Absorption coefficients of polyenes in heated poly(vinyl alcohol) film and distribution of polyenes formed by its photodegradation

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The absorption coefficients of polyenes $(\text{-CH=CH-})_n$ with $n=2-5$ in heat-treated poly(vinyl alcohol) (PVA) film were determined approximately by the analysis of selective photodegradation. The distribution of polyenes formed by photodegradation of the heat-treated PVA film was estimated using the absorption coefficients obtained. It indicated that the reactivity of the terminal double bond of polyenes decreased as the conjugation number increased.

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

INTRODUCTION

The change in the absorption spectrum upon light irradiation of a mixture of polyenes $(\text{-CH=CH-})_n$ produced in poly(vinyl alcohol) (PVA) by heat treatment is peculiar[1], i.e. photodegradation of polyenes occurs preferentially for those with $n \leqslant 5$. Photodegradation of polyenes produced in poly(vinyl chloride) (PVC) has also been reported[2]. In this case, photo-induced dehydrochlorination of PVC occurs at the same time to give a polyene structure, so that the photodegradation of polyenes produced in PVC is more complicated than in the case of PVA and the analysis is difficult.

Since the photodegradation of polyenes in PVA is dependent on the wavelength of irradiation, each individual absorption spectrum of *n* conjugated polyene (*n*-polyene for short) with $n=2-5$ was extracted separately by selective photodegradation[3].

In this report, the absorption coefficients of the polyenes are determined approximately by the idea that the decrement in absorbance of *n*-polyene and the increment in absorbance of the formed polyenes are equal at the isosbestic point, which is observed by irradiation with selected wavelengths of light. Concomitantly, the distribution of polyenes formed by photodegradation of *n*-polyene is discussed.

EXPERIMENTAL

Some 8 g of PVA powder (Koso Chemical Co. Ltd), of which the average degree of polymerization was 1400 and alkaline saponification was 99–100%, was heated in air at 160°C for 5 h. After heating it turned pale yellow. This powder was washed repeatedly with distilled water, dissolved in 200 cm^3 distilled water at 90°C, and the solution cast on a horizontal plate of poly(methyl acrylate) (30 cm × 25 cm). After drying at room temperature for 7 days, the PVA film thus obtained was heated for 2 h at 120°C under a flow of nitrogen.

The pale-yellow PVA film was swollen with distilled water and digested in a mixed solution of 0.2 M ($1\ \text{M} = 1\ \text{mol dm}^{-3}$) $NaBH_4$ and 0.01 M NaOH for 3 days in order to reduce the carbonyl groups[4], and then in water for 1 day, in 0.1 M CH_3COOH for 1 day and in distilled water for 10 days. This film was then heated at 120°C for 2 h under a flow of nitrogen.

Another sample film used for the analysis of photodegradation of polyene with $n=5$ was prepared according to a method reported previously[4], using the powder without heat treatment before casting. Heat treatment of this film at 170°C gave a yellow film in which the content of $n=5$ was much more than in the above pale-yellow films.

The above procedure was carried out in a darkroom. Distilled water prepared under a flow of nitrogen was used.

A sample film was irradiated in nitrogen with a 500 W xenon lamp. The selection of the wavelength of the irradiating light was carried out using a Shimadzu RF-502 Spectrofluorophotometer having a slit width of 10–15 nm. The absorption spectrum was measured on a Shimadzu UV-360 Spectrophotometer.

RESULTS

When a pale-yellow PVA film was irradiated with 325 nm light (this wavelength corresponds to that of the $1 \leftarrow 0$ transition of the polyene with $n=4$), the spectrum changed as shown in *Figure 1a*. The difference spectrum between the spectra before and after irradiation is shown in *Figure 1b*, where the parts above and below the line through zero represent a decrease and an increase in absorbance, respectively.

Figure 1b indicates that on light irradiation the absorption of $n=4$ in general decreases but that there is an increase at short wavelengths. The crossing points of the spectra observed after 16–420 min irradiation show an isosbestic point at 279 nm.

