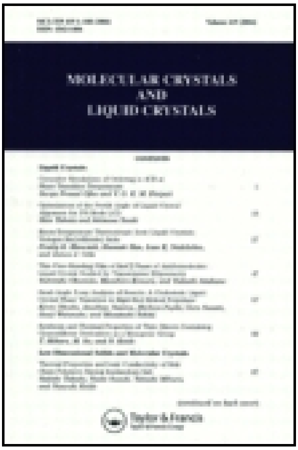

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New Ferroelectric Mixtures of Liquid Crystalline α-Halogen Carboxylates

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New Ferroelectric Mixtures of Liquid Crystalline α-Halogen Carboxylates

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Novel binary, ternary and four component mixtures of (S)-4-(2-chloro-3-methylbutanoyloxy)phenyl-4-[(n-alkoxy)benzoates] and 4-n-alkoxyphenyl 4-n-alkoxybenzoates were prepared exhibiting SmC* phase in a wide range near to room temperature. Phase diagrams and physical properties e.g. electro-optical response, spontaneous polarization and switching time have been determined. The appearance and disappearance of different mesophases has been studied.

Keywords: Ferroelectric mixtures; liquid crystalline α-halogen carboxylates; spontaneous polarization; tilt angle; switching time

INTRODUCTION

In fast switching ferroelectric liquid crystal displays, the materials should exhibit numerous advantageous properties such as high chemical, photochemical, electrochemical stability, broad chiral smectic C* (SmC*) phase around room temperature, moderate spontaneous polarization and low rotational viscosity. Although, some calculations (1) have been made on creating such mixtures, there are numerous questions to be answered. Why do some additives cause the disappearance of some mesophases? An even more interesting question is, how the intermolecular interactions can induce ferroelectricity and high spontaneous polarization in mixtures, even if none of the constituents has a SmC* phase. According to our earlier studies, two non chiral SmC compounds mixed with a chiral, non-liquid crystalline one gave a relatively high spontaneous polarization (200 nC/cm^2) in their ternary mixtures (2). For a better understanding of the rela-

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tionship between the molecular length and the tilt angle of liquid crystals, numerous mixtures exhibiting chiral and achiral SmC phase have been investigated (3). There is an indication (4), that if the tilt angle of the single components differ significantly, the originally observable SmC phase will not appear in their mixture.

The amino acids are good chiral starting materials for the preparation of liquid crystalline compounds with ferroelectric behavior. Numerous compounds exhibiting SmC* phase have been synthesized from L- or D- valine. Depending on their optical purity, some of them also have a TGB A* phase. When the (S)- or (R)-2-chloro-3-methylbutyric acid moiety derived from the corresponding amino acid was connected to a diarylethane group containing core, the above mentioned TGB A* phase was detectable only in the high optically pure liquid crystalline derivatives (5,6). Chiral alcohols have also been prepared from α-amino acids via replacement of the amino group with a halogen atom and reduction of the acid function to an alcohol. Mesogens prepared from these, such as (2S,3S)-(2-bromo-3-methylpentyl)-4-alkoxybenzylidene-4-aminocinnamates, also exhibit a SmC* phase above room temperature (7). When a 2-hydroxybenzylideneamino part was built into these molecules, more ordered smectic phases were also observed below the SmC*phase (8). Numerous liquid crystalline compounds containing the 1-chloro- or 1-bromo-2-methylbutyric acid moiety as the chiral groups derived from amino acids, also exhibited a SmC*phase in a wide temperature range. Some of these compounds have also been investigated in mixtures (9).

A large variety of core structures, as well as variations in the chiral group, liquid crystals have been investigated in ferroelectric mixtures for the better understanding of the importance of the molecular geometry. Basic mixtures, prepared from 4′-n-alkoxyphenyl-4-n-alkoxybenzoate derivatives as achiral host materials, were doped with optically active biphenylene diesters and other chiral guests. These produced a fast response and high contrast ratio, and were useful mixtures for optical shutter multiplex-driving liquid crystal displays (10). Some liquid crystalline 1,4-disubstituted bicyclo[2,2,2]octane (11), pyrimidine derivatives (12), and laterally substituted phenylene and biphenylidene derivatives (12) have been used as achiral host materials to create ferroelectric mixtures. Optically active cyanocyclohexane derivatives (13) have been applied as chiral dopants to induce ferroelectric SmC* phase in an achiral host mixture.

Our aim was to extend the use of liquid crystalline α-halogen carboxylic acid derivatives derived from chiral amino acids to ferroelectric mixtures which have SmC* phases in a wide temperature range around room temperature. Two main strategies were followed : a) mixing chiral liquid crystals to widen their SmC* phase temperature range and to create mixtures with a preferred phase sequence of

I →N^* →SmA^* →SmC^* on cooling. b) using these mixtures as dopants or additives for mixtures of achiral liquid crytalline compounds exhibiting a SmC phase.

