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Antiferroelectric Behaviors of the SmCP Phase in Liquid-Crystalline Compounds with Achiral Bent-Core Liquid-Crystalline Molecules Containing Salicylaldimine-Based

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Antiferroelectric Behaviors of the SmCP Phase in Liquid-Crystalline Compounds with Achiral Bent-Core Liquid-Crystalline Molecules Containing Salicylaldimine-Based

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A new series of bent-shaped mesogens has been synthesized and their mesomorphic properties studied. All compounds exhibit the B2 (SmCP) phase. Compounds with a 3,4'-biphenyldiol central core containing salicylaldimine-based and two terminal tetradecyloxy tails are reported. In addition, the effects of lateral substituent (R=F and Cl) at the biphenyl core into 3'-position are examined. These substituents have a strong influence in reducing the clearing temperatures and increasing temperature range of the SmCP phase. The electro-optical switching characteristics have been investigated using both triangular-wave and DC electric fields. For several compounds, chirality switching from racemic to the homochiral state was seen after application of a low-frequency AC field. We studied spontaneous polarization, switching time, tilt angle, switching time, voltage-transmittance effect, and dielectric parameters (namely dielectric strength, relaxation frequency, distribution parameter) of a 7.5-μm-thick planar-oriented sample of a highly tilted anti-ferroelectric liquid-crystal material and investigated the correlation between their electro-optical properties and the chemical structures of these compounds.

Keywords Antiferroelectric properties; bent-core liquid crystals; homochiral state; racemic; salicylaldimine-based

Introduction

Akutagawa *et al.* [1] reported a series of bent-core molecules, as 1,3-phenylene bis[4-(4-n-octyloxyphenyliminomethyl) benzoate] derivatives. Liquid-crystalline mesophases formed by bent-core (banana-shaped) mesogens have attracted particular interest since their first observation [2]. The B2 (SmCP) phase, which exhibits electro-optic switching, is the most studied banana mesophase. In a structural

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evolution paralleling that of the calamitic SmC* liquid crystals (LCs), most bent-core (bent-shaped, or bow-shaped) mesogens [3] exhibiting the remarkable SmCP antiferroelectric and ferroelectric [4] phases are Schiff bases. Though SmCP mesogens without Schiff's base units have been reported [5], deviations on the theme of the bis-Schiff's base bent-core system have proven remarkably useful for providing interesting polar smectics. Several results on bent-core liquid crystals considered as new supramolecular functional materials with potential for applications are reviewed [6]. Various topics are discussed where these materials present unique attributes with clear advantages over conventional mesogens [7]. In the present article, a series of achiral bent-shaped liquid-crystalline molecules based on a 3,4'-biphenyldiol central core containing salicylaldimine-based and two terminal tetradecyloxy tails were synthesized and characterized. In addition, we report the effect of a lateral substituent ($R=F$ and Cl) at the biphenyl core into 3'-position, leading to the influence of the mesomorphic properties. We expected to obtain a wider range and lower temperature of the SmCP phase. We studied the mesomorphic behavior of a new series with asymmetrical bent cores [8]. In this article, the material parameters such as dielectric permittivity, switching time, rotational viscosity, tilt angle, and spontaneous polarization were also studied. The experimental results were analyzed using dielectric relaxation spectroscopy, polarizing optical microscopy, and other electro-optical studies.

Experimental

Materials

The chemical structures and phase transition behavior of series **SB** are shown in Table 1. The series **SB** contain salicylaldimine-based and two terminal tetradecyloxy tails in the mesogenic group. It was prepared in the same manner as described in previous literature [8]. All of the products were purified by column chromatography

Table 1. Phase Transition Temperatures ($^{\circ}C$) and Enthalpies ($kJ\ mol^{-1}$; in Parentheses) for the Bent-Core Compounds as Determined by DSC (Scan Rate = $5^{\circ}C\ min^{-1}$)^a

Compound	R	Cr	Second heating first cooling	SmCP	Second heating first cooling	I
SB-H	H	•	113.1 (67.8) 107.8 (68.6)	•	214.2 (25.1) 213.3 (25.2)	•
SB-F	F	•	108.7 (32.7) 85.8 (33.0)	•	205.9 (26.6) 204.6 (25.7)	•
SB-Cl	Cl	•	132.0 (29.5) 51.6 (26.7)	•	184.0 (20.8) 180.5 (21.0)	•

