Ferroelectric Liquid Crystals from Bent-Core Molecules with Vinyl End Groups

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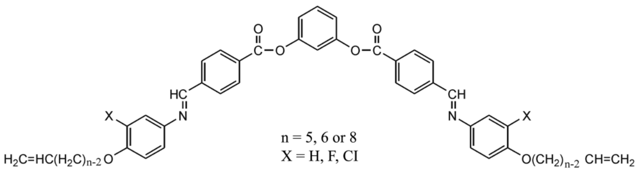
New banana-shaped achiral compounds, 1,3-phenylene bis [4-{4-(alkenyloxy) phenyliminomethyl}benzoate]s were synthesized by varying the length of alkenyl group; their ferroelectric properties are described. The smectic mesophases, including a switchable chiral smectic C (Sm C*) phase, were characterized by differential scanning calorimetry, polarizing optical microscopy and triangular wave method. The presence of vinyl groups at the terminals of linear side wings in the banana-shaped achiral molecules containing Schiff's base mesogen induced a decrease in melting temperature and formation of the switchable Sm C* phase in the melt. The smectic phases having the octenyloxy group such as $(CH_2)_6CH{=}CH_2$ showed ferroelctric switching, and their values of spontaneous polarization on reversal of an applied electric field were 120 nC/cm^2 (X=H) and 225 nC/cm^2 (X=F), respectively. We could obtain ferroelectric phases by controlling the number of carbon atom in alkenyloxy chain of a bent-core molecule.

Key Words : Banana-shaped liquid crystal, Switchable smectic C, Spontaneous polarization, Ferroelectric properties, Bent-core molecule

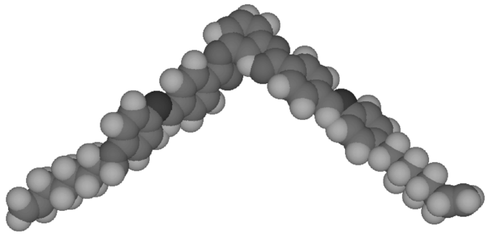
Introduction

A mesogenic compound of non-linear molecular structure was discovered for the first time by Voländer.[1] Most chiralities of liquid crystal phases are due to the introduction of a chiral group containing chiral carbon. The chiral phase can also occur without chiral structure by spontaneous polarization derived from symmetry breaking.[2-5] A fascinating example of the achiral symmetry breaking was found in the tilted smectic phases of banana-shaped molecules.[6,7] Because of the director tilt and the simultaneous polar ordering, each smectic layer loses its inversion symmetry and becomes chiral, although the molecules contain no chiral carbons. Recently, ferroelectric liquid crystal phases formed from achiral molecules have been reported in which smectic phases of banana-shaped molecules could show ferroelectric switching.[8-10] The existence of such a mesophase depends upon the length of the rigid core and the number of carbon atom in linear side wings as well as the magnitude of bent and its position. Since the bent-core molecules are closely packed and are all aligned in the direction of bending, they form a unique smectic phase.[11]

Niori *et al.*[7] reported the first obvious example of ferroelectricity in banana-shaped achiral molecules, ascribing the polar packing of the molecules with C_{2V} symmetry. Link *et al.*[6] 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.*[12] reported that ferroelectricity could be detected for one of the mesophases in some achiral banana-shaped molecules by varying direction of connecting groups and substituents. Currently, ferroelecric liquid crystals that exhibit spontaneous polarization due to their self-organizing character are regarded as one of the most promising groups of optoelectronic materials.[13,14]



1,3-phenylene bis [4-{4-(alkenyloxy)phenyliminomethyl}benzoate]



Skeleton of the compound with n = 8 and X = H

In this study, new banana-shaped achiral molecules having vinyl end groups were synthesized, and their ferroelectric liquid crystalline properties were investigated to determine the relationship between the liquid crystallinity and structural changing of the vinyl groups. We could obtain ferroelectric phases by controlling the number of carbon atom in alkenyl-

