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An X-ray diffraction study of terminally bromo substituted side chain polysiloxanes

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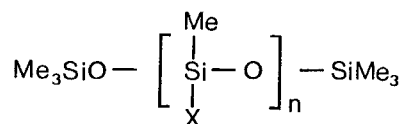
(Received 11 February 1990; accepted 12 December 1990)

X-ray diffraction results are reported for two bromo substituted side chain liquid crystal polymers with polysiloxane backbones. Both exhibit a smectic A phase with the observed lamellar d spacings being consistent with an almost totally overlapped interdigitated structure. Below the S_A phase the biphenyl derivative gives an X-ray pattern with sharp 110, 200 and 210 reflections which can be interpreted as smectic E.

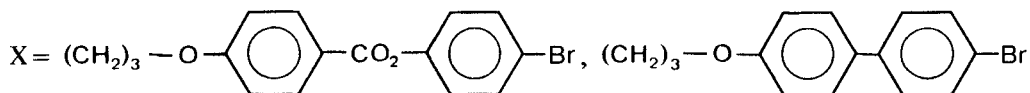
1. Introduction

As part of a program involving a study of liquid crystal side chain polymers it was of interest to examine the structure when the mesogenic units attached to the backbone with a short spacer group were terminated by bromine atoms.

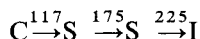
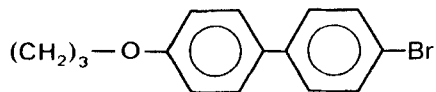
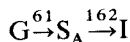
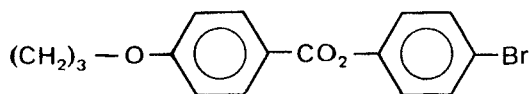
This paper describes an X-ray investigation of two side chain polysiloxanes with the structure



where n is approximately 35, the polydispersity, γ , is 2 and



DSC measurements and microscopy studies gave the following transition temperatures (°C)



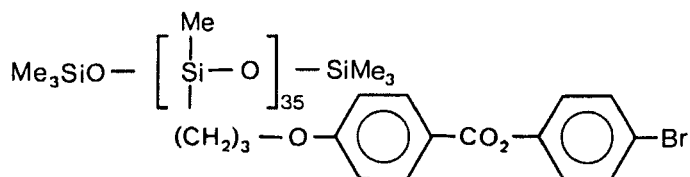
Although DSC measurements indicated two smectic phases for the second material, their designation was not clear.

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2. Experimental

The X-ray diffraction experiments were performed using Cu-K α radiation ($\lambda=1.5418 \text{ \AA}$) obtained with a graphite monochromator. The patterns were recorded on flat photographic films with a sample to film distance in the range 6–10 cm; sodium chloride was used for distance calibration. The samples were placed in glass capillaries either in the form of a powder or as aligned samples drawn from heated material. The sample in its capillary was attached to a metal heating block whose temperature, measured with a chromel alumel thermocouple, could be controlled to $\pm 0.2^\circ\text{C}$. X-ray diffraction photographs were taken at regular intervals during heating from room temperature to the isotropic phase.

3. Results

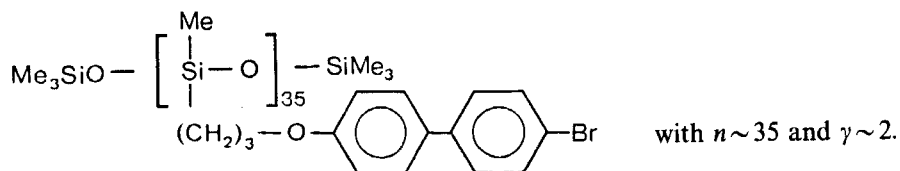


X-ray diffraction photographs were taken in 20°C steps from 20°C up to the isotropic for non-aligned and mechanically aligned samples. Photographs taken at room temperature using freshly prepared non-aligned material showed (i) a sharp but weak inner ring with d spacing of 20.4 \AA surrounded by a region of diffuse scattering; (ii) a very faint diffuse ring at approximately 6.3 \AA ; (iii) a very strong ring with $d=4.53 \text{ \AA}$ and a slightly weaker ring with $d=4.0 \text{ \AA}$, both rings associated with a region of diffuse scattering lying between them and (iv) a weaker ring with a d spacing of 3.2 \AA .

