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Dichroism Analysis of Oriented Polyenes Produced in Poly(vinyl alcohol) Film

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Dichroic spectra of polyenes $-(CH=CH)_n-$ produced in heat-treated poly(vinyl alcohol) [PVA] film were determined for two cases; stretch (at 85 °C) after heat (120 °C), (Δ,S), and heat after stretch, (S,Δ). The dichroic ratios Rd_n of component polyenes (n=2—6) were estimated by means of simulation. In both cases (Δ,S) and (S,Δ), the relation of Rd_n vs. Rs (stretch ratio) kept the theoretical equation of the dichroism analysis. The relative angles among the transition moments μ_n (n=2—6) were in accordance with those obtained by drawings of *trans*-polyenes. The idea of an azimuth vector in the stretched PVA substrate was justified. The relation of $Rd_n(\Delta,S) > Rd_n(S,\Delta)$ was always observed at any Rs. This was explained by the thermal orientation-relaxation of polymer chains.

Stretched PVA film colored by heating is utilized as a polarizing film.[1] In such a film, various kinds of π electron systems must be produced and oriented to the stretched direction. Therefore, the whole dichroism has to be dependent upon the respective polarization characteristics of the π electron systems. But the detailed analysis of the dichroism has not been investigated yet, though the dichroic ratio of the stretched and heat-treated PVA film has been reported.[2]

Up to date, the conventional dichroism analysis by the technique of stretching the PVA film[3] has succeeded in explaining the correlation between the transition moment and the geometrical structure of many molecules.[4] This analysis is based on a distribution function of an azimuth vector postulated for the PVA substrate.[3]

Previously, we have made assignments for the polyenes produced in heat-treated PVA film[5] and have further attempted to estimate the concentrations of the polyenes by simulations.[6]

When the dichroism analysis is combined with the method of simulation, it is expected that the correlation between the whole and the component dichroisms of the polyenes in a stretching state can be analyzed. Since the polyenes should be formed along the polymer chains in this case, the orientation aspect of the polyenes is regarded to be the same as that of the polymer chains. In other words, the orientation vector of the polyenes as an absorption species is the same as the azimuth vector of the substrate. This is important because, in the conventional dichroism analysis, it is assumed that an orientation vector of a guest molecule acts with the same behavior as the azimuth vector concomitant with the substrate itself. For that reason, the respective orientation directions of polyenes must be identical with a single direction which is common to all. This will be checked by the geometrical relation between the common azimuth direction and the molecular structure of the polyene.

The purpose of the present study is the following. The first is to seperate the total dichroism of polyenes into the component dichroisms by simulation and then to determine the relative directions of the transition moments μ_n. The second is to verify the justification of an azimuth vector, for which the distribution function is fundamental to the conventional dichroism analysis.

Experimental

PVA films treated with $NaBH_4$ according to the method reported previously[5] were digested in 0.05 M HCl solution (1 M=1 mol dm^{-3}) or 0.05 M H_2SO_4 solution for 3 h and dried for 1 d at room temperature. Further, they were treated by the following processes (A) or (B).

(A) After the film was heated at 120 °C to turn it red, it was digested in distilled water for 1 d, dried at room temperature for 1 d, and then stretched. The stretched film was fixed on a metal holder.

(B) At first the film was stretched and fixed on a metal holder. Then it was heated at 120 °C for about 15 min.

In order to distinguish between (A) and (B) by the sequence of heating (Δ) and stretching (S), the notations (Δ,S) and (S,Δ) will be used, respectively.

The film was uniaxially stretched at 85±5 °C and the stretch ratio (Rs) was defined in the same way as reported previously.[3] That the stretched film is ideally deformed was checked by assuring that the dimensional requirement for the theory of dichroism analysis was satisfied with respect to the length, width and thickness of film before and after stretching.[7] The heat treatment of the sample film was carried out in a heating compartment under conditions of 0.5 dm^3 min^{-1} flow of nitrogen.

The absorption spectra were measured using a Shimadzu UV-360 Spectrophotometer equipped with a rotatory Rochon-type prism. The net absorption of the sample film was obtained by compensation for the absorption of a colorless PVA film before heating. The dichroic ratio Rd is defined as $A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are the absorbances for the incident polarized light, of which the electric vector is parallel and perpendicular to the stretching direction of film, respectively. The Rd curves were obtained by a data processor, Sapcom-1, attached to the spectrophotometer.

