Chiral-racemic phase diagram of a blue-phase liquid crystal

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We have measured the phase diagram for mixtures of chiral and racemic cholesteric S-(+)-4-(2-methylbutyl)phenyl-4-decyloxybenzoate (CE6) in order to study the effect of changing chirality on the appearance of the cholesteric blue phases. We have also measured the latent heats at the isotropic transitions. Our phase diagram is compared with the Landau theory of Hornreich and Shtrikman and the data of Marcus and Goodby.

I. INTRODUCTION

Studies of the blue phases of cholesteric liquid crystals have been in progress for several years.[1-3] It has been well established that there are, in general, three distinct blue phases: two cubic phases (BPI and BPII) and one amorphous phase (called either BPIII or the fog phase). From a theoretical point of view, Hornreich and Shtrikman (HS)[4] have shown that blue phases are caused by the addition of a chiral term to the free energy of a nematic liquid crystal. When the chirality (i.e., the coefficient of the chiral term) is small, this term leads to the usual low-temperature cholesteric phase. For high chirality, however, new phases—the blue phases—become energetically preferable to the cholesteric near the cholesteric-isotropic boundary. From the HS theory, Grebel, Hornreich, and Shtrikman (GHS) have derived a number of phase diagrams in which phase-transition temperature is plotted versus chirality, the latter treated as an independent thermodynamic parameter.[3,5] These diagrams show clearly how the blue phases appear and become wider in temperature as chirality increases.

Another effect, predicted theoretically by Brazovskii,[6] which may potentially influence the appearance of blue phases, is that due to the possible onset of large order-parameter fluctuations at the phase boundary of a high-temperature spatially uniform phase and a low-temperature spatially periodic phase. Brazovskii has shown that, due to the topology of the minimum surface of the free energy for this system in wave-vector space, a transition which is ostensibly second order by simple Landau theory can become a fluctuation-induced first-order transition. The isotropic-cholesteric transition is a candidate for such a transition due to its phase-space topology, except that it is already weakly first order due to the cubic term in the nematic part of the free energy. Nevertheless, it is reasonable to enquire whether such effects will cause enhanced first-order behavior, for example, as an increased latent heat at larger chiralities.

Experimentally, the effect of chirality on the blue phases has most commonly been studied by mixing nematic compounds with chemically different cholesteric materials.[2,7-9] Such a mixing causes an alteration of the basic chemical nature of the mixture and also alters the chirality. In terms of a Landau theory, one would expect a variation of all the coefficients of the Landau free energy instead of just the chiral coefficient as assumed by HS in their theory. It is difficult to isolate the effects of chirality alone with such experiments, and phase diagrams obtained by this method cannot be reasonably compared with those predicted by GHS. A procedure which avoids this complication is to combine both left- and right-handed (or alternatively, chiral and racemic) versions of the same cholesteric material in a mixture. To good approximation, the resulting mixtures will vary only in chirality, i.e., in the size of the chiral coefficient. The other Landau coefficients will remain essentially unchanged.

Chiral-racemic phase diagrams have been previously reported by Flack, Crooker, Johnson, and Long[10] and by Marcus and Goodby (MG).[11] The former diagram is for a mixture of three nematics and either a chiral or racemic cholesteric; such a system is too complicated to compare with theoretical phase diagrams. The latter diagram of MG shows rather complex behavior which we will compare with our present measurements.

We report here the chiral-racemic phase diagram of S-(+)-4-(2-methylbutyl)phenyl-4-decyloxybenzoate (CE6).[12] The chirality of this mixture is shown to increase linearly with chiral fraction, so that our temperature and chirality axes are proportional to those of GHS.[3,5] The latent heats of the transition have also been measured, allowing us to examine the potential effects of fluctuations on the transitions. The diagram turns out to be qualitatively different from that of MG.

II. EXPERIMENT

Our chiral CE6 was obtained from British Drug House and used as received. The racemic ester was prepared by reacting properly substituted benzoic acid and phenol. Racemic 4-(2-methylbutyl)phenol was prepared by the Fries rearrangement of phenyl 2-methylbutyrate followed by reduction of the resulting ketone. The ester was then purified by column chromatography followed by recrystallization from ethanol. Both proton NMR and high pressure liquid chromatography (HPLC) were used to check for impurities in both materials; none were detected.

