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Ferroelectric liquid crystals from banana-shaped achiral molecules with vinyl end groups

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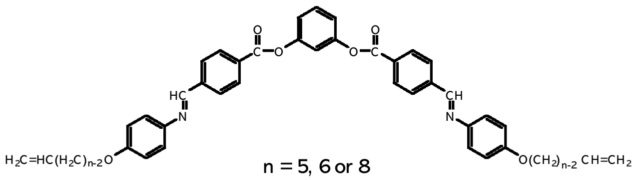
Banana-shaped achiral compounds, the 1,3-phenylene bis[4-(alkenyloxyphenyliminomethyl)-benzoate]s, were synthesized with varying length of the alkenyl group; their ferroelectric properties are described. The smectic mesophases, including a switchable chiral smectic C (SmC*) phase, were characterized by differential scanning calorimetry, polarizing optical microscopy and the triangular wave method. The presence of vinyl groups at the ends of the linear side-wings in the banana-shaped achiral molecules, containing a Schiff's base mesogen, induced a decrease in melting temperature and formation of the switchable SmC* phase in the melt. The compound having the octenyloxy group exhibited a spontaneous polarization of 120 nC cm^{-2} on reversal of an applied electric field.

1. Introduction

Most chiralities of liquid crystal phases are due to the introduction of a group containing a chiral carbon. The chiral phase can also occur without a chiral structure by spontaneous polarization derived from symmetry breaking [1–4]. A fascinating example of achiral symmetry breaking was found in the tilted smectic phases of some banana-shaped molecules [5, 6]. Because of the director tilt and simultaneous polar ordering, each smectic layer loses its inversion symmetry and becomes chiral, although the molecules contain no chiral carbons. Recently, ferroelectric liquid crystal (FLC) phases formed from achiral molecules have been reported in which the smectic phases of banana-shaped molecules could show ferroelectric switching [7, 8]. For a system to be ferroelectric, a spontaneous polarization must exist and be switchable with an electrical triangular wave.

Niori *et al.* [6] reported the first obvious example of ferroelectricity in banana-shaped achiral molecules, ascribing it to the polar packing of the molecules with C_{2V} symmetry. Link *et al.* [5] reported the first spontaneous formation of chirality in a smectic phase of banana-shaped achiral molecules, a chiral layer structure with a handedness depending on the tilted molecular direction. Weissflog *et al.* [9] reported that ferroelectricity could be induced in one of the mesophases in some achiral banana-shaped molecules by varying the direction of connecting groups and substituents. FLCs that exhibit spontaneous polarization due to their self-organizing character are now regarded as one of the most promising groups of optoelectronic materials [10, 11].

In this study, a new banana-shaped achiral molecule having vinyl end groups has been synthesized, and its FLC properties investigated to determine the relationship between liquid crystallinity and structural effect of the vinyl group. We could obtain a ferroelectric phase simply by controlling the number of carbon atoms in the alkenyloxy chains of a banana-shaped molecule. Its structure is indicated below.



1,3-Phenylene bis[4-(alkenyloxyphenyliminomethyl)benzoate]

