Extraction of absorption spectra of some poly(vinyl alcohol) film utilizing photodegradations by monochromatic light

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Individual absorption spectra of $-(CH=CH)_n-$ ($n=2-5$) produced in heated poly(vinyl alcohol) (PVA) films can be extracted separately by selective photodegradation. Difference spectra between the two spectra obtained at various different irradiation times did not show the spectra of individual polyenes owing to overlapping of the spectra due to degraded and produced polyenes. By proper combination of irradiations, however, the other spectra could be eliminated, and each spectrum of $n=2-5$ could be extracted. For $n=4$ and 5, the second bands were revealed.

INTRODUCTION

Absorption spectra of heat-treated poly(vinyl alcohol) (PVA) film have been interpreted as those of a mixture of $-(CH=CH)_n-$ polyenes and vibrational peaks have been assigned to the $\pi-\pi^*$ transitions of linear polyenes[1]. The same authors have also investigated the kinetics of polyene formation by heat treatment[2] and dichroism of polyenes oriented by stretching the film[3]. In those investigations[2,3], the concentrations of polyenes were calculated by means of simulation by combination of absorption spectra of free polyenes of the type of R–$(CH=CH)_n$–R (R=H, CH_3)[4,5]. The simulated absorption and dichroic spectra reproduced well the experimental ones with respect to the absorption maxima, but did not agree with the minima. This may indicate that the spectra of polyenes formed along the PVA chains do not always correspond to those of free polyenes. Accordingly, in order to improve the reliability of analysis by simulation of the polyene spectra of PVA, it is necessary to obtain the absorption profiles of individual polyenes as they are.

As reported previously[6], the absorption spectrum of a mixture of polyenes produced in PVA film shows characteristic changes upon heat treatment and light irradiation; the heat- and photodegradation of polyenes is undergone preferentially for those of $n \geqslant 6$ and $n \leqslant 5$, respectively. If the photodegradation of polyenes is dependent on the wavelength, absorption of a particular polyene can be decreased by irradiation at a selected light wavelength. In such a case, the difference between the two spectra for samples at different irradiation times should give an absorption spectrum of the polyene in question. Furthermore, if successive irradiation with various monochromatic light wavelengths is properly applied, the undesired polyenes can be selectively removed so that only the desired polyene remains. In this paper we will use the word 'extraction' to mean obtaining an absorption of a defined polyene by such a procedure.

The main purpose of this investigation was to extract the absorption spectra of n-polyenes separately from one another.

EXPERIMENTAL

PVA films were prepared by the method reported previously[1] using a commercial PVA powder (Koso Chemical Co. Ltd) for which the average degree of polymerization was 1400 and alkaline degree of saponification was 99–100%. Film not subjected to chemical treatment is called PVA-1, while the film for which the treatment described below was carried out to reduce carbonyl groups is called PVA-2. The treatment was to soak the sample in 0.05 M $NaBH_4$–0.05 M NaOH solution for 1 day, then to wash with distilled water before again soaking in 0.05 M HCl solution for 3 h and then finally drying for 1 day at room temperature.

The PVA-1 and PVA-2 films were fixed on, respectively, metal holders and heated at 170°C (PVA-1) and 120°C (PVA-2) in a 0.5 dm³ min⁻¹ flow of nitrogen. The films after heat treatment were soaked in distilled water for 1 day, 0.05 M $NaBH_4$–0.05 M NaOH solution for 1 day, 0.05 M HCl solution for 1 day, distilled water for 2 days, and then dried at room temperature for 3 days. They were used as starting materials for experiments.

A sample film was irradiated in air with a 500 W xenon lamp and the absorption spectrum was measured on a Shimadzu UV-360 spectrophotometer at various time intervals. The selection of the wavelength of irradiating light was carried out using a Shimadzu RF-502 spectrofluorophotometer having a slit width of 10–15 nm.

