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# An X-ray diffraction study of a chromophoric liquid crystal polysiloxane

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# An X-ray diffraction study of a chromophoric liquid crystal polysiloxane

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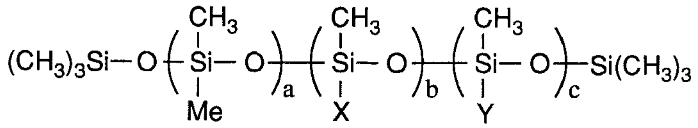
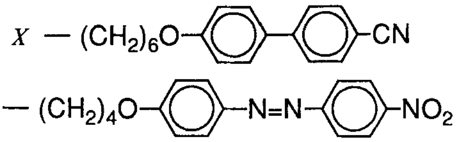
Polymeric materials of composition,



$$(CH_3)_3Si-O\left(\underset{Me}{\overset{CH_3}{Si}}-O\right)_a\left(\underset{X}{\overset{CH_3}{Si}}-O\right)_b\left(\underset{Y}{\overset{CH_3}{Si}}-O\right)_c Si(CH_3)_3$$

where



$a$ = 0·54, $b + c$ = 0·46 and $c$ = 0·000, 0·029, 0·059, 0·107, 0·234 have been characterized using X-ray diffraction and found to have bilayer $S_A$ structures. The smectic layer spacing of 39 Å at 20°C was found to decrease by 0·04 Å $K^{-1}$ with increasing temperature for all the materials.

## 1. Introduction

This paper is part of a series describing side-chain liquid crystal polymers. Thermotropic liquid crystal side-chain polymers can have mesogenic groups bonded either directly or via spacer groups to the main-chain of a macromolecule. It is of interest to study the effect of the addition of a dye. The synthesis of the polymers studied was reported by Gray *et al.* [1].

## 2. Experimental

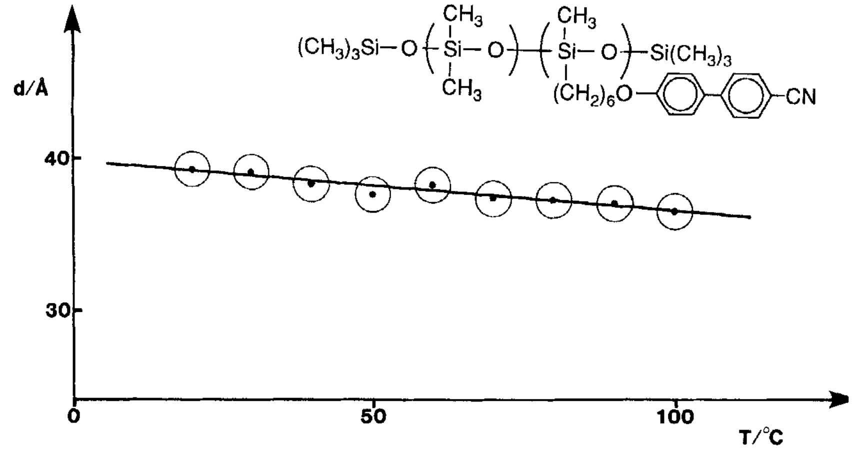
The X-ray diffraction patterns were recorded on flat photographic films with a sample to film distance of 7 cm; sodium chloride was used for distance calibration. The radiation used was CuK$\alpha$, obtained using a graphite monochromator. The samples were first mechanically aligned by stretching the polymers at room temperature, cooled, then inserted into a 0·3 mm diameter glass capillary and attached to a heating block whose temperature (measured using a chromel-alumel thermocouple) was controlled to ± 0·2°C. For alignment in a magnetic field, the mechanically aligned sample was heated into the isotropic phase, placed in a magnetic field of 1·5 T and then cooled slowly to room temperature. X-ray diffraction patterns were taken at regular intervals during heating into the isotropic phase.

