Mesomorphic Properties in Asymmetric Bent-shaped Molecules with Different Linkage Moieties as Side Wings

Sungmin Kang,* Seng-Kue Lee, Xiadong Li, Masatoshi Tokita, and Junji Watanabe
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552

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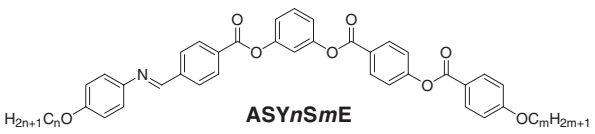
A new homologous series of asymmetric bent-shaped molecules with two different side wings composed of Schiff base and ester linkage moieties were synthesized. The effects of asymmetric shape on the liquid crystalline properties were investigated and discussed in comparison with the conventional symmetric bent-shaped molecules.

Liquid crystalline phases of bent-shaped (or banana) molecules have evoked considerable interest, in particular due to their exotic banana shape.[1] They can spontaneously form ferroelectric phases, and further chiral phases by breaking mirror symmetry[2] and forming twisted conformation[3] in spite of an absence of chiral carbon. A number of bent-shaped molecules have been prepared and characterized, and at least seven different banana phases (Bn; $n = 1$–7) have been identified.[4,5] One of the major research targets in the bent-shaped molecular field is to clarify how the molecular structure relates to mesophase properties such as polarity, chirality, and frustration.

Bent-shaped molecules are composed of three units; central bent core, side wings, and alkyl tails. Generally, resorcinol is used as a central bent core. Side wings in many bent-shaped molecules are based on a Schiff base azomethine moiety, but ester[6–8] and stilbene bent-shaped molecule have been synthesized to adjust the temperature region of mesophase and discover novel phases. In most of cases, side wings, and tail groups are symmetrically introduced and there are only a few reports of asymmetric banana molecules.[6,9,10] To clarify the effects of asymmetric shape on liquid crystalline properties, we synthesized a new homologous series of asymmetric banana molecules, 3-{4-[*N*-(4-*n*-alkoxyphenyl)iminomethyl]benzoyloxy}phenyl 4-(4-*n*-alkoxybenzoyloxy)benzoate (ASY*n*S*m*E: see Scheme 1[13]), which have a Schiff base moiety (S) in wing and an ester moiety (E) in the other wing. Carbon numbers (n, m) in the alkoxy tail groups were varied from 4 to 18. Polarized optical microscopy (POM), electrooptical and X-ray diffraction measurements have been utilized for the investigation of the mesomorphic properties and phase structures.

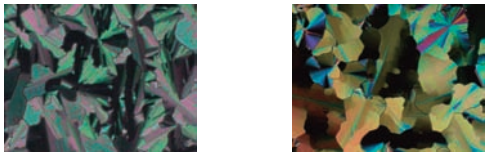
All the asymmetric ASY*n*S*m*Es show enantiotropic transitions. Mesomorphic transition temperatures and enthalpy changes were collected from DSC in conjunction with POM, and are listed in Table 1. ASY*n*S*m*Es with $n, m \leqq 8$ form a typical B1 phase[11,12] which exhibits mosaic texture (Figure 1) and



Scheme 1.

Table 1. Phase-transition temperatures and enthalpies for ASY*n*S*m*Es collected from cooling DSC thermograms at a rate of 10 °C min^{-1}

n	m	Transition temperature/°C (enthalpy/kJ mol^{-1})
4	4	Iso 166 (14.9) B6 150 (0.28) B1 130 (14.0) Cr
6	6	Iso 149 (15.4) B1 110 (11.3) Cr
8	8	Iso 137 (26.7) B1 103 (20.1) Cr
10	10	Iso 139 (31.9) B2 78 (16.6) Cr
12	12	Iso 133 (37.6) B2 72 (30.5) Cr
14	10	Iso 137 (26.1) B2 72 (14.8) Cr
18	10	Iso 137 (23.5) B2 81 (15.5) Cr



(a) (b)

Figure 1. POM images of mosaic texture in the B1 phase. (a) ASY6S6E and (b) ASY8S8E.

have a two-dimensional frustrated structure as clarified from X-ray profiles.[11] ASY4S4E shows an additional specific B6 phase in higher temperature region than the B1 phase, hence, Iso–B6–B1–Cr phase sequence. When both n and m are longer than 8, the highest temperature B1 phase is replaced by B2 phase. Thus, it shows an Iso–B2–Cr phase sequence.

The polar structure of the B2 phase was investigated through an electrooptic measurements. As shown in Figure 2a, B2 phase shows two switching current peaks within a half period of triangular voltage. Further, microscopic texture simultaneously observed indicates anticlinic to clinic transformation (Figures 2b and 2c). Thus, B2 phase has a homochiral antiferroelectric structure, that is a SmC_AP_A type of layer structure. The tilt angle was elucidated as 35° from the rotation angle of POM extinction brushes on electrooptical switching from off-state to on-state.

In comparison to classical symmetric molecules, P-*n*-O-PIMBs,[3] the effects of the asymmetric introduction of the side wings are clearly detected. First, the isotropic–liquid crystal transition temperature, T_i, is significantly lowered. For example, T_i for ASY12S12E is 133 °C while it is 165 °C for P-12-O-PIMB. Secondly, the temperature region of B2 phase is more expanded in the asymmetric system; 60 °C for ASY12S12E in comparison with 30 °C for P-12-O-PIMB. Thirdly, the racemic nature of B2 phase in P-*n*-O-PIMB is altered to the homochiral nature in this asymmetric system and the lowest temperature B4 phase is replaced by the crystal phase.

