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# Synthesis, Characterization, and Electro-Optic Properties of Novel Bent-Core Mesogens Based on Cinnamoyloxy Derivatives

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*The new series of bent-core molecules based on a 3,4'-biphenyldiol central core has been synthesized. The influence of the central core as well as that of a fluorine and chlorine substituent on the diphenyl rings in the bent-core compound has also been examined. A few novel series of bent-core compounds containing cinnamoyloxy or  $\alpha$ -methylcinnamoyloxy groups in the side arms have been synthesized, and the mesophases exhibited by them have been compared. The mesophases under discussion were investigated by means of polarizing microscopy, differential scanning calorimetry, X-ray diffraction, as well as electro-optical experiments. The influence of the molecular structure on the occurrence of the SmCP phase was investigated. Finally, the electro-optical properties of the SmCP phase, such as voltage-transmittance effect, tilt angle, dielectric permittivity, and switching behavior, were also measured. As a consequence, the correlation between their electro-optical properties and chemical structures of these compounds is investigated.*

**Keywords** Bent-core mesogens; cinnamoyloxy; dielectric permittivity; tilt angle; voltage-transmittanceeffect

## Introduction

The chiral mesophases could be obtained by using achiral molecules with a bent core since the proposal by Watanabe et al. [1–9]. The type of liquid crystal has attracted a great deal of attention. The different liquid crystal-phases, generally denoted as B-type mesophases, have already been described and reviewed in the literature [10–13]. Together with the B<sub>1</sub> mesophase, which is characterized by a columnar disposition of the molecules, the B<sub>2</sub> arrangement, also called the SmCP (smectic C polar) mesophase, is the most commonly observed for bent-shaped molecules. It has been stated that this mesophase can exhibit either ferroelectric or antiferroelectric properties. The design and synthesis of novel achiral bent-shaped mesogens forming ferroelectric

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and/or antiferro-electric smectic or columnar mesophases is one of the most exciting research activities in the area of thermotropic liquid crystals. Bent-shaped mesogens broadly require two units: (i) a central unit, which provides the bending angle, and (ii) two rod-like units with a terminal aliphatic chain that could be attached to the central unit. In general, the relationship between molecular structure and the mesomorphic behavior involves different aspects; for example, the position and magnitude of the bending angle, the number of phenyl rings present in the bent-core, the type and influence of lateral substituent [14–16], the nature and orientation of linking groups, and length of the terminal chains. In this article, two new series of symmetrical bent-shaped mesogens have been synthesized and their mesomorphic properties studied. We examine some novel series of bent-core compounds containing 3, 4'-positions of a diphenol ring as the central unit with the side wings containing a cinnamoyloxy or an  $\alpha$ -methylcinnamoyloxy group. We investigate the relation between the structure and the mesomorphic properties. In addition, we add the halogen (F and Cl) in the 3'-position of the diphenol and research the affect in the mesomorphic properties. The electro-optical properties of the SmCP phase is also measured. As a consequence, the correlation between their electro-optical properties and chemical structures of these compounds is investigated.

## Experimental

### *Characterization Techniques*

$^1\text{H}$  nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance-500 spectrometer (National Taiwan University of Science and Technology (Taiwan)) (500 MHz), using  $\text{CDCl}_3$  as solvents. Elemental analyses for C and H were performed on a Heraeus Vario EL-III elemental analyzer. The optical textures of mesophases were characterized by polarizing optical microscopy (POM; model Olympus BH5 (National Taiwan University of Science and Technology (Taiwan))) equipped with a hot stage (Mettler Toledo FP82HT (National Taiwan University of Science and Technology (Taiwan))) and a programmable temperature controller (Mettler Toledo FP90 central processor (National Taiwan University of Science and Technology (Taiwan))). Temperatures and enthalpies of transitions were determined by differential scanning calorimetry (DSC; model Perkin Elmer Diamond (National Taiwan University of Science and Technology (Taiwan))). Powder samples of ca. 3.0 mg were examined at heating and cooling rates of  $5^\circ\text{C min}^{-1}$  under a nitrogen atmosphere.

Synchrotron powder X-ray diffraction (XRD) measurements were performed in transmission geometry with synchrotron radiation at beamline BL17A of the National Synchrotron Radiation Research Center (NSRRC), Taiwan, where the X-ray wavelength was 1.33366 Å. The XRD data were collected using a Mar345 image plate detector mounted orthogonal to the beam with sample-to-detector distance of 280 mm. The diffraction signals were accumulated for 10 s. The powder samples were packed into a capillary tube and heated by a heat gun, where the temperature controller is programmable by a PC with a proportional-integral-derivative (PID) feedback system. The scattering angle theta was calibrated by a mixture of silver behenate and silicon. For the 2D XRD patterns, the surface-aligned samples of the mesophases were obtained by very slow cooling ( $1^\circ\text{C min}^{-1}$ ) of a small droplet of the compound from the isotropic melt on a glass plate treated with commercially available homeotropic agent.

Electro-optical investigations were carried out using commercially available liquid crystal cells with indium tin oxide (ITO) electrodes coated with antiparallel rubbed polyimide (from Mesostate Corp. (Taiwan), cell gap = 7.5  $\mu\text{m}$  for active area = 1  $\text{cm}^2$ ). The sample was filled into the cell in the isotropic phase. A digital oscilloscope (Yokogawa Electric, DL1640, Taiwan) was used in these measurements, and a high-power amplifier was connected to an arbitrary function generator (Tektronix AWG2005). For the switching polarization experiment was measured by using triangular waveform voltage method under slowly cooling from the isotropic phase. The optical transmission experiments were probed by monochromatic light using an He-Ne laser beam (632.8 nm). The cell was placed between crossed polarizers and its orientation was adjusted to obtain the minimum transmission of light (detected by a photodiode) without any electric field. The photodiode detector was set at about 20 cm away from the cell sample and the incident laser beam was normal to the cell. A digital oscilloscope was used in these measurements, and a high-power amplifier was connected to a function generator and a dc power supply was utilized in the dc field experiments. During electro-optical measurements, the modulations of textures by applying electric fields were observed using a polarizing optical microscope. Finally, we also measured the complex dielectric permittivity (detected by HP4192A) in the frequency range  $10^2$ – $10^7$  Hz for the planar-aligned (measuring field is normal to the director) sample on cooling at a rate of about  $1^\circ\text{C min}^{-1}$ , keeping the temperature of the sample stable during frequency sweeps.

### Materials

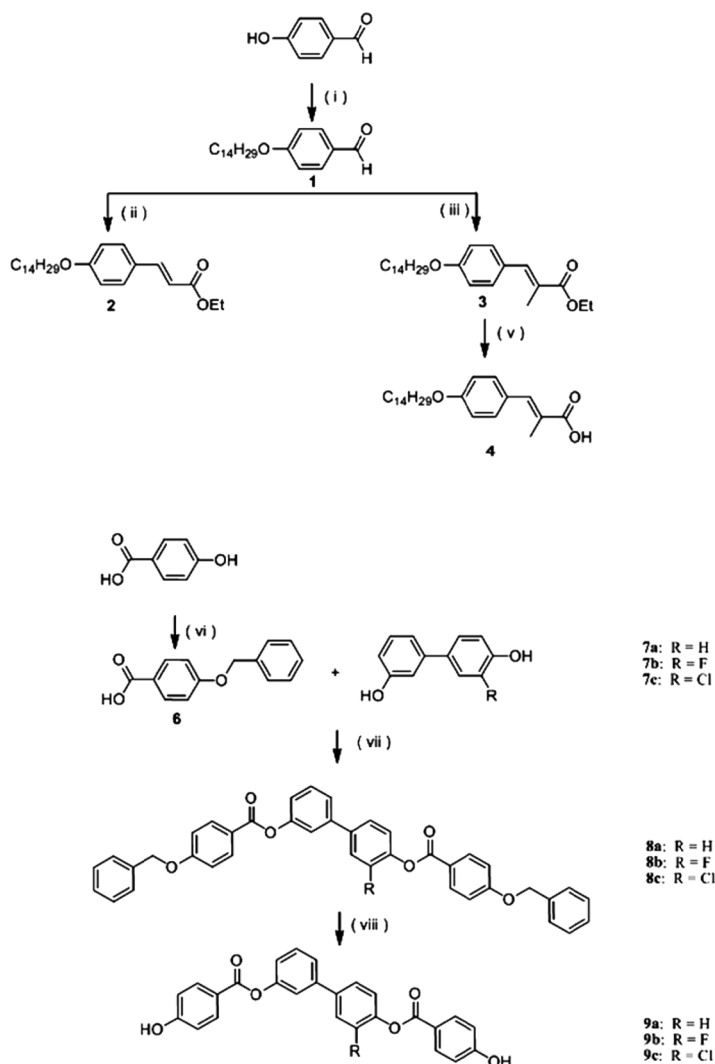
All reagents (from Taiwan) and chemicals were purchased from commercial sources (Alfa (USA), TCI (Japan), and Fluka (USA)) and used as received without further purification. Tetrahydrofuran (THF) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) were distilled to keep anhydrous before use. Reactions were monitored by thin-layer chromatography (TLC) on silica gel plates (Merck TLC silica gel 60 F<sub>254</sub> aluminum sheets), which were examined under ultraviolet (UV) light and iodine vapor. Column chromatography was performed using Merck 60-mesh silica gel.