Theoretical

When a PVA film undergoes an ideal uniaxial stretching, the width and thickness of the film shrink at the same rate. In this case, the following relation must hold,

$$A = k(A_{\parallel} + 2A_{\perp}) \tag{1}$$

where A is the absorbance before stretching and k is a constant depending on the film dimensions deformed. Equation 1 also holds in the case of respective polyenes. Using the same constant k, the absorbance of n-polyene -(CH=CH)$_n$- is given by

$$A_n = k(A_{n\parallel} + 2A_{n\perp}) = \varepsilon_n C_n d \tag{2}$$

where ε_n and C_n are the extinction coefficient and the concentration of n-polyene, and d is the film thickness. The dichroic ratio is defined as usual:

$$R\mathrm{d}_n = A_{n\parallel}/A_{n\perp} \tag{3}$$

From Eqs. 2 and 3, the $A_{\parallel}$ and $A_{\perp}$ spectra of the whole system can be represented as follows,

$$\left.\begin{aligned} A_{\parallel} &= \sum_n A_{n\parallel} = (d/k) \sum_n \varepsilon_n C_n (1+2/R\mathrm{d}_n)^{-1} \\ A_{\perp} &= \sum_n A_{n\perp} = (d/k) \sum_n \varepsilon_n C_n (2+R\mathrm{d}_n)^{-1} \end{aligned}\right\} \tag{4}$$

Therefore, the following relation between Rd and Rd$_n$ is obtained.

$$R\mathrm{d} = \frac{\sum_n \varepsilon_n C_n (1+2/R\mathrm{d}_n)^{-1}}{\sum_n \varepsilon_n C_n (2+R\mathrm{d}_n)^{-1}} \tag{5}$$

Strictly speaking, on account of the molecular vibration, the ratio of $A_{n\parallel}$ to $A_{n\perp}$ of the dichroic spectra of A_n depends on the wavelength, namely, Rd$_n$ is not constant over the whole absorption region. But, its variation in the main part is generally small. At the present stage, therefore, all of Rd$_n$ are assumed to be invariable in the respective absorption regions.

By simulation of the absorption spectra of polyenes produced in PVA film,6) the concentrations C_n of Eq. 2 can be estimated, using the known ε_n, from the simulated spectrum A of Eq. 1 together with the relation $A=\sum_n A_n$. From these and the observed Rd values, Rd$_n$ of respective polyenes can be determined so as to satisfy Eq. 5.

According to the theory of dichroism analysis using uniaxially stretched PVA film,3) the anisotropy of the substrate can be described by a distribution function $f(R\mathrm{s})$ of an azimuth vector (OD vector) for the stretching direction. And the dichroic ratio Rd$_n$ is derived from $f(R\mathrm{s})$. An important point to be noticed here is that the direction which keeps the distribution $f(R\mathrm{s})$ is not the transition vector μ_n itself but the projective part (μ_{na}) of μ_n upon the direction of OD. For that reason, the Rd$_n$ equation involves Rs and a parameter r_n, $R\mathrm{d}_n = F(R\mathrm{s}, r_n)$, where r_n is defined as $r_n = |\mu_{na}/\mu_{nb}|$, and μ_{na} and μ_{nb} are the components of μ_n along OD and its normal direction, respectively.

