Sensitive Measurements of Photodichroism of Anthracene by Spectropolarimeter

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Anthracene molecules dispersed in polyvinylchloride (PVC) films were irradiated by polarized light of wavelength 257 or 383 nm. The induced photodichroism (Weigert effect) was recorded sensitively by means of a spectropolarimeter. The sample irradiated by polarized light of 257 nm shows perpendicular dichroism at 257 nm and parallel dichroism at 383 nm. While, the sample irradiated by polarized light of 383 nm shows parallel dichroism at 257 nm and perpendicular dichroism at 383 nm. The several bands in the region of 300–400 nm were analized as superposition of absorptions polarized to the short axis direction of the anthracene molecule upon those polarized to the long axis direction of the molecule.

INTRODUCTION

When silver halides or photosensitive dyes dispersed in polymer films are irradiated by polarized light, those show optically anisotropic nature. This phenomenon is well known as photodichroism or Weigert effect,[1] which is ascribed to the anisotropic orientation of the crystals or molecules as the results of anisotropic photochemical reaction.

R. Gotoh and the present authors investigated previously the effect on a system of photosensitive dyes dispersed in collogion or gelatine films.[2] Many dyes or photosensitive dyes have complicated structures, and assignments of their absorption bands are scarcely obvious. Therefore, the quantitative interpretation of the effect has not been established yet.

Anthracene molecule has high symmetry and the assignments of the absorption bands have determined with confidence. The present authors choose it as a sample for a quantitative investigation.

EXPERIMENTAL

The polymer used in this study was commercially available polyvinyl chloride (PVC) having the degree of polymerization of 1000 in average. Zonerefined anthracene and the purest grade of cyclohexanone (Tokyo Kasei Co. LTD) were used without further purification. The film sample was prepared from cyclohexanone solution of mixture of anthracene and PVC (0.03–1.0 W %) by casting on a glass plate at room temperature. Before use, the films were washed to remove cyclohexanone with mixed solvent of alcohol and water at 70°C for one hour, and then dried at

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90°C for two fours in a dry box. The film shows no absorption of the solvent at 280 nm, and has thickness of about 20 μm. The film was cut into a small rectangular strip (1.0×1.5 cm^2), and mounted on a sheet holder with a window (0.5×0.5 cm^2). These films were comfirmed to be optically isotropic by using a spectropolarimeter.

The PVC film containing anthracene was irradiated by monochromatic polarized light. The light was obtained by using an Ushio Electric xenon short arc lamp model UXL-500DV and Baush & Lomb grating monochromator model 33–86–45 and a Glan-Thomson polarizer. Wavelength of the light for irradiation was accorded with each of the two strong absorption bands of anthracene at 257 and 383 nm. The entrance and exit slits of monochromator were set on 1 mm that gives a optical slit width of 3.1 nm. This width is sufficiently narrow compared with half band widths of the absorption bands, and provides sufficient intensity for irradiation. The light passed through the monochromator and the polarizer was properly focused on the sample film using a quartz lens.

The method of the dichroic measurements was the same as that in a previous work,[2] in which a Yanagimoto recording spectropolarimeter model 185 was used. If the rotatory angle α^λ of the polarized light is small, dichroic difference D^λ at a wavelength λ can be expressed by the following relation,

$$D^\lambda = A^\lambda_{//} - A^\lambda_{\perp} = 2 \log \tan (45° - \alpha^\lambda) = -0.0303\alpha^\lambda \qquad (1)$$

were $A^\lambda_{//}$ and $A^\lambda_{\perp}$ are the absorbances for the light polarized parallel and perpendicular, respectively, to the direction of the electric vector of the polarized light used for irradiation. When the electric vector of the incident light for measurement rotates toward the direction of the electric vector of the polarized light for irradiation, α^λ is defined to be positive.

The absorption spectrum in the region 210 to 500 nm was recorded by a Hitachi spectrophotometer model 3.