RESULTS

Spectral changes by irradiation

When λ, the wavelength of irradiating light, is in accord with or close to the wavelength of a vibrational transition
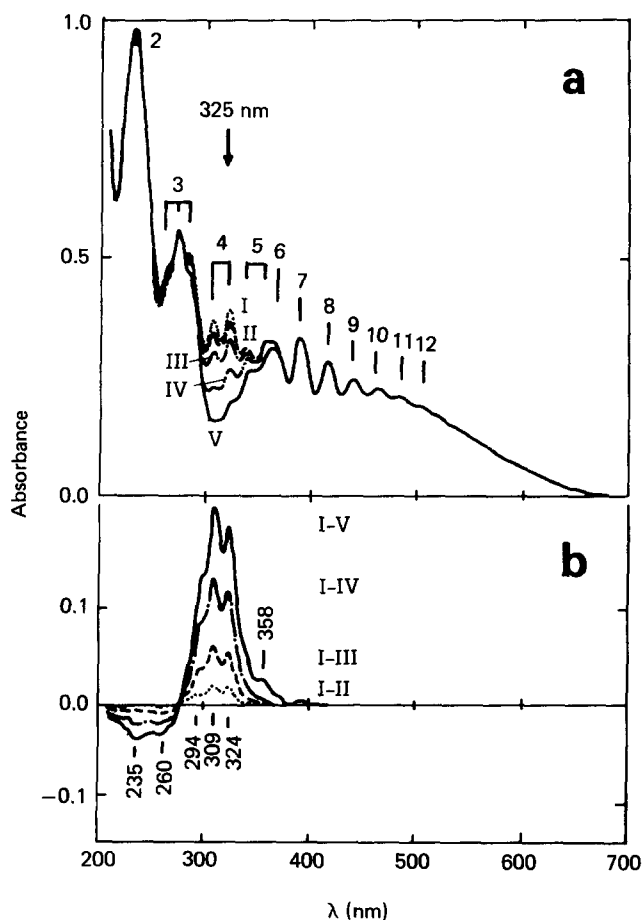
Figure 1 (a) Absorption spectra of heat-treated PVA-2 film irradiated with 325 nm light for 0 (I), 5 (II), 30 (III), 120 (IV) and 420 min (V). Integer n indicates the conjugation number of $-(CH=CH)_n-$. (b) Difference spectra between I and II–V. Upper and lower parts of the zero line represent decrease and increase in absorbance, respectively. Figures along curves indicate the peak wavelength

$v\leftarrow 0$ of n-polyene, it is expressed by $\lambda n(v)$. For instance, since 235 nm corresponds to the $1\leftarrow 0$ transition of diene $(n=2)$, it is denoted by $\lambda 2(1)$.

The absorption spectra of a film were measured at various time intervals. The spectrum of a red film obtained by heat treatment of PVA-2 is shown in *Figure 1a* as spectrum I. The fine structures are already classified into the respective n-polyenes, $-(CH=CH)_n-$, which are indicated by integers[1]. When the film was irradiated with 325 nm light $(\lambda 4(0))$, spectrum I successively changed to II, III, IV and V; i.e. the absorption decreased in the 300–380 nm region and at the same time increased in the region below 278 nm.

Figure 1b shows the difference spectra between I and others, II–V, where the upper and lower parts of the line through zero represent a decrease and an increase in absorbance, respectively. Most of the absorption decrease can be attributed to the degradation of tetraene $(n=4)$, because the peaks at 324, 309 and 294 nm correspond to the $0\leftarrow 0$, $1\leftarrow 0$ and $2\leftarrow 0$ transition peaks for $n=4$, respectively. In the difference spectra (I–V), there is an additional peak at 358 nm which corresponds to the $0\leftarrow 0$ transition for $n=5$. This means that the small amount of pentaene is degraded concomitantly. In the case of increased absorption, the formation of triene $(n=3)$ and diene $(n=2)$ are considered because the peaks are recognized at 260 and 235 nm, which correspond to

$2\leftarrow 0$ of $n=3$ and $1\leftarrow 0$ of $n=2$, respectively. Consequently, it can be said that the photodegradation of $n=4$ and $n=5$ produce $n=2$ and $n=3$.

