Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Decobert, G. , Dubois, J. C. , Esselin, S. and Noel, C.(1986) 'Some Novel Smectic* Liquid-Crystalline Side-Chain Polymers', Liquid Crystals, 1: 4, 307 — 317
To link to this Article: DOI: 10.1080/02678298608086664
URL: http://dx.doi.org/10.1080/02678298608086664

Liquid Crystals, 1986, Vol. 1, No. 4, 307–317

Some novel smectic C* liquid-crystalline side-chain polymers

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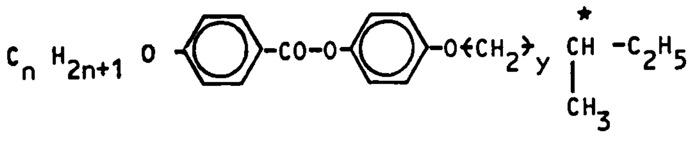
(*Received 26 February 1986; accepted 16 April 1986*)

Three acrylate 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. For shorter flexible spacers ($n = 2$) both smectic A and C* phases are observed thus making this polymer interesting for the fabrication of electro-optical devices based on ferroelectric properties (a smectic A phase is required for alignment purposes). For longer flexible spacers, ($n = 6$, 11) only the smectic A phase remains.

1. Introduction

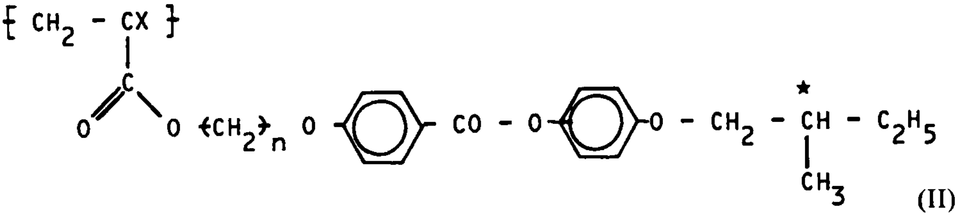
Ferroelectricity in liquid crystals was first demonstrated by Meyer *et al.* [1] in the chiral C and H phases, referred to as smectic C* and H* phases respectively, of *p*-decyloxybenzylidene *p*′-amino-2-methylbutyl-cinnamate (DOBAMBC). The structure of the smectic C* phase is essentially the same as that for the achiral C phase except for the distribution of molecular tilt directions. In the smectic C* phase, the molecules are parallel to one another and are arranged in layers, with the long axes tilted with respect to the normal to the layer planes. However, the structure is helicoidal with a ‘precession’ of the director about the layer normal. The symmetry plane and the inversion centre of the ordinary smectic C phase are absent, which stems directly from the chirality of the compounds. The only symmetry element which remains is a two-fold rotation axis parallel to the layers and normal to the molecular long axis. If there is any transverse electric molecular dipole moment (as in almost all liquid-crystalline molecules) its component parallel to this axis cannot be averaged to zero; this results in a spontaneous polarization. When an electric field, E, is applied normal to the helical axis, the helix becomes distorted; above a critical field, E_c, it is completely unwound and the sample is poled with the molecules tilted along a preferred direction normal to E.

Interest in the synthesis of chiral smectic C liquid crystals has increased considerably since the advent of a fast switching, bistable, electro-optical device based on their ferroelectric properties [2–4]. Materials of the type



(I)

have been reported to exhibit Ch, S_A and/or S_C^* phases depending on their chemical structure [5,6]. As part of a continuing effort to produce new chiral smectic C liquid crystals, the side-chain polymers



(II)

where $n = 2, 6, 11$ and $X = H, CH_3, Cl$ were prepared by two of the authors [7]. These materials are analogous to those prepared by Shibaev *et al.* [8]. Here we restrict our attention to the thermotropic mesomorphic behaviour of three acrylate polymers of structure (II) where X is hydrogen and n is equal to 2, 6, 11.