THEORY

Absorption spectrum of anthracene has been investigated by many workers using the quantum mechanical and the experimental methods.[4~6] It has been shown that the electric vector of the transition must lie in the plane of the molecule. The 257 nm band, the most intense band, has been assigned to the ^1B_b band, due to $^1B_{1u} \leftarrow ^1A_{1g}$ transition. The transition moment is along the long axis of the molecule. The band at 383 nm has been assigned to the ^1L_a band, due to $^1L_a \leftarrow ^1A_{1g}$ transition, polarized along the short axis.[7] The several bands in the 300–370 region have been interpreted as superposition of the bands polarized to the direction of the short axis (^1L_a) upon those polarized to the direction of the long axis (^1L_b) of the molecule.[8]

The cartesian coordinate system with X, Y, and Z is adopted to the sample shape as shown in Fig. 1. It will now be chosen that the XY-plane coincides with the plane of the film, and the direction of propagation of the light for irradiation as well as for measurment of dichroism coincides with the Z axis. The direction of the electric vector of the irradiating light is chosen to be parallel to the Y axis . The
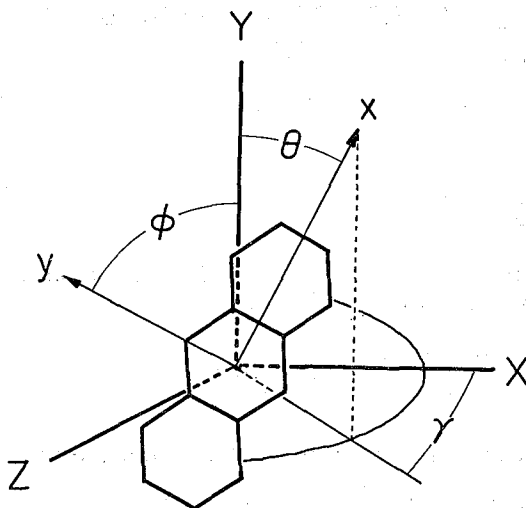
Fig. 1. Coordinate systems and Eulerian angles.

long and short axes of anthracene molecule coincide with the x and y axes, respectively. The orientation of the molecule is defined by using Eulerian angles θ, ϕ and γ.

The molar extinction coefficients at a given wavelength for the long and short axes of the molecule are defined to be K_l^λ and K_s^λ, respectively. These are related with the optical densities, $A_{//}^\lambda$ and $A_\perp^\lambda$, which are observed by the polarized light with the electric vectors parallel to the Y and X axes, respectively. The relations are given by

$$A_{//}^\lambda = (K_l^\lambda \,\overline{\cos^2 \theta} + K_s^\lambda \,\overline{\cos^2 \phi})Cd \tag{2a}$$

$$A_\perp^\lambda = \frac{1}{2}(K_l^\lambda \,\overline{\sin^2 \theta} + K_s^\lambda \,\overline{\sin^2 \phi})Cd \tag{2b}$$

where C and d are the concentration and the thickness of the sample, respectively. The coefficient 1/2 in equation (2b) comes from an average about the Y axis which is principal axis of the uniaxial orientation. The usual extinction coefficient K^λ for random orientation relates with K_l^λ and K_s^λ as follows:

$$K^\lambda = \frac{1}{3}(K_l^\lambda + K_s^\lambda) \tag{3}$$

The decreasing of concentration by irradiation is assumed to be proportional to the energy of the light absorbed by the molecule during irradiation. The absorbed energy is proportional to the square of the direction cosine between the direction of transition moment of a band and that of electric vector of the irradiating beam. Then, the parameters $P(l)$ and $P(s)$, which denote the decrease of concentration by the irradiation of the light whose wavelength were in agreement with that of the long and short axes transition, respectively, are introduced. The ratio of the resultant concentration C to the original concentration C_0 is then given by an integration of the form

(215)

$$\frac{C}{C_0} = \frac{\int (1 - P(l) \cos^2 \theta - P(s) \cos^2 \phi) d\Omega}{\int d\Omega}$$

$$= 1 - \frac{1}{3} P(l) - \frac{1}{3} P(s) \tag{4}$$

where

$$d\Omega = \sin \theta d\theta d\phi$$

The ratio i of the concentration decreased by irradiation to that of the original concentration can also be given by

$$i = \frac{C_0 - C}{C_0} = \frac{1}{3} P(l) + \frac{1}{3} P(s) \tag{5}$$

This ratio i can be obtained experimentally from the absorbance observed by unpolarized light for the original sample A_0^λ and these measured by polarized light for the irradiated sample $A_{//}^\lambda$ and $A_\perp^\lambda$.

