Polar Smectic Phases of Bent-Core Liquid Crystals with Vinyl End Groups

Chong-Kwang Lee[1], Soon-Sik Kwon[1], Tae-Sung Kim[1], Sung-Tae Shin[2], Lee-Tack Oh[2], E-Joon Choi[3], Wang-Choel Zin[4], and Liang-Chy Chien[5]

[1]Dept. of Chemistry, Gyeongsang National University, Chinju 660-701, Korea
[2]Dept. of Physics, Korea University, Chungnam 339-700, Korea
[3]Dept. of Polymer Science and Engineering, Kumoh National University of Technology, Kumi 730-701, Korea
[4]Dept. of Materials science and Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea
[5]Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA

New banana-shaped achiral compounds, 1,3-phenylene bis [4-{4-(7-octenyloxy)phenyliminomethyl} benzoate](PBOEB), 1,3-phenylene bis [4-{3-fluoro-4-(7-octenyloxy)phenyliminomethyl}benzoate] (PBFOEB), 1,3-phenylene bis [4-{4-(10-undecyloxy)phenyliminomethyl}benzoate](PBEUB), and 1,3-phenylene bis [4-{3-fluoro-4-(10-undecyloxy)phenyliminomethyl}benzoate](PBFEUB) were obtained by general synthetic methods. PBOEB and PBFOEB having the octenyloxy groups such as $-(CH_2)_6CH=CH_2$ showed ferroelectric switching, and their values of spontaneous polarization on reversal of an applied electric field were 120 nC/cm^2 and 225 nC/cm^2, respectively. PBEUB and PBFEUB having the undecyloxy groups such as $-(CH_2)_9CH=CH_2$ showed antiferroelectric switching, and their values of spontaneous polarization on reversal of an applied electric field were 120 nC/cm^2 and 140 nC/cm^2, respectively. We could obtain ferroelectric and antiferroelectric phases by controlling the number of carbon atom in alkenyloxy chains of bent-core molecules.

1. Objective and Background

A mesogenic compound of non-linear molecular structure was discovered for the first time by Voländer [1]. The chiral phase can also occur without chiral structure by spontaneous polarization derived from symmetry breaking [2]. A fascinating example of the chiral symmetry breaking was found in the tilted smectic phases of banana-shaped molecules [3].

Recently, ferroelectric or antiferroelectric liquid crystal phases formed from achiral molecules have been reported in which smectic phases of banana-shaped molecules could show ferroelectric or antiferroelectric switching[4].

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

2. Experimental

The syntheses of new banana-shaped achiral compounds were achieved by a general synthetic method [5,6].

The phase transition temperatures were determined by differential scanning calorimetry (DSC) and polaring optical microscopy (POM). DSC measurements were performed in a N_2 atmosphere with a cooling rate of 10 °C/min. Texture observation was carried out using a polarizing microscope with a hot plate. The switching current was obtained

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

Number of carbon atom(n) (X : lateral substituent)	Transition temperature/°C (Enthalpy/J · mol^{-1})	Switching property
8 (X=H)	Cr 130.8(27.2) SmX_1 142.9(17.0) SmC^* 159.8(25.4) I	Switchable(ferroelectric)
8 (X=F)	Cr 105.4(26.7) SmC^* 139.2(7.9) I	Switchable(ferroelectric)
8 (X=Cl)	Cr 108.3(14.1) I	None
11 (X=H)	Cr 136.4(28.4) SmC^* 156.6(11.1) I	Switchable(Antiferroelectric)
11 (X=F)	Cr 59.0(4.5) SmX_1 99.6(33.0) SmC^* 143.7(15.1) I	Switchable(antiferroelectric)
11 (X=Cl)	Cr 117.9(13.3) I	none

by the triangular wave method [7]. The sample cell was mounted in a microfurnace for measuring the spontaneous polarization with varing temperature. The polarization current, converted into a 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 Properties

The synthetic route for the banana-shaped compounds 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 accordance with expected formulae. The relationships of the transition temperatures between the number of carbon atoms in the alkenyloxy chains(n) and the presence of lateral halogen-substituents in the Schiff's base moiety are shown in Table 1. In the table, all the molecules of alkenyloxy groups with n=8, and 11 were switchable in their liquid crystal phases, while the molecules with Cl-substituents in the Schiff's base moiety were not switchable in their mesophases but could form smectic phases.

