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S. Esselin [a] , C. Noel [b] , G. Decobert [a] & J. C. Dubois [a]

[a] Laboratoire Central de Recherches, Thomson-CsF, Domaine de Corbeville, BP 10, F-91401, Orsay, Cedex, France

[b] Laboratoire de Physicochimie Structurale et Macro-moléculaire, 10 rue Vauquelin, 75231, Paris, Cedex 05, France

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SYNTHESIS AND PROPERTIES OF SMECTIC LIQUID CRYSTALLINE SIDE-CHAIN POLYMERS

S. ESSELIN, C. NOEL*, G. DECOBERT and J.C. DUBOIS
* Laboratoire de Physicochimie Structurale et Macromoléculaire, 10 rue Vauquelin, 75231 Paris Cedex 05, France.
Laboratoire Central de Recherches, Thomson-CsF, Domaine de Corbeville, BP 10, F-91401 Orsay Cedex, France

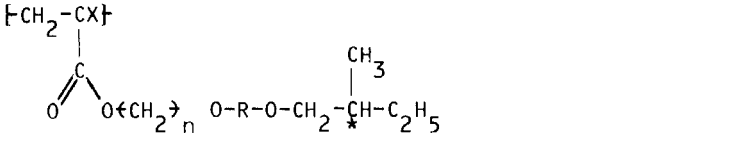
1. INTRODUCTION

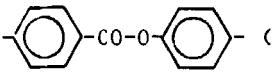
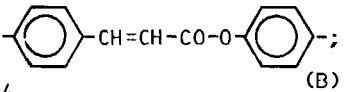
In the chiral smectic phase (i.e. the C^* phase), the molecules are arranged randomly in layers and tilted with respect to the normal layer. The symmetry plane of the ordinary smectic C structure is absent because the molecules are chiral. The only symmetry element is a twofold rotation axis which allows molecules to "flip-flop" head-to-tail. If there is any transverse electric molecular dipole moment, its component along this axis cannot be averaged to zero and so each layer is spontaneously polarized. However, on passing from layer to layer the tilt direction of the molecules is turned through a small angle about an axis perpendicular to the layers and hence a helical structure is formed. The spontaneous polarization is rotated from one layer to the next about the helical axis and averages to zero in a bulk sample. Hence, the chiral smectic phase is ferroelectric only if the helical arrangement is suppressed.

In 1980, Clark and Lagerwall described the surface-stabilized Ferroelectric Liquid Crystal (SSFLC) device concept

based upon the use of C^* phase [1, 2]. This created considerable interest in the synthesis of new compounds which exhibit smectic C^* phases.

Liquid crystalline polymers offer several chemical design possibilities which are not available in low molar mass systems. Over the past few years, we have been particularly interested in exploring the possibility of obtaining ferroelectric smectic liquid crystals and we have synthesized polymers having the general structure :



where R =  (A),  (B)

n = 2, 6, 11 and X = H, CH_3, Cl [3,4]. Here we restrict our attention to the thermotropic mesomorphic behavior of polymethacrylates BCH n and poly α chloroacrylate BCl11.

2. EXPERIMENTAL

Polymerizable monomers were prepared by standard methods [4] via the scheme described in Figure 1. Polymers were prepared by free radical polymerization in toluene at 60°C with azo-bis-isobutyronitrile as the initiator. Purification was accomplished by two 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) operating at 20°C/minute. Indium was used as the calibration standard.