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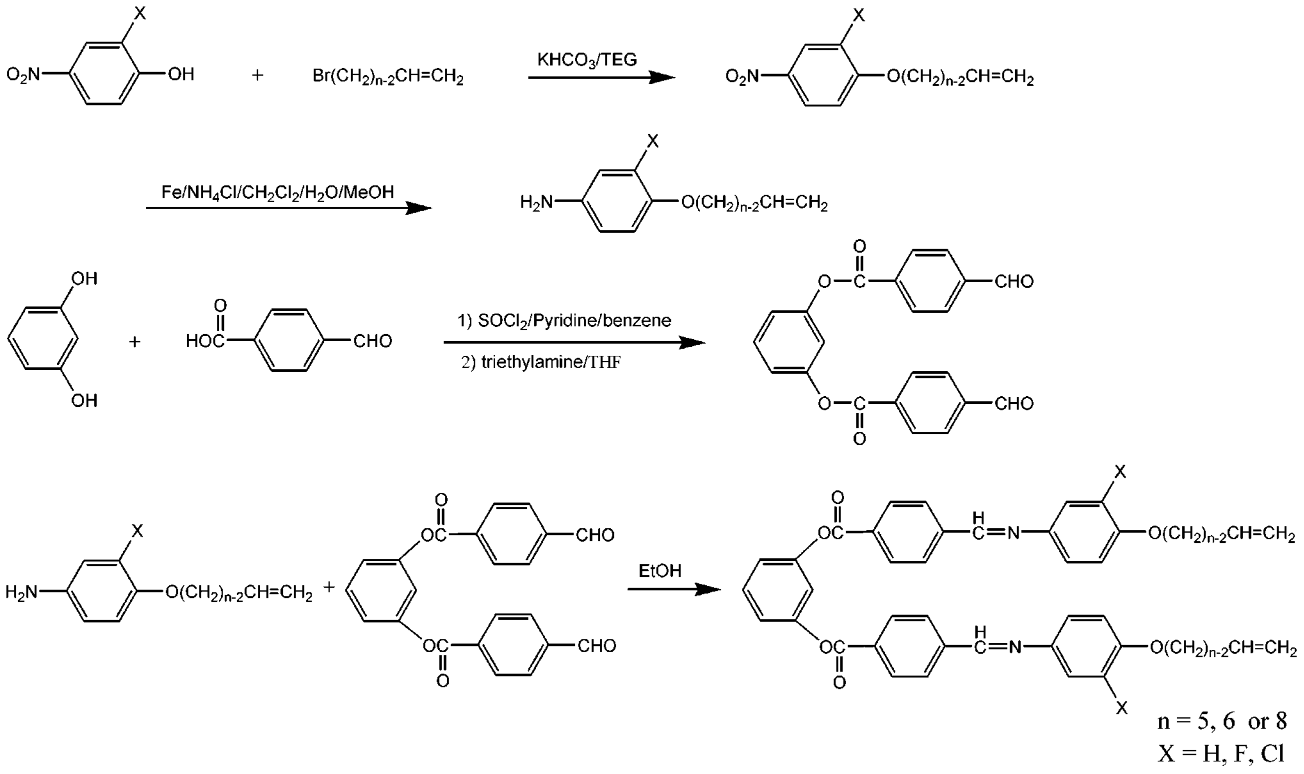

Scheme 1

oxy chain and introducing the lateral substituent in the 3-position of Schiff's base moiety of a bent-core molecule.

