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Some novel smectic C* liquid-crystalline side-chain polymers
Polymethacrylates and poly α-chloroacrylates†

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Novel methacrylate and α-chloroacrylate side-chain polymers in which the mesogenic moieties are based on the 4-n-alkoxyphenyl-4'-(4"-methylhexyloxy) benzoates have been characterized by differential scanning calorimetry, optical microscopy and X-ray diffraction. Polymethacrylates give smectic A phases although the homologue where $n = 11$ exhibits a smectic C*–smectic A transition. There is no real evidence for liquid-crystalline properties in the poly-α-chloro-acrylates where $n = 2$ or 6. The poly-α-chloroacrylate for which $n = 11$ exhibits a layer structure with the side chains orthogonal to the layer planes as in the smectic A phase. However, this smectic phase has a higher order of the molecules within the layers; the chlorine atoms do impose a local ordering of the mesogenic side groups.

1. Introduction
In the first paper of this series, the synthesis of a number of polymers of structure

$$\{CH_2 - CX\}$$

(I)

$$X = H, CH_3, Cl, \quad n = 2, 6, 11$$
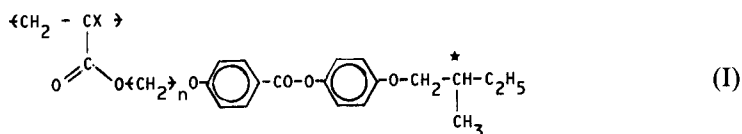
was described [1]. In a latter paper, polarized optical microscopy, D.S.C. and X-ray structural characterization showed that all the polyacrylates ($X = H$) give smectic A phases; the polyacrylate where $n = 2$ exhibits a smectic C*–smectic A transition [2]. In the present paper we report on the characterization of the polymethacrylates ($X = CH_3$) and poly α-chloroacrylates ($X = Cl$).

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The object of this work was threefold:

> to investigate the effect of lengthening the flexible spacer group (which links the mesogenic side group to the polymer backbone) upon the liquid crystal behaviour of the polymers;
> to compare the liquid crystal properties of a series of related polymers;
> to determine as much structural detail as possible about the mesophases by X-ray diffraction.

2. Experimental

A detailed description of the synthesis of polymerizable monomers is given elsewhere [1]. Polymerizations were free radical and initiated at 70°C with azo-bis-isobutyronitrile as described previously [1].

A differential thermal analyser (Du Pont 1090) was used for determining phase transition temperatures and enthalpies; the heating rate was 20°C min^{-1}. The D.S.C. curves obtained on second heating were used to obtain all of the experimental data. The positions of peak maxima were taken as phase transition temperatures. The glass transition temperature, T_g, was estimated from the point of intersection between the initial base line and the sloping portion of the line obtained as the base line shifts during the glass transition. For the evaluation of the transition enthalpies, an indium sample was used as the standard.

Microscopic investigations were carried out on a polarizing light microscope (Olympus BHA-P) fitted with a Mettler FP52 microfurnace in conjunction with a FP5 control unit.

The layer spacings were measured by X-ray diffraction usually on powder specimens but sometimes using aligned samples contained in 1 mm Lindemann glass tubes. CuKα radiation, monochromated by a flat graphite crystal in conjunction with a pinhole collimator was used. Exposure times of 1 to 3 hours were required using flat photographic films. The sealed capillary tubes were mounted in an electrically heated oven, the temperature of which was controlled with a precision of 0·5°C using a platinum resistor as the sensing element. The whole diffraction equipment was contained inside a tank which was evacuated during experiments to reduce the scattering of X-rays by air. It was found that some of the polymers could be aligned by warming lumps of them and pulling thin strings with a pair of tweezers.

3. Results and discussion

3.1. *Thermal properties*

The table gives some of the previous results on polyacrylates and compares them with our present data. It is useful to summarize some general points.

(*a*) Relative to conventional poly(*n*-alkylacrylates) ($T_g = -80°C$–$0°C$) and poly(*n*-alkylmethacrylates) ($T_g = -20°C$–$72°C$), the glass transition temperatures of the materials studied are quite high. It is evident that the bulky mesogenic group causes severe hindrance to main chain motions [3].

(*b*) Replacement of hydrogen in the polymer backbone by another substituent such as a methyl group or a chlorine atom enhances T_g values. This results mainly from a stiffening of the polymer backbone.

(*c*) Extending the length of the flexible spacer lowers the glass transition temperature. For example, T_g is decreased by 50°–70°C on passing from the polymers

Thermal properties of the polymers studied.

Polymer		Transition temperatures °C				
n	X	T_g	T_m	$T_{S_1 S_2}$	T_1	$\Delta H_1/\text{kJ/m.u.}\|$
2	H	65		110	146	1·80
6	H	15	46†	68‡	87	4
11	H	32	59		108	6·56
2	CH$_3$	110§			155	3·51
6	CH$_3$	40			90	5·02
11	CH$_3$	10–40§	58	90	106	6·94
2	Cl	97§	172			4·85
6	Cl	37	94			5·02
11	Cl	10–40§	62	86‡	112	7·48

† Small endotherm which appears only after sample annealing at 30°C for 6 hours.
‡ Very small endotherm. We were unable to detect any differences in the diffraction patterns and in the texture at this temperature.
§ These glass transitions were hard to detect.
‖ m.u.: monomer unit.

where $n = 2$ to their homologues where $n = 6$. This behaviour is very general for polyacrylate and polymethacrylate series and reflects the increased plasticizing action of the flexible spacers [4, 5]. It is also quite clear that long flexible spacers move the bulky mesogenic groups farther away from the polymer backbone which causes less hindrance to main chain motions. The remaining anomaly is that the glass transition temperature of polymer H11 (32°C) is higher than that of polymer H6 (15°C) and not lower, as would be expected. This unusual behaviour for a homologous series is again reminiscent of results obtained for poly(n-alkyl acrylates) and poly(n-alkyl methacrylates): above a critical value of n, partial crystallization of the aliphatic side chains occurs which results in an increase in T_g.

