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Pretransitional optical activity in a liquid-crystal system of high chirality

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Optical activity measurements in the isotropic phase just above the liquid-crystal transition temperature were performed for various concentrations of the chiral liquid crystal 4″-(2-methylbutylphenyl)-4′-(2-methylbutyl)-4-biphenylcarboxylate (CE2) in the nonchiral liquid crystal 4-*n*-pentylbenzenethio-4′-*n*-heptyloxybenzoate ($\bar{7}$S5). The mixtures investigated possessed extremely high chirality, with pitches varying from about 250 nm in the 40-wt.%-CE2 sample to approximately 100 nm in pure CE2. The pretransitional optical activity results clearly show that coupling between the structural modes of the ordered phase grow more and more important as the chirality increases. The agreement between these data and theory is quite good, thus permitting an estimation of the critical temperature for two of the structural modes.

INTRODUCTION

There has been significant work over the past few years concerning the effect of chirality in liquid-crystal systems. Recent theoretical and experimental progress on understanding the blue phases of chiral liquid crystals has demonstrated that the presence of chirality can have an important effect on the behavior of such systems. One area which has received little attention is the effect of chirality on the isotropic–liquid-crystal phase transition itself.

Theoretical work in this area is usually directed to the study of pretransitional properties with the use of a Landau–de Gennes free energy.[1–4] Short-range order over some correlation radius in the isotropic phase increases as the temperature approaches the transition to the ordered phase, so properties which normally vanish in the isotropic phase (but are nonzero in the ordered phase) do not vanish, and in fact appear to be heading for a divergence at a temperature slightly below the transition temperature. One property which behaves this way is the optical activity in the isotropic phase, and several authors have reported experimental confirmation of the theoretical prediction.[1,3,5] Unlike nematic liquid crystals where one simple structural mode is required to describe the orientational order, chiral liquid crystals require five basic modes.[2–4] Fluctuations in these modes possess different temperature dependences, so pretransitional behavior in chiral systems has the potential of being much richer than in nematic liquid crystals. Most of the theoretical work has assumed that fluctuations in the different modes are uncoupled. Since most experiments measure a property which depends on a single mode, diverging behavior with respect to a single temperature is therefore predicted. However, in the one theoretical approach which considers the effect of mode coupling, the result is quite different. If the chirality is high enough, the optical activity should no longer diverge as the transition is approached, but reach a maximum and decrease.[6]

Two experiments have been performed to test this prediction. Demikhov and Dolganov reported observation of a slight decrease in the optical activity of cholesteryl nonanoate within 0.02 K of the transition to the ordered phase.[7] Data taken in our laboratory did not confirm this, but the temperature inhomogenity within the sample (0.05 K) was high enough so that such a small effect was probably not observable.[5] Whether or not the effect of mode coupling can be observed in cholesteryl nonanoate, it is obvious that the effect is extremely small. For that reason we decided to (i) improve our temperature homogeneity, and (ii) investigate a system with a chirality higher than cholesteryl nonanoate. The effect should be more pronounced the higher the chirality, so these two changes should provide strong evidence for or against the prediction.

We report here measurements of the optical activity in the isotropic phase of a mixed system of a highly chiral liquid crystal and a nematic liquid crystal. The chirality of the system studied varies from that of cholesteryl nonanoate to a value at least twice as great. The data show without a doubt the effect of mode coupling, and even allow us to estimate the second-order transition temperatures of two of the modes.

