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Ferroelectric smectic meso-phase formed by banana-shaped achiral liquid crystals

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A new banana-shaped achiral molecule, 1,3-phenylene bis[4-(3-chloro-4-*n*-octyloxyphenyl-iminomethyl)benzoate] (PBCOB) has been synthesized, and its ferroelectric properties and homeotropic alignment investigated. The presence of a lateral chloro-substituent in the Schiff's base moiety prevents the regular stacking of molecules and results in lowering the transition temperature and the degree of crystallinity of the switchable banana phase. Their smectic mesophases, including a switchable banana phase B_7, were characterized by differential scanning calorimetry, X-ray scattering and polarizing optical microscopy. Both the left- and right-handed helical domains are spontaneously formed upon cooling from the isotropic liquid to the switchable banana phase B_7. By X-ray study, the smectic phases showed a layer spacing of 38.1 Å, compatible with the end-to-end distance of the molecule with a bent conformation. Significantly, the smectic B_7 phase exhibited a periodicity of 292 Å that corresponds to a helical structure with periodicity about 7.5 times 38.1 Å. The spontaneous polarization for PBCOB is about 50 nC cm^{-2} and shows a temperature dependence. The ferroelectric lyo-mesophase of PBCOB showed a ferroelectric electro-optical switching range extending more than 50°C, switchable at room temperature.

1. Introduction

Since Meyer *et al.* [1] discovered ferroelectricity in the chiral smectic C phase (smectic C*), ferroelectricity has been considered to appear only in dopant chiral molecules which are used to reduce the overall symmetry of a liquid crystal mixture. In the ferroelectric phase, dipoles are aligned parallel to each other, so that the system must have a polar symmetry. If the molecules could form a polar arrangement in their own systems, ferroelectricity may appear even in systems consisting of achiral molecules. Considering that it is not essential for ferroelectric liquid crystals to be chiral, much attention has been given to the formation of new ferroelectric liquid crystalline structures in non-chiral systems [2]. Niori *et al.* [3] observed the first obvious example of ferroelectricity in a smectic phase formed by achiral banana-shaped molecules, which have been accepted as a single new ferroelectric liquid crystal system [4, 5]. For a system to be ferroelectric, a spontaneous polarization must exist and be switchable with a triangular wave. The ferroelectricity is attributed to the polar packing of molecules with C_{2v} symmetry where the molecules are packed in the same direction. Weissflog *et al.* [6] have reported that ferroelectricity could be detected only for one of the phases in some liquid crystals consisting of achiral banana-shaped molecules. The existence of such a mesophase depends on the length of the rigid core of molecules as well as on the magnitude of the bend and its position. Recently it has been reported that the smectic phase of achiral banana-shaped molecular systems could form helical superstructures [7–10]. On one hand, Link *et al.* [7] reported that achiral molecules with bent cores could form a chiral layer structure with a handedness that depends on the sign of the tilt. On the other hand, Sekine *et al.* [9, 10] reported an achiral banana-shaped molecular system in which helical domains of both handednesses are formed in the smectic phases.

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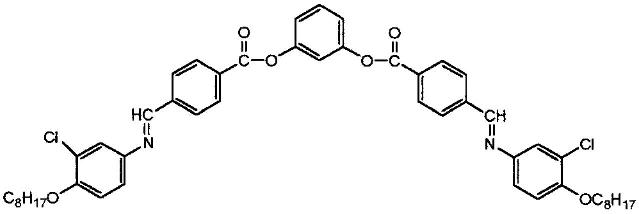
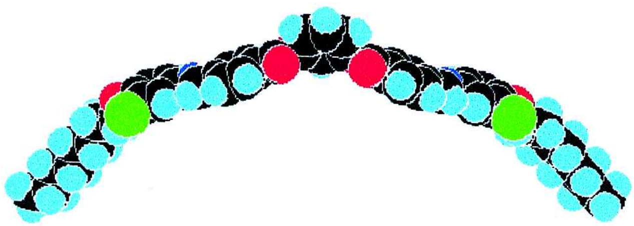
In this work, we report the synthesis and characterization of a new liquid crystalline banana-shaped molecule, with the introduction of a chlorine substituent into the 3-position of the *p*-alkoxyaniline Schiff's base moiety. The ferroelectric liquid crystalline properties of 1,3-phenylene bis[4-(3-chloro-4-*n*-octyloxyphenyliminomethyl)benzoate] (PBCOB) have been investigated in order to modify and improve knowledge of the relationship between the structure of angled mesogens and their mesomorphic properties, including the ferroelectricity arising from achiral molecules.