### Synthesis

The general synthetic routes of intermediates and target bent-core molecules are shown in Schemes 1 and 2. The purity and chemical structures of the intermediates and target compound can be easily verified by TLC,  $^1\text{H}$  NMR spectroscopy, and elemental analysis. The synthetic procedures and chemical analyses of each product are described sequentially below.

*4-(Tetradecyloxy)benzaldehyde, 1.* This compound was prepared by a modified literature procedure [17], as a white solid in 84% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.95 (t,  $J$  = 6.7 Hz, 3H), 1.21–1.62 (m, 22H), 1.87 (m, 2H), 4.01 (t,  $J$  = 6.6 Hz, 2H), 7.44 (d,  $J$  = 8.7 Hz, 2H), 7.82 (d,  $J$  = 8.4 Hz, 2H), 9.70 (s, 1H). Anal. Calc. for  $\text{C}_{21}\text{H}_{34}\text{O}_2$ : C, 79.19; H, 10.76. Found: C, 79.40; H, 10.66.

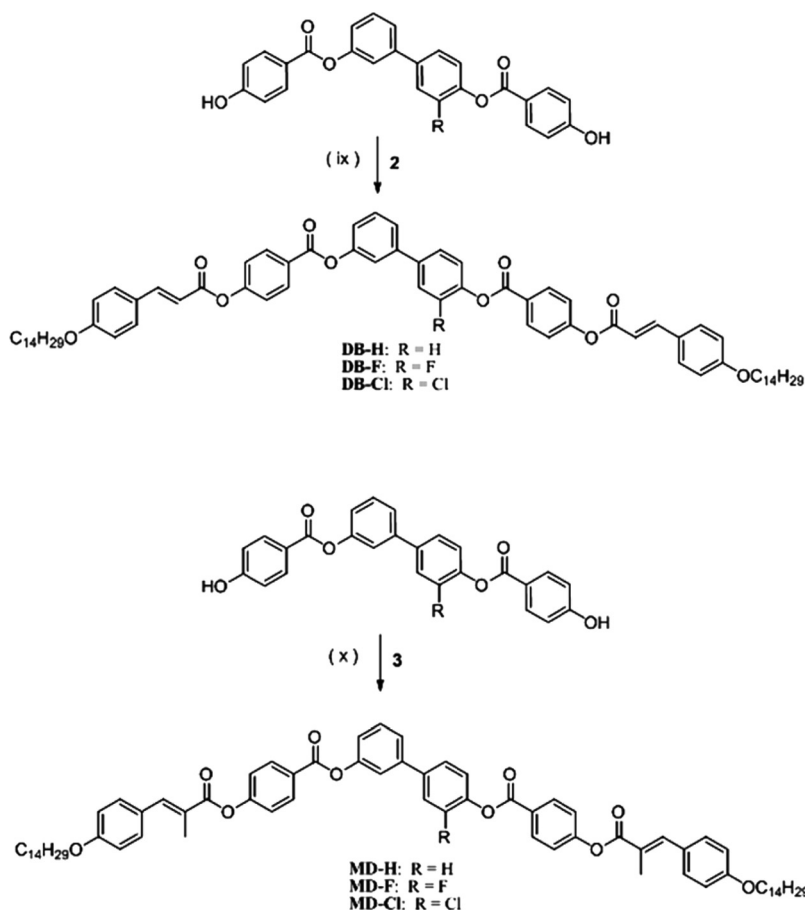
*(E)-4-tetradecyloxy cinnamic acid, 2.* A mixture of 4-(tetradecyloxy)benzaldehyde, **1** (10.0 g, 31.4 mmol), malonic acid (4.9 g, 47.1 mmol), and piperidine (1 mL) in dry pyridine (20 mL) was stirred and heated for 2 h at  $60^\circ\text{C}$  and 3 h at  $120^\circ\text{C}$  and then



**Scheme 1.** Synthetic routes of intermediates.

cooled down to room temperature. The solution was poured into 3 N HCl (250 mL). The precipitate was collected by filtration and washed with water. After drying, the residue was purified by recrystallization from ethanol to give a product as white solid in 87% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.88 (t,  $J = 6.9$  Hz, 3H), 1.23–1.47 (m, 25H), 1.76–1.85 (m, 2H), 3.96 (t,  $J = 6.6$  Hz, 2H), 4.25 (m, 2H), 6.95 (m, 2H), 7.29 (m, 2H), 7.71 (s, 1H). Anal. Calc. for  $\text{C}_{25}\text{H}_{40}\text{O}_3$ : C, 77.27; H, 10.38. Found: C, 77.19; H, 10.44.

*Ethyl 2-methyl-3-(4-(tetradecyloxy) phenyl) acrylate*, **3**. To a suspension of sodium hydride (NaH) (0.97 g, 40.3 mmol, 60% dispersion in mineral oil) in anhydrous THF (50 mL) under a nitrogen atmosphere was added drop-wise triethyl 2-phosphonopropionate (5.8 g, 24.2 mmol) in THF (20 mL) over 0.5 h, on cooling in



**Scheme 2.** Synthetic routes of target bent-core molecules.

an ice bath. The mixture was stirred for an additional 0.5 h at room temperature to form a clear solution. After being cooled in an ice bath, compound **1** (7.0 g, 22.0 mmol) in anhydrous THF (20 mL) was added over 0.5 h. The reaction mixture was allowed to warm to room temperature for 2 h and then quenched with water and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was separated and dried over anhydrous magnesium sulfate. After removal of the solvent by evaporation under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 20:1) to give a product as white solid in 92% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.86 (t,  $J = 6.9$  Hz, 3H), 1.26–1.49 (m, 25H), 1.74–1.83 (m, 2H), 2.13 (s, 3H), 3.98 (t,  $J = 6.6$  Hz, 2H), 4.26 (m, 2H), 6.90 (m, 2H), 7.36 (m, 2H), 7.63 (s, 1H). Anal. Calc. for  $\text{C}_{26}\text{H}_{42}\text{O}_3$ : C, 77.56; H, 10.51. Found: C, 77.34; H, 10.34.

**2-Methyl-3-(4-(tetradecyloxy) phenyl) acrylic acid, 4.** A solution of **3** (6.5 g, mmol) in ethanol (150 mL) was treated with 5 N solution of potassium hydroxide (KOH). The reaction mixture was stirred under reflux overnight. The resulting mixture was acidified with 6 N HCl (200 mL). The white precipitate was collected by filtration and washed with water. After drying, the residue was purified by

recrystallization from ethanol to give a product as white solid in 93% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.88 (t,  $J=6.9$  Hz, 3H), 1.26–1.46 (m, 22H), 1.74–1.82 (m, 2H), 2.15 (s, 3H), 3.99 (t,  $J=6.6$  Hz, 2H), 6.93 (d,  $J=8.7$  Hz, 2H), 7.42 (d,  $J=9.0$  Hz, 2H), 7.70 (s, 1H). Anal. Calc. for  $\text{C}_{24}\text{H}_{38}\text{O}_3$ : C, 76.96; H, 10.23. Found: C, 76.88; H, 10.33.

