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Simulation of Absorption Spectra of Polyenes Produced in PVA Film by Heating and Kinetics of Polyenes Formation

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Characteristics of absorption spectra of heated PVA film could be simulated as combinations of absorption spectra of free polyenes corresponding to the type -(CH=CH)$_n$- (n=1—13). The change in concentrations of polyenes produced in PVA films was calculated by means of simulation. Each polyene -(CH=CH)$_n$- was assumed to be produced by a first order reaction with rate constant k_n with respect to the concentration of -(CH=CH)$_{n-1}$-. k_n values (n=1—13) at several temperatures were obtained. Arrhenius plots of k_n from straight lines, giving activation energies 57—63 kJ mol^{-1} for the reaction catalyzed by H_3PO_4 and 94—100 kJ mol^{-1} for that by H_2SO_4. The activation entropies are negative in both cases.

At the initial stage of heating, thermal decomposition of poly(vinyl alcohol) [PVA] leads to formation of polyene structures in main polymer chains.1) The authors have already assigned peaks and bands in absorption and excitation spectra of heated PVA films to 0←0, 1←0, and 2←0 π-π* transitions of -(CH=CH)$_n$- type polyenes and -(CH=CH)$_n$-CO- type polyenones.2) These types are distinguished from each other according as the spectrum is accompanied with a fine structure or not; the former shows a fine structure and the latter a broad band. Under certain conditions, the type of polyenes is preferentially produced. In such cases, a proper combination of absorption spectra of free polyenes is expected to reproduce the experimental spectrum, provided that the concentration of polyenones produced may be disregarded relative to that of polyenes. Moreover, by using the concentration of polyenes determined by simulation, a kinetic study on the polyenes formation is expected to be made.

The present purpose is to simulate absorption spectra of polyenes produced in heated PVA film and to try a kinetic study on the polyenes formation.

Experimental

The PVA used was a commercial one (Koso Chemical Co., Ltd.), of which the average polymerization degree was 1400 and the alkaline saponification was 99—100%. Ten grams of PVA powder was dissolved in distilled water of 200 cm^3 at 90 °C and the solution was poured on a horizontal plate of glass. After it was dried at room temperature for 10 d, a PVA film about 100 μm thick was obtained. This film was kept for 2 h at 80 °C, digested in a mixed solution of 0.1 M(1 M=1 mol dm^{-3}) $NaBH_4$ and 0.1 M NaOH for 1 d to reduce the carbonyl group contained, and then washed successively with 0.05 M HCl solution and with distilled water.

Subsequently, the PVA film was digested in 0.05 M H_3PO_4 or 0.05 M H_2SO_4 solution for 1 d and then dried at room temperature. The PVA film thus treated was fixed on a metal holder and heated in a heating compartment at a constant temperature in a 0.5 dm^3 min^{-1} flow of nitrogen. After a period of time, it was taken out from the compartment and cooled rapidly to room temperature by keeping the holder in contact with a metal plate, and then the absorption spectrum of the film was measured. The above-mentioned procedure from heating to absorption measurement was repeated until the maximum absorbance became 2.0.

Absorption spectra were measured on a Shimadzu UV-360 spectrophotometer, and simulation and kinetic calculation were carried out with a micro computer, an NEC model-N6300 system.

Results

Simulation. The solid line in Fig. 1 shows an example of absorption spectra of PVA film heated at 170 °C. The arrows in Fig. 1 indicate positions of 1←0 transition peaks for respective n values which were already assigned to π-π* transitions of polyenes, -(CH=CH)$_n$-, produced along polymer chains.2)

A simulation for the spectrum was made as follows by combination of absorption spectra of free polyenes corresponding to -(CH=CH)$_n$- with n=1—13. The absorption spectra of free polyenes3—7) were shifted in wave number so that the 1←0 transition peaks were in accord with those assigned by the authors.8) As for the absorption coefficients of polyenes, reported values9) were used. Figure 2 shows examples of the shifted absorption spectra of H(CH=CH)$_n$H used for the simulation where n=6 and 13.

