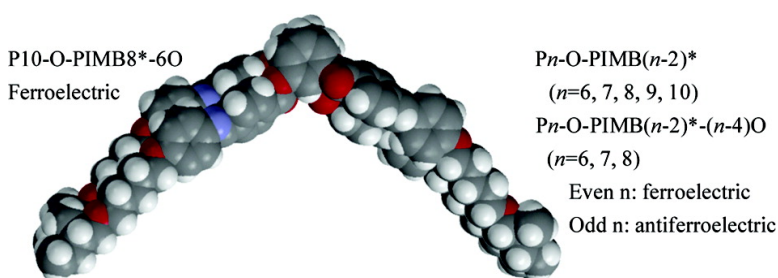


## Odd–Even Behavior of Ferroelectricity and Antiferroelectricity in Two Homologous Series of Bent-Core Mesogens

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## Odd–Even Behavior of Ferroelectricity and Antiferroelectricity in Two Homologous Series of Bent-Core Mesogens

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**Abstract:** Two chiral bent-core mesogens  $Pn-O-PIMB(n-2)^*$  ( $n = 9$  and  $10$ ) and their oxygen analogues  $Pn-O-PIMB(n-2)^*-(n-4)O$  ( $n = 8, 9,$  and  $10$ ) with  $\omega$ -[(S)-amyloxy]alkoxy terminal groups were prepared, and their phase structures were investigated by means of electro-optic, polarization reversal current and second harmonic generation measurements in order to clarify the effect of the interlayer steric interaction on the emergence of polar orderings. The odd–even behavior for the alternative appearance of ferroelectricity and antiferroelectricity was observed in two homologous series; the bent-core mesogens  $P10-O-PIMB8^*$ ,  $P8-O-PIMB6^*-4O$ , and  $P10-O-PIMB8^*-6O$  in addition to the previously reported  $P6-O-PIMB4^*$  and  $P8-O-PIMB6^*$ , where the length of chains  $n$  is even, exhibited ferroelectric phases. On the contrary, the mesogens  $P7-O-PIMB5^*$ ,  $P9-O-PIMB7^*$ , and  $P9-O-PIMB7^*-5O$ , where  $n$  is odd, showed antiferroelectric phases. It is obvious that the interlayer steric interaction plays a major role for the emergence of a variety of phase structures.

### 1. Introduction

Since Niori et al.<sup>1</sup> discovered that achiral bent-core (banana-shaped) molecules possess unusual and interesting properties, i.e., unique polarity and supramolecular chirality, much attention has been paid for these materials. The investigation of the relationship between the molecular structure and mesomorphic properties is very important to liquid crystal chemistry. That is, a series of liquid crystals with a systematic structural variation have to be synthesized to examine the relationship between the chemical structures and their physical properties, particularly the polar orders in the bent-core mesogens. For that purpose, new synthetic methods have to be developed.

Among seven phases, B1–B7, the most widely studied is the B2 phase, in which four structures are known to exist depending on tilt and polar correlations between adjacent layers;  $SmC_{S,APFA}$ . Here the first two subscripts, S and A, specify syn- and anticlinicity, and the second two subscripts, F and A, specify ferro- and antiferroelectricity, respectively. As in  $Pn-O-PIMB$  with achiral terminal alkoxy chains, most of bent-core mesogens exhibit the antiferroelectric mesophase,<sup>2–6</sup>

and only a few ferroelectric bent-core mesogens have been reported.<sup>7–14</sup> This is quite natural from the viewpoint of interlayer steric interaction. Namely,  $SmC_5P_A$  is the only structure that satisfies the condition that the terminal chains in adjacent layers are parallel to each other. An intentional attempt to suppress  $SmC_5P_A$  and to obtain the ferroelectric phase was made by Walba et al.<sup>15</sup> by introducing the same chiral terminal chain as that of a material (MHPOBC) showing the smectic  $C_A^*$  ( $SmC_A^*$ ), anticlinic organization of rodlike molecules.

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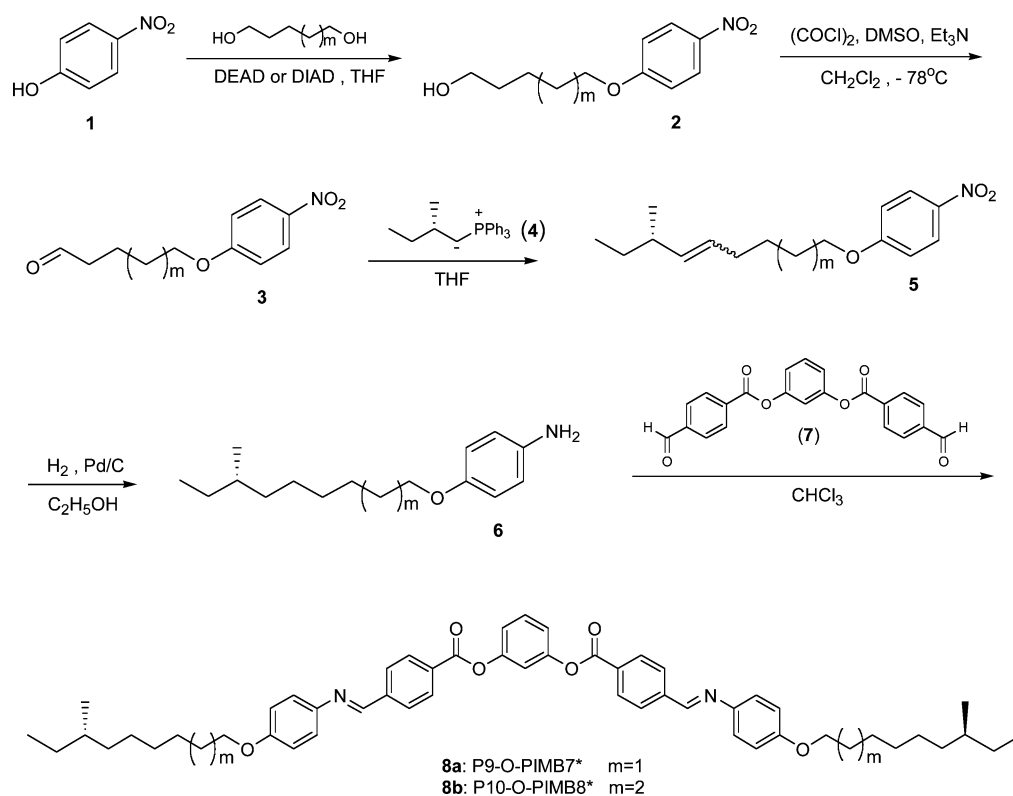
<sup>‡</sup> Department of Organic and Polymeric Materials, Tokyo Institute of Technology.