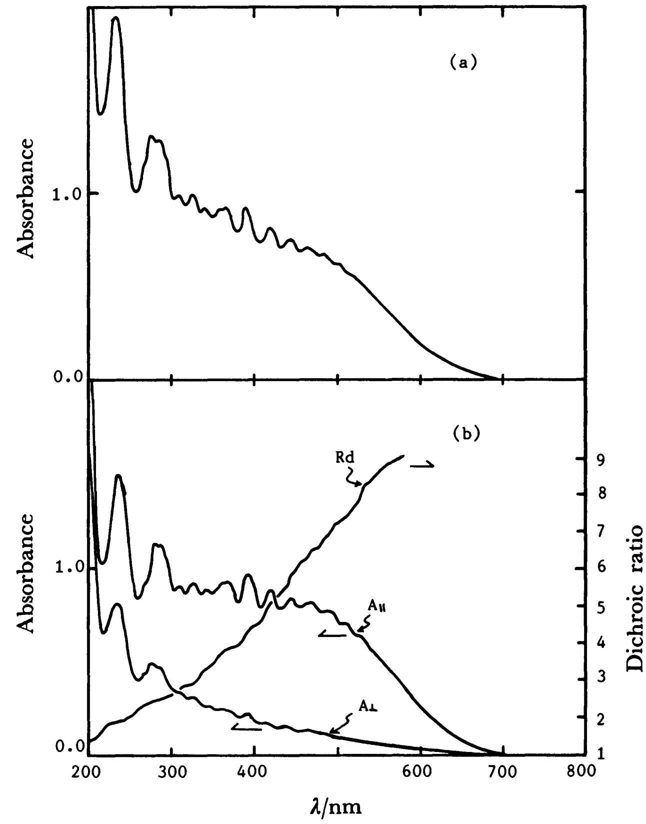

Fig. 1. Isotropic (a) and polarized absorption spectra (b) of PVA film for the case of (Δ,S), which is stretched (Rs=5.7) after heating at 120 °C for 15 min. Rd is dichroic ratio. Film thickness is 195 μm (a) and 110 μm (b).

Finally, Rd$_n$ is expressed by Rs and r_n as follows.3)

$$\left.\begin{aligned} R\mathrm{d}_n &= \frac{2+2(r_n{}^2-1)T}{(2r_n{}^2+1)-(2r_n{}^2-1)T} \\ &\text{where} \\ T &= \frac{R\mathrm{s}^2}{R\mathrm{s}^2-1}\left[1-\left\{\frac{\pi}{2}\tan^{-1}(R\mathrm{s}^2-1)^{-1/2}\right\}(R\mathrm{s}^2-1)^{-1/2}\right]. \end{aligned}\right\} \tag{6}$$

The inclination of μ_n for OD can be given by

$$\alpha_n = \cot^{-1} r_n \tag{7}$$

where α_n is called the orientation angle of μ_n.

Results

Figure 1(a) shows the absorption spectrum of a PVA film heated to red, and Fig. 1(b) the dichroic spectra and the Rd curve of the same film stretched to Rs=5.7. The spectrum A calculated by Eq. 1 using $A_{\parallel}$ and $A_{\perp}$ of Fig. 1(b) coincided with that of Fig. 1(a) when k=0.66. This indicates that the deformation of PVA substrate was ideal and that the absorption species did not change chemically by stretching.

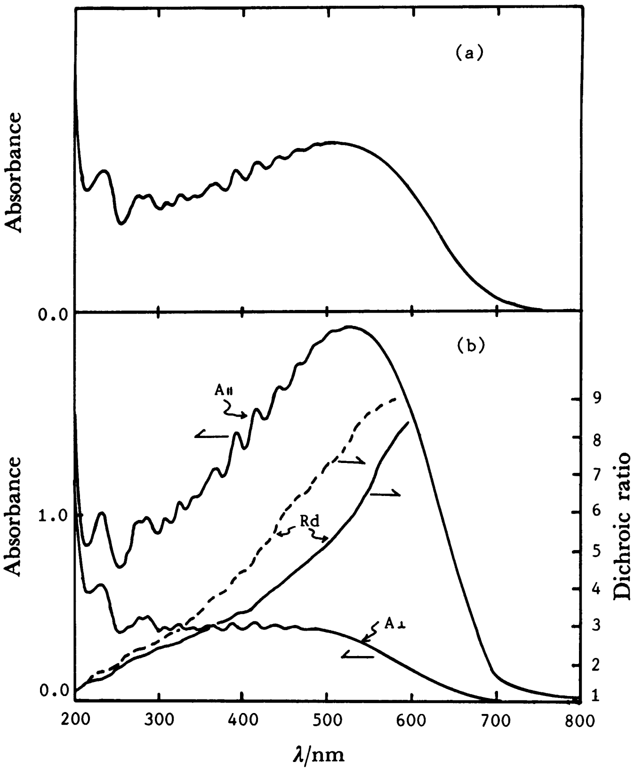

Fig. 2. Isotropic (a) and polarized absorption spectra (b) of PVA film for the case of (*S*,*Δ*), which is heated at 120 °C for 15 min after stretching (*R*s=6.2). Fig. (a) is obtained from $(A_{\parallel}+2A_{\perp})/3$ of Fig. (b). Film thickness is 98 μm. Broken line in (b) indicates *R*d curve in Fig. 1(b).