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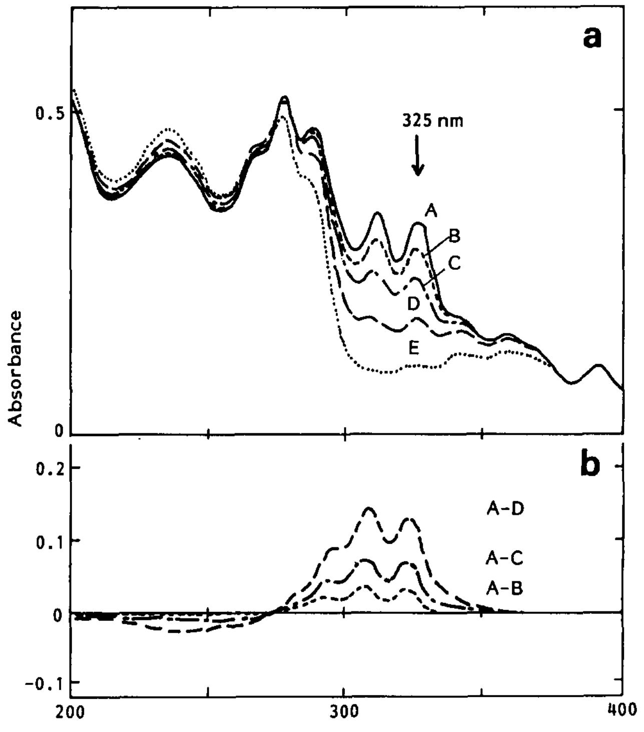

Figure 1 (a) Absorption spectra of sample PVA film irradiated with 325 nm light for 0 (A), 16 (B), 90 (C), 420 (D) and 3000 min (E). (b) Difference spectra between A and B to D. Parts above and below the zero line represent a decrease and an increase in absorbance, respectively

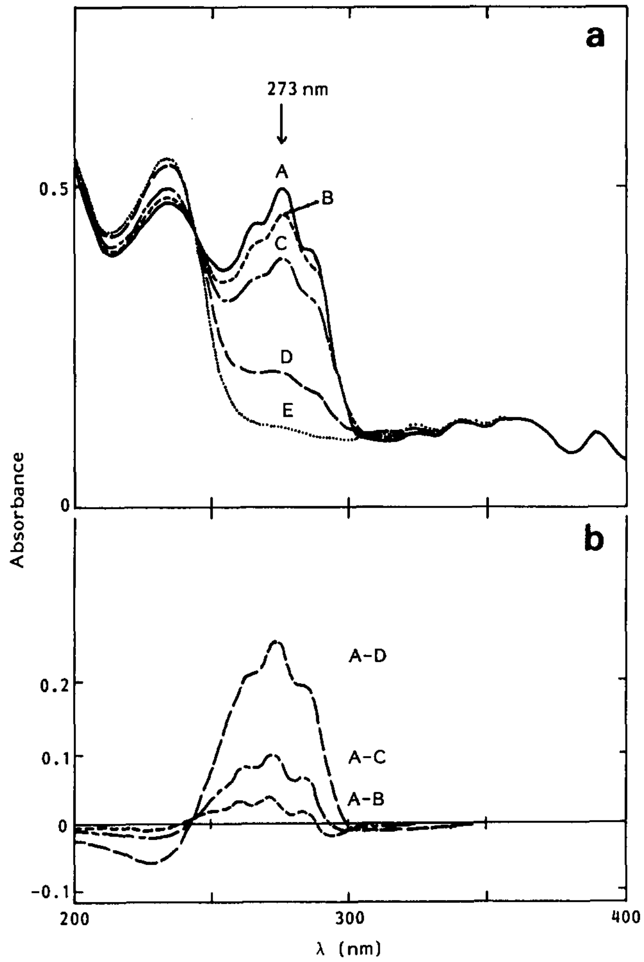

Figure 2 (a) Absorption spectra of sample PVA film irradiated with 273 nm light for 0 (A), 40 (B), 240 (C), 540 (D) and 5940 min (E). (b) Difference spectra between A and B to D

After irradiation with 325 nm light for 50 h to remove $n=4$ polyenes completely, 273 nm light ($1 \leftarrow 0$ of $n=3$) was used to reduce the absorption of $n=3$ and to increase that in the region shorter than 246 nm and the region longer than 280 nm, as shown in *Figures 2a* and *2b*. On irradiation for 40–540 min, the isosbestic point was observed at 246 nm.