The difference spectra for various irradiating lights are shown in *Figures 2a–2f* for the heat-treated PVA-2 in the same way as *Figure 1b*. The arrows denote the positions of wavelengths of irradiating light and the integers indicate the peak wavelengths.

The evidence provided by the spectral changes shown in *Figures 2a–2f* and the reasons are as follows.

(a) $n=2$ (245, 234 nm) and $n=3$ (274 nm) are decreased by light irradiation at 235 nm $(\lambda 2(1))$. The peak at 274 nm is due to the $1\leftarrow 0$ transition of $n=3$.

(b) $n=3$ (287, 274, 263 nm) and $n=4$ (324, 309 nm) are decreased and $n=2$ (232 nm) is increased by 275 nm light $(\lambda 3(1))$.

(c) $n=4$ (324, 309, 295 nm) and $n=5$ (358 nm) are decreased and $n=2$ (238 nm) is increased by 310 nm light $(\lambda 4(1))$.

(d) $n=4$ and $n=5$ are decreased and $n=2$ and $n=3$ are increased by 325 nm light $(\lambda 4(0))$. This finding has already been explained for the results in *Figure 1b*.

(e) $n=4$ (324, 309, 295 nm) and $n=5$ (358, 340 nm) are decreased and $n=2$ and $n=3$ are increased by 340 nm light $(\lambda 5(1))$. The reason why the absorption of $n=4$ is decreased by the light $\lambda 5(1)$ is that the absorption train of the $0\leftarrow 0$ transition of $n=4$ extends to the spread region of $\lambda 5(1)$.

(f) $n=4$ (324, 310 nm) and $n=5$ (358, 339 nm) are decreased and $n=2$ (234 nm) and $n=3$ (274 nm) are increased by 360 nm light $(\lambda 5(0))$, where the reduced amount of $n=5$ is much more than in the case of (e).

The intersecting points of the difference spectra of *Figures 2a–2f* moved within about 5 nm accordingly as a sample film was irradiated. This may be due to the mixture of polyenes in the system for which multiple reaction proceeds simultaneously.

Extraction of absorption spectra of polyenes

The difference spectra give much information about peak wavelengths of fine structures of polyenes. However, they do not show the true difference spectra of individual polyenes because there are other spectra present in the longer and shorter wavelength regions of the spectrum for a given n-polyene; i.e. a reduction of polyenes larger than n in the longer part and an increase of polyenes smaller than n in the shorter. For this reason, in order to obtain the absorption spectrum of a particular n-polyene, it is necessary to remove completely the other polyenes by means of proper combination of irradiation of various monochromatic or filtered lights. *Figures 3a–3f* show the absorption spectra thus obtained for the PVA-1 and heat-treated PVA-1 films.

The procedures for extraction of the respective spectra of *Figures 3a–3f* were as follows.

Figure 3a. A PVA-1 was irradiated with xenon light from a light source without filter. Spectrum I changed into II. When this film was then soaked in $NaBH_4$ solution for 2 days, spectrum II changed to III. The very small change from II to III suggests that the amount of carbonyl group by light irradiation is very small. As a result, the final curve shows an absorption edge of $n=1$.

