

## Sensitive Measurements of Photodichroism of Dyes by Spectropolarimeter

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Cyanin dyes dispersed in films of collodion or gelatin were irradiated by monochromatic polarized light of various wavelength and the induced photodichroism-(Weigert Effect) was recorded sensitively as an optical rotatory dispersion curve by a spectropolarimeter. The effect was ascribed to orientation of dye molecules due to anisotropic fading.

The induced optical rotatory power was related to the absorbed energy and the orientation function of unaffected dye molecules with respect to the direction of the transition moment.

The optical rotatory dispersion curves due to photodichroism appeared corresponding to the absorption spectrum of the dye independently of the wavelength of the light for excitation and so called color-correspondence was not observed, while the wavelength of the light for excitation was the shorter, the effect was the stronger.

### INTRODUCTION

It has been known as Weigert Effect<sup>1-4)</sup> that silver halides or photosensitive dyes dispersed in films of collodion or gelatin show optically anisotropic nature or photodichroism when irradiated by polarized light. Formerly the photodichroism was observed with a polarimeter at various frequencies of light. Present authors have found that a recording spectropolarimeter is very sensitive and convenient for measuring the photodichroism, and dichroism caused by molecular orientation was discussed in terms of optical rotatory power.

Further, some experimental discrepancies were found with the former results reported.

### EXPERIMENTAL

#### 1. Specimen

Dyes: Several kinds of photosensitizing dyes among Cyanin groups produced by Japanese Research Institute for Photosensitizing Dyes Co. (Okayama) were used. Following results in this report obtained mainly with Pinachrome (abbreviated to NK 914)<sup>\*\*\*</sup>.

Collodion film: A glass plate (1.5×2.0 cm) was dipped in the 2.5% alcohol-

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ether solution of Collodion, dried at the room atmosphere, dyed in ethanol solution of Pinachrome (2~3 mg/10 ml alcohol) and dried in the room atmosphere. The collodion films stripped from the glass plate were about  $10\mu$  thick.

Gelatin film: Ethanol solution of Pinachrome (2 mg/4 ml alcohol) mixed

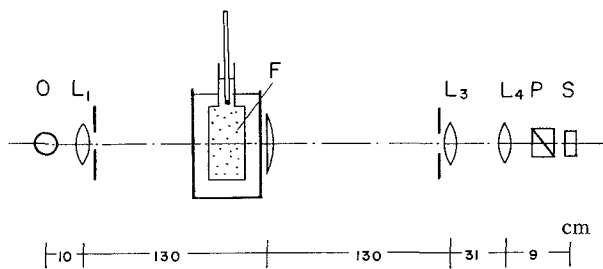


Fig. 1. Apparatus of excitation by polarized light.

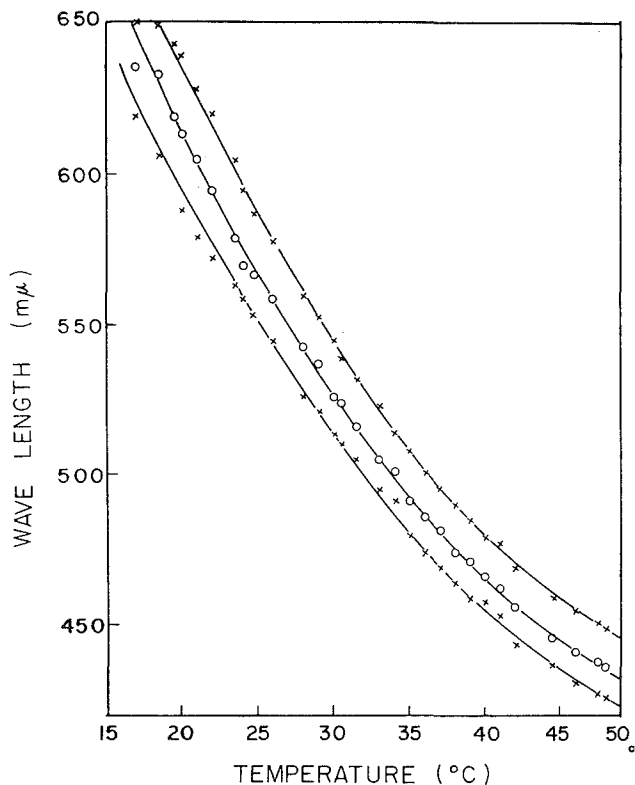
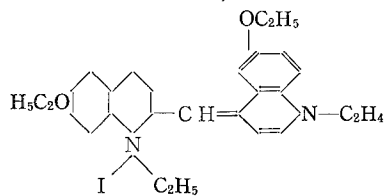