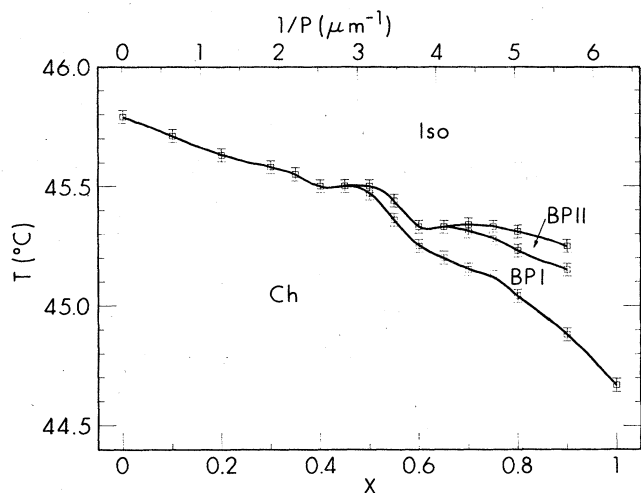Phase transitions were obtained by observation of tex-

FIG. 1. Phase diagram of chiral-racemic CE6. Bottom axis is the mole fraction x of chiral material; top axis is the chirality $1/P$, where P is the pitch in the associated cholesteric phase. Ch and Iso refer to the cholesteric and isotropic phases, BPI and BPII refer to the blue phases, and the line is a guide to the eye. At $x=1$ the BPI and BPII textures are in the ultraviolet region and visually undetectable.

tures, using a polarizing microscope in the back-reflecting configuration. Figure 1 shows the phase diagram as a function of mole fraction x of chiral CE6. In this diagram the uncertainty in mole fraction was $\Delta x = \pm 0.003$, while the transition temperatures were reproducible on our microscope stage to $\Delta T = \pm 0.03\,°C$. BPI and BPII were both present in this material; a fog phase, however, was not observed. As x is increased BPI appears by itself between $x=0.45$ and 0.5. BPII then appears at a higher concentration very near $x=0.65$. Unlike MG, we show the actual line of temperatures T_{clear} at which the isotropic phase appears; the slope of this line is not constant but undergoes undulations near the onset of the BPI and BPII phases.

The selective reflection wavelengths associated with each phase were obtained by a grating spectrometer attached to the microscope camera tube.[13] Figure 2 shows typical data at $x=0.70$. We associate the BPI wavelength with the body-centered-cubic (110) Bragg plane; the (200) line,
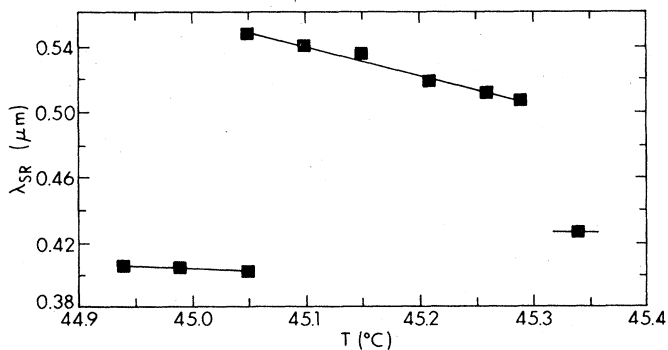

FIG. 2. Selective reflection wavelengths λ_{SR} vs temperature in the cholesteric, BPI, and BPII phases for $x=0.7$. Lines are guides to the eye.
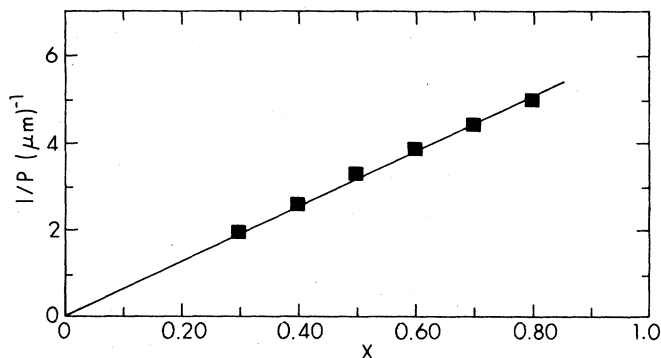

FIG. 3. Chirality $1/P$ vs mole fraction x of chiral CE6. P is the pitch of the cholesteric phase just below the cholesteric-BPI transition. The line is a best linear fit to the data.

which is the next lower wavelength line, has a wavelength too short to be detected by our equipment. The single BPII point evolves out of the BPI line and is either the simple cubic (100) or the bcc (110) reflection. The selective reflection wavelength λ of the cholesteric is used to find the pitch P of the cholesteric according to $P=\lambda/n$, where n is the average refractive index. We found both λ and n by using the Cano wedge method[14] in which the sample is placed between a thin planoconvex lens and a microscope slide. This technique also allowed us to find values of the pitch in the ultraviolet region.

Figure 3 shows the reciprocal pitch vs x. The graph is linear to within our experimental error, which allows us to plot a chirality scale (where chirality is defined as $1/P$) on the phase diagram of Fig. 1. From Fig. 1 we note that, for CE6 material, the blue phases cease to exist at the relatively short pitch of about $0.33\ \mu$m. For other materials, blue phases have been shown to exist at pitches up to $0.500\ \mu$m.