1,3-phenylene bis[4-(3-chloro-4-octyloxyphenyliminomethyl)benzoate] (PBCOB)



Skeleton of PBCOB

2. *Experimental procedures*

The synthesis of 1,3-phenylene bis[4-(3-chloro-4-*n*-octyloxyphenyliminomethyl)benzoate] (PBCOB) was achieved by a general synthetic method [11, 13] as shown in the scheme. 3-Chloro-4-*n*-octyloxyaniline (**1**) was prepared by reaction between 3-chloro-4-*n*-nitrophenol and 1-bromo-octane, followed by hydrogenation with H_2 gas in the presence of palladium on activated carbon. 1,3-Phenylene bis(4-formyl benzoate) (**2**) was then prepared by esterification of resorcinol and 4-carboxybenzaldehyde. This reaction was performed in methylene chloride with dicyclohexylcarbodiimide and a catalytic amount of dimethylaminopyridine. PBCOB was finally obtained by condensation of the 3-chloro-4-*n*-octyloxyaniline and 1,3-phenylene bis(4-formyl benzoate). The product was purified by chromatography on silica gel, and recrystallized several times from ethanol/dimethylformamide. Yield after purification was 20–30%. Spectroscopic data: ^{1}H NMR ($CDCl_3$, 200 MHz); $\delta = 0.6$ (6H, t), 1.0–1.9 (24H, m), 4.0–4.1 (4H, t), 6.9–7.5 (10H, m), 8.01–8.05 (4H, d), 8.2–8.3 (4H, d), 8.5 (2H, s).

The phase transition temperatures were determined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). DSC measurements were performed in a N_2 atmosphere with a cooling rate of 10°C min^{-1}. Texture observation was carried out using a polarizing microscope with a hot plate. Wide angle X-ray diffraction (XRD) and low angle X-ray scattering measurements were carried out using a Siemens D5000 X-ray diffractometer.

X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the Pohang Accelerator Laboratory, Korea. In order to investigate structural changes on heating, the sample was held in an aluminum sample holder which was sealed with a window of 7 µm thick Kapton films on both sides. The sample was heated with two cartridge heaters and its temperature monitored by a thermocouple placed close to the sample. Subtracting the scatterings from the Kapton gave a background scattering correction.

To prepare the ferroelectric lyo-mesophase of the banana-shaped molecules, PBCOB was mixed with xylene in various ratios. The isotropic–B_7 transition temperatures and ferroelectric electro-optical switchable range were then investigated.

3. Results and discussion

3.1. *Mesogenic properties*

Figure 1 displays the DSC thermogram of PBCOB. Three endothermic peaks at 56.2, 64.5 and 132.1°C on heating indicate the existence of two mesophases, SmX_2 and SmX_1. In this study the SmX_1 phase was identified as B_7. On cooling, only a smectic phase appears from the isotropic phase to the supercooled region. In the literature the introduction of a central substituent in the 1,3-phenylene moiety is reported to decrease the smectic thermal stability [14, 15]; in the present study the presence of a lateral chlorine substituent at the 3-position of the Schiff's base moiety prevents the regular stacking of molecules so that the melting and isotropic transition temperatures are depressed without destabilizing the smectics.

