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# 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 parameters, 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 the specific heat-capacity critical exponent found from the mean-square fluctuations of the tilt angle <δθ2(T)> and the critical exponent ($\alpha'$) explored from the birefringence differential quotient $Q(T)$ for the SmA-SmC* phase transition has also been undertaken 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

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## 1. Introduction

The study of antiferroelectric liquid crystals (AFLCs), exhibited by elongated chiral molecules, has become a subject of significant interest not only in the scientific community but also from technological points of view after the discovery of antiferroelectricity in liquid crystals [1,2]. The presence of delicately balanced ferroelectric and antiferroelectric ordering interplay shows variant chiral smectic-C (SmC) subphases characterized by the layer-to-layer tilt-azimuthal angles, which is one of the prominent features in AFLCs. The different properties of chiral antiferroelectric (smectic-CA*), ferroelectric (smectic-C*), and the intermediate phases (smectic-C*, smectic-C$\gamma$*) 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, which have great potential for application in flat panel displays. At the same time, the wide variety of structures that are observed in the antiferroelectric chiral smectic materials has initiated the development of new theoretical approaches for the description of phase transitions between these novel phases.

## 2. Results and Discussion

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

The determination of critical exponent from a specific heat capacity anomaly:

In order to determine the critical exponent, the $\Delta C_p$ data were analyzed with the following renormalization-group expression including the corrections-to-scaling terms [3,4]:

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

The 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 $\Delta n$. The $Q(T)$ data were been analyzed in detail with the renormalization-group expression including the correction-to-scaling terms [7,8]:

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

where, $\tau = (T - T_C)/T_C$ is the reduced temperature and the superscripts $\pm$ denote those above and below $T_C$, where $T_C$ represents the phase transition temperature, $A^{\pm}$ represents the critical amplitudes, $\alpha'$ is the critical exponent similar to the specific heat critical exponent $\alpha$, $D^{\pm}$ 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.

### 2.1. Iso-SmA Phase Transition

The isotropic to SmA phase transition characterized the formation of the ordered phase, having both rotational and translational ordering from a fluid-like disordered isotropic phase. The molecules are arranged in a random fashion in the isotropic phase; by lowering the temperature, the disordered molecules arranged themselves in such a way that both positional and orientational ordering comes into play. On moving from the isotropic phase to the SmA phase, a large peak was observed in the specific heat capacity, and a large jump occurred in the birefringence value, which indicated the first-order nature of this transition as shown in Figure 1. To check the behaviour, the critical exponent extracted from both $\Delta C_P(T)$ and $Q(T)$ using the renormalization group expression gave a value of about 0.5, which confirmed that the Iso to SmA phase transition was first-order in nature.

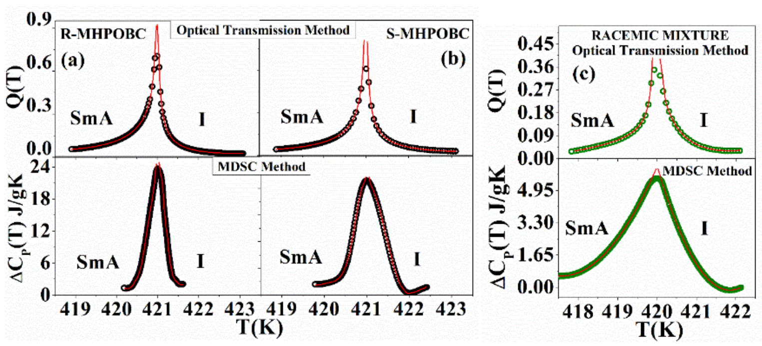


**Figure 1.** Plot of $Q(T)$ and $\Delta C_P(T)$ as a function of temperature ($T$) in the Section 2.1. for the compounds (**a**) R-MHPOBC (**b**) S-MHPOBC, and (**c**) Racemic mixture of MHPOBC. The red solid lines indicate fits to Equations (1) and (3).

### 2.2. SmA-SmC$_\alpha$* Phase Transition

SmA is the paraelectric phase in which the molecules arrange themselves in a regular pattern and has both orientational as well as short-range positional ordering, such as in bookshelf geometry. The *SmC$_\alpha$** 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 as shown in Figure 2. The extracted critical exponent clearly indicates the second-order nature of this transition.

