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A structural investigation of some terminally cyano-substituted side chain liquid-crystalline polysiloxanes

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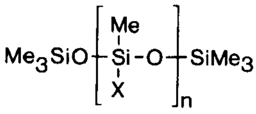
A series of terminally cyano substituted side chain polysiloxanes have been characterized using optical microscopy, D.S.C., and X-ray diffraction. Values for the lamellar spacings, *d*, of the interdigitated smectic A phases were obtained, and the variations in *d* with temperature and length of the flexible aliphatic spacer are discussed. The spacing for $m = 4$, 5, and 6 increased regularly with *m* whereas the short $m = 3$ spacer gave an anomalously high value.

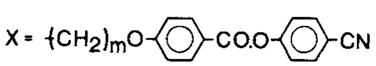
1. Introduction

Thermotropic liquid-crystalline side chain polymers can form when mesogenic groups are bonded directly or via spacer groups such as an aliphatic chain to the main chain of a macromolecule—the polymer backbone. This paper describes a structural investigation of a series of terminally cyano-substituted side polysiloxanes with the structure



$$Me_3SiO\left[\begin{matrix}Me\\ | \\ -Si-O- \\ | \\ X\end{matrix}\right]_n SiMe_3$$

where



and *n* is approximately 35. The polydispersity, γ, is two. The materials were prepared on a Dow 1107 polyhydrogen methyl siloxane backbone.

D.S.C. measurements gave the following values for T_g, the crystal to smectic and the smectic to isotropic transition temperatures together with the enthalpy of transition $\Delta H_{S_A I}$

m	$T_g/°C$	C–S_A	S_A–I	$\Delta H_{S_A I}/J g^{-1}$
3	18	—	133	1·59
4	16	—	130	2·05
5	—	84	162	3·18
6	8	22	148	3·68

The S_A–I transition temperatures are taken as the peak maxima on the D.S.C. traces; the actual full clearing temperature as obtained from microscopy are higher.

2. Experimental

The X-ray diffraction patterns were recorded on flat photographic plates with a sample to plate distance of 6 cm. The radiation used was copper $K\alpha$ obtained using a graphite monochromator. The samples were aligned mechanically by stretching the polymer at a temperature either in the region of the crystal–smectic transition or for samples $m = 3$ and $m = 4$ of about 30°C. The samples were inserted into 0·3 mm diameter glass capillaries and attached to a metal heating block. The temperature was measured using a chromel–alumel thermocouple and could be controlled to ± 0·2°C. X-ray diffraction photographs were taken at regular intervals during heating from room temperature up to the isotropic phase.

3. Results and discussion

The main features of the X-ray diffraction patterns of the smectic phase (cf. figure 1) are the following.

(*a*) A sharp low angle equatorial diffraction maximum with *d* spacing in the range 26–32 Å depending on the temperature and length of the spacer together with a second order reflection. The sample $m = 4$ gave a very much weaker first order reflection than the other three compounds; in addition the second order was barely visible.

(*b*) There were two somewhat broader equatorial reflections with *d* spacings of approximately 10 Å and 7 Å. The values of the spacing varied with *m*. The intensity of these reflections was weaker than the second order low angle maximum except for the sample $m = 4$.

(*c*) A diffuse outer axial maximum at a large diffraction angle corresponding to an intermolecular distance, *D*, of approximately 5 Å. Apart from the two reflections at 7 and 10 Å the photographs resemble those given by low molar mass smectic A phases.

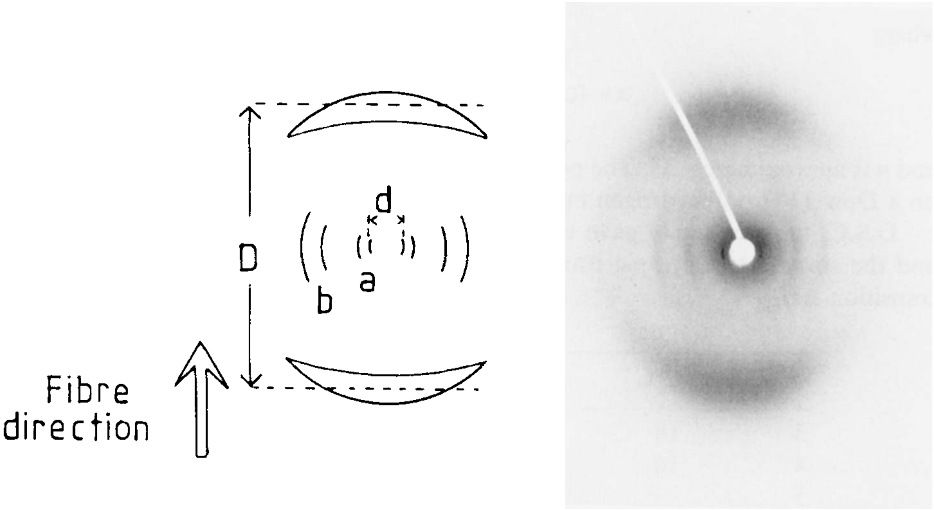


Figure 1. The main features of the X-ray diffraction patterns.