Experimental Section

The syntheses of 1,3-phenylene bis [4-{4-(4-pentenyloxy)-phenyliminomethyl}benzoate] (PBPEB), 1,3-phenylene bis [4-{4-(5-hexenyloxy)-(PBHEB), 3-fluoro-5-hexenyloxy-(PBFHEB), 3-chloro-5-hexenyloxy-(PBCHEB), 7-octenyloxy-(PBOEB), 3-fluoro-7-octenyloxy-(PBFOEB) and 3-chloro-7-octenyloxy-(PBCOEB)-phenyliminomethyl}benzoate] were achieved by a general synthetic method[15,16] as shown in Scheme 1. First, 4-nitro-1-alkenyloxybenzene was prepared by substitution reaction of 4-nitrophenol and bromoalkene. Then, 4-alkenyloxyaniline (I) was obtained by hydrogenation of 4-nitro-1-alkenyloxybenzene with iron in the presence of $CH_2Cl_2/MeOH/H_2O$ solvent mixture. Next, 1,3-phenylene bis(4-formyl benzoate) (II) was prepared by reaction of resorcinol and 4-formyl benzoyl chloride in tetrahydrofuran with triethylamine at 0 °C. Finally, the product was prepared by condensation reaction 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%. The representative spectroscopic data obtained by means of NMR and Mass spectroscopy: ^1H NMR ($CDCl_3$, 500 MHz) for PBOEB; δ=1.3-1.5 [m, 12H, -$(CH_2)_3$-], 1.8 (m, 4H, -$0CH_2CH_2$-), 2.0 (m, 4H, -CH_2CH=), 4.0 (t, 4H, -$0CH_2$-), 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. The remaining banana-shaped compounds were prepared and confirmed by the same method with PBOEB.

NMR spectra were obtained by Brucker DRX NMR spectrometer. Mass spectra were measured on a JEOL JMS-700 spectrometer. The transition behaviors were characterized by differential scanning calorimetry (Perkin-Elmer DSC7) and by polarizing microscopy (Nikon Eclipse E400 POL). DSC measurements were performed in N_2 atmosphere with heating and cooling rate of 5 °C/min. Optical texture observation was carried out using a polarizing microscope with a hot plate. The switching current was examined by the triangular wave method.[17] The sample cell was mounted in a microfurnace for measuring the spontaneous polarization with varying temperature. The temperature fluctuations inherent to 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 in a digitizing oscilloscope and fed into a computer for data analyses.

Results and Discussion

Synthesis and mesogenic behaviors. The synthetic route for the banana-shaped compound is rather straightforward and each reaction step is relatively well-known. The obtained compounds were characterized by means of NMR and Mass spectroscopy. NMR and Mass spectral data were in accor-

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

Number of Carbon Atom (n)	Transition Temperature/°C (Enthalpy/J mol^{-1})	Switching Property
5 (X=H)	Cr 107.0 (47.1) I	None
6 (X=H)	Cr 146.8 (18.5) SmX$_1$ 157.2 (10.9) SmX$_2$ 160.9 (8.1) I	None
6 (X=F)	Cr 45.5(5.8) SmX$_1$ 115.7 (35.7) SmX$_2$ 138.4 (10.1) I	None
6 (X=Cl)	Cr 103.7(9.0) I	None
8 (X=H)	Cr 130.8 (27.2) SmX$_1$ 142.9 (17.0) SmC* 159.8 (25.4)	Switchable
8 (X=F)	Cr 105.4 (26.6) SmC* 139.2 (7.9) I	Switchable
8 (X=Cl)	Cr 108.0(14.0) I	None

