

Binary mixtures of liquid crystalline compounds with a reentrant smectic- A^* phase

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Binary mixtures of chiral liquid crystalline homologs have been studied. One compound designated 9ZBL exhibited reentrancy of a paraelectric smectic- A^* phase, SmA_{RE}^* , below the ferroelectric SmC^* phase in the $\text{SmA}^*-\text{SmC}^*-\text{SmA}_{\text{RE}}^*$ phase sequence. Stabilization of the SmA_{RE}^* phase is established from studying binary mixtures of 9ZBL with its neighboring homologs 8ZBL and 10ZBL. Compound 8ZBL exhibits only SmA^* phase in a wide temperature range and for 10ZBL the $\text{SmA}^*-\text{SmC}^*$ phase sequence is observed on cooling. X-ray studies, dielectric spectroscopy, polarization, and tilt angle measurements have been carried out to characterize studied materials. For binary mixtures 9ZBL-10ZBL the reentrant SmA_{RE}^* phase is observed for all studied concentrations. For binary mixtures 9ZBL-8ZBL a very small amount of 8ZBL (up to 0.5 mole %) causes disappearance of the SmC^* phase. Nevertheless, a small anomaly in the temperature dependencies of the layer spacing, $d(T)$, accompanied by a significant decrease in diffracted x-ray intensity occurs within the SmA^* phase for mixtures containing up to 20 mole % of 8ZBL. This anomaly is evidence of the existence of a boundary between the SmA^* and SmA_{RE}^* phases, thus proving their different nature.

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I. INTRODUCTION

Liquid crystalline (LC) materials are known to exhibit a rich polymorphism. The ordering of phases typically increases upon temperature lowering. In some cases the regular sequence is broken due to different competing interactions in these systems. If a less ordered phase appears below the more ordered ones we call such a phenomenon reentrancy. This rather unusual effect has been observed in different LC systems [1-6]. First it was discovered in binary mixtures of strongly polar materials [7]. The reentrant nematic phase appeared upon cooling after the smectic- A (SmA) phase. Later a multiple reentrancy of nematic and SmA phases was found in rodlike materials with strong longitudinal dipole moments [8]. SmA reentrancy occurred in these cases due to the dimerization of molecules, which was confirmed by x-ray studies. The lower SmA phase was found to contain a higher percentage of dimers, while the upper one was composed mostly of monomers. Further, the reentrant behavior was also observed under pressure [9], when dimers were formed by overlapping aromatic parts of two molecules. However, different types of molecular association are possible depending on interactions between molecules and within their constituent parts.

In chiral smectics the reentrancy of the ferroelectric phase has been reported [10,11] in the ferroelectric smectic C^* (SmC^*)-antiferroelectric smectic C^* (SmC_A^*)- SmC^* phase sequence. The stabilization of the SmC_A^* phase in mixtures with the next regular homologs was studied in Ref. [12].

Recently a homolog series $n\text{ZBL}$ (n is a number of carbon atoms in the nonchiral chain) of chiral liquid crystalline compounds with two biphenyls connected by an ester group, one biphenyl being laterally substituted by a chlorine atom, was synthesized and studied [13]. One representative of this series (9ZBL) appeared to be very interesting due to the unique phase sequence of paraelectric $\text{SmA}^*-\text{SmC}^*-\text{reentrant SmA}_{\text{RE}}^*$ phases upon cooling. X-ray measurements were performed and temperature dependence of the layer

spacing, d , showed the formation of dimers can be excluded in the SmA_{RE}^* phase. An attempt to describe a reentrancy phenomenon for this system was done by Novotná *et al.* [14] on the basis of Landau theory. It was supposed that the temperature dependence of the lowest-term coefficient in the free energy expansion must be nonmonotonous and change sign from positive to negative at least twice in contrast to the simplest mean-field model. To achieve such a behavior the quadratic and cubic terms were included in the temperature dependence of the lowest-term coefficient in the Landau expansion.

For 9ZBL with the unusual $\text{SmA}^*-\text{SmC}^*-\text{SmA}_{\text{RE}}^*$ phase sequence an applied electric field strongly influences the values of the tilt angle, Θ , and polarization, P , within the whole range of the SmC^* phase. The electroclinic coefficient has been evaluated [13] for 9ZBL reaching maxima up to $2^\circ \text{ V } \mu\text{m}^{-1}$ at the $\text{SmA}^*-\text{SmC}^*$ and $\text{SmC}^*-\text{SmA}_{\text{RE}}^*$ phase transitions. The neighboring homolog 10ZBL exhibits a $\text{SmA}^*-\text{SmC}^*$ phase sequence. Nevertheless also for this compound rather unusual temperature dependencies of P and Θ have been detected in the SmC^* phase, evidencing the tendency of this compound to diminish both values after reaching a maximum upon cooling [13].

