Effect of Lateral Substituents on the Formation of Smectic Phases in Banana-Shaped Molecules

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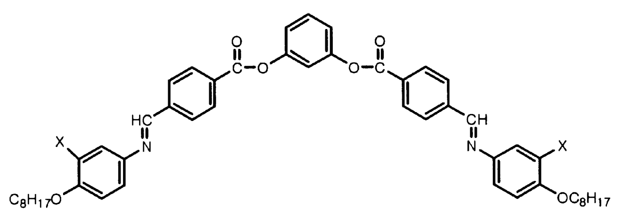
Ferroelectric liquid crystals formed from chiral molecules exhibiting smectic C phase are of great interest in theoretical and technological aspect.[1,2] Although the symmetry of most liquid crystalline phases is too high to allow spontaneous polarization, it has been recognized that a tilted smectic phase made up of chiral molecules can be ferroelectric, owing to a reduction in the overall symmetry of the material.[3] On the other hand, considering the point that the essential requirement to be ferroelectric liquid crystals need not necessarily be chiral, much attention has been given to the foundation of new ferroelectric liquid crystalline systems with achirality.[4,5] One new ferroelectric liquid crystal in achiral systems is the banana-shaped molecules with a bend-core structure in the middle of the mesogenic part.[6-9] It was first demonstrated by Niori *et al.*[10] that achiral banana-shaped molecules could produce ferroelectricity in its smectic phase. Recently, Sekine *et al.*[11] reported that helical domains of both handedness are formed in the smectic phase of banana-shaped molecules although the constituent molecules are achiral.



x = H, F, Cl, CH_3, OCH_3 or OC_2H_5

In this study, we have described the synthesis, effect of substituents and characterization of new six banana-shaped achiral compounds with the introduction of substituents onto the 3-position of the *p*-alkoxyaniline Schiff's base moiety.

Experimental Section

The banana-shaped compounds, 1,3-phenylene bis[4-(4-*n*-octyloxyphenylimino methyl)benzoate] (PBOB) and 1,3-phenylene bis[4-(3-fluoro-(PBFOB), 3-chloro- (PBCOB), 3-methyl-(PBMLOB), 3-methoxy-(PBMYOB) and 3-ethoxy-(PBEOB) 4-*n*-octyloxyphenyliminomethyl)benzoate] were prepared by using a general synthetic methods.[12-14] For the PBCOB, at first, 3-chloro-4-*n*-octyloxyaniline was prepared by hydrogenation of 2-chloro-4-nitro-1-octyloxybenzene with H_2 gas in the presence of palladium on activated carbon (10 wt. %), which was obtained by substitution reaction of 3-chloro-4-nitrophenol and 1-bromooctane. Then, 1,3-phenylene bis(4-formyl benzoate) was prepared by esterification reaction of resorcinol with 4-carboxybenzaldehyde in the presence of dicyclohexylcarbodiimide and a catalystic amount of dimethylaminopyridine in methylene chloride. The final Schiff's base product, PBCOB, was prepared by condensation reaction of the 3-chloro-4-*n*-octyloxyaniline and the 1,3-phenylene bis(4-formyl benzoate). The product was purified by chromatography on silica gel, and recrystallized several times from ethanol/dimethylformamide. Yield after purification was 20-30%. Spectroscopic data: ^{1}H NMR ($CDCl_3$, 200 MHz); δ=0.87 (t, 6H, $-CH_3$), 1.15-1.62 (m, 20H, $-(CH_2)_5-$), 1.87 (m, 4H, $-OCH_2CH_2-$), 4.07 (t, 4H, $-OCH_2-$), 7.20-7.52 (m, 8H, Ar-H), 6.95, 8.05, 8.31 (d, 10H, Ar-H), 8.56 (s, 2H, -CH=N-). IR (cm^{-1}, KBr), 3085 (aromatic CH), 2981 (aliphatic CH), 1734 (C=O), 1626 (C=N), 1600, 1491 (aromatic C=C), 1274 (C-O).

