Novel Unsymmetrical Achiral Banana-shaped Molecules Having Different Lengths of Alkyl Terminal Chains

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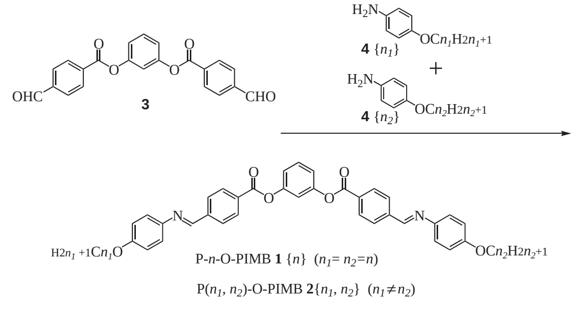
New unsymmetrical banana-shaped molecular series having different lengths of alkyl flexible chain on both side wings designated by "P-(n_1, n_2)-OPIMB", are studied comparing with the symmetric banana molecules in P-*n*-O-PIMB homologues.

Up to the present, the banana-shaped molecular systems have been extensively studied since their unconventional properties have intrigued scientists in this field and have opened a new era for polarity and chirality in soft materials. The well-known mesophases that had been revealed in the early of 1996 by Niori et al.[1] were the so called "B2" and "B4" phases formed in 1,3-phenylene bis[4-{(4-*n*-alkoxyphenyl)iminomethyl}benzoate] (P-*n*-O-PIMB) **1** homologous molecules. The former phase (B2) was found to exhibit electro-optic switching under applied external field[1] and both of them are apparently chiral liquid crystalline phases. In the B2 phase, the molecules are tilted in the smectic layers as in SmC phase formed by calamitic mesogens. However, in the special structural bent shape of molecule, this tilting builds up a particular packing which gives rise to a formation of enantiotropic structures, i.e. chirality.[2] Consequently, four types of layer structures can be formed by the tilting of the banana-shaped molecule in the smectic layers; (1) two homochiral layer structures [SmC_SP_F and SmC_AP_A], and (2) two racemic layer structures [SmC_AP_F and SmC_SP_A].[3] This combination of the tilt and molecular tip directions in the smectic layers causes the extraordinary properties in the B2 phase.[2,4–6] We wish to report how unsymmetrical banana-shaped molecules P-(n_1, n_2)-O-PIMB **2**, analogue to the P-*n*-O-PIMB homologous molecules, are affected by the combination of alkyl tail groups on the mesomorphic behavior and mesophase structure.[7,8]

The synthetic pathway of the materials used is shown in Scheme 1.[9] For example, condensation of dialdehyde **3** and a mixture of 4-butoxyaniline **4**{*4*} and 4-decyloxyaniline **4**{*10*} in refluxing ethanol, followed by removing the residue of aldehyde using PS-$TsNHNH_2$™ resin, provided a 1:2:1 mixture of P-4-O-PIMB **1**{*4*}, P-(4,10)-O-PIMB **2**{*4,10*}, and P-10-O-PIMB **1**{*10*}.[10] Complete separation was accomplished by gel permeation chromatography (GPC) eluting with chloroform recycled nine times.[11] The product was recrystallized from ethanol-chloroform to provide analytically pure **2**{*4,10*} in 22% isolated yield. P-(4,8)-O-PIMB **2**{*4,8*}, P-(4,10)-O-PIMB **2**{*4,10*}, P-(4,12)-O-PIMB **2**{*4,12*}, P-(6,14)-O-PIMB **2**{*6,14*}, and P-(8,14)-O-PIMB **2**{*8,14*} were synthesized in the same manner using the combination of the corresponding two 4-alkoxyanilines **4**, respectively. The combination of three 4-alkoxyanilines **4**{*4*}, **4**{*7*}, and **4**{*11*} also provided the desired P-(4,7)-O-PIMB **2**{*4,7*}, P-(4,11)-O-PIMB **2**{*4,11*}, and P-(7,11)-O-PIMB **2**{*7,11*} with homo coupling products P-4-O-PIMB **1**{*4*}, P-7-O-PIMB **1**{*7*}, and P-11-O-PIMB **1**{*11*}.[10] It should be noted that hetero coupling products were easily obtained by separation of the mixture of the coupling products if the difference of the molecular weight of the products is more than 50. Thermodynamic data of all materials are summarized in Table 1 and Figure 1.