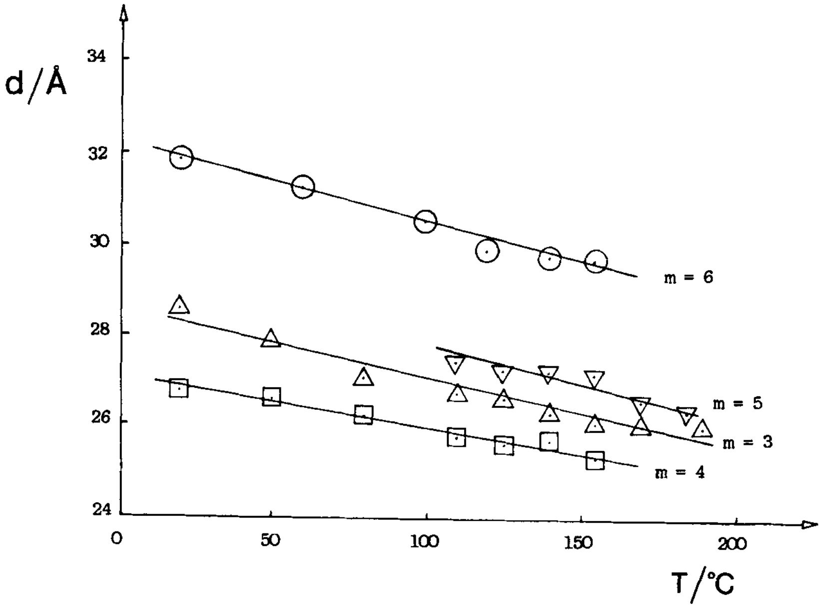


Figure 2. Variation of the layer spacing with temperature.

The smectic layer spacing was obtained as a function of temperature for the four values of m the results and are shown in figure 2. All the samples showed that the d spacing in the smectic region decreased as the temperature was increased; for example the sample $m = 6$ showed a decrease of $-0{\cdot}016\,\text{Å}\,{}^{\circ}\text{C}^{-1}$. Sample $m = 5$ shows that the spacing is almost constant in the crystalline region, then there is a sudden increase of about 1·5 Å at the C–S_A transition, and once in the smectic region as the temperature increases the d spacing decreases (see figure 3). All of the points for the

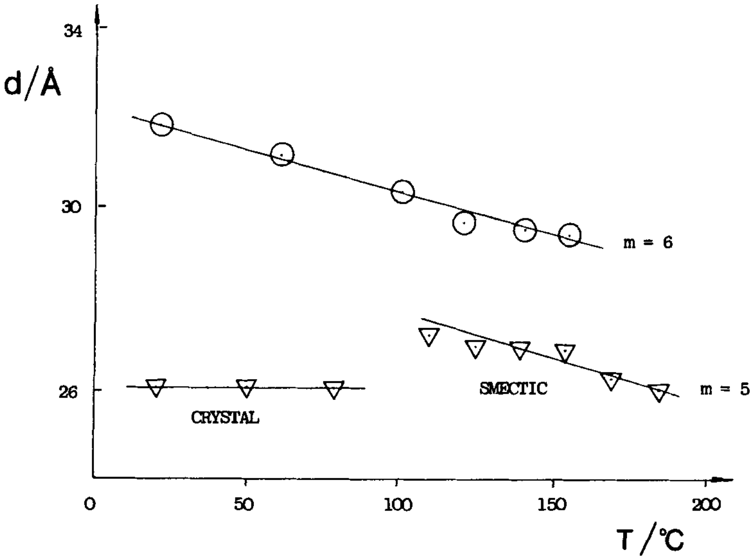


Figure 3. Variation of the spacing in the crystal and smectic phases for the sample with $m = 5$.