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(1) Niori, T.; Sekine, T.; Watanabe, J.; Furukawa, T.; Takezoe, H. *J. Mater. Chem.* **1996**, *6*, 1231–1233.  
(2) Pelzl, G.; Schroeder, M.; Dunemann, U.; Diele, S.; Weissflog, W.; Jones, C.; Coleman, D.; Clark, N.; Stannarius, R.; Li, J.; Das, B.; Grande, S. *J. Mater. Chem.* **2004**, *14*, 2492–2498.

(3) Nakata, M.; Link, D. R.; Thisayukta, J.; Takanishi, Y.; Ishikawa, K.; Watanabe, J.; Takezoe, H. *J. Mater. Chem.* **2001**, *11*, 2694–2699.  
(4) Niwano, H.; Nakata, M.; Thisayukta, J.; Link, D. R.; Takezoe, H.; Watanabe, J. *J. Am. Chem. Soc.* **2004**, *108*, 14889–14896.  
(5) Niori, T.; Yamamoto, J.; Yokoyama, H. *Mol. Cryst. Liq. Cryst.* **2004**, *411*, 1325–1333.  
(6) Thisayukta, J.; Niwano, H.; Takezoe, H.; Watanabe, J. *J. Am. Chem. Soc.* **2002**, *124*, 3354–3358.  
(7) Olson, D. A.; Veun, M.; Cady, A.; D’agostino, M. V.; Johnson, P. M.; Nguyen, H. T.; Chien, L. C.; Huang, C. C. *Phys. Rev. E* **2001**, *63*, 041702–1–5.  
(8) Keith, C.; Reddy, R. A.; Hahn, H.; Lang, H.; Tschierske, C. *Chem. Commun.* **2004**, 1898–1899.  
(9) Dantgraber, G.; Eremin, A.; Diele, S.; Hauser, A.; Kresse, H.; Pelzl, G.; Tschierske, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2408–2412.  
(10) Nadasi, H.; Weissflog, W.; Eremin, A.; Pelzl, G.; Diele, S.; Das, B.; Grande, S. *J. Mater. Chem.* **2002**, *12*, 1316–1324.  
(11) Bedel, J. P.; Rouillon, J. C.; Marcerou, J. P.; Laguerre, M.; Nguyen, H. T.; Achard, M. F. *Liq. Cryst.* **2000**, *27*, 103–113.  
(12) Bedel, J. P.; Rouillon, J. C.; Marcerou, J. P.; Laguerre, M.; Nguyen, H. T.; Achard, M. F. *Liq. Cryst.* **2001**, *28*, 1285–1292.  
(13) Reddy, R. A.; Sadashiva, B. K. *J. Mater. Chem.* **2002**, *12*, 2627–2632.  
(14) Reddy, R. A.; Schroeder, M. W.; Bodyagin, M.; Kresse, H.; Diele, S.; Pelzl, G.; Weissflog, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 774–778.  
(15) Walba, D. M.; Korblova, E.; Shao, R.; MacLennan, J. E.; Link, D. R.; Glaser, M. A.; Clark, N. A. *Science* **2000**, *288*, 2181–2184.

Scheme 1



Recently it was reported that the emergence of ferroelectricity and antiferroelectricity is dependent upon the number of carbons and the position of the chiral carbon along the terminal chains in the banana-shaped molecules 1,3-phenylene bis[4-(4-alkoxyphenyliminomethyl)]benzoates [ $P_n$ -O-PIMB( $n-2$ )\*] with chiral terminal alkoxy groups  $\text{CH}_3\text{CH}_2\text{C}^*\text{H}(\text{CH}_3)(\text{CH}_2)_x\text{O}$  ( $n = x + 3$ ), where  $n$  stands for the number of carbons in each end chain and ( $n-2$ )\* for the chiral position from the oxygen next to the core; namely, the third carbon from the chain end (methyl carbon) is always chiral.<sup>16–19</sup> P7-O-PIMB5\* exhibits a stable antiferroelectric phase, while P8-O-PIMB6\* shows a ferroelectric phase. Although P6-O-PIMB4\* has no mesogenic phase, inherent ferroelectric nature was proved by second harmonic generation (SHG) and texture observation using binary mixture with antiferroelectric P8-O-PIMB. The interlayer steric interaction between the chiral terminal groups was suggested to be the most important factor for the emergence of particular phase structures.

To understand the reason  $P_n$ -O-PIMB( $n-2$ )\*, where  $n$  is even, exhibits ferroelectric  $\text{SmC}_A\text{P}_F^*$  and to generalize this odd–even behavior findings further, bent-core mesogens had to be systematically synthesized. Two more mesogens  $P_n$ -O-PIMB( $n-2$ )\* ( $n = 9$  and 10) and some of their oxygen analogues were prepared to confirm the odd–even effect for the appearance of ferroelectricity in these homologues.

A number of oxygen analogues of  $P_n$ -O-PIMB( $n-2$ )\* were also prepared, assuming that the overall conformation of the molecules is hardly affected by replacing one methylene unit with an oxygen. It was reported that the valency of the angle, preferred conformation, torsional barriers, and all other conformational consequences are strikingly retained when a methylene group in a molecule was replaced with an ethereal oxygen.<sup>20</sup> Thus we replaced one methylene unit in the terminal chain of  $P_n$ -O-PIMB( $n-2$ )\* with an oxygen atom and synthesized mesogens of  $P_n$ -O-PIMB( $n-2$ )\*-( $n-4$ )O ( $n = 8, 9$ , and 10) bearing a  $\omega$ -[(*S*)-amyloxy]alkoxy terminal  $\text{CH}_3\text{-CH}_2\text{C}^*\text{H}(\text{CH}_3)\text{CH}_2\text{O}(\text{CH}_2)_y\text{O}$  group ( $n = y + 5$ ), where ( $n-4$ )O stands for the position of O in the end chains from O next to the core; namely, the fourth carbon from the chain end (methyl carbon) is always replaced by O.