The remaining banana-shaped compounds were prepared by same method with PBCOB.

The phase transition temperatures were determined by differential scanning calorimetry (Perkin-Elmer DSC 7) and by polarizing optical microscopy (Nikon Eclipse E400 POL). DSC measurements were performed in N_2 atmosphere with a heating and cooling rate of 10 °C/min. Texture observation was carried out using a cross-polarizing microscope with a hot stage.

Results and Discussion

Mesomorphic Behavoir. The transition temperatures and Hammett substituent constants (σ) for the introduction of substituents onto the 3-position of the *p*-alkoxy aniline Schiff's base moiety are listed in Table 1. As it can be seen from the table, of the six banana-shaped molecules obtained, only the three molecules with x=H, F and Cl are of thermotropic liquid crystalline compounds. Compound PBCOB (x=Cl) has the lowest melting temperature among all the banana-shaped molecules because of the bulky lateral chloro-substituent. The presence of lateral halogens such as F and Cl in the 3-position of the Schiff's base moiety prevents the regular stacking of layers, and so the melting and isotropic temperatures are depressed.[15] On cooling the isotropic phase, PBCOB exhibits a smectic phase at about 138 °C and continuously cooling the smectic phase to room temperature could not induce the crystallization. Although indi-

Table 1. The transition temperatures of the banana-shaped liquid crystals and Hammett substituent constants (σ) of lateral substituents

X	Transition temperature (°C)	Hammett substituent constant[a] (σ)
H	K 158.2 SmB_3 162.1 SmB_2 175.2 I	0.00
F	K 118.8 SmX 147.2 SmB_2 154.4 I	0.06
Cl	K 56.2 SmX 64.5 SmB_2 138.1 I	0.23
CH_3	K 78.7 I	-0.17
OCH_3	K 105.3 I	-0.27
OC_2H_5	K 112.6 I	-0.24

[a]The σ values for x=H, F, Cl, CH_3, OCH_3 and OC_2H_5 have been reported by Taft *et al.*[17]

vidual banana-shaped molecules may be strongly polar, due to the large volume of molecules the dipole-dipole interaction is usually too weak to produce long-range polar ordering.[16] As shown in Table 1, comparing Hammett substituent constants (σ)[17] of electron withdrawing groups with those of electron donating groups, σ of electron withdrawing groups such as -H, -Cl and -F are zero or positive, while σ of electron donating groups such as -CH_3, -OCH_3 and -OC_2H_5 are negative. The introduction of lateral substituents with negative σ in the 3-position of Schiff's base moiety is expected to enhance the intralamellar electrostatic repulsion in the direction of their longitudinal dipoles. And so, the molecules which was made up of lateral substituents with negative σ value could not form smectic liquid crystals. But, 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 σ value could exhibit smectic phases.

Microscopy Textures. Figure 1 shows optical micrographs of the mesophase of PBCOB (x=Cl). The helical domains are observed upon cooling from isotropic to the smectic mesophase. Note that the formation of the helical domains in the banana-shaped molecules is unique in the sense that it occurs in a fluid system in which molecular interaction is weak and also thermal fluctuation is extensive.[18,19] As shown in Figure 1, different radii of helical domains can appear depending on the angle of inclination of molecules from the surface of plate or their nucleation site. Particularly, PBCOB shows the most texture variants, depending on the rate of cooling isotropic liquid to the smectic phase and interactions with surface of plate, including fan, focal conic and myelinic textures. The optical micrographs of PBOB (x=H) and PBFOB (x=F) show the textures containing small focal conic domains [see Figure 2(a)].

