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V-shaped switching in binary mixtures of an achiral swallow-tailed material with the antiferroelectric liquid crystal (*S*)-MHPOBC

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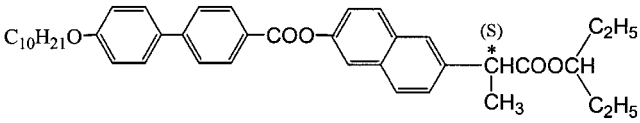
An achiral swallow-tailed material, 2-propylpentyl 4-(4′-decyloxybiphenyl-4-carbonyloxy)-benzoate, **p**, showing SmA and SmC_{alt} phases was prepared for mixing (by weight percentage) with an antiferroelectric liquid crystal, (*S*)-MHPOBC, **m**, for the study. The binary mixture **p**15/**m**85 using (*S*)-MHPOBC (85%) as a host doped with achiral material (15%) resulted in a phase sequence SmA–SmC*–SmC_A^*. The electro-optic response of this mixture in the ferroelectric SmC* phase displayed V-shaped switching, while that in the antiferroelectric SmC_A^* phase displayed a double hysteresis switching. The mixture **p**85/**m**15 possessed SmA* and SmC_A^* phases; V-shaped switching was found in the antiferroelectric SmC_A^* phase of this mixture. These optical phenomena implied that a binary mixture containing a larger amount of achiral swallow-tailed material and/or possessing relatively lower polarization favours the occurrence of V-shaped switching in the antiferroelectric phase. The results of this work also suggested that thresholdless V-shaped switching in chiral smectic liquid crystals can be achieved by mixing an achiral swallow-tailed material with an antiferroelectric liquid crystal.

1. Introduction

Thresholdless, V-shaped switching in chiral smectic liquid crystals [1] has become a very attractive subject for research due to the unique properties of these materials for display applications [1–8]. So far, only two mixtures (Inui and Mitsui mixtures) showing V-shaped switching properties have been reported [1, 2]. The components in the mixtures are generally derived from a homologous series of chiral tail groups with a highly polar trifluoromethyl substituent attached to the chiral centre. Consequently, the mixtures possess high polarization, e.g. the maximum $\mathbf{p}_s$ value for the Inui mixture is about 170 nC cm^{-2} [8].

Recently, Wu and Hsieh reported a novel chiral swallow-tailed compound, 1-ethylpropyl (*S*)-2-{6-[4-(4-decyloxyphenyl)benzoyloxy]-2-naphthyl}propionate, (*S*)-EP10PBNP, as sketched below, showing an antiferroelectric liquid crystal phase possessing thresholdless, V-shaped switching [9]. The material design was based primarily on a chiral molecule in which a methyl substituent at the chiral centre is attached close to the core of the molecule, in conjunction with a swallow-tailed group in the chiral tail. The antiferroelectric phase of this material was found to possess a relatively low polarization (maximum $\mathbf{p}_s = 30$ nC cm^{-2}) as compared with that reported for Inui and Mitsui mixtures. This suggests that V-shaped switching could also be obtained in other materials with low polarization in the antiferroelectric phase. Moreover, it has been shown that achiral materials with swallow-tailed terminal moieties encourage the formation of an 'antiferroelectric-like' phase, a so-called SmC_{alt} phase, and can be doped with small quantity of antiferroelectric liquid crystal to induce antiferroelectricity [10–12]. Therefore, we decided to investigate a binary mixture of an achiral swallow-tailed compound with an antiferroelectric liquid crystal, to explore V-shaped switching phenomena further.



