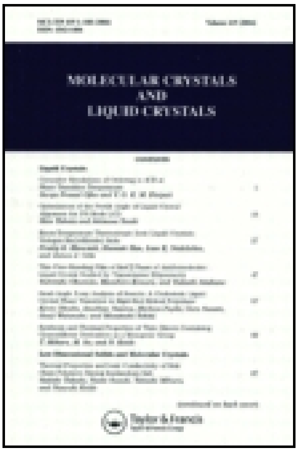

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Distinct Ferroelectric Smectic Liquid Crystals Consisting of Achiral Molecules with Banana Shape

Teruki Niori [a], Tomoko Sekine [a], Junji Watanabe [a], Tomoo Furukawa [a b] & Hideo Takezoe [a b]

[a] Department of Polymer Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, 152, Japan

[b] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, 152, Japan

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DISTINCT FERROELECTRIC SMECTIC LIQUID CRYSTALS CONSISTING OF ACHIRAL MOLECULES WITH BANANA SHAPE

TERUKI NIORI, TOMOKO SEKINE, JUNJI WATANABE,
TOMOO FURUKAWA* and HIDEO TAKEZOE*
Department of Polymer Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan
*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

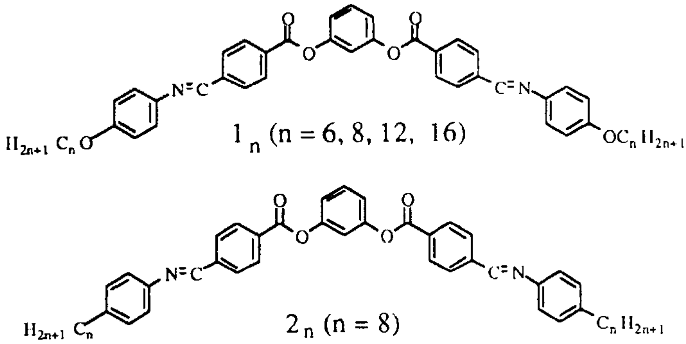
Abstract We found three smectic phases, SmX_1, SmX_2 and SmX_3, in achiral compounds with banana shape. The SmX_1 phase has a biaxial single molecular layer, along which polarization exists. The polarization precesses along the layer normal, and is aligned by applying an electric field. The spontaneous polarization is about 60 nC/cm^2 and shows a slight temperature dependence. The dielectric constant shows a larger value in SmX_1 than those of the other phases, suggesting the Goldstone mode. The relaxation frequency is below 100 Hz.

INTRODUCTION

In the ferroelectric phase, dipoles are aligned parallel to each other, so that the system must be noncentrosymmetric. For a system to be ferroelectric, a spontaneous polarization must exist and is switchable with a single hysteresis loop. In liquid crystals, the chirality was introduced to realize noncentrosymmetric systems. Actually many chiral materials showing the chiral smectic C (SmC*) phase have been synthesized, since the discovery of ferroelectricity in 1975 by Meyer et al.[1] However, chirality is not necessary to be introduced to have ferroelectric liquid crystals. If a polar structure is formed and the polarization is switchable by applying an electric field, the system is ferroelectric. A great deal of effort has been made to realize ferroelectric liquid crystals in nonchiral systems. Polyphilic molecules comprising chemically different subunits synthesized by Tournilhac et al.[2] are one of them. Recently, we also reported a ferroelectric switching in a smectic liquid crystal consisting of achiral molecules of banana shape.[3] In this report, we describe some details of the structure of the smectic phase and the electric properties.

MATERIALS

The compounds used are illustrated in Fig. 1, together with their phase sequences. The ester linkages of two benzylideneaniline to 1,3-dihydroxybenzene maintain the molecules to be banana shape. According to DSC, there are three smectic phases, which are designated as SmX_1, SmX_2 and SmX_3 in this paper.



