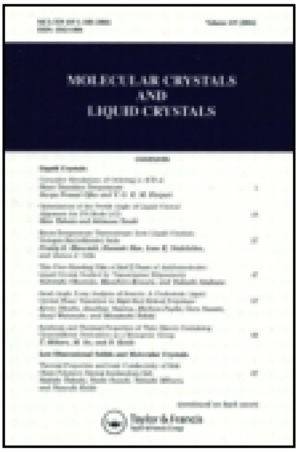

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X-RAY DIFFRACTION STUDY OF THE SMECTIC C MESOPHASE OF A SIDE CHAIN POLYACRYLATE CONTAINING A SULFIDE SUBSTITUTED MESOGEN

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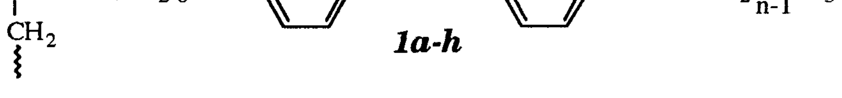
Abstract An X-ray study was performed on powder specimen and oriented fibers of a side chain liquid-crystalline polyacrylate containing a sulfide substituent. The X-ray diffraction patterns showed the presence of a bilayer smectic C mesophase with the mesogenic groups tilted by an angle $\beta \approx 40°$ with respect to the layer normal. The electron density profile $\rho(z)$ along the direction normal to the smectic layers was calculated by Fourier inversion and the results suggest a minor interdigitation of the aliphatic chains. The positional smectic order parameter was also determined.

INTRODUCTION

In recent papers[1-3], we reported the synthesis and mesophase behavior of a new series of side chain liquid-crystalline polyacrylates ***1a-h***, containing prochiral sulfide groups:



1a-h

	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*
n	*1*	*2*	*3*	*4*	*5*	*6*	*8*	*10*

The length of the sulfide substituent was varied regularly from $n= 1$ to $n= 10$. This class of polymers is viable to modification by asymmetric oxidation yielding the corresponding chiral sulfoxide-containing polymers[1]. The introduction of the strong dipole moment of the sulfoxide moieties, directly located at the chiral center and perpendicular to the long axis of the mesogenic groups should facilitate the formation of a chiral smectic C* mesophase, with potential applications in electrooptics and non-linear optics.

A preliminary X-ray diffraction investigation provided evidence for the existence of a complex smectic polymorphism including smectic A, B and C mesophases with monolayer and interdigitated bilayer structures. In particular, the lower polymer homologues in the series ($n\leq 6$) displayed smectic B1 and A1 mesophases, whereas the higher homologue ($n= 10$) showed a smectic C mesophase. Polymer ***1g***, with an intermediate terminal substituent length ($n= 8$), revealed a unique behavior in that it showed both monolayer and interdigitated bilayer smectic mesophases coexisting over extremely wide temperature ranges[3].

The effects of changing the length and nature of the flexible spacer and terminal substituent on the mesophase properties of a variety of side chain polymers have been investigated rather extensively[4]. However, alkyl sulfide segments were never incorporated before into the molecular framework of the repeating unit of other side chain liquid-crystalline polymers. It was, therefore, of interest to start a more detailed structural analysis of the phase behavior of the present liquid-crystalline polyacrylates, in which the peculiar dipolar and steric factors of the sulfide moiety could be expected to affect the structure and order of the smectic phase.

The present paper reports on the results of the X-ray investigation of the structure and molecular organization of polymer ***1h*** ($n= 10$) in the smectic mesophase, obtained from the analysis of the diffraction spectra of both unoriented and oriented mesophases. In particular, the electron density distribution along the normal to the smectic layers and the smectic layer positional order parameters were determined.

