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X-ray diffraction study of the smectic mesophase of some azobenzene-containing polyacrylates

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X-ray diffraction study of the smectic mesophase of some azobenzene-containing polyacrylates

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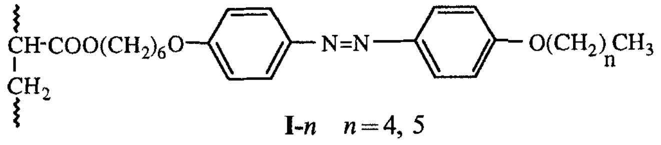
An X-ray study is performed on powder specimens and on stretched oriented fibres of two liquid crystalline polyacrylates containing the azobenzene mesogenic unit with either a 4'-*n*-pentyloxy (sample **I-4**) or 4'-*n*-hexyloxy (sample **I-5**) substituent. The X-ray diffraction patterns of both samples showed the presence of a bilayer smectic C mesophase with the mesogneic groups tilted by an angle $\beta \sim 45°$ (**I-4**) or $\beta \sim 38°$ (**I-5**) 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 possible structural models of the smectic mesophase are discussed. A partial interdigitation of the terminal alkyloxy substituents appears to occur.

1. Introduction

Considerable interest is presently being focused [1–6] on side chain liquid crystalline polymers containing azobenzene mesogenic units. Due to the reversible *trans–cis* photochemical or thermal isomerization of the azobenzene moieties, these materials may find applications in erasable optical memory discs and tapes, holographic storage devices, optical sensors and non-linear optics systems.

In recent papers we have described [7–10] the synthesis and liquid crystalline properties of a large variety of polymers and copolymers containing the azobenzene mesogen. A careful control of the structural and molecular parameters allows us to obtain polymeric materials with tailored mesomorphic behaviour. In particular, several samples of a polymer series **I-*n*** whose general structure is represented in the formula



I-*n* $n = 4, 5$

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were prepared [7] and characterized with respect to their liquid crystalline properties by differential scanning calorimetry and optical microscopy observations. A highly differentiated mesomorphic behaviour was observed including nematic and smectic mesophases. In order to identify better these mesophases and to provide a detailed description of the molecular organization in polymeric smectic mesophases, in the present paper we report an X-ray investigation of the samples **I-4** and **I-5** having a 4′-*n*-pentyloxy and 4′-*n*-hexyloxy substituent, respectively. X-ray diffraction spectra were recorded on powder specimens and on stretched oriented fibres and a model of the molecular structural packing in the smectic mesophases is given. The electron density distribution, along the normal to the smectic layers, which follows from the model, is compared with the one obtained by Fourier analysis.

2. Experimental

Polyacrylates **I-4** and **I-5** were prepared as previously described [7]. X-ray diffraction measurements were performed both on powder samples and on stretched oriented fibres. Oriented samples were produced by drawing fibres out of the mesophase, at a temperature of ~ 105°C in both cases, with a pair of tweezers at a speed of about $0{\cdot}1\,\mathrm{m\,s^{-1}}$ and subsequently quenching them in liquid nitrogen. X-ray diffraction measurements on powder samples were performed by an 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°. Ge(101) monochromatized Cu–K_α radiation ($\lambda = 1{\cdot}54$ Å) was used. X-ray diffraction photographs on oriented samples were obtained by means of a Rigaku–Denky RV300 rotating anode generator equipped with a pin-hole flat camera. Ni-filtered Cu–K_α radiation was used. The optical density of the X-ray diffraction photographs was measured with a microdensitometer. The 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 is proportional to $\sin\theta^{-2}$ [11, 12] and the Ge monochromator induces [13] a polarization factor $P(\theta)$

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

with $\alpha = 11{\cdot}1°$. Accordingly, the experimental results were corrected for the combined Lorentz–polarization factor $LP(\theta)$

$$LP(\theta)=\frac{0{\cdot}538+0{\cdot}461\cos^2 2\theta}{\sin^2\theta}. \qquad (2)$$