THEORY

Long-range orientational order is represented by the anisotropic part of the dielectric tensor. When this tensor lacks inversion symmetry, optical activity results. In the isotropic phase this tensor is zero (ignoring the molecular optical activity), but short-range order over some correlation radius results in a nonzero average over a small volume element. Near the transition to the liquid-crystal phase, this correlation radius grows, causing an increase in the small amount of optical activity present due to the short-range order. The anisotropic local dielectric tensor is a symmetric tensor with zero trace, so it can be represented in terms of five independent modes or basis tensors. Using the notation of Ref. 4, the planar spiral mode where two local principal axes rotate around a spiral axis, remaining perpendicular to the spiral axis, is called the $m=2$ mode. The $m=1$ mode represents a conical spiral mode where two local principal axes rotate around a spiral axis, but each makes an angle of 45° with this axis. Finally, the nonchiral, nematiclike mode is called the $m=0$ mode. The $m=-2$ and $m=-1$ modes are similar to the $m=2$ and $m=1$ modes, respectively, but represent rotations of the opposite sense. A structure with long-range orientational order can be represented by a linear combination of these five modes; for example, the cholesteric phase with a right-handed helix can be represented by the proper combination of the $m=0$ and $m=2$ modes.

Next the Landau–de Gennes free energy is written in terms of the anisotropic part of the local dielectric tensor. The four quadratic terms have coefficients a, b, c, and d, with $a=a_0(T-T^*)$. T^* is the second-order transition temperature for the racemic mixture. The coefficients for the third- and fourth-order terms are given the symbols μ and λ, respectively. When the anisotropic part of the local dielectric tensor is expressed in terms of the five modes and only terms up to second order are retained, the free energy takes the form

$$F-F_0=\frac{1}{2}\sum_m \int d^3q \left[a-mdq + \left[b+\frac{c}{6}(4-m^2) \right] q^2 \right] |\varepsilon_m(q)|^2 , \tag{1}$$

where m is the label for the mode, q is the wave vector, and $\varepsilon_m(q)$ is the amplitude of the mode. Each mode possesses a value of q which minimizes the free energy. In addition, using the expression for the coefficient a, one can find the temperature at which this minimized free energy vanishes for each mode. This is the temperature at which the correlation radius for each mode diverges:

$$\begin{aligned} T^*_{\pm 2} &= T^* \pm \frac{bq_0^2}{a_0} , \\ T^*_{\pm 1} &= T^* \pm \frac{1}{4(1+c/2b)} \frac{bq_0^2}{a_0} , \\ T^*_0 &= T^* , \end{aligned} \tag{2}$$

where q_0 represents the chirality of the system, $q_0=d/b=4\pi/P$. P is the pitch of the system. Of course, the first-order transition to the ordered phase occurs at a temperature T_C, which is greater than the five T^* temperatures.

If no coupling between the modes is allowed, each mode contributes to the optical activity independently. Since only the $m=1$ and -1 modes affect the optical activity directly,[2] this property tends to diverge at a temperature equal to T^*_1. Expressing the optical activity tensor in terms of these two modes, then applying the equipartition theorem to determine the amplitude of the fluctuations in each mode, and finally integrating over all wave vectors, one obtains the following expression for the pretransitional optical activity:

$$\phi=\frac{k_B T k_0^2 q_0}{48\pi\bar{\epsilon}\sqrt{a_0 b}} \left[1+\frac{c}{2b} \right]^{-3/2} \frac{1}{(T-T^*_1)^{1/2}} + \phi_0 , \tag{3}$$

where k_B is Boltzmann's constant, k_0 is the wave vector of the light, $\bar{\epsilon}$ is the average dielectric constant, and ϕ_0 is the molecular optical activity.

If the free energy includes higher than second-order terms, the modes of the structure are mixtures of the five original modes. Coupling of the $m=2$ and 1 modes now occurs. Since the $m=2$ mode has a second-order transition temperature above the one for the $m=1$ mode, it may be possible for the fluctuations of the $m=2$ mode to become quite large in the isotropic phase. This will cause a significant $m=2$ component to appear in the mixed mode, causing the optical activity to change from its simple divergence due to the $m=1$ component. According to Filev,[6] the effect of the $m=2$ mode is to introduce optical rotation in the opposite sense from that due to the $m=1$ mode, and thus cause a peak in the optical activity just before the transition to the ordered phase. Reference 6 does not include all the details of the calculation, but the result is given in the following form:

$$\phi=\frac{k_B T k_0^2 q_0}{48\pi\bar{\epsilon}\sqrt{a_0 b}} \left[1+\frac{c}{2b} \right]^{-3/2} \left[\frac{1}{(T-T^*_1)^{1/2}} - \frac{\left[1+\frac{c}{2b} \right]^{3/2} f(x,\tau)}{(T-T^*_2)^{1/2}} \right] + \phi_0 , \tag{4}$$

where $f(x,\tau)$ is a function which represents the mixing of the two modes. x is simply $q_0/2k_0$ (the ratio of the wavelength to pitch) and $\tau=T-T^*_2$.