2. Experimental

The synthesis and purification of polymerizable monomers are described in detail elsewhere [7]. Polyacrylates were prepared by radical polymerization in toluene at 70°C with azo-bis-isobutyronitrile (AIBN) as initiator. Typically, mixtures of solvent and monomer (containing AIBN) were thoroughly outgassed by the conventional freeze–thaw technique before sealing and removing from the vacuum apparatus. Polymerization was allowed to proceed before the mixture was poured into an excess of methanol. Purification was accomplished by two further re-precipitations in methanol after which the polymers were dried *in vacuo*.

Phase transition temperatures and enthalpies were measured using a differential thermal analyser (Du Pont 1090). The samples were examined under dry nitrogen flow and a scanning rate of 20°C/min was used. 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. Peak maximum positions were taken as the melting and clearing temperatures. The textures of the mesophases were observed with a polarizing microscope (Olympus BHA-P) equipped with a programmable heating stage (Mettler FP5) without special preparations of support and cover slide.

For the X-ray measurements, the samples were contained in 1 mm diameter Lindemann glass tubes. Diffraction patterns were recorded on flat films using Ni-filtered CuK_α radiation. The sealed capillary tubes were mounted in an electrically heated oven, the temperature of which was controlled with a precision of 0·2°C using a platinum resistor as sensing element. The sample holder was contained inside a tank evacuated to reduce air scattering. Oriented samples were produced by drawing fibres out of the mesophase with a pair of tweezers.

3. Results and discussion

3.1. *Thermal properties*

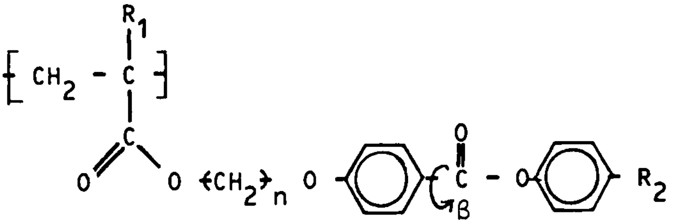
The transition temperatures for the polymers are listed in the table. Below the glass transition temperature, the D.S.C. curves for the three polyacrylates investigated show a small base-line shift which has the appearance of a β-transition. Recently, Zentel *et al.* [9] reported that side-chain polymers having the repeating unit

Thermal properties of the polymers.

Polymer		Transition temperature/°C					ΔH_c	
X	n	T_β	T_g	T_m	$T_{M_1M_2}$	T_c	J/g	kJ/monomer unit
H	2	−5	65		110	146	4·52	1·80
H	6	−18	15	46†	68‡	87	8·74	3·97
H	11	−15	32	59		108	12·51	6·57

† Small endotherm which appears only after sample annealing at 30°C for 6 hours.

‡ Very small endotherm. No transition was detected at this temperature by optical microscopy and X-ray diffraction.



(III)

R_1 = H, CH_3 n = 2, 6 R_2 = CN, OCH_3, $O(CH_2)_3CH_3$

exhibit a β-relaxation associated with reorientations of dipoles located at the centre of the mesogenic group. This interpretation is supported by dielectric measurements showing that the β-relaxation is found for all polymers independent of R_1, R_2 and n.

The data in the table can be used to make some remarks about the variation of glass transition temperature as the length of the flexible spacer varies. Polymer H2 has a glass transition temperature of 65°C, much higher than that of poly(propyl acrylate) [10]. It is evident that the bulky mesogenic group causes severe hindrance to main chain motions. This results mainly from a stiffening of the polymer backbone. Lengthening the aliphatic spacer from $n = 2$ to $n = 6$ decreases the glass transition temperature from 65 to 15°C. The same sort of behaviour has been observed in other polyacrylate and polymethacrylate series. This is understandable because (i) long flexible spacers have a plasticizing action similar to that of the aliphatic side-chains in poly(n-alkyl acrylates) and poly(n-alkyl methacrylates) and (ii) the bulky mesogenic group is moved farther away from the polymer backbone and causes less hindrance to main chain motions. This is easy to see in the series poly(phenyl acrylate), poly(benzyl acrylate), poly(2-phenyl ethyl acrylate) in which the glass transition temperatures are 55°, 6° and −3°C respectively. It is to be noted, however, that polymer H11 has a glass transition of 32°C, higher than that of polymer H6. Studies carried out on poly(n-alkyl acrylates), and poly(n-alkylmethacrylates) have shown that at and above a critical value of n partial crystallization of the aliphatic side chains occurs, which results in an increase in the glass transition temperature. The same phenomenon is probably observed in the series which we have investigated at $n = 11$. Such an interpretation is consistent with the experimental findings that polymers H2 and H6 are essentially non-crystalline in character whereas polymer H11 is semicrystalline ($\Delta H_m = 15{\cdot}1\,J\,g^{-1}$).

