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Ferroelectric Mixtures of Chiral and Achiral Thioesters

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The aim of this paper is to present a ferroelectric mixture with low eutectic point based on chiral and achiral thioesters. Nine ferroelectric mixtures of two thioesters have been studied by Dielectric Spectroscopy (DS) and Reversal Currents Method (RCM). DS and RCM measurements have been performed on the well aligned mono-domains by means AC electric field. Spontaneous polarization vs. temperature for each concentration has been measured to study the character of the transition between the para- and ferroelectric phases in view of the mean-field theory. The Influence of the chiral dopant on the nature of ferroelectric behaviour was also investigated.

Keywords Eutectic point; ferroelectric mixture; liquid crystals; spontaneous polarization

1. Introduction

Since the discovery [1] of ferroelectric liquid crystals (FLCs) many compounds have been synthesized showing ferroelectric behaviour [2–7]. However, display applications of FLCs proposed by Clark and Lagerwall [2] need uniformly planar aligned thin layers in the form of book-shelf geometry displaying a uniform texture known as SSFLC. It was possible to obtain such conditions for small size micro-displays (up to few inches). Large area displays based on FLCs have not been designed up to now due to disclination lines which show up for SSFLCs.

Nine mixtures, based on two thioester compounds: chiral (S)-4-(1-methylheptyloxy)biphenyl 4′-decylthiobenzoate (in short MHOBS10) and achiral 4-n-pentylphenyl-4′-n-octyloxythiobenzoate (in short 8OS5), have been studied by complementary methods to explore a possibility of obtaining a ferroelectric SmC^* phase in a wide temperature range incorporating room temperature range. The aim of this work was to find the phase diagram and an eutectic point, at which the ferroelectric SmC^* would have the widest temperature range.

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All these mixtures have been investigated by Differential Scanning Calorimetry (DSC), Frequency Domain Dielectric Spectroscopy (FDDS) and Reversal Currents Methods (RCM). In this paper a report is given on research done by these techniques to find physical parameters important for potential applications of thioester mixtures which are stable in time and under electric fields. Each mixture had different concentration of the chiral compound. The concentrations were computed as a molar fractions of the chiral compound in achiral matrix of 8OS5, for example MHOBS10-0.3/8OS5-0.7.

2. Molecular Structure of Substance Studied

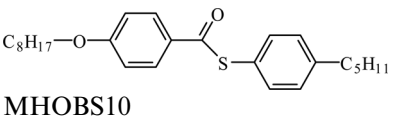
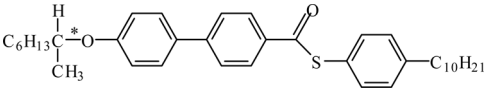
Both compounds are characterized in a few publications [1–5]. The compounds belong to thioesters group, and one of them is achiral and the other – chiral. Table 1 shows chemical structures and temperature range of each phase for pure compounds. Both substances display reach polymorphism. Especially the presentence of a monotropic SmC phase for 8OS5 in a wide temperature range, from 50°C to 28°C seems to be promising. The other compound MHOBS10 exhibits ferroelectric SmC* phase in the temperature range from 108°C to 85°C [8–13]. Phase transition temperatures were determined using Perkin-Elmer DSC8000 set-up. The presence of nematic N for 8OS5 and cholesteric – N* phase for MHOBS10 is also desirable from the point of view of better alignment of the mono-domain in the presence of an external electric field. These four specific characteristics predispose these compounds to make mixtures of different molar fractions of chiral compound (MHOBS10) admixed to the achiral matrix (8OS5).

3. Texture Observations

Textures of liquid crystalline phases were observed using polarizing microscope Nicon Eclipse 100POL equipped with INSTEC HCS410 heating stage. The samples being in the isotropic were introduced into ITO 5.3 μm planar AWAT cells by means of the capillary action. Selected images taken with CCD camera are presented in Figure 1 which shows liquid crystal phases for selected mixtures aligned by external electric field.