Figure 3b. Spectrum I changed into II for 1 day exposure to xenon light with a filter transparent above 308 nm, for which polyenes of $n\geq 4$ disappeared.
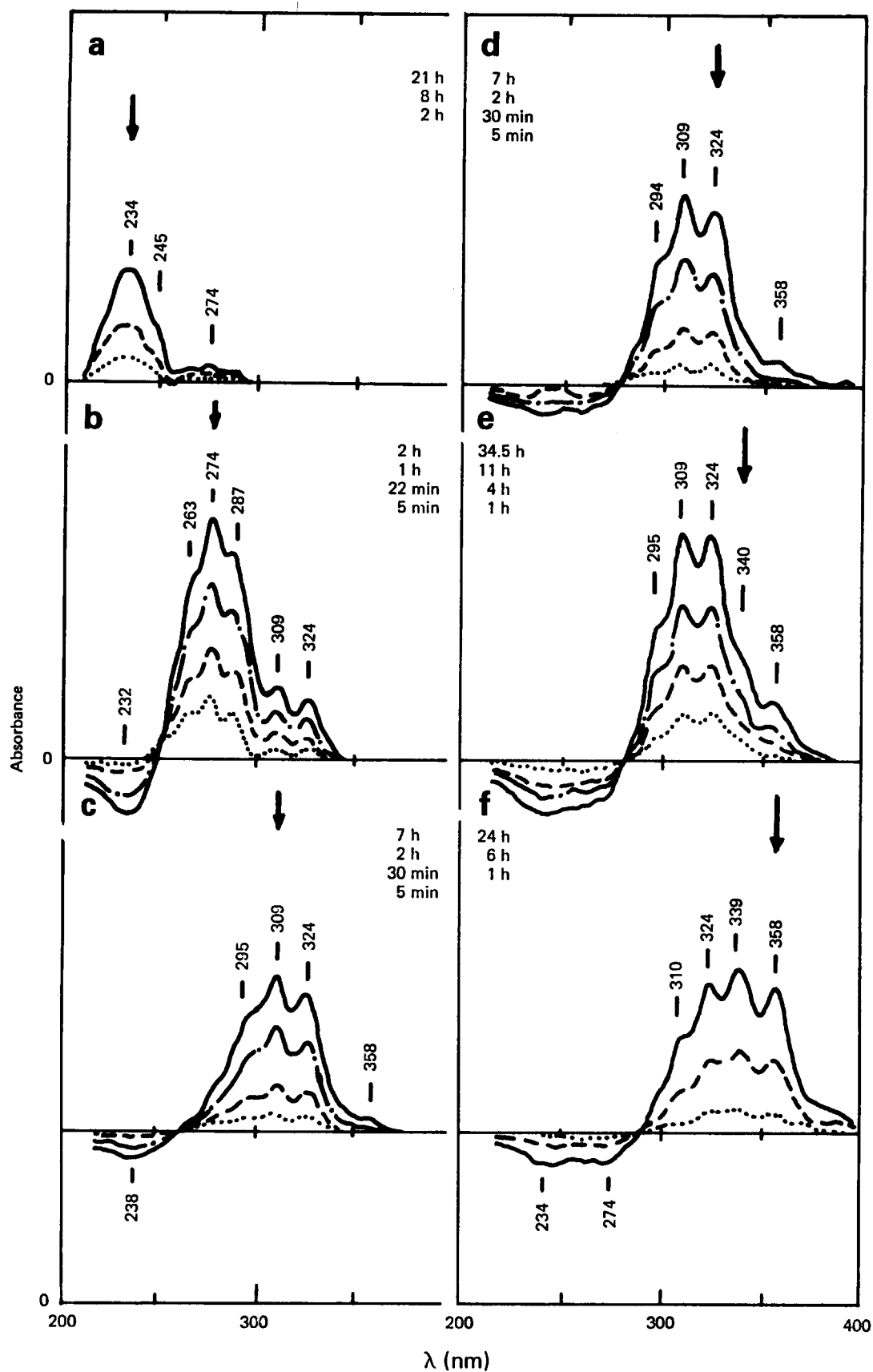
Figure 2 Difference spectra for irradiation of variour monochromatic lights (see the caption to *Figure 1b*) for heat-treated PVA-2. The order of the irradiation times is recorded and that of curves correspond to one another. The arrows