After irradiation with 273 nm light for 99 h to remove $n=3$ completely, 234 nm light ($1 \leftarrow 0$ of $n=2$) was used to reduce the absorption of $n=2$. On irradiation for 0–130 min, the absorption of the 250 nm band increases slightly. On further irradiation, the broad absorption in the region longer than 250 nm increases, as shown in *Figures 3a* and *3b*. On irradiation for 130–1263 min, the isosbestic point is observed at 204 nm.

For the irradiation of $n=5$, a sample film was first irradiated with 295 nm light for 77.5 h in order to reduce $n=3$ and 4. The sample film was irradiated with 360 nm light ($1 \leftarrow 0$ of $n=5$) to reduce the absorption of $n=5$. After 1594 min irradiation, the isosbestic point is observed at 294 nm, as shown in *Figure 4*.

Logarithms of concentration ($\ln C_n$) for respective n are plotted against irradiation time in *Figure 5a* for $n=2$–4 and in *Figure 5b* for $n=5$, where C_n is the normalized amount of polyene assuming that the difference in absorbance between the spectra before and the last one after irradiation is equal to 1.0. The plots for respective n give straight lines after the isosbestic point has appeared. This indicates that the photodegradation of $n=2$–5 is of first order in this irradiation time range.

DISCUSSION

The difference spectra in *Figures 1–4* suggest that the photodegradation of n-polyene gives polyenes shorter than itself. If it is assumed that the scission of a π-bond

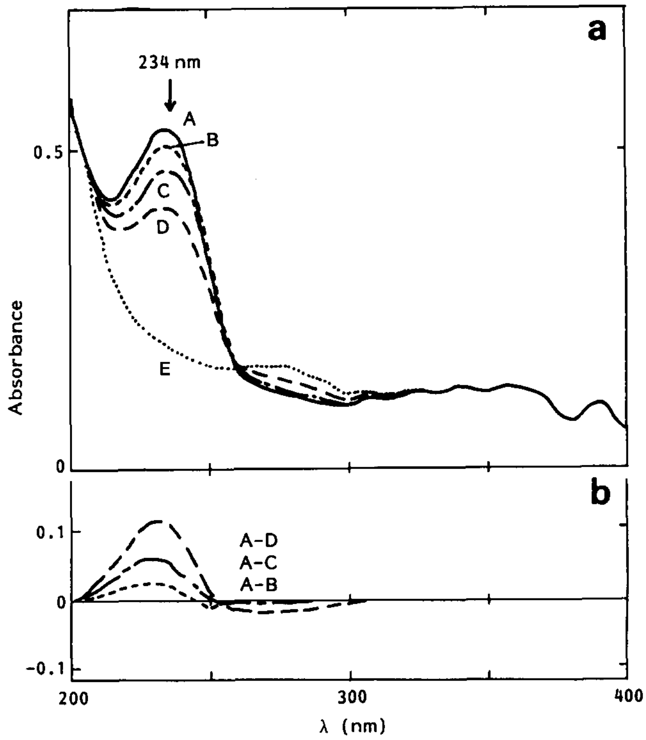

Figure 3 (a) Absorption spectra of sample PVA film irradiated with 234 nm light for 0 (A), 130 (B), 420 (C), 1263 (D) and 10230 min (E). (b) Difference spectra between A and B to D