3.2. *Texture observation*

All the polyacrylates investigated exhibit mesophases, the textures of which are reminiscent of those of conventional liquid crystals [11, 12].

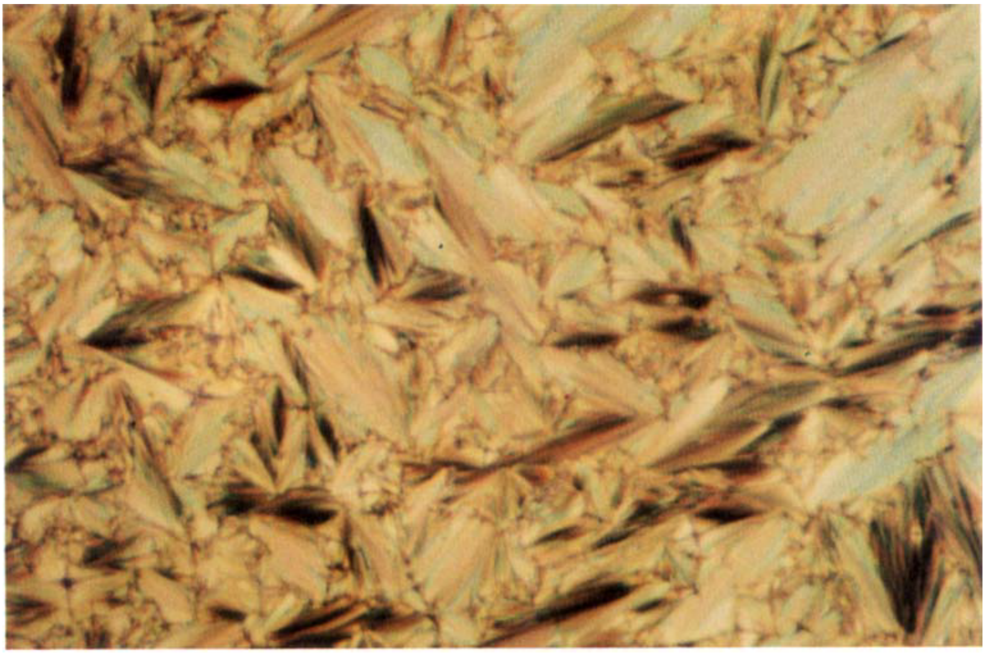


Figure 1. Photomicrograph of the high-temperature smectic phase of polyacrylate H2 (crossed polarizers; 121°C).