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The achiral swallow-tailed compound 2-propylpentyl 4-(4′-decyloxybiphenyl-4-carbonyloxy)benzoate **p** was prepared, and a well known antiferroelectric liquid crystal,

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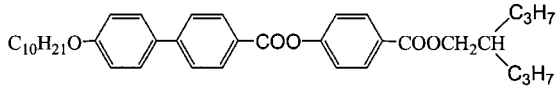
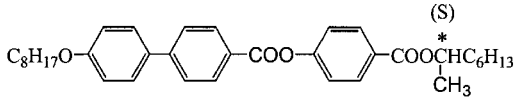
(*S*)-4-(1-methylheptyloxy)carbonylphenyl 4′-octyloxy-4-biphenylcarboxylate (*S*)-MHPOBC **m** was used for mixing with **p** for the investigation. The structures of both materials are shown below.

p 

m 

2. Experimental

2.1. *Characterization of the materials*

The chemical structures of the materials were analysed by nuclear magnetic resonance spectroscopy using a Jeol EX-400 FT-NMR spectrometer. The purity of the achiral material was checked by thin layer chromatography and further confirmed by elemental analysis using a Perkin-Elmer 2400 spectrometer.

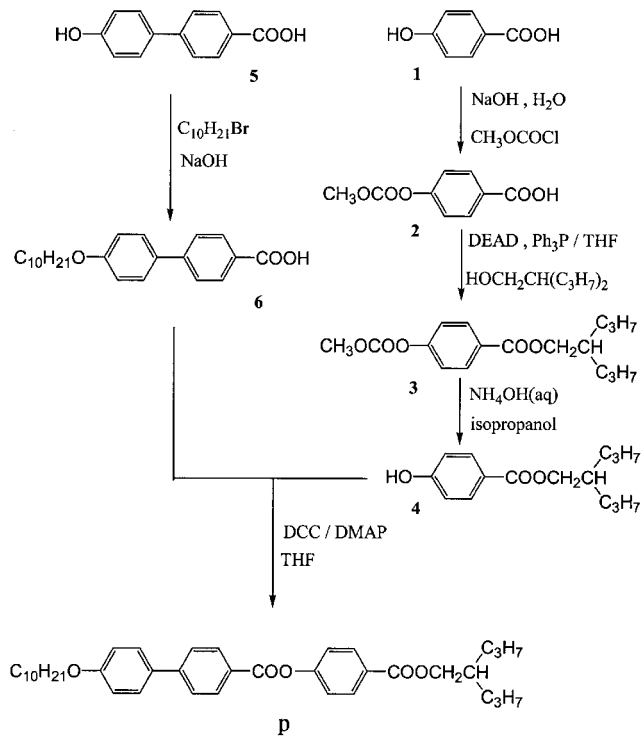
Mesophases of the achiral material and the mixtures were identified principally from microscopic textures of the materials sandwiched between two glass plates under a polarizing microscope using a Nikon Microphot-FXA in conjunction with an Instec HS1 heating stage. Transition temperatures and phase transition enthalpies were determined by differential scanning calorimetry using a Perkin-Elmer DSC7 calorimeter at heating/cooling rates of 1–20°C min^{-1}. The antiferroelectric phase of the mixtures was further characterized by switching behaviour and electro-optic response in homogeneous cells. The commercially available homogeneous cells coated with polyimide as alignment film were purchased from E. H. C. Co. Japan. The sample was filled into the cell by capillary action in the isotropic state. Two wires were then fixed separately to the ITO coated glass plates of the sample cell by silver paint.

The spontaneous polarization ($\mathbf{p}_s$) was measured by a triangular wave method [13]. A triangular waveform was applied to the sample from a Yogaw AG1200 arbitrary waveform generator. The induced current was displayed by the measuring the voltage across a wire-wound resistor using a Hewlett-Packard HP54502A digital storage oscilloscope.

The measurement of optical transmittance versus applied electric field was conducted by using a He-Ne laser (5 mW, 632.8 nm) as a probe beam [14, 15]. The optical transmittance of the probe beam passing through the cell between crossed polarizers, whose axes were parallel and perpendicular to the smectic layer normal, was detected by a photodiode. The signals were monitored by the digital oscilloscope (HP54502A). The voltage applied to the cell was produced by the arbitrary waveform generator (AG1200) and amplified by a homemade power preamplifier.