3.2. Texture observation

Optical microscopy of the smectic phase of the $n = 2$ and $n = 6$ members of the polymethacrylate series does not reveal any specific textures (cf. figure 1). In contrast, polymer CH$_3$11 exhibits two mesophases, the textures of which are reminiscent of those of low molar mass smectics [6, 7]. At the transition from the isotropic liquid to the high-temperature smectic phase ($T_c \sim 105$°C), bâtonnets appear first similar to those of smectic A phases. On further cooling, they grow, merge and result in a focal-conic fan texture (cf. figure 2). Occasionally it is possible to observe a variant of the focal-conic texture with spherulitic domains. These microscopic observations are consistent with the existence of a smectic A phase. As the temperature falls below 90°C the low temperature smectic phase appears. The texture obtained is either focal-conic (cf. figure 3) or Schlieren (cf. figure 4). The focal-conic texture is obtained from the clear, focal-conic texture of the preceding smectic A phase while the Schlieren texture is obtained from the homeotropic regions of the A phase. This suggests a smectic C* or smectic F* phase as the low temperature smectic phase.

There is no real evidence for liquid crystal properties in polymers where $X = $ Cl and $n = 2$ or 6. Rather these homopolymers resemble typical semicrystalline polymers. They melt as ordinary polymers to give a clear, isotropic fluid phase. In
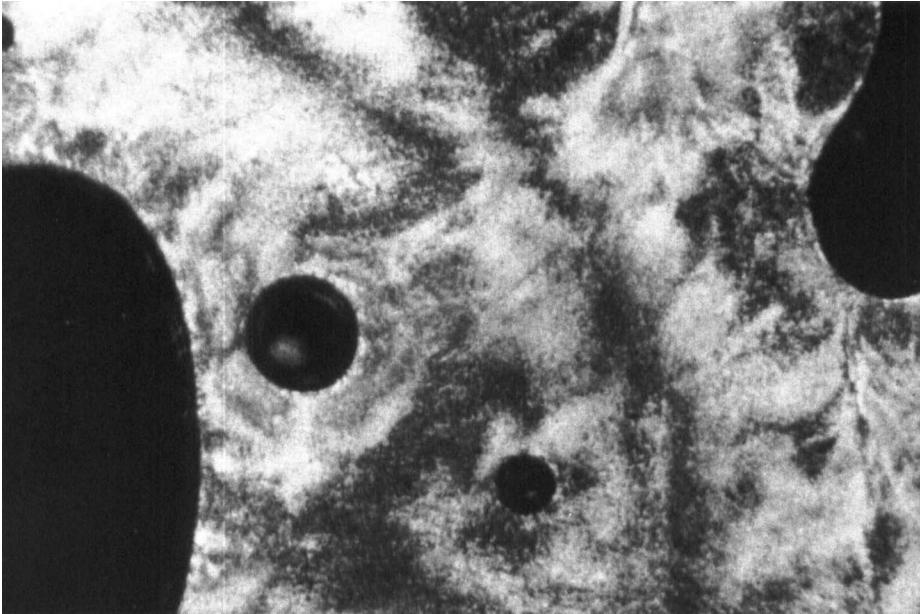
Figure 1.   The rough texture of the smectic phase from polymethacrylate where $n = 6$, crossed polarizers, magnification $\times 200$.
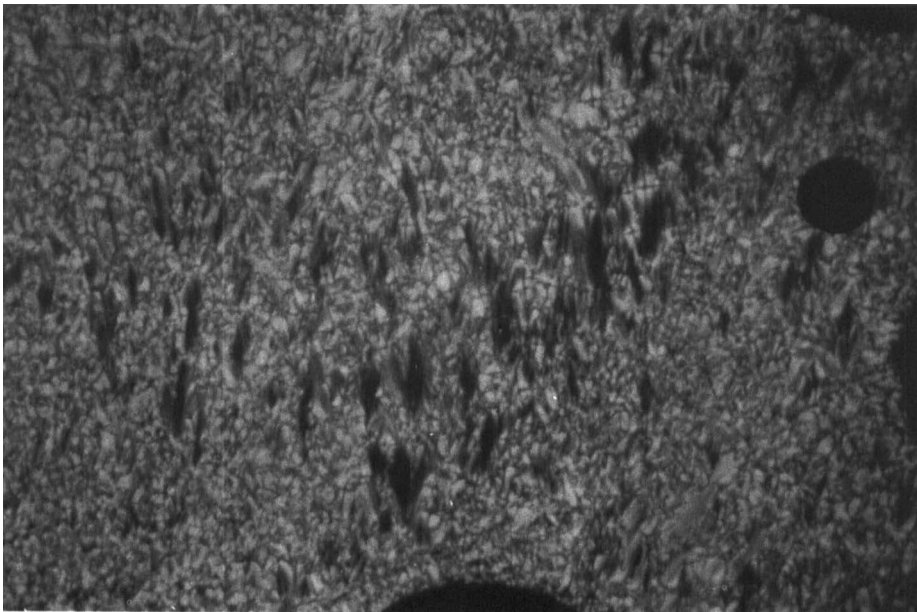