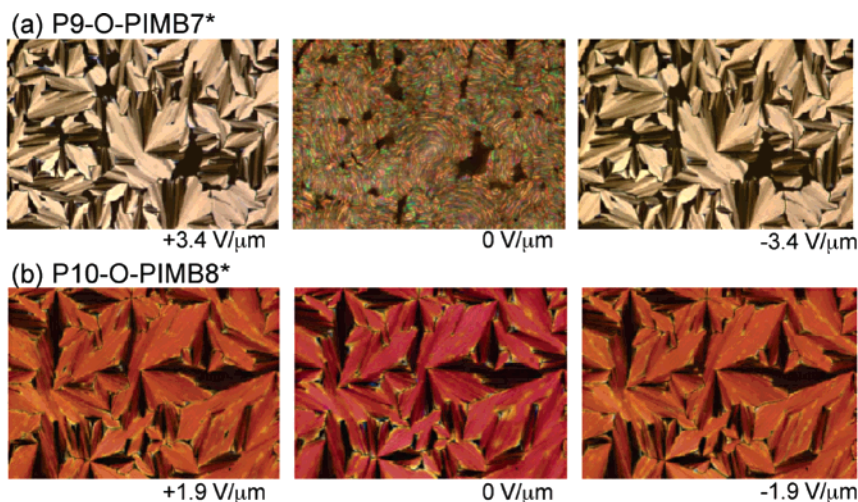
## 2. Results and Discussion

### 2.1. Synthesis.

Since (*S*)-7-methyl-1-nonanol and (*S*)-8-methyl-1-decanol are not commercially available, P9-O-PIMB7\* (**8a**) and P10-O-PIMB8\* (**8b**) were synthesized from the combination of an aldehyde **3** and (*S*)-1-bromo-2-methylbutane as shown in Scheme 1. Aldehyde **3** was prepared from 4-nitrophenol and diol in 2 steps using the Mitsunobu reaction and the Swern oxidation. (*S*)-1-Bromo-2-methylbutane was converted to the phosphonium salt by heating with triphenylphosphine (3 days at 130°C in a sealed tube). Wittig reaction of **3** with the phosphorus ylide **4** generated in situ from the phosphonium salt, and butyllithium provided **5**, which was reduced to aniline **6** by catalytic hydrogenation. The anilines were reacted with bisaldehyde **7** to produce chiral banana-shaped liquid crystals **8**.

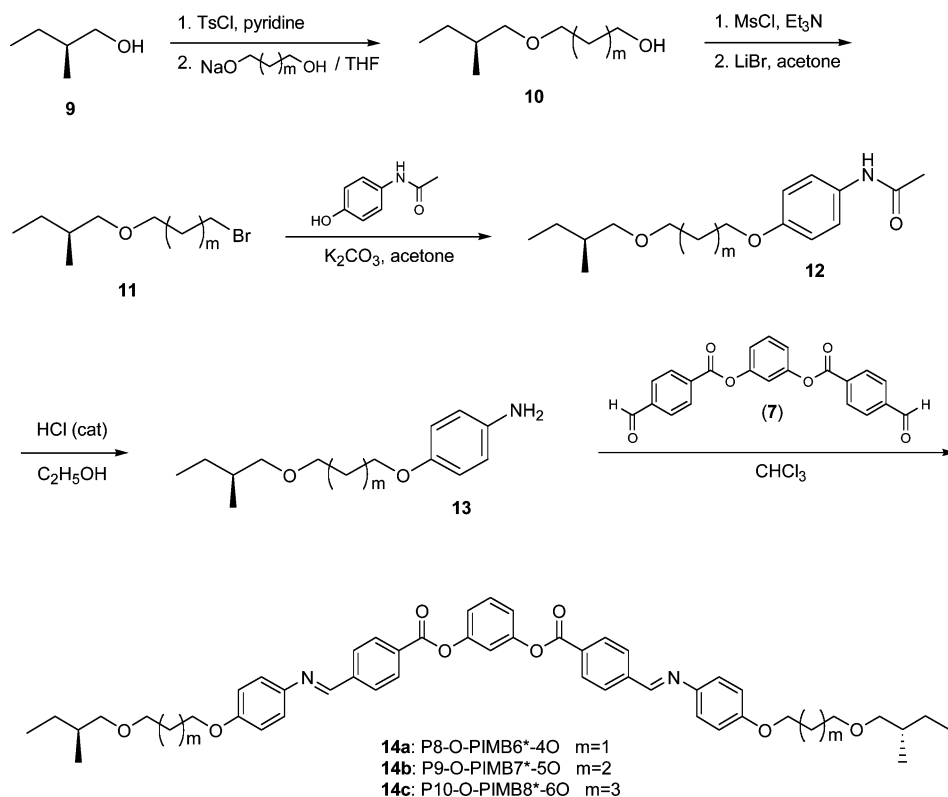
- (16) Gorecka, E.; Pocięcha, D.; Araoka, F.; Link, D. R.; Nakata, M.; Thisayukta, J.; Takanishi, Y.; Ishikawa, K.; Watanabe, J.; Takezoe, H. *Phys. Rev. E* **2000**, *62*, R4524–R4527.
- (17) Nakata, M.; Link, D. R.; Araoka, F.; Thisayukta, J.; Takanishi, Y.; Ishikawa, K.; Watanabe, J.; Takezoe, H. *Liq. Cryst.* **2001**, *28*, 1301–1308.
- (18) Kumazawa, K.; Nakata, M.; Araoka, F.; Takanishi, Y.; Ishikawa, K.; Watanabe, J.; Takezoe, H. *J. Mater. Chem.* **2004**, *14*, 157–164.
- (19) Araoka, F.; Thisayukta, J.; Ishikawa, K.; Watanabe, J.; Takezoe, H. *Phys. Rev. E* **2002**, *66*, 21705–1–5.