Optical observations were made using a polarizing micros-

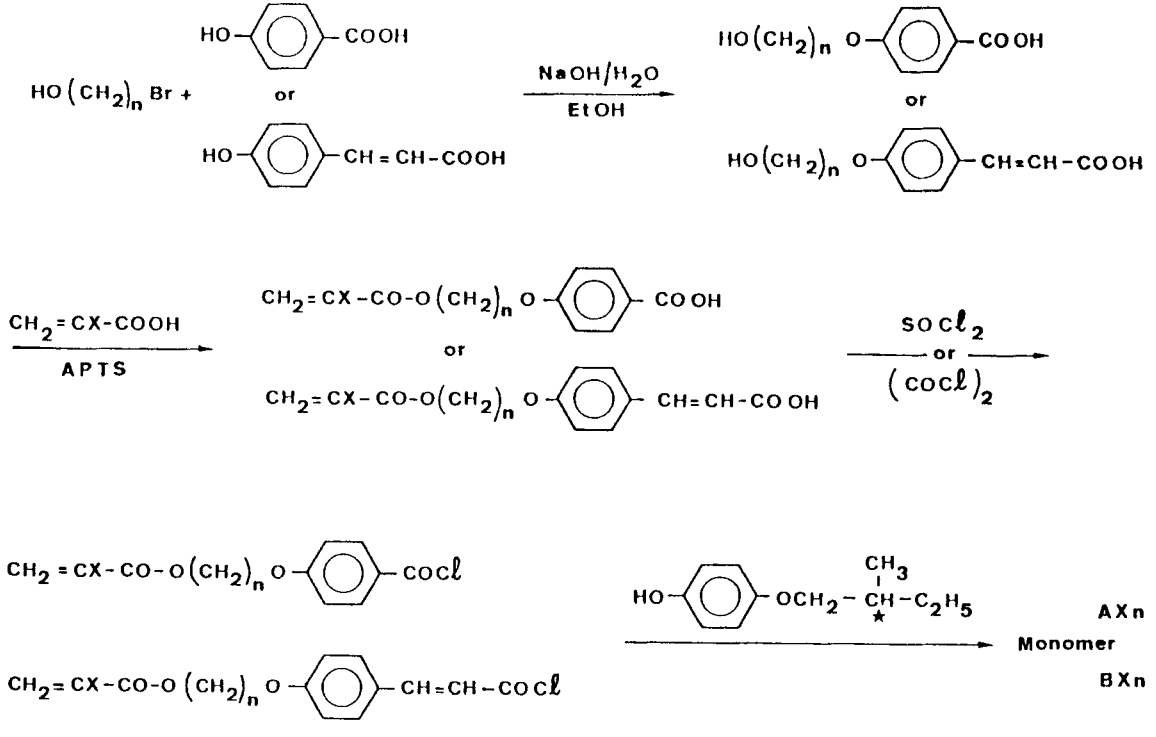


FIGURE 1 - Synthetic route for the preparation of monomers

cope (Olympus BHA-P) in conjunction with a Mettler FP52 hot-stage and 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. CuK_α radiation, monochromated by a flat graphite crystal in conjunction with a pinhole collimator was used. Exposure times of 2-3 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 $\pm$ 0.5°C. The whole diffraction apparatus was placed inside a tank which was evacuated during measurement to reduce the scattering of X-rays by air.

3. RESULTS AND DISCUSSION

3.1. Thermal properties

The table gives some of previous results [5, 6] on polymers AXn and compares them with our present data. Several interesting results emerge :

1/ The bulky mesogenic groups severely hinder main chain motions and so the glass transition temperatures for the side chain polymers investigated are higher than those for conventional poly(n-alkyl acrylates) and poly(n-alkyl methacrylates)

2/ The change from H to Me or Cl results in a stiffening of the polymer backbone and the glass transition temperature is increased. The effects of X = Me and X = Cl are nearly the same.