2.2. *Preparation of materials*

The achiral compound 2-propylpentyl 4-(4′-decyloxybiphenyl-4-carbonyloxy)benzoate **p** was synthesized as indicated in the scheme, according to the method described in [16]. Methy chloroformate was added to 4-hydroxybenzoic acid **1** in an aqueous sodium hydroxide solution to protect the hydroxy group, giving 4-methoxycarbonyloxybenzoic acid **2**. The acid **2** was then esterified with 2-propyl-1-pentanol by treatment with triphenylphosphine (Ph_3P) and diethylazodicarboxylate (DEAD) to generate 2-propylpentyl 4-methoxycarbonyloxybenzoate **3**. This benzoate compound **3** was converted to 2-propylpentyl 4-hydroxybenzoate **4** by the removal of protecting group with a solution of ammonia in isopropanol. Esterification of **4** with 4-(4-decyloxyphenyl)benzoic acid **6**, which was prepared previously by the Williamson synthesis involving 4′-hydroxybiphenyl-4-carboxylic acid **5** with 1-bromodecane, produced the target material **p**. Elemental analysis for $C_{38}H_{50}O_5$: calc. C 77.82, H 8.53, found C 77.58, H 8.52%. ^1H NMR ($CDCl_3$): δ (ppm) 0.87–1.55 (m, 34H, RCH_2CH_3), 1.77–1.8 (m, 1H, OCH_2CH), 4.0–4.03 (t, 2H, $ArOCH_2$), 4.22–4.23 (d, 2H, $COOCH_2$), 6.98–8.26 (m, 12H, ArH).



Scheme.

The antiferroelectric liquid crystal (*S*)-4-[(1-methylheptyloxyl)carbonyl]phenyl 4′-octyloxy-4-biphenylcarboxylate, (*S*)-MHPOBC **m**, with 99% purity was purchased from Aldrich, US, and used directly for preparing mixtures without further purification. The reported mesophase sequence is I(151.5°C)SmA(123.0°C)SmC* (121.0°C)SmC_A^*(73.5°C)Cr. More detailed mesophases have been well studied and reported as I(156.0°C) SmA(122.0°C)SmC_α^*(120.7.0°C)SmC_β^*(119.0°C)SmC_γ^* (118.3°C)SmC_A^*(66.0°C)SmI_A^*(30°C)Cr [18–23].

The mixtures were prepared by weight percentage and mixed thoroughly with the addition of anhydrous dichloromethane. The dichloromethane was then evaporated and the mixtures further dried under vacuum. The mixture of **p**15/**m**85 refers to the mixture of 85% **m** doped with 15% **p**, while that of **p**85/**m**15 refers to the mixture of 85% **p** doped with 15% **m**.

3. Results and discussion

The mesophases of the achiral swallow-tailed compound and the binary mixtures were primarily characterized by their microscopic textures. The achiral material exhibited SmA and SmC_{alt} phases. The SmA phase displayed a focal-conic texture. The SmC_{alt} phase was characterized by the appearance of a schlieren texture with the presence of a small number of two-brush and many four-brush singularities [12] as shown in circles and squares, respectively, in figure 1. The binary mixtures **p**15/**m**85 and **p**85/**m**15 gave phase sequences SmA*–SmC*–SmC_A^* and SmA*–SmC_A^*, respectively. The SmA* phase showed a focal-conic texture and the SmC* phase showed a broken focal-conic texture. The SmC_A^* phase displayed a striated focal-conic texture in the thicker sample region, and was further characterized by the schlieren texture with two-brush and four-brush singularities [23] in the thinner sample region. A representative schlieren texture obtained from mixture **p**85/**m**15 is shown in figure 2. The ferroelectric and antiferroelectric phases for the mixtures were further confirmed by the measurement of physical properties.

