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Plenary Lecture. Phase transitions and critical phenomena in polar smectic A liquid crystals

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Plenary Lecture

Phase transitions and critical phenomena in polar smectic A liquid crystals

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Since the discovery of a phase transition between two polymorphic forms of the smectic A phase, there has been a considerable amount of experimental as well as theoretical work on strongly polar materials exhibiting different smectic A phases. These studies have led to the observation of a variety of new phase transitions and critical phenomena which are rarely encountered in any other area of condensed matter physics. We review briefly some of these important results.

1. Introduction

The first observation of a transition between two forms of the smectic A phase was made by Sigaud *et al.* [1] in binary mixtures of benzoyloxy-(4'-*n*-pentylphenyl)benzoate (DB5) and terephthalidene bis-(4-*n*-butylaniline) (TBBA). Although this first order transition was seen by differential scanning calorimetry (D.S.C.) studies, optical microscopy did not show any difference in the textures of the two smectic A phases. X-ray studies [2] revealed that the higher and lower temperature S_A phases are, respectively, monolayer (or S_{A_1}) with the layer thickness, d , being approximately equal to the molecular length (l) and bilayer (or S_{A_2}) with $d \approx 2l$. The existence of a partially bilayer smectic A or S_{A_d} phase with $l < d < 2l$ being already known, it became clear that the S_A phase can exist in several polymorphic forms. This was soon followed by the discovery of several other types of new phases, viz. the antiphase or $S_{\bar{A}}$, the crenellated phase or $S_{A_{cre}}$ and the ribbon phase or S_C [3, 4]. So far, these phases have been observed only in strongly polar systems, i.e. materials in which the molecules possess a strongly polar cyano or nitro group at one end. (In the case of binary mixtures at least one of the constituent compounds belongs to this category.)

A phenomenological theory which attempts to explain the origin of the different forms of S_A phase was proposed by Prost [5] almost concomitantly with the first observation of the $S_{\bar{A}}-S_A$ transition. This theory, which was enlarged in its scope by Prost and Barois [6], defines the free energy of a strongly polar smectic A in terms of two order parameters, viz. the dipolar order parameter, ψ_1 , associated with an antiparallel pair of dipolar molecules and the usual density order parameter ψ_2 . The competition between these two types of order trying to condense at two incommensurate length scales leads to different types of S_A phases. (The same competition also

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leads to the occurrence of the re-entrant nematic behaviour [5, 7] but we are not concerned with this aspect here.) In this definition the nematic phase is identified as that for which $\psi_1 = 0$ and $\psi_2 = 0$, while $\psi_1 = 0$ and $\psi_2 \neq 0$ defines the S_{A_1} phase. In the case of both S_{A_d} and S_{A_2} phases ψ_1 as well as ψ_2 has a non-zero value, but $\psi_1 \gg \psi_2$ in the case of the S_{A_d} phase while $\psi_1 \approx \psi_2$ in the case of the S_{A_2} phase. This theory also predicts, under certain conditions, the existence of an incommensurate phase, i.e. a phase in which two collinear incommensurate density modulations coexist. Prost and Barois [6] have, in fact, discussed the probability of the existence of two types of incommensurate phases, viz. the weakly coupled incommensurate phase in which the two modulations exist independently of each other and the strongly coupled incommensurate phase where the two periodicities are modulated in one dimension, leading to a structure consisting of defects walls or solitons [8]. The theory of Prost and Barois [6] has been extended by Barois *et al.* [9] within the framework of the mean field theory to calculate the various phase diagrams that are possible involving the different types of S_A phases. These theoretical phase diagrams also predict several types of critical-multicritical points: (a) the N- S_{A_2} tricritical point, (b) S_{A_1} - S_{A_2} tricritical point, (c) the S_{A_d} - S_{A_2} critical point and (d) the S_{A_1} -N_{re}- S_{A_d} bicritical point.

On the experimental side, investigations that have been carried out during the past few years have resulted in the observation of both types of incommensurate phases and most of the critical or multicritical points mentioned here. There have also been more-rigorous theoretical treatments which take into account fluctuations. These fluctuations corrected theories have made some important predictions regarding the universality class of the S_{A_d} - S_{A_2} critical point and also concerning the different possible ways in which the S_{A_1} - S_{A_d} transition boundary can terminate. Experiments to verify these predictions have begun only very recently. The aim of this paper is to give an overview of the experimental situation concerning the incommensurate phases and the critical or multicritical points involving the different S_A phases. The results are discussed in relation to the predictions of the mean field and the fluctuation corrected theories.

2. Incommensurate phases

Although the theory of polar smectics (also referred to as frustrated smectics) clearly predicts the existence of the incommensurate phase, all of the experiments seem to yield only the biaxial smectic (\tilde{A} , A_{cre} and \tilde{C}) phases. These biaxial phases, unlike the uniaxial S_A phases which are liquid-like within the layer, possess an additional periodicity in the plane of the layer. It appeared that when two competing lengths are involved the system prefers to escape frustration by going over to a two dimensional modulated antiphase rather than a one dimensional modulated incommensurate phase [10]. However, there have been several experimental observations of incommensurate fluctuations in nematic and smectic phases [11–14]. In the nematic phase, X-ray diffraction studies have detected the presence of two diffuse scattering peaks corresponding to fluctuations at wavelengths incommensurate with each other. In the case of the S_{A_d} phase (with a condensed peak at a wavevector $q'_0 = 2\pi/l'$; $l < l' < 2l$), the fluctuations are generally seen at a wavevector corresponding to monolayer periodicity ($2q_0 = 2\pi/l$), whereas in the case of S_{A_1} (with a condensed peak at $2q_0$) the fluctuations were at q'_0 . The diffraction pattern in the S_{A_2} phase consists of two condensed reflections at $q_0 = 2\pi/2l$ and at its second harmonic $2q_0$, but no diffuse scattering appears to have been seen.

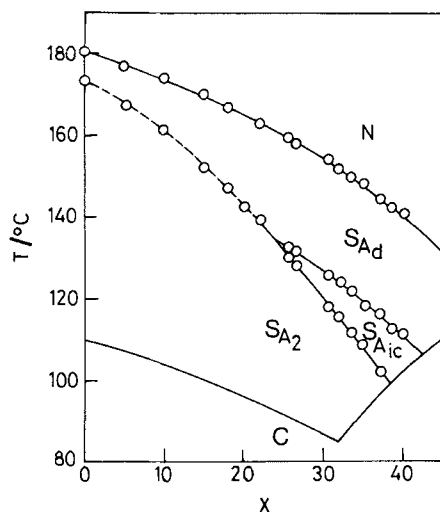


Figure 1. Partial temperature-concentration (T - X) diagram for mixtures of 4- n -octyloxy-4'-cyanobiphenyl (8OCB) and 4- n -heptyloxyphenyl-4'-cyanobenzoyloxybenzoate (DB7OCN). X is the molar percentage of 8OCB in the mixture. The incommensurate $S_{A_{ic}}$ phase intervenes between the partially bilayer (S_{A_d}) and bilayer (S_{A_2}) phases. The broken line signifies the temperature at which calorimetric studies show a peak corresponding to a supercritical transformation of S_{A_d} to S_{A_2} . (From [15].)

The first observation of an incommensurate smectic A or $S_{A_{ic}}$ phase was by Ratna *et al.* [15] in binary mixtures of 4- n -heptyloxyphenyl-4'-cyanobenzoyloxybenzoate (DB7OCN) and 4-octyloxy-4'-cyanobiphenyl (8OCB) (see figure 1). This phase, whose characteristic diffraction pattern consists of both S_{A_d} and S_{A_2} periodicities, intervenes between S_{A_d} and S_{A_2} phases. The possibility of this phase being a two phase region has been ruled out by a detailed measurement of the layer spacing as a function of temperature for a series of concentrations [16] (see figure 2). Although initially it was reported that there exists an S_{A_d} - S_{A_2} transition for 8OCB concentrations (X) < 0.24 , subsequent high resolution X-ray and calorimetric studies showed that there is in fact no S_{A_d} - S_{A_2} transition in this concentration range, but only a continuous evolution of S_{A_d} from S_{A_2} . (This aspect of the S_{A_d} - S_{A_2} transition will be discussed later.) Thus, the phase diagram shown in figure 1 depicts a situation where the S_{A_d} phase evolves into the S_{A_2} phase either continuously or via the $S_{A_{ic}}$ phase. High resolution calorimetric studies [17] on mixtures of DB7OCN and 8OCB (see figure 3) also support this deduction. The heat capacity curve for the 12.5 per cent mixture shows a pronounced rounding of the peak, which is characteristic of a continuous supercritical transformation (or transformation without a phase change) from S_{A_d} to S_{A_2} . The C_p behaviour for the 27 per cent mixture looks completely different; there are two kinks or regions of very rapid change in dC_p/dT . These kinks occur exactly at the same temperatures at which the S_{A_d} - $S_{A_{ic}}$ and $S_{A_{ic}}$ - S_{A_2} transformations were identified on the basis of X-ray measurements [16]. Also, more importantly, no hysteresis in C_p was seen and no anomalous change in the phase shift, ϕ , of the temperature oscillation was observed, providing thereby that $S_{A_{ic}}$ is definitely not a two phase region.

