Bull. Chem. Soc. Jpn., **65**, 1342—1348 (1992) [Vol. 65, No. 5

Rate Constants of the Photodegradation and Photoisomerization of Polyenes Produced in Heat-Treated PVA Film

Kazunori MARUYAMA,* Yasunori KURAMOTO, Yoshié TANIZAKI,
Michio KOBAYASHI, and Kozo KUCHITSU
Department of Chemistry, Nagaoka University of Technology,
Nagaoka 940-21

(Received November 5, 1991)

The rate constants of two parallel reactions, photodegradation and photoisomerization of polyenes, $\{CH=CH\}_n$ with n=2—5, produced in heat-treated PVA film are estimated by an analysis of the spectral changes on monochromatic irradiation (200—250 nm). The rate constants for isomerization is found to be ten times as large as that of degradation.

Linear polyenes, $\{CH=CH\}_n$, with various conjugation numbers, n, are produced in poly(vinyl alcohol) [PVA] on heat treatment. Polyenes with n=2—5 in PVA are photo-sensitive and degraded on ultraviolet irradiation.[1] The photodegradation of these polyenes is a complex of consecutive and parallel reactions such as isomerization, ring formation, and addition reaction of other chemicals.

There are a large number of reports on the photoisomerization of polyenes such as diene,[2] triene,[3] and tetraene.[4] Furthermore, the ring formation and opening reactions of polyenes[5] and the addition reactions of water and alcohol to the double bonds of polyenes[6] have also been reported.

As for the irradiation on polyenes in PVA, the relationship between the irradiation time and the logarithm of net absorbance of $\{CH=CH\}_n$ with n=2—5 shows an asymptotic curve.[1] This curve is analyzed in the present paper in terms of the parallel reactions of photoisomerization and photodegradation, and the rate constants of these reactions are estimated for triene.

Experimental

A sample film, prepared by the procedure reported in Ref. 1, was irradiated in nitrogen atmosphere with a 500 W xenon lamp. The wavelength was selected using a spectrofluorophotometer (Shimadzu RF-502) having a spectral slit width of 10—15 nm. The absorption spectrum was measured on a spectrophotometer (Shimadzu UV-360).

Results

Method of Analysis. A previous paper[1] has shown that irradiation of monochromatic light to a mixture of polyenes produced in PVA causes a decrease of longer polyenes and an increase of shorter polyenes. At an initial stage of irradiation, the relation between the irradiation time and the logarithm of the net absorbance of polyenes with n=2—5 shows asymptotic curves.[1] For example, the irradiation to polyenes in the PVA film with 273 nm light causes a decrease in the absorption of triene as shown in Fig. 1 (a). The logarithm of this absorbance is plotted against the irradiation time in Fig. 2, where the net absorbance of triene before irradiation is assumed to be the difference in absorbance between the spectra A and E in Fig. 1 (a).

The curve shown in Fig. 2 is analyzed in terms of the parallel reactions of photoisomerization and photodegradation shown in Fig. 3; the photoisomerization

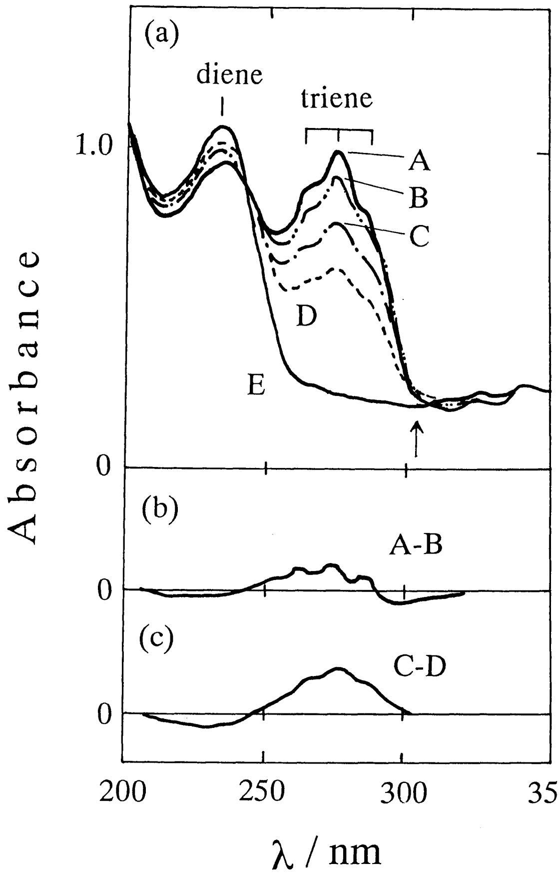


Fig. 1. (a) Absorption spectra of PVA film irradiated with 273 nm light[1] for (A) 0, (B) 40, (C) 240, (D) 540, and (E) 5940 min, with assignments for triene peaks. (b) Difference spectrum between A and B. (c) Difference spectrum between C and D.