X-ray diffraction photographs taken at 20°C for a mechanically aligned sample contained the following features as shown in the figure (a) (i) on the meridian a strong inner first order reflection with a d spacing equal to 21.52 \AA and four weak reflections at 7.23 , 5.41 , 4.28 and 3.55 \AA corresponding to orders 3 to 6 respectively: these are reflections from the smectic layers; (ii) on the equator there was a faint reflection at 8.20 \AA ; (iii) in addition there were three complete rings which exhibited preferred orientation with maximum intensity on the equator; these had Bragg spacings of 4.58 , 4.03 and 3.23 \AA with relative intensities strong, medium and weak respectively.

Photographs taken at 20°C , 40°C and 60°C were similar. From 80° upwards the diffraction patterns were typical of a S_A phase. The non-aligned samples showed (i) an inner ring with d spacing in the range $22\text{--}20 \text{ \AA}$; (ii) a weak ring at 6.9 \AA ; and (iii) a strong outer diffuse ring with $D=5.04$ where $1.117 \lambda = 2D \sin \Theta$; at 200°C the material had entered the isotropic region.

The aligned samples (see the figure (b)) gave (i) on the meridian a sharp inner maximum at 21.19 \AA ; (ii) two diffuse weak reflections at 6.85 and 5.33 \AA respectively; (iii) on the equator a very weak diffuse reflection with d spacing of 8.2 \AA ; and (iv) an outer diffuse ring with D of 4.98 \AA . In the smectic region the lamellar d spacing decrease slightly from 21.19 \AA at 80°C to 21.01 \AA at 170°C . The intensity of the first order and the outer diffuse reflection increases with increasing temperature reaching a maximum value at 130°C , then decreases as the isotropic phase is approached.



