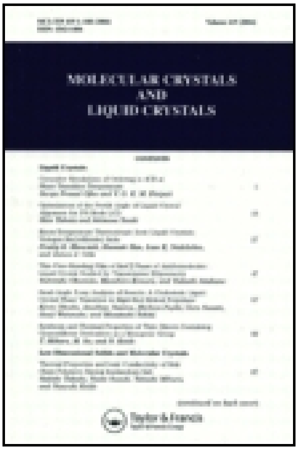

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Phase Diagrams and Electro-Optical Properties of Novel Ferroelectric Mixtures

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Phase Diagrams and Electro-Optical Properties of Novel Ferroelectric Mixtures

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Two binary mixtures were prepared, based on three members of the homologous series of 4-*n*-alkoxyphenyl esters of the 4′-*n*-alkoxybenzoic acids. Three structurally different chiral compounds were used to make novel ternary and four-component mixtures with chiral smectic *C* phase. The phase diagrams of two-component, the ternary and four-component mixtures are presented and the corresponding physical and electro-optical properties such as spontaneous polarization, tilt angle and switching time are discussed. Spontaneous polarization values up to 200 nC/cm^2 were found and two distinct modes of electro-optical switching, associated with different stages of helix distortion, were observed.

Keywords: Ferroelectric mixtures; spontaneous polarization; tilt angle; switching time; helix distortion

INTRODUCTION

Ferroelectric materials used in displays and display related research must posses a well defined set of physical and physicochemical properties [1]. These are as follows: high chemical stability, wide temperature range of the chiral smectic *C* (S_C^*) phase, appropriate value of spontaneous polarization (P_S), low viscosity, a phase sequence $S_C^* \rightarrow S_A^* \rightarrow N^* \rightarrow I$ to facilitate alignment, etc. Mixing of different compounds is a useful method for making novel type of liquid crystal materials with the required thermochemical and physical properties. The aim of this work is to describe the preparation of some ferroelectric mixtures with chiral smectic *C* phase in the temperature range from 20 °C to 80 °C. The corresponding physical and electro-optical properties such as spontaneous polarization, tilt angle and switching time are also described.

2. PHASE DIAGRAMS

2.1. Experimental Technique

The textures of liquid crystal mixtures were observed in thin film form between glass slides using polarized light with crossed polarizers. The phase transition temperatures were measured by polarizing microscopy and scanning calorimetry. Microscopic observations of the textures and phase transition temperatures together with miscibility studies were carried out using an Amplival pol-u polarizing microscope equipped with a Boetius hot stage.

2.2. Results

Table I summarizes the formulae and transition temperatures (in °C) of compounds used for miscibility and phase diagram studies.

The 4-*n*-alkoxyphenyl 4′-*n*-alkoxybenzoates are well known achiral materials which strongly favour smectic *C* properties [2].

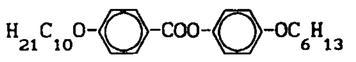
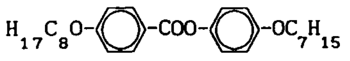
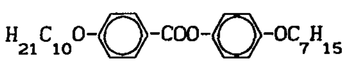
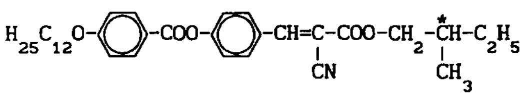
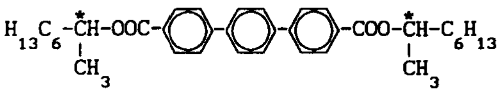
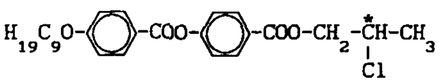
The phase diagram of two members of this homologoues series, 4-*n*-hexyloxyphenyl-4′-*n*-decyloxybenzoate (compound 1, see Tab. I) and 4-*n*-heptyloxyphenyl-4′-*n*-octyloxybenzoate (compound 2) is shown in Figure 1.