Figure 2.   Smectic A focal-conic fan texture of polymethacrylate where $n = 11$ at 92°C, crossed polarizers, magnification $\times 200$.
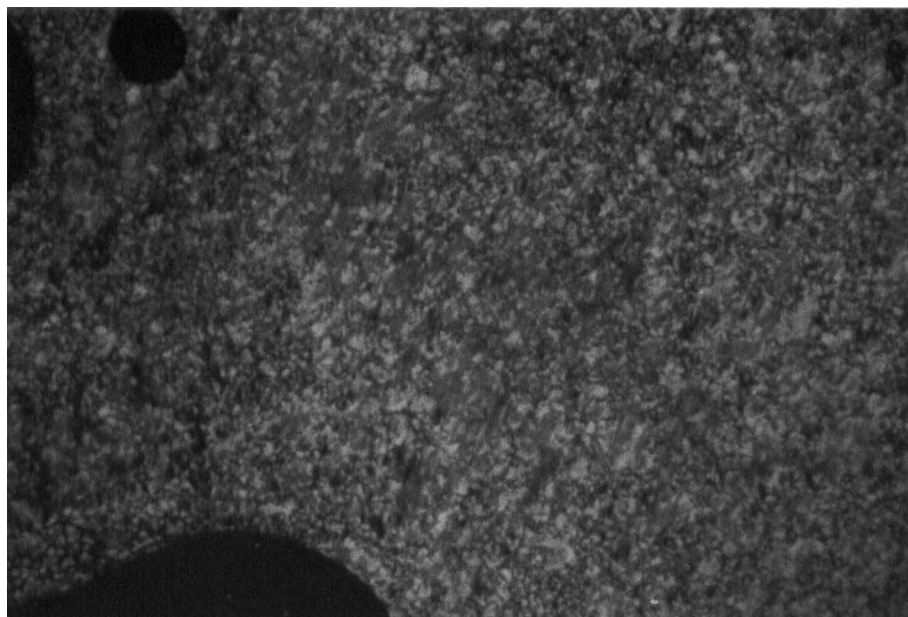
Figure 3. Focal-conic texture of the low-temperature smectic phase from polymethacrylate where $n = 11$, 79°C, crossed polarizers, magnification × 200.
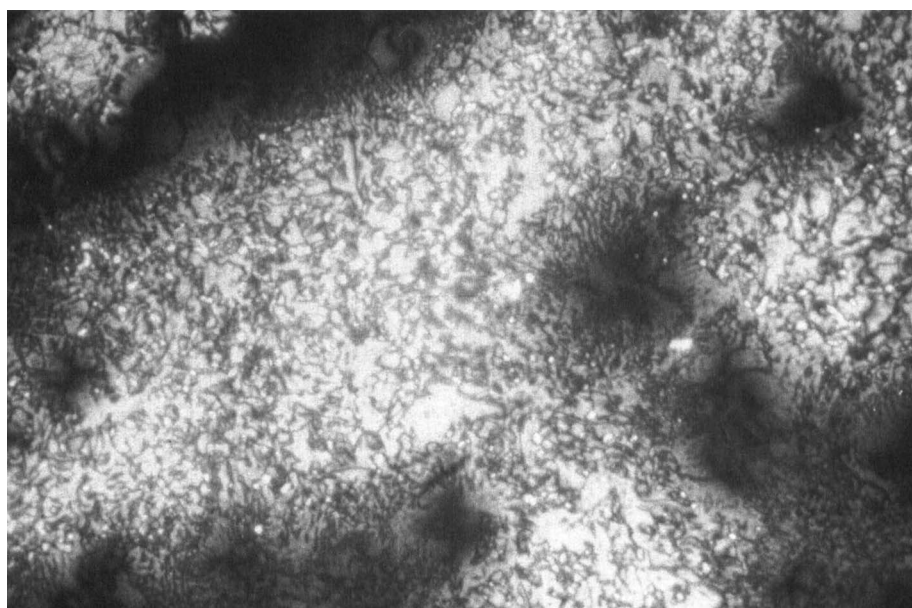

Figure 4. Schlieren texture of the low-temperature smectic phase from polymethacrylate where $n = 11$, crossed polarizers magnification × 200.

