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

Chong-Kwang Lee,* Soon-Sik Kwon, Liang-Chy Chien,† and E-Joon Choi‡

Dept. of Chemistry, Gyeongsang National University, Chinju 660-701, Korea
†Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA
‡Dept. of Polymer Science and Engineering, Konkuk National University of Technology, Kumi 730-701, Korea

Received September 4, 2009

Ferroelectric liquid crystals formed from chiral molecules exhibiting smectic C phase are of great interest in theoretical and technological aspects. 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. 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 formation of new ferroelectric liquid crystalline systems with achirality. 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. It was first demonstrated by Niori et al. that achiral banana-shaped molecules could produce ferroelectricity in its smectic phase. Recently, Sekine et al. reported that helical domains of both handedness are formed in the smectic phase of banana-shaped molecules although the constituent molecules are achiral.

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)]benzene (PBOB) and 1,3-phenylene bis[4-(3-fluoro-PFOB), 3-chloro- (PBCOB), 3-methyl- (PBMILOB), 3-methoxy- (PBMYOB), and 3-ethoxy- (PBEOB) 4-n-octyloxyphenylimino methyl)]benzene] were prepared by using a general synthetic methods. For the PBCOB, at first, 3-chloro-4-n-octyloxyaniline was prepared by hydrogenation of 2-chloro-4-nitro-1-octyloxybenzene with H2 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 benzene] was prepared by esterification reaction of resorcinol with 4-carboxybenzaldehyde in the presence of dicyclohexylcarbodiimide and a catalytic 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 benzene]. The product was purified by chromatography on silica gel, and recrystallized several times from ethanol/dimethylformamide. Yield after purification was 20-30%.

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 N2 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 Behavior. The transition temperatures and Hammett substituent constants (α) 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. 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-
individual 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. As shown in Table 1, comparing Hammett substituent constants \( \sigma \) of electron withdrawing groups with those of electron donating groups, \( \sigma \) of electron withdrawing groups such as \(-\text{H}, -\text{Cl} \) and \(-\text{F} \) are zero or positive, while \( \sigma \) of electron donating groups such as \(-\text{CH}_3, -\text{OCH}_3 \) and \(-\text{OC}_2\text{H}_5 \) are negative. The introduction of lateral substituents with negative \( \sigma \) in the 5-position of Schif'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 \( \sigma \) 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 \( \sigma \) could exhibit smectic phases.

Microscopy Textures. Figure 1 shows optical micrographs of the mesophase of PBCOB \((x=F)\). 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. 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 myelamic textures. The optical micrographs of PBOB \((x=H)\) and PBOB \((x=F\) show the textures containing small focal conic domains [see Figure 2(a)].

Alignment and Ferroelectric Properties. On a treated surface \((C_{18} \times \text{silane coated glass plates})\) 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,
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=C), 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 Hamnett substituent constant ($\sigma$) 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.

Acknowledgment. This work was supported by NSF ALCOM DMR 89-20147 and Foundational Juridical Person of Gyeongsang National University & Scholarship Foundation.

References

Notes