EXPERIMENTAL PART

The synthesis and liquid crystalline properties of the polymer ***1h*** were described in Ref. 1. The number average molecular weight (Mn) and first polydispersity index (Mw/Mn) were evaluated by SEC to be Mn=195000 and Mw/Mn= 3.2, in terms of polystyrene standards. X-ray diffraction measurements on powder samples were performed using the INEL CPS 120 powder diffractometer, equipped with a position sensitive detector covering 120° in the scattering angle 2θ, with an angular resolution of 0.018° in θ. Ge(101) monochromatized CuKα radiation was used. The sample, ~1 mm thick, was placed between two thin Al sheets, fixed to an Al sample holder. Heating was achieved by a hot stage whose temperature was controlled within ±0.5°C by an automatic temperature regulator. The relative integrated intensities of the Bragg reflections in the smectic phases were measured from the corresponding spectra after background subtraction, deconvolution for the instrumental resolution function and correction for the Lorentz and polarization factors. In our geometry, the Lorentz factor L(θ) was proportional[5,6] to $(\sin\theta/\lambda)^2$, and the use of the (101) reflection on the Ge monochromator induces[7] a polarization factor P(θ)

$$P(\theta) = \frac{1+\cos^2 2\alpha \cos^2 2\theta}{1+\cos^2 2\alpha} \qquad [1]$$

with α= 11.1°. The experimental data were therefore corrected for the combined Lorentz-polarization factor LP(θ)

$$LP(\theta) = \frac{0.538+0.461\cos^2 2\theta}{\sin^2\theta} \qquad [2]$$

Oriented smectic phases were obtained by drawing a fibre out of the mesophase, at a temperature of ~20 K lower than the smectic-isotropic transition, with a pair of tweezers and cooling it in air at room temperature. X-ray diffraction photographs of the oriented specimens were taken on a Rigaku-Denky RV300 rotating anode generator equipped with a pin-hole flat camera. Ni-filtered CuKα radiation (λ= 1.54 Å) was used. The optical density of the X-ray diffraction photographs was measured by a conventional microdensitometer.

RESULTS AND DISCUSSION

Polyacrylate ***1h*** is amorphous[2] and displays a smectic C mesophase with the following phase sequence:

$$g \xrightarrow{318\ K} S_C \xrightarrow{394\ K\ (21.9\ Jmol^{-1}K^{-1})} I$$

Figure 1 shows the X-ray powder diffraction pattern of the smectic mesophase of polymer *1h* recorded at 343 K in the cooling cycle. The spectrum is constituted by three sharp Bragg peaks in the small angle region corresponding to periodicities of 55.0 , 27.5, and 18.3 Å (the first order reflection on the smectic layers and its first two harmonics) and a wide angle diffuse halo centered at about 4.5 Å. consistent with a disordered smectic mesophase. The layer spacing d= 55.0 Å is much longer than the length of the repeating unit in the fully extended conformation, L=37 Å (as estimated from the Dreiding stereomodels), thus suggesting some form of bilayer arrangement of the side chain groups.

Figure 2 reports the diffraction spectrum of the oriented smectic mesophase. In the small angle region, eight sharp spots corresponding to the first four orders of Bragg reflection on the smectic layers are visible.

