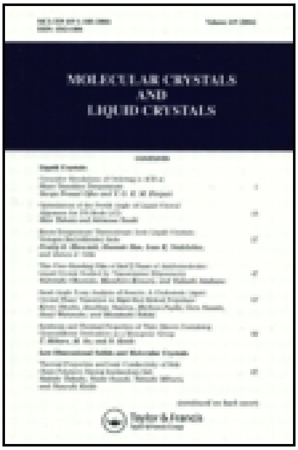

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X-ray Diffraction from Side Chain Liquid Crystal Polymerst

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X-ray Diffraction from Side Chain Liquid Crystal Polymers†

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X-ray diffraction results are reported on a number of side chain liquid crystal polymers with polymethylsiloxane and polyacrylate backbones. Identifications of the phase types have been made and models for the local packing of the mesogenic units proposed. Most of the smectic polymers with terminally cyano-substituted side chains show the partially overlapping structure common in their low molecular weight analogues, but for polymer liquid crystals this structure is not confined to cyano-compounds. The temperature dependence of the intensity of the smectic layer reflection and the layer spacing is discussed.

1. INTRODUCTION

We report here an exploratory X-ray diffraction study of a number of side chain liquid crystal polymers prepared at the University of Hull by P. A. Gemmell, G. W. Gray, and D. Lacey. Several of the materials are polysiloxanes[1] with terminally cyano-substituted side chains.[2] The molecular structures of all materials are shown in Table I together with the phase identifications made at Hull‡ by microscopy and differential scanning calorimetry. The first object of this work was to confirm these identifications. The second object was to investigate the local packing of the mesogenic units and the polymer backbones by comparing the X-ray diffraction results with distances obtained from molecular models.

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†Presented at the Tenth International Liquid Crystal Conference, York, July 15-21, 1984.

‡Except in the case of polymer P5, which we now believe to be smectic.

TABLE I

Molecular structures and transition temperatures between the glass (G), smectic (S), nematic (N) and isotropic (I) phases of the materials studied. X and Y are unclassified phases. Where indicated the degree of polymerisation is only approximate and the samples are believed to be polydisperse.

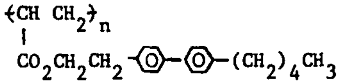
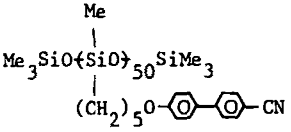
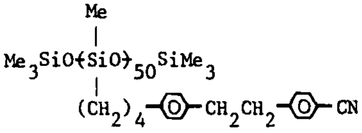
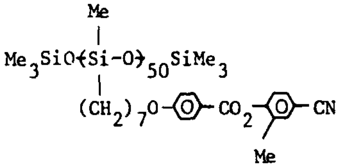
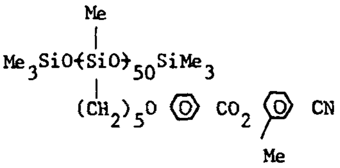
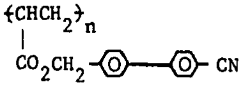
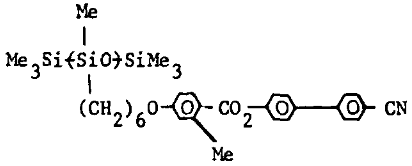
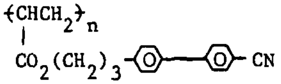
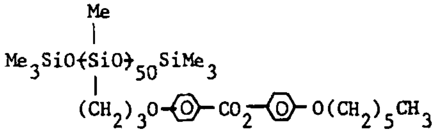
Code	Molecular Formula	Transition temperature/°C (heating)
P1		G 65 S 192 I
P2		G 14.6 S 169.5 I
P3		G -4 X 33 Y 73 I
P4		G 9 S 89 I
P5		G 19 S 65
P6		G 105 N 136 I

TABLE I (*continued*)

Code	Molecular Formula	Transition temperature/°C (heating)
P7		G 31 S_2 289 S_2 315 I
P8		G 68 N 94 I
P9		G 15 S 112 I

2. EXPERIMENTAL

The X-ray diffraction experiments were carried out using graphite monochromated copper *K*α radiation (40 kV, 16 mA). Exposure times of 20 to 30 h were required using a flat photographic plate at 10 cm from the sample. For speed, the temperature variation of the scattered intensities was followed using a linear position sensitive detector. The temperature of the sample was kept constant to ± 1°C with an accuracy of ±2°C. A mylar window to the oven gives a weak additional reflection on some of the diffraction patterns at about 15° scattering angle (corresponding to d = 5.8Å).