- (20) Dale, J. *Tetrahedron* **1974**, *30*, 1683–1694.



**Figure 1.** Photomicrographs showing the switching behavior in the B2 phase under the application of an electric field. (a) 2.7- $\mu\text{m}$ -thick cell of P9-O-PIMB7\* at 145 °C.  $\text{SmC}_8\text{P}_A^*$  ( $E = 0 \text{ V } \mu\text{m}^{-1}$ ) switches to  $\text{SmC}_A\text{P}_F^*$  under  $E = \pm 3.4 \text{ V } \mu\text{m}^{-1}$ . (b) 5.5- $\mu\text{m}$ -thick cell of P10-O-PIMB8\* at 135 °C.  $\text{SmC}_A\text{P}_F^*$  ( $E = 0 \text{ V } \mu\text{m}^{-1}$ ) switches to  $\text{SmC}_A\text{P}_F^*$  under the application of an electric field  $E = \pm 1.9 \text{ V } \mu\text{m}^{-1}$ .

### Scheme 2



Oxygen-replaced chiral banana-shaped liquid crystals **14** were synthesized in a different sequence of reactions. The tosylates of (*S*)-2-methyl-1-butanol **9** were allowed to react with monosodium alkoxides of diol. Thus prepared  $\omega$ -amyoxy-1-alkanols **10** were transformed to  $\text{P}_n\text{-O-PIMB}(n-2)^*-(n-4)\text{O}$  homologues **14** as shown in Scheme 2.

**2.2. Phase Structures of  $\text{P}_n\text{-O-PIMB}(n-2)^*$  Homologues.** The bent-core mesogen **8a** (P9-O-PIMB7\*) enantiotropically showed the B2 phase [Iso (164 °C) B2 (118 °C) Cryst, on cooling; Cryst (123 °C) B2 (167 °C) Iso, on heating]. On cooling from the isotropic phase to the B2 phase, randomly oriented domains appeared. By application of an electric field, however, fan-shaped domains were changed to smooth domains.

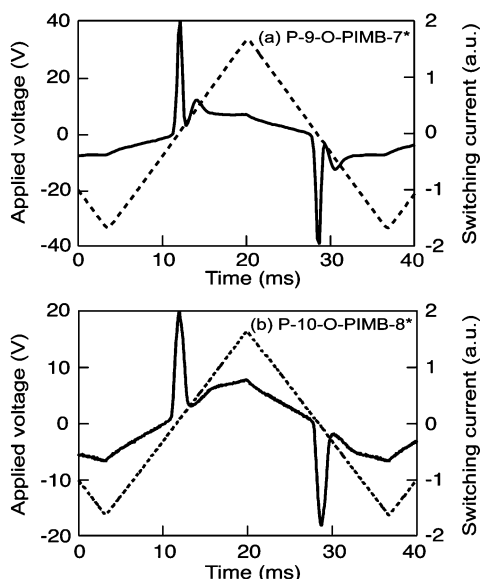
The photomicrographs shown in Figure 1a display the switching behavior by applying a rectangular-wave field. The texture in the absence of a field suggests the typical B2 phase observed in the standard bent-core mesogens,<sup>21,22</sup> and the texture change shown in Figure 1a is attributed to the electro-optic switching between  $\text{SmC}_8\text{P}_A^*$  and  $\text{SmC}_A\text{P}_F^*$  in the racemic state. Hence the ground state is antiferroelectric ( $\text{SmC}_8\text{P}_A^*$ ).

The compound **8b** (P10-O-PIMB8\*) enantiotropically exhibited the B2 phase [Iso (163 °C) B2 (124 °C) Cryst, on

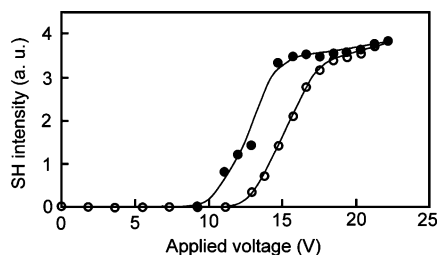
(21) Zennoji, M.; Takanishi, Y.; Ishikawa, K.; Thisayukta, J.; Wstanabe, J.; Takezoe, H. *J. Mater. Chem.* **1999**, *9*, 2775–2778.

(22) Zennoji, M.; Takanishi, Y.; Ishikawa, K.; Thisayukta, J.; Wstanabe, J.; Takezoe, H. *Jpn. J. Appl. Phys.* **2000**, *39*, 3536–3541.





**Figure 2.** The polarization reversal current in the B2 phase by applying a triangular-wave voltage of 30 Hz. (a) P9-O-PIMB7\* at 145 °C by applying a 66-V<sub>pp</sub> triangular-wave voltage. (b) P10-O-PIMB8\* at 135 °C by applying a 32-V<sub>pp</sub> triangular-wave voltage.

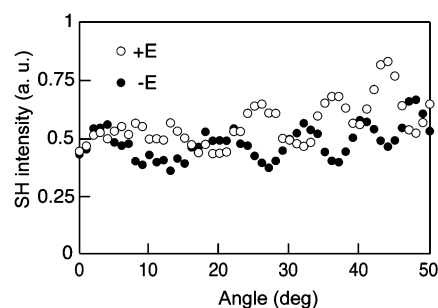


**Figure 3.** Applied voltage dependence of the SH intensity in a 7.6- $\mu\text{m}$ -thick cell of P9-O-PIMB7\*. Hysteresis behavior is seen in the field-induced antiferroelectric-ferroelectric transition.

cooling; Cryst (130 °C) B2 (166 °C) Iso, on heating], but this material showed different electro-optical switching behavior, as shown in Figure 1b. In these photomicrographs, we observed orange domains with an extinction direction parallel to the layer normal under an electric field ( $E > E_{\text{th}}$ ), but texture remained unchanged except for a slight birefringence color change after terminating the electric field. This feature indicates a bistable switching between two  $\text{SmC}_A\text{P}_F^*$  states.<sup>17</sup>

The switching current measurements were conducted in **8a** (P9-O-PIMB7\*) and **8b** (P10-O-PIMB8\*) by applying a triangular-wave electric field. The mesogens **8a** and **8b** revealed double and single switching current peaks in a half cycle, as shown in Figure 2, being consistent to the antiferroelectric and ferroelectric phases, respectively.