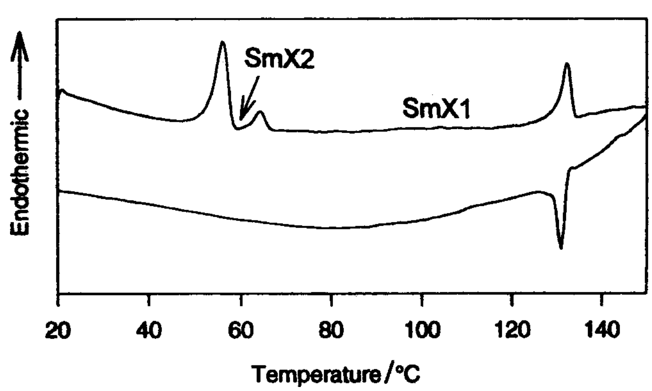
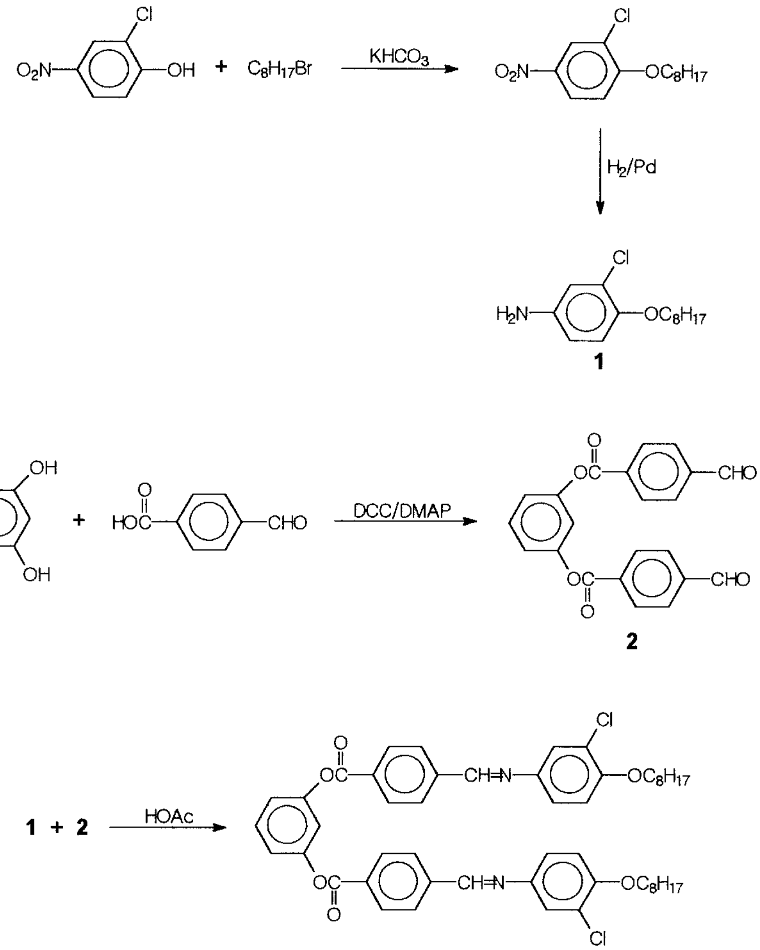


Figure 1. DSC thermogram of PBCOB.



Scheme.

3.2. *Microscopy textures*

When the isotropic liquid of PBCOB is cooled slowly, unusual and complicated optical textures of the smectic B_7 phase are observed and the texture variants mostly occur simultaneously within the same preparation. Figure 2 shows optical micrographs of PBCOB, where the phase transition takes place from the isotropic to the B_7 phase. Upon cooling slowly from the isotropic melt, the B_7 phase appears in several forms, such as double-twisted helices, filaments and fan-shaped textures. Figure 2 (*a*) shows double-twisted helices initially formed in the B_7 phase. They tend to transform into fan-shaped textures with a fringe pattern showing a helical structure, although the system contains only achiral molecules. Simultaneously, as shown in figures 2 (*b–d*), the homeotropic domains begin to occupy the space between double-twisted helices. Similarly, Pelzl *et al.* [8] observed that on slow cooling of the isotropic liquid to the B_7 phase, a nitro-substituted banana-shaped compound showed a double-spiral character in its optical texture with a roughly equal number of right and left-handed helices.

