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X-ray Investigation of Liquid Crystalline Side Chain Polymers

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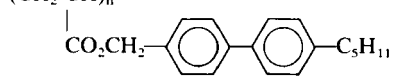
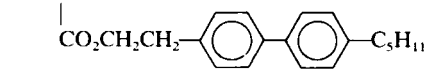
An X-ray investigation has been carried out on two smectic polymers with polyacrylate backbones. Values for the lamellar spacing, and the lateral distance between the mesogenic groups, were obtained and their variation with temperature investigated. The differences in the diffraction patterns of the two polymers studied, appear to be related to the length of the flexible spacer linking the mesogenic group to the backbone, —with the longer spacer allowing a more ordered mesophase structure to develop.

Keywords: liquid crystals, X-ray diffraction, polymers

INTRODUCTION

X-ray diffraction studies have been performed on two side chain liquid crystal polymers with polyacrylate backbones. The preparation of the liquid crystal polymers together with the phase identification by microscopy and differential scanning calorimetry were made by Gemmell.[1] The structural formulae and the transition temperatures for the studied polymers are:

code	Molecular formula	Transition temp. (C) (heating)
P1		G 67 S 130°C I
P2		G 65 S 192°C I

EXPERIMENTAL

The X-ray experiments were performed with a flat plate camera using graphite monochromated CuK_α radiation. The specimen to film distance was 8 cm and exposure times were of 2 to 3 hours. The powder samples were contained in Lindemann glass capillaries of diameter 0.3 mm placed in a heating block whose temperature, measured with a chromel-alumel thermocouple, was kept constant to ± 0.2°C.

RESULTS AND DISCUSSION

Polymer P1

X-ray diffraction photographs were taken in 10°C steps during the heating of the polymer from 20°C when it is in a glassy phase up to 140°C when it is in the isotropic phase. All the photographs up to the isotropic phase were similar, showing a low angle broad diffraction maximum with d-spacing of 35.9 Å together with a broad diffuse ring whose position corresponded to an intermolecular distance D of 5.1 Å and, a sharp spotty ring with a d-spacing of 2.96 Å, possibly corresponding to a periodicity along the backbone.

The 35.9 Å reflection was broader and weaker than the typical diffraction maximum obtained for the S_A or S_C phase and there was no indication of a second order reflection. This suggests that the order is of a shorter range than that normally obtained in these phases. This weaker value for the intensity has been previously observed in two cyano substituted side chain liquid crystal polysiloxanes (Sutherland and Rawas).[2] During heating, the lamellar spacing was found to be constant and there was no obvious indication of any variation in its intensity. The spacing of 35.9 Å is only 3 Å smaller than the molecular length of 38.9 Å assuming a polymer chain with mesogenic groups extended in a direction perpendicular to the main polymer chain. Such a reduction is commonly observed in low molecular weight smectic A compounds and can be accounted for by a random tilt of the molecules within the individual layers. A tilt of some 23° would give the necessary reduction.

Polymer P2

The X-ray diffraction investigations were performed using virgin samples which were heated in 10°C steps from 20°C, the glassy phase to 200°C when the sample was in the isotropic phase. The introduction

of an additional CH_2 group in the alkyl spacer gave somewhat different X-ray diffraction results from the previous compound. At 20°C the X-ray diffraction pattern of the virgin material as prepared showed a sharp first order low angle maximum with a d-spacing of 37.0 Å together with the usual broad outer maximum corresponding to an intermolecular distance D of 5.0 A. This outer maximum was sharper than normally observed for a S_A or S_C but broader than a S_B and somewhat similar to those of the S_F, S_I or hexatic B phase.

On heating, second and third order maxima of the 37 Å spacing appeared. The d-spacing of the first order diffraction maximum remained constant with temperature at 37.0 Å up to the isotropic phase. However, its intensity increased reaching a maximum value in the temperature range 140–150°C and then decreases as the isotropic phase is approached. Two X-ray diffraction patterns taken at 20°C

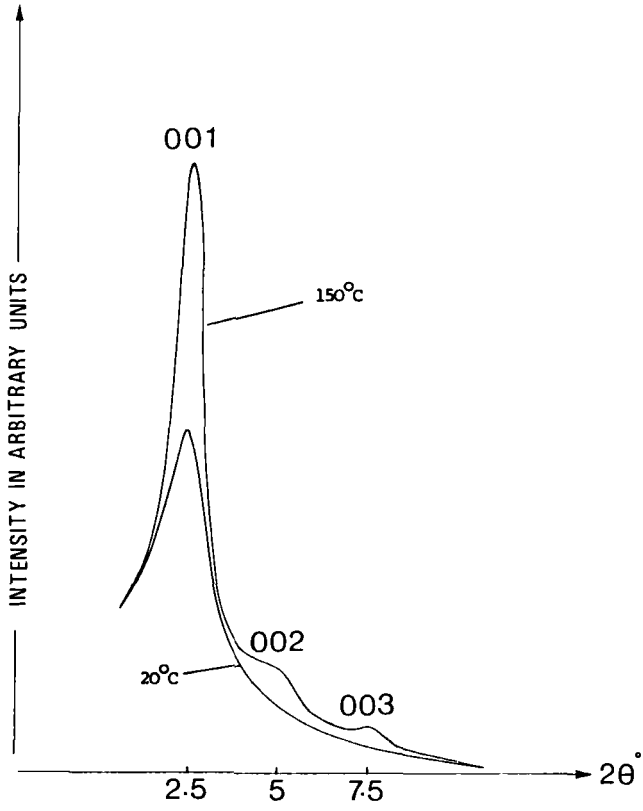


FIGURE 1 The intensity of the layer reflection of P2 and 20°C and 150°C.