3.2 Microscopy Texture

Using an optical microscope with crossed polarizer, on cooling the isotropic liquid compounds, we could identify every phase transitions shown in Table 1. When the isotropic liquids of the compounds are cooled slowly, optical textures of SmB_7 phases with n=8 appear as domains with granual patterns

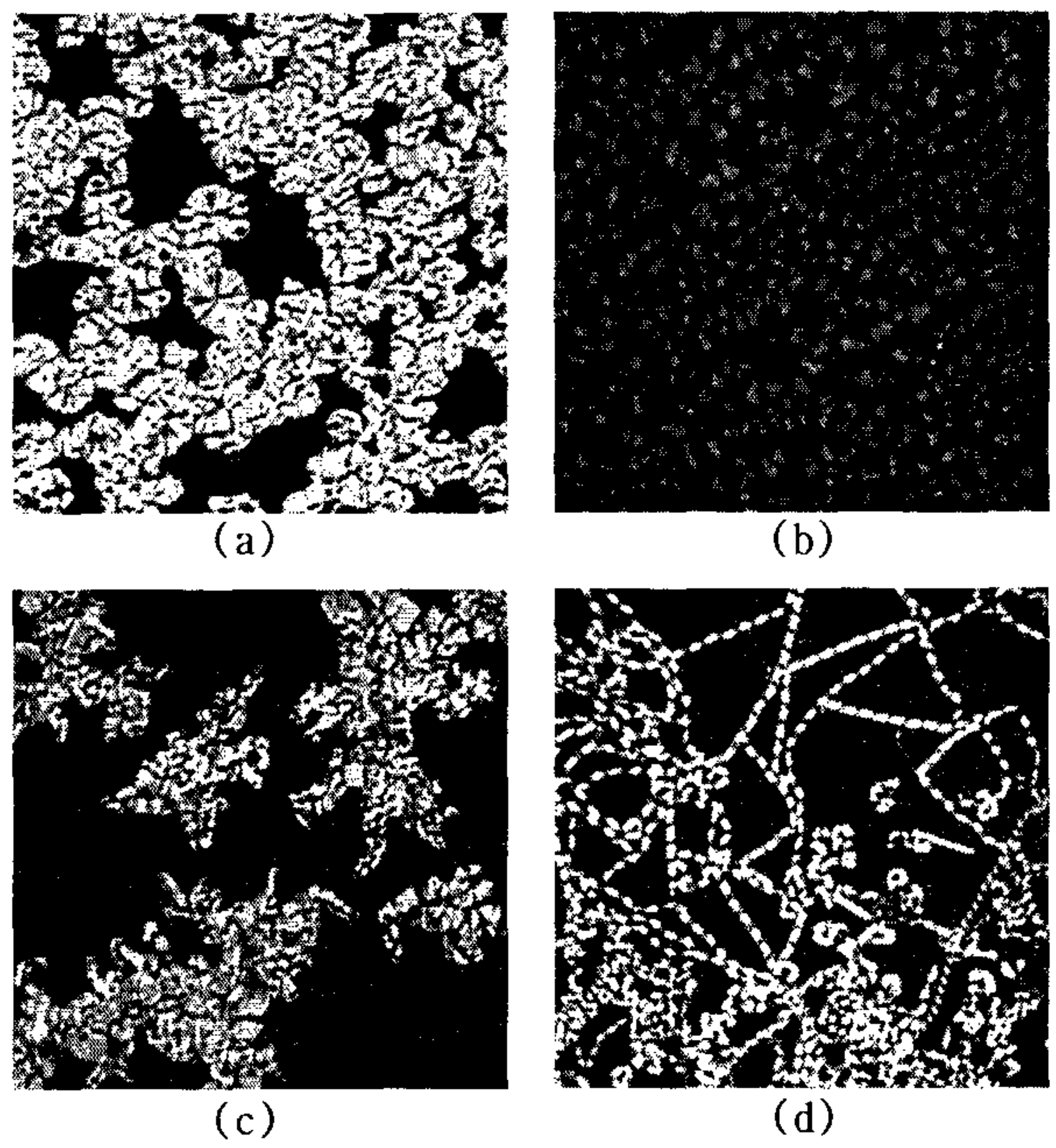
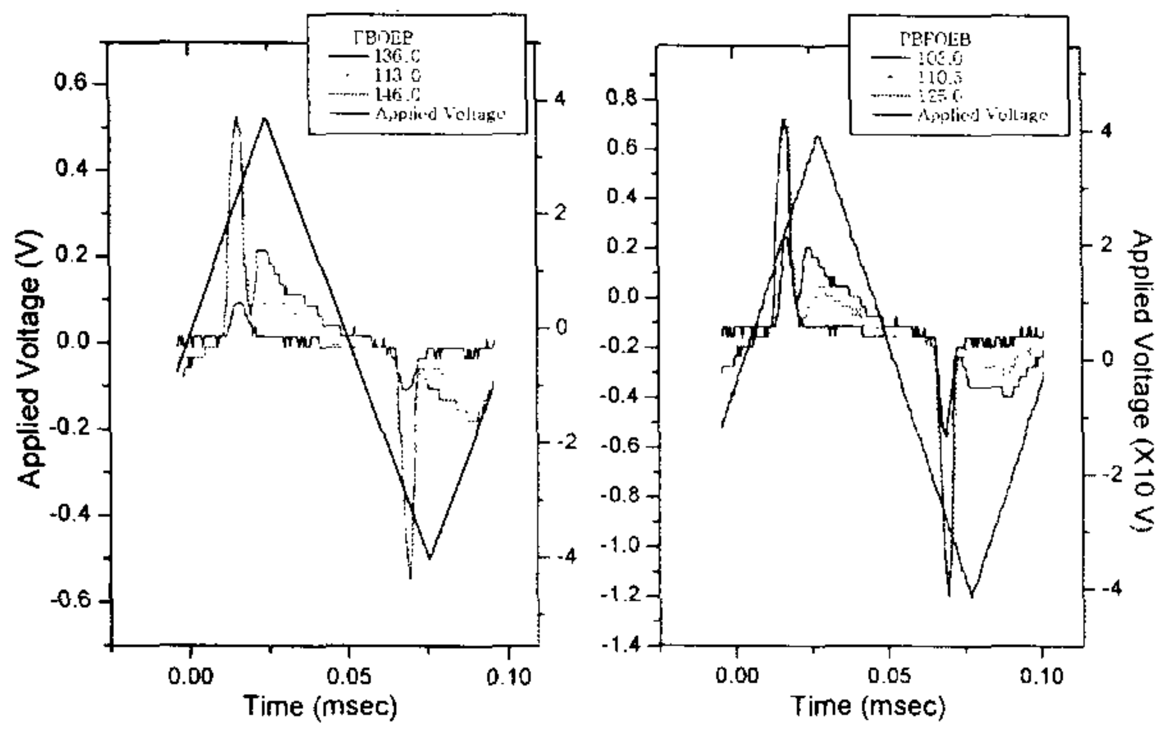


Figure 1. Optical micrographs of the switchable banana phases on cooling from the isotropic melt: (a) the switchable banana phase of PBOEB with n=8 at 160.0 °C, (b) the switchable banana phase of PBFOEB with n=8 at 139.1 °C, (c) the switchable banana phase of PBUEB with n=11 at 161.2 °C, (d) the switchable banana phase of PBFUEB with n=11 at 142.9 °C.

in Figure 1(a) and (b). While, optical textures of SmB_2 with n=11 appear as mesomorphic domain in Figure 1(c) and double-twisted helical germs in Figure 1(d).