^aCr = crystalline phase; SmCP = polar SmC phase (i.e., B_2 phase); I = isotropic phase; (• = phase exists).

using silica gel and then recrystallized. A differential scanning calorimeter (LT-Modulate DSC 2920, Taiwan) was used to determine the thermal transitions. The thermal transitions were read at their maximum endothermic or exothermic peaks. Heating and cooling rates were $5^{\circ}\text{C min}^{-1}$ in all of these compounds. Moreover, the transition temperatures were obtained from the specified second heating and cooling scans. A polarized optical microscope (POM; Olympus BH5) equipped with a hot stage (Mettler Toledo FP82HT) and a programmable temperature controller (Mettler Toledo FP90 central processor) was then used to observe the thermal transitions and analyze the anisotropic textures. The heating/cooling rate for POM was $1^{\circ}\text{C min}^{-1}$.

Characterization Techniques

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., cell gap = $7.5\text{ }\mu\text{m}$ for active area = 1 cm^2). The sample was filled into the cell in the isotropic phase. A digital oscilloscope (Yokogawa Elect., DL1640) 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 a triangular waveform voltage method under slowly cooling from the isotropic phase. The cell was placed between a crossed polarizer 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 measured the complex dielectric permittivity (detected by HP4192A) in the frequency range 10^3 – 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.

Results and Discussion

Spontaneous Polarization (P_s)

The switching behavior was observed in the SmCP phase of the studied compound **SB-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 160 Vpp at 60 Hz (see Fig. 1a). This is a strong indication of an antiferroelectric switching process. The temperature dependence of the magnitude of the P_s value for the compound **SB-F** obtained by integrating the area under the two peaks is shown in Fig. 1b and spontaneous polarization (P_s) was about 550 nC cm^{-2} at 120°C . It can be seen that the P_s is dependent on temperature for compound **SB-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

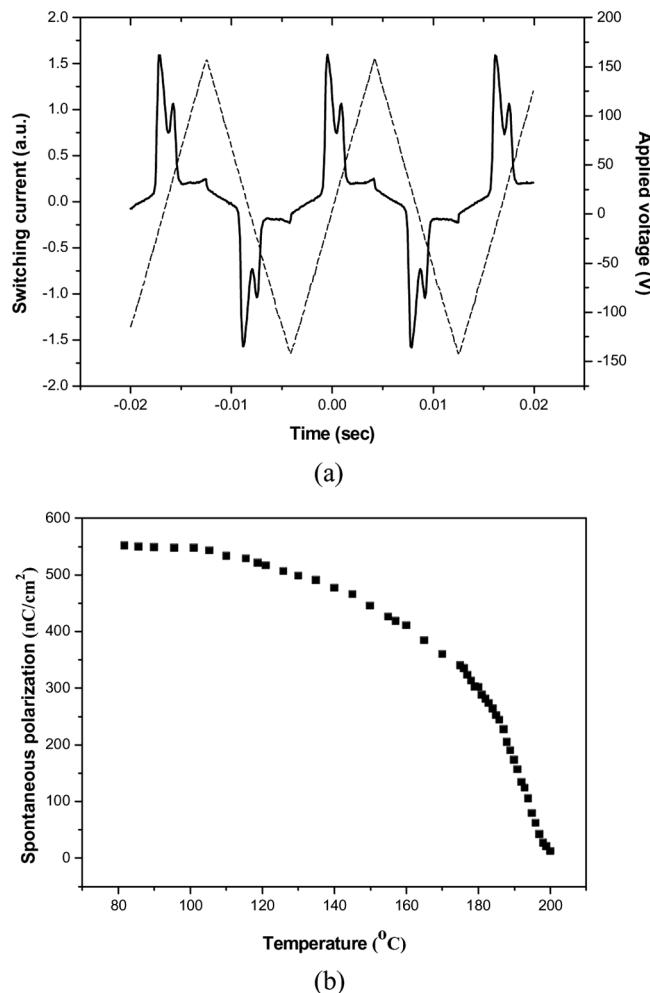


Figure 1. (a) Switching current response observed in the SmCP phase of compound **SB-F** at 120°C under the applied triangular wave voltage (7.5 μ m antiparallel rubbed polyimide-coated ITO cell, 160 Vpp, 60 Hz) and (b) spontaneous polarization (P_s) as a function of temperature.

transformation. The P_s value exhibits a maximum polarization of 615 nC cm^{-2} for compound **SB-H** at 115°C, 550 nC cm^{-2} for compound **SB-F** at 120°C, and 606 nC cm^{-2} for compound **SB-Cl** at 100°C. It appears that the spontaneous polarization is similar in the core containing the halogen substituent.

