Activation parameters for degradation of polyenes produced in heated poly(vinyl alcohol) film

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Polyenes $-(CH{=}CH)_n-$ produced in heated poly(vinyl alcohol) film degrade on successive heat treatment after the film has been washed well with distilled water. The change in concentration of polyenes was calculated by means of simulation. Each polyene with $n = 10$ and 11 degrades by a first-order reaction with respective rate constant k_n. Arrhenius plots of k_n form straight lines, giving an activation energy of 82 kJ mol^{-1} and a negative activation entropy. These values are consistent with that of Diels–Alder reactions of polyenes.

(Keywords: poly(vinyl alcohol); polyene; bleaching; activation parameters)

INTRODUCTION

It is well known that the primary degradation product of poly(vinyl alcohol) (PVA) on heat treatment is a distribution of conjugated polyene sequences along PVA polymer chains, and that the degraded PVA has a reddish-brown colour[1]. Assuming that each polyene $-(CH{=}CH)_n-$ is formed by first-order consecutive dehydration of a PVA unit adjacent to a polyene $-(CH{=}CH)_{n-1}-$, a kinetic study reveals that the average activation energy for polyene formation with $n = 3$–12 on heat treatment is 95 kJ mol^{-1} for the reaction catalysed by H_3PO_4 and 60 kJ mol^{-1} for that catalysed by H_2SO_4 (ref. 2). However, when a red PVA film was heated after the film had been washed with distilled water to remove the catalyser for polyene formation, the coloration of the PVA film proceeds in the early stage of heating and then the bleaching reaction occurs[3]. If the PVA film coloured on heat treatment is washed well with distilled water, coloration does not proceed on further heat treatment but only the bleaching reaction occurs. This phenomenon is interpretable as degradation of polyenes, especially those with $n \geqslant 6$.

We report here a kinetic study and present the activation parameters for degradation of polyenes $-(CH{=}CH)_n-$ where $n = 10$ and 11.

EXPERIMENTAL

PVA films were prepared by casting an aqueous PVA solution on a glass plate according to the method reported previously[2]. These films were swollen with 0.01 M aqueous HCl solution, i.e. doping PVA with a catalyser for polyene formation, and dried at room temperature. Then they were fixed on metal holders and heated at 100°C in a 0.5 dm^3 min^{-1} flow of nitrogen.

The films coloured red by heat treatment as mentioned above were soaked in distilled water/0.05 M $NaBH_4$/0.05 M NaOH mixed solution for 1 day in order to reduce the content of carbonyl groups. They were then washed with 0.1 M aqueous CH_3COOH solution to neutralize NaOH, soaked in distilled water for 5 days and dried at room temperature. The red films thus obtained were used as the starting films for the experiments.

The absorption spectrum of this red film is shown as a full curve in *Figure 1*. The fine structures in *Figure 1* have already been classified into the respective polyenes[4], where integer n indicates the conjugation number of $-(CH{=}CH)_n-$.

The PVA film thus treated was heated at a constant temperature in a 0.5 dm^3 min^{-1} flow of nitrogen. It was removed after various time intervals and cooled to room temperature by keeping the metal holder in contact with a metal plate. Then the absorption spectrum of the film was measured on a Shimadzu UV-360 spectrophotometer.

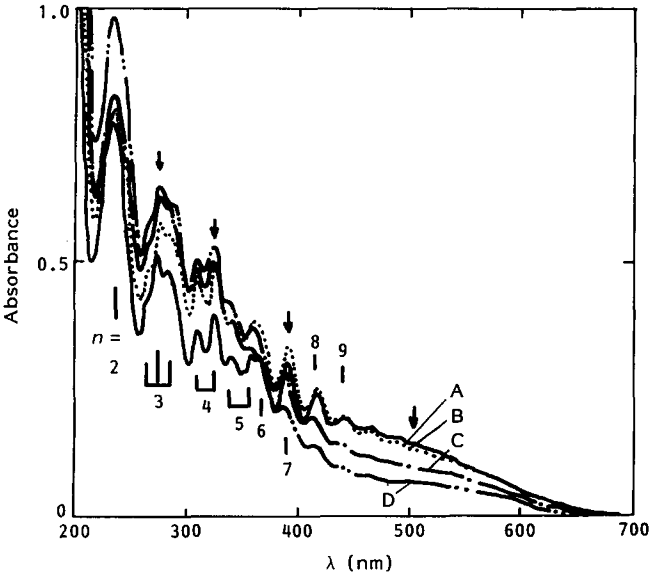

Figure 1 Absorption spectra of PVA film (200 μm thick) heated at 200°C for (A) 0, (B) 9, (C) 25 and (D) 80 min, respectively. Integer n indicates the conjugation number of $-(CH{=}CH)_n-$. Arrows indicate the positions of monitoring wavelengths in *Figure 2*