We have also measured the latent heat along the isotropic boundary using a Perkin-Elmer DSC-4 differential scanning calorimeter. Three chiral concentrations were measured: 0% (0.57 cal/g), 50% (0.59 cal/g), and 100% (0.60 cal/g). We consider all these values to be the same to within experimental error.

III. DISCUSSION

Our phase diagram appears to be qualitatively different from that presented by MG.[11] For example, MG observe a fog phase between BPII and the isotropic phase, whereas none was found in CE6. Furthermore, in their diagram BPI and BPII appear in the same sequence as in our diagram, but their BPI region then narrows and disappears completely as x is increased, despite the fact that BPII and the fog phase both persist and become larger in temperature width. We find this behavior to be more complex than that of CE6, in which both blue phases appear to increase their widths monotonically until the highest chirality is reached. Theoretically, GHS predict increasing widths as we see, rather than the vanishing phases present in MG's material.

The line of clearing temperatures T_{clear} has interesting structure. In the first place, T_{clear} slopes downward with increasing chirality, while in the theoretical HS diagrams the slope is upward. (This slope is not obtained by MG.) This

downward slope can perhaps be phenomenologically explained within the framework of the HS theory by allowing the Landau transition temperature T_c to be chirality dependent, perhaps as a simple expansion of T_c in powers of chirality.[15]

A more detailed feature of the T_{clear} line is a flattening out of the slope at the points where new blue phases appear. This feature does not appear in the HS diagrams. It does not appear explicitly in the MG phase diagram either, since the temperatures are plotted relative to T_{clear}. Nevertheless, MG's data show an interesting narrowing of the BPII region at a chirality near that at which the fog phase appears. If we plot our data in the same way as MG we observe a similar narrowing of BPI at the appearance of BPII. In CE6 this effect is due to the behavior of T_{clear}; possibly T_{clear} has the same behavior in MG's material. Furthermore, if a flattening out of the T_{clear} line is a signature of the onset of a new blue phase, then the lack of any high-chirality flat region in our data may indicate that there is, in fact, no fog phase in this material. Alternatively, it is possible that the fog-phase texture was not observable visually. The question of whether CE6 has a fog phase is therefore still unresolved.

Figure 3 shows that the chirality of CE6 increases linearly with increasing x with a slope of 6.3 μm^{-1}. MG's data show a similar linearity, except that their material has a slope which we calculate from their data to be 3.5 μm^{-1}. With these numbers, we can now calculate the minimum chiralities at which the blue phases appear. For CE6, BPI appears at $1/P = 3.00$ μm^{-1}, or $P = 0.33$ μm. For MG's mixture, BPI appears at $1/P = 1.0$ μm^{-1}, or $P = 1.0$ μm which is an unusually long cholesteric pitch for the appearance of blue phases. Further comparison of these numbers with those given by HS is not possible without knowing the values of the coefficients in their Landau theory.

We finally discuss our latent-heat measurements. The constancy of the latent heat as the chirality is increased indicates that the fluctuation effects of Brazovskii[6] do not significantly affect our transitions. Within the Landau theory, for which fluctuations are neglected, GHS[5] have calculated transition entropies ΔS for the isotropic-cholesteric transition, for two isotropic–blue-phase transitions, and for two blue-phase–cholesteric transitions. They observe, like us,

that ΔS at the isotropic transitions is essentially independent of chirality, except that, unlike our data, there may be smaller ΔS when the lower phase is one of the blue-phase space groups O^5 or O^2. The most likely space-group candidate for BPI is actually O^8, for which ΔS has not yet been worked out.

IV. CONCLUSIONS

We have measured the chiral-racemic phase diagram of CE6 and compared it to the theoretical phase diagrams of GHS and the experimental phase diagram of MG. We observe qualitative differences between our data and that of MG. Both sets of data have features which are not predicted by the HS theory. The latent heats at the CE6 isotropic transitions indicate that fluctuations do not play an important role in these transitions; probably, the Brazovskii mechanism is irrelevant for these transitions.

An important question still to be answered is whether there is common behavior for the phase diagrams of different chiral-racemic mixtures. The fact that our and MG's chiral-racemic phase diagrams are qualitatively different is of interest and bears on the question of what common behavior exists between different chiral-racemic systems. In the Landau theory of HS, this behavior depends on the size of the chiral coefficient relative to the other Landau coefficients. The elucidation of other chiral-racemic phase diagrams, currently underway in our laboratory, should clarify this issue.

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$$C_{10}H_{21}O(C_6H_4)COO(C_6H_4)CH_2CH(CH_3)C_2H_5.$$
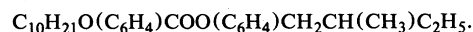
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