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Light Scattering Study on Orientations in the Smectic Modifications

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Abstract—The scattering of light by smectic liquid crystals is discussed in terms of theories which have been applied to the scattering from crystalline polymers. The $I_\perp$ patterns observed from the smectic A and B states are of the four leaf clover form in which the scattering intensity increases continuously in going toward the center, while the smectic C gives circularly symmetric patterns for both $I_\parallel$ and $I_\perp$. These indicate that the scattering, at least in the smectic A and B mesophases is due to an assembly of anisotropic rods having random-orientation. Some new experimental facts observed for the cholesteric and pseudo-isotropic nematic states are described.

1. Introduction

The light scattering in liquid crystals has been studied by several authors[1–3] and analyzed in terms of theories which are commonly applicable to the scattering from crystalline polymer. Furthermore, it was also shown that the scattering in liquid crystals primarily arises from the existence of regions having a correlated orientation with dimensions comparable with the wave length of light. However, such light scattering studies have been mainly carried out on the cholesteric and nematic states, and no light scattering study on the smectic phase has been so far reported although it would serve to characterize the shape and arrangement of correlated regions in the smectic state. It is well known that the smectic phase can be most commonly classified into the smectic A, B and C according to the microscopic texture.[4,5]

In this paper, the light scattering in the smectic A, B and C modifications was studied using a laser as a light source and the type of orientation correlations is qualitatively discussed on the basis of the polarization of the scattered light and its angular dependence.

Some experimental results for the cholesteric and pseudo-isotropic nematic states are also described briefly.

2. Experimental

Use of a laser for light scattering permits rather precise measurement of the angular dependence of scattering light from scattering objects which are large compared with the wave length of light. A NEC Model 105 He-Ne laser was employed as a light source which has the output of about 10 mW and the wavelength $\lambda_0 = 6328$ Å. The polarized laser beam was incident normally upon a sample cell, which was fashioned from microscopic slide plates, on the heating stage. The scattered light from a sample was passed through an analyzing polaroid and allowed to fall on a photographic film. A thickness of a sample cell was varied from about 3 to 30 μm. The temperature of the sample was measured using chromel–alumel thermocouples.

Liquid crystal compounds used in this study are as follows; *p*-*n*-octyloxybenzoic acid (OOBA), *p*-*n*-octadecyloxybenzoic acid (ODOBA), ethyl-*p*-(4-ethoxybenzylideneamino-)cinnamate (EEBAC), ethyl-*p*-(4-methoxybenzylideneamino-)cinnamate (EMBAC), *p*-*n*-decyloxybenzylidene *p*-aminoazobenzene (DOBAB) and cholesteryl *n*-nonanoate (CN). CN and EMBAC were commercially obtained from Tokyo Kasei Co. Other compounds were synthesized in our laboratory. All liquid crystal compounds were recrystallized several times from ethanol. EEBAC, EMBAC and DOBAB exhibit two smectic modifications, namely, the smectic *A* and *B*, but the smectic *B* phase of EMBAC was monotropic with respect to the crystal state.[5–8] OOBA and ODOBA exhibit only the smectic *C* state.[5,9] CN exhibits the smectic mesophase as well as the cholesteric state at a lower temperature.[10]

3. Results and Discussion

Typical scattering patterns obtained for the smectic *A* state of DOBAB are shown in Fig. 1. The pattern (a) was obtained when the analyzer direction was perpendicular to the polarization direction of the incident light beam ($I_\perp$ pattern), and the pattern (b) when