Tilt Angle

To study the tilt angle in the SmCP phase we carried out DC field experiments. A sample of compound **SB-F** was cooled slowly from the isotropic phase under a DC voltage of 100 Vpp. 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 was reversed, the

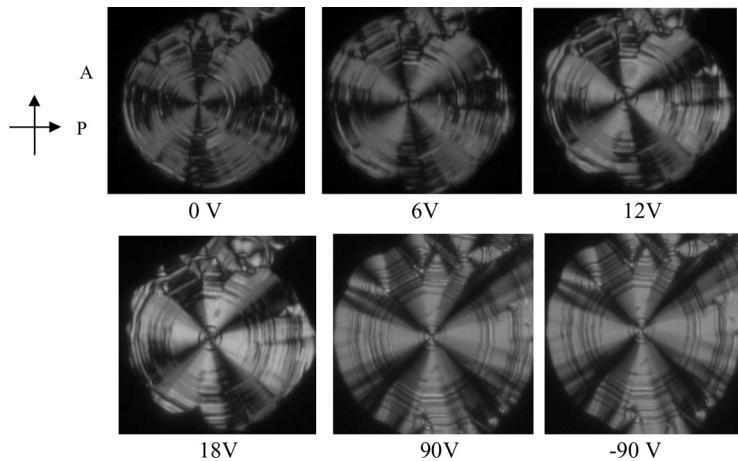


Figure 2. Polarizing optical micrographs of the circular domains in the SmCP phase for compound **SB-F** (on antiparallel rubbing direction LC cells with 7.5- μm thickness). Chiral domains obtained by various DC fields: 0 V ($\text{SmC}_\text{A}\text{P}_\text{A}$), 6, 12, 18, 90, and 90 V ($\text{SmC}_\text{S}\text{P}_\text{F}$) at 120°C in compound **SB-F**. (Arrows are the directions of polarizers and analyzers.)

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 anticlinic tilt in the antiferroelectric ground state ($\text{SmC}_\text{A}\text{P}_\text{A}$). As shown in Fig. 2, by applying electric fields with different voltages and 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 as in the off state. The angles between the extinction directions and the crossed polarizer positions are about 41° for ± 90 V at 120°C in compound **SB-F**,

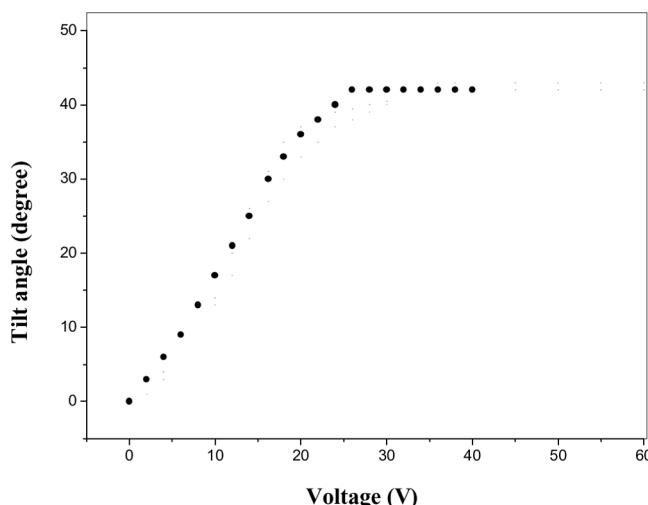


Figure 3. Tilt angle of the SmCP phase as a function of the DC electric fields in compound **SB-F** at 120°C (on antiparallel rubbing direction LC cells with 7.5- μm thickness).