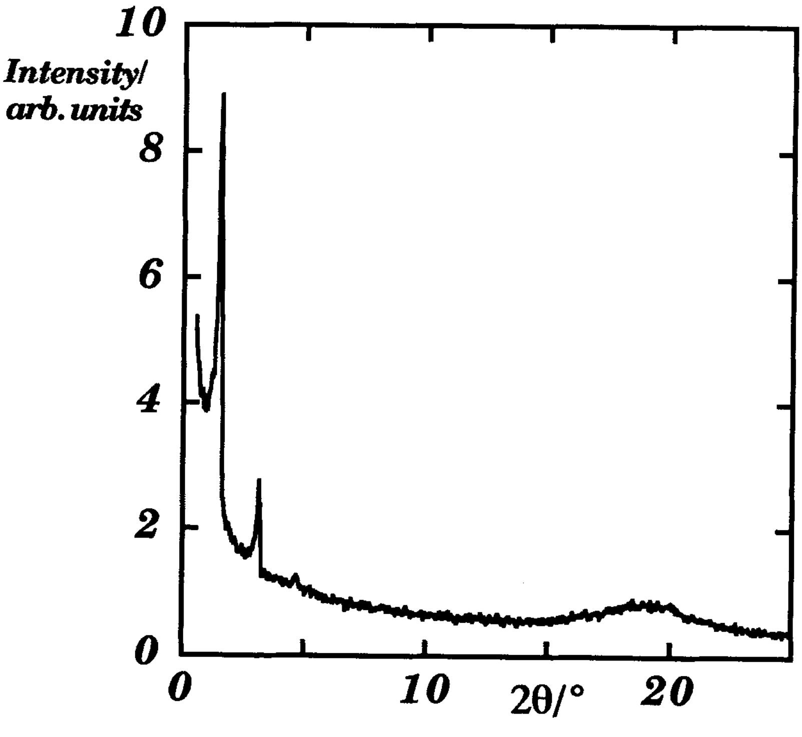


FIGURE 1 X-ray diffraction diagram of polymer *1h* at 343 K after cooling from the isotropic melt.

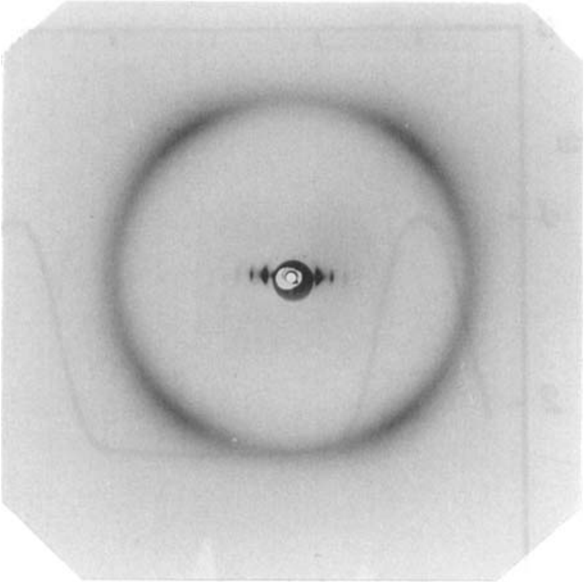


FIGURE 2 Fiber X-ray diffraction pattern of the smectic mesophase of polymer ***1h***. Fiber axis aligned along the vertical direction.

They are aligned on the equator thus indicating that the smectic layers and consequently the polymer chains are parallel to the fiber axis. In addition, a diffuse four-spot pattern is observed in the wide angle region. These diffuse reflections are equidistant from the origin and their centers form pairs on straight lines making an angle β of about 40° with respect to the fiber axis. Figure 3 shows the microdensitometric profile of the intensity distribution function I(β) as a function of the azimuthal angle. The tilt angle β was estimated as the angle corresponding to the maximum of the intensity I(β). The above features reveal the smectic C nature of the mesophase with the mesogenic side groups tilted by an angle $\beta \approx 40°$ with respect to the layer normal. The shape of the I(β) profile suggests a relatively wide angular distribution of the side chain orientation with respect to the layer normal. Two possible structural arrangements of the polymer smectic C phase consistent with the above X-ray evidences are sketched in Figure 4. Comparison of d with L indicates that only a little interdigitation should be present. However, the value of L considered above does not include the thickness of the backbone contribution, estimated between ≈ 1 Å and ≈ 3 Å, depending on its degree of confinement.

