

## **Reversible change in the optical rotatory power of poly(L-glutamate) thin film induced by photochromism of a spiropyran**

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### Summary

When the thin film of poly(L-glutamate) containing 6'-nitroindolino-spiropyran was exposed to uv light (mainly 365nm), measurable change in the optical rotatory power was observed, accompanied with the coloration due to the formation of the photo-merocyanine. The change was reversible upon exposure to visible light (>480nm). The extent of the reversible change of the optical rotatory power was found to depend on the concentration of the spiropyran as well as casting concentration. Discussion was made on the mechanism of the appearance of the optical rotatory power.

### Introduction

While photochromism has been proposed to reversible optical recording (1), discussion has been made on the disadvantages of the photochromic materials for a bit-oriented recording where absorptive readout process destructs the information (2). Many works have been done on the reversible change in physical as well as chemical properties of polymeric materials which show upon photoirradiation reversible change in molecular structure of photochromic unit attached to or mixed with polymers (3). These types of photoresponsiveness may have a potential value for nondestructive readout since the change in the optical properties can be detected with light of wavelength other than that of photochromic reaction.

Reversible change of optical rotatory power may be one of the candidates for nondestructive readout process. Although chiro-optical properties of polymers having azobenzene residue in the side chain have been reported (4), the systems have been so far restricted to the solution phase of the polymers. These situation led us to study the reversible change of optical rotatory power in solid polymer film.

### Experimental

1,3,3-Trimethylindolino-6'-nitrospiropyran was purchased from Tokyo Kasei Co. Poly(benzyl-L-glutamate) of D.P.=130 and 822 were available from Sigma Co. and Miles Yeda Co., respectively. Poly(benzyl-L-glutamate) (PBLG) and poly(amyL-L-glutamate) (PALG) of D.P.=1500 were prepared by the ester exchange of the corresponding methyl ester gifted by Ajinomoto Co., Ltd., according to the literature(5). Optical rotatory power was taken on a Horiba SEPA-200 High Sensitive Polarimeter and was measured at sodium D-line(589nm) unless otherwise noted. For the photoreaction of the spiropyran, a 500W mercury arc lamp was used as a light source, and the combination of color glass filters was employed to obtain uv light(Corning filters 1-59 and 7-59, mainly 365nm) and visible light(Corning filters 1-59 and 3-70, >480nm). Measurements of CD and ORD spectra were performed with use of J-40S and ORD/UV-5(Japan Spectroscopic Co., Ltd.), respectively.

### Sample preparation

After the poly(glutamate) and the spiropyran was dissolved in dioxane or dichloroethane, then viscous solution was left standing in the dark for 24h. Sample films were prepared by following two methods. First, a few drops of the solution was put on a slide glass followed by spreading with use of automatic coating apparatus with a wire bound bar which made by Tester Sangyo Co., Ltd.(Method A). The casting speed was about 2 cm/sec. The thickness of the air-dried film was controlled by exchanging the wire bound bar. Second, the sample solution on a glass plate was spreaded with a glass applicator with 75 $\mu$ m space(Method B). The procedure was carried out in a dry box to obtain a transparent film. Film thickness was measured with a stylus equipment of Rank Taylor Hobson(Talystep) or an outside micrometer of Mitutoyo Mfg., Co.,Ltd. Film thickness obtained by Method B varies widely(3-15  $\mu$ m) and therefore, Method A was almost used unless otherwise noted.

### Measurement of reversible change of optical rotatory power

The poly(glutamate) film containing the spiropyran was exposed with uv light until the absorbance of the photo-merocyanine reached saturated value, and then the optical rotatory power was measured. Since the rate constant of the thermal recovery of the spiropyran in the film state was  $2-6 \times 10^{-4}$ /sec at ambient temperature, measurement of the optical rotatory power carried out as rapidly as possible. Subsequent exposure to visible light was performed until the color due to the merocyanine disappeared completely.