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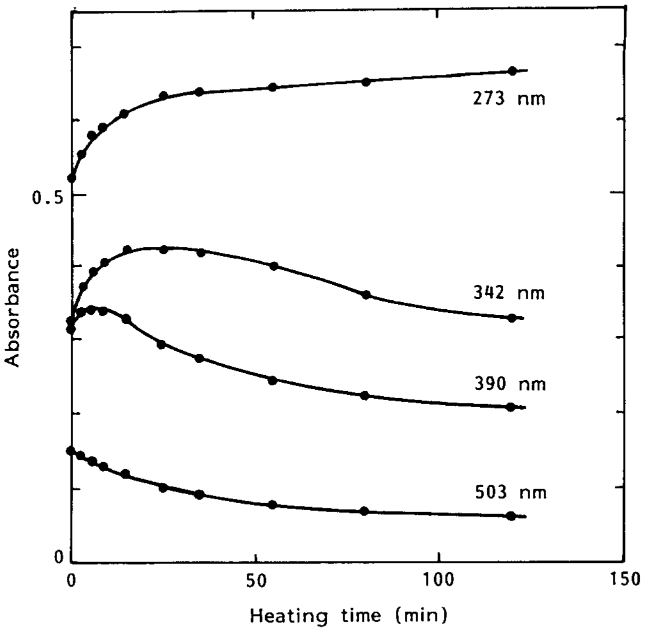

Figure 2 Change in absorption of PVA film monitored at 273, 342, 390 and 503 nm, which are pointed out by arrows in *Figure 1*

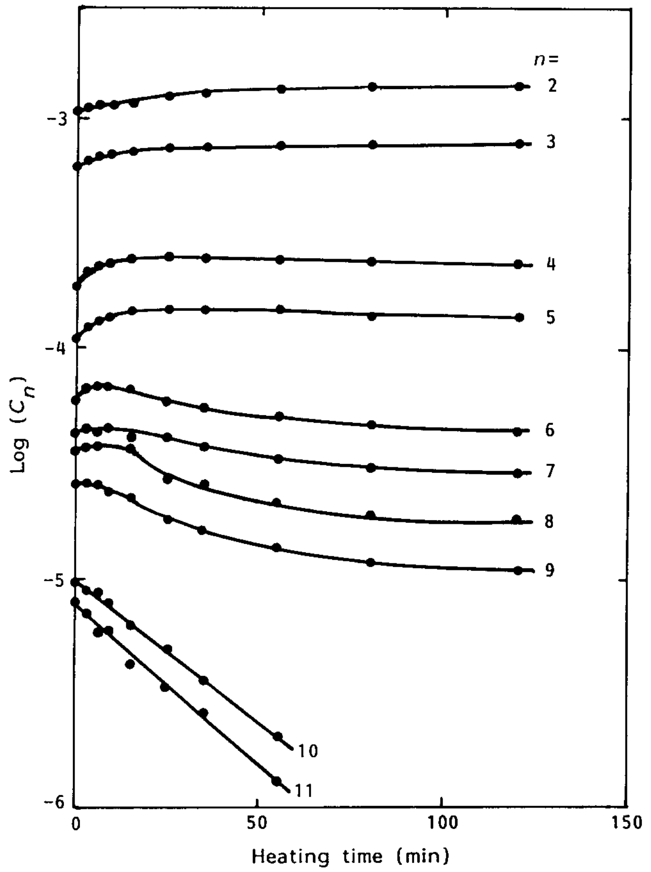

Figure 3 Relation between log(C_n) and heating time at 200°C for respective n

RESULTS

When a red PVA film was heated at 200°C, it turned to pale yellow and the absorption spectrum (A) changed to (B), (C) and (D) as shown in *Figure 1*, i.e. absorption increases in the shorter-wavelength region (<380 nm) while it decreases in regions longer than 420 nm. *Figure 2* shows the change in absorbance monitored at specific wavelengths, which are indicated by arrows in *Figure 1*. The absorption in the region below 300 nm increases in two stages according as the PVA film was heated, as shown by the curve monitored at 270 nm in *Figure 2*. The absorption between 300 and 420 nm increases in the initial stage of heating and then decreases, as shown by the curve monitored at 342 nm. The absorption above 420 nm decreases monotonically, as shown by the curve monitored at 503 nm. The concentration of each polyene for each absorption spectrum measured at various time intervals is calculated by means of a simulation reported previously[3] using the absorption spectra and the absorption coefficient of free polyenes.

