Confinement effects at the transition from a chiral fluid SmC* to a hexatic SmI* liquid crystal phase

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Abstract
The temperature dependence of the spontaneous polarization across the phase transition from the fluid smectic C* to the hexatic smectic I* phase of a chiral liquid crystal was investigated with respect to confinement effects, due to closely spaced substrates. A strong thickness dependence of the polarization was observed in both the SmC* and SmI* phases, which cannot be interpreted either by polarization screening due to ionic impurities, or by the polarization self-screening model. A possible explanation is given in terms of non-switching interface regions close to the substrates, caused by strong anchoring conditions. It is demonstrated that the occurrence of bond-orientational order does not affect the anchoring behaviour of the liquid crystal. Confinement effects were observed for decreasing cell gap below 4 μm, while the first order character of the SmC*–SmI* phase transition is retained.

1. Introduction

Since the discovery of SmC* ferroelectric liquid crystals [1], the spontaneous polarization (P_S) has been one of the most extensively investigated parameters, but surprisingly few reports have been given on its cell gap dependence. Meyer *et al* [1] have shown by symmetry arguments that the occurrence of a spontaneous polarization is a property of every tilted smectic phase composed of chiral molecules, thus placing them into the class of pyroelectric materials. Only when the spontaneous polarization can be reversed between two stable states by application of an external electric field do we speak of ferroelectricity. In contrast to the intrinsic helielectric behaviour of the bulk SmC* phase, true ferroelectricity can be observed when the helical superstructure is suppressed. This can be achieved by elastic interactions between the liquid crystal and the substrate, i.e. in the surface stabilized ferroelectric liquid crystal (SSFLC) state,

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discovered by Clark and Lagerwall [2]. The ferroelectric properties of liquid crystals have been investigated in great detail for the fluid smectic C* phase, but reports are rare for the tilted hexatic phases, namely SmI* and SmF* [3–7].

For a SmC* material with low spontaneous polarization ($P_S \sim 10$ nC cm^{-2}), Patel and Goodby [8] demonstrated that the polarization may exhibit a sample thickness dependence, which was interpreted in terms of space charge accumulation of ions and a depolarizing field within the liquid crystal cell. Later, Galerne [9] gave a theoretical interpretation of the self-screening effect in terms of distortions of the director field close to the electrodes, due to anchoring conditions. In this model, the polarization reverses its direction through a wall of thickness d_0, accounting for cell gap dependent polarization values in cells of gap smaller than approximately 10 μm. Analysing the experimental data of [8], Galerne obtained a value in the order of $d_0 = 0.8$ μm for the polarization inversion wall thickness of the SmC* phase [9]. In a recent report, Shenoy *et al* [10] observed no significant dependence of the SmC* polarization on cell thickness for materials with large spontaneous polarization ($P_S \sim 250$ nC cm^{-2}). Employing the polarization self-screening model of Galerne, they consequently obtained a very small value for the wall thickness in the order of $d_0 = 0.08$ μm. In this study, we present for the first time detailed cell gap dependent polarization data across the fluid SmC* to hexatic SmI* transition, in order to analyse possible influences of bond-orientational order on confinement conditions.