Figure 3 shows the optical microscopic texture observed in the homeotropically aligned B_7 phase prepared by shearing between glass plates. The most notable observation from the microscopy is that the homeotropic texture, which can be seen by shearing a thin specimen between glass plates, shows distinct birefringence. This means that the bent molecules are packed with alignment in the direction of bending, and parallel to the layers.

Figure 4 shows the temperature dependence of spontaneous polarization; this indicates that this switchable smectic phase exhibits a maximum polarization of about 50 nC cm^{-2}.

3.3. *X-ray study*

XRD patterns of PBCOB obtained by glass capillary are shown in figure 5. The X-ray pattern obtained at room temperature shows three inner sharp peaks, so-called layer reflections, and an outer broad peak with a spacing of about 4.5 Å. The sample quenched from the isotropic liquid state at 152°C shows only broad diffuse inner and outer peaks.

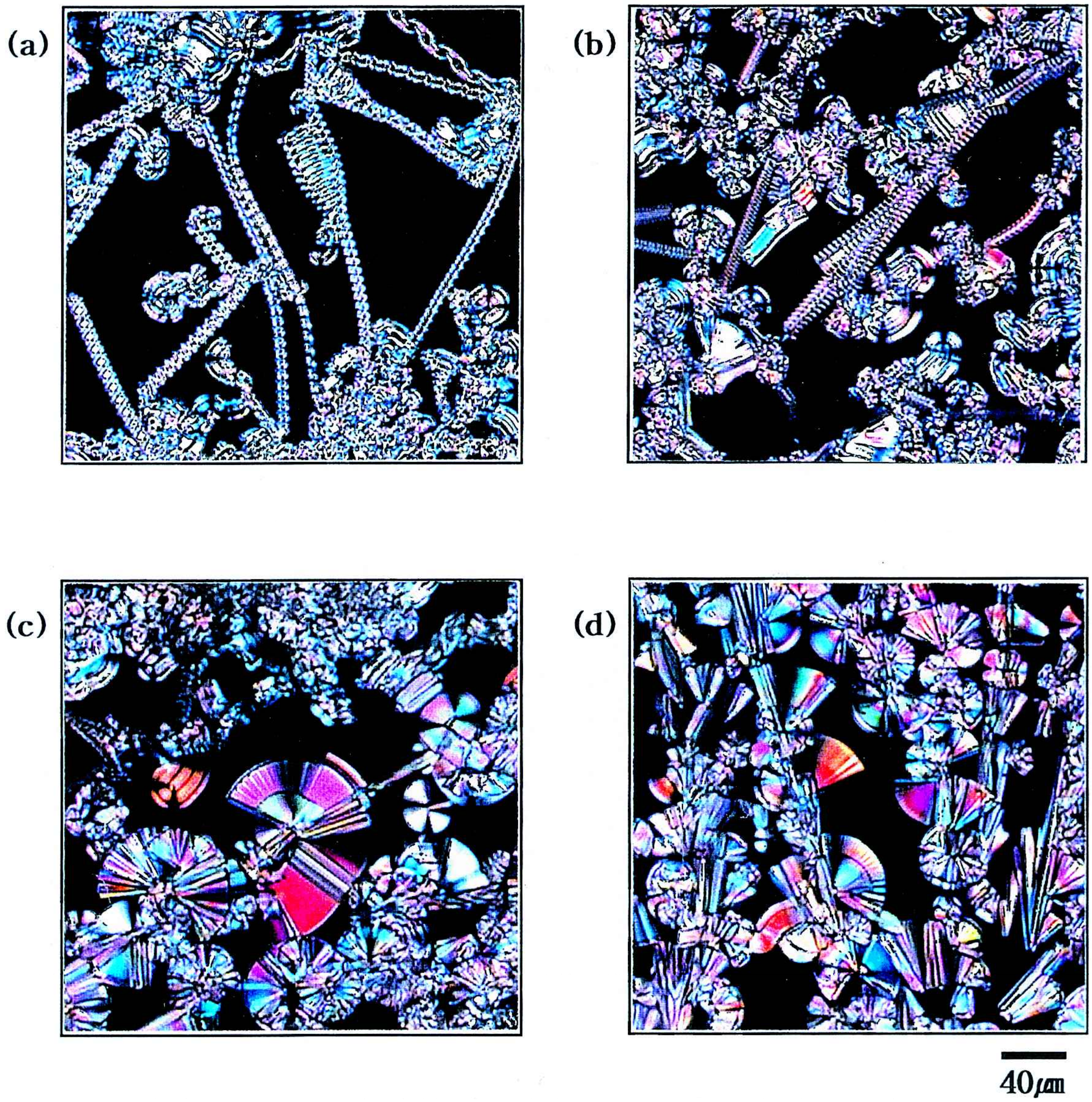


Figure 2. Optical micrographs of the B_7 phase of pure PBCOB on cooling from the isotropic melt. (*a*) B_7 phase initially appears as double-twisted helices; the helices tend to transform into a fan-shaped texture with a fringe pattern. (*b–d*) Simultaneously, the homeotropic domains begin to occupy the space between double-twisted helices.

