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S. Haldar [a], D. Sinha [a], D. Goswami [a], P. K. Mandal [a], K. C. Dey [b] & A. Lapanik [c]

[a] Physics Department, North Bengal University, Siliguri, India

[b] Physics Department, ABN Seal College, Cooch Behar, India

[c] Institute of Physical Chemistry, Darmstadt University of Technology, Darmstadt, Germany

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S. HALDAR,[1] D. SINHA,[1] D. GOSWAMI,[1]
P. K. MANDAL,[1] K. C. DEY,[2] AND A. LAPANIK[3]

[1]Physics Department, North Bengal University, Siliguri, India
[2]Physics Department, ABN Seal College, Cooch Behar, India
[3]Institute of Physical Chemistry, Darmstadt University of Technology, Darmstadt, Germany

Six multi-component room-temperature ferroelectric liquid crystal mixtures are investigated using X-ray diffraction and polarization studies. Layer spacing and average intermolecular distance in SmC phase are found to differ marginally. In two mixtures layer spacings show slightly increasing trend with temperature whereas in three other mixtures it shows slightly decreasing trend, in the remaining mixture it remains almost constant. Tilt angles determined from X-ray data are found to be similar to those observed from optical measurements. Spontaneous polarisations are found to vary widely and associated critical exponent is observed to deviate from the mean field value.*

Keywords Average intermolecular distance; critical exponent; room temperature FLC mixtures; SmC* layer spacing and tilt angle; spontaneous polarization; X-ray diffraction study

1. Introduction

Ferroelectric liquid crystals (FLCs) have been the subject of intense investigation for their intriguing properties for fundamental condensed matter research. These materials combine the ferroelectric, electrooptic, piezoelectric and pyroelectric properties of solid polar dielectric materials with the flow characteristics of the liquids. These materials are also important for their application in fast switching flat panel displays, optical light modulators, optical signal processing and computing [1,2]. In order to realize the possible and contemplated applications of FLC materials they must have properties like temperature range, rise time, birefringence, polarization, tilt angle, length of pitch, viscosity, thermal and UV stability properties tailored to the needs of specific application. In general, no single FLC compound can satisfy all the requirements. Multi-component mixtures are, therefore, formulated to optimize

Address correspondence to P. K. Mandal, Physics Department, North Bengal University, Siliguri-734013, India. Tel.: +91-3532776338; Fax: +91-3532699001; E-mail: mandal_pradip@yahoo.com

the required properties for practical applications. Keeping these in mind we have selected proper host materials to control the temperature range and tilt angle; chiral dopants to control the switching speed and helical pitch and birefringence dopants to adjust the birefringence to the desired level [3]. Six multi-component room-temperature ferroelectric liquid crystal mixtures have been formulated and investigated using optical polarizing microscopy, dielectric spectroscopy, electro-optic as well as small angle X-ray diffraction methods. In all the mixtures SmC^* phase is either induced or enhanced. Effect of various dopants on the occurrence and thermal stability of different phases, spontaneous polarizations and different types of dielectric absorption behaviour have been discussed in previous publication [4]. Here we report results of small angle X-ray diffraction studies on the randomly oriented samples of these mixtures. Temperature dependence of spontaneous polarization has also been reported.

2. Experimental Methods

2.1. *Preparation of Mixtures*

Mixtures were prepared using two multi-component matrices as hosts; non-fluorinated and partially fluorinated chiral molecules as dopants. Molecular structures of the mixing components are shown in Figure 1. Host1 is a mixture of three phenyl pyrimidines (with $n = 8$ and $m = 6,8,9$ of molecule I, Fig. 1) and one biphenyl pyrimidine (with n, $m = 8$ of molecule II, Fig. 1) whereas Host2 is mixture

