Crystals 2022

Type of the Paper (Proceedings, Abstract, Extended Abstract, Editorial, etc.)

Study of the Critical Behaviour in the Vicinity of Various Phase Transitions Associated with Two Antiferroelectric Enantiomers R-Mhpobc, S-Mhpobc and their Racemic Mixture †

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Abstract: High resolution birefringence measurements and modulated differential scanning calorimetry have been carried out in order to investigate the critical behaviour near the isotropic to smectic-A, smectic-A to smectic-C * phase transitions associated with two well known antiferroelectric liquid crystalline materials R- and S-enantiomers of MHPOBC [4-(1-methylheptyloxycarbonyl) phenyl 4 -octyloxybiphenyl-4-carboxylate] and their racemic mixture. The heat capacity anomaly and the birefringence data serve as order parameter and the critical exponents extracted from these order parameters corresponding to the various transitions associated with the investigated materials indicates the nature of the transition whether it is first order or second order. The data have been analyzed in detail with the renormalization-group expression with correction-to-scaling terms. A comparison of specific heat-capacity critical exponent found from the mean-square fluctuations of the tilt angle <δ 2(T)> and the critical exponent (α') explored from the birefringence differential quotient Q(T) for the SmA-SmC * phase transition has also been done for pure R-MHPOBC. The nature of phase transition associated with the racemic mixture of MHPOBC has also been discussed in the light of precise birefringence and specific heat capacity measurements.

Keywords: Specific heat capacity, Optical birefringence, Critical behaviour, Birefringence suppression, Tilt angle fluctuation, Critical exponent.

Citation: Lastname, F.; Lastname, F.; Lastname, F. Title. *Chem. Proc.* **2021**, *3*, x. https://doi.org/10.3390/xxxxx

Published: date

1. Introduction

Study of antiferroelectric liquid crystals (AFLCs) exhibited by elongated chiral molecules becomes a subject of significant interest not only in scientific but also in technological points of view after the discovery of antiferroelectricity in liquid crystals [1-2]. The presence of delicate balancing of ferroelectric and antiferroelectric ordering interplay shows variant chiral smectic-C (SmC) subphases characterized by the layer-to-layer tilt-azimuthal angles is one of the prominent features in AFLCs. Different properties of chiral antiferroelectric (smectic-CA*), ferroelectric (smectic-C*) and intermediate phases (smectic-C *, smectic-Cγ*) of chiral smectic liquid crystals have attracted a lot of attention so far because of the extraordinary optical and electro-optical properties of these novel phases have great potential for application in flat panel displays. At the same time, the rich variety of structures that are observed in the antiferroelectric chiral smectic materials has initiated the development of new theoretical approach for the description of phase transitions between these novel phases.

2. Results and Discussions

Critical behaviour in the vicinity of I-SmA and SmA-SmC$^*_\alpha$ phase transitions of R, S-MHPOBC and their racemic mixture:

Determination of critical exponent from specific heat capacity anomaly:

In order to determine the critical exponent, the ΔC_P data have been analyzed with the following renormalization-group expression including the corrections-to-scaling terms [3-4]:

$$\Delta C_P(T) = \frac{A^{\pm}}{\alpha}|\tau|^{-\alpha}(1 + D^{\pm}|\tau|^{\Delta}) + E(T - T_C) + B \tag{1}$$

Determination of critical exponent from birefringence:

The differential quotient Q(T) is defined as [5-6]:

$$Q(T) = -\frac{\Delta n(T) - \Delta n(T_C)}{T - T_C} \tag{2}$$

where $\Delta n(T_C)$ is the birefringence value at T_C (phase transition temperature) as obtained by differentiating the temperature dependence of Δn. The Q(T) data have been analyzed in detail with the renormalization-group expression including the correction-to-scaling terms [7-8]:

$$Q(T) = \frac{A^{\pm}}{\alpha'}|\tau|^{-\alpha'}(1 + D^{\pm}|\tau|^{\Delta}) + E(T - T_C) + B \tag{3}$$

where, $\tau = (T-T_C)/T_C$ is the reduced temperature and the superscripts ± denote those above and below T_C, where T_C *represents the phase transition temperature,* $A^{\pm}$ represents the critical amplitudes, α' is the critical exponent similar to the specific heat critical exponent α, $D^{\pm}$ are the co-efficients of the first order corrections-to-scaling terms. The term $E(T-T_C)$ corresponds to a temperature dependent part of the regular background while B is a constant giving the combined critical and regular backgrounds.