Fig. 2. Range of wavelength transmitted through Christiansen-Weigert filter.

\*\*\* Pinachrome (NK 914)



with 25 ml of 5% aqueous solution of gelatin was poured on a glass plate (15×20 cm), dried at 2~5°C. The film was about 20 $\mu$  thick.

Both kinds of films were cut into strips of a size 1.0×1.5 cm and mounted on paper sheets with a window (0.5×1.0 cm).

## 2. Excitation apparatus

Figure 1 shows an apparatus used for excitation of dyes which is similar to that shown by Shidei.<sup>5)</sup>  $O$  is a xenon lamp (500 W),  $F$  the Christiansen-Weigert filter composed of methyl benzoate and granules of crashed optical glass.<sup>6)</sup> Figure 2 shows the range of the wavelength of the transmitted light through the filter at various temperatures. The center line shows the mean values of the wavelengths.

The filtered light was collimated by lenses  $L_3$  and  $L_4$ , polarized by Glan-Thomson polarizer  $P$  and projected to the specimen  $S$ .

## 3. Measurement of dichroism

The dyed film excited by the polarized light is mounted on a test position of a Yanagimoto Recording Spectropolarimeter ORD-Model 3, so that the direction of the electric vector of the polarized light for excitation rotates at an angle +45° (to the right) or -45° (to the left) with respect to the direction of the electric vector of the polarized light for measurement. Thus a pair of optical rotatory dispersion (ORD) curves is obtained for two kinds of arrangements of the specimen which are symmetrical with respect to that for unexcited specimen. From these curves we get twice the rotatory angle  $2\alpha$ , independent of the optical rotatory power of the film itself. The full scale for the rotatory angle  $\alpha$  can be changed in five steps from  $\pm 2^\circ$  to  $\pm 0.1^\circ$ . The wavelength ranges from 200 to 700  $m\mu$ . The absorption spectrum of the specimen was measured by a Hitachi Spectrophotometer Model 3.

## 4. Theory for measurement

Taking  $OP$  in Fig. 3 as the direction of the electric vector of the polarized light used for measurement,  $OP$  may be considered to be composed of the com-

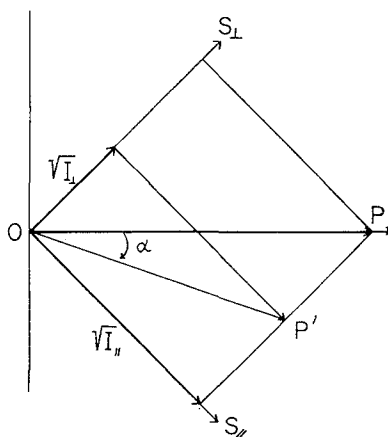


Fig. 3. Optical rotation due to anisotropic absorption.

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ponents  $OS_{//}$  and  $OS_{\perp}$ , which are parallel and perpendicular to the direction of the electric vector of the polarized light for excitation, that is, the direction of excitation of the specimen make angles  $+45^{\circ}$  and  $-45^{\circ}$  to  $OP$  respectively. Taking  $I_{//}$  and  $I_{\perp}$  as the intensity of the transmitted light of the components  $OS_{//}$  and  $OS_{\perp}$ , respectively, of the polarized light for measurement, we have a relation

$$\sqrt{\frac{I_{\perp}}{I_{//}}} = \tan(\pm 45^{\circ} - \alpha) \quad (1)$$

or

$$\log \frac{I_{\perp}}{I_{//}} = 2 \log\{\tan(\pm 45^{\circ} - \alpha)\}, \quad (2)$$

