Birefringence study of reentrant-nematic liquid-crystal mixtures

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The birefringence in mixtures of 4-cyano-4′-octyloxybiphenyl (8OCB) and 4-cyano-4′-hexyloxybiphenyl (6OCB) has been studied near the nematic–to–smectic-A (NA) and smectic-A–to–reentrant-nematic (AN') transitions. There is an overall increase in the birefringence at the NA transition and an overall decrease at the AN' transition. The birefringence change at the transitions decreases with increasing concentration x of 6OCB and vanishes at $x=0.28$. The birefringence and the transition enthalpy behave similarly.

Reentrant phenomena in liquid crystals have been observed in mixtures[1,2] and in single compounds at high pressure[3] or at atmospheric pressure.[4,5] The occurrence of the reentrant nematic phase has been investigated thermodynamically[6] and with a Landau theory, assuming the existence of an optimum density for smectic ordering.[7] A tentative model with antiparallel pairing of molecules has been suggested.[8]

There have been questions on whether the reentrant nematic and the high-temperature nematic phases are identical, and on the nature of the nematic–to–smectic-A (NA) and smectic-A–to–reentrant nematic (AN') transitions.[1,2] X-ray measurements suggested that the two nematic phases are similar.[9] Critical anomalies above the NA transition and below the AN' transition have also been observed in the bend elastic constant[1,10] and the twist viscosity.[11] It is interesting to note that one of the Miesowicz viscosities was found to be larger in the reentrant nematic phase than the value extrapolated from the high-temperature nematic phase.[11] A calorimetric study did not indicate any first-order nature of the NA and AN' transitions, nor did it yield any critical behavior in the heat capacity.[12] The behavior of the nematic order parameter near the NA and AN' transitions is also of interest. The coupling of the nematic and smectic order parameters has been suggested to be important in describing the reentrant phase diagram.[13] However, an electron-spin-resonance study failed to reveal changes in the nematic order parameter at the NA and AN' transitions.[14] In this Communication, we report the results of a high-resolution measurement of the birefringence in reentrant mixtures of 4-cyano-4′-octyloxybiphenyl (8OCB) and 4-cyano-4′-hexyloxybiphenyl (6OCB).

Our samples of 8OCB and 6OCB were obtained from BDH Chemicals. Mixtures with various concentrations x by weight of 6OCB were studied. Planar samples were formed between glass slides, with the director aligned in a direction parallel to the slides. By decreasing the temperature slowly from the high-temperature nematic phase, sample alignment was maintained in the smectic-A and reentrant nematic phases. The temperature was controlled to a stability of 1 mK. The temperature gradient in the illuminated part of the sample was estimated to be less than 6 mK. The birefringence was measured using a rotating-analyzer technique with a sensitivity of 4×10^{-6}.[15] The intensity of light scattered by the sample was monitored simultaneously to locate the phase transition temperatures.

The phase transition temperatures of the mixtures studied are shown in Fig. 1. The phase diagram is in good agreement with those previously reported for

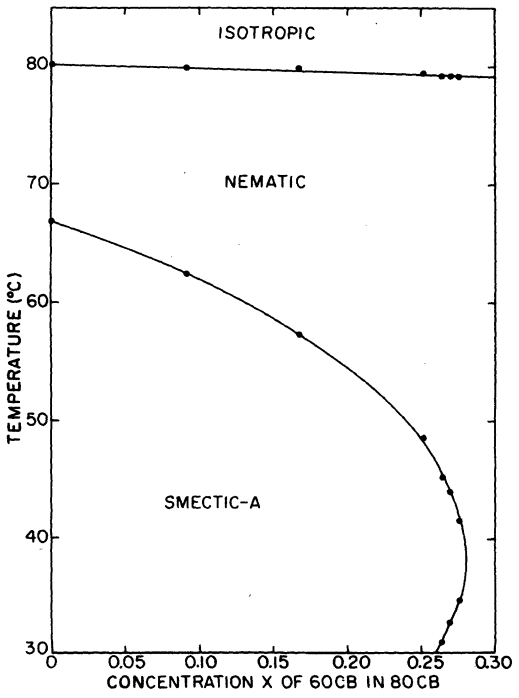

FIG. 1. Phase diagram of 8OCB–6OCB mixtures as a function of the concentration x by weight of 6OCB.