Iso-SmA phase transition: The isotropic to SmA phase transition characterize the formation of ordered phase having both rotational and translational ordering from fluidlike disordered isotropic phase. The molecules are arranged in random fashion in the isotropic phase; with lowering the temperature the disordered molecules arranged themselves in such a way that both positional and orientational ordering comes into play. On entering from isotropic phase to SmA phase a large peak is observed in specific heat capacity and a large jump occurs in the birefringence value which indicates the first order nature of this transition. To check the behaviour the critical exponent extracted from both $\Delta C_P(T)$ and $Q(T)$ using the renormalization group expression gives a value of about 0.5 which confirms that the Iso to SmA phase transition is first order in nature.

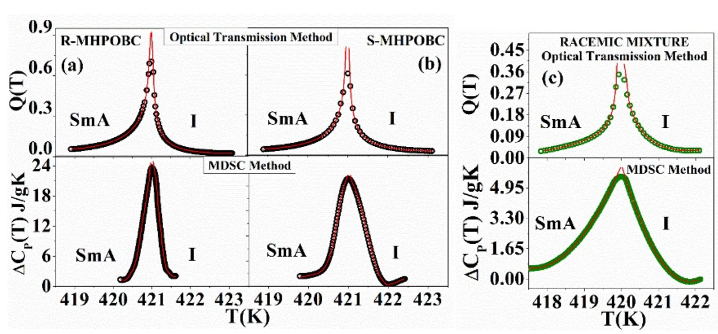

Figure 1. Plot of $Q(T)$ and $\Delta C_P(T)$ as a function of temperature (T) in the **I-SmA** phase transition for the compounds **(a)** R-MHPOBC **(b)** S-MHPOBC and **(c)** Racemic mixture of MHPOBC. The red solid lines indicate fits to Equation (1 and 3).

SmA-SmC$_\alpha^*$ phase transition: SmA is the paraelectric phase in which the molecules arrange themselves in a regular pattern which has both orientational as well as short range positional ordering like bookshelf geometry. The SmC_{α}^{*} phase is the chiral ferroelectric tilted phase. The specific heat capacity anomaly also shows a small peak corresponding to this transition both for R and S-enantiomers. The extracted critical exponent clearly indicates the second order nature of this transition.

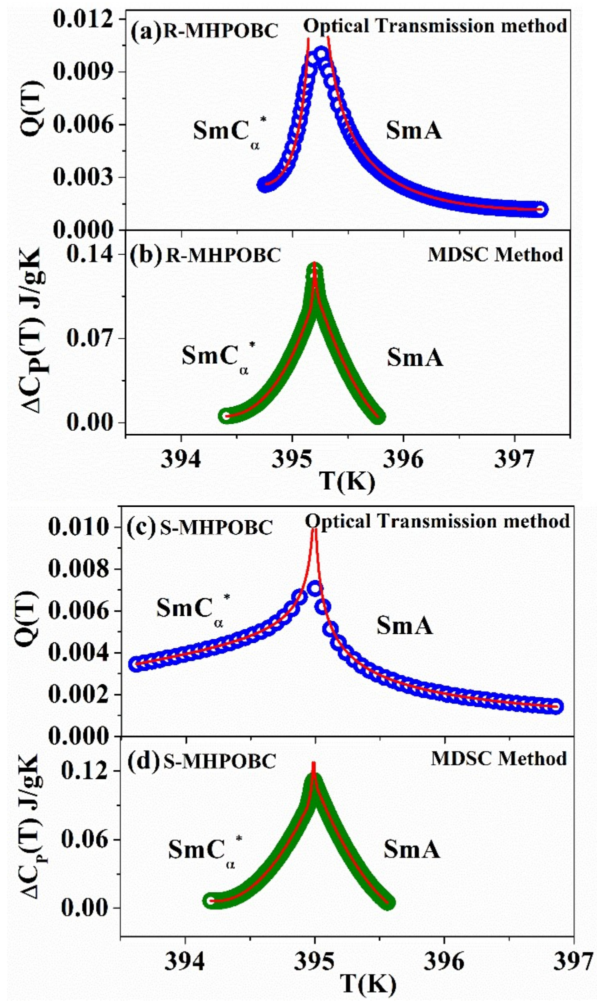

Figure 2. Plot of $Q(T)$ and $\Delta C_P(T)$ as a function of temperature (T) for the compound **(a,b)** R-MHPOBC and **(c,d)** S-MHPOBC for the **SmA-SmC**$_{\alpha}^{*}$ phase transition; The red solid lines indicate fits to Equation (1 and 3).