It is assumed that the excited specimen shows no anisotropic nature of refractive indices induced on irradiation of polarized light. Assuming that the intensity of the components of the incident light are equal, from Eq. (2) we have

$$\log \frac{I_{\perp}}{I_{//}} = A_{//} - A_{\perp} \equiv D \quad (3)$$

where  $A_{//}$  and  $A_{\perp}$  are the absorbancies for the polarized light in the directions of  $OS_{//}$  and  $OS_{\perp}$  respectively.  $D$  can be called "Dichroic difference" and can be evaluated by the relations (2) and (3) using the experimental value of  $\alpha$ .

When the direction of excitation is  $+45^{\circ}$  and  $45^{\circ} > \alpha > 0$ ,  $I_{//} > I_{\perp}$  or  $A_{//} < A_{\perp}$ . In this case, the direction of the transition moment tends to orient perpendicularly to that of excitation. This kind of optical rotation or dichroic nature arises from an anisotropic absorption of light due to the molecular orientation, and is distinguished from the optical rotatory power due to the asymmetric carbon structure in the molecule. The latter effect is generally independent of the setting direction of the specimen, while the former depends on it.

Assuming that the dye molecules are oriented uniaxially, and taking  $\theta$  as the average angle between the directions of excitation  $OS_{//}$  and that of the transition moment of the dye molecule\* with respect to the frequency of absorbed

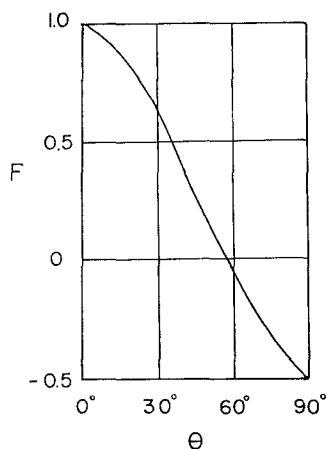


Fig. 4. Relation between  $F$  and  $\theta$ .

\* There are few dyes transition moments of which have been determined.

light, we have

$$F = \frac{1}{2}(3 \overline{\cos^2 \theta} - 1) = \frac{A_{//} - A_{\perp}}{A_{//} + 2A_{\perp}} \quad (4)$$

where  $F$  is called the orientation function. When  $A_{//} \doteq A_{\perp}$ , Eq. (4) is written

$$F = \frac{A_{//} - A_{\perp}}{3A} = \frac{D}{3A}$$

where  $A$  is the absorbance of the same specimen for unpolarized light. Thus  $F$  and  $\theta$  can be estimated by experimental value of  $\alpha$  and  $A$ .

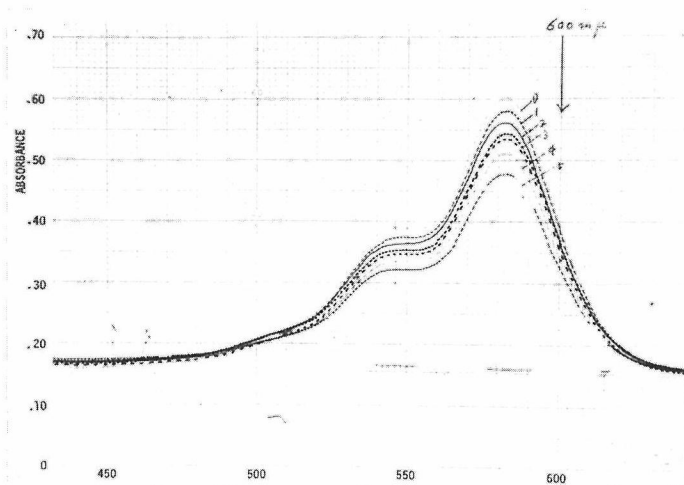


Fig. 5. Absorption spectra of Pinachrome in collodion film during irradiation by polarized light.