The absence of X-ray reflections at wavevectors corresponding to combinations of q_0 and q'_0 in the $S_{A_{ic}}$ phase indicates that this is probably the weakly coupled

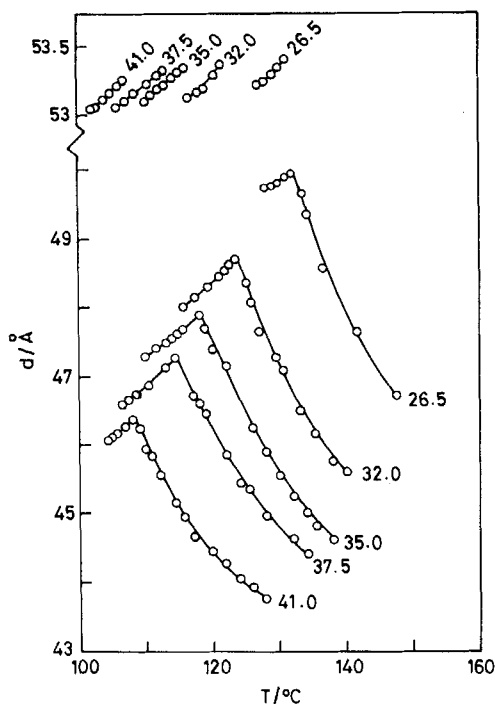


Figure 2. Temperature variation of the layer spacing (d) in the S_{A_d} , $S_{A_{ic}}$ and S_{A_2} phases for different concentrations of the 8OCB-DB7OCN mixtures. The concentrations shown correspond to the molar percentage of 8OCB. The data in the $S_{A_{ic}}$ phase for different concentrations do not fall on a single curve, showing that $S_{A_{ic}}$ is not a two phase region. (From [16].)

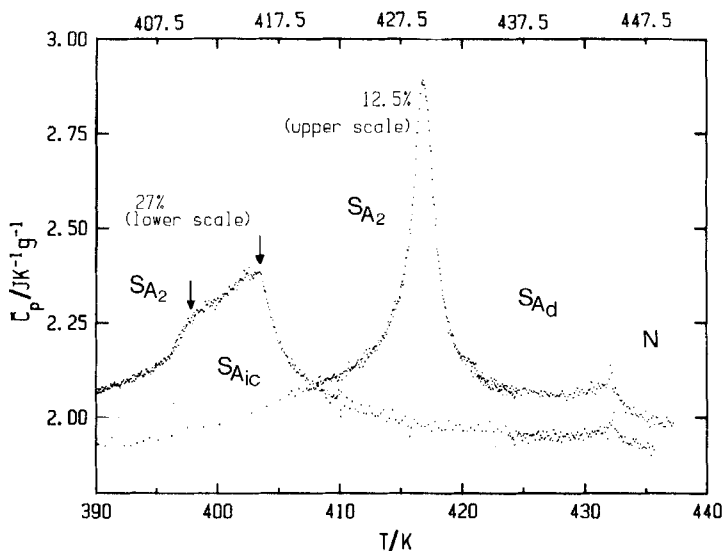


Figure 3. Variation of the heat capacity for two 8OCB-DB7OCN mixtures, viz. $X = 12.5$ and 27 . The 12.5 mol % mixture shows a continuous (supercritical) transformation from S_{A_d} to S_{A_2} . The arrows shown for the 27 mol % mixture denote the temperatures at which the S_{A_d} - $S_{A_{ic}}$ and $S_{A_{ic}}$ - S_{A_2} transformations have been seen by X-ray experiments. (From [17].)

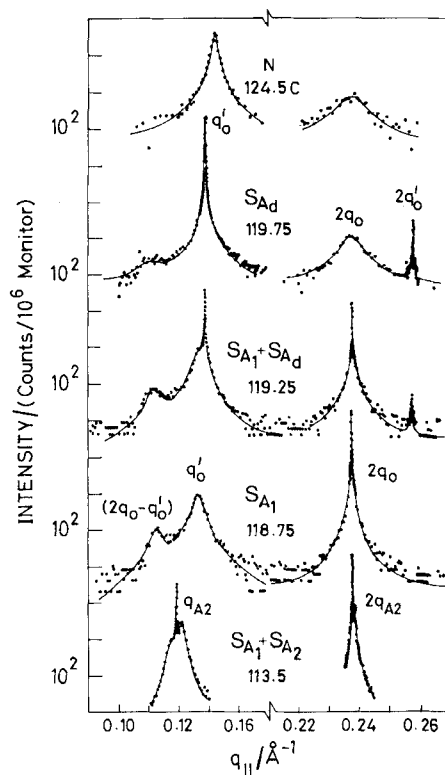


Figure 4. X-ray scattering intensity data for scans taken along $q_{||}$ for the DB5-T8 mixture with 22.88 mol % of T8. The lines are the least squares fit of the data to a lorentzian shape. The temperature as well as the phase corresponding to each scan is marked. In the S_{A_d} phase there are two resolution-limited peaks at q'_0 and $2q_0$ in addition to a broad peak (due to fluctuations) centred at $2q_0$. The main feature is that in the S_{A_1} phase a resolution-limited peak is seen at $2q_0$ along with two diffuse maxima at q'_0 and at $q_- = 2q_0 - 2q'_0$. This signifies the existence of strong incommensurate fluctuations in the S_{A_1} phase. (From [18].)

incommensurate phase predicted by Prost, i.e. the two interpenetrating incommensurate density modulations exist independently of each other.

Fontes *et al.* [18] have carried out high resolution X-ray studies on the DB5-T8 binary system. They found that for the mixture with 22.88 mol % of T8, the S_{A_1} phase shows two collinear diffuse maxima at incommensurate wavevectors in addition to the fundamental quasi-Bragg peak at $2q_0$ (see figure 4). The diffuse peaks are at q'_0 and $q_- = 2q_0 - q'_0$. The existence of q_- is evidence of strong coupling between ψ_1 and ψ_2 , the order parameters associated with density and dipolar waves [5]. With lowering of temperature these incommensurate fluctuations evolve towards off-axis or $S_{A_{\bar{\lambda}}}$ -like fluctuations before condensing into the commensurate S_{A_2} phase with condensed reflections at q_0 and $2q_0$. Thus, although strong incommensurate fluctuations have been observed, the strongly coupled incommensurate phase predicted by theory has remained elusive.

Recently Ratna *et al.* [19] have found evidence for the existence of the strongly coupled incommensurate or $S_{A_{is}}$ phase over a very narrow concentration region in mixtures of 4-*n*-octyloxyphenyl-4'-cyanobenzoyloxybenzoate (DB8OCN) and 4-octyloxybenzoate-4'-cyanoazobenzene (8OBCAB) (see figure 5). In fact, this phase diagram

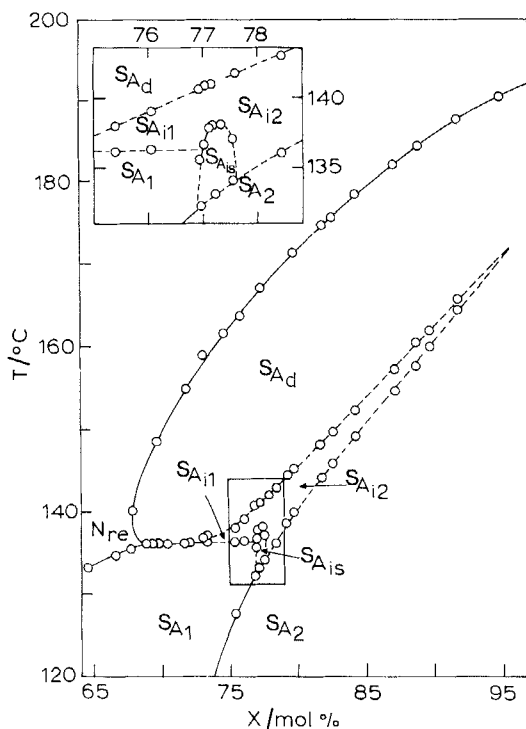


Figure 5. Partial T - X diagram for binary mixtures of 4-*n*-octyloxyphenyl-4'-cyanobenzoyloxybenzoate (DB8OCN) and 4-*n*-octyloxybenzoate-4'-cyanoazibenzene (8OBCAB). X is the molar percentage of DB8OCN in the mixture. Two weakly coupled incommensurate phases $S_{A_{i1}}$ and $S_{A_{i2}}$ are seen in addition to the strongly coupled incommensurate phase $S_{A_{iS}}$.