3/ Decreases in glass transition temperatures accompany lengthening of the flexible spacer. This is understandable because i/ long flexible spacers have a plasticizing

Polymer			Transition temperatures(°C)									
R	X	n		Tg	Tm		T_{S1S2}		T_I		ΔH_I KJ/m.u[c]	ΔS_I J/K m.u.
A	H	2		65		S_C^*	110	S_{A2}	146	I	1.8	4.29
A	H	6		15	46[a]		S_{A1}		87	I	4	11.1
A	H	11		32	59		S_{A1}		108	I	6.6	17.2
A	CH_3	2	S_C^*	110			S_{A2}		155	I	3.5	8.2
A	CH_3	6		40			S_{A1}		90	I	5.0	13.8
A	CH_3	11		10-40[b]	58	S_C^*	90	S_{A1}	106	I	6.9	18.3
A	Cl	2		97	172	I					4.8	
A	Cl	6		37	94	I					5.0	
A	Cl	11		10-40	62		S_A-like		112	I	7.5	19.4
B	CH_3	2		125			S_{A2}		172	I	2.8	6.2
B	CH_3	6		50	92		S_{A1}		125	I	3.5	8.8
B	CH_3	11		35	65	S_C^*	115	S_{A1}	142	I	5.4	12.9
B	Cl	11		35	76		S_A-like		140	I	4.6	11.1

a/ Small endotherm which appears only after sample annealing at 30°C for 6 hours; b/ These glass transitions were hard to detect; c/ m.u : monomer unit.

Table 1-Thermal properties of polymers AXn and BXn

action similar to that of the aliphatic side-chains in poly(n-alkylacrylates) and poly(n-alkylmethacrylates) and ii/ the bulky mesogenic group is moved farther away from the polymer backbone and causes less hindrance to main chain motions. However, the glass transition temperature of polymer AH11 (32°C)is higher than that of polymer AH6 (15°C). This unusual behavior for a homologous series is again reminiscent of results obtained for poly(n-alkylacrylates) : above a critical value of n, partial crystallization of the aliphatic side chains occurs which results in an increase in Tg.

The ordered-to-isotropic phase transition has a smaller gain in entropy than expected for the fully oriented mesogen alone (25-45 J/Kmol). Thus, the mesophases must contain considerable disorder, even for the mesogens. For a given series, the replacement of hydrogen in the polymer backbone by a methyl group or a chlorine atom seems to result in higher orientational order in liquid crystals. As in the low molar mass materials, longer flexible spacers increase the transition entropy, but less than expected for a fully extended aliphatic chain. Additive values to the entropy change of 0.75-1.4 J/K and to the enthalpy change of 0.3-0.5 KJ can be calculated for each methylene unit. From such values one can conclude that over 60 % of the methylene groups are in the trans conformation thus providing evidence that the flexible spacer is in a rather extended state in the mesophase.

3.2. Texture observation

Optical microscopy of the smectic phase of polymers $BCH_3 2$,

$BCH_3$6 and BCl11 does not reveal any specific textures. In contrast, polymer $BCH_3$11 exhibits smectic phases, the textures of which are reminiscent of those of low molar mass liquid crystals [7, 8]. Typically, the smectic A phase separates from the isotropic liquid in the form of bâtonnets these coalesce to produce an unbroken focal conic fan texture (Fig.2). The phase also exhibits the homeotropic texture. On cooling the A phase, a transition to the C^* phase takes place with the fans becoming broken and mottled in appearance (Fig.3). The homeotropic areas become birefringent and exhibit a schlieren texture.

3.3 - X-ray diffraction

Polymer $BCH_3$2

For polymer $BCH_3$2, X-ray diffraction patterns obtained with powder samples in the temperature range 125-172°C are characteristic of a disordered lamellar structure. They present a broad, diffuse outer ring in the $q = 4\pi \sin\theta/\lambda$ range 1.3-1.4 Å^{-1} reflecting the absence of ordering within the layer planes and two well-defined inner rings corresponding to a spacing d, of ~ 49 Å (Fig. 4). It is clear that d is approximately twice the length L of the side chain in its most extended conformation as calculated by assuming standard bond lengths, angles and van der Waals radii. These results are consistent with the formation of a "bilayer" smectic A phase. In addition a diffuse ring can be also seen. It corresponds to a distance of 12.5 Å, which is approximately half the length L. It is impossible to establish the origin of this diffuse ring solely from the X-ray patterns of powder samples. Unfortunately it was not possible to align this sample for further X-ray study.