	Iso		SmX_1		SmX_2		SmX_3	Cryst
1_6	•	176°C	•	172°C	•	159°C	• (h)	–
	•	174°C	•	158°C	•	146°C	• (h)	
1_8	•	176°C	• (h)	163°C	•	157°C	• (h)	–
	•	173°C	• (h)	152°C	•	141°C	• (h)	–
1_{12}	•	172°C	• (h)	149°C	–		• (h)	–
	•	169°C	• (h)	142°C	–		• (h)	–
1_{16}	•	163°C	• (h)	143°C	–		• (h)	–
	•	161°C	• (h)	138°C	–		• (h)	–
2_8	•	161°C	• (h)	155°C	•	96°C	–	•
	•	157°C	• (h)	138°C	•	73°C	–	•

(h): existence of helical structure (refer to the text).

FIGURE 1 Molecular structures and phase sequences.

EXPERIMENTAL RESULTS

Figure 2 shows the temperature dependence of the layer spacing of the compounds $\mathbf{1}_n$. It shows a jump between SmX_1 and SmX_2 phases. According to the computer simulation, there exist three stable conformations, as shown in Fig. 2. The layer spacing in SmX_1 corresponds to the conformation (a), and those in SmX_2 and SmX_3 to the conformation (b). Thus, the smectic structure is of single molecular layer.

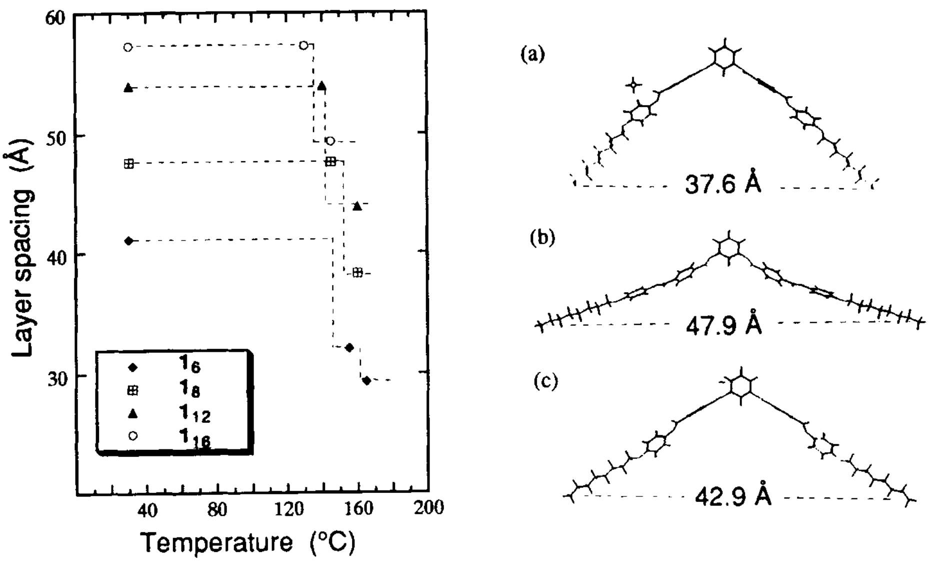


FIGURE 2 Layer spacing of $\mathbf{1}_n$ as a function of temperature. Simulated molecular configurations of $\mathbf{1}_8$ are also shown.

Three smectic phases exhibit different textures, as shown in Figs. 3 and 4. In the SmX_1 phase of $\mathbf{1}_6$, a fan texture is clearly seen. Very strikingly, a fringe pattern suggesting a helical structure is observed in the SmX_1 phase of $\mathbf{2}_8$. The fringe pattern was observed in all the compounds except for $\mathbf{1}_6$, though the system contains only achiral molecules. We confirmed that the fringe disappears by applying an electric field.