The eutectic concentration of these compounds was used as a *basic mixture A* for further measurements. It has the following phase sequence:

$$\mathrm{Cr}(S_B 33)\ 43\ S_C\ 74\ S_A\ 79\ N\ 87\ I$$

The phase diagram of another combination of the same homologous series, 4-*n*-heptyloxyphenyl 4′-*n*-octyloxybenzoate (compound 2) and 4-*n*-heptyloxy- phenyl 4′-*n*-decyloxybenzoate (compound 3), is shown in Figure 2. It can be seen that if a mixture is needed without the monotropic S_B (S_B) phase, concentrations around the eutectic mixture have to be avoided. In spite of this, the eutectic mixture from this phase diagram was used as a

TABLE I

Compound	*Structural formula*	*Phase sequence*
1		*Cr* (S_B 45) 62 S_C 77 S_A 83 *N* 89 *I*
2		*Cr* 62 S_C 69 *N* 88 *I*
3		*Cr* 67 S_C 79 S_A 82 *N* 89 *I*
4		*Cr* (S_C^* 76) 82 S_A^* 90 *I*
5		*Cr* 82 *I*
6		*Cr* 52 S_A^* 69 *I*

basic mixture B. It has the following phase sequence:

$$Cr(S_B\ 33)\ 51\ S_C\ 76\ S_A\ 78\ N\ 89\ I$$

While the single compounds 2 and 3 do not have any other smectic phase below the S_C phase their mixtures have induced (S_B) phase, in the vicinity of the eutectic concentration.

The ferroelectric α-cyano-4-(2′-methylbutyl) cinnamate ester of 4′-*n*-dodecyloxy-benzoic acid (compound 4) was used as a third component to transform *basic mixture A* to a ferroelectric mixture. Compound 4 does not have any *N** phase therefore it starts to destabilize the *N** phase in the mixture. The *N** phase disappears at 30 wt% of compound 4 as shown in

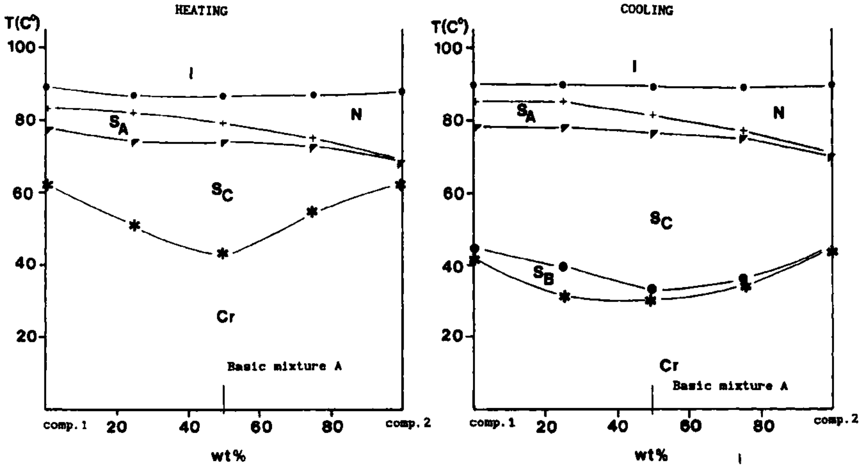


FIGURE 1 Phase diagram of binary mixture (wt%) composed of compound 1 and compound 2.

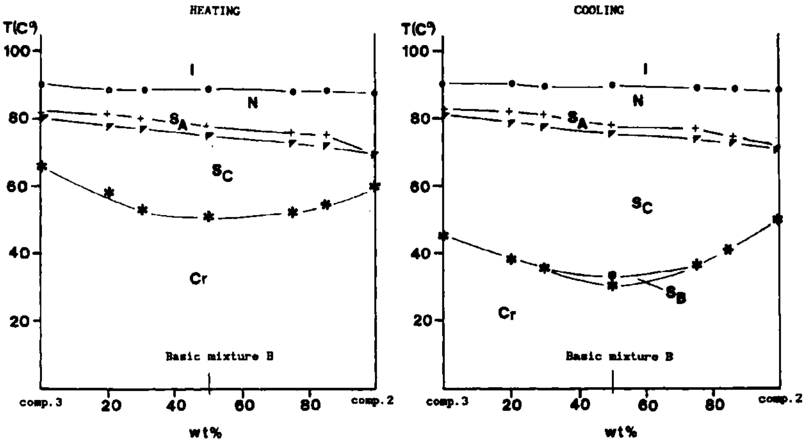


FIGURE 2 Phase diagram of binary mixture (wt%) composed of compound 3 and compound 2.

