the meridian. Such an effect is seen when the various normals to the smectic layers are tilted and rotated about the field direction so as to give cylindrical symmetry around the director. This effect makes a direct determination of the unit cell parameters from the diffraction pattern difficult.

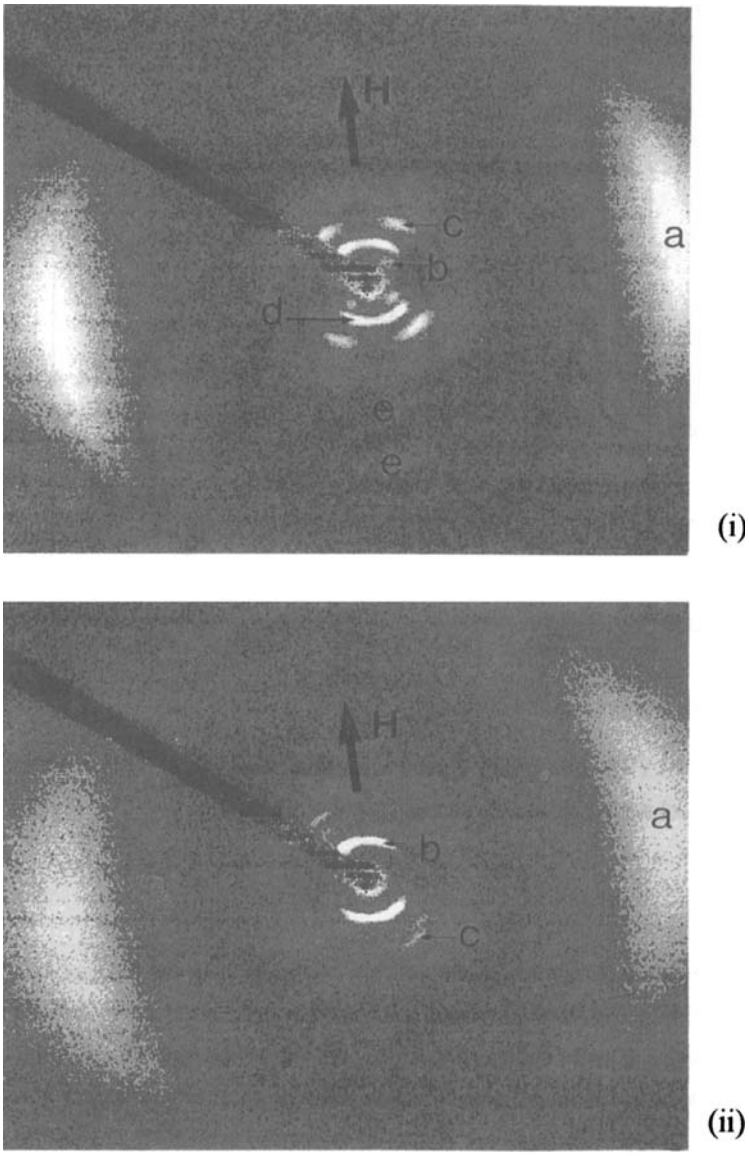

FIGURE 8 X-ray diffraction pattern obtained from a magnetically aligned bulk sample of Polymer 3 (i) at 30°C, (a) diffuse wide-angle crescent, (b) (101) reflection, (c) (103) reflection, (d) split (00$\bar{2}$) reflection, (e) diffuse streaks; (ii) at 70°C , (a) wide angle diffuse crescent; (b) split (001) reflection; (c) split (00$\bar{2}$) reflection; H is the direction along which the magnetic field had been applied (meridian). See Color Plate XII.

