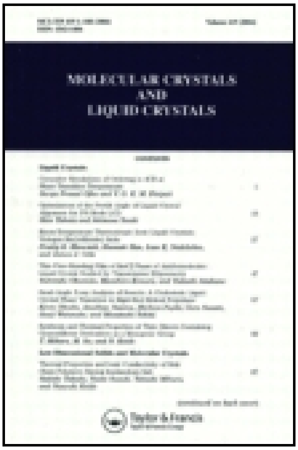

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An X-ray Investigation of Terminally Cyano-substituted Side Chain Liquid Crystalline Polysiloxanes

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An X-ray Investigation of Terminally Cyano-substituted Side Chain Liquid Crystalline Polysiloxanes

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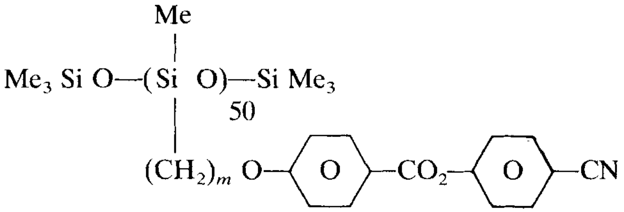
X-ray diffraction results are reported for a number of cyano substituted side chain liquid crystal polymers with polysiloxane backbones. The *d*-spacing of the smectic layer increases linearly with increasing length of the aliphatic spacer and, for each compound, shows a steady decrease with increasing temperature. The variation of intensity of the smectic layer reflection with temperature indicates that the length of the flexible aliphatic spacers linking the mesogenic units to the polymer determines the ease with which liquid crystalline order is obtained. The smectic order increases steadily with temperature for short spacers whereas the orientational freedom conferred by the longer spacers reduces the temperature dependence. The structural parameters, obtained from the X-ray studies, are compared with repeat distances obtained from molecular models involving either interdigitation or tilting of the mesogenic units.

Keywords: liquid crystals, x-ray diffraction polymers, polysiloxanes.

INTRODUCTION

Thermotropic liquid crystal side chain polymers can have mesogenic groups bonded either directly or *via* spacer groups (usually an aliphatic chain) to the main chain of a macromolecule.

This paper describes X-ray diffraction studies of the temperature variation of the mobility of the main chain, the liquid crystal order of the smectic phases and the lamellar spacing for a series of terminally cyano-substituted side chain liquid crystalline polysiloxanes. These polymers have the general formula shown below, and the seven different polymers listed in Table I with values of *m* ranging from 3 to 11, were investigated.



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 (λ = 1.5418 Å). Where possible the samples were mechanically aligned by stretching the polymer, either at room temperature or at a temperature in the region of the glass-smectic or crystal-smectic transition with subsequent rapid cooling to room temperature. The samples had a diameter of 0.3 mm and were placed between aluminium or mylar sheets and attached to an aluminium heating block. The temperature, measured using a chromel-alumel thermocouple, was controlled to ±0.2°C.

RESULTS

X-ray diffraction photographs were taken of the aligned samples at room temperature and then during heating in 10° to 20°C steps from the glassy or crystal phase to the isotropic phase. The diffraction

TABLE I

m	Transition (°C) temperatures
3	*G* 29 *S* 161.5 *I*
4	*G* 26 *S* 150 *I*
5	*K* 107 *S* 183.6 *I*
6	*K* 54.9 *S* 184 *I*
7	*K* 88 *S* 189 *I*
8	*G* 22 *K* 62 *S* 193.8 *I*
11	*K* 76 *S* 198.5 *I*

G, glass
K, crystalline
S, smectic
I, isotropic

patterns of samples in the smectic state contained the following features as shown in Figure 1;

(a) a sharp low angle equatorial diffraction maximum with *d* spacing in the range 24 to 40 Å, corresponding to the smectic layer spacing together with its second order, except for the polymers $m = 3, 4$ where only a weak first order was present. However, after annealing these samples the second order was observed.
(b) two broad and weak equatorial maxima with *d* spacings of approximately 12 and 8 Å respectively. These maxima were observed in all the samples except in the polymer $m = 11$.
(c) a diffuse outer axial maximum at a large diffraction angle corresponding to an intermolecular distance of approximately 5 Å.

Apart from the two broader maxima observed for the compounds $m = 3$ to 8 the photographs resemble those given by S_A phases. The various interplanar spacings are shown in Table II.