Figure 1(b) is for the case of (*Δ*,*S*). In contrast to this, the film for (*S*,*Δ*) is reddish purple and its dichroic spectra at *R*s=6.2 are measured as shown in Fig. 2(b). Figure 2(a) shows the isotropic spectrum *A* determined by Eq. 1 using $A_{\parallel}$ and $A_{\perp}$ of Fig. 2(b).

From the comparison of Figs. 1(a) and 2(a), it is clear that the absorption spectrum of a film is changed by reversing the procedure, heat (*Δ*) and stretch (*S*); the relative intensities in the short and long wavelength regions are exchanged. The absorption in the long wavelength region is more intensive for the case of (*S*,*Δ*) than for (*Δ*,*S*).

The *R*d curve rises toward the long wavelength in either case (Figs. 1(b) and 2(b)), but the *R*d value at each wavelength is smaller for (*S*,*Δ*) (solid line in Fig. 2(b)) than for (*Δ*,*S*) (broken line), though *R*s of the former is larger than that of the latter.

The concentrations C_n of Eq. 2 were obtained using litetature values of ε_n.[8] The Rd_n values at *R*s=5.7 were calculated from the data of Fig. 1(b), in such a way that *R*d of Eq. 5 becomes equal to the observed *R*d. The Rd_n values thus determined at the wavelength corresponding to the 1←0 transition of *n*-polyenes are listed in Table 1 together with the *R*d values at the same wavelengths. In Table 1, only the results of *n*=2—7 are presented, being left out those of *n*≧8,

Table 1. Simulated Rd_n and Observed *R*d at 1←0 Transitions of *n*-Polyenes[a)]

n	Rd_n	*R*d
2	1.9	1.9(234)
3	2.3	2.3(274)
4	2.6	2.8(310)
5	3.1	3.3(342)
6	4.2	3.9(366)
7	4.3	4.5(390)

a) Observed *R*d is the case of *R*s=5.7 (Fig. 1(b)). ( ) indicates wavelength of 1←0 transition of *n*-polyene.

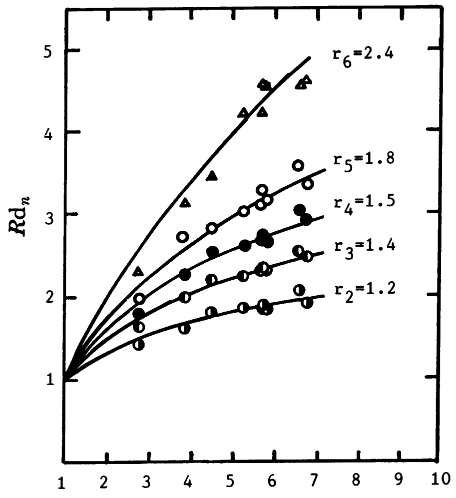

Fig. 3. Relationship of $Rd_n(\Delta,S)$ vs. *R*s for *n* which is the number of double bonds of *n*-polyene. Marks are experimental and lines are obtained from Eq. 6 using the parameters r_n listed in Table 2. ◑: *n*=2, ◐: *n*=3, ●: *n*=4, ○: *n*=5, △: *n*=6.

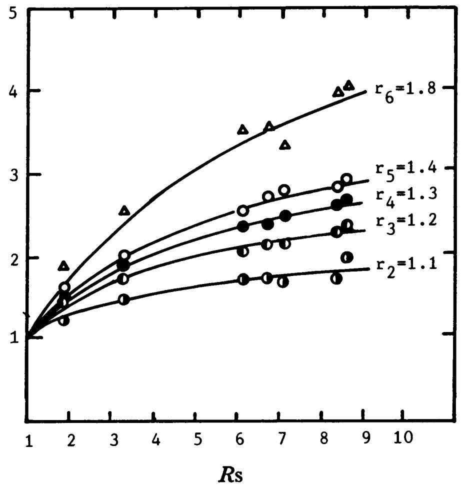

Fig. 4. Relationship of $Rd_n(S,\Delta)$ vs. *R*s for *n* which is the number of double bonds of *n*-polyene. Marks are experimental and lines are obtained from Eq. 6 using the parameters r_n listed in Table 2. ◑: *n*=2, ◐: *n*=3, ●: *n*=4, ○: *n*=5, △: *n*=6.