$$i = \frac{A_0^\lambda - \frac{1}{3}(A_{//}^\lambda + 2A_\perp^\lambda)}{A_0^\lambda} \tag{6}$$

The averages of the squares of the cosines and sines of the angles formed by Y axis against the x and y axes are found to be

$$\overline{\cos^2 \theta} = \frac{\int (1 - P(l) \cos^2 \theta - P(s) \cos^2 \phi) \cos^2 \theta d\Omega}{\int (1 - P(l) \cos^2 \theta - P(s) \cos^2 \phi) d\Omega}$$

$$= \frac{C_0}{C}\left(\frac{1}{3} - \frac{1}{5} P(l) - \frac{1}{15} P(s) \right) \tag{7a}$$

$$\overline{\sin^2 \theta} = \frac{\int (1 - P(l) \cos^2 \theta - P(s) \cos^2 \phi) \sin^2 \theta d\Omega}{\int (1 - P(l) \cos^2 \theta - P(s) \cos^2 \phi) d\Omega}$$

$$= \frac{C_0}{C}\left(\frac{2}{3} - \frac{2}{15} P(l) - \frac{4}{15} P(s) \right) \tag{7b}$$

$$\overline{\cos^2 \phi} = \frac{\int (1 - P(l) \cos^2 \theta - P(s) \cos^2 \phi) \cos^2 \phi d\Omega}{\int (1 - P(l) \cos^2 \theta - P(s) \cos^2 \phi) d\Omega}$$

$$= \frac{C_0}{C}\left(\frac{1}{3} - \frac{1}{15} P(l) - \frac{1}{5} P(s) \right) \tag{7c}$$

$$\overline{\sin^2 \phi} = \frac{\int (1 - P(l) \cos^2 \theta - P(s) \cos^2 \phi) \sin^2 \phi d\Omega}{\int (1 - P(l) \cos^2 \theta - P(s) \cos^2 \phi) d\Omega}$$

$$= \frac{C_0}{C}\left(\frac{2}{3} - \frac{4}{15} P(l) - \frac{2}{15} P(s) \right) \tag{7d}$$

Using equations (2), (7) and the relation $A_0^\lambda = K^\lambda C_0 d$, dichroic difference $D^\lambda (= A_{//}^\lambda - A_\perp^\lambda)$ at a given wavelength (λ) is given by

$$D^\lambda = \frac{1}{15} A_0^\lambda \left\{ P(l) \frac{(K_s^\lambda - 2K_1^\lambda)}{K^\lambda} + P(s) \frac{(K_1^\lambda - 2K_s^\lambda)}{K^\lambda} \right\} \qquad (8)$$

When there is a band polarized to the long axis and the molecule is irradiated by the polarized light in accordance with the wavelength of the band, $P(s)$ in the above equations should be zero. The dichroic difference $D^\lambda(l)$ in this case becomes

$$D^\lambda(l) = \frac{P(l)}{15} A_0^\lambda \left(\frac{K_s^\lambda - 2K_1^\lambda}{K^\lambda} \right) \qquad (9)$$

and the value of $P(l)$ is obtained from equations (5) and (6)

$$P(l) = \frac{3A_0^\lambda - (A_{//}^\lambda(l) + 2A_\perp^\lambda(l))}{A_0^\lambda}$$

Similarly, in the case of irradiation by the polarized light in accordance with wavelength of the band polarized to short axis of a molecule, the equation becomes

$$D^\lambda(s) = \frac{P(s)}{15} A_0^\lambda \left(\frac{K_1^\lambda - 2K_s^\lambda}{K^\lambda} \right) \qquad (10)$$

and also

$$P(s) = \frac{3A_0^\lambda - (A_{//}^\lambda(s) + 2A_\perp^\lambda(s))}{A_0^\lambda}$$