Experimentally it is useful to compare the actual transition temperature T_C to the temperature at which fluctuations in the various modes diverge. The first-order transition to the ordered phase can be to the cholesteric phase or one of the three blue phases. By equating the free energy of the isotropic phase to that of the cholesteric phase or to that of one of the structures proposed to represent the blue phases, one can determine the transition temperature to the ordered phase.[8] Only the transition to the cholesteric phase can be expressed in closed form:

$$T_C=T^*+\frac{\mu^2}{27\lambda a_0}+\frac{3}{4}\frac{bq_0^2}{a_0} . \tag{5}$$

Comparing this temperature to the second-order mode transition temperatures, one finds that as the chirality is increased the separation between T_C and T^*_1 increases,

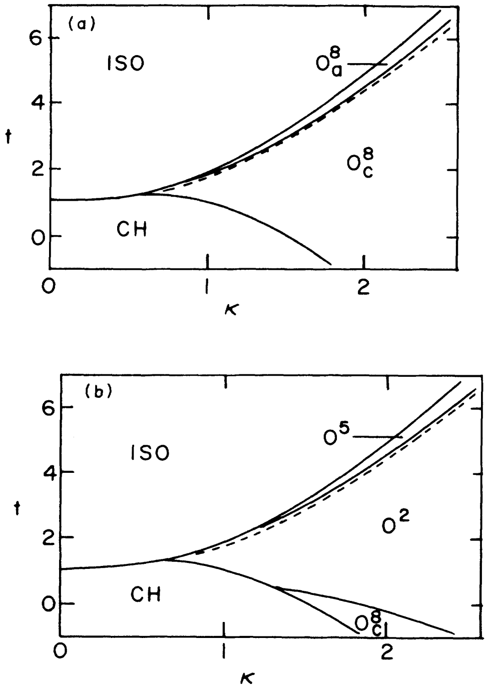

FIG. 1. Phase diagrams of cubic structures which represent the blue phases (Ref. 8). t is the reduced temperature and k is the chirality. Theoretical phase boundaries are given by solid lines; the dotted line is the isotropic-cholesteric phase transition line, assuming no other phases exist.

while the separation between T_C and T_2^* decreases. Thus the effect of mode coupling should increase as the chirality of the system is increased. Of course, this assumes that only the chirality changes, while the coefficients of the free-energy expansion remain constant.

Even though the transition to the ordered phase for highly chiral systems is from the isotropic phase to one of the blue phases, using the expression for the isotropic-cholesteric phase transition for these transitions as well may be in fact quite legitimate. As shown in Fig. 1, if one graphs the theoretical expression for the isotropic-cholesteric transition on the phase diagram of Ref. 8 (showing the various blue-phase structures), one finds that this line does not lie far below the line for the highest blue-phase–to–isotropic-phase transition. This means that the theoretical expression for the isotropic-cholesteric transition is not a bad approximation for the isotropic–blue-phase transition. It is therefore more correct to say that the blue phases have lower free energy than the cholesteric phase, thus depressing the transition to the cholesteric phase, than it is to say the blue phases have lower free energy than the isotropic phase.