Some attempt was made to align the samples (about 1 mm^3 in a Lindemann glass capillary) by cooling them from the isotropic phase in a magnetic field of 1.5 T over a period of a few hours. Although generally successful for low molecular weight liquid crystals, this procedure had no effect on the liquid crystal polymers. It was found that polymer P4 could be aligned by gently warming a lump of it and pulling a thin string (1 mm diameter) with tweezers. Polymer P3, however, was not susceptible to this treatment.

3. RESULTS

X-ray diffraction photographs of some polymer liquid crystals are shown in Figure 1. Polymers P6 and P8 gave diffraction patterns consisting of two diffuse rings (e.g., Figure 1a) which suggests that they are nematic although, since we were unable to align these samples, the X-ray data alone could not distinguish them from isotropic phases. The outer ring corresponded to a *d* spacing of 5.4 Å which is a typical lateral spacing for two mesogenic molecules.

The remaining materials all showed a sharp inner ring giving *d* spacings in the range 29 Å to 49 Å which we have interpreted as a smectic layer spacing, e.g. Figure 1b and 1c. (Unfortunately only the lower smectic phase of P7 was at an accessible temperature.) Second and third order rings were also visible in some materials. They all showed a diffuse outer ring of scattering corresponding to a spacing in the range $4\frac{1}{2}$ to $5\frac{1}{2}$ Å, so all these materials must be either of the smectic A or smectic C types with unstructured layers (including P5 which was originally thought to be nematic). The stretched sample