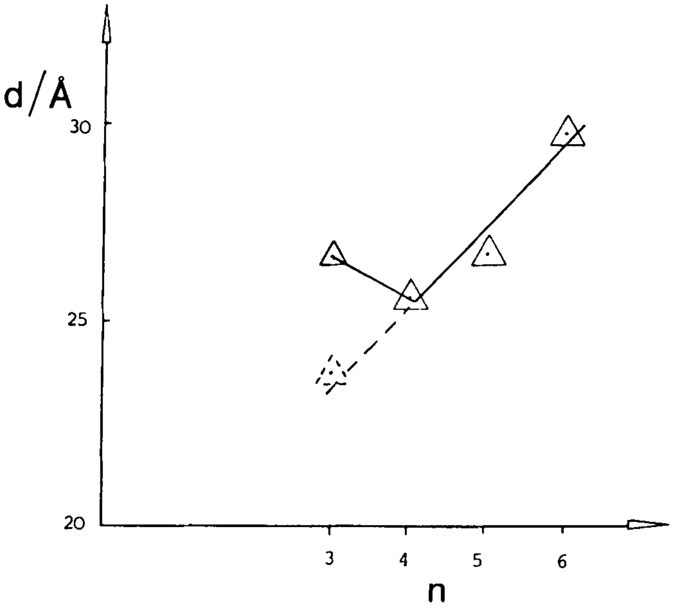


Figure 4. Variation of the layer spacing with the length of the alkyl chain.

sample $m = 3$ have a d spacing higher than the corresponding points for $m = 4$ but lower than those for $m = 5$. This is seen more clearly if the values obtained for the samples at $T_I - 30°C$ are plotted as shown in figure 4. For $m = 4$ to 6 the increase in the d spacing is 2·05 Å per methylene group. This can be compared with the corresponding increment of 1·27 Å for a methylene group in a crystalline paraffin in its fully extended conformation. However, on going from $m = 4$ to $m = 3$ there is an increase in the observed spacing of 1·0 Å. One probable explanation, based on overlapping mesogenic units, is that the short $m = 3$ spacer is more rigid and this will reduce the amount of overlap. It is of interest to compare these results with those of a similar series obtained with $n = 50$ where the catalyst was not fresh and resulted in dark coloured end products. In this series the d value for the $m = 3$ spacer was about 24 Å [1]. In this material it is highly probable that not all of the possible sites on the polymer backbone for the mesogenic units were occupied thus leaving room for closer packing. The preparation of these materials has recently been discussed by Gray *et al.* [2].

When the photographs of the four compounds are compared, it is very obvious that the intensity of the first order reflection for the sample $m = 4$ is very much weaker than that of the other three compounds. This suggests that the order for $m = 4$ is of a shorter range than that of the others which are in turn comparable to that of a low molecular weight smectic A phase. The intensity of the first order reflection increases with temperature, reaching a maximum at about 110°C, then gradually reducing, disappearing when the isotropic phase is reached. The second order reflection was not visible at 15°C but as the temperature increases it became visible and its intensity continued to increase. However it did reduce rapidly as the isotropic phase was reached. These processes are reversible.

The intensity of the low angle smectic layer maxima depend on the translations at order parameter, τ, of the smectic layers and the form factor, F, of the mesogenic unit with the backbone; $I \propto (\tau F)^2$. If F is taken to be constant then the order parameter is proportional to $\sqrt{I}$. The increase in intensity with increasing temperature for the first and second order reflections suggests therefore a higher degree of order being present as the temperature is increased. When the other three materials are examined, $m = 3$, 5 and 6 the first order reflection at best remains constant or decreases with temperature. The second order intensity on the other hand increases to a maximum just before the transition to the isotropic phase. It should be remembered that the d spacing decreased with increasing temperature.

There are two possible explanations of what is happening. Either the backbone remains where it is with the mesogenic units becoming more mobile and thus disordered or the backbone disorders as it becomes more mobile with the mesogens becoming more ordered. It is this second possibility which is more probable. The second order reflection is always very much weaker than the first order. The fact that the second order reflection is initially very weak and gradually increases with temperature and the first order intensity decreases could be accounted for by some alteration of the packing which occurs because of the change in d spacing thus affecting the form factor F. Some asymmetry could be introduced into the packing thus increasing the intensity of the second order reflection and allowing only a small reduction in the intensity of the first order.

A comparison of the diffuse reflections is shown in table 1. These are second and third order reflections with the first order being very weak which result from a d spacing which is just smaller than the sum of the molecular length, l, and the thickness of the backbone. The spacings appear to remain constant with temperature but vary with the length of the spacer. Such a d spacing would be obtained from columns of mesogenic units and backbones as shown in figure 5; the columns are not directly related to the smectic layer structure. The widths of these diffuse peaks suggest a coherence length in the range of three to five layers. Similar diffuse scattering involving only second and third order reflections was observed by Davidson *et al.* [3] for a related mesogenic unit attached to a polymethacrylate backbone. In this case the material was nematic, however, a similar coherence length of approximately five layers was obtained.