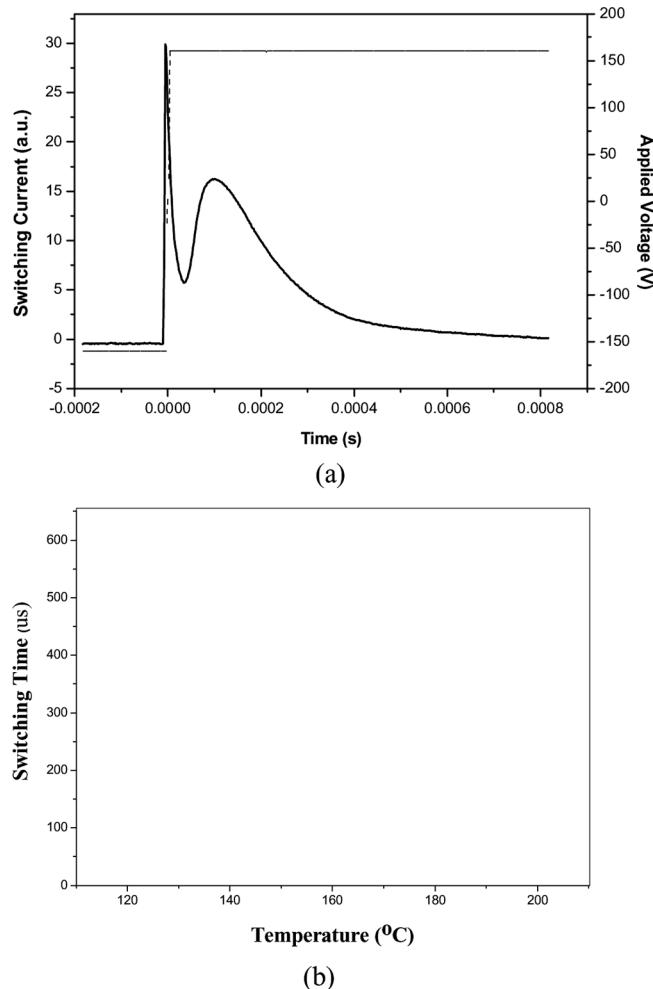


Figure 4. (a) The time dependences of the switching current under a square wave field for compound **SB-H** at 140°C and (b) switching time as a function of temperature for compound **SB-H** (on antiparallel rubbing direction LC cells with 7.5- μ m thickness as V_{pp} = 150 V, f = 10 Hz).

which corresponds to the optical tilt angle. The switching behavior of the extinction crosses of the domains rotated in opposite directions depending on the sign of the field, which is a characteristic field-responsive texture for chiral domains of the SmCP phase [9]. Furthermore, the switching process can be studied by measuring the tilt angle as a function of the applied DC electric field in the SmCP phase of compound **SB-F** (at 120° C), as shown in Fig. 3. The tilt angles are estimated from the rotating angles between the extinction brushes and crossed polarizer by applying electric fields, which indicates that the rotated phase structure from the anticlinic-antiferroelectric (Sm_C_AP_A) state to the synclinic-ferrelectric (Sm_C_SP_F) state occurred. The tilt angles of compound **SB-F** rise with increasing the applied voltage and saturate at the fields of 30–35 V. Thus, it can be demonstrated that the halogen-substituent materials have similar spontaneous polarization and tilt angles.

Switching Time

In order to investigate the dynamics of the polarization switching behavior, the switching currents of compound **SB-H** were measured with an applied square wave field (as $V_{pp} = 150$ V, $f = 10$ Hz) in the SmCP phase (at 140°C upon cooling from the isotropic phase). The switching current curves of compound **SB-H** at 140°C are shown in Fig. 4 a as a function of time. The switching time (τ) values are determined from the time elapsed between the appearance of the maximum of the current signal and the field reversal [10]. The switching time as a function of the temperature is shown in Fig. 4b 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 **SB-H** (in the range of 600 – 17 μs) was observed due to the viscosity decrease. The switching time values were measured at the temperature of $T_c - T = 15^\circ\text{C}$. Therefore, the order of switching time values regarding molecular design is as follows: without lateral substituent at the biphenyl core (17 μs) < fluoro-substituent at the biphenyl core (27 μs) < chloro-substituent at the biphenyl core (40 μs). The results show that switching time may be influenced by tilt angle and P_s , the decrease of the switching time with decreasing tilt angle, or increasing of the P_s .