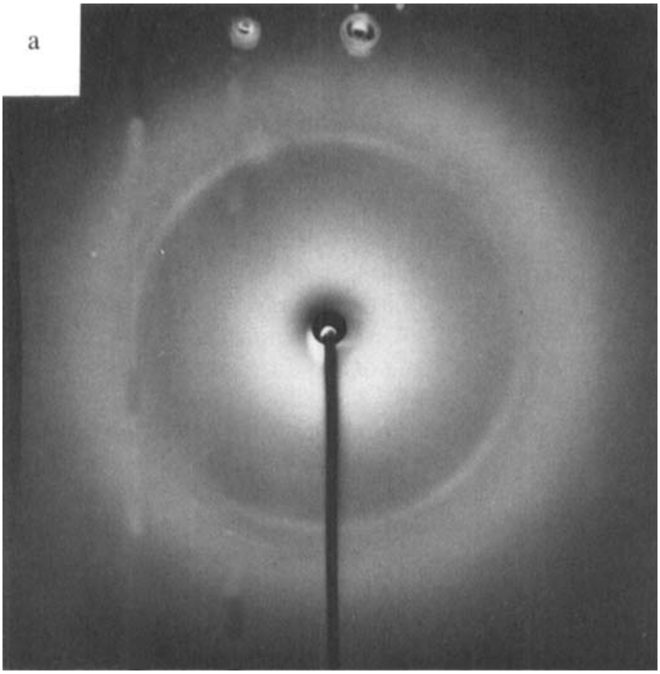
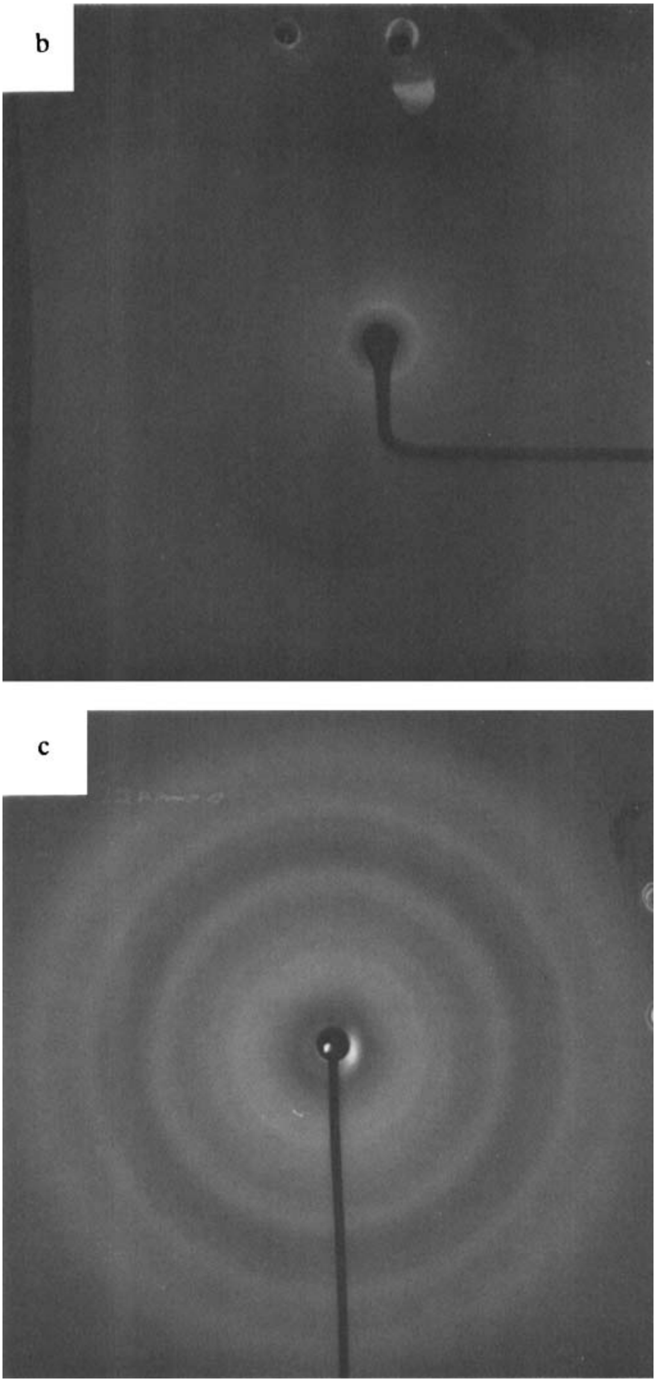
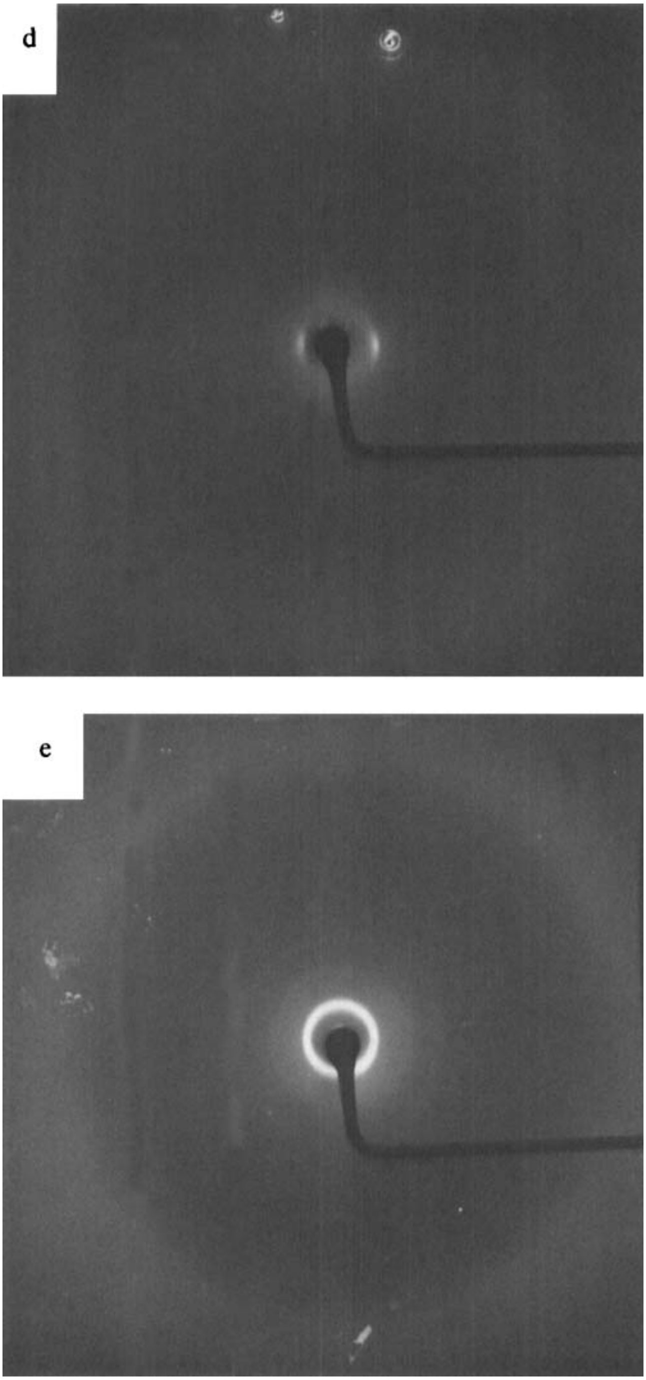