EXPERIMENT

The samples used in these experiments were mixtures of the chiral liquid crystal 4″-(2-methylbutylphenyl)-4′-(2-methylbutyl)-4-biphenylcarboxylate (CE2) and the nonchiral liquid crystal 4-n-pentylbenzenethio-4′-n-heptyloxybenzoate ($\overline{7}$S5). The CE2 was obtained from BDH Chemicals and the $\overline{7}$S5 was provided by the Liquid Crystal Institute at Kent State University.[9] Both compounds were used without further purification. This system possesses an interesting phase diagram in that the second blue phase disappears at 45 wt. % CE2.[10] For the mixtures used in this investigation, the transition to the ordered phase was between the isotropic phase and the third blue phase (fog phase). Optical activity measurements on thin samples in the blue phases indicated that the pitch of these mixtures varied from roughly 250 nm for the 40-wt. % sample down to about 100 nm in the 100-wt. % sample.

The sample was contained in a glass spectrophotometer cell (1 cm path length) located in a double-oven arrangement. The inner oven was controlled by an Instec mK1 temperature control card in an Apple IIe computer. The temperature homogeneity across the sample was 0.03 K. The optical activity was measured using a rotating-analyzer system which achieved a precision of ±0.01°. Light from a He-Ne laser was split into two beams, one of which then passed through the sample. Both beams then passed through the same analyzer rotating at about 13 Hz, finally being detected by two silicon photodiodes. The phase difference between the two outputs was measured repeatedly by a computer, producing an average optical rotation angle of the required precision.

Measurements of the pretransitional optical activity were taken with increasing temperature, starting at a temperature in the ordered phase. For the samples containing low concentrations of CE2, the transition from the ordered phase to the isotropic phase was quite obvious, in that there was a discontinuity in the optical activity and a momentary decrease in the transmitted intensity. As the concentration of CE2 increased, however, the discontinuity in the optical activity and the decrease in transmitted intensity became quite small. For the highest concentrations of CE2, the transition revealed itself only as a change in the temperature dependence of the transmitted intensity. In the third blue phase the intensity increased slowly with increasing temperature, whereas in the isotro-

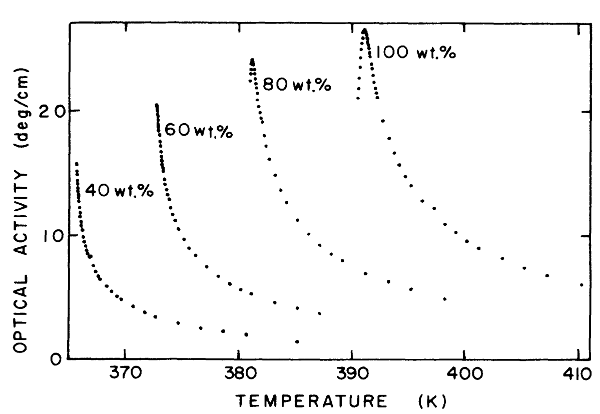

FIG. 2. Optical activity in the isotropic phase for the CE2-$\overline{7}$S5 system. The wt. % of CE2 is shown for each data set. The wavelength of light is 633 nm.

TABLE I. Least-squares-fit values for the three parameters of Eq. (3) (40 wt. % CE2) and five parameters of Eq. (4) (60, 80, and 100 wt. % CE2). A is the factor in front of the square brackets in Eq. (4). The isotropic transition temperatures are 365.54, 372.53, 380.83, and 390.30 K for the 40-, 60-, 80-, and 100-wt. % CE2 samples, respectively.

	wt. % CE2			
Parameter	40	60	80	100
ϕ_0 (deg/cm)	−0.9	−0.9	−1.7	−4.8
A ($K^{1/2}$/cm)	0.21	0.49	0.73	1.25
$f(x,\tau)$		0.16	0.15	0.17
T_1^* (K)	365.07	372.01	380.14	389.28
T_2^* (K)		372.32	380.73	390.17

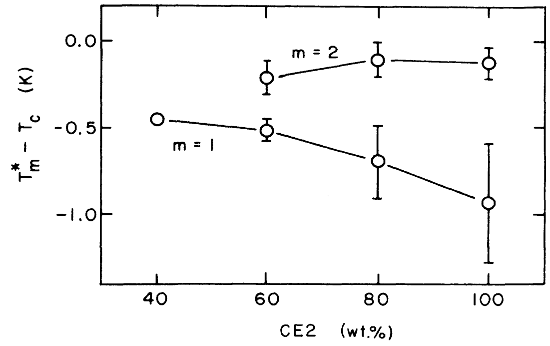

FIG. 4. Second-order mode transition temperatures relative to the liquid crystal to isotropic transition for the CE2-$\overline{7}$S5 system. $m = 2$, planar spiral mode; $m = 1$, conical spiral mode.

pic phase it increased quite rapidly just above the transition. This rapid increase was due to the large amount of scattering in our thick sample just above the transition.

