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Computer simulation of diffuse X-ray scattering by an aligned smectic C-like nematic phase

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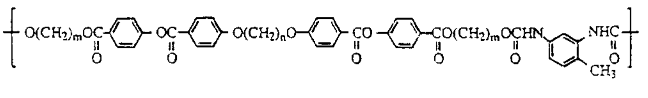
We report a new method for the quantitative analysis of diffuse X-ray scattering by some disordered smectic phases. Computer simulations of diffuse X-ray scattering are compared with actual diffraction patterns of a series of oriented liquid crystalline polymers TDI-C$_m$C$_n$. The simulation shows that both Bragg peaks (spots) and equidistant streaks (diffuse scatterings) are diffracted by one smectic C-like structure in which each of the molecular chains is displaced from its mean position by a random distance Δ_z, along the chain axis (z). This is a first type of disorder. By assuming a Gaussian distribution of the disordered displacements, the mean value of Δ_z has been determined from the position and intensity of the streaks and Bragg peaks for the polymers.

1. Introduction

We have investigated by computer simulation a typical X-ray diffraction pattern which displays both lower angle Bragg peaks (spots) and diffuse streaks. This type of diffraction pattern is produced by oriented smectic liquid crystals, in particular main-chain polymer smectics. There are two traditional ways to analyse such diffuse scattering. One is to assume some partially ordered structure; the other is to assume that the Bragg peaks and streaks are contributed by two coexisting phases: the nematic and smectic phases. Here we show that computer simulations of the X-ray diffraction patterns of the series of main-chain polymers TDI-C$_m$C$_n$ can give a very clear picture of the partial order of the smectic phase. It has led to a new method of analysis of this type of diffuse scattering.

2. Experimental

The main-chain polymers TDI-C$_m$C$_n$ are synthesized from various mesogenic alkylene di[4-(ω-hydroxyalkyloxy-4-oxybenzoyl)oxybenzoate]s [1]. The chemical structures of the polymers are:



TDI denotes 2,4-toluenediisocyanate. The diffraction patterns of oriented samples were recorded on films by using a pin-hole flat camera, at room temperature. Our experiments have been described elsewhere [1, 2]. On each of the patterns, pairs of Bragg diffraction spots and series of streaks are displayed; they have a common periodicity along the fibre axis. The positions of Bragg peaks correspond to a smectic C-like structure in which the molecular axis is aligned parallel to the fibre director. This type of diffuse scattering has been observed in other liquid crystal (LC) systems [3–6] and in protein crystal [7].

There are two ways to interpret such diffraction patterns. One way is to assume that both the streaks and Bragg peaks may be attributed to one disordered structure, for example as in the Doucet and Benoit investigation of crystalline lysozyme [7]. Their study confirmed that the diffuse streaks are induced by coupled displacement of molecules along one axis of the crystal. A contrary interpretation is to assume that Bragg peaks and streaks are diffracted respectively by two different phases: smectic and nematic [2]. This raises the question: what is the real structure of the polymer TDI-C$_m$C$_n$?

The actual X-ray diffraction patterns of aligned TDI-C$_m$C$_n$ samples are very similar for different m and n numbers. As an example, figure 1 (*a*) shows a real pattern and a schematic representation of the pattern of TDI-C$_6$C$_{10}$. The high angle region consists of a pair

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Figure 1. X-ray diffraction pattern and the corresponding structure of polymer TDI-C_6C_{10}. (*a*) Actual pattern and a schematic representation of the pattern; (*b*) the packing of the molecular chains in the fibre.

of broad crescents (centred at $d_m = 4.3$ Å), lying on the line: $z = 0$. It indicates that the molecules are apparently aligned parallel to the fibre axis (z) and form a liquid-like array. In the low angle region, the pattern displays both equidistant Bragg peaks (spots) and equidistant streaks. The Bragg peaks are located in one direct line which passes through the centre of the pattern and forms an angle ($\beta = 53°$ for TDI-C_6C_{10}) with respect to z. These peaks are respectively the first, second and third order of peaks by a smectic C-like structure with a layer thickness of 36.5 Å, see figure 1 (*b*). Moreover, some higher order of streaks, orthogonal to the z axis, are observed. For all the samples, we can always find that both the Bragg peaks and the streaks correspond to a common periodicity along z. For Bragg peaks, the periodicity: $P_B = \langle nd_n \rangle / \cos \beta$; where the d_n is the nth order of the spacing of reflection plane, n denoting the order number. For the streaks, the periodicity: $P_s = \langle nd_{ns} \rangle$; where $d_{ns} = n\lambda / \sin 2\theta$, is obtained from the positions of the streaks. The table shows the experimental data, and that the value of P_B is equal to P_s, for each of the samples under test. The observed periodicity also agrees with that measured from the molecular chain model with a fully extended conformation.

