Mean-Field to Tricritical Crossover Behavior near the Smectic-A–Smectic-C^* Tricritical Point

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Precise x-ray measurements of the tilt angle near the smectic-A–smectic-C^* tricritical point show clear evidence of mean-field to tricritical crossover behavior; the mean-field region shrinks to zero at the tricritical point.

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Smectic-A (hereafter denoted as A) and smectic-C (denoted C) liquid crystals are orientationally ordered fluids which possess quasi-long-range positional order in one dimension represented by a mass-density wave. The wave vector of this density wave is along the director in the case of the A phase, while it is tilted in the case of the C phase. When the constituent molecules are optically active, a chiral C (or C^*) phase is observed which exhibits ferroelectric properties.[1] Experimental evidence[2–4] indicates that the A-C^* transition is mainly driven by intermolecular forces producing the C phase and hence the primary order parameter associated with the A-C^* transition is, as in the case of the A-C transition, the tilt angle.

The nature of the A-C or A-C^* transition is of considerable interest. Although it was initially proposed that this transition should exhibit heliumlike critical behavior,[5] subsequent studies[6–11] have clearly shown that the A-C as well as the A-C^* transition is mean-field-like with a sixth-order term in the Landau free-energy expansion. As first pointed out by Huang and Viner,[11] the presence of the sixth-order term implies that the mean-field-like A-C transition is always close to a mean-field tricritical point with a concomitant existence of a "crossover" behavior from a mean-field-like region to a tricritical-like region. It is also to be expected that as the

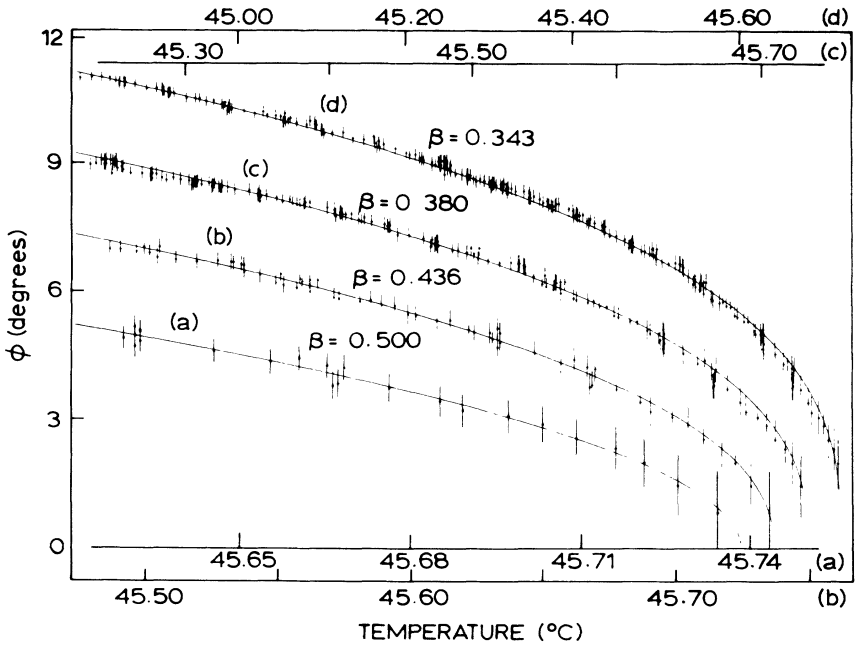

FIG. 1. Tilt angle (ϕ) vs temperature plots in the C^* phase of the $X=16.92$ mixture of 7OPDOB in C_7. The solid lines are fits of the data by a power law. The exponent β has been evaluated by our limiting the data (see text) to four temperature ranges, viz., (a) 103 mK, (b) 240 mK, (c) 490 mK, and (d) 930 mK. The corresponding β values are marked. The error bars represent one standard deviation statistical error.

tricritical point (TCP) is approached the mean-field (MF) region should shrink, going to zero at the TCP. Recent x-ray studies[12] on 4-(3-methyl-2-chloropentanoyloxy)-4′-heptyloxy biphenyl or C_7, a material exhibiting large spontaneous polarization,[13] have established that the A-C^* transition in this material is first order. It was also shown that addition of a second compound, viz., 4-heptyloxy-4′-decyloxybenzoate (7OPDOB), drives the transition towards second order, leading to a TCP.

In this Letter we present the results of our high-resolution x-ray measurements of the tilt angle on the second-order side of the TCP in the C_7-7OPDOB binary system. These results clearly show a mean-field to tricritical crossover behavior, the mean-field range shrinking to zero at the TCP. We also show that the data for a concentration very close to the TCP yield a tricritical exponent (0.25) for the tilt angle.