Values of log(C_n) at 200°C are plotted against heating time in *Figure 3*, where C_n is the concentration of $-(CH=CH)_n-$. The plots give straight lines for $n = 10$ and 11. This indicates that the degradation of $n = 10$ and 11 polyenes is of first order. The other plots at 160, 190 and 210°C also give straight lines for $n = 10$ and 11. Thus the rate constants for each polyene and each temperature could be obtained; Arrhenius plots of k_{10} and k_{11} form straight lines (*Figure 4*) and give the activation energies. *Table 1* summarizes the rate constants of $n = 10$ and 11 and the activation energy, together with other activation parameters, where each parameter is the average value of $n = 10$ and 11 since they are not essentially different from each other.

In *Figure 3*, the concentrations of $n = 2$ and 3 do not decrease in the whole stage of heating but increase in two

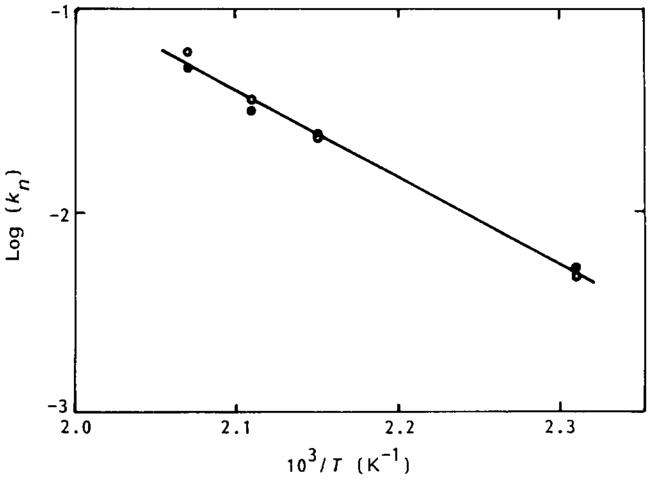

Figure 4 Arrhenius plots of k_n for degradation of $n = 10$ (○) and 11 (●)

Table 1 Rate constants and activation parameters for degradation of polyenes

	Rate constant (min^{-1})				Activation parameters		
	160°C	190°C	200°C	210°C	E (kJ mol^{-1})	H_{473} (kJ mol^{-1})	S_{473} (J K^{-1} mol^{-1})
k_{10}	0.0048	0.024	0.032	0.051	82	78	−141
k_{11}	0.0041	0.023	0.036	0.061			

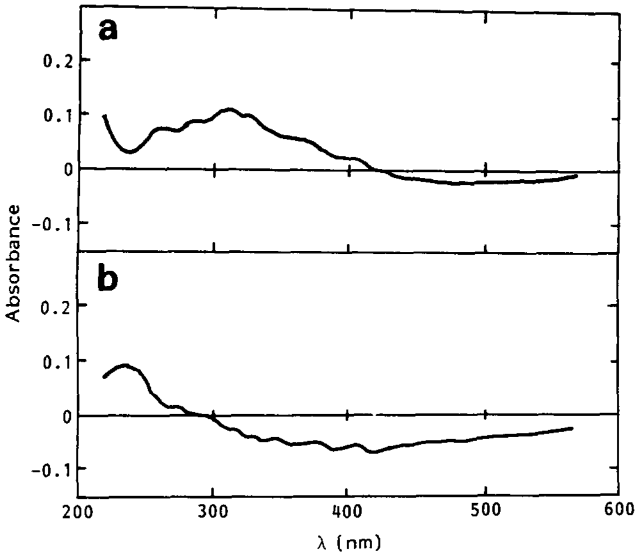

Figure 5 Difference spectra: (a) between A and B in *Figure 1*; (b) between C and D in *Figure 1*

stages according as the film was heated. Although the concentrations of $n=4$–9 increase in the initial stage of heating, they decrease after 20 min. This indicates that the polyenes with $n=4$–9 also degrade on heat treatment. The fine structure of $n \leqslant 6$ tends to broaden as it was heated, so that the increment of absorption should not only be caused by the produced linear polyenes under consideration.

Figures 5a and *5b* show the difference spectra between A and B, and between C and D, respectively, in *Figure 1*, where the positive and negative parts represent a decrease and an increase in absorbance, respectively. In *Figure 5b*, i.e. in the last stage of heating, the bleaching reaction proceeds and the 230 nm band increases, along with a slight increase of the 280 nm band. The absorption bands of both diene and monoene carbonyl are at 230 nm and those of triene and diene carbonyl are at 280 nm[4]. The absorption of polyene $-(CH=CH)_n-$ and polyene carbonyl $-(CH=CH)_nCO-$ are distinguishable from each other according as the spectrum is accompanied by fine structure or not: the former shows fine structure and the latter a broad band[4]. Since the fine structure in *Figure 1* tends to broaden as the film was heated and the treatment of this film with $NaBH_4$ caused the absorption to decrease in the short-wavelength region, the increase of these 230 and 280 nm absorption bands indicates the production of polyene carbonyl of $n=1$ and 2.