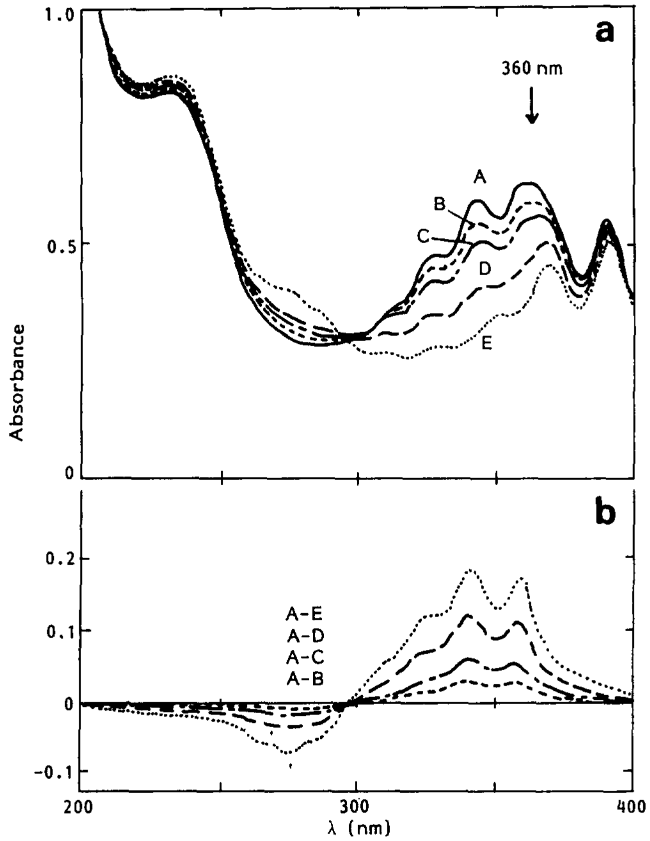

Figure 4 (a) Absorption spectra of sample PVA film irradiated with 360 nm light for 0 (A), 300 (B), 1594 (C), 4242 (D) and 15 500 min (E). (b) Difference spectra between A and B to E

system occurs at only one double bond, the photodegradation can be expressed as follows:

$$(\text{-CH=CH-})_n \xrightarrow{h\nu} (\text{-CH=CH-})_m + (\text{-CH=CH-})_{n-m-1}$$

For an isosbestic point to appear on light irradiation, it is necessary that equation (1) is satisfied:

$$\varepsilon_n^{\mathrm{i}}|\Delta C_n| = \varepsilon_{n-1}^{\mathrm{i}}|\Delta C_{n-1}| + \varepsilon_{n-2}^{\mathrm{i}}|\Delta C_{n-2}| + \cdots \quad (1)$$

where $\varepsilon_n^{\mathrm{i}}$ and ΔC_n indicate the absorption coefficient at the isosbestic point and the increment or decrement in n-polyene.

There is no absorption besides that due to n- and $(n-1)$-polyenes at the wavelength of the isosbestic point for $n=2$–4, and also none except that due to n-, $(n-1)$- and $(n-2)$-polyenes for $n=5$ (cf. ref. 3). Equation (1) for respective n is summarized in *Table 1*, where, for $n=3$ and $n=5$, $\Delta C_1/2$ and $\Delta C_2/2$ are introduced in the material balance so that scission at the centre of 3-polyene and 5-polyene gives twice $n=1$ and $n=2$, respectively.

The absorption spectrum for each of $n=2$–5 produced in PVA has already been obtained by selective photodegradation[3], so that the relative absorption coefficients at various absorption wavelengths for each n-polyene can be obtained. Some of them, at the various isosbestic points used in the calculation, are summarized in *Table 2*. In order to determine the concentrations of m component polyenes by simulation of the spectrum of a mixture of polyenes, the following m simultaneous equations were solved so that the calculated absorbances at m wavelengths λ_m agreed with those observed[5]:

$$A_{\text{obs}}(\lambda_m) = \sum_{n=1}^{m} C_n \varepsilon_n(\lambda_m) d \quad (2)$$