shows in addition to $S_{A_{iS}}$, two types of weakly coupled incommensurate phases, viz. $S_{A_{i1}}$ (in which the S_{A_d} -like and S_{A_1} -like modulations coexist) and $S_{A_{i2}}$ (which is synonymous with the phase referred to as S_{A_c} earlier). The diffraction pattern in the $S_{A_{iS}}$ phase consists of three condensed reflections (see figure 6(a)) at two incommensurate wavevectors $2q_0$ and q_0'' , and at $q_s = 2q_0 - q_0''$. The presence of the combination reflection q_s shows that there exists a coupling between the two basic wavevectors $2q_0$ and q_0'' . The correlation length as obtained from the longitudinal width of q_s was found to be about 1000 Å. Thus, there is sufficient evidence to support the idea that $S_{A_{iS}}$ is indeed the strongly coupled incommensurate phase whose structure consists of solitons or an array of domain walls. Another important feature can be seen from figures 6(a) and (b); as the $S_{A_{iS}}$ phase is cooled towards the S_{A_2} phase, the soliton periodicity $Z = 2\pi/(q_0'' - q_s)$ appears to diverge as predicted by theory [8]. However, the resolution of these experiments is not sufficient to probe the exact nature of this divergence close to the lock-in transition to the S_{A_2} phase.

Thus, both types of incommensurate phases predicted by Prost and Barois [6] have been observed experimentally. It should also be mentioned that a theoretical phase diagram evaluated on the basis of the phenomenological model predicts a tetracritical point at which the incommensurate phase joins the intersection of the S_{A_1} -N and N- S_{A_d} boundaries. The theory also envisages the alternative possibility that the domain of the incommensurate phase may be disconnected from the nematic phase

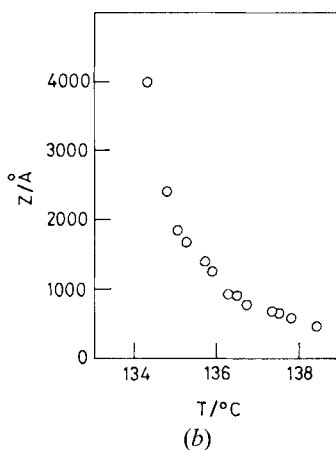
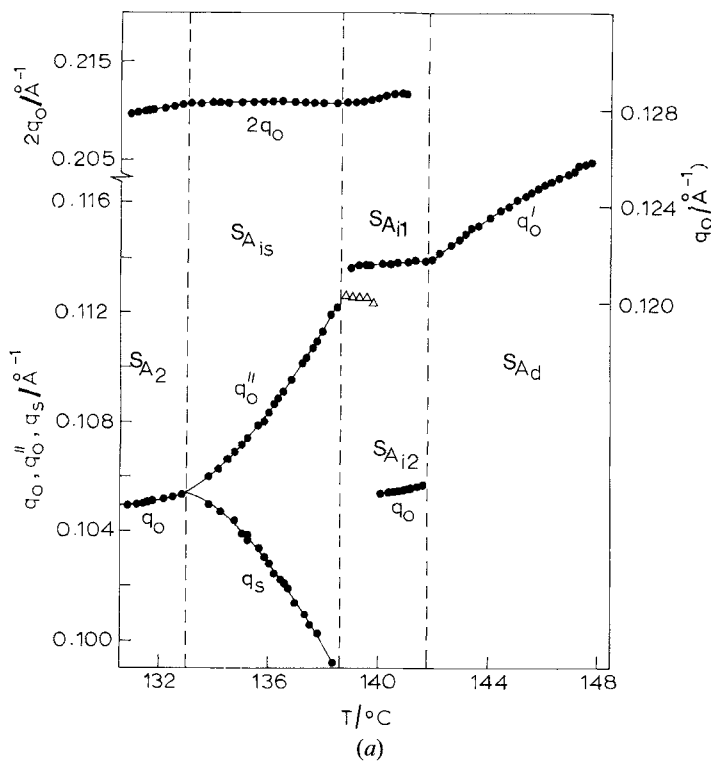


Figure 6. (a) Temperature variation of the wavevectors characterizing the different phases for the 77.2 mol% mixture of DB7OCN–8OBCAB. Three condensed reflections are seen in the $SA_{i,s}$ phase, these being at $2q_0$, q_0'' and $q_s = 2q_0 - q_0''$. (b) Variation of the soliton periodicity $Z = 2\pi/(q_0'' - q_s)$ in the $SA_{i,s}$ phase.

by an SA_d – SA_i phase boundary. The latter picture is in qualitative agreement with the experimental phase diagram of figure 5. It is truly remarkable that a binary system of DB8OCN and 8OBCAB, whose constituent compounds have nearly the same molecular length, produces such a rich variety of phases with six different types of SA phases. This shows that the polymorphism of smectic A should be very delicately dependent on the nature of molecular interactions.

Lubensky *et al.* [20] have investigated theoretically the static and dynamic properties of the incommensurate phase. According to them, the incommensurate phase can be characterized by two density waves whose Fourier components are non-zero only on a discrete incommensurate set of reciprocal lattice points. Such a description leads to an elastic theory involving two variables: the layer displacement field and the phason or the relative displacement of the two fundamental density waves which are incommensurate. Formulating the elastic free energy in terms of these variables, Lubensky *et al.* [20] have predicted that although the first and second sound modes of the incommensurate smectic A should be identical to those in ordinary smectics, the sound attenuations are expected to have a different dependence. In addition, there should also be a diffusive phason mode which is not found in ordinary smectics. This, in turn, is expected to lead to an anomalously slow mechanical response analogous to that predicted in quasicrystals. Experiments to verify these predictions would be of considerable interest.

3. Phase transitions and critical phenomena involving smectic A phases

Phase transitions between the different forms of the smectic A phase are of considerable current interest because they are transitions between two phases with quasi-long range order. The smectic phases A_1 , A_d and A_2 have the same macroscopic symmetry, differing from each other only by the wavelength of their periodic modulations. Hence, it should be possible to go from S_{A_1} to S_{A_d} or from S_{A_d} to S_{A_2} by only varying the layer spacing. There can also be a first order transition between these phases at which the wavevector characterizing the phase should show a discontinuous jump. A line of such first order transitions can terminate at a critical point when the difference between the wavevectors in the S_A phases goes to zero, this critical point providing a continuous path between S_{A_1} or S_{A_2} and S_{A_d} phases. On the other hand, the S_{A_1} - S_{A_2} transition can be either first or second order because of the exact doubling of the layer periodicity, i.e. the layer spacing doubles as a result of the continuous vanishing of a spatial subharmonic. We summarize in this section the current theoretical as well as the experimental situation concerning the phase transitions as well as critical/multicritical points involving S_{A_1} , S_{A_2} and S_{A_d} phases.

3.1. S_{A_1} - S_{A_2} transition

This transition, which was the first S_A - S_A transition to be observed [1], is of intrinsic interest for two reasons. First, it can be either second or first order. Secondly, an understanding of the critical nature of the fluctuations near the S_{A_1} - S_{A_2} transition could conceivably help in the understanding of the S_A -N transition, a transition which has remained one of the principal unsolved problems in equilibrium statistical physics, despite considerable theoretical and experimental efforts [21].

