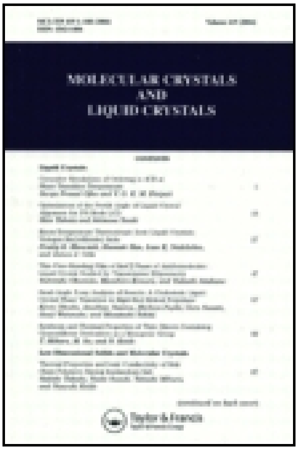

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An X-Ray Diffraction Study of Liquid Crystal Polysiloxane Copolymers

H. H. Sutherland [a] , Z. Ali-adib [a] , B. Gasgous [a] & G. Nestor [b]

[a] Dept. of Physics, University of Hull, Hull, England

[b] Dept. of Chemistry, University of Hull, Hull, England

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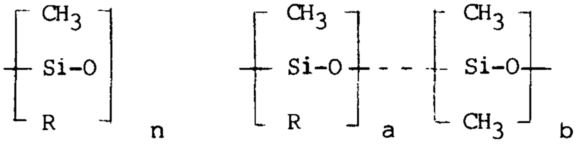
AN X-RAY DIFFRACTION STUDY OF LIQUID CRYSTAL POLYSILOXANE COPOLYMERS

H.H. SUTHERLAND, Z. ALI-ADIB, B. GASGOUS
Dept. of Physics, University of Hull, Hull, England

G. NESTOR
Dept. of Chemistry, University of Hull, Hull, England

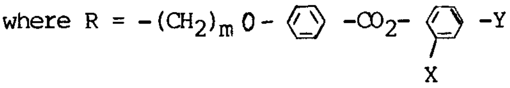
<u>Abstract</u> The smectic and nematic phases of a series of liquid crystal polymers based on (I) a poly (hydrogenmethylsiloxane) backbone and (II) a poly (hydrogenmethyldimethylsiloxane) copolymer backbone have been investigated by X-ray diffraction.

The polymers have the form



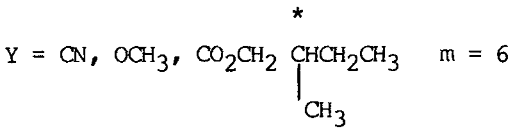
$$\left[\begin{array}{c} CH_3 \\ -Si-O \\ R \end{array}\right]_n \qquad \left[\begin{array}{c} CH_3 \\ -Si-O- \\ R \end{array}\right]_a - - \left[\begin{array}{c} CH_3 \\ -Si-O- \\ CH_3 \end{array}\right]_b$$

(I) (II)



where $R = -(CH_2)_m O - C_6H_4 - CO_2 - C_6H_3(X) - Y$

$X = H, CH_3$ when $m = 8$, $Y = CN$



$Y = CN, OCH_3, CO_2CH_2\overset{*}{C}H(CH_3)CH_2CH_3$ $m = 6$

A comparative study of results obtained from the homopolymer and the statistically random copolymer is presented. The dependence of spacing on the length of the flexible spacer and terminal grouping of the mesogenic side chain is discussed and possible packing models deduced.

INTRODUCTION

Thermotropic liquid crystal 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 liquid crystal polymers based on a poly(hydrogen methyl dimethyl siloxane) backbone.

The copolymer materials were prepared using a Petrarch PS122.5 polyhydrogen methyldimethyl siloxane backbone and the homopolymer materials on a DOW 1107 polyhydrogen methyl siloxane backbone.

EXPERIMENTAL

The X-ray diffraction patterns were recorded on flat photographic plates with sample to plate distance between 6 and 10 cms. The radiation used was CuKα obtained using a graphite monochromator. The samples were initially mechanically aligned by stretching, inserted into 0.3, 0.5 or 1 mm diameter glass capillaries and attached to a metal heating block. The temperature, measured using a chromel-alumel thermocouple, could be controlled to $\pm 0.2^{o}$ C. In subsequent experiments several of the samples were found to align in a magnetic field of 1.6T.

X-ray diffraction photographs were taken at regular intervals during heating from 15°C up to the isotropic phase.