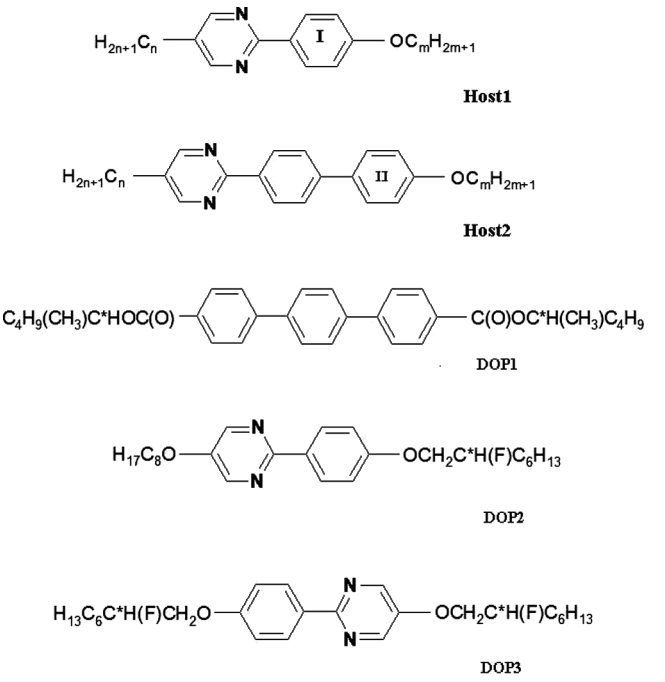

Figure 1. Molecular structures of the non-chiral host molecules (I and II) and the chiral dopant molecules (Dop1 – Dop3).

Table 1. Phase transition temperatures of the mixtures

Mixtures	Transition temperatures (°C)
LAHS1 (Host1 + Dop1)	Cr < 20 SmC* 80.6 SmA* 81.1 N* 87.0 I
LAHS2 (Host2 + Dop1)	Cr < 20 SmC* 58 SmA* 66 I
LAHS3 (Host2 + Dop2)	Cr < 20 SmC* 59.8 N* 69.7 I
LAHS4 (Host1 + Dop3)	Cr < 20 SmC* 75.5 N* 92 I
LAHS5 (Host2 + Dop3)	Cr < 20 SmC* 60 SmA* 70 N* 72 I
LAHS6 (Host2 + Dop1 + Dop3)	Cr < 20 SmC* 43 SmA* 73 I

of only three phenyl pyrimidines (with n = 8, m = 6,8 and n = 10, m = 8 of molecule I, Fig. 1). Mixing components of the mixtures and their transition temperatures are shown in Table 1.

2.2. *X-ray Diffraction Studies*

Small angle X-ray diffraction photographs of the randomly oriented samples were taken using custom built high temperature camera [5]. Scanned photographs were analyzed to find the smectic layer spacing (d) and the average intermolecular distance (D) between the molecules following procedure described before in [6]. Tilt angles in smectic phase were calculated using weighted average molecular lengths, individual lengths were determined building most extended molecular models.

2.3. *Polarization and Tilt Measurements*

Home-made ITO-coated cells, pre-treated for planar alignment, were used (cell thickness was around 3 μm and area about 1 cm^2). Cell temperature was controlled using Mettler FP 80/82 controller. Spontaneous polarization (P_S) was measured by reversal current method [7–9] using triangular wave (10 Hz) from HP 34401A function generator. Detail procedure has been described in earlier communication [10]. Tilt angles were measured by recording the two angular positions of the cell corresponding to the maximum transmitted light intensity when the cell was switched by a square wave pulse. Intensity was measured using a photodiode and oscilloscope.

3. Results and Discussion

All the mixtures exhibit ferroelectric phase from below room temperature over a considerable range. Stability of SmC* phase is maximum (60.6 °C) in LAHS1 followed by LAHS4. Mixtures (LAHS3 and LAHS5) having dopants with same core structure but with chirality at one or both ends produce similar thermal stability of SmC* phase. Presence of the two dopants (DOP1 and DOP3) with chirality at both ends reduces thermal stability drastically (LAHS6).

Temperature variations of layer spacings (d) in the ferroelectric phase SmC* phase are depicted in Figure 2. Layer spacings are found to differ marginally among the mixtures. This is expected behaviour since the weighted average length of the molecules in the mixtures varies from 30.3 to 31.1 Å. In mixtures LAHS1 and LAHS6 layer spacings show slightly increasing trend with temperature whereas in