FIGURE 1 X-ray diffraction photographs from (*a*) nematic P6, (*b*) smectic P4 unaligned, (*c*) smectic P3, (*d*) aligned smectic P4, (*e*) smectic P1.


b
c


d
e

of polymer P4 indicated that the 33 Å spacing corresponded to planes parallel to the stretching axis and the 4.1 Å spacing to interference between mesogenic units within one plane. The polymers P2, P3, and P5 showed some extra rings, some of which were quite sharp and well defined. The spacings corresponding to all the reflections are tabulated in Table II and their interpretation is discussed in the next section. There was no noticeable change in the diffraction patterns below the glass transition.

The differential scanning calorimeter (DSC) traces (Figure 2) of P3 show that the isotropic phase supercools by about 20°C and then transforms to a phase X at 45°C. On a heating cycle it undergoes a strong, exothermic transition at 26°C to a phase Y. We were unable to detect any differences in the diffraction patterns at 25°C, 50°C, or at 25°C after cooling from the isotropic phase. The exposures took 24 h each, so we believe that the phase X is probably a metastable phase that first forms on cooling from the isotropic phase, but then converts to the stable phase Y over a period of a few hours.

4. DISCUSSION

4.1 Layer spacings in the smectic phases

If the smectic planes consist of syndiotactic polymer chains lying parallel with the mesogenic groups extended in a direction perpendicular to the planes, we would expect the layer thickness to be twice the length of the mesogenic unit, plus ~5 Å for the backbone. This distance has been estimated using molecular models (e.g., Figure 3) for all the materials studied and is given in Table III together with the observed layer spacing. In every case (except P1 and P3) the observed layer spacing is considerably less than the extended model length, so we are forced to invoke either some form of interdigitation of the mesogenic units such as is now established for many cyanobiphenyls[3] or that the long axes of the mesogenic units are tilted with respect to the layer normal. The tilts or overlaps that are necessary are shown in Table III. To distinguish between these two possibilities, we divide the smectic phase into three categories and consider the arrangements that would allow the polarizable parts (e.g., cyanobiphenyl units) to lie together in planes to maximise dispersion forces, while maintaining efficient filling of space by the less polarizable parts (e.g., alkyl chains).

i) P1 has an observed layer spacing only 10% shorter that the model length. This can be easily accounted for by some disorder in the alkyl

TABLE II

Showing *d* spacing in Å for the observed reflections. The measurements quoted were made in the middle of mesophase range.

Polymer	Layer Reflections			Extra Reflections			Intra-Layer Reflections	
P1	37	18.5	12.3					4.5
P2	29	14.5		10.2 (diffuse)	7.2 (diffuse)			4.3
P3	49 ±2			13.2 (sharp)	10.5 (sharp)	7.2 (diffuse)	5.2	4.4
P4	33							4.1
P5	29	14.3		9.0 (sharp)	7.7 (sharp)	6.2 (sharp)		4.4
P6	16.5 (v.diffuse because nematic)							5.4
P7	33	16						4.5
P8	~20 (v.diffuse because nematic)							4 to 5
P9	38	19						4 to 5