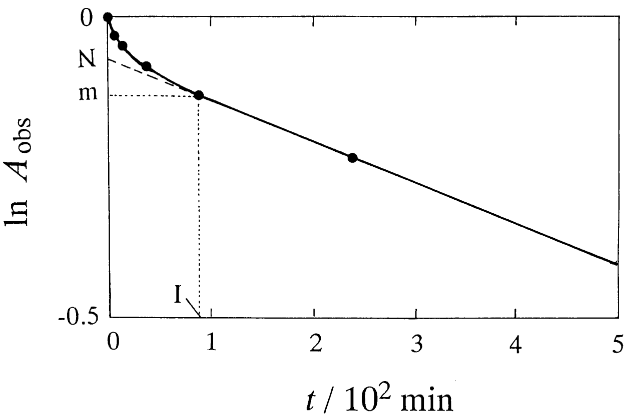


Fig. 2. Relationship between ln A_{obsd} at 278 nm and irradiation time t for triene, where the absorption of triene before irradiation is denoted as A_{obsd}=1.0.

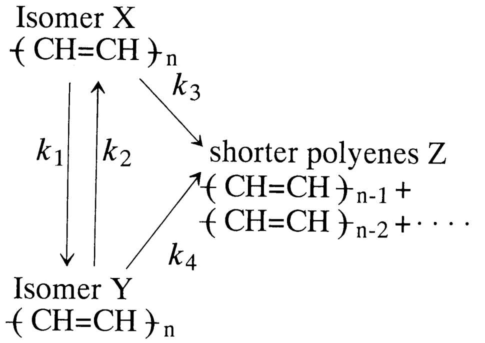
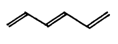
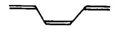
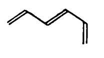
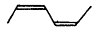
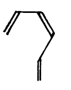


Fig. 3. Reaction scheme and definition of the rate constants.

Table 1. Peak Wavelengths and Absorption Coefficients for Isomers of 1,3,5-Hexatriene[a)]

	Compound Structure	Peak wavelength λ/nm Obsd	Calcd	Absorption coefficient Obsd[b)]	Calcd
1		255	240	53000 (1.00)	37485
2		255	241	41000 (0.77)	36255
3		286	252	14500 (0.27)	21420
4		284	259	16200 (0.31)	21420
5			283		18900

a) Taken from Ref. 7. b) The absorption coefficient relative to that for compound **1** is shown in parentheses.

between two geometrical isomers, X and Y, of n-conjugated polyene proceeds with rate constants k_1 and k_2, and both isomers are degraded with rate constants k_3 and k_4 to form a mixture of polyenes, denoted as Z, with conjugation numbers smaller than n. Since the diene (n=2) has only two geometrical isomers, *s-trans* and *s-cis*, this scheme holds automatically. Polyenes with $n \geqslant 3$ have many geometrical isomers; for example, triene has six geometrical isomers as shown in Table 1. However, it seems permissible for the present purpose to assume this simple scheme; some justification is presented in section 2.

It is further assumed that both reactions are of the first order as discussed further in section 3. Thus the following three differential equations are set up to represent the absorbances of polyenes X, Y, and Z, where ε, A, and C are the absorption coefficient, the absorbance at a certain wavelength, and the concentration of each polyene, respectively:

$$\mathrm{d}A_{\mathrm{X}}/\mathrm{d}t = \mathrm{d}(\varepsilon_{\mathrm{X}}C_{\mathrm{X}})/\mathrm{d}t = -(k_1+k_3)\varepsilon_{\mathrm{X}}C_{\mathrm{X}} + k_2\varepsilon_{\mathrm{X}}C_{\mathrm{Y}} = -(k_1+k_3)A_{\mathrm{X}}\,k'_2A_{\mathrm{Y}}, \tag{1-1}$$

$$\mathrm{d}A_{\mathrm{Y}}/\mathrm{d}t = k'_1A_{\mathrm{X}} - (k_2+k_4)A_{\mathrm{Y}}, \tag{1-2}$$

$$\mathrm{d}A_{\mathrm{Z}}/\mathrm{d}t = k'_3A_{\mathrm{X}} = k'_4A_{\mathrm{Y}}, \tag{1-3}$$

where

$$k'_1 = k_1(\varepsilon_{\mathrm{Y}}/\varepsilon_{\mathrm{X}}),\quad k'_2 = k_2(\varepsilon_{\mathrm{X}}/\varepsilon_{\mathrm{Y}}),\quad k'_3 = k_3(\varepsilon_{\mathrm{Z}}/\varepsilon_{\mathrm{X}}),$$