Figure 3. On the other hand, compound 4 has a monotropic chiral smectic C (S_C^*) phase. When compound 4 is mixed with *basic mixture A* a stabilization of the previously monotropic S_C^* phase can be observed and, in the concentration range above 50 wt% of *basic mixture A*, the (S_C^*) phase becomes enantiotropic. This is because *basic mixture A* has an enantiotropic Sc phase. It is also seen from the phase diagram (Fig. 3) that mixtures do not have any monotropic S_B phases. For further studies the special ternary

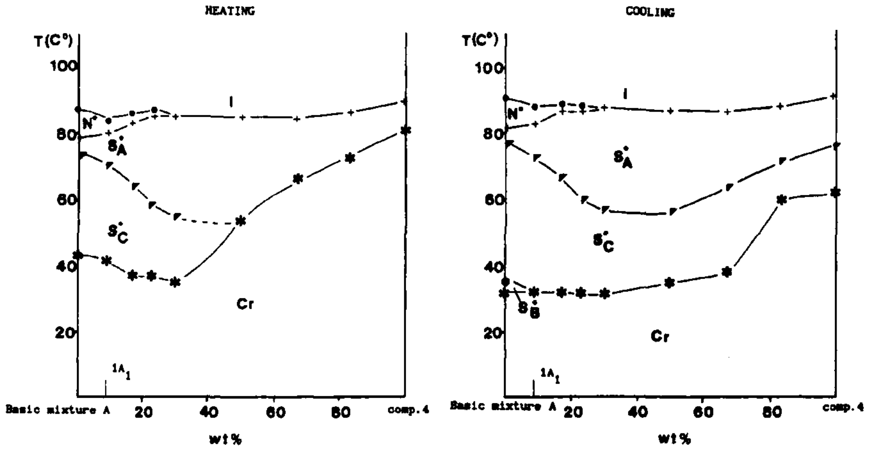


FIGURE 3 Phase diagram of ternary mixture (wt%) composed of *basic mixture 1* and compound 4.

composition $1A_1$ (marked in Fig. 3) where the S_C^* phase has the widest temperature range was selected.

The next chiral additive is the bis (R)-(1-methylheptyl)-1, 1′-4′1″-terphenyl-1, 4″-dicarboxylate (compound 5) which does not exhibit any liquid crystalline phase [3]. Compound 5 was used as a chiral additive to *basic mixture A* and its phase diagram is shown in Figure 4. Compound 5 has a stabilizing effect on the S_C^* phase in mixtures [1]. Introduction of compound 5 instead of compound 4 into *basic mixture A* leads not only to the stabilization of N^* phase but the S_C^* phase as well, as seen in Figure 4. The special composition $1A_2$(marked in Fig. 4) shows a much larger supercooling than for composition $1A_1$ (see Fig. 3). It is also seen that the terphenyl derivative (compound 5) results in a mixture with wider chiral S_C^* phase.The phase transition temperatures for $1A_1$ and $1A_2$ are summarized in Table II.

A similar phase transition behaviour was observed by introducing compound 5 either into *basic mixture A* or *B* and thus obtaining the mixtures $1A_2$ and $1B_c$ (compare Fig. 4 with Fig. 5). The shapes of the curves in the phase diagrams are similar except that the N^* phase disappeared at 38.3 wt% of compound 5 (Fig. 5). We did not increase the concentration of compound 5 higher than 34 wt% because the lack of N^* phase usually makes the alignment of the samples more difficult.

We have also introduced the (R)-(2-chloropropyl)4-[4′-(*n*-nonyloxy) benzoyloxy] benzoate (compound 6) [4] into the *ternary mixture* $1B_A$ with increasing concentrations and thus producing the mixture $3B_A$ (see Tab. II). This material has a larger dipole moment and therefore might change the

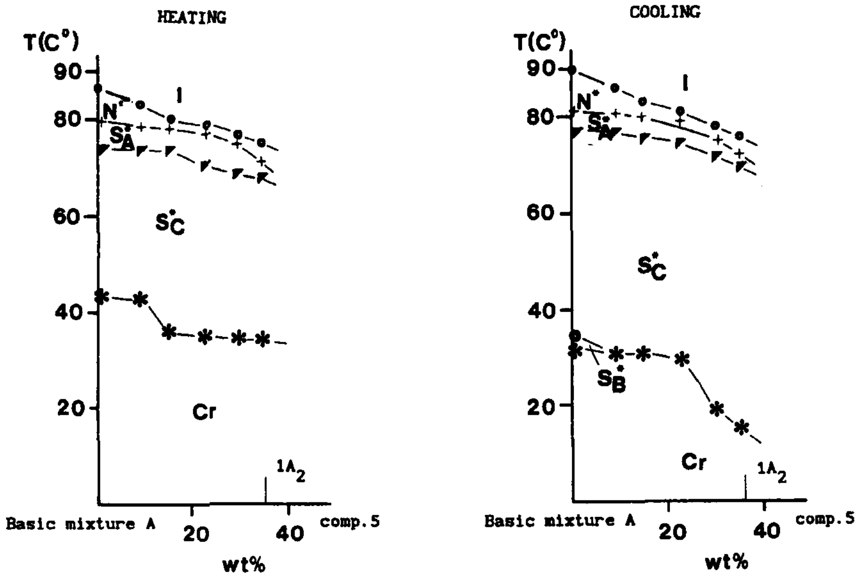


FIGURE 4 Phase diagram of ternary mixture (wt%) composed of *basic mixture 1* and compound 5.

