CHEMISTRY LETTERS, pp. 823-826, 1974. Published by the Chemical Society of Japan

INDUCED CIRCULAR DICHROISM OF DYES BURIED IN SOLID "LIQUID CRYSTAL" FILMS OF POLY-γ-METHYL-D-GLUTAMATE

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Induced circular dichroism was found for achiral molecules when buried in the solid film of PMDG made by casting from solution. This circular dichroism is regarded to be induced by the dissymmetric field due to the supramolecular helical structure of PMDG molecules retained in the solid film.

Saeva et al. reported that optically inactive achiral dye molecules become optically active when they are dissolved in a thermotropic cholesteric phase and that induced circular dichroism (CD) bands can be observed in their electronic transitions.[1]

This phenomenon has been extended to achiral dyes dissolved in a lyotropic liquid crystalline phase such as those dissolved in the solutions of poly-γ-benzyl-L- or D-glutamate,[2,3] poly-γ-ethyl-D-glutamate[4] and poly-γ-methyl-D-glutamate (PMDG).[4] When the dyes were dissolved in the lyotropic liquid crystalline phase formed in the concentrated solutions of these polyglutamates, induced CD bands appeared in the wavelength regions corresponding to the electronic transitions of the dye molecules. Polyglutamates in the α-helical conformation are known to form a cholesteric structure in many kinds of solvents,[5] and the circular dichroism for the dyes in the lyotropic liquid crystalline phase has been considered to arise from the dissymmetric field of the cholesteric helical structure in the lyotropic liquid crystalline phase.

Such a helical structure in the concentrated solution can be retained in the solid films of poly-γ-benzyl-L-glutamate[6] and PMDG[7] when the films are made by casting from solutions. This leads us to the idea that an extrinsic optical activity must be detected for an achiral dye when the dye is buried in a solid film of a polyglutamate. In the present communication, we wish to report that achiral dyes display optical activities when they are buried in the solid film of PMDG made by casting from solution, as detected by the circular dichroism in their electronic transitions.

EXPERIMENTAL

Dyes were dissolved in the 15%(w/w) ethylene dichloride solution of PMDG (DP= 250) at the concentrations of 10^{-2}-10^{-3} M. A small amount of the solution including a dye was spread as a thin film on the surface of a glass plate, rubbed to one direction with a glass plate edge and the solvent was evaporated slowly in a closed vessel at room temperature. A thin film formed on the glass plate was then stripped off the glass surface by introducing the film-covered glass plate into water. A sample film with uniform thickness and suitable area was selected and cut out from the film obtained, and was mounted on a holder with a window (8 mm in diameter).

The CD and the absorption (AB) spectra were recorded on a JASCO J-20A spectropolarimeter and a Hitachi EPS-3T spectrophotometer, respectively.

RESULTS AND DISCUSSION

Definite CD bands with negative sign were observed for pyrene and acridine orange (AO) buried in the solid PMDG film in the wavelength regions of the absorption of dyes. The CD spectra are given in Figs. 1 and 2 together with the AB spectra. This induced circular dichroism of the dyes manifests that the achiral dyes in the solid film of PMDG are no longer symmetric but are subjected to a dissymmetric field.

In addition to the above-mentioned circular dichroism in the electronic transitions of the dyes, a positive CD band was observed around 500 nm for the film containing pyrene or AO. In the case of the sample including AO, which has absorption around 500 nm, this positive CD band was superposed by the negative CD bands due to the electronic transitions of AO. Since the sample films showed birefringence on polarizing microscopic observation and had an iridescent color, the positive circular dichroism, whose wavelength region does not correspond to those of the electronic transitions of any components of the samples, indicates that a "cholesteric" structure exists in the films.

The cholesteric structure in the fluid liquid crystal is known to induce the circular dichroism in the electronic transitions of an achiral dye buried in the liquid crystal.[1-4] The possibility that the dissymmetric field of the α-helix constituting the cholesteric structure is the origin of this circular dichroism has been negatived on the basis of the following facts; i) the circular dichroism disappears when the cholesteric phase including the dye is diluted to a concentration where no cholesteric structure is retained and ii) the circular dichroism is not observed when the cholesteric structure is expanded to the nematic structure keeping constant the