$$k'_4 = k_4(\varepsilon_{\mathrm{Z}}/\varepsilon_{\mathrm{Y}}). \tag{2}$$

The solution of Eq. 1 under the initial conditions that $A_{\mathrm{X}}=A_{\mathrm{X.0}}$, $A_{\mathrm{Y}}=A_{\mathrm{Y.0}}$, and $A_{\mathrm{Z}}=0$ at t=0 min is given by

$$A_{\mathrm{X}} = p_1\exp(-\kappa_1t) - p_2\exp(-\kappa_2t), \tag{3-1}$$

$$A_{\mathrm{Y}} = q_1\exp(-\kappa_1t) - q_2\exp(-\kappa_2t), \tag{3-2}$$

$$A_{\mathrm{Z}} = r_1\{1-\exp(-\kappa_1t)\} - r_2\{1-\exp(-\kappa_2t)\}, \tag{3-3}$$

where

$$p_1 = \{-(k_1+k_3-\kappa_2)A_{\mathrm{X.0}} + k'_2A_{\mathrm{Y.0}}\}/(2\gamma),$$

$$p_2 = \{-(k_1+k_3-\kappa_1)A_{\mathrm{X.0}} + k'_2A_{\mathrm{Y.0}}\}/(2\gamma), \tag{4-1}$$

$$q_1 = \{-(k_2+k_4-\kappa_2)A_{\mathrm{Y.0}} + k'_1A_{\mathrm{X.0}}\}/(2\gamma),$$

$$q_2 = \{-(k_2+k_4-\kappa_1)A_{\mathrm{Y.0}} + k'_1A_{\mathrm{X.0}}\}/(2\gamma), \tag{4-2}$$

$$r_1 = (k'_3p_1 + k'_4)q_1/\kappa_1,\quad r_2 = (k'_3p_2 + k'_4)q_2/\kappa_2, \tag{4-3}$$

$$\kappa_1 = \alpha - \gamma,\quad \kappa_2 = \alpha + \gamma,\quad \gamma = (\alpha^2 - \beta)^{1/2}, \tag{4-4}$$

$$\alpha = (k_1+k_2+k_3+k_4)/2,\quad \beta = k_1k_4 + k_2k_3 + k_3k_4. \tag{4-5}$$

At the wavelength outside the absorption region of Z, the observed absorbance, A_{obsd}, is equal to the sum of the absorbances for X and Y. Substitutions of Eqs. (3-1) and (3-2) into Eq. 4 lead to

$$A_{\text{obsd}} = A_X + A_Y = a\exp(-\kappa_1 t) - b\exp(-\kappa_2 t), \tag{5}$$

where

$$a = p_1 + q_1, \qquad b = p_2 + q_2. \tag{6}$$

Equation (5) reproduces well the experimental curve shown in Fig. 2 by selection of an appropriate set of the parameters. Therefore, Eq. 5 is adopted for an empirical expression of the experimental results.

Equation (4-4) and (4-5) lead to

$$\kappa_1 + \kappa_2 = 2\alpha = k_1 + k_2 + k_3 + k_4, \tag{7}$$

$$\kappa_1\kappa_2 = \beta = k_1k_2 + k_2k_3 + k_3k_4. \tag{8}$$

In order to determine the rate constants k_1—k_4, two other independent equations derivable from experimental results are available besides Eqs. 7 and 8. The third equation is concerned with the intercept N of the asymptote of the curve in Fig. 2 (See Appendix 1),

$$2\exp(N) - 1 = \alpha/\gamma - \{(k_1 + k_3 - k'_1)A_{X.0} + (k_2 + k_4 - k'_2)A_{Y.0}\}/(\gamma A_{X.0} + \gamma A_{Y.0}). \tag{9}$$

The fourth equation is based on the isosbestic point (See Appendix 2),

$$\kappa_1 = k_1 + k_3 - (k_2/R_I) = k_2 + k_4 - k_1R_I, \tag{10}$$

where

$$R_I = C_{X.I}/C_{Y.I}. \tag{11}$$

Constants κ_1 and κ_2 for Polyenes with n=2—5. It is possible to reproduce the asymptotic curve shown in Fig. 2 for triene, Eq. 5, by assuming κ_1=9.9×10^{-4} min^{-1} and κ_2=3.6×10^{-2} min^{-1}. Other asymptotic curves for polyenes with n=2—5 reported in a previous paper[1] are also reproducible by assuming the values of κ_1 and κ_2 summarized in Table 2. This implies that the scheme for the photoreaction of polyenes with $n \geqslant 3$ can be assumed, at least phenomenologically, to occur between two isomers X and Y, like that for diene, as shown in Fig. 1.