3. Simulations

Simulated diffraction patterns are calculated by the square of the modulus of the Fourier transformation (FT) of a 2D monoclinic lattice with the first type disorder [8]. A band of parallel molecular chains is represented by a 2D pixel lattice, in which each of the pixels represents a repeating unit and each column of pixels represents a molecular chain. The unit cell of the lattice is defined by three constants: a, c and α, see figure 1 (*b*). It was assumed that all the pixels in hth column shift together along the z axis by a distance of Δz_h; with respect to their position in a perfect lattice. There is no correlation between the displacements of different columns. Moreover, the probability of the displacements Δz_h is assumed as a Gaussian distribution, that is:

$$p(\Delta z_h) = \frac{1}{\sqrt{2\pi}\Delta_z} \exp\left(-\frac{\Delta z_h^2}{2\Delta_z^2} \right) \tag{1}$$

where Δ_z^2 is the mean-square of the displacements. The relative mean displacement is defined as: $D_z = \Delta_z / c$.

The simulations are very realistic, in that both the 'Bragg' peaks and streaks appear in the pattern whenever $D_z > 0$. The main features are located at the lines of $q_z = 2\pi n / c$; Bragg peaks appear at lower q_z while streaks display at higher q_z range, and some of them are overlapped. Figure 2 (*a*) shows the simulated diffraction pattern by a disordered lattice ($D_z = 0.1$). The simulations also reveal that the intensities of Bragg peaks can be fitted perfectly by the function: $I_{\mathrm{Bragg}} = n_x^2 n_z^2 \exp(-q_z^2 \Delta_z^2)$, and that the streak intensities can be expressed as: $I_{\mathrm{Streak}} = n_x n_z^2 [1 - \exp(-q_z^2 \Delta_z^2)]$. Figure 2 (*b*) illustrates the intensities of Bragg peaks and the streaks as a function of q_z together with the best fit curves. It is reasonable to expect the square of the FT of the distribution function (1) has the form: *Constant* $\times \exp(-q_z^2 \Delta_z^2)$ since the effective electron density profile along z is the convolution of the density of a perfect lattice and the distribution function.

Table 1. The X-ray diffraction data and the longitudinal displacements of molecular chains of the polymers TDI-C_mC_n.

Parameter		Polymer, TDI-				
		C_2C_6	C_4C_6	C_6C_4	C_6C_6	C_6C_{10}
Bragg Peaks/Å	d_1	31.2	32.5	35.4	37.4	36.5
	d_2		16.2	17.6	18.6	18.2
	d_3					12.2
	$\beta/°$	46.4	49.8	49.0	46.7	53.4
	L_x/Å	132	259	262	322	560
	L_{B}	$45.2\pm.8$	$50.4\pm.8$	$54.0\pm.8$	$54.5\pm.8$	$61.2\pm.6$
Streaks/Å	d_2	22.7				
	d_3	14.9	16.4	17.6	17.9	19.8
	d_4			13.2	13.5	15.2
	d_5		9.9	10.7	10.9	
	P_{S}	$45.1\pm.8$	$49.4\pm.8$	$53.1\pm.8$	$54.2\pm.8$	$60.1\pm.8$
Crescent/Å	$\langle d_{\mathrm{m}}\rangle$	4.30	4.27	4.27	4.30	4.28
$I_{\mathrm{Streak}}/I_{\mathrm{Bragg}}$		1	1	1	1	0.4
$D_z=\Delta_z/P_{\mathrm{B}}$		0.63	0.45	0.45	0.48	0.39

The result can also be applied to 3D lattices. By taking the structure factor into account, we have:

$$I_{\mathrm{Bragg}}=(n_xn_yn_z)^2|F|^2\exp(-q_z^2\Delta_z^2) \tag{2}$$

$$I_{\mathrm{Streak}}=n_xn_yn_z^2|F_z|^2[1-\exp(-q_z^2\Delta_z^2)] \tag{3}$$

where F is the structure factor of a perfect cell and F_z denotes the structure factor of a perfect cell along z. The integers n_x, n_y and n_z represent the number of the lattice cells in the x, y and z directions. Equations (2) and (3) are analogous to the Debye–Waller factor [8, 9], where thermal diffuse scattering is replaced by the streaks because of the disordered displacements of the molecular chains instead of individual atoms. When the lattice constants $c\gg a$, then $|F|^2\approx|F_z|^2$. Combining the formulas (2) and (3), yields:

$$\Delta_z=\frac{1}{q_z}\ln\left(1+N\,\frac{I_{\mathrm{Streak}}}{I_{\mathrm{Bragg}}}\right) \tag{4}$$

where, $N=n_xn_y$. This equation allows us to evaluate directly the displacement Δ_z of molecular chain for some real samples.