In the present work we study binary mixtures of 9ZBL with its neighboring homologs 8ZBL and 10ZBL. Homolog 8ZBL with a shorter chain exhibits only the SmA^* phase in a wide temperature range and 10ZBL shows the $\text{SmA}^*-\text{SmC}^*$ phase sequence. The tendency to form the ferroelectric SmC^* and reentrant SmA_{RE}^* phases is studied by different experimental techniques: x-ray diffraction, dielectric spectroscopy, and electro-optical and tilt angle measurements. The goal of our work is to establish stabilization of the SmA_{RE}^* phase and to study the tendency for its formation in the binary mixtures. Finally, speculation about the origin of paraelectric SmA^* phase reentrancy and microscopic mechanism of this phenomenon are presented.

II. EXPERIMENT

Different experimental techniques were used to characterize the physical properties of the mixtures. Both small-angle and wide-angle x-ray diffraction (XRD) experiments were performed to evaluate the layer thickness and to study possible in-plane order, respectively. X-ray experiments were carried out using the Bruker D8 Discover (CuK α radiation), equipped with the Anton Paar DCS-350 heating stage (temperature stability, 0.1 K), in the reflection mode for nonoriented samples with one free surface. For broad-angle XRD studies the Bruker D8 GADDS was used (CuK α line, Goebel mirrors, point beam collimator, HiStar area detector). The samples were prepared as droplets on the heated plate. The layer thickness, d , was calculated from the Bragg law:

$$n\lambda = 2d \sin \theta, \tag{1}$$

where λ is the x-ray wavelength and θ is the incident ray angle.

The tilt angle, Θ , was measured using a rotating analyzer method [15]. The He-Ne laser beam is circularly polarized with a Glan-Thompson prism and a quarter-wave plate. A rectangular switching voltage of frequency 120 Hz is applied to a sample. After passing through the analyzer rotating with a frequency of 90 Hz the light is detected by a photodiode and the signal is fed to the oscilloscope input. The intensity data wave form is decomposed into two sinusoidal curves and numerically analyzed to obtain a phase difference, which is equal to 2Θ .

Measurements of spontaneous polarization were performed by integration of polarization current measured under an alternating triangular electric field (up to 40 V/ μ m). A modified Sawyer-Tower bridge completed with a Tektronix TDC70 oscilloscope enabled us to reveal the hysteresis loop profile.

Frequency dispersion of permittivity was measured upon cooling using a Schlumberger 1260 impedance analyzer in a frequency range of 10 Hz to 1 MHz. The temperature of the sample was kept stable within 0.1 K during the frequency sweeps. The data were analyzed using the Cole-Cole formula for the frequency-dependent complex permittivity:

$$\varepsilon^* - \varepsilon_\infty = \frac{\Delta\varepsilon}{1 + (if/f_r)^{1-\beta}} - i \left(\frac{\sigma}{2\pi\varepsilon_0 f^n} + Af^m \right). \tag{2}$$

The second and the third terms are added to eliminate the low-frequency contribution to conductivity due to dc and the high frequency contribution from the resistance of indium tin oxide (ITO) electrodes, respectively. Here f_r is the relaxation frequency of the mode, $\Delta\varepsilon$ is the dielectric strength, β is the distribution parameter of relaxation, ε_0 is the permittivity of the vacuum, ε_∞ is the high frequency permittivity, and n , m , and A are the parameters of fitting. All electro-optical measurements were performed on commercial glass cells with transparent ITO electrodes, which were filled by means of capillary action in the isotropic phase. In such cells the liquid crystalline molecules are parallel to the sample plane (planar alignment).

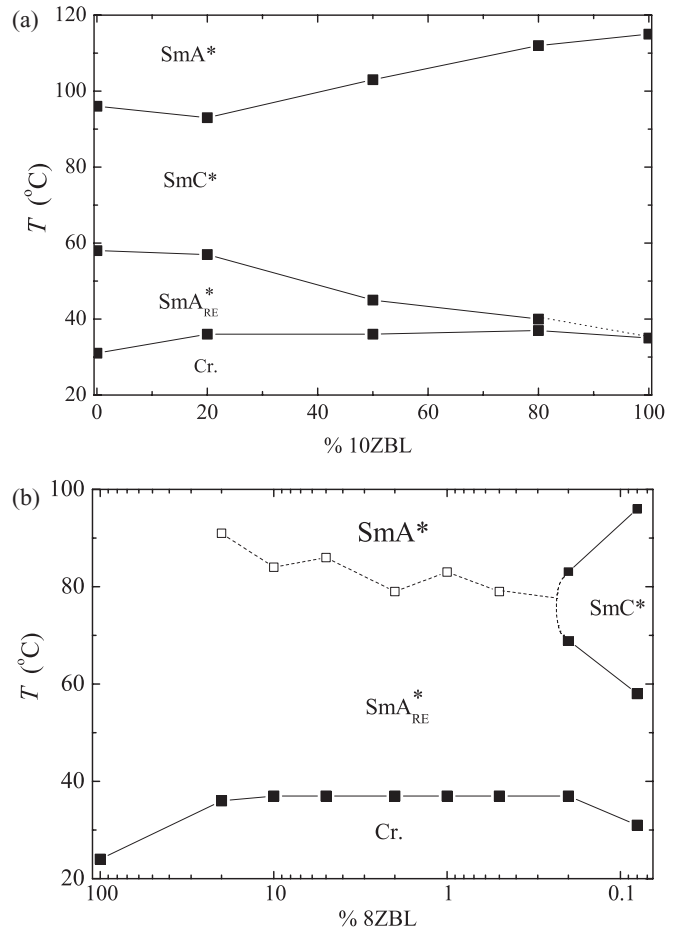


FIG. 1. Phase diagrams of (a) 9ZBL-10ZBL mixtures and (b) 9ZBL-8ZBL mixtures. The dotted line in panel (b) joins possible phase transitions between the SmA and SmA_{RE}^* phases.