Ratio $\varepsilon_X/\varepsilon_Y$ for Triene. If each absorption spectrum of isomer X or Y for each polyene is available, the ratio $\varepsilon_X/\varepsilon_Y$ at any wavelength can in principle be determined . In practice, however, sufficient experimental information is obtained only for triene in the present study.

Three spectra are available in this study for a mixture of X and Y of triene with different relative concentrations: The absorption spectrum shown in Fig. 4 (b), taken from our previous report,[1] the difference spectrum A—B shown in Fig. 1 (b), and that of C and D shown in Fig. 1 (c). The latter two difference spectra contain information on the isomerization and degradation of triene. In order to determine the spectra of X and Y by using these three spectra, difference spectra should be separated into the component spectra representing the isomerization and degradation. For this purpose, the difference spectrum representing photoisomerization only is determined by the following procedure.

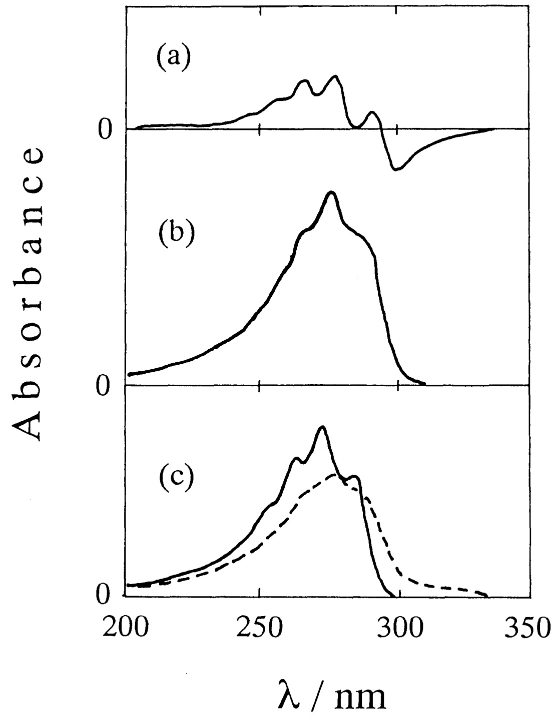


Fig. 4. (a) Difference spectrum showing the effect of photoisomerization of triene. (b) Absorption spectrum of triene in PVA, taken from Ref. 1. (c) Absorption spectrum of isomers X (solid line) and Y (broken line).

The spectrum shown in Fig. 1 (b), obtained in the initial stage of irradiation, is ascribed to the isomerization and degradation of triene; namely, the relative concentrations of X and Y in spectra A and B are different. On the other hand, the difference spectrum shown in Fig. 1 (c), obtained in the later stage of irradiation can be ascribed to photodegradation only, because all the difference spectra obtained in the latter stages have similar features. In other words, the relative concentrations of X and Y in spectra C and D are essentially equal. In addition, the constant κ_1, observed after the irradiation exceeding 40 min is approximately equal to the rate constants of photodegradation, $k_3 \approx k_4$ (see Discussion). Therefore, the spectrum shown in Fig. 1 (c) represents the photodegradation of triene, and the change in its intensity is caused by the irradiation for 300 min. The corresponding difference spectrum showing the effect of photoisomerization is estimeted in Fig. 4 (a); this curve is obtained by subtracting the spectrum shown in Fig. 1 (c) from that in Fig. 1 (b) after proper normalization to an identical irradiation time.

A combination of the spectra shown in Figs. 4 (a) and 4 (b) leads to the spectra of the isomers: the whole spectrum of one of the isomers mixed in Fig. 4 (b) can be transformed to that of the other isomer by using the difference spectrum for photoisomerization shown in Fig. 4 (a). Thus the spectrum of isomer X is estimeted, as shown by a solid line in Fig. 4 (c), by subtracting the original spectrum of triene shown in Fig. 4 (b) from that shown in Fig. 4 (a) after proper normalization so as to make the baseline flat in the region of $\lambda>310$ nm. This condition is adopted by the following argument.

The absorption in the region of $\lambda>300$ nm increases with the irradiation time, as indicated by an arrow in Fig. 1 (a); this increase is noticeable more clearly in Fig. 1 (b) as a negative part of the spectrum in the same region. This increase indicates that only one of the two isomers has the absorption in this region. In fact the irradiation of 310 nm light to triene caused a systematic change in the spectrum with an isosbestic point at 278 nm, as shown in Fig. 5. The presence of this isosbestic point demonstrates isomerization of Y to X. In summary, only isomer Y has absorption in the region of $\lambda>310$ nm.