value of spontaneous polarization. On the other hand, due the presence of chlorine atom the viscosity of the ferroelectric mixture should decrease. Although compound 6 has only S_A^* phase, the four-component *mixture* $3B_A$ has an enantiotropic S_C^* phase in a wide enough temperature range below S_A^* phase (Fig. 6).

In order to study further the effect of adding compound 6 to the ferroelectric mixtures, ternary mixture $1B_B$ was also selected and mixed with this compound producing the new four-component mixture of $3B_B$. The comparison of phase diagrams in Figure 6 and Figure 7 shows that mixture $3B_B$ has a wider range of S_C^* phase than mixture $3B_A$ (see Tab. II) and therefore $3B_B$ provides a more suitable material for physical measurements because of the existence of its N^* phase.

3. PHYSICAL PROPERTIES

We studied the physical properties of a number of mixtures in the $1B_C$; $1B_D$; $2B$; $3B_C$.

The experiments were carried out on samples sandwiched between indium tin-oxide coated glasses. The thicknesses of the cells were varied between 7

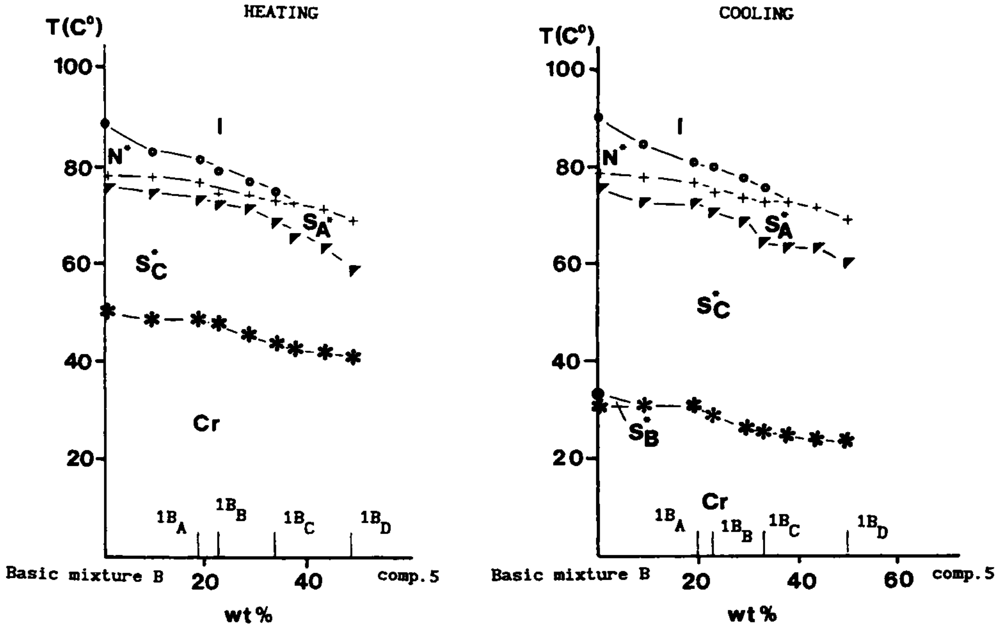


FIGURE 5 Phase diagram of ternary mixture (wt%) composed of *basic mixture 2* and compound 5.