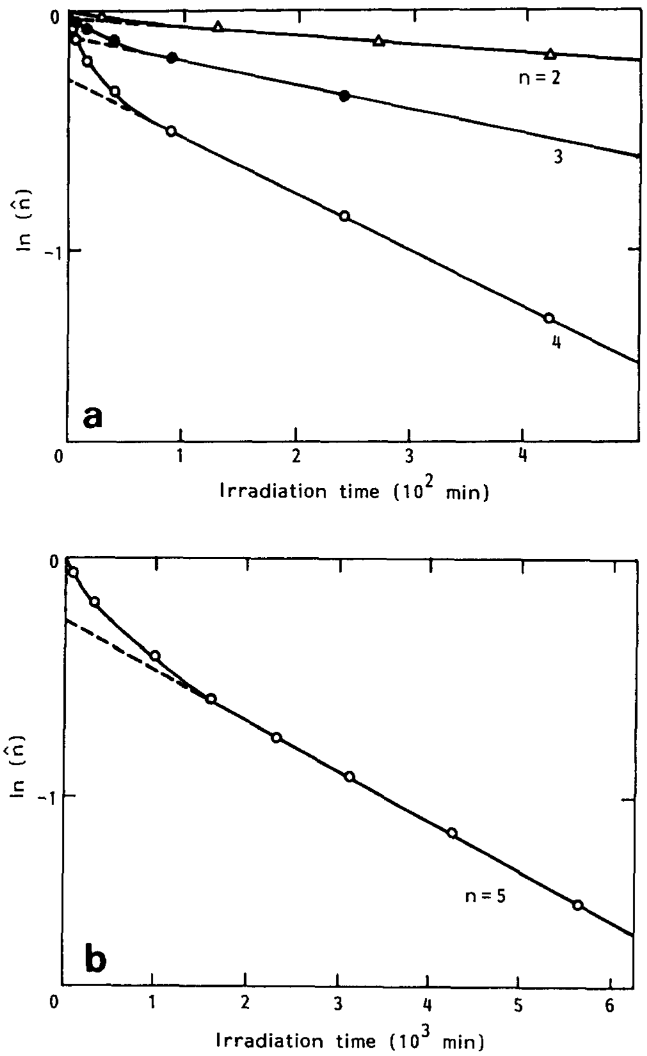

Figure 5 Relations between ln C_n and irradiation time for $n=2$–4 (a) and $n=5$ (b), where the amount of n-polyene before irradiation is normalized to 1.0

Table 1 Relation between absorption coefficient at isosbestic point and concentration of polyenes

Wavelength at isosbestic point (nm)	Relation	
204	$\varepsilon_2^{\mathrm{i}} = \varepsilon_1^{\mathrm{i}}$	
246	$\varepsilon_3^{\mathrm{i}} = \varepsilon_2^{\mathrm{i}}\|\Delta C_2/\Delta C_3\|$	$(\|\Delta C_3\| = \|\Delta C_2 + \Delta C_1/2\|)$
279	$\varepsilon_4^{\mathrm{i}} = \varepsilon_3^{\mathrm{i}}\|\Delta C_3/\Delta C_4\|$	$(\|\Delta C_4\| = \|\Delta C_3 + \Delta C_2\|)$
294	$\varepsilon_5^{\mathrm{i}} = \varepsilon_3^{\mathrm{i}}\|\Delta C_3/\Delta C_5\| + \varepsilon_4^{\mathrm{i}}\|\Delta C_4/\Delta C_5\|$	$(\|\Delta C_5\| = \|\Delta C_3 + \Delta C_4 + \Delta C_2/2\|)$

Table 2 Relative absorption coefficients for each n-polyene at various wavelengths

n	Normalization[a]	ε(246 nm)	ε(279 nm)	ε(297 nm)
2	ε(234 nm) = 100	57.4	0	0
3	ε(274 nm) = 100	35.3	90.3	20.7
4	ε(309 nm) = 100	3.4	37.8	74.1
5	ε(340 nm) = 100	10.3	5.3	17.4

[a] Absorption coefficients at 1 ← 0 transition wavelength for each n-polyene (234, 274, 309 and 340 nm for $n=2$, 3, 4 and 5, respectively) are normalized to 100

where m indicates the number of component polyenes, $A_{\mathrm{obs}}(\lambda_m)$ 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.

In the practical calculation, the value of ε_2 for $CH_3(\text{-}CH{=}CH\text{-})_2CH_3$ (Tokyo Kasei Co. Ltd) in n-hexane (namely 24 000 at the 1←0 transition) was used as the standard value. On photodegradation of $n=3$, however, the increment of $n=1$ could not be estimated owing to the unreliability of difference spectra in the 200 nm region, so that we calculated $\varepsilon_3^{\mathrm{i}}$ for various amounts of ΔC_1. For instance, if 10% and 90% of $n=3$ are broken at the middle and terminal bonds, respectively, then $|\Delta C_2|/|\Delta C_3|=0.9/1.0=0.9$. The value of $\varepsilon_2^{\mathrm{i}}$ at 246 nm (isosbestic point on photodegradation of $n=3$) is calculated to be $(57.4/100)\times 24000=13776$ using the values in *Table 2*. The equation in *Table 1* gives $\varepsilon_3^{\mathrm{i}}=\varepsilon_2^{\mathrm{i}}\times 0.9=13776\times 0.9=12398$, and ε_3 at the $1\leftarrow 0$ transition (274 nm) is equal to $(12398/35.39)\times 100=35033\approx 35000$. Other results at various ratios of $|\Delta C_2|/|\Delta C_3|$ are shown in the upper part of *Table 3*.

