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REENTRANT CHOLESTERIC PHASE*

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ABSTRACT - We report on a variant of the reentrant phenomena whereby a chiral compound has been added to a liquid crystalline material to form the sequence of phases cholesteric smectic A cholesteric as the temperature is varied. We present here a phase diagram which shows the effects of different concentrations of chiral additive and describe an unusual texture which appears under a polarizing microscope in the vicinity of the transition from the smectic A phase to either the reentrant cholesteric or the cholesteric phases.

In this study we made use of binary mixtures of 4-cyano-4'-*n*-hexyloxybiphenyl (6OCB) and 4-cyano-4'-*n*-octyloxybiphenyl (8OCB) which have been previously reported to exhibit the reentrant nematic phase.[1] To this material we added the chiral compound 4"-(2-methylbutylphenyl)-4'-(2-methylbutyl)4-biphenylcarboxylate (CE-2) in order to twist the nematic and, therefore, obtain the cholesteric phase. A reentrant cholesteric phase was observed to form below the smectic A phase as expected. Figure 1 shows the phase diagram obtained by adding CE-2 (from zero to 12 wt%) to several different mixtures of 6OCB and 8OCB. The phase transitions could be identified under a polarizing microscope[2] from textures typical of those which characterize the cholesteric and smectic A phases.[3] Several features can be readily noticed from Figure 1. (i) There is a

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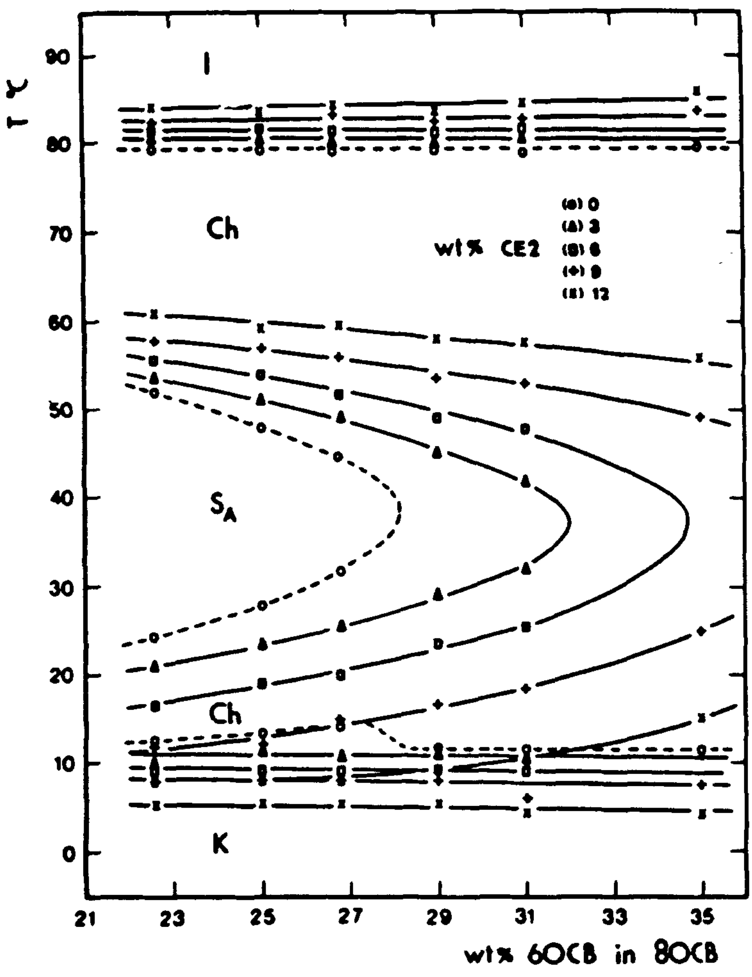

Figure 1

Portion of the phase diagram obtained by adding to several binary mixtures of 6OCB and 8OCB the chiral compound CE2 in the following concentrations: zero wt% (open circles), 3 wt% (open squares), 6 wt% (open triangles), 9 wt% (+), and 12 wt% (x). The inner dashed line separates the smectic A from the nematic phases and the inner solid lines separate the smectic A from the cholesteric phases.

substantial increase in the range of concentrations of 6OCB and 8OCB for which the reentrant phase occurs. (ii) The cholesteric-smectic A transition temperature increases with increasing concentration of CE-2 while the smectic A-reentrant cholesteric transition temperature decreases. In other words, the temperature range of the smectic A phase measured at a particular concentration of 6OCB and 8OCB increases with increasing concentration of CE-2. (iii) The clearing point increases roughly in direct proportion to the concentration of added CE-2 while the crystallization temperature decreases.