Figure 6 displays the low angle X-ray scattering patterns of PBCOB obtained at room temperature, 60°C, 80°C and 150°C. The scattering pattern obtained at room temperature shows three sharp reflections at reciprocal space ratios of 1:2:3, indicative of a lamellar structure with layer spacing of 38.1 Å. The 38.1 Å is compatible with the end-to-end distance of the molecule with bent conformation. The scattering pattern shows no significant change at 60°C even though DSC shows an enthalpy change at about 55°C. In the smectic X_1 phase at 80°C, six additional reflections at very low angle are developed at the relative positions 1, 2, 3, 4, 5 and 6, where the *d*-space of the first peak is 292 Å. It has been reported that both the left- and right-handed helical domains are spontaneously formed upon cooling from isotropic liquid to the switchable banana phase (B_7) [16]. The periodicity of 292 Å, about 7.5 times 38.1 Å, may correspond to a helical pitch distance of the smectic B_7 phase. All these peaks disappear at 150°C in the isotropic state as shown in figure 6 (*d*).

In order to characterize the enthalpy change at 55°C, wide angle XRD has been taken at room temperature and 60°C as shown in figures 7 (*a*) and 7 (*b*). A broad amorphous peak centered at $q = 14\,\text{Å}^{-1}$ together with

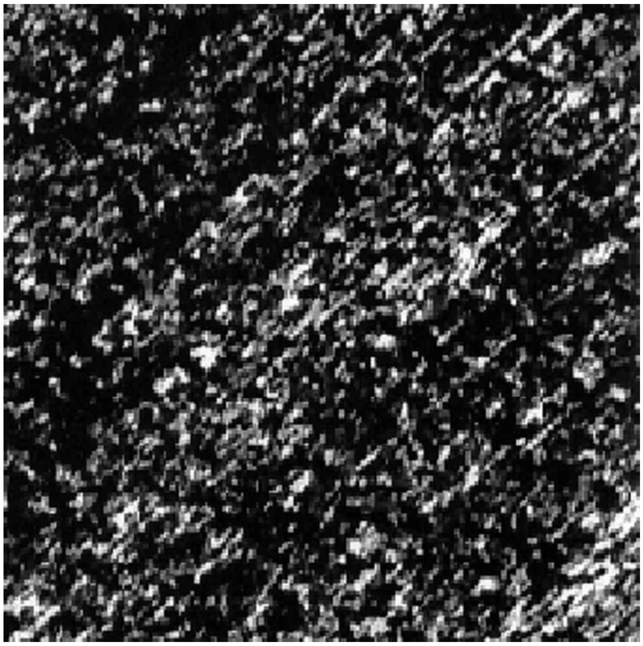


Figure 3. Optical mircoscopic texture observed in the homeotropically aligned B_7 phase which was prepared by shearing between glass plates.