**4-Benzoyloxybenzoic acid, 6.** This compound was prepared according to published procedures [18], as a white solid in 85% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 5.50 (s, 2H), 7.03 (d,  $J=8.4$  Hz, 2H), 7.25 (m, 5H), 8.15 (d,  $J=8.7$  Hz, 2H). Anal. Calc. for  $\text{C}_{14}\text{H}_{12}\text{O}_3$ : C, 73.67; H, 5.30. Found: C, 73.58; H, 5.45.

**3,4'-Biphenyl bis(4-benzoyloxybenzoate), 8a.** To a suspension of compounds **6** (6.82 g, 29.9 mmol) and **7a** (2.5 g, 13.6 mmol), dissolved in dry dichloromethane (100 mL), *N,N*-dicyclohexylcarbodiimide (DCC; 6.2 g, 29.9 mmol) and 4-(*N,N*-dimethylamino) pyridine (DMAP; 0.33 g, 2.72 mmol) were added to react under nitrogen. The reaction mixture was stirred for 12 h at room temperature. The precipitated dicyclohexylurea (DCU) was filtered off and washed with an excess of dichloromethane (50 mL). The filtrate was washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent by evaporation under reduced pressure, the residue was purified by column chromatography on silica gel using chloroform as an eluent. The collected product was crystallized from a mixture of dichloromethane and 2-propanol to give **8a** as a white solid in 84% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 5.17 (s, 4H), 7.07 (d,  $J=8.7$  Hz, 4H), 7.18–7.50 (m, 16H), 7.64 (d,  $J=9.0$  Hz, 2H), 8.16–8.20 (m, 4H). Anal. Calc. for  $\text{C}_{40}\text{H}_{30}\text{O}_6$ : C, 79.19; H, 4.98. Found: C, 79.13; H, 5.01.

**3'-Fluoro-3,4'-biphenyl bis(4-benzoyloxybenzoate), 8b.** This compound was obtained from the reaction of compounds **6** and **7b** by using a similar procedure as described for compound **8a**. The product was isolated as a white solid in 80% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 5.16 (s, 4H), 7.08 (d,  $J=8.7$  Hz, 4H), 7.32–7.54 (m, 17H), 8.19 (d,  $J=8.7$  Hz, 4H). Anal. Calc. for  $\text{C}_{40}\text{H}_{29}\text{FO}_6$ : C, 76.91; H, 4.68. Found: C, 76.83; H, 4.87.

**3'-Chloro-3,4'-biphenyl bis(4-benzoyloxybenzoate), 8c.** This compound was obtained from the reaction of compounds **6** and **7c**, following a similar procedure as described for compound **8a**. The product was isolated as a white solid in 89% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 5.16 (s, 4H), 7.04–7.08 (m, 4H), 7.20–7.61 (m, 17H), 8.11–8.22 (m, 4H). Anal. Calc. for  $\text{C}_{40}\text{H}_{29}\text{ClO}_6$ : C, 74.93; H, 4.56. Found: C, 74.88; H, 4.67.

**3,4'-Biphenyl bis(4-hydroxybenzoate), 9a.** A mixture of compound **8a** (5.7 g, 9.4 mmol) was dissolved in THF (150 mL) containing a suspension of 10% Pd-C catalyst (1 g). The mixture was stirred under a hydrogen atmosphere at room temperature until no further hydrogen was taken up (*ca.* 10 h). The catalyst was removed by filtration through Celite and washed with an excess of THF (150 mL). The solvent was removed by evaporation under reduced pressure and the crude product was purified by column chromatography on silica gel (chloroform/ethyl acetate, 50:1) to give a white solid in 90% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 6.55 (d,  $J=8.4$  Hz, 4H), 7.26 (m, 1H), 7.36–7.69 (m, 7H), 8.06 (m, 4H), 10.49 (s, 2H). Anal. Calc. for  $\text{C}_{26}\text{H}_{18}\text{O}_6$ : C, 73.23; H, 4.25. Found: C, 73.13; H, 4.34.

*3'-Fluoro-3,4'-biphenyl bis(4-hydroxybenzoate)*, **9b**. This compound was obtained from compound **8b**, following a similar procedure as described for compound **9a**. The product was isolated as a white solid in 75% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 6.93 (m, 4H), 7.28 (m, 1H), 7.46–7.83 (m, 6H), 8.00 (m, 4H), 10.65 (s, 2H). Anal. Calc. for  $\text{C}_{26}\text{H}_{17}\text{FO}_6$ : C, 70.27; H, 3.86. Found: C, 70.23; H, 3.97.

*3'-Chloro-3,4'-biphenyl bis(4-hydroxybenzoate)*, **9c**. This compound was obtained from compound **8c**, following a similar procedure as described for compound **9a**. The product was isolated as a white solid in 80% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 6.95 (m, 4H), 7.24 (m, 1H), 7.49–7.85 (m, 6H), 8.03 (m, 4H), 10.53 (s, 2H). Anal. Calc. for  $\text{C}_{26}\text{H}_{17}\text{ClO}_6$ : C, 67.76; H, 3.72. Found: C, 67.90; H, 3.50.

Compounds of the series **DB** and **MD** were prepared by a similar method as described for compound **8a**. After workup, the crude products were purified by column chromatography on silica gel using chloroform as an eluent and twice recrystallization from a mixture of chloroform and ethanol as a white solid. The yields of these products after purification were *ca.* 57–71%.

*Biphenyl-3,4'-diyl bis(4-(3-(4-(tetradecyloxy) phenyl) acryloyloxy) benzoate)*, **DB-H**. The compound was prepared from compounds **2** and **9a**. The product was isolated as a white solid in 76% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.88 (t,  $J=6.9$  Hz, 6H), 1.20–1.47 (m, 44H), 1.81 (m, 4H), 4.01 (t,  $J=6.6$  Hz, 4H), 6.48 (s, 1H), 6.53 (s, 1H), 6.94 (d,  $J=8.7$  Hz, 4H), 7.22–7.36 (m, 7H), 7.45–7.68 (m, 9H), 7.84 (s, 1H), 7.89 (s, 1H), 8.29 (m, 4H, Ar-H). Anal. Calc. for  $\text{C}_{72}\text{H}_{86}\text{O}_{10}$ : C, 77.81; H, 7.80. Found: C, 77.73; H, 7.75.

*3'-Fluorobiphenyl-3,4'-diyl bis(4-(3-(4-(tetradecyloxy) phenyl) acryloyloxy) benzoate)*, **DB-F**. The compound was prepared from **2** and **9b**. The product was isolated as a white solid in 72% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.89 (t,  $J=6.3$  Hz, 6H), 1.20–1.55 (m, 44H), 1.81 (m, 4H), 4.01 (t,  $J=6.6$  Hz, 4H), 6.48 (s, 1H), 6.53 (s, 1H), 6.94 (d,  $J=9.0$  Hz, 4H), 7.23–7.56 (m, 15H), 7.84 (s, 1H), 7.90 (s, 1H), 8.27–8.31 (m, 4H). Anal. Calc. for  $\text{C}_{72}\text{H}_{85}\text{FO}_{10}$ : C, 76.57; H, 7.59. Found: C, 76.51; H, 7.52.

*3'-Chlorobiphenyl-3,4'-diyl bis(4-(3-(4-(tetradecyloxy) phenyl) acryloyloxy) benzoate)*, **DB-Cl**. The compound was prepared from **2** and **9c**. The product was isolated as a white solid in 78% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.89 (t,  $J=6.3$  Hz, 6H), 1.21–1.49 (m, 44H), 1.81 (m, 4H), 4.01 (t,  $J=6.6$  Hz, 4H), 6.48 (s, 1H), 6.53 (s, 1H), 6.94 (d,  $J=8.7$  Hz, 4H), 7.24–7.58 (m, 15H), 7.84 (s, 1H), 7.90 (s, 1H), 8.29 (m, 4H). Anal. Calc. for  $\text{C}_{72}\text{H}_{85}\text{ClO}_{10}$ : C, 75.47; H, 7.48. Found: C, 75.43; H, 7.56.