Figure 1(a) illustrates Frederiks transition in paraelectric SmA* phase for MHOBS10-0.1/8OS5-0.9 mixture at 42°C. It is interesting that all mixtures as well

Table 1. Chemical structure, phase sequence and temperature range for each phase for 8OS5 and MHOBS10

Acronym	Chemical structure/phase sequence
8OS5 	Table 1 Figure 8OS5 Cooling: I 87°C N 68°C SmA 50°C SmC 28°C SmB (18°C) Cr
MHOBS10 	Table 1 Figure MHOBS10 Cooling: I 120°C N* 108°C SmC* 85°C SmG* 22°C Cr

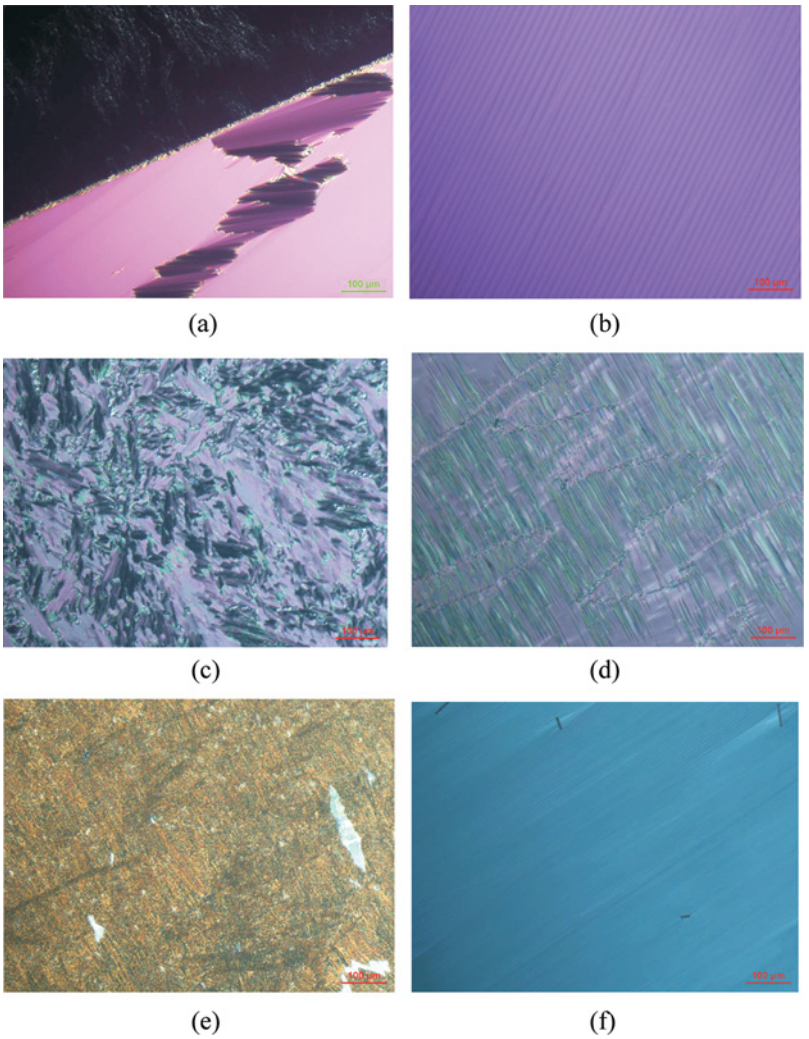


Figure 1. (a) Planar and homeotropic texture (upper part) for the SmA* phase of MHOBS10-0.1/8OS5-0.9 mixture at 42°C. Aligning voltage was 160 $V_{p\text{-}p}$. (b) Mono-domain of N* phase aligned in a few minutes time by electric field for MHOBS10-0.6/8OS5-0.4 at 81°C. Aligning voltage was 100 $V_{p\text{-}p}$. (c) Texture of the highly ordered SmG* phase obtained for MHOBS10-0.8/8OS5-0.2 at 55°C. No electric field was applied. (d) Texture of the SmG* phase for MHOBS10-0.2/8OS5-0.8 at 60°C. Alignment voltage was 160 $V_{p\text{-}p}$. (e) Texture of crystalline phase for MHOBS10-0.8/8OS5-0.2 mixture at −10°C. (f) Texture of SmC* for MHOBS10-0.3/8OS5-0.7 mixture at 55°C. Aligning voltage was 160 $V_{p\text{-}p}$, $\nu = 50$ Hz. (Figure appears in color online.)

as pure compounds studied display positive dielectric anisotropy in the SmA* phase far from the critical temperature, where the soft mode contribution to the dielectric anisotropy is negligible. It is important to notice that the concentration of chiral compound is only 0.1 molar fraction and despite of this the paraelectric SmA* phase is observed. One should note that the Frederiks transition is irreversible in the case of the SmA* phase and the threshold voltage for re-orientation of molecules

$U_0 = 160\,V_{p\text{-}p}$. For the planar texture, the molecules' long axes are arranged on the average parallel to the electrodes and in a direction perpendicular to the external electric field. For homeotropic texture, the long axes of molecules are arranged perpendicularly to the glass plates, and parallel to the electric field. In Figure 1 the upper part is a homeotropic texture – between the electrodes, whereas the bottom part – being outside of the electrodes – exhibits a planar texture.