## Results

Indolinospiropyran, one of the most representative photochromic compounds, possesses one chiral carbon atom at the spiro position, whereas the dissymmetry disappears upon the formation of the photo-merocyanine. We have thus initially expected that the optical activity may be introduced when the photochromic reaction of the racemic spiropyran is carried out in chiral reaction medium.

When a dioxane solution of the polymer containing the photochromic

Table 1 Effect of the concentration of the spiropyran on the difference in optical rotatory power of the PALG film before and after exposure to uv light.

Concentration of the spiropyran (mol%)	Difference in optical rotatory power <sup>a)</sup> ( $ \Delta\alpha $ )
1	0.106
2	0.328
4	1.225

a)  $\Delta\alpha$  represents the difference in optical rotation angle before and after exposure to uv light for 80 sec.

Preparation conditions of the film : Method B, casting concentration = 4.5 wt%, solvent = dioxane. Film thickness is about 4 $\mu$ m.

Table 2 Effect of casting concentration of PBLG on the difference in optical rotatory power before and after exposure to uv light.

Casting concentration (wt%)	Film thickness ( $\mu$ m)	Reduced optical rotation <sup>a)</sup> ( $ \Delta\alpha /\mu$ m)
5	0.45	0.344
10	0.90	2.10
15	1.30	2.24

a) The value represents the difference in optical rotatory power before and after exposure to uv light for 60 sec per 1 $\mu$ m film thickness.

Preparation conditions of the film : D.P. of PBLG = 1500, solvent = dichloroethane, concentration of the spiropyran = 2 mol%.

compound was spread on a flat plate and allowed to form air-dried film, the film demonstrated large optical rotation even though the film thickness was very small in  $\mu\text{m}$  order as shown in Tables 1 and 2. This is based on the formation of cholesteric liquid crystal structure. The steep increase in the reduced optical rotatory power above 10wt% in Table 2 is due to the increase in the content of the cholesteric mesophase in PBLG solid film since the cholesteric liquid crystalline mesophase of PBLG is formed above a critical concentration which is a function of solvent, temperature, and degree of polymerization(6). It was found that exposure to the thin film to uv light resulted in the change of optical rotatory power measurable at D-line and that the optical rotatory power altered reversibly, accompanied with the photochromic reaction of the spiropyran.

Careful examination of the reversible change in the optical rotatory power revealed that the extent of the change in optical rotatory power is affected not only by the amount of the spiropyran but essentially also by

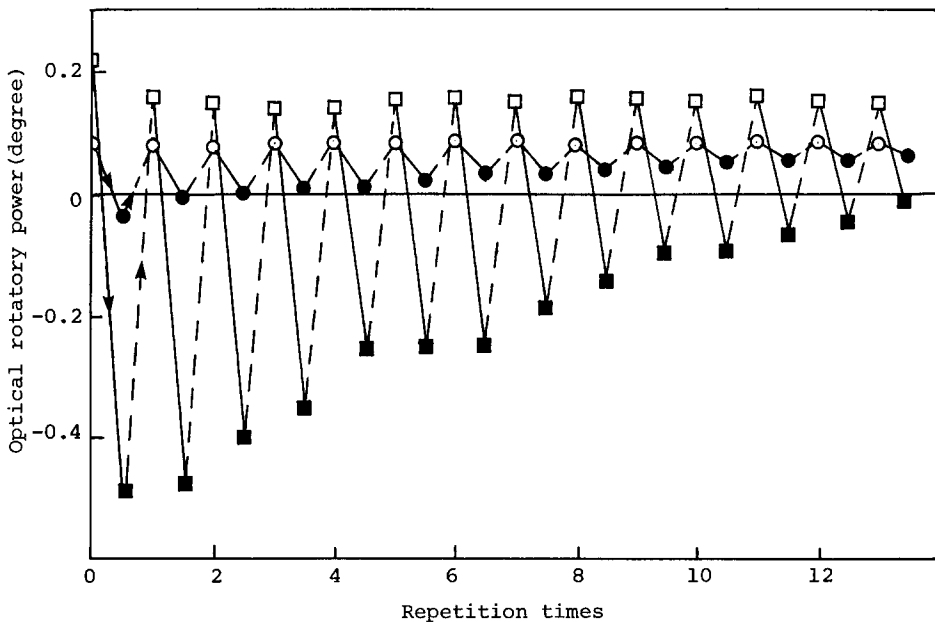


Fig. 1 Reversible change in optical rotatory power of PALG thin films containing the spiropyran of 1 mol% (—○—) and 4 mol% (—□—) in alternative illumination with uv (—) and visible light (---) for 20 sec.