In the model proposed by Prost [5], the order parameter associated with the dipolar modulation develops in the presence of non-zero ψ_2 (the order parameter associated with the monolayer modulation) at the S_{A_1} - S_{A_2} transition. Because of the coupling between ψ_1 and ψ_2 , the phase of ψ_1 is locked to that of ψ_2 and, consequently, only the amplitude of ψ_1 is expected to exhibit critical behaviour at the S_{A_1} - S_{A_2} transition. The model predicts this transition to be in the three dimensional Ising class. However, as we are dealing with a transition to a phase with only quasi-long range order (rather than to a system with true long range order as in a three dimensional crystal lattice), there are complications which are important to the phase transition

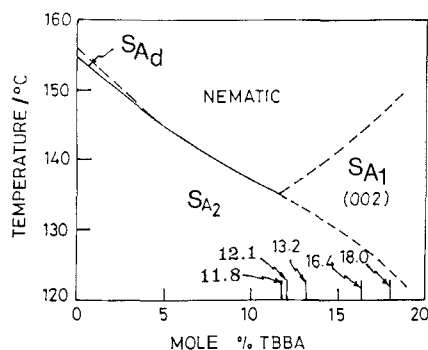


Figure 7. Schematic phase diagram for mixtures of hexylphenyl cyanobenzoyloxybenzoate (DB6) and terephthalylidene-bis-(4-*n*-butylaniline) (TBBA). Broken curves indicate second order phase boundaries while the full curve denotes a first order boundary. The S_{A_1} - S_{A_2} transition has a tricritical point. (From [23].)

problem involving the smectic A phase, viz. anisotropy, quasi-long range order and coupling between smectic layering and the nematic director. All of these effects have been considered in the theoretical model of Wang and Lubensky [22]. To a first order ϵ expansion they find that the S_{A_1} - S_{A_2} transition should be in the same universality class as the Ising model with isotropic correlation exponents; $\nu_{\parallel} = \nu_{\perp} = 0.63$. However, a non-uniform susceptibility exponent (σ) which is expected to be less than the Ising value of 1.242 is predicted.

High resolution X-ray scattering measurements of the critical fluctuations have been carried out near the S_{A_1} - S_{A_2} transition in the hexylphenyl cyanobenzoyloxybenzoate (DB6)-TBBA binary liquid crystal system [23, 24]. The transition is found to be first order over a narrow region of concentrations close to the N- S_{A_1} - S_{A_2} triple point, whereas it is second order over the rest of the region (see figure 7). The first order nature of the transition has been deduced by the deviation from the power-law behaviour of the correlation length over a region of about 20 mK close to the transition (see figure 8(a)), the coexistence region in which a sharp, resolution limited q_0 peak was seen superimposed over the diffuse scattering peak. Power law fits on the second order side (see figure 8(b)) yielded critical exponents $\nu_{\parallel} = \nu_{\perp} = 0.74 \pm 0.03$ and $\sigma = 1.46 \pm 0.05$. It was also found that the exponents are invariant along the second order S_{A_1} - S_{A_2} line; no crossover behaviour as reported for the S_A -N transition was seen. That the correlation length exponents are isotropic provides the first experimental support for the hypothesis that the divergent phase fluctuations of the smectic order parameter are responsible for the anisotropy of the correlation lengths in the case of the N- S_A transition, these fluctuations are presumably quenched in the case of the S_{A_1} - S_{A_2} transition. The critical exponents are also consistent with the measured specific heat exponent [25, 26] via the scaling relation $3\nu + \alpha = 2$. However, the correlation length as well as the susceptibility exponents disagree with both the theoretical predictions, the simple three dimensional Ising behaviour predicted by mean field theory as well as the Ising-like transition on a quasi-long range order lattice as discussed by Wang and Lubensky [22]. Huse [27] has pointed out that the exponents determined for the S_{A_1} - S_{A_2} transition should be Fisher renormalized [28] since the measurements were made at constant concentration and not at constant chemical potential, particularly since the rate at which the S_{A_1} - S_{A_2} transition temperatures vary with concentration is quite appreciable. The measured exponents, in fact, agree with

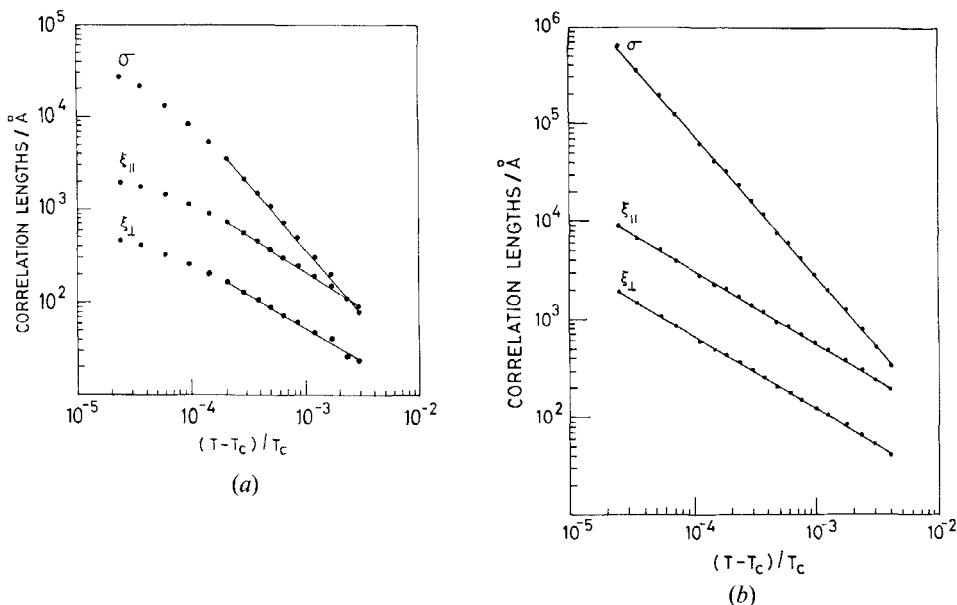


Figure 8. Power-law fits for the S_{A_1} - S_{A_2} transition in mixtures of DB6 and TBBA, the concentrations (expressed in mol% of TBBA) are 12.1 for (a) and 13.2 for (b). σ is the susceptibility exponent while ξ_{\parallel} and ξ_{\perp} are correlation length exponents along and perpendicular to the director, respectively. In the case of the 12.1 mol% mixture the S_{A_1} - S_{A_2} transition is first order and the data deviate from the power-law behaviour. No such deviations are seen for the 13.2 mol% mixture and the transition is second order. (From [23].)

the Fisher renormalized exponents. However, this Fisher renormalization approach need not necessarily be the only explanation of the experimental results. It should be pointed out that in the S_{A_1} phase the diffuse X-ray scattering peak (due to the S_{A_2} fluctuations) is not exactly at $q_0 = 2\pi/2l$ but at an incommensurate wavevector whose periodicity lies between l and $2l$. This suggests that coupling between ψ_1 and ψ_2 may not be in the strong field limit. This could conceivably be responsible for the differences between the observed exponents and the bare Ising values. Further experiments on other systems exhibiting the S_{A_1} - S_{A_2} transition are necessary to see whether the behaviour seen in DB6-TBBA mixtures is universal.

3.2. S_{A_d} - S_{A_2} critical point

Since the S_{A_d} and S_{A_2} phases have the same macroscopic symmetry and since the layer spacing ratio is not exactly equal to 2, there can only be a first order transition between them. The theory of Barois *et al.* [9], which has referred to S_{A_d} as S_{A_2} , identifying both the phases to be of the bilayer type, makes several interesting predictions concerning the S_{A_d} - S_{A_2} transition. (a) The X-ray scattering profiles in the S_{A_d} and S_{A_2} phases are expected to be equivalent with quasi-Bragg peaks at 001 and 002. In the case of S_{A_2} the diffraction peaks would be at $q_0 (= 2\pi/2l)$ and $2q_0 (= 2\pi/l)$ whereas for the S_{A_d} phase they are at q'_0 and $2q'_0$, where $q_0 < q'_0 < 2q_0$. Also, in the S_{A_d} phase the 002 peak intensity is predicted to be significantly lowered and almost completely overshadowed by a pronounced diffuse scattering centred around a wavevector close to $2q_0$. These features have in fact been confirmed recently by high resolution X-ray studies (see [18, 23]). (b) The signature of the S_{A_d} - S_{A_2} transition

should be a discontinuous jump in the wavevector associated with the two phases. There should also be an accompanying discontinuity in the ratio of the 001 and 002 intensities at the transition. (c) The first order S_{A_d} - S_{A_2} phase boundary can terminate at a critical point similar to the gas-liquid Ising-like critical point. As the critical point is approached the difference in the wavevectors q'_0 and q_0 goes to zero and the distinction between S_{A_d} and S_{A_2} phases disappears. Beyond the critical point the S_{A_d} phase can change continuously into the S_{A_2} phase. Predictions (b) and (c) have been verified experimentally, as we shall now see.

