Tricriticality near the Smectic-*A*–Smectic-*C* Transition of a Liquid-Crystal Compound

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High-resolution calorimetric investigations have been carried out on the chiral and racemic versions of 4-(3-methyl-2-chlorobutanoyloxy)-4′-heptyloxybiphenyl. While the chiral compound shows a weakly first-order smectic-*A*–chiral-smectic-*C* transition, the racemic one exhibits a continuous smectic-*A*–smectic-*C* transition. The latter transition is found to be at a mean-field tricritical point, within our experimental resolution.

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The smectic-*A* (Sm*A*) and smectic-*C* (Sm*C*) liquid-crystal mesophases can be characterized as orientationally ordered two-dimensional fluids with one-dimensional mass-density waves. The wave vector is either along (*A*) or at an angle (*C*) to the long axis of the molecule (molecular director). If the constituent molecules are optically active, the chiral smectic-*C* (Sm*C**) phase[1] will be observed instead of the Sm*C* phase. In the Sm*C** phase, as a consequence of the molecular chirality, the molecular director exhibits a helical structure precessing around the one-dimensional mass-density wave vector. The helical pitch is usually about several microns. If the molecule has a net transverse dipole moment, there will be spontaneous polarization within each smectic layer. From symmetry arguments, the net spontaneous polarization points in a direction perpendicular to both the mass-density wave vector and the molecular director. Experimental results[2] indicate that the Sm*A*-Sm*C** transition is mainly driven by intermolecular forces producing the molecular tilt from the direction of the mass density wave vector and not by a coupling between molecular dipoles. Consequently, the tilt angle (θ) is the primary order parameter for both Sm*A*-Sm*C* and Sm*A*-Sm*C** transitions, while the spontaneous polarization of the Sm*C** phase is a secondary order parameter for the Sm*A*-Sm*C** transition.

Experimentally, the Sm*A*-Sm*C* and Sm*A*-Sm*C** transitions are generally found to be continuous. While compiling all of the available high-resolution data near the Sm*A*-Sm*C* (or -Sm*C**) transitions, Huang and Lien[3] discovered that, in principle, if a compound showing a mean-field tricritical behavior can be found, then "properly" reducing the Sm*A*-phase temperature range will make the transition become first order. In this Letter a mean-field tricritical point is identified in the Sm*A*-Sm*C* transition of one racemic mixture; the corresponding chiral compound with a smaller Sm*A* temperature range shows a first-order Sm*A*-Sm*C** transition. These experimental results give a strong support to our previous observation and suggest the role of the polarization in the determination of the tricritical point.

In 1980, Clark and Lagerwall[4] demonstrated that the helical pitch can be suppressed in the surface-stabilized ferroelectric liquid-crystal cell (SSFLC). This results in macroscopic domains with almost uniform polarization. Consequently, the coupling between the molecular director and polarization allows one to use the SSFLC cell as an electro-optical switching device with a reasonably fast switching speed (better than 1 μsec has been achieved). Numerous applications using the SSFLC cell have been proposed and/or demonstrated. Meanwhile, in order to improve device applications, many new ferroelectric liquid-crystal compounds have been synthesized with very large values of spontaneous polarization in the Sm*C** phase.[5,6] One of them prepared by Bahr and Heppke[5] is 4-(3-methyl-2-chlorobutanoyloxy)-4′-heptyloxybiphenyl (A7) which has a first-order Sm*A*-Sm*C** transition.[7] Its transition sequence is isotropic (I) (81.6 °C) Sm*A* (73.04 °C) Sm*C** (71.1 °C) crystal-*G* (Cry*G*). The racemic mixture has a similar transition sequence, namely, I (82.0 °C) Sm*A* (72.23 °C) Sm*C* (70.2 °C) Cry*G*.

Details of our calorimetric system have been published.[8] Figures 1 and 2 display the heat-capacity anomalies in the vicinity of the Sm*A*-Sm*C** and Sm*A*-Sm*C* transitions of the chiral and racemic compounds of A7, respectively. In both compounds, we measured heat capacity for successive heating and cooling runs through the transition temperature to detect the thermal hysteresis. The results for the chiral A7 compound are shown in Fig. 1. Thermal hysteresis of about 18 mK is clearly discernible and the transition is first order. Except for the thermal hysteresis, the overall temperature variation of heat capacity behaves in a mean-field fashion. The temperature scan rate used in the vicinity of the transition is approximately 3 mK/min. Our slow-