2. Experimental details

The chiral liquid crystal used for this investigation has the following structural formula:
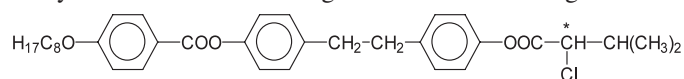
Its phase sequence on cooling was originally reported as [6] Iso.* 134.5 N* 129.4 TGBA* 129.2 SmA* 125.6 SmC* 92.9 SmI* 83.7 SmF*, while the crystal transition can be greatly supercooled, depending on cooling rate. It should be noted, though, that the above stated (absolute) transition temperatures were determined with a completely different experimental set-up, allowing for variations in the order of 1–2 K as compared to the presently used equipment. This is however not of significant importance to the phenomena discussed here, as all of the measurements presented below were indeed carried under the same experimental conditions and temperatures are relevant only on a relative scale (accuracy below 0.1 K). The material has a medium bulk spontaneous polarization in the order of $P_S \sim 100$ nC cm^{-2} at temperatures well below the para- to ferro-electric transition. It was introduced into commercially available liquid crystal sandwich cells (EHC, Japan, parallel rubbing, planar anchoring conditions) of various cell gaps by capillary filling in the isotropic phase. Samples were investigated in the SSFLC bookshelf geometry. The spontaneous polarization was determined by employing the well known triangular wave technique [11] at frequency $f = 27$ Hz and field amplitude $E = 2$ MV m^{-1} across the SmC*–SmI* transition. Saturated switching of both phases in the vicinity of the transition was assured. High resolution current reversal curves were recorded by use of a digital storage oscilloscope (Agilent Infinium, 500 MHz) for subsequent data analysis. A minimum of 256 curves were averaged to reduce statistical noise and the estimated error of the determined polarization values lies in the range of 1%. Samples were slowly cooled in a self-constructed hot stage of large heat capacity at a rate smaller than 0.1 K min^{-1}, regulated by a EuroTherm temperature controller. The error of (relative) temperatures lies within ± 0.1 K, which is believed to cause a larger uncertainty in the determined polarization values than the actual integration procedure.
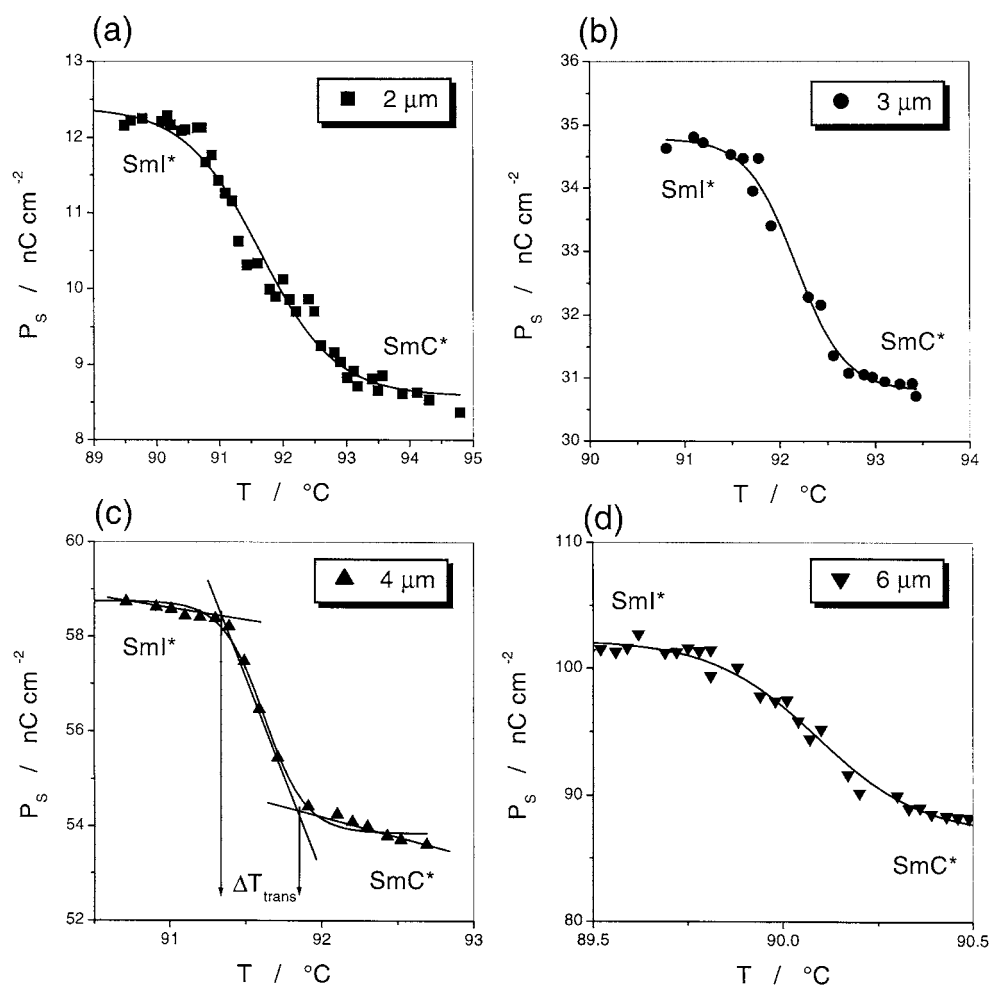
Figure 1. Temperature dependence of the spontaneous polarization across the fluid SmC* to hexatic SmI* liquid crystal phase transition at varying confinement conditions: (a) $D = 2$ μm, (b) $D = 3$ μm, (c) $D = 4$ μm and (d) $D = 6$ μm. Note the significantly different scales of the polarization and the temperature axes. Solid curves are a guide to the eye.