3. Results and discussion

3.1. *Analysis of the X-ray diffraction spectra*

The liquid crystalline properties of polymers **I-4** and **I-5** were previously described [7]. Both polymers exhibit a smectic mesophase. A nematic mesophase is also shown by **I-4**. The phase transition data of the polymers are collected in table 1. Figures 1 and 2 illustrate the X-ray diffraction diagrams, obtained at different temperatures from room temperature up to the isotropization point, of powder samples of **I-4** and **I-5**, respectively. The X-ray diagrams of both samples recorded at room temperature consist of three small angle peaks and several diffuse wide angle peaks thus indicating that the thermal untreated samples are nearly amorphous with a relatively small degree of crystallinity ($X_c \approx 5$–10 per cent). The above X-ray patterns do not change with increasing temperature until the melting temperature of the corresponding sample is reached. Above the melting point, X-ray diffraction patterns, constituted by three sharp small angle signals, corresponding to three orders of reflection, and a wide angle diffuse signal, are observed in both samples. Similar X-ray diffraction patterns are characteristic of a disordered layered structure consistent with a smectic phase of A or C type. Above the smectic to isotropic and the smectic to nematic transition temperatures of samples **I-4** and **I-5**, respectively, the X-ray diffraction patterns display only a broad halo at wide angles with a maximum at about 4·5 Å. The X-ray diffraction patterns recorded on samples cooled to temperatures within the smectic mesophase closely parallel those obtained on heating, whereas at room temperature a highly ordered lamellar phase is observed for both samples. The smectic interlayer spacings d at temperatures 10° above the melting point are $d = 47\cdot5$ Å and $d = 51\cdot5$ Å for **I-4** and **I-5**, respectively, and increase slightly with increasing temperature. A variation of ~ 5 per cent in d is observed in both samples when the temperature is raised from the lower to the upper limit of the smectic mesophase. The smectic interlayer spacings are much longer than the length L of the repeating unit in the fully extended conformation as estimated from the Dreiding stereomodels ($L \approx 34$ Å for **I-4** and $L \approx 35$ Å for **I-5**). This implies some form of bilayer arrangement of the side chains in the smectic mesophase.

To gain a better view of the structure of the smectic mesophases of **I-4** and **I-5**, X-ray diffraction measurements on the stretched fibres were performed. Figure 3 (*a*) shows the X-ray diffraction pattern of the oriented smectic mesophase of polymer **I-4** and figure 3 (*b*) shows for the convenience of clarity its schematic representation. The X-ray diffraction pattern of the oriented sample **I-5** is very similar to the one of sample **I-4**. The anisotropy shown in the X-ray pattern clearly demonstrates that a high degree of molecular orientation can be achieved by drawing fibres from the mesophases. There are two basic features to be noted in the X-ray patterns. In the small angle region there are six Bragg spots corresponding to the first, second and third orders of reflection of the smectic interlayer spacing. They are aligned on the equator thus indicating that the smectic layers and consequently the polymer chains are parallel to the fibre axis. In addition, a diffuse four spots wide angle pattern is observed consistent with liquid-like order within the layers. These diffuse spots are roughly equidistant from the origin and form pairs on straight lines making an angle β of $45 \pm 2°$ for **I-4** and $38 \pm 2°$ for **I-5** with respect to the fibre axis. Therefore we conclude that for both samples the mesogenic side groups are tilted by this angle with respect to the layer normal such as in the smectic C mesophase [14, 15]. Two possible structural arrangements of the polymer smectic C phase are sketched in figure 4.

Table 1. Physicochemical properties of liquid crystalline polyacrylates **I-4** and **I-5**.

Sample	M_n/g mol^{-1}†	T_m/K	T_{SCN}/K	T_i/K	ΔS_{SCN}/J mol^{-1} K^{-1}	ΔS_i/J mol^{-1} K^{-1}
I-4	79000	378	402	416	2·7	1·9
I-5	99000	373	—	420	—	11·4

† By SEC, in chloroform at 25°C.