FIGURE 2 - High-temperature smectic phase of polymer $BCH_3 11$

See Color Plate XIV.

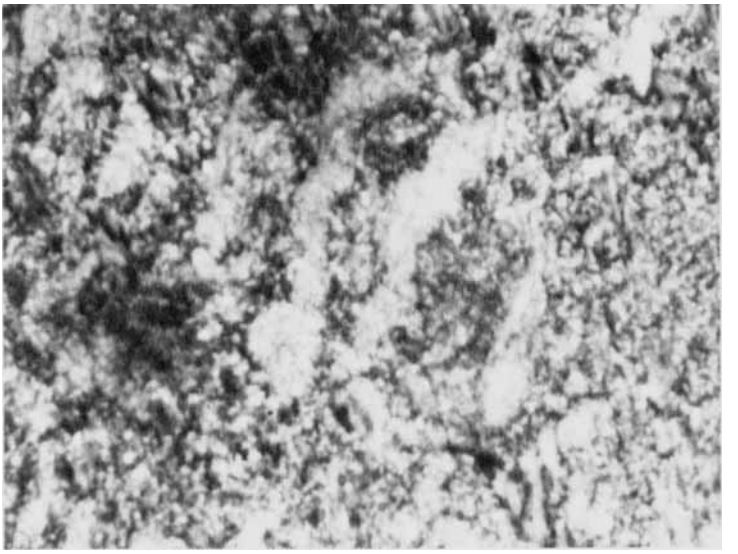


FIGURE 3 - Low-temperature smectic phase of polymer $BCH_3 11$

See Color Plate XV.

