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Optical Rotatory Dispersion Induced by Molecular Orientation

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The orientation of anthracene dispersed in a stretched film of polyvinylchloride (PVC) was recorded as an optical rotatory dispersion curve by means of a spectropolarimeter at various degree of elongation of the film. The orientation of the polymer molecules was measured by the polarized infrared spectrum.

The orientation functions of anthracene was compared with those of PVC with respect to the transition moments of their absorption bands.

It was concluded that some definite relations were held between the orientation functions of anthracene and that of the polymer during elongation of the polymer film.

INTRODUCTION

In the previous paper,¹⁾ the present authors reported that the photodichroism of a cyanin dye induced by polarized irradiation was recorded sensitively as an optical rotatory dispersion (ORD) curve by means of a spectropolarimeter. The photodichroism was ascribed to the orientation of dye molecules due to anisotropic photochemical reaction. This result suggests that the molecular orientation caused by various methods can be discussed in terms of optical rotatory power.

Several kinds of method have been used for investigation of molecular orientation, for instance, birefringence, x-ray diffraction, dichroism of dyes, and polarized visible or infrared absorption spectrum.

In order to discuss the orientation of amorphous parts in polymers, dichroism of dyes in fibers or films of polymers has been investigated by means of a polarimeter or a spectrophotometer with a polarizer.²⁻⁵⁾ But both methods are not so sensitive for molecular orientation and there are few dyes transition moments of which have been determined.

As the transition moments of the absorption of anthracene has been determined with some confidence, the present authors used anthracene in order to investigate the relation between dichroism and molecular orientation.

The ORD due to orientation of anthracene in stretched polyvinylchloride films was observed by means of a spectropolarimeter. The dichroism of anthracene was measured by polarized absorption spectra. The orientation of polyvinylchloride (PVC) was measured by the polarized infrared spectra. The orientation functions of anthracene and PVC were compared with respect to the transition

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moments of their absorption bands.

EXPERIMENTAL

1. Specimen

Polyvinylchloride (PVC) was commercial material from Wako Pure Chemical Industries, L. T. D. Anthracene was zone-refined chemical pure one from Tokyo-Kasei L. T. D. Anthracene (4 mg) and PVC (300 mg) were dissolved into tetrahydrofuran (10 ml), developed on a glass plate (10×15 cm) and dried at the room temperature. The stripped film was ca. 20 μ thick. The film was cut into a small rectangular strip (1.0×1.5 cm) and mounted on a stretching apparatus. The specimen was elongated to various lengths in hot water at 80°C and cooled at the room atmosphere.

2. Procedure

The PVC specimen was fixed in the test position of Nihon-Bunko (JASCO) spectropolarimeter Model ORD/UV-5, so that the direction of stretching makes an angle +45° (to the right) or -45° (to the left) to the direction of the electric vector of the polarized light for measurement as shown in the previous paper. The full scale for measurement of the optical rotatory angle α is changeable within the range below $\pm 2^\circ$. The maximum sensitivity is $\pm 0.0005^\circ$.

When the optical rotatory angle exceeds 1° on large elongation over 50%, orientation of anthracene was discussed in terms of polarized spectra obtained with the same instrument. Orientation or dichroism of PVC was measured by polarized infrared spectra obtained with a Perkin-Elmer Grating Spectrophotometer Model 521.

3. Molecular orientation and optical rotation

It is assumed that anthracene molecules in a PVC film orient uniaxially along the direction of stretching of the film. Taking $A_{//}$ and A_{\perp} as the absorbances for the polarized radiation with electric vector parallel and perpendicular to the stretching direction respectively, we have,

$$2 \log\{\tan(\pm 45^\circ - \alpha)\} = A_{//} - A_{\perp} \equiv D \quad (1)$$

where α is the angle of optical rotation. D is likely called the dichroic difference.

Taking θ as an angle between the stretching direction and the transition moment of an absorption band, the orientation function F is given by a relation

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

When the difference between $A_{//}$ and A_{\perp} is small, Eq. (2) can be written approximately,

$$F = \frac{D}{3A}, \quad (3)$$

where A is the absorbance of the same specimen for unpolarized light.

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F or θ is estimated from the experimental values of the optical rotatory angle α or the dichroic difference at various elongation of the film.

RESULTS

The upper part of Fig. 1 shows the ORD curves of anthracene in the PVC film stretched by 0, 6.1 and 13.2%. The optical rotatory dispersion of anthracene appears increasingly with the elongation of the film and corresponds with the absorption spectra shown in the lower part of Fig. 1. Decrease in the absorbances on elongation arises from thinning of the specimen. The characteristic absorption bands of anthracene at 256 and 379 $m\mu$ have been assigned to be associated with the transition moments in a longitudinal direction of the molecule and that in a transverse direction, respectively.⁴⁾ The absorption at 250 $m\mu$ is too strong to have an exact record of the optical rotation.

