Circular Dichroism in Lyotropic Liquid Crystals of Polyglutamate Solutions

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A poly-γ-ethyl-L-glutamate solution with a cholesteric color exhibits a circular dichroism due to the selective reflection of circularly polarized light of one sense by the cholesteric helical structure existing in the solution. On the other hand, an induced circular dichroism is observed in the wavelength region corresponding to the absorption bands of an achiral dye molecule when the molecule is dissolved in the poly-γ-benzyl-D-glutamate liquid crystalline phase. The two modes of circular dichroism are correlated to the structure and the chirality of the cholesteric phase of concentrated polyglutamate solutions.

Polyglutamate having α-helical conformation forms a lyotropic liquid crystalline phase when dissolved in various organic solvents in concentrations exceeding a critical value.[1,2] Robinson *et al.*[2] have extensively studied the structure of the liquid crystalline phase, and suggested two types of supramolecular structure, cholesteric and nematic, for the lyotropic liquid crystalline phase of a polyglutamate solution.

The cholesteric structure, which is the most common for the liquid crystalline phase of the polyglutamate solution, has been described as follows. In any given domain of the solution, rigid rod-like polyglutamate molecules are packed in a set of equispaced parallel planes in which the polyglutamate molecules lie parallel to one another. The molecules in one plane have a slight twist relative to those in adjacent planes about an axis of torsion perpendicular to the set of planes. Incorporation of successive layers of appropriately oriented polyglutamate molecules results in a helical structure, causing an extraordinarily high optical rotatory power to the solution. The sign of the optical rotation changes with variation of the solvent species, reflecting the inversion of the helical sense by the variation of the solvent species.[2a,2e] Robinson *et al.* presumed this optical rotation to be due to the selective reflection of circularly polarized light of one sense by the helical structure. They demonstrated by their experiment using a quarter-plate that the light reflected by the concentrated poly-γ-ethyl-L-glutamate solution in ethyl acetate is right circularly polarized.[2e]

The nematic structure has been elucidated as the untwisted array of equispaced parallel planes in which polyglutamate molecules are packed parallel to one another; the nematic structure is regarded as the cholesteric structure where the pitch of the helix is expanded to infinity, no optical rotatory power being caused. The nematic structure can be realized by dissolving polyglutamate in a particular solvent mixture[2d] or by untwisting the cholesteric structure by the application of magnetic field.[3]

Saeva and Wysocki[4,5] reported that the achiral dye molecule becomes optically active when the dye molecule is dissolved in a thermotropic cholesteric phase, and in this case, a strong circular dichroism (CD) is induced in the wavelength region of the absorption (AB) bands of the dye molecule. Saeva[6] also indicated that the induced circular dichroism of the achiral molecule in the thermotropic liquid crystalline phase can be used as a probe to determine the existence and the chirality of the cholesteric liquid crystalline phase.

We detected the circular dichroism corresponding to the optical rotation due to the selective reflection of circularly polarized light of one sense by the cholesteric helical structure in the liquid crystalline phase of the polyglutamate solution. We found the induced circular dichroism due to the achiral molecule dissolved in the lyotropic liquid crystalline phase of the polyglutamate solution. The two modes of circular dichroism are discussed in relation to the structure and the chirality of the cholesteric liquid crystalline phase of the concentrated polyglutamate solution.

Experimental

Materials. A lyotropic liquid crystal with a cholesteric color was obtained by the polymerization of 27 g of *N*-carboxyanhydride of γ-ethyl-L-glutamate in 50 ml of vinyl acetate using a mixture of triethylamine and β-dimethylaminoethanol (95: 5 in molar ratio) as an initiator. The resulting solution was directly used for CD measurement.

Poly-γ-benzyl-D-glutamate (PBDG) was obtained by the polymerization of *N*-carboxyanhydride of γ-benzyl-D-glutamate, the degree of polymerization of the resultant polymer being 910. The liquid crystalline phase of the PBDG solution was formed when PBDG was dissolved in dichloromethane, chloroform or 1,1,2,2-tetrachloroethane at a concentration of 0.75 M of the glutamyl residue. Achiral dyes were added to this concentrated PBDG solution. Acridine orange (AO) was purified by the method described elsewhere.[7] The solvents used were spectral grade ones and used without further purification.