The results of this procedure are shown in Fig. 2 for four different mixtures of varying chirality. Notice that the data for the lowest chirality (40 wt %) show no evidence for mode coupling. A fit to the simple relationship given by Eq. (3) is excellent, and the best fit values for the three parameters are given in Table I. This is not the case for the three mixtures with higher chirality. As evident in Fig. 2, the effect due to mode coupling becomes more and more apparent as the chirality is increased. Since $x = q_0/2k_0 > 2$ for all of these mixtures, the theory indicates that $f(x,\tau)$ should be a weak function of τ and thus can be treated as one of five adjustable parameters for a least-squares fit. The two second-order transition temperatures are two of the other adjustable parameters along with the molecular optical activity and the factor in front of the brackets in Eq. (4). The best-fit values for the 60, 80, and 100-wt % samples are also given in Table I.

Figure 3 shows the result of the five-parameter fit for the 100-wt %-CE2 sample. The large number of fitting parameters allows for considerable variability in these parameters while maintaining a good fit. Obviously such a procedure is not the best method to measure T_1^* and T_2^*; it would be much better to perform two experiments, one which measured each temperature directly. Nevertheless, even with this large amount of variability, these fits indicate that $T_C - T_1^*$ seems to increase and $T_C - T_2^*$ seems to decrease slightly as the chirality is increased (see Fig. 4). This agreement with theory is in spite of the fact that as the chirality is increased not only is the transition temperature increasing, but the different concentrations should also change the coefficients in the free-energy expression.

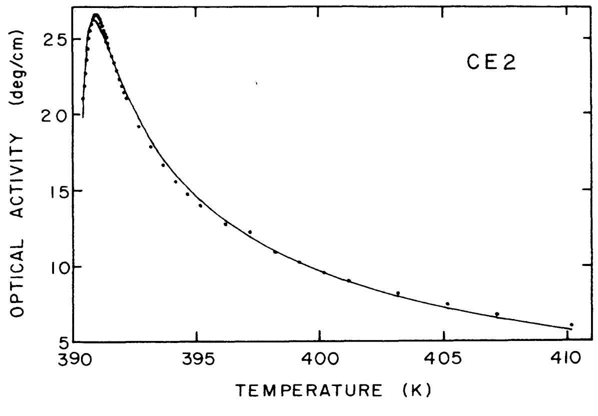

FIG. 3. Theoretical fit to the optical activity data of pure CE2. The fitting parameters are given in Table I. The wavelength of light is 633 nm.

DISCUSSION

These results are quite consistent with the data from experiments with systems of less chirality. For example, $T_C - T_1^*$ for the system of cholesteryl esters never drops below 0.5 K.[5] This is about where these measurements begin. In the cholesteryl esters, however, $T_C - T_1^*$ decreases with increasing chirality. One possible reason for this different dependence is the fact that in the cholesteryl esters the transition temperature decreases with increasing chirality, instead of just the opposite for the CE2-$\overline{7}$S5 system.

One interesting feature of the five-parameter fits is that the value of $f(x,\tau)$ for some of the fits is much larger than the theory would predict. The best-fit $f(x,\tau)$ values are between 0.15 and 0.20, about four times larger than predicted. In addition, the theoretical curve for the 100-wt % CE2 sample differs slightly from the data in the region just above the transition (see Fig. 3). Since the details of the calculation are absent in Ref. 6, it is difficult to ascertain which parts of the theory might be changed to produce better agreement. Certainly more theoretical work is needed.