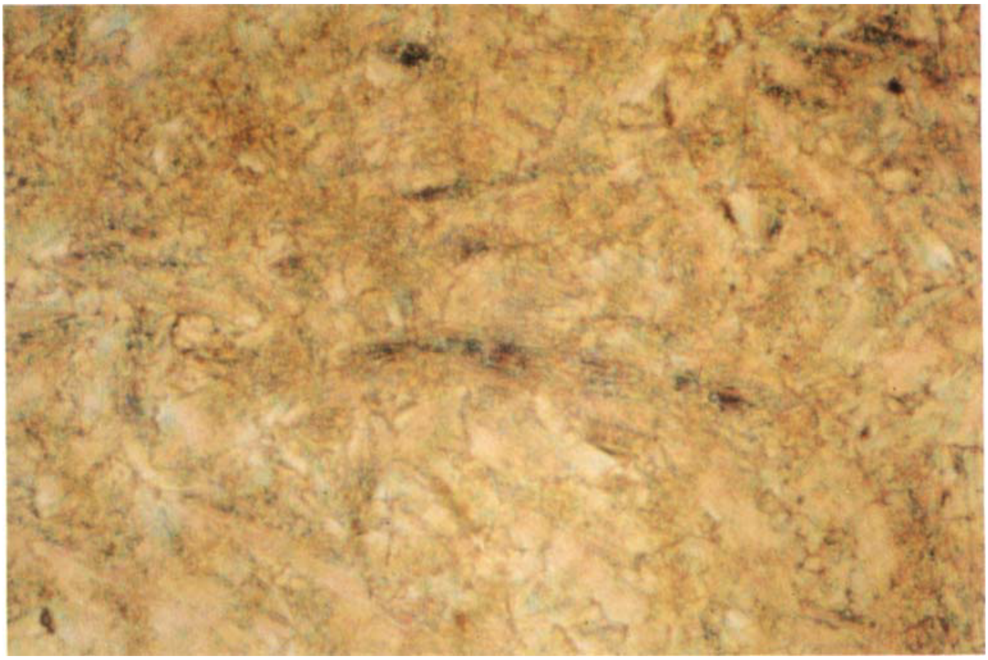


Figure 2. Photomicrograph of the low-temperature smectic phase of polyacrylate H2 (crossed polarizers; 105°C).

Figure 3. Photomicrograph of the smectic A phase of polyacrylate H6 (crossed polarizers; 71°C).

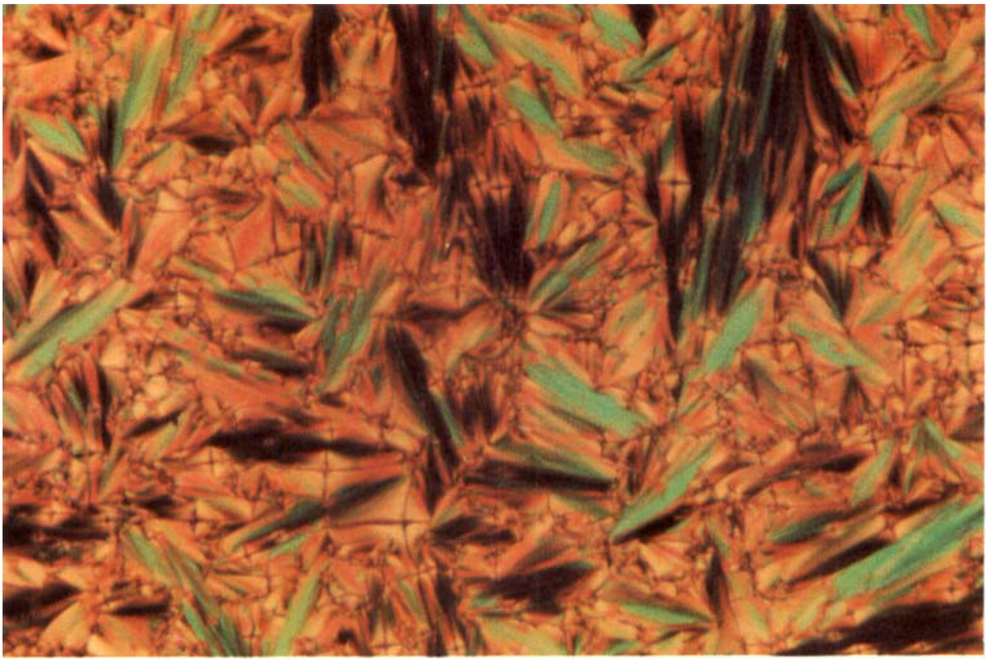


Figure 4. Photomicrograph of the smectic A phase of polyacrylate H11 (crossed polarizers; 79°C).

Polarized-light photomicrographs depicting the appearance of the two mesophases of polyacrylate H2 exhibit characteristic features of smectic phases as illustrated in figures 1 and 2. Upon cooling the isotropic melt, the high-temperature smectic phase begins to separate at the clearing point in the form of typical bâtonnets which, after further cooling grow, coalesce and reorganize their shape until a final focal-conic fan texture is established (figure 1). Occasionally it is possible to observe a variant of the focal-conic texture with spherulitic domains. These microscopic observations are consistent with a smectic A phase. As the temperature falls below 110°C, the low-temperature smectic phase appears suddenly as a poorly defined texture (cf. figure 2) which suggests a smectic C* or smectic F* phase.

