Synthesis and Properties of Photosensitive Rubbers. II. Photosensitivity of Cyclized Polydienes and Polypentenamer with Pendent Cinnamate Groups

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Synopsis

Photosensitivity of cyclized polydienes such as *cis*-1,4-polybutadiene, 1,2-polybutadiene, and polypentenamer having pendent cinnamate groups has been studied in terms of the influence of polymer structure. The photosensitivity, which was based on the photodimerization of cinnamate groups in these polymers, was greatly affected by the mobility of the cinnamate groups. The observed rates (k_{obs}^u) could be estimated by using the reciprocal of the difference between an irradiated temperature (T) and a standardized temperature ($T_g - 50$), at which the free volume of the polymer could be considered as zero by taking the glass transition temperature (T_g) of the polymer as a standard. Furthermore, the photosensitivity of the cyclized rubber decreased with an increase in the amount of the cyclized units in the polymer. The overall rate of the photodimerization did not linearly correlate with the amount of the incorporated cinnamate groups, because the glass transition temperature of the cyclized rubber was not dependent on the small amount of the incorporated cinnamate groups, but on the amount of the cyclized units in the polymer. Theoretical treatment of the photodimerization reaction in the solid polymer was carried out, which was consistent with experimental results.

INTRODUCTION

Cyclized polydiene rubbers containing photocrosslinking reagents, such as bisazides, are widely used as typical photoresists.[1] Advantages of these polydiene rubbers can be summarized as follows: better solubility in organic solvents and better adhesion to metal plates and silicone wafers, which are favorable to developing characteristics; also fewer pinholes formed in the thin film; and a high resistence to etchants. However, these photoresists are not stable enough for long storage, and photosensitivity decreases considerably in the presence of oxygen and antioxidants.

The advantages of poly(vinyl cinnamate)-type photoresists are attributed to long storage stability and high resolving power, and the photosensitivity not only changes in the presence of oxygen and antioxidants, but also can be enhanced by photosensitizers. On the other hand, these have several disadvantages including low resistivity to etchants and pinholes in a thin film state. Therefore, it is desirable to synthesize cyclized polydienes having cinnamate groups, which may have the advantages of both cyclized rubbers and poly(vinyl cinnamate).

In a previous article,[2] we reported synthetic conditions needed to obtain cyclized rubbers having desired amount of cinnamate groups; and their properties were primarily investigated. The structures of the products obtained were identified as cyclized polydiene rubbers with pendent cinnamate groups. The amount of the incorporated cinnamate groups increased up to a maximum of

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around 20 mol %, and the amount of the residual unsaturated groups in the polymer backbone decreased because of cyclization of the double bond. The products had two glass transition temperatures.

These glass transition temperatures were identified as follows: a lower transition, owing to the original polydiene segment where the incorporated cinnamate groups were located; and a higher one, owing to the cyclic segment. These two thermal transitions on the polymer backbone suggested that the cyclic structure existed as a block segment in the polymer and the cinnamate groups were incorporated at random in a polymer.

The glass transition temperature of photosensitive polymers greatly influences the photosensitivity,[3,4] because the photocrosslinking reaction takes place in a solid state, where the mobility of the polymer influences the topochemical reaction. A theoretical elucidation of the relationship between the photosensitivity and the glass transition temperature of uncyclized polypentenamer having pendent cinnamate groups has previously been reported by us.[5-7] This report deals with the photosensitivity of cyclized polydienes and polypentenamer having pendent cinnamate groups in order to study the influence of the polymer structure in terms of the role of the glass transition temperature.