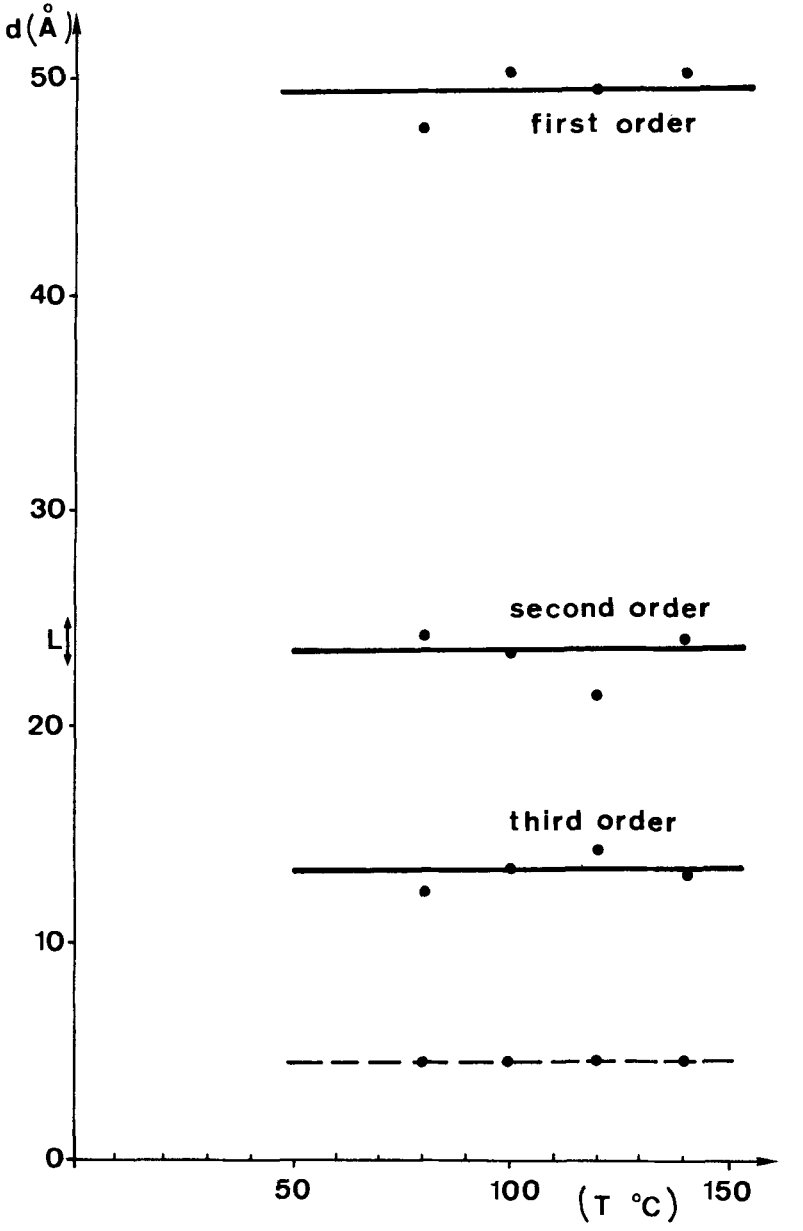


FIGURE 4 - Intermolecular distance (---) and layer spacing (——) in polymer BCH_3^2

Polymer $BCH_3 6$

For polymer $BCH_3 6$, X-ray diffraction patterns of powder samples are consistent with a smectic A phase. They present a diffuse outer ring indicating the absence of periodic lateral order and two well-defined inner rings which are related to the lamellar thickness. The observed layer spacings vary only slightly in the temperature range 92-125°C and are almost identical with the molecular length $L \simeq 30$ Å so that a "monolayer" structure is implied (Fig.5).

The diffraction patterns obtained using stretched oriented fibers (Fig.6) consist mainly of :

(i) equatorial Bragg spots showing the existence of extensive layer-like correlations

(ii) two diffuse crescents at large angles. The relative positions of these diffuse crescents and of the Bragg spots with respect to the fiber axis show that the side-chains are perpendicular to the fiber axis while the smectic layers and, as a consequence, the main chains are parallel to the stretching direction.

(iii) parallel diffuse lines which arise from uncorrelated periodic columns (9). The periodicity in these columns is the same as the smectic periodicity (i.e. the molecular length L) but they are out of the mean position in the layer plane. The correlation length can be measured from the width of the diffuse lines and is of the order of 240 Å (i.e. 8 side-chains). From the q dependence of the intensity of the diffuse lines, the amplitude of the displacement from the layer plane can be evaluated (~ 3 Å).

(iv) four diffuse spots. In fact, these spots are the intersection of two diffuse rings located in reciprocal planes (00ℓ) with ℓ close to $\pm 2^{10}$. They originate in a periodic

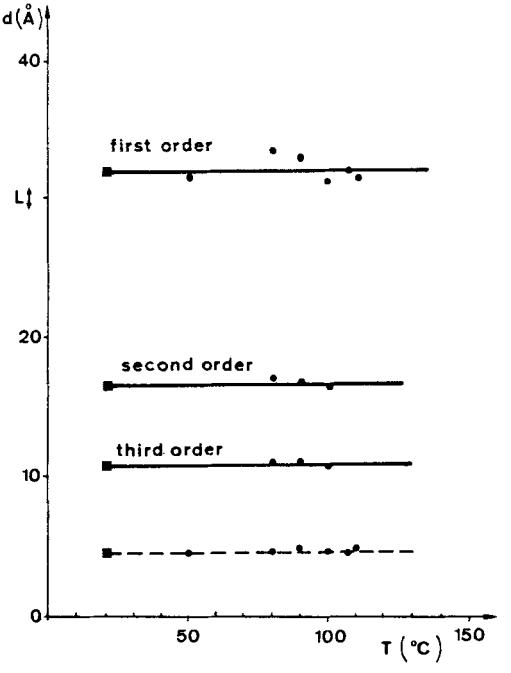


FIGURE 5 - Intermolecular distance (---) and layer spacing (——) in polymer BCH_36