dance with expected formulae. The relationship of the transition temperature and the number of carbon atom in the alkenyloxy chains (n) at the linear terminal side wings are shown in Table 1. In the table, among the seven banana-shaped molecules synthesized, molecules (X=H, and F) of alkenyl group with n=8 were switchable in their liquid crystal phases. Comparing these molecules with n=8 to the molecules with n=5, the alkenyl group length could be reasoned to be too short to form mesophase. The molecules of the alkenyl group with n=6 were not switchable in their mesophases but could form smectic phase. Banana-shaped molecules with electron withdrawing groups are expected to decrease the intralamellar electrostatic repulsion in the direction of their longitudinal dipoles and thus the molecules consisted of substituents with positive Hammett Substituent Constant (σ)[18] value could exhibit smectic phases. In the literature the introduction of a central substituent in the 1,3-phenylene moiety is reported to decrease the smectic thermal stability;[19,20] in the present study the presence of a lateral chlorine substituent at 3-position of the Schiff's base moiety prevents the regular stacking of the molecules so that they could not form mesophase. Figure 1(a) shows DSC thermogram of PBOEB with n=8. In the heating DSC thermogram, three endothermic peaks were appeared: the first one for the melting at 148.8 °C, the second one for smectic X$_1$ (SmX$_1$)-to-Sm C* phase at 157.3 °C, and the third one for the clearing at 162.3 °C. In the cooling DSC thermogram, three exothermic peaks were observed: the first one for isotropic liquid-to-Sm C* phase at 159.9 °C, the second one for Sm C*-to-SmX$_1$ at 143.0 °C, and the third one for crystallization at 130.8 °C. Figure 1(b) shows DSC thermograms of PBFOEB with n=8. In the heating DSC thermogram, three endothermic peaks were appeared: the first one for the melting at 71.4 °C, the second one for smectic X$_1$ (SmX$_1$)-to-Sm C* phase at 114.7 °C, and the third one for the clearing at 139.2 °C. In the cooling DSC thermogram, two exothermic peaks were observed: the first one for isotropic liquid-to-Sm C* phase at 139.18 °C, the second one for crystallization at about 105.4 °C.

Microscopy texture. Using an optical microscope with crossed polarizer, on cooling the isotropic liquid samples we could identify every phase transitions shown in Table 1. As shown in Figure 2, when the isotropic liquid of PBOEB with n=8 and X=H is cooled slowly, optical texture of smectic phase appears as a striped granual pattern at the isotropic-to-Sm C* phase transition temperature. The texture tends to transform into mesomorphic domain. At about 134 °C, smectic phase is changed abruptly to paramorphic texture that grows to become mosaic texture with schlieren remnants to room temperature. Figure 3 shows optical texture of PBFOEB with n=8 and X=F. On cooling, optical texture of smectic phase of PBFOB appears as very small granual pattern at the isotropic-to-Sm C* phase transition temperature. The texture tends to transform into mosaic texture with small domains gradually. As it was further cooled, smectic phase is changed abruptly at 103.5 °C. Then, the texture grows to become schlieren texture of the twisted smectic state to room temperature.

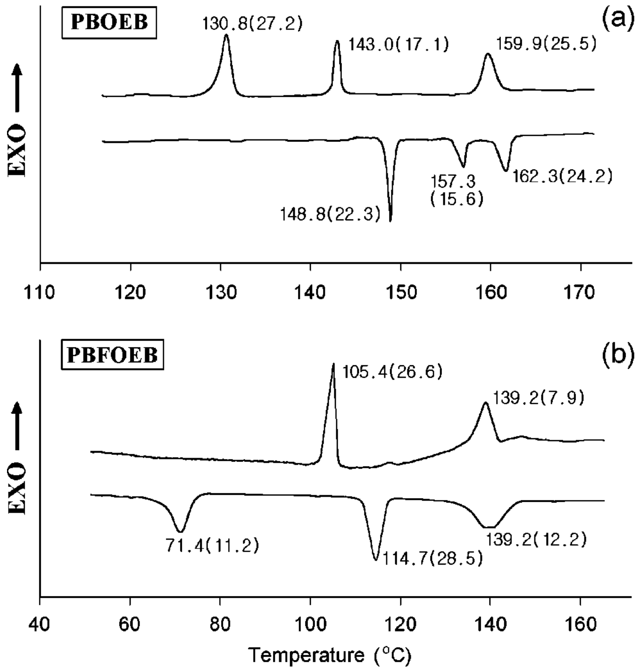

Figure 1. (a) DSC thermogram of heating and cooling of PBOEB with n=8. (b) DSC thermogram of heating and cooling of PBFOEB with n=8.