For concentrations of CE-2 in excess of 20 wt% the formation of a reentrant cholesteric phase would persist but with new variants in liquid crystalline polymorphism which are to be presented elsewhere.[4]

Observations under the polarizing microscope revealed that the reentrant cholesteric phase exhibits textures similar to those of the cholesteric phase, namely a fan-like texture with fingerprints[3] or, after shearing the glass slides, a planar texture with oil streaks.[3] The spacing between the fingerprints appeared to be the same in both cholesteric phases suggesting a similar pitch distance in each phase which increases as the smectic A is approached either from below coming from the reentrant cholesteric phase or from above coming from the cholesteric phase. Furthermore, very near the phase transition from the smectic A proceeding into either the cholesteric or reentrant cholesteric phases a texture with the appearance of evenly spaced "needles" would form at natural boundaries of the sample or at point defects and extend into the homeotropically aligned regions of the sample as illustrated in Figure 2. These "needles" were always observed to extend in a direction normal to the local curvature of the natural boundaries and radially along circular boundaries). Only one dark line along the center of each needle could be brought into focus and the needles appeared to extend over long distances without curvature. The needles did not appear to have the characteristic texture of elongated spherulitic domains that have been observed in long pitch cholesterics under homeotropic boundary alignment in other cholesteric systems.[5] Upon further cooling the needles would evolve into the fingerprint pattern. These observations suggest that the needles have a width of one pitch length. Furthermore, it is suggestive that the dark homeotropically aligned

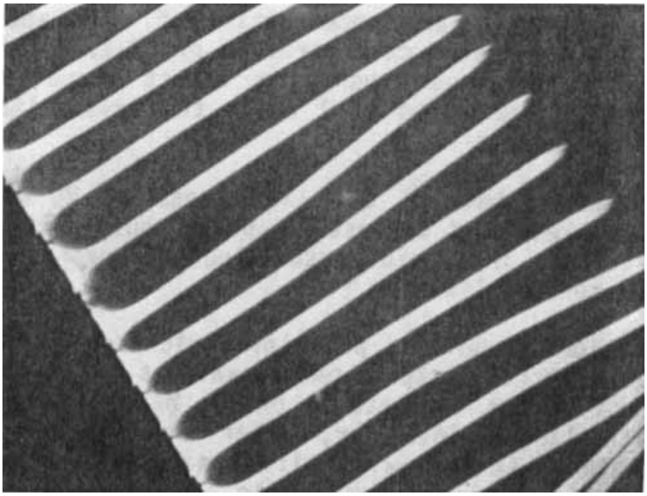

Figure 2

Needle-like texture observed in thin samples (no spacer other than the sample itself) upon cooling from the smectic A into the reentrant cholesteric. The material is composed of 75 wt% 8OCB, 25 wt% 6OCB to which is added 5% CB-15. The dark region on the lower left corner of the photograph is void of material. The needles originally at this boundary grow in a direction toward the upper right of the photograph. It is suggested that the dark region between the needles is homeotropically aligned nematic and that beyond the points of the needles is homeotropic smectic A. The photograph was made with one second exposure and with a Leitz objective of 50x on the polarizing microscope.

region between two needles is nematic, that is, untwisted by the surface imposed alignment. This type of distortion appears similar to that observed in bulk cholesteric samples placed in a large magnetic field which is very near to the critical untwisting field. In support of this interpretation is the observation that the width of the dark line that can be brought into focus in the central region of each needle and that corresponds to a pseudo-isotropic alignment is much smaller than the width of each of the bright bands on either side of the needle.

Finally, we mention that we also used the chiral compound 4-cyano-4'-(2-methylbutylbiphenyl) (CB-15) in order to twist the nematic and reentrant nematic phases. This compound is of similar chemical structure as that of 6OCB and 8OCB, but of less twisting power than CE-2. Another difference between the two chiral materials is that the clearing point of CB-15, which is below room temperature, is much lower than that of CE-2 (T_C=118.7°C). With these considerations in mind it is easy to understand that, although with CB-15 we still observed a reentrant cholesteric phase, the transition temperatures were all much lower. For example, with a mixture of 25 wt% of 6OCB in 8OCB to which 5 wt% CB-15 has been added, the polymorphism was observed to be as follows:

I (67.7°C Ch (17°C) S_A (8°C) Reentr. Ch (2°C) solid.

Also, the extent of concentrations of 6OCB in 8OCB for which a reentrant phase occurs is much shorter, i.e., at 35 wt% of 6OCB no reentrant phase could be observed to occur at all independent of the concentration of CB-15.

Independent studies by Billard[6] and Tinh et al.[7] have recently come to our attention in which different systems of compounds were used to form the reentrant cholesteric phase.

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