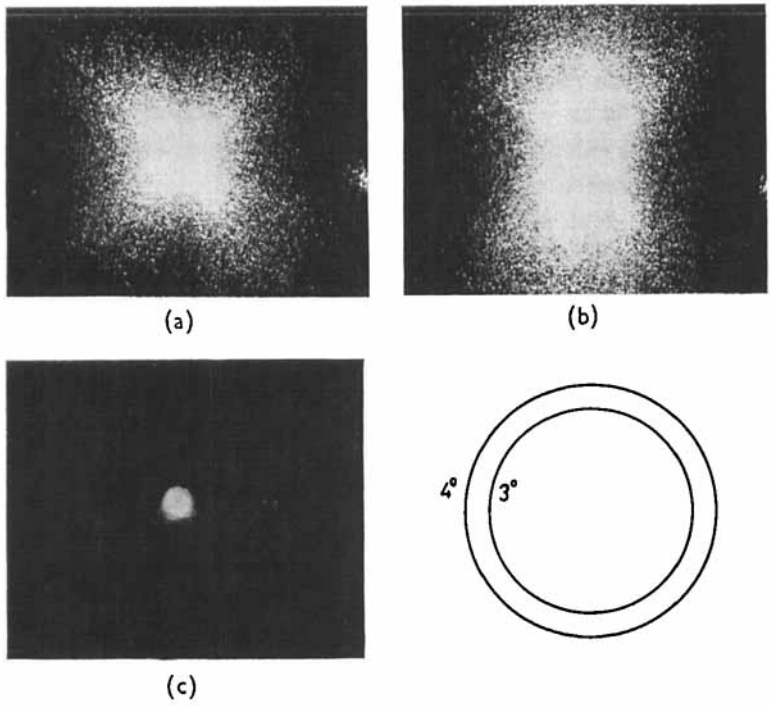

Figure 1. Light scattering patterns obtained in the smectic A state of DOBAB with (a) crossed and (b) parallel polarization. The parallel polarization direction is horizontal. The spot at the right side is due to the reflection of the laser beam from glass covering the polarizer. Pattern (c) shows the unscattered laser beam. The circles represent the scattering angle. Sample thickness; 5 μm.

the analyzer direction was parallel ($I_{\parallel}$ pattern). Scattering patterns for the smectic A state of EMBAC and EEBAC were very similar to those of DOBAB. All patterns can be reversibly observed both on heating and cooling.

As shown in Fig. 1, it should be noted that the $I_{\perp}$ pattern has the four leaf clover shape which has its maximum intensity at 45° to the polarization direction, and which has not been so far observed in the smectic state. Such an azimuthally dependent pattern became more remarkable in a thinner sample cell, and was observed even in the cell of thickness 30 μm. Furthermore, its crystalline state did not exhibit such a characteristic pattern. In this case, therefore,

it seems reasonable to consider that the observed pattern results from a molecular orientation characteristic of the smectic A state but not from the effect of the glass surface.

At present it is concluded that the light scattering for liquid crystal systems essentially arises from orientation fluctuations having correlation distance of the order of several thousands of Angstrom units.[3] The four leaf $I_\perp$ pattern has so far been reported for polymer spherulites[11] and cholesteric state[1-3] in which the light scattering is considered to result from fluctuations of non-random orientation correlations classified into two types, i.e., rod or fiber-like and disk-like types.[12] However, the pattern in the smectic A state differs from that obtained for the polymer spherulites and cholesteric state in that the scattering intensity increases continuously in going toward the center of the pattern, rather than showing a maximum intensity at a certain small scattering angle. This indicates that the smectic A state does not have non-random orientation correlations.

It is known that there is no scattering for a randomly oriented assembly of isotropic rods under crossed polarization. However, for an assembly of anisotropic rods, it has been also shown that the scattering pattern becomes dependent upon the azimuthal angle, μ, even though there is no orientation. A theory of the scattering of light from such a system has been obtained by Stein *et al.*[13] The total scattered intensity is

$$I = KL^2 \int_0^{2\pi} (\mathbf{M} \cdot \mathbf{O})^2 N(\alpha) \left\{ \frac{\sin [g \cos (\alpha - \mu)]}{g \cos (\alpha - \mu)} \right\}^2 \mathrm{d}\alpha \qquad (1)$$

where K is a proportionality constant, L length of a rod, N the total number of rods, and α angle between the polarization direction and an extended direction of a scattering element. When a light with wave length λ is scattered at angle θ, $g = (L/\lambda) \sin \theta$.

For the assembly of anisotropic rods with the optic axis lying along the rod axis, $(\mathbf{M} \cdot \mathbf{O})$ in Eq. (1) is presented by

$$(\mathbf{M} \cdot \mathbf{O})_{I_\perp} = E \cos \rho_1 [\delta \cos^2 \alpha + \alpha_2]$$

and

$$(\mathbf{M} \cdot \mathbf{O})_{I_\parallel} = E \cos \rho_2 [\delta \sin \alpha \cos \alpha]$$

where E is the amplitude of scattering from a rod, ρ_1 and ρ_2 are the fluctuations in scattering amplitude, and δ is the anisotropy, namely,

$\delta = \alpha_1 - \alpha_2$, and α_1 and α_2 the polarizabilities parallel and perpendicular to the rod. Stein *et al.* evaluated numerically Eq. (1) by use of a computer. The resulting contour plots, which were obtained for the anisotropic rods with the optic axis almost parallel to the rod axis, have maxima at $\mu = 45°$ for crossed polarizers and are extended in the vertical plane (perpendicular to the plane of polarization) for parallel polarizers.