Because of the overlap of streak and third order Bragg peak, for the sample TDI-C_6C_{10}, Δ_z may be calculated directly by using equation (4). The translational correlation length (L_x) of the smectic layer corresponds to the inverse of the full width at half-maximum of Bragg peaks along x. N corresponds to the average number of molecular chains in a domain and can be approximated as: $N=(\pi/6\sqrt{3})(L_x/d_{\mathrm{m}})^2\approx 0.3(L_x/d_{\mathrm{m}})^2$, by assuming the correlated area (domain) normal to the fibre axis has a circular shape with diameter of L_x, and that the molecular chain packing is in a quasi hexagonal array in the area.

For other samples, there is no overlap of Bragg peaks and streaks. Here, we assume that: $I_{\mathrm{Streak}}/I_{\mathrm{Bragg}}=1$, at the position $q_z=\sqrt{q_{z\mathrm{B}}q_{z\mathrm{s}}}$, where $q_{z\mathrm{B}}$ and $q_{z\mathrm{s}}$ denote, respectively, the position of the highest order of the observed Bragg peak and the lowest order of observed streak ($q_{z\mathrm{s}}$) in the pattern along the z direction. The ratio Δ_z/P_{B} calculated from our samples (see the table), varies from 0.39 to 0.63. These molecular chain displacements are quite large compared with the conventional smectic phase [5], and yet they are less than one would expect for a conventional nematic phase. Thus it seems appropriate to refer to this structure as a smectic C-like nematic phase.

With respect to the determination of Δ_z, there are some differences between our method and that of Hosemann [10]. Hosemann's theory is based on a disordered lattice of the second type, in which the fluctuation (same as Δ_z) is a function of $q_{z\mathrm{B}}$. Our method is based on the existence of first type of disorder in the lattice, where Δ_z depends not only on $q_{z\mathrm{B}}$ but also on other factors. In fact, real LC systems usually exhibit both the first and the second type disorder, and one type of disorder may dominate the structure: we must therefore choose an appropriate method to evaluate the fluctuation.

Our results confirm that it is sufficient to consider only the deformation of the lattice and ignore the deformation inside a unit cell. An advantage of the method is that we use the structural factor of a perfect

(*a*)

(*b*)

(*c*)

Figure 2. (*a*) The simulated diffraction pattern of a disordered lattice in real space with the parameters: $c=50$ Å, $D_z=0.1$. (*b*) Based on the different D_z values, the intensities of the 'Bragg peaks' and (*c*) the streaks, as a function of q_z, with best fit curves.

cell that is more easily calculated than the 'average structural factor' $\langle F \rangle$ in the traditional method of diffuse scattering analysis. With regard to streak intensity, the traditional method and our technique yield similar results. An equation similar to formula (3) has been reported [7], based on the traditional method, where the mean-square of molecular displacements in the protein crystal was evaluated according to the intensities of the streaks. However, a satisfactory result was obtained only with small amplitude displacements, because a harmonic type of displacement was assumed; our method employs a strict solution and may be applied to calculate any displacement.

The interpretation of the nematic cybotactic phase [2] is unsatisfactory for the samples TDI-C_mC_n, because it does not explain the experimental observations: the absence of lower order streaks and higher order Bragg peaks. According to this model, the polymer coexists in two phases: nematic and smectic phase (in cybotactic clusters), which contribute to the Bragg peaks and streaks, respectively. However, for a conventional nematic phase, the lower order streaks should also be displayed in the patterns, because the streaks are attributed to the diffraction of individual molecular chains. For a conventional smectic phase, some higher order Bragg peaks should be observed in the patterns, because of its ordered structure. The absence of lower order streaks is also observed in the patterns of other aligned LC systems [3]. It has been suggested that this is because of a special shape of the electron density profile along the molecular chain, so that the structural factor(s) of the first order of diffraction is equal to zero. It is difficult to believe in the existence of such a strange and very sharp electron density profile along the molecular chain, in some quite disordered LC systems. In addition, it is also difficult to explain, for the same molecular chain, why the electron density profiles (which are determined according to the intensities of streaks) are so different from those determined from the intensities of Bragg peaks. We consider that equations (2) and (3) give a preferable explanation of this fact.

4. Conclusions

Our study leads to the following inferences. (1) The longitudinal disorder displacements of molecular chains in an aligned smectic-like structure can eliminate the higher order Bragg peaks and create higher order diffuse streaks simultaneously in the patterns. (2) The value of the displacements can be quantitatively determined by analysis of the diffuse scattering. (3) Each of the polymers TDI-C_mC_n, forms a smectic C-like nematic phase.

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