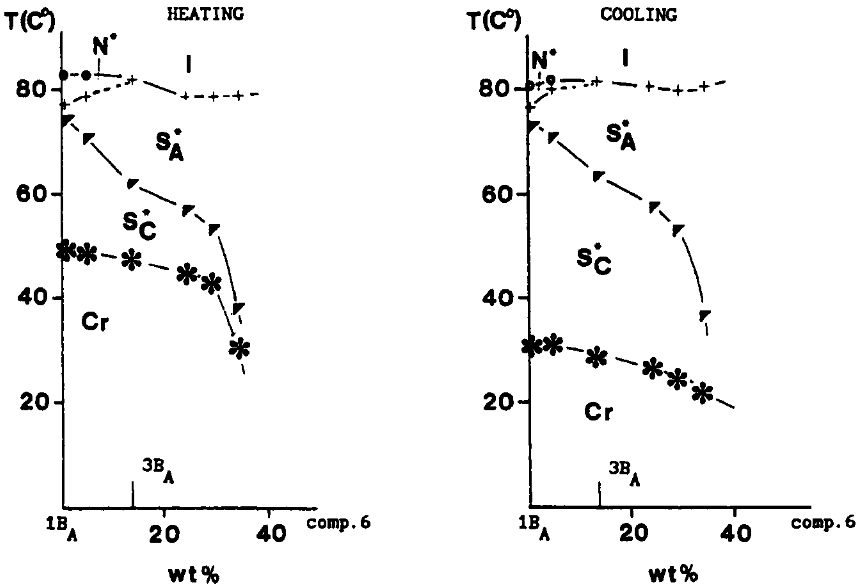


FIGURE 6 Phase diagram of four-component mixture (wt%) composed of ternary mixture ($1B_A$) and compound 6.

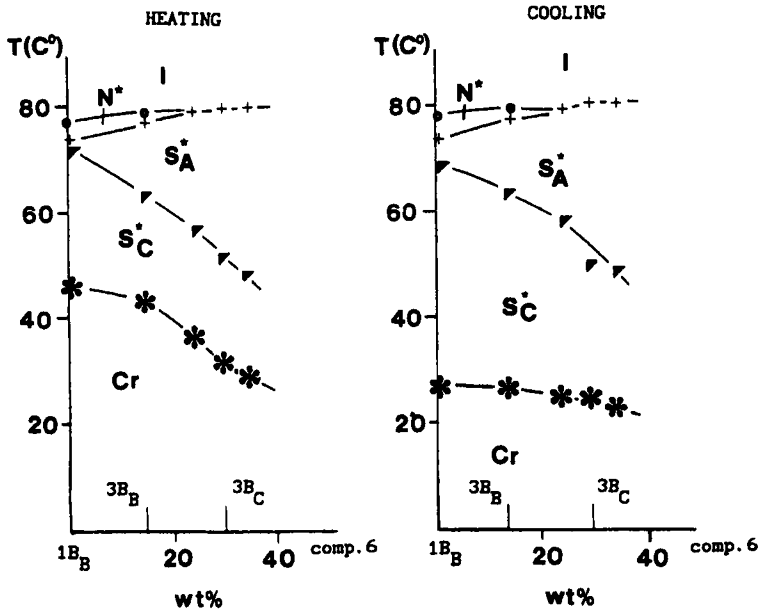


FIGURE 7 Phase diagram of four-component mixture (wt%) composed of ternary mixture ($1B_B$) and compound 6.

TABLE II

	Two-Component Mixtures	
Basic mixture A:	comp. 1, 2	(50:50 wt%) Cr (S_B 33) 43 S_C 74 S_A 79 N 87 I
Basic mixture B:	comp. 2, 3	(50:50 wt%) Cr (S_B 33) 51 S_C 76 S_A 78 N 89 I
	Ternary mixtures	
Mixture $1A_1$:	comp. 1,2,4	(45.4:45.4:9.2 wt%) Cr 41 S_C^* 70 S_A^* 80 N^* 85 I
Mixture $1A_2$:	comp. 1,2,5	(32.7:32.7:35.6 wt%) Cr 35 S_C^* 68 S_A^* 71 N^* 75 I
Mixture $1B_A$:	comp. 2,3,5	(40.2:39.8:20.0 wt%) Cr 49 S_C^* 74 S_A^* 77 N^* 82 I
Mixture $1B_B$:	comp. 2,3,5	(38.4:38.4:23.2 wt%) Cr 48 S_C^* 73 S_A^* 75 N^* 79 I
Mixture $1B_C$:	comp. 2,3,5	(33.0:33.0:34 wt%) Cr 44 S_C^* 69 S_A^* 73 N^* 75 I
Mixture $1B_D$:	comp. 2,3,5	(25.1:25.9:49 wt%) Cr 42 S_C^* 59 S_A^* 69 I
Mixture 2B:	comp. 2,3,6	(43.5:43.5:13.0 wt%) Cr (S_C^* 45) 47 S_A^* 83 N^* 87 I
	Four-component mixtures	
Mixture $3B_A$:	comp. 2,3,5,6	(35.6:35.9:14.9:13.6 wt%) Cr 48 S_C^* 62 S_A^* 82 I
Mixture $3B_B$:	comp. 2,3,5,6	(33.6:33.3:20.1:13.0 wt%) Cr 43 S_C^* 63 S_A^* 78 N^* 79.5 I
Mixture $3B_C$:	comp. 2,3,5,6	(29.1:29.1:18.2:23.6) Cr 36 S_C^* 57 S_A^* 78 I

and 15 μm. The spontaneous polarization was deduced from transient current measurements, following the triangular wave method described by Patel and Goodby [5]. The tilt angle was determined from observations of the extinction directions in the presence of strong positive and negative applied voltages [5].