EXPERIMENTAL

The textures of liquid crystal mixtures were observed in thin films placed between cross polarizers. The phase transition temperatures of mesophases were measured by hot-stage polarizing microscopy and scanning calorimetry. Miscibility studies and texture observations were carried out using an Amplival pol-u polarizing microscope equipped with a Boetius heating stage. The spontaneous polarization was determined in applied EHC cells of 2–10µm thicknesses by measuring the electric current flowing through the sample with a triangular shape ac voltage.

RESULTS AND DISCUSSION

Two representatives of a homologous series of phenylbenzoates derived from L-valine : (S)-4-(2-chloro-3-methylbutanoyloxy)phenyl 4-[(n-octyloxy)-benzoate] (**1**) and (S)-4-(2-chloro-3-methylbutanoyloxy)phenyl 4-[(n-decyloxy)benzoate] (**2**) were prepared according to (9) and used in binary mixtures. Compound (**1**) exhibits an enantiotropic chiral smectic A (SmA^*) phase (Table I). whereas in compound (**2**) this phase is monotropic. Both compounds have a monotropic SmC^* phase. Compound (**1**) has an enantiotropic chiral nematic (N^*) phase, while compound (**2**) does not have. These compounds were mixed in three different concentrations labelled by mixtures **M1-M3** (Figure 1.). In mixtures **M1** and **M2**, the enantiotropic SmA^*phase has been stabilized and the temperature range of the monotropic SmC^*phase became wider compared with compound (**1**) (Table II). Mixture **M2** has been chosen for further investigations.

The ferroelectric (S)-4-[n-nonyloxybenzoyloxy)phenyl 4-[(2-chloro-3-methylbutanoyloxy)benzoate (**3**) was added as a third component to enlarge the temperature range of the mesophases of **M2**. Three ternary mixtures (**M4-M6**) were prepared using compound (**3**). Their phase diagrams have also been investigated on heating and cooling (Figure 2). The phase transition temperatures are summarized in Table II. After adding the third component (**3**) to mixture **M2**, an N^* phase appeared and the SmA^* phase has been broadened. Increasing the concen-

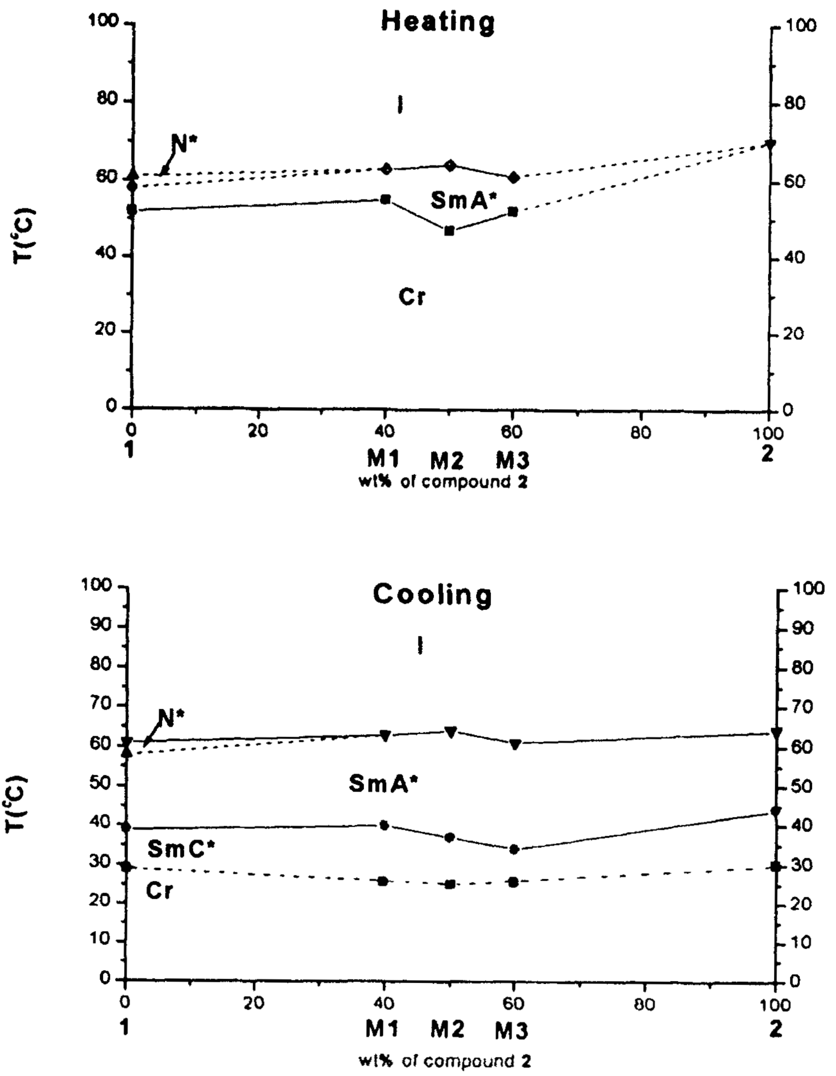
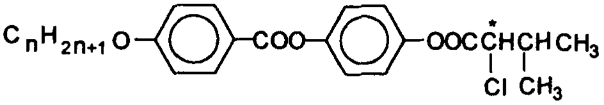