A typical example of Group I is P-(4,8)-O-PIMB **2**{*4,8*}, which exhibits B1 and B4 phases as found in Figure 1. By com-



Scheme 1.

Table 1. Phase transition temperature (°C) of P-(n_1,n_2)-O-PIMB homologous molecules measured on cooling at a rate of 10 °C min^{-1a}

P-(4,7)-O-PIMB **2**{*4,7*}	B4 150(28.0) B1 173(7.89) Iso[b]
P-(4,8)-O-PIMB **2**{*4,8*}	B4 150(27.7) B1 167(15.1) Iso
P-(4,10)-O-PIMB **2**{*4,10*}	B4 156(32.8) B2 165(18.6) Iso[b]
P-(4,11)-O-PIMB **2**{*4,11*}	B4 155(31.1) B2 166(18.5) Iso
P-(4,12)-O-PIMB **2**{*4,12*}	B4 156(32.1) B2 166(20.0) Iso[b]
P-(7,11)-O-PIMB **2**{*7,11*}	B4 138(33.3) B2 167(21.1) Iso
P-(6,14)-O-PIMB **2**{*6,14*}	B4 144(27.6) B2 165(21.9) Iso
P-(8,14)-O-PIMB **2**{*8,14*}	B4 138(33.8) B2 167(24.4) Iso

The mesomorphic behavior and physical properties of P-(n_1, n_2)-O-PIMB were studied by means of optical microscopy, DSC, X-ray diffraction measurements. [a]The transition enthalpies ($-kJ$ mol^{-1}) are given in parentheses. [b]Monotropic.

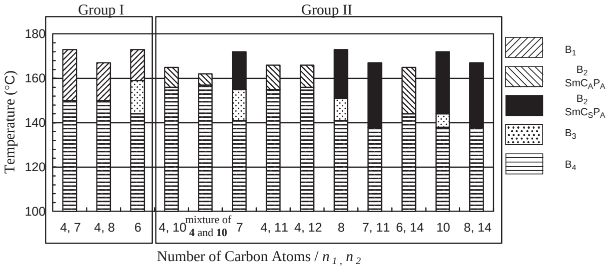


Figure 1. Phase behavior of P-(n_1,n_2)-O-PIMB determined on the cooling process with a rate of 10 °C min^{-1}.

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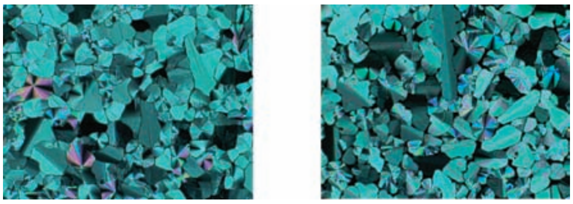

Figure 2. Polarized optical microscopic textures for the B1 phase of (a) P-(4,8)-O-PIMB 162 °C (left) and (b) P-6-O-PIMB 169 °C (B4 144 B3 159 B1 173 Iso) (right).

paring with symmetric counter-part (P-6-O-PIMB **1**{*6*}), one knows that they exhibit almost similar phase sequence except for the disappearance of the B3 phase in the unsymmetrical one. Optical micrographs of the B1 phase[12] of unsymmetrical **2**{*4,8*} are displayed in Figure 2a, showing large platelets of mosaic texture as observed in the B1 phase of symmetric **1**{*6*} (Figure 2b). The X-ray diffraction data of the B1 phase in **2**{*4,8*} indicate a frustrated structure with a unit lattice of $a = 46.3$ and $c = 39.6$ Å. These lattice parameters are approximately equivalent to those of **1**{*6*} ($a = 49.5$ and $c = 40.4$ Å). The layer spacings of the B4 phase are also similar 43 Å for **2**{*4,8*} and 42.4 Å for **1**{*6*}. It should be stated that this similarity in the layer spacing of the B4 phase with the symmetric counter-parts is observed for all other unsymmetrical materials.

