Smectic-A_d–Smectic-A_2 Critical Point

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The first observation of the smectic-A_d–smectic-A_2 critical point is reported. Detailed x-ray studies show that a first-order phase transition between the partially bilayer smectic-A_d and the bilayer smectic-A_2 phases which have the same symmetry terminates in a critical point in the temperature-concentration plane.

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The smectic-A phase can be characterized as a one-dimensional density wave in an orientationally ordered fluid.[1,2] When the constituent molecules are symmetric only one type of smectic-A phase occurs, viz., the monolayer A_1 phase in which the periodicity of the density wave (or the layer spacing d) is approximately equal to the molecular length (l). When the molecules have a strongly polar end group, several types of A phases are seen.[3] In addition to the monolayer A_1 phase, there are the partially bilayer A_d phase, the bilayer A_2 phase, and the incommensurate A_{ic} phase.[4] They can be identified unambiguously on the basis of the x-ray diffraction patterns obtained from monodomain samples. The A_1 phase gives a strong diffraction maximum (quasi-Bragg peak) at a wave vector $2q_0=2\pi/l$; the A_2 phase two maxima, the fundamental at q_0 and the second harmonic at $2q_0$. The A_d phase also has two maxima, these being at $q_0'=2\pi/l'$ (where $l<l'<2l$) and $2q_0'$. In addition, a diffuse maxima centered around $2q_0$ is seen in the A_d phase.

The smectic-A polymorphism exhibited by the terminally polar compounds has been successfully explained in terms of a phenomenological model.[5-8] More recently, the nature of the A_d phase and its relation to the A_1 and A_2 phases were examined theoretically by Barois, Prost, and Lubensky.[9] They used the phenomenological model within the framework of the mean-field theory to study phase diagrams as well as x-ray scattering intensities. It has been argued that, the symmetries of the A_d and A_2 phases being identical, there cannot be a second-order phase transition between them. (These arguments should, in principle, be valid for the A_1-A_d transition also. The A_1-A_2 transition can, however, be second order[10] because of the exact doubling of the layer periodicity.[11]) The theory of Barois, Prost, and Lubensky[9] also predicts that a first-order phase boundary along which the A_d and A_2 phases coexist can terminate at a critical point similar to the gas-liquid critical point. There have been some experimental attempts[12-14] to observe the A_d-A_2 critical point, but they have so far remained unsuccessful.

We present in this Letter the results of our miscibility and x-ray studies on binary mixtures of 4-n-undecyloxyphenyl-4′-(4″-cyanobenzyloxy) benzoate (or 11OPCBOB) and 4-n-nonyloxybiphenyl-4′-cyanobenzoate (or 9OBCB) which have led to the first observation of the A_d-A_2 critical point (CP). We show that the first-order A_d-A_2 transition characterized by a jump in the wave vectors terminates at a CP in the temperature-concentration plane. We also show that the width of the coexistence region associated with the A_d-A_2 transition, as well as the difference in the wave vectors at the transition, goes to zero at a CP.

The phase diagram of the 11OPCBOB-9OBCB binary system is shown in Fig. 1. This diagram has been obtained by observing under a polarizing microscope the optical textures exhibited by the different phases. It is seen that for the mole fractions of 11OPCBOB (X) less than 0.52, the ribbon phase $\tilde{C}$ intervenes between the A_d and A_2 phases. However, with increasing X the $\tilde{C}$ gets suppressed leading to a direct A_d-A_2 transition which is seen optically as a readjustment of the focal conic texture. We shall show in the following that the first-order A_d-A_2 transition terminates at a critical point (CP) in the temperature-concentration plane.

The results of x-ray studies for a number of concentrations on either side of CP are shown in Fig. 2. These high-precision data were obtained using a computer controlled Guinier diffractometer (Huber model 644). Cu $K\alpha_1$ and $K\alpha_2$ lines were separated by using a bend quartz monochromator in the Johansson geometry and only the $K\alpha_1$ line was used for the experiment. The sample filled in a Lindemann glass capillary (0.5 mm in diameter) was oriented by slow cooling from the nematic to the A_d phase in the presence of a 2.4-T magnetic field. The oriented sample was then transferred along with the temperature controlled oven to the goniometer of the diffractometer. Temperatures were held constant to ± 5 mK or better during any measurement of the Bragg angle θ. The precision in the determination of the wave