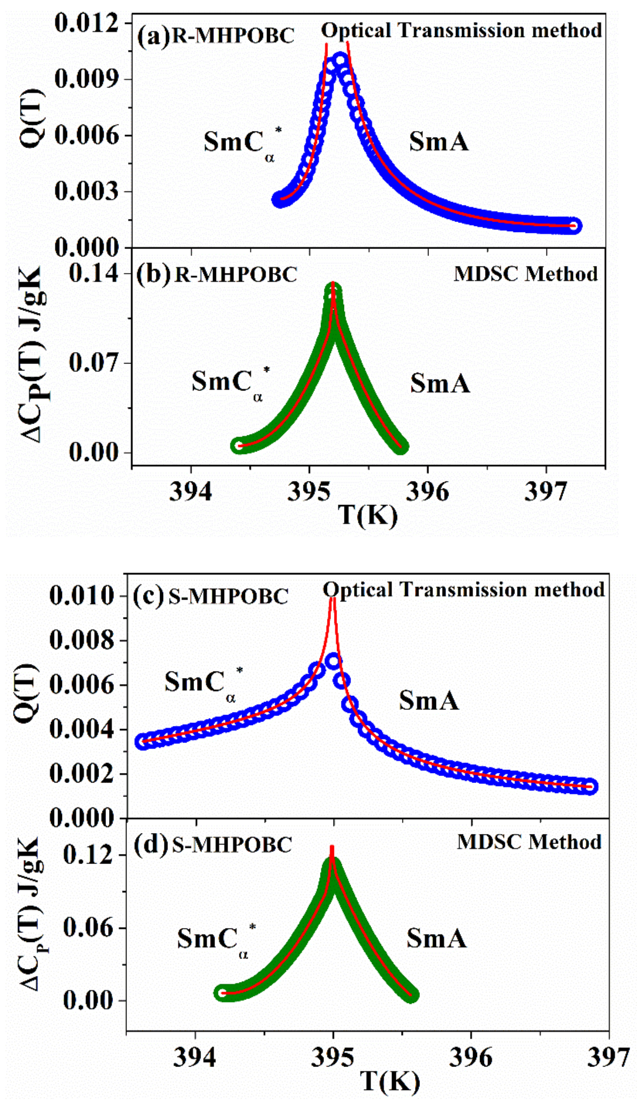


**Figure 2.** Plot of $Q(T)$ and $\Delta C_P(T)$ as a function of temperature ($T$) for the compound (**a**,**b**) R-MHPOBC and (**c**,**d**) S-MHPOBC for the Section 2.2; The red solid lines indicate fits to Equations (1) and (3).

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

The experimentally measured optical birefringence $\Delta n$, in the smectic-A phase, is directly related to the mean-square fluctuations of the tilt angle $\Delta n = \Delta n_0\ (1 - (3/2)\ (<\delta\theta^2>)$ [9] as shown in Figure 3a,b. The term $<\delta\theta^2(T)>$ 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 ($\alpha$) [9]

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

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 $(1-\alpha)$ was 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 ($\alpha$) for R-MHPOBC found from the critical part of the tilt angle fluctuations <δ$\theta^2$(T)> is 0.177, which is equal to the critical exponent ($\alpha'$) explored from Q(T) fitting.

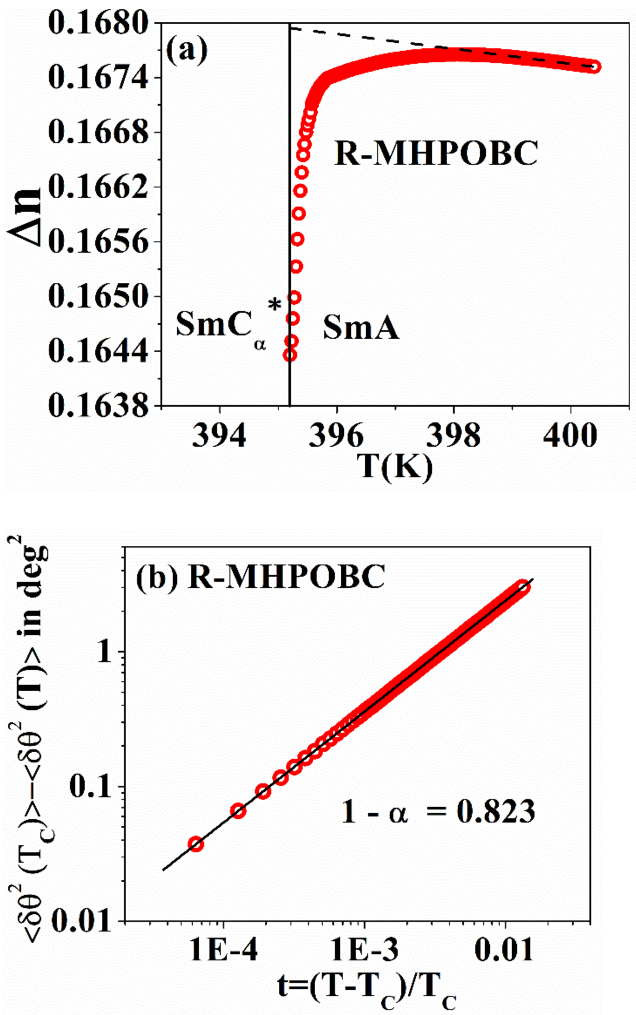


**Figure 3.** (**a**) Birefringence suppression in the smectic-A phase near the vicinity of the Section 2.2. of R-MHPOBC. The dashed line is a background curve, describing a gradual increase in the birefringence due to the increased orientational order. The vertical solid line shows the Section 2.2. temperature; (**b**) Log-log plot of $\left[< \delta\theta^2(T_{AC}) > - < \delta\theta^2(T) >\right]$ versus reduced temperature $(T)$ for R-MHPOBC.

## 3. Conclusions

High-resolution optical birefringence ($\Delta n$), as well as the specific heat capacity $C_P$ measurements, have been carried out to probe the critical behaviour at phase transitions on the 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 $\Delta n$ values and using $\Delta C_P$. 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 $\alpha$ values came out to be $0.177 \pm 0.005$ and $0.176 \pm 0.002$, respectively. These values are found to be in excellent agreement with those obtained from the high-resolution adiabatic scanning calorimetry by others. We also studied the critical pre-transitional behaviour of optical birefringence in the smectic-A phase of the 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 the specific heat-capacity critical exponent ($\alpha$) found from the mean-square fluctuations of the tilt angle <δ$\theta^2$(T)> and the critical exponent

($\alpha'$) explored from the birefringence differential quotient $Q(T)$ has also been undertaken for R-MHPOBC. This is reflected in the corresponding critical exponents $\alpha$ that exhibit nonuniversal effective values.

**Supplementary Materials:** The poster presentation can be downloaded at: https://www.mdpi.com/article/10.3390/IOCC_2022-12148/s1.

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