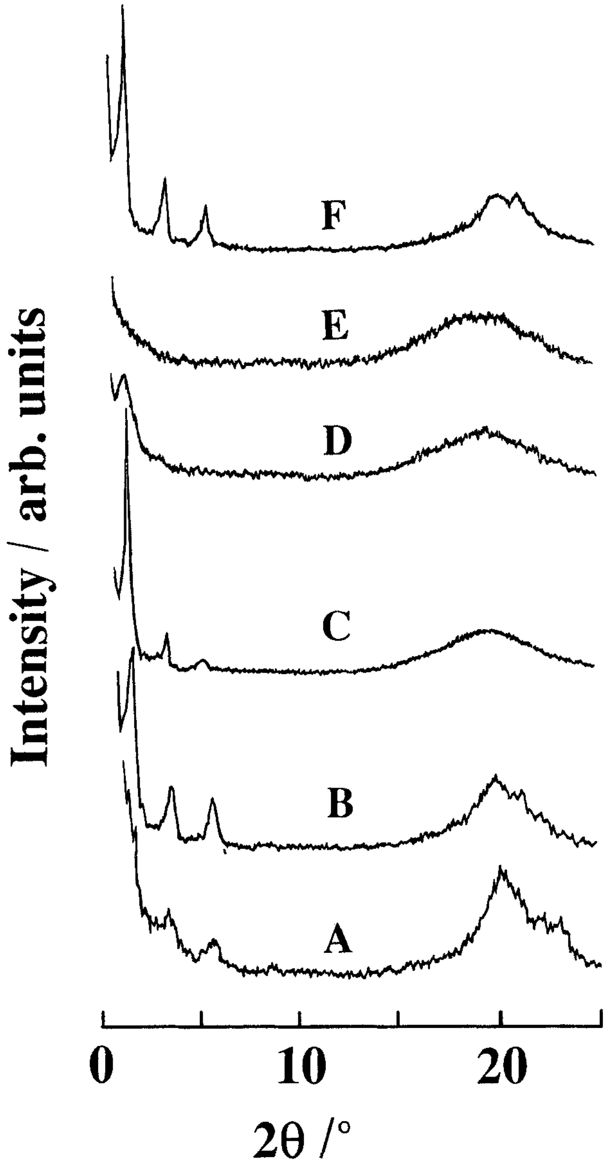


Figure 1. X-ray diffraction diagrams of polymer **I-4** at different temperatures: 300 K (A) (virgin sample); 368 K (*B*); 393 K (*C*); 408 K (*D*); 416 K (*E*); 300 K (*F*) (after cooling from the isotropic melt).