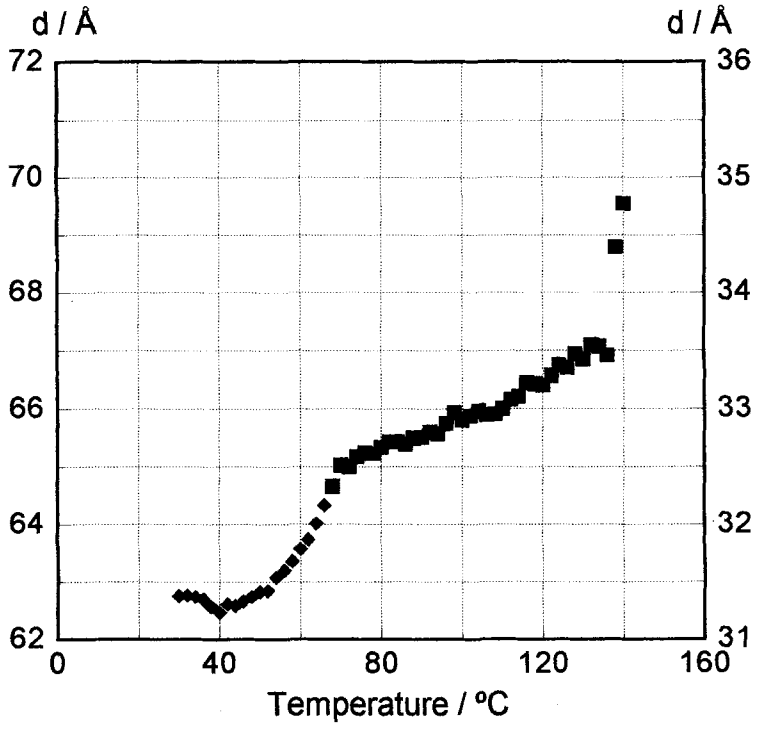

FIGURE 9 Temperature dependence of polymer 3 smectic periodicity, d; ■ correspond to a monolayer structure and the 31-36Å scale; ◆ correspond to a bilayer structure and the 62-72Å scale.

The relative positions of the small and wide-angle diffraction features therefore show that the magnetic field has aligned the side-chain mesogenic units within disordered smectic layers. The layers themselves being tilted with respect to the aligning field direction.

At 30°C the smectic periodicity was measured at 62.8Å (see figure 9) which is less than $2L_{ext}$, and confirms the tilt of the side-chains as predicted by the relative positions of the observed diffraction features. A set of parallel diffuse lines, at equal intervals of Q, are also observed in the diffraction pattern from polymer 3 at 30°C. These are characteristic of disorder along the director[6,7]. Such scattered intensity arises from uncorrelated periodic columns and is often seen in those smectic phases having 3-dimensional order e.g., S_B. The diffuse lines are not curved implying that all the colums are oriented in the same direction. The observation of these weak features in the diffraction from polymer 3 but not polymers 1 and 2 is probably a consequence of the fact that the mesogenic side-chains (rather than the layer normals) have aligned in this material. There may be more opportunity for end to end correlation of the mesogenic units to exist

and less possibility of the resulting layer lines to be smeared out and then not observed. On heating polymer 3 the measured smectic periodicity remains fairly constant up to 40°C, and then increases steadily to a maximum of 64.7Å at 68°C. This implies that the tilt angle of the side-chains with respect to the layer normal has decreased slightly. The diffraction patterns obtained between 30°C and 68°C were all qualitatively similar suggesting that they originate from the same phase and that this phase shares the same structural characteristics as the polyacrylate polymer 1 between 54°C and 78°C. Methyl substitution along the backbone would therefore seem to destabilise the periodic modulation of the smectic layers.

Figure 8(ii) shows the diffraction pattern recorded at 70°C. The (*h*0*l*) reflections have disappeared and the previously assigned (00±2) and (00±4) diffraction peaks now represent the first and second order (00±1) and (00±2) (see figure 8(ii), (b) and (c) respectively) reflections from the smectic layers. The wide-angle crescents remain diffuse indicating that the liquid-like order still prevails within the smectic layers. A measured layer spacing of 32.5Å and the splitting of the small angle peaks either side of the meridian shows that the phase has monolayer character and is tilted. This suggests that a transition to an S^*_{C1} phase has taken place. The splitting of the (00*l*) reflections as seen on the diffraction patterns was found to decrease on heating with a concomitant increase in the measured smectic periodicity to 34.8Å at 140°C. This suggests that the tilt angle of the side-chain mesogenic units is decreasing with increasing temperature causing an expansion of the smectic layers and that the phase remains S^*_{C1} until the polymer forms an isotropic liquid at 141°C.

