Dichroism analysis of polyenes produced in heat-treated PVA

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Dichroism analysis of polyenes produced in PVA films was carried out for films stretched (at 80°C) after heat treatment (at 170°C) and films heat-treated after stretch. The relation between R_s (stretch ratio of the film) and $R_{d,n}$ (dichroic ratio of n conjugated polyene) in the former case fitted the theoretical curves, but in the latter, high $R_{d,n}$ values regardless of R_s were observed. Stretching of the film might promote both polyene formation and cross-linking dehydration, especially on the segments oriented in the stretch direction.

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

INTRODUCTION

When a poly(vinyl alcohol) (PVA) film was heat-treated, even at 100°C, in the presence of acid it coloured to produce polyene sequences in the PVA film[1]. When this PVA film containing polyene sequences was washed well with distilled water to reduce acid, however, the film did not become coloured for heat treatment up to 200°C[2].

As mentioned in a previous paper[3], when a PVA film containing polyene sequences was washed well to remove acid and then heated at 120°C, which is low enough to cause no polyene formation out of acid, orientation of long polyenes unexpectedly proceeded, in spite of the orientation relaxation of short polyenes. These orientation aspects were explained by considering two different reactions: orientation relaxation of polymer chains and *cis–trans* isomerization of polyenes (see below). More relaxation of polymer chains by thermal motion is expected to occur at higher temperature. The present work is an extension of the previous study. It aims to discover the extent to which orientation relaxation will occur and overcome the *cis–trans* isomerization effect at higher temperature.

BACKGROUND

Dichroism analysis

In dichroism analysis on stretching a PVA film[4,5], the following parameters are characteristic: stretch ratio (R_s), dichroic ratio (R_d), orientation direction (OD) and orientation angle (α).

If the length L_1, width W_1 and thickness T_1 of a PVA film containing a certain molecule to be analysed change to L_2, W_2 and T_2 on stretching, the film must satisfy the following equations for dichroism analysis:

$$\left.\begin{aligned}(L_1/L_2)^{1/2}=W_2/W_1=T_2/T_1\\ L_1W_1T_1=L_2W_2T_2\end{aligned}\right\} \tag{1}$$

The stretch ratio (R_s) is defined as[4,5]:

$$R_s=(L_2/L_1)(W_1/W_2) \tag{2}$$

On stretching a PVA film, the long axis of a molecule in PVA generally orients in the stretched direction according to the R_s value to give anisotropy in absorbance. The dichroic ratio (R_d) is defined as $A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are the absorbances for polarized incident light, the electric vectors of which are parallel and perpendicular to the stretch direction of a film, respectively.

The orientation direction (OD) of a molecule in a PVA film is defined to be the direction such that, when the PVA film is stretched to infinity, the stretch direction coincides with OD and the molecules in PVA are aligned with a certain angle (the orientation angle, α) between the transition moment of the molecule and the stretch direction[4–6]. The OD of a molecule in PVA is related to the steric configuration of the molecule and it cannot be decided *a priori.*

If the stretched film is ideally deformed to satisfy equation (1), the relation between R_s and R_d, which is not derived here, is[4–6]:

$$R_d=[2+2(r^2-1)T]/[(2r^2+1)+(2r^2-1)T] \tag{3a}$$

where

$$T=[1-\{(\pi/2)\tan^{-1}(R_s^2-1)^{-1/2}\}(R_s^2-1)^{-1/2}]R_s^2/(R_s^2-1) \tag{3b}$$

$$r=|\mu_a/\mu_b| \tag{3c}$$

and μ_a and μ_b are the components of the transition vector μ along OD and its normal direction, respectively. The orientation angle of μ, written as α, is defined as follows:

$$\alpha=\cot^{-1} r \tag{4}$$

Using the conventional dichroism analysis mentioned above, the orientation angle, α_n, of n conjugated polyenes (n polyenes for short) produced in the PVA was obtained for $n=2$–5[6]. Note that it is not α_n that changes on stretching the film but the distribution of molecular-axis orientation (strictly speaking, the distribution of the projective part of the transition moment of n-polyene μ_n, on the orientation direction).