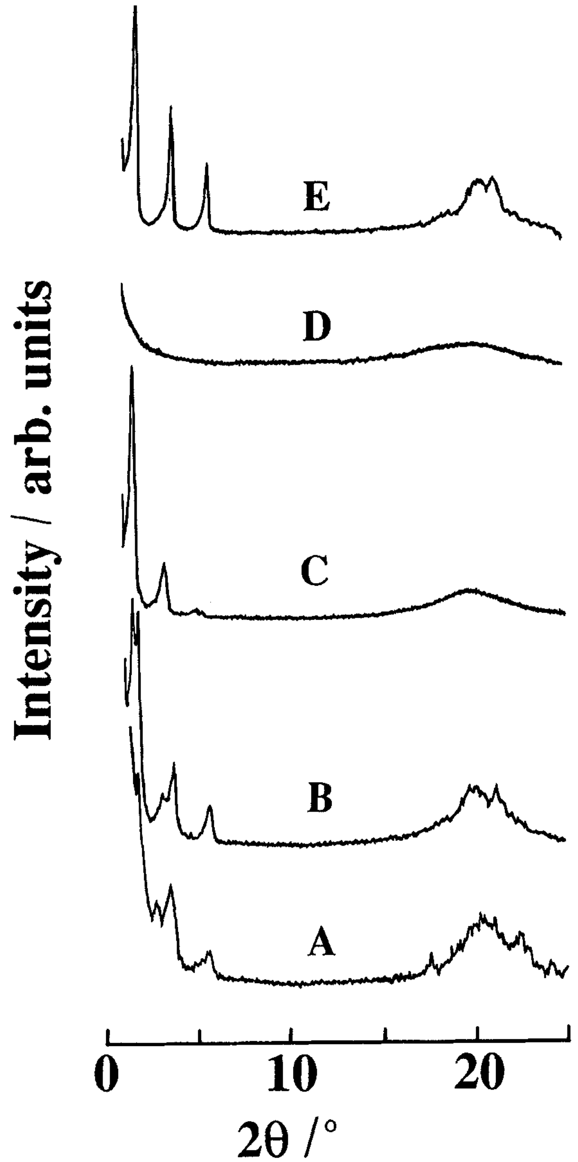
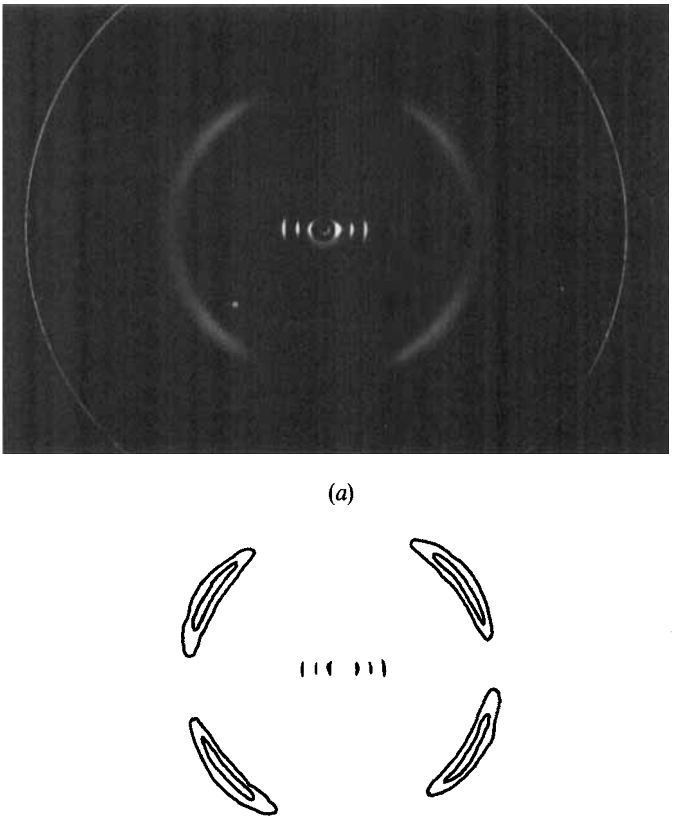


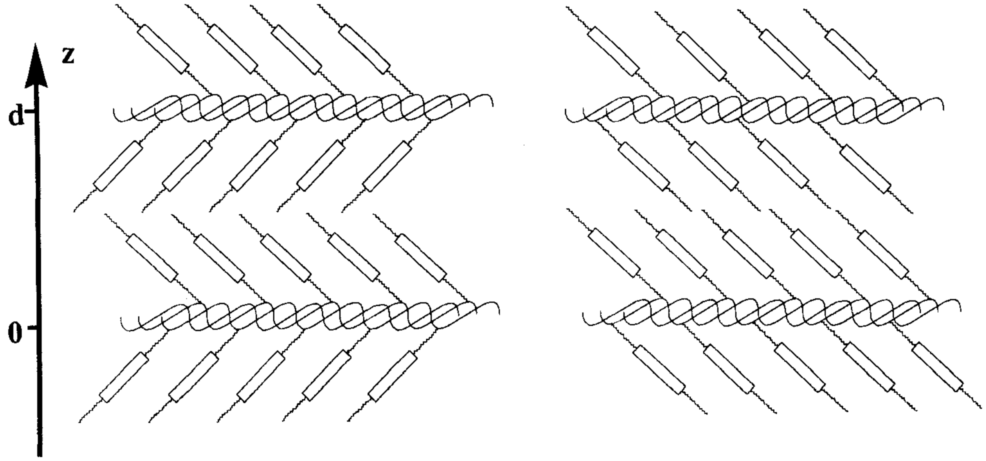
Figure 2. X-ray diffraction diagrams of polymer **I-5** at different temperatures: 300 K (*A*) (virgin sample); 363 K (*B*); 378 K (*C*); 423 K (*D*); 300 K (*E*) (after cooling from the isotropic melt).