In Figure 1(b) a planar texture of cholesteric phase N^* is presented for MHOBS10-0.6/8OS5-0.4 at 81°C. This texture was grown up after applying an external electric voltage of $100\,V_{p\text{-}p}$. It was found that the pitch of the helix is 15.4 μm.

In Figures 1(c) and 1(d) the textures for the highly ordered ferroelectric SmG^* phase are presented for two different mixtures MHOBS10-0.8/8OS5-0.2 and MHOBS10-0.2/8OS5-0.8 at temperature of about 55°C without and with $U = 160$ Vp-p external voltage. As seen there is a great influence of electric field on the highly ordered SmG^* phase.

In Figure 1(e) a texture of crystalline phase is presented for MHOBS10-0.8/8OS5-0.2 mixture at −10°C. In Figure 1(f) texture of the aligned ferroelectric SmC^* phase for MHOBS10-0.3/8OS5-0.7 mixture at 55°C – aligning voltage was $160\,V_{p\text{-}p}$, $\nu = 50$ Hz. As seen it is possible to grow a mono-domain which can switch in external electric field.

4. Electro-Optic Measurements

For all samples under investigation spontaneous polarization has been measured – using Reversal Current Method (RCM) – at different frequencies of the driving triangular wave.

Temperature dependence of spontaneous polarization was obtained for nine mixtures. As seen in Figure 2(a), spontaneous polarization is strongly dependent on concentration of the chiral compound. Spontaneous polarization was computed by using the formula:

$$P_S = \frac{1}{R} \cdot \frac{A}{2S}, \tag{1}$$

where R – resistance of the resistor being in series with the electro-optic cell, A – area under the response current spectrum, and S – area of ITO electrode.

As found spontaneous polarization P_S decreases with decreasing concentration of chiral compound and also the freezing temperature changes monotonically with concentration, what is seen in Figure 2(a).

Figure 2(b) presents a phase diagram of the mixture of two compounds with eutectic point being 10°C for the composition: MHOBS10-0.7/8OS5-0.3, where the ferroelectric SmC^* phase changes to crystalline (Cr) phase. This mixture could be applied in some liquid crystal devices which could work at room temperature. It is important that this mixture possesses the cholesteric N^* phase, which facilitates the ordering and growing of the mono-domain.

As found in this study spontaneous polarization measured at 10°C below the transition to the SmC^* phase is a linear function [14] of molar concentration (X) of chiral compound as illustrated in Figure 2(c). Due to the fact that P_o is negative one would presume that at low concentrations there is a non-linear dependence. Based on the electro-optic and DSC studies a phase diagram has been found, which is shown in Figure 2(b).