The spectrum shown in Fig. 4 (a), after multiplication by a certain factor, is subtracted from that in Fig. 4 (b). The provisional spectrum obtained by this procedure is normalized so as to cross the spectrum of isomer X at the isosbestic point (278 nm). Then the spectra of isomers X and Y are prepared, and the ratio $\varepsilon_X/\varepsilon_Y$ at a proper wavelength outside the absorption region of the dienes can be calculated. Other parameters, R_0 and R_I, can be calculated by the procedures mentioned in sections 4 and 5. The provisional values of k_1—k_4 are then obtained by Eqs. 7—10.

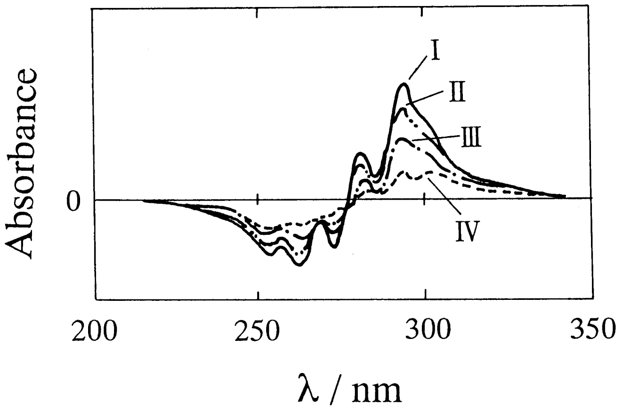


Fig. 5. Difference spectra for triene in PVA after irradiation of 310 nm light; I, II, III, and IV are obtained by subtraction of those obtaind after 5, 15, 30, and 60 min of irradiation, respectively, from the original absorption spectrum shown in Fig. 4(b).

If the provisional spectrum of Y adopted in the above procedure is correct, this same spectrum should be reproducible by the other combinations of the spectra shown in Figs. 4 (a) and 5 by taking the provisional values of k_1—k_4 thus obtained. The difference spectra shown in Fig. 5 are derived by the isomerization Y→X and degradation Y→Z after the irradiation of 310 nm light. The ratios in the decrement by Y→X and Y→Z are $k_2/(k_2+k_4)$ and $k_4/(k_2+k_4)$, respectively. The spectrum shown in Fig. 4 (a), obtained by 40 min irradiation, is normalized as $(60/40)\,(k_2/(k_2+k_4))$ so as to represent the decrement of Y by isomerization after the irradiation of 60 min and is added to spectrum I shown in Fig. 5 to compensate for the decrement in the absorbance by isomerization. This difference spectrum represents the degradation Y→Z. If the provisional spectrum of Y and the values of k_1—k_4 adopted in this procedure are all correct, the spectrum thus obtained should be consistent with the provisional spectrum in the region of $\lambda>278$ nm.

The above calculations are repeated until full consistency is obtained. The spectrum of isomer Y estimated by this method is shown in the broken line in Fig. 4 (c). The values of k_1—k_4 and $\varepsilon_X/\varepsilon_Y$ estimated by this method are summarized in Table 2; the rate constant of isomerization is found to be ten times as large as that of degradation.

As for polyenes with $n=2$, 4, and 5, it is impossible to determine the spectrum of isomer Y and the rate constants k_1—k_4 because no difference spectra representing the isomerization can be obtained.

Constant R_I for Triene. The value of $R_I(=C_{X.I}/C_{Y.I})$ is determined by taking the spectrum based on X and a provisional one of Y. Figure 6 shows the procedure when the spectra of isomers X and Y shown in Fig. 4 (c) are used. If the value of R_I is 47/(100−47), the spectrum of isomer X multiplied by 0.47 is added to the spectrum of isomer Y multiplied by 0.53; the spectrum thus obtained coincides with the difference spectrum in Fig. 1 (c) in the region of $\lambda>280$ nm, where diene have no absorption.

Constant R_0 for Triene. The total amount of n-conjugated polyene before irradiation is approximately equal to the amount at intersept N shown in Fig. 3; it thus

Table 2. Parameters Used for Determination of Rate Constants

$n^{a)}$	$\kappa_1/\mathrm{min}^{-1\,b)}$	$\kappa_2/\mathrm{min}^{-1\,b)}$	$\mathrm{N}^{c)}$	$R_0^{d)}$	$R_I^{d)}$	$\varepsilon_Y/\varepsilon_X^{e)}$	$\lambda/\mathrm{nm}^{f)}$
2	3.8×10^{-4}	1.3×10^{-2}	−0.035				234 (0.14)
3	9.9×10^{-4}	3.6×10^{-2}	−0.11	3.3	0.89	0.72	273 (1.0)
4	2.4×10^{-3}	5.1×10^{-2}	−0.28				325 (3.9)
5	2.4×10^{-4}	2.0×10^{-3}	−0.22				360 (6.1)

a) Conjugation number of polyenes. b) Defined in Eq. 3. c) Defined in Fig. 2. d) Defined in Eq. 1. e) Ratio of the absorption coefficients for Y and X. f) Wavelength of radiation. The intensity relative to that for $n=3$ is shown in parentheses.