A calorimetric study indicated that the shape of the SmA–SmC_{alt} transition peak for the achiral material was clearly first order in nature, supporting the assignment of the SmC_{alt} phase [10, 12]. The SmA*–SmC_A^* transition peak for the mixture **p**85/**m**15 displayed a first order characteristic, and indicated the existence of the SmC_A^* phase. The SmA*–SmC* and SmC*–SmC_A^* transitions for the mixture **p**15/**m**85 showed second and weak first order characteristics, respectively. The phase sequence, transition temperatures and corresponding phase transition enthalpies of mesophases for the achiral material and the binary mixtures obtained by DSC are given in

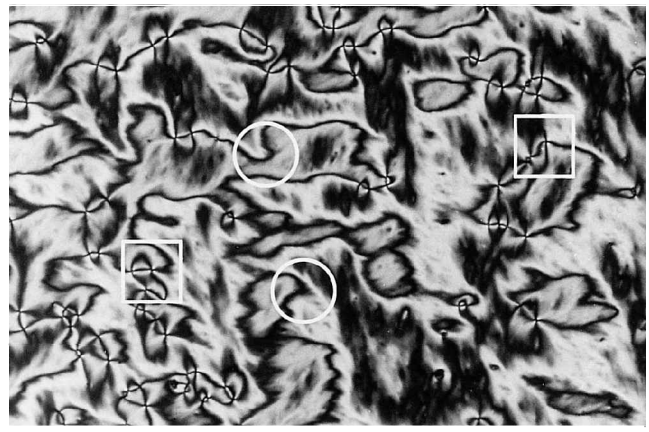


Figure 2. Schlieren texture of the SmC_A^* phase obtained from **p**85/**m**15 showing two- and four-brush singularities, as shown in circles and squares, respectively.

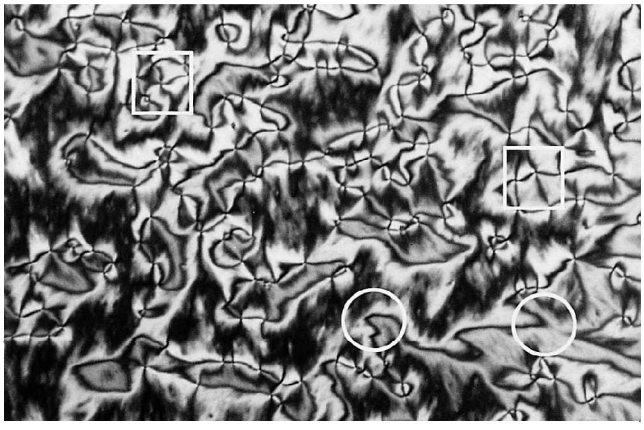


Figure 1. Schlieren texture of the SmC_{alt} phase obtained from the achiral swallow-tailed material **p** showing both two- and four-brush singularities, as shown in circles and squares, respectively.

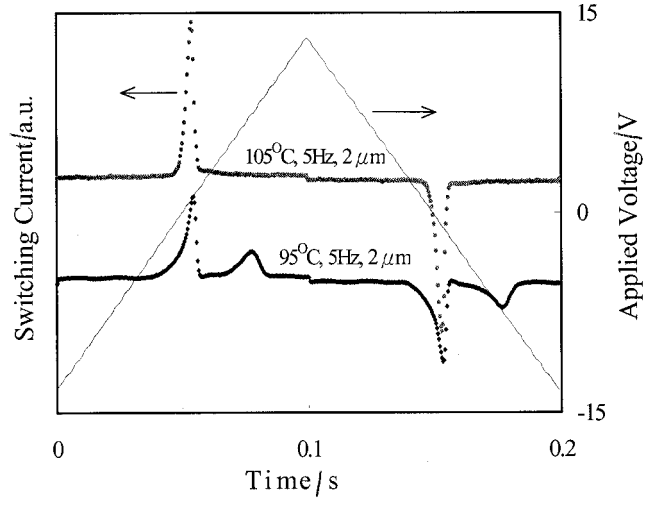


Figure 3. Switching behaviour of **p**15/**m**85 in the SmC* phase at 105°C and the SmC_A^* phase at 95°C.

the table. The thermal stability of the SmC* phase is enhanced in the mixture **p**15/**m**85 as compared with that of (*S*)-MHPOBC. The ferroelectric phase seems to be suppressed on increasing the amount of achiral material, as indicated in the mesophases on going from **p**15/**m**85 to **p**85/**m**15.