*Biphenyl-3,4'-diyl bis(4-(2-methyl-3-(4-(tetradecyloxy) acryloyloxy) benzoate)*, **MD-H**. The compound was prepared from **4** and **9a**. The product was isolated as a white solid in 82% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.88 (t,  $J=6.9$  Hz, 6H), 1.27–1.49 (m, 44H), 1.81 (m, 4H), 2.26 (s, 6H), 4.01 (t,  $J=6.6$  Hz, 4H), 6.95 (d,  $J=8.7$  Hz, 4H), 7.21–7.53 (m, 14H), 7.61–7.69 (m, 2H), 7.92 (s, 2H), 8.29 (m, 4H). Anal. Calc. for  $\text{C}_{74}\text{H}_{89}\text{O}_{10}$ : C, 77.79; H, 7.75. Found: C, 77.63; H, 7.85.

*3'-Fluorobiphenyl-3,4'-diyl bis(4-(2-methyl-3-(4-(tetradecyloxy) acryloyloxy) benzoate)*, **MD-F**. The compound was prepared from **4** and **9b**. The product was isolated as a white solid in 85% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.88 (t,



$J = 6.9$  Hz, 6H), 1.20–1.56 (m, 44H), 1.81 (m, 4H), 2.28 (s, 6H), 4.01 (t,  $J = 6.6$  Hz, 4H), 6.96 (d,  $J = 8.7$  Hz, 4H), 7.24–7.56 (m, 15H), 7.92 (s, 2H), 8.28–8.31 (m, 4H). Anal. Calc. for  $C_{74}H_{89}FO_{10}$ : C, 76.79; H, 7.75. Found: C, 76.87; H, 7.63.

*3'-Chlorobiphenyl-3,4'-diyl bis(4-(2-methyl-3-(4-(tetradecyloxy) acryloyloxy) benzoate, MD-Cl*. The compound was prepared from **4** and **9c**. The product was isolated as a white solid in 80% yield.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  (ppm): 0.89 (t,  $J = 6.3$  Hz, 6H), 1.27–1.48 (m, 44H), 1.80 (m, 4H), 2.29 (s, 6H), 4.02 (t,  $J = 6.6$  Hz, 4H), 6.97 (d,  $J = 8.7$  Hz, 4H), 7.27–7.60 (m, 15H), 7.75 (s, 2H), 8.29–8.35 (m, 4H). Anal. Calc. for  $C_{74}H_{89}ClO_{10}$ : C, 75.71; H, 7.64. Found: C, 75.56; H, 7.70.

## Results and Discussion

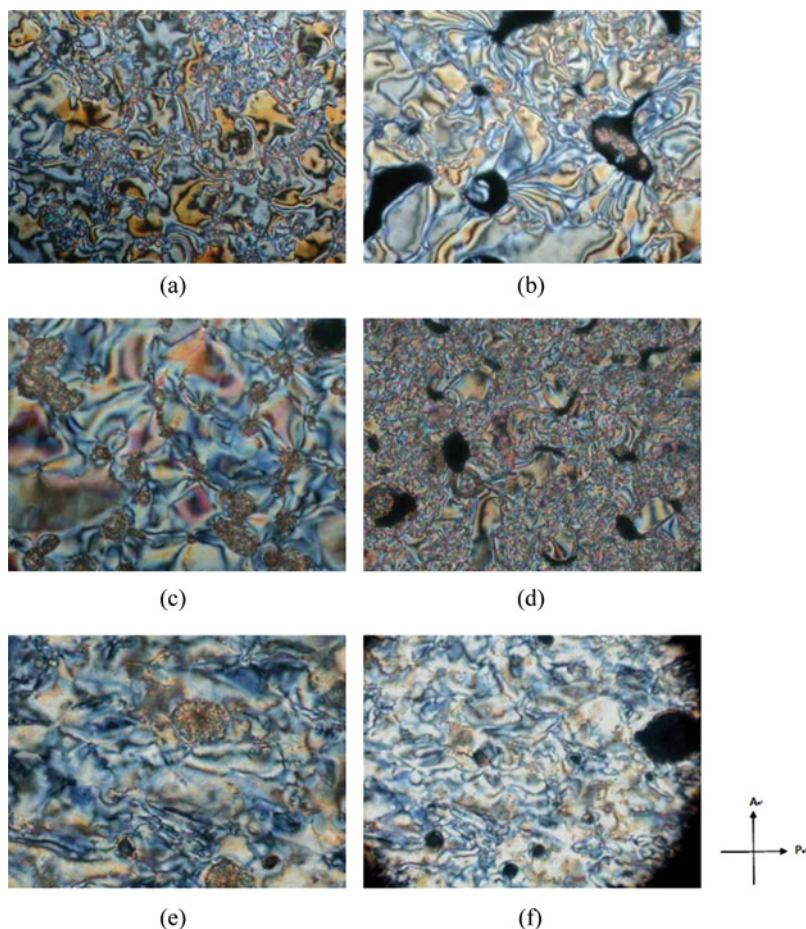
### Thermal Properties and Optical Textures

The phase behaviors of all compounds were investigated by combining different techniques, including POM, DSC, and XRD. Phase transition temperatures observed by POM match well with the corresponding DSC thermograms. The mesomorphic properties of the studied compounds, the phase sequence, phase transition temperatures, and enthalpy data are summarized in Table 1. Upon cooling from the isotropic state, the compound **DB-H** displays a characteristic Schlieren texture and broken fan textures of the mesophase at 110°C (see Fig. 1a), indicating the formation of the SmCP phase. The other compounds show similar optical texture, thus implying that they have the same mesophase. All of the compounds exhibit enantiotropic mesomorphic behavior and only a mesophase. A typical DSC curve of compound **DB-H** is shown in Fig. 2a, which shows that one mesophase can be obtained and that there are no significant differences for different heating or cooling rates. In the DSC

**Table 1.** Phase transition temperatures (°C) and enthalpies ( $kJ\ mol^{-1}$ ; in parentheses) for the bent-core compounds as determined by DSC (scan rate =  $5^\circ C\ min^{-1}$ )<sup>a</sup>

Compound	R	Cr	Second heating first cooling	SmCP	Second heating first cooling	I
<b>DB-H</b>	H	•	119.2 (29.5) 98.0 (27.8)	•	153.9 (15.2) 151.4 (14.2)	•
<b>DB-F</b>	F	•	130.6 (26.7) 109.8 (28.0)	•	149.9 (13.1) 142.9 (13.1)	•
<b>DB-Cl</b>	Cl	•	111.2 (30.9) 56.2 (21.0)	•	127.9 (14.8) 125.1 (14.2)	•
<b>MD-H</b>	H	•	99.6 (19.3) 73.1 (18.8)	•	131.5 (15.5) 125.5 (15.8)	•
<b>MD-F</b>	F	•	89.4 (23.6) 45.8 (18.1)	•	119.6 (12.3) 112.3 (11.9)	•
<b>MD-Cl</b>	Cl	•	58.9 (22.3) 39.6 (21.2)	•	97.8 (12.5) 91.8 (12.3)	•

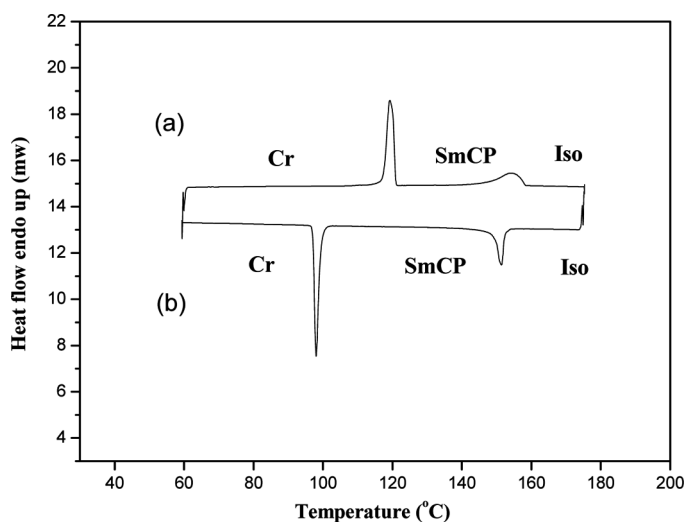
<sup>a</sup>Abbreviations: Cr = crystalline phase; SmCP = polar SmC phase (i.e.,  $B_2$  phase); I = isotropic phase (• = phase exists).