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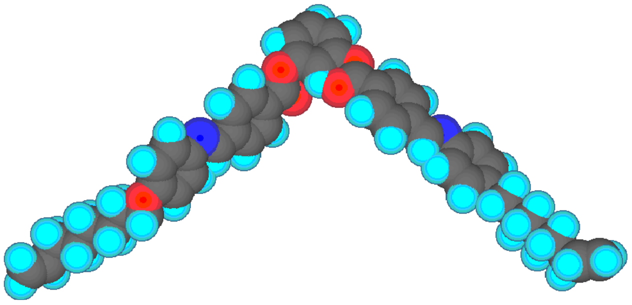
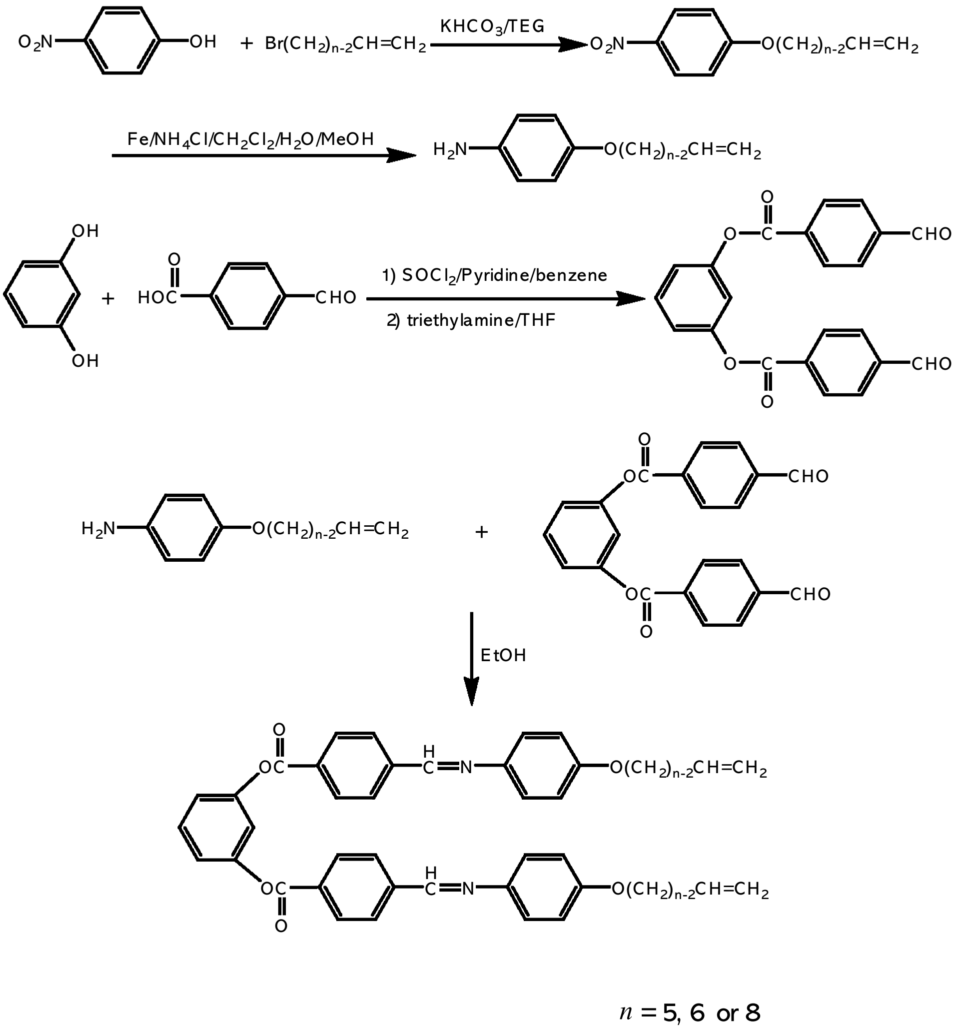


Skeleton of the compound with n = 8

2. Experimental procedures

The syntheses of 1,3-phenylene bis[4-(4,7-octenyloxyphenyliminomethyl)benzoate] (PBOEB), 1,3-phenylene bis[4-(4,5-hexenyloxyphenyliminomethyl)benzoate] (PBHEB), and 1,3-phenylene bis[4-(4,4-pentenyloxyphenyliminomethyl)benzoate] (PBPEB) were achieved by a general synthetic method [12, 13] as shown in the scheme. First, the 4-nitro-1-alkenyloxybenzene was prepared by the substitution reaction of 4-nitrophenol with bromoalkene. Then, the 4-alkenyloxyaniline (**I**) was obtained by hydrogenation of the 4-nitro-1-alkenyloxybenzene with iron in the presence of $CH_2Cl_2/MeOH/H_2O$ solvent. Next, the 1,3-phenylene bis(4-formylbenzoate) (**II**) was prepared by the reaction of resorcinol with 4-formylbenzoyl chloride in tetrahydrofuran with triethylamine at 0°C. Finally, the required product was prepared by a condensation between the aniline (**I**) and the dialdehyde (**II**). The final product was purified by chromatography on silica gel, and recrystallized several times from a mixture of ethanol and dimethylformamide (20/1, v/v); yield after purification was 20 ~ 30%. ^{1}H



Scheme.