III. RESULTS

A. Phase diagrams

Binary mixtures of 9ZBL compound with 10ZBL compound were prepared in concentrations 20 mole %, 50 mole %, and 80 mole % of 10ZBL in 9ZBL host. All studied mixtures exhibit the SmA^* - SmC^* - SmA_{RE}^* phase sequence [see Fig. 1(a)]. The temperature range of the reentrant SmA_{RE}^* phase becomes narrower while the range of the SmC^* phase increases with increasing concentration of 10ZBL.

In a binary mixture of 9ZBL with 8ZBL the SmC^* phase is induced only for very low concentrations of 8ZBL up to 0.2 mole %. For higher concentrations only the SmA phase occurs [see Fig. 1(b)]. Phase diagrams of 8ZBL-9ZBL mixtures are presented in Fig. 1(b) in logarithmic scale for better resolution. The phase transitions are not visible in differential scanning calorimetry study, which is typical for transitions between smectic phases with no order within the smectic layers. The phases and transitions between them have been identified from texture observation and confirmed by experiments described below, namely, temperature dependence of the layer spacing and dielectric properties (see Figs. 2 and 5, respectively).

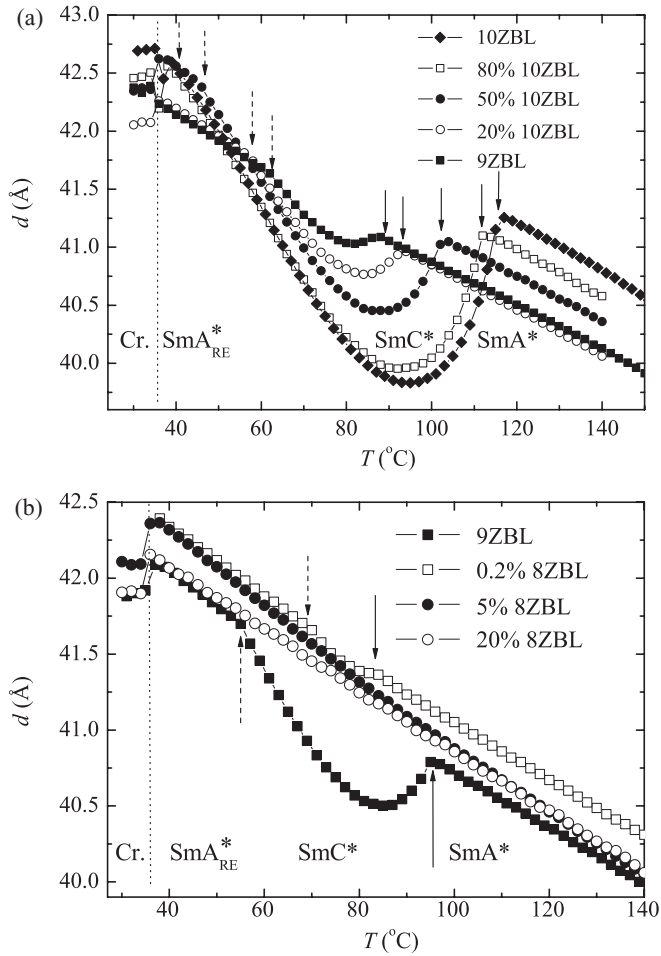


FIG. 2. Temperature dependencies of the layer spacing, d , for (a) 9ZBL-10ZBL and (b) 9ZBL-8ZBL mixtures and for pure 9ZBL. The SmA^* - SmC^* phase transitions are designated by solid arrows and the SmC^* - SmA_{RE}^* phase transitions by dashed arrows.

B. X-ray diffraction

The experiments have been carried out upon cooling from the isotropic phase. The layer spacing, d , has been evaluated from the peak in diffracted intensity using Eq. (1). The wide-angle diffraction did not detect any long-range positional or orientational order in the smectic layers; therefore hexatic order is excluded in all observed mesophases [13].

For pure 9ZBL and 10ZBL and their binary mixtures temperature dependencies of d are presented in Fig. 2(a). Layer spacing values grow upon cooling and by linear extrapolation we can establish a thermal expansion coefficient, α , in both upper SmA^* and lower SmA_{RE}^* phases (see Table I).

The layer spacing increase in the SmA^* phase has been explained by stretching of the molecular lateral chains and increase of the orientational order upon cooling. At the SmA^* - SmC^* transition temperature a clear drop in the layer spacing is observed, which is connected with the increasing of the molecular tilt angle. Nevertheless, a tendency of d to increase prevails and after reaching a local minimum, d values continue to increase upon cooling within the SmC^* phase. For all studied mixtures the SmC^* - SmA_{RE}^* phase transition has been established upon cooling. It is distinguishable on the

TABLE I. Thermal expansion coefficients, α , in $\text{\AA}/\text{K}$ for pure 8ZBL, 9ZBL, and 10ZBL compounds and in 9ZBL-10ZBL binary mixtures in SmA^* and SmA_{RE}^* phases.