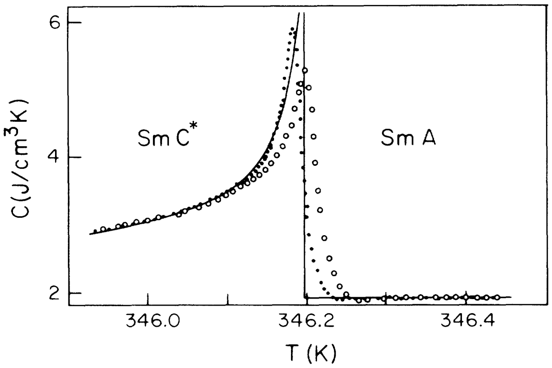

FIG. 1. Measured heat capacity near the SmA-SmC^* transition of a chiral A7 compound (l enantiometer). Dots are data for a cooling run; circles are data for the successive heating run. The thermal hysteresis between heating and cooling runs is very clear. Solid line is the fitted curve, Eq. (2), for the cooling run.

ing down the temperature scanning rate will cause some irregularities in the reading of the average sample temperature which is detected by one pair of tiny thermocouple junctions attached to the top side of our sample package.[8] We believe that the irregularities in the measured sample temperature are due to the release (in cooling) or absorption (in heating) of the latent heat associated with the first-order phase transition. Similar irregularities have been observed near the first-order hexatic-B-crystal-E transition in 65OBC. Here 65OBC refers to n-hexyl-4′-n-pentyloxybiphenyl-4-carboxylate.

The racemic compound for our heat-capacity investigations was prepared by 50%-50% mixture of the d and l enantiomer. Optical microscopic studies of the same mixture show a clear SmA-SmC transition without helical pitch which is the hallmark for the SmC^* phase. Within our experimental resolution (3 mK) no hysteresis can be detected. The irregularities observed in the pure chiral compound did not show up in our experimental run for the racemic mixture even though the heating or cooling rate was significantly reduced to less than 1 mK/min near the transition. In comparison with the heat-capacity anomaly associated with the other SmA-SmC (or SmC^*) transitions, except that this anomaly is much larger and sharper, the overall features are similar and are characteristic of the mean-field transitions with the free-energy expansion including a large sixth-power term of the order parameter.[9] One way to characterize the quality of the sample is the 10%-90% width of the heat-capacity jump on the high-temperature side of the anomaly. For the racemic A7 compound this width is 5.8×10^{-5} on the reduced temperature scale. In comparison with other SmA-SmC (or -SmC^*) transitions, this 10%-90% width is comparable to the best sample among the compounds without a chiral center[10] and is about 10 times smaller than the best one among the compounds with a chiral center.[11] Furthermore, this width is approximately the same as the one for the starting chiral compound as shown in Fig. 1. This indicates that the starting chiral materials are very pure and our mixing of two enantiomers does not induce any additional impurity rounding.

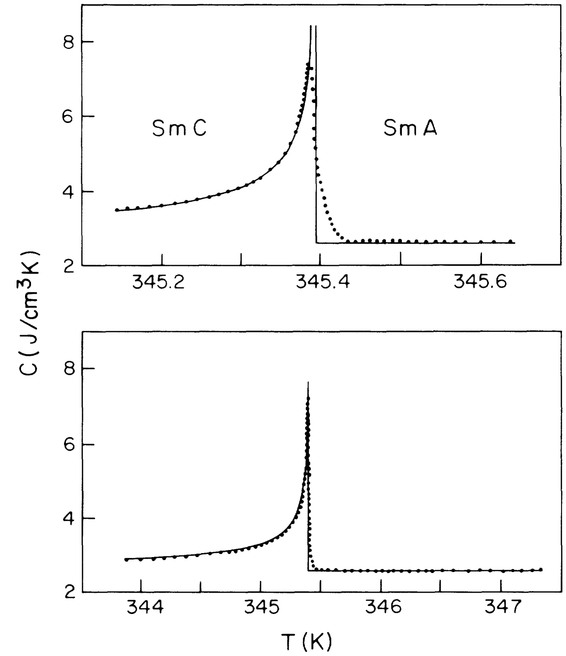

FIG. 2. Heat-capacity anomaly near the SmA-SmC transition of racemic A7 compound. Dots are experimental data; solid line is the fitted curve.

On the basis of their high-resolution heat-capacity studies near one SmA-SmC transition, Huang and Viner[9] proposed the following mean-field free energy with three expansion terms to describe the nature of this transition:

$$G=G_0+at\theta^2+b\theta^4+c\theta^6. \tag{1}$$

Here G_0 is the nonsingular part of the free energy. The constants a, b, and c are >0 for a continuous transition. $t=(T-T_c)/T_c$ is the reduced temperature and T_c the transition temperature chosen to be the midpoint of the mean-field heat-capacity jump for a continuous transition. The temperature dependence of the heat-capacity anomaly can be derived from Eq. (1) and is given as

$$C=\begin{cases}C_0, & T>T_c,\\ C_0+AT(T_m-T)^{-1/2}, & T<T_c.\end{cases} \tag{2}$$