For polymer H6 only one smectic A phase is observed from 46°C up to 87°C. For this polyacrylate smectic A liquid crystal comes directly from the isotropic liquid in the form of bâtonnets which grow and coalesce into a focal-conic fan texture (cf. figure 3).

Above its melting point (~ 59°C), polymer H11 gives a birefringent melt which exhibits characteristic features of smectic A phases as illustrated in figure 4. There is some indication that this polymer also forms a cholesteric phase at about 100°C. However, the appearance of the isotropic phase in the same temperature range obscures subtle changes in the texture such as could be expected for a S_A/Ch transition. Indeed, while conventional liquid crystals have well defined transition temperatures, in the polyacrylates under investigation, because of the polydispersity of the samples, the transitions occur over a range of temperatures within which there is an equilibrium two-phase microstructure. It is to be noted, however, that the endotherm which appears between 97°C and 120°C in the D.S.C. curves (cf. figure 5) is much broader than that observed at the clearing point for either polymer H2 or polymer H6, which is consistent with two overlapping peaks resulting from S_A/Ch and Ch/I transitions.

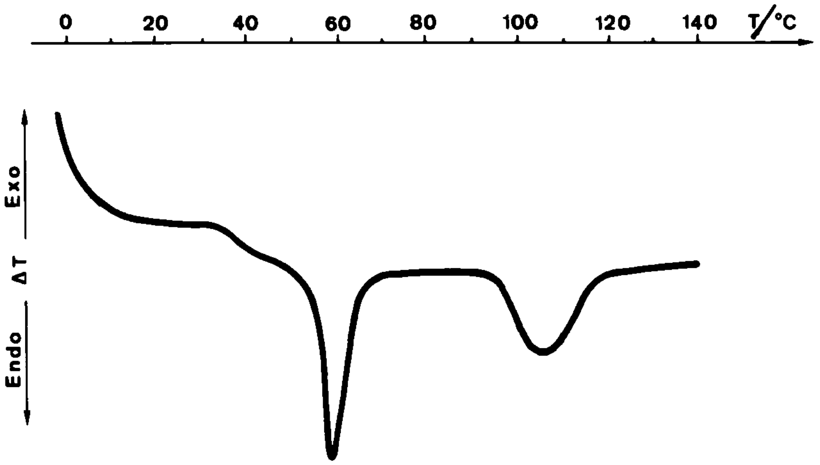


Figure 5. D.S.C. heating trace of polymer H11 (6·8 mg).

3.3. *X-ray diffraction patterns*

For polymer H2, X-ray diffraction patterns obtained with powder samples in the temperature range 110–145°C are characteristic of a disordered lamellar structure. They present a diffuse outer ring reflecting the absence of ordering within the layer planes and two well-defined inner rings corresponding to a spacing, *d*, of 42·6 ± 1 Å

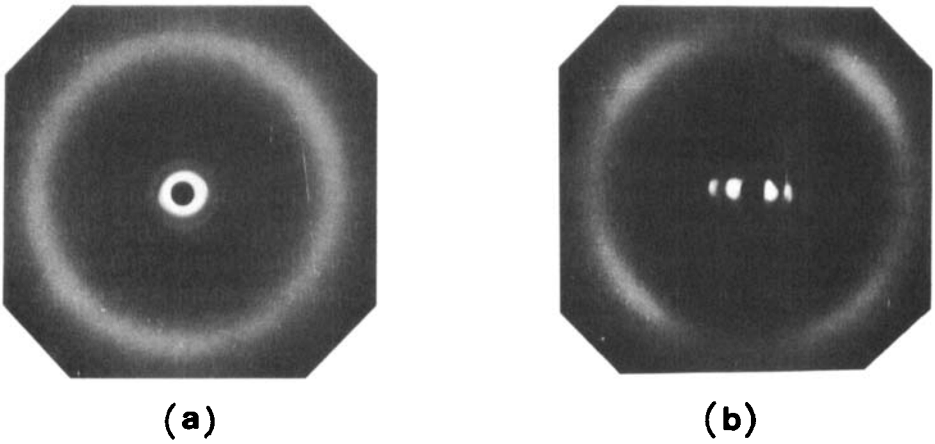


Figure 6. X-ray diffraction patterns of polymer H2. (*a*) Smectic A phase (125°C). (*b*) Stretched oriented fibre drawn out of the smectic C phase.