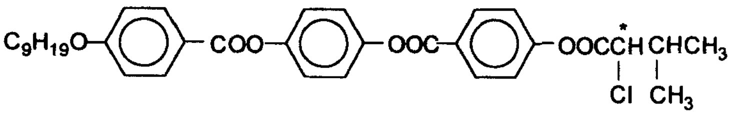
FIGURE 1 Phase diagrams of binary mixtures **M1-M3** prepared from compounds (**1**) and (**2**)

tration of compound (**3**), the monotropic SmC* phase disappeared in mixtures **M5** and **M6**. These phase diagrams are depicted in Figure 2, and the phase transition sequences are summarized in Table II.

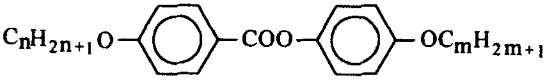
TABLE I Compounds used in ferroelectric mixtures and their phase transition temperatures



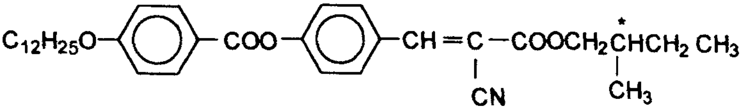
(1) n=8 Cr 52 (SmC*39) SmA* 58 N* 61 I
(2) n=10 Cr 70 (SmC*44) (SmA*64) I



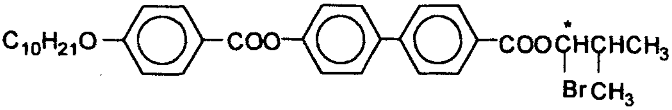
(3) Cr 106 SmC* 111 N* 190 I



(4) n=8, m=7 Cr 62 SmC 69 N 88 I
(5) n=10, m=7 Cr 67 SmC 79 SmA 82 N 89 I



(6) Cr 82 (SmC*76) SmA* 90 I



(7) Cr 86 SmC* 148 N* 174 I

( ) monotropic phase transition

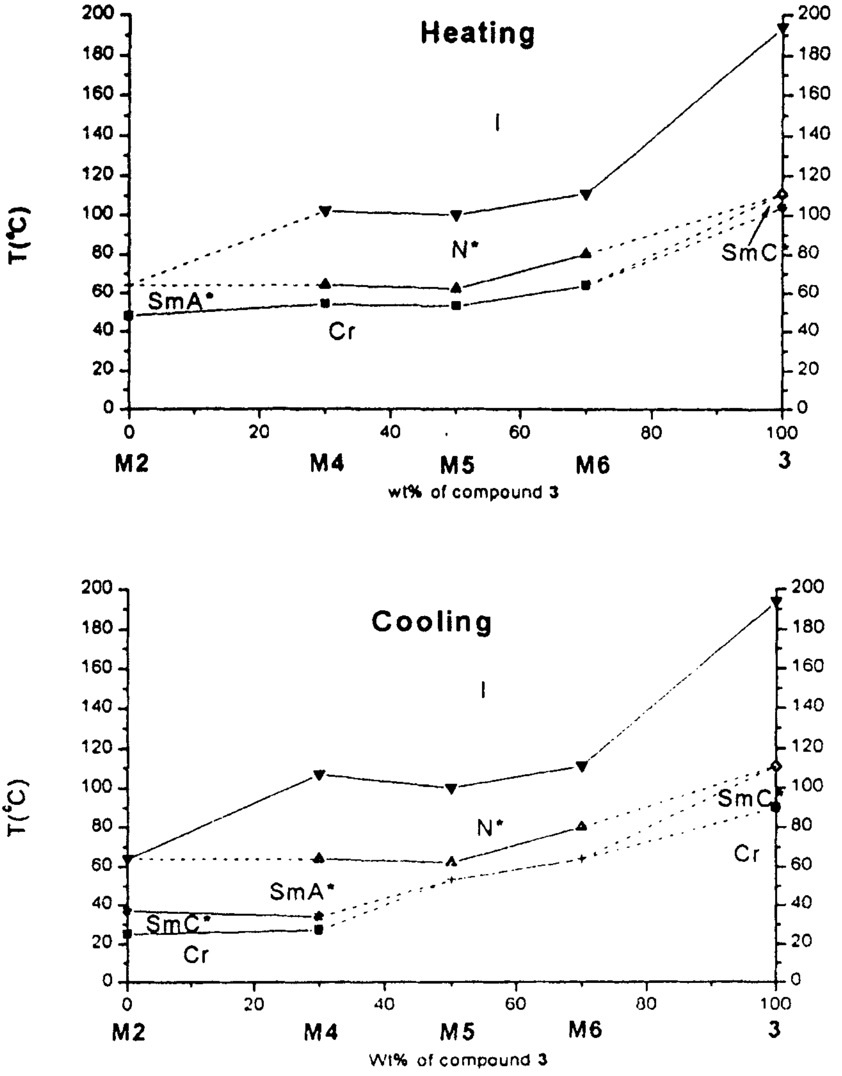


FIGURE 2 Phase diagrams of ternary mixtures **M4-M6** prepared from mixture **M2** and compound (**3**)