Compound	SmA^*	SmA_{RE}^*
8ZBL	-0.018	
9ZBL	-0.018	-0.023
20% of 10ZBL	-0.019	-0.024
50% of 10ZBL	-0.019	-0.026
80% of 10ZBL	-0.020	-0.030
10ZBL	-0.021	

temperature dependencies of the layer spacing as a distinct kink and as a minimum on the diffracted intensity. Let us point out that at low temperatures d exceeds slightly the molecular length, which is about 41 \AA . The minima of diffracted intensity at both phase transitions (SmA^* - SmC^* and SmC^* - SmA_{RE}^*) reflect fluctuations of the molecular director. One can see that for higher concentrations of 10ZBL the SmC^* phase becomes wider and the layer shrinkage and, thus, the tilt angle become higher.

For some binary mixtures of 9ZBL with the neighboring homolog 8ZBL the temperature dependencies of the layer spacing, d , obtained from x-ray data, are presented in Fig. 2(b). One can see a small drop in d for the mixture of concentrations of 8ZBL of 0.2 mole % evidencing the SmA^* - SmC^* dependencies. For higher concentrations monotonous $d(T)$ dependencies have been detected. For pure 8ZBL exhibiting the SmA^* phase only the thermal expansion coefficient $\alpha = -0.018 \text{ \AA}/\text{K}$, which is identical with the value of α in the SmA^* phase of 9ZBL (see Table I), has been detected.

For the mixtures presented in Fig. 2(b) the deviations of $d(T)$ from linearity can be better visualized calculating the function $d(T) - d_{\text{LF}}(T)$, where d_{LF} is a linear fit of $d(T)$ over the whole smectic phase temperature range studied. The results are shown in Fig. 3. A remarkable minimum for the mixture with 0.2 mole % of 8ZBL corresponds to the SmC^* phase. For concentrations higher than 0.2 mole % of 8ZBL up to 20 mole % (where the SmC^* phase is not present) there is a clear turn in the slope of $d - d_{\text{LF}}(T)$ (see Fig. 3) corresponding to a

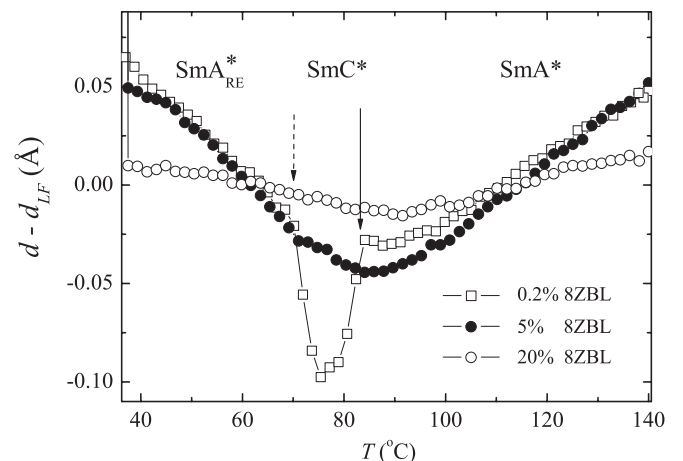


FIG. 3. Deviation from linear fit of the layer spacing, $d - d_{\text{LF}}$, for some of the 9ZBL-8ZBL mixtures.

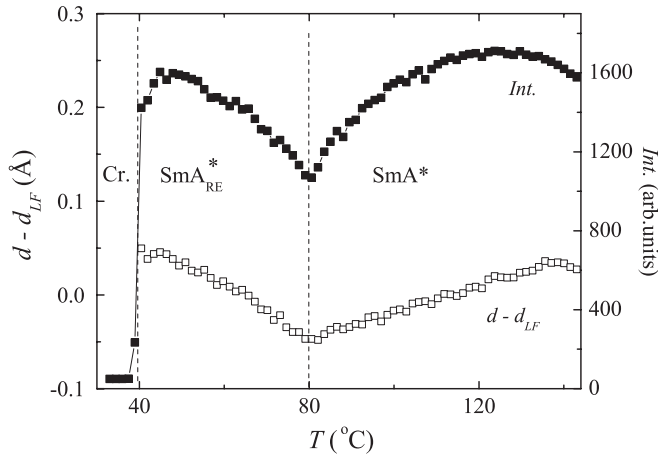


FIG. 4. Temperature dependence of the x-ray diffracted intensity, $Int.$, and deviation from linear fit of the layer spacing, $d - d_{LF}$, for 5 mole % of 8ZBL in 9ZBL host mixture.

change of the thermal expansion coefficient at a temperature of about 80 °C. Moreover, the plot of the diffracted x-ray intensity exhibits a distinct anomaly at the same temperature (Fig. 4). This minimum reflects fluctuations and evidences transition between the upper and lower SmA^* phases. We designated corresponding phases as SmA^* and SmA_{RE}^* despite the absence of a ferroelectric phase between them. In Fig. 4 the temperature dependence of the diffracted x-ray intensity together with $d - d_{LF}(T)$ for 5 mole % of 8ZBL in 9ZBL host mixture is presented and the border between SmA^* and SmA_{RE}^* is depicted by a dotted line.