3. Experimental results and discussion

Figure 1 depicts the temperature dependence of the spontaneous polarization across the SmC*–SmI* transition for different cell gaps below 10 μm, the range where screening effects are expected to be observed. Indeed, it can clearly be seen that P_S is strongly dependent on cell thickness in both the SmC* and the SmI* phase. An interpretation of this behaviour in accordance to the model of ionic screening, as introduced by Patel and Goodby [8], can be excluded. Following their interpretation, the measured spontaneous polarization should exhibit a pronounced frequency dependence in the range of saturated switching, with increasing polarization for increasing frequency. This is not the case for the present measurements, as demonstrated in figure 2, where a constant P_S is observed for increasing frequency in the range of saturated switching. Only for frequencies $f > 40$ Hz is the polarization found to decrease, which is simply caused by a non-saturated switching process.
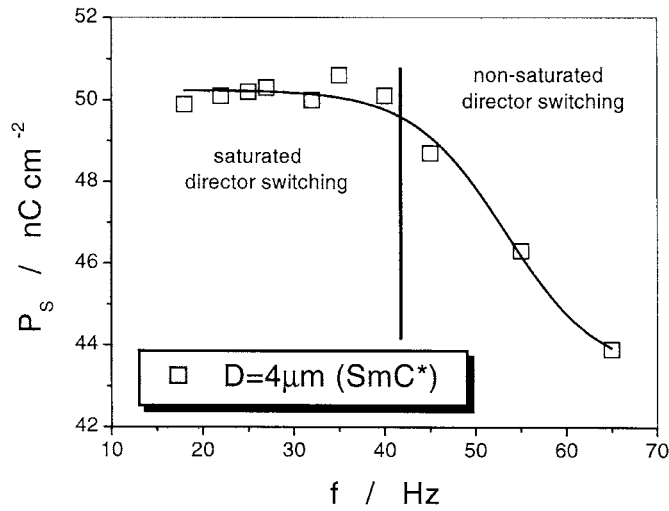
Figure 2. Screening due to ionic impurities [8] can be disregarded, as this would imply a frequency dependence of the spontaneous polarization P_S in the regime of saturated switching ($f < 40$ Hz), which is not observed for the present material.

Alternatively, following Galerne's polarization self-screening approach [9], the measured spontaneous polarization P_S should be related to the true polarization P_0, according to equation (1):

$$P_S = P_0 - \frac{2P_0 d_0}{D} \tag{1}$$

with d_0 the thickness of the polarization inversion wall and D the cell gap. The model is schematically depicted in figure 3(a). Equation (1) implies a linear relationship between the measured polarization and the inverse cell gap, which is apparently not fulfilled for the present measurements, as shown in figure 3(b). Forcing an analysis according to equation (1) onto the measured data for small cell gaps (2–4 μm, lines in figure 3(b)), we obtain values for d_0 of 0.92 and 0.90 μm for the SmC* and SmI* phase, respectively. These values would be in good agreement with that determined for the SmC* phase of the low polarization compound (data [8], analysis [9]). The calculated true bulk polarization P_0 is obtained to be 95 nC cm^{-2} for SmC* and 99 nC cm^{-2} for SmI*. The determined values are larger than the measured ones for SmC*, but in fact slightly smaller than the actually measured values for SmI* in thicker cells (compare to figure 1(d)). This contradiction indicates the problems with the polarization self-screening approach to explain the present data, which is of course not surprising, as we had noted the non-linearity between P_S and $1/D$ before. This makes the respective analysis only a crude approximation, leading to errors in the order of at least 20%. We nevertheless note that the values for d_0, obtained from the slope of the linear approximation, are equivalent for both the fluid SmC* and the hexatic SmI* phase. Thus, the development of bond-orientational order would seemingly have no influence on the polarization self-screening mechanism.