TABLE II Phase transition temperatures of the chiral and achiral mixtures

Mixtures	*Components (wt. %)*							*Phase transition temperatures (°C)*
	1	*2*	*3*	*4*	*5*	*6*	*7*	
M1	40.00	60.00						Cr 55 (SmC*40) SmA* 63 I
M2	50.00	50.00						Cr 49 (SmC*37) SmA* 64 I
M3	60.00	40.00						Cr 52 (SmC*34) SmA* 61 I
M4	38.46	38.46	23.07					Cr 54 (SmC*34) SmA* 64 N* 102 I
M5	33.33	33.33	33.33					Cr 53 SmA* 62 N* 100 I
M6	29.41	29.41	41.17					Cr 64 SmA* 80 N* 111 I
M7				50.00	50.00			Cr 51 (SmB33) SmC 76 SmA 78 N 89 I
M8	13.04			43.47	43.47			Cr 52 (SmB*32) SmC* 72 SmA* 77 N* 89 I
M9	23.08			38.46	38.46			Cr 46 (SmB*31) SmC* 62 SmA* 74 N* 85 I
M10	33.33			33.33	33.33			Cr 40 (SmB*25) SmC* 50 SmA* 71 N* 80 I
M11	41.17			29.41	29.41			Cr 43 (SmB*26) SmC* 46 SmA* 70 N* 78 I
M12	28.57			28.57	28.57	14.29		Cr 38 (SmC*32) SmA* 73 I
M13	25.00			25.00	25.00	25.00		Cr 43 (SmC*39) SmA* 79 I
M14	22.22			22.22	22.22	33.34		Cr 54 (SmC*41) SmA* 82 I
M15	28.57			28.57	28.57		14.29	Cr 42 (SmB*32) SmC* 59 SmA* 77 N* 90 I
M16	25.00			25.00	25.00		25.00	Cr 45 (SmB*37) SmC* 72 SmA* 87 N* 106 I
M17	27.72			27.72	27.72		16.84	Cr 46 (SmB*41) SmC* 76 SmA* 91 N* 109 I

The compound (**3**) in structure, is a hydroquinone derivative exhibiting an enantiotropic SmC* phase itself, but in its mixtures (between 50–70% of compound (**3**)), the desirable SmC* phase disappeared. If we consider that compounds **1–3** have the same chiral centers at the same distance from the core, and they all have the same spatial configuration, with the same electronegative group connected to the chiral center (chlorine), we get the same inductive effect there (Table III). Accordingly, we conclude that the disappearance of the SmC*phase is due to the different chemical structure of the compound **3**. This structure does not fit into the helical structure formed by the other two compounds e.g. (**1**) and (**2**).

TABLE III Characterization of the chiral centers of the molecules applied in mixtures

Compounds	*Absolute configuration*	*Parity*	*Inductive effect on the chiral center*	*Twist sense*
1	S	odd	-I	LH
2	S	odd	-I	LH
3	S	odd	-I	LH
6	S	even	+I	LH
7	S	odd	-I	LH

We have continued our investigations according to the second strategy. In our previous studies (2,14), we prepared achiral basic mixtures consisting of two members of a homologous series of 4-n-alkoxyphenyl-4-n-alkoxybenzoates. In this paper, we used the eutectic mixture of 4-(n-heptyloxy)phenyl 4-(n-octyloxy)benzoate (**4**) and 4-(n-heptyloxy)phenyl 4-(n-decyloxy)benzoate (**5**). The phase transitions data of the individual compounds are given in Table I, whereas that of the mixture **M7** is shown in Table II. None of the compounds (**4**) and (**5**) had a smectic B phase, although other members of this homologous series do (2). In the mixture, we could observed this so called latent SmB phase (14). In mixtures **M8-M11** and **M15–17**, obtained from the basic mixture **M7**, this smectic B* phase was observed below the SmC* phase. This is likely due to the larger supercooling of the latent SmB* phase, could be, that these compounds can be easily supercooled in mixtures.

When we added compound (**1**) to the achiral mixture **M7** in different concentrations, we obtained the ternary **M8-M11** mixtures exhibiting enantiotropic SmC*, SmA*, N* and monotropic SmB* phases. Increasing the amount of compound (**1**) caused the melting points of the mixtures to decrease and narrowed the range of the SmC* phase (Figure 3).

