Synthesis and Characterization of banana-shaped achiral molecules

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New banana-shaped achiral compounds, 4-chloro-1,3-phenylene bis [4-4(3-fluoro-9-alkenyloxy)phenyl-iminomethylbenzoate]s and 4-chloro-1,3-phenylene bis [4-4-(3-fluoro-10-alkanyloxy)phenyliminomethyl benzoate]s were synthesized by varying the substituent (X=H, F, or Cl); their electrooptical properties are described. The smectic phases, including a switchable chiral smectic C (SmC*) phase, were characterized by differential scanning calorimetry, polarizing optical microscopy, and triangular method. The presence of vinyl end group at the terminals of linear side wings in the banana-shaped molecules induced a decrease in melting temperature. The smectic phase having the undecenyloxy group such as -$(CH_2)_9CH=CH_2$ showed ferroelectric switching, and its value of spontaneous polarization on reversal of an applied electric field was 2250 nC/cm^2, while the value of spontaneous polarization of the smectic phase having the decanyloxy group such as -$(CH2)_9CH_3$ was 3700 nC/cm^2. We could obtain the ferroelectric phase with low isotropic temperature by varying the end group at the terminals of linear side wings in the banana-shaped achiral molecules.

Poster presentation

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Abstract

New banana-shaped achiral compounds, 4-chloro-1,3-phenylene bis [4-4(3-fluoro-9-alkenyloxy)phenyl-iminomethylbenzoate]s and 4-chloro-1,3-phenylene bis [4-4-(3-fluoro-10-alkanyloxy)phenyliminomethyl benzoate]s were synthesized by varying the substituent(X=H, F, or Cl); their electrooptical properties are described. The smectic phases, including a switchable chiral smectic C (SmC^*) phase, were characterized by differential scanning calorimetry, polarizing optical microscopy, and triangular method. The presence of vinyl end group at the terminals of linear side wings in the banana-shaped molecules induced a decrease in melting temperature. The smectic phase having the undecenyloxy group such as -$(CH_2)_9CH=CH_2$ showed ferroelectric switching, and its value of spontaneous polarization on reversal of an applied electric field was 2250 nC/cm^2, while the value of spontaneous polarization of the smectic phase having the decanyloxy group such as -$(CH2)_9CH_3$ was 3700 nC/cm^2. We could obtain the ferroelectric phase with low isotropic temperature by varying the end group at the terminals of linear side wings in the banana-shaped achiral molecules.

1. Objective and Background

Since Meyer et al. [1] discovered ferroelectricity in the chiral smectic C phase formed by a chiral compound, molecular chirality has been accepted as the essential requirement for the smectic phase to show ferroelectricity. In the case molecular chirality is used to reduce the overall symmetry of the smectic phase. If other structural factors decrease the symmetry of the liquid crystal phase in the same manner as molecular chirality, ferroelectricity or antiferroelectricity could appear even in liquid crystal systems derived from achiral molecules. The chiral phase can also occur without chiral structure by spontaneous polarization derived from symmetry breaking[2-4]. A fascinating examples of the chiral symmetry breaking was found in the tilted smectic phases of banana-shaped molecules[5,6]. Recently, ferroelectric liquid crystal phases from achiral molecules [7] were reported in which smectic phases of the compounds with banana-shaped molecules show ferroelectric switching [8,9]. Moreover, liquid crystal phases formed from achiral molecules have been reported in which smectic phases of banana-shaped molecules could show ferroelectric or antiferroelectric switching[10-12]. In this study, new banana-shaped achiral molecules having vinyl and alkyl end groups were synthesized, and their ferroelectric liquid crystalline properties were investigated to determine the relationshipn between the liquid crystallity and structural changing of the end groups. We could obtain the ferroelectric phase with low isotropic temperature by varying the end group at the terminals of linear side wings in the banana-shaped achiral molecules.