EXPERIMENTAL

Photosensitive Rubbers

Cyclized polydienes and polypentenamer having pendent cinnamate groups were prepared as previously described.[2] Characteristics of the samples used

TABLE I
Cyclized Polydienes and Polypentenamer with Pendent Cinnamate Groups

Polymer	X, mol %[a]	Y, mol %[b]	Z, mol %[c]	n^d	η_{sp}/C, dL/g[e]	T_1, °C[f]	T_2, °C[f]	T_3, °C[f]
cis-1,4-BR-CA-6	76.0	1.7	22.3	2.25	3.18	−103	−72, −20[g]	(112)[h]
-12	66.1	3.0	30.9		3.02	−98	−65, −20[g]	(125)[h]
-20	49.7	4.1	46.2		2.21	−87	−16	(120)[h]
-44	46.7	7.2	46.1		0.95	−66	−33	(122)[h]
-No. 1	24.7	8.2	67.1		1.90	−72	−35	(123)[h]
1,2-BR-CA-10	17.8	7.2	75.0	2.85	0.46	0	75	
-20	12.6	6.5	80.9		0.36	1	80	
-40	3.7	3.9	92.5		0.27	2	90	113
-2-20-79	1.4	3.9	94.8		0.20	0	86	
PP-CA-10	74.9	6.5	18.6	1.79	3.95	−72		
-20	72.1	9.0	18.9		1.89	−43	22	
-40	51.7	10.8	37.5		1.73	−35	80	
-110-40	26.1	9.7	64.2		0.54	−10	80	112
-2-20-79	23.5	14.7	61.8		1.00	−19	80	115

[a] Residual double bond of polydienes and polypentenamer.
[b] Incorporated cinnamate groups.
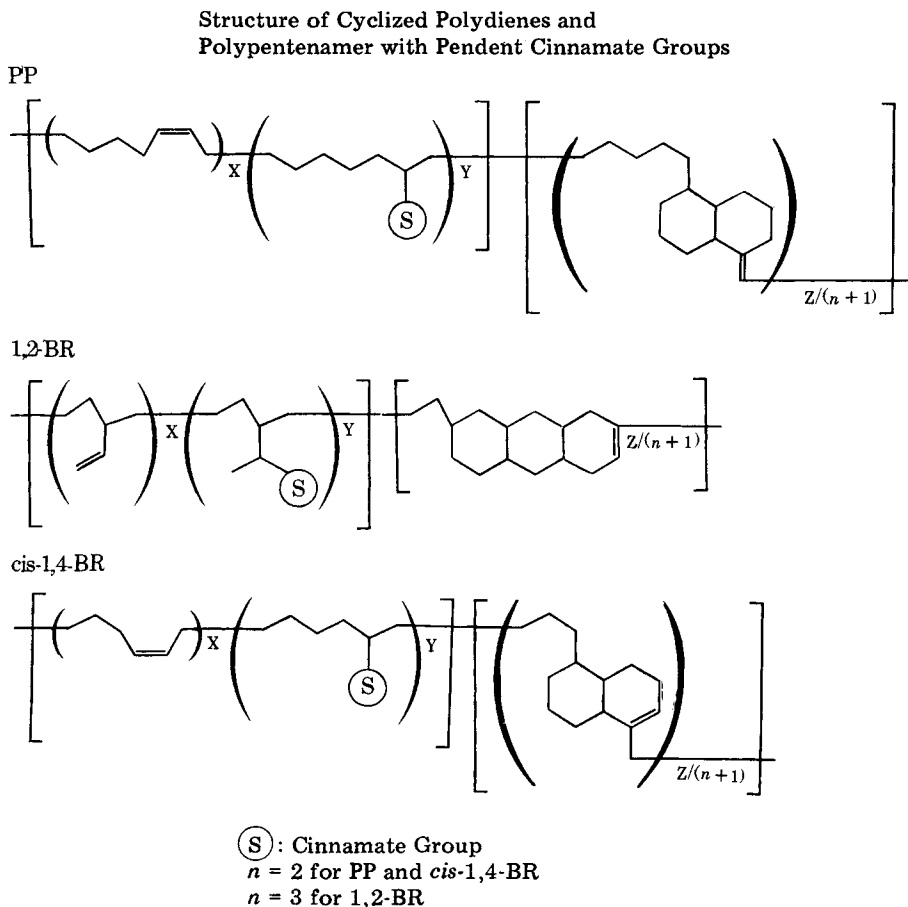[c] Degree of cyclization.
[d] Cyclicity.
[e] In chloroform at 30°C.
[f] Thermal transition of products measured by DSC.
[g] Melting temperature.
[h] Small transition.