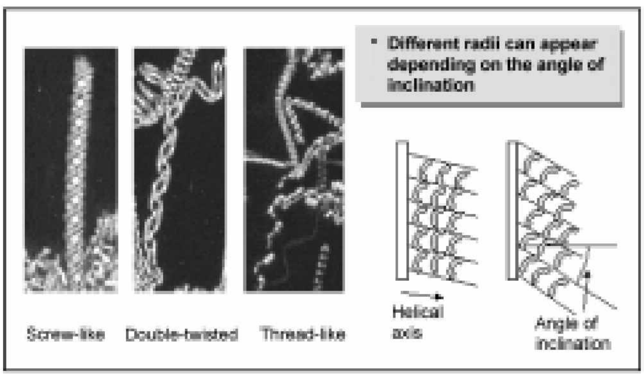


Figure 1. Optical microscopic textures observed on smectic mesophase of PBCOB (x=Cl). The helical structures such as screw-like, thread-like and double-twisted helices were obtained on cooling isotropic melt into the smectic phase.

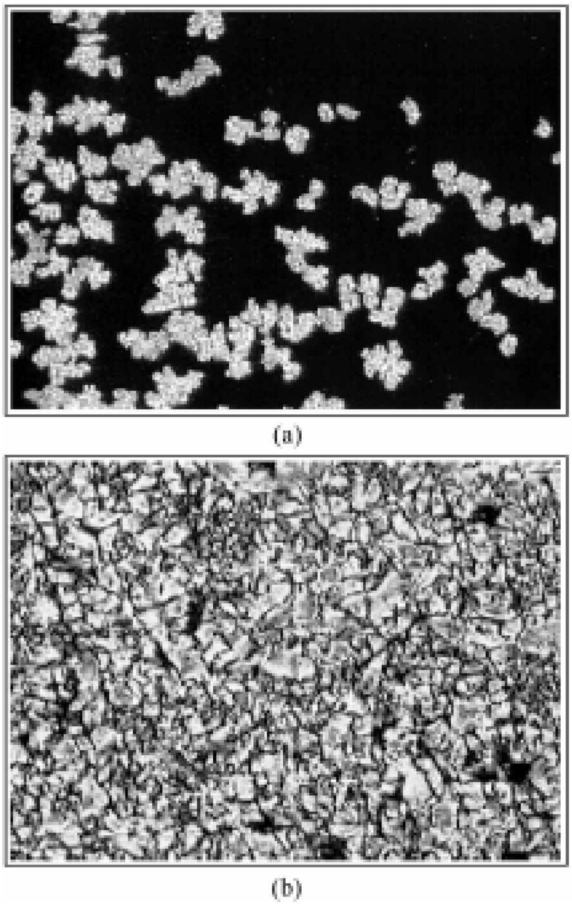


Figure 2. Optical microscopic textures observed on smectic mesophase of PBFOB (x=F). (a) Mesophase initially appears as the texture with granular pattern (magnification, × 200). (b) They tend to grow to be mosaic texture consisting of small domains (room temperature, × 40).

Alignment and Ferroelectric Properties. On a treated surface (C_{18} silane coated glass plates) for homeotropic alignment, a moderate uniform alignment was observed from a cross-polarizing microscope with a hot stage. As shown in Figure 3, the notable observation from microscopy is that the homeotropic texture can be seen by shearing a thin specimen between glass plates, showing distinct birefringence and a moderate uniform alignment. This means that the bent molecules are packed in the direction of bending and parallel to the layers, while by shearing the bending molecules become aligned parallel to the surface of plate. The ferroelectric properties of banana molecule PBCOB were further studied using a commercial display cell with a cell gap of 2 micron and polyimide alignment layer coated on inner surfaces and assembled in an antiparallel fashion. The ferroelectricity,

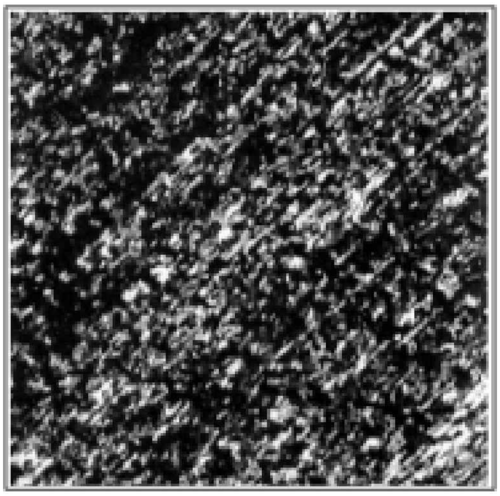


Figure 3. The alignment of PBCOB obtained from shearing a thin specimen between glass plates with the C_{18} silane coated surface.