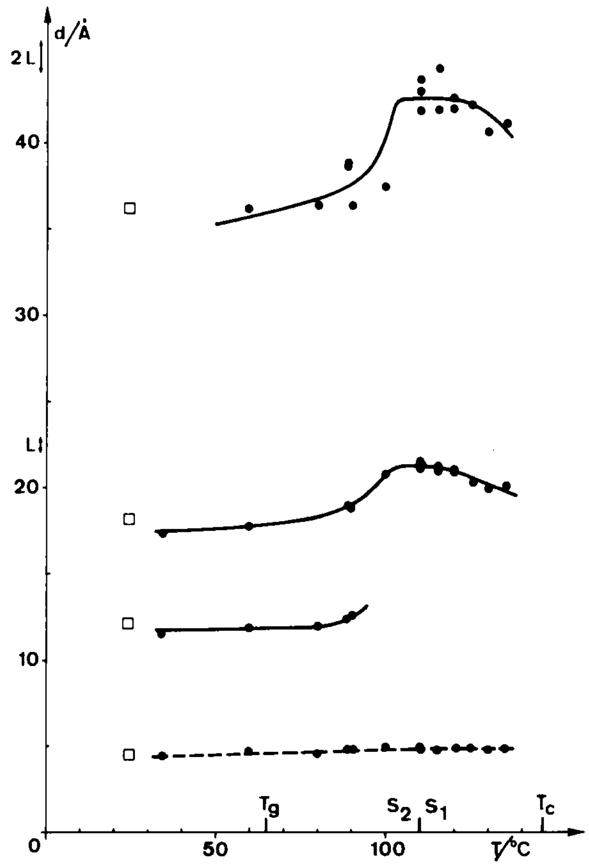


Figure 7. Intermolecular distance (- - -) and layer spacing (——) in polymer H2 as a function of temperature. (□) Stretched oriented fibre.

(cf. figure 6). The layer spacings, *d*, vary only slightly in the temperature range 110–130°C and then decrease as the temperature reaches 130°C, the beginning of the smectic A–isotropic liquid transition (cf. figure 7). This decrease of *d* can be associated with a decrease of the order parameter. It is worth comparing these spacings with the length *L* (of approximately 22–23 Å) of the side-chain in its most extended conformation which was calculated assuming standard bond lengths, angles and van der Waals radii. It is clear that $d \simeq 2L$ so that some form of bilayer structure is implied.

Below 110°C, the diffraction patterns of powder samples are essentially the same as those for smectic A phases except that three well-defined inner rings are observed. They correspond to a Bragg spacing of 36–38 Å (cf. figure 7), which is less than twice the molecular length *L*. This gives rise to two possible models for the side-chain ordering:

(i) A smectic A-like structure in which the side chains would overlap in an antiparallel, interdigitated arrangement.
(ii) A tilted smectic-like ordering.

It should be noted that optical microscopy of this smectic phase (cf. figure 2) does not in fact reveal any smectic A characteristics. Therefore, the system would have smectic C-like properties. Support for such an interpretation has been obtained using stretched oriented fibres. As shown in figure 6, the diffraction patterns of oriented samples consist of:

(i) Six small-angle Bragg spots corresponding to the three first orders of reflection on the layer planes ($d \simeq 36{\cdot}2$ Å). They are located on the equator which indicates that the smectic layers and, as a consequence, the main chains are parallel to the fibre axis.
(ii) Four diffuse crescents at large angles indicating a liquid-like order within the layers. These diffuse spots are roughly equidistant from the origin and form pairs aligned on straight lines making an angle of about 35–40° with respect to the fibre axis.

Therefore, we can conclude that the mesogenic side groups are tilted with respect to the layer planes. The two distinct orientations for the mesogenic side groups could be readily explained, as indicated in figure 8.