Spontaneous polarization and switching current. In order to characterize the smectic phase, we measured spontaneous polarization of the sample. For the measurement, a cell is made up of conductive indium-tin-oxide coated glasses, treated with rubbed polyimide for the alignment. The cell gap was maintained by patterned organic spacer of 1.5 μm thickness. The spontaneous polarization was measured by applying triangular shape voltage, and the switching was also observed by using a polarized microscope. Figure 4

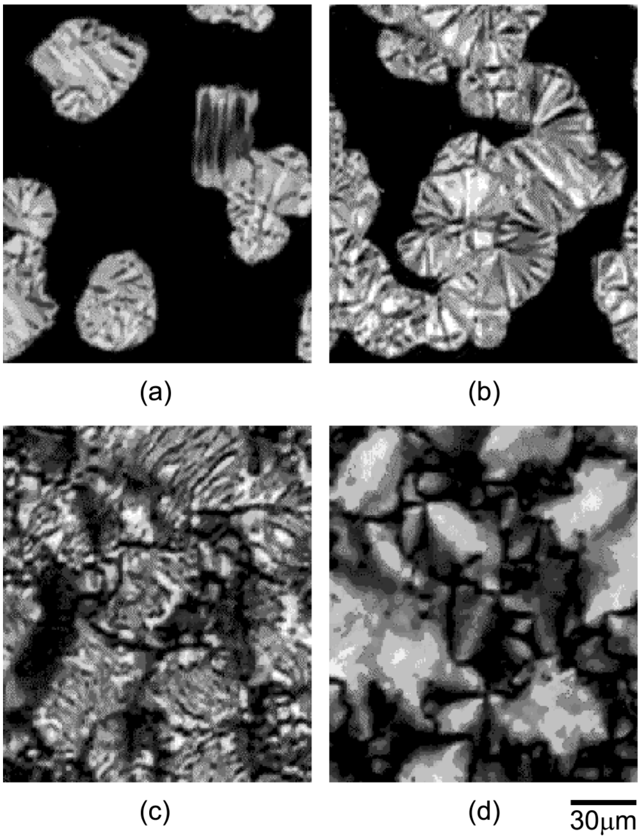

Figure 2. Optical micrographs of Sm C* phase for PBOEB with n=8 on cooling from the isotropic liquid. (a) Sm C* phase appears as a striped granual pattern at the isotropic-to-Sm C* phase transition temperature. (b) The texture tends to transform into mesomorphic domain. (c) As it was further cooled, the smectic phase is changed abruptly to paramorphic texture at 134 °C. (d) Then, the texture grows to become mosaic texture with schlieren remnants to room temperature.