**Figure 1.** Polarized optical microscopic textures obtained Schlieren with broken fan-shaped textures in the SmCP phase on cooling ( $1^{\circ}\text{C min}^{-1}$ ) from the isotropic state for (a) compound **DB-H** at  $110^{\circ}\text{C}$ , (b) compound **DB-F** at  $136^{\circ}\text{C}$ , (c) compound **DB-Cl** at  $123^{\circ}\text{C}$ , (d) compound **MD-H** at  $119^{\circ}\text{C}$ , (e) compound **MD-F** at  $72^{\circ}\text{C}$ , and (f) compound **MD-Cl** at  $70^{\circ}\text{C}$ . (Arrows are the directions of polarizers and analyzers.).

thermograms, the enthalpy values obtained for the SmCP mesophase-to-isotropic phase transition were in the range of about  $11.9$  to  $15.8 \text{ kJ mol}^{-1}$  (see Table 1).

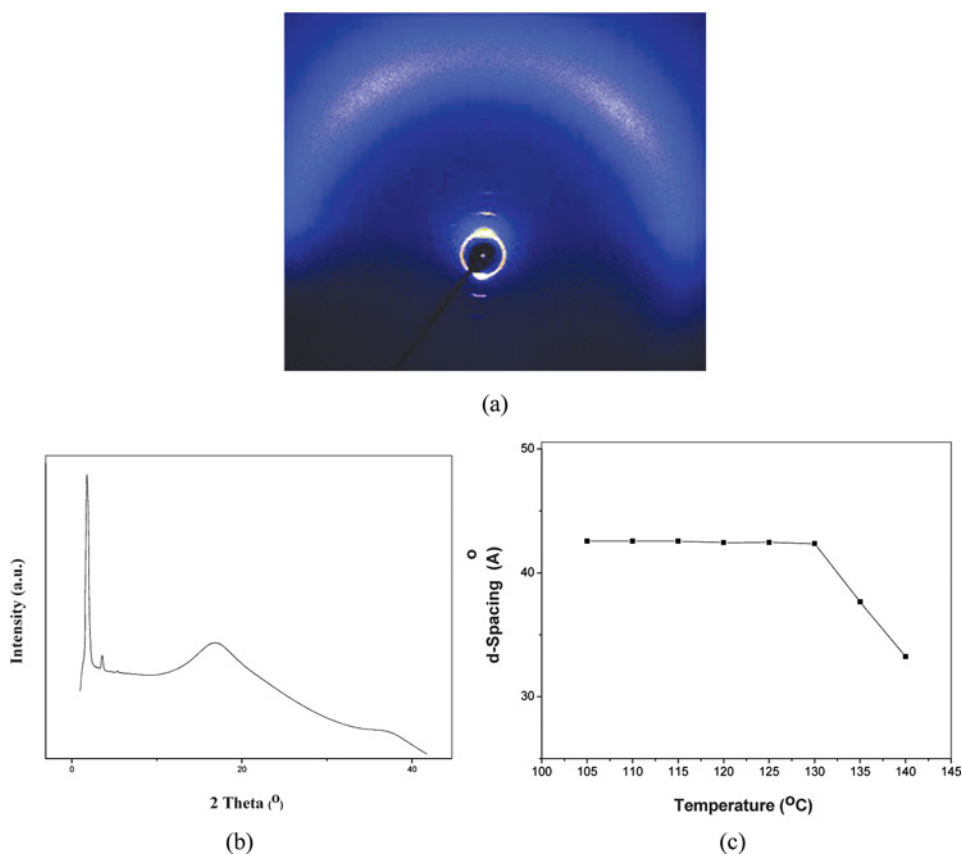
Comparison of compounds **DB-H** and **DB-F**, shows that the compound **DB-Cl** is due to the lowest clearing transition temperature upon cooling from the isotropic liquid. In this case, the chlorine atom has a larger size atom than the fluorine and hydrogen atoms. As a result, when introduction of the lateral substituent was at the biphenyl core into the 3'-position, the clearing temperature of the compound was decreased. Thus, size of the lateral substituent has a profound influence on their mesomorphic behavior. However, series MD, which contain an  $\alpha$ -methylcinnamoyloxy group in the side wings, showed smaller clearing transition temperature than series DB. The presence of a methyl group in the cinnamoyl moiety of these five-ring esters completely destroys the mesophase, probably due to steric reasons.



**Figure 2.** DSC curves of compound **DB-H** obtained at a rate of  $5^{\circ}\text{C min}^{-1}$ : (a) second heating and (b) first cooling cycle with respective transition temperatures.

### *X-ray Diffraction Studies*

To further identify the type of mesophases, the determination of structural parameter has been further performed by XRD. The theoretical molecular length of **DB-F** determined from molecular model estimated using CS Chem3D Ultra 7.0 software (National Taiwan University of Science and Technology, Taiwan) gave molecular length of *ca.* 55.0 Å, where we suppose that the molecular structure is coplanar and the alkyl chains are in the fully extended all-*trans* conformation. As shown in Fig. 3a, the 2D diffraction pattern including two symmetric intense arcs in the small-angle region on the meridian XRD pattern of compound **DB-F** and the data were integrated in Fig. 3b, as an illustrative example. The resulting XRD pattern of compound **DB-F** at 110°C exhibits three Bragg reflections in the small-angle region at  $2\theta = 1.78, 3.54,$  and  $5.39^{\circ}$  with the *d*-spacing of 42.5, 21.6, and 14.2 Å, respectively, corresponding to the reciprocal spacing in the ratios 1, 2, and 3 and to the indexation  $(hk) = (10), (20),$  and  $(30)$ , which can imply the formation of a layered structure. On the other hand, a diffuse scattering halo in the wide-angle region centered at  $2\theta$  around  $16.91^{\circ}$  with *d*-spacing of *ca.* 4.5 Å indicates a liquid-like arrangement of the molecules within the layers. As shown in Fig. 3c, the temperature dependence of the layer *d*-spacing of compound **DB-F** in the SmCP phase was recorded upon cooling from the isotropic phase. The values of the layer *d*-spacing only change slightly within the temperature range of the SmCP phase. Therefore, the layer *d*-spacing value of 42.5 Å for compound **DB-F** by XRD measurement is smaller than the calculated theoretical molecular length of 55.0 Å, which suggests a tilted arrangement of the smectic structure; that is, smectic C phase with tilt angle of  $39.4^{\circ}$  along the layer normal direction. Series **DB** and **MD** also revealed similar diffraction pattern at temperatures within the respective mesophase temperature range. The *d*-spacing and tilt angle of series **DB** were smaller than the series **MD** (see Table 2) due to the steric effect of the methyl group in the series **MD**.



**Figure 3.** (a) 2D XRD pattern of a partially surface-aligned sample of compound DB-F obtained in the SmCP phase at 110°C (upon cooling from the isotropic phase). (b) X-ray diffraction intensity against angle profile obtained in the SmCP phase of (DB-F) at 110°C and (c) layer  $d$ -spacing as a function of the temperature dependence (upon cooling from the isotropic phase).