The mixtures containing a large amount of compound 5 ($1B_C$ and $1B_D$) showed selective reflection in the visible range of light. This fact indicates that the pitch is of the order of 0.2–0.4 μm in these materials. Partial substitution of compound 5 with compound 6 (Mixture $3B_C$), led to a large increase of the pitch. The stripes characterising the helical structure became directly observable in a polarising microscope; from their separation the pitch was estimated to be around 5 μm.

In the relatively thick electro-optical cells used in our experiments, the short-pitch mixtures ($1B_C$ and $1B_D$) formed a more or less undistorted helical structure (selective reflection was observable). The unwinding of the helix by an applied field occured in two distinct steps. At low voltages, the selective reflection gradually disappeared, but in a polarising microscope no dramatic change of the texture could be seen. At this stage the helix was distorted, but the periodic structure was still present. At a threshold field, a *discontinuous* texture change was observed, corresponding to a transition to a homogenous, completely unwound structure. A similar phenomenon was described by Beresnev *et al.*, in another ferroelectric mixture [6]. These authors attribute the effect to a domain structure of the material.

The discontinuity of the process is demonstrated in Figure 8 where the area below the transient current peak is shown as a function of the applied voltage. The transition takes place at 3.2 V; above this value the area is constant and can be considered as a measure of the spontaneous polarisation of the material. In this range the tilt angle could also be measured.

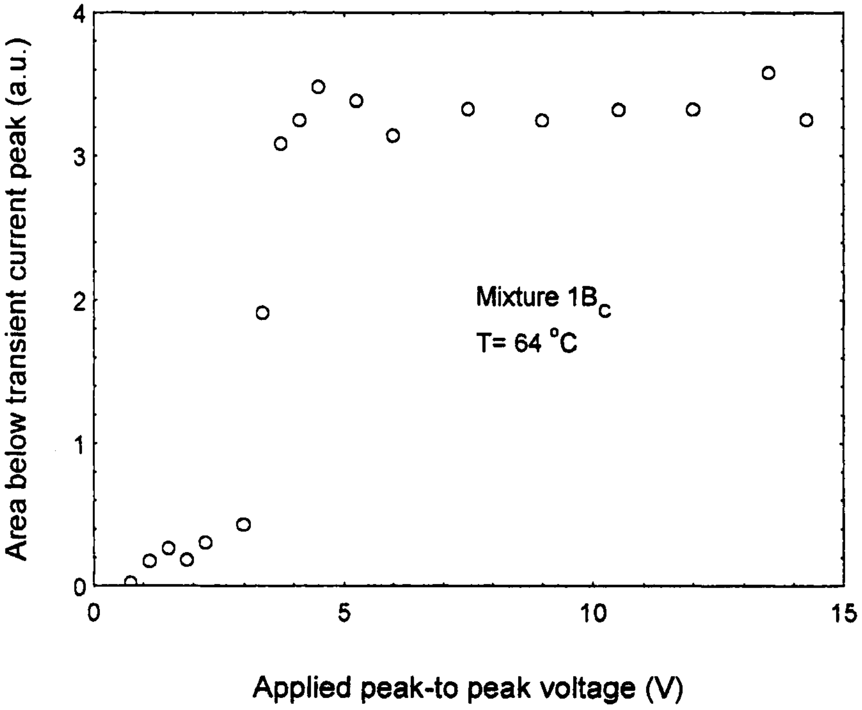


FIGURE 8 The area below the transient current peak as a function of the peak-to-peak amplitude of the applied triangular voltage.

The spontaneous polarization (P_S) and the tilt angle (θ) as a function of the temperature for $1B_C$ and $1B_D$ are shown in Figures 9 and 10 respectively. In the case of $1B_C$, P_S and θ go to zero continuously as the S_A^* phase is approached, indicating a second order phase transition. The temperature dependence of the spontaneous polarization is proportional to $(T_{AC} - T)^{1/2}$ where T_{AC} is the smectic A-C phase transition temperature (see the fitted curve in Fig. 9), corresponding to a mean-field behaviour. For $1B_D$, the decrease of these quantities were observed in the S_C^* phase, but isotropic droplets formed before their value had reached zero.