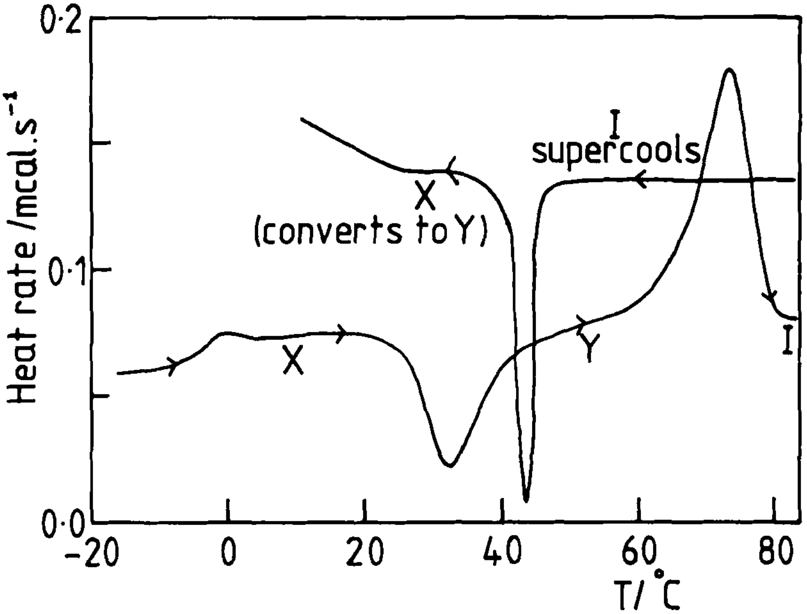


FIGURE 2 Showing DSC traces from P3 taken with a scan rate of 10 degrees per minute[7] (base line is arbitrary). Diffraction patterns at 25°C and 50°C (on heating) were identical.

chain and there is no need to invoke interdigitation. Figure 4a shows a schematic structure. P9 has an observed layer spacing 25% less than the model span which implies either a tilt of 41° or an overlap of 13 Å (2 Å more than the length of the hexyloxy chain). We will return to a discussion of this compound later.

ii) P2, P4, P5, and P7 have layers between 28% and 35% shorter than found for a fully extended model. This would imply a tilt angle of between 43° and 52° which is possible but would greatly reduce the contact between the polarizable parts of neighbouring mesogenic units on a chain and so we consider it unlikely. If we note in Table III the strong correlation between the discrepancy between the model and observed spacings, and the length of the polarizable part of the mesogenic unit, it seems most probable that the mesogenic units in adjacent layers are interdigitated sufficiently for the polarizable parts to overlap as shown in Figure 4b. The flexibility of the alkyl spacers and the polymer backbone allow the space filling to occur on either side of the plane of the polarizable cores. The additional rings in the diffraction pattern from P5 probably result from some additional three dimensional crystal like ordering. These were not observed in P4 and

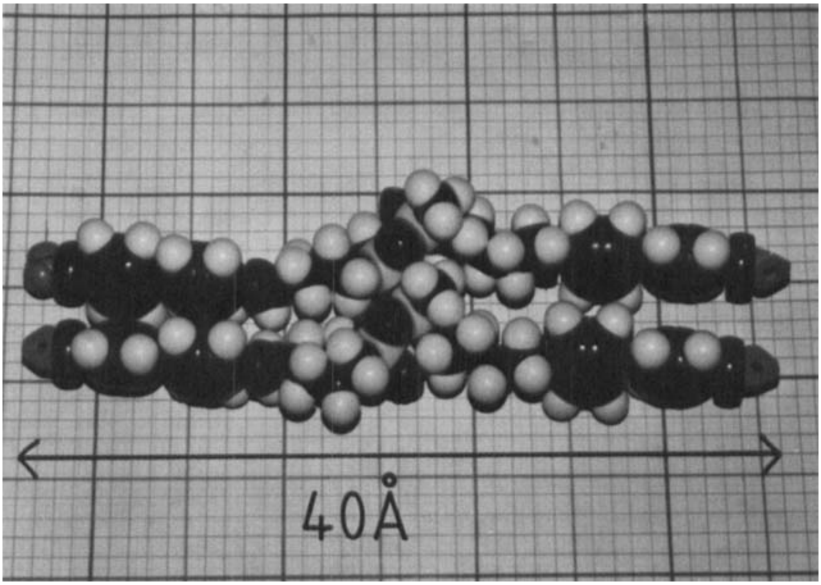


FIGURE 3 Model of part of the chain of polymer P2 showing the span of extended mesogenic units.
See Color Plate XII, located in the final volume of these conference proceedings.

it is tempting to associate the extra ordering with shorter flexible spacers.

iii) P3 is different from the other smectic polymers in that its observed layer spacing is considerably greater than the length predicted by the model of extended mesogenic units. A packing in the layers with alternate backbones displaced can be constructed from models,

TABLE III

Comparing measured smectic layer spacing with model dimensions.

