Orientation-relaxation of polyenes produced in heated PVA film

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The dichroism analysis of polyenes produced in heat-treated and stretched PVA film revealed the orientation-relaxation of PVA polymer chains by successive heat treatment. The degree of orientation-relaxation was estimated by a change of orientation vector.

(Keywords: poly(vinyl alcohol); polyenes; orientation-relaxation)

INTRODUCTION

Conventional dichroism analysis using the technique of stretching poly(vinyl alcohol) (PVA) film[1] has succeeded in explaining the correlation between the transition moment and the geometrical structure of many molecules[2]. Using this technique, dichroism analysis of polyenes $-\!(CH{=}CH)_n\!-$ produced in heat-treated PVA film has already been carried out[3]. In this paper[3], the dichroism ratios of component polyenes (Rd_n, where $n = 2 \sim 5$) were estimated by means of simulation for two cases; stretch after heat (△, S for short), and heat after stretch (S, △). In both cases the relation Rd_n vs stretch ratio (Rs) kept to the theoretical equation of the dichroism analysis, with the Rd_n value in (△, S) being larger than that in (S, △) for respective n values. PVA is stretched at 85°C in the case of (△, S) and at 120°C for (S, △), so with the latter temperature being higher than the former the polymer chains in the latter case are much more in favour of thermal orientation-relaxation.

There have been some reports on the relaxation of stretched polymer film, such as an analysis by polarized fluorescence spectra of degraded PVA[4], and an analysis by birefringence of degraded poly(vinyl chloride) (PVC)[5]. These indicate that the higher the temperature, the more the relaxation. In our previous paper[3], owing to insufficient washing of the PVA film, there remained catalysts (such as HCl) in the PVA for polyene formation, so that the change in Rd accompanies the coloration and it is not possible to determine whether the change in Rd is caused by the orientation-relaxation of PVA polymer chains or by polyene formation. In the present study, the dichroism analysis of polyenes was carried out using well-washed PVA film and the degree of orientation-relaxation was estimated by a change of orientation vector.

EXPERIMENTAL

PVA powder (20 g, Koso Chemical Co. Ltd), with average degree of polymerization of 1400 and degree of alkaline saponification 99–100%, was dissolved in 0.01M HCl (250 cm^3). This solution was heated to 80°C and casted on a horizontal glass plate (30 x 30 cm). After it was dried at room temperature for 7–10 days, the PVA film obtained was kept for 1 h at 100°C to give a red colour. The film was swollen with distilled water for 1 day, and digested in a mixed solution of 0.2M $NaBH_4$ and 0.01M NaOH for 1 day in order to reduce the carbonyl group. It was also digested in 0.1M CH_3COOH for 1 day to neutralize NaOH, and in distilled water for 5 days. It was then dried at room temperature.

A sample film was uniaxially stretched ($Rs \fallingdotseq 5.5$) at a certain temperature. The value of Rs was defined as reported previously[1]. That the stretched film is ideally deformed was checked by assuming that the dimensional requirement for the theory of dichroism analysis was satisfied with respect to length, width and thickness of a film before and after stretching.

After the film was stretched, it was fixed on a metal holder, and then it was heated to 90°C and the absorption spectrum was measured at various time intervals.

The temperatures on stretching and heat treatment of a PVA film were: stretched at 60°C and then heated to 90°C; and stretched at 90°C and then heated at 90°C.

The absorption spectra were measured using a Shimadzu UV-360 spectrophotometer equipped with a rotary Rochon-type prism. The net absorption of the sample film was obtained by comparison with the absorption of a colourless PVA film before heating. The dichroic ratio (Rd) is defined as $A\| / A\perp$, where $A\|$ and $A\perp$ are the absorbances for the incident polarized light, with the electric vector parallel and perpendicular to the stretching direction of a film, respectively. The Rd values were obtained as reported previously[3] using a KADEC-L1 A/D converter and NEC PC-9801 microcomputer.

RESULTS AND DISCUSSION

Figure 1a shows the polarized absorption spectra of a sample PVA film stretched at 60°C (Rs = 5.58), and heated to 90°C for 2.5 min. The fine structures in *Figure 1* are classified into several groups of linear polyenes $-\!(CH{=}CH)_n\!-$, where the integer n indicates the conjugation number. *Figure 1b* shows the difference spectra between the spectra before and after heat treatment in *Figure 1a*, where the upper and the lower parts of the line through zero represent a decrease and increase in absorbance, respectively.