In order to determine concentrations of 13 polyenes produced in the heated PVA film, the following 13 simultaneous equations were solved so that calculated absorbances at 13 wavelengths λ_m (m=1—13) agreed with those observed:

$$A_{\text{obsd}}(\lambda_m) = \sum_{n=1}^{13} C_n \cdot \varepsilon_n(\lambda_m) \cdot d \quad (\text{for } m=1\text{—}13), \tag{1}$$

where $A_{\text{obsd}}(\lambda_m)$ is the absorbance observed at λ_m, C_n, and $\varepsilon_n(\lambda_m)$ are the concentration and molar absorption coefficient of -(CH=CH)$_n$- at λ_m, respectively, and d is the film thickness.

The simulated spectrum is shown by the dotted

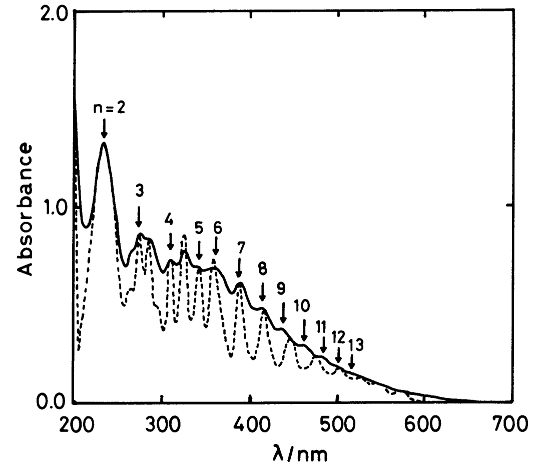

Fig. 1. Absorption spectrum of the heated PVA film (solid line) and that by simulation (dotted line). PVA film was digested in 0.05 M H_3PO_4 solution and heated at 170 °C for 40 min. n indicates conjugation number and arrows indicate 1←0 positions of $-(CH=CH)_n-$.

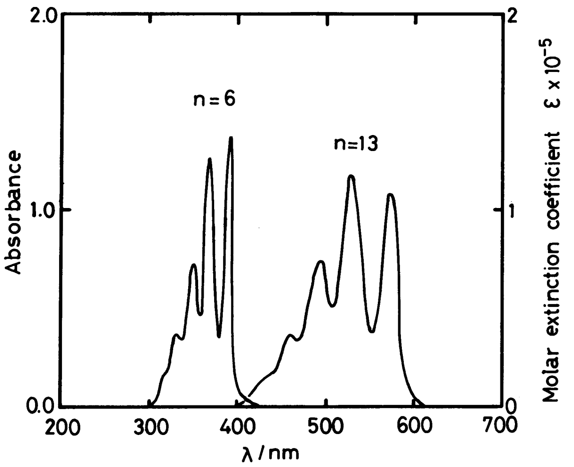

Fig. 2. Shifted absorption spectra of $H(CH=CH)_nH$. The concentration of each polyene is 1 mmol dm^{-3} and the film thickness is 100 μm.

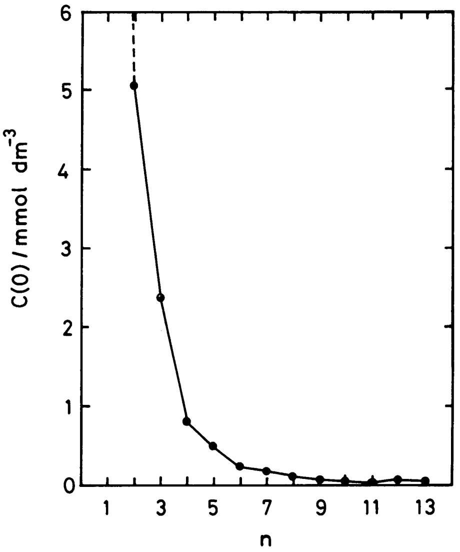

Fig. 3. Concentrations of calculated polyenes produced in the heated PVA film whose absorption spectrum is shown in Fig. 1. The concentration of monoene ($n=1$) is 2.95×10^{-1} mol dm^{-3}.

line in Fig. 1. It is in good agreement with the observed absorption maxima in the region 200—400 nm.