For polymers H6 and H11 the assignment of S_A phases founded on texture observations is confirmed by X-ray diffraction. The X-ray patterns obtained with powder samples are characterized in the wide-angle region by a diffuse halo associated

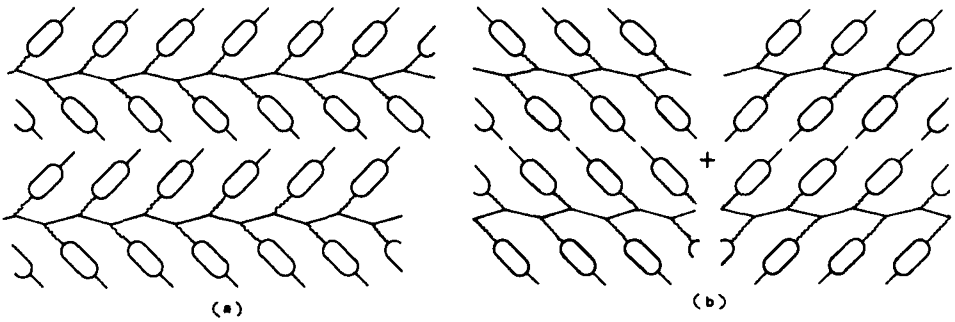


Figure 8. Possible models for side-chain ordering in the smectic C phase of polyacrylate H2.

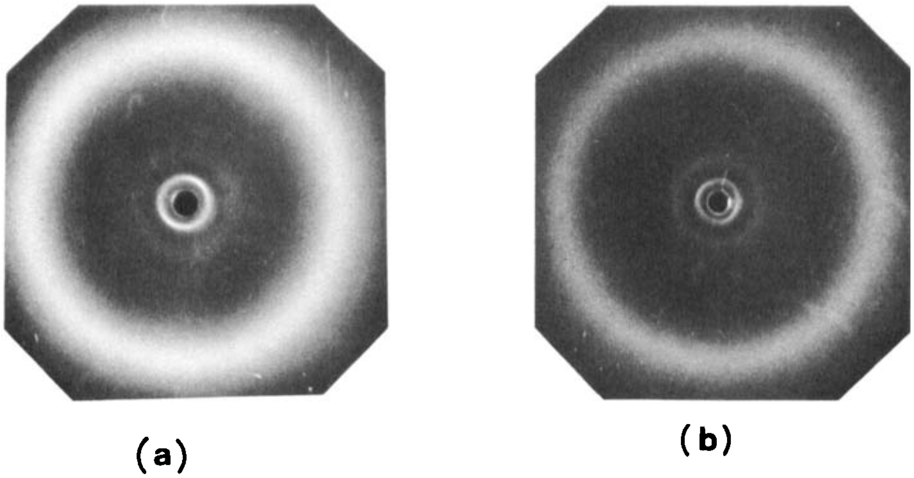


Figure 9. X-ray diffraction patterns of the smectic A phases of polymers H6 (*a*) and H11 (*b*).

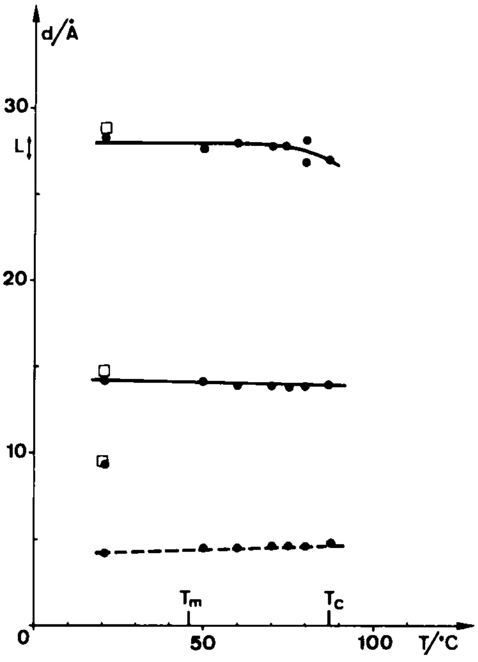


Figure 10. Intermolecular distance (- - -) and layer spacing (——) in polymer H6 as a function of temperature. (□) Stretched oriented fibre.

with the unstructured nature of the layers and in the small-angle region by two sharp rings namely a base reflection and a second-order reflection, corresponding to the lamellar thickness (cf. figure 9). As shown in figures 10 and 11, the layer spacings, *d*, in the S_A phases vary very slightly with temperature. It is clear that $d \simeq L$ (of approximately 27·5 ± 1 Å for polyacrylate H6 and 34 ± 1 Å for polyacrylate H11) so that a monolayer structure is implied.