In the calculation of ε_4 and ε_5, the simulation was carried out for the difference spectra after an isosbestic point has appeared on photodegradation of $n=4$ (*Figure 6a*) and $n=5$ (*Figure 6b*), shown by full curves. If ε_2 and ε_3 are 24 000 and 39 000, respectively, the difference spectrum in *Figure 6a* can be separated into fractional spectra of $n=2$, 3 and 4, as shown in the figure, and $\Delta C_2:\Delta C_3:-\Delta C_4$ is calculated to be 0.75:1.0:1.75 $(-\Delta C_4=\Delta C_2+\Delta C_3)$ by equation (2). In other words, 1.75 (1.00) mol of $n=4$ changed to 0.75 (0.43) mol of $n=2$ and 1.0 (0.57) mol of $n=3$. The value of $\varepsilon_3^{\mathrm{i}}$ at 279 nm (isosbestic point for photodegradation of $n=4$) is $(90.3/100)\times 38926=35150$, and the equation in *Table 1* gives $\varepsilon_4^{\mathrm{i}}=\varepsilon_3^{\mathrm{i}}|\Delta C_3|/|\Delta C_4|=35150\times 1.0/1.75=20085$ and $\varepsilon_4=(100/37.8)\times 20085=53136\approx 53000$.

In the case of ε_5, the simulation of the difference spectrum in *Figure 6b* was carried out by equation (2). If ε_2, ε_3 and ε_4 are 24 000, 39 000 and 53 000, respectively, the difference spectrum in *Figure 6b* can be separated into fractional spectra of $n=2$, 3, 4 and 5, as shown in the figure, and $\Delta C_2:\Delta C_3:\Delta C_4:-\Delta C_5$ is calculated to be 8:11.9:5.4:21.3 $(-\Delta C_5=\Delta C_3+\Delta C_4+\Delta C_2/2)$ by equation (2). In other words, 21.3 (1.00) mol of $n=5$ changed to 8 (0.38) mol of $n=2$, 11.9 (0.56) mol of $n=3$ and 5.4 (0.25) mol of $n=4$. The values of $\varepsilon_3^{\mathrm{i}}$ and $\varepsilon_4^{\mathrm{i}}$ at 297 nm (isosbestic point for photodegradation of $n=5$) are $39000\times 20.7/100=8150$ and $53000\times 74.1/100=39273$, respectively, and

$$\varepsilon_5^{\mathrm{i}}=\varepsilon_3^{\mathrm{i}}|\Delta C_3/\Delta C_5|+\varepsilon_4^{\mathrm{i}}|\Delta C_4/\Delta C_5|$$
$$=8150\times 11.9/21.3+39273\times 5.4/21.3=14009$$

Therefore, $\varepsilon_5=(14009/17.4)\times 100\approx 83000$.

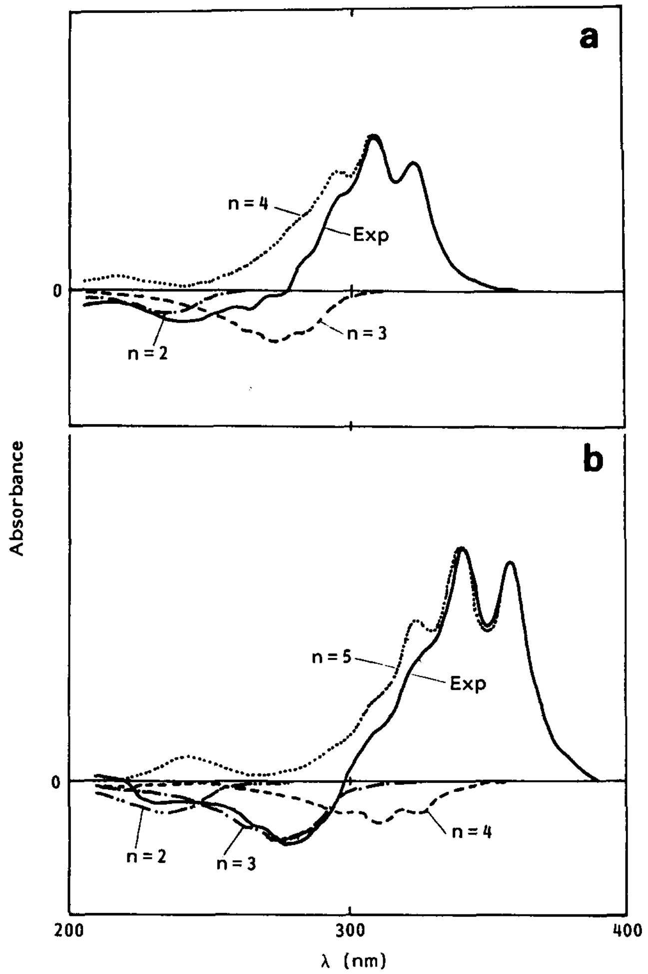

Figure 6 Difference spectra (full curves) after an isosbestic point has appeared on photodegradation of $n=4$ (a) and $n=5$ (b), and the fractional spectra (other curves) of each component polyene