2. Experimental

New banana-shaped achiral compounds, 4-chloro-1,3-phenylene bis [4-4(3-fluoro-9-alkenyloxy)phenyliminomethylbenzoate]s and 4-chloro-1,3-phenylenebis [4-4-(3-fluoro-10-alkanyloxy)phenyliminomethylbenzoate]s were achieved by a general synthetic methods [13,14]. 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. Texture observation was carried out using a polarizing microscope with a hot plate. The switching current was obtained by the triangular wave method[15]. The sample cell was mounted in a microfurnace for measuring the spontaneous polarization with varying the

Table 1. Phase transition temperatures of the smectic phases with alkanyloxy and alkenyloxy chains on cooling

	Transition temperature/°C (Enthalpy/J · mol^{-1})	Switching property
-$(CH2)_9CH_3$ (X=H)	Cr 32.7(4.0) SmX_1 83.71(14.3) SmC* 134.9(11.9) I	switchable
-$(CH2)_9CH_3$ (X=F)	Cr 37.3(12.1) SmC* 132.7(10.2) I	Ferroelectric switchable
-$(CH2)_9CH_3$ (X=Cl)	Cr 110.7(8.9) I	switchable
-$(CH_2)_9CH=CH_2$ (X=H)	Cr 78.0(14.9) SmC*121.0(11.2) I	switchable
-$(CH_2)_9CH=CH_2$ (X=F)	Cr 36.3(11.2) SmC* 111.8(6.4)I	Ferroelectric switching
-$(CH_2)_9CH=CH_2$ (X=Cl)	Cr 82.1(1.4) SmX_1 92.8(3.4) I	switchable

temperature. The temperature fluctuations inherent to the furnace were approximately 0.1 K. For direct measurements of the polarization, the triangular wave method was used for ease of subtracting the background current. 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.

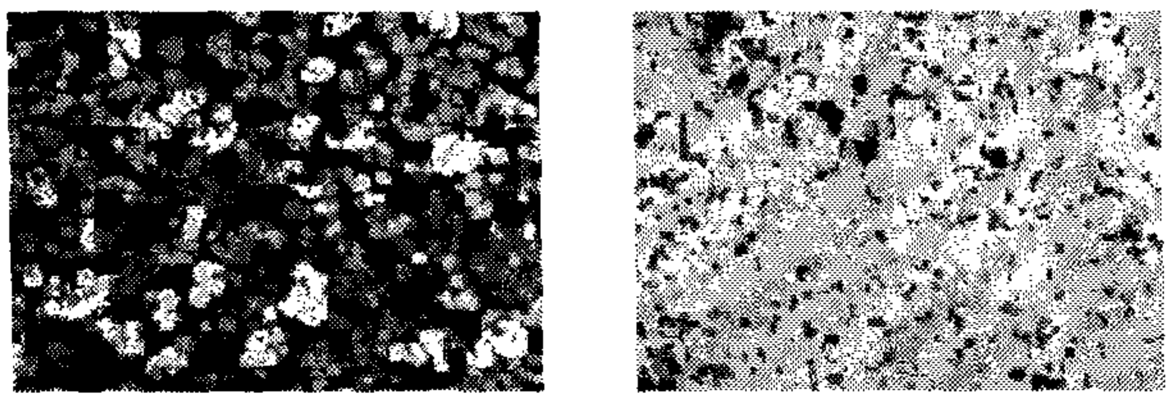
3. Results and Discussion

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 alkenyloxy chains and alkanyloxy chains, and the presence of lateral halogen-substituents in the Schiff's base moiety are shown in Table 1. In the table, the molecules with alkenyloxy group and alkanyloxy group were switchable in their liquid crystal phases, but only the molecules with F-substituent in the Schiff's base moiety showed ferroelectricity