Optical Transmission

Optical transmission studies were carried out in the SmCP phase of compound **SB-F** at 120°C by a triangular voltage wave ($V_{pp} = 60$ V, $f = 1$ Hz). The electric field dependence of the transmitted intensity of light is shown in Fig. 5. The switching process in transmittance exhibits a V-shaped like switching behavior (*i.e.*, highest transmittance at around 35 V) in compound **SB-F**; a similar phenomenon has also been observed in another bent-core structure [11]. This result should coincide with the previous tilt angle experiment of compound **SB-F**, where the highest transmittance around 35 V is due to the saturated tilt angle around 35 V (see Fig. 3).

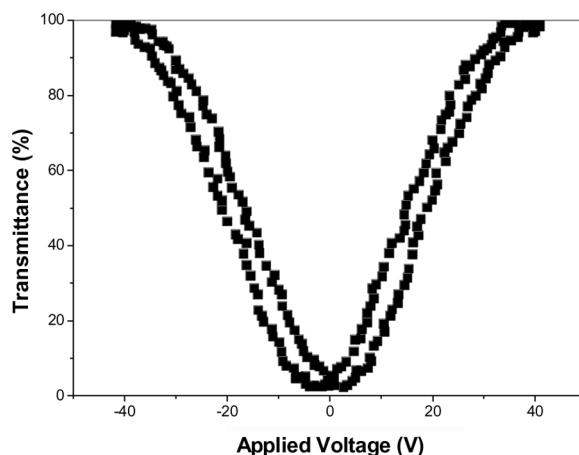


Figure 5. Transmittance versus applied voltage (triangular wave, $V_{pp} = 60$ V, $f = 1$ Hz) in the SmCP phase of compound **SB-F** at 120°C (on antiparallel rubbing direction LC cells with $7.5\text{-}\mu\text{m}$ thickness).

Dielectric Permittivity

Finally, we measured the complex dielectric permittivity in the frequency range 10^3 – 10^7 Hz for the planar-aligned (measuring field is normal to the director) sample on cooling at a rate of about 1°C min^{-1} , keeping the temperature of the sample stable during frequency sweeps. The temperature and frequency dependence of the dielectric constant [12] for compound **DB-H** are shown in Fig. 6a. The study of the dielectric behavior of compound **DB-H** by the Cole-Cole plot (ϵ'' versus ϵ') is practice. The Cole-Cole plot provides valuable information with regard to the

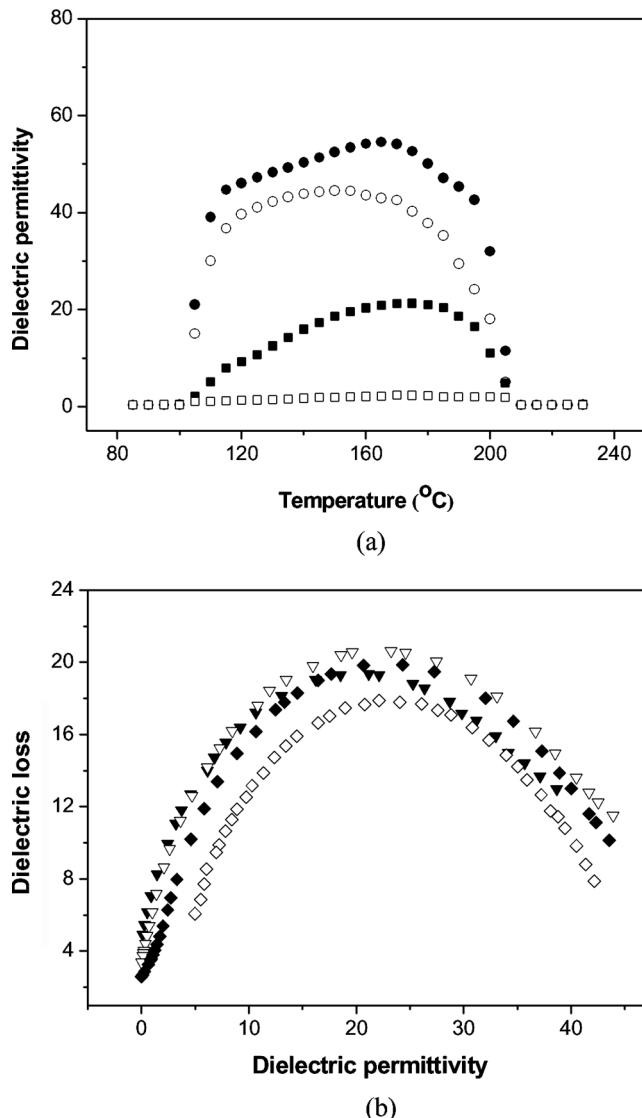


Figure 6. (a) Temperature dependence of the dielectric constant (ϵ') at 10^3 (●), 10^4 (○), 10^5 (■), and 10^6 (□) Hz for **SB-H**. (b) Cole-Cole plot of γ relaxation for **SB-H** at different temperatures: 170°C (▼), 150°C (▽), 130°C (◆), and 110°C (◊).