indicate the position of wavelengths of irradiation light: (a) 235 nm, (b) 275 nm, (c) 310 nm, (d) 325 nm, (e) 340 nm, (f) 360 nm
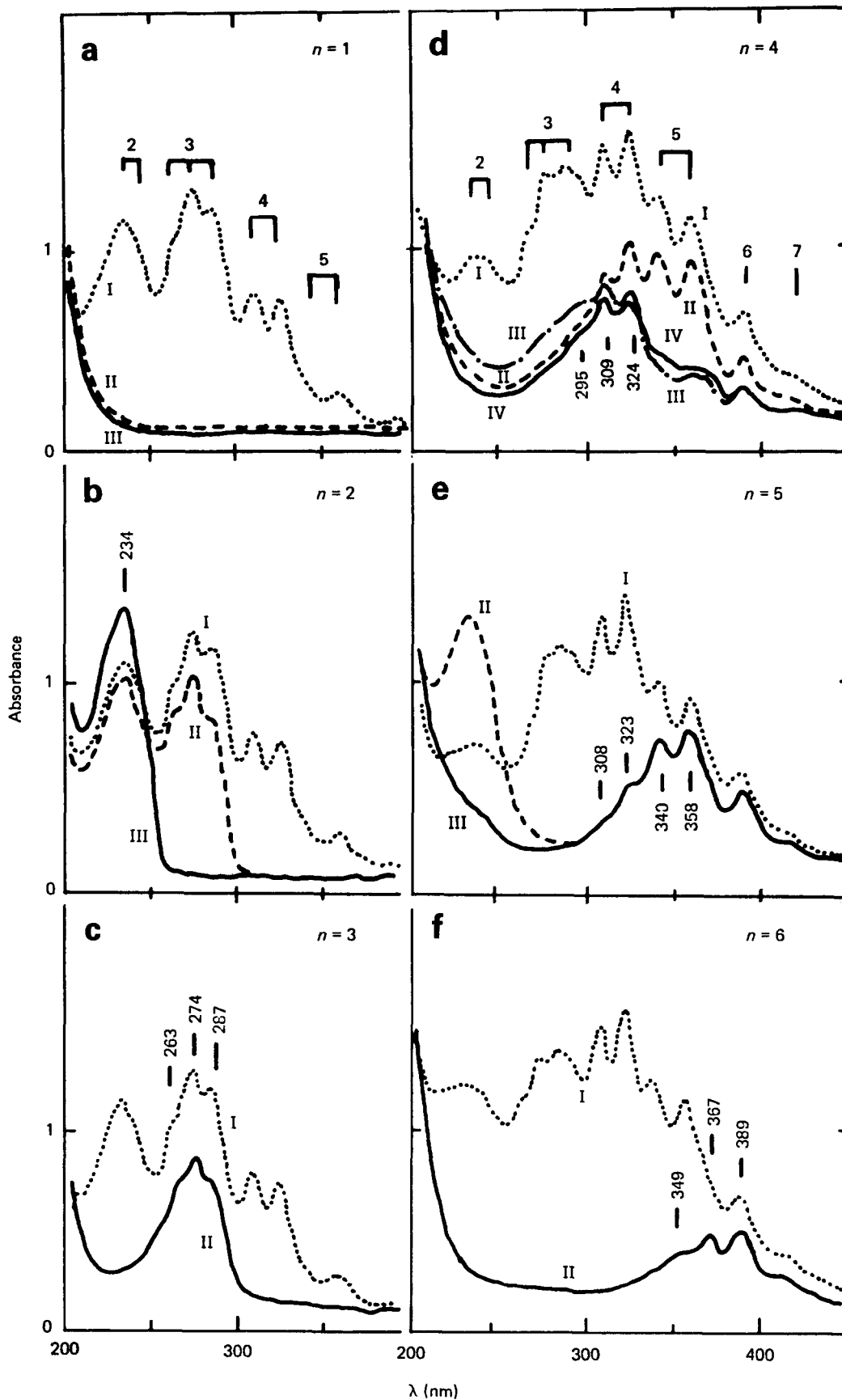
Figure 3 Absorption spectra of PVA-1 and heat-treated PVA-1 films irradiated with various lights. A detailed description is given in the text
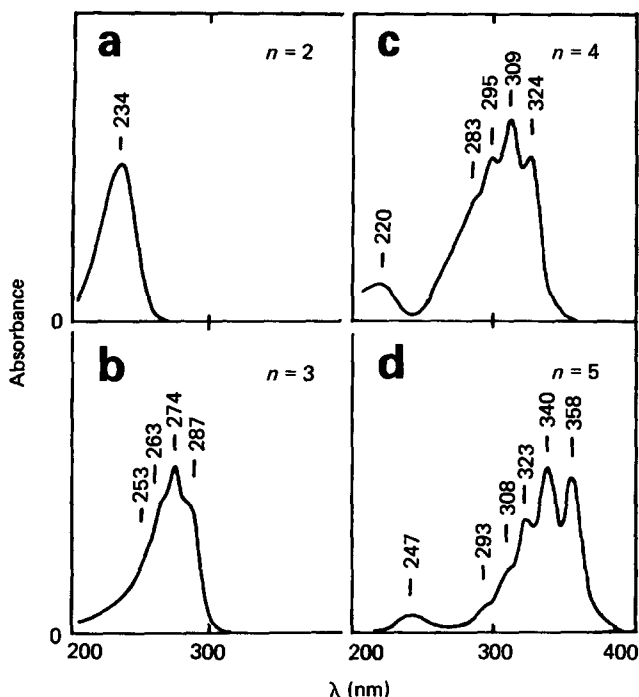
Figure 4 Extracted absorption spectra of $-(CH=CH)_n-$ ($n=2-5$) produced in PVA film