Methods. The CD measurement of the poly-γ-ethyl-L-glutamate (PELG) solution was carried out with a JASCO MOE-7 magnetorotatory dispersion spectropolarimeter with a CD attachment. The CD and the AB spectra of the systems of the dyes dissolved in the PBDG solution were recorded on a JASCO J-20A or J-15 spectropolarimeter. In all cases, the sample solutions were slowly introduced into a quartz cell having a 0.5 mm path length.

Results and Discussion

Circular Dichroism Due to the Selective Reflection by the Cholesteric Structure. Robinson *et al.* found a cholesteric color in the PELG solution in ethyl acetate, where the cholesteric pitch is comparable with the wavelength of the visible light. They demonstrated that the origin of this cholesteric color is the selective reflection of circularly polarized light of one sense by the cholesteric pitch.[2d,2e)]

We found a brilliant iridescent color also for the PELG solution in vinyl acetate. This gives evidence to the existence of a cholesteric structure in this solution. The solution was thus expected to exhibit a circular dichroism due to the selective reflection by the cholesteric structure. A positive CD band was observed for the PELG solution in the visible region with a peak around 800 nm (Fig. 1). This is attributable to the selective reflection of circularly polarized light of one sense by the cholesteric pitch since no AB band exists in this wavelength region for any component of the PELG solution.

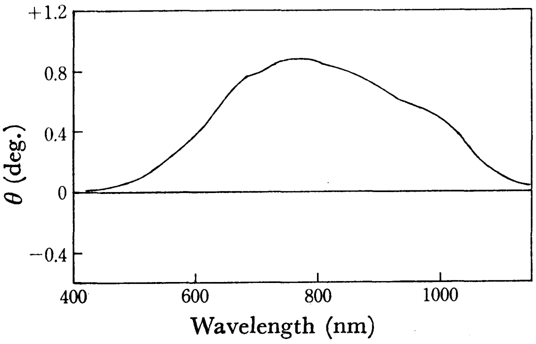

Fig. 1. CD spectrum due to the selective reflection of the lyotropic cholesteric phase of the PELG solution in vinyl acetate.

The circular dichroism due to the selective reflection by the cholesteric structure for the lyotropic liquid crystalline phase enables us to determine the cholesteric helical sense on the basis of the observed CD sign in comparison with the results of Saeva and Wysocki[4-6)] concerning the thermotropic liquid crystalline phase, where the sign of the circular dichroism due to the selective reflection by the cholesteric structure is positive for the right-handed cholesteric helical sense and negative for the left-handed one. The PELG solution in vinyl acetate is concluded to be the cholesteric phase of right-handed helical sense, since the solution displays a positive CD band due to the selective reflection by the cholesteric structure.

The magnitude of a CD band is defined as the absorbance for the left circularly polarized light minus that for the right circularly polarized light. The sample in the Robinson experiment would thus exhibit a negative CD band, since the light reflected by their sample was right circularly polarized, indicating that the apparent absorbance for the right circularly polarized light is larger in their sample. The CD sign, the cholesteric helical sense of the PELG solution in vinyl acetate, is opposite to that of the Robinson sample, while polyglutamate in both studies is the same in configuration. It has been confirmed by observation of the circular dichroism due to the selective reflection of circularly polarized light of one sense by the cholesteric helical structure that the helical sense of the lyotropic cholesteric structure in the PELG solution depends on the solvent in which polyglutamate is dissolved. An analogous situation has already been shown by the optical rotatory measurements for the PBLG cholesteric phase.[2a,2e)]

We have the well-known relationship between the cholesteric pitch P and the wavelength of the maximum reflectivity λ_m:

$$\lambda_m = n \times P$$

where n is the average refractive index of the cholesteric phase. The value of λ_m can be determined from the wavelength of the CD peak due to the selective reflection by the cholesteric structure. Thus, the cholesteric structure in the PELG solution in vinyl acetate is found to have a cholesteric pitch *ca.* 570 nm, the value of n being 1.4.

Induced Circular Dichroism of Dye Molecules in PBDG Liquid Crystalline Phase. We found that achiral dye molecules become optically active when they are dissolved in the PBDG liquid crystalline phase and that definite CD bands appear in the wavelength region where the AB bands of the dyes exist. Acridine orange gave a large positive circular dichroism around 500 nm when dissolved in the concentrated solution of PBDG in 1,1,2,2-tetrachloroethane. Positive CD peaks were also observed for *N*-ethylcarbazole in the solution of PBDG in tetrachloroethane in near ultraviolet region. Typical CD spectra of the systems of AO and *N*-ethylcarbazole dissolved in the concentrated PBDG solution are given in Figs. 2 and 3, respectively, together with their AB spectra. Due to the existence of many strong AB bands in the systems, CD measurement in a wavelength region shorter than 280 nm could not be carried out successfully.