The SmB* phase could be eliminated by adding (S)-(2-methylbutyl)-4-[4′-(n-dodecyloxybenzoyloxyl)] 2-cyanocinnamate (**6**) to mixture **M10** (15) in three

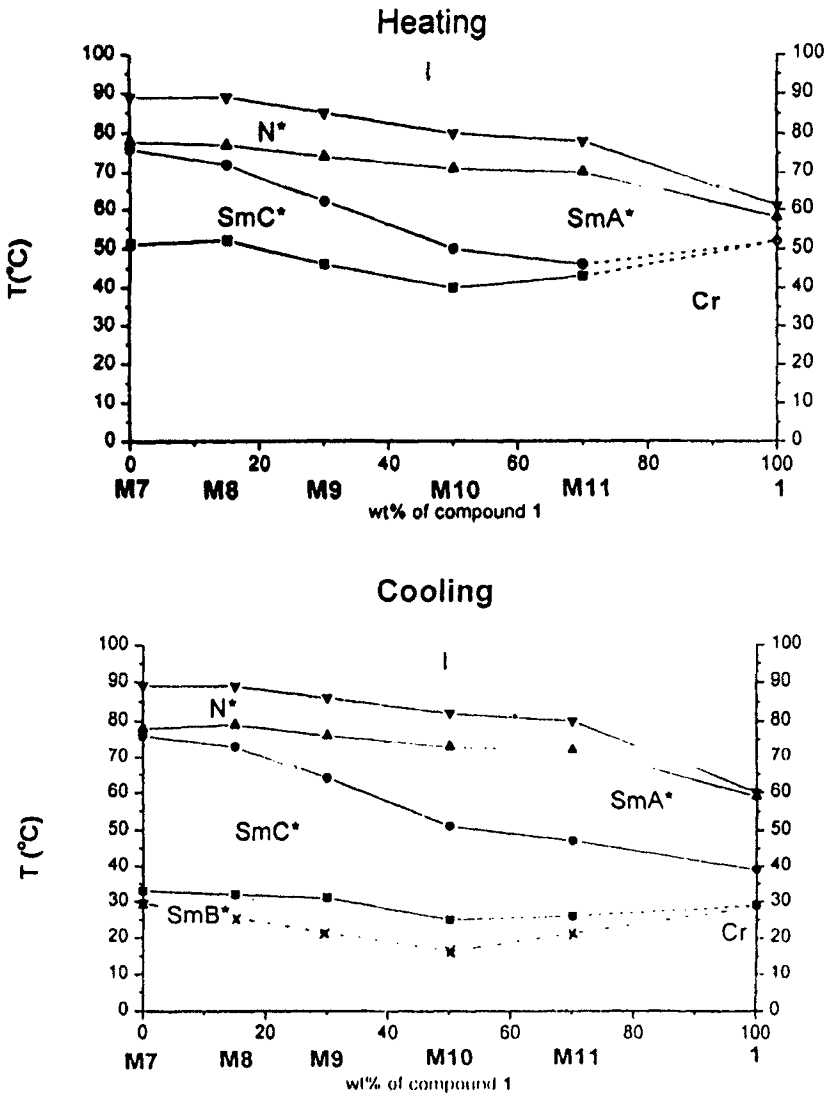


FIGURE 3 Phase diagrams of ternary mixtrues **M8-M11** prepared from mixture **M7** and compound **(1)**

different concentrations obtaining mixtures **M12-M14**. The phase sequences of compound **(6)** and its mixtures **M12-M14** are given in Table I and Table II, respectively. The phase diagrams are shown in Figure 4. In comparison with the ternary basic mixture **M10**, the SmA* phase broadened depressing the appear-