Cis–trans *isomerization effect of polyenes on $R_{d,n}$*

If a decrease in $R_{d,n}$ of n-polyene is observed on

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heat treatment under conditions of no further polyene formation, then an increase in α_n at constant R_s, or a decrease in R_s at constant α_n is expected. Both mean that the film is returned to a less stretched state, i.e. orientation relaxation of PVA polymer chains occurs. The orientation change in this paper will be shown by α_n because it is easy to illustrate the orientation change by a diagram such as *Figure 1*.

If an increase in $R_{d,n}$ is observed, it indicates a structural change of polyenes by a reaction such as the following *cis–trans* isomerization. Each *n*-polyene is regarded as a mixture of isomers[7] and α_n obtained by dichroism analysis for each *n*-polyene is an average value for a mixture of isomers[3]. Considering a certain *n*-polyene, e.g. tetraene in *Figure 1*, isomer A has a smaller orientation angle than isomer B because the polyenes in PVA should be formed along the polymer chains, and the respective orientation directions of isomers A and B in *Figure 1* must be identical[6]. The isomerization of *n*-polyene from *cis* to *trans* type, for example from B to A in *Figure 1*, causes a decrease in α_n. On the other hand, orientation relaxation of polymer chains causes an increase in α_n. Therefore, when both isomerization and relaxation of PVA polymer chains occur at the same time and the decrement in α_n due to such isomerization is larger than the increment in α_n due to relaxation of polymer chains, the observed α_n of *n*-polyene should decrease as if orientation proceeds.

EXPERIMENTAL

The PVA powder used (Koso Chemical Co. Ltd) had an average degree of polymerization of 1400 and degree of alkaline saponification 99–100%. It was heated under a flow of nitrogen at 170°C for 5 h to give pale yellow powder. It was digested in distilled water at room temperature for 2 d to remove CH_3COONa, which is a saponification product that catalyses the coloration of PVA, and then dissolved in hot water. The solution was poured onto a horizontal plate of glass. It was dried at room temperature for 7 d to give a pale yellow PVA film. The film was treated with $NaBH_4$ to reduce the carbonyl groups and washed well with distilled water by the method reported previously[6]. Using another white PVA powder without heat treatment, transparent PVA film containing CH_3COONa was also prepared without washing and $NaBH_4$ treatment.

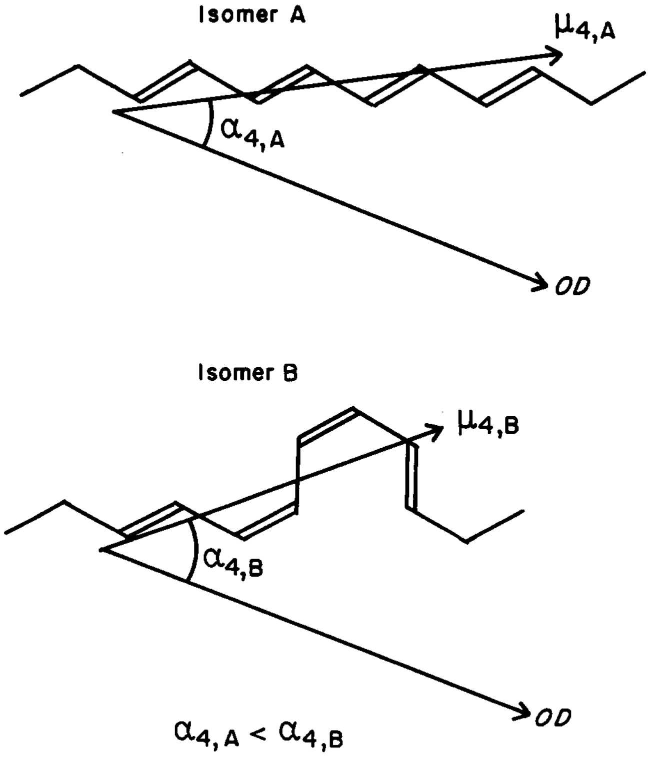

Figure 1 Transition vector (μ), orientation vector (*OD* vector), and orientation angle (α) of isomers A and B of tetraene in PVA

Both pale yellow and transparent PVA films were uniaxially stretched at 80°C. Ideal deformation of one of the stretched films was checked by using equation (1).