Strictly speaking, the absorption spectra (solid lines) in Fig. 1 should be a mixture of spectra of polyenes and polyenones. But the concentrations of polyenones were disregarded for the simulation, because the excitation spectra of this sample film indicated that the intensities of polyenones were very low compared to those of polyenes.[2]

The concentrations of polyenes calculated by the present simulation, which are given in Fig. 3, are very low and decrease with increasing conjugation number n.

Kinetics. It has been pointed out that the concentrations of polyenones produced in the heated PVA film are much lower than that of polyenes when HCl, H_2SO_4, or H_3PO_4 is used as a catalyzer.[2] For such cases, therefore, a kinetic study on the polyenes formation could be made by repeating the heating process and absorption measurement as described in the Experimental section.

Figure 4 shows the change of absorption spectra of a PVA film with heating time at 170 °C. The concentrations of polyenes $-(CH=CH)_n-$ were determined from the well fitted simulation curves. The marks in Fig. 5 indicate the concentrations of polyenes thus obtained for n=2—6 against heating time. The concentration of each polyene increases rapidly according as the specimen is heated.

Since the concentrations of polyenes are very low at the initial stage of the heating, it is reasonable to consider that each polyene is formed by a dehydration of the PVA unit adjacent to the polyene as follows:

$$-(CH=CH)_{(n-1)}-CH_2CH(OH)- \xrightarrow{k_n} -(CH=CH)_n- + H_2O.$$

Accordingly, the concentration of PVA monomer unit $-CH_2CH(OH)-$, $C(0)$, is calculated by

$$C(0) = C(0)_0 - \sum_{n=1}^{13} n\cdot C(n), \tag{2}$$

where $C(0)_0$ is the initial concentration of PVA unit, which was calculated to be 30.1 mol dm^{-3} from the volume and weight of PVA film before heating, and $C(n)$ is the concentration of $-(CH=CH)_n-$. Values of log $C(0)$ at various heating temperatures were plotted against heating time in Fig. 6. The plots give

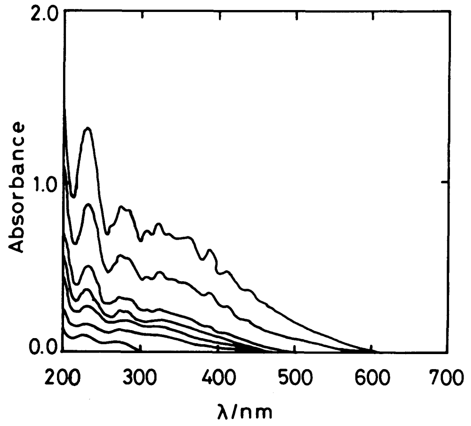

Fig. 4. Absorption spectra of PVA film (106 μm thick) which was digested in 0.05 M H_3PO_4 and heated at 170 °C for 0 (the lowest line), 5, 10, 15, 20, 30, and 40 min (the highest line) respectively.

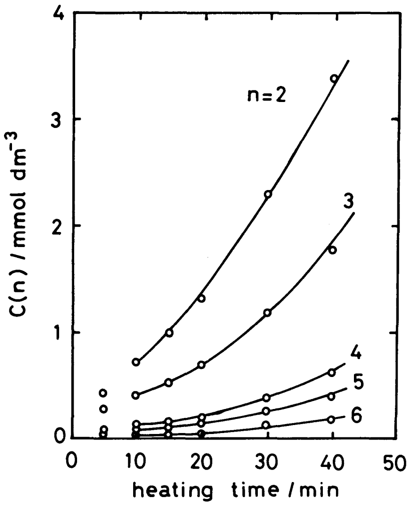

Fig. 5. Comparison of observed concentrations of polyenes (n=2—6) with calculated ones at 170 °C. Marks are experiments, lines are obtained by calculations using the rate constants shown in Table 1 and the concentrations of polyenes at 10 min of heating time as initial condition of the calculation.

straight lines in all cases for 160, 170, 180, and 190 °C. This indicates that the polyene formation is of the first order as a whole.