Open and full marks represent colorless and photo-merocyanine form, respectively.

Preparation conditions of the films : Method B, casting concentration = 4.5 wt%, solvent = dioxane. Film thickness : about  $4 \mu\text{m}$ .

casting concentration of poly(glutamate) as shown in Tables 1 and 2. Furthermore, the preparative condition of the glutamate film is important for the reversible change in the optical rotatory power of the polymeric thin film. Slow evaporation of the solvent is necessary condition. Thus, reproducibility was not good if the film was formed by means of spin-coating technique.

Fig. 1 shows the reversible change in the optical rotatory power of the films which were illuminated alternatively with uv and visible light. The difference in the degree of optical rotatory power before and after exposure to uv light became larger when the content of the spiroopyran in the polymer film increased. As seen in Fig. 1, the amplitude of the change of the optical rotatory power decreases as the repetition of the alternative irradiation with light of uv and visible light is accumulated. This is caused by the photo-induced degradation of the spiroopyran as shown in Fig. 2; coloration was scarcely observed on exposure to uv light after 32 times of alternative irradiation. Fig. 1 shows also that the degree of the optical rotatory power of the film after exposure to uv light decreases as the number of alternative irradiation increases whereas the degree of the optical rotatory power of the film after exposure to visible light is almost unchanged. This confirms that the appearance of the optical rotatory power arises from the formation of the photo-merocyanine structure.

### Discussion

The optical rotatory power of the poly(glutamate) film after exposure to uv light is a few degree per  $\mu\text{m}$  as already shown in Table 2. This value

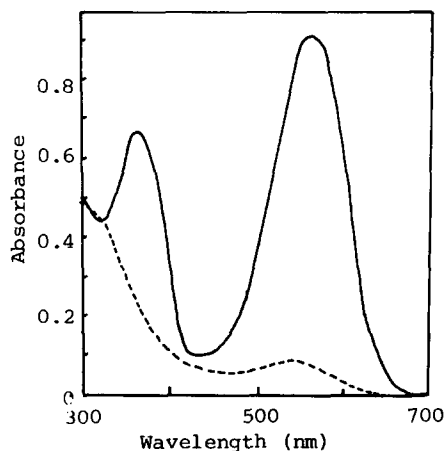


Fig. 2 Absorption spectra of PALG thin film containing the spiroopyran after first cycle (—) and 32nd cycles (-----) alternative illumination.

Preparation conditions:  
 Method B,  
 casting concentration=4.5wt%  
 spiroopyran concentration=4mol%  
 Film thickness is about  $4\mu\text{m}$ .