The existence of an S_{A_d} - S_{A_2} transition was reported in DB7OCN soon after the observation of the S_{A_1} - S_{A_2} transition [29]. However, recent high resolution X-ray studies [30] on the same material have shown that there is, in fact, no phase transition in this compound, but only a continuous evolution of S_{A_2} from S_{A_d} . High resolution A.C. calorimetric results have also yielded the same conclusion. The first clear evidence of the existence of the S_{A_d} - S_{A_2} transition as well as the S_{A_d} - S_{A_2} critical point has been provided by Shashidhar *et al.* in 4-*n*-undecyloxyphenyl-4'-(4''-cyanobenzoyloxy) benzoate (11OPCBOB)-4-*n*-nonyloxybiphenyl-4'-cyanobenzoate (9OBCB) mixtures [31]. We now discuss these results in some detail.

The phase diagram of 11OPCBOB-9OBCB is shown in figure 9. For molar fractions of 11OPCBOB (X) less than 0.52, the ribbon phase S_C intervenes between the S_{A_d} and S_{A_2} phases. However, with increasing X , S_C is suppressed, leading to a direct S_{A_d} - S_{A_2} transition. This first order S_{A_d} - S_{A_2} boundary then terminates at a critical point in the temperature-concentration plane. All of these features have been deduced from the results of accurate X-ray experiments for a series of binary mixtures (see

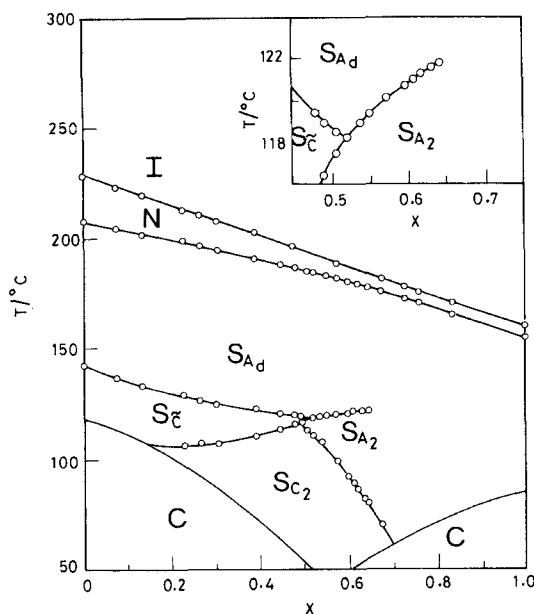


Figure 9. T - X diagram for the binary mixtures of 4-*n*-undecyloxyphenyl-4'-(4''-cyanobenzoyloxy) benzoate (11OPCBOB) and 4-nonyloxybiphenyl-4'-cyanobenzoyloxy benzoate (9OBCB). X is the molar fraction of 11OPCBOB in the mixture. The S_{A_d} - S_{A_2} transition terminates at the critical point. The phase diagram in the vicinity of the critical point is shown in the inset on an enlarged scale. (From [31].)

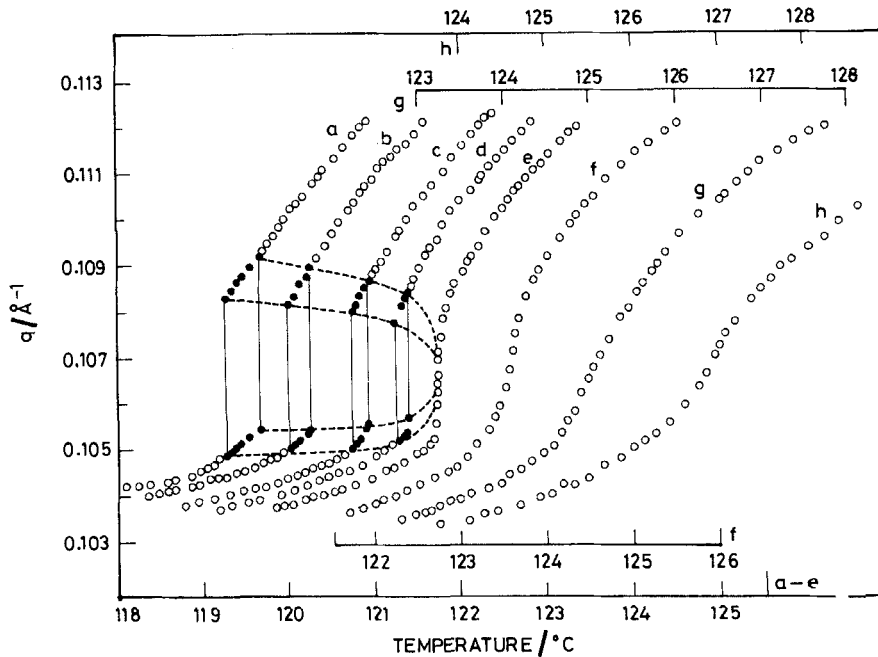


Figure 10. Plots of wavevectors q_0 and q'_0 versus temperature (T) for different mixtures of 11OPCBOB in 9OBCB. The X values for the mixtures are: (a) 0.55, (b) 0.571, (c) 0.597, (d) 0.619, (e) 0.642, (f) 0.715, (g) 0.80 and (h) 1.0, i.e. 11OPCBOB. The corresponding temperature scales are identified. For $X < 0.642$ (plots (a)–(d)), a first order S_{A_d} – S_{A_2} transition is seen which manifests as a jump in the wavevector. The data in the two phase region are shown as closed circles, and the vertical line represents the approximate width of this region. Broken curves are envelopes of the ends of the two-phase regions and are only guides to the eye. The critical point is identified by the vertical variation of the wavevector seen for the 0.642 mixture (plot (e)). (From [31].)

figure 10). For all $X < 0.642$, an S_{A_d} – S_{A_2} transition is seen whose signature is the existence of a two phase region in which the diffraction pattern consists of both q_0 and q'_0 (as well as their second harmonics, which are not shown) as seen in figures 10(a)–(d). This is exactly as expected for a first order transition between two smectic phases with different layer periodicities. These figures also show that the variations of q'_0 and q_0 in the coexistence region are nothing but continuations of the trends in the variation of the corresponding wavevectors in the S_{A_d} and S_{A_2} phases, respectively. We can also associate the observed jump in the wavevector with the S_{A_d} – S_{A_2} transition. With increasing X , the magnitude of the wavevector jump decreases with an accompanying decrease in the width of the two phase region until at $X = 0.642$ no jump is observed. At this point the wavevector variation is almost vertical and there is a point of inflection. All of these features, the shrinking of the two phase region associated with a first order transition and the accompanying decrease in the difference between q_0 and q'_0 at the transition, the extremely steep variation of the wavevector with point of inflection, are clearly indicative of the existence of a critical point at $X = 0.642$. For higher X , i.e. on moving away from the critical point in the supercritical region, the point of inflection becomes progressively less pronounced and S_{A_2} evolves continuously from S_{A_d} to S_{A_2} without a phase transition. Thus, it has been established that the two smectic A phases S_{A_d} and S_{A_2} have the same macroscopic symmetry.

The mean field theory of Barois *et al.* [9] predicts that the S_{A_d} - S_{A_2} critical point should have Ising symmetry, i.e. should be similar to the liquid-gas critical point. However, as pointed by these authors themselves, the situation may be more complicated. Park *et al.* [32] have carried out a more extensive theoretical investigation of the critical point. They have developed a non-linear elastic model to describe this critical point and have analysed its critical properties using the ε expansion. The theory predicts that the S_{A_d} - S_{A_2} critical point should be of a new universality class with d_c , the upper critical dimension, being six. (The upper critical dimension is defined as that above which the system should exhibit mean field behaviour.) The theory also makes several important predictions that should be valid in three dimensions. For instance, anisotropic scaling is predicted for the correlation length exponents ν_{\parallel} and ν_{\perp} ; the specific heat at constant pressure as well as the stiffness elastic constant, B , measured along the critical path should diverge with an exponent γ/Δ . On the other hand, the specific heat at constant layer spacing is expected to yield the exponent α .