The diffraction patterns obtained using stretched oriented fibres (cf. figure 12) consist mainly of:

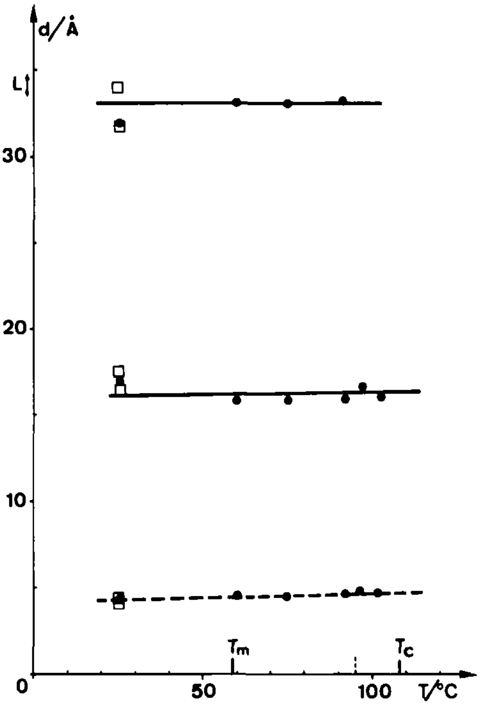


Figure 11. Intermolecular distance (– – –) and layer spacing (——) in polymer H11 as a function of temperature. (□) Stretched oriented fibre.

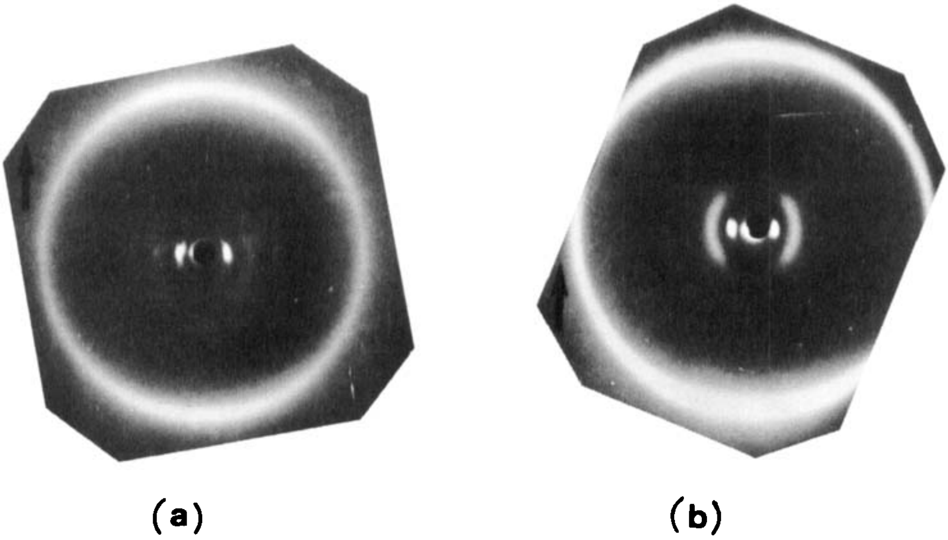


Figure 12. X-ray diffraction patterns obtained for polymers H6 (*a*) and H11 (*b*) using stretched oriented fibres.

(i) Four equatorial Bragg spots at small-angle showing the existence of extensive layer-like correlations. Again the *d* spacings of the layers are found to be almost identical with the length *L* of the side-chains in their most extended conformation.

(ii) Two large-angle arcs on the meridian.

The relative position of the large-angle arcs and the small-angle reflections with respect to the fibre axis shows that the side-chains are perpendicular to the fibre axis while, as observed for polymer H2, the main-chains are parallel to the stretching direction.

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