The x-ray diffraction experiments have been conducted with use of a computer-controlled Guinier diffractometer (Huber model 644). The details of the setup have been described earlier.[14,15] In order to acquire the exhaustive data that are necessary for an accurate determination of the critical exponent (β) associated with the tilt angle, the temperature of the sample was varied at a slow rate ($\simeq$100 mK/h) and the data were collected at temperature intervals of $\simeq$5 mK, the temperature being constant to about 2 mK during any data collection. The relative accuracy in the determination of the wave vector was 2×10^{-4} Å^{-1}. In all, five mixtures of the C_7-7OPDOB system was studied whose concentrations (X, expressed in mole percent of 7OPDOB) were 16.92, 15.49, 14.02, 13.60, and 13.30. The tilt angle in the C^* phase was evaluated from the expression $\phi=\cos^{-1}(d_{C^*}/d_A)$, where the subscripts denote the phases in which the layer spacing d ($=2\pi/q$) was measured. The efficacy of such an evaluation (which assumes a "rigid-rod" behavior[16]) has been verified by a direct determination of ϕ from the "four-spot" x-ray diffraction photographs.[17] The values of ϕ obtained by these two methods agreed exactly.

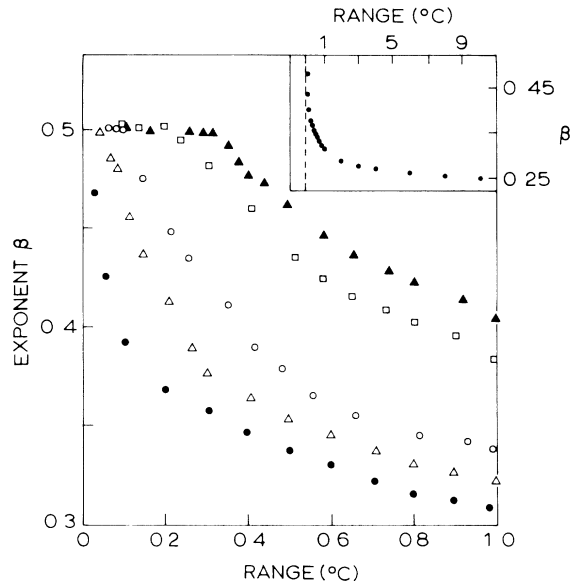

FIG. 2. Variation of β with temperature range for different mixtures of the C_7-7OPDOB binary system. The concentrations are 16.92 (filled triangles), 15.49 (squares), 14.02 (open circles), 13.60 (open triangles), and 13.30 (filled circles). In the mean-field (MF) region $\beta=0.5$ and is independent of the temperature range. In the crossover region β values are strongly dependent on the range. The MF range is seen to shrink with decreasing X. The mixture with $X=13.30$ for which no MF region is seen by power-law fit is practically at the tricritical point (TCP). Inset: Plot of β vs range for this mixture over an extended temperature range ($\simeq$10 °C) shows the saturation of β at the tricritical value of 0.25.

The tilt-angle data were analyzed with use of a power law,[16] viz., $\phi=\phi_0[(T_{AC^*}-T)/T_{AC^*}]^\beta$ and a "variable-range" procedure—we chose (arbitrarily) different limiting values of temperature (T_l) in the C^* phase and in each case the data between T_l and T_{AC^*} were fitted by the power law and the exponent β was evaluated. A nonlinear least-squares-fit program was used, with ϕ_0, T_{AC^*}, and β being free parameters. For each concentration, about fifteen limiting ranges varying from 40 mK to 1 K were chosen and the χ^2 values for the fits were typically in the range 0.6–2.0. The accuracy in the determination of β is reckoned to be ±0.01 or better. Fits carried out with use of the data for the 16.92 mixture for four typical ranges, viz., 103, 250, 490, and 930 mK are shown in Fig. 1. It is seen that for the lowest range (103 mK) the power-law fit gives a mean-field exponent, i.e., $\beta=0.50$. With increasing range, β decreases, signifying mean-field to tricritical crossover behavior. Figure 2 shows the plot of β versus temperature range for the different concentrations. It is seen that with decreasing X, i.e., as the TCP is approached, the temperature range (T_{MF}) over which the mean-field β value of 0.5 is obtained gets progressively smaller, until finally, for the $X=13.30$ mixture, there appears to be no mean-field range at all. For this mixture, we have also evaluated β over a wide range of temperature ($\simeq$10 °C) in the C^* phase. Such an

TABLE I. The transition temperature (T_{AC^*}), mean-field range (t_{MF}), crossover temperature (t_0), and the range of the smectic-A phase for the different mixtures of C_7-7OPDOB system. (T_{IA} is the isotropic–smectic-A transition temperature.)