Therefore, spectrum II consists of those of polyenes of $n=1,2$ and 3. By the following irradiation of 275 nm light ($\lambda3(1)$) for 1 day, the polyene of $n=3$ disappeared. Curve III is the final spectrum obtained after the sample had been soaked in $NaBH_4$ solution. Spectrum III indicates the absorption mixture of $n=1$ and $n=2$. The spectrum of $n=1$ could not be eliminated, because a light source was not available. (The following is the same.)

Figure 3c. Spectrum II was obtained from II in *Figure 3b* by the irradiation of 230 nm light ($\lambda2(1)$) for 5 days. It consists of the spectra of $n=1$ and $n=3$.

Figure 3d. Heat-treated PVA-1 (spectrum I) was irradiated with 250 nm light ($\lambda2(0)$, $\lambda3(3)$) for 5 days, and then turned into II by exhaustion of $n=2$ and $n=3$. Spectrum II changed to III upon irradiation by xenon light with a filter transparent above 360 nm for 6 days. In this case, the absorption of $n=5$ and higher are evidently decreased, but increased in the absorption region of $n=2$ and $n=3$ (230–300 nm). Therefore, the film was irradiated again with 250 nm light ($\lambda2(0)$, $\lambda3(3)$) for 1 day. The final spectrum IV indicated the absorption mixtures of $n=1, 4, 5$ and 6. The amounts of $n=5$ and $n=6$ are considered to be small compared with that of $n=4$ (324, 309, 295 nm).

Figure 3e. Heat-treated PVA-1 (spectrum I) was irradiated with 290 nm light ($\lambda3(0)$, $\lambda4(2)$) for 1 day. The spectrum I changed to II, being exhausted of $n=3$ and $n=4$ and produced $n=2$. Spectrum II became III by further successive irradiation at 245 nm ($\lambda2(0)$, $\lambda4(3)$) for 19, 22 and 6.5 h, respectively. Spectrum III shows the absorption mixtures of $n=1, 5, 6$ and 7. The amounts of $n=6$ and $n=7$ are considered to be small compared with that of $n=5$ (358, 340, 323, 308 nm).

Figure 3f. Spectrum I changed to II by irradiation with xenon light through a saturated $NiSO_4$ aqueous solution in 1 cm thick transparent cell in 240–360 nm region for 2 days and by further irradiation without filter for 1 day. Spectrum II shows the absorption mixtures of $n=1, 6, 7$

and 8. In the spectrum, the peaks at 328–390 nm may be assigned to $n=6$ (389, 367, 349 nm).