Polymer	Measured Layer Spacing, d/Å	Model Span ℓ/Å	Tilt required, β/deg $\beta = \cos^{-1} d/\ell$	Overlap Required $(\ell - d)$/Å	Length of polarizable core in model/Å
P1	37	41	25	4	—
P2	29	40	43	11	11
P3	49 ±2	39	—	—	—
P4	33	48	47	15	14
P5	29	44	48	15	15
P7	33	54	52	19	17
P9	38	51	41	13	—

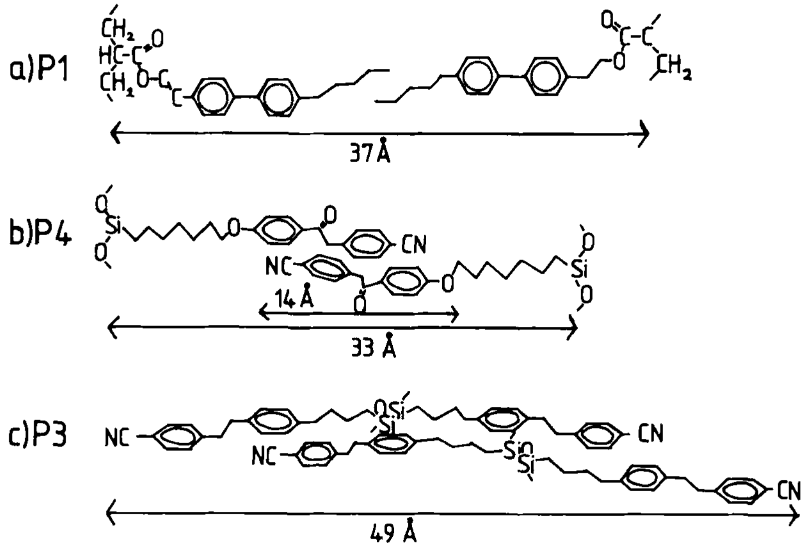


FIGURE 4 Proposed schematic structures of smectic layers. Dimensions are taken from space filling molecular models. The backbones lie approximately perpendicular to the plane of the paper.

so that the layer thickness is 48 Å as shown in Figure 4c. This arrangement might be energetically favourable because some of the cyano-group dipoles are adjacent to polarizable benzene rings. The overlapping core structure proposed for P2, P4, P5, and P7 is probably not possible for P3 because the alkyl chain spacer is not long enough to bend and fill the space around the chains. It remains to find a detailed explanation of the observed spacings at 10 Å and 13 Å, but if there are three dimensional crystal like correlations in the structure, it is not surprising that some extra reflections are seen. High degrees of crystallinity have also been observed[4] in other materials.

From a study of the crystal and smectic phases of a well aligned sample, Zugenmaier and Mügge[4] have developed a model for the packing in a smectic liquid crystal polymer. In their materials, the observed layer spacing corresponds to approximately half the span of a model, thus implying complete overlap of the mesogenic units. A simple extension of their model for the packing is shown in Figure 5 and can account for any lesser degree of overlap as observed in P2, P4, P5, and P7. The degree of overlap actually adopted by a particular material will depend upon the relative lengths of the flexible spacers, cores and tails of the mesogenic units, the effect of any specific in-

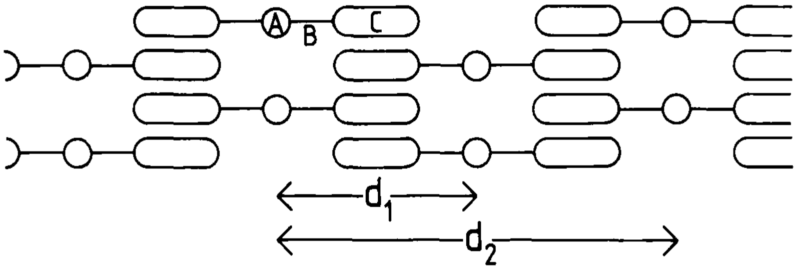


FIGURE 5 Schematically possible local packing scheme for overlapping or interdigitated structures. The backbones (A) are perpendicular to the plane of the paper. The flexibility of the backbones (A) and spacers (B) is essential to fill the gaps between the cores (C) of the mesogenic units. Although the cell dimension in the layer normal direction is d_2, it will not be observable in a smectic phase because of the glide plane symmetry element. The layer d_1 will, however, give a strong Bragg reflection. The actual layer spacing will depend upon the degree of overlap of the mesogenic units.