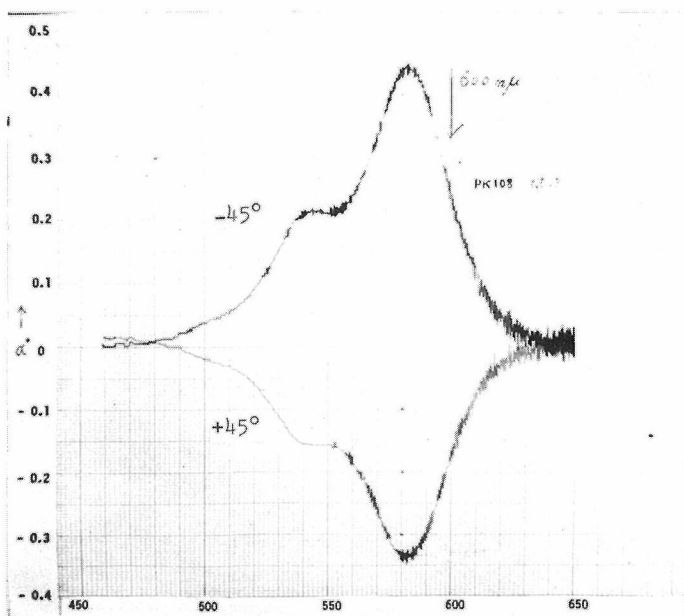


Fig. 6. Optical rotatory dispersion curve of Pinachrome irradiated by polarized light (600 mμ) for 6'33''.

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Figure 4 shows the relation between the numerical value of the orientation function of  $F$  and the angle of orientation  $\theta$ . When the specimen has entirely random orientation or  $\theta=54^{\circ}44'$ ,  $F=0$ .

EXPERIMENTAL RESULTS

1. Photodichroism and absorption spectra

Figure 5 shows the absorption spectra of the collodion film dyed by Pinachrome and irradiated by polarized light with a wavelength of  $600\text{ m}\mu$  for various duration of time. The absorbance decreased almost homogeneously with respect to the wavelength. In other words, the color of the dye fades down with time without change in the tone and at the same time, the dichroic changes appear as the optical rotatory dispersion as is shown in Fig. 6 which was obtained from the specimen irradiated for the time  $6'33''$ . The symmetrical ORD curves were obtained with the specimen, the direction of excitation rotated by  $+45^{\circ}$  and  $-45^{\circ}$  with respect to the direction of the polarized light for measurement. Figure 5 means that the dye molecules with the transition moment parallel to the direction of excitation are decomposed photochemically and fade down on polarized irradiation resulting in perpendicular orientation of the remaining molecules as

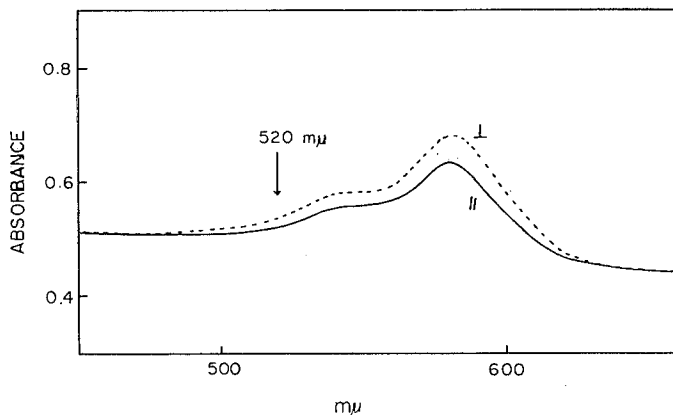


Fig. 7. Polarized spectra of NK 914 irradiated at  $520\text{ m}\mu$  for 40 min.

Table 1. Ranges for Measurement.