these mixtures.[2,10,12] The behavior of the birefringence Δn near the NA transition in three mixtures with $x=0.091$, 0.167, and 0.251 is shown in Fig. 2. The origin of the Δn axis for each mixture has been shifted arbitrarily to prevent overlapping of the data. The temperatures for each mixture are plotted relative to its NA transition temperature T_{NA}, which was determined from the light scattering data taken simultaneously. To within our experimental resolution, there is no discontinuity in Δn at T_{NA} in all the data, suggesting a second-order NA transition for the mixtures. Even though Δn changes smoothly at T_{NA}, there is also clearly an overall increase in Δn due to the NA transition. The temperature dependence of Δn near T_{NA} is fairly linear on both the nematic and the smectic-A sides, except for a pretransitional region of about 0.04 °C in the immediate vicinity of T_{NA}. The absolute value of the slope decreases typically by 20% in going from the nematic to the smectic-A phase. By extrapolating the linear region on either side of T_{NA}, one can define an overall change $\delta(\Delta n)$ in Δn at T_{NA}. This is illustrated in Fig. 2 for the $x=0.091$ mixture. Such an extrapolation has also been applied to the Δn data on pure 8OCB.[16] The sensitivity of $\delta(\Delta n)$ to the concentration x of 6OCB is quite striking. For example, $\delta(\Delta n)$ changes from 1.95×10^{-3} for $x=0$ to 1.00×10^{-3} for $x=0.091$, even though T_{NA} only decreases from 66.8 to 62.4 °C. The further decrease in $\delta(\Delta n)$ with increasing x is also apparent from Fig. 2.

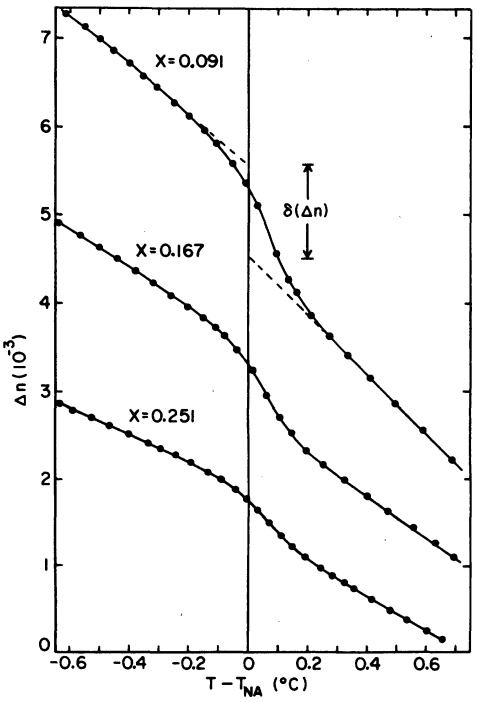

FIG. 2. Temperature dependence of the birefringence Δn in three 8OCB–6OCB mixtures with various concentrations x of 6OCB. The origin of the Δn axis for each mixture has been shifted arbitrarily. The temperatures are measured relative to the NA transition temperature T_{NA} of the respective mixtures.

At $x=0.270$, the reentrant nematic phase is stable. The Δn and light scattering intensity data for this mixture are shown in Fig. 3. The reentrant behavior is clearly evident from the light scattering intensity, which decreases as T_{NA} is approached from above, remains at a constant, low level in the smectic-A phase, and increases again below the AN' transition temperature $T_{AN'}$. With the experimental sensitivity, changes in the birefringence Δn near T_{NA} and $T_{AN'}$ are clearly discernible. The pretransitional region appears to be considerably wider than that in pure 8OCB. By extrapolating the linear regions, an overall change $\delta(\Delta n)$ in Δn at both transitions is indicated in Fig. 3. The value of $\delta(\Delta n)$ at T_{NA} for $x=0.270$ is more than an order of magnitude smaller than that for pure 8OCB. The change in Δn near the AN' transition is particularly interesting. There is an overall *decrease* in Δn by an amount which is comparable to the increase in Δn at the NA transition. The change in Δn can originate from changes in both the nematic order parameter S and the density ρ.[17] However, density measurements near the AN' transition at $x=0.253$ showed a relative change in ρ or 1.15×10^{-4},[18] which is an order of magnitude smaller than the relative change in Δn. Thus the change in Δn at $T_{AN'}$ is predominantly due to a change in S. Our results therefore imply that the orientational order in the reentrant nematic phase is smaller than what it would be in the absence of the AN' transition.

The change $\delta(\Delta n)$ in Δn at the NA and AN' tran-

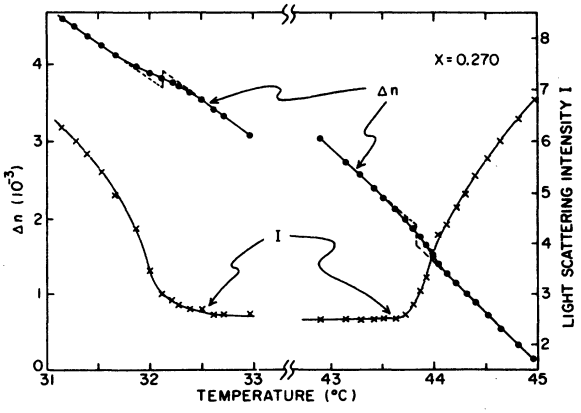

FIG. 3. Temperature dependence of the birefringence Δn (points) and the light scattering intensity I (crosses) in a mixture with 6OCB concentration $x=0.270$. The origin of the Δn axis has been shifted arbitrarily in the two temperature regions. Arbitrary units are used for I.

