

Optical Bragg Diffraction of the Helical Smectic A Liquid Crystal

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Optical properties of the mixture of cholesteryl-n-nonanoate (CN) and n-nonyloxybenzoic acid (NOBA) in weight proportion 7:3 have been investigated. As it was early found by us (*Ukrainian Fiz. Zhurn.*, 35, 221 (1990)) this mixture possesses a new liquid-crystalline helical smectic A (SmA*) phase between the low-temperature smectic A (SmA) and high-temperature cholesteric (Ch) phases. It is shown experimentally that there are three temperature regions of the optical Bragg diffraction for the mixture. The first two regions correspond to the different states of the SmA* phase and the third one corresponds to the Ch phase. Inside each region the temperature dependence of the Bragg reflection wavelength λ is in excellent agreement with an empirical formula $\lambda = \lambda_0 + a/(T - T^*)^2$, where $T^* = 82.4^\circ\text{C}$ is the temperature of the SmA - SmA* transition and λ_0 as well as a are constant within each region but differ for different regions.

Keywords: helical smectic A, optical Bragg diffraction

The cholesteric (Ch)-to-smectic A (SmA) phase transition in liquid crystals is analogous to the normal metal-to-superconductor transition under the action of an external magnetic field.¹ Recognizing this analogy, Renn and Lubensky² have theoretically predicted a new liquid crystalline phase which is analog of the Abrikosov phase in superconductors. This phase is a helical smectic A (SmA*), which intervenes between the low-temperature SmA phase and high-temperature Ch phase. The new phase is constructed from a rotated blocks of a usual SmA layers, in which long molecular axes are arranged normally to the layer planes. In the direction of the layer planes there is a twist of the molecular axes. Thus the helical axis of SmA* is parallel to the smectic planes and perpendicular to the molecular axes. Mutual rotations of the individual smectic blocks are provided by the network of screw dislocations.

The preliminary experimental evidence of the unusual properties of some liquid crystalline materials in the vicinity of the Ch-SmA* transition have been presented in Reference 3 for the mixture of cholesteryl-n-nonanoate (CN) and n-nonyloxy-

benzoic acid (NOBA). Further investigations of this mixture^{4,5} confirmed the existence of the new liquid crystalline SmA^* phase within the broad temperature range $82.6 \leq T \leq 90^\circ C$ between the SmA and Ch phases. In addition it was found that the SmA^* phase may contain two different states.

The helical ordering of the SmA^* phase as well as the Ch phase must give rise to a circular dichroism for light propagating parallel to the helical ordering axis. For a range of wavelengths centered about $\lambda = Pn$, where λ is the optical wavelength in air, P is the helical pitch, and n is the average index of refraction, light of one sense of circular polarization is transmitted without attenuation and light of the opposite sense is totally reflected (Bragg reflection). It is well known that in the Ch phase P and consequently λ are extremely sensitive to the temperature changes in the vicinity of the $Ch-SmA$ transition.⁶ One can expect that dependence $\lambda(T)$ should also possess informative peculiarities in the vicinity of the $Ch-SmA^*$ and SmA^*-SmA transitions as well as inside the SmA^* phase.

In this article we report the experimental investigations of transmittance spectra of CN:NOBA mixture (in weight proportion 7:3) in Ch and SmA^* phases. The variation of the Bragg reflection wavelength λ , at which transmission is a minimum, as a function of T , has been determined on the planar anchored samples using the spectrophotometer "Specord". The error in λ was estimated to be 1 nm; T was recorded accurate to $0.05^\circ C$ and varied at a rate $0.1^\circ C/min$. Quartz cells with thickness $5 \mu m$ were used.

As seen in Figure 1, the behaviour of $\lambda(T)$ within the temperature range $82.4 \leq T \leq 101.1^\circ C$ is typical for helical phase: λ drastically increases with decreasing T just before a transition to the SmA phase; away from this transition λ is relatively temperature-independent. It is practically impossible to identify in Figure 1 the

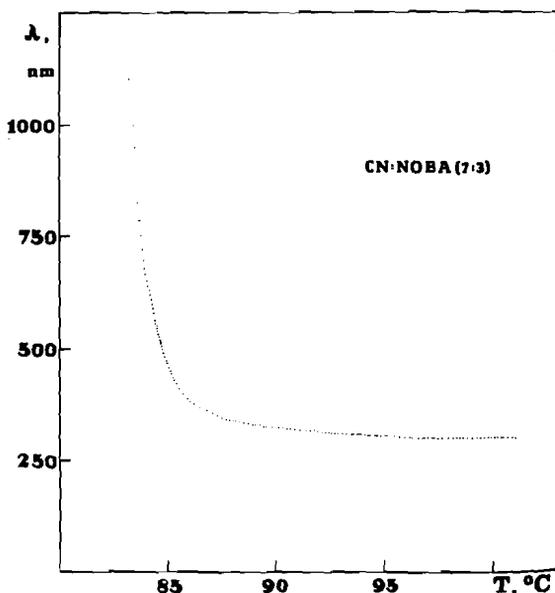


FIGURE 1 Temperature dependence of the Bragg reflection wavelengths in the CN:NOBA (7:3 by weight) mixture.