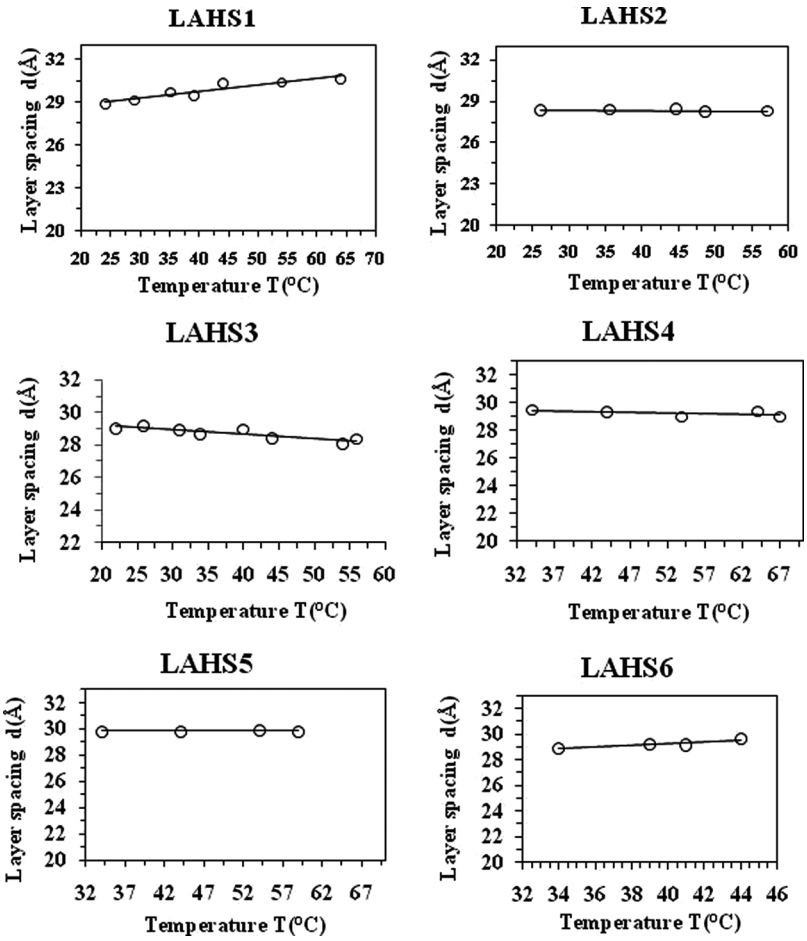

Figure 2. Layer spacing of the mixtures in the SmC* phase as a function of temperature.

mixtures LAHS2, LAHS3 and LAHS4 it shows slightly decreasing trend, in LAHS5 it remains almost constant.

Variations of average intermolecular distance (D) with temperature are shown in Figure 3. Mixtures of DOP1 and DOP3 in Host1 (LAHS1 and LAHS4) show slightly increasing trend in D with temperature. Mixtures of DOP1 and DOP2 in Host2 (LAHS2 and LAHS3) also show same behaviour. On the other hand, LAHS5 and LAHS6 which are mixtures of DOP3 or DOP1 + DOP3 in Host2 show slightly decreasing trend.

The lengths of the mixing molecules were determined by building stereo models of the molecules and considering their most extended conformation. From layer spacing tilt angles in SmC* phase have been calculated using the weighted average length of molecules in the mixtures. Near ambient temperature observed tilt angles are found to be 21.9, 22.2, 16.8, 16.9, 10.0 and 18.2° respectively in mixtures LAHS1 to LAHS6. Optical tilt angles were also measured and found to be close to the value observed from X-ray study. High tilt angle is observed in LAHS2 containing only phenyl pyrimidines in host (Host2) and non-fluorinated molecule with chirality at