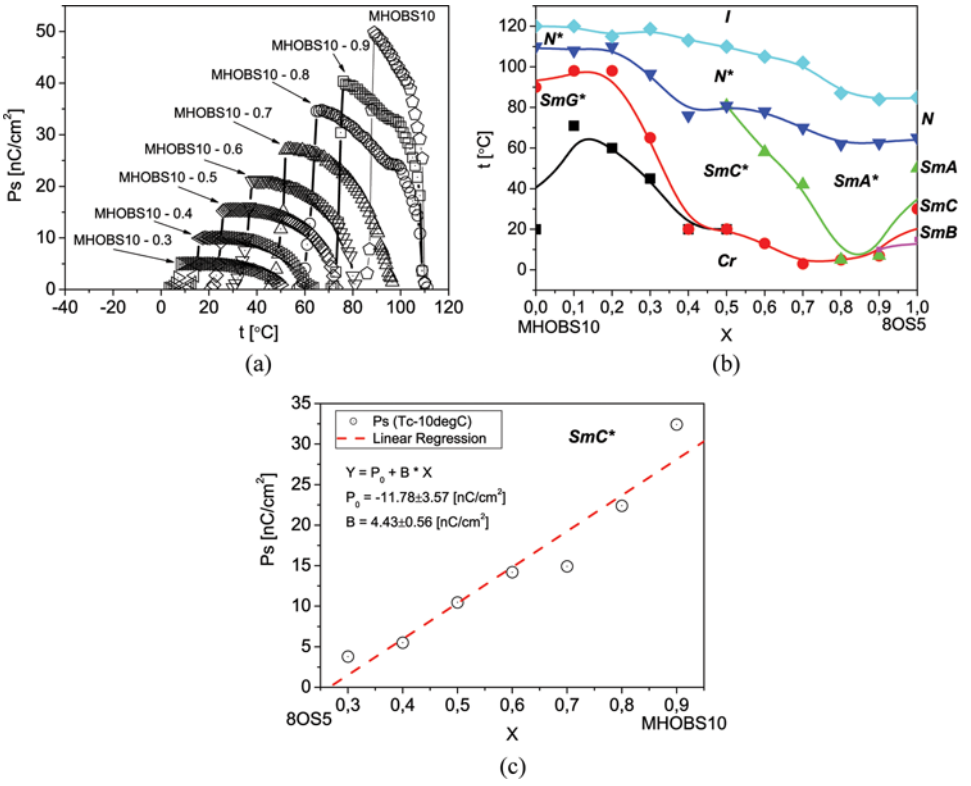


Figure 2. (a) Spontaneous polarization vs. temperature for 7 ferroelectric mixtures. (b) Phase diagram for the mixture studied. (c) Spontaneous polarization measured at 10°C below T_C vs. concentration of the chiral MHOBS10 component. (Figure appears in color online.)

5. Dielectric Spectra

Dielectric measurements were performed using two dielectric spectrometers one based on Agilent 4294A impedance analyzer and Novocontrol-Turnkey dielectric spectrometer. Both were connected to a sample holder containing a gold 5 μm planar cell filled with the substance under test. The dielectric spectra were obtained by frequency domain dielectric spectroscopy. The value of measuring voltage was equal to 0.1Vrms from 40 Hz to 10 MHz. Dielectric spectra were measured on cooling of the sample. Figures 3(a) and 3(b) present a selected dielectric spectrum. Solid lines in the Cole-Cole plots were obtained by fitting Eq. (2).

$$\varepsilon_\perp^*(\nu) = \varepsilon_\perp'(\nu) - i\varepsilon_\perp''(\nu) = \varepsilon_\perp(\infty) + \sum_{k=1}^{2} \frac{\Delta\varepsilon_{\perp k}(\nu)}{1 + \left(i\frac{\nu}{\nu_{Rk}}\right)^{1-\alpha_k}} - i\frac{A}{\varepsilon_0 \nu^M} + \frac{B}{\nu^N} \tag{2a}$$

$$\Delta\varepsilon_{\perp k} = \varepsilon_{\perp k}(0) - \varepsilon_{\perp k}(\infty) \tag{2b}$$