The $I_\perp$ pattern observed for the smectic A state is quite similar to these results obtained by Stein *et al.* The smectic A state is an assembly of anisotropic elements, and thus the observed $I_\perp$ pattern suggests that the smectic A state has random orientation correlations.

On the other hand, the $I_\parallel$ pattern has a shape elongated in the direction perpendicular to the polarization as shown in Fig. 1 and is similar to that predicted theoretically by Stein *et al.* As discussed above, by analogy with the light scattering in the polymer spherulites it can be reasonably concluded from the $I_\perp$ and $I_\parallel$ patterns that in the smectic A state the assembly of anisotropic rods orients randomly and the optic axis lies close to the rod axis, i.e., random rod-like orientation correlation.

The samples discussed above exhibit another smectic state, i.e., the smectic B state, at a lower temperature. The $I_\perp$ and $I_\parallel$ patterns observed for the smectic B state of DOBAB are shown in Fig. 2. Patterns observed for the other samples were similar to those of

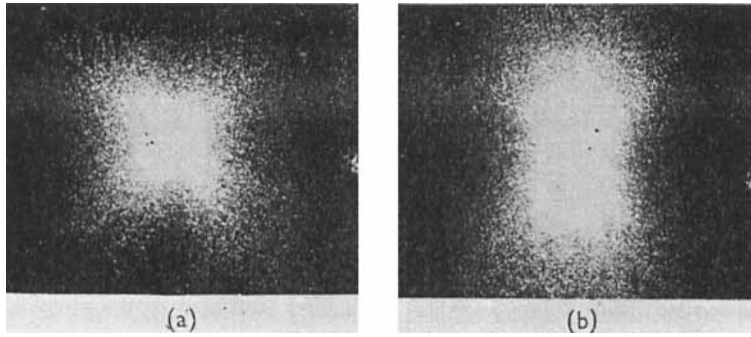

Figure 2. Light scattering patterns obtained in the smectic B state of DOBAB with (a) crossed and (b) parallel polarization. Sample thickness; 5 μm.

DOBAB. It has been well established from microscopic observations that the smectic B state exhibits different optical textures from those of the smectic A, and furthermore, the heat capacity considerably changes at the transition between the smectic A and B states according to measurements of thermal analysis.[4,6] However, no change was observed in the light scattering patterns at the smectic A–B transition, and both $I_{\perp}$ and $I_{\parallel}$ patterns of the smectic B state were identical with those of the smectic A state with respect to their intensity and shape. These are not surprising results because large transition heats are closely connected with the change of intermolecular force, on the other hand, the light scattering pattern is mainly attributed to the orientation correlations. It has been so far considered that the smectic B has the molecular axis tilted or perpendicular to the layers and, in addition, has an order within the layers, while the smectic A has the long molecular axis perpendicular to the layers.[14,15] Such a structural difference between the smectic A and B would correspond to large transition heats at the A–B phase transition and the change of the microscopic textures. Despite the difference of the molecular arrangements, the fact that there is no change in the light scattering patterns at the smectic A–B phase transition suggests that the smectic B state adopts orientation correlations essentially identical with the smectic A.

Light scattering patterns obtained for OOBA, which exhibits the smectic C state, are shown in Fig. 3. Patterns of ODOBA were

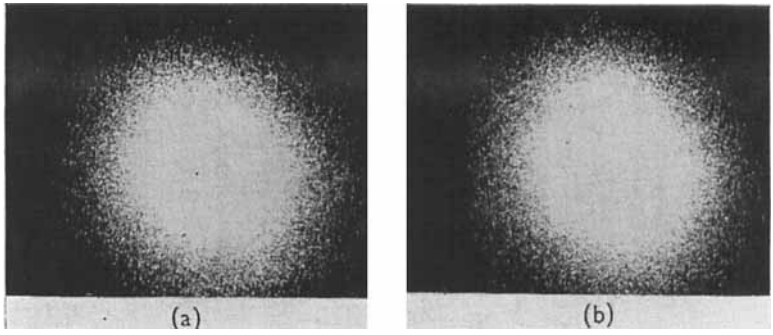

Figure 3. Light scattering patterns obtained in the smectic C state of OOBA with (a) crossed and (b) parallel polarization. Sample thickness; 5 μm.