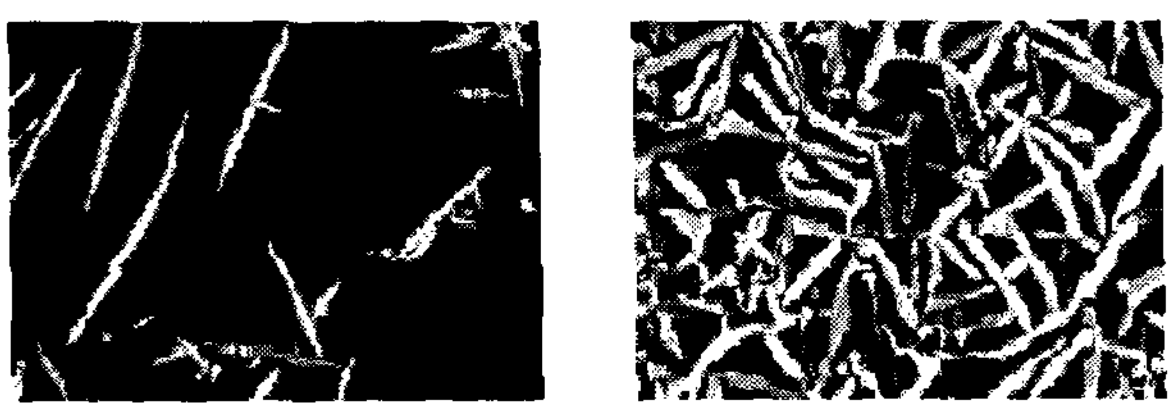
3.2 Microscopy Texture

Using an optical microscope with crossed polarizer, on cooling the isotropic liquid compounds, we could identify every phase transitions shown in Table 1. As shown in figure 1, when the isotropic liquids of CPBFDB (liquid crystal with alkanyloxy chain) are cooled slowly, optical textures of smectic phase of alkanyloxy group with F-substituent appear as granular patterns with white and blue colours (a). The granular textures grow to become amorphous mosaic textures consisting of small domains (b). On further cooling the textures begin to disappear gradually into background with blue colour from about 50.0 °C. Figure 2 shows optical micrographs of CPBFUEB (liquid crystal with alkenyloxy chain). When the isotropic liquids are cooled slowly, optical textures show as sharp needle-bar (a). The pattern become a texture with network at 111.8 °C (b). The textures then develop with amorphous pattern at 105.0 °C (c) and changes into colourful pattern at 36.6 °C (d).

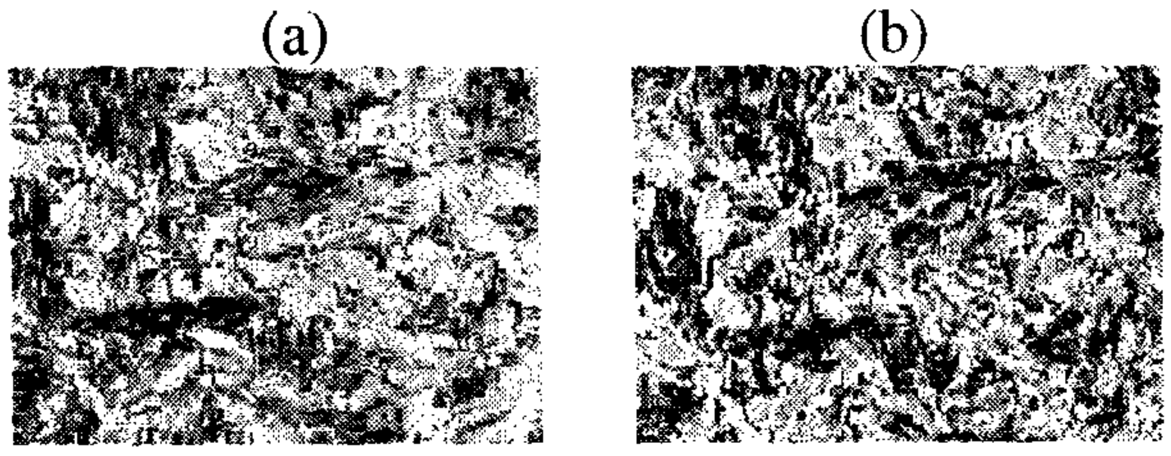


(a) (b)

Figure 1. Optical micrographs of the switchable banana phases for compounds with $-(CH2)_9CH_3$ group on cooling from the isotropic melt. (a) Textures of smectic phase of alkanyloxy group with F-substituent appear as granular patterns with white and blue colours (a). The granular textures then grow to become amorphous mosaic textures consisting of small domains (b). And then the mosaic textures begin to disappear gradually from about 50.0 °C.



