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Liquid Crystals

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Preliminary communication

Thermotropic liquid crystals of polyesters having a mesogenic p,p' -bibenzoate unit

X. Distinct orientation of molecules in a thin SmCA film stretched from isotropic melt, providing evidence for the biaxiality of the SmCA phase

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A thin oriented SmCA film of a main-chain polyester was prepared by drawing from the isotropic melt, and X-ray patterns were observed by irradiation from three characteristic positions relative to the film. The results clarify the biaxiality of the SmCA phase, with a distinct molecular orientation where the mesogenic groups are tilted in a zigzag manner in a direction perpendicular to the film surface. Such a biaxial orientation is considered to result from the relaxation from the extended arrangement of the mesogenic groups on stretching to the stable zigzag arrangement.

The SmCA phase was initially proposed from the oriented X-ray pattern of BB- n polyesters with an odd n [1, 2]. The qualitative model that emerges from the X-ray pattern and conformational analysis is one in which the mesogenic groups are tilted to the layer normal, and their tilt direction (c -director) is opposite between neighbouring layers [see figure 1(a)] [3-5]. In other words, the polymer chain lies along the direction perpendicular to the layers [z -direction in figure 1(a)], assuming the average conformation, with successive mesogenic groups tilted by around 50° with respect to each other. Crystallographically, SmCA structure can be illustrated by a doubling of the period in the z -direction, giving rise to a second order screw axis [3]. Further, it is invariant under gliding reflection in the xz -plane [see figure 1(a)], i.e. reflection combined with a translation in the z -direction by a half of the period. The space group is analogous to the crystallographic D_{2h} group, although the local symmetry of each layer is C_{2h} as in a SmC phase. The structure is optically biaxial and its optical index ellipsoid can be illustrated for each of two neighbouring layers in the period as shown in figure 1(b). The optic plane is located in the xz -plane and optic axes lie symmetrically on both sides of the Oz -axis.

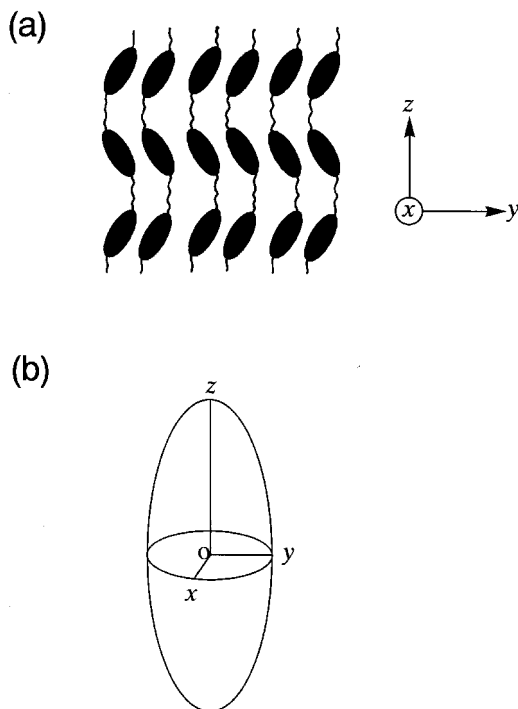


Figure 1. (a) Molecular ordering of the SmCA phase; (b) the optical index ellipsoid of the SmCA phase.

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In addition to the X-ray data, the two following observations support this peculiar structure of the SmC_A phase. First is that the schlieren texture with the singularities of $s = 1/2$ is observed in the homeotropically aligned cell [3, 6, 7]. This is due to the D_{2h} packing symmetry; the head and tail of c -directors are globally indistinguishable and a continuous stacking of layers takes place around the singularity of $s = 1/2$ if a screw dislocation is coupled. This type of defect, produced by a coupling of wedge disclination and helical dislocation, is called a wedge dispiration [8], and was first observed in this phase [6]. Second, a specific property of the light reflection can be seen due to the helical structure induced on the chiral SmC_A^* phase. In this phase, the O_z -axis in the index ellipsoid of figure 1(b) is equivalent to the helical axis and hence the optical property always has a