In equations (9) and (10), the values of A_0^λ, $D^\lambda(l)$, $D^\lambda(s)$, $P(l)$ and $P(s)$ can be obtained from the experiments. Thus the plots of $D^\lambda(l)$ vs. $P(l)A_0^\lambda(l)/15$ and $D^\lambda(s)$ vs. $P(s)A_0^\lambda(s)/15$ give the straight lines having the slopes of $H^\lambda(l)$ and $H^\lambda(s)$, respectively, which are difined as follows.

$$H^\lambda(l) = \frac{K_s^\lambda - 2K_1^\lambda}{K_0^\lambda} = \frac{3(K_s^\lambda - 2K_1^\lambda)}{K_1^\lambda + K_s^\lambda} \qquad (11a)$$

$$H^\lambda(s) = \frac{K_1^\lambda - 2K_s^\lambda}{K_0^\lambda} = \frac{3(K_1^\lambda - 2K_s^\lambda)}{K_1^\lambda + K_s^\lambda} \qquad (11b)$$

If the wave length for measurement λ coincides with the wavelength of absorption polarized to the long- or short-axis of the molecule, these values would be given as follows.

$$H^l(l) = -6 \qquad (12a)$$
$$H^s(s) = 3 \qquad (12b)$$
$$H^l(s) = 3 \qquad (12c)$$
$$H^s(s) = -6 \qquad (12d)$$

In this theory, it is assumed that the molecular orientation is fixed during the irradiation and the observation of dichroism. If the molecule librates about the three axes of the molecule, values in equations (12a)-(12b) are in the range from 3 to -6.

RESULTS AND DISCUSSION

Figure 2 illustrates the absorption spectrum of anthracene dispersed in the PVC film. This spectrum is quite similar to that in various solutions of low concentration but differs from that in crystalline state.[9~10] Therefore, it may be analogized that anthracene molecules are dispersed monomolecularly in the PVC film.

Figure 3 shows an optical rotatory dispersion (ORD) curve of a sample irradiated by polarized light with a wavelength of 257 nm. The dotted line is the curve for original sample and shows no dichroism before irradiation. The solid and broken lines show the symmetrical ORD curves obtained by rotation of the direction of the electric vector of irradiation by $+45°$ and $-45°$, respectively, with respect to the direction of the electric vector of the polarized light for measurement. Solid line ($+45°$) indicates negative values in the regions of longer wavelength than 346 nm and in the region shorter than 227 nm, and positive values in the region from 346 to 227 nm. The broken line shows reverse of the solid line. In the other words, the sample shows parallel dichroism in the region above 346 nm and in that below 227 nm, and perpendicular dichroism in the region from 346 to 227 nm.

The ORD curves of the original sample and that of the sample irradiated with the polarized light of 383 nm are shown in Fig. 4. In this case, the solid line ($+45°$) shows positive values (perpendicular dichroism) in the region above 297 nm and in the region below 227 nm, and negative values (parallel dichroism) in the region from 297 to 227 nm.

The plots of D^{257} (257) $vs.\ P(257)A_0^{257}/15$ for various irradiation times are shown
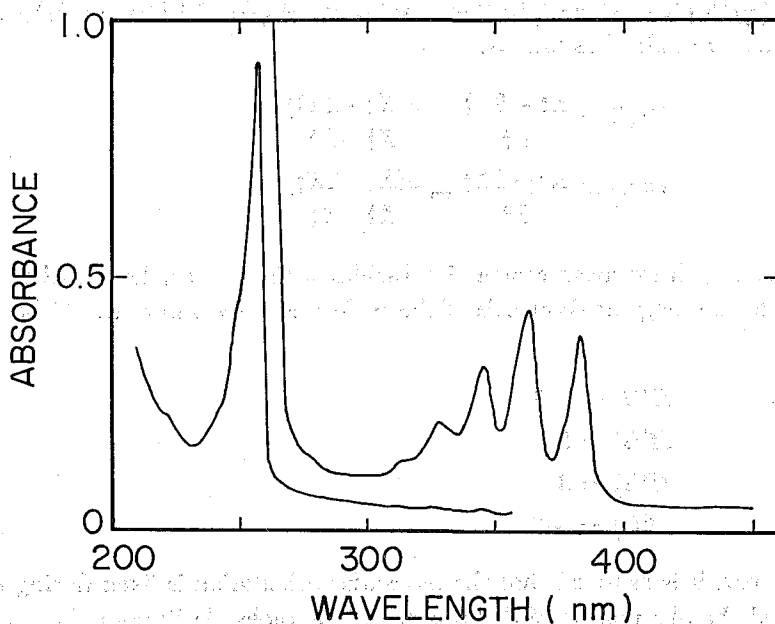