dielectric relaxation process. The Cole-Cole plots at various temperatures are shown in Fig. 6b for the γ relaxation of compound **DB-H**. The results show that the relaxation strength (diameter of the circle) is similar with increasing temperature. Figure 7a and 7b show the frequency dispersions of real and imaginary parts of dielectric constants, ϵ' and ϵ'' in the SmCP phase of compound **DB-H**. A relaxation mode was detected at about 200 kHz in Fig. 7a. A similar result has also been observed in another bent-core structure [13–15]. It was tentatively explained that

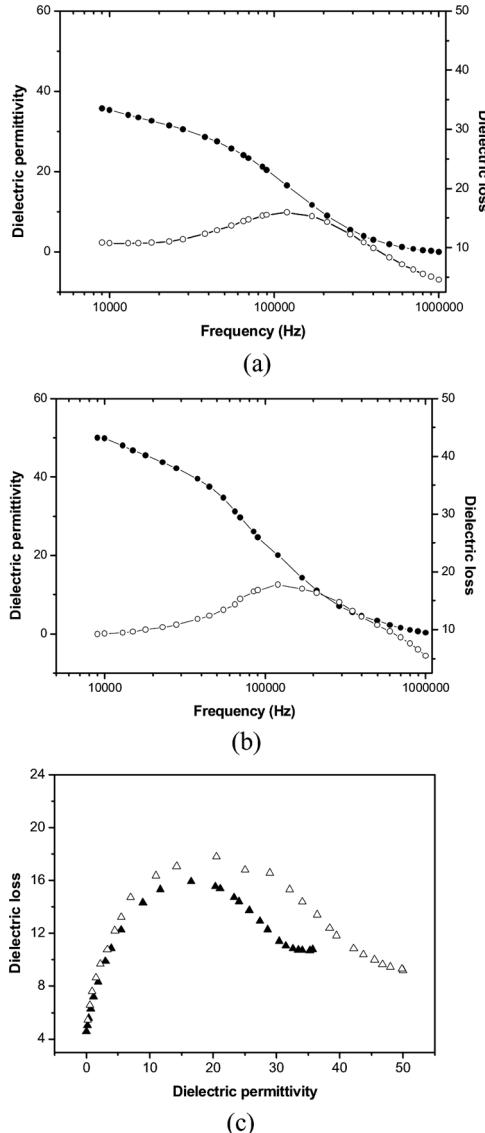


Figure 7. Frequency dispersions of real and imaginary parts of dielectric constants, ϵ' and ϵ'' (a) without a DC bias field and (b) under a 35 V DC bias field (relative dielectric permittivity (●) and the dielectric loss (○)) at $T_c-T=25^\circ\text{C}$. (c) Cole-Cole plots without a DC bias field and under a 35 V DC bias field in the SmCP phase of compound **SB-H** (no bias (▲), bias 35 V (△)).

the relaxation is due to the rotation around the molecular short axis [16]. The explanation was based on the untilted ferroelectric structure instead of the tilted antiferroelectric one. The results show the relaxation 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 [17]. In order to understand the relaxation mode in detail, a DC bias field was applied [18]. When a 35 V DC bias field was applied, the dielectric strength increased in Fig. 7b. The Cole-Cole diagrams are shown in Fig. 7c, from which the dielectric strength and the relaxation frequency were obtained. The enhanced dielectric strength is attributed to induced polarization by a DC bias field.

Conclusions

Electrical switching and molecular tilt angle as functions of temperature were investigated in the SmCP phase. The tilt angle of compound **SB-Cl** can reach 42° at low fields (40 V), and the switching times of all target compounds were very fast at 150 Vpp in the SmCP phase. We also observed the molecular switching behaviors for the V-shaped like switching LC cell by monitoring the optical anisotropy. Finally, we observed the relaxation process from the Cole–Cole plots.

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