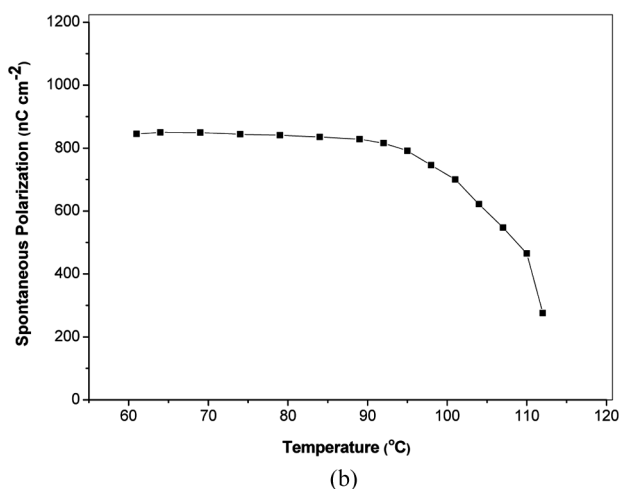
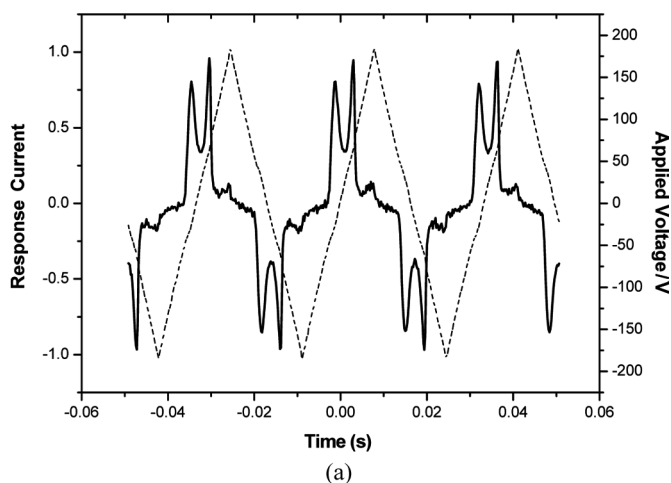
**Table 2.** Summary data of series MD and DB

Compound	DB-H	DB-F	DB-Cl	MD-H	MD-F	MD-Cl
Mesophase	SmCP	SmCP	SmCP	SmCP	SmCP	SmCP
Parameters (Å)	55.0	55.0	55.0	57.0	57.0	57.0
Measured Spacings (Å)	42.3	42.5	42.6	43.7	43.9	43.8
Tilt angle (°)	39.7	39.4	39.2	39.9	39.6	39.7
Optical tilt angle (°)	40	40	42	42	42	43
Switching time ( $\mu$ s) <sup>a</sup>	15.4	18.0	32.2	15.9	32.0	61.7
Maximum $Ps/nC$ (cm <sup>-2</sup> )	890	833	800	903	850	804

<sup>a</sup>The data were measured in the range  $T_C - T = 15^\circ\text{C}$ .

### Electro-Optical Behavior

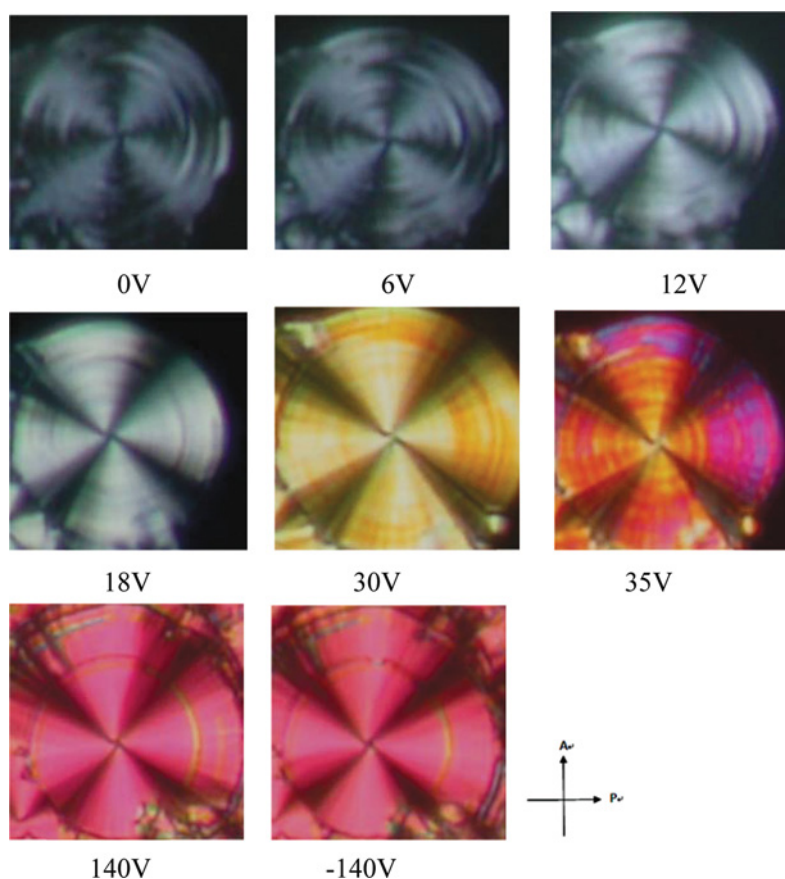
The switching behavior has been observed in the SmCP phase of the studied compound **MD-F** using the triangular wave method. Two distinct sharp peaks per half period of an applied triangular wave voltage are clearly seen under a triangular wave field of about 180 Vpp at 60 Hz (see Fig. 4a). This is a strong indication of an antiferroelectric switching process. The temperature dependence of the magnitude of the  $P_s$  value for the compound **MD-F** obtained by integrating the area under the two peaks is shown in Fig. 4b and spontaneous polarization ( $P_s$ ) is about 850 nC cm<sup>-2</sup> at 75°C. It can be seen that the  $P_s$  is dependent on temperature for compound **MD-F**. A similar tendency was also observed in the other compounds. The abrupt increase of  $P_s$  around the isotropization temperature indicates that the phase transformation from the isotropic phase to the SmCP phase is a first-order phase



**Figure 4.** (a) Switching current response observed in the SmCP phase of compound **MD-F** at 92°C under the applied triangular wave voltage (7.5  $\mu$ m antiparallel rubbed polyimide-coated ITO cell, 180 Vpp, 60 Hz) and (b) spontaneous polarization ( $P_s$ ) as a function of temperature.

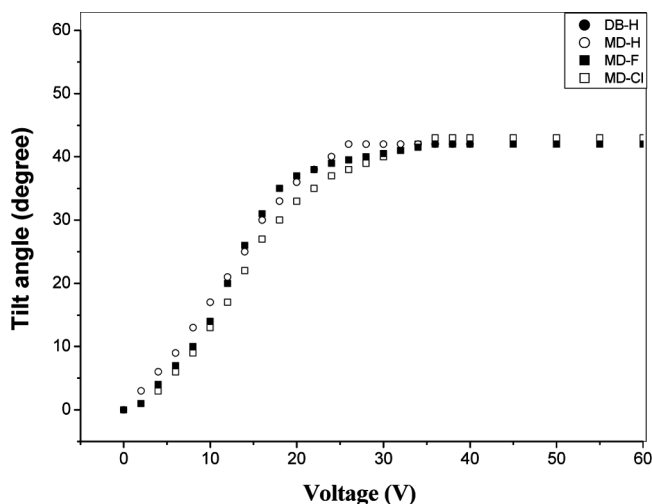
transformation. The  $P_s$  value exhibits a maximum polarization (see Table 2). Comparably, the spontaneous polarization value of series **DB** (800–890 nC cm<sup>-2</sup>) without the methyl group is similar to the analogous series **MD** (804–903 nC cm<sup>-2</sup>) which have methyl group. It seems that an additional methyl group at linking group in the core is not able to abate rotation of the molecular. Therefore, the order of  $P_s$  values regarding molecular design is as follows:  $P_s$  (without lateral substituent at the biphenyl core) >  $P_s$  (fluoro-substituent at the biphenyl core) >  $P_s$  (chloro-substituent at the biphenyl core). It seems that the dipole moment originating in the core containing the halogen substituent depresses spontaneous polarization.

To study the tilt sense in the SmCP phase, we carried out dc field experiments. A sample of compound **MD-Cl** was cooled slowly from the isotropic phase under a dc voltage of 100 Vpp to induce the chiral domain. Circular domains with dark brushes making an angle with respect to the analyzer were obtained, which indicates a synclinal tilt of the molecules in a field-induced state. When the polarity of the applied field



**Figure 5.** Polarizing optical micrographs of the circular domains in the SmCP phase for compound **MD-Cl** (on antiparallel rubbing direction LC cells with 7.5  $\mu\text{m}$  thickness) is shown. Chiral domains obtained by various dc fields: 0 V (SmC<sub>A</sub>P<sub>A</sub>), 6 V, 12 V, 18 V, 30 V, 35 V, 140 V, -140 V (SmC<sub>S</sub>P<sub>F</sub>) at 85°C in compound **MD-Cl**. (Arrows are the directions of polarizers and analyzers.)