After the films were stretched, the transparent PVA film was fixed on a metal holder and then heated at 170°C under a flow of nitrogen. After heating, it turned yellow and was successively treated with $NaBH_4$ and washed with distilled water.

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 comparing the absorption with that of a colourless PVA film. The R_d values were obtained by a method reported previously[3], using a NEC PC-9801 microcomputer with a KADEC-L1 A/D converter.

RESULTS AND DISCUSSION

The solid line in *Figure 2a* shows the absorption spectrum of a PVA film prepared from pale yellow powder heated at 170°C for 50 min. *Figure 2b* shows the polarized absorption spectra of the film after stretching at 80°C ($R_s = 6.4$). The fine structures in *Figure 2* are classified into several groups of linear polyenes $\text{-(}CH{=}CH\text{)-}_n$, where the integer *n* indicates the conjugation number[8]. This film has undergone ideal uniaxial stretching and the thickness of the film changed from 200 μm to 106 μm, so the solid line is expected to coincide with the dotted line in *Figure 2a*, which was calculated from $(200/106)(A_{\parallel} + 2A_{\perp})/3$ using the $A_{\parallel}$ and $A_{\perp}$ in *Figure 2b*. However, the dotted line shows higher absorbance than the solid line. The temperature 170°C often causes crosslinking reactions among PVA polymer chains[1], so the physical properties of the PVA should not be the same as before heating. In addition, the all-*trans* type *n*-polyene generally has the largest absorption coefficient among the isomers*. Therefore, in the 170°C heated PVA film, if the *cis–trans* isomerization of polyenes was promoted by 80°C stretching to give an increase in the *trans* isomer population, the spectrum shown by the dotted line calculated by using $A_{\parallel}$ and $A_{\perp}$ of *Figure 2b* without changing the concentrations of polyenes might give higher absorbance than that before stretching.

The R_d curve in *Figure 2b* is for a polyene mixture, and the respective $R_{d,n}$ for each polyene can be estimated from a simulation by assuming that all $R_{d,n}$ of polyenes are constant in the respective absorption regions[10]. The $R_{d,n}$ calculated by simulation plotted in *Figure 3* fits the theoretical curves drawn by using equation (3) with parameters $\alpha_n = 44$, 37 and 31° for $n = 2$, 3 and 4, respectively.

A transparent PVA film was stretched at 80°C

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* See, for example, Reference 9, which gives the absorption coefficients of six isomers of triene

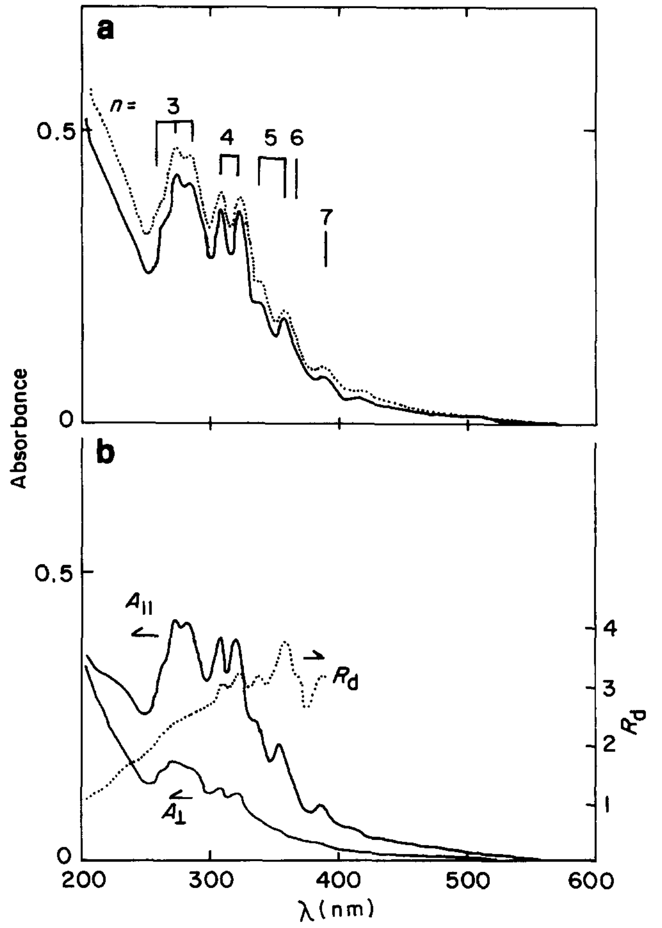

Figure 2 (a) Isotropic and (b) polarized absorption spectra of PVA film stretched ($R_s = 6.4$) after heat treatment at 170°C for 50 min. Film thickness: (a) 200 μm; (b) 106 μm. ······, Spectra calculated from $(200/106)(A_{\parallel}/2A_{\perp})/3$ using the $A_{\parallel}$ and $A_{\perp}$ in (b). Symbols are explained in text