Here C_0 is the background heat capacity obtained from G_0, $A=(a/T_c)^{3/2}/2(3c)^{1/2}$, and $T_m=T_c(1+t_0/3)$. An important dimensionless parameter to measure the relative importance of the sixth-order term is $t_0=b^2/ac$. So far it has been demonstrated that this free energy can describe the heat-capacity anomalies associated with all the reported SmA-SmC^* transitions[3] or a weakly first-order nematic-SmC transition with the coefficient b being negative.[12]

On the reduced temperature scale, the value of t_0 equals the full width at half height of the theoretical $(C-C_0)/T$ vs T curve.[9] Actually, the parameter t_0 describes the crossover from an ordinary mean-field behavior near the transition temperature with $b\theta^4/c\theta^6$ to a mean-field tricritical-like one away from the transition temperature for $c\theta^6 > b\theta^4$. In the case of a tricritical point ($b=0$), the heat-capacity anomaly diverges toward T_m ($=T_c$ in this special case) and the theoretical full width at half height of the anomaly becomes zero. In reality, because of the rounding caused by impurities and/or finite resolutions of experimental measurements, a heat-capacity peak with a finite width will be obtained. From the heat-capacity data in Fig. 2, we obtain 8.1×10^{-5} for the value of the experimental full width at half height on the reduced temperature scale. This value is comparable to the 10%-90% width ($\simeq 5\times10^{-5}$) of the mean-field jump. Consequently, we conclude that the value of t_0 ($=8\times10^{-5}$) obtained in this way is really limited by the rounding of our data and should be the upper bound for the true value of t_0. Here, the fact that this upper bound value of t_0 is about 10 times smaller than any reported one[3] leads us to conclude that the SmA-SmC transition of racemic A7 compound is in the immediate vicinity of a mean-field tricritical point. Employing x-ray diffraction to measure temperature variation of tilt angle, Ratna *et al.*[13] have studied the nature of the first-order SmA-SmC^* transition of another liquid crystal compound with large spontaneous polarization. The addition of a second-compound drives the SmA-SmC^* transition toward a continuous one. This suggests the existence of a mean-field tricritical point in the binary mixture system.

Equation (2) gives an excellent fit to our heat-capacity data near the SmA-SmC transition of racemic A7. The fitting result is shown in Fig. 2 as the solid line. The important parameters obtained through this fitting are $A=1.36\times10^{-3}$ J/K$^{3/2}\cdot$cm^3 and $|t_0| \lesssim 1\times10^{-5}$ which is the limit of our experiment resolution. This value of t_0 confirms our argument that the value obtained from the full width at half height of the heat-capacity anomaly is the upper bound for the parameter t_0. Thus we conclude that the SmA-SmC transition of racemic A7 exhibits the mean-field tricriticality within our experimental resolution. Similarly, the heat-capacity data of pure A7 near the SmA-SmC^* transition can be fitted by Eq. (2), with a larger value χ^2. The result is also shown in Fig. 1 as the solid line for one cooling run.

In searching for an explanation of the large sixth-order term in the Landau mean-field free-energy expansion [Eq. (1)] in describing SmA-SmC or SmA-SmC^* transitions, Huang and Lien[3] have found that the behavior of these two phase transitions is strongly dependent on the size of the SmA-phase temperature range which, to a good approximation, is directly related to the fluctuations of SmA order near the given SmA-SmC or SmA-SmC^* transition. Two salient features that result from this investigation are the following. First, all the SmA-SmC (or -SmC^*) transitions are not too far from a mean-field tricritical point. Thus the sixth-order term is essential to describe these two kinds of phase transitions unless a compound with SmA temperature range much larger than 100 K can be found. Second, the compound with a sufficiently small SmA-phase temperature range will have a first-order SmA-SmC (or -SmC^*) transition. Thus a compound with a mean-field tricritical SmA-SmC (or -SmC^*) transition will become a first-order transition, provided that the SmA temperature can be "properly" reduced. Here we have reported a continuous mean-field tricritical SmA-SmC transition in a racemic mixture, while the pure chiral compound with a smaller temperature range for the SmA phase has a weakly first-order SmA-SmC^* transition. These results give a strong confirmation of the previous observation. However, it remains to be answered why some other compounds with smaller SmA temperature ranges[3] than that of the racemic A7 compound still have continuous SmA-SmC (or -SmC^*) transitions. The fact that the chiral A7 compound has a large spontaneous polarization[14] leads us to speculate that this may be related to the size of the spontaneous polarization which the pure chiral compounds have. Recent theoretical investigations by Selinger[15] suggest that an increase of the molecular-tilt stiffness constant will drive the SmA-SmC (or -SmC^*) transition first order. In principle, the increase of the molecular tilt stiffness constant will stabilize the SmC (or SmC^*) phase at a higher temperature and consequently reduce the SmA-phase temperature range. Further investigations of these ideas are in progress.

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