SHORT COMMUNICATION

Cholesteric Twisted Structure in Solid Films of Poly(γ-methyl-D-glutamate)

Junji WATANABE, Shintaro SASAKI, and Ichitaro UEMATSU

Department of Polymer Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan.

It is well known that the concentrated solutions of synthetic polypeptides have a cholesteric liquid crystal structure.[1] This liquid crystal structure consists of rotating layers of the rod-like molecules and is characterized by the presence of a helical twist of uniform pitch. In consideration of the concentration dependence of pitch,[1] it is easy to envisage that a similar structure with a small pitch is retained in the solid films when all the solvent is removed. If the films have a cholesteric pitch comparable to the wavelength of visible light, it is expected from de Vries' theory, that they will show the cholesteric color and the form circular dichroism.[1,2] Such observations have been reported for a concentrated solutions of poly(γ-ethyl glutamate) in ethyl acetate,[1] poly(γ-methyl-D-glutamate) film,[3] and in the cuticles of some species of adult beetles.[4] In this paper, it will be shown that the colored poly(γ-methyl-D-glutamate) (PMDG) films can be prepared for reproduction from 1,2-dichloroethane (EDC), dichloromethane (DCM)—N,N-dimethylformamide (DMF), and chloroform—DMF solutions, and also that the color of the film is due to the selective reflection of the visible light caused by the uniform cholesteric twisted structure. Furthermore, the nature of the cholesteric twisted structure in the solid films of PMDG was studied by circular dichroism measurements.

The PMDG used has a molecular weight of about 100,000. In the preparation of films, the solutions (about 3 vol%) were poured onto a glass plate on a mercury surface. The solvents were allowed to evapolate slowly at room tem-perature. After being dried, the solid films were stripped off the glass surface by immersing the film-covered glass into methyl alcohol, and then were dried again *in vacuo*. The circular dichroism (CD) was measured by using a JASCO automatic recording spectropolarimeter Model J-5. Samples were cut from solid films, 10 to 20 μm thick, and mounted on a window of 10 mm diameter. The incident light was irradiated at right angles to the film surface. The shape of the circular dichroism curve was not modified by the macroscopic rotation of the film about the normal to film surface. Therefore, the effect of the birefringence due to orientation, which may probably occur in the casting process, was insignificant. X-Ray measurements were carried out with a Rigaku Denki X-ray generator (Ni-filtered CuK$_\alpha$ Radiation).

The colored films were prepared for reproduction from three different solutions. One of the films was cast from EDC solution, as reported by Tachibana, *et al.*[3] The other films were cast from DCM—DMF and chloroform—DMF solutions; 1-g PMDG was dissolved in 30-ml DCM (or chloroform) and then 0.4-ml DMF was added. The colorless films were prepared from chloroform or DCM solution but found from X-ray measurements not to contain the cholesteric twisted structure.[5] Therefore, DMF seems to play an important part in the preparation of colored films. When observed at right angles to the film surface, the films cast from EDC and DCM—DMF solutions showed green or yellow color, while blue or violet colored films were prepared from chloroform—DMF solution.
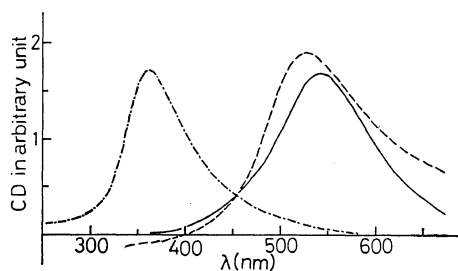
Figure 1. Circular dichroism of PMDG films cast from EDC solution (——), from DCM—DMF solution (– – –), and from chloroform—DMF solution (—·—).