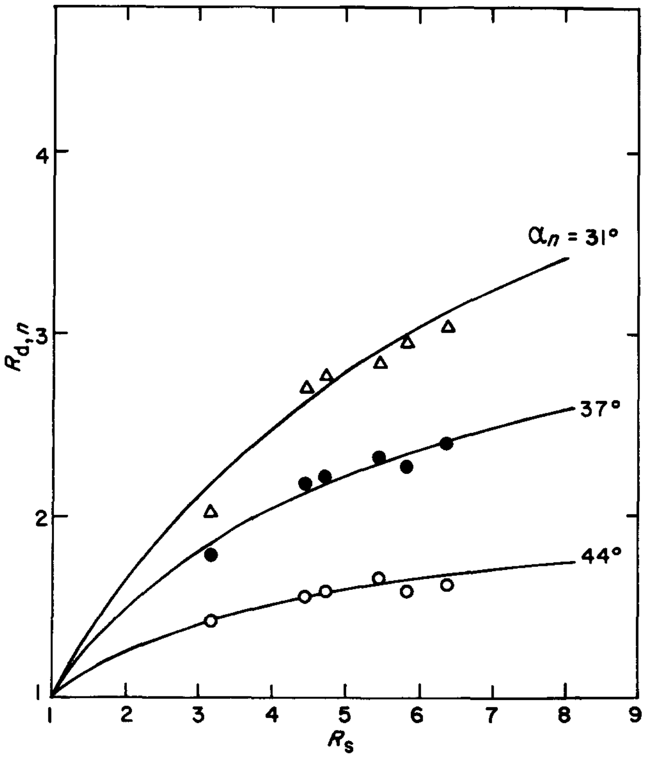

Figure 3 $R_{d,n}$ *versus* R_s for various n. Experimental results: ○, $n=2$; ●, $n=3$; △, $n=4$. ——, Theory

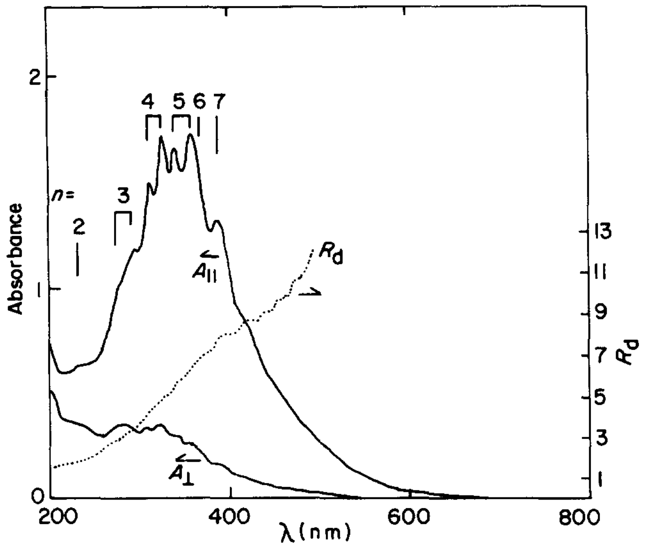

Figure 4 Polarized absorption spectra of PVA film heated at 170°C for 10 min after stretching ($R_s = 5.7$) at 80°C. Film thickness is 90 μm