Angle of Optical Rotation	Dichroic Difference
$\alpha^{\circ}$ (degree)	$D(=A_{//}-A_{\perp})$
0.001°	0.00003
0.005°	0.00015
0.010°	0.00030
0.050°	0.00151
0.100°	0.00303
0.500°	0.01516
1.000°	0.03032
2.000°	0.06064

was suggested by Weigert *et al.*

The dichroism can be detected as the polarized spectrum (Fig. 7) which is not so sensitive as compared with the ORD method shown above. Table 1 shows the sensitivity ranges for measurements of dichroism comparing different methods. The angle of optical rotation is exceedingly sensitive in comparison with the dichroic difference observed directly. Arrows in Table 1 show the measurable ranges of scales of the recording paper for various kinds of instruments.

## 2. Photodichroism and energy absorbed

As is shown above, the photodichroism is induced by absorption of polarized light and accordingly that effect depends upon the absorbed quantity of light energy.

The energy  $E_t^\lambda$  absorbed by the dye during the time ( $t$ ) of excitation at a definite wavelength  $\lambda$  of polarized light may be given by a relation :

$$E_t^\lambda = E_0^\lambda \int_0^t \left(1 - \frac{I}{I_0}\right) dt \quad (6)$$

where  $E_0^\lambda$  is the intensity of the light source given for excitation, and  $I/I_0$  is the transmittance of the specimen excited.

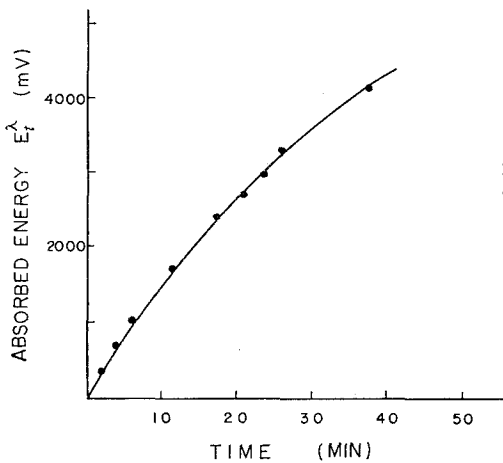


Fig. 8. Absorbed energy at 580  $m\mu$  during polarized irradiation at 615  $m\mu$ .

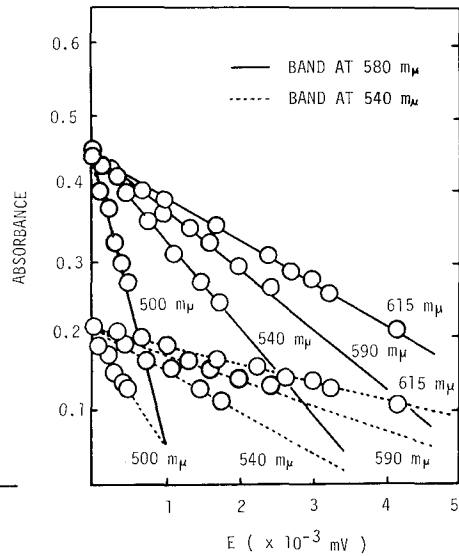


Fig. 9. Relation between absorbance and absorbed energy at various wavelengths.

The relative value of  $E_0^\lambda$  was measured by a photocell in mV. Figure 8 shows an example of the integrated value of relative absorbed energy during the time of excitation at the wavelength 615  $m\mu$ . Figure 9 gives the relations between the absorbances of the specimen at the wavelengths 540 and 580  $m\mu$  and the absorbed energy obtained for various wavelengths of excitation, 500, 540, 590 and 615  $m\mu$  respectively. These results show that the absorbances or the concentration of the dye in the specimen decrease almost linearly with the

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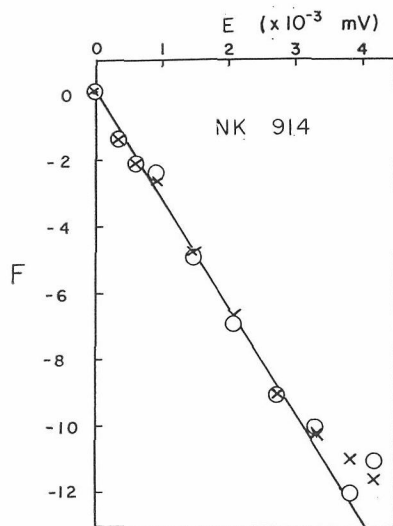