In the initial stage of heating, the increase of broad absorption in the difference spectrum of *Figure 5a* also indicates the production of polyene carbonyl. However, the decrement of absorbance in the long-wavelength region in *Figure 5a* is so small compared with the increment of absorption in the short-wavelength region that it is difficult to speculate that the degradation of long polyenes leads to an increase of short polyene carbonyls. *Figures 6a* and *6b* show the absorption spectra and the change in absorbance, respectively, at specific wavelengths of colourless PVA film heated at 200°C, in which the film was washed well before heat treatment; the absorption increased slowly as it was heated. As mentioned in the 'Experimental' section, the coloured PVA film swelled in water before heat treatment, so that these conditions may influence the production of polyene carbonyls in the initial stage of heating since the rapid increase in the initial stage of heating is also observed in *Figure 6b*.

DISCUSSION

The thermal degradation of poly(vinyl chloride) (PVC) also gives rise to polyene structures in the polymer chains[5]. On the addition of trifluoroacetic acid to dichloromethane solution of degraded PVC, new species are formed with strong bands at 730 and 790 nm which are assigned to the polyenylic ions formed by protonation of the polyenes[6]. The mechanism of bleaching of thermally degraded PVC by solvent impurities such as peroxide was investigated systematically[7]. In the present study of PVA, these reactions can be neglected since an increase in absorbance in the 800 nm region was not observed as the film bleached, and the heat treatment was carried out in the solid state, out of solvent, and in a flow of nitrogen.

The rate constants for formation of polyenes with $n=10$ are $1.2\times10^{-1}\,\mathrm{min}^{-1}$ catalysed by H_3PO_4 at 160°C and $6.6\times10^{-1}\,\mathrm{min}^{-1}$ catalysed by H_2SO_4 at 130°C as reported previously[3]. The rate constant for polyene degradation of $n=10$ is relatively very small, $4.8\times10^{-3}\,\mathrm{min}^{-1}$ at 160°C. By comparison of these rate constants, polyene formation, coloration of PVA in other words, proceeds as an overall reaction in the presence of acid.

The thermal degradation of polyenes is a complex of consecutive and parallel reactions which can involve ionic, molecular and radical mechanisms. In the present study, the negative activation entropy suggests the activated state to be rigid. Tudes *et al.*[8] reported that proportionality between the amount of polyenes and the degree of dehydrochlorination is observed only at the

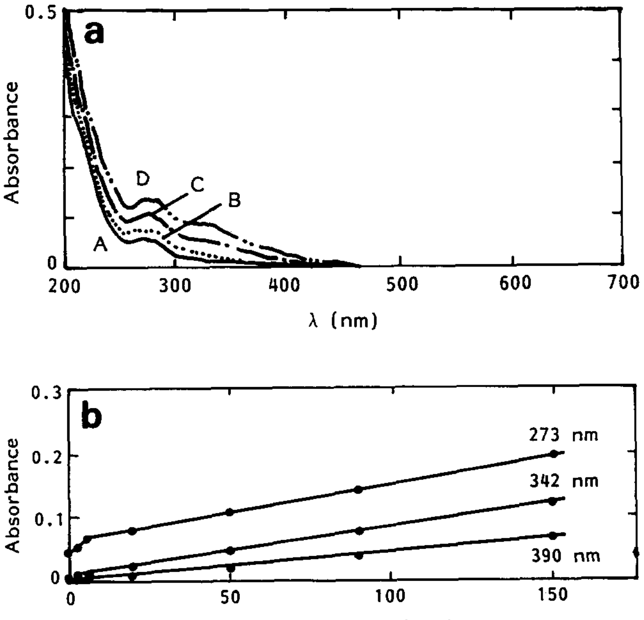

Figure 6 (a) Absorption spectra of PVA film (200 μm thick) heated at 200°C for (A) 0, (B) 20, (C) 50 and (D) 90 min, respectively, and (b) change in absorbance monitored at 273, 342 and 390 nm

initial stage of degradation and, later on, the number of double bonds in the system is much lower than the amount of hydrogen chloride molecules split off. This phenomenon is interpreted by intramolecular cyclization of polyenes, namely Diels–Alder reactions[8]. Kinetic studies of Diels–Alder reactions of polyenes revealed that they require relatively small enthalpies of activation and strongly negative entropies of activation[9]. Activation parameters obtained in the present study are consistent with the values of Diels–Alder reaction. However, it is difficult at present to interpret the large increment of short polyenes compared with the decrement of long polyenes as shown in *Figure 5a* and contrary small increment of short polyenes in *Figure 5b*.

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