teractions between the cores, and the flexibility of the backbone. In the case of mesogenic units with terminal cyano-groups, the accommodation of the cyano-group in a region of high polarizability will be an important factor which will tend to favour the partially overlapping (i.e., interdigitated) structure. However in side chain liquid crystal polymers, there seems no reason to suppose that this phenomenon is confined to compounds with terminal dipoles as appears to be the case in low molecular weight liquid crystals. Sample P9 is an example.

4.2 Smectic order parameter

The intensity of the layer reflections will depend on the form factor of the chain plus mesogenic units and the order parameter,[5] τ_1, of the smectic layers. If we assume that the form factor remains constant, we can study the temperature dependence of the order parameter by measuring the intensity:

$$\tau_1 \propto I^{1/2}$$

Figures 6(a) and (b) show the temperature variation of the intensity of the first order layer reflection from P1 and P4. The intensity first increases with increasing temperature and then decreases to zero, suggesting some mobility of the polymer backbone is conducive to smectic ordering, but eventually at higher temperatures the motion

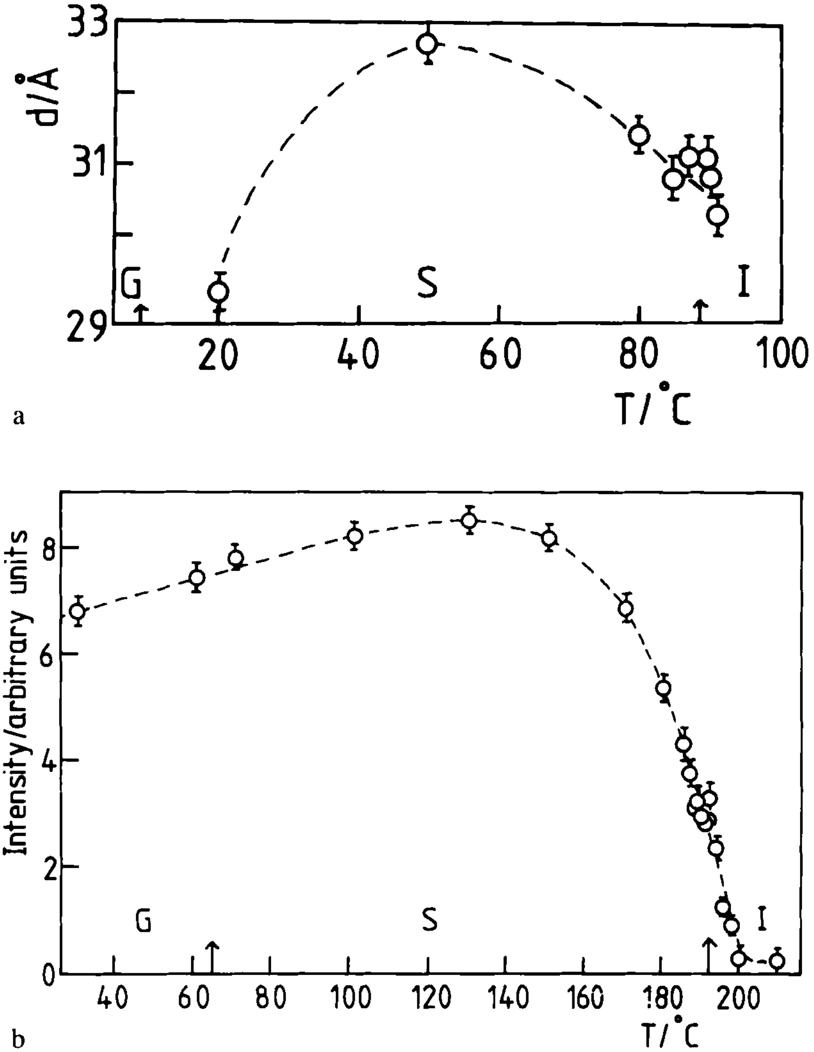
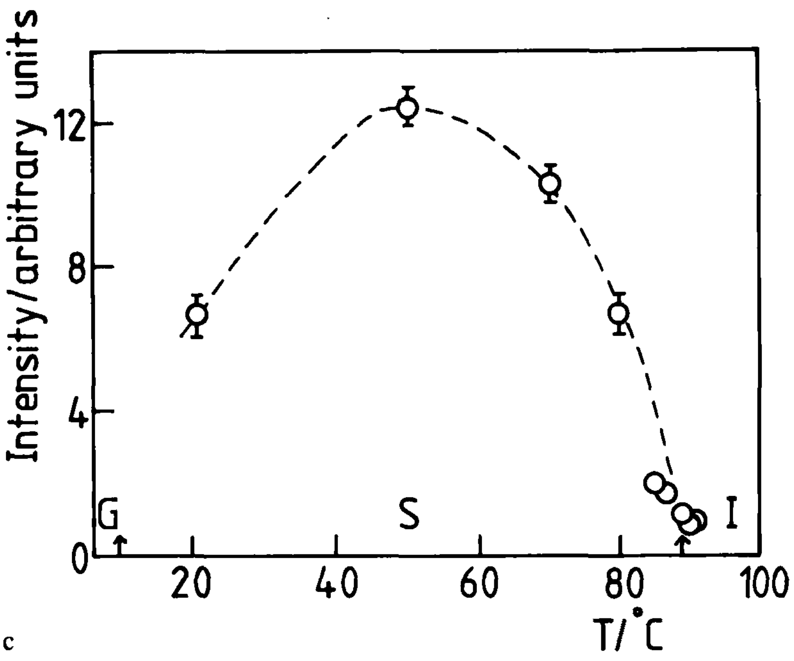