The switching current behaviour of **p**15/**m**85 in the SmC* and SmC_A^* phases were investigated in 2 μm homogeneous cells and are illustrated in figure 3. A single and sharp switching current peak, representing a switching between two ferroelectric states, appears in the whole temperature range of the SmC* phase. In the temperature range of the antiferroelectric phase, two current peaks appear as the characteristics of antiferroelectric–ferroelectric switching among three states, i.e. one stable antiferroelectric state in the absence of an applied electric field and two field-induced ferroelectric states. The switching behaviour of **p**85/**m**15 in the SmC_A^* phase, as shown in figure 4, displays two current peaks which are slightly overlapped.

The magnitudes of spontaneous polarization for both mixtures were measured as a function of temperature on cooling in 2 μm homogeneous cells and are illustrated in figure 5. It is seen that the spontaneous polarization increases with decreasing temperature, and the mixture **p**15/**m**85 containing the larger amount of (*S*)-MHPOBC

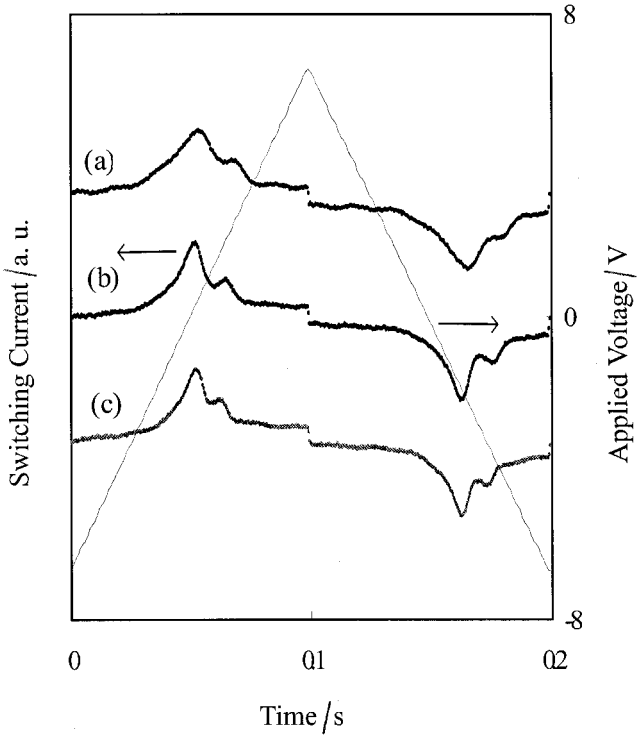


Figure 4. Switching behaviour of **p**85/**m**15 in the SmC_A^* phase at several temperatures: (*a*) 70°C, (*b*) 90°C, (*c*) 100°C.

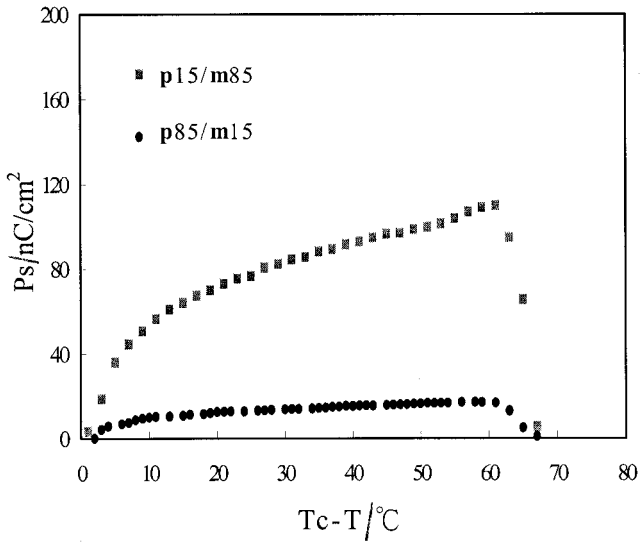


Figure 5. Spontaneous polarization plotted as a function of temperature for the binary mixture **p**15/**m**85 and **p**85/**m**15.