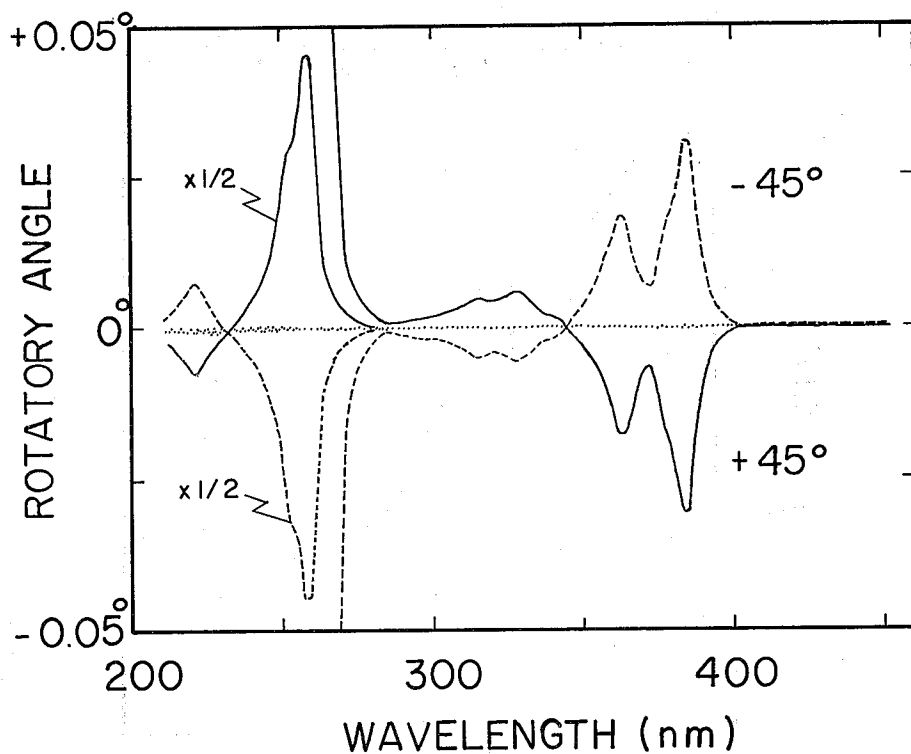Fig. 2. Absorption spectrum of anthracene dispersed in PVC film.

Fig. 3. Optical rotatory dispersion (ORD) curves of the sample irradiated with polarized
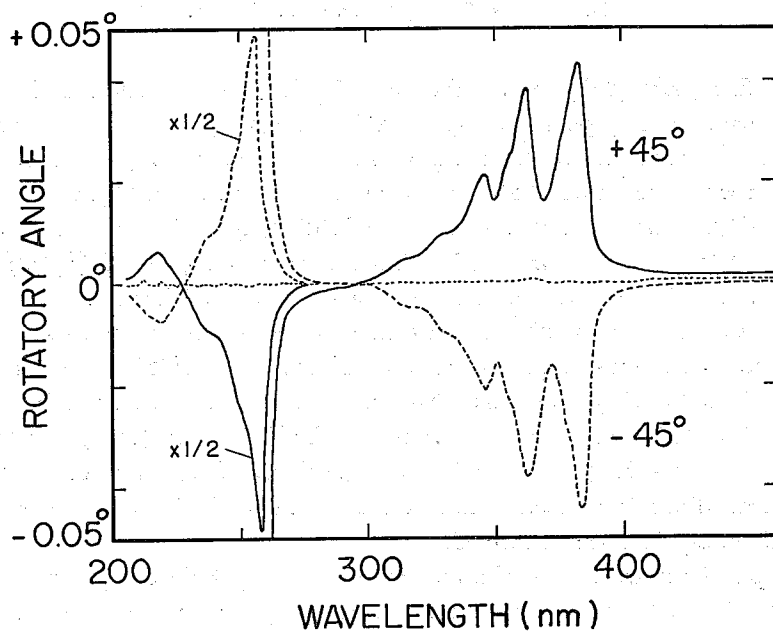light at 257 nm.