## 3. Results and discussion

A mechanically aligned sample of the copolymer material with $c = 0{\cdot}0$ at 20°C shows a sharp low angle equatorial first order maximum with a *d*-spacing of 39 Å together with a diffuse equatorial reflection of 11·5 Å. In addition there is a diffuse ring with a spacing of 7·8 Å and an outer axial diffuse arc with $D = 4{\cdot}9$ Å at right angles to the equatorial reflections where $1{\cdot}117\lambda = 2D\sin\theta$. This indicated that the polymer backbones are aligned parallel to the drawing direction.

The sample aligned in a magnetic field of 1·5 T acting along the drawn fibre axis and perpendicular to the X-ray beam showed; (*a*) on the meridian a sharp intense low angle reflection together with a diffuse region of scattering which appeared to show two maxima, one at approximately 12·2 Å and the other at 11·1 Å; (*b*) on the equator, there was a diffuse arc with a $D$ of 4·9 Å; (*c*) at 7·8 Å a broad ring of scattering was observed which is similar to and occurs at approximately the same position as the first ring of scattering from the liquid backbone material.

The smectic layer spacing was obtained as a function of temperature, see the figure; the spacing decreases by 0·04 Å $K^{-1}$ with increasing temperature. The spacing of the diffuse ring at 7·8 Å and the outer diffuse arcs remained constant with temperature. The intensity of the layer spacing and the outer diffuse reflection decreased with increasing temperature.



The variation of the the layer spacing with temperature.

The observed interlayer spacing of 39 Å at 20°C is approximately 10 per cent smaller than the 42·7 Å for the length of the mesogenic moiety plus spacer unit calculated using standard bond lengths and angles, assuming that the mesogenic groups are perpendicular to the main polymer chain. This difference is common in low molar mass smectic A materials and can be accounted for either by random tilts of the mesogenic units of up to 23° or by an overlap of the cyano groups of 3·5 Å. These results suggest that the material has a bilayer $S_A$ structure.

Richardson *et al.* [2] and Sutherland *et al.* [3] found in studies of a homopolymer $C_5$ cyanobiphenyl polysiloxane that the layer spacing was appreciably less than the length of the mesogenic unit plus spacer and could be explained in terms of interdigitation with a 10·7 Å overlap of the polarizable cores. The 39 Å layer spacing for the current material, a copolymer, is some 8–9 Å larger than would be obtained from the overlap of 10·7 Å of the polarizable cores. In a comparative investigation of homo- and copolymers, Sutherland *et al.* [4] showed that the copolymer layer spacing was approximately 8–9 Å larger than the corresponding homopolymer layer spacing.

In the mechanically drawn samples, the layers and consequently the backbones are parallel to the drawing direction with the mesogenic units perpendicular to the drawing direction. When the magnetic field is applied, the mesogenic units lie parallel to the field direction with the smectic layers perpendicular to the field. Similar results have been described by Zugenmaier and Mugge [5].

The four samples which had different amounts of the chromophore, $c = 0{\cdot}029$, $c = 0{\cdot}059$, $c = 0{\cdot}107$, $c = 0{\cdot}234$, gave X-ray diffraction data for mechanically and magnetically aligned samples which was essentially the same as for the basic copolymer. The *d*-spacings of the various maxima were, within experiment error, the same; the lamellar spacing of 39·2 Å at 20°C decreased by 0·04 Å $K^{-1}$ with increasing temperature. The main difference was in the intensity behaviour of the region of diffuse scattering at 12·2 and 11·1 Å in the magnetically aligned samples. As the percentage of dye increased, the relative intensities altered with the region around 12·2 Å becoming more intense than that around 11·1 Å.

Since all the materials gave similar lamellar spacings, the packing arrangements must be similar and defined by the cyanobiphenyl mesogenic units and the backbone, the azo compounds having a minimal effect. The length of two dye units lying perpendicular to the backbone is 43·3 Å which is comparable with the 42·7 Å for the cyanobiphenyl mesogenic unit and the observed *d*-spacing of 39·2 Å at room temperature. The basic, non dye material has a bilayer $S_A$ structure; the dye molecules must lie parallel to the cyano groups.

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