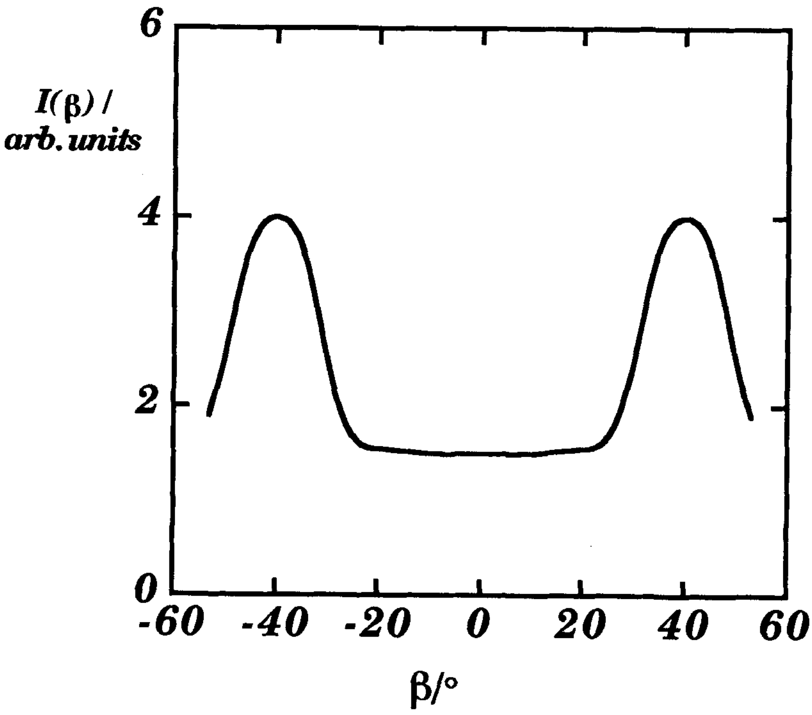


FIGURE 3 Intensity distribution I(β) of polymer *1h* as a function of the azimutal angle β at a diffraction angle 2θ= 20°.

In order to obtain more information on the molecular organization within the smectic planes and, in particular, on the extent of interdigitation of the side chains and the confinement of the polymer backbone, we determined the electron density distribution along the normal to the smectic layers.

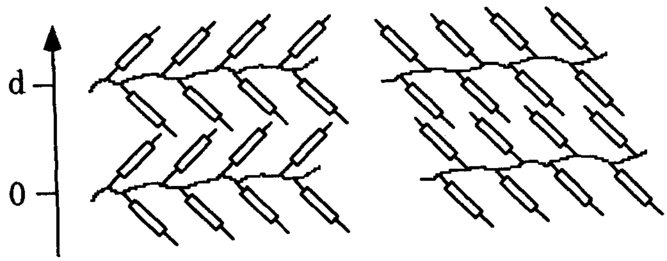


FIGURE 4 Schematic representation involving tilting of the side chains of polymer *1h* in two possible bilayer smectic C mesophase.

TABLE I Intensities (I) and amplitude (a) values for the 00*l* Bragg reflections in the smectic mesophase of polymer ***1h***

00*l*	I_{00l}/I_{001}	a_l/a_1
001	1	1
002	0.74(2)	0.86(1)
003	0.25(1)	0.50(1)
004	0.025(15)	0.15(5)

Electron Density Profile along the Layer Normal

The presence of several reflection orders in the diffraction pattern of the smectic mesophase implies that the projection of the electron density along the normal to the smectic layers cannot be described by the ideal model of a single sinusoidal modulation[8] and allows a more detailed electron density profile to be obtained by Fourier inversion of the X-ray intensity data. An accurate evaluation of the intensities of the different Bragg reflections was performed from the powder diffraction spectra after background subtraction, deconvolution for the instrumental resolution function and correction for Lorentz and polarization factors. The results obtained for the first three orders of reflection are reported in Table I. Since no absolute intensity could be obtained, the results are collected as the ratio I_{00l}/I_{001} of the intensity of the *l*-th order of reflection to the first one. The ratio I_{004}/I_{001} of the intensity of the fourth harmonic to the first one was obtained from the diffraction pattern of the oriented mesophase. This was done by performing microdensitometer scans along straight lines at different angles with respect to the equatorial direction, thus obtaining the intensity profile for a set of azimuthal angles β. From the numerical integration of this set of intensity profiles we obtained the ratio I_{004}/I_{001}. Due to the lower accuracy of the results obtained from the fiber pattern, this value is affected by a considerably greater error with respect to the intensity ratios calculated from the powder spectra, as shown by the error bands in Table I. If we indicate by z the normal to the smectic layers and take the origin of the z axis in the middle of the layer, the electron density ρ(z) is centrosymmetric and can be expressed by a Fourier series containing only cosine terms

$$\rho(z) = \rho_0 + \sum_{l=1}^{\infty} a_l \cos(2\pi l \frac{z}{d}) \qquad [3]$$