It was confirmed by CD measurements for the concentrated PBDG solution without dye molecules that no CD band due to the selective reflection exists in the wavelength region in which the CD bands due to the

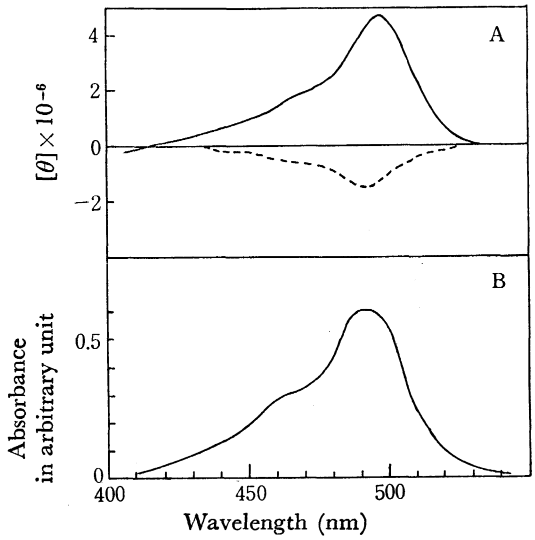

Fig. 2. (A) CD spectra of AO induced in the cholesteric phases of the PBDG solutions in tetrachloroethane (——), and in dichloromethane (------) and (B) absorption spectrum of AO in the PBDG solution in tetrachloroethane. [θ] was calculated on the basis of the concentration of AO.

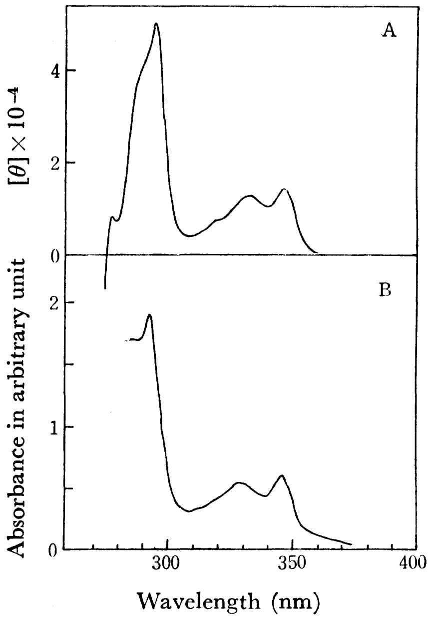

Fig. 3. (A) CD spectrum of *N*-ethylcarbazole induced in the cholesteric phase of the PBDG solution in tetrachloroethane and (B) absorption spectrum of *N*-ethylcarbazole in the PBDG solution in tetrachloroethane. [θ] was calculated on the basis of the concentration of *N*-ethylcarbazole.

dye molecules appear. No CD band could be detected in the dilute solution of PBDG containing AO. The circular dichroism observed for the system of AO dissolved in the cholesteric liquid crystalline phase of the PBDG solution in dichloromethane or tetrachloroethane disappeared when the cholesteric structure in this system was untwisted to the nematic structure by the application of magnetic field.

The possibility that the dissymmetric field of the α-helix constituting the cholesteric phase causes the circular dichroism can be eliminated. We see that the circular dichroism observed for the achiral dyes dissolved in the concentrated solution of PBDG are induced by the dissymmetric field effect of the cholesteric helical structure formed in these systems on the electronic transitions of the dyes. This is similar to cases of dyes buried in thermotropic liquid crystalline phases.[4–6,8]

Thus, the achiral dyes in the cholesteric liquid crystalline phase of the PBDG solution are intercalated in the helical structure in this phase and are oriented relative to this helical structure. As a result, they appear in the dissymmetric field due to the cholesteric helical structure.

The CD bands observed for *N*-ethylcarbazole in the PBDG solution in tetrachloroethane is simply positive in sign in the wavelength region 280—370 nm (Fig. 3). This is not the case in Saeva's results[5] where the CD curve for *N*-ethylcarbazole in the thermotropic liquid crystalline phase consists of two regions with opposite signs. As Sackmann and Voss[8] indicated, the CD sign depends on the polarization character of the corresponding electronic transition of the dye molecule only when the helical arrangement of the dye molecule along the cholesteric helical axis is realized. Our results show that such a helical arrangement is absent for the dye molecule in the lyotropic liquid crystalline phase.