(*a*)

(*b*)

Figure 3. Fibre X-ray diffraction pattern of the smectic mesophase of polymer **I-4** (*a*) and schematic representation of its intensity contour map (*b*) (vertical fibre axis).



(*a*) (*b*)

Figure 4. Schematic representations involving tilting of the side chains of polymers **I-4** and **I-5** in the bilayer smectic C mesophase.

3.2. *Determination of the electron density profile along the smectic layer normal*

The presence of several orders of reflection in the diffraction spectra means that the projection of the electron density profile along the normal to the smectic layers cannot be described by ideal single sinusoidal modulation [16, 17]. On the other hand, the knowledge of the electron density profile gives information both on the degree of confinement of the backbones and the organization of the chains in the mesophase. To this purpose, the electron density profile $\rho(z)$ along the direction normal to the smectic layers (z axis) was determined by Fourier inversion. Since no absolute intensities could be obtained, the results are presented as the ratio $I_{(00l)}/I_{(001)}$ of the intensity of the lth order of reflection to the intensity of the first one. The corrected integrated intensities of the three reflection orders, measured at 110°C for **I-4** and at 105°C for **I-5**, are reported in table 2. Referring to the model with a herring-bone structure sketched in figure 4 (*a*), let us take the origin of the z axis in the middle of the layer. With this choice, $\rho(z)$ is symmetric and can be expressed by a Fourier series containing only cosine terms according to

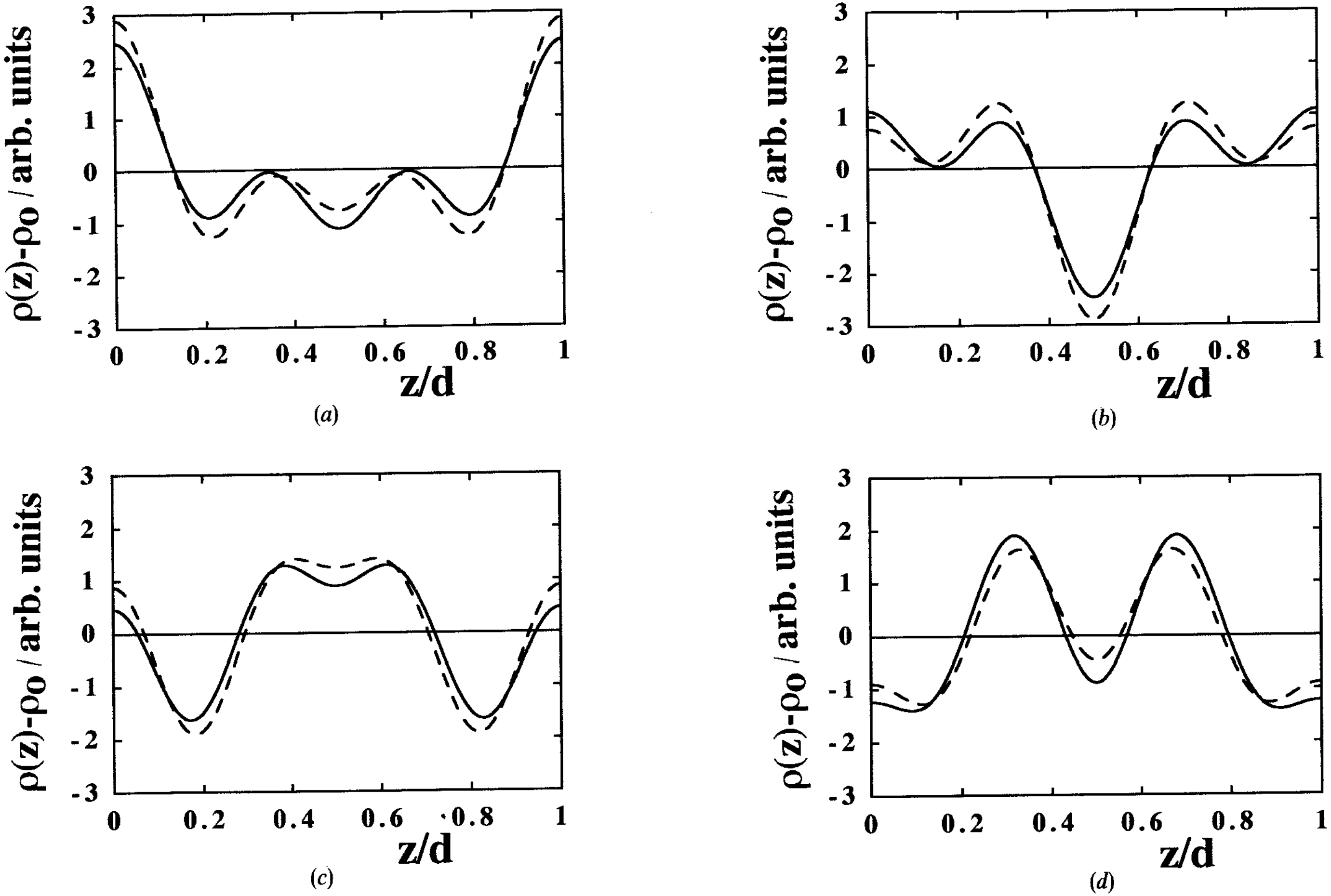
$$\rho(z)=\rho_0+\sum_{l=1}^{\infty} a_l \cos\left(2\pi l \frac{z}{d}\right), \tag{3}$$