C. Dielectric spectroscopy

Dielectric spectroscopy was carried out to study polar fluctuations in the smectic phases. One distinct mode was found in each phase. In the SmA^* phase it corresponds to the soft mode, which reflects fluctuations of the molecular tilt magnitude. In the ferroelectric SmC^* phase the soft mode also exists, but it is overwhelmed by large phase fluctuations of the tilt (Goldstone mode). Real and imaginary parts of complex dielectric permittivity $\epsilon^*(f) = \epsilon' - i\epsilon''$ were simultaneously fitted to Eq. (2) to obtain the temperature dependence of the relaxation frequency, f_r , and the dielectric strength, $\Delta\epsilon$.

For 9ZBL-10ZBL binary mixtures temperature dependencies of the relaxation frequency, f_r , and reciprocal values of dielectric strength, $1/\Delta\epsilon$, are shown in Fig. 5. A linear decrease (softening) of f_r and $1/\Delta\epsilon$, which corresponds to the soft mode, is observed in both paraelectric phases (SmA^* and SmA_{RE}^*) when approaching the ferroelectric phase (Curie-Weiss regime). Only below the SmC^* - SmA_{RE}^* transition is the expected increase of f_r surpassed by the increase of viscosity upon cooling, which results in the decrease of f_r . Besides, the lower increase of f_r upon cooling in the SmA_{RE}^* is explained by the mean-field model presented in Ref. [14], which assumes nonmonotonous temperature dependence of the first coefficient in the free energy expansion. In the SmC^* phase the parameters of the Goldstone mode should be temperature independent, which is true for Fig. 5(b). The decrease in f_r upon cooling is again a result of the viscosity increase.

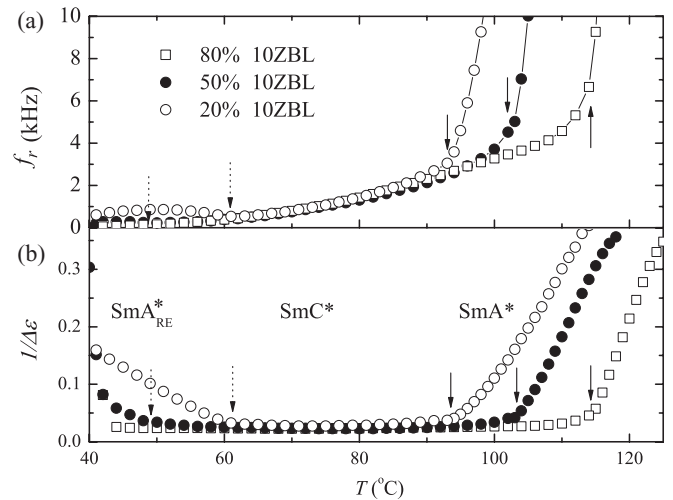


FIG. 5. Temperature dependence of (a) the relaxation frequencies, f_r , and (b) the inverse dielectric strength, $1/\Delta\epsilon$, for 9ZBL-10ZBL mixtures. Phase transition temperatures are marked by arrows (solid-line arrows for SmA^* - SmC^* phase transitions and dashed arrows for SmC^* - SmA_{RE}^* phase transitions).

The bias field has been applied to suppress the Goldstone mode in the SmC^* phase and to study the soft mode behavior in the ferroelectric phase as well. Dielectric spectroscopy measurements in different bias fields (1 V/μm and 2 V/μm) have been performed for binary mixtures. The inverse dielectric strength of 20 mole % of 10ZBL in 9ZBL host mixture is presented in Fig. 6. Under a bias field, softening of $1/\Delta\epsilon(T)$ is clearly seen in the vicinity of the SmA^* - SmC^* and SmC^* - SmA_{RE}^* phase transitions even from the SmC^* phase side. One can see that the temperature range of the ferroelectric phase becomes broader under increasing bias electric field. This fact is in agreement with the model of the reentrant SmA^* phase proposed in Ref. [14].

For selected 9ZBL-8ZBL binary mixtures temperature dependencies of the relaxation frequency, f_r , and the reciprocal dielectric strength, $1/\Delta\epsilon$, are presented in Fig. 7. Softening of the relaxation mode is reflected in the critical decrease of

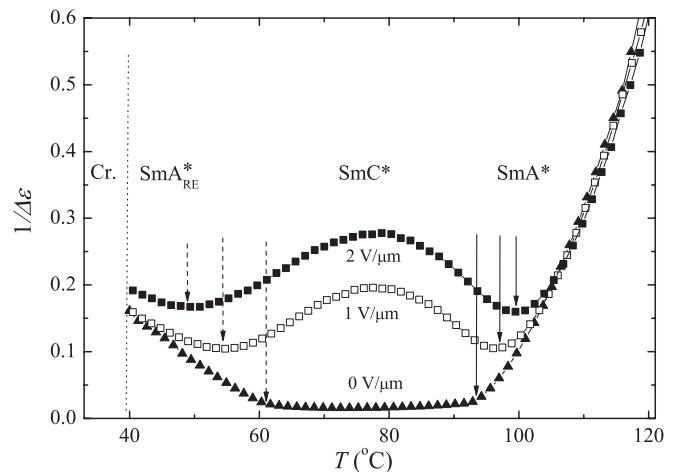


FIG. 6. Inverse dielectric strength, $1/\Delta\epsilon$, for 20 mole % of 10ZBL in 9ZBL host mixture without field and in various bias fields. The arrows show phase transitions.