Fig. 4. Optical rotatory dispersion (ORD) curves of the sample irradiated with polarized
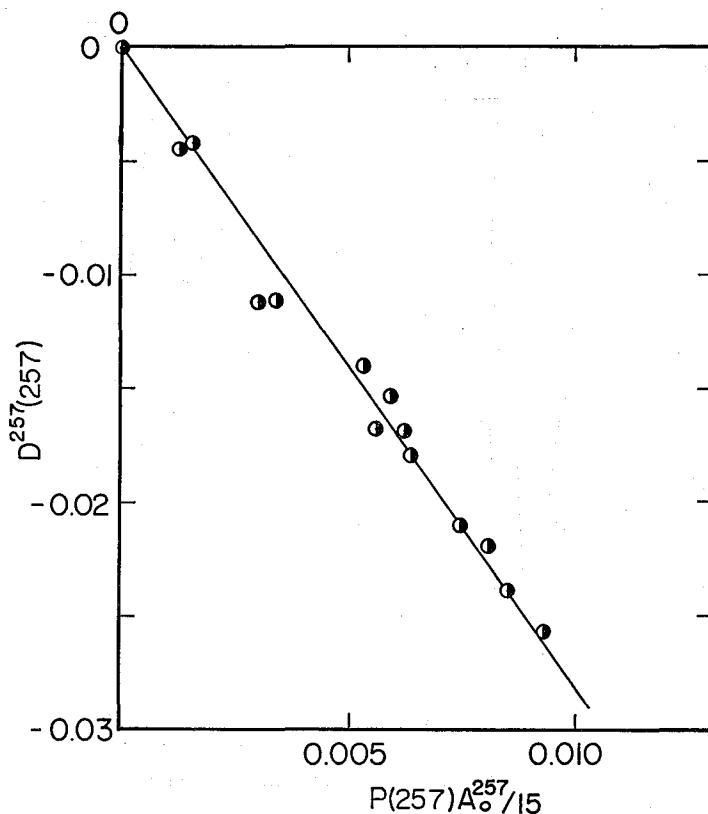light at 383 nm.

Fig. 5.   Plots of D^{257} (257) $vs.$ $P(257)A_0^{257}/15$.

in Fig. 5.   Here, D^{257} (257) denotes the dichroic difference measured at 257 nm for the sample irradiated by polarized light of 257 nm, $P(257)$ is the parameter showing the decrease of concentration by the irradiation of polarized light of 257 nm, and A_0^{257} is absorbance measured at 257 nm for original sample.   In Fig. 6, the dichroic differences $D^\lambda(257)$ are plotted as a function of $P(257)A_0^\lambda/15$.   The plots of $D^\lambda(383)$ $vs.$ $P(383)$ $A_0^\lambda/15$ for various irradiation time are given in Fig. 7. $D^{257}(383)$ was not obtained, because it needs very long time to produce photodichroism.

If the bands at 257 and 383 nm are assumed to be the purely long-axis and purely short-axis polarized transitions, respectively, $H^\lambda(257)$ and $H^\lambda(383)$ are obtained by using equations (9)–(11) and Figs. (5)–(7).   The results are shown in Table I. Equations (12a)-(12d) show that the values of $H^{257}(257)$, $H^{383}(257)$, $H^{257}(383)$ and $H^{383}(383)$ could be -6, $+3$, $+3$ and -6, respectively, if the assumption of purely polarized transitions is correct.   However, the values obtained in the experiment differ considerably from that expected.