In Group II, we can know how the unsymmetrical tails affect the nature of the B2 phase. Typical example is P-(4,10)-O-PIMB **2**{*4,10*} in which the molecule exhibits the B2 and B4 phases. Again, we understand that the phase behavior is similar to that of its symmetric counter-part, P-8-O-PIMB **1**{*8*}, but the B3 phase disappears. WAXD data for the B2 phase of **2**{*4,10*} show a conventional smectic layer structure with a layer spacing of 38.0 Å, which is also similar to 38.1 Å in the symmetric counter-part, **1**{*8*}. The reversal switching current under applying triangular wave form (8.3 Vpp/μm, 100 Hz) for a switchable B2 mesophase of compounds in this group exhibited the appearance of the two reversal current peaks. It indicates antiferroelectricity of the phase.

It is worth noting that on cooling from the isotropic state, the B2 phase showed the domain which has an extinction direction along the layer normal (see Figure 3a). This domain can be switched into the synclinic state having extinction direction sprays away from the layer normal under the electric field (Figure 3b). Both evidences confine to SmC_AP_A (anticlinic and antiferroelectric polar order) as layer structure for the B2 phase of P-(4,10)-O-PIMB **2**{*4,10*}. This formation of SmC_AP_A structure in the unsymmetrical derivative is unusual since the P-*n*-O-PIMB **1**{*n*} molecules form SmC_SP_A (synclinic and antiferroelectric polar order) layer type as a ground-state layer structure.[13,14] It is obvious that the introduction of different alkyl terminal tails induces the SmC_AP_A structure.

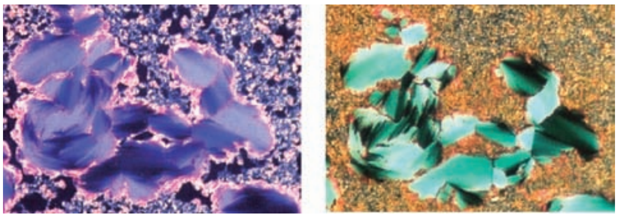

Figure 3. Polarized optical texture for the B2 phase of P-(4,10)-O-PIMB; (a) without electric field (left) and (b) in the field (right).

Type of the layer structure of the B2 phase has carefully been determined for other unsymmetrical P-(n_1, n_2)-O-PIMB **2**{n_1, n_2} molecules. As found from Figure 1, the simple conclusion was obtained if $(n_1 - n_2)$ is bigger than n_2, the ground-state B2 layer structure is altered from SmC_SP_A to SmC_AP_A.

In a summary, unsymmetrical P-(n_1, n_2)-O-PIMB molecules exhibit similar mesophase behavior to the P-*n*-O-PIMB with *n* corresponding to $(n_1 + n_2) / 2$, although the B3 phase disappears in all cases. It is thus likely that the two types of tails are not segregated from each other, but mix randomly. The disappearance of the B3 phase suggests that the B3 phase is fairly ordered phase which needs the uniform tail length. The most significant effect of unsymmetry is that the ground-state structure of the B2 phase becomes SmC_AP_A as alterated from SmC_SP_A when the difference of the two alkyl terminal chain lengths becomes larger. This suggests that the interaction of alkyl tails at layer interface is a significant key for the banana-shaped molecular alignment, i.e., the layer structure. Moreover, a comprehensive study will be reported in due course.

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