It is interesting to note that the value of spontaneous polarization and the tilt angle is almost the same for $1B_C$ and $1B_D$, although the latter contains considerably more of the chiral dopant. Such a "saturation" effect has been described earlier by Loseva *et al.* [3].

Mixture $3B_C$, in which compound 5 is partially replaced by compound 6, exhibits a much smaller spontaneous polarization than $1B_C$ or $1B_D$ (Fig. 9). In mixture $2B$, where compound 6 was the only chiral component, P_S turned out to be even lower; in fact, our apparatus was not sensitive enough to get reliable values of it.

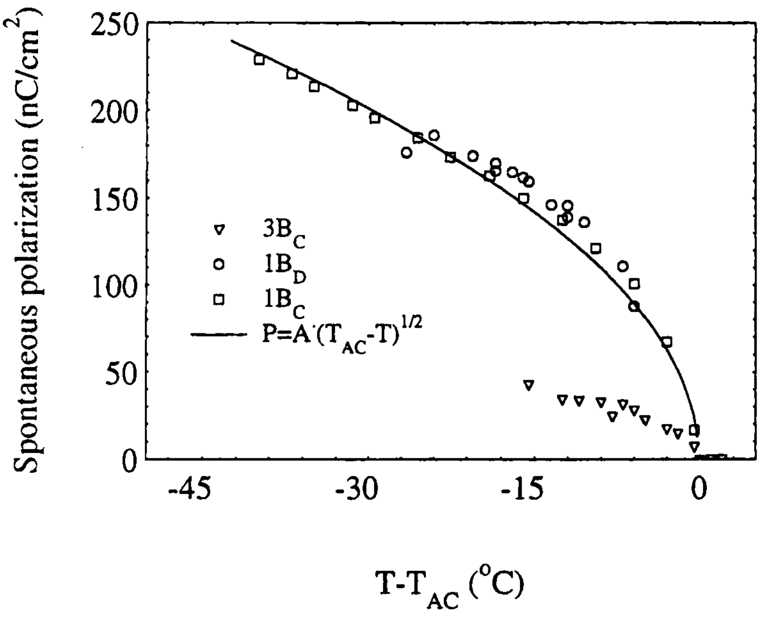


FIGURE 9 Spontaneous polarization as a function of the temperature for three mixtures. The fitted curve refers to mixture $1B_C$.

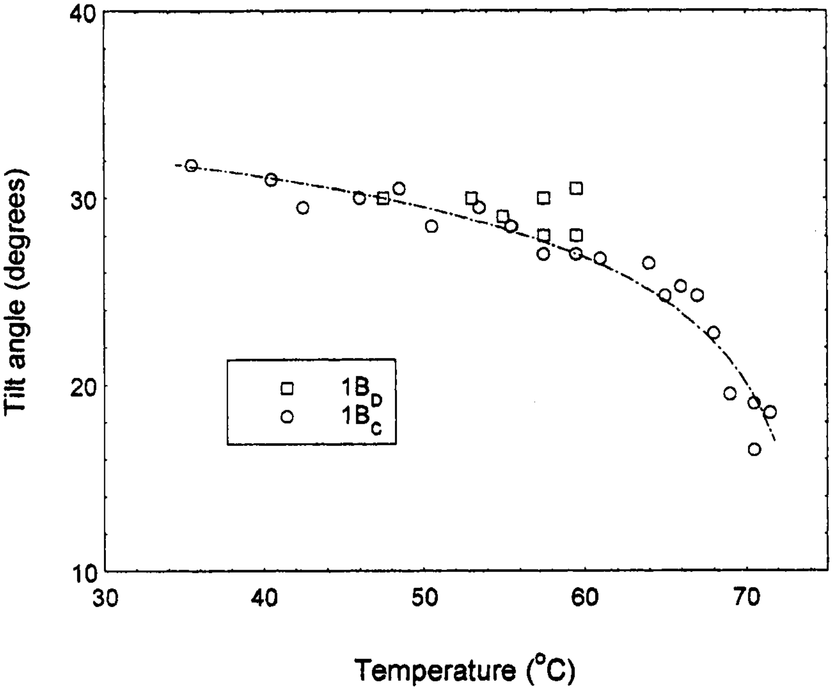


FIGURE 10 Tilt angle as a function of the temperature for mixtures $1B_C$ and $1B_D$.