Table 3 Calculated absorption coefficients of polyenes at $1\leftarrow 0$ transition and molar ratios of polyenes formed by photodegradation of *n*-polyenes in PVA

$\lvert\Delta C_2\rvert/\lvert\Delta C_3\rvert$ [a]	1.0/1.0	0.9/1.0	0.8/1.0	0.7/1.0
ε_2(234 nm)	24 000	24 000	24 000	24 000
ε_3(274 nm)	39 000	35 000	31 000	27 000
ε_4(309 nm)	53 000	50 000	46 000	42 000
ε_5(340 nm)	83 000	77 000	70 000	66 000

Degraded polyene		Formed polyenes				
n	mole	*n*	mole			
3	1.00	1	0.00	0.20	0.40	0.60
		2	1.00	0.90	0.80	0.70
4	1.00	2	0.43	0.40	0.37	0.34
		3	0.57	0.60	0.63	0.66
5	1.00	2	0.38	0.35	0.32	0.29
		3	0.56	0.58	0.60	0.61
		4	0.25	0.25	0.25	0.24

[a] Assumed molar ratio of the amounts of formed $n=2$ and degraded $n=3$ on the photodegradation of $n=3$

The calculated ε_n at the $1\leftarrow 0$ transition for $n=2$–5 are summarized in the upper part of *Table 3* together with other results for various values of $|\Delta C_2|/|\Delta C_3|$. The relation (molar ratios) between the amounts of degraded polyene and of produced polyenes is summarized in the lower part of *Table 3*, in which the amount of each degraded polyene is normalized to 1.0.

Some absorption coefficients of polyenes already reported are shown in *Table 4*. The differences between reported values for each n may be due to differences in purity and in ratio of isomers. In fact, the absorption coefficients of respective isomers of n-polyene are different from each other. For instance, each coefficient ε_3 of six isomers of triene H(-CH=CH-)$_3$H has been calculated

Table 4 Some absorption coefficients of polyenes reported at 1 ← 0 transition

n	$H(-CH{=}CH-)_nH$	Ref.	$CH_3(-CH{=}CH-)_nCH_3$	Ref.
2	23 000	6	24 000	6
	21 000	7		
3	42 700	8	30 200	9
	51 700	10[a]	33 400	9
	53 000	7, 11[a]	55 000	10[a]
4	64 000	7	76 500	9
			78 000	12[a]
5	51 000	7	122 000	9
	115 000	8		

[a] All-*trans* type

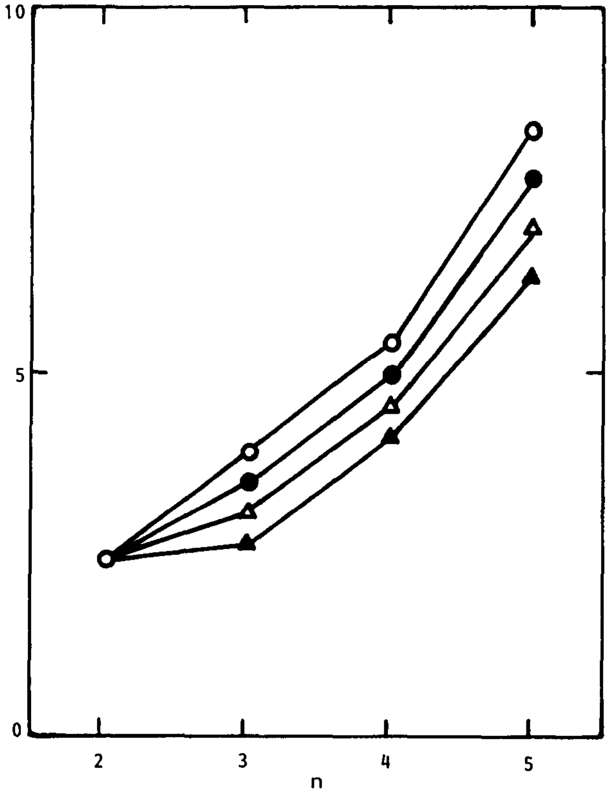

Figure 7 Relations between the molar absorption coefficients of polyenes and n, which is the number of conjugated double bonds. The ratio of polyenes $|\Delta C_2|/|\Delta C_3|$ as a parameter produced in the case of photodegradation of $n=3$ is 1.0 (○), 0.9 (●), 0.8 (△) and 0.7 (▲), respectively