A possible interpretation, which consistently explains our measured data, is the assumption of a non-switching interface region of thickness ξ close to both substrates (figure 4(a)). This can qualitatively be motivated by strong anchoring conditions fixing the director at each of the substrates along the direction of uniform rubbing of the polymer layers. The elastic properties of the liquid crystal extend this region into the bulk of the sample. We thus have a non-switching liquid crystal region directly at the substrates and reduced director reorientation in
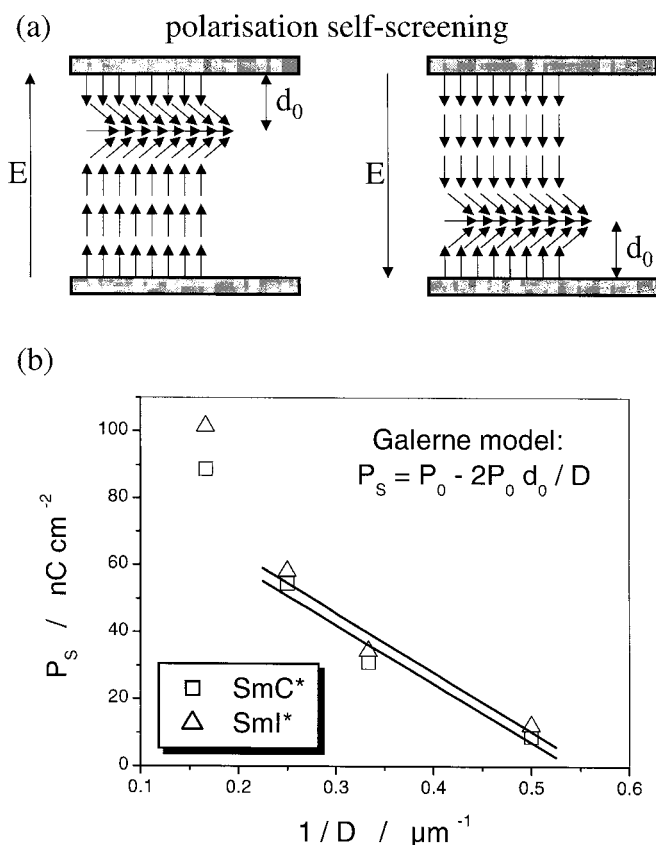
Figure 3. (a) The polarization self-screening model of Galerne [9] predicts a linear dependence of the measured spontaneous polarization P_S on the reciprocal cell gap $1/D$. (b) This is not observed for the present data.

the vicinity of the surfaces. In reality, there will be a profile of increasing switching angle (and thus increasing polarization reversal) the further we proceed towards the middle region of the cell. As we currently have no means to determine this profile, a non-switching surface layer is assumed for simplicity. In a first approximation, this would lead to a linear dependence between the measured spontaneous polarization P_S and the cell gap D, according to equation (2):