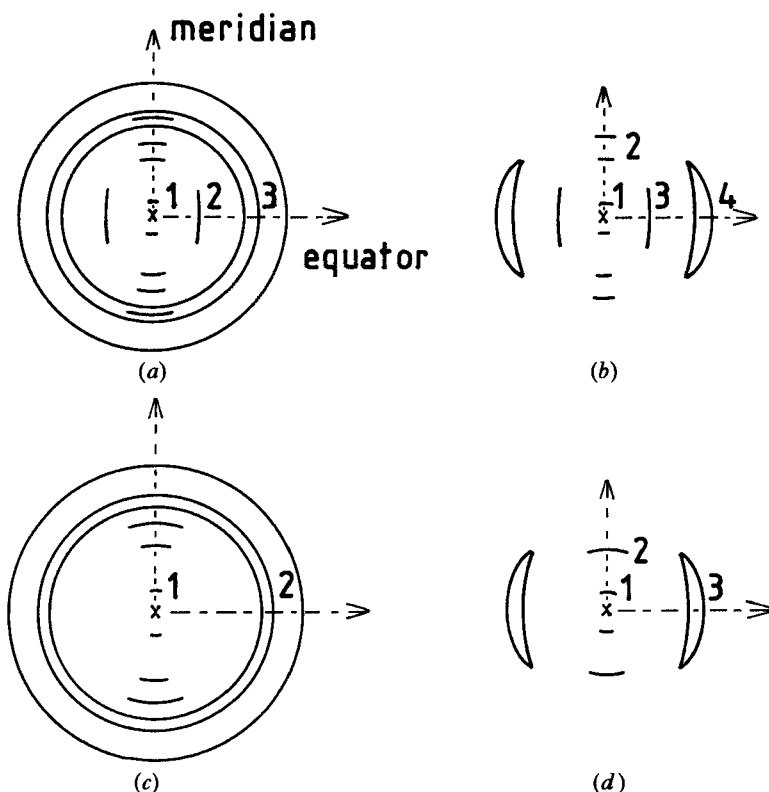


Figure 1. Schematic representation of X-ray diffraction patterns. (a) Polymer 1; $T = 20^{\circ}\text{C}$. (1) 001 reflections, (2) weak diffuse 8.2 \AA reflection, (3) $hk0$ reflections. (b) Polymer 1; $T = 80^{\circ}\text{C}$. (1) 001 reflection, (2) diffuse reflections, (3) weak diffuse 8.2 \AA reflection, (4) diffuse arc. (c) Polymer 2; $T = 20^{\circ}\text{C}$. (1) 001 reflections, (2) $hk0$ reflections. (d) Polymer 2; $T = 225^{\circ}\text{C}$. (1) 001 reflection, (2) sharp 003 reflection, (3) diffuse arc.

DSC and microscopy studies had identified transitions at 117°C , 175°C and a smectic–isotropic transition at 225°C . Mechanical alignment of the samples proved difficult. An X-ray diffraction photograph of a partially aligned sample, figure (c), taken at 20°C shows: (i) on the meridian a moderately intense reflection with d spacing equal to 19.28 \AA , a sharp third order reflection with similar intensity at 6.38 \AA and a weaker fourth order at 4.78 \AA ; (ii) three complete rings with maximum intensity on the equator are observed at 4.40 , 3.92 and 3.17 \AA with strong, medium and weak intensities respectively. Similar photographs were obtained as the temperature was increased up to 190°C . Above this the photographs were typical of a S_A , for example at 225°C the photograph showed (i) on the meridian a weak reflection with d spacing of 18.75 \AA , (ii) a sharp reflection with medium intensity at 6.35 \AA and (iii) on the equator a diffuse reflection with a value for D of 5.12 \AA . At 240°C the first order layer spacing disappeared but a faint maximum of 9.29 \AA appeared with the 6.35 \AA maximum becoming slightly stronger and the outer diffuse reflection gave D of 5.04 \AA . By 255°C all the sample material had entered the isotropic phase and on subsequent cooling to 20°C gave the original 20°C photograph.

4. Discussion

The three outer rings found on the low temperature forms of both compounds can be indexed as the 110, 200 and 210 reflections; cell parameters of $a = 7.84$, $b = 5.32$ Å and $c = 19.28$ Å are obtained for the bromobiphenyl and $a = 8.06$, $b = 5.57$ Å and $c = 21.52$ Å for the bromoester assuming orthogonal axes. The strong 110 reflection suggests a concentration of electron density in this direction and is the probable line of the backbone.

The photographs of the bromoester above 60°C showed a S_A phase. The calculated length of the molecule, assuming that the mesogenic groups lie perpendicular to the main polymer chain, is 38.4 Å. The observed lamellar d spacing of 21.2 Å could be explained in terms of interdigitation with an almost total overlap of 17.2 Å. The diffuse reflection at 8.20 Å is due to a periodicity associated with the backbone either between the backbones or within the backbone.

DSC data for the bromobiphenyl predicted two smectic phases above the crystalline phase. The higher temperature smectic phase for the bromobiphenyl is smectic A. The calculated molecular length is 34.2 Å which requires interdigitation with complete overlap to satisfy the 18.75 Å first order layer spacing. As the isotropic temperature is approached the S_A arrangement alters and the first order equatorial reflection disappears and a 9.29 Å spacing appears. This could be the second order of the S_A arrangement or it could arise from columns of mesogenic units and backbones. As the temperature reaches the isotropic this order breaks down with the increased mobility of the backbones and these reflections disappear.

X-ray diffraction photographs for the bromobiphenyl in the temperature range of the lower smectic phase were indistinguishable from those at room temperature.

Various studies [1] have ascribed similar diffraction patterns to either crystalline or smectic E phases and a recent structure report on a side chain polymethacrylate by Duran *et al.* [2] stated that such a pattern indicated a smectic E phase. Since the form of these can be ascribed to either a crystalline phase or a smectic E phase it is possible that this phase is smectic E.

5. Conclusions

The X-ray studies indicate that the bromoester polymer has a smectic A phase and the bromobiphenyl polymer has smectic E and smectic A phases.

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