and/or determined experimentally to be 8000–53 000[11], in which the largest value is for the all-*trans* type triene. Accordingly, it is not possible to estimate whether the ε_n obtained are reasonable or not by comparing them with reported values.

From considerations of effective chromophore area, a linear relation between absorption coefficients for allowed transitions of polyenes and conjugation number had been expected and observed[7,13]. The best linearity in the present study is obtained in the case of $|\Delta C_2|/|\Delta C_3| = 1.0/1.0$ for $n=2$–4 and $|\Delta C_2|/|\Delta C_3| = 0.7/1.0$ for $n=3$–5, as shown in *Figure 7*. The observed wavelength of the isosbestic point in the case of $n=5$ is less reliable than that in other cases of $n=2$–4 because photodegradation of $n=5$ accompanies successive degradation of $n=4$ formed from $n=5$. Therefore we are in favour of linearity in the case of $|\Delta C_2|/|\Delta C_3| = 1.0/1.0$, i.e. ε_n in the left column in *Table 3* may be most reliable.

The formation of $(n-1)$-polyene on photodegradation of n-polyene normally requires the disappearance of a terminal π-bond, while the formation of $(n-2)$-polyene and others requires the disappearance of an inner π-bond. A brief molecular-orbital calculation indicates that the more conjugation, the more extreme is the electron density on a terminal p-orbital. Therefore, the reactivity of a terminal π-bond is expected to increase as n increases. In contrast to this expectation, the ratio of formed $(n-1)$-polyene decreased as n increases, as shown in *Table 3*. This may suggest that, because the zigzag bending of the π-bond system is so extensive, it could not form and still keep its coplanar structure over the whole chain, since polyene sequences should be formed along the polymer chains. Therefore, the overlapping of the p-orbital is not sufficient on an inner π-bond and this may cause the increase in reactivity of an inner π-bond as n increases.

The mechanism of polyene degradation is not clear at present. However, on considering many reports about the photo-reactions of polyenes, it is possible to conjecture about the reaction mechanism. The photolysis of hexa-1,3,5-triene produced many species of diene and monoene, some containing three-, four-, five- or six-membered ring systems[10]. If photolysis of polyenes is carried out in the presence of water or alcohol, an addition reaction with the π-bond occurs[14,15]. Srinivasan reported that rate studies on irradiation of a mixture of *cis*- and *trans*-1,3-pentadiene indicated that the *trans* compound was the sole source of $n=1$ (3-methylcyclobutene) and at the same time *trans–cis* photoisomerization of 1,3-dienes occurs[16].

In the present study, some characteristic phenomena suggest a reaction mechanism. As shown in *Figure 3*, on irradiation with 234 nm light (photodegradation of $n=2$) after irradiation with 273 nm light (to degrade $n=3$), the absorption in the long-wavelength region, which is the absorption region of $n=3$, increased slightly. Since irradiation of colourless PVA film with this light does not produce polyene structures in it, this increase suggests that some of the degraded $n=3$, i.e. $n=2$, re-form $n=3$ on irradiation. In other words, the photo-reaction in this case is reversible. Therefore, one of the reactions may be an intramolecular Diels–Alder type of reaction on irradiation. Also, there should be free water in the PVA film, so that the addition reaction of water may also occur.

The relation between ln C_n and irradiation time (*Figure 5*) is a straight line after the isosbestic point has appeared. Concomitantly, the difference spectra in the initial stage of irradiation show more clear fine structures than that in the latter stages. These facts indicate that the reaction in the initial stage of irradiation is different from the later reaction. The *cis–trans* isomerization reaction of polyenes is likely to occur especially in the initial stage of irradiation. The study of the photo-isomerization reaction in detail is now in progress.

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