identical with those of OOBA. As seen in Fig. 3, both the $I_{\perp}$ and $I_{\parallel}$ patterns were circularly symmetric and azimuthally independent, although they have nearly the same intensity. This suggests that the light scattering in the smectic C state arises from orientation correlations in which scattering elements are on the average spherical in shape, i.e., random orientation correlations. Recently, the authors have proposed that the smectic C state has a twisted smectic structure on the basis of the polarizing microscope observations on these compounds,[16] although Taylor *et al.* have proposed that the smectic C state has a tilted smectic structure.[17] The twisted smectic state has a structure where the molecules are arranged in layers with the long molecular axes lying tilted at an angle to the layer interface, and the angle of the molecular axis to the layer interface changes successively through the twisted smectic strata in a helicoidal fashion. When such a twisted molecular arrangement is applied to the smectic C state, the scattering elements are reasonably supposed to orient at random in the bulk. Thus, azimuthally dependent patterns would not be observed on this smectic C state differing from the smectic A and B states.

CN exhibits the smectic state besides the cholesteric state at a lower temperature. At present the smectic substances that also adopt the cholesteric state have been usually classified as the smectic A state.[18] Therefore, if the smectic state of CN has the identical molecular structure with the smectic A as discussed above, the $I_{\perp}$ pattern should have the four leaf clover shape. However, the observed pattern was circularly symmetric as shown in Fig. 4. This fact suggests that the smectic state of CN has different orientation correlations from the ordinary smectic A state although this mesophase certainly exhibits focal conic textures characteristic of the smectic A state on cooling from the isotropic state. When the cover glass of the sample cell containing CN is slid smoothly in the polarization direction, a four leaf clover pattern appears as shown in Fig. 5. The appearance of this pattern is possibly due to scattering elements forcibly oriented by displacement of the cover glass. However, such an effect is not observed on the smectic A state discussed above. The observed azimuthally independent patterns, thus, seem to suggest that this smectic state of CN is more likely associated with the smectic C state, although the microscopic texture for the smectic

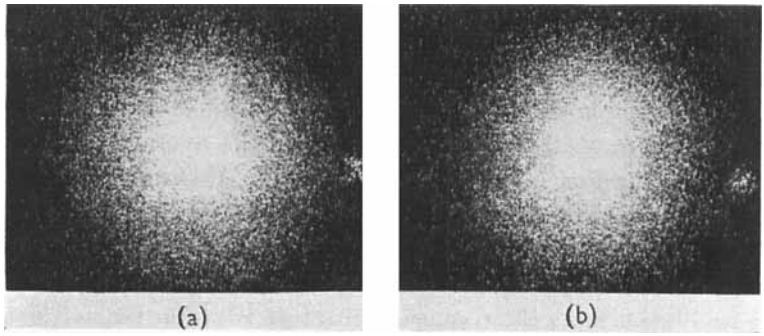

Figure 4. Light scattering patterns obtained in the smectic state of CN with (a) crossed and (b) parallel polarization. Sample thickness; 5 μm.

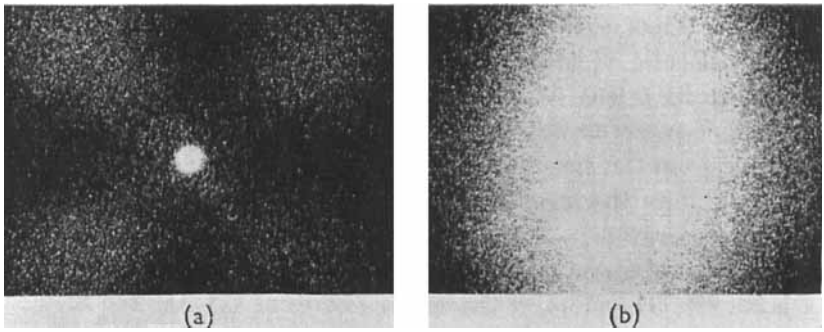

Figure 5. Light scattering patterns for the smectic state of CN obtained by moving the cover glass in the polarization direction with (a) crossed and (b) parallel polarization. Sample thickness; 5 μm.

state of CN is distinctly different from that for the smectic C state of OOBA. The smectic state of CN may be another smectic modification which is different from the smectic A or C with respect to the orientation correlations.