Spectra of n-polyenes of $n>6$ could not be obtained by the same techniques as above. It was owing to their very slow change in absorption and low power of the light source used.

DISCUSSION

Absorption spectra of polyenes

As mentioned in the Results section, the final curve in *Figure 3a* shows the absorption edge of $n=1$, and those of *Figures 3b* and *3c* show the spectra of mixtures of $n=1$ and 2 and $n=1$ and 3, respectively. Therefore, by a suitable subtraction of spectrum of $n=1$ (*Figure 3a*) from that of *Figure 3b* or *Figure 3c*, an actual spectrum of $n=2$ or 3, respectively, may be determined. In the case of $n=3$, for instance, the curve $n=1$ (*Figure 3a*) is subtracted from that of *Figure 3c* so that the slope of $n=3$ resembles the reported curve[5]. Thus, the spectra shown in *Figures 4a* and *4b* were obtained for $n=2$ and $n=3$, respectively.

In order to obtain a spectrum of $n=4$ included in the final curve IV of *Figure 3d*, it is necessary to exclude the spectra of $n=1$ and $n\geqslant5$. To achieve this, a complex procedure for subtraction of *Figures 3a* and *3e* from *Figure 3d* is required. This gave a spectrum for $n=4$, as shown in *Figure 4c*. A spectrum for $n=5$, shown in *Figure 4d* was obtained in the same way, by subtraction of *Figures 3a* and *3f* from *3e*.

Figures 4c and *4d* show the second absorption bands of $n=4$ and $n=5$ at 220 nm and 247 nm, respectively, which are not detectable in *Figures 3d* and *3e*. Since the second bands of $CH_3(CH=CH)_nCH_3$ have been reported present at 215 nm for $n=4$ and 235 nm for $n=5$ in hexane solution[5], the above identification is reasonable.

As mentioned above, the respective absorption spectra of $n=2-6$ produced in PVA film could be successfully extracted. In fact, an experimental absorption spectrum of heated PVA film can be reproduced well using the extracted spectra, as shown in *Figure 5*.

The peak wavelengths shown in *Figures 3* and *4* are summarized in *Table 1*. Peaks not evident in *Figure 4* but
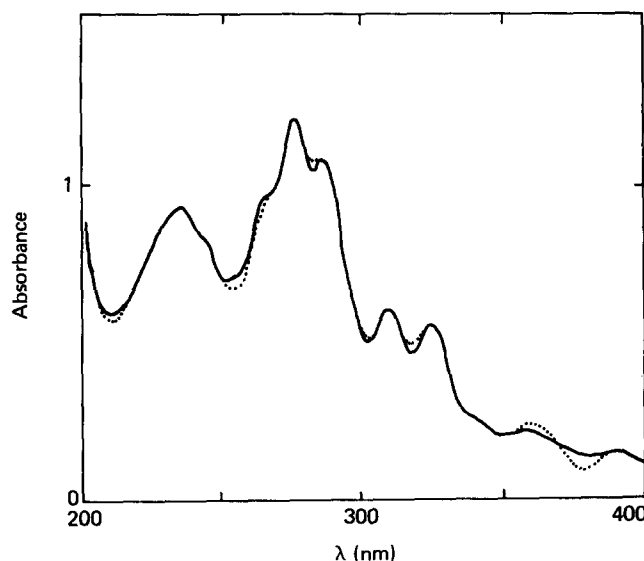

Figure 5 Absorption spectra of heated PVA film determined by experiment (————) and simulation (-----)

Table 1 Assignment of absorption peaks of $-(CH=CH)_n-$ produced in PVA films

n	Second band	First band				
		4←0	3←0	2←0	1←0	0←0
2			(220)	(228)	234	(245)
3			253	263	274	287
4	220		283	295	309	324
5	247	293	308	323	340	358
6			(329)	349	367	389

( ) indicates the wavelength determined by the secondary differential spectra of *Figure 3*

determined by the secondary differential spectra of *Figure 3* are indicated in parentheses in *Table 1*. A Lewis–Calvin plot[7] of the square of peak wavelength in *Table 1* against the conjugation number n gives straight lines for each classified transition, as shown in *Figure 6*.