$$P_S = P^*(D - 2\xi) \tag{2}$$

where P^* is a polarization per unit length, i.e. the spontaneous polarization per micrometre cell gap, or alternatively a charge per unit volume, i.e. the charge density. Such a relation is indeed observed for the present measurements, as demonstrated in figure 4(b), for both the SmC*, as well as the SmI* phase. From an analysis of the data according to equation (2), we obtain a constant thickness for the interface region on each substrate of $\xi = 0.72\,\mu$m across the SmC*–SmI* transition. The value of P^* increases from 200 C m^{-3} in SmC* to 224 C m^{-3} in SmI*, which is in perfect agreement with the expected and commonly observed increase of the spontaneous polarization across the SmC*–SmI* transition. Errors in the analysis according to the latter interpretation are smaller than 3%. At this point it may also be worthwhile to mention the coupling between polarization charges due to Coulomb interaction [12], caused by a partial lifting of the ionic screening during the switching process, which can similarly contribute to the observed effect.
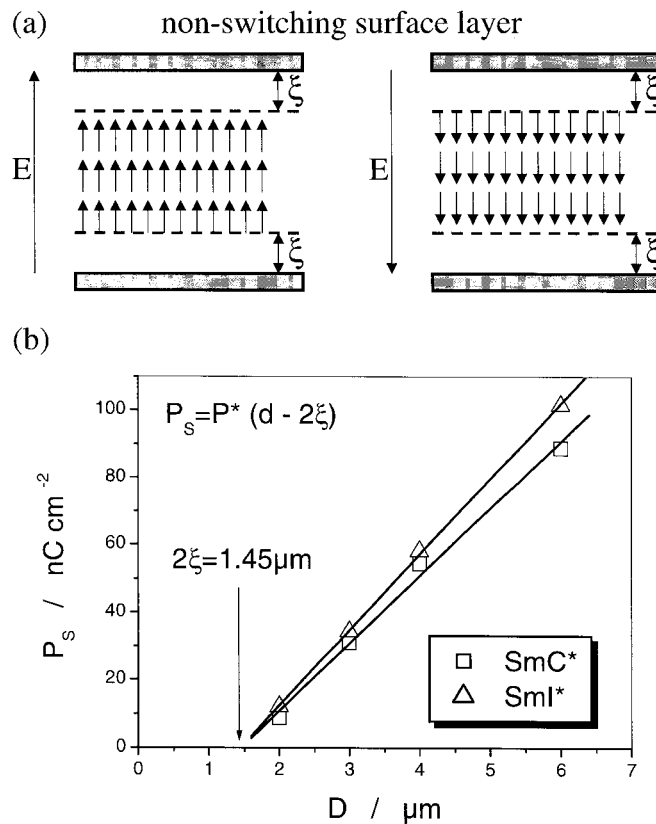
Figure 4. (a) Assuming a non-switching liquid crystal–substrate interface region leads to a linear dependence of the spontaneous polarization P_S on cell gap D. (b) This behaviour is indeed observed experimentally.

Let us briefly discuss the influence of decreasing cell gap on the actual phase transition behaviour, determined from the polarization measurements. The cell gap dependent transition temperatures (figure 5(a)) were determined according to a procedure which is essentially equivalent to that commonly employed in the determination of the onset temperature of a phase transition in differential scanning calorimetry (DSC). This is the temperature at which the line of steepest slope intersects with the baseline, which in our case is the temperature dependent curve of the spontaneous polarization in the SmC* phase (approaching the transition from above) and that of the SmI* phase (approaching the transition from below, see figure 1(c)). As shown in figure 5(a), the SmC*–SmI* phase transition temperature, taken at the onset of the transition on cooling, increases with decreasing cell gap, indicating a strong liquid crystal–substrate interaction. The temperature range ΔT_{trans} of the SmC*–SmI* transition, taken from the onset in SmC* to the final formation of the SmI* phase, i.e. the temperature width of the region of phase coexistence, strongly increases as the cell gap is lowered below $D = 4\ \mu$m (figure 5(b)). This type of smearing out of a phase transition is typical for confined systems [13] and can most pronouncedly be observed in systems subjected to strong confinement by (random) nanopores [14].