are summarized in Table I. The relationship among X, Y and Z in Table I is illustrated in the following scheme:

**Structure of Cyclized Polydienes and
Polypentenamer with Pendent Cinnamate Groups**

PP

1,2-BR

cis-1,4-BR

(S): Cinnamate Group
$n = 2$ for PP and cis-1,4-BR
$n = 3$ for 1,2-BR

Irradiation of Photosensitive Rubbers

Film specimens for UV irradiation were prepared by casting from chloroform solution on NaCl plates. Their film thickness used was about 5×10^{-3} cm, which was measured by using the standard calibration curve of 1460 cm^{-1} absorption intensity in infrared spectra and the film thickness estimated from the film weight divided by the film area as the polymer density was unity. The UV irradiation was carried out at 25°C at a distance of 45 cm from a high pressure mercury lamp (250 W) made by Ushio Denki Co. The photodimerization rate of cinnamate groups was determined by the intensity change in the infrared (IR) absorption at 1637 cm^{-1} due to the carbon–carbon double bond of cinnamate groups by using Hitachi 215 Grating Infrared Spectro Photometer. In the case of 1,2-polybutadiene (1,2-BR), however, the IR absorption at around 1637 cm^{-1} due to the terminal vinyl group (CH$_2$=CH—) of 1,2-BR overlaps the IR absorption due to the cinnamate group. Therefore, in order to obtain the actual

intensity of the IR absorption at 1637 cm^{-1} due to the cinnamate group, the total intensity of the IR absorption at 1637 cm^{-1} was substracted by the intensity of the IR absorption at 1637 cm^{-1} due to 1,2-BR, which was calculated by using the ratio between the IR absorption at 1637 and at 910 cm^{-1} due to the terminal vinyl group.

RESULTS AND DISCUSSION

Process of Photodimerization of Cinnamate Groups

There is a detailed report by Tsuda[8] on the photodimerization of cinnamate groups in poly(vinyl cinnamate), in which the photodimerization of cinnamate groups, which proceeds through several complicated reaction paths, is finally summarized by four basic reaction paths, as follows:
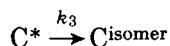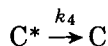
I. Excitation:

$$C^{so} \xrightarrow{h\nu, k_1} C^*$$

II. Dimerization:

$$C^* + C^{so} \xrightarrow{k_2} C\text{—}C^* \rightarrow C\text{—}C$$
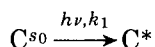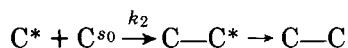
III. Isomerization:

$$C^* \xrightarrow{k_3} C^{isomer}$$

IV. Deactivation:

$$C^* \xrightarrow{k_4} C$$

where C^{so} and C^* denote the cinnamate group at the ground singlet state and the lowest excited state consisting of the singlet or triplet states, respectively.

Kinetics of Photodimerization of Cinnamate Groups[6]

The kinetic equation for the photodimerization of the cinnamate groups can be derived by using the previous basic four reaction equations and by assuming the steady state of the excited species and the isomerization reaction of the cinnamate groups does not take place because the cinnamate group in a solid film of poly(vinyl cinnamate)[9,10] and in a liquid of ethyl cinnamate[10,11] is known not to isomerize, as in the following equation:

$$[C^*] = \frac{k_1[C]}{k_2[C] + k_4}$$
$$= \frac{k_1[C]}{k_4} \qquad (\because k_2[C] \ll k_4) \qquad (1)$$

where the photodimerization is assumed to be slower than the deactivation ($k_2[C] \ll k_4$).[9] The photodimerization rate can be expressed to be half of the conversion rate of the cinnamate group, as follows:

$$\frac{-d[C]}{dt} = k_1[C] - k_4[C^*] + 2k_2[C^*][C]$$

$$= \frac{2d[\text{C—C}]}{dt} \tag{2}$$

The rate of the excitation reaction ($k_1[\text{C}]$) can be rewritten by using the absorbed light intensity (I_{abs}) and the film thickness (l), as in the following equations:

$$k_1[\text{C}] = \frac{I_{\text{abs}}}{6.023 \times 10^{23}h\nu \cdot l}$$

$$= \frac{\alpha I_{\text{abs}}}{l} \tag{3}$$

where $\alpha = 1/(6.023 \times 10^{23}h\nu)$; and h and ν denote Plank's constant and wave number, respectively. The photodimerization rate can be expressed from eqs. (1), (2), and (3) as follows:

$$\frac{-d[\text{C}]}{dt} = \frac{2d[\text{C—C}]}{dt}$$

$$= 2\alpha I_{abs} \frac{k_2[\text{C}]}{lk_4} \tag{4}$$

Therefore, the photodimerization rate can be expressed by considering the condition of the absorbed light intensity, as follows:

(a) If the absorbed light intensity is less than the incident light intensity ($I_{\text{abs}} < I_0$), the absorbed light intensity can be expressed by Lambert–Beers's equation and its approximation:

$$I_{\text{abs}} = I_0(1 - 10^{-\epsilon[\text{C}]l})$$
$$= 2.303 \, \epsilon[\text{C}]lI_0 \tag{5}$$

From eqs. (4) and (5), the photodimerization rate can be represented as a second-order reaction rate equation based on the concentration of the cinnamate groups. The observed rate constant (k_{obs}) is independent of film thickness, as follows:

$$\frac{-d[\text{C}]}{dt} = 4.606\alpha\epsilon I_0 \frac{k_2[\text{C}]^2}{k_4} \tag{6}$$

$$k_{\text{obs}} = 4.60\alpha\epsilon I_0 \frac{k_2}{k_4} \tag{7}$$

$$\frac{1}{[\text{C}]} - \frac{1}{[\text{C}_0]} = k_{\text{obs}}t \tag{8}$$

(b) If the absorbed light intensity is nearly equal to the incident light intensity ($I_{\text{abs}} \doteq I_0$), the photodimerization rate can be represented as a first-order reaction rate equation from eq. (4), and the thickness term of the film is included in the observed rate constant, as follows:

$$\frac{-d[\text{C}]}{dt} = \frac{2d[\text{C—C}]}{dt}$$

$$= 2\alpha I_0 \frac{k_2[\text{C}]}{lk_4} \tag{9}$$

$$k_{\text{obs}} = 2\alpha I_0 \frac{k_2}{lk_4}$$

$$= \frac{k^u_{\mathrm{obs}}}{l} \tag{10}$$

$$\frac{\ln[C_0]}{[C]} = k_{\mathrm{obs}}t \tag{11}$$

where $[C_0]$ denotes the initial concentration of the cinnamate group. Therefore, the observed rate constant on the unit film thickness (k^u_{obs}) was used for a comparison of the photosensitivity of the polymers.

Irradiation of Photosensitive Rubbers

When the film specimen of the photosensitive rubbers was irradiated with UV light, the absorption intensity of the IR spectrum due to the carbon–carbon double bond of the cinnamate group at 1637 cm^{-1} decreased and that due to the ester carbonyl at 1700 cm^{-1} shifted to 1720 cm^{-1}. Moreover, absorptions due to the double bond of cyclized polydienes and polypentenamer did not change (Fig. 1). Therefore, only the photoreaction between the cinnamate groups was traced in this system.

Figure 2 shows the time–conversion curve for the cinnamate group by irradiation, where most of the cinnamate group in cyclized cis-1,4-BR was dimerized within 30 min, and the photodimerizability changed in the following order: cis-1,4-BR-CA-6 > PP-CA-10 > PP-CA-20 > 1,2-BR-CA-20 ≳ cis-1,4-BR-CA-No 1 > 1,2-BR-CA-40.