FIGURE 6 Showing the temperature dependence of (*a*) the intensity of the layer reflections of P1, (*b*) the intensity of the layer reflections of P4 and (*c*) the layer spacing of P4.

of the backbone is sufficient to destroy the smectic plans. A similar effect was found by Tsukruk *et al.*[6] It was noticed that as the intensity of the sharp ring decreased, it was replaced by a diffuse ring (at approximately the same scattering angle) which remained in the is-



otropic phase. This is consistent with the idea of a two phase region (S_A and isotropic) forming below the clearing point as has been observed[7] in many of these materials. No temperature variation in the layer spacing could be detected in P1 but a small effect shown in Figure 6(c) was observed in P4. It seems plausible that the layer thickness in an interdigitated structure (P4) is sensitive to the chain mobility, while in a "normal" structure (P1), this is not the case because the structure fills space more efficiently without relying on chain mobility.

4.3 Nematic Phases

The two nematic phases both show a very diffuse inner ring of scattering whose maximum (using the Bragg equation) corresponds to a distance of 16.5 Å in P6. This distance corresponds closely to half the full extended length of two mesogenic units either side of the backbone. This suggests that the tendency to form the partially overlapping structure is not so strong as in low molecular weight nematics with similar mesogenic units. This may be because the shortness of the flexible spacer in P6 and P8 means the mesogenic units do not have the freedom of movement to achieve a partially overlapping antiparallel configuration with mesogenic units on neighbouring chains. X-ray diffraction results from a homologous series (preferably exhibiting smectic and nematic phases) of a terminal cyano-substituted liquid crystal polymer are needed to clarify this.

5. CONCLUSION

We have successfully identified the phase types of all the materials and have proposed models for the packing of the mesogenic units[8]. These models are consistent with the X-ray diffraction data and are plausible in terms of the forces between different parts of the molecules. It seems that the overlapping core structures found in many low molecular weight liquid crystals containing terminal cyano-groups are also favoured in liquid crystal polymers. However, there are variants to the types of structure adopted by liquid crystal polymers with terminal cyano-groups (e.g., P3) and the overlapping structure is not confined to terminal cyano-compounds (e.g., P9).

It should be emphasised that some of the materials identified as smectic show additional sharp reflections (e.g., P3, P5) which are not observed in classical low molecular weight smectic A phases. This implies some additional degree of crystallinity in these materials, but its precise nature and its dependence on the molecular structure and sample preparation remains to be investigated.

It is now important to develop methods of aligning samples suitable for diffraction studies so that the structures may be studied in detail and so enabling the different types of smectic phases (e.g., S_A and S_C) to be distinguished.

Acknowledgment

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