Fig. 10. Relation between orientation function between energy absorbed at 600  $m\mu$ .

absorbed energy and the wavelength of the polarized light for excitation is the shorter, the effect is the stronger. The latter fact does not agree with the result previously reported by Weigert *et al.* that the light of longer wavelength was more effective for excitation and peak of the effect appeared at the wavelength of the light irradiated *i.e.* color correspondence. In Fig. 10, the orientation functions calculated from the photodichroism at the wavelengths 540 (O) and 580 ( $\times$ )  $m\mu$  induced by polarized irradiation at 600  $m\mu$  are plotted against the absorbed energy.

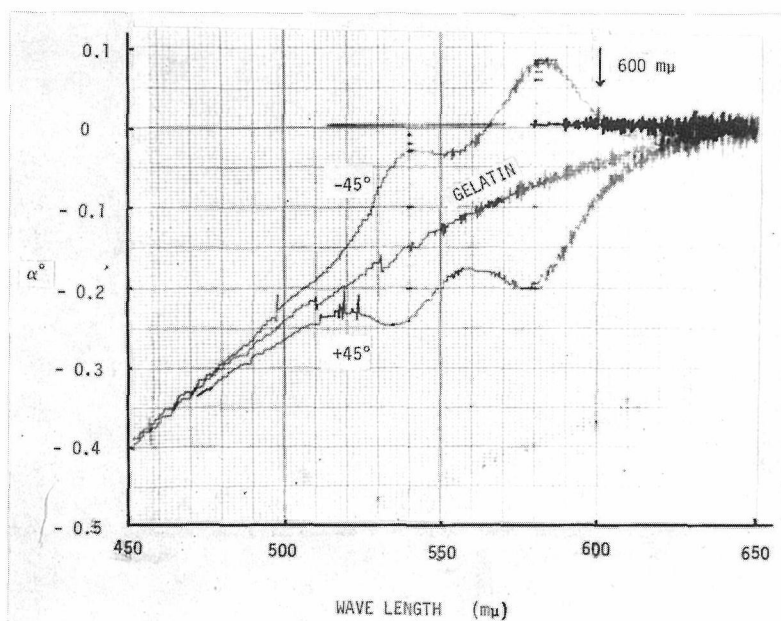


Fig. 11. ORD curves of Pinachrome in gelatin film irradiated by polarized light (590  $m\mu$ ).



Both orientation functions obtained at different wavelength almost coincide with each other suggesting that different parts of the dye molecule are affected in the same way by irradiation of polarized light.

#### 4. Photodichroism in gelatin films

When the specimen is composed of optically active material, gelatin for instance, the pair of ORD curves of the dye appears symmetrically along the optical rotatory dispersion curve of gelatin as is shown in Fig. 11.

#### 5. Relaxation of photodichroism

It was reconfirmed that the photodichroism relaxes gradually for several days as was reported by Yamamoto previously.<sup>8)</sup> In this report, the data of photodichroism was taken about three minutes after excitation.

### CONCLUSION

The experimental results are summarized as follows :

1) Pinachrome, a dye of cyanin series, dispersed in collodion shows photodichroism after irradiation of polarized light, which can be recorded sensitively by means of a spectropolarimeter.

2) The photodichroism is induced by polarized light absorbed by dye and appears corresponding with its absorption spectrum. Reported color correspondence is not observed.

3) Polarized light of shorter wavelength is more effective than that of longer wavelength.

4) In the gelatin film, the photodichroism of dye appears overlapping with the optical rotatory dispersion of gelatin, but they can be distinguished clearly with each other.

5) The photodichroism is ascribed to anisotropic fading of dye molecule induced by absorption of polarized light parallel to the transition moment of the dye molecule and to orientation of dye molecule remaining unchanged.

6) It was reconfirmed that the photodichroism relaxes gradually as is reported previously.

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