NMR ($CDCl_3$, 500 MHz) for PBPEB: $\delta = 1.9$ (m, 4H, $-OCH_2CH_2-$), 2.2 (m, 4H, $-CH_2CH=$), 4.0 (t, 4H, $-OCH_2-$), 5.0 (q, 4H, $=CH_2$), 5.8 (m, 2H, $-CH=$), 6.9–8.3 (m, 20H, Ar–H), 8.5 (s, 2H, $-CH=N-$); EIMS *m/z* 692 (M^+). HRMS (EI) calcd for $C_{44}H_{40}N_2O_6$ (M^+) 692.2886; found 692.2879. For PBHEB: $\delta = 1.6$ [m, 4H, $-CH_2-$], 1.8 (m, 4H, $-OCH_2CH_2-$), 2.1 (m, 4H, $-CH_2CH=$), 4.0 (t, 4H, $-OCH_2-$), 5.0 (q, 4H, $=CH_2$), 5.8 (m, 2H, $-CH=$), 6.9–8.3 (m, 20H, Ar–H), 8.5 (s, 2H, $-CH=N-$); EIMS *m/z* 720 (M^+). HRMS (EI) calcd for $C_{46}H_{44}N_2O_6$ (M^+) 720.3199; found 720.3195. For PBOEB: $\delta = 1.3$–1.5 [m, 12H, $-(CH_2)_3-$], 1.8 (m, 4H, $-OCH_2CH_2-$), 2.0 (m, 4H, $-CH_2CH=$), 4.0 (t, 4H, $-OCH_2-$), 5.0 (q, 4H, $=CH_2$), 5.8 (m, 2H, $-CH=$), 6.9–8.3 (m, 20H, Ar–H), 8.5 (s, 2H, $-CH=N-$); EIMS *m/z* 776 (M^+). HRMS (EI) calcd for $C_{50}H_{52}N_2O_6$ (M^+) 776.3825; found 776.3827.

NMR spectra were obtained by a Brucker DRX NMR spectrometer; mass spectra were measured on a JEOL JMS-700 spectrometer. The transition behaviours were characterized by differential scanning calorimetry (Perkin-Elmer DSC7) and by polarizing optical microscopy (Nikon Eclipse E400 POL). DSC measurements were performed in N_2 with heating and cooling rates of 5°C min^{-1}. Optical texture observation was carried out using the polarizing microscope with a hot plate. The switching current was examined by the triangular wave method [14].

For measurement of the spontaneous polarization with varying temperature, the sample cell was mounted in a microfurnace; the temperature fluctuations inherent in the furnace were approximately 0.1°C. For direct measurement of the polarization, we used the triangular wave method for ease of subtracting the background current. The polarization current, converted into voltage signal through an amplifier, was measured with a digitizing oscilloscope and fed into a computer for data analysis.

3. Results and discussion

3.1. *Synthesis and mesogenic behaviour*

The synthetic route for the banana-shaped compounds is quite straightforward and each reaction step is relatively