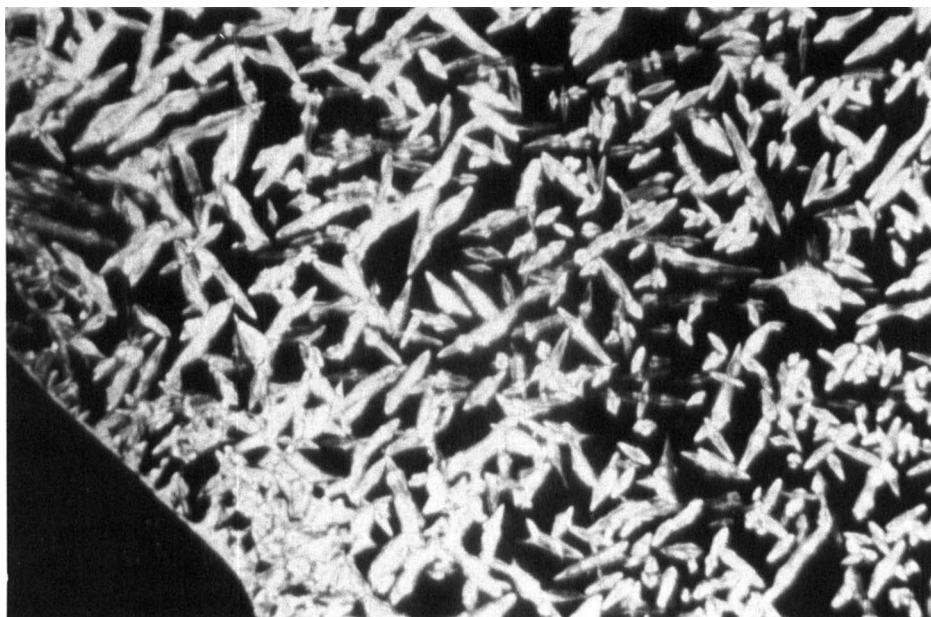Figure 5.   Bâtonnets at the smectic–isotropic phase transition for polymer Cl11, 105°C, crossed polarizers, magnification × 200.
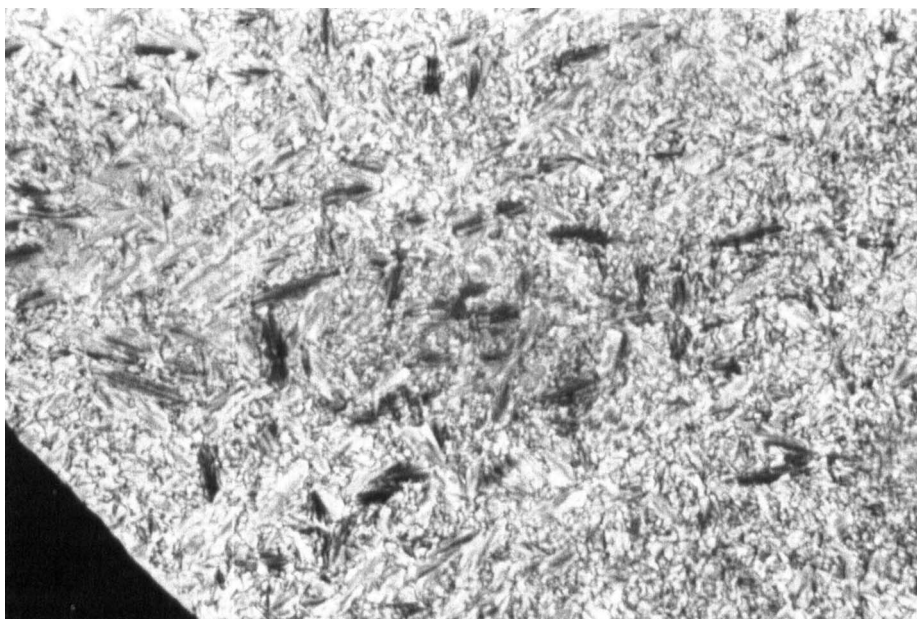

Figure 6.   Smectic focal-conic texture of polymer Cl11 at 100°C, crossed polarizers, magnification × 200.

contrast, the $n = 11$ member of this series exhibits a smectic phase. Upon cooling the isotropic melt, the smectic phase begins to separate at the clearing point in the form of bâtonnets (cf. figure 5) which, after further cooling, join together to form larger domains with either a focal conic texture (cf. figure 6) or a mosaic texture (cf. figure 7).
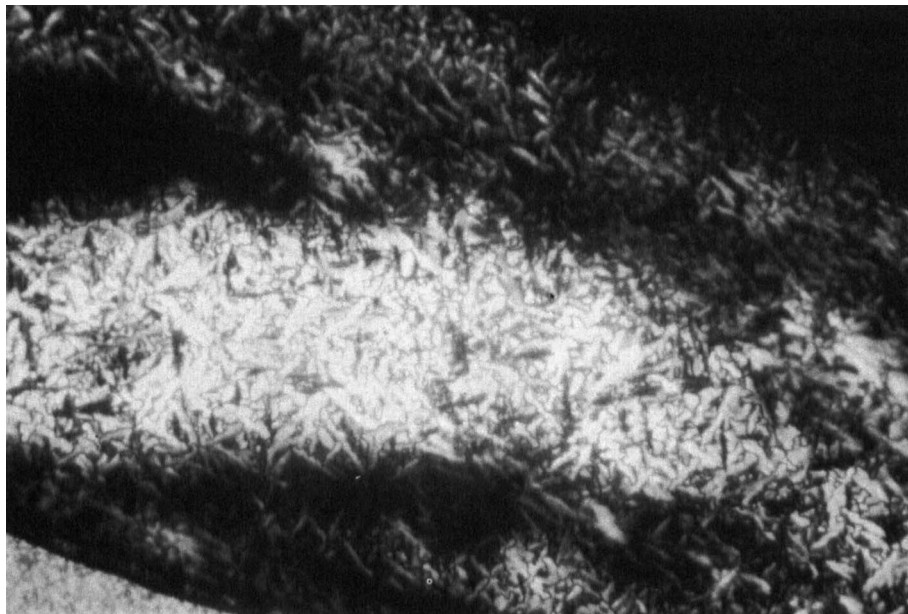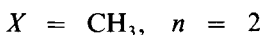

Figure 7. Unidentified texture of the smectic phase from polymer Cl11 at 97°C, crossed polarizers, magnification × 200.