where ρ_0 is the average electron density value along the director, d is the smectic interlayer spacing and a_l is the amplitude of the $00l$ reflection. The density ρ_0 was evaluated by dividing the total number of the electrons within a smectic layer by the layer spacing d, thus obtaining ρ_0= 10.3 e^-/Å. The difference $\rho(z)$-ρ_0 gives the fluctuations of the electron density around the calculated average value. The intensity of the l-th reflection is directly proportional to $|a_l|^2$. The ratios $|a_l|/|a_1|$ are also collected in Table I. The coefficients a_l are positive or negative real numbers and the phase problem is then reduced to choosing the right combination of signs for the amplitudes a_l. With four coefficients a_l, sixteen different sign combinations are possible, which results in as many density distributions. We indicate, for example, ρ_{+-++} the combination where a_1, a_3 and a_4 are positive whereas a_2 is negative. Due to the small amplitude of the fourth order reflection, only slight differences are observed between the distributions differing only in the sign of the a_4 coefficient. Therefore, we considered at first the eight distributions corresponding to the different sign combinations of a_1, a_2, a_3. The fourth harmonic contribution was then introduced as a refinement to the density profile obtained.

The choice of the most likely density profile was done on the basis of simple physical considerations. Due to the relatively high electron density contrast between the rigid part of the molecule, i.e. the mesogenic core including the sulfur atom, and the flexible polymethylene chains, an electron density profile was expected with a broad central minimum, corresponding to the aliphatic chains, and two pronounced maxima associated with the rigid cores and roughly centred at a distance of about d/3 from the polymer backbones (Figure 5). Only four of the eight possible distributions display a central minimum and among these only two, namely the ρ_{+--} and ρ_{--+}, reported in Figure 5a and 5b respectively, match the above expectations. In particular, the ρ_{+--} distribution exhibits a physically unlikely deep minimum corresponding to the polymer backbones whereas the relatively high central minimum (at z=0) would require an appreciable degree of interdigitation of the side chains. Accordingly, the ρ_{--+} distribution seems to be the best appropriate to describe the smectic phase of this polymer.

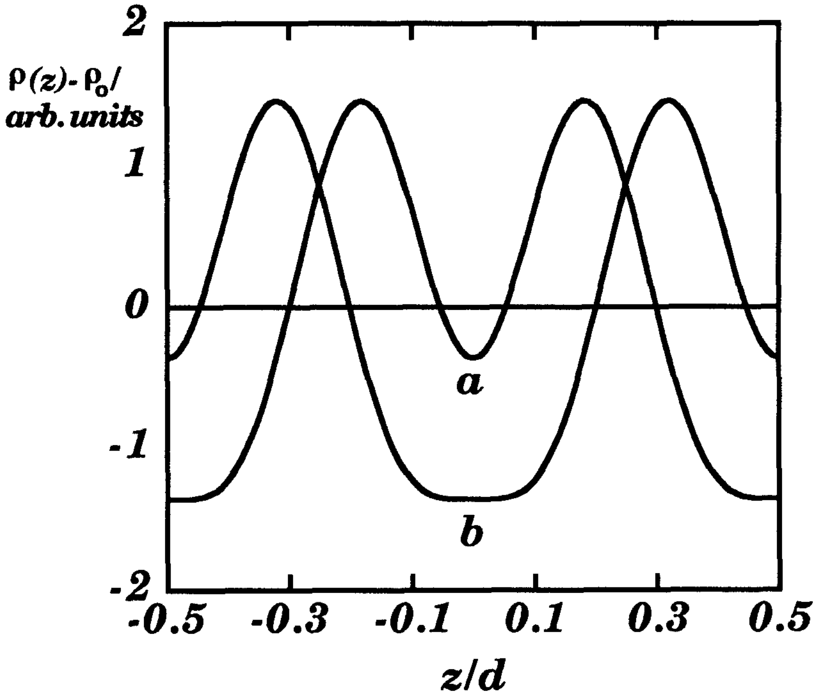


FIGURE 5 Projection of the electron density profile $\rho(z)$ along the layer normal for polymer **1h** corresponding to the different sign combinations of the a_l coefficients. (a) ρ+--; (b) ρ--+.