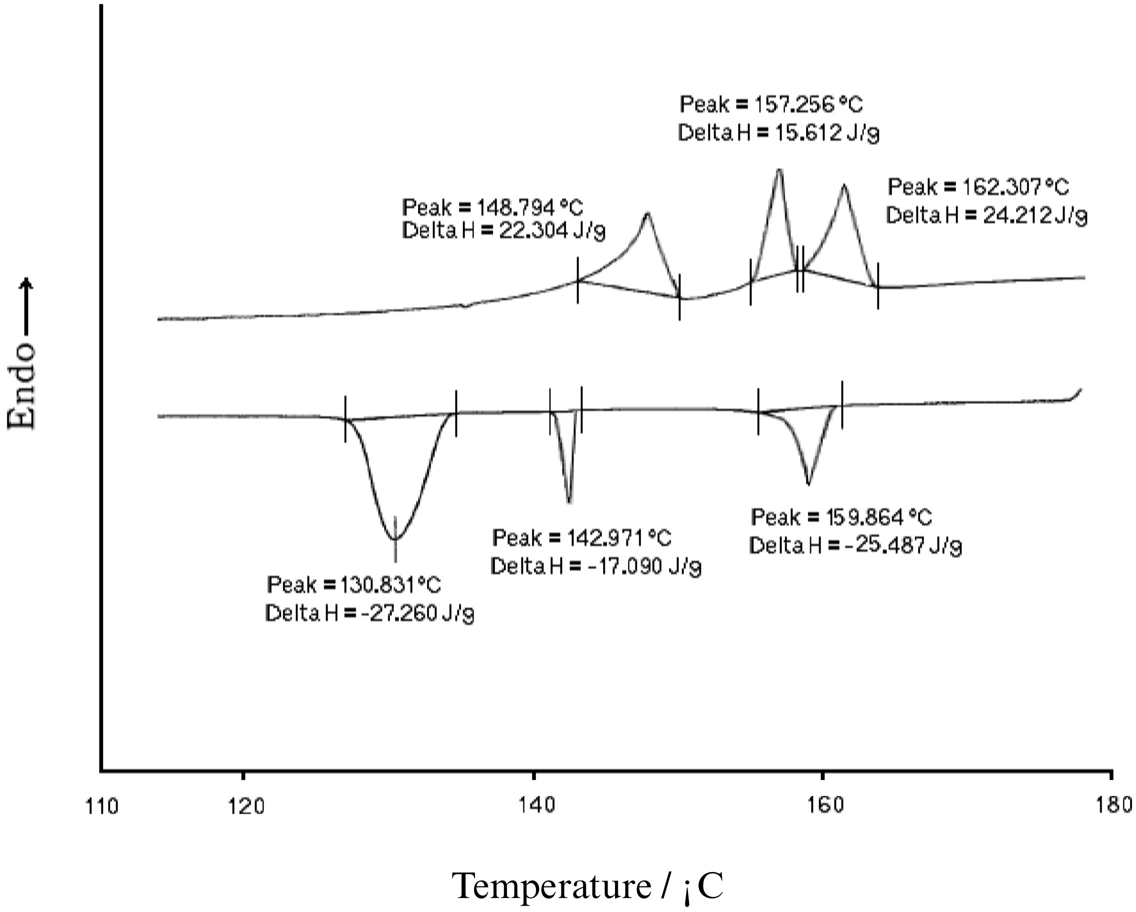


Figure 1. DSC thermogram for heating and cooling of the compound with $n = 8$.

well known. The compounds obtained were characterized by means of NMR and mass spectroscopy; the spectral data were in accordance with expected formulae. The relationship of the transition temperatures with the number of carbon atoms (n) in the alkenyloxy chains at the linear terminal side wings are shown in table 1. Among the three banana-shaped compounds obtained, only one ($n = 8$) was switchable in its liquid crystal phase. Comparing the $n = 8$ molecule with that with $n = 5$, the alkenyl group length could be reasoned to be too short to form mesophase. The compound with $n = 6$ was not switchable in its mesophase but could form a smectic phase.

Table 1. Phase transition temperatures on cooling and the number of carbon atoms (n) in the alkenyloxy chains.

n	Transition temperature/°C (enthalpy/J mol^{-1})	Switching property
5	Cr 107.0 (47.1) I	None
6	Cr 39.6 (2.8) SmX$_1$ 113.6 (47.2) SmX$_2$ 132.8 (9.8) I	None
8	Cr 130.8 (27.2) SmX$_1$ 142.9 (17.0) SmC* 159.8 (25.4) I	Switchable

Figure 1 shows DSC thermograms of the compound with $n = 8$. In the heating thermogram, three endothermic peaks appeared: the first for the melting at 148.7°C, the second for a smectic X (SmX) to smectic C* (SmC*) transition at 157.2°C, and the third for clearing at 162.3°C. In the cooling thermogram, three exothermic peaks were observed: the first for isotropic liquid to SmC* phase at 159.8°C, the second for SmC* to SmX at 142.9°C, and the third for crystallization at 130.8°C.

3.2. *Microscopy texture*

Using an optical microscope with crossed polarizer, on cooling the isotropic liquid samples we could identify every phase transition shown in table 1. As shown in figure 2, when the isotropic liquid of the compound with $n = 8$ is cooled slowly, the optical texture of the SmC* phase appears as a striped granular pattern at the isotropic to SmC* phase transition temperature. The texture then tends to transform into fan-shaped texture