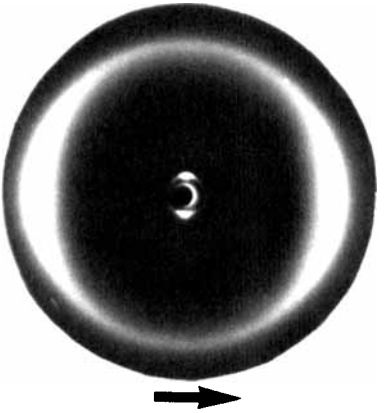


FIGURE 6 - X-ray diffraction pattern obtained for polymer BCH_36 using oriented fibers

modulation of adjacent layers with a wave vector a parallel to the layer plane. Knowing the position of the diffuse spots and taking into account that the reflections are not seen for $h > 1$ and $\ell > 2$, we can deduce that the period of undulation is $a \simeq 20$ Å with mean square fluctuations of about 5 and 4 Å in a direction parallel and perpendicular to the layer planes, respectively.

Polymer $BCH_3$11

For polymer $BCH_3$11, X-ray diffraction patterns obtained with powder samples in the temperature range 115-145°C are consistent with a "monolayer" smectic A phase (Fig.7). Below 110°C, the diffraction patterns are essentially the same as those for the smectic A phase except that the inner rings correspond to a Bragg spacing which is less than the molecular length L. This suggests a tilted smectic-like ordering. A tilt angle of 20° would account for the difference between the extended model length L and the layer spacing d. A pure fiber diagram for the smectic phase could not be obtained because of the strong tendency of polymer $BCH_3$11 to crystallize. However, the diffraction patterns obtained using stretched oriented fibers (Fig. 8) are characterized by i/ equatorial Bragg spots from which the d spacings of the layers are found to be 33.5 Å which is smaller than the molecular length L and ii/ four large-angle arcs which are roughly equidistant from the origin and which form pairs aligned on straight lines making an angle with respect to the fiber axis. Therefore one can conclude that the mesogenic groups are tilted with respect to the layer planes.

Polymer BCl11

In the temperature range 76-140°C, polymer BCl11 gives diffraction patterns characteristic of a disordered lamellar

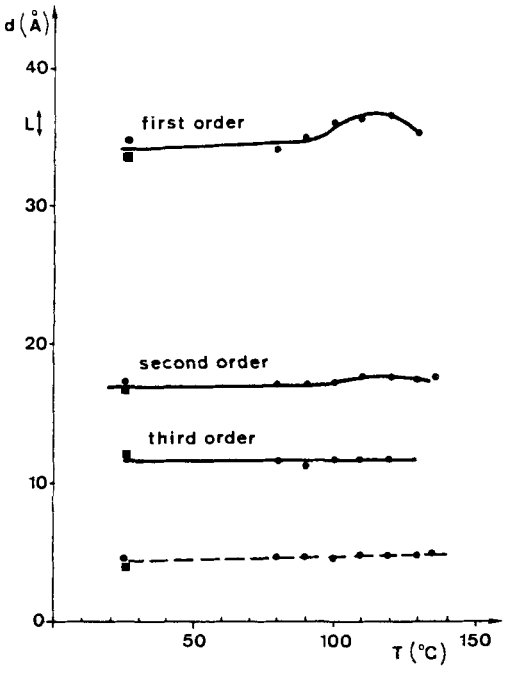


FIGURE 7 - Intermolecular distance (---) and layer spacing (——) in polymer $BCH_3 11$

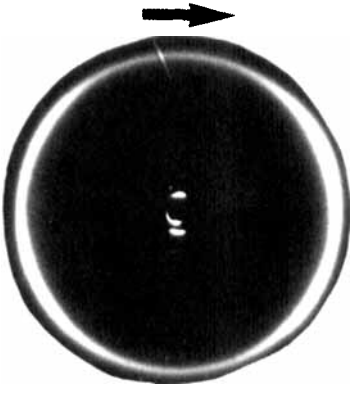


FIGURE 8 - X-ray diffraction patterns obtained for polymer $BCH_3 11$ using oriented fibres.