RESULTS AND DISCUSSION

$R = (CH_2)_m-O-\langle O \rangle-CO_2-\langle O \rangle CN$ $m = 3 - 6$

The homopolymer and copolymer samples of mechanically aligned specimens have some common features. Both give sharp low angle equatorial first and second order reflections, and a diffuse meridianal maximum corresponding

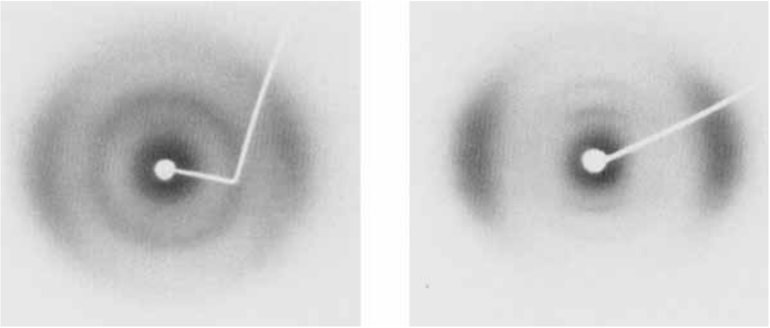

(a) (b)

FIGURE 1. X-ray photographs for (a) copolymer and (b) homopolymer for m = 4.

to an intermolecular distance, D, of approximately 5A. In addition, the homopolymers gave two broader equatorial reflections with d-spacings of approximately 10A and 7A, the values varying with the lengths of the spacer unit; whereas the copolymers gave a diffraction ring with d-spacing of 7-8A. In the case of the homopolymer these are due to columns of mesogenic units and backbone and in the copolymer to the backbone. The smectic layer spacing was obtained as a function of temperature for both sets of polymer Fig.1 and was found to decrease as the temperature

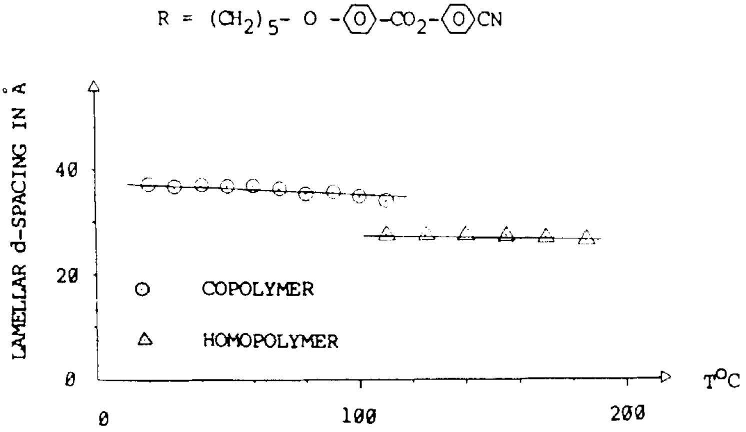


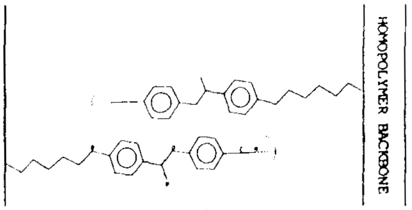
FIGURE 2. Variation of the layer spacing with temperature.

was increased, the average value for the copolymer was -.03A K^{-1} and for the homopolymers -.014A K^{-1}. In addition the copolymer layer spacing for m of 4,5 and 6 was approximately 8-9A larger than that for the corresponding homopolymer, Table I. The observed interlayer spacings are