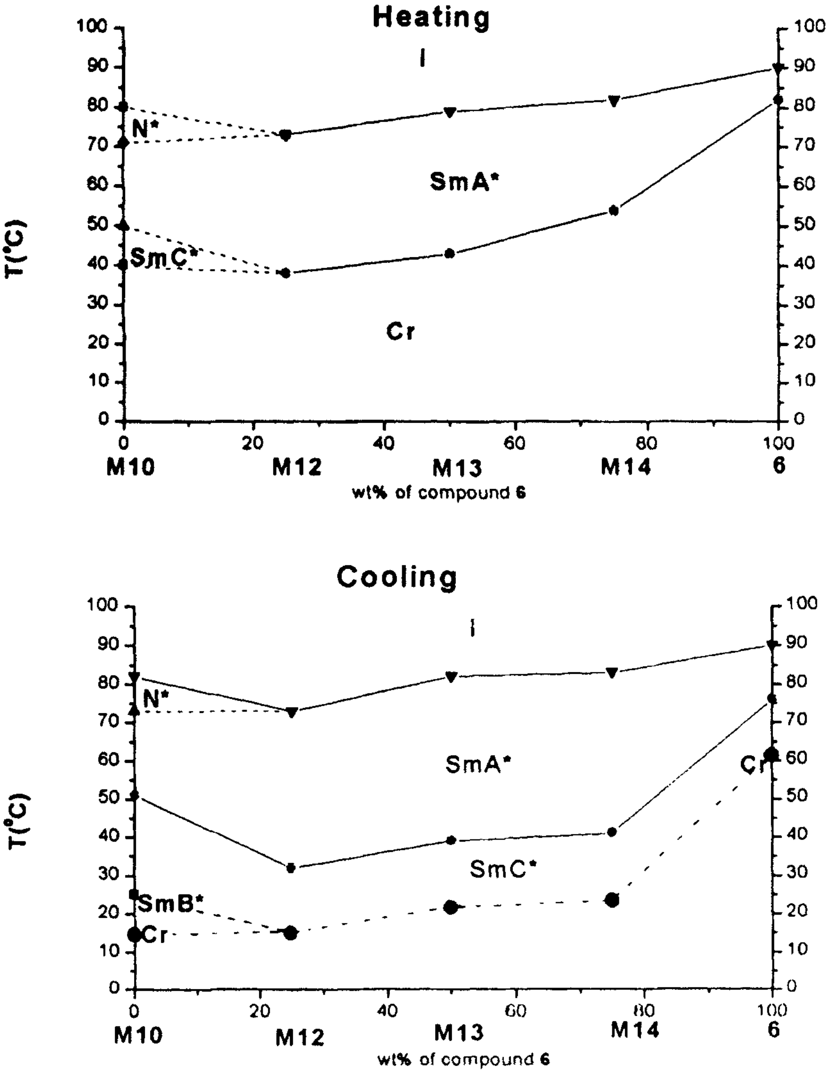


FIGURE 4 Phase diagrams of four-component mixtures **M12-M14** prepared from mixture **M10** and compound (**6**)

ance of the N^*phase. The four-component mixtures containing compound (**6**) have a monotropic SmC^* phase above room temperature. The range of the SmC^*phase decreased and the mixtures could not be supercooled as much as in **M10**. Compound (**6**) has a large dipole moment perpendicular to its long axis, with the combination of the large dipole moments of both the α-halogencarboxylic acid and (S)-2-methylbutyl-α-cyanocinnamicate derivatives, moderate depression of the SmC* phase was observed. If we take into consideration the parity, spatial configuration, and dipole moments around the chiral centers (Table III), additionally the dipolar interactions and the steric packing of the components in the mixtures **M12-M14**, we can understand, that the left hand helix (LH) inducing or forming components of these mixtures presumably are not compatible with each other in a wide temperature range.

In order to enlarge the SmC* phase range of the mixture **M10** towards the higher temperature end, (S)-[4-(2-bromo-3-methyl-butanoyloxy)biphenyl 4-(n-decyloxy) benzoate (**7**) was added to it in three different concentrations. These new four-component mixtures, **M15-M17**, have the advantageous phase sequence as it is seen in Table II and the phase diagrams are depicted in Figure 5. Compound (**7**) (Table I) has enantiotropic SmC* and N* phases, but compound (**6**) does not. Inspite of the fact that compound (**7**) does not have any SmA*phase, it stabilizes and preserves this phase in mixtures, further broadening the SmC* phase in mixture **M10**. The phase transition temperatures of the four-component mixtures **M15–17** appeared at a higher temperature range than they did for **M10**. With increasing ratio of compound (**7**), the SmC*phase broadened at higher temperatures. **M16-M17** exhibited the widest temperature range of the enantiotropic SmC* and N*phases. Both the melting and clearing temperatures of the mixtures were observed at higher temperatures compared with the chiral ternary basic mixture **M10**. These mixtures can be easily supercooled, leading to the appearance of the SmB* phase.

In this paper we describe good supercoolable mixtures exhibiting the SmC* phase in a wide temperature range with components of left-handed helical structure (Table III). Earlier, it was shown, that mixing compounds having the opposite sense of their helical structure is more favourable for good mixtures (16). Using this principle, we intend to continue our investigations of mixtures composed of chiral materials exhibiting or inducing helixes of opposite sense.

To characterise the main physical properties of the mixtures, we measured the time dependencies of the electric current flowing across the samples under triangular ac voltages. This provides information about the spontaneous polarization, dielectric constant and conductivity.