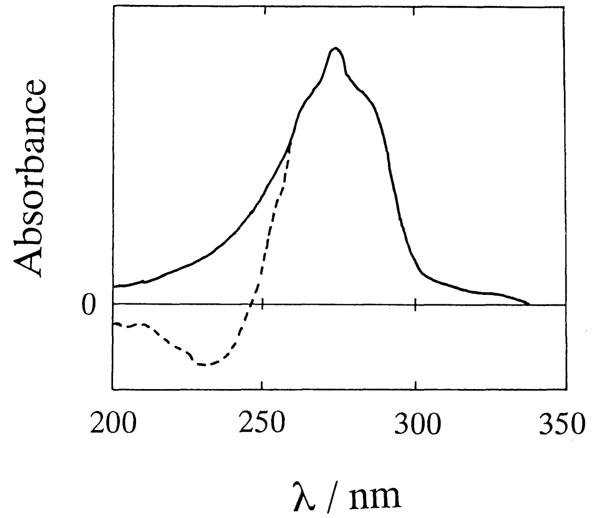


Fig. 6. Estimation of R_I for triene. If $R_I=C_{X,I}/C_{Y,I}$ is 47/(100−47), the spectrum of isomer X (solid line in Fig. 4(c)) multiplied by 0.47 is added to the spectrum of isomer Y (broken line in Fig. 4(c)) multiplied by 0.53 to make the spectrum thus obtained (solid line) coincide with the difference spectrum shown in Fig. 1(c) (broken line in this figure) in the region of λ>280 nm.

Table 3. Rate Constants for Triene[a)]

Photoisomerization		Photodegradation	
k_1/min^{-1}	k_2/min^{-1}	k_3/min^{-1}	k_4/min^{-1}
1.8×10^{-2}	1.7×10^{-2}	9.9×10^{-4}	1.0×10^{-3}

a) Rate constants k_1—k_4 are defined in Fig. 3.

follows that

$$C_{X.N.0}+C_{Y.N.0}=C_{X.0}+C_{Y.0}=C,$$

$$C_{X.N.0}/C_{Y.N.0}=C_{I.0}/C_{I.0}=R_I. \tag{12}$$

It further follows from Eq. 9 that

$$\begin{aligned}\exp N &= (A_{X.N.0}+A_{Y.N.0})/(A_{X.0}+A_{Y.0}) \\ &= (\varepsilon_X C_{X.N.0}+\varepsilon_Y C_{Y.N.0})/(\varepsilon_X C_{X.0}+\varepsilon_Y(C-C_{X.0})).\end{aligned} \tag{13}$$

The normalized values of $C_{X.0}$ and $C_{Y.0}$ can be calculated by using Eq. 13. The calculation for triene is shown in Appendix 3.

Discussion

The rate constants k_1 and k_2 are larger than k_3 and k_4 by an order of magnitude, as shown in Table 2. The approximation that $k_1=k_2\gg k_3=k_4$ simplifies Eq. 2—5 as

$$\kappa_1=\alpha-(\alpha^2-\beta)^{1/2}\approx\beta/2\alpha=k_3, \tag{14}$$

$$\kappa_2=\alpha+(\alpha^2-\beta)^{1/2}\approx 2\alpha=2k_1. \tag{15}$$

Therefore, the slope at a later stage of irradiation, represented by κ_1 in Fig. 2, implies degradation. The appearance of an isosbestic point at this stage also implies that the ratio of the concentration of isomers, C_X/C_Y, is constant. In fact, any difference spectrum in this stage has a similar form. The non-linearity at the initial stage of irradiation, shown in Fig. 2, can be ascribed to the result of the fast isomerization of polyenes.

For identification of the triene isomers designated as X and Y in the present study, it is helpful to consider the electronic transitions of the five isomers of *1,3,5-hexatriene* shown in Table 1.[7)] All-*trans* triene (compound **1** in Table 1) has the largest absorption coefficient and the peak maximum at the shortest wavelength among the isomers listed in the table. The ratio of the maximum absorption coefficients of compounds **1** and **2** is 1 : 0.77. The distance between the peaks of compounds **1** and **2** is small, whereas those for compounds **3**, **4**, and **5** from **1** are much larger, exceeding 30 nm.

The ratio of the maximum absorption coefficients of the triene isomers X and Y is estimated from the spectra shown in Fig. 4 (c) to be 1.00 : 0.72. The distance between their peak wavelengths, 274 and 278 nm, is only 4 nm. From these characteristics, isomers X and Y are likely to be compounds **1** and **2** listed in Table 1.