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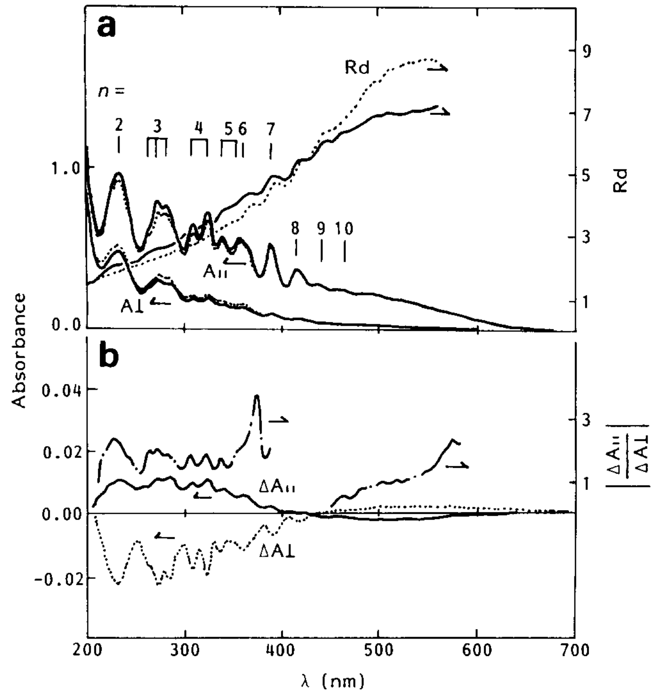

Figure 1 (a) Polarized absorption spectra of heat-treated PVA film stretched at 60°C (Rs = 5.58, ——) and heated at 90°C for 2.5 min (····). Rd is dichroic ratio, over n indicates the conjugation number of $\text{-(CH=CH)}_n\text{-}$. Film thickness is 110 μm. (b) Difference spectra of $A\|$ and $A\perp$ in (a)

The Rd curve in *Figure 1a* indicates a decrease in the longer wavelength region and an increase in the shorter region than 430 nm. This is caused by an increase in $A\|$ and a decrease in $A\perp$ in the longer wavelength region, but by a decrease in $A\|$ and an increase in $A\perp$ in the shorter region (*Figure 1b*). Since coloured PVA film was washed as well as possible with distilled water in order to eliminate the catalysts for polyene formation, the film coloration does not proceed at this temperature[6]. PVA film was fixed tightly on a metal holder during the heat treatment. Therefore, the change in Rd should be caused by the orientation change of polymer chains, in other words, relaxation of short polyenes and the orientation of long polyenes.

Figure 2 shows the relation of Rd vs heating time monitored at 234, 274, 310, 340, and 503 nm corresponding to the $1 \leftarrow 0$ transition of $n = 2$, 3, 4, 5, and 12, respectively. It reveals that the orientation change occurs rapidly, i.e., in the initial stage of heating Rd values decrease and then they scarcely change for $n = 2$–5, whilst the Rd value increases for $n = 12$.

Rd values plotted in *Figure 2* are from a polyene mixture, and the Rd_n value for each polyene can be estimated by means of simulation[3] by assuming that the Rd_n values are invariable in the respective absorption regions. The results from simulation are plotted in *Figure 3* as the relation of observed orientation angle (θ) between orientation direction and transition moment vs heating time. Orientation direction in dichroism analysis using PVA film is defined to be the direction such that when PVA film is stretched to ∞, the stretch direction coincides with the orientation direction and a molecule doped in PVA aligned with a certain angle (orientation angle) between the long axis of a molecule and the stretch direction[1]. Orientation direction is related to the steric configuration of a molecule and it is not defined a priori, but determined by molecular orbital calculations and dichroism analysis. In addition, it is noticed that when PVA film is stretched to ∞, even a rod-like molecule such as anthracene doped in PVA aligns with the stretch direction and is not in the direction of the long axis of a molecule[7].