where ρ_0 is the average value for the electron density along the director, d is the smectic interlayer spacing and a_l is the amplitude of the $00l$ reflection. We evaluate ρ_0 by dividing the total number of electrons of the repeating unit by d and obtain $\rho_0=9{\cdot}6\,\mathrm{e}^-\,\text{Å}^{-1}$ for **I-4** and $\rho_0=9{\cdot}2\,\mathrm{e}^-\,\text{Å}^{-1}$ for **I-5**. The intensity $I(00l)$ of the lth order of reflection is directly proportional to the square of the modulus of a_l. The moduli of the amplitudes a_l are collected in table 2. Due to the centrosymmetric nature of the electron density distribution, the phase of the amplitude a_l can be 0 or π and consequently a_l can be positive or negative. The phase problem then reduces to choosing the right combination of signs for the amplitudes a_l. Eight different electron density distributions can be obtained corresponding to the different sign amplitude combinations. Let us call, for example, ρ_{+-+} the combination where a_1 and a_3 are chosen positive whereas a_2 is chosen negative. The electron densities of the mesogenic cores (ρ_{core}) and of the aliphatic (spacer and terminal substituent) chains (ρ_{al}), under the assumption that the aliphatic chains are in the fully extended conformation, are evaluated by dividing the total number of electrons of each unit by the z-projection of their respective size and results in $\rho_{\mathrm{core}}=12{\cdot}0\,\mathrm{e}^-\,\text{Å}^{-1}$ for **I-4** and $10{\cdot}6\,\mathrm{e}^-\,\text{Å}^{-1}$ for **I-5**, and $\rho_{\mathrm{al}}=8{\cdot}9\,\mathrm{e}^-\,\text{Å}^{-1}$ for **I-4** and $8{\cdot}0\,\mathrm{e}^-\,\text{Å}^{-1}$ for **I-5**. The electron density of the backbone ρ_{b} depends on its degree of confinement. We can estimate for ρ_{b} an upper value, corresponding to its maximum confinement, of $\rho_{\mathrm{b(max)}}=15{\cdot}0\,\mathrm{e}^-\,\text{Å}^{-1}$ and a lower value,

Table 2. Intensities I and amplitude a values† of the $00l$ Bragg reflections of the smectic mesophase for samples **I-4** (at 110°C) and **I-5** (at 105°C).

Sample	$00l$	$I_{(00l)}/I_{(001)}$	a_l/a_1
I-4	001	1	1
	002	0·47	0·68
	003	0·62	0·79
I-5	001	1	1
	002	1·12	1·06
	003	0·69	0·83

†Corrected for the Lorentz–polarization factor and normalized to the intensity and amplitude of the corresponding first order reflection.