Polyenes with $n\geqslant 4$ have many geometrical isomers. However, plots of ln f (Eq. 5 is modified as $[A_{\text{obsd}}-a\exp(\kappa_1 t)]/b=\exp(\kappa_2 t)\equiv f(t)$) against t calculated by using A_{obsd} and κ_1 show essentially straight lines, and the asymptotic curves are reproducible only by the two

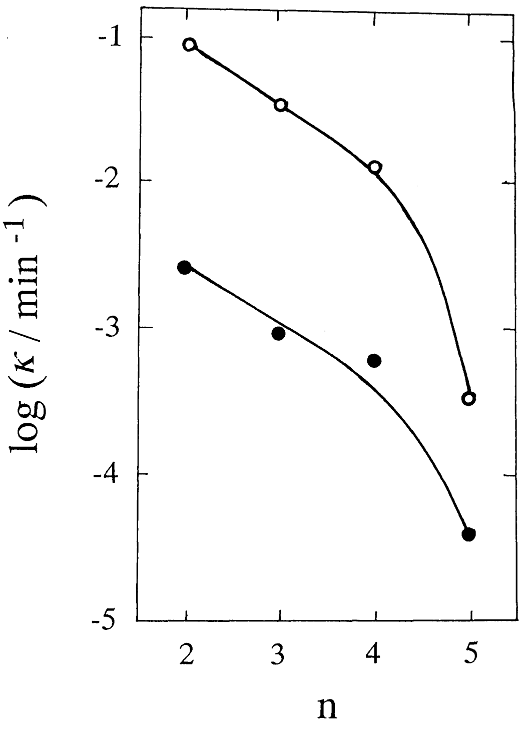


Fig. 7. Dependence of κ_1 and κ_2 on the conjugation number n.

values of κ_1 and κ_2 listed in Table 2. This implies that the isomerization occurs essentially between these two species. In the absence of reliable spectra of polyene isomers, no further analysis of the rate constants k_1—k_4 can be made.

The rate constants for triene estimated directly in the present study, κ_1 and κ_2, are nearly equal to that of k_3 and $2k_1$, respectively. The κ_1 and κ_2 values obtained for other polyenes can also be assigned to the rate constants for the degradation and isomerization, respectively. The values of κ_1 and κ_2, corrected for the relative intensities of irradiation shown in Table 2 and plotted against the conjugation number n in Fig. 7, decrease with n. This decrease corresponds to the low photoreactivity of polyenes with $n \geqslant 6$.

The detailed mechanism of photodegradation is not clear at present. The peresence of oxygen does not affect the rate of photodegradation, but the presence of water accelerates the degradation.[8] Therefore, the probable reaction is the addition of water to the carbon–carbon double bonds.

Appendix

Appendix 1. The introduction of hyperbolic functions into Eq. 2 leads to

$$A_X = \{\exp(-\alpha t)\}\{A_{X.0}\cosh(\gamma t) + 2\sigma_1 \sinh(\gamma t)\},$$

$$A_Y = \{\exp(-\alpha t)\}\{A_{Y.0}\cosh(\gamma t) + 2\sigma_2 \sinh(\gamma t)\}, \qquad \text{(A1)}$$

where

$$\sigma_1 = p_1 - A_{X.0}/2 = p_2 + A_{X.0}/2,$$

$$\sigma_2 = q_1 - A_{Y.0}/2 = q_2 + A_{Y.0}/2. \qquad \text{(A2)}$$

At the wavelength outside the absorption region of Z, the observed absorbance can be written by the substitution of Eq. A1 as

$$\begin{aligned} A_{\mathrm{obsd}} &= A_X + A_Y \\ &= (A_{X.0} + A_{Y.0})\{\exp(-\alpha t)\}\{\cosh(\gamma t) + \omega \sinh(\gamma t)\}, \end{aligned} \qquad \text{(A3)}$$

where

$$\begin{aligned} \omega &= 2(\sigma_1 + \sigma_2)/(A_{X.0} + A_{Y.0}) \\ &= \alpha/\gamma - \{(k_1 + k_3 - k_1')A_{X.0} \\ &\quad + (k_2 + k_4 - k_2')A_{Y.0}\}/\gamma/(A_{X.0} + A_{Y.0}). \end{aligned} \qquad \text{(A4)}$$

Since the plots in Fig. 2 are normalized, it is represented by

$$\begin{aligned} &\ln\{(A_X + A_Y)/(A_{X.0} + A_{Y.0})\} \\ &\quad = -\alpha t + \ln\{\cosh(\gamma t) + \omega \sinh(\gamma t)\} \equiv y(t). \end{aligned} \qquad \text{(A5)}$$