The above observations indicate that compound 6 does not contribute significantly to the chiral properties of the mixtures. This is somewhat surprising, because the molecule has a strong perpendicular dipole moment, associated with the chlorine atom in the chiral centre. It is possible that the chiral centre, which is linked to the core through a methylene group, can rotate freely around the long molecular axis and therefore the perpendicular component of the dipole is averaged out. This effect can lead to a significant reduction of the macroscopic spontaneous polarization of the system [5].

4. ELECTRO-OPTICAL INVESTIGATIONS

For the electro-optical studies, we used similar cells as in the case of the physical measurements. A square wave was applied to the cell and the transmitted light was detected in a polarizing microscope. The signal variations, triggered by polarity changes of the voltage, were recorded with the help of a digital storage oscilloscope. We calculated the switching time according to the conventional definition, i.e. the interval between the times at which 10% and 90% of the total intensity modulation were achieved.

The electro-optical switching was investigated in the mixtures $1B_C$ and $3B_C$. In $1B_C$, the switching process showed markedly different features below and above the threshold voltage for helix unwinding (Fig. 11). In the former case, the modulation amplitude of the transmitted light increased linearly with the square-wave amplitude, whereas the switching time did not change significantly. Contrary to this, above the threshold, the switching time decreased with increasing field while the modulation amplitude remained constant.

These observations are in agreement with our assumptions about the mechanism of the unwinding process. For relatively small deformations, the variation of the transmitted signal is proportional to the amplitude of the helix distortion, which, in turn, is proportional to the perturbing field. The response time in this case is determined by the ratio γ/K, where γ is the rotational viscosity and K is an elastic constant. In the unwound structure,

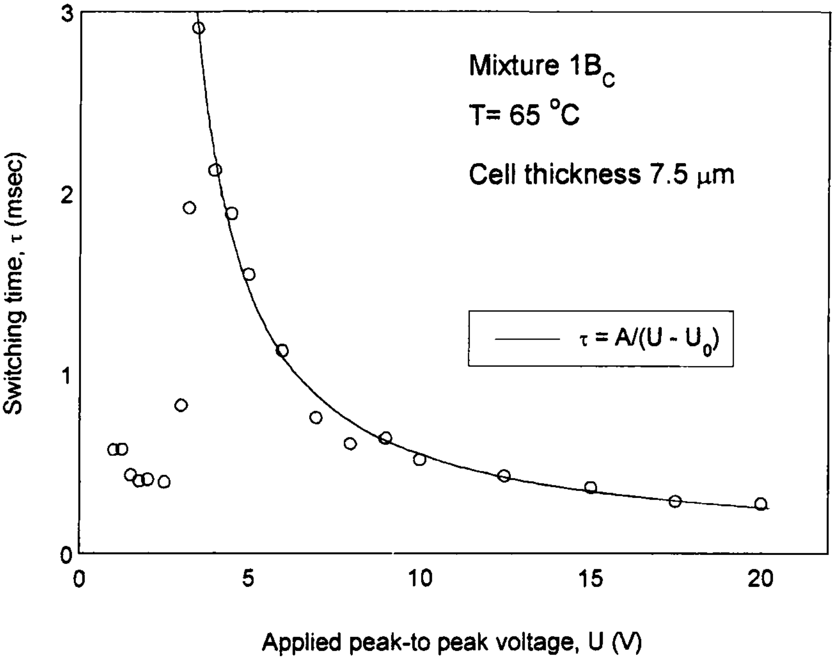


FIGURE 11 Switching time as a function peak-to-peak amplitude of an applied square wave for a 7.5 μm thick cell. The fitted curve refers to the switching times above the threshold for helix unwinding; the fitting parameters are $A = 4.4$ msec V, $U_0 = 2.0$ V.

the director rotates from an angle $+\theta$ to $-\theta$, independently from the field amplitude. The switching time of this process is, however, inversely proportional to the field strength [7]. This found to hold, at least asymptotically, in our samples as well (see the fitted curve in Fig. 11).

In $3B_C$, the contrast and switching speed increased continuously with the applied voltage. A typical value of the switching time at 35°C, in a cell with thickness of 10 μm and 10V peak-to-peak amplitude was 300 μsec. A comparison with the data for $1B_C$, presented in Figure 11, indicates that the presence of compound 6, although decreases P_S, leads to an increase of the switching speed of the mixture.

SUMMARY

Adding chiral compounds into the mixtures having broad temperature range of smectic C phase is a useful method for the creation of the ferroelectric mixtures with $S_C^* - S_A^* - N^*$ phase sequence.

Acknowledgements

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