The optical slit width and the incompleteness of polarized light was checked. The optical slit width was measured experimentally by using the mercury arc source, and was obtained to be 3.1 nm, that was sufficiently narrow to prevent absorption of the neighboring band.   The polarized beam passed through the sample was closed
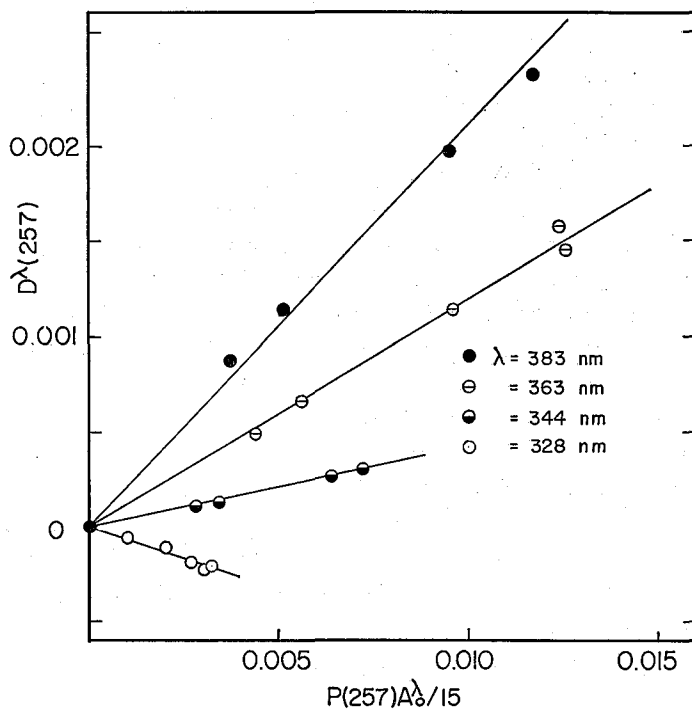
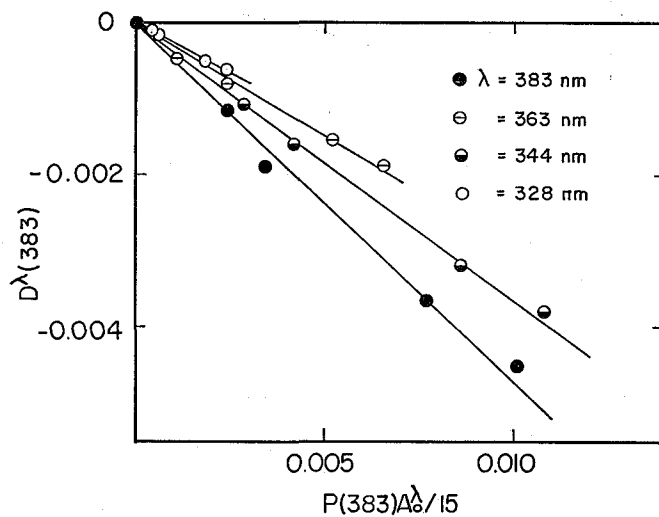Fig. 6. Plots of $D^\lambda(257)$ *vs.* $P(257)A_0{}^\lambda/15$.

Fig. 7. Plots of $D^\lambda(383)$ *vs.* $P(383)A_0{}^\lambda/15$.

Table I. The values of H^λ (257) and H^λ (383) for Each Band

Wavelength (nm)	383	363	344	328	257
H^λ (257)	0.21	0.12	0.04	−0.07	−2.80
H^λ (383)	−0.48	−0.37	−0.30	−0.27	*

* the positive value is observed.

completely with an analizer placed in front of the detector.

The relaxation effect of the orientation after irradiation was slightly detected, but the relaxation time was very long, order of some weeks, and did not affect on dichroic measurements.

Deviation of the experimental value of $H^{257}(257)$ (-2.8) from the theoretical values (-6.0) might be caused by librational motions of the anthracene molecule during irradiation and measurment. However, deviation of $H^{383}(383)$ (-0.48) from the theoretical value (-6.0) seems to be too large to interprete by librational motions.