3.3. *X-ray diffraction patterns*

$$X = CH_3, \quad n = 2$$

Above the glass transition temperature (~ 110°C), the polymethacrylate where $n = 2$ gives diffraction patterns consisting of a broad, diffuse outer ring in the $q = 4\pi \sin\theta/\lambda$ range 1·3 to 1·4 Å^{-1} related mainly to the lateral spacing between mesogenic side groups and a sharp inner ring giving d spacings of about 43 Å; these we have interpreted as a smectic layer spacing (cf. figures 8, 9). A second order ring is also visible. It is to be noted that the layer spacings correspond approximately to twice the length $L = 22.5$ Å of the side chain, calculated from standard bond lengths and angles with the assumption of an all-trans molecular conformation. These results are consistent with the formation of a bilayer smectic A$_2$ phase, in agreement with texture observations.

At the glass transition, the value of d decreases with decreasing temperature but this decrease tapers off, and at lower temperatures the layer spacings lie in the range 40·5–41 Å, which is less than twice the extended model length of the side chain. We are forced therefore, to invoke either some form of interdigitation of the mesogenic side groups or a tilted smectic-like ordering (the difference between the layer spacing d and the extended model length L would imply a tilt angle of 19°). It is impossible to distinguish between these two models from the X-ray patterns of powder samples.
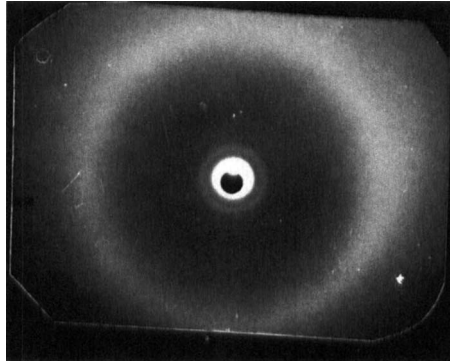
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Figure 8.   X-ray diffraction photograph from polymethacrylate where $n = 2$, powder sample at 130°C.
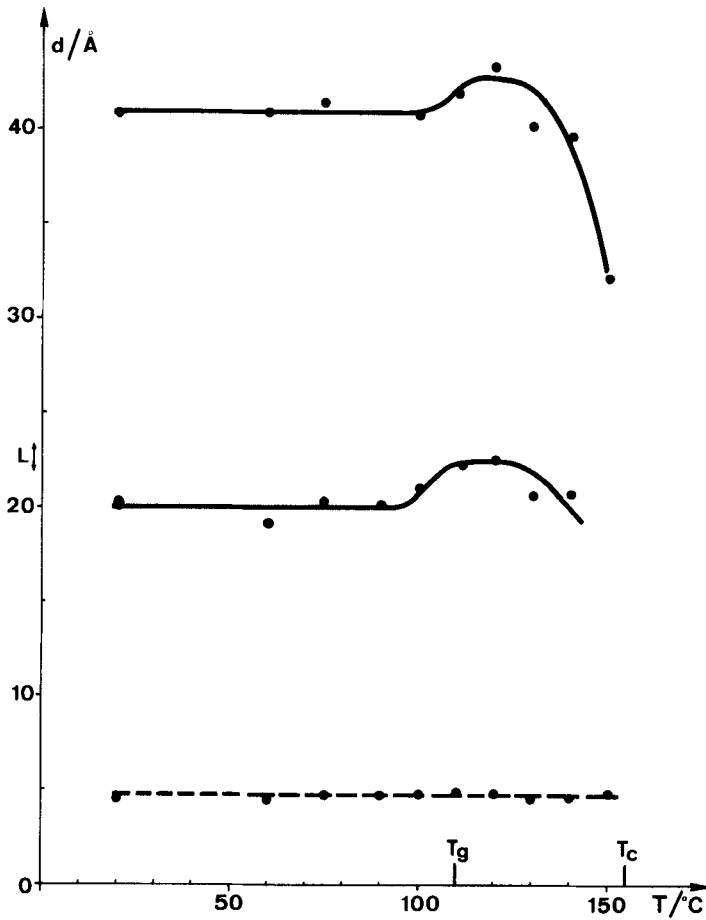

Figure 9.   Intermolecular distance (– – – –) calculated assuming that $d = 2\pi/q$ and layer spacing (———) in polymer CH_32 as a function of temperature. T_g and T_c are the glass transition and the isotropic liquid temperature respectively.

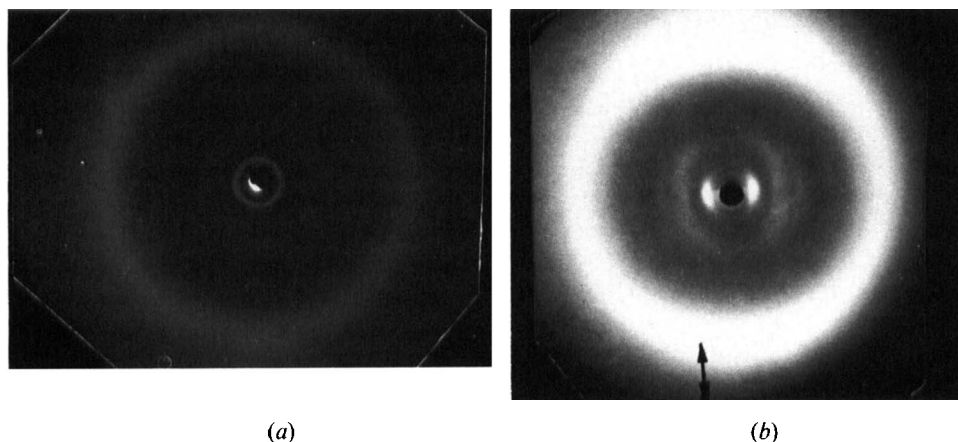(a)   (b)

Figure 10.   X-ray diffraction photographs from polymethacrylate where $n = 6$. (a) Powder sample at 70°C; (b) Stretched oriented fibre (the X-ray beam is perpendicular to the fibre axis).