Mole percent	T_{AC^*} (°C)	$10^3 t_{MF}$	$10^3 t_0$	$T_{IA}-T_{AC^*}$ (°C)
16.92	44.668	1.03	2.17	15.5
15.49	45.120	0.72	1.41	14.8
14.02	45.738	0.31	0.71	14.1
13.60	46.095	0.13	0.39	13.7
13.30	46.271	···	0.05	13.4

evaluation (inset of Fig. 2) shows that β *gets saturated at 0.25, the tricritical value.*

We have also fitted our tilt-angle data for all the concentrations to an equation derived from the extended mean-field expression with a sixth-order term,[7] i.e.,

$$\phi=\phi_0[(1+3t/t_0)^{1/2}-1]^{1/2},$$

where t_0 is the mean-field to tricritical crossover temperature expressed in reduced temperature. The values of t_0, obtained from such fits, are listed in Table I along with the mean-field range, t_{MF} (i.e., T_{MF} expressed in reduced temperature), as obtained from power-law fits. It is clear that both t_0 and t_{MF} become smaller as TCP is approached. Interestingly, for $X=13.30$, t_{MF} is nearly zero, while the value of t_0 is also extremely small, viz., 5×10^{-5}, showing that this concentration is practically at or extremely close to the TCP. This inference is also substantiated by the power-law fit which yields $\beta=0.25$. Thus we have shown clear evidence of mean-field to tricritical crossover behavior near the A-C^* mean-field tricritical point. The mean-field range, as determined from the power-law fit, shrinks and goes to zero at TCP. This scenario is represented in Fig. 3.

Finally, it is relevant to comment on the origin of the A-C^* tricritical point. It has been shown[18] that the temperature range of the A phase plays an important role in determining the nature of the A-C or A-C^* transition. The decrease of the A phase range appears to lead to smaller t_0 values, i.e., the mean-field-like transition is driven towards a tricritical point and subsequently

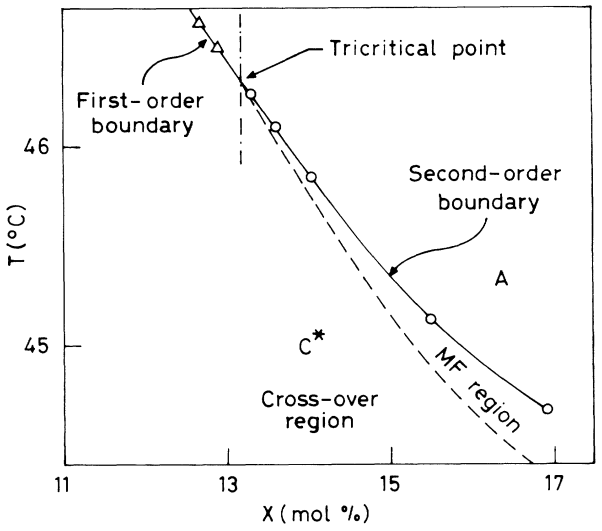

FIG. 3. Phase diagram for the C_7-7OPDOB system showing the mean-field to tricritical crossover behavior near the smectic-A-smectic-C^* tricritical point. The A-C^* phase boundary on the first-order (triangles) as well as on the second-order (circles) side of TCP have been obtained optically. The dashed line representing the MF to tricritical crossover has been identified by power-law fits of the tilt-angle data (see Fig. 2). The MF region shrinks to zero at TCP.

to a first-order transition. The range of the A phase for C_7, which exhibits a first-order A-C^* transition, is $\simeq7$ °C. Recently another material[19] 4-(3-methyl-2-chlorobutanoyloxy)-4′-heptyloxybiphenyl (A_7) also exhibiting large spontaneous polarization and with an A phase range of $\simeq8$ °C has been found to exhibit a first-order A-C^* transition. On the other hand, a number of chiral substances with a similar or even smaller A range are known to exhibit only a second-order A-C^* transition.[18] These are, however, materials with a small spontaneous polarization. Thus the first-order nature of the A-C^* transition in C_7 and A_7 may perhaps be associated with large spontaneous polarization. Clearly, further studies are needed to understand the origin of the A-C^* tricritical point.

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