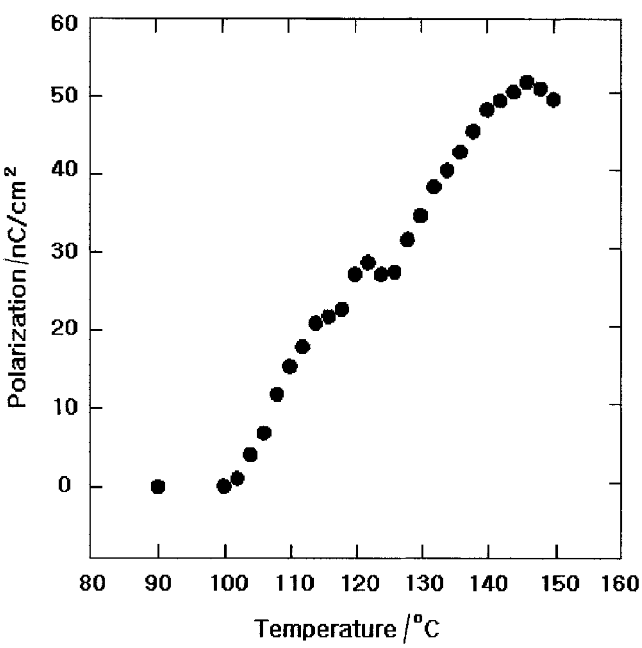


Figure 4. Temperature dependence of spontaneous polarization.

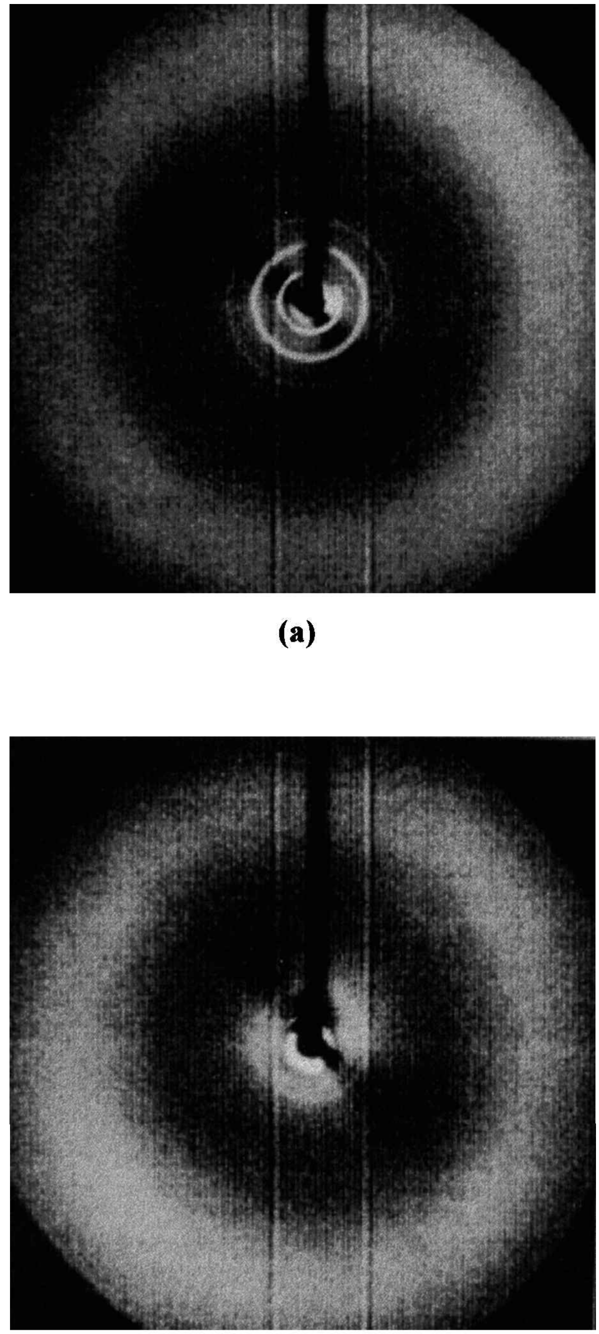


Figure 5. X-ray diffraction patterns of PBCOB obtained by glass capillary: (*a*) as-prepared sample at room temperature; (*b*) sample quenched from isotropic state at 152°C.

very small narrow peaks at $q = 11$ and $16.5\,\text{Å}^{-1}$ were obtained at room temperature; the small peaks disappear at 60°C. Considering the negligible difference in the lamellar space (38 Å) above and below 55°C, together with the size of the narrow peaks, we assume that the central bent-core part may be very loosely packed even at room temperature, possibly due to the chlorine substituent. The enthalpy change at 55°C and small X-ray peak may indicate the partial crystallization of side alkyl groups.