(a) (b)

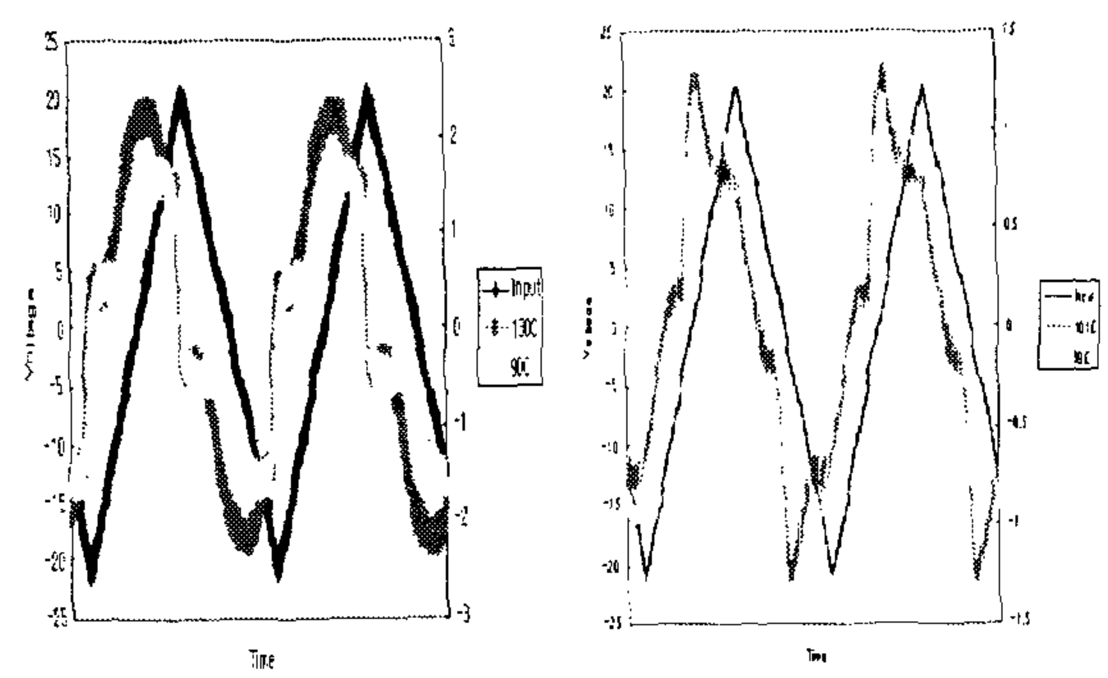


(c) (d)

Figure 2. Optical micrographs of the switchable phases for compounds with $-(CH_2)_9CH{=}CH_2$ group on cooling from the isotropic melt. (a) Textures of smectic phase of alkenyloxy group with F-substituent show as sharp needle-bar (a). The pattern then become a texture with network at 111.8 °C (b). The texture develops with amorphous schlieren pattern at 105.0 °C (c) and then changes into colourful texture pattern at 36.6 °C (d).