(when it is in the glassy phase) and at 150°C (when in the smectic A phase) with a virgin sample under the same operating and processing conditions were scanned using a Joyce Loebl densitometer, Figure (1). The intensity of the first order maximum for the 150°C increased by about 100% and the half width at half maximum was reduced by 50%. These results suggest that the long range order within the layer increases with increasing temperature, a similar finding was previously reported by Tsukruk et al.[3]

During heating a virgin sample, the broad outer ring maintained

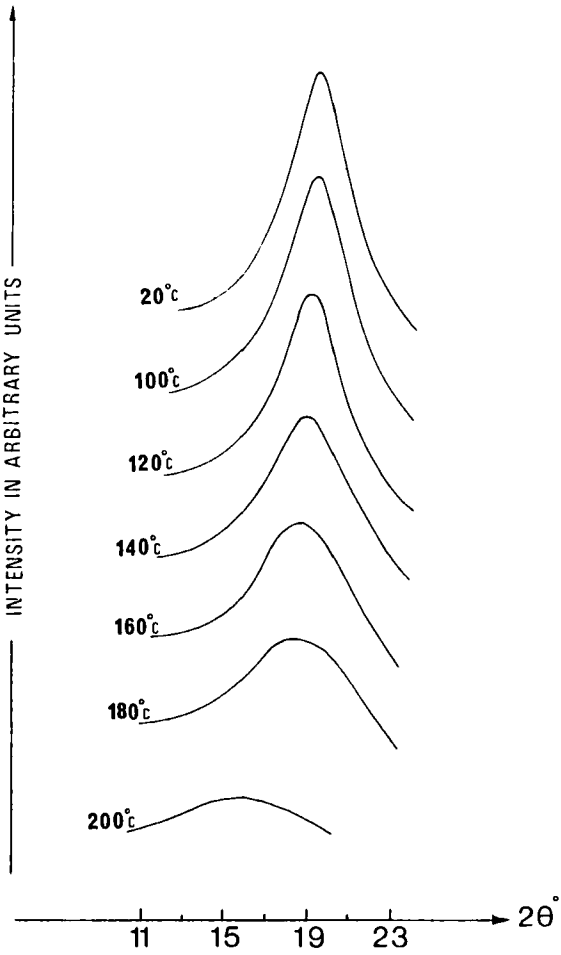


FIGURE 2 Variation of the intensity of the diffuse outer ring with the temperature for the sample P2.

its appearance (sharper than normal) up to 120°C when it became more diffuse and by 140°C was typical of that observed for a S_A or S_C phase, as shown in Figure (2). If the sample was heated up to the isotropic phase and allowed to cool to 20°C the X-ray diffraction pattern obtained at 20°C was different from that of the virgin material but similar to that recorded at 140°C showing 1st, 2nd and 3rd orders of the low angle maxima and an outer diffuse ring typical of S_A or S_C. The lateral distance D between the mesogenic groups is constant with the glassy phase and increases with increasing temperature in the smectic phase, finally giving a value of 6.2 Å in the isotropic phase, Figure 3. This can be attributed to a change in the organisation of the mesogenic groups around the main chain.

The low angle d spacing of 37.0 Å can be related to the length of the mesogenic unit and the backbone thickness. As in the first compound the observed d spacing is less than the calculated length of 40.7 A. The reduction of 3.7 Å can be accounted for by a random tilt of approximately 25° and there is probably no need to invoke some form of interdigitation of the mesogenic units as suggested by Gudkov & Chistyakov.[4] A similar value for the smectic layer spacing has been obtained by Richardson.[5] The differences in the diffraction patterns of these two polymers at room temperature and during heating, together with the lack of annealing in P1 (as shown by the non-

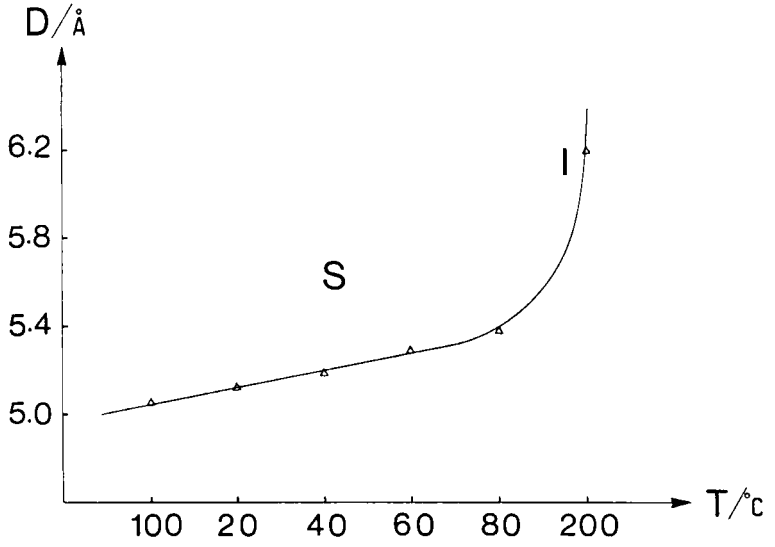


FIGURE 3 Temperature dependence of the spacing, D, for the outer ring for P2.

appearance of a second order) can be understood in terms of the short spacers in P1. These restrict the movement of the mesogenic groups and hence make it more difficult for the smectic ordering to be established.

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