DISCUSSION

The *d*-spacing of the smectic layer increases linearly with increasing length of the aliphatic spacer. The increment in thickness varies from 1.93 Å per CH_2 at 90°C to 1.66 Å per CH_2 at 160°C. This should be compared with the corresponding increment of 1.27 Å for a methylene group in a crystalline paraffin in its fully extended conformation. The smectic layer spacing was obtained as a function of

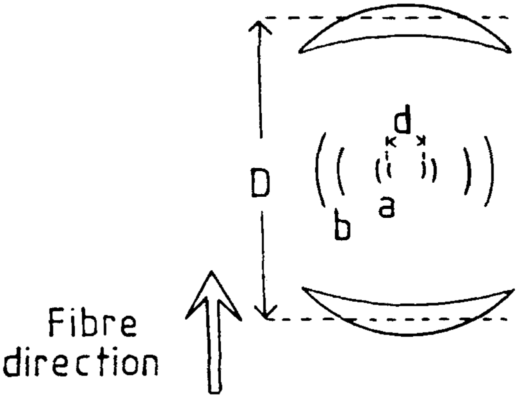


FIGURE 1 Principal features on the x-ray diffraction pattern.

TABLE II

Summary of the x-ray diffraction results

Polymer m	d-spacing for the first order of the smectic layer at (125°C) in Å	The second order of the smectic layers at:		ϕ° The angle between the direction of the stretch with the normal to the layer	d-spacing for the two broad maxima in (Å)	The intermolecular distance, D in Å
		Room temperature	The transition g or $k \rightarrow S$			
3	24.0	not observed	not observed	15	7.1 10.5	4.81
4	25.8	not observed	not observed	15	7.0 11.5	4.81
5	27.0	not observed	observed	0	7.8 11.6	5.0
6	29.1	not observed	observed	10	8.1 12.1	5.03
7	31.4	not observed	observed	10	8.3 13.1	5.06
8	32.9	not observed	observed	30	8.6 13.5	5.05
11	38.0	observed	observed	0	not observed	5.09

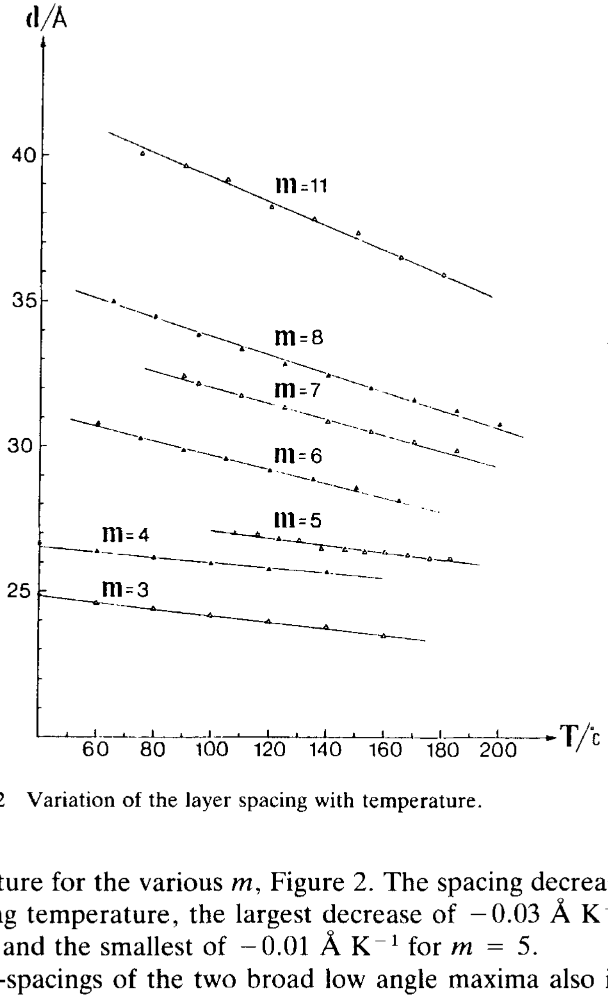


FIGURE 2 Variation of the layer spacing with temperature.

temperature for the various *m*, Figure 2. The spacing decreases with increasing temperature, the largest decrease of -0.03 Å K^{-1} is for $m = 11$ and the smallest of -0.01 Å K^{-1} for $m = 5$.

The *d*-spacings of the two broad low angle maxima also increase with increasing *m*. However when $m = 11$ these maxima were no longer observed. Their presence is probably indicative of some additional order which does not occur in the normal low molecular weight smectic A and C phases.

The observed interlayer spacings are smaller by approximately 40% than the calculated length of the molecule, assuming that the mesogenic groups lie perpendicular to the main polymer chain. There are a number of possible explanations as shown in Figure 3.

