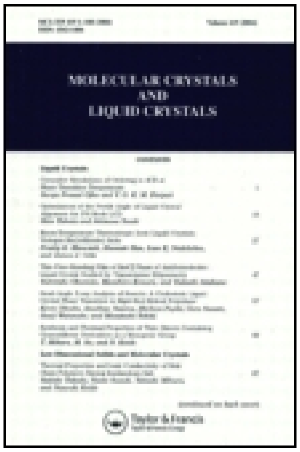

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X-ray Photograhic Study of Some Cyano Biphenyl Sidechain Liquid Crystalline Polysiloxanes

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X-ray Photographic Study of Some Cyano Biphenyl Sidechain Liquid Crystalline Polysiloxanes

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X-ray diffraction results are reported for a number of cyano substituted sidechain liquid crystal polymers with polysiloxane backbones. The structural parameters obtained from the X-ray studies are compared with repeat distances of models involving interdigitation of side chains. Where partial overlap occurred the *d*-spacing of the smectic layer decreased linearly with temperature; but for a mixed compound with complete overlap there was a small increase in *d*-spacing with temperature. Where a short flexible aliphatic spacer was used to link the mesogenic units to the polymer backbone, although there was also interdigitation, a different packing arrangement occurred from that normally observed when longer spacer units are present. Two diffuse equatorial maxima were observed in the diffraction patterns of all the samples, suggesting that these were columns consisting of groups of mesogenic units plus backbone. One of the compounds had an additional diffuse axial reflection suggesting a six mesogenic unit periodicity along the backbone.

Keywords: liquid crystal, x-ray diffraction polymers, polysiloxanes

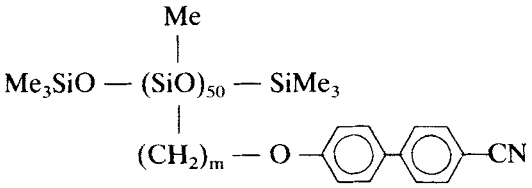
INTRODUCTION

This paper is part of a series describing sidechain liquid crystal polymers. Polysiloxanes have a very flexible backbone and in order to decouple the motions of the mesogenic moieties and the backbone, a flexible alkylene spacer is introduced. The effect of varying the length of the spacer is therefore of interest.

EXPERIMENTAL

The X-ray diffraction photographs were recorded on flat films with sample to film distance in the range 6 cm – 10 cm using monochromatic CuKα radiation ($\lambda = 1.5418\text{Å}$). The samples were mechanically aligned by stretching the polymer either at room temperature or at a temperature close to the glass-smectic transition. The samples, of diameter approximately 0.3 mm, were placed in an aluminium heating block whose temperature (measured with a chromel-alumel thermocouple) could be controlled to ±0.2 °C.

The materials have the general formula



Three compounds listed in Table I with $m = 3,4,5$ were investigated.

RESULTS AND DISCUSSION

m = 5

For the material with m = 5, in the temperature range up to 88°C the X-ray photographs contained the following features as shown in Figure 1;

TABLE I

m	Transition (°C) Temperatures				
3	G	$\xrightarrow{40}$	S	$\xrightarrow{152}$	I
4	G	$\xrightarrow{28}$	S	$\xrightarrow{132.5}$	I
5	G	$\xrightarrow{14.5}$	S	$\xrightarrow{169.5}$	I

G, glass
S, smectic
I, isotropic

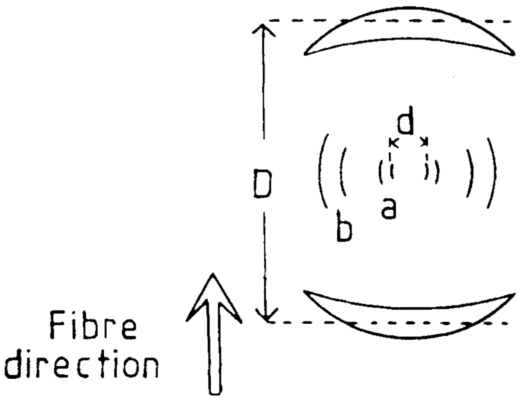


FIGURE 1 Principal features of the x-ray diffraction pattern.