Unfortunately we were unable to align this sample.

$$X = CH_3, \quad n = 6$$

In the liquid-crystalline state (40–90°C) the polymethacrylate, where $n = 6$, gives X-ray patterns consistent with a smectic A phase (cf. figure 10(a)). They present a diffuse outer ring indicating a lack of periodic lateral order and two well-defined inner rings which are related to the lamellar thickness. The average intermolecular spacing gives rise to the broad ring around 1.4Å^{-1} (cf. figure 11). The observed layer spacings vary only slightly in the temperature range 20–90°C and are almost identical with the length, $L = 28 \text{Å}$, of the side chains in an extended all-trans conformation, so that a monolayer structure is implied.

The X-ray patterns obtained using stretched oriented fibres are qualitatively like those for oriented samples of low molar mass smectic A phases. The anisotropy is clearly shown (cf. figure 10(b)) and there are correlations of two distinct periods, parallel and perpendicular to the fibre axis which correspond to an average molecule width ($\approx 4.5 \text{Å}$) and layer thickness ($d \approx 27.4 \text{Å}$), respectively. The two symmetrical wide-angle crescents are associated with the unstructured liquid-like nature of the layers. The Bragg spots along the equator show the existence of extensive layer-like correlations. The relative position of the wide-angle crescents and the small-angle reflections with respect to the fibre axis indicates that the side chains are perpendicular to the fibre axis while, as observed for polyacrylate H6 [2], the main chains are parallel to the direction of stretching.

In addition to these common features, parallel diffuse lines, equally spaced versus q, are observed along the equator. This is characteristic of disorder along the director. As shown in figure 12, the extra scattered intensity arises from uncorrelated periodic columns [8]. Such diffuse features do not usually appear in smectic A diffraction patterns of low molar mass liquid crystals. They often occur in smectic phases which exhibit three-dimensional order as, for example, smectics B, and so the most obvious explanation of their appearance in the X-ray diffraction patterns of polymer $CH_3 6$ is in terms of a rigidity effect of the smectic layers due to the macromolecular nature of the compound. Evidence in support of this interpretation comes from the fact that, recently, Davidson *et al.* [9, 10] have also observed this kind of linear disorder in the smectic A or smectic C phases of polymers of similar structure:
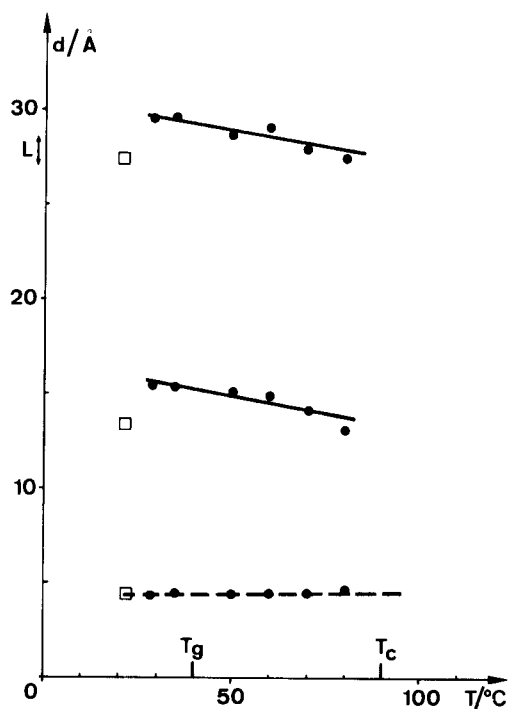
Figure 11.   Intermolecular distance (– – –) and layer spacing (——) in polymer $CH_3 6$ as a function of temperature. Powder samples ●; stretched oriented fibre □.
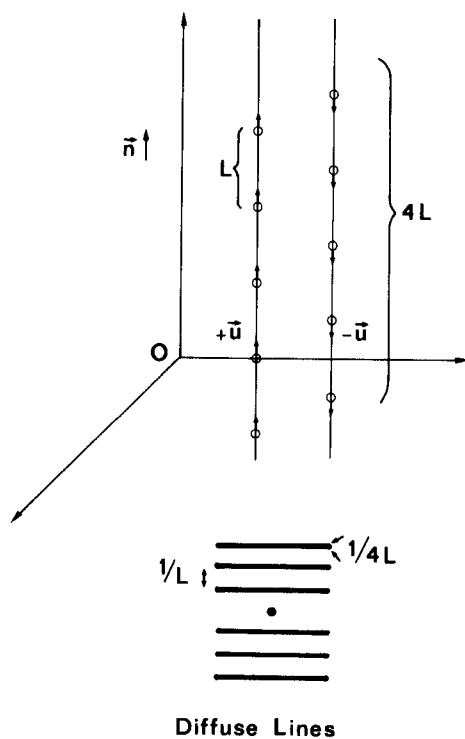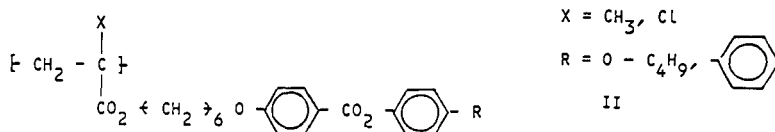

Figure 12.   Linear disorder with longitudinal motion.