3.3 Spontaneous Polarization and Switching Current

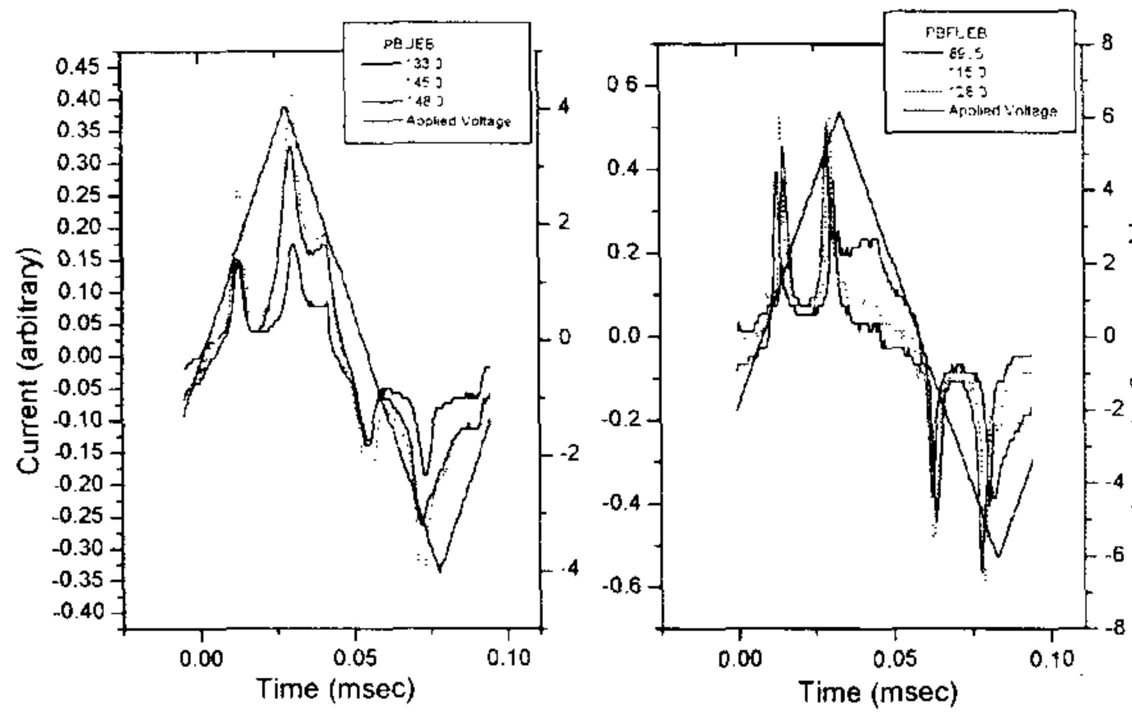
In order to characterize the smectic phases, we measured spontaneous polarization of the samples. A cell is made up of conductive indium-oxide coated glasses, treated with rubbed polyimide for the alignment. The cell gap was maintained by patterned organic spacer of 1.5 μm thickness. The spontaneous polarization was measured by applying triangular shape voltage, and the switching was also observed by using a polarized Microscope. Figure 2 shows the polarization reversal currents of the cell at



(a) (b)

Figure 2. The switching current curves for compounds with n=8 were obtained by appling a triangular voltage. (a) The switching current curves for PBOEB with n=8 at different temperaures. (b) The switching current curves for PBFOEB with n=8 at different temperatures.

temperatures corresponding to clear isotropic liquid and the SmB_7 phases for PBOEB and PBFOEB with n=8. In Figure 2(a), the one sharp peak of reversal current for every half period was observed at 146 °C (temperature within SmB_7 phase forming region) and the broad pattern at 136 °C (temperature within Sm X_1 forming region). In Figure 2(b), the one sharp peak of reversal current for every half period was observed at 125.0 °C (temperature within SmB_7 phase forming region). Thus, we can conclude that the SmB_7 phases of the compounds with n=8 are ferroelectric, with the tip of the bent molecules orienting along the electric field and reversing their orientation on the polarity of the field.