Table 1 clarifies more peaks of fine structures of n-polyenes which are masked by strong bands due to other mixed polyenes.

Photodegradation of polyenes

According to *Figure 2d*, the absorption due to $n=2$ and $n=3$ increase as those of $n=4$ and $n=5$ diminished by the $\lambda 4(0)$ light. Stoichiometric increase and decrease of these species can be calculated approximately using the simulation method reported previously[2], provided that the extracted specta obtained above are used. If the amount of $n=4$ lost is equal to 1.00 mol, then the amount of $n=5$ lost is estimated to be 0.09 mol and as a result 0.43 mol of $n=2$ and 0.65 mol of $n=3$ are produced. This implies that polyenes produced of $n=2$ and $n=3$ are mainly related to a reduced amount of $n=4$, since the amount of $n=5$ is small. The formation of $n=3$ from $n=4$ requires the disappearance of a terminal π-bond, while the formation of $n=2$ from $n=4$ requires that of a π-bond adjacent to terminal.

Owen and Williams reported that $Ph(CH=CH)_4Ph$ degrades photochemically to produce $Ph(CH=CH)_3-$ and $Ph(CH=CH)_2-$, successively, in hexane solution in the presene of HCl[8]. This fact suggests that the terminal π-bonds of linear polyenes are more reactive than the inner ones under light irradiation. In this investigation, from the semiquantitative analysis of photodegradation of $n=4$, it has been demonstrated that both the terminal and inner π-bonds can disappear by light irradiation, the former more readily than the latter.

Concerning photooxidation[9] and photoinduced hydrochlorination[10] of conjugated polyenes produced in poly(vinyl chloride), the qualitative analysis of absorption spectra has been reported. However,
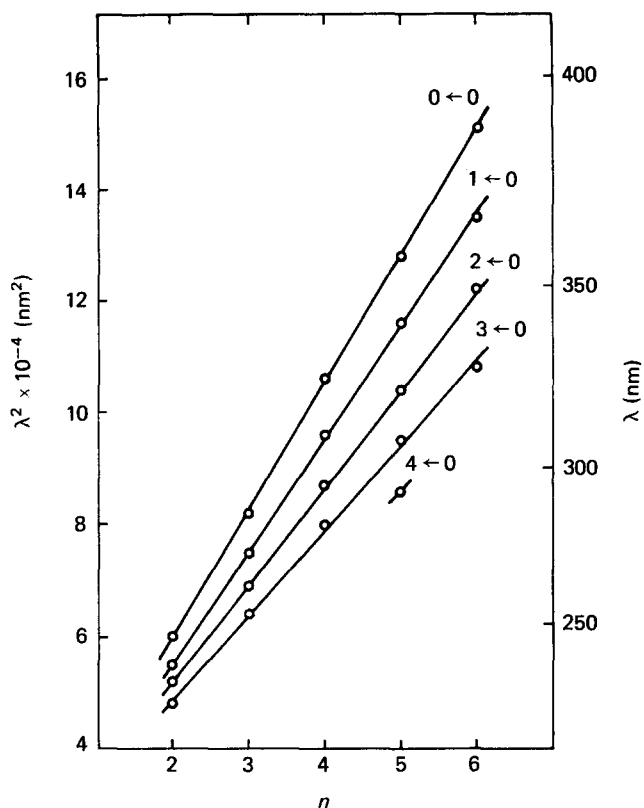

Figure 6 Lewis–Calvin plot of relation between the square of peak wavelength, λ^2, and the conjugation number, n, of $-(CH=CH)_n-$

quantitative analysis of the amount of formed and degraded polyenes has not been discussed, possibly due to difficulty in estimating the quantities of formed or degraded polyenes for the absorption spectra owing to the overlap of the component polyenes.

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