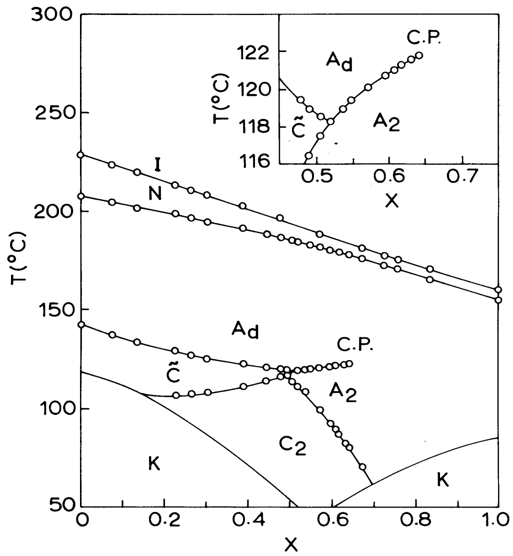

FIG. 1. Temperature-concentration (T-X) diagram for the binary mixtures of 11OPCBOB in 9OBCB. X is the mole fraction of 11OPCBOB in the mixture. The A_d-A_2 transition terminates at the critical point (CP). The phase diagram in the vicinity of CP is shown in the inset on an enlarged scale: K, crystalline; N, nematic; I, isotropic; $\tilde{C}$, bidimensional ribbon (Ref. 15); and C_2, bilayer C phases (Ref. 15).

vectors characterizing the A_d and A_2 phases was $\pm 2\times 10^{-4}$ Å^{-1}.

The x-ray diffraction pattern in the A_d phase was found to consist of quasi-Bragg peaks at wave vectors q_0' and $2q_0'$, while that in the A_2 phase showed peaks at q_0 and $2q_0$ (Fig. 2). We also sometimes observed, depending on the mosaicity of the aligned sample, diffuse scattering centered around $2q_0$ in the A_d phase. The signature of the A_d-A_2 transition was a two-phase region whose diffraction pattern consisted of both q_0 and q_0', as well as the wave vectors corresponding to the second harmonic [Fig. 2(b)]. This is exactly as is expected and indeed seen earlier[16] for a first-order transition between two smectic phases with different layer periodicities. Figure 3 gives the temperature variation of q_0 and q_0' for binary mixtures with X=0.550, 0.571, 0.597, 0.619, 0.642, 0.715, 0.80, and 1.0 (or 11OPCBOB). For all $X<0.642$, the A_d-A_2 transition is seen. Figure 3 also shows the data in the coexistence region. It is seen that the variations of q_0' and q_0 in this region are nothing but continuations of the trends in the variation of the wave vectors in the A_d and A_2 phases, so much so, we can associate a jump in the wave vector at the A_d-A_2 transition. (Exactly similar results have been obtained for the wave vector of the second harmonic also, but these will not be discussed here.)

It is clear from Fig. 3 that the magnitude of the wave vector jump which is about 0.0037 Å^{-1} (this corresponds to a layer spacing change of 2 Å) for X=0.550,

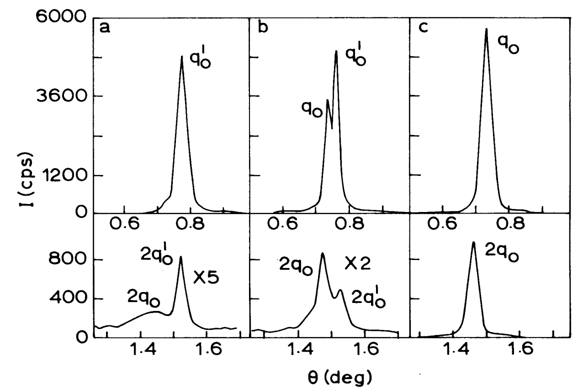

FIG. 2. Raw diffractometer scans taken along the equitorial direction ($q_\perp=0$) for the X=0.608 mixture showing the x-ray scattered intensity I (counts per second) as a function of the scattering angle (θ). (a) A_d phase, T=121.5 °C. The quasi-Bragg peaks are at q_0' and $2q_0'$; the latter one is seen overriding on the diffuse scattering centered around $2q_0$. (b) Two-phase region (T=121.1 °C) showing the coexistence of q_0 and q_0' as well as of $2q_0$ and $2q_0'$. (c) A_2 phase (T=120.3 °C) with the diffraction peaks at q_0 and $2q_0$. The intensities of the second harmonics in (a) and (b) have been multiplied by a factor of 5 and 2, respectively.