Assuming that each polyene of -(CH=CH)$_n$- is formed by a first order consecutive reaction, we may handle the following 14 differential equations

$$\left.\begin{aligned} &\mathrm{d}[C(0)]/\mathrm{d}t = -\sum_{n=1}^{13} k_n[C(n-1)], \\ &\mathrm{d}[C(n)]/\mathrm{d}t = k_n[C(n-1)] - k_{n+1}[C(n)] \\ &\qquad\qquad\qquad\qquad (\text{for } n=1\text{—}12), \\ &\mathrm{d}[C(13)]/\mathrm{d}t = k_{13}[C(12)]. \end{aligned}\right\} \quad (3)$$

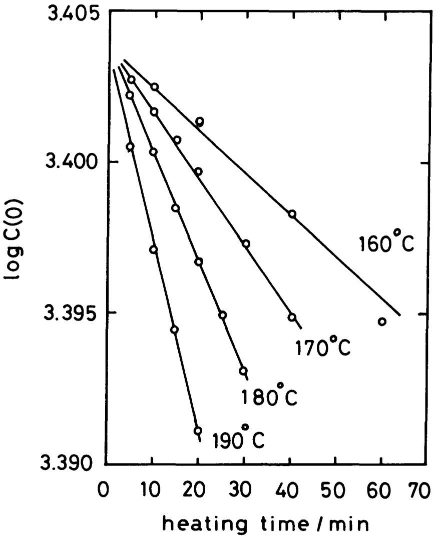

Fig. 6. Relation of log C(0) and heating time at 160, 170, 180, and 190 °C.

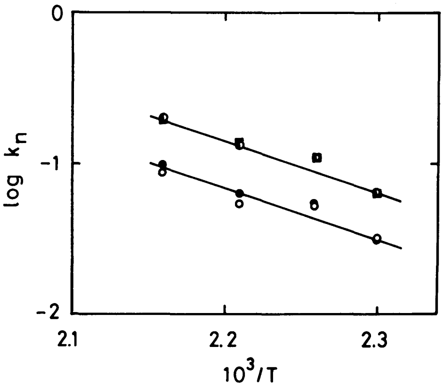

Fig. 7. Arrhenius plots of k_n for PVA film containing H_3PO_4. ○: k_3, ●: k_4, ◐: k_5, ■: k_6.

Such simultaneous differential equations could be solved numerically by the Runge-Kutta method with trial values for rate constants k_1—k_{13}. The most reliable rate constants k_1—k_{13} were determined by making calculated concentrations of polyenes fit experimental ones. The rate constants thus obtained are summarized in Table 1. The calculated curves in Fig. 5, which have been obtained by using the rate constants in Table 1, are in good agreement with the experimental concentrations of polyenes.

Figure 7 shows some of the Arrhenius plots for k_n (n=3—6). They make straight lines for respective rate constants and, therefore, activation energies of the polyenes formation can be calculated. They are summarized in Table 2 together with other activation parameters.

Tables 3 and 4 also shows rate constants k_1—k_{13} and activation parameters determined for the case using H_2SO_4 as a catalyst.

Table 1. Rate Constants for Polyenes Formation Catalyzed by H_3PO_4

Temp	Rate constant/min^{-1}			
°C	160	170	180	190
k_1	0.0001326	0.0002065	0.00033	0.000587
k_2	0.0006784	0.00107	0.00121	0.00211
k_3	0.0346	0.0532	0.052	0.0857
k_4	0.0307	0.0531	0.059	0.0974
k_5	0.0649	0.107	0.125	0.198
k_6	0.0613	0.106	0.128	0.190
k_7	0.112	0.181	0.22	0.31
k_8	0.060	0.174	0.21	0.29
k_9	0.120	0.178	0.21	0.30
k_{10}	0.12	0.20	0.24	0.30
k_{11}	0.22	0.25	0.38	0.56
k_{12}	0.10	0.31	0.28	0.35
k_{13}	0.05	0.09	0.10	0.17