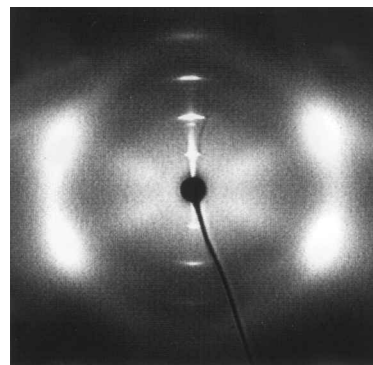


Figure 2. X-ray diffraction pattern for an oriented SmC_A fibre taken at 170°C . The fibre was prepared by drawing from the isotropic melt and its axis is placed in a vertical direction.

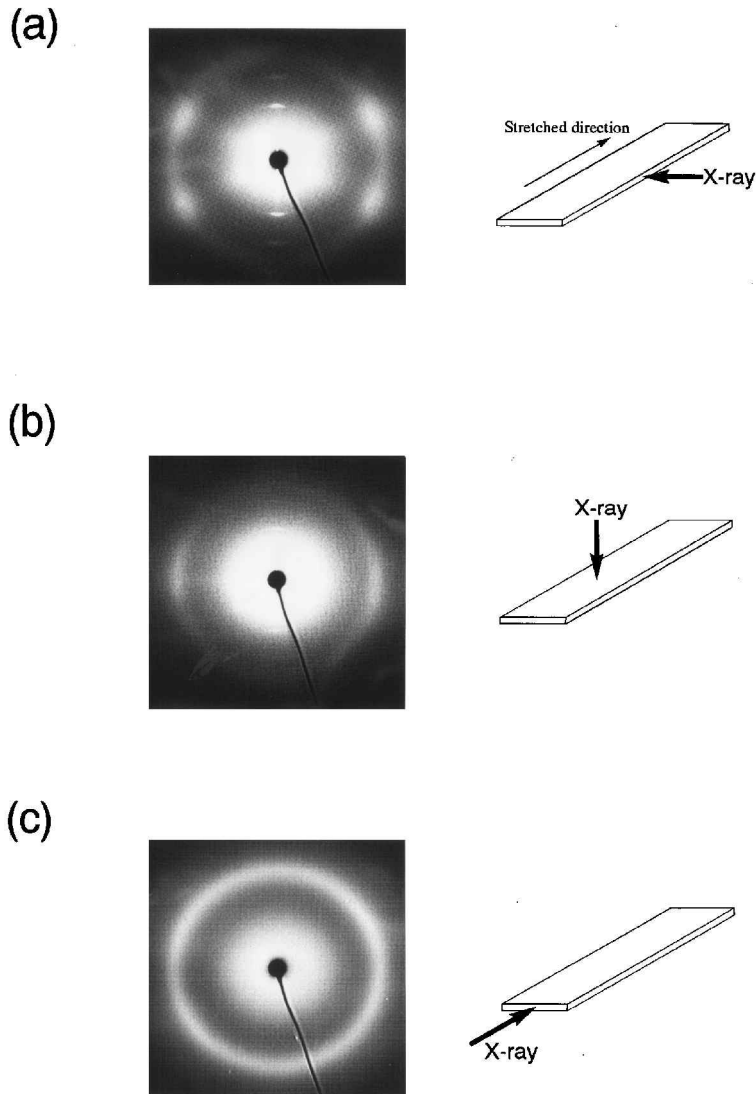


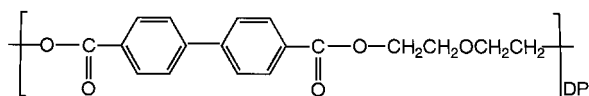
Figure 3. X-ray diffraction patterns of the oriented SmC_A film taken by irradiation from three characteristic positions. (a) Parallel to the film surface and perpendicular to the chain axis; (b) perpendicular to the film surface; (c) parallel to both the film surface and chain axis. In (a) and (b) the chain axis is placed in the vertical direction; in (c) the film surface is parallel to the horizontal direction.

period equal to half the pitch in any view, or on any propagation of light to the helical axis. This situation is similar to that in cholesterics [3], but completely different from that in the chiral SmC^* phase which has a periodicity of the full pitch for light propagating in any direction except for the direction along the helical axis [9].