structure. They show a diffuse outer ring located at $q = 1.3\text{-}1.4\ \text{Å}^{-1}$ which corresponds to the average intermolecular spacing. It is to be noted that the first order reflection at about 35 Å is weak in comparison with the second and third reflections. The latter correspond to d spacings of 11.8 Å and 17.6 Å in good agreement with the extended molecular length $L \simeq 35\text{-}36$ Å. These results are consistent with a "monolayer" smectic A-like structure. The low intensity of the first order transition may be interpreted as arising from some organization in the smectic layers : the chlorine atoms in the main chain do impose a local ordering of the mesogenic side groups. Similar results were obtained for polymer ACl11 [6]

A pure fiber diagram for the smectic phase could not be obtained because of the strong tendency of polymer BCl11 to crystallize. However, the diffraction patterns obtained using stretched oriented fibers (Fig.9) are characterized by two sets of strong reflections: one on the equator with a d-spacing of ~ 35 Å which corresponds approximately to the length of a side-chain, the other on the meridian which can be assigned to the average distance between successive mesogenic side groups. From the position of the two sets of reflections, it follows that the side-chains are perpendicular to the fiber axis while the main-chains are parallel to the stretching direction.

In addition, parallel diffuse lines are observed along the equator. As observed for polymer BCH_36, these lines arise from uncorrelated periodic columns which have the same periodicity as the smectic layers, i.e. $L \simeq 35$ Å, but are out of the mean position in the layer plane. The correlation length is of the order of 220 Å (i.e. 6 side-chains)

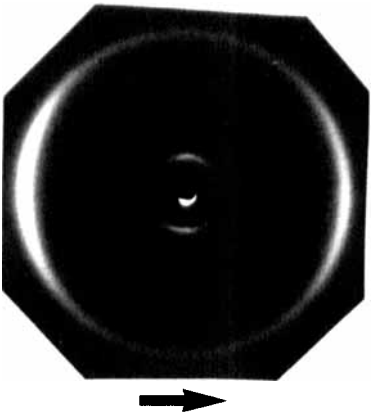


FIGURE 9 - X-ray diffraction pattern obtained for polymer BCl11 using oriented fibers

and the displacement from the mean position is $u \simeq 4$ Å.

Finally, the four diffuse spots seen out of the equatorial line can be ascribed to a periodic modulation of wave vector a parallel to the layer plane. However, they are of very low intensity which makes it difficult to determine the period of undulations.

4. CONCLUSIONS

The data obtained for polymers AX_r [5,6] and BX_n reveal change in the structure of the mesophases as X and n are varied. The following remarks should be noted :

- The layer spacings determined for polymers where n = 2 are consistent with the formation of "bilayer" structures
- The layer spacings calculated for polymers with longer flexible spacers imply "monolayer" structures. The X-ray patterns obtained using oriented fibers present parallel

diffuse lines. These lines arise from uncorrelated columns which have the same periodicity as the smectic layers but are out of the mean position in the layer plane.

- In monolayer smectics, the change from H to Me or Cl in the polymer backbone seems to constrain the polymer which results in a periodic modulation of adjacent layers.
- For polymers ACl11 and BCl11, the radial extension of the outer ring in the X-ray patterns of powder samples is small compared to ordinary S_A liquid crystals and the first order reflection is weak. Therefore the chlorine atoms in the main chain do impose a local ordering on the mesogenic side groups.

For polymers AH2, $ACH_3$2, $ACH_3$11 and $BCH_3$11 both smectic A and C^* phases are observed thus making these polymers interesting for the fabrication of electro optical devices based on ferroelectric properties.

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