3.3 Spontaneous Polarization and Switching Current

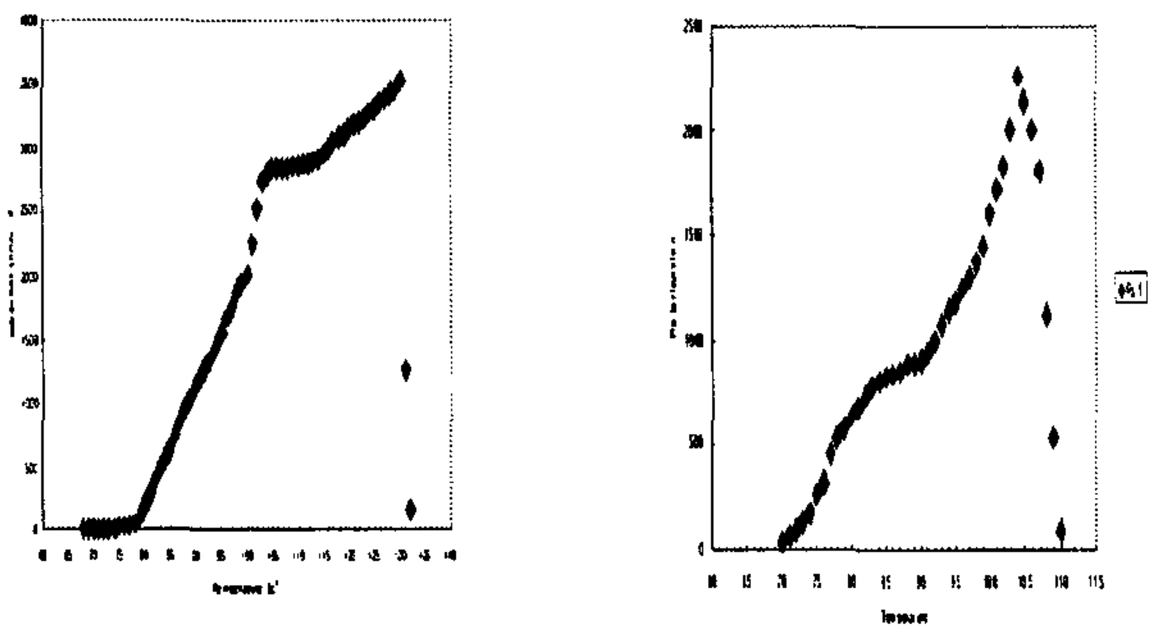
In order to characterize the smectic phases, we measured spontaneous polarization of the samples. For the measurements, a cell is made up of conductive indium-oxide coated glasses, treated with rubbed polyimide for the alignment. The cell gap was maintained by patterned organic spacer of 1.5 μm thickness.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



(a) (b)

Figure 3. The switching current curves of the smectic phases for CPBFDB and CPBFUEB were obtained by appling a triangular voltage. (a) The switching current curves for CPBFDB at different temperaures. (b) The switching current curves for CPBFUEB at different temperatures.

Figure 3 shows the polarization reversal currents of the cell at temperatures corresponding to clear isotropic liquid and the smectic phases for CPBFDB and CPBFUEB. In figure 3(a), the one sharp reversal current peak for every half period was observed at 130 °C (temperature within smectic phase forming region). In figure 3(b), the one sharp peak of reversal current for every half period was observed at 101.0 °C (temperature within smectic phase forming region). Thus, we can conclude that the smectic phases of the compounds are ferroelectric, with the tip of the bent molecules orienting along the electric field and reversing their orientations on the polarity of the field.



(a) (b)

Figure 4. (a) The temperature dependence of spontaneous polarization for for CPBFDB. (b) The temperature dependence of spontaneous polarization for CPBFUEB.

Figure 4 shows the temperature dependence of spontaneous polarization of the compounds of CPBFDB and CPBFUEB. In Figure 4(a), the switchable smectic phase exhibits a maximum polarization of about 3200 nC/cm^2 for CPBFDB. In Figure 4(b), the smectic phase exhibits a maximum polarization of about 2350 nC/cm^2 for CPBFUEB.

On heating the liquid crystals, the spontaneous polarizations are increased with increasing temperature. The spontaneous polarizations dramatically decreased with increasing temperature above each isotropic liquid. The sharp decrease of polarization suggested that the smectic phase-to-isotropic phase transition is first order.

4. Conclusions

The introduction of alkyl end group and vinyl end group onto the terminals of bent-core molecule containing Schiff's base mesogen reduced the melting and the clearing temperature. The banana-shaped molecules with alkyl end group and vinyl end group at terminals could form the switchable smectic phases. Considering the switching current corresponding to the spontaneous polarization of compounds with octanyloxy group and undecenyloxy group, the aligned smectic phases are ferroelectric. We could obtain new ferroelectric liquid crystals by introducing the different end group in the terminals of banana molecules.

5. Acknowledgement

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6. References

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