In most types of liquid crystal so far observed, uniaxial orientation has been achieved for the long axes of mesogens. In this sense, the SmC_A phase discovered in main chain polyesters [1–3] is quite novel and interesting, since uniaxial ordering cannot be observed for the n -director (the long axis of the mesogenic group) but only for the c -director. This discovery leads to the finding of the antiferroelectric chiral SmC_A^* phase [10] and to the ferroelectric smectic phase composed of achiral molecules [11–13].

In this paper, we report distinct molecular orientation in a thin film of SmC_A phase where the zigzag tilting of mesogenic groups takes place preferentially in a direction perpendicular to the film surface. This is direct evidence for the biaxiality of the SmC_A phase.

The polymer used here is $\text{BB}-(\text{OEt})_2$ with the following structure,



$\text{BB}-(\text{OEt})_2$

which belongs to the odd homologue of polymers since the number of atoms in the spacer is five. The polymer was synthesized by melt transesterification from dimethyl p,p' -bibenzoate and diethylene glycol with isopropyl titanate as catalyst. The inherent viscosity of the polymer is 1.3 dl g^{-1} which was measured at 30°C using 0.5 g dl^{-1} solutions in a 60/40 w/w mixture of phenol and tetrachloroethane. The DSC thermogram, measured with a Perkin Elmer DSC-II, indicated only a SmC_A -isotropic transition at 199°C on heating and at 180°C on cooling. No crystallization took place at a normal cooling rate.

Oriented fibre and film were prepared by stretching the viscous isotropic melt; the rate of stretching was around 1 m s^{-1} . The diameter of fibre and thickness of film were around $20 \mu\text{m}$. X-ray patterns were taken at the smectic temperatures with a Rigaku Denki X-ray generator (RU-200). Figure 2 shows a typical X-ray pattern observed for the oriented fibre. The inner layer reflections are observed on the meridian while the outer broad reflections are split above and below the equator, as observed so far for the SmC_A phase [3].

Figures 3(a)–3(c) show the X-ray patterns of film specimens obtained by X-ray irradiation from three

characteristic positions. The X-ray patterns exhibit a fairly good orientation of the chain axis and appear different depending on the direction of X-ray irradiation. In the photograph of figure 3(a), where the beam is irradiated parallel to the film surface and perpendicular to the oriented axis (chain axis), the X-ray pattern includes layer reflections on the meridian and broad reflections split above and below the equator. The splitting of the broad reflections can be seen more clearly in curve (a) of figure 4 where the intensity distribution $I(\beta)$ was measured as a function of the azimuthal angle β at constant diffraction angle of the reflection ($2\theta = 20.5^\circ$). In contrast, when the X-ray beam is irradiated perpendicular to the film surface, the layer reflections are invariably observed on the meridian, but the broad reflections are concentrated on the equator [see figure 3(b) and curve (b) of figure 4]. For X-ray irradiation parallel to both the film surface and chain axis, only broad reflections can be observed without any orientation [figure 3(c)]. These diffraction profiles dictate the biaxiality of the SmC_A phase, in which the zigzag tilting of mesogenic groups takes place in a direction perpendicular to the film surface, as illustrated in figure 5(a).

The layer spacing is 16.0 \AA and the tilt angle of the repeat unit is around 25° , as estimated from curve (a) of figure 4. There is no difference between the spacings of the broad reflections in the two directions parallel and perpendicular to the tilt direction of the mesogenic