The best-fit values given in Table I allow certain thermodynamic parameters to be evaluated and compared with measurements in this system and other systems. Since an approximate value for the pitch is known for these samples, subtracting the first two equations of Eqs. (2) produces a value for b/a_0. Likewise, the best-fit value for the term in front of the square brackets in Eq. (4) can be used to obtain a value for $a_0 b$. The index of refraction for CE2 and $\overline{7}$S5 has been measured (1.6 is a very reasonable value for all of these mixtures[11]) and the ratio c/b is known to be about 1.[3,12] The values for b/a_0 and $a_0 b$ thus obtained allow a_0 and b to be calculated, the results of which are included in Table II. These a_0 values are very similar to a value measured in a nematic liquid crystal, 1.08×10^6 erg/cm^3 K, whereas the b values are less than the measured value of 1.05×10^{-6} erg/cm.[3] Consistent with this is the fact that the ratio b/a_0 calculated from these data, approximately 0.7×10^{-12} cm^2 K, is less than the value measured in a nematic liquid crystal, 1.45×10^{-12} cm^2 K,[12] and in another cholesteric liquid crystal, 3.7×10^{-12}cm^2 K.[13]

The latent heat L for the isotropic–to–liquid crystal transition can be evaluated from the relationship[4]

$$L=\tfrac{1}{3}a_0(\epsilon_\parallel-\epsilon_\perp)^2 T_C \ , \tag{6}$$

where $\epsilon_\parallel-\epsilon_\perp$ is the anisotropy of the dielectric constant. Using a value for the density and dielectric anisotropy for $\overline{7}$S5 (1.0 g/cm^3 and 0.32, respectively[11]), the latent heat for the 60, 80, and 100-wt % CE2 samples can be determined. These values are also given in Table II, along with the results of differential scanning calorimetry (DSC) on this same system.[11] The agreement is surprisingly good, considering that (i) a mean-field theory is being used, (ii) certain constants have been estimated, and (iii) large pretransitional effects make the DSC latent-heat measurements difficult to interpret. The consistency between the values calculated from the least-squares fits and the independent measurements is encouraging, and seems to indicate that both the theory and this experimental technique can yield useful information.

One last finding of interest is the fact that the transition to the isotropic phase seems to appear more continuous as the chirality is increased. This is obvious experimentally and confirmed by both the decrease in a_0 and the decrease in $T_C-T_2^*$. In the chiral systems studied to date, most of the latent heat is contained in the isotropic–to–blue-phase transition, regardless of which blue phase exists just below the isotropic phase.[14] As the chirality is increased, however, the smallness of a_0 and the closeness of T_2^* to T_C causes a significant amount of order to build up in the isotropic phase, producing less of a change at the transition to the ordered phase itself. This effect is also aided by the fact that the third blue phase seems to be amorphous, having the least orientational order of all the blue phases. Whether in the limit of extremely high chirality this transition could theoretically be second order is a difficult question, since many theoretical assumptions break down in this limit. The important point is that there are good theoretical reasons to expect the transition to grow weaker as the chirality is increased, and the results presented in this report certainly support that prediction. Whether the transition in pure CE2 is continuous or not is a difficult experimental question. After all, the optical activity in the blue and isotropic phases is small in these experiments because the pitch is so much shorter than the wavelength of light being used. As a result, any discontinuity in the optical activity at the transition is much more difficult to observe. In addition, a two-phase region due to the presence of impurities could also be present, making a weak first-order transition appear continuous. The answer to this last question must therefore await careful thermodynamic experiments on extremely pure samples.

TABLE II. Values calculated from the least-squares fits to Eq. (4) together with measured values of the latent heat from Ref. 11.

	wt. % CE2		
Parameter	60	80	100
a_0 (erg/cm^3 K)	1.3×10^6	1.1×10^6	0.92×10^6
b (erg/cm)	8.9×10^{-7}	8.4×10^{-7}	6.2×10^{-7}
L (cal/g)	0.40	0.34	0.29
L_{measured} (cal/g)	0.39 ± 0.03	0.33 ± 0.02	0.30 ± 0.03

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