There have been some experimental attempts to verify the predictions of the theory developed by Park *et al.* [32]. The most precise of these is due to Jeong *et al.* [33] who have carried out high resolution heat capacity measurements in the vicinity of the S_{A_d} - S_{A_2} critical point in 11OPCBOB-9OBCB mixtures. Detailed views of the C_p data for three concentrations are shown in figure 11. The specific heat measurements confirm the X-ray results on the existence of the S_{A_d} - S_{A_2} critical point in these mixtures. The data for the $X = 0.615$ mixture (see figure 11) show a pronounced hysteresis over a temperature range. The measured value of the phase was also found to exhibit an anomalous behaviour in the same range, showing thereby that there exists a first order S_{A_d} - S_{A_2} transition for this concentration. For $X > 0.642$ no hysteresis in C_p or anomalous behaviour of ϕ was observed. We now discuss the data for a concentration close to (or at) the critical point, i.e. the results for $X = 0.642$. These data are shown in figure 12. It can be seen that there is a pronounced rounding of the C_p peak over a temperature region of about 600 mK. The fits of the data carried out after excluding the data in this region yield an exponent of 0.54 ± 0.04 . The

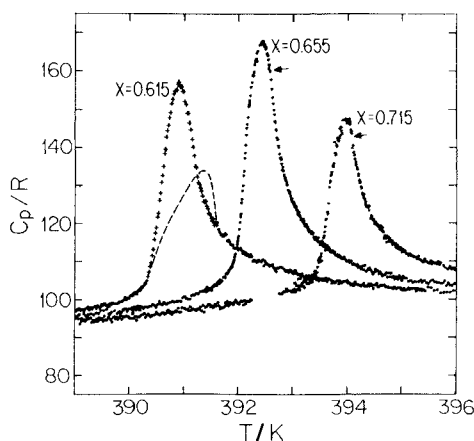


Figure 11. Variation of the specific heat (C_p) for three 11OPCBOB-9OBCB mixtures. The $x = 0.615$ mixture exhibits a first order S_{A_d} - S_{A_2} transition; the C_p variation obtained on cooling and heating (broken curve) shows hysteresis and there is a coexistence region (shown as +). On the other hand, the data for the 0.655 and 0.715 mixtures show no such effects and signify a continuous transformation of S_{A_2} from S_{A_2} . (From [33].)

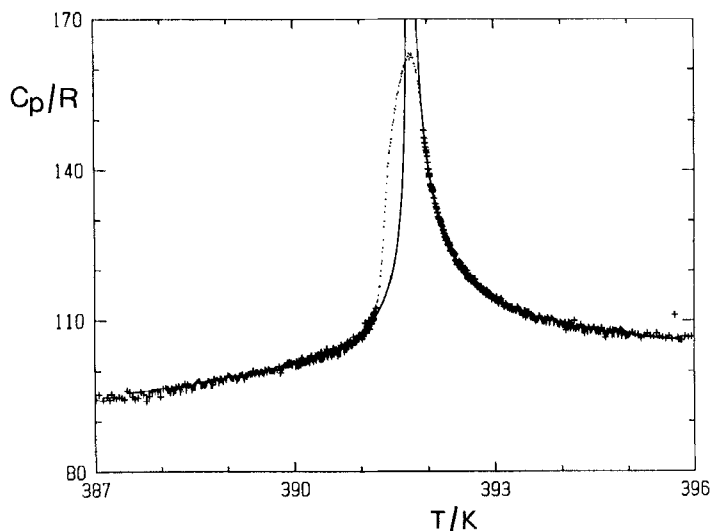


Figure 12. Least squares fit of the C_p data for a mixture ($X = 0.642$) in the immediate vicinity of the critical point, which yields an exponent $\gamma/\Delta = 0.54$. There is a pronounced rounding of the signal near the peak. The data in this region have been omitted from the fit. (From [33].)

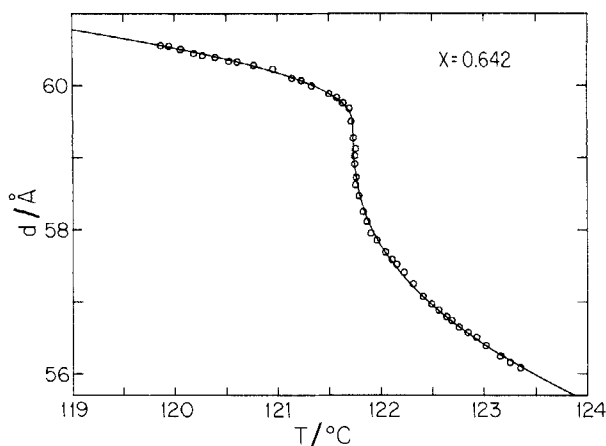


Figure 13. Least squares fit of the layer spacing (d) data for the 0.642 mixture to an equation which is the smectic analogue of the liquid-gas density variation along the critical isobar. Such a fit yields an exponent of $1/\delta = \beta/\Delta = 1 - \gamma/\Delta$. The value of γ/Δ evaluated in this manner is 0.62 ± 0.03 . (From [33].)

theory of Park *et al.* [32] has predicted that for the S_{A_4} - S_{A_2} critical point (which is of a new universality class with $d_c = 6$) this exponent should be γ/Δ instead of α . Another way to evaluate γ/Δ is to fit the X-ray data for the layer spacing variation to an equation which is the smectic liquid crystal analogue of the gas-liquid point with regard to the density variation along the critical isobar [34]. The result of such a fit (see figure 13) yields 0.62 ± 0.03 , which is in reasonable agreement with the figure obtained from C_p measurements. Although the experimentally determined value of the exponent γ/Δ appears to be somewhat lower than either the three dimensional

Ising (0.79) or the mean field value (0.67), this cannot be taken as sufficient evidence for the correctness of the theory of Park *et al.* [32].

It should also be mentioned that Park *et al.* [35] have recently considered the theory for the S_{A_d} - S_{A_2} critical point in the presence of a symmetry breaking field such as an electric or magnetic field or even a dislocation layer. They postulate that under such a condition, $d_c = 2.5$, i.e. in three dimensions the critical point might exhibit mean field-like behaviour. Hence, the exact universality class of the S_{A_d} - S_{A_2} critical point is still to be established.

3.3. On the termination of the S_{A_1} - S_{A_d} phase boundary

One of the predictions of the phenomenological theory proposed by Barois *et al.* [9] is the occurrence of a bicritical point where the second order nematic-smectic A_1 (N - S_{A_1}) and nematic-smectic A_d (N - S_{A_d}) boundaries meet the first order smectic A_1 -smectic A_d (S_{A_1} - S_{A_d}) line. However, when the effect of fluctuations is considered in the theory, the existence of such a bicritical point becomes questionable. It has been argued [9] that since both the S_{A_d} and S_{A_1} phases have the same symmetry, the N - S_{A_d} and N - S_{A_1} transitions should belong to the same universality class, viz. the inverted x - y universality class [21] with negative values of the specific heat exponent for both transitions. Renormalization group calculations [36] show that under such circumstances the resulting multicritical point is a tetracritical point and not a bicritical point. It has also been predicted [37] that an offshoot of this situation would be an incommensurate smectic A phase with both S_{A_d} -like and S_{A_1} -like periodicities.

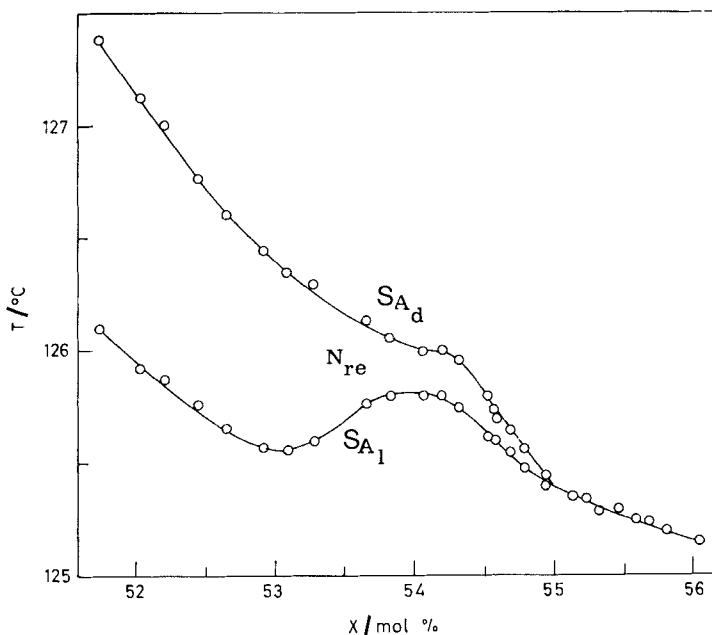


Figure 14. High resolution T - X diagram for binary mixtures of 4-*n*-octyloxyphenyl-4'-(4'-nitrobenzoyloxy) benzoate (DB8ONO₂) and 4-*n*-decyloxyphenyl-4'-(4'-nitrobenzoyloxy) benzoate (DB10ONO₂) in the vicinity of the smectic A_1 -re-entrant nematic-smectic A_d or S_{A_1} - N_{re} - S_{A_d} point. (From [42].)