Critical exponent from Birefringence Suppression near SmA-SmC$_{\alpha}^{*}$ phase transition of R MHPOBC:

The experimentally measured optical birefringence Δn, in the smectic-A phase is directly related to the mean-square fluctuations of the tilt angle $\Delta n = \Delta n_0 (1-(3/2) (\langle\delta\theta^2\rangle)$ [9]. The term $\langle\delta\theta^2(T)\rangle$ is due to the director fluctuations. The critical exponent for the mean-square tilt angle fluctuations is simply related to the specific heat-capacity exponent (α) [9]

$$\langle\delta\theta^2(T)\rangle = t^{1-\alpha} \quad (4)$$

where $t=(T-T_{AC\alpha^*})/T_{AC\alpha^*}$ is the reduced temperature. This shows a straightforward comparison between the critical exponents, as obtained from specific heat-capacity and optical birefringence experiments. In this work the value of (1-α) has been found to be 0.823 which agrees quite well with ref. [10]. One can see that the value of the specific heat capacity critical exponent (α) for R-MHPOBC found from the critical part of the tilt angle fluctuations $<\delta\theta^2(T)>$ is 0.177 which is equal to the critical exponent (α') explored from Q(T) fitting.

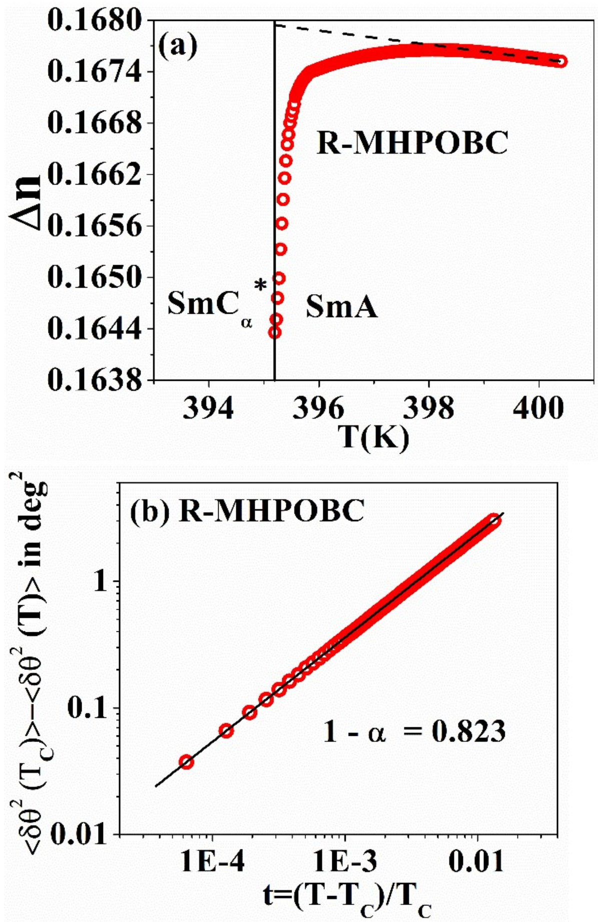

Figure 3. **(a)** Birefringence suppression in the smectic-A phase near the vicinity of the **SmA-SmC$_\alpha^*$** phase transition of R-MHPOBC. The dashed line is a background curve, describing a gradual increase of the birefringence due to the increased orientational order. The vertical solid line shows the **SmA-SmC$_\alpha^*$** phase transition temperature; **(b)** Log-log plot of $[<\delta\theta^2(T_{AC})> - <\delta\theta^2(T)>]$ *versus* reduced temperature (t) for R-MHPOBC.

3. Conclusion

High-resolution optical birefringence (Δn) as well as the specific heat capacity C_P measurements have been carried out to probe the critical behaviour at phase transitions on chiral tilted smectic phase of R- and S-enantiomers of MHPOBC and their racemic mixture. The critical behaviour of this transition has been explored with the aid of a differential quotient extracted from the Δn values and using ΔC_P. The data have been analyzed in detail with the renormalization-group expression with correction-to-scaling terms. For the pure R- and S-enantiomers of MHPOBC, the evaluated α values comes out to be 0.177±0.005 and 0.176 ± 0.002 respectively. These values are found to be in excellent agreement with those obtained from the high-resolution adiabatic scanning calorimetry by others. It has also been studied the critical pretransitional behaviour of optical birefringence in the smectic-A phase of chiral and polar tilted smectics in a different way by observing the power law behaviour of the mean square of the tilt angle fluctuations, as deduced from birefringence. A comparison of specific heat-capacity critical exponent (α) found from the mean-square fluctuations of the tilt angle $\langle\delta\theta^2(T)\rangle$ and the critical exponent (α') explored from the birefringence differential quotient Q(T) has also been done for R-MHPOBC. This is reflected in the corresponding critical exponents α that exhibit nonuniversal effective values.

Acknowledgments: Financial support was provided by the Department of Science and Technology, DST, New Delhi. Barnali Barman is grateful to Department of Science and Technology, DST-INSPIRE, New Delhi [DST/INSPIRE Fellowship/2015/IF 150049] for the financial support as a Junior Research Fellowship.

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