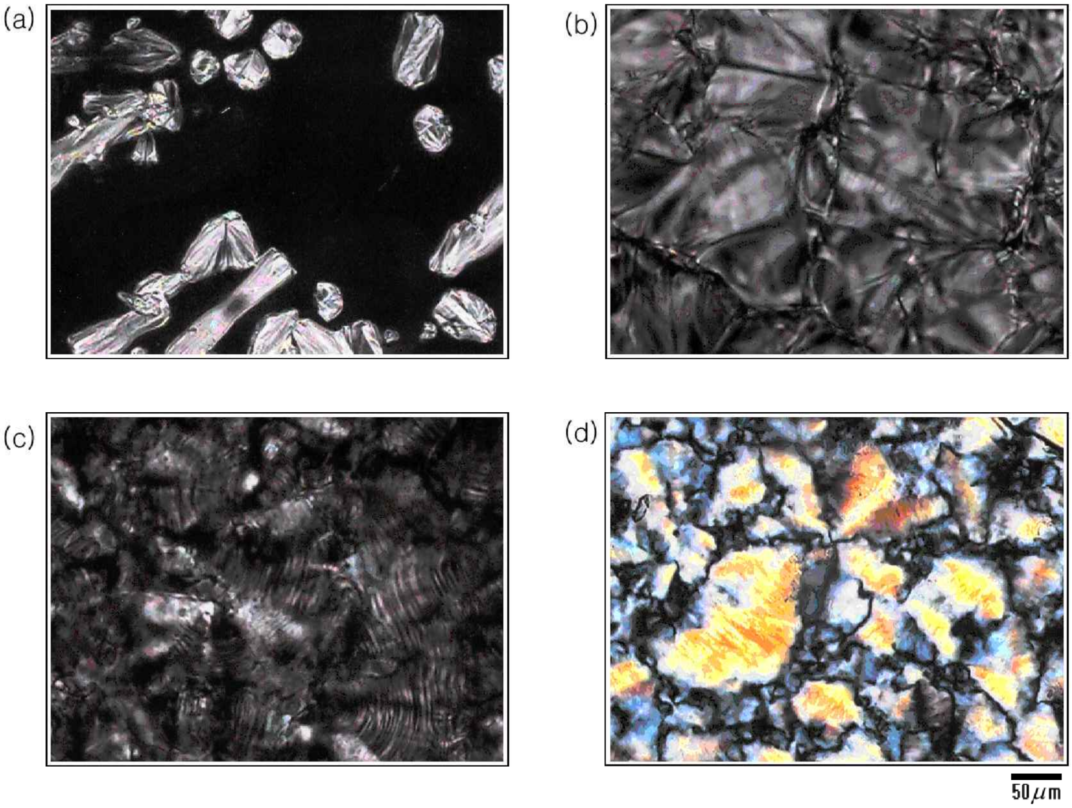


Figure 2. Optical micrographs of the SmC* phase for the compound with $n = 8$, on cooling from the isotropic liquid. (*a*) SmC* phase initially appears as a texture with striped grandular pattern; (*b*) the pattern become a fan-shaped texture with focal-conics; (*c*) on further cooling the fan-shaped texture changes abruptly at 151°C; (*d*) a mosaic texture then develops with schlieren remnants at room temperature.

with focal-conics. At about 150°C, the SmC* phase changes abruptly to paramorphic textures that grow to become a mosaic texture with schlieren remnants at room temperature.

3.3. *Spontaneous polarization and switching current*

In order to characterize the smectic phase, we measured the spontaneous polarization of the sample. For this measurement, a cell was made up from conductive indium tin oxide coated glass plates, treated with rubbed polyimide for alignment. The cell gap was maintained by a patterned organic spacer of 1.5 µm thickness. The spontaneous polarization was measured by applying a triangular shape voltage, and the switching was also observed by using a polarizing microscope. Figure 3 shows the polarization reversal current for the compound with $n = 8$ at temperatures corresponding to two smectic phases, SmX_1 and SmC*. A reversal current peak for every half-period was observed at 146°C (within the SmC* phase-forming region) and a broad pattern at 136°C (temperature within the SmX_1-forming region). Thus, we can conclude that the SmC* phase of the compound with $n = 8$ is ferroelectric, with the tip of the bent molecule orienting along the electric field and reversing its orientation with the polarity of the field. Figure 4 shows the temperature dependence of spontaneous polarization for the compound with $n = 8$ in the cooling experiment. The data indicate that this switchable smectic phase exhibits a maximum polarization of about 120 nC cm^{-2} at 140°C. On cooling the isotropic liquid, the spontaneous polarization increased with decreasing temperature and saturated at about 140°C.