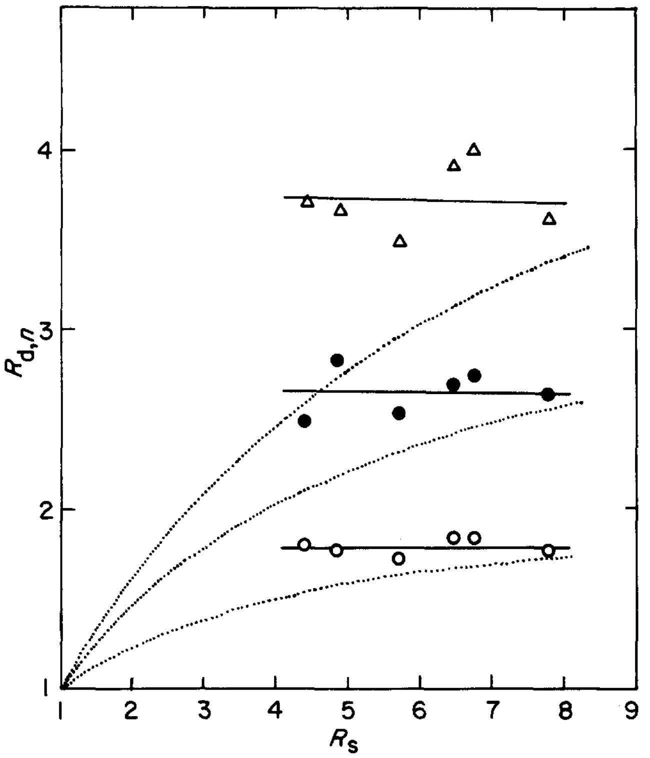

Figure 5 $R_{d,n}$ *versus* R_s for various n. Experimental results: ○, $n=2$; ●, $n=3$, △, $n=4$. ——, Theory; ······, $R_{d,n}$ curves from *Figure 2* for $n=2$, 3 and 4

($R_s = 5.7$) and then heated at 170°C for 10 min. It was treated successively with $NaBH_4$ to remove carbonyl groups. Then it coloured pale yellow and turned hard. Throughout these procedures, it did not deform, probably owing to the structural change of the PVA by crosslinking reactions. The polarized absorption spectra of the film are shown in *Figure 4*. The respective $R_{d,n}$ calculated from the simulation mentioned above are plotted in *Figure 5*. The dotted lines in *Figure 5* give the $R_{d,n}$ curves in *Figure 3*. This PVA film also underwent an ideal deformation by stretching at 80°C and the crosslinking reactions at this stage can be neglected because of low temperature, but the $R_{d,n}$ values do not fit the theoretical curves drawn by using equation (3) for any α. The $R_{d,n}$ values are high and almost constant, regardless of R_s. When a similar PVA film was stretched and then heated at 120°C[3], the respective $R_{d,n}$ obtained were reported to be lower than those shown here in *Figure 5*. In addition, a decrease of $R_{d,n}$ by successive heat treatments was apparently observed, i.e. an orientation relaxation of PVA polymer chains occurs at 120°C. For heat-treatment at 170°C, in the case of this paper, high $R_{d,n}$ values in *Figure 5* do not support the expected orientation relaxation by thermal motion of PVA polymer chains but the formation of polyenes oriented in the stretch direction. The *cis–trans* isomerization of polyenes in this case can be picked out, because the PVA is transparent and consequently it has no polyene sequence before heat treatment.

The stretching of the film apparently promoted both the formation of polyenes and the crosslinking reactions. Because the spectrum of the film stretched after heating was obtained after heating for 50 min (*Figure 2*), the film swelled in water. On the other hand, the spectrum of the film heated after stretch was obtained after heating for 10 min (*Figure 4*) and it did not swell in water in spite of the shorter heating time. Crosslinking reactions may proceed through intermolecular and intramolecular dehydration reactions. On the other hand, polyene formation reactions may proceed through intramolecular dehydrations. If the stretching of the film promoted the dehydration reactions, especially on the segments oriented in the stretch direction, the high $R_{d,n}$ regardless of R_s in *Figure 5* can be acceptable. However, the mechanism relating the stretching of the PVA film with those reactions is not clear at present.

A comparison of the orientation behaviour of polyenes with that of other free molecules using PVA films heated at 170°C is in progress.

CONCLUSIONS

Two important results were obtained when the PVA film was heated after stretching: first, constant and high R_d values regardless of R_s were observed; second, the PVA film heated after stretching did not swell in water. We conclude that the stretching of a PVA film promoted dehydration reactions, especially on the segments oriented in the stretch direction.

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