Table I. Values of λ_m, P, and the angle of twist, Ψ

Casting solvent	Color	λ_m, nm	P, nm	Ψ, degree
1,2-Dichloroethane	Green	540	386	1.1
Dichloromethane—DMF	Green	520	371	1.2
Chloroform—DMF	Violet	360	257	1.7

The circular dichroism was observed in the films mentioned above. Figure 1 shows the CD curve, where the CD is expressed as the apparent absorbance for the left circularly polarized light minus that for the right circularly polarized light. The CD curves for the green colored films from EDC and DCM—DMF solutions exhibit a large positive band with a peak in the region 500—600 nm. For the violet colored film from the chloroform—DMF solution, a peak is observed in the 300—400 nm. As shown in Table I, the values of the wavelength, λ_m, at peaks in the CD curves are in good agreement with the wavelength of visible color observed at right angles to the film surface. Thus, the colors of the films are due to the selective reflection of visible light. The large positive bands in 300—600 nm further show that the reflected light is left circularly polarized. The result indicates that the cholesteric twisted structure in the concentrated solution can be maintained in solid films of PMDG.

The pitch of the solid cholesteric structure is estimated from the equation $\lambda_m = nP$, where n (=1.4) is the average refractive index and P the pitch,[2] since the axis of the macro-helix is likely to be vertical to the film surface.[3,6,7] The values of P are listed in Table I. Robinson

has shown that the cholesteric twisted structure consists of rotating layers of rod like molecules.[1] We make the assumption that the distance between the twisted molecular layers, a, is of the order of molecular diameter in the solid films. The value of a is about 12 A as estimated from the hexagonal structure of the film cast from the chloroform solution.[5] Thus, the angle of twist per layer, Ψ (=$360a/P$), is 1—2 degrees, as shown in the last column of Table I. It is of interest that these values of the angle of twist are much larger than those in the cholesteric phase of concentrated solutions.

It has been predicted that the range of total reflection should expand from $P(n-\Delta n/2)$ to $P(n+\Delta n/2)$,[1,8] where Δn is the birefringence of untwisted material. Therefore, the width of the reflection is given by the equation

$$\Delta\lambda = P\Delta n \quad \text{or} \quad \Delta\lambda/\lambda_m = \Delta n/n$$

From Figure 1,

$$\Delta n/n = \Delta\lambda/\lambda_m = 0.20—0.25$$

Using $n = 1.4$, Δn is estimated as about 0.3 which is of the different order from the birefringence ($\Delta n = 0.026$) measured for the nematic phase in the solution which contained equal quantities of the L and D enantiomorphs of poly(γ-benzyl glutamate).[9] This discrepancy may be probably caused by the wide distribution of pitch length and/or the disordering of the twisted axes.

All the PMDG films showing the form circular dichroism give a characteristic X-ray diffraction pattern which is quite different from the hexagonal pattern of that film cast from the chloroform solution[5] (Table II). This characteristic pattern is also observed in colored poly(γ-benzyl-D-glutamate) films and may be attributed to the cholesteric twisted structure.

The structural change of the PMDG films immersed in methyl alcohol elicits much interest. Methyl alcohol has a considerable effect on the X-ray diffraction pattern of colored films. As Table II shows, several new reflections appear, and all reflections are rather sharp. Such a situation means that the twisted PMDG molecules form a kind of complex phase with the methyl alcohol. It was found that the peak of the CD curve shifts to the higher wavelength for that film immersed in methyl alcohol (Figure 2).

This shift can be attributed to the expansion of molecular distance due to swelling, and not to a change of refractive index since the refractive index of methyl alcohol is about 1.33 as close to that of the polymer, 1.4. The expansion of the distance between the twisted layers estimated from λ_m, is 15—20%. These results certainly clarify the nature of the cholesteric twisted structure of PMDG films, since methyl alcohol has no effect on the hexagonal crystalline phase of PMDG films cast from chloroform or from DCM solution. The examination for these phenomena is in progress.