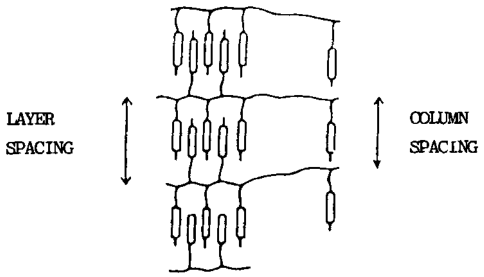


Figure 5. Molecular packing showing interdigitation and columns of mesogenic units with the backbone.

The observed interlayer spacings are considerably smaller than the calculated length of the molecule, assuming that the mesogenic groups lie perpendicular to the main polymer chain. It has been shown by Leadbetter *et al.* [4] for low molar mass smectic A cyanobiphenyls that the ratio of the molecular length, l, to the X-ray layer spacing, d, is 1·4 which can be explained in terms of interdigitation. There are a

Table 1. X-ray scattering results for the side chain liquid-crystalline polysiloxanes.

Polymer	Smectic layer *d* spacing/Å at 110°C		*d* spacing Å for the two broad maxima		Calculated first order diffuse spacing/Å	Molecular length plus backbone/Å	The intermolecular distance, *D*/Å ($2D\sin\theta = 1{\cdot}117\lambda$)
	First order	Second order					
m							
3	26·8	13·5	6·7	10·4	20·5	21·5	5·04
4	25·8	12·8	6·9	11·0	21·5	22·9	4·75
5	27·4	13·8	7·5	11·5	22·8	23·9	4·94
6	30·5	15·0	7·5	12·4	23·7	25·2	4·91

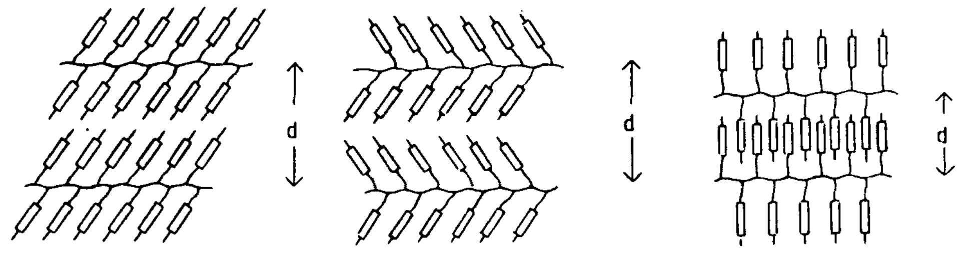


Figure 6. Schematic representation of the molecular packing.

number of possible explanations for a reduction in the spacing either involving tilting or interdigitation. Three possible arrangements are shown in figure 6. The first involving tilting is typical of a smectic C phase and there is no evidence for this from the X-ray photographs. The second involving tilting has a herring bone configuration. The third involves interdigitation. The possible tilt angles or overlap distances are given in table 2. A tilt of between 44° and 52° is required to explain the observed d spacing at the beginning of the smectic phase and that just before the isotropic phase the tilt angle would increase by about 4°. If the case of overlapping layers is considered then the overlap for $m = 3$ would be about 11·1 Å and for the other three samples approximately 15 to 17 Å at the beginning of the smectic phase. At $T_{\mathrm{I}} - 30$°C phase the overlap increases for the sample $m = 3$ to 13.0 Å and for $m = 4$, 5 and 6 to 16·8, 17·7 and 17·3 Å respectively (see table 2).

Table 2. Overlap distances or tilt angles required for the observed layer spacing.

Polymer m	The calculated length of the fully extended sidechain, L/Å	d/Å	The overlap distance/Å	The calculated length of the sidechain, l/Å	Tilt required β/° = $\cos^{-1} d/l$
3	39·7	28·6	11·1	18·2	43·9
4	42·5	26·7	15·8	19·6	51·1
5	44·4	27·5	17·0	20·6	51·7
6	47·1	31·9	15·2	21·9	47·4

The most probable model is that of the interdigitated bilayer smectic A structure with overlap of the polarizable core. The degree of overlap depends on the length of the flexible spacer and the rigidity of the $m = 3$ spacer reduces the degree of overlap. Richardson and Herring [5], on the basis of packing also favoured an interdigitated structure for a number of polymeric materials which showed a similar reduction in layer spacing. They concluded that the tilt angles necessary for a tilted model would greatly reduce the contact between the polarizable parts of neighbouring mesogenic units.

4. Conclusion

The length of the aliphatic spacer determines the ease with which liquid-crystalline order is obtained. For the spacer $m = 4$ the smectic order increases steadily with temperature whereas the orientational freedom conferred by the longer spacers $m = 5$ and 6 reduces the temperature dependence. The rigidity of the spacer $m = 3$ is such that the packing is different from that of the other compounds.

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