A similar induced circular dichroism was reported recently by Saeva and Olin,[9] their results agreeing with ours.

Relations between the CD Profile and the PBDG Cholesteric Structure. The CD spectra of AO were observed not only in the solution of PBDG in tetrachloroethane but also in the solutions of PBDG in dichloromethane and in chloroform. The CD sign observed for AO around 500 nm changed with solvent, being negative in the dichloromethane solution and positive in the tetrachloroethane solution. The CD sign in the region for the chloroform solution turns positive from negative with time. For all the cases investigated, the CD magnitude around 500 nm increased when the solution was left to stand after being introduced into the observation cell. It took several hours or even days for the equilibration of the CD magnitude. Figure 4 shows the change of the CD magnitude with time for AO in the solution of PBDG in tetrachloroethane. Such a time dependent character of the circular dichroism was also observed for the system containing *N*-ethylcarbazole.

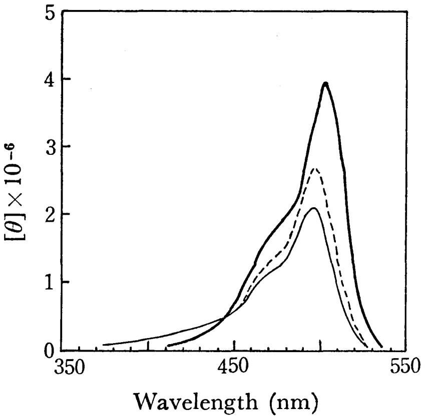

Fig. 4. Change in the CD magnitude observed for AO in the cholesteric phase of the PBDG solution in tetrachloroethane; (——) recorded immediately after the introduction of the sample into the observation cell, (------) 1 hour after and (——) 2 days after. [θ] was calculated on the basis of the concentration of AO.

In the course of maturation of the PBDG cholesteric phase in the observation cell, the microscopic observation showed that the cholesteric phase which had been disturbed through the introduction into the cell attained to its equilibrated state, exhibiting the retardation lines characteristic of the cholesteric phase on a time scale comparable with that of the change in CD magnitude. It is assumed that the recovery of the PBDG cholesteric structure to its equilibrium state increases the CD magnitude of the bands. Such a long relaxation is observed also in the NMR studies[3] on the magnetic field induced reorientation of the PBLG liquid crystalline phase and regarded as characteristic of polyglutamate liquid crystalline solutions.

We postulate that the circular dichroism is brought about by the dissymmetric field of the cholesteric helix. The sign of the dissymmetric perturbation from the helical structure is known to change by the inversion of the helical sense. Thus, the fact that the sign of the circular dichroism induced for the dye molecule in the solution of PBDG in dichloromethane is opposite to that in tetrachloroethane leads to the conclusion that the helical sense of the cholesteric structure is inversed by the change of the solvent from dichloromethane to tetrachloroethane. The cholesteric helical sense is determined not only by the steric isomerism of polyglutamate in the solution but also by the mode of the interaction of polyglutamate with the solvent. Inversion of the CD sign with time for AO in the solution of PBDG in chloroform suggests that the interaction between PBDG and chloroform reduces the energy difference between the cholesteric helical senses in this system.

We could detect no circular dichroism due to the selective reflection for the PBDG cholesteric phase as a result of very large cholesteric pitch in this phase. Robinson *et al.* reported that the sign of the optical rotation is positive for the cholesteric liquid crystalline phase of the solution of PBLG in dichloromethane.[2a,2e] This might show that there exists a negative Cotton effect at the longer wavelength region corresponding to the cholesteric pitch band. If so, the sense of the cholesteric helix for the solution of PBLG in dichloromethane is left-handed. We can therefore expect the right-handed helical sense to exist in the PBDG cholesteric phase in dichloromethane. On combining this and the above-mentioned result concerning the induced circular dichroism, the negative sign of the circular dichroism induced for the dye in the PBDG cholesteric phase in dichloromethane is taken as diagnostic of the right-handed cholesteric helical sense in this system.

Thus, the inversion of the cholesteric helical sense is demonstrated again by the observation of the sign of the induced circular dichroism for the achiral dyes dissolved in the cholesteric liquid crystalline phase of polyglutamate.

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