The electric current, I flowing through a sandwich cell of area A, thickness d, filled with a ferroelectric material of dielectric constant, ε, and of ferroelectric polarization, P can be written as follows.

$$I(t) = U\sigma A/d + \varepsilon_0 \varepsilon A/d \bullet \frac{\partial}{\partial t} U + A \frac{\partial}{\partial t} P$$

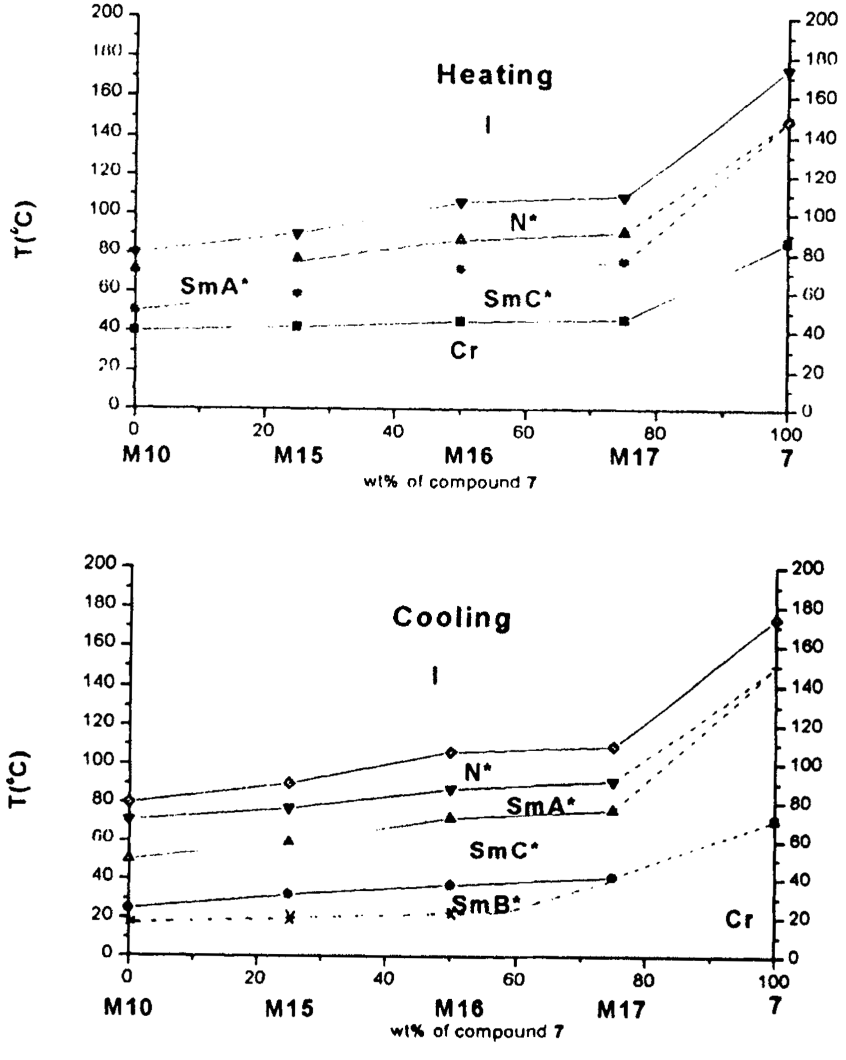


FIGURE 5 Phase diagrams of four component mixtures **M15-M17** prepared from mixture **M10** and compound (7)

In this equation the first term is due to the conductivity σ, and is proportional to the applied voltage U (Ohmic term). The second (capacitive) term appears as a step, when the time derivative of the applied voltage changes sign. From the amplitude of this step one can determine the dielectric constant, ε parallel to the polarization. The third term gives a hump due to the switching of the polarization (polarization term). The area of the hump above the slope determined by the electric conductivity σ gives the value of the spontaneous polarization, *P*.

A typical example for the measured I(t) is illustrated in Figure 6 for the mixture **M8**. The dielectric constants, the conductivity and the polarization of these materials were found to be typical of most SmC*mixtures, see for example, **M8** at 30 °C ε=5.5 and $\sigma = 10^{-9}\ 1/\Omega m$. In Figure 7, we plotted the temperature dependence of the polarization of mixture **M8**. The data were fitted by the equation $P(T) = P_0(T_C - T)^{\alpha}$, where P_0 is constant and T_C is the SmA*-SmC* phase transition temperature. Theoretical arguments predict that α should be 0.5 (17). Experimentally (especially for mixtures), however α is found to be less than 0.5 (16). This is true also for our case, where α= 0.29.

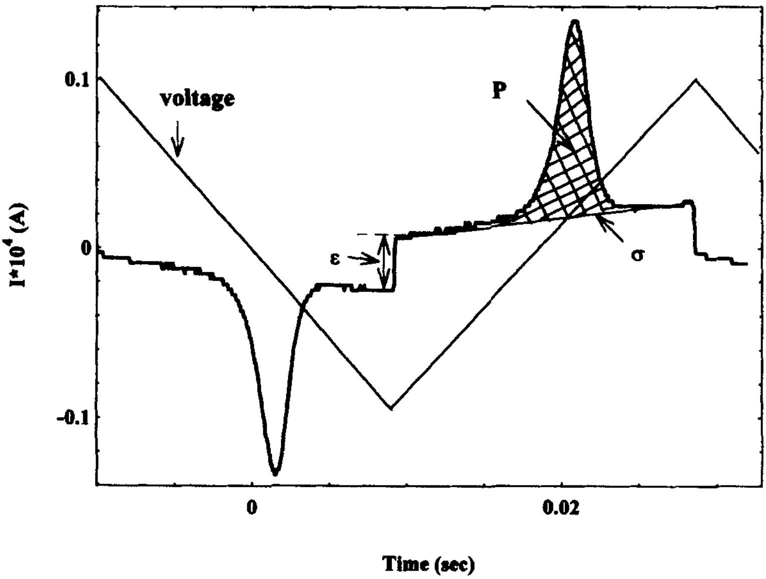


FIGURE 6 Time dependence of the electric current at 98.5 °C of mixture **M8** under 12 $V_{p\text{-}p}$ triangular voltage