The structure assignment mentioned above was confirmed by SHG under an electric field along the substrate normal. Figure 3 shows the electric field dependence of the SH intensity at 45° incidence of light in a 7.6- $\mu\text{m}$ -thick cell of P9-O-PIMB7\*. In the absence of a field, no SHG is observed. The SHG signal shows a sharp onset at about 11 V and saturates at about 19 V. With a decrease in the field, the system becomes SHG inactive, and hysteresis behavior is observed. This result clearly indicates that the stable state of this material is antiferroelectric, and a field-induced antiferroelectric-ferroelectric phase transition occurs. On the contrary, P10-O-PIMB8\* was SHG active even in the absence of a field, indicating the ferroelectric nature. As



**Figure 4.** SHG interferograms after the application of either positive (+250 V/mm) or negative (−250 V/mm) voltage along the cell surface in a 5.6- $\mu\text{m}$ -thick cell of P10-O-PIMB8\* at 148 °C in the absence of a field.

**Table 1.** Polar Structures of the B2 Phase in  $P_n\text{-O-PIMB}(n-2)^*$  Homologues<sup>a</sup>

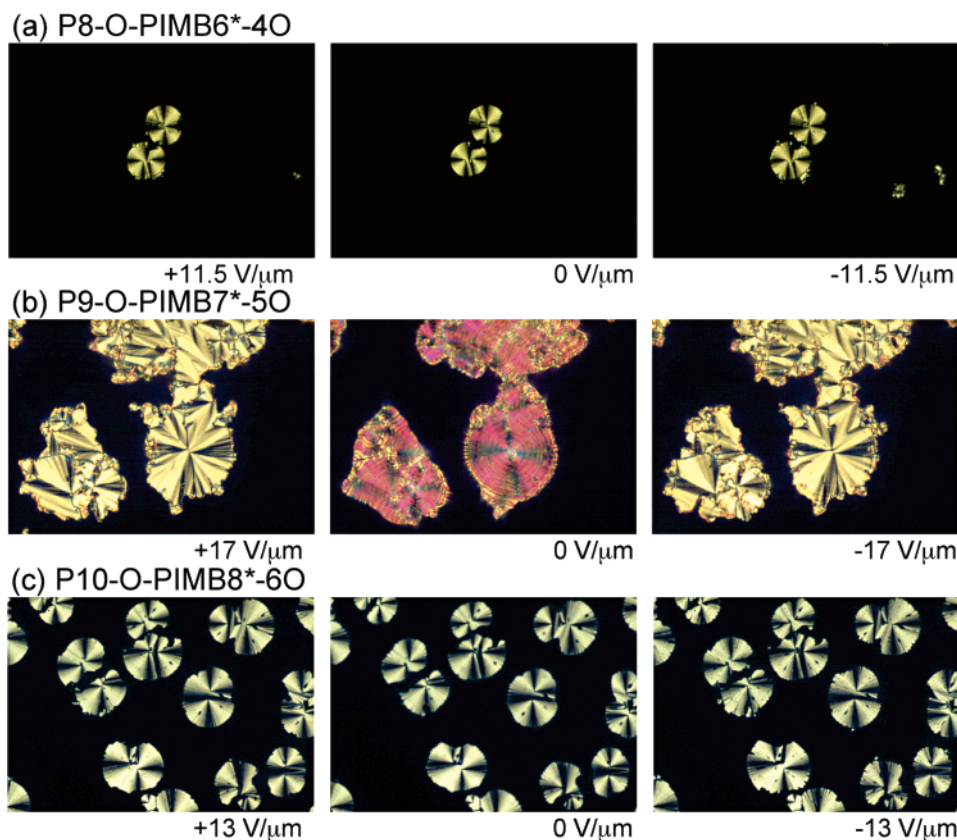
mesogen	( $n-2$ )	polar order	polar structure
P6-O-PIMB4*	4	(ferroelectric)	( $\text{SmC}_A\text{P}_F^*$ )
P7-O-PIMB5*	5	antiferroelectric	$\text{SmC}_S\text{P}_A^*$
P8-O-PIMB6*	6	ferroelectric	$\text{SmC}_A\text{P}_F^*$
<b>8a</b> P9-O-PIMB7*	7	antiferroelectric	$\text{SmC}_S\text{P}_A^*$
<b>8b</b> P10-O-PIMB8*	8	ferroelectric	$\text{SmC}_A\text{P}_F^*$

<sup>a</sup> The previous results in  $P_n\text{-O-PIMB}(n-2)^*$  ( $n = 6-8$ )<sup>18</sup> are also included in the table. Parentheses mean the inherent properties in the non-mesogenic P6-O-PIMB4\*.

reported already in our previous paper,<sup>17</sup> well-aligned cells were prepared by applying an in-plane electric field. Interferograms of the SHG signal were observed at normal incidence at  $V = 0$  V after the application of positive (+250 V/mm) and negative (−250 V/mm) in-plane voltages. The results are shown in Figure 4. The  $\pi$  phase difference indicates a reversal in the direction of the polarization in the cell and the bistable ferroelectric states.

The polar structures of the newly synthesized **8a** (P9-O-PIMB7\*) and **8b** (P10-O-PIMB8\*) are summarized in Table 1 along with previous results. Table 1 clearly shows that the ferroelectric phase is brought about from  $P_n\text{-O-PIMB}(n-2)^*$ , where  $n$  is even. The position of the chiral center ( $n-2$ ) from the phenoxy oxygen in the terminal group is also even. In contrast,  $P_n\text{-O-PIMB}(n-2)^*$ , where  $n$  is odd, exhibits the antiferroelectric phase.