The ORD curves show evidently that the transverse direction of the anthracene molecule tends to orient perpendicularly to the direction of elongation of the film. In Fig. 2 the optical rotations at absorption maxima, 328, 344, 360 and 380

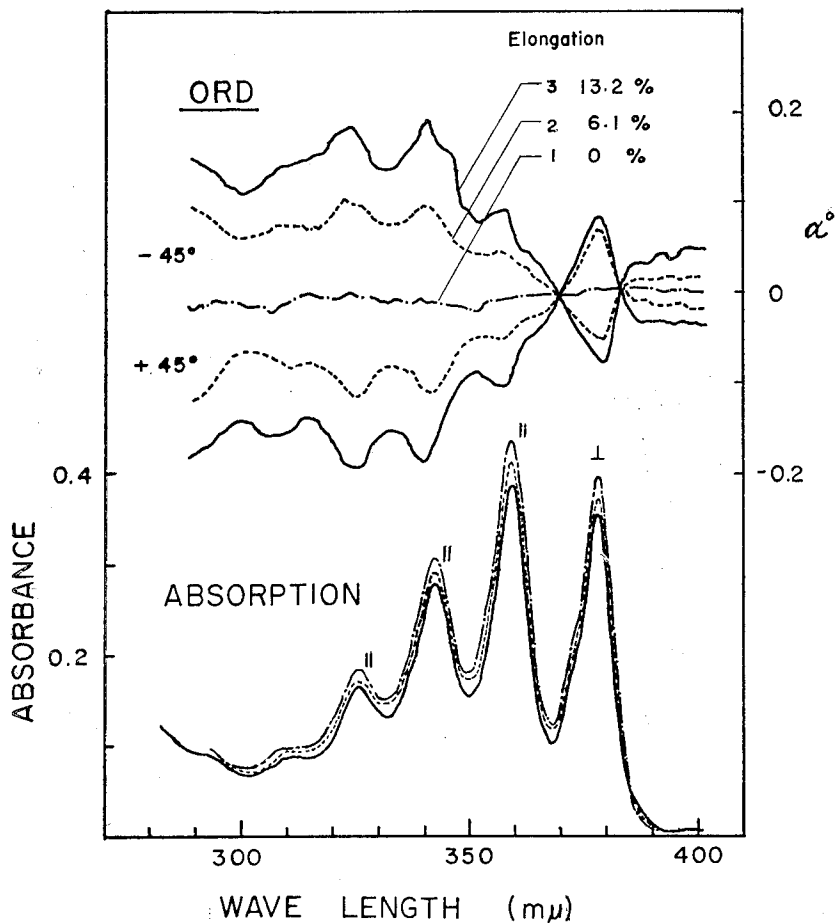


Fig. 1. ORD curves and absorption spectra of anthracene in stretched PVC film.

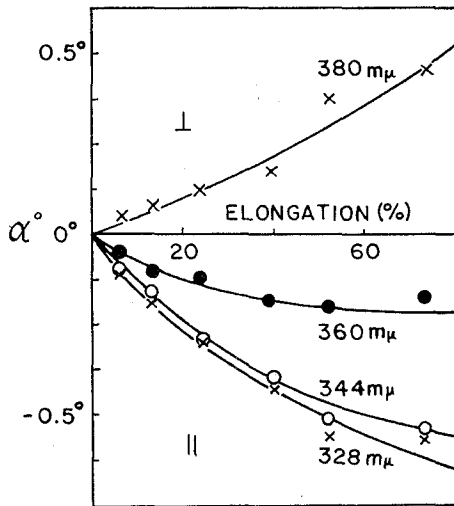


Fig. 2. Optical rotation of anthracene at various degrees of elongation.

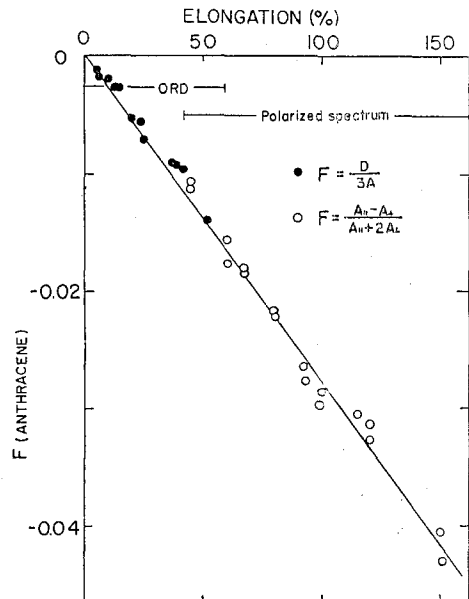


Fig. 3. Orientation functions of anthracene at various degrees of elongation.

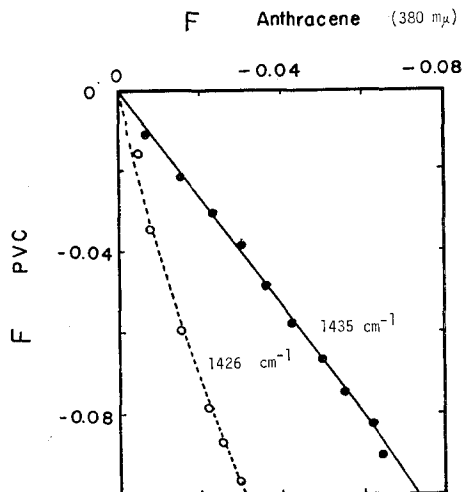


Fig. 4. Orientation functions of anthracene and PVC.

$m\mu$ are plotted against the degree of elongation. In this case, the stretching direction of the specimen was tilted by $+45^\circ$ to the direction of the polarized radiation for measurement. Figure 3 shows the relation between the orientation function and the degree of elongation. In Fig. 4, the orientation function of anthracene at $380 m\mu$ is plotted against those of PVC at 1426 and 1435 cm^{-1} . The absorptions at both frequencies have been assigned to scissoring vibration of the CH_2 groups, and determined to be perpendicular bands.^{6,7)} It is concluded from the result shown in Fig. 4 that the transverse axes of the anthracene molecules

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tend to orient perpendicularly with the direction of elongation holding an almost constant relation with the orientation of PVC for various degrees of elongation of the film.

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