Table. The transition temperatures and associated enthalpy data for the achiral swallow-tailed material and binary mixtures.

	Transition temperature/°C[a]											
Code	I		SmA			SmC/SmC*		SmC_{alt}/SmC_A^*			Cr	m.p.[b]
p	•	136.9 [9.9][c]	•			—		116.2 [1.4]	•	60.4 [68.3]	•	94.8 [85.8]
p85/**m**15	•	140.3 [12.5]	•			—		119.2 [1.8]	•	49.9 [52.44]	•	87.0 [62.2]
p15/**m**85	•	148.8 [15.66]	•	124.3[d] [e]		•		100.2[d] [e]	•	59.2 [3.62]	•	80.6 [54.9]

[a] Recorded by DSC thermograms at cooling rates of 5°C min^{-1}.
[b] The m.p. refers to the melting point taken from DSC thermograms recorded at a heating rate of 5°C min^{-1}.
[c] Figures in square parenthesis denote enthalpies in J g^{-1}.
[d] The transition temperature was obtained by switching current measurement.
[e] The enthalpy was too small to be measured by DSC.

displays a higher polarization. The maximum $\mathbf{p}_s$ value in mixture **p**85/**m**15 is approximately 17 nC cm^{-2}; that in mixture **p**15/**m**85 is approximately 110 nC cm^{-2}.

Optical transmittance versus electric field was measured for both mixtures in 5 µm homogeneous cells at various frequencies of applied triangular waveform. Some representative results are presented in figures 6–8. The electro-optic response of **p**15/**m**85 at 1 Hz applied frequency, as presented in figure 6, shows a slight hysteresis at the V-shape tip appearing like W-shaped switching as indicated with arrows for the switching directions; this appears in the SmC* phase, whereas a double hysteresis switching appears in the antiferroelectric SmC_A^* phase. The maximum value of optical