**2.3. Phase Structures of  $P_n\text{-O-PIMB}(n-2)^*-(n-4)\text{O}$  Homologues.** The compound **14a** (P8-O-PIMB6\*−4O) enantiotropically showed the B2 phase [Iso (120.3 °C) B2 (119.6 °C) Cryst, on cooling; Cryst (122 °C) B2 (130 °C) Iso, on heating]. On cooling from the isotropic phase to the B2 phase, circular domains were formed, as shown in Figure 5a. The photomicrographs were taken at 119.9 °C in the absence and presence of an electric field. The texture suggests  $\text{SmC}_A\text{P}_F^*$ . The mesogen **14b** (P9-O-PIMB7\*−5O) enantiotropically showed the B2 phase [Iso (138.3 °C) B2 (111.2 °C) Cryst, on cooling; Cryst (117 °C) B2 (145 °C) Iso, on heating]. The photomicrographs shown in Figure 5b display the switching behavior by applying a rectangular-wave field. In the presence of  $E > E_{\text{th}}$ , yellow domains with an extinction direction parallel to the layer normal were observed, whereas red-stripe domains were observed in the absence of an electric field. This is a field-induced change from the racemic  $\text{SmC}_S\text{P}_A^*$  to the  $\text{SmC}_A\text{P}_F^*$  state. Hence the ground state in this material is antiferroelectric. The bent-core mesogen **14c** (P10-O-PIMB8\*−6O) enantiotropically exhibited the B2 phase [Iso (128.3 °C) B2 (110.8 °C) Cryst, on cooling; Cryst (120 °C) B2 (134 °C) Iso, on heating]. The photomicrographs shown in Figure 5c are similar to those



**Figure 5.** Photomicrographs of the switching behavior in the B2 phase under the application of an electric field. (a) 2.6- $\mu\text{m}$ -thick cell of P8–O–PIMB6\*–4O at 119.9 °C; (b) 2.9- $\mu\text{m}$ -thick cell of P9–O–PIMB7\*–5O at 126.4°C; (c) 3.0- $\mu\text{m}$ -thick cell of P10–O–PIMB8\*–6O at 110.0 °C.

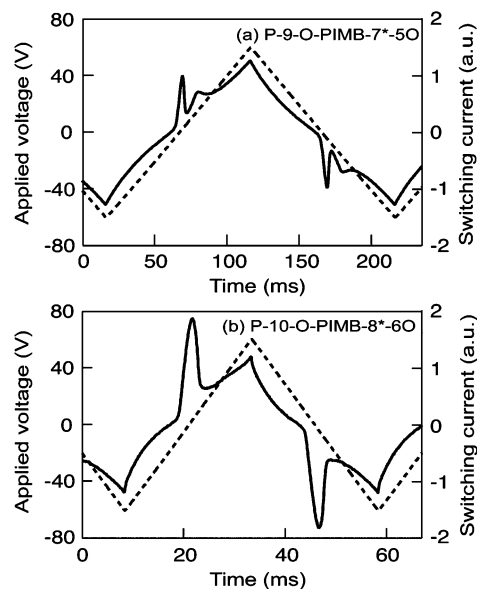
of P8–O–PIMB6\*–4O, indicating a bistable switching between two  $\text{SmC}_{\text{AF}}^*$  states with opposite polarizations and racemic layer structures.

The polarization reversal current behaviors could not be observed in P8–O–PIMB6\*–4O because of a very narrow liquid crystal temperature range. P9–O–PIMB7\*–5O and P10–O–PIMB8\*–6O showed double and single switching current peaks by applying a triangular wave electric field, as shown in parts a and b of Figure 6. The behaviors are similar to those in P9–O–PIMB7\* and P10–O–PIMB8\*, confirming antiferroelectric and ferroelectric behavior, respectively.

To convincingly demonstrate the polar order of these compounds, we carried out SHG measurements as a function of temperature without applying an electric field. Despite a narrow temperature range of P8–O–PIMB6\*–4O, we confirmed the SHG activity, as shown in Figure 7. No SHG was observed in P9–O–PIMB7\*–5O. Thus, we can conclude that P9–O–PIMB7\*–5O is antiferroelectric. In P10–O–PIMB8\*–6O, on the other hand, an onset of SH intensity was observed at the Iso-B2 phase transition and the SH intensity increases with decreasing temperature, as shown in Figure 7. Hence the stable state of P10–O–PIMB8\*–6O has ferroelectric nature just like P10–O–PIMB8\*.

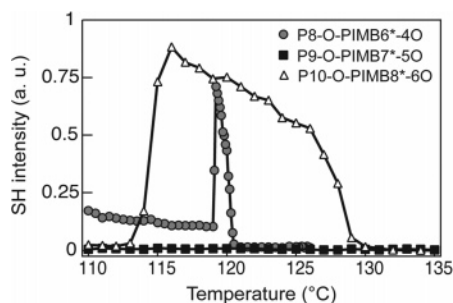
As summarized in Table 2, odd–even behavior of ferroelectricity and antiferroelectricity in a  $P_n\text{--O--PIMB}(n-2)^*-(n-4)\text{O}$  homologous series is also observed.

**2.4. Role of the Terminal Chains for the Emergence of Phase Structure.** On the basis of the observed polar structure of the B2 phase in a series of  $P_n\text{--O--PIMB}(n-2)^*$  ( $n = 9$  and 10) and their oxygen analogues  $P_n\text{--O--PIMB}(n-2)^*-(n-4)\text{O}$  ( $n = 8, 9,$  and 10) combined with the previously reported results on the  $P_n\text{--O--PIMB}(n-2)^*$  ( $n = 6, 7,$  and 8), it becomes clear that the emergence of particular polar order of the SmCP phase depends on the length and the position of the chiral carbon in the terminal chains. Namely, the ferroelectric and antiferroelectric phases emerge in case the number of carbons including an oxygen atom in the terminal chains is even and odd, respectively. As the other part of mesogens remaining



**Figure 6.** The polarizing reversal current in the B2 phase under the application of a triangular-wave voltage. (a) P9–O–PIMB7\*–5O at 115 °C, 120  $\text{V}_{\text{pp}}$ , and 5 Hz. (b) P10–O–PIMB8\*–6O at 110.0 °C, 120  $\text{V}_{\text{pp}}$ , and 20 Hz.