The patterns observed for the cholesteric state of CN both on heating and cooling are shown in Fig. 6. The $I_{\perp}$ pattern observed on cooling is different from that observed on heating, and the former corresponds to the latter rotated through 45° about the center. Such a behavior has not been so far reported for any of the cholesteric mesophases. This can be explained qualitatively by assuming that

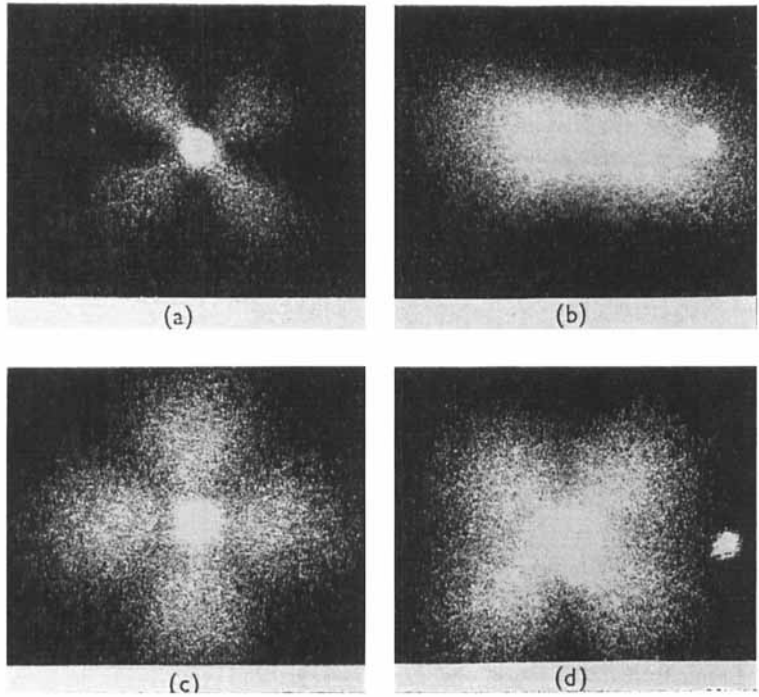

Figure 6. Light scattering patterns obtained in the cholesteric state of CN with (a) crossed and (b) parallel polarization on heating, (c) crossed and (d) parallel polarization on cooling. Sample thickness; 5 μm.

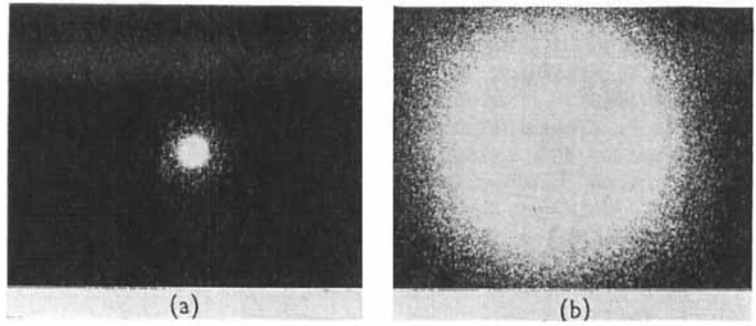

Figure 7. Light scattering patterns obtained in the pseudo-isotropic nematic state of EMBAC with (a) crossed and (b) parallel polarization. Sample thickness; 5 μm.

the optic axis of the mesophase on cooling lies at an angle of 45° to the scattering body radius.

EMBAC exhibits a pseudo-isotropic nematic state in which it has been considered that the long molecular axis lies nearly perpendicular to the glass surface of the sample cell. The $I_{\perp}$ and $I_{\parallel}$ patterns in the pseudo-isotropic state are shown in Fig. 7. The $I_{\perp}$ pattern has a very weak intensity of scattered light and small size compared with that of an ordinary nematic mesophase. This indicates that the orientation is restricted to a small range of angles.

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