The orientation angle between orientation direction and transition moment does not change at any stretch ratio[1], so that the positive change of observed orientation angle means that it reverted to the less stretched conditions. Hence the change of the distribution function relates to the vector of orientation direction (OD vector). The change in angle of the average OD vector ($\triangle\theta$) for each polyene before and after heat treatment are given in *Table 1* for $n = 2$–5 with $n \geq 6$ being omitted because the concentrations computed are not reliable[3].

Since the polyenes in this case should be formed along the polymer chains, the orientation aspect of the polyenes is regarded to be the same as that of the polymer chains. In other words, the OD vector of the polyenes as an absorption species is the same as for the PVA substrate. The change of OD vector is equivalent for all directions, so that the change in absorption for the stretched direction ($\triangle A\|$) and for the perpendicular direction ($\triangle A\perp$), should satisfy the following equation:

$$\triangle A\| = -2\triangle A\perp \tag{1}$$

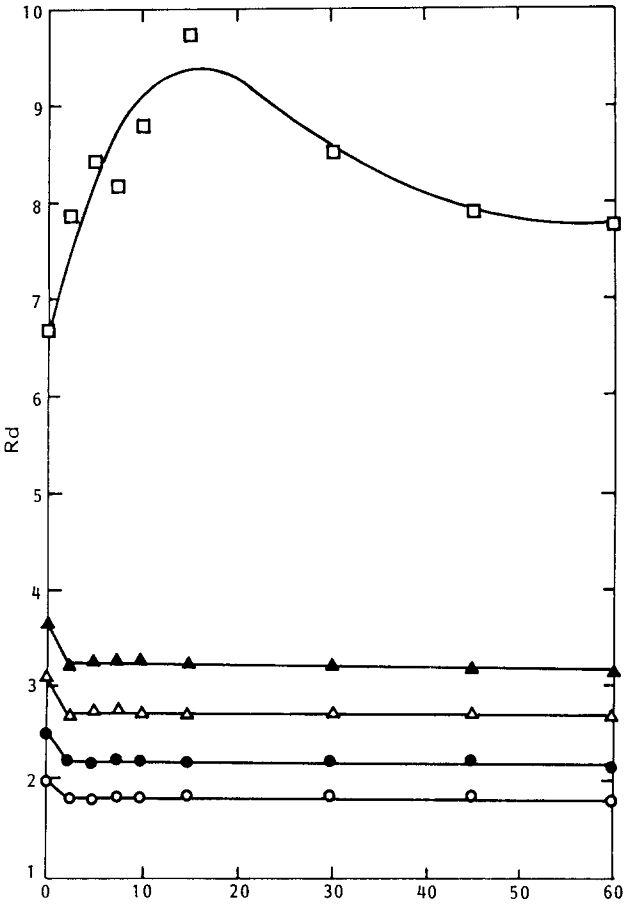

Figure 2 Relation between Rd of polyenes and heating time. PVA was stretched at 60°C (Rs = 5.58) and heated at 90°C. Monitored at: ○, 234 ($n = 2$); ●, 274 ($n = 3$), △, 310 ($n = 4$), ▲, 340 ($n = 5$); □, 503 nm ($n = 12$)