$(n-4)\text{O}$  ( $n = 8, 9,$  and 10) combined with the previously reported results on the  $P_n\text{--O--PIMB}(n-2)^*$  ( $n = 6, 7,$  and 8), it becomes clear that the emergence of particular polar order of the SmCP phase depends on the length and the position of the chiral carbon in the terminal chains. Namely, the ferroelectric and antiferroelectric phases emerge in case the number of carbons including an oxygen atom in the terminal chains is even and odd, respectively. As the other part of mesogens remaining



**Figure 7.** Temperature dependence of the SH intensity in  $P_n\text{-O-PIMB}(n-2)^*-(n-4)\text{O}$  ( $n = 8, 9,$  and  $10$ ).

**Table 2.** Polar Structures of the B2 Phase in  $P_n\text{-O-PIMB}(n-2)^*-(n-4)\text{O}$  Homologues

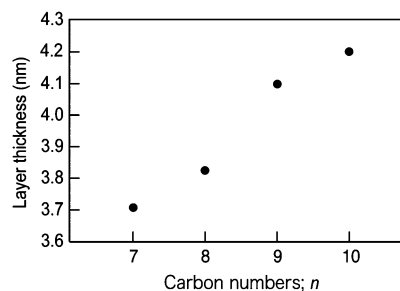
mesogen	$(n-2)$	polar order	polar structure
<b>14a</b> P8-O-PIMB6*-4O	6	ferroelectric	$\text{SmC}_A\text{P}_F^*$
<b>14b</b> P9-O-PIMB7*-5O	7	antiferroelectric	$\text{SmC}_S\text{P}_A^*$
<b>14c</b> P10-O-PIMB8*-6O	8	ferroelectric	$\text{SmC}_A\text{P}_F^*$

unchanged, it is obvious that such as odd–even behavior must be caused by the structure of terminal chains. Both simple alkyl terminal chains and their oxygen analogues, which have fairly polar etheral bonds, bring about the same odd–even phenomenon. It is reasonable to say that what causes overall arrangement of the polar order is not the polar dipole–dipole interaction but the interlayer steric interaction between the terminal alkyl or alkoxy chains of mesogens. The steric demands of the alkyl chain and their oxy analogues are supposed to be nearly identical because bond lengths, bond angles, and conformations along C–C–C and C–O–C bonds are approximately same.<sup>20</sup>

As mentioned in introduction,  $P_n\text{-O-PIMB}$  having achiral straight alkyl chains exhibits the antiferroelectric phase.<sup>3</sup> The antiferroelectric  $\text{SmC}_S\text{P}_A$  phase is the only structure where terminal chains in adjacent layers are parallel to each other, providing stabilization by an excluded volume effect. In contrast, the situation is not the case in  $\text{SmC}_S\text{P}_F$ , because the terminal chains of bent-core molecules in adjacent layers are not parallel despite synclinc order. Thus, it is rather surprising that the otherwise most stable antiferroelectric  $\text{SmC}_S\text{P}_A^*$  state is destabilized and the ferroelectric  $\text{SmC}_A\text{P}_F^*$  states is stabilized only by changing the terminal chain lengths. Why  $P_n\text{-O-PIMB}(n-2)^*$  and  $P_n\text{-O-PIMB}(n-2)^*-(n-4)\text{O}$  have an ability to show the ferroelectric  $\text{SmC}_A\text{P}_F^*$  states only when  $n$  is even? To be ferroelectric, the terminal chains in adjacent layers are not parallel in the polar plane. Therefore, a certain type of stabilizing interlayer interaction other than parallel arrangement of the linear alkyl chains has to exist.

The interlayer distances of the smectic phase in the series of  $P_n\text{-O-PIMB}(n-2)^*$  were determined in order to get some insight into the interdigitation of the terminal end between the adjacent layers. The measurement was carried out at a temperature 5 °C below the isotropic–SmCP phase transition. Unfortunately, the interlayer distance of P6–O–PIMB4\* was not determined because it does not exhibit the liquid crystalline mesophase.

As shown in Figure 8, the layer spacing increases as the length of the terminal alkyl chain increases. As the number of carbons ( $n$ ) in the terminal groups increases from 7 to 8 and from 9 to 10, 1.17 and 1.03 Å increments were observed, respectively, which are much smaller than half of the increment of 2.73 Å



**Figure 8.** Layer spacing for the  $\text{SmCP}^*$  phases of  $P_n\text{-O-PIMB}(n-2)^*$  ( $n = 7\text{--}10$ ).

shown by going from  $n = 8\text{--}9$ . Thus, considerably higher increment of interlayer spacing was observed from going even to odd number of the carbons (from 8 to 9) compared with that observed from going odd to even number of carbons in the terminal chains. If the layer spacing is largely dependent on the interdigitation of the terminal groups, the increment of layer spacing in going from synclinc antiferroelectric to anticlinic ferroelectric structure should be larger than that of layer spacing in the reverse case. This is not in agreement with the experimental observation. The degree of layer spacing increment in going from antiferroelectric to ferroelectric, that is, from the number of carbons in the terminal chains of 7–8 ( $\text{P7-O-PIMB5}^* \rightarrow \text{P8-O-PIMB6}^*$ ) and 9–10 ( $\text{P9-O-PIMB7}^* \rightarrow \text{P10-O-PIMB8}^*$ ) is smaller than that observed for ferroelectric to antiferroelectric change (the number of carbons 8–9,  $\text{P8-O-PIMB6}^* \rightarrow \text{P9-O-PIMB7}^*$ ). Therefore the odd–even behavior in the interlayer spacing increment does not necessarily reflect the degree of interdigitation of the terminal groups. Actually, similar odd–even behavior in the interlayer spacing increment was reported in calamitic molecules which show the odd–even behavior in the emergence of synclinc ferroelectric and anticlinic antiferroelectric phases.<sup>23</sup> The degree of tilting and the direction of the terminal methyl group can also be another factor governing the interlayer spacing. In addition to ref 23, the odd–even behavior in the emergence of synclinc and anticlinic phases has been observed in calamitic molecules.<sup>24,25</sup> It is noted, however, that the bent core provides complexity that does not appear in calamitic molecules. Namely, the interdigitation of the terminal groups can be discussed only in the tilt plane in calamitic molecules, whereas it must be considered not only in the tilt plane but also in the plane parallel to the polarization (polarization plane). Actually, only the  $\text{SmC}_S\text{P}_A$  structure gives parallel terminal groups in adjacent layers both in the tilt and polarization planes, and  $\text{SmC}_S\text{P}_F$  and  $\text{SmC}_A\text{P}_A$  gives parallel terminal groups only in the tilt and polarization planes, respectively.<sup>18</sup>