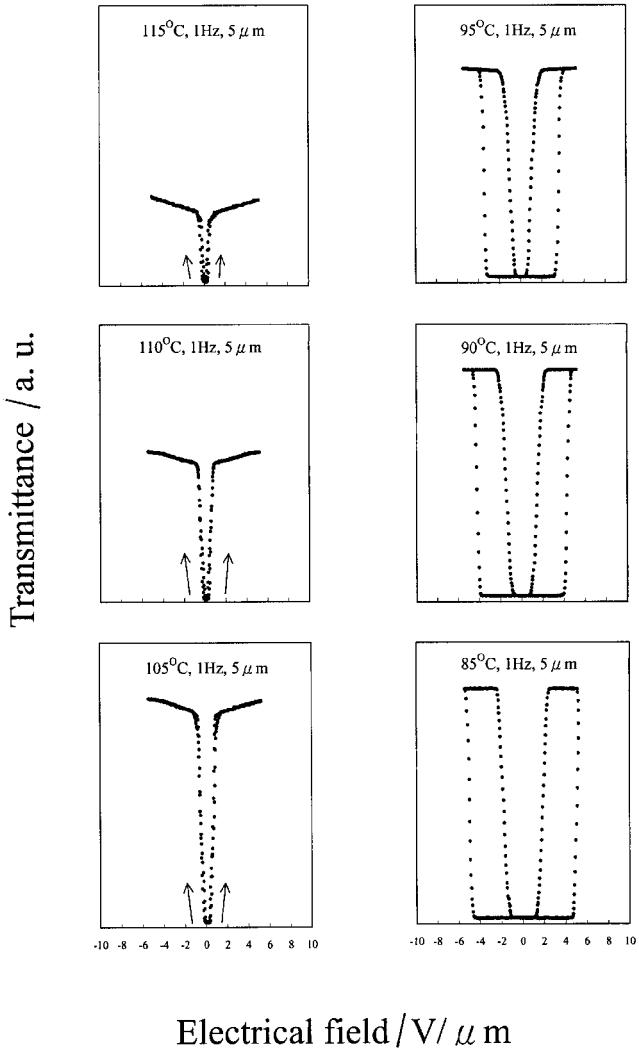


Figure 6. Optical transmittance versus electric field for **p**15/**m**85 in a 5 µm homogeneous cell on application of a 1 Hz triangular waveform at 115, 110 and 105°C of the SmC* phase, and at 95, 90 and 85°C of the SmC_A^* phase. The arrows indicate the directions of W-shaped switching.

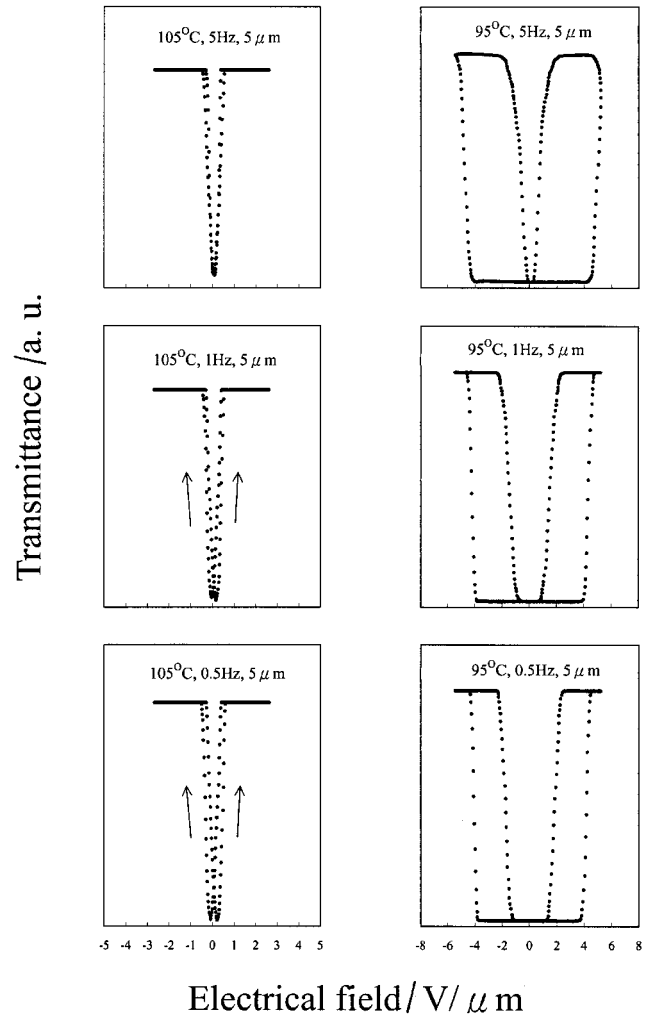


Figure 7. Optical transmittance versus electric field for **p**15/**m**85 in a 5 µm homogeneous cell at various frequencies of the applied triangular waveform at 105°C in the SmC* phase and 95°C in the SmC_A^* phase. The arrows indicate the switching directions of W-shaped switching.

transmittance in V-shaped switching significantly increases with decreasing temperature in the SmC* phase due to the increasing tilt angle [6]. This hysteresis and W-shaped switching in the SmC* phase can be confined to a V-shaped switching as indicated in figure 7 at 5 Hz of applied frequency. As the frequency decreases from 5 to 0.5 Hz, V-shaped switching in the SmC* phase alters to W-shaped switching, but double hysteresis switching in the SmC_A^* phase remains, although the width of the hysteresis becomes narrower.