The cholesteric twisted structure in the solid state was so stable on heating that it was not destroyed at temperatures below 180°C. Above 200°C, however, this cholesteric twisted structure was gradually destroyed depending on the heating duration, as shown in Figure 3; the films mounted on a sample holder were annealed *in vacuo*. In Figure 4, the nomalized peak heights in the CD curves are plotted against the an-
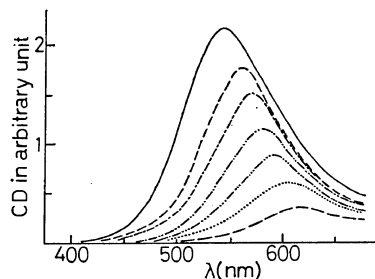
Table II. X-Ray diagram of PMDG films cast from 1,2-dichloroethane solution

As cast film, A		Swollen in methanol, A	
		33.0	?
		23.1	m
		19.2	w
11.9	*vs.*	14.8	m
10.5	*vs.*	13.2	s
		11.6	m
		10.8	m
		9.81	vw
7.76	m	9.06	w
		7.60	vvw
5.7	Diffuse		
5.2	Diffuse		

Figure 2. Circular dichroism of PMDG films cast from chloroform—DMF solution: ——, original; ----, immersed in methanol.

Figure 3. Circular dichroism of PMDG films (cast from EDC solution) annealed at 200°C for 0 hr (——), 2 hr (----), 3 hr (—·—), 4 hr (—··—), 5 hr (—···—), 6 hr (····), and 7 hr (——).
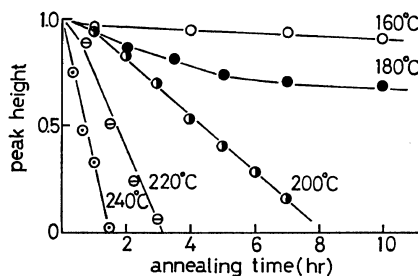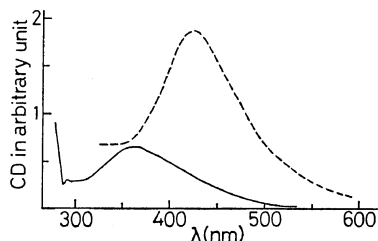

Figure 4. Plots of the peak height in the CD curves against the annealing time for PMDG films (cast from EDC solution) annealed at various temperatures.

nealing time at various temperatures. The peak height decreased with heat application and reached zero after 3 hr at 220°C or 1 hr at 240°C. This destruction of the cholesteric twisted structure was reflected in the X-ray diffraction pattern. The characteristic pattern of the colored films gradually changed to the hexagonal pattern due to annealing above 200°C. The film annealed at 240°C for 1 hr, clearly showed the same hexagonal pattern as in the film cast from the chloroform solution. The results show that the destruction of the solid cholesteric structure is caused by the molecular rearrangement from the twisted array of α-helices to the parallel one and also, that the anharmonic molecular motion of the individual twisted α-helices may occur above 200°C.

REFERENCES

1. (a) C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956); (b) C. Robison, J. C. Ward, and R. B. Beevers, *Discuss. Faraday Soc.*, **25**, 29 (1958);

    (c) C. Robinson, *Tetrahedron*, **13**, 219 (1961);

    (d) C. Robinson, *Mol. Cryst.*, **1**, 467 (1966).

2. Hl. de Vries, *Acta Cryst.*, **4**, 219 (1951).

3. T. Tachibana and E. Oda, *Bull. Chem. Soc. Jpn.*, **46**, 2583 (1973).

4. A. C. Neville and S. Caveney, *Biol. Rev.*, **44**, 531 (1969).

5. J. Watanabe and I. Uematsu, *Rep. Prog. Polym. Phys. Jpn.*, **19**, 559 (1976).

6. E. T. Samulski and A. V. Tobolsky, *Nature*, **216**, 997 (1967).

7. A. J. Mackinnon and A. V. Tobolsky, *J. Phys. Chem.*, **70**, 1453 (1966).

8. T. L. Fergason, *Mol. Cryst.*, **1**, 293 (1966).

9. C. Robinson and J. C. Ward, *Nature*, **180**, 1183 (1957).