BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2583—2584 (1973)

Circular Dichroic Evidence for the Cholesteric Phase in Solid Films of Poly-γ-methyl-glutamate

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(Received October 21, 1972)

Concentrated solutions of synthetic polypeptides are known to have a cholesteric liquid crystal structure.[1)] Samulski and Tobolsky[2)] presented evidences for such a structure in solid films of poly-γ-benzyl-L-glutamate (PBLG) made by casting from solution. The structure in the solid films was inferred from swelling and birefringence studies and X-ray observation. Thus, if the solid films in which the periodicity is comparable to the wavelength of light can be prepared, it is reasonable to expect them to show the cholesteric colors, since the cholesteric liquid crystal exhibits selective reflection of circularly polarized light. Such an example has been reported[3)] only for a concentrated solution of poly-γ-ethyl-glutamate in ethyl acetate.

Recently a patent[4)] was published in which it was described that solid films with iridescent colors were obtained from poly-γ-methyl-D(or L)-glutamate (PMDG or PMLG). In order to confirm our presumption that the colors are due to cholesteric color, we have performed circular dichroic studies with colored films.

Experimental

Concentrated solutions (24 wt%) of PMDG and PMLG (D. P., *ca* 230) in 1,2-dichloroethane (provided from Central Research Laboratories, Ajinomoto Co., Inc.)[5)] were used after being diluted to 8 weight percent with the same solvent. A small amount of the solution was spread as thin films on the surface of a plate glass, rubbed in one direction with a glass rod. The solvent was then allowed to evaporate freely in air at room temperature. After being dried completely, thin solid films were formed on the glass surface. They were then stripped off the glass surface by introducing the film-covered glass plates into water. Solid films 10 to 30 micron thick were preferred for the optical study. Although they were more or less opaque and colorless for transmitted light, they assumed a uniform reflection color varying from blue to red depending on the angle of view and incidence. The color depended also on the initial concentration of solution and the evaporation rate; when the rate was slower, the color was displaced from blue to red when viewed at a certain angle.

Samples with uniform thickness and area suitable for measuring the circular dichroism were cut out from the films and mounted on a holder with a window, 6 mm×6 mm. Circular dichroism was measured by using a JASCO Automatic Recording Spectropolarimeter Model J-10. Unless otherwise stated, incident light was cast at right angle to the sample film.

Results and Discussion

As expected, circular dichroism (CD) was observed for the sample films reflecting blue to red light. Typical circular dichroic curves for a PMDG film are illustrated in Fig. 1, where the CD (ordinate) is

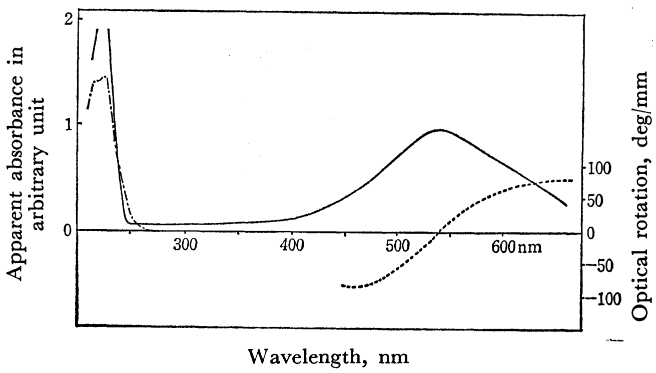

Fig. 1. Circular dichroism (——) and optical dispersion (····) of solid films (20 μ thick) of PMDG.
Line (–·–·–) shows a CD curve of dilute solution (0.04 wt%) of PMDG in 1,2-dichloroethane.

expressed as the apparent absorbance of the left circularly polarized light minus that of the right one. The CD curve exhibited a large band with a peak in the region 450—650 nm and a small band with a peak in the region 220—230 nm. The latter band, also observed for the solutions of PMDG in chloroform, was the same as the CD band which has been attributed to the n-π* transition in the α-helix of PMDG molecules.[6)] The 450—650 band is due to selective reflection of circularly polarized light of one sense in that wavelength region, since no absorption is found here for the solution. Since the apparent absorbance is actually due to the reflection, it is concluded from Fig. 1 that the PMDG films reflect selectively the left circularly polarized light. On the other hand, the PMLG films were found to give the CD curve of the opposite sense. The result indicates the presence of a cholesteric liquid crystal structure in the solid films of PMDG or PMLG.

