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LIQUID CRYSTALS COMPOSED OF N-ACYLAMINO ACID. I. CIRCULAR DICHROISM IN LIQUID CRYSTALS COMPOSED OF N-LAUROYL-L-GLUTAMIC ACID AND AROMATIC SOLVENTS

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Amorphous powdered N-lauroyl-L-glutamic acid (LGA) soaked into aromatic solvents such as benzene showed birefringence under a polarizing microscope and a positive CD band. An achiral dye molecule dissolved in this system showed induced CD. From these results it is concluded that the LGA-benzene system is a cholesteric liquid crystalline phase.

The authors found that the amorphous powdered N-lauroyl-L-glutamic acid$^{1,2)}$ soaked into benzene showed a positive circular dichroism (CD) band at 330 nm (Fig.1). The N-lauroyl-L-glutamic acid-benzene (LGA-B) system exhibited an iridescent color like typical thermotropic cholesteric liquid crystals. The color varied reversibly with temperature, and the color of the scattered light was complementary to the transmitted light. The LGA-B system is a suspension of swelling powder, and showed birefringence under a polarizing microscope. The microscopic structure of the LGA-B system differed from that of dry powdered LGA. From these results, it was deduced that the LGA-B system is liquid crystalline phase. The 330 nm CD band may be attributable to the selective reflection of circularly polarized light of one sense, because any component in the LGA-B has no absorption band around 330 nm.

According to the de Vries' theory,$^{3)}$ which first explained the very high rotatory power of the cholesteric liquid crystal as the reflection of the circularly polarized light, the cholesteric pitch, p, and the average refractive index of the cholesteric phase, n, is related to the wavelength of the maximum reflectivity as follows;

$$\lambda = n \times p \qquad (1)$$

The value of λ can be determined from the wavelength of the CD peak due to the selective reflection by the cholesteric structure. Thus, by using λ= 330 nm and n = 1.5 the cholesteric pitch of the LGA-B system was estimated to be about 220 nm.

An iridescent color and CD band appeared also when LGA was soaked into other aromatic solvents such as toluene, xylene, chlorobenzene or dimethylphthalate. The LGA was not dissolved but swelled or suspended in these solvents as the case of the LGA-B system. The CD spectrum of the LGA-toluene system is illustrated in Fig.2 as an example. When LGA was completely dissolved in methanol or ethanol, the iridescent color and CD band around 300~400 nm were not observed.

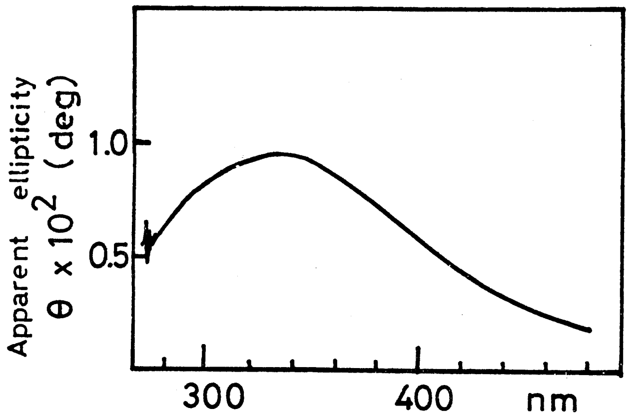

Fig. 1. CD spectrum of LGA-B system. Amorphous powdered LGA was suspended in a cell with 0.1 mm light path. The measurement was conducted with the sediment formed in the cell at room temp.

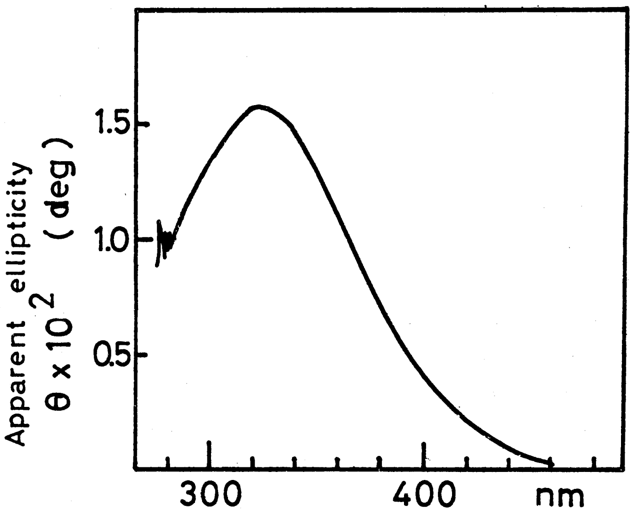

Fig. 2. CD spectrum of LGA-toluene system.
The measurement was made in the same way as for LGA-B.
0.1 mm light path, room temp.