The tangent at a point $(t, y(t))$ on the curve, shown in Fig. 2, can be written as

$$\begin{aligned} \xi = (\mathrm{d}t/\mathrm{d}y)(\eta - t) + y(t) = [-\alpha + \gamma\{(\tanh(\gamma t) + \omega)/ \\ (1 + \omega \tanh(\gamma t))\}]\eta + \ln\{\cosh(\gamma t) + \omega \sinh(\gamma t)\} \\ - \gamma\{(\tanh(\gamma t) + \omega)/(1 + \omega \tanh(\gamma t))\}]t. \end{aligned} \qquad \text{(A6)}$$

In the limit of $t \to \infty$, Eq. A6 leads to an asymptote

$$\xi(t \to \infty) = -(\alpha - \gamma) \times \eta + \{\ln(1 + \omega)\}/2. \qquad \text{(A7)}$$

The intercept of $\xi(t \to \infty)$ equals to

$$N = \{\ln(1 + \omega)\}/2. \qquad \text{(A8)}$$

Equations (A3) and (A8) lead to

$$\begin{aligned} 2\exp N - 1 = \alpha/\gamma - \{(k_1 + k_3 - k_1')A_{X.0} \\ + (k_2 + k_4 - k_2')A_{Y.0}/\gamma/(A_{X.0} + A_{Y.0}). \end{aligned} \qquad \text{(9)}$$

Appendix 2. After irradiation ($t \geqslant$I in Fig. 2), an isosbestic point appears inside the absorption region of polyenes X, Y and Z. This fact is expressed as

$$\mathrm{d}A_X/\mathrm{d}t + \mathrm{d}A_Y/\mathrm{d}t + \mathrm{d}A_Z/\mathrm{d}t = 0. \qquad \text{(A9)}$$

The substitution of Eq. 1 in Eq. A9 leads to

$$\begin{aligned} &\{k_1(\varepsilon_X - \varepsilon_Y) + k_3(\varepsilon_X - \varepsilon_Z)\}C_X \\ &\quad + \{k_2(\varepsilon_Y - \varepsilon_X) + k_4(\varepsilon_Y - \varepsilon_Z)\}C_X = 0, \end{aligned} \qquad \text{(A10)}$$

and consequently,

$$\begin{aligned} C_{X.\mathrm{I}}/C_{Y.\mathrm{I}} = \{k_2(\varepsilon_Y - \varepsilon_X) + k_4(\varepsilon_Y - \varepsilon_Z)\}/\{k_1(\varepsilon_X - \varepsilon_Y) \\ + k_3(\varepsilon_X - \varepsilon_Z)\} = \text{constant} \equiv R_\mathrm{I}. \end{aligned} \qquad \text{(A11)}$$

Therefore, Eqs. (1-1) and (1-2) can be expressed for $t \geqslant$I as

$$\mathrm{d}A_X/\mathrm{d}t = -(k_1 + k_3 - k_2/R_\mathrm{I})A_X, \qquad \text{(A12)}$$

$$\mathrm{d}A_Y/\mathrm{d}t = -(k_2 + k_4 - k_1/R_\mathrm{I})A_Y. \qquad \text{(A13)}$$

After irradiation ($t \geqslant$I), the term $\exp(-\kappa_2 t)$ in Eq. (3) is negligible. Then Eqs. (2-1) and (2-1) lead to

$$\mathrm{d}A_X/\mathrm{d}t = -\kappa_1 A_X, \qquad \text{(A14)}$$

$$\mathrm{d}A_Y/\mathrm{d}t = -\kappa_1 A_Y. \qquad \text{(A15)}$$

Equations (A12)—(A15) lead to

$$\kappa_1 = k_1 + k_3 - k_2/R_\mathrm{I} = k_2 + k_4 - k_1/R_\mathrm{I}. \qquad \text{(10)}$$

Appendix 3. If R_I is 47/53 for triene, the values of $\varepsilon_Y/\varepsilon_X$ and N are 0.68 and −0.284, respectively. Substitution of these values into Eq. 13 leads to

$$C_{X.0} = 0.77, \qquad \text{(A16)}$$

and

$$C_{Y.0} = 1 - 0.77 = 0.23, \quad R_0 = 0.77/0.23 = 3.3. \qquad \text{(A17)}$$

References

1) K. Maruyama, Y. Kuramoto, and Y. Tanizaki, *Polymer,* **30**, 1419 (1989).

2) R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 4141 (1962); *ibid.*, **90**, 4499 (1968).

3) Y. Furukawa, H. Takeuchi, I. Harada, and M. Tasumi,

J. Mol. Struct., **100**, 341 (1983).

4) J. R. Ackerman and B. E. Kohler, *J. Am. Chem. Soc.*, **106**, 3681 (1984).

5) W. G. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

6) W. G. Dauben and W. A. Spitzer, *J. Am. Chem. Soc.*, **90**, 802 (1968).

7) N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **99**, 4918 (1977).

8) K. Maruyama, unpublished data.