Table 2. Activation Parameters for Polyenes Formation Catalyzed by H_3PO_4 at 175 °C

k_n	Act. E	Act. H_{448}	Act. S_{448}
	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}
k_3, k_4	57	53	−191
k_5, k_6	63	59	−174

Table 3. Rate Constants for Polyenes Formation Catalyzed by H_2SO_4

Temp	Rate constant/min^{-1}			
°C	100	111	120	130
k_1	0.0000369	0.000108	0.0001976	0.000592
k_2	0.000206	0.000648	0.001012	0.002845
k_3	0.0174	0.0512	0.07123	0.181
k_4	0.0167	0.0549	0.07513	0.197
k_5	0.043	0.122	0.1565	0.414
k_6	0.052	0.145	0.1855	0.502
k_7	0.0808	0.205	0.2715	0.766
k_8	0.0930	0.275	0.2668	0.828
k_9	0.0620	0.200	0.2255	0.675
k_{10}	0.0525	0.214	0.212	0.66
k_{11}	01610	0.453	0.368	1.25
k_{12}	0.6075	0.400	0.368	1.65
k_{13}	0.0191	0.075	0.081	0.25

Table 4. Activation Parameters for Polyenes Formation Catalyzed by H_2SO_4 at 115 °C

k_n	Act. E	Act. H_{388}	Act. S_{388}
	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}
k_3, k_4	100	97	−65
k_5, k_6	94	91	−71

Discussion

Simulation. As shown in Fig. 1, the simulated spectrum reproduces well the experimental one with respect to the number and wavelengths of peaks in the region 200—400 nm. Nevertheless, the simulated spectrum does not agree with the absorption minima. Two reasons for this disagreement are conceivable: One is that the broad bands of polyenones form the foundation of the spectrum although the concentrations of polyenones have been judged to be low from the excitation spectra, and the other is concerned with the matter of valleys of the spectrum, which is considered as the determinant. The valleys of the reported spectra of $H(CH=CH)_nH$[5] are deeper than those of $CH_3(CH=CH)_nCH_3$.[10] Considering that the polyenes in the PVA film are formed from part of the polymer chains, their spectra should resemble those of substituted polyenes, $CH_3(CH=CH)_nCH_3$, rather than $H(CH=CH)_nH$. In fact, the excitation spectrum of tetraene produced in the heated PVA film[2] shows shallower absorption minima than the reported spectrum of $H(CH=CH)_4H$[5] as shown in Fig. 8. The absorption spectra of $CH_3(CH=CH)_nCH_3$, however, could not be used for the present simulation, because the spectrum of each polyene described in the report is part of itself. For that reason, such a spectrum with very deep constrictions as shown in Fig. 2 was obliged to be adopted for all the polyenes under consideration.

In the longer wavelength region over 400 nm, the simulated spectrum does not reproduce the number and wavelengths of absorption peaks. One reason is that the absorption spectrum of octaene has been used for $-(CH=CH)_n-$ of n=9—13.

Kinetics. For evaluation of k_n, 30.1 mol dm^{-3} was used as the initial concentration of PVA monomer unit. Taking into consideration the free water remaining in the PVA film before heating, we should assign $C(0)_0$ a smaller value than 30.1 mol

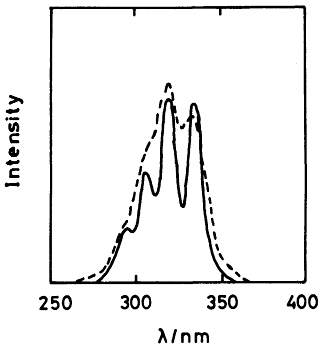

Fig. 8. Shifted absorption spectrum of $H(CH=CH)_4H$ (solid line) and the excitation spectrum of heated PVA film monitored at 383 nm (dotted line).