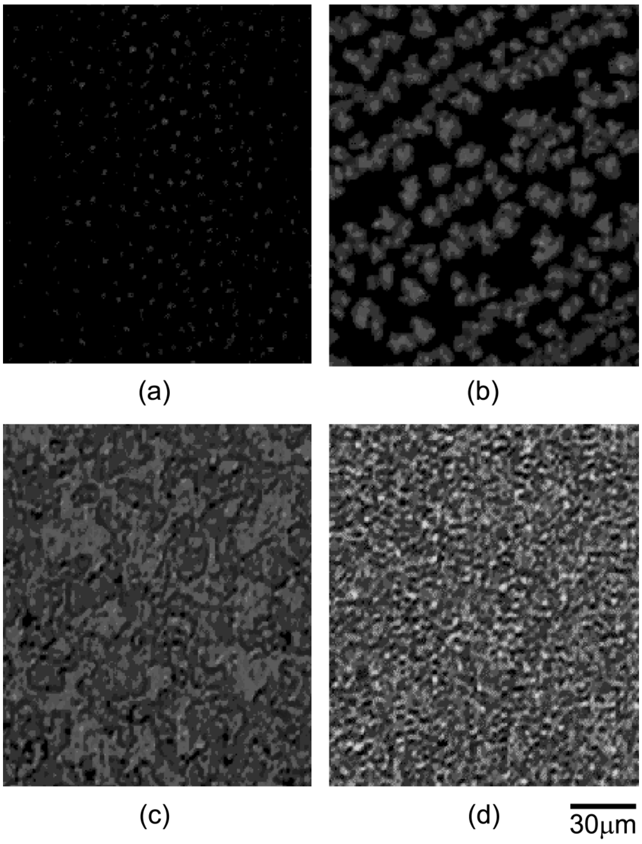

Figure 3. Optical micrographs of Sm C* of PBFOEB with n=8 on cooling from the isotropic liquid. (a) Sm C* phase appears as very small granual pattern at the isotropic-to-Sm C* phase transition temperature. (b) The texture grows to become granual pattern. (c) The texture tends to transform into mosaic texture with small domains gradually. (d) As it was further cooled, smectic C phase is changed abruptly at 103.5 °C. Then, the texture grows to become schlieren texture of the twisted smectic state to room temperature.

shows the polarization reversal current for PBOEB and PBFOEB with n=8 at the temperature corresponding to two smectic phases, SmX_1 and Sm C*. In Figure 4(a), the one sharp peak of reversal current for every half period was observed at 146 °C (temperature within Sm C* phase forming region) and the broad pattern at 136 °C (temperature within

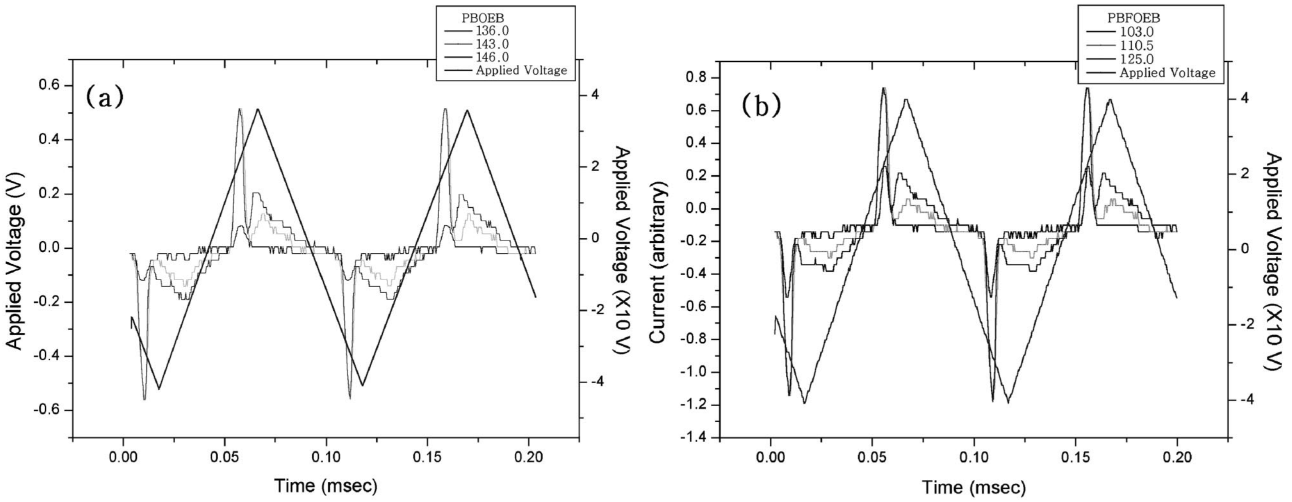

Figure 4. (a) The switching current curve obtained by applying a triangular voltage wave for PBOEB with n=8. (b) The switching current curve obtained by applying a triangular voltage wave for PBFOEB with n=8.