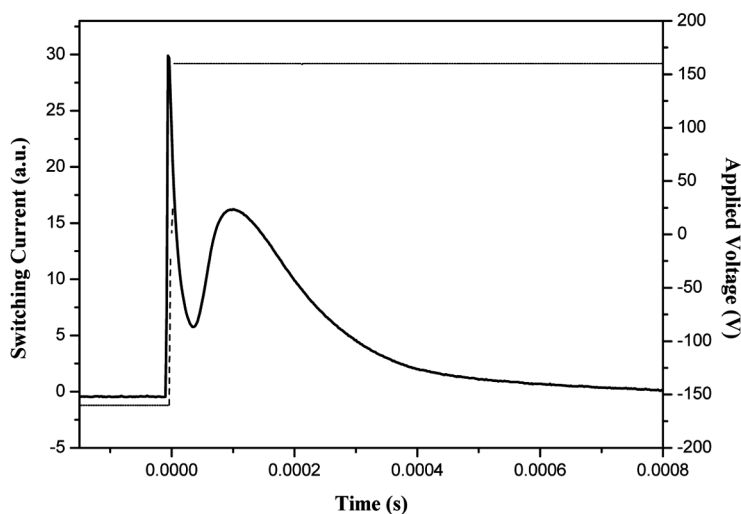
was reversed, the orientation of the brushes rotated in an anticlockwise direction and the mesophase shifted to another ferroelectric state. After removing electric fields, the extinction crosses were reoriented along the crossed polarizer position in the off state, indicating an antclinic tilt in the antiferroelectric ground state ( $\text{SmC}_\text{A}\text{P}_\text{A}$ ). As shown in Fig. 5, by applying electric fields with reverse polarities, the extinction crosses rotated counterclockwise (positive field) and clockwise (negative field). The extinction crosses in the switched-on state did not coincide with the crossed polarizer positions in the off state. The angles between the extinction directions and the crossed polarizer positions are about  $43^\circ$  for  $\pm 35$  V at  $85^\circ\text{C}$  in compound **MD-Cl**, which corresponds to the optical tilt angle. The inclined position of the majority of dark extinction brushes obtained under a dc field indicates a field induced synpolar smectic phase with a predominately uniform tilt direction of the molecules in adjacent layers ( $\text{SmCsP}_\text{F}$  phase). In the highly birefringent domain the extinction crosses are inclined with the directions of the polarizers by about  $40\text{--}45^\circ$ . Hence, the molecules in these domains seem to have  $40\text{--}45^\circ$  tilted synclinic organization. The switching behavior of the extinction crosses of the domains rotated in opposite directions depending on the sign of the field, which are characteristic field-responsive textures for chiral domains of the  $\text{SmCP}$  phase [19, 20]. Furthermore, the switching process can be studied by measuring the tilt angle as a function of the applied dc electric fields in the  $\text{SmCP}$  phase of series **MD** (at  $T_\text{C} - T = 10^\circ\text{C}$ , respectively), as shown in Fig. 6. The tilt angles are estimated from the rotating angles between the extinction brushes and crossed polarizers by applying electric fields, which indicates the rotated phase structure from the antclinic-antiferroelectric ( $\text{SmC}_\text{A}\text{P}_\text{A}$ ) state to the synclinic-ferroelectric ( $\text{SmCsP}_\text{F}$ ) state had occurred. The tilt angles of series **MD** rise with increasing the applied voltage and saturate at the fields of  $\sim 35$  V. In addition, both series **DB** and **MD** have similar tilt angles at lower applied voltages and similar saturated tilt angles around  $40^\circ$ , as shown in Table 2. However, comparing materials with series **DB** and **MD**, the compound containing the halogen-substituent has a similar tilt angle. The results also show that, in general, the halogen-substituted materials



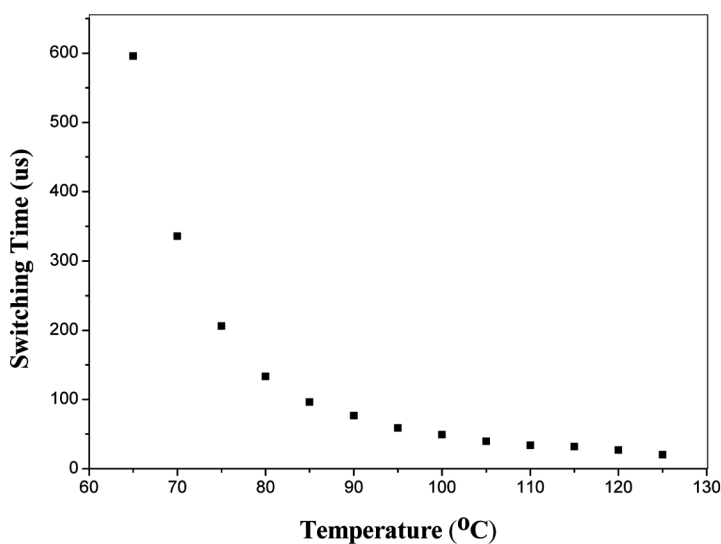
**Figure 6.** Tilt angle of the  $\text{SmCP}$  phase as a function of the dc electric fields in compounds (on antiparallel rubbing direction LC cells with  $7.5\text{ }\mu\text{m}$  thickness) respectively.

have similar tilt angles as nonsubstituted materials. Thus, it can be demonstrated that the halogen-substituent materials decrease the spontaneous polarization but the tilt angle is similar.

In order to investigate the dynamics of the polarization switching behavior, the switching currents of compound **DB-Cl** were measured with an applied square wave field (as  $V_{pp} = 150$  V,  $f = 10$  Hz) in the SmCP phase (at  $85^\circ\text{C}$  upon cooling from the isotropic phase). The switching current curves of compound **DB-Cl** at  $85^\circ\text{C}$  are



(a)



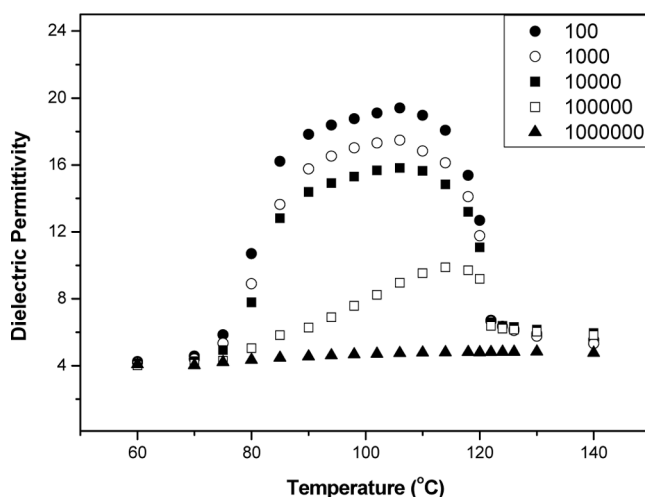
(b)

**Figure 7.** (a) Time dependences of the switching current under a square wave field for compound **DB-Cl** at  $85^\circ\text{C}$  and (b) switching time as a function of temperature for compound **DB-Cl** (on antiparallel rubbing direction LC cells with  $7.5\mu\text{m}$  thickness as  $V_{pp} = 150$  V,  $f = 10$  Hz).