$$\tau_{Rk} = \frac{1}{2\pi\nu_{Rk}} \tag{2c}$$

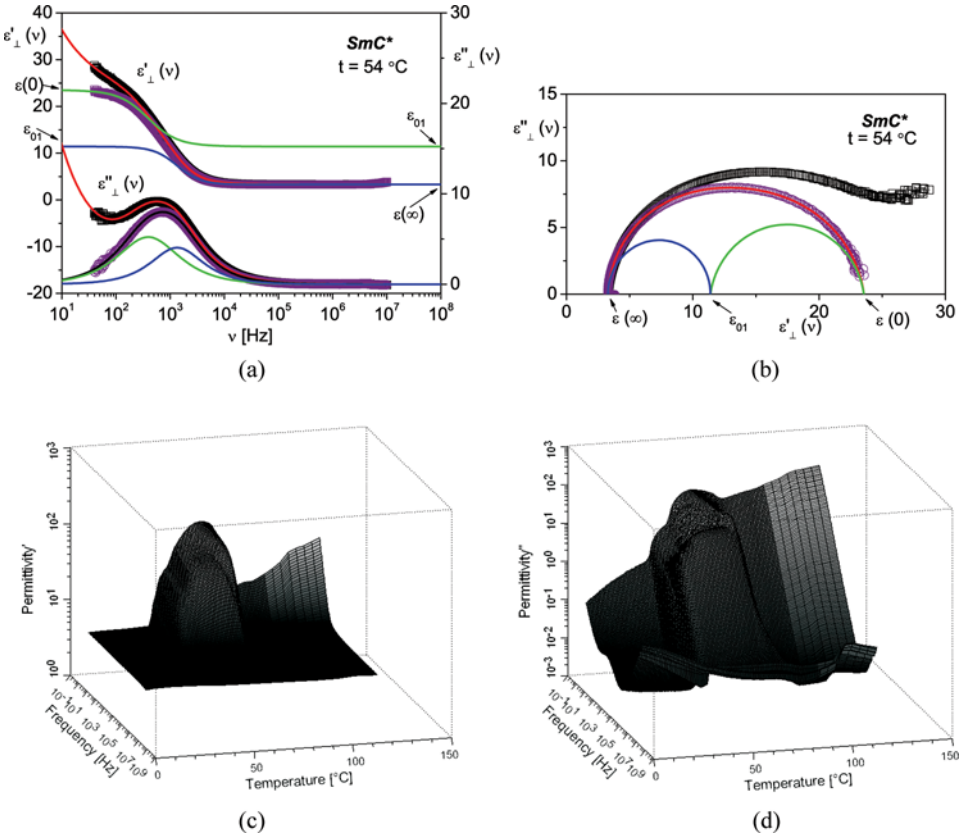


Figure 3. (a) Dielectric dispersion and absorption of SmC* phase for MHOBS10-0.5/8OS5-0.5 mixture. (b) Cole-Cole diagram of SmC* phase for MHOBS10-0.5/8OS5-0.5 mixture. (c) Dielectric dispersion vs. temperature for MHOBS10-0.4/8OS5-0.6 mixture. (d) Dielectric absorption vs. temperature for MHOBS10-0.4/8OS5-0.6 mixture.

where $\Delta\varepsilon$ is the dielectric increment, ν is frequency of measuring electric field (in Hz), τ_{Rk} is the dielectric relaxation time [s], $\varepsilon_\perp(\infty)$ is electric permittivity at high frequencies, $\varepsilon_\perp(0)$ is static electric permittivity, ε_o is electric permittivity in free space [F/m], ν_{Rk} is the relaxation frequency for k-th process, α_k is a distribution parameter of the relaxation times, A is ionic conductivity [S/m], B is a parameter related to electrode polarization, M and N are other fitting parameters.

Such a fitting model has successfully been used by Kresse et al. [15] for other systems. However, the conductivity term in Eq. (2a) gives only a simplified description of the low frequency dielectric absorption due to ionic conductivity. A more general model is presented in [16].

Dielectric spectra of the compounds studied show two kinds of relaxation processes shown in Figures 3(a) and 3(b). The fitting parameters are gathered in Table 2.

As seen there is a great influence of conductivity on the dielectric properties in the low frequency range below 1 kHz. That's why Turnkey Dielectric Spectrometer has been used to study the dielectric behaviour of the mixtures in the sub-hertz frequency range. As found in addition to conductivity there are some low frequency relaxation processes that influence the dielectric spectrum. The low frequency

Table 2. Fitting parameters for Cole-Cole plot shown in Figures 3(a) and (b)

Parameter	Value	Uncertainty
$\Delta\varepsilon_1$	12.15	±0.57
ν_{R1} [Hz]	394.05	±5.42
α_1	0.10	±0.01
$\varepsilon(\infty)$	3.29	±0.01
$\Delta\varepsilon_2$	8.10	±0.24
ν_{R2} [Hz]	1341.97	±8.88
α_2	~0 (fixed)	0
B	59.22	±2.33
N	0.66	±0.03
$A \cdot E + 10$ [S/m]	5.49	±0.33
M	0.61	±0.02
$\varepsilon(0)$	23,54	±0,82
ε_{01}	11.40	±0.25

dielectric spectrum in sub-hertz range originates from the space charge polarization and Maxwell-Wagner dielectric relaxation. Both these effects are theoretically described in [16] and will be discussed in detail in our next paper.

6. Conclusions

Mixing of the chiral MHOBS10 and achiral 8OS5 compounds allowed us to obtain a ferroelectric phase at room temperature.

The SmC* obtained aligns well in external electric field – forming a planar mono-domain.

The SmC* phase exhibits two collective dielectric relaxation processes of Debye-type. One of them seems to be a Goldstone mode and the other may be connected with Maxwell-Wagner relaxation.

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