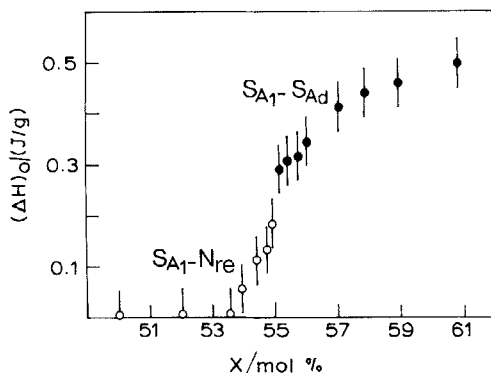


Figure 15. Plot of the latent heat $(\Delta H)_0$ associated with the S_{A_1} - S_{A_d} (●) and S_{A_1} - N_{re} (○) transitions in the neighbourhood of the S_{A_1} - N_{re} - S_{A_d} point for DB8ONO₂-DB10ONO₂ mixtures. X is the molar percentage of the latter. (From [42].)

On the experimental side, the S_{A_1} - N_{re} - S_{A_d} point (where N_{re} refers to the re-entrant nematic phase) has been observed in the T - X diagram of binary mixtures [38, 39] and it has been pointed out [10] that the shape of the phase diagram near this point is similar to the typical topology of a magnetic bicritical point [40–42]. However, a high resolution phase diagram evaluated by Raja *et al.* [42] on the basis of data obtained in the immediate vicinity of the S_{A_1} - N_{re} - S_{A_d} point shows that this is not the case (see figure 14). Detailed D.S.C. studies [42] conducted on the S_{A_1} - N_{re} and S_{A_d} - S_{A_1} transitions have revealed an interesting different situation (see figure 15). The change in the latent heat $(\Delta H)_0$ associated with the S_{A_d} - S_{A_1} transition does not go to zero at the S_{A_d} - N_{re} - S_{A_1} point, confirming that it is not a bicritical point. The data shown in figure 15 also show that the S_{A_1} - N_{re} boundary is second order ($\Delta H_0 \approx 0$) for concentrations less than about 53 mol %, but becomes first order as the S_{A_d} - N_{re} - S_{A_1} point is approached indicating that a tricritical point should exist for the S_{A_1} - N_{re} transition. Thus, it appears that the bicritical point has split into a tricritical point (for the S_{A_1} - N_{re} boundary) and a critical end point (for the S_{A_d} - N_{re} boundary) [42]. High resolution specific heat measurements [43] support this conclusion. The heat capacity data for the 51.3 per cent mixture are shown in figure 16 along with the fit carried out with $\alpha = 0.5$ (see [43] for details concerning the fitting procedure). It is clear that the fit is extremely good, showing that the S_{A_1} - N_{re} transition for this mixture is at (or nearly at) its tricritical point.

It should also be mentioned that this new alternative, i.e. the splitting of the bicritical point into a tricritical point and a critical end point has not been envisaged by the theory of frustrated smectics, although such a situation has been predicted in magnetic systems [44, 45]. However, the recent, exact calculations of Prost and Pommier [46] do predict such a splitting of the bicritical point for the case with $d = 3$.

The dislocation-loop melting theory of Prost and Toner [47] envisages different ways in which the S_{A_d} - S_{A_1} phase boundary can terminate. In the mean field limit the theory predicts the existence of a smectic- A_d -smectic A_1 critical point similar to the S_{A_d} - S_{A_2} point discussed in §3.2. However, when the effect of fluctuations is considered the theory predicts that the S_{A_d} - S_{A_1} boundary can end either as a critical point or as a nematic island (see figure 17). The smectic layer compression elastic constant, B , would have a minimum but non-zero value at the critical point, whereas $B = 0$ leads to the nematic island. The theory, in fact, predicts several interesting topological

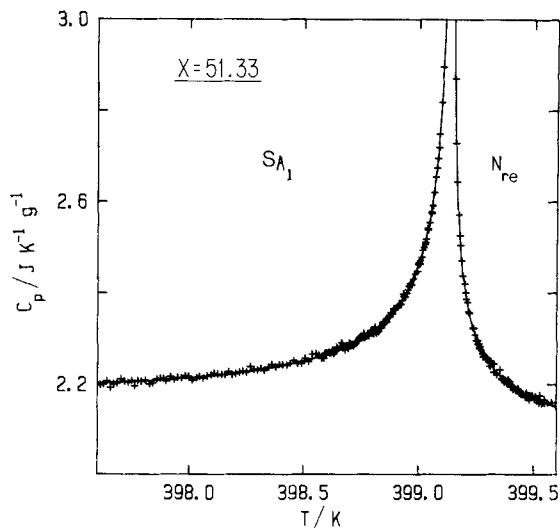


Figure 16. Fit of the heat capacity data for the N_{re} - S_{A_1} transition in the $X = 51.0$ mol % mixture carried out by fixing the specific heat exponent (α) at a value of 0.5, i.e. at the tricritical value and with the additional scaling constraint $B^+ = B^-$. The fit is seen to be extremely good, showing that this mixture is at or very near the tricritical point for the N_{re} - S_{A_1} transition. (From [43].)

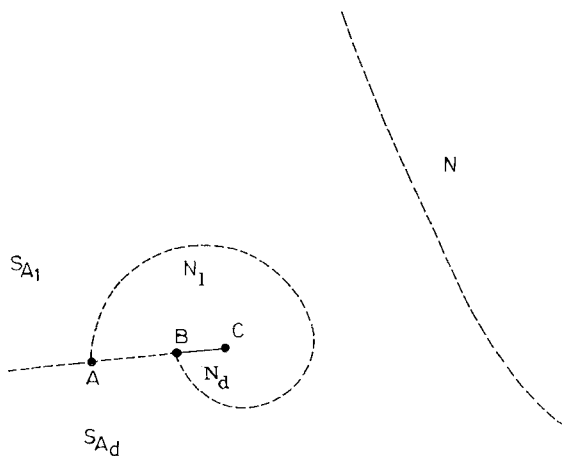


Figure 17. Theoretical phase diagram predicted by the dislocation-loop theory of Prost and Toner [47], showing the nematic island at the terminus of the S_{A_d} - S_{A_1} phase boundary. There are two types of nematics in this island, viz. N_d and N_1 . C is the critical point at which a first order N_d - N_1 transition ends. A and B are critical end points for the N_1 - S_{A_1} and N_d - S_{A_d} boundaries, respectively. This nematic island is seen separated from a main domain nematic region.

features for the nematic island (see figure 17). (a) The nematic island, which is seen separated from a main domain nematic region, has two types of nematic phases, viz. N_d and N_1 , (b) there exists an N_d - N_1 transition which ends as a nematic-nematic critical point (C) and the two nematics become indistinguishable beyond C, and (c) there are two critical end points A and B involving the S_{A_1} - N_1 and S_{A_d} - N_d phase

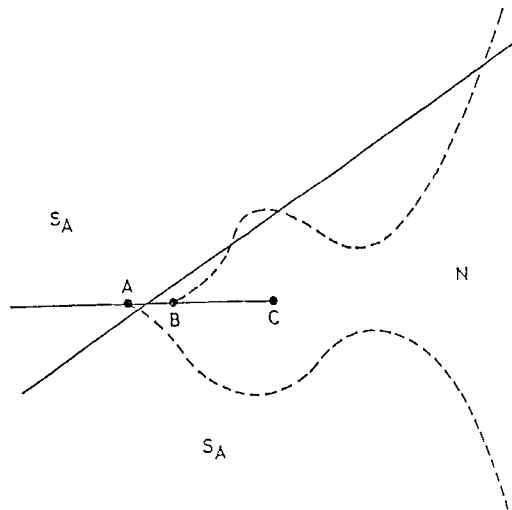


Figure 18. Topology of the theoretical phase diagram when the nematic island merges with the main nematic region. (From [47].)

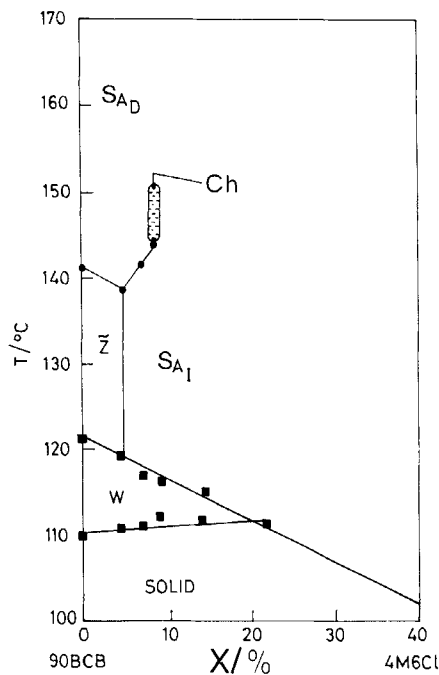


Figure 19. Partial phase diagram for mixtures of 90BCB and 1-4-di(4-methylhexyloxybezoate) (4M6Cl), showing the cholesteric island at the end of the S_{A_D} - S_{A_1} phase boundary. (From [48].)

boundaries, respectively. Prost and Toner [47] have also worked out a variety of possible phase diagrams. Figure 18 represents one of these; it shows interesting topological features that are expected when the nematic island merges with the main domain nematic.