Table 2. r_n and Orientation Angle of n-Polyene[a)]

n	(Δ, S)			(S, Δ)		
	r_n	α_n°	α_n	r_n	α_n°	α_n
2	1.2	41°	41°	1.1	44°	44°
3	1.4	36°	36°	1.2	39°	39°
4	1.5	33°	33°	1.3	37°	36°
5	1.8	29°	31°	1.4	35°	34°
6	2.4	22°	30°	1.8	29°	33°

a) Orientation angle: α_n° is observed, α_n is from drawing (see Fig. 6).

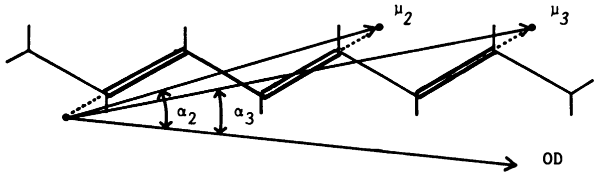

Fig. 6. Drawing of $\mu_n (n=2, 3)$ and OD for polyene skeleton. Terminals of transition vector μ_n are at two points taken at halves as long as the terminal bond on the outer extension lines. α_n is the orientation angle of μ_n against OD (orientation direction) of polymer chain.

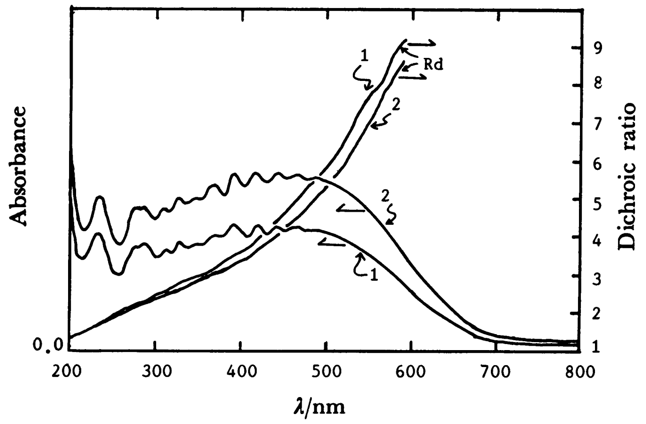

Fig. 5. Absorption spctra of PVA film for the case of (S,Δ), stretched (Rs=6.8) and heated at 120 °C for 16 min (curve 1) and 20 min (curve 2). Film thickness is 68 μm.

because these concentrations computed are not dependable.[6)]

In the same way as above, the $R\mathrm{d}_n$ values at various Rs were determined. The relation $R\mathrm{d}_n$ vs. Rs is plotted in Fig. 3 for individual polyenes. The curves drawn in Fig. 3 are those obtained theoretically by Eq. 6 using the parameters which fit for the $R\mathrm{d}_n$–Rs plot. Figure 4 shows the same relation for the case (S,Δ), where the heating times were kept at 15 min, because the Rd value was dependent upon the length of the heating period (see Fig. 5). The r_n values of Figs. 3 (Δ,S) and 4 (S,Δ), and the orientation angles α_n° obtained from Eq. 7 are listed in Table 2.

Figure 5 shows the absorption spectra and the Rd curves for the different heating times (1: 16 min, 2: 20 min) of a film for the case of (S,Δ), in which the spectra are derived from Eq. 1 using the observed $A_{\parallel}$ and $A_{\perp}$. Figure 5 reveals an interesting phenomenon that the longer the heating time, the stronger the absorption and at the same time the lower the Rd values.

Discussion

Orientation Angles of Polyenes. As shown in Figs. 3 and 4, the $R\mathrm{d}_n$ values agree well with the theoretical curves. This means that μ_{n_a} is acting with the same behavior as the OD vector which is common to all polyenes. For that reason, the inclinations of μ_n can be compared by the orientation angles α_n° against only one OD vector.