$$X = CH_3, \quad CL$$

$$R = O - C_4H_9,$$

II

For polymer $CH_3 6$, the periodicity in the uncorrelated columns is the same as the smectic layer periodicity, i.e. the extended model length L, but it is worth noting that they are out of the mean position in the layer plane. The correlation length can be measured from the width of the diffuse lines (cf. figure 12) and is of the order of $110\,\text{Å}$ (approximately four times the layer thickness). It should be noted that correlation lengths are generally less than about five molecular dimensions for low molar mass liquid crystals. From the q dependence of the intensity of the diffuse lines, the amplitude of the displacement u from the layer plane can be evaluated; taking account of the variation of the atomic scattering factors and assuming that the highest intensity arises for $q \sim 0.6\,\text{Å}$, the mean displacement u is found to be of the order of $3\,\text{Å}$. Finally, the diffuse lines are not curved; this implies that all the columns are oriented in the same direction; there are almost no fluctuations in the direction of the strings.

A second diffuse zone can be seen in the diffraction patterns for polymer $CH_3 6$: four spots are visible at the $l = \pm 2$ level and out of the equator line. Such extra scattering has been assigned to a distinct kind of disorder, i.e. a periodic modulation of adjacent layers with a wave vector **a** parallel to the layer plane [9]. From the position of the diffuse spots and taking into account that the reflections are not seen for $h > 1$ and $l > 2$ we can deduce that the period of undulations is $a = 15$–$25\,\text{Å}$ with mean square fluctuations of about $4\,\text{Å}$ and $3\,\text{Å}$ in a direction parallel and perpendicular to the layer planes, respectively. From these observations we can infer that the monolayer smectic A structure constrains the polymer which results in an undulation of the polymer backbone as in the example in figure 6 of [9] for polymers of structure (II).

$$X = CH_3, \quad n = 11$$
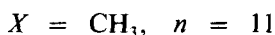
The X-ray diffraction patterns obtained at and above 90°C for powder samples of polymethacrylate where $n = 11$ are consistent with a smectic A phase, in agreement with microscopic observations (cf. figure 2). The observed layer spacings are almost identical with the length $L = 34\,\text{Å}$ of the side chains in their most extended conformation so that a monolayer structure is implied. Below 90°C, the diffraction patterns are essentially the same as those for S_{A_1} except that the layer spacings are smaller (cf. figure 13); the lamellar thickness is less than the length predicted by the model of extended side chains. We are forced therefore, to invoke either some form of interdigitation of the mesogenic side groups or a tilted smectic-like ordering. The textures (cf. figures 3 and 4) observed in this temperature range argue for a tilted smectic-like ordering. A tilt angle of some 20° would account for the difference between the extended model length L and the layer spacing determined at 60°C.

From the comparison of the two homologous series (I) where $R = $ H [2] and CH_3 we can conclude that

(i) the layer spacings determined for both acrylate and methacrylate polymers where $n = 2$ are consistent with the formation of bilayer structures; these polymers exhibit a high temperature S_{A_2} phase and a low temperature tilted smectic C*-like phase;
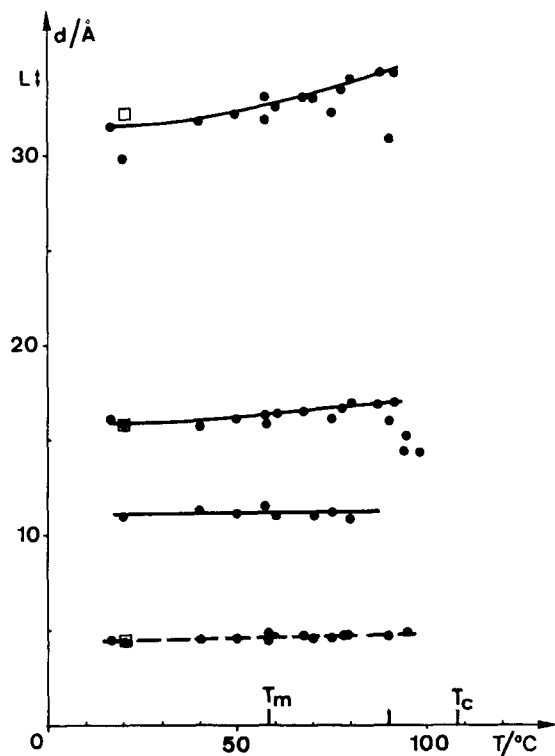
Figure 13.   Intermolecular distance (– – –) calculated assuming that $d = 2\pi/q$ and layer spacing (——) in polymer $CH_3 11$ as a function of temperature. Powder samples ●; stretched oriented fibre □.

(ii) the layer spacings measured for polyacrylates and polymethacrylates with longer flexible spacers ($n = 6, 11$) are consistent with monolayer structures; these polymers give S_{A_1} phases, polymer $CH_3 11$ exhibiting a chiral tilted smectic phase–S_{A_1} transition;

(iii) in monolayer smectics, the replacement of an hydrogen in the polymer backbone by a methyl group seems to constrain the polymer.

$$X = Cl, \quad n = 11$$

The X-ray patterns obtained from powder samples in the temperature range $60°–110°C$ are characterized by a diffuse outer ring, located at $q = 1\cdot3–1\cdot4\,Å^{-1}$ corresponding to the average intermolecular spacing and three inner rings (cf. figure 14). This polymer must then be of the smectic type with unstructured layers. It is to be noted, however, that the radial extension of the outer ring is small compared to ordinary smectic A or C liquid crystals which indicates a more ordered structure. Another major difference arises from the fact that the first order reflection, corresponding to a spacing of about $29\cdot4$ Å, is weak in comparison with the second and third order reflections. The latter correspond to d spacings of about $16\cdot4–17$Å and $10\cdot8–11\cdot4$ Å in a better agreement with the fully extended model length $L \approx 34$ Å than the former.