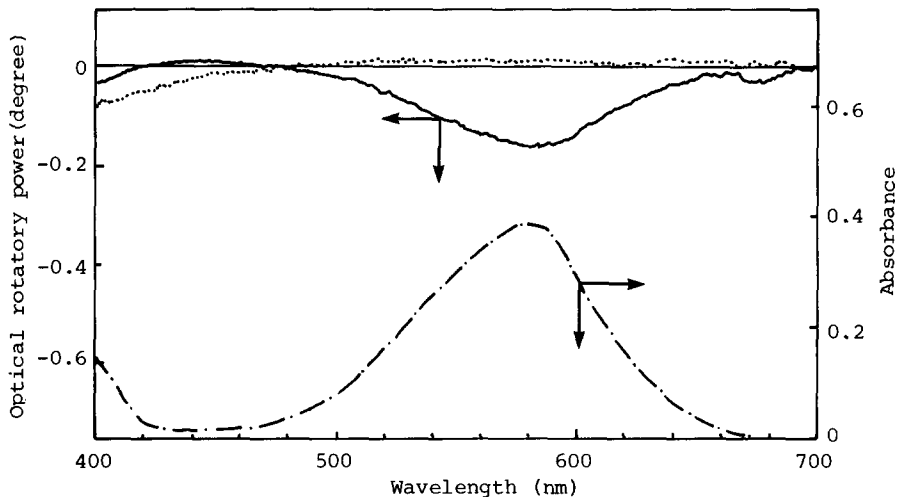


Fig. 3 ORD and absorption spectra of PBLG thin films containing the spiro-merocyanine before (.....) and after (—) uv light exposure. Absorption spectrum (— · —) represents the photo-merocyanine form of the spiro-merocyanine.

Preparation conditions of the film : D.P. of PBLG = 1500, casting concentration = 15 wt%. Film thickness is 1.8  $\mu\text{m}$ .

is extremely large in comparison with optical rotation of ordinary chiral compounds since the observation of  $\alpha_D = 1^\circ$  in  $1\mu\text{m}$  thickness requires to be  $[\alpha]_D = 100000^\circ$  (assume the concentration of  $1\text{ g/cm}^3$  and the cell length of 10 cm). This consideration eliminates the possibility that the reversible change in the optical rotatory power is due to the formation of the optically active spiro-merocyanine in the poly(glutamate) films. The larger value of optical rotatory power of the colored form in comparison with the colorless film confirms that the appearance of the optical rotatory power is caused by the formation of the merocyanine structure. This is supported by the fact that the wavelength of the maximum rotation angle in the ORD spectrum coincides with that of absorption maximum of the photo-merocyanine structure as shown in Fig. 3.

Thus there exist two possibilities to induce the reversible change of optical rotatory power; reversible change of the cholesteric liquid crystal structure caused by the molecular change of the photochromic compound and the interaction of the colored chromophore with the chiral super-molecular structure. The former possibility is very unlikely since the cholesteric pitch of the solid state of polymer seems to be stable(7) and may be hardly altered. At the present stage, we believe that the chiro-optical properti-

es are resulted from the latter mechanism related to the induced circular dichroism(ICD) of the photo-merocyanine doped in cholesteric liquid crystal state. In fact, ICD was observed for the photo-merocyanine in PBLG as shown in Fig. 4.

If the reversible change of optical rotatory power is related to the ICD, this may be general phenomenon induced by photochromism in the polymeric thin film containing cholesteric liquid crystalline structure. The investigation of the reversible change of optical rotatory power using other photochromic systems are now under way.

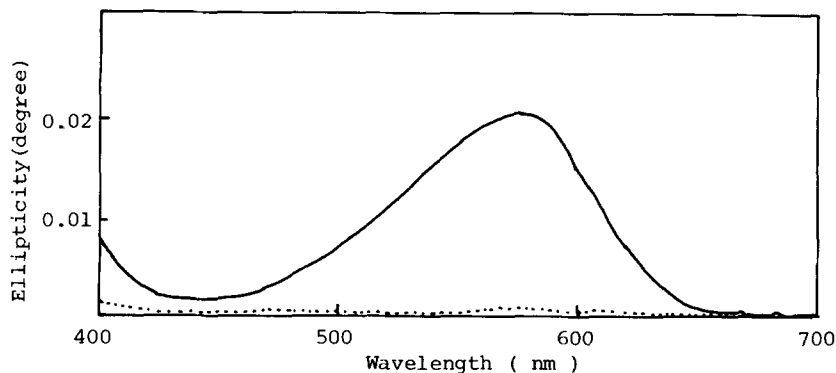


Fig. 4 ICD spectra of PBLG thin film containing the spiroopyran before(.....) and after(—) uv light exposure.

Preparation conditions of the film : D.P. of PBLG = 1500  
 casting concentration = 10 wt%, solvent = dichloroethane.  
 Film thickness is 0.86 $\mu$ m.

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