The most important effect of the asymmetric introduction of side wings is reflected in the layered structure of B2 phase. Figure 3 shows the X-ray diffraction pattern typically observed for the B2 phase of ASY10S10E (See Figure S2[13] for

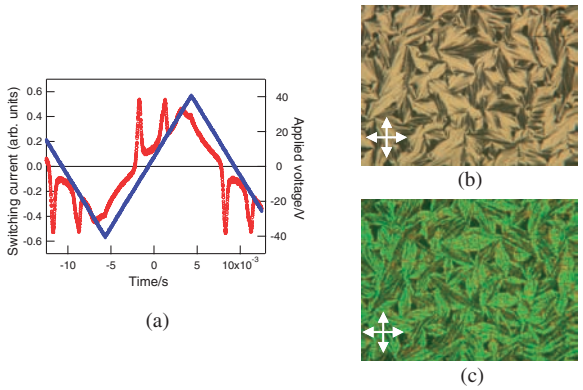


Figure 2. (a) Reversal switching current for the B2 phase of ASY14S10E which is indicative of antiferroelectricity, and (b) and (c) POM images of electrooptic measurement at DC-off-state and DC-on-state, respectively (4.7 µm cell, 80 Vpp, 50 Hz). White arrows indicate the direction of cross-polarization. See Figure S3[13] result for ASY10S10E.

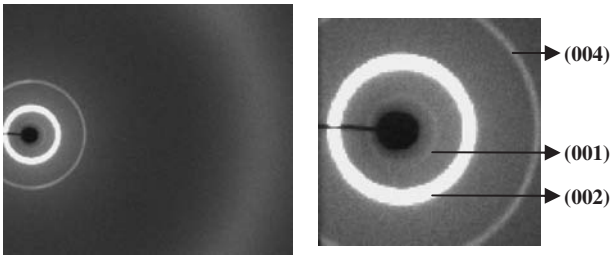


Figure 3. (a) X-ray pattern observed for B2 phase of ASY10S10E. (b) is the enlarged view of the small angle region of (a).

ASY12S12E and ASY18S10E). There are three sharp inner reflections in addition to the diffuse outer halo. The latter indicates the liquid-like association of molecules within a layer. Spacings of the inner reflections are 74.2, 37.3, and 18.6 Å, which correspond to (001), (002), and (004), respectively. The (002) reflection with a spacing of 37.3 Å comparable to the molecular length (44.7 Å) is strongest, indicating that each layer is constructed by each molecule. The smaller value of the observed spacing than the molecular length means the molecules tilt in the layer. The calculated tilt angle 33° corresponds to the microscopically determined value of 35°. Of interest is an observation of a reflection with a spacing of 74.2 Å that is twice the molecular length, since it is indicative of a bilayer structure in which two layers are included in a repeating unit. Such a bilayer structure can be constructed only by a segregation of the two different side wings. Since the molecules are tilted by 33° to the layer and the layer structure is essentially homochiral SmC_AP_A, the bilayer structure is illustrated in Figure 4a and compared with the conventional homochiral SmC_AP_A structure in Figure 4b. In our previous study,[8] we prepared asymmetric banana molecules in which different tail groups were introduced. In this case however, there is observed neither the segregation of two tail groups nor the formation of bilayer structure, showing that the tail chains can fill randomly the space between mesogenic layers (interlayer space). In the present system, in contrast, the mixing of two different side-wings may be energetically unfavorable because of the chemically different nature and different length.

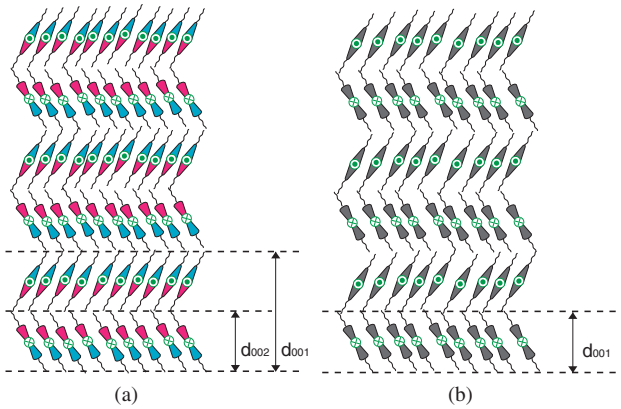


Figure 4. Schematic illustration of layer structures in the B2 phases of (a) asymmetric ASY10S10E and (b) symmetric P-10-O-PIMB. In (a), the red and blue color indicate two different side wings composed of Schiff base and ester-linkage moieties, respectively. The segregation of two side wings results in the bilayer structure which exhibits (001) reflection with a spacing corresponding to twice the molecular length.

In summary, novel bent-shaped ASY*n*S*m*Es with asymmetric side wings composed of a Schiff base moiety in one side and ester linkage moiety in the other side were synthesized. The ASY*n*S*m*Es ($n = m$ and $n \neq m$) enable us to evaluate the effects on the mesomorphic properties. The isotropization temperature of the mesophase is appreciably decreased and the temperature range of the mesophase is effectively expanded. The most significant effect is that the asymmetric introduction of side wings results in the formation of bilayer SmC_AP_A B2 phase. The formation of bilayer structure is important since it reduces the packing symmetry. While the current SmC_AP_A structure possesses a D_2 packing symmetry, it has a polar symmetry of C_2. The examination of the polar symmetry is now proceeding from the observation of second harmonic generation for a perfect aligned sample. The details will be published elsewhere.

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