The diffraction patterns obtained from stretched oriented fibres (cf. figure 15) enlightened us on these peculiarities; the first inner ring seen in powder diagrams is in fact the combination of two kinds of scattered intensity.
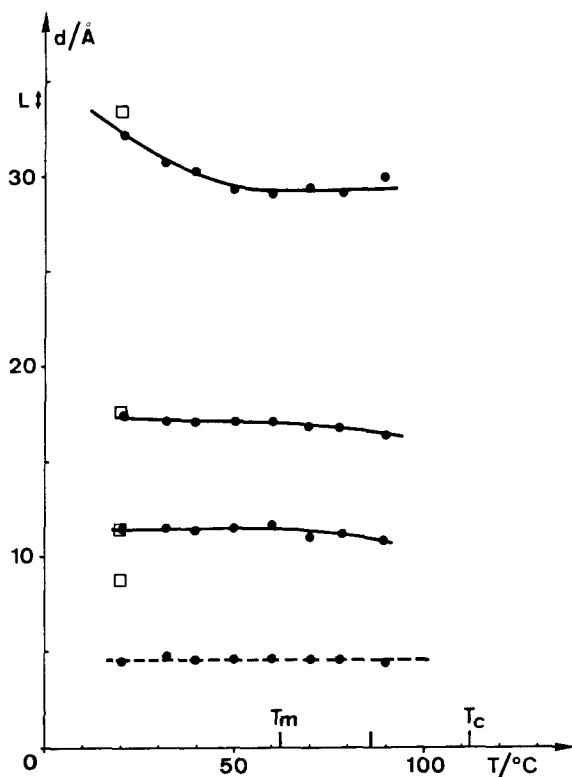
Figure 14. Intermolecular distance (– – – –) calculated assuming that $d = 2\pi/q$ and layer spacing (——) in polymer Cl11 as a function of temperature. Powder samples ●; stretched oriented fibre □.
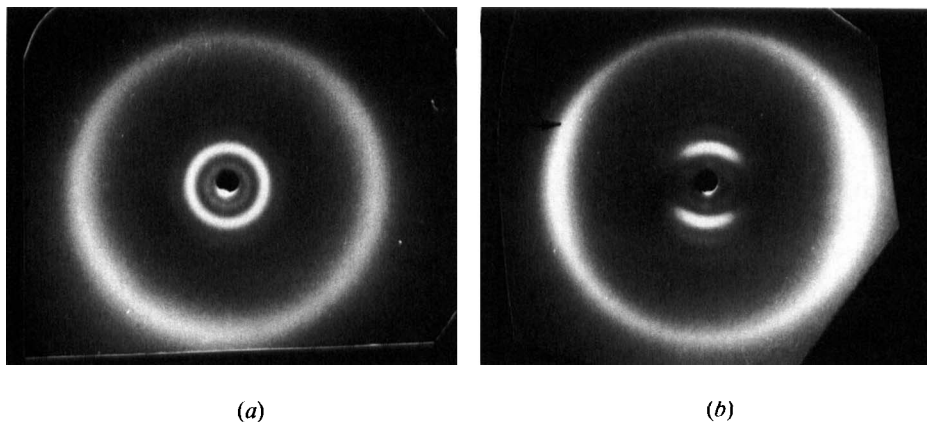

| (a) | (b) |

Figure 15. X-ray diffraction photographs from the polymer where $X = $ Cl and $n = 11$. (a) Powder sample at 70°C; (b) Stretched oriented fibre (the X-ray beam is perpendicular to the fibre axis).

(i) Two Bragg spots are seen in the direction perpendicular to the fibre axis; they can be related to the layer thickness. They correspond to a d spacing of $C \approx 33$–34 Å which is almost identical with the molecular length L implying a monolayer structure. Thus, the side chains are perpendicular to the smectic layers, these being parallel to the direction of stretching.

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The weakness of the 001 diffraction may be interpreted as arising from some organization in the smectic layers as expected from the small radial extension of the outer ring (cf. figure 14). The chlorine atoms in the main chain do impose a local ordering of the mesogenic side groups so that the presence of a [001] screw axis or a centred lattice results in the quasi-extinction of the 001 reflection.

(ii) Four diffuse spots, the intensity of which is quite similar to that of the 001 reflections, are seen out of the equatorial line. They can be ascribed to a distinct kind of disorder induced by a periodic modulation of wave vector a parallel to the layer plane; the period of undulations is $a \simeq 29$ Å. In powder patterns these spots give rise to a ring, corresponding to a spacing of ~ 29 Å, which merges in the Bragg reflection so that the layer thickness cannot be determined accurately from unoriented samples.

In addition, parallel diffuse lines, equally spaced versus q, are observed along the equator. As we have seen for polymer CH_36, such diffuse features are characteristic of disorder along the director. The scattered intensity results from uncorrelated columns which have the same periodicity as the smectic layers, i.e. $L = 34$ Å, but are out of the mean position in the layer plane. The correlation length determined from the width of the diffuse lines is of the order of 180 Å which is almost identical with 5C. The displacement from the mean position in the layer plane is $u \approx 4$ Å.

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