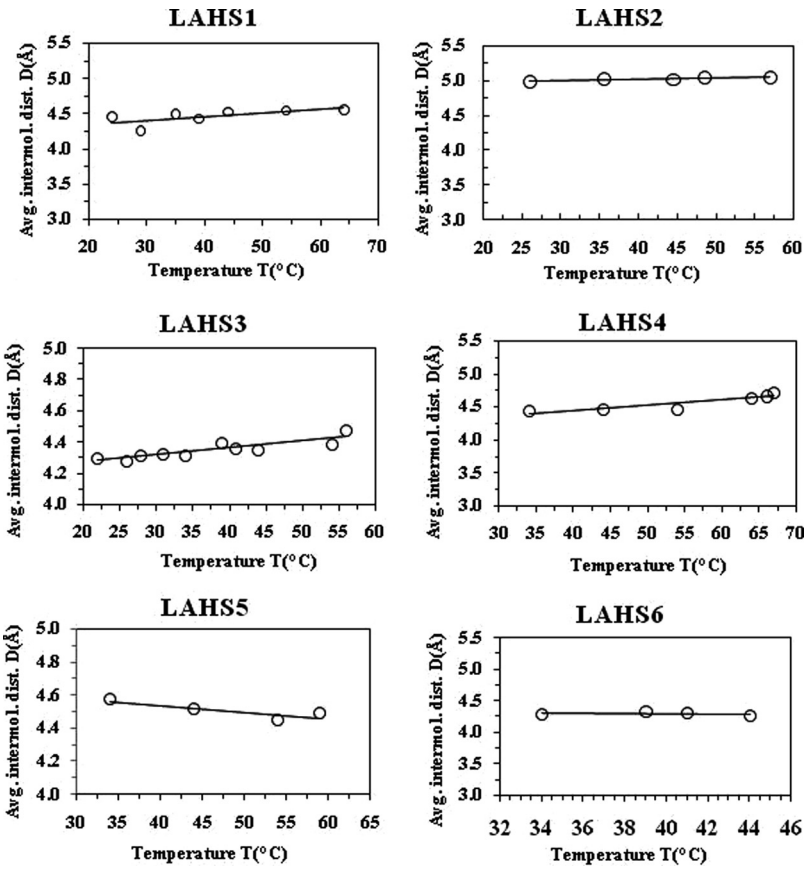

Figure 3. Average intermolecular distance of the mixtures in the SmC* phase as a function of temperature.

both ends as dopant (DOP1). Tilt angle is found to be least in LAHS5 when singly fluorinated molecule with chirality at both ends is used as dopant (DOP3), the host remaining same. Temperature variation of tilt angle is shown in Figure 4. Observed behaviour is opposite to that observed in layer spacing.

We also measured spontaneous polarisations (P_s) of the mixtures and their variation with temperature is shown in Figure 5 for mixtures LAHS1, 3, 4 and 6, data for other mixtures were reported before [4]. P_s values are found to vary widely (12.9–62.2 nC/cm^2) at room temperature. It is observed that mixtures with dopants having chiral centres at both ends posses relatively high P_S compared to mixtures with dopant having one chiral centre. Mixture with two chiral compounds having opposite optical rotations is found to have minimum P_S. Measured P_S data were fitted nicely to the mean-field model $P_S = P_0 (T_C - T_0)^{\beta}$ where T_C is the SmC*– SmA* transition temperature and β is critical exponent for the secondary order parameter [11]. Fitted T_C values, shown in Table 2, are found to be within ±4°C of the observed temperatures except in LAHS1 and LAHS5. Moreover, since fitted β-values (Table 2) are found to deviate from the mean field value (0.5) the SmC*– SmA* transition may not be strictly the second order in nature in these mixtures.

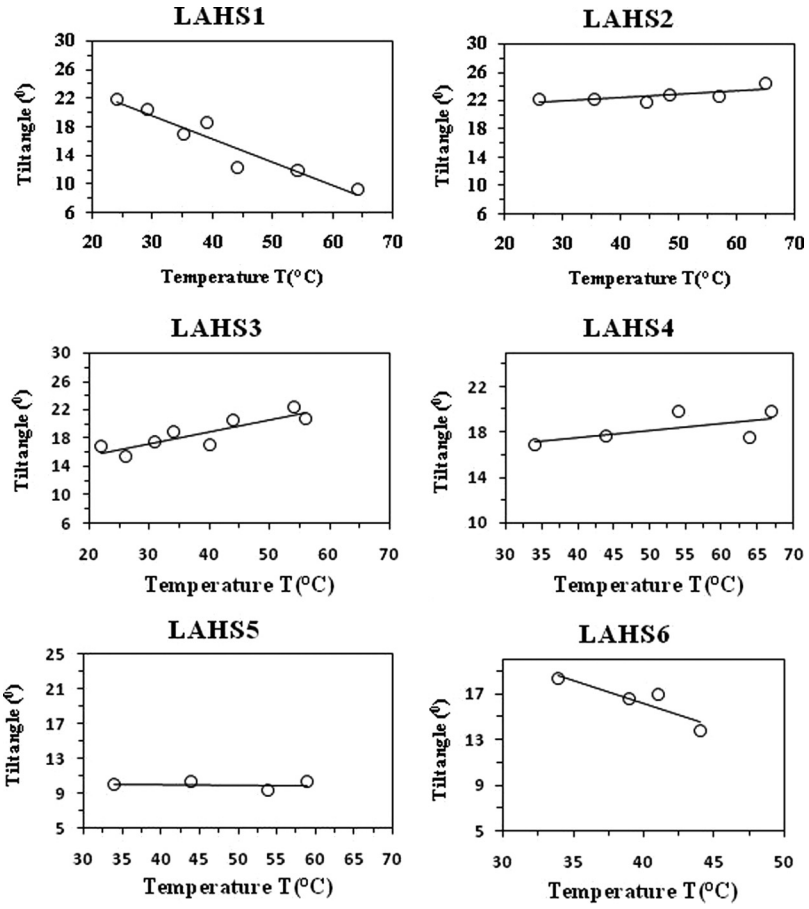

Figure 4. Tilt angle of the mixtures in the SmC* phase as a function of temperature.