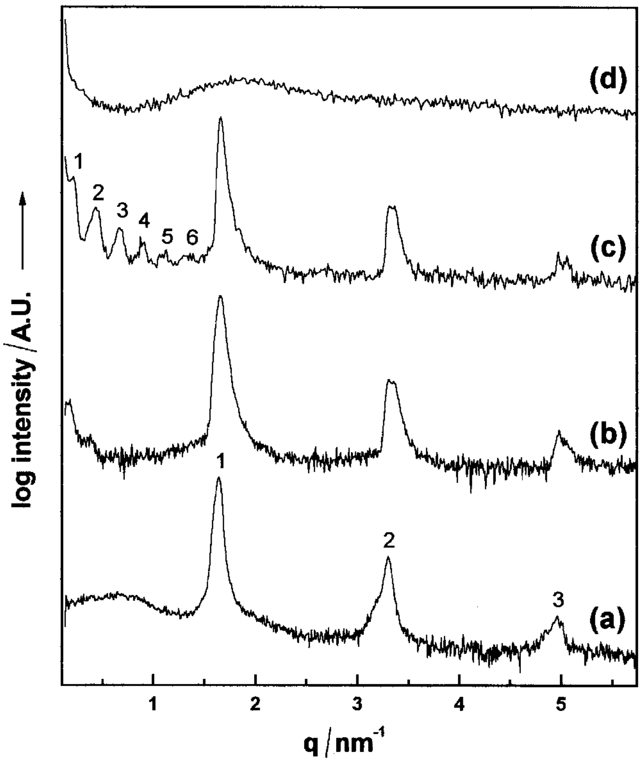


Figure 6. Small angle X-ray scattering patterns obtained at (*a*) room temperature, (*b*) 60°C, (*c*) 80°C and (*d*) 150°C.

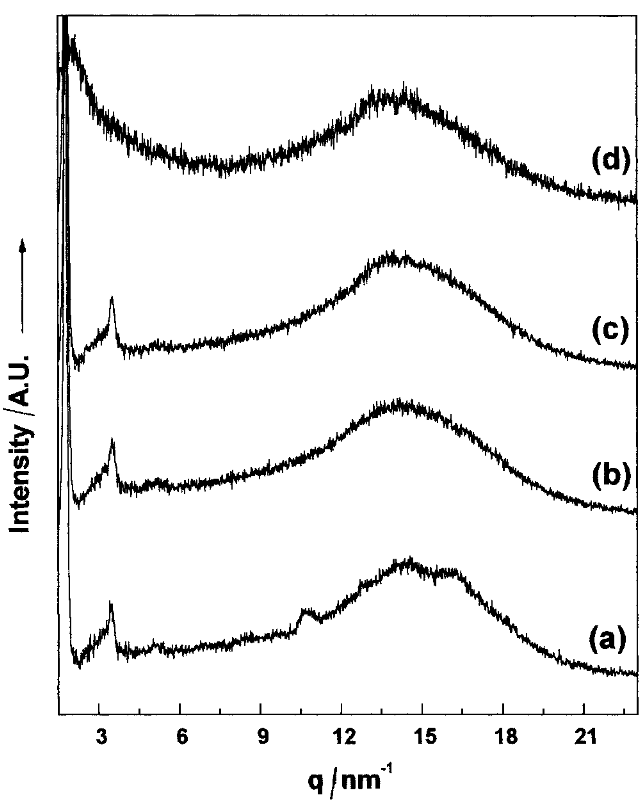


Figure 7. Wide angle X-ray diffraction patterns obtained at (*a*) room temperature, (*b*) 60°C, (*c*) 80°C and (*d*) 150°C.