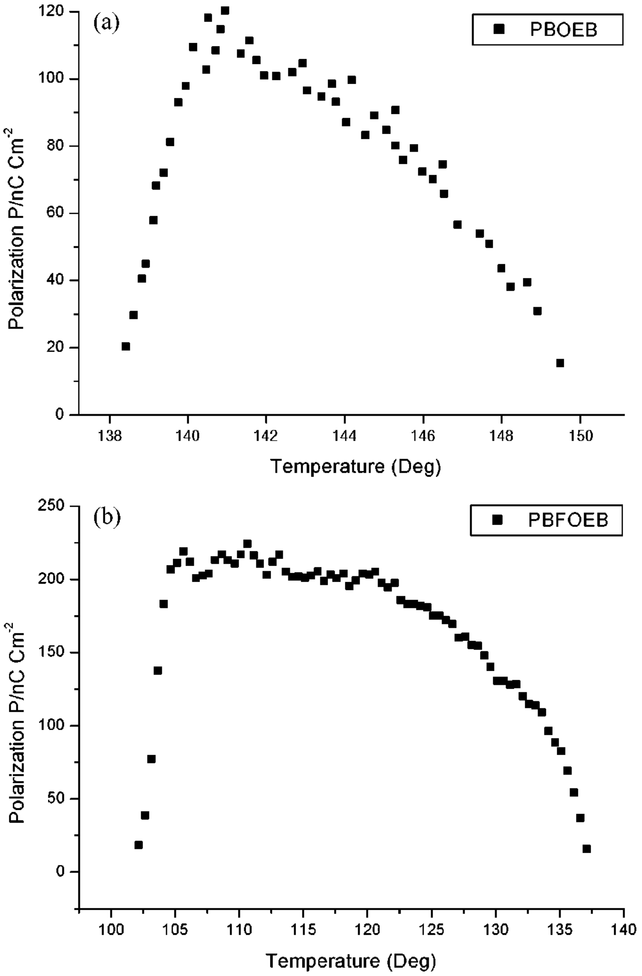

Figure 5. (a) The temperature dependence of spontaneous polarization for PBOEB with n=8. The temperature dependence of spontaneous polarization for PBFOEB with n=8.

SmX$_1$ forming region). In Figure 4(b), the one sharp peak of reversal current for for every half period was observed at 125 ^{o}C (temperature within Sm C* phase forming region) and the broad pattern at 103 ^{o}C (temperature within SmX$_1$ forming region). Thus, we can conclude that the Sm C* phase of the compounds (PBOEB and PBFOEB) is ferroelectric with the tip of the bent molecule orienting along the electric field and reversing its orientation on the polarity of the field. Figure 5 shows temperature dependence of spontaneous polarization for PBOEB and PBFOEB in the cooling experiment. In Figure 5(a), the switchable smectic phase exhibits a maximum polarization of about 120 nC/cm^2 for PBOEB. In Figure 5(b), the smectic phase exhibits a maximum polarization of aboput 225 nC/cm^2 for PBFOEB. On cooling the isotropic liquid, the spontaneous polarizations are increased with decreasing temperature. The spontaneous polarization dramatically decreased with lowering temperature below each critical temperature. The sharp decrease of polarization suggested that the smectic phase-to-solid phase transition is the first order. On further lowering the temperature, the polarization was vanished, because of crystallization of the central rod parts of the molecules.

Conclusions

The introduction of a lateral substituent (halogen atom) in the 3-position of a Schiff's base moiety reduced the transition temperature and the degree of crystallinity of the switchable banana liquid crystal. Also, the introduction of vinyl groups onto the terminals of bent-core molecules containing Schiff's base mesogen reduced the melting and the clearing temperature. The bent-core molecules with vinyl groups at the terminals could form the switchable smectic phase with octenyl group (n=8) even though the constituent molecules are achiral. We concluded that the smectic phase of the banana-shaped molecule having octenyl group except one with chlorine substituent was a chiral smectic C. Considering the switching current corresponding to the spontaneous polarization and optical microscopic textures, the aligned smectic phase was ferroelectric.

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