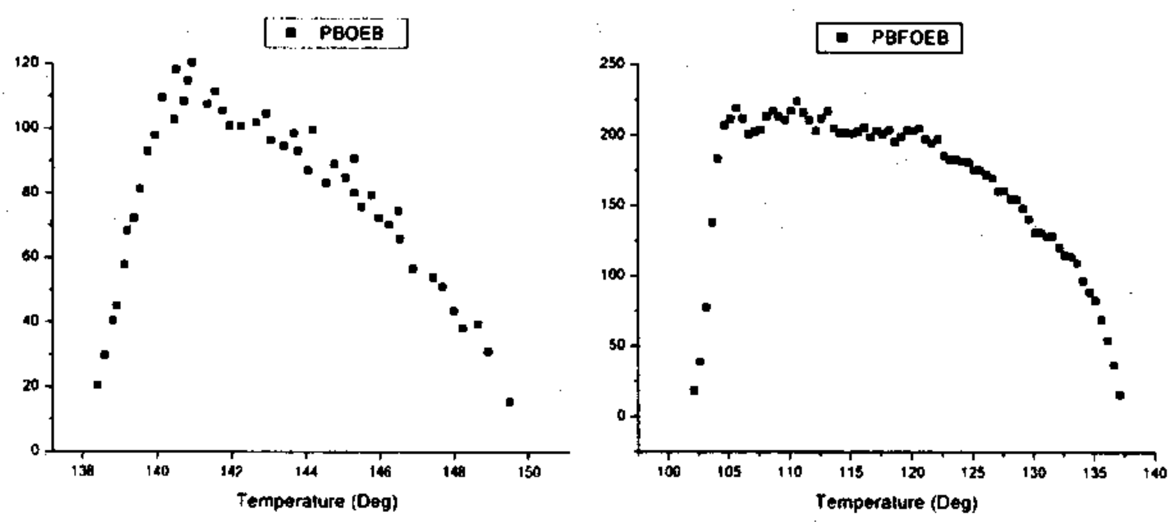


(a) (b)

Figure 3. The switching current curves for compounds with n=11 were obtained by appling a triangular voltage. (a) The switching current curves for PBUEB with n=11 at different temperatures. (b) The switching current curves for PBFUEB with n=11 at different temperatures.

Figure 3 shows the polarization reversal currents of the cell at temperatures corresponding to clear isotropic liquid and the SmB_2 phases for PBUEB and PBFUEB with n=11. In Figure 3(a), the two sharp reversal current peaks for every half period were observed at 148 °C. In Figure 3(b), the two sharp peaks of reversal current for every half period were observed at 128.0 °C (temperature within SmB_2 phase forming region). Thus, we can conclude that the SmB_2 phases of the compounds with n=11 are antiferroelectric, with the tip of the bent molecules orienting along the electric field and reversing their orientations on the polarity of the field.

Figure 4 shows the temperature dependence of spontaneous polarization of the compounds of PBOEB, and PBFOEB with n=8. In Figure 4(a), the switchable smectic phase exhibits a maximum polarization of about 120 nC/cm^2 for PBOEB. In Figure 4(b),