The switching time and the director tilt angle were determined optically. The voltage dependence of the switching time of a 2μm thick cell containing mixture **M17** is represented in Figure 8. Above a threshold field the switching time is inversely proportional to the applied field, which is normal for surface stabilised SmC* films under high fields (18). The main physical parameters of the studied substances are summarised in Table IV.

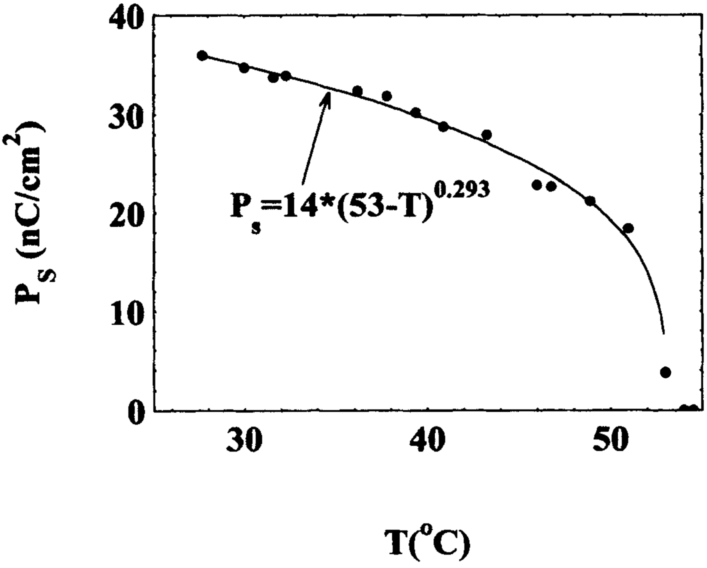


FIGURE 7 Temperature dependence of the polarization of mixture M8. Solid line is the best fit

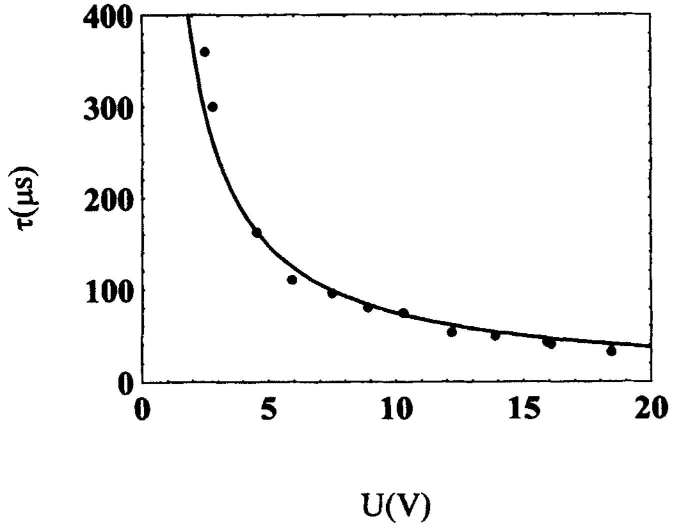


FIGURE 8 Voltage dependence of the switching time 2°C below the phase transition to the SmA phase of a 2μm thick cell containing mixture **M17**. The solid line is the best fit with equation (18) $\tau \cong 2 \cdot \frac{\gamma d}{PU} \approx 750/U$. From this we can determine that the rotational viscosity γ ~5cPoise

TABLE IV Physical parameters of selected mixtures

Mixture	$P_s(nC/cm^2)$	$\tau(\mu s)$ *at* $4V/\mu s$	$\theta(°)$
M1	38	47	22
M2	34	56	24
M8	36	52	17
M17	18	40	20

SUMMARY

Seventeen multicomponent mixtures have been prepared according to two different strategies. The physical properties were investigated in four mixtures. Mixtures **M1** and **M2** were prepared from two chiral liquid crystalline α-halogen carboxylates. These mixtures have spontaneous polarizations of about 35nC/cm^2. The ternary mixture **M8** was composed of two non-chiral and a small amount of one of the chiral derivatives. It has similar Ps value as in case of **M1** and **M2**. Larger concentrations of the chiral components did not give a larger spontaneous polarization. The four-component mixture **M17**, composed of structurally different core containing derivatives, gave a quicker response time and higher tilt angle. The effect of the molecular geometry and the structure around the chiral center has been discussed.

Acknowledgements

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