Saeva and Wysocki[4 - 6] reported that an achiral dye molecule becomes optically active when dissolved in a thermotropic cholesteric phase. In Saeva's case, a strong CD band is induced in the region of the absorption bands of the dye molecule. More recently, we observed the similar behavior in the lyotropic liquid crystals of polyglutamate solution.[7] In the LGA-B system, the induced CD (ICD) was detected for achiral molecules such as azulene or anthracene (Figs. 3,4). The ICD spectrum of anthracene showed a single sign, and the profile of the CD spectrum was nearly identical with the profile of absorption spectrum. A similar single-sign ICD was reported by Saeva for anthracene in lyotropic cholesteric liquid crystals of polyglutamate solution.[8] These ICD spectra support the assumption that LGA-B system is a lyotoripic liquid crystal with a supra-molecuar helical structure. The LGA has a chirality due to an asymmetric carbon in the molecule, but has no helical structure in solid state. Then the added aromatic solvent may partially release the intermolecular interaction among the LGA molecules, and the released LGA molecules may form a supramolecular helical structure. An achiral molecule intercalated in this system may be helically oriented, and perturbed by the asymmetric fiels of liquid crystalline phase.

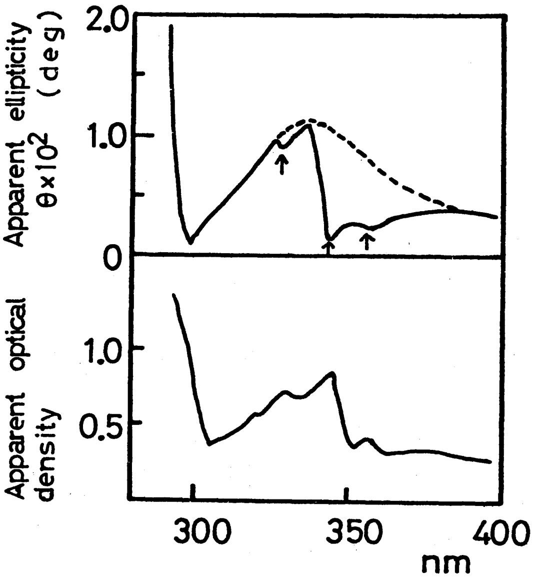

Fig. 3. ICD and absorption spectra of azulene dissolved in the LGA-B system.

The measurement was made in the same way as for LGA-B. 24°C, 0.2 mm light path, azulene 1×10^{-2} M. Arrows show the ICD, dotted line shows the CD band by the selective reflection estimated from Fig. 1.

Since CD and ICD band were not detected in the liquid crystalline phase composed of the racemic N-lauroylglutamic acid, it is necessary to use a chiral LGA for the formation of the new cholesteric phase. The dye molecule in this system is held more loosely than in the case of typical thermotropic cholesteric liquid crystals.8)

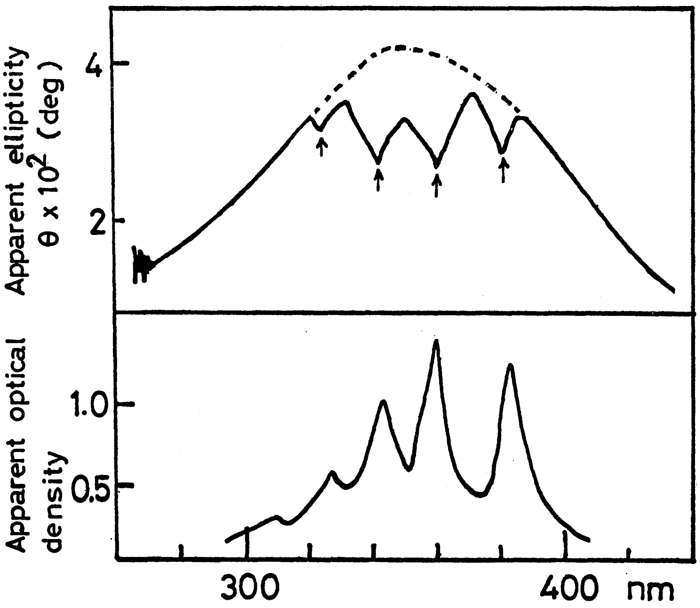

Fig. 4. ICD and absorption spectra of anthracene dissolved in the LGA-B system.

The measurement was made in the same way as for LGA-B. 24°C, 0.5 mm light path, anthracene 2×10^{-2} M. Arrows show the ICD, dotted line shows the CD band by the selective reflection estimated from Fig. 1.

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