POLYMER 4

The diffraction pattern recorded from the magnetically aligned poly-α-chloroacrylate at 30°C is shown in figure 10. It has the same small-angle scattering features as found with both polymer 1 and polymer 3 which again points towards the formation of ribbons as in figure 4. Two scattering arcs are observed at wide angles. These are centred on the equator indicating that the long axes of the side-chains have oriented on average parallel to the direction of the magnetic field. The radial extension of the arcs is small compared to the normal disordered S_A and S_C phases implying a more ordered structural arrangement of the side-chains within the smectic layers. Esselin[8,9] *et al* have reported similar observations in a poly-α-chloroacrylate liquid crystal polymer where the ordering of the side-chains is attributed to the presence of the chlorine atoms along the polymer backbone. The (00*l*) relections are split either side of the meridian. The relative positions of the small

and wide-angle diffraction features therefore show that the magnetic field has aligned the side-chain mesogenic units within ordered smectic layers, the layers being tilted with respect to the aligning field direction. A set of parallel diffuse lines as seen for polymer 3, again at equal Q intervals, are also observed in the diffraction pattern. These probably result from end to end correlation units as described for polymer 3.

At 30°C the smectic periodicity was measured at 65.4Å (see figure 11) which is less than $2L_{ext}$ showing that the phase has bilayer character and confirming the tilt of the side-chains as predicted by the relative positions of the observed diffraction features. As shown by figure 10, heating the polymer causes an initial slight decrease in the measured smectic periodicity to 64.1Å at 80°C. It then remains fairly constant until approximately 100°C after which a rapid regular increase to 68.8Å at 134°C occurs. This is unusual and is not readily explained by observation of the diffraction patterns obtained in the same temperature range. Measurement of the angular width of the wide-angle scattering arcs shows that the phase becomes less ordered as the polymer is heated over the same temperature range. Further investigations are in progress.

When the polymer was heated above 134°C the diffraction pattern obtained was completely analogous to that shown in figure 8(ii) obtained from the methacrylate polymer. The (*h*0*l*) reflections were seen to disappear and the previously assigned (00±2) and (00±4) diffraction peaks become the first and second order (00±1) and (00±2) reflections from the smectic layers. The wide-angle crescents are diffuse indicating that the liquid-like order within the smectic layers. A measured layer spacing of 34.6Å and the splitting of the small angle peaks either side of the meridian shows that the phase has both monolayer character and is tilted. As with polymer 3, this suggests that a transition to an S^*_{C1} phase has taken place. The splitting of the (00*l*) reflections as seen on the diffraction patterns was found to decrease on heating with a concomitant increase in the measured smectic periodicity to 35.3Å at 150°C suggesting that the tilt angle of the side-chain mesogenic units decreases with increasing temperature and that the S^*_{C1} phase remains until the polymer forms an isotropic liquid at 151°C.

Clearly, substitution hydrogen atoms with chlorine along the backbone has had a remarkable effect on phase behaviour when polymer 4 is compared to polymer 1. The periodic modulation of the smectic layers is stabilised to a much higher temperature (134°C compared with 78°C). Both methyl groups and chlorine atoms tend to restrain the polymer backbone leading to an increased rigidity of the smectic layers. However the presence of the methyl groups in polymer 3 were seen to cause a decrease in the temperature at which the S^*_{C1} to modulated phase transition took place. It therefore seems likely that a contribution to the modulated phase stabilisation in polymer 4 must be a

consequence of some type of dipolar ordering between the backbones in the smectic layers due to the relatively high polarity of the chlorine atoms. A possible mechanism is that attraction between neighbouring backbones is enhanced so the "ribbons" (as depicted in figure 4) are stable to a higher temperature.