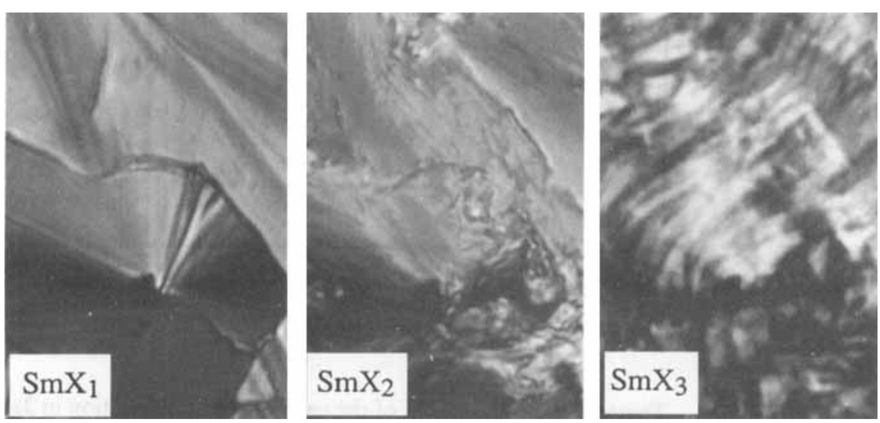


FIGURE 3 Optical micrographs of SmX_1, SmX_2 and SmX_3 of $\mathbf{1}_6$. (See Color Plate VII).

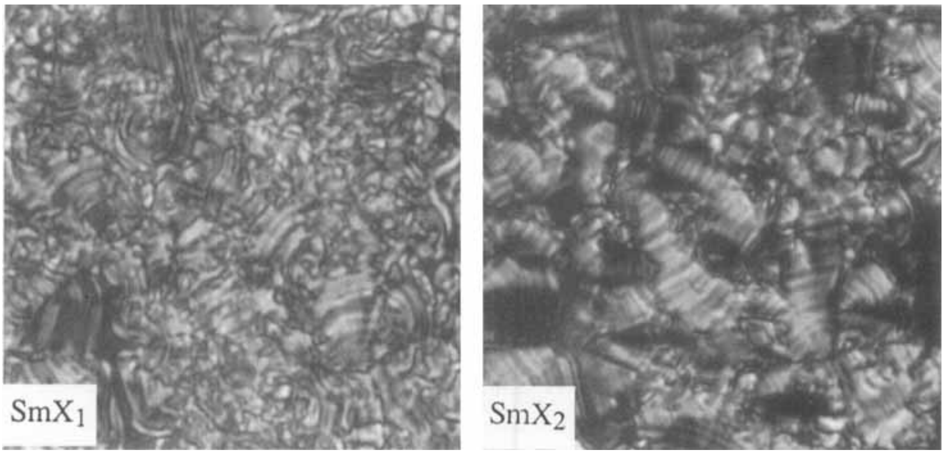


FIGURE 4 Optical micrographs of SmX_1 and SmX_2 of $\mathbf{2}_8$. (See Color Plate VIII).

We have already confirmed the ferroelectric switching in the compound $\mathbf{2}_8$ using a triangular method.[3] Figure 5 shows the temperature dependence of the spontaneous polarization. The switching current peak observed is also shown in the inset of the figure. The spontaneous polarization is about 60 nC/cm^2 and shows only a slight temperature dependence.

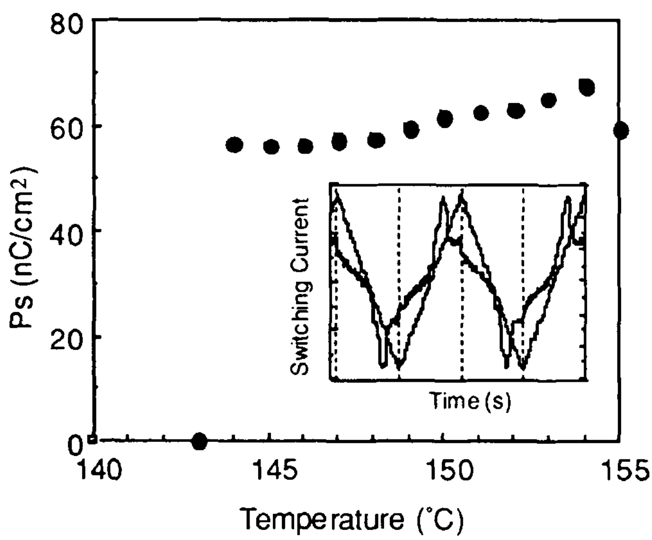


FIGURE 5 Temperature dependence of the spontaneous polarization in $\mathbf{2}_8$. The switching current profile is also shown.