Recently, Etherington et al.[9] have introduced for the evaluation of the electron density of low molar mass liquid crystals a parameter r defined as

$$r = \frac{\rho_0 - \rho_{al}}{\rho_{core} - \rho_{al}} \qquad [4]$$

where ρ_{al} and ρ_{core} are the electron densities of the aliphatic chains and the mesogenic cores respectively, along the normal to the smectic layers. This parameter may be useful as a qualitative criterion for the choice of the proper electron density solution even in polymers, as previoulsy discussed[9,10]. The values of ρ_{al} and ρ_{core} were calculated from the structural model (Figure 4) by dividing the total number of electrons of each unit by the z-projection of the respective size, and result ρ_{al}= 8.2 e^-/Å and ρ_{core}=12.6 e^-/Å. With these values, the estimated r is 0.48 which is equal to the value as calculated for the ρ_{--+} distribution. Therefore, the ρ_{--+} density

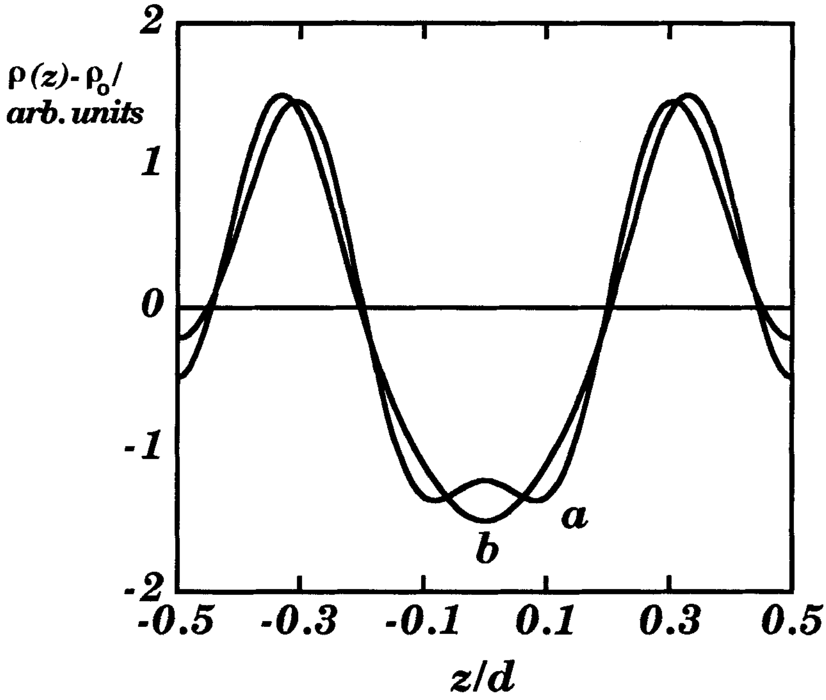


FIGURE 6 Projection of the electron density profile ρ(z) along the layer normal for polymer ***1h*** corresponding to the different sign combinations of the a_4 coefficient. (a) ρ_{--++}; (b) ρ_{--+-}.

profile appears to be the most likely one, in agreement with the above conclusions. The distribution ρ_{--+} can be better refined by considering the contribution of the fourth harmonic. The profiles corresponding to the positive and negative signs of a_4 are shown in Figures 6a and 6b respectively. The ρ_{--+-} distribution was discarded since it produces a lowering of the central minimum which is difficult to justify. Consistent with our results, we conclude that the ρ_{--++} electron density profile should occur in the smectic mesophase of polymer ***1h***. In this electron density distribution, the presence of the weak central relative maximum confirms the existence of only a limited extent of interdigitation of the side chains. In addition, two density maxima, corresponding to the rigid mesogenic cores including the heavy sulfur atom, are localized at a distance of about 11 Å from the backbone. Their extension along z axis corresponds approximately to the z-projection of the length of the mesogenic core, thus indicating only a small spread out due to the translational fluctuations of the chains. This point is more quantitatively treated in the next paragraph. Finally, a slight microsegregation of the backbone should be present as indicated by the value of the electron density at z= ±d/2.