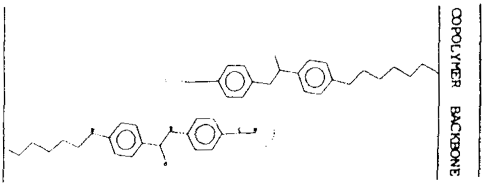
TABLE I Overlap distances for the observed layer spacing at T_{I-30}

m	The calculated length of the fully extended side chain (A)	Copolymer		Homopolymer	
		d,A	The overlap distance (A)	d,A	The overlap distance (A)
3	39.7	33.0	6.7	27.0	12.7
4	42.3	34.3	8.0	25.7	16.6
5	44.3	35.5	8.8	27.0	17.3
6	47.1	39.9	8.1	30.0	17.1

considerably smaller than the calculated length of the molecule, assuming that the mesogenic groups lie perpendicular to the main polymer chain. Such a decrease can be explained in terms of tilting or interdigitation. However there is no evidence for a smectic C phase and an interdigitated smectic A arrangement is most likely. In the copolymer there is a partial overlap of the core and in the homopolymer total overlap of the core but not of the flexible spacer, Fig.3. Both arrangements are



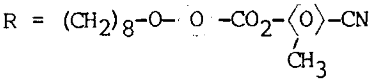
HOMOPOLYMER OVERLAP



COPOLYMER OVERLAP

FIGURE 3. Schematic representation of packing.

energetically favourable and are consistent with the greater flexibility of the copolymer backbone and the weaker forces between the reduced number of mesogenic units in the copolymer.



$R = (CH_2)_8\text{-O-}\langle O\rangle\text{-}CO_2\text{-}\langle O\rangle\text{-}CN$, CH_3

The diffraction photographs of the copolymer and homopolymer were similar to those obtained from the previous samples. The copolymer gave first and second order lamellar spacings of 43.8 and 21.5A at 25°C, which decreased at -.12A K^{-1} as the temperature was increased, Fig.4. This spacing is consistent with the spacing obtained for the series without the methyl group and can be explained in terms of an interdigitated smectic A structure with a core overlap of 8.4A. There were the diffuse circular ring at 8.4A and the outer diffuse meridianal

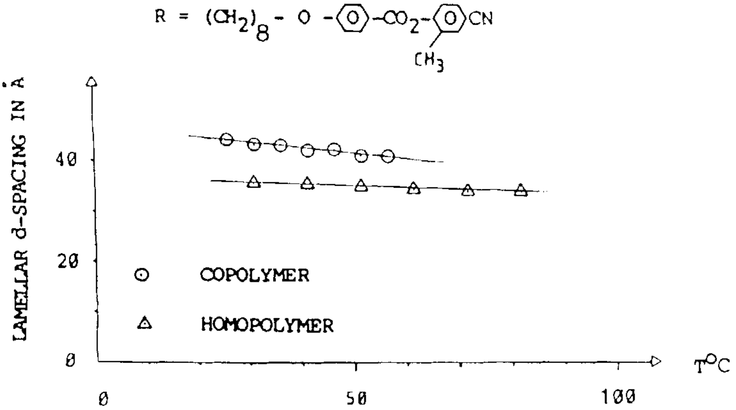
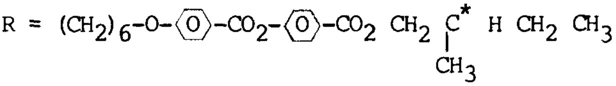


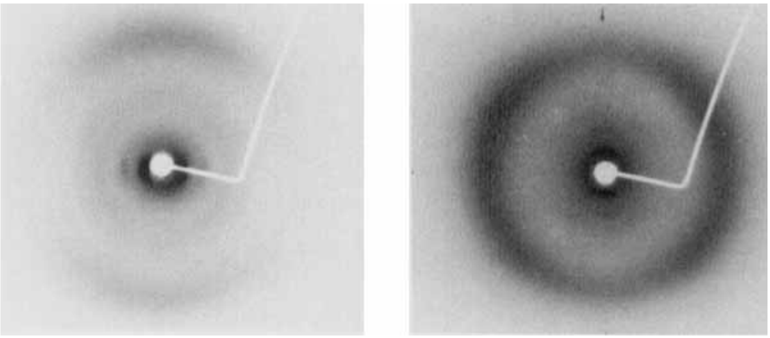
FIGURE 4. Variation of layer spacing with temperature.

reflection. The homopolymer at 20°C gave a first order lamellar spacing of 35.6A and when the temperature was raised above 30°C a second order reflection was observed. The spacing which is approximately 8A smaller than that for the copolymer is due to a smectic A interdigitated structure with a core overlap of 16.4A - a result which is similar to those obtained for the previous group compounds.