decreases with increasing X with an accompanying decrease in the width of the two-phase region until at X=0.642, no jump is seen within the resolution of our experimental setup. Instead, a "vertical inflection point" is observed for this concentration. All these features—the shrinking of the two-phase coexistence region associated with the first-order A_d-A_2 transition and the accompanying decrease in the difference between q_0 and q_0' at the transition, the vertical inflection point—are clearly indicative of the existence of a critical point at X=0.642. For higher X values, the inflection point becomes less pronounced as is expected on moving away from the critical point and A_2 evolves continuously from the A_d phase without a phase transition. Thus, we have shown that two smectic-A phases with different layer spacings can coexist along a line (of first-order transitions) terminating at a critical point beyond which the distinction between the two phases ceases to exist.

The mean-field theory of Barois, Prost, and Lubensky[9] had initially suggested that the A_d-A_2 critical point might be similar to a gas-liquid type of critical point. However, a recent theoretical approach[17] based on renormalization-group theory appears to indicate that because of layer fluctuations and coupling of the order parameter to elastic degrees of freedom this critical point may belong to a new universality class, with $d_c=6$ and anisotropic correlation length exponents. Clearly, further high-resolution experiments are needed to classify the A_d-A_2 critical point.

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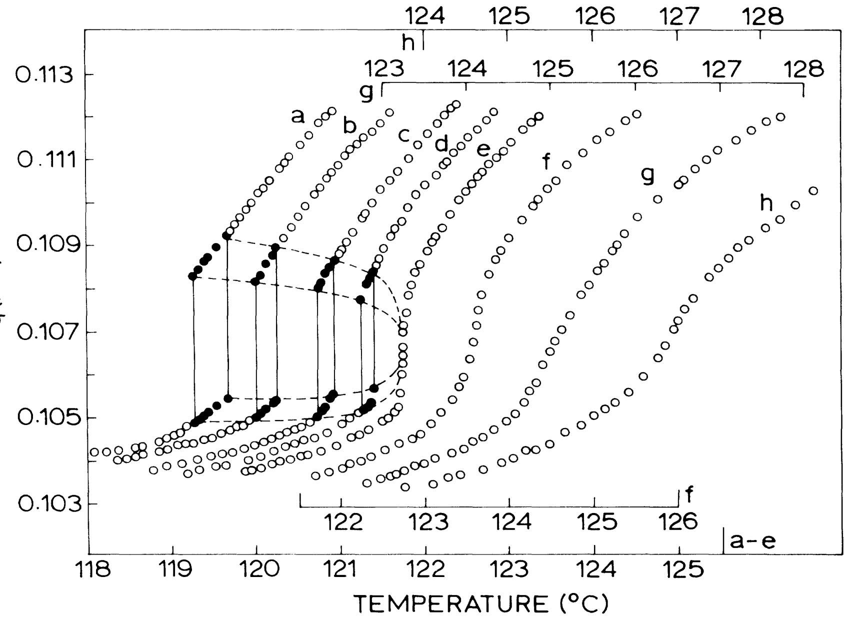

FIG. 3. Plots of wave vectors q_0 and q_0' vs temperature (T) for different mixtures of 11OPCBOB in 9OBCB. The mole fractions (X) of 11OPCBOB in the mixture are (a) 0.55, (b) 0.571, (c) 0.597, (d) 0.619, (e) 0.642 (f) 0.715, (g) 0.80, and (h) 1.0 or 11OPCBOB. The corresponding temperature scales are identified. For $X < 0.642$ (plots a-d), a first-order A_d-A_2 transition is seen which manifests as a jump in the wave vector. The data in the two-phase region are shown as circles, while the vertical lines represent the approximate width of this region. Dashed lines are envelopes of the ends of the two-phase regions and are only guides to the eye. The critical point (CP) is identified by the vertical inflection point seen for $X = 0.642$ (plot e).

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