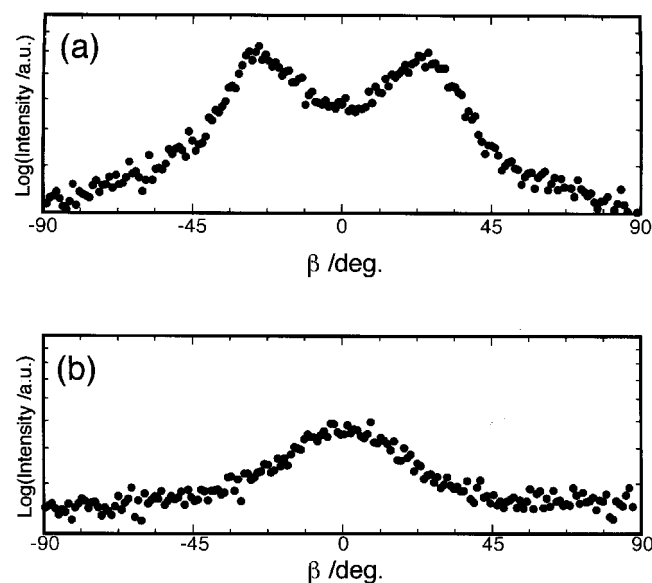


Figure 4. Intensity distribution $I(\beta)$ measured as a function of the azimuthal angle β at a diffraction angle of $2\theta = 20.5^\circ$. Curves (a) and (b) are collected from figures 3(a) and 3(b), respectively. Here, the equatorial direction corresponds to $\beta = 0^\circ$.

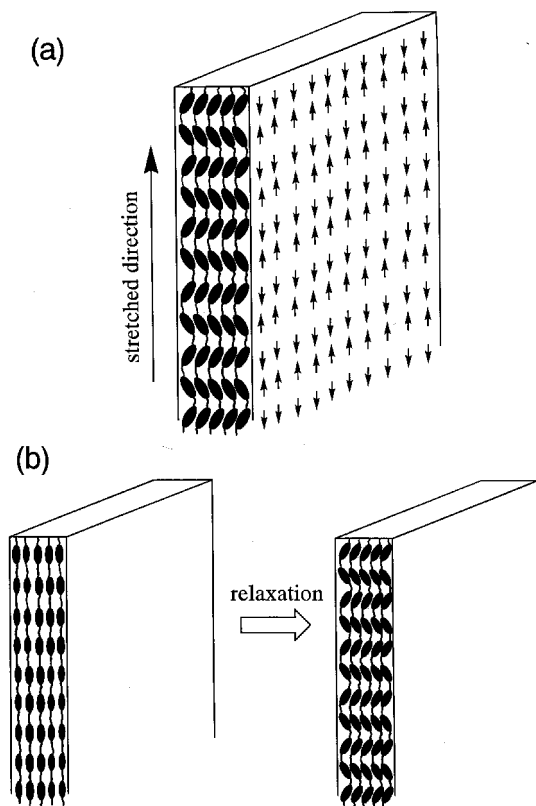


Figure 5. (a) Illustration of the biaxial orientation of zigzag molecules in the SmC_A film where the mesogenic groups are tilted in a direction perpendicular to the film surface. This preferential orientation may be caused by relaxation from the extended arrangement of mesogenic groups on drawing to the stable zigzag arrangement illustrated in (b).

groups. This indicates that there is no significant difference between the molecular interactions in these two directions and so the relatively free rotation of biphenyl mesogens takes place around their long axis. This is reasonable since the biaxiality of the SmC_A phase is produced by the conformational constraint exerted on the individual chain rather than by intermolecular interaction.

A question arises here as to why such a characteristic orientation takes place in the film specimen. At the present time, it is considered to result from the relaxation from the stretched deformation on drawing, as illustrated in figure 5(b). To obtain well oriented films, we applied

a high stretching velocity of around 1 m s^{-1} . With such a high velocity or such a large flow deformation, the polymer chain is somewhat extended; in fact this behaviour has been observed in stretched fibre specimens [14, 15]. Immediately after the sample is cooled to the SmC_A phase, the stretching is completed since the SmC_A phase is far more viscous than the isotropic phase and the extended chains are rapidly relaxed by an elastic rebound to take up the stable conformation with the zigzag arrangement of mesogenic groups. It is conceivable that the relaxation in a thin film specimen takes place in a preferential direction perpendicular to the film surface, since the mesogenic groups may rearrange more easily in this direction than along the film surface. Finally, we note that such a preferential orientation has been observed at least for thin films less than $50 \mu\text{m}$ thick, and found to be stable on a time scale of several hours even at the SmC_A temperatures.

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