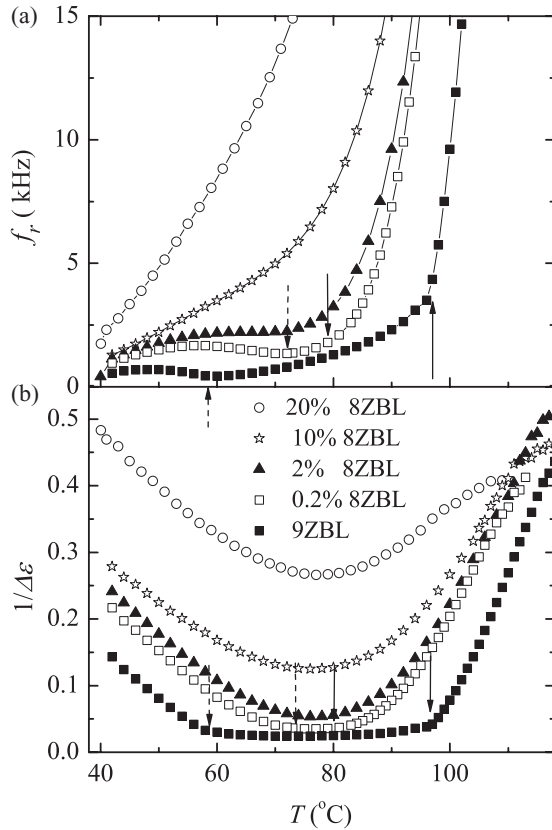


FIG. 7. (a) Relaxation frequencies, f_r , and (b) inverse dielectric strength, $1/\Delta\epsilon$, for 9ZBL-8ZBL mixtures of designated concentrations. The solid-line arrows denote the SmA^* - SmC^* phase transitions and the dashed-line arrows denote the SmC^* - SmA_{RE}^* phase transitions.

f_r and $1/\Delta\epsilon$ when approaching the SmC^* phase on cooling (Fig. 7). Similarly as in the 9ZBL-10ZBL system the softening is not seen in the temperature dependence of f_r in the SmA_{RE}^* phase. The magnitude of the dielectric strength increases with increasing 9ZBL concentration [seen as decreasing for $1/\Delta\epsilon(T)$ in Fig. 7(b)]. A horizontal part in the $1/\Delta\epsilon$ plot occurs for pure 9ZBL and 0.2 mole % of 8ZBL in 9ZBL host mixture, both exhibiting the ferroelectric SmC^* phase. In $1/\Delta\epsilon(T)$ dependence, the softening is also seen from the SmA_{RE}^* phase side. A tendency toward softening of the relaxation mode has been found even for mixtures without the SmC^* phase up to concentrations of 20 mole % of 8ZBL in 9ZBL host. In these mixtures $1/\Delta\epsilon(T)$ is decreasing upon cooling, but then continuously increases again after reaching a local smooth minimum at a temperature of about 80 °C. Let us point out that this temperature is approximately the same as that at which the change of thermal expansion coefficient, taken from x-ray data, has been detected.

Dielectric spectroscopy measurements were performed under various bias fields (1–3 $\text{V}/\mu\text{m}$). For bias fields higher than 1 $\text{V}/\mu\text{m}$, in the mixture of concentration of 0.5 mole % of 8ZBL in 9ZBL host, with the SmA phase only, we detected specific anomalies typical for the SmA^* - SmC^* and SmC^* - SmA_{RE}^* phase transitions (Fig. 8, cf. with Fig. 6). These anomalies indicate that even under such a low bias a narrow

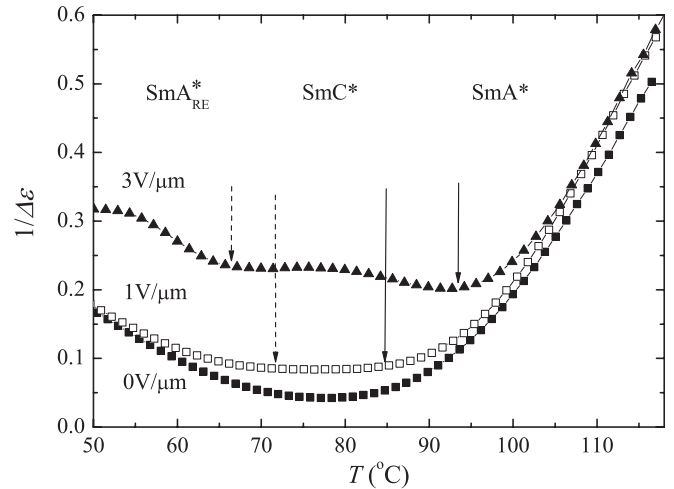


FIG. 8. Inverse dielectric strength, $1/\Delta\epsilon$, for a mixture of 0.5% 8ZBL in 9ZBL host, measured without bias and under indicated bias fields. Phase transitions are indicated by arrows.