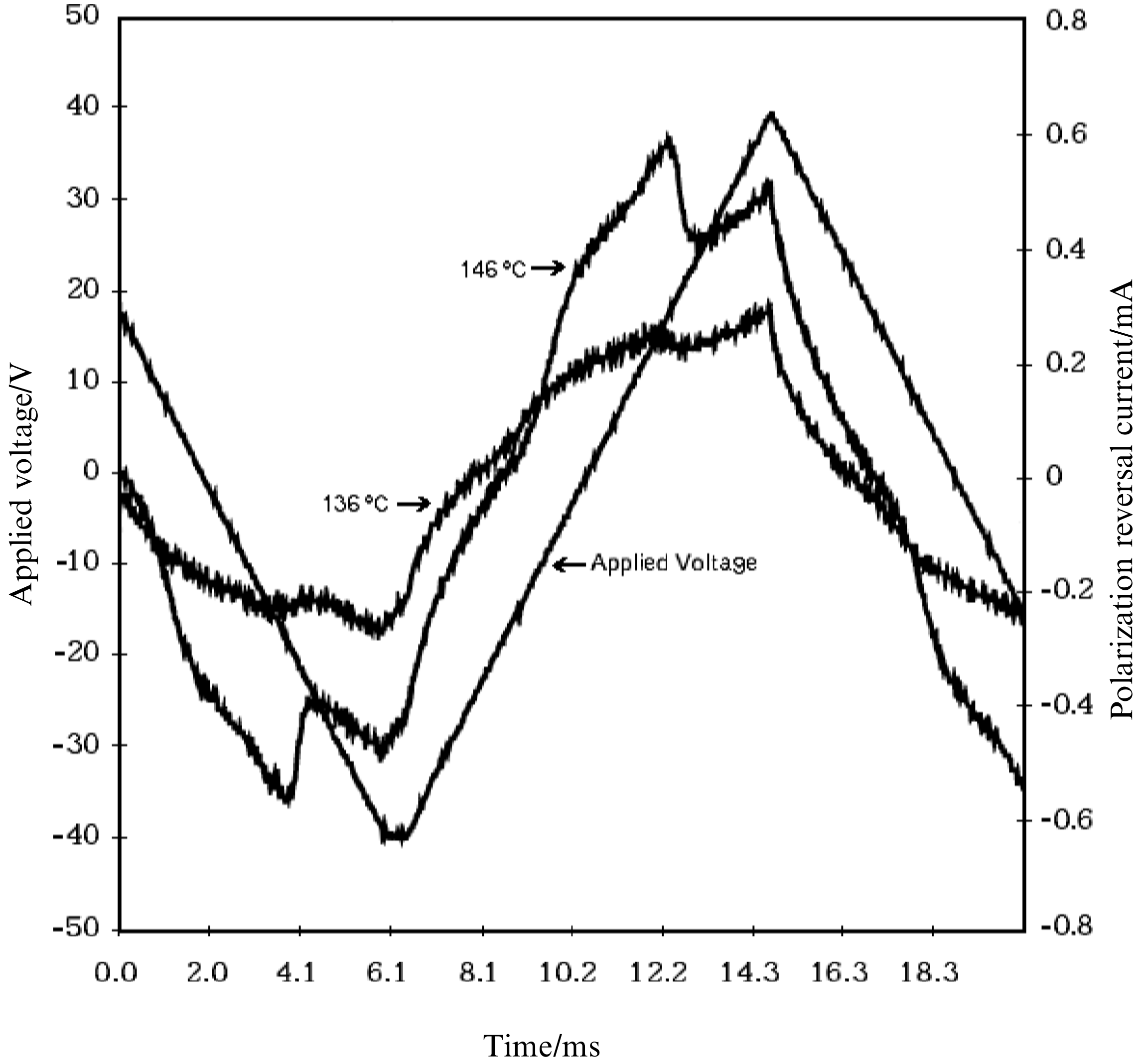


Figure 3. Switching current curve obtained by applying a triangular wave voltage at 146°C for the compound with $n = 8$.