sitions for the mixtures studied are summarized in Fig. 4. There is a monotonic decrease in $\delta(\Delta n)$ as a function of decreasing T_{NA} or $T_{AN'}$. The two points with negative $\delta(\Delta n)$ changes correspond to the data near the AN' transition. The value of $\delta(\Delta n)$ vanishes at $T_{NA} = 37.5\,^{\circ}\mathrm{C}$, which is in good agreement with the transition temperature at the maximum 6OCB concentration of $x = 0.28$ in the phase diagram in Fig. 1 for the smectic-A phase to exist. The decrease in $\delta(\Delta n)$ is quite similar to the decrease in the transition enthalpy with increasing x that has been observed.[12] This implies that the changes in Δn may be proportional to the changes in the internal energy in the vicinity of the transitions. Such a relation has been previously suggested[16] and has recently been found to be true by comparing the birefringence[19] and heat-capacity[20] data near the smectic-A–to–smectic-B transition in N-(p-butoxybenzylidene)-p-n-octylaniline (40.8). Unfortunately, this proportionality cannot be tested extensively in the 8OCB–6OCB mixtures because the transition enthalpy was not measurable for mixtures with x beyond 0.20.[12]

Finally, we would like to comment on the implication of our results on the coupling between the nematic and smectic-A order parameters. Although Δn is not an exact measure of the nematic order parameter S because of the local-field corrections, approximate corrections, such as that proposed by Vuks,[21] have been quite successfully applied. Experimentally, Δn and S are found to be proportional to each other in the nematic and smectic phases through quantities such as the density and the mean refractive index, which are not very sensitive to temperature.[17,22–24] Thus our results on Δn largely reflect the effect on S caused by the buildup and breakup of smectic-A order near the NA and AN' transitions, respectively. de Gennes has suggested that the coupling between S and the smectic-A order parameter ψ can be represented by a coupling term $-C(S-S_0)\psi^2$ in the free energy, where $C > 0$ and S_0 is the value of S in the absence of the smectic-A order.[25] This implies

$$S = S_0 + \chi C \psi^2 \ , \tag{1}$$

where χ is a positive constant. This is in qualitative agreement with the observed behavior of S near the NA transition, with the additional increase in S above T_{NA} attributed to short-range smectic-A order.[16] When applied to a reentrant system, Eq. (1) predicts an enhancement of S in the temperature range in which the smectic-A phase exists, which is what has been observed in the 8OCB–6OCB mixtures. On the other hand, Cladis has proposed that the reentrant phase diagram of the 8OCB–6OCB mixtures can be described by a Landau expansion of the free energy in both S and ψ, with a coupling term $(\eta/2)S^2\psi^2$, where $\eta > 0$.[13] This implies that

$$S^2 = S_0^2 - (\eta/\beta)\psi^2 \ , \tag{2}$$

where β is a positive constant. This model predicts an overall drop in S upon cooling through T_{NA} and an increase through $T_{AN'}$. Our data thus suggest that the effect of Eq. (1) is the predominant one near T_{NA} and $T_{AN'}$ in the 8OCB–6OCB mixtures. One might speculate that the decrease in the temperature dependence of S in the smectic-A phase compared to the nematic phase may be considered evidence for the existence of the coupling leading to Eq. (2). However, this change of slope at the NA transition is quite universal, and occurs even in nonpolar materials, such as 40.8,[19] which do not show reentrant behavior.

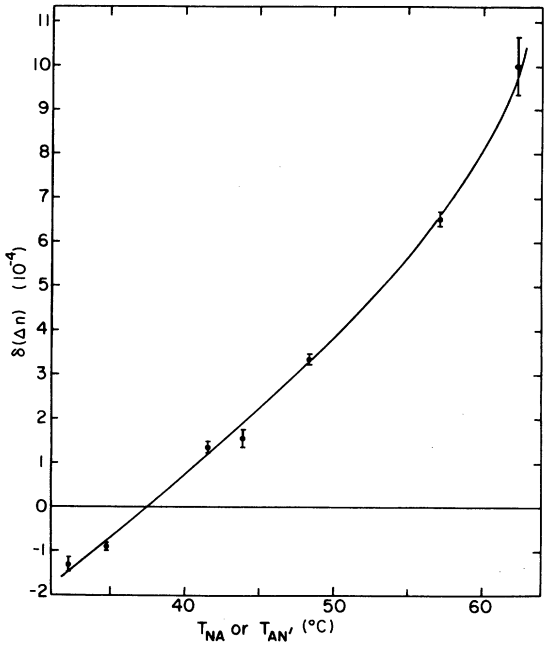

FIG. 4. Overall birefringence change $\delta(\Delta n)$ at the NA and AN' transitions.

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