SmC^* phase is induced. With increasing bias the anomalies become more pronounced and the SmC^* phase broadens.

D. Spontaneous quantities

Dependence of the tilt angle and spontaneous polarization on electric field as well as on temperature has been studied for binary mixtures of the studied compounds. For 9ZBL-10ZBL binary mixtures, the tilt angle and polarization measured in a 15 $\text{V}/\mu\text{m}$ electric field are shown in Fig. 9 in dependence of temperature. One can see that the higher the concentration of 10ZBL the higher the spontaneous quantities detected are. Similar to the 9ZBL compound, a strong electroclinic effect [16] is detected in the vicinity of the SmA^* - SmC^* and SmC^* - SmA_{RE}^* phase transitions, which is manifested as induction of the tilt by the electric field in the SmA^* or SmA_{RE}^* phases rather far from the transition to the SmC^* phase [14]. The induced tilt can reach values comparable with the tilt deduced from the x-ray data in the SmC^* phase. The susceptibility of the tilt to the electric field is also pronounced in the whole SmC^* phase region. It was necessary to apply 15 $\text{V}/\mu\text{m}$ to obtain the saturated value of the tilt, similar to pure 9ZBL [14].

For 9ZBL-8ZBL binary mixtures the temperature dependence of the tilt angle and spontaneous polarization was measured for several concentrations. For 0.5 mole % of 8ZBL in 9ZBL host mixture, exhibiting only the SmA^* phase in the field-free state, the temperature dependence of the tilt under different measuring fields (up to 25 $\text{V}/\mu\text{m}$) is presented in Fig. 10. Qualitatively the same behavior as that for the 9ZBL-10ZBL system was observed, but the saturation occurs for the electric field of about 25 $\text{V}/\mu\text{m}$ and the maximum tilt reaches only 12.5°. The nonmonotonous temperature dependence of the tilt angle indicates that the SmA^* phase was transformed under the field.

The temperature dependencies of the polarization measured at 15 $\text{V}/\mu\text{m}$ are shown for different 9ZBL-8ZBL mixtures in Fig. 11. The behavior is similar to that found for the tilt angle; polarization first increases and after reaching a

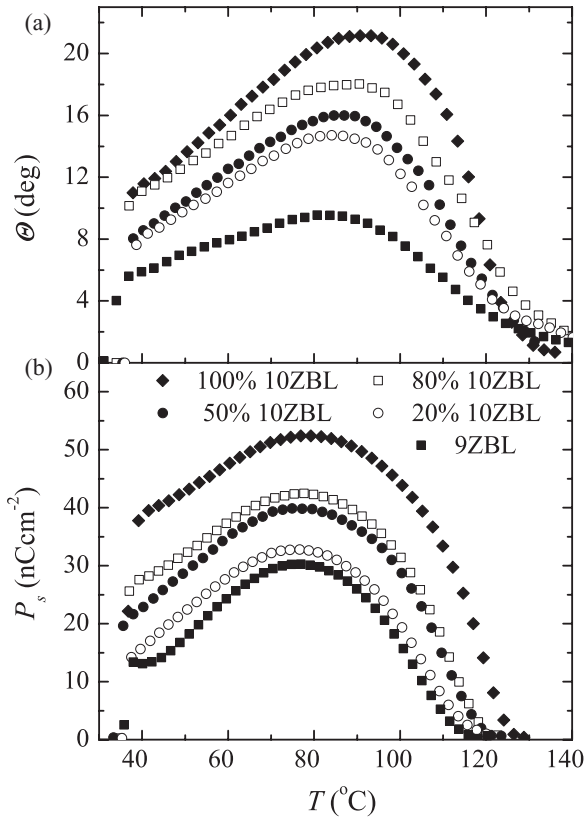


FIG. 9. Temperature dependence of (a) tilt angle, Θ , and (b) spontaneous polarization, P_s , for 9ZBL-10ZBL mixtures (concentrations are designated) measured in an electric field of $15 \text{ V}/\mu\text{m}$.

maximum decreases upon cooling. The characteristic peaks in the switching current are seen for mixtures up to 20 mole % of 8ZBL, where the SmC^* phase does not exist without the electric field. This proves that in these mixtures the SmC^* phase is induced by the measuring field. The value of the maximum polarization, as well as the maximum tilt, is higher for mixtures with higher concentrations of 9ZBL compound. In both studied binary systems the phase transitions are smeared