Liquid crystals in the cholesteric phase are well-known to form a macroscopic helical structure. Polarizing microscope examination showed that the birefringence of the film of PMDG or PMLG is optically negative and the optical axis is almost normal to the

1) C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956).
2) E. T. Samulski and A. V. Tobolsky, *Nature*, **216**, 997 (1967); *Pure Appl. Chem.*, **23**, 145 (1970).
3) C. Robinson, *Mol. Cryst.*, **1**, 467 (1966).
4) N. Okuda, S. Mori, Y. Takagi, and Y. Takeda, Japanese, No. 5154 (1970).
5) PMG was prepared by ring-opening polymerization of γ-methyl-glutamate NCA in 1,2-dichloroethane using *N,N*-dimethylethylenediamine as initiator (S. Mori and N. Iwatsuki, private communication).
6) G. Holzwarth and P. Doty, *J. Amer. Chem. Soc.*, **87**, 218 (1965).

film surface, *i.e.* the axis of the macrohelix is almost vertical to the film surface. Thus, for normal incidence, the pitch p of the macrohelix is inferred from the equation[7] $\lambda_m = n \cdot p$, where λ_m is the wavelength of the maximum reflection and n is the average refractive index. The value for λ_m was obtained from the peak of the CD curve and n was experimentally estimated as about 1.4. For a sample which showed the CD curve of Fig. 1, the pitch was estimated as 350 nm by using $\lambda_m = 500$ nm and $n = 1.4$.

The helical sense can be deduced from the sense of the circularly polarization of the reflected light or from the sign of the optical rotatory dispersion; a left-handed helical structure reflects left circularly polarized light and it shows negative optical rotation on the short wavelength side of the reflection band[7,8,9,10]. Figure 1 shows that the PMDG films reflect left circularly polarized light and that they show negative optical rotation at the short wavelength side of the inversion. It is thus concluded that the PMDG films have a left-handed macrohelix. For the PMLG films a right-handed macrohelix was found. Since the molecular helix (α-helix) of PMDG (or PMLG) is known to be left-handed (or right-handed), this result indicates that the sense of the macrohelix is the same as that of the molecular helix of each enantiomer.

The dependence of the reflection on the angle of incidence was also measured. The wavelength peak was compared with the value calculated by Fergason's formula[11] which gives the wavelength of maximum reflection as a function of the angle of incidence and of reflection for cholesteric liquid crystal. The observed value of the peak was in good agreement with the value calculated by assuming that the reflection planes are placed parellel to the film surface. This shows that the reflection planes of the cholesteric phase are parallel to the film surface, being consistent with the result of the polarizing microscope examination.

The cholesteric structure of the films was so heat-resistant that it was not destroyed until near the decomposition temperature of this polymer.

The colors of the solid films of PMDG were found to change reversibly by absorbing organic vapor such as chloroform or benzene. With the progress of absorption, the color turned red, becoming finally faint. Corresponding to the visual color change, the peak of the CD curve shifted to longer wavelength region. This indicates the increase of the pitch of the macrohelix by absorbing organic vapor between the planes in which the molecules lie, since the change of the refractive index is not so sensitive in this case.

Colored films were not obtained from a racemic mixture of PMDG and PMLG. Among polyglutamate esters, PBLG is also reported to form a solid film with a cholesteric structure,[2] but it did not exhibit cholesteric color. Formation of the solid film with cholesteric color was most favorable from solutions of PMDG or PMLG which was prepared according to the method in Ref. (5). This explanation is still not clear.

The result we presented has a new significance for the observation[12] that the light reflected from certain iridescent beetles is also circularly polarized, suggesting the presence of a cholesteric structure in their cuticles.

7) Hl. de Vries, *Acta Crystallogr.*, **4**, 219 (1951).
8) S. Chandrasekhar and K. N. S. Rao, *ibid.*, **A24**, 445 (1968).
9) M. Aihara and H. Inaba, *Opt. Commun.*, **3**, 77 (1971).
10) Here it should be noted that confusion occurs regarding the sense of circular polarization in the literature. For example, according to Conners' paper (*J. Opt. Soc. Amer.*, **58**, 875 (1968)), a right-handed helix reflects left circularly polarized light. Then, he adopted a definition contrary to the normal usage for the sense of circularly polarized light.
11) J. L. Fergason, *Mol. Cryst.*, **1**, 293 (1966).
12) A. C. Neville and S. Caveney, *Biol. Rev. Cambridge Phil. Soc.*, **44**, 531 (1969).