PP-CA-10

1,2-BR-CA-10

cis-1,4-BR-CA-44

1800 1600   1000 800 500
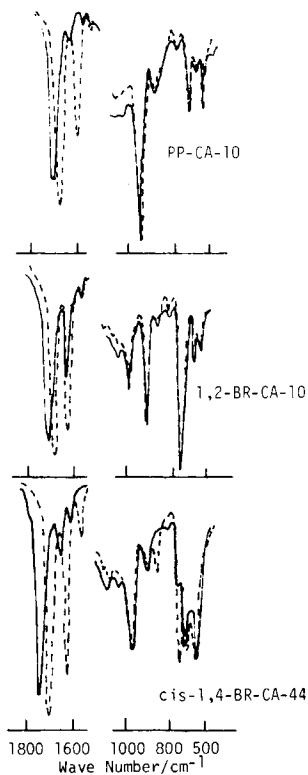Wave Number/cm^{-1}

Fig. 1. Infrared spectra of cyclized polydienes and polypentenamer with pendent cinnamate groups (film): (- - -) virgin; (——) UV irradiated.
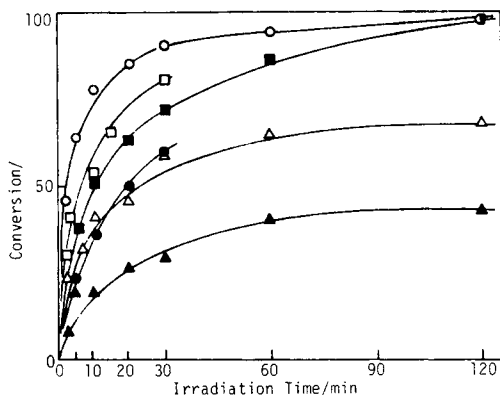
Fig. 2. Time conversion of cinnamate groups in cyclized polydienes and polypentenamer by UV irradiation at 25°C: (O) *cis*-1,4-BR-CA-6; (●) *cis*-1,4-BR-CA-No. 1; (Δ) 1,2-BR-CA-20; (▲) 1,2-BR-CA-40; (□) PP-CA-10; (■) PP-CA-20.

The film specimen used for irradiation showed a large UV absorption around 300 nm, which is the effective wavelength for the dimerization of cinnamate groups.   In this case, the kinetic treatment was carried out by using eqs. (9), (10), and (11), and the observed rate constant depended on the film thickness.   The first-order kinetics are shown in Figure 3.   The observed rate constants (k_{obs}) were obtained as the initial slopes because the slopes decreased with reaction time.   The crosslinking of the polymers may cause a decrease in the mobility of the cinnamate group, leading to a slowdown in the photodimerization reaction. The glass transition temperature of the polymers increased with UV irradiation, as indicated in a previous report.[2]

Figure 4 shows the relationship between the observed rate constant and the reciprocal of the film thickness, where the rate constant increased linearly with an increase in the reciprocal of the film thickness.   Therefore, the photodimer-
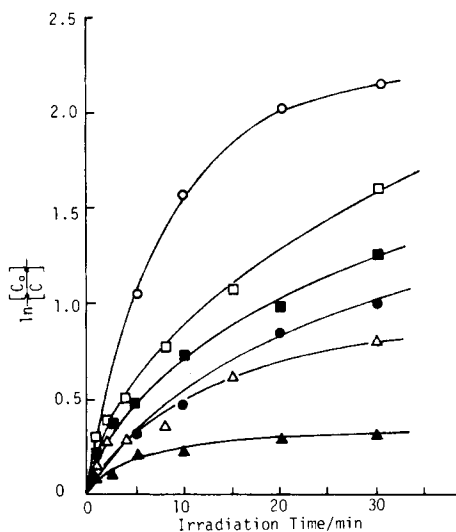

Fig. 3. Photodimerization of cinnamate groups in polydienes and polypentenamer at 25°C: (O) *cis*-1,4-BR-CA-6; (●) *cis*-1,4-BR-CA-No. 1; (Δ) 1,2-BR-CA-20; (▲) 1,2-BR-CA-40; (□) PP-CA-10; (■) PP-CA-20.