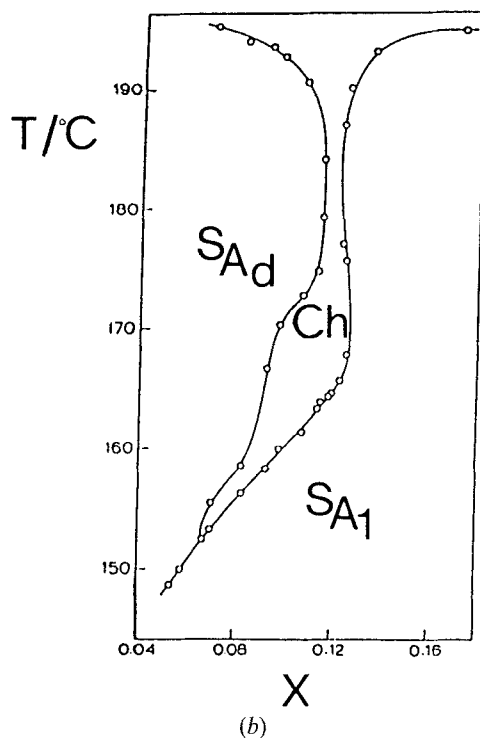
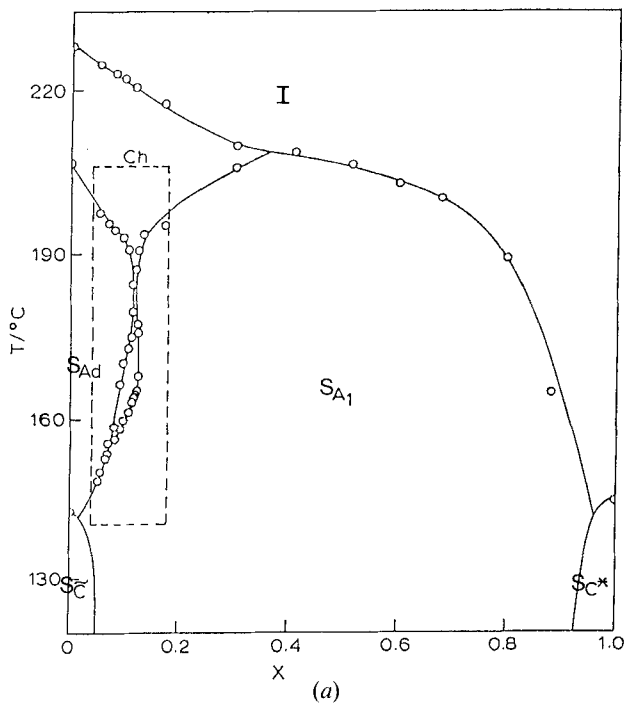


Figure 20. T - X diagram for binary mixtures of 9OBCB and *p*-*n*-hexylphenyl-5[*p*-(2-chloro-4-methylpentanoyloxy)-phenyl] pyrimidene, abbreviated as A. The cholesteric island emerges from the main cholesteric domain. The region inside the broken lines is shown on an enlarged scale in (b). X represents the molar fraction of A in the mixture.

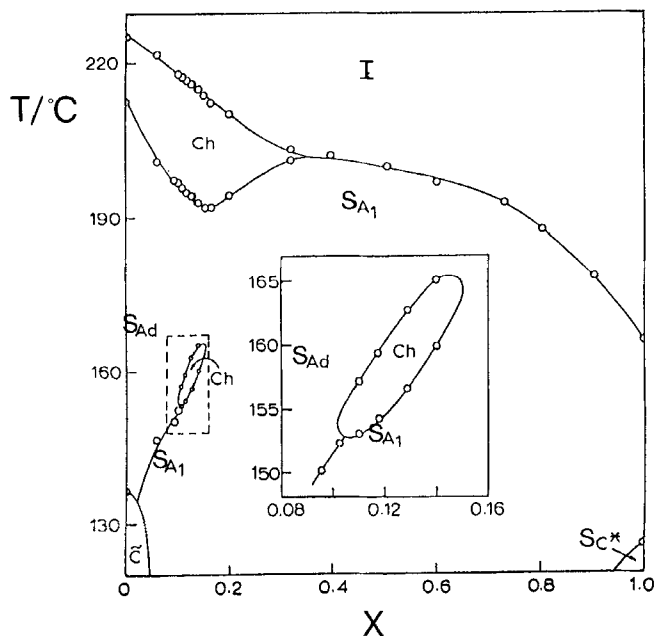


Figure 21. T - X diagram for the system in which one of the constituents is 9-25OBCB (which is a 25 wt % mixture of 9OBCB with its higher homologue 10OBCB) and A is the other constituent. The concentration has been expressed as the molar fraction of A in the mixture. The area within the broken lines is shown in the inset on an enlarged scale. The cholesteric island is now fully separated from the main cholesteric region.

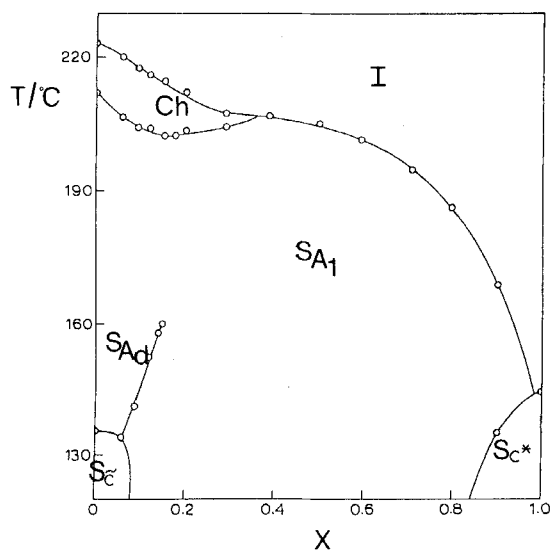


Figure 22. T - X diagram for binary mixtures of 10OBCB in A. X is the molar fraction of A in the mixture. The cholesteric island has disappeared completely, leading to the S_{A_d} - S_{A_1} critical point.

On the experimental side, Cladis and Brand [48] have discovered the cholesteric island (see figure 20) surrounded by a sea of smectic A at the terminus of the S_{A_d} - S_{A_1} phase boundary. In fact, this observation preceded the theoretical prediction. They also found that beyond this island the layer spacing in the S_{A_d} phase varies smoothly to the monolayer value in the S_{A_1} phase. Hardouin *et al.* [49] have shown that by continuously varying the chain length the nematic island can merge with the main domain nematic. Heppke *et al.* [50] have made a more detailed study on mixtures involving a strongly polar material with terminally non-polar chiral materials. These diagrams (see figures 20–22) clearly show that as the concentration of the latter is varied, the cholesteric island evolves out of the main cholesteric region, separates and finally vanishes altogether to form a smectic A_d -smectic A_1 critical point. These results support the theoretical idea [47] that the occurrence of the nematic (or cholesteric) island at the terminus of the S_{A_d} - S_{A_1} boundary is not necessarily universal. None of the experimental studies described here has the resolution to probe the details of the nematic island. Hence, the theoretical predictions regarding the existence of two types of nematic phases (inside the island) and two critical end points are still to be verified experimentally.

4. Summary

Strongly polar liquid crystals exhibit an extremely rich variety of phases, phase transitions and critical phenomena. These can be understood on the basis of the phenomenological model of a frustrated smectic in which there is a competition between two length scales, viz. the thickness of the smectic layer and the molecular length. Most of the predictions of this mean field approach have been verified experimentally. High resolution experiments to understand the nature of the different phase transitions and multicritical points have just begun. The results emerging from these studies, coupled with the recent developments in the fluctuation-corrected theories, should lead to a better understanding of the interesting and new physics of polar smectic A liquid crystals.

We are extremely grateful to Professor S. Chadrsekhar for many invaluable suggestions and discussions. Several of the experimental results described in this paper would not have been possible but for the help of several collaborators, in particular Mr V. N. Raja, Dr S. Krishna Prasad, Mr S. Somasekhara, Professor G. Heppke and Professor C. W. Garland whose help is gratefully acknowledged. We are also highly grateful to Dr J. Prost, Professor C. W. Garland, Professor T. C. Lubensky and Dr P. Barois for several important discussions.

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