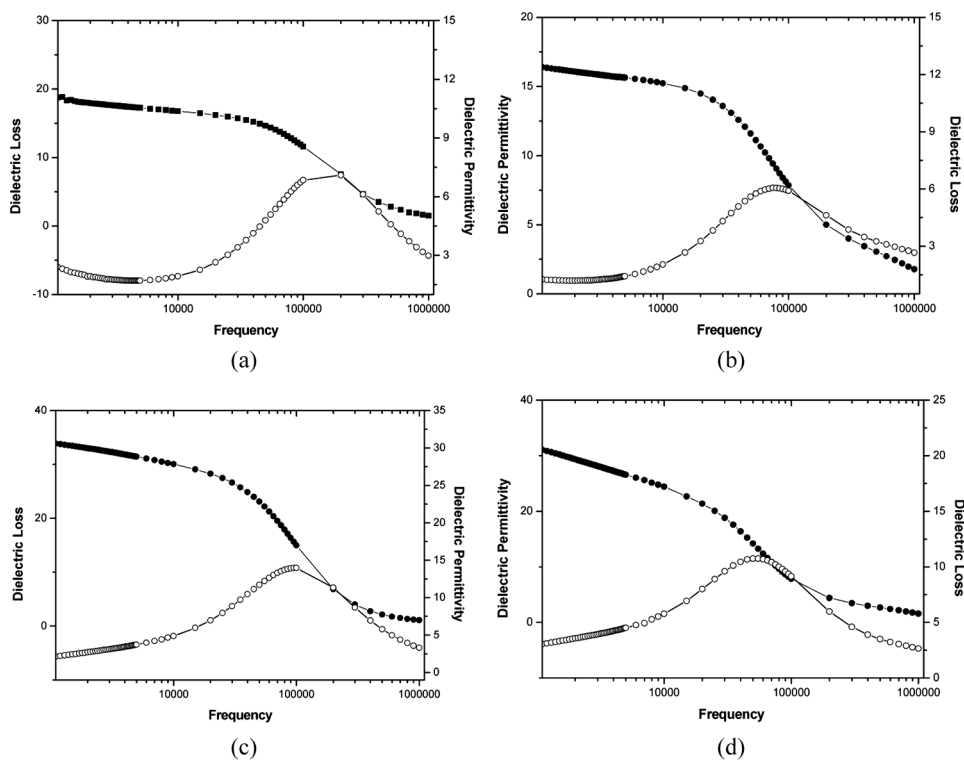


shown in Fig. 7a as a function of time. The switching time ( $\tau$ ) values are determined from the time elapsed between the appearance of the maximum of the current signal and the field reversal [21,22]. The switching time as a function of the temperature is shown in Fig. 7b with the same field and frequency (i.e.,  $V_{pp} = 150$  V,  $f = 10$  Hz). The decrease of the switching time with increasing temperature for compound **DB-Cl** (in the range of 600–17  $\mu$ s) was observed due to the viscosity decrease. The switching time values were measured at the temperature of  $T_C - T = 15^\circ\text{C}$  (see Table 2). Comparably, the switching time value of series **DB** (15–32  $\mu$ s) is smaller than that of the analogous series **MD** (16–62  $\mu$ s). Therefore, the order of switching time values regarding molecular design is as follows: without lateral substituent at the biphenyl core < fluoro-substituent at the biphenyl core < chloro-substituent at the biphenyl core. The results show that switching time may be influenced by viscosity as a decrease of the switching time with a decrease in viscosity. Therefore, the viscosity decreases due to the substituent destruction of the molecular interactions.

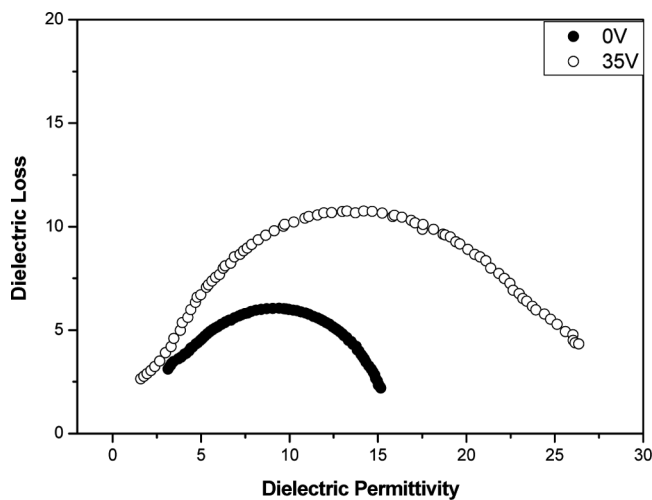
Finally, we also measured the complex dielectric permittivity in the frequency range  $10^2$ – $10^6$  Hz for the planar-aligned (measuring field is normal to the director) sample on cooling at a rate of about  $1^\circ\text{C min}^{-1}$ , keeping the temperature of the sample stable during frequency sweeps. The temperature dependence of the relative dielectric permittivity ( $\epsilon'$ ) of compound **DB-H** at various frequencies [23] is shown in Fig. 8. The large variation in  $\epsilon'$  with frequency in the SmCP phases is due to the dielectric relaxation modes present in the phase. The large change in the value of  $\epsilon'$  at Iso to SmCP phase transitions is due to the transformation of the paraelectric structure into an antiferroelectric structure. As the result, highest value of  $\epsilon'$  is observed at  $\sim 19.4$  in the SmCP phase at 100 Hz. Figures 9a and 9b show the frequency dispersions of real and imaginary parts of dielectric constants,  $\epsilon'$  and  $\epsilon''$  in the SmCP phase of compounds **DB-H** and **MD-H**. A relaxation mode was detected at about 500 k Hz. A similar result has also been observed in another bent-core structure [24–26]. The results were tentatively explained such that relaxation is due to the rotation around the molecular short axis [27]. The explanation was based on the



**Figure 8.** Temperature dependence of the dielectric constant ( $\epsilon'$ ) at  $10^2$ ,  $10^3$ ,  $10^4$ ,  $10^5$ , and  $10^6$  Hz for **MD-H**.



**Figure 9.** Frequency dispersions of real and imaginary parts of dielectric constants,  $\epsilon'$  (●) and  $\epsilon''$  (○), (a) (b) without a dc bias field and (c) (d) under a 35 V dc bias field in the SmCP phase of compound **DB-H** and **MD-H** at  $T^C - T = 25^\circ\text{C}$ .



**Figure 10.** Cole-Cole plots without a dc bias field and under a 35 V dc bias field in the SmCP phase of compound **MD-H** at  $T_C - T = 25^\circ\text{C}$ .

untilted ferroelectric structure instead of the tilted antiferroelectric one. The relaxation was explained as the reorientation around the long axis. As mentioned above, the SmCP phase was confirmed to be antiferroelectric and the dielectric response due to the Goldstone mode was essentially small in the absence of a dc bias field, because net polarization in neighboring layers was canceled out [28]. In order to understand the relaxation mode in detail, a dc bias field was applied [29] (Figs. 9c and 9d). When a 35 V dc bias field was applied, the antiferroelectric ordering was distorted due to the molecular rotation on the cone, so that a net polarization emerged. The dielectric strength increased in the higher frequency and an additional relaxation was detected in the lower frequency range. The Cole-Cole plot ( $\epsilon''$  versus  $\epsilon'$ ) provides valuable information with regard to the dielectric relaxation process. The relaxation process of compound **MD-H** was observed from the Cole-Cole plots (see Fig. 10) at various biases (0 and 35 V). The relaxation strength (diameter of the circle) increased with added bias. The center of the circles was shifted along the  $\epsilon'$  axis to larger  $\epsilon'$  values with added bias. The result that the dielectric strength of a small relaxation mode increased with adding dc bias field was explained by the distortion of the antiferroelectric ordering.

## Conclusions

We have achieved the molecular design, synthesis, and characterization of bent-core liquid crystals that have different linking groups ( $\alpha$ -methylcinnamoyloxy group and cinnamoyloxy group) and different lateral substituents (fluorine and chlorine). Specifically, we have explored the possibility of stabilizing a wide thermal range SmCP phase. It exhibits the SmCP phase over a 60°C thermal range. Electro-optic studies were carried out for the majority of the compounds exhibiting the SmCP phase. Electrical switching and molecular tilt angle as functions of temperature were investigated in the SmCP phase. The tilt angle of compound **MD-Cl** can be up to 43° at low fields (40 V), and the switching time of all target compounds were very fast at 150 Vpp in the SmCP phase. Finally, we observed the relaxation process from the Cole-Cole plots.

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