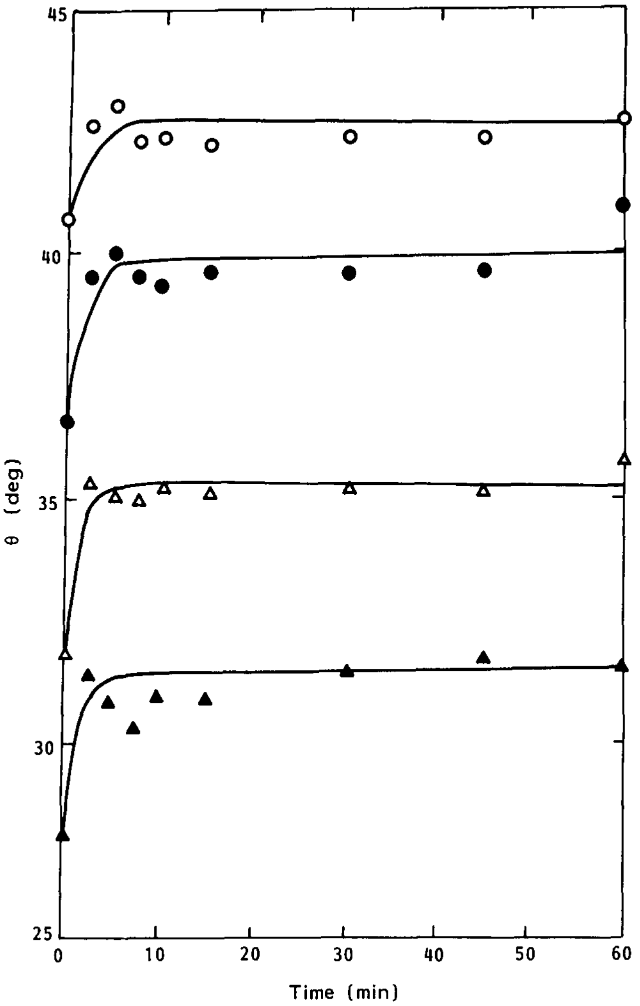

Figure 3 Relation between θ of polyenes and heating time. PVA was stretched at 60°C (Rs = 5.58) and heated at 90°C; $n=2$ (○), 3 (●), 4 (△) and 5 (▲)

Table 1 Change in angle of orientation vector for each polyene[a]

n	$\Delta\theta$ (deg)
2	1.8
3	3.0
4	3.5
5	3.3

[a] Positive value indicates an increment in θ after heat treatment

As shown in *Figure 1b*, equation (1) is satisfied in the absorption region shorter than 430 nm. This means that the orientation-relaxation of polyenes with $n=2$–7 occurs by heat treatment. The degree of relaxation estimated by the change in θ ($\Delta\theta$) should be the same for all polyenes because the transition moment of each polyene acts in the same way as only one OD vector. However, $\Delta\theta$ for $n=2$ is less than for $n=3$ and 4, as shown in *Table 1*. As reported previously[8], the second bands of some long polyenes appear in the absorption region for $n=2$. This should decrease the observed Rd for $n=2$, so that the average value of $n=3$–5, which is 3.3°, may be accepted to be the degree of relaxation for the OD vector.

In the absorption region longer than 430 nm, the increase in Rd indicates the orientation of long polyenes in the stretched direction by heat treatment. Since the orientation angle of the polyenes does not change through stretching the PVA substrate[1], and assuming that the polyene structure does not change, the above phenomena may be interpreted as the selective orientation-relaxation of polymers. This suggests that the oriented segments having longer polyenes tend to orient much more to the stretched direction by heat treatment, whereas the segments having shorter polyenes show orientation-relaxation by heat treatment.

The orientation-relaxation by heat treatment of molecules doped in a stretched PVC film is reported to be related to the molecular length using diphenyl polyenes $Ph{-}(CH{=}CH)_n{-}Ph$ where $n=2\sim4$ (ref. 5). This means that longer molecules lose their orientation more rapidly and shorter ones more slowly than the polymer segments on average. This may be interpreted as the longer molecules tending to align preferentially to the higher-oriented sequences of polymer segments, and orientation-relaxation first causes disorientation of the higher sequences of segments. This hypothesis cannot be rejected for the case of PVA. However, each polyene produced in PVA is revealed to be a mixture of isomers[8], and θ for each polyene observed is an average value of a mixture of isomers. Comparing θ values of various isomers of some linear polyenes, the all-*trans* isomer has smallest θ (*Figure 4*). A number of isomers tend to isomerize to the thermally stable all-*trans* type polyene[9]. The number of isomers of each polyene increases rapidly as the conjugation number increases, so that the average θ of long polyenes tends to be far from the θ value of the all-*trans* type polyene. If the isomerization and orientation relaxation of polymer chains occur at the same time and $\Delta\theta$ of the former is larger than the latter, Rd should change as if orientation occurs. In the Rd curve in the long wavelength region it is therefore expected that the longer the wavelength, the higher the Rd. In fact, as shown in *Figure 1b*, this is satisfied.