dm^{-3}. Further, the concentration of monoene, $C(1)$, is not so reliable as those for n=2—7, because the intensity of the absorption shoulder at 200 nm was adopted in the simulation instead of that of the absorption maximum of monoene. However, the unreliabilities of $C(0)_0$ and $C(1)$ influence only k_1 and k_2, having no effect on the other constants k_3—k_{13}. Because, for instance, if 25.0 mol dm^{-3} is used for $C(0)_0$ instead of 30.1 mol dm^{-3}, the value of k_1 is changed to 2.492×10^{-4} from 1.326×10^{-4} min^{-1}, but the k_2—k_{13} values are not changed and kept almost the same as shown in Table 1.

The values of k_8—k_{13} also are less reliable for the reason that the concentrations of polyenes for n=8—13 in PVA were calculated without using the absorption data for longer conjugate polyenes than tridecaene. For the same reason, there is a disagreement of the simulated spectrum with the experimental one in the longer wavelength region over 400 nm.

A few kinetic studies have been reported about the degradation of PVA by heating. Yamaguchi et al.[11] investigated the first order rate constant for degradation of PVA by the thermobalance method. According to their report, activation energies for degradation of commercial PVA powder are about 96—230 kJ mol^{-1}, which are affected by the polymerization degree, the degree of oxidation of PVA, and others. Perepelkin and Borodina[12] postulated that the change in transmittance of PVA film was dependent on the decrease in concentration of PVA monomer unit, and determined the activation energy to be 67—176 kJ mol^{-1} for the PVA film containing CH_3COONa and 192—263 kJ mol^{-1} without CH_3COONa. In the present study, as shown in Tables 2 and 4, the activation energies are 53—64 kJ mol^{-3} for the reaction catalyzed by H_3PO_4, and 94—100 kJ mol dm^{-3} for H_2SO_4, which are comparatively low, probably reflecting the effect of catalyzers.

The activation entropies in Tables 2 and 4 are negative, suggesting some sterical restriction operating in the transition state of the polyenes formation. The difference in numerical values of activation energy and entropy between Tables 2 and 4 may be taken to suggest a difference between the roles of H_3PO_4 and H_2SO_4 as catalysts.

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3) The spectrum of *trans*-$(CH_3)CH=CH(CH_3)$ was cited from Ref. 4, the spectrum of $CH_3(CH=CH)_2CH_3$ being measured with a commercial product (Tokyo Kasei Co., Ltd.). The spectra of $H(CH=CH)_nH$ with n=3, 5, 6, and 8 were cited from Ref. 5; $H(CH=CH)_4H$, from Ref. 6 and $H(CH=CH)_7H$, from Ref. 7. No spectra of $H(CH=CH)_nH$ for n=9 and 11—13 have been reported, however the reported spectrum of decaene (n=10) is very similar to the shifted octaene (n=8). Therefore, the spectrum of octaene was used for these of polyenes of n=9—13.

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8) Since the peak maximum of monoene, $-CH=CH-$, was not detected in the measured absorption range (190—800 nm) in this study, the spectrum of *trans*-$CH_3(CH=CH)CH_3$ was used as it was, i. e., without any shifting applied for the simulation. Since both $0\leftarrow0$ and $1\leftarrow0$ transitions of tetraene and pentaene were observed in the experimental spectrum, the experimental spectra of $H(CH=CH)_nH$ (n=4 and 5) were shifted so that both the absorptions of $0\leftarrow0$ and $1\leftarrow0$ agreed with their experimental positions.

9) The molar absorption coefficent of $H(CH=CH)_4H$ was not described in Ref. 6; the molar coefficient of $CH_3(CH=CH)_4CH_3$ given in Ref. 10 was used. Since the molar absorption coefficient of heptaene reported for the $1\leftarrow0$ transition (33000) is so small compared with those of hexaene (127000) and octaene (112000), the average value (119500) for hexaene and pentaene was used as the absorption coefficient of heptaene.

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