(*a*) (*b*) (*c*) (*d*)

Figure 5. Projection of the electron density profile $\rho(z)$ along the normal to the smectic layers for polymers **I-4** (solid curve) and **I-5** (dashed curve) corresponding to the different sign combinations of the a_l coefficients: (*a*) ρ_{+++}; (*b*) ρ_{+-+}; (*c*) ρ_{-++}; and (*d*) ρ_{--+}.

corresponding to its minimum confinement, of $\rho_{b(\min)}=9\cdot5\,e^{-}\,\text{Å}^{-1}$. In both cases ρ_b is higher than the one of the aliphatic chains ρ_{al}. Accordingly, the electron density $\rho(z)$ should have a maximum corresponding to the polymer backbone and two maxima corresponding to the two mesogenic groups. Four electron density distributions, namely the ρ_{---}, ρ_{++-}, ρ_{-+-} and ρ_{+--}, do not possess such a maxima and were discarded. The remaining four electron density distributions, namely the ρ_{+++}, ρ_{+-+}, ρ_{--+} and ρ_{-++} matching the above expectation are illustrated in figure 5 (*a*)–(*d*). The ρ_{+++} distribution (see figure 5 (*a*)) is characterized by an exceedingly high density in the region of a strongly confined backbone. The ρ_{+-+} distribution (see figure 5 (*b*)) exhibits a physically unlikely deepest minimum in the middle of the interlayer region. By contrast, an excessive degree of interdigitation of the mesogenic units would result according to the ρ_{-++} profile (see figure 5 (*c*)). Finally, the ρ_{--+} electron density distribution (see figure 5 (*d*)) suggests that some interdigitation of the mesogenic units and a limited microsegregation of the polymer backbone should be present. Consistent with our results, we may conclude the ρ_{--+} electron distribution profile to occur in the smectic mesophase of polymers **I-4** and **I-5**. In this model, a higher extent of interdigitation is expected for polymer **I-5** that was found to have a smaller tilt angle.

Recently, Etherington *et al.* [18] have introduced for the evaluation of electron density of low molar mass liquid crystals a parameter r defined as

$$r=\frac{\rho_0-\rho_{al}}{\rho_{core}-\rho_{al}}. \tag{4}$$

This parameter may serve as a qualitative criterion for the choice of the proper electron density solution even in polymers, as discussed in [17, 19]. The values of r calculated for the electron density distribution of **I-4** are $r=1\cdot05$ for ρ_{+++}, $r=0\cdot56$ for ρ_{+-+}, $r=0\cdot56$ for ρ_{-++} and $r=0\cdot44$ for ρ_{--+}, while those of **I-5** are $r=1\cdot09$ for ρ_{+++}, $r=0\cdot70$ for ρ_{+-+}, $r=0\cdot58$ for ρ_{-++} and $r=0\cdot42$ for ρ_{--+}. We estimate a value of $r=0\cdot23$ and $r=0\cdot46$ for **I-4** and **I-5**, respectively, and therefore the ρ_{--+} electron density distribution appears to be the actual one for both polymers, in agreement with the above conclusions.

4. Conclusions

The analysis of the X-ray diffraction spectra of polymers **I-4** and **I-5** on powder specimens and on stretched oriented fibres evidenced in both samples a bilayer smectic C mesophase in which the mesogenic groups are tilted by an angle $\beta\sim45°$ (**I-4**) or $\beta\sim38°$ (**I-5**) with respect to the layer normal. In addition, the presence of the first three orders of reflection of the smectic interlayer spacings allowed for a Fourier inversion calculation of the electron density profile $\rho(z)$ along the normal to the smectic layers. It is suggested that the electron density profile best complying with the steric packing requirements of the smectic C mesophase is the ρ_{--+} for both samples. In this profile there exist three maxima relevant to the polymer backbone and to the mesogenic groups, and two minima relevant to the aliphatic spacers and terminal alkyloxy substituents. The electron density value observed in correspondence to the terminal alkyloxy substituents in the middle of the smectic layer is higher than that corresponding to the alkylene spacers. This result points to the presence of a partial interdigitation between the terminal substituents.

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