The necessary tilt angles or overlap distances are listed in Table III. The packing involving tilting, although possible, is less likely than that involving interdigitation. Both modes of packing could account

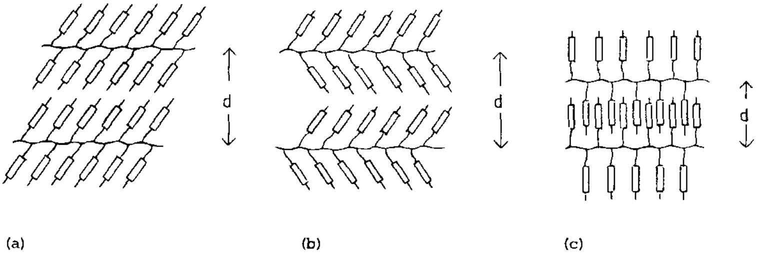


FIGURE 3 Schematic representation of packing: (a) tilted S_c arrangement, (b) tilted herring bone arrangement, (c) mesogenic units interdigitated in a way similar to a bilayer structure.[1,2]

for the decrease in *d*-spacing with temperature, either as an increase in tilt angle or as an increase in overlap. The increase in overlap is more probable when we consider the rapid decrease of the lamellar spacing observed for the long spacer polymers. There will, in addition, be an increase in the mobility of the spacer unit with temperature.

The relationship between the length of the spacer and the smectic order can be shown by considering the variation in the diffraction pattern with increasing spacer length and with temperature. The small angle reflections obtained using fresh samples in the smectic phase can be classified in three groups for this series of polymers as shown in Table II.

I Only a weak first order reflection is observed for the polymers with short spacers with $m = 3$, 4 and this is considerably weaker than that normally observed for S_A phases suggesting that the order is of a shorter range than that of a low molecular weight

TABLE III

Overlap distances or tilt angles required for the observed layer spacing

Polymer *m*	The calculated length of the fully extended side chain (Å)	*d*, Å	The overlap distance (Å)	The calculated length of the side chain (Å)	Tilt required β(°) $\beta = \cos^{-1} d/l$
3	40.1	24.0	16.1	18.4	53.2
4	43.0	25.8	17.2	19.85	53.1
5	44.7	27.0	17.7	20.7	52.8
6	48.3	29.1	19.2	22.5	52.9
7	50.3	31.4	18.9	23.5	51.4
8	53.3	32.9	20.4	25.0	51.9
11	60.7	38.0	22.7	28.7	51.2

S_A material. The first order intensity increases quite rapidly with increasing temperature. Only after annealing the sample does the second order appear.

II The second order reflection in the polymers (5, 6, 7, 8), start to appear at the glassy-smectic phase transition and its intensity increases gradually with increasing temperature. At the same time a strong first order reflection is observed.

III First and second order reflections are obtained in the polymer ($m = 11$) with only a small increase in intensity with increasing temperature.

The intensity of the low angle smectic layer maxima depends on the order parameter τ_l of the smectic layers and the form factor F of the mesogenic unit plus backbone. $I \propto (\tau_l F)^2$. If we take F to be constant then the order parameter is proportional to $\sqrt{I}$. The intensities of the second order reflections of the smectic layers for $m = 5$ and 11 were measured and the variation of $(I/I_{\max})$, the normalized intensities, with temperature for the compounds with $m = 5$ and $m = 11$ is shown in Figure 4. The increase in intensity with increasing temperature suggests a higher degree of order of the smectic layers. This could be due to the increased mobility of the main chain, allowing a higher degree of smectic ordering. However as the temperature increases beyond a certain value, the intensity decreases suggesting that the motion of the backbone is sufficient to destroy the smectic ordering. Similar results have been obtained by Tsukruk et al.[3]

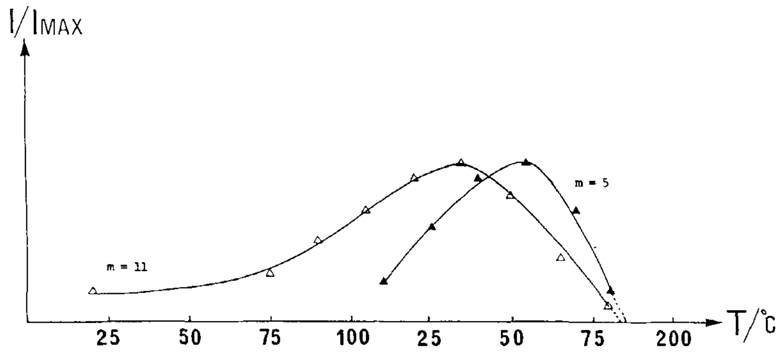


FIGURE 4 Intensity of the second order maximum for $m = 5$ and $m = 11$ as a function of temperature.

CONCLUSION

Our observations confirm that the length of the flexible aliphatic spacers linking the mesogenic units to the polymer main chain is of crucial importance in determining the ease with which liquid crystalline order can be established. For short spacers with 3 or 4 methylene units the X-ray diffraction patterns indicate a steady increase of smectic ordering with temperature. The orientational freedom conferred by the longer spacers makes it easier for the liquid crystalline order to be attained and hence appreciably reduces the temperature dependence.

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