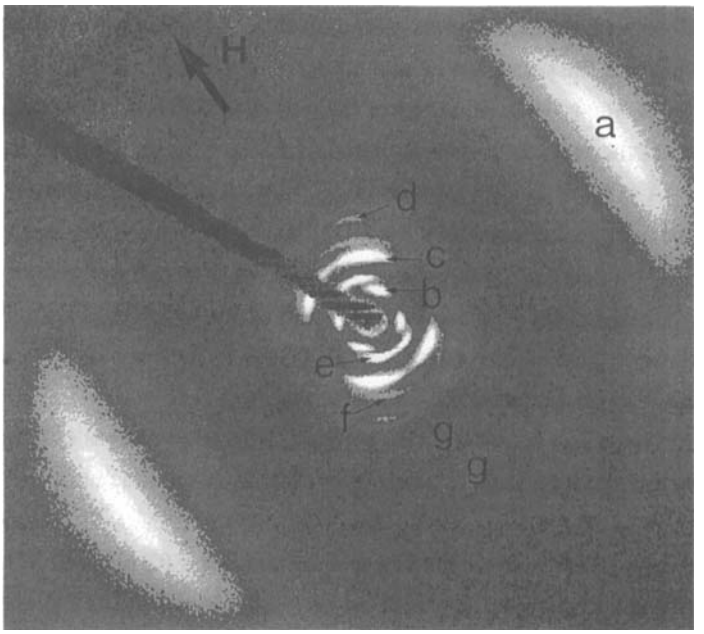

FIGURE 10 X-ray diffraction pattern obtained from a magnetically aligned bulk sample of Polymer 4 at 30°C, (a) wide angle sharp arc centred on the equator, (b) (101) reflection, (c) (103) reflection, (d) (105) reflection, (e) split $(00\bar{2})$ reflection, (f) split $(00\bar{4})$ reflection and (g) diffuse streaks; H is the direction along which the magnetic field had been applied (meridian). See Color Plate XIII.

CONCLUSION

From these observations we can conclude that the layer spacings for the acrylate, methacrylate and chloroacrylate polymers are consistent with a transition from a higher temperature $S^*_{C_1}$ phase to a lower temperature phase which has bilayer character and a modulation of smectic layers into ribbons based upon a two-dimensional face-centred rectangular superlattice. The layer spacings measured for the polysiloxane in comparison

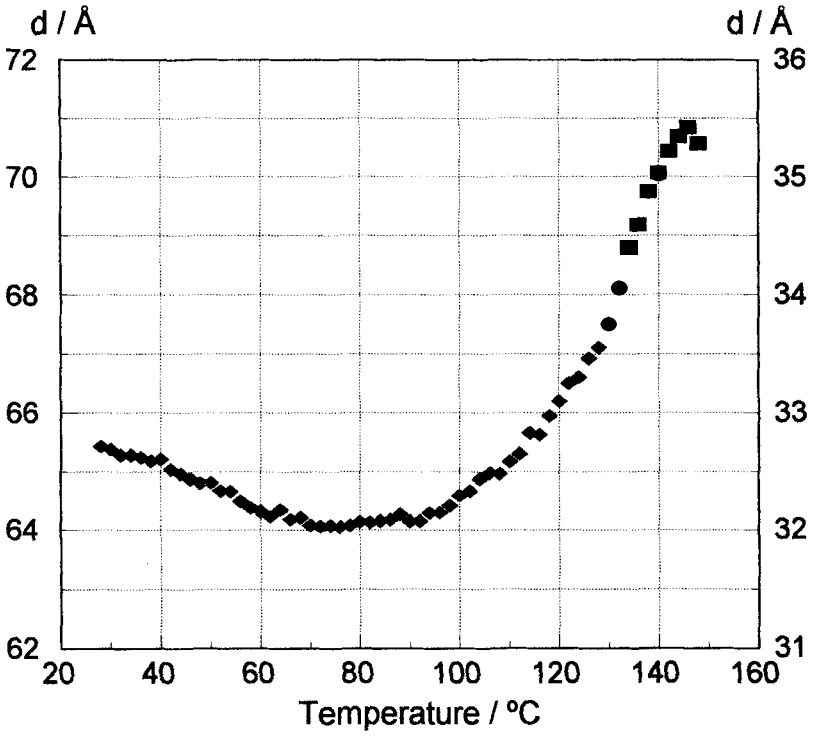

FIGURE 11 Temperature dependence of LCP127 smectic periodicity, d; ■ correspond to a monolayer structure and the 31-36Å scale; ◆ correspond to a bilayer structure and the 62-72Å scale.

are consistent with a broad monolayer S_C^* phase which forms directly from the isotropic phase and remains down to room temperature. The enhanced flexibility of the siloxane backbone compared to the polyacrylates therefore seems to allow the liquid-crystalline, as opposed to polymeric, properties of the system to dominate. Given an identical side-chain mesogenic unit, substitution of hydrogen atoms with methyl groups along the backbone in the acrylate series has been shown to destabilise the formation of the "ribbon" phase. One possible reason for this is that the increased volume of the backbone tends to destabilise the ribbons by reducing the discrepancy between the volume requirement of the backbone and mesogenic units. However, when chlorine atoms were substituted for hydrogens such a modulation appears to be favoured, possibly because the stronger polar interaction between adjacent backbones stabilises the ribbons illustrated in figure 4. The large effect of the chloro-substituent can be anticipated from other polymer properties. For instance, the T_g of poly(vinyl chloride) is some 166°C higher than poly(ethylene) whereas

poly(propylene) has a T_g that is only 65°C higher.

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