In a previous paper[3], dichroic measurements were made of anthracene in PVC films stretched at various degree of elongation. The rations of extinction coefficient for the long $(a=K_l^\lambda/K_l^\lambda+K_s^\lambda)$ and the short $(b=K_s^\lambda/K_l^\lambda+K_s^\lambda)$ axes to the total extinction coefficient at wavelength λ are estimated on the assumption that the bands at 257 and 383 nm are completely polarized.

In this work, it is assumed that the 257-nm band is due to a completely polarized transition along the long axis of anthracene molecule, but the 383-nm band is due to a superposed band of a polarized transition along long axis upon a polarized transition along short axis. On this assumption, equation (9) can be used, but equation (10) can not be used.

The plots of $(A_{//}^\lambda(257)-A_\perp^\lambda(257)/(A_{//}^\lambda(257)+2A_\perp^\lambda(257))$ with respects of absorbed
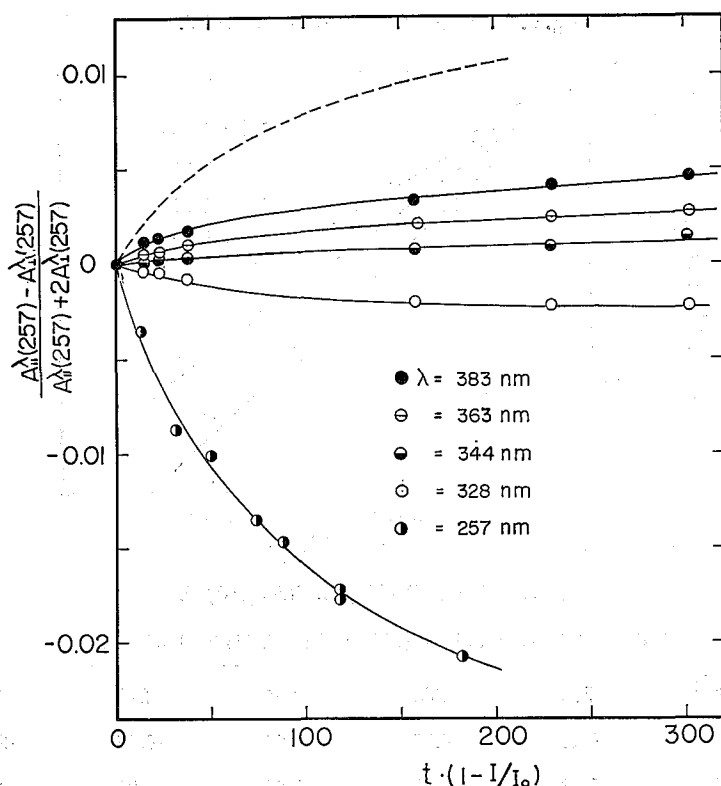

Fig. 8. Plots of $(A_{||}{}^\lambda(257)-A_\perp{}^\lambda(257))/(A_{||}{}^\lambda(257)+2A_\perp{}^\lambda(257))$ vs. $t(1-I/I_0)$

energy by the sample are illustrated in Fig. 8. The absorbed energy is proportional to the time t(hr) of irradiation and to the quantities $(1-I/I_0)$, where I_0 and I are intensities of the incident and the transmitted lights. In the case of photodichroism, it is not necessary to consider the orientation of the plane of anthracene molecule, although the orientation should be considered in the case of stretching of polymer film.[3] Therefore, the orientation function of the long axis (F_1) is related with that of the short axis (F_s) and that of normal to molecular plane (F_π).

$$F_1 = -2F_s = -2F_\pi$$

Table II shows the ratios of extinction coefficient for the long (a) and short axes (b) to the total extinction coefficient at wavelength λ, which are estimated in this work. These values seems to be more reliable than those obtained in a previous work.[3]

Table II. The Parameters a and b for Each Band of Anthracene

Wavelength (nm)	383	363	344	328	257*
a	0.21	0.26	0.31	0.40	1.00
b	0.79	0.74	0.69	0.60	0

* see the text.

ACKNOWLEDGMENT

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