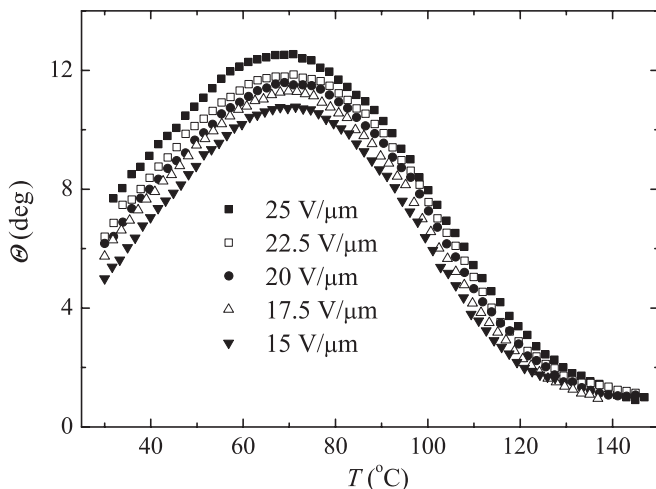


FIG. 10. Temperature dependence of the tilt angle, Θ , for 0.5 mole % of 8ZBL mixture measured under different electric fields.

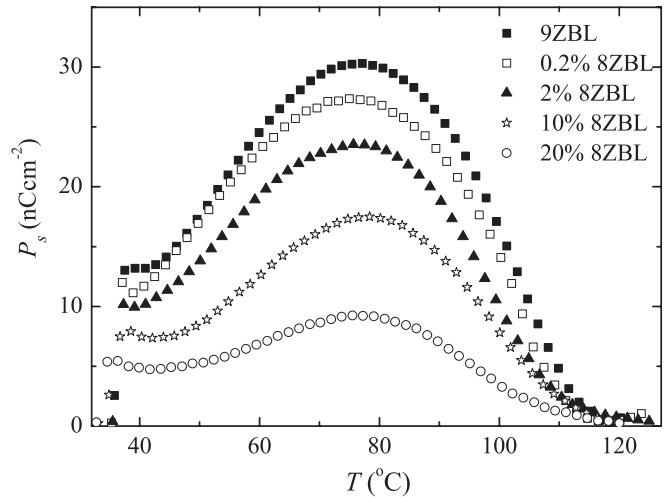


FIG. 11. Temperature dependence of spontaneous polarization for 9ZBL-8ZBL mixtures (concentrations are designated) measured in an electric field of $15 \text{ V}/\mu\text{m}$.

under the electric field and thus it is difficult to establish the phase transition temperatures.

IV. DISCUSSIONS AND CONCLUSIONS

Binary mixtures of 9ZBL compound, which exhibits a unique reentrancy phenomenon, with its neighboring homologs were studied.

The prepared mixtures with 10ZBL compound, possessing a paraelectric SmA^* -ferroelectric SmC^* phase sequence, exhibit the reentrant SmA^* phase for all studied concentrations. The SmA_{RE}^* temperature range gradually decreases and simultaneously the range of the ferroelectric SmC^* phase broadens with increasing the concentration of 10ZBL [see Fig. 1(a)]. The layer spacing of both high-temperature and low-temperature SmA^* phases is not very different, contrary to the SmA phase reentrancy investigated in Refs. [17,18].

In the series prepared with the 8ZBL homolog, possessing only the SmA^* phase, the ferroelectric SmC^* phase does not occur for concentrations of 8ZBL higher than 0.2 mole %. Nevertheless, mixtures with concentrations of 8ZBL up to 20 mole % show a small anomaly in the thermal expansion coefficient within the SmA^* phase (see Fig. 3). The temperatures of the anomaly can be regarded as a borderline between the SmA^* and SmA_{RE}^* phases for various concentrations. Let us point out that in the vicinity of this temperature also derivation of the temperature dependence of the reciprocal dielectric strength changes a sign [see Fig. 7(b)]. One can find an analogy between this line and the so-called Widom line, which has been identified in supercritical fluids as a border between liquidlike and gaslike behavior [19] or in supercooled liquid water as a border between two different liquids [20]. At the Widom line, emanating from the critical point in the pressure-temperature phase diagram some properties show anomalies, for example, dispersion of acoustic waves [19] or compressibility [20]. At the borderline found here within the SmA^* phase, in addition to the anomaly in the thermal expansion, a significant decrease in diffracted x-ray intensity takes place, evidencing

increased fluctuations. This phenomenon is typical also for phase transitions.

We suppose that the anomaly in the expansion coefficient reflects a difference in the expansion mechanisms in both SmA^* phases. In the SmA^* phase the thermal expansion is expected to be predominantly a consequence of the stretching of the lateral molecular chains. We suppose that in the SmA_{RE}^* phase the expansion can be explained by sterical hindrance in the packing of the molecules, caused by the presence of a bulky Cl atom. This mechanism is described in detail in Ref. [11]. The existence of the soft mode in the vicinity of the borderline within the SmA phase suggests that in this temperature region the SmC^* phase is energetically rather close, but the softening is not completed. This is the reason why a weak electric field stabilizes the SmC^* phase in this temperature region. This SmC^* phase can be broadened by increasing the applied electric field.

To conclude, the present study of mixtures enables us to establish the stabilization of phases induced by the 9ZBL

compound and the reentrancy of the SmA phase. Some of the mixtures exhibit anomalies in physical properties at distinct temperatures inside the SmA phase, demarking a change in the nature of these phases. The extremely high sensitivity to the electric field of all the studied materials, revealed namely in electro-optical experiments, is promising for applications.

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