resulting from the symmetry breaking and in-plane polar order in the smectic layer, was observed in PBCOB. Figure 4 shows the temperature-dependent spontaneous polarizations of PBCOB (*x*=Cl), PBOB (*x*=H) and PBFOB (*x*=F). The temperature-dependent polarization studies show that these switchable smectic phases exhibit maximum polarizations of about 50 nC/cm^2 for PBCOB, 60 nC/cm^2 for PBOB and 250 nC/cm^2 for PBFOB, respectively. Particularly, as temperature increases above the isotropic, measuring the polarization could be converted into measuring the ionic conductivity.

Conclusions

The introduction of lateral substituents in the 3-position of Schiff's base moiety reduced the transition temperature and the degree of crystallinity of the switchable phase. As the banana-shaped molecules containing electron-withdrawing groups with positive Hammett substituent constant (σ) are expected to decrease the intralamellar electrostatic repulsion in the direction of their longitudinal dipoles, the molecules could form smectic liquid crystals. The homeotropic texture showing birefringence and moderate uniform alignment can be seen by shearing a thin specimen between display cells. The PBOB, PBFOB and PBCOB could show the spontaneous polarization resulting from the symmetry breaking and in-plane polar order in the smectic layer.

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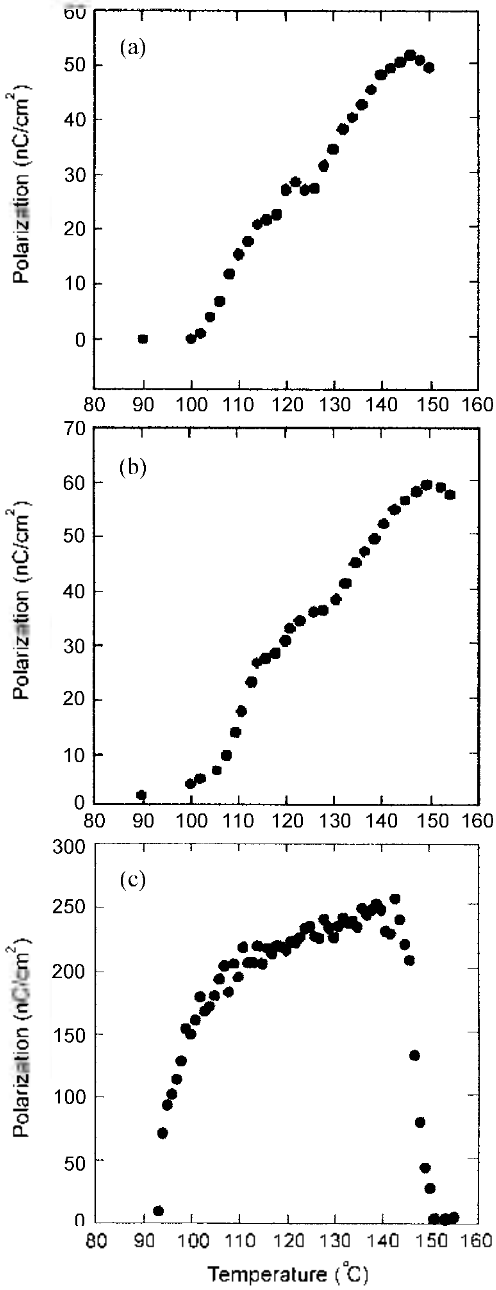

Figure 4. Temperature-dependence of spontaneous polarizations for (a) PBCOB (*x*=Cl), (b) PBOB (*x*=H) and (c) PBFOB (*x*=F).

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