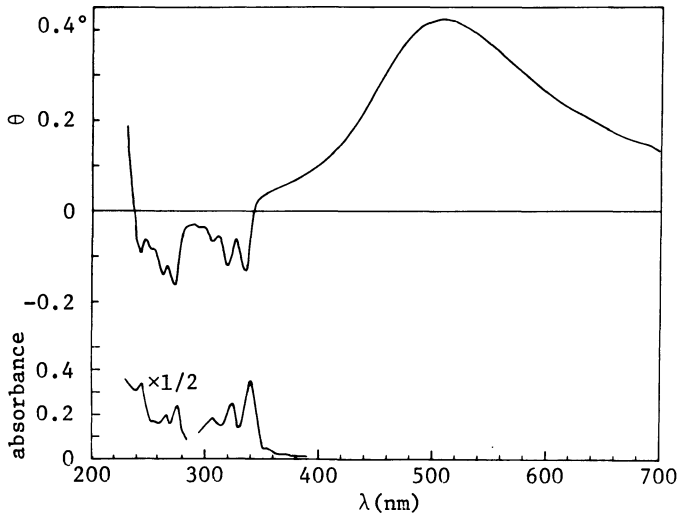

Fig. 1. CD (upper) and AB (lower) spectra of PMDG film containing pyrene.

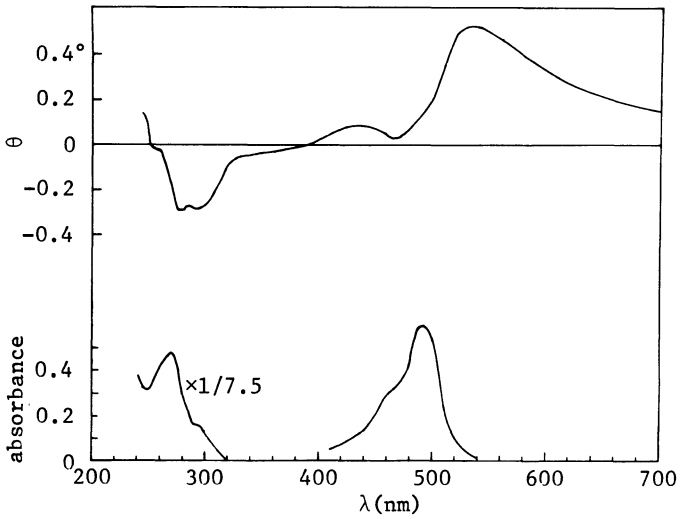

Fig. 2. CD (upper) and AB (lower) spectra of PMDG film containing AO.

concentrations of the dye and the polyglutamate.[2,3] Therefore, we can naturally assume that the induced circular dichroism in the absorption regions of pyrene and AO buried in the solid PMDG film is caused by the dissymmetric field of the "cholesteric" structure existing in the film.

In the sample films investigated in this paper, rigid rod-like PMDG molecules lie in equispaced parallel planes. The PMDG molecules in one plane are slightly twisted relative to those in adjacent planes about an axis of torsion perpendicular to the set of planes. The incorporation of such successive layers results in a helical structure, which gives rise to a high optical retatory power.[5] Thus the achiral dyes in the solid film are oriented relative to the "cholesteric" helix of PMDG molecules and they suffer the dissymmetric perturbation of the helix.

The circular dichroism induced in the absorption regions of the dyes in the solid film is simply negative in sign regardless of the polarization direction of the

corresponding electronic transitions. Sackmann and Voss,[8] however, indicated from their experiments about the induced circular dichroism of dyes in a thermotropic cholesteric phase that the signs of the induced CD bands of the achiral dyes depend upon the polarization character of the corresponding electronic transitions of the dyes when the dyes have a helical arrangement along the cholesteric helix. This discrepancy might be explained by assuming that the dyes in the solid film are not ordered in such a helical arrangement as in a thermotropic cholesteric phase, but are only exposed to the large dissymmetric field of the "cholesteric" helix. This situation is analogous to that of the dye dissolved in a fluid lyotropic cholesteric phase, where the induced circular dichroism of simple sign is observed,[2,3] and is considered to be characteristic of a less ordered arrangement of the dye in the cholesteric phase. Thus, on forming a solid PMDG film from solution, such a cholesteric structure including less ordered dye molecules is retained as it is in the solution.

An extrinsic optical activity is induced to an achiral dye buried in a solid PMDG film by the dissymmetric field due to the supramolecular helical structure in the film. There seems no discontinuity on passing from the fluid to the solid state with regard to the optical activity measurement, which has been proposed in NMR and X-ray studies.[9]

We are gratefully indebted to Professor K. Seto and Mr. Y. Sato for stimulating discussions and encouragements in this investigation.

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(Received May 28, 1974)