4. Conclusions

Six multi-component room-temperature FLC mixtures have been formulated using two different types of host mixtures and three dopants. Rigidity of the core structure, nature of chirality and extent of fluorination of the host and dopant molecules were reported earlier to have pronounced effect on various mixture properties like ferroelectric phase stability, spontaneous polarization and collective mode relaxation behaviour [4]. However, layer spacing in the ferroelectric SmC* phase, determined from X-ray study, are found to differ marginally among the mixtures. This is expected since the weighted average lengths of the molecules in the mixtures do not differ much. In mixtures LAHS1 and LAHS6 layer spacings show slightly increasing trend with temperature whereas in mixtures LAHS2, LAHS3 and LAHS4 it shows slightly decreasing trend, in LAHS5 it remains almost constant. Average intermolecular distances of the molecules are also found to be similar in the mixtures. It shows slightly increasing trend with temperature in LAHS1 to LAHS4, opposite trend is observed in remaining two mixtures. Tilt angles in SmC* phase have also been determined using the weighted average lengths of the mixing molecules and

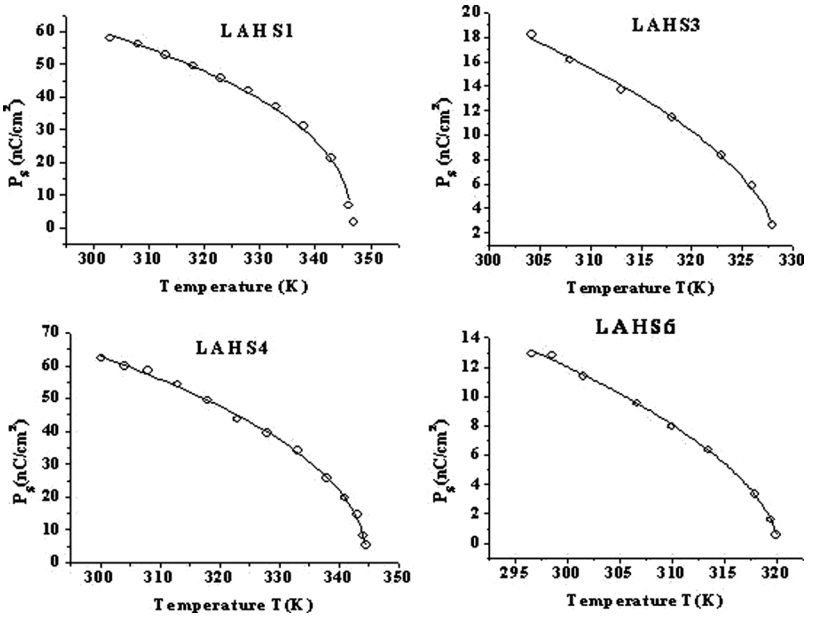

Figure 5. Variation of spontaneous polarization P_S of the mixtures with temperature.

Table 2. Fitted transition temperatures (SmC*– SmA*) and critical exponents β

	Transition temperatures (°C)		
Mixtures	Observed	Fitted	Critical exponent β
LAHS1	80.6	73.7 ± 0.2	0.42 ± 0.02
LAHS2	58.0	58.2 ± 0.2	0.42 ± 0.03
LAHS3	59.8	55.8 ± 0.4	0.53 ± 0.03
LAHS4	75.5	71.7 ± 0.2	0.47 ± 0.01
LAHS5	60.0	53.7 ± 0.8	0.43 ± 0.05
LAHS6	43.0	47.1 ± 0.1	0.57± 0.02

are found to be similar to those observed from optical measurements. High tilt angle is found in LAHS2 containing only phenyl pyrimidines in host and non-fluorinated molecule with chirality at both ends as dopant. Tilt angle is found to be least in LAHS5 when singly fluorinated molecule with chirality at both ends is used as dopant, the host remaining same. Spontaneous polarisations of the mixtures shows wide variation and the critical exponent β is observed to deviate from the mean field value at SmC*– SmA* transition suggesting that the nature of transition may not be strictly second order.

Acknowledgment

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