Finally, we can determine the change of the (secondary) order parameter P_S, i.e. the jump of $\Delta P_{S,trans}$ in spontaneous polarization on passing the SmC*–SmI* transition. For purely bulk
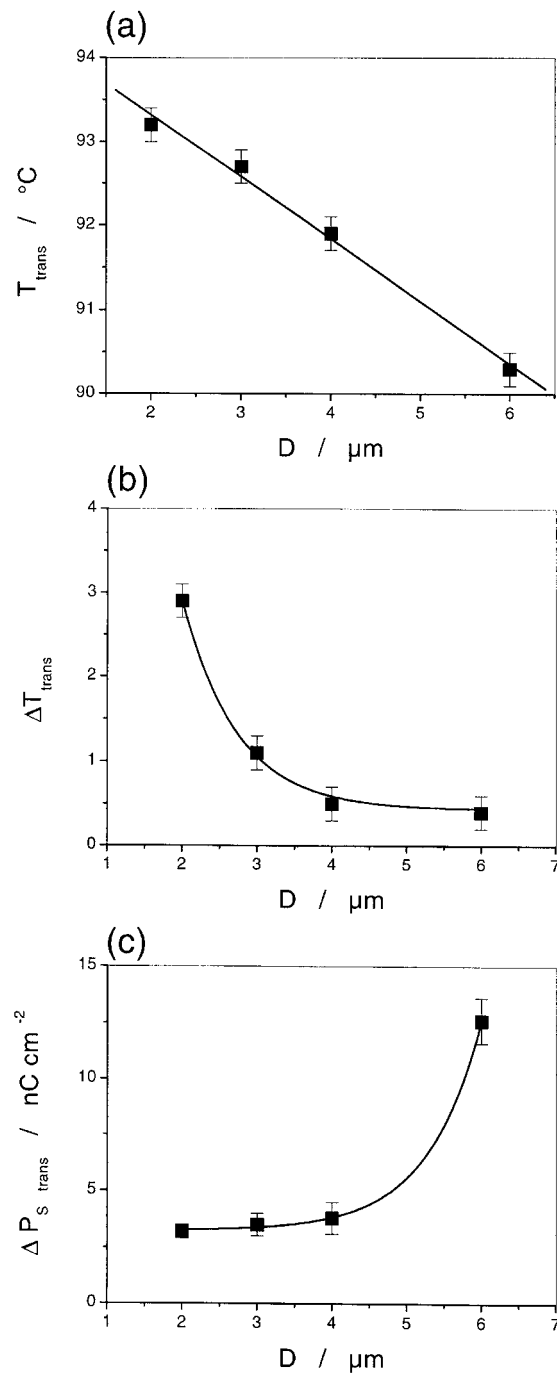
Figure 5. Demonstration of confinement effects at the transition from the fluid SmC* to the hexatic SmI* phase: (a) increase of the transition temperature T_{trans} for decreasing cell gap D, (b) smearing out of the transition temperature interval ΔT_{trans} for decreasing cell gap D and (c) reduction of the change in spontaneous polarization $\Delta P_{S\ trans}$ across the transition for decreasing cell gap D. Solid lines are a guide to the eye.

samples a sharp, discontinuous increase in P_S would be expected, as the SmC*–SmI* transition is commonly of first order, although this discontinuity may be small and only be revealed by high resolution measurements, such as reported in the present investigation. Indeed, this is the general behaviour observed, while $\Delta P_{S,trans}$ is strongly reduced for decreasing cell gap, as shown in figure 3(c). Its finite saturation value for small cell gaps nevertheless indicates that the first order character of the SmC*–SmI* transition is retained under planar confinement conditions.

4. Conclusions

We have presented detailed spontaneous polarization measurements across the transition from the fluid SmC* to the hexatic SmI* phase of a ferroelectric liquid crystal for varying degrees of confinement. The cell gap dependence of the spontaneous polarization cannot be accounted for either by screening effects due to ionic impurities [8], or by the polarization self-screening approach [9]. The measurements indicate a non-switching interface region of a thickness in the order of 0.7 μm in the vicinity of the substrates, which we attribute to strong surface anchoring. The thickness of this interface layer remains constant during the transition from SmC* to SmI*, thus the liquid crystal–substrate interactions are not significantly altered by the development of bond-orientational order. The smearing of the transition suggests noticeable confinement effects for cell gaps smaller than 4 μm, while the first order character of the SmC*–SmI* transition is retained.

Acknowledgment

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