To get better insight into the ground-state conformation of multistacked molecules, systematic conformer searches were performed for the two-stacked molecules with the Spartan'02 program.<sup>26</sup> Optimized geometries of all conformers were obtained by using the MMFF method. The stacking mode of two molecules of P9–O–PIMB7\* and P10–O–PIMB8\* were drawn in Figure 9. In the present homologues, the chiral carbon locates close to the end of the terminal chains and always at

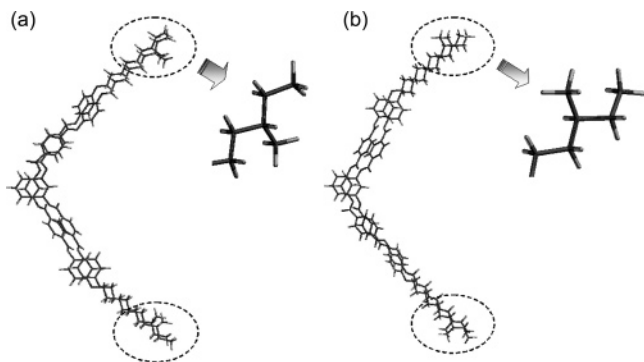
(23) Ikeda, A.; Takanishi, Y.; Takezoe, H.; Fukuda, A. *Jpn. J. Appl. Phys.* **1993**, *32*, L97–L100.

(24) Goodby, J. W.; Patel, J. S.; Chin, E. *J. Mater. Chem.* **1992**, *2*, 197–207.

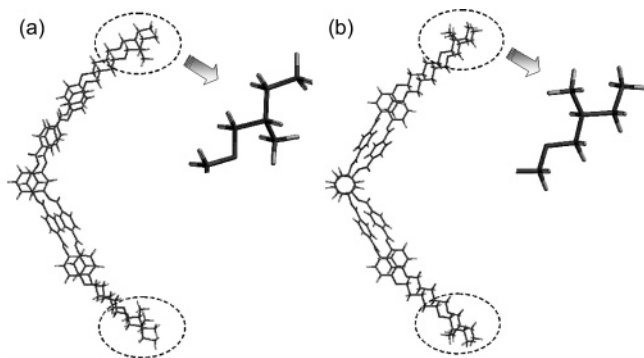
(25) Thisayukta, J.; Samulski, E. T. *J. Mater. Chem.* **2004**, *14*, 1554–1559.

(26) Kong, J. et al. *J. Comput. Chem.* **2000**, *21*, 1532–1548.





**Figure 9.** Optimized modeling of the conformers (a) P9–O–PIMB7\* and (b) P10–O–PIMB8\*.



**Figure 10.** Optimized modeling of the conformers (a) P9–O–PIMB7\*–5O and (b) P10–O–PIMB8\*–6O.

the same position from the ends. Hence, the directions of methyl groups connected to the chiral centers must be a key factor to determine the phase structures. In their most stable conformations, the two methyl groups are oriented inward and outward in the stacking plane of molecules in P9–O–PIMB7\* (Figure 9a) and P10–O–PIMB8\* (Figure 9b), respectively. Each conformation near the chiral center of molecules was shown in circles. The orientation of the methyl group (inward and outward) repeats alternatively, as the chain length (number of carbon) of the terminal alkyl group varies from odd to even and even to odd. The same phenomenon was observed in the oxygen analogues P9–O–PIMB7\*–5O and P10–O–PIMB8\*–6O (Figure 10). That is, the chain length (number of carbons plus an oxygen) is odd; two methyl groups connected to the chiral centers are oriented inward. Likewise when it is even, they are oriented outward. This difference in the conformational

arrangement in the vicinity of the chiral centers with odd–even alkyl chain is believed to result in the difference in the interlayer steric interaction, which in turn results in the odd–even behavior for the emergence of ferroelectricity and antiferroelectricity of the present bent-core liquid crystals.

In our previous paper,<sup>27</sup> we reported that all the B2 phases in a homologue with chiral 3-(alkoxy)propoxy terminal groups (P*n*–O–PIMB5\*–4O, *n* = 7, 8, 9, and 10) show the antiferroelectric SmC<sub>5</sub>P<sub>A</sub>\* state. In this homologue, the position of the chiral center is fixed at the 5 position from the phenoxy oxygen in the terminal group. As shown in Figures 9 and 10, the antiferroelectricity is well expected when the chiral carbon is at the odd position. The elongation in chain length outside the chiral center does not affect on the phase behavior of the homologue.

### 3. Conclusion

The phase behavior of two homologues, P*n*–O–PIMB(*n* – 2)\* and oxygen analogues P*n*–O–PIMB(*n* – 2)\*–(*n* – 4) O\*, has been studied by means of texture observation, switching current, and SHG measurements. It was found that emergence of ferroelectricity and antiferroelectricity is determined by the position (odd or even) of the chiral center from the chain end (methyl carbon) without any exceptions. The compounds of the two homologues show ferroelectric and antiferroelectric when *n* is even and odd, respectively. For the emergence of either of the polar orders, a possible role played by the interlayer steric interaction, particularly by the directions of methyl groups connected to the chiral centers, was discussed.

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**Supporting Information Available:** Experimental procedures for the synthesis of the bent-core mesogens and the intermediates, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, and the electro-optic measurements and the complete citation for ref 26. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(27) Lee, S. K.; Park, C. W.; Lee, J. G.; Kang, K.-T.; Nishida, K.; Shimbo, Y.; Takamishi, Y.; Takezoe, H. *Liq. Cryst.*, submitted.