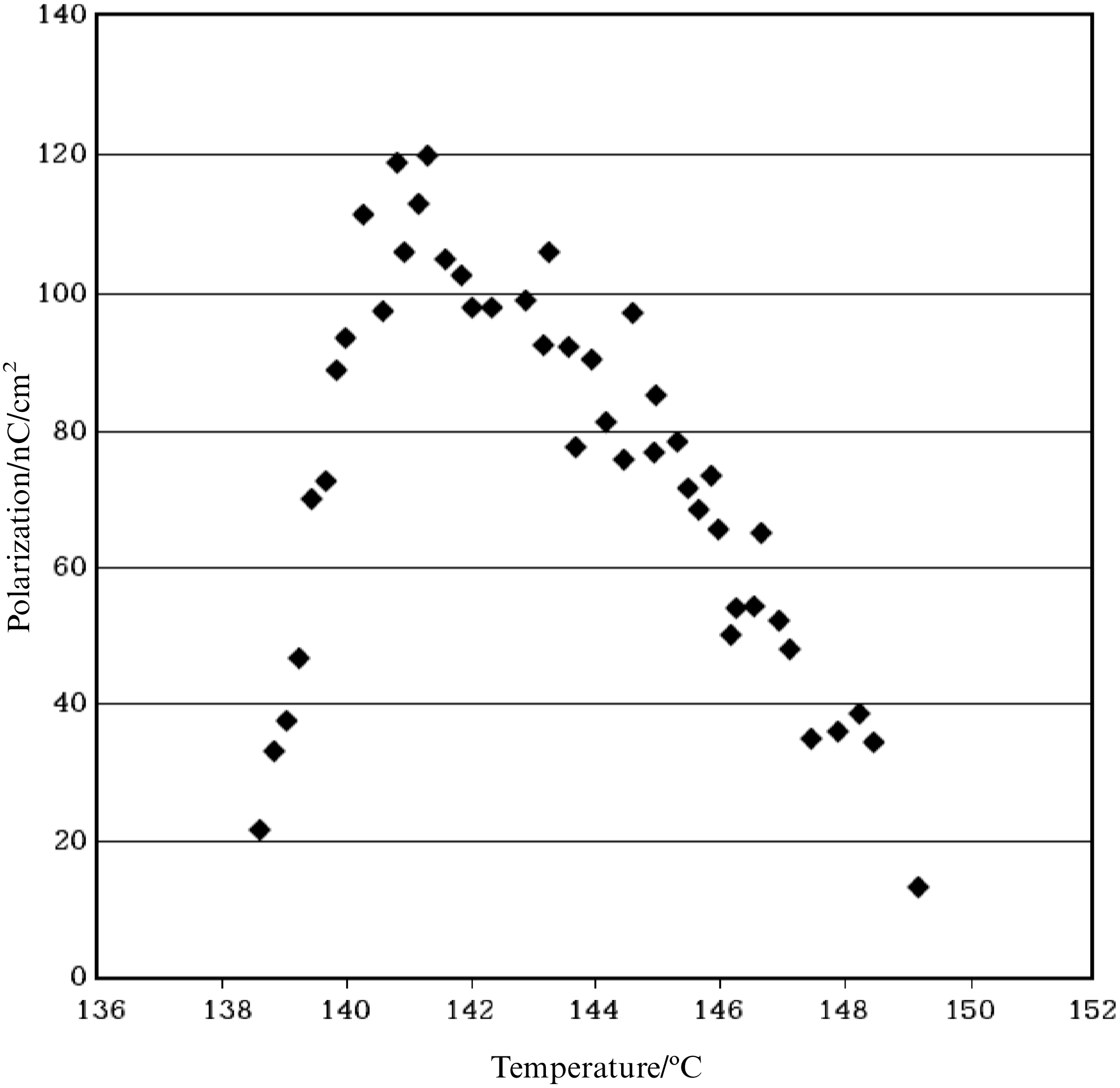


Figure 4. Temperature dependence of spontaneous polarization for the compound with $n = 8$.

The spontaneous polarization dramatically decreased on lowering the temperature below 140°C. The sharp decrease of polarization confirms that the SmX_1 to solid phase transition is first order. On further reduction in temperature, the polarization vanished at about 130°C, because of crystallization of the central rod parts of the molecules.

4. Conclusions

The introduction of terminal vinyl groups onto banana-shaped molecules containing a Schiff's base mesogen reduces the melting and clearing temperatures. The banana-shaped compound with terminal octenyl groups forms a switchable smectic phase, even though the constituent molecules are achiral. We conclude that the smectic phase of this banana-shaped compound is a chiral smectic C phase. From consideration of the switching current corresponding to spontaneous polarization, and optical microscopic textures, the aligned smectic phase is seen to be ferroelectric.

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