The electro-optical response of **p**85/**m**15 at 1 Hz applied frequency, as presented in figure 8, shows V-shaped switching in the vicinity of the SmA*–SmC_A^* phase transition temperature. This is followed by the

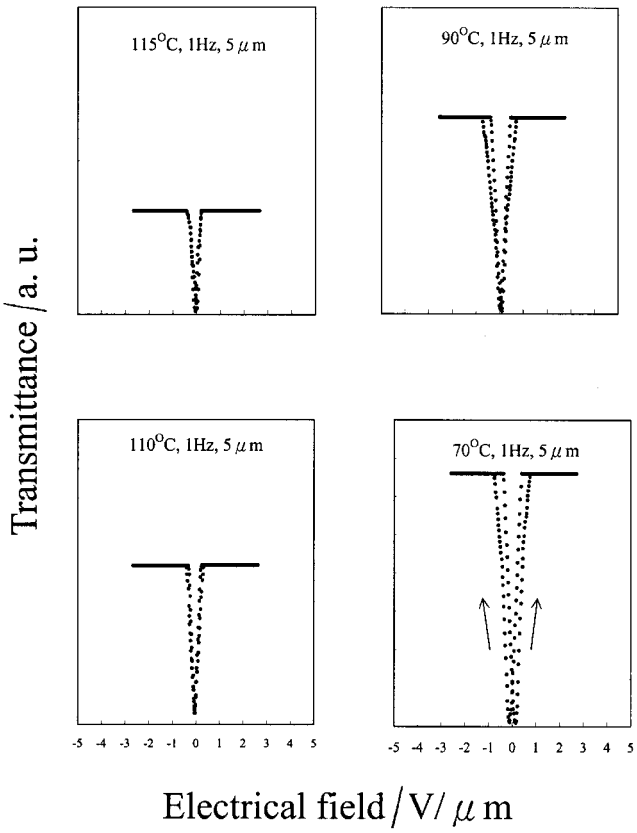


Figure 8. Optical transmittance versus electric field for **p**85/**m**15 in a 5 μm homogeneous cell on application of a 1 Hz frequency triangular waveform at several temperatures of the SmC_A^* phase. The arrows indicate the directions of W-shaped switching.

appearance of a hysteresis and W-shaped switching at lower temperatures. However, it is worth pointing out again that this hysteresis and W-shaped switching may be confined to V-shaped switching by changing the applied frequency and/or the thickness of the homogeneous cell.

These optical phenomena suggest that an antiferroelectric liquid crystal mixture using an achiral swallow-tailed material as a host, doped with (*S*)-MHPOBC, favours the formation of V-shaped switching in the SmC_A^* phase. In other words, the larger amount of achiral swallow-tailed material in the mixture encourages the formation of V-shaped switching. Moreover, the relatively low polarization of mixture **p**85/**m**15 as compared with that of **p**15/**m**85 also implies that an antiferroelectric mixture with lower polarization more easily gives V-shaped switching. This phenomenon is in agreement with our previous observation of V-shaped switching in an antiferroelectric liquid crystal (*S*)-EP10PBNP which contains a swallow-tailed group in the chiral tail and possesses low polarization (maximum $\mathbf{p}_s = 30\ \mathrm{nC\,cm^{-1}}$). However, the reasons that V-shaped switching is affected by either an achiral swallow tailed material or the polarization of a mixture, or both, are not clear at present.

4. Conclusion

Our results demonstrate that thresholdless, V-shaped switching in ferroelectric and antiferroelectric liquid crystals can be achieved by mixing an achiral swallow-tailed material with ferroelectric and antiferroelectric liquid crystals. We hope this finding may provide a new way of assessing the nature of V-shaped switching, and a new method of formulating chiral smectic liquid crystal mixtures possessing thresholdless, V-shaped switching for display application.

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