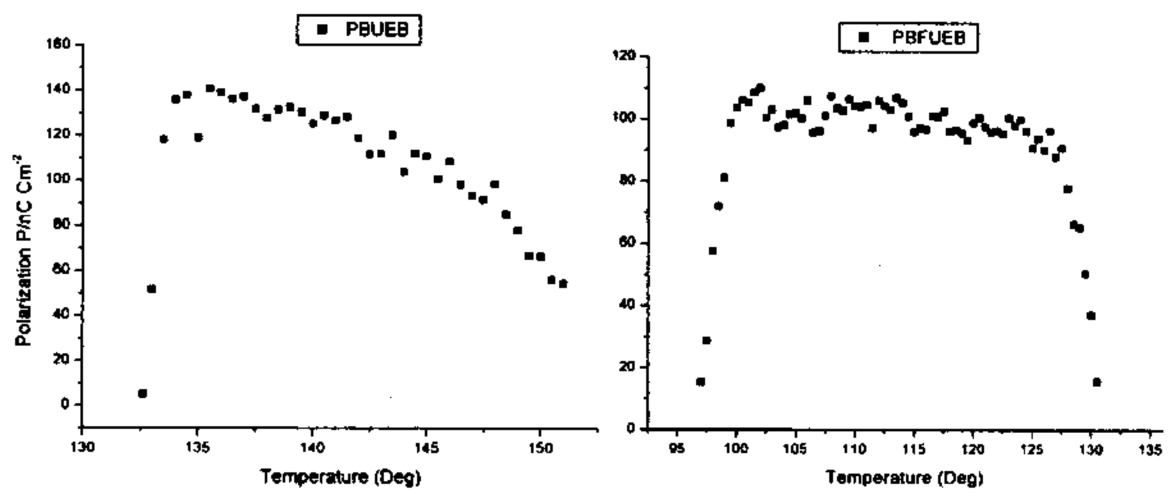


(a) (b)

Figure 4. (a) The temperature dependence of spontaneous polarization for PBOEB with n=8. (b) The temperature dependence of spontaneous polarization for PBFOEB with n=8.

the smectic phase exhibits a maximum polarization of about 225 nC/cm^2 for PBFOEB.

Figure 5 shows the temperature dependence of spontaneous polarization of the compounds of PBUEB and PBFUEB with n=11. In Figure 5(a), the switchable smectic phase exhibits a maximum polarization of about 140 nC/cm^2 for PBUEB. In Figure 5(b), the smectic phase exhibits a maximum polarization of about 110 nC/cm^2 for PBFUEB.



(a) (b)

Figure 5. (a) The temperature dependence of spontaneous polarization for PBUEB with n=11. (b) The temperature dependence of spontaneous polarization for PBFUEB with n=11.

On cooling the isotropic liquids, the spontaneous polarizations are increased with decreasing temperature. The spontaneous polarizations dramatically decreased with lowering temperature below each critical temperature. The sharp decrease of polarization suggested that the smectic phase-to-solid phase transition is first order.

4. Conclusions

The banana-shaped molecules with vinyl end group at terminal could form the switchable SmB_7 phases with octenyloxy group (n=8) and SmB2 phases with dodecyloxy group (n=11).

Considering the switching current corresponding to the spontaneous polarization with octenyloxy group (n=8), the aligned smectic phases are ferroelectric, while considering the switching current corresponding to the spontaneous polarization with dodecyloxy group (n=11), the aligned smectic phases are antiferroelectric. We could obtain ferroelectric and antiferroelectric phases by controlling the number of carbon atom in alkenyloxy chains of banana molecules.

Acknowledgement

This work was supported by grant No. R01-2001-00433 from the Korea Science & Engineering Foundation.

References

[1] D. Vorländer, Ber., **63**, 2831 (1920).
[2] D. Kondepudi, R. J. Kauffmann, and N. Singh, Science, **250**, 975 (1990).
[3] M. Lennan, and M. Seul, Phys. Rev. Lett., **69**, 2082 (1992).
[4] C.-K. Lee, J.-H. Kim, E-J. Choi, W.-C. Zin, and L.-C. Chien, Liq. Cryst., **28**, 12, 1749 (2001).
[5] A. Hussan, and V. Alexanian, Tetrahe dron Lett., 4475 (1978).
[6] C.-K. Lee, and L.-C. Chien, Liq. Cryst., 26, 609 (1999).
[7] K. Miyasato, H. Abe, A. Takezoe, and E. Kuze, Jpn. Phys., **22**, L661 (1983).