Positional Smectic Order Parameter

The distribution function of the molecular positions normal to the layers in the smectic phase can be written in terms of a Fourier series[11,12]

$$f(z) = \left(1 + \sum_{l=0}^{\infty} 2\tau_l \cos\left(2\pi l \frac{z}{d}\right)\right) / d \qquad [5]$$

where d is the layer spacing and $\tau_l = \langle\cos(2\pi l\, z/d)\rangle$ is a smectic layer order parameter, which ranges from 1 for the perfect layer structure to 0 for absence layer structuring. The scattering factor F_{00l} for the scattering vector $\boldsymbol{Q}$ along the z direction can be written

$$F_{00l} = \sum_{m} \langle f_m \exp(2\pi i l z'_m / d)\rangle \qquad [6]$$

where m denotes the atoms in the molecule, f_m is the atomic form factor of the m-*th* atom and the average is taken over all molecular configurations. If we indicate by z_{mo} the z coordinates for a perfectly ordered smectic ($\tau_{00l} = 1$) then $z'_m = z_{mo} + z_m$, where z_m gives the fluctuation of the m-*th* atomic position around z_{mo}. Then Eq.6 can be written

$$F_{00l} = \sum_{m} \langle \exp(2\pi i l z_m / d)\rangle a_m \exp(2\pi i l z_{m0} / d) \qquad [7]$$

If z_m is supposed to be the same for all atoms in the molecule, then the intensity of the 00*l* reflection can be written

$$I_{00l} = C|F_{00l}|^2 = \tau_l^2 I^{\circ}_{00l} \qquad [8]$$

where C is a proportionality constant and I^{o}_{00l} is the intensity for a perfectly ordered smectic layer. By assuming a Gaussian distribution for f(z)

$$f(z) = [2\pi\langle z^2\rangle]^{-1/2} \exp(-z^2 / 2\langle z^2\rangle) \qquad [9]$$

the smectic layer order parameters take the form

$$\tau_{00l} = \exp(-2\pi^2 l^2 \langle z^2\rangle / d^2) \qquad [10]$$

where $<z^2>$ is the mean square displacement of the atoms. From Eq.8 we obtain

$$\frac{I_{002}}{I_{001}} = \frac{\tau_2^2}{\tau_1^2}\frac{I^\circ_{002}}{I^\circ_{001}} \qquad [11]$$

The intensity ratio I^o_{002}/I^o_{001} can be calculated for a simple model where the side chains assume a planar fully extended conformation with an average tilt of 40° with respect to the layer normal. The value obtained is 1.07 and is not very sensitive to the details of the model. From I_{002}/I_{001}= 0.74 (Table I) we obtain τ_2/τ_1=0.83 (Eq.11), and $(<z^2>)^{1/2}$=3.1 Å (Eq.10). This value corresponds to a smectic layer order parameter τ_1= 0.94, thus further indicating a strong confinement of the repeatings unit into a regular registry.

CONCLUSIONS

The analysis of the X-ray diffraction spectra of polymer ***1h*** on powder specimens and on stretched oriented fibers evidenced a bilayer smectic C mesophase where the mesogenic groups are tilted by an angle $\beta \approx 40°$ with respect to the layer normal. The presence of four orders of reflection on the smectic layers allowed Fourier inversion calculation of the electron density profile $\rho(z)$ along the normal to the smectic layers. The electron density profile best complying with the steric packing requirements of the smectic C mesophase is the ρ_{--++}. In this profile there exist two maxima relevant to the rigid parts (the mesogenic core including the sulfur atom) and a wide minimum relevant to the aliphatic segments. The width of the maxima suggests only a very limited extent of mesogenic core dislocation due to the translational fluctuations whereas the slight maximum of the density profile in the middle of the layer points to the presence of a partial interdigitation between the aliphatic chains. The positional smectic layer order parameter was calculated and its value complies with a well ordered layer structure.

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