3.4. *Ferroelectric lyo-mesophase*

Although the thermotropic ferroelectric and antiferroelectric aspects of these banana-shaped molecules are extremely interesting from an academic point of view [17], their applications are strongly restricted due to the high temperature range (above 100°C) of the switchable phases [18]. Recently it has been reported that ferroelectric lyotropic liquid crystals can be formed by dissolving disc-shaped molecules in a non-polar organic solvent [19]. The electro-optical switching properties of the lyo-mesophase are to some extent better than those of the bulk columnar liquid crystals: the switching threshold voltage and the phase transition temperatures are decreased [20]. We therefore dissolved the PBCOB in a non-polar, non-aqueous solvent to form a lyo-mesophase. By adding only 15 wt % of xylene to the PBCOB, the isotropic-to-smectic B_7 phase transition temperature was lowered from 138°C to 69°C. The ferroelectric electro-optical switching range now extended from about 2°C to more than 50°C in range; this solution of PBCOB in xylene thus became switchable even at room temperature. The lyo-mesophase of PBCOB in xylene shows homeotropic properties, which can be seen by shearing a thin specimen between glass plates (see figure 8).

Generally, banana phases showing the B_2 or B_7 textures are antiferroelectric, however Walba *et al.* [21] have proposed a structure for the B_7 switching phases in the ferroelectric phases formed from achiral banana molecules. Although the achiral structure of PBCOB switches between ferroelectric phases, it is not clear yet

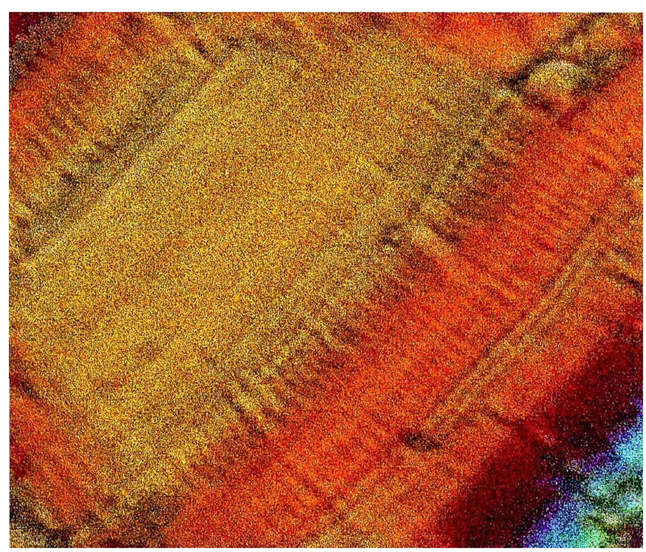


Figure 8. Homeotropic textures in the B_7 phase of the mixture of 5 wt % xylene and 95 wt % PBCOB. The pictures represent 1 mm^2 areas.

that the banana phase showing B_7 texture is ferroelectric. A detailed discussion of these points will appear elsewhere [22].

4. Conclusions

The introduction of a lateral substituent in the 3-position of a Schiff's base moiety reduced the transition temperature and the degree of crystallinity of the switchable banana phase of the new compound 1,3-phenylene bis[4-(3-chloro-4-*n*-octyloxy phenyliminomethyl)benzoate]. This system of banana-shaped molecules formed B_7 smectic phases in which both left- and right-handed helical domains with a periodicity of 292 Å were spontaneously formed, even though the constituent molecules are achiral. Moreover, the B_7 phase appeared in several forms, such as double-twisted helices, filament and fan-shaped texture. The switching current corresponding to the spontaneous polarization, and the optical microscopic texture, indicated that the homeotropically aligned smectic mesophase was ferroelectric. By adding 15 wt % of xylene to the PBCOB, the temperature range for ferroelectric electro-optical switching was extended by a factor of more than 25; the ferroelectric lyo-mesophase became switchable even at room temperature.

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