The dielectric measurement also supports the existence of the spontaneous polarization. Figure 6 shows the dispersion of the dielectric constant in the SmX_1 and SmX_2 phases of $\mathbf{2}_8$. The dielectric constant in the SmX_1 phase is larger than that in the SmX_2 phase and shows a relaxation below 100 Hz in the SmX_1 phase. The relaxation is clearly attributed to the Goldstone mode, in which the polarization responds to an applied electric field retaining the helical structure.

The model structure of the helix in SmX_1 is shown in Fig. 7. Since the banana-shaped molecules stack to form a single layer, the polarization appears along the molecular tip direction (arrows in Fig. 7) parallel to the smectic layer. The polarization precesses along the layer normal, as shown in Fig. 7. The helix is caused by molecular conformational chirality and/or flexoelectric effect, as described in a separate paper.[4] In any event, the existence of the macroscopic polarization is canceled by forming the helix, so that the ferroelectricity stably exists. Actually, $\mathbf{1}_6$ shows no helical structure and no ferroelectricity. In this compound, the formation of a frustrated bilayer smectic structure, which was observed in main-chain polymers,[5] microscopically cancels the polarization, preventing the appearance of ferroelectricity.

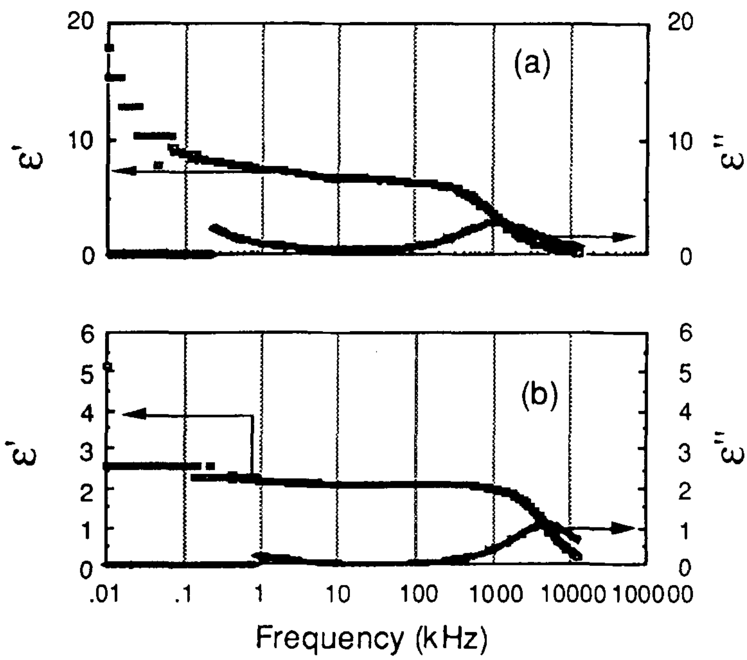


FIGURE 6 Dielectric dispersion in (a) SmX_1 and (b) SmX_2 of $\mathbf{2}_8$.

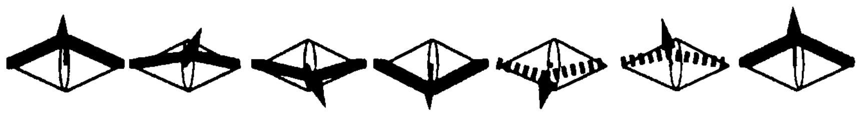


FIGURE 7 Model structure of helix in the SmX_1 phase.

As for the SmX_3 phase of $\mathbf{1}_n$, a blue color was observed. We confirmed that the blue color originates from the selective reflection due to a helix with the helical axis along the smectic layer. The structure suggests the twist-grain-boundary (TGB) phase. A circular dichroism (CD) signal due to the selective reflection was observed in SmX_3, and the absolute value and even the sign of the CD signal varies around zero for sequential measurements after heating the cell up to the isotropic phase.[4] The detailed measurements are in progress.

CONCLUSION

Distinct ferroelectric smectic phase was found in compounds consisting of achiral banana-shaped molecules. The existence of the helical structure was confirmed in the SmX_1 and SmX_3 phases of all the compounds except for $\mathbf{1}_6$. The macroscopic cancellation of the polarization along the smectic layer due to the helix is suggested to be very important for the appearance of the ferroelectricity.

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