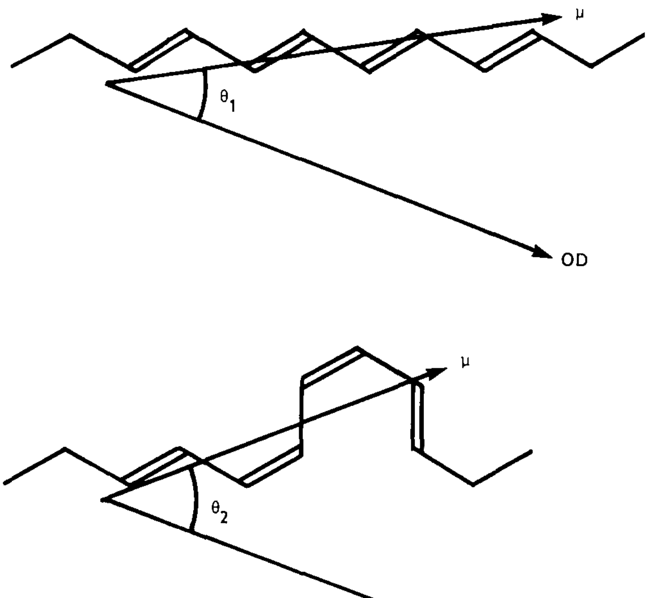

Figure 4 Drawing of μ (transition vector) and OD (orientation direction) for polyene skeleton. θ is the orientation angle of μ against OD of polymer chain

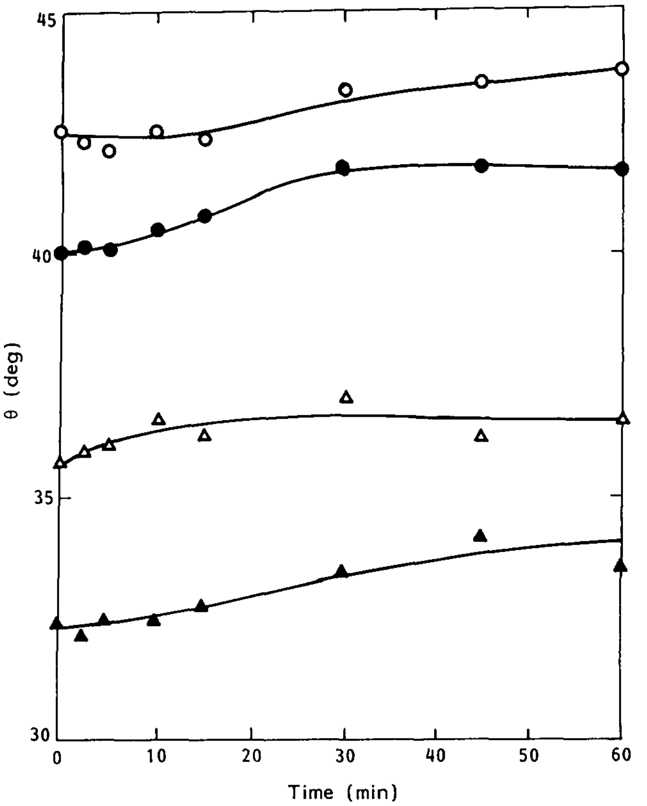

Figure 5 Relation between θ of polyenes and heating time. PVA was stretched at 90°C (Rs = 5.44) and heated at 90°C. Monitored at: ○, 234 ($n=2$); ●, 274 ($n=3$); △, 310 ($n=4$); ▲, 340 nm ($n=5$)

Figure 5 shows the relation of θ vs heating time for the case stretched at 90°C (Rs = 5.44) and then heated to 90°C. θ for the respective n values after stretching shows a rather large value which is almost the same as that observed in the case stretched at 60°C and heated to 90°C after relaxation has occurred (*Table 1*), and θ increases a little by further heat treatment. The glass transition temperature of PVA is reported to be about 80°C (ref. 10), so that the stretching may simultaneously accompany the orientation-relaxation. These phenomena also occur using PVA or PVC film doped with various dyes. In these cases, when the stretching ratio is identical, the higher the temperature of stretching, the more relaxation[11].

When PVA sample film was stretched at 60°C (Rs = 5.33) and then heated to 60°C, its absorption spectrum and Rd curve did not change essentially as with 60 min heat treatment.

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