Table 2 shows that α_n° becomes smaller with increase of n in both cases, (Δ,S) and (S,Δ). This indicates that the OD vector points to a certain lengthwise direction close to the zigzag chain of polyene skeleton.

In order to investigate α_n° in Table 2 by a molecular diagram, the transition directions of μ_n with respect to the same geometry of polyene-skeleton were made in the following way. The direction of μ_n is regarded as the direction through the two points which are respectively half as long as the C–C bond on the outer extension line of each of the terminal double bonds of n-polyene as shown in Fig. 6. Assuming that an angle α_2 between μ_2 and OD by drawing is equal to α_2°, other α_n are obtained as listed in the right columns of (Δ,S) and (S,Δ) in Table 2.

In both cases, (Δ,S) and (S,Δ), the experimental α_n° are in good agreement with the drawing α_n in the range $n=2$—5. This fact indicates that the distribution of the OD vector agrees with the theoretical distribution function and that the concept of an azimuth vector is justified.

Relaxation Phenomenon of Orientation. Inspecting the same n, the following relations are recognized: $\alpha_n^\circ(\Delta,S) < \alpha_n^\circ(S,\Delta)$ in Table 2 and $R\mathrm{d}_n(\Delta,S) > R\mathrm{d}_n(S,\Delta)$ at any Rs in Figs. 3 and 4. The latter relation may correspond to some reduction of $R\mathrm{s}(S,\Delta)$ by heating after stretching. However the film was fixed tightly on a metal holder during the heat treatment and any appreciable deformation of film could not be observed by heating, accordingly the reduction of the Rs of the film itself cannot be considered. Therefore, the apparent reduction of Rs by heating may be due to some orientation-relaxation by the thermal motion of the polyene chains.

If the reduction of apparent Rs is regarded as a relaxation phenomenon, a stationary state of orientation must exist at a given temperature. Let f_1 and f_2 be the distribution functions for stationary states at temperature T_1 and T_2 $(T_1 < T_2)$, respectively, the time dependent change from f_1 to f_2 may be described as follows,

$$f(t)=f_2+(f_1-f_2)\exp(-t/\tau) \quad (8)$$

where τ is the relaxation time.

Since the orientation relaxation is induced by thermal motion, the change of Eq. 8 should be directed towards the isotropic state. Consequently, *R*d must be lowered with the period of heating time. In fact, as shown in Fig. 5, the *R*d curve in the whole wavelength region is lowered with the heating time. This is considered evidence for the relaxation phenomenon of orientation.

Stretching Effect on Polyenes Formation. In spite of the equal heating temperature (120 °C), the relative intensity of absorption in the long wavelength region was greater for the stretched film (Fig. 2(a)) than for the unstretched one (Fig. 1(a)). This stretching effect on polyenes formation, however, cannot be analyzed at the present stage.

References

1) E. H. Land and H. G. Logers, U. S. Patent, 2173304 (1939); C. A. Finch, "Poly Vinyl Alcohol," John Wiley & Sons, New York (1973), p. 505.

2) Y. Nishijima, Y. Onogi, and T. Asai, *J. Polymer Sci.*, **C-15**, 237 (1966).

3) Y. Tanizaki, *Bull. Chem. Soc. Jpn.*, **38**, 1978 (1965); *ibid.*, **32**, 75 (1959).

4) As one of the most recent reports: M. Kobayashi, T. Hoshi, J. Okubo, H. Hiratsuka, T. Harazono, M. Nakagawa, and Y. Tanizaki, *Bull. Chem. Soc. Jpn.*, **57**, 2905 (1984).

5) K. Maruyama, H. Akahoshi, M. Kobayashi, and Y. Tanizaki, *Chem. Lett.*, **1983**, 1863; *Bull. Chem. Soc. Jpn.*, **58**, 2923 (1985).

6) K. Maruyama, M. Také, N. Fujii, and Y. Tanizaki, *Bull. Chem. Soc. Jpn.*, **59**, 13 (1986).

7) Y. Tanizaki, T. Kobayashi, and N. Ando, *Bull. Chem. Soc. Jpn.*, **32**, 1362 (1959).

8) F. Sondheimer, D. A. Ben-Efrain, and R. Molovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961).