SmA*—Ch transition between two helical phases as well as any transitions between different states inside the SmA* region. Nevertheless, these transitions may be made clear by replotting the data in coordinates $(\lambda, 1/(T - T^*)^2)$, where $T^* = 82.4^\circ\text{C}$ is temperature of the SmA*—SmA transition. The result is shown in Figure 2. Three different temperature regions of λ behaviour are now easily distinguished: (I) $82.4 \leq T \leq 84.2^\circ\text{C}$; (II) $84.2 \leq T \leq 90.5^\circ\text{C}$; and (III) $T \geq 90.5^\circ\text{C}$. As it follows from the comparison of these data with the independent ones of References 4 and 5, the above mentioned regions correspond to the SmA* phase (I and II regions) and to the Ch phase (III region). The small discrepancies of the transition temperatures ($\leq 1^\circ\text{C}$) may be caused by the different degrees of the aging of substances.

It is impossible as a matter of principle to describe the temperature dependences of λ in all regions by one common approximating formula due to the sharp changes of λ in the vicinity of the transition points $T = 84.2$ and 90.5°C , which correspond to $(T - T^*)^{-2} = 1.5 \cdot 10^{-2} (\text{C}^\circ)^{-2}$ and $31 \cdot 10^{-2} (\text{C}^\circ)^{-2}$ in Figure 2, respectively. However, inside each of these regions the data of Figure 2 are in good agreement with an empirical formula⁷:

$$\lambda = \lambda_0 + a/(T - T^*)^2,$$

where λ_0 and a are constants. Keep $T^* = 82.4^\circ\text{C}$ constant for all regions, one finds $\lambda_0 = 423 \text{ nm}$ and $a = 0.625 \cdot 10^3 \text{ nm} \cdot (\text{C}^\circ)^2$ for the I region of the SmA* phase; $\lambda_0 = 303 \text{ nm}$ and $a = 1.11 \cdot 10^3 \text{ nm} \cdot (\text{C}^\circ)^2$ for the II region of the SmA* phase, and $\lambda_0 = 292 \text{ nm}$, $a = 1.93 \cdot 10^3 \text{ nm} \cdot (\text{C}^\circ)^2$ for the Ch phase (III region).

The data presented by us confirm the earlier conclusions of References 4 and 5 that the CN:NOBA mixture possesses the new liquid crystalline SmA* phase, which contains two different states. The temperature dependences of the Bragg reflection wavelengths in these two SmA* states as well as in the Ch phase can be described

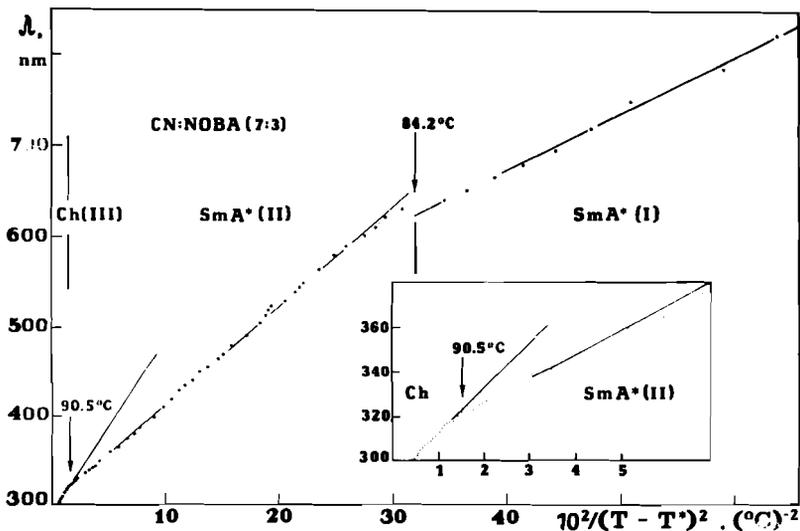


FIGURE 2 The plot $\lambda - 1/(T - T^*)^2$ for the CN:NOBA (7:3 by weight) mixture.

by straight lines in coordinates $(\lambda, 1/(T - T^*)^2)$ but the slopes of lines in these phases are unambiguously different.

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