$$R = (CH_2)_6-O-\langle O\rangle-CO_2-\langle O\rangle-CO_2\;CH_2\;\underset{\underset{CH_3}{|}}{\overset{*}{C}}\;H\;CH_2\;CH_3$$

Non-aligned samples of the copolymer gave a first order reflection at 30.1A, a broad diffuse band at approximately 7-9A and the diffuse reflection at d = 4.6A. Alignment in a 1.6T magnetic field gave at 20°C an intense first order meridianal reflection of 30.1A and weaker second order of 14.6A, two extended diffuse arcs of 8.18 and 6.0A and a diffuse equatorial reflection of D = 4.96A. The lamellar spacing, which decreased -.04A K^{-1}, with increasing

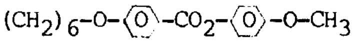


(a) (b)

FIGURE 5. X-ray photographs for (a) copolymer and (b) homopolymer.

temperature, is considerably less than the length of two mesogenic units plus backbone, 52.8A. This discrepancy can be accounted for if the copolymer has an interdigitated smectic A structure with an overlap of 22.7A which indicates almost total overlap. The two diffuse arcs at 8.8 and 6.9A probably arise from columns of mesogenic units and backbone which are perpendicular to the layers.

The diffraction pattern from non-aligned samples of the homopolymer gave a series of concentric circles. Mechanically aligned samples produced a strong first order equatorial reflection of 24.6A and moderately strong second order of 12.2A at 20°C. The lamellar spacing was constant with increasing temperature. The spacing of 24.6A is smaller than even the length of one mesogenic unit and can be explained in terms of an interdigitated structure with the mesogenic units inclined at 30° to the layer. In addition there were two sets of diffuse reflections at 8.85 and 6.91A. These took the form of four sectors whose maxima lay along two lines which were inclined at 30° to the equator. The diffuse reflections arise from columns of mesogenic units and backbone which are lying at 30° to the mesogenic units in the layers.

R =


The copolymer and the homopolymer were aligned in a 1.6T magnetic field; both gave similar diffraction patterns exhibiting nematic phases; those for the homopolymer are in agreement with the results of Zugenmaier and Mügge[1]. Although the homopolymer at 20°C was observed to crystallise with time, no such effect was noted for the copolymer. At 20°C the copolymer on the meridian gave a strong first order maximum of 30.1A in the form of four spots, together with a weak second order reflection, a diffuse 10.9A reflection in the form of 4 segments with the maximum inclined at ~25° to the meridian; a ring of spacing 8.0A with maximum intensity on the meridian; and diffuse arcs with spacing of 6.23 and 4.58A. On the equator there was the usual diffuse reflection with D of 4.92A. Since the length of two mesogenic units plus backbone is 46.0A, the lamellar spacing of 30A implies interdigitation with core overlap of 15.4A. This can be compared with the corresponding homopolymer spacing of 23A which requires total overlap of core and alkyl chain together with a random tilt of 20°.

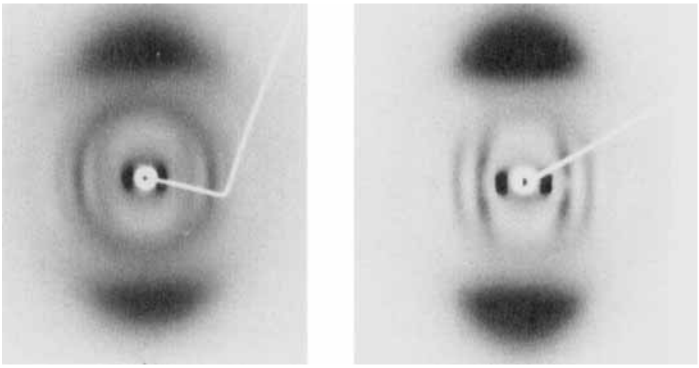

(a) (b)

FIGURE 6. X-ray photograph of (a) copolymer and (b) homopolymer.

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