(a) a sharp low angle equatorial first order maximum with a *d*-spacing of approximately 28Å together with a less sharp second order of 14Å,

(b) two diffuse equatorial reflections at 10.5 and 7.35Å

(c) an outer axial diffuse arc with D = 4.86Å at right angles to the low angle diffraction maxima.

Above 88°C the diffuse equatorial reflections at 10.5 and 7.35Å disappeared and the X-ray pattern resembled that of typical low molecular weight S_A phase. It was found that the *d*-spacing of the smectic layer decreases from 28.8Å at 0°C to 27.2Å just below the transition to the isotropic phase. These spacings are appreciably less than the length of two mesogenic units plus backbone (39.5Å). This discrepancy can be explained in terms of either a tilt of some 45° of the molecules to the layer normal or of interdigitation of the mesogenic units from adjacent layers with an overlap of 10.7Å (a distance which corresponds to the polarizable core of the model). A similar result was found by R. M. Richardson *et al.*[1] The appearance of the two diffuse reflections of 10.5 and 7.35Å (whose *d*-spacings remain constant with temperature) can be explained if we assume that they are 2nd and 3rd order reflections—the first order being very weak. This implies a repeat distance of approximately 21.5Å which correspond to the sum of the molecular length plus the thickness of the backbone (21.4 Å). This suggests that there are columns, consisting of mesogenic units plus backbone, as shown in Figure 2 and since the reflections are diffuse we infer that the columns are relatively short. The disappearance of the 10.5 and 7.35Å maxima above 88°C is

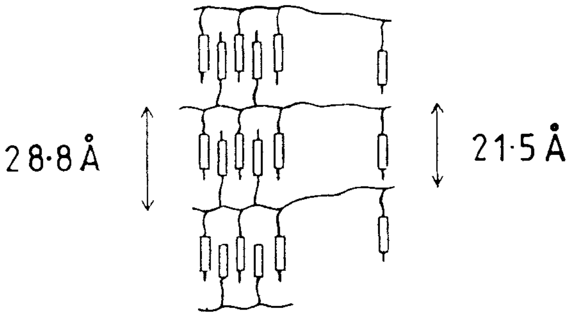


FIGURE 2 Schematic representation of packing showing interdigitation and columns of mesogenic units plus backbone.

probably due to the increased mobility of the backbone which together with the freedom given by the length of the spacer, $(CH_2)_5$, destroys the columns and thus allows the mesogenic units to achieve a degree of packing similar to that observed in low molecular weight compounds.

m = 3,4

The reduction in the length of the spacer group modifies the X-ray diffraction pattern. Both materials give similar diffraction patterns. For *m* = 4 the pattern consists of (1) an inner equatorial arc of *d*-spacing 12.55Å, (2) two wider equatorial arcs at 9.8 and 6.0Å and (3) a diffuse outer axial maxima with D = 5.0Å. The corresponding spacings for m = 3 were 11.7, 9.2, 6.5 and 5.0Å respectively. However the sample m = 3, gave an additional relatively weak, diffuse axial maximum at 7.6Å. The diffraction patterns of both compounds were apparently of the S_A type with the two additional diffuse equatorial maxima. The inner maxima at 11.7 and 12.55Å for m = 3 and 4 respectively are almost half the value 28.8Å obtained for m = 5. However the molecular lengths for m = 3 and 4 are 34.9 and 37.9Å respectively which are only slightly smaller than that for m = 5. The smallest calculated *d*-spacings for an arrangement with complete interdigitation (with the model used for m = 5) are 19.2 and 20.6Å respectively. A possible explanation for the observed *d*-spacing is an interdigitated pattern (with the molecular units tilted at an angle of approximately 42°). However it is more probable that the 11.7 and 12.55Å maxima are second order, the first being systematically absent because of the effect of a glide plane as shown in Figure 3. This would give repeat units in the two materials of 23.4 and 25.1Å and corresponds to an overlap of 11.5Å for m = 3 and 12.8Å for m = 4.

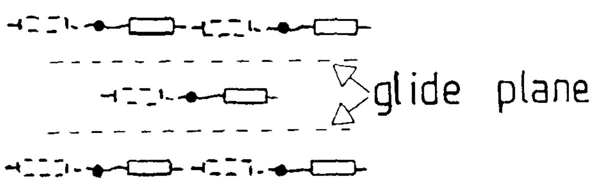
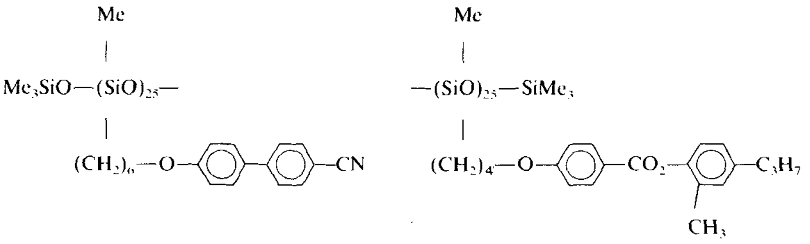


FIGURE 3 Schematic representation of packing for samples m = 3 and m = 4 looking down the backbone.

The equatorial diffuse reflections are consistent with the picture of columns consisting of mesogenic unit, spacer and backbone. For m = 4, the average repeat unit distance, assuming the diffuse reflections are second and third order, is 20.15Å and this can be compared with the sum of the length of the sidechain and thickness of the backbone of 20.6Å. Similar values of the repeat distance from the X-ray data and from molecular models for m = 3 are 18.95Å and 19.1Å respectively.

The diffuse axial reflection of 7.6Å is probably due to some periodicity in the backbone as shown in Figure 4. The repeat distance is 15.2Å but because there is the action of a glide plane we only observe the 7.6Å second order. This repeat distance would require a group of six mesogens in the repeat unit.

The fourth compound was



The diffraction pattern at 20°C gave a sharp equatorial low angle maximum with a *d*-spacing of 23.8Å together with a strong second order and weaker third order and an outer diffuse axial maximum with D of 5.1Å. The pattern was that of a S_A phase. The smectic layer spacing increased from 23.8Å at 20°C to 24.4Å at 82°C. The size of the spacing indicates interdigitation. The lengths of the two mesogens are similar with L_{CN} of 20.0Å and $L_{C_3H_7}$ of 20.4Å leading to a molecular length including backbone of 43.7Å. The observed *d*-

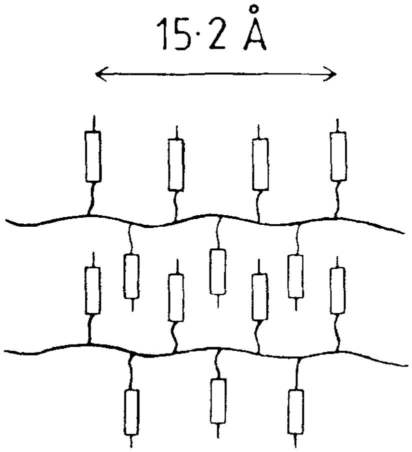


FIGURE 4 Periodicity in the backbone.

spacing of 24Å can be obtained assuming complete overlap of the mesogens in an interdigitation process. The fact that there is total overlap would account for the small variation in the smectic layer spacing with temperature. It is of interest to note that in this material the calculated position of the equatorial diffuse maxima which appear in compounds m = 3 to 5 would occur at the same position as the second and third orders of the 23.8Å reflection. Examination of the X-ray photographs do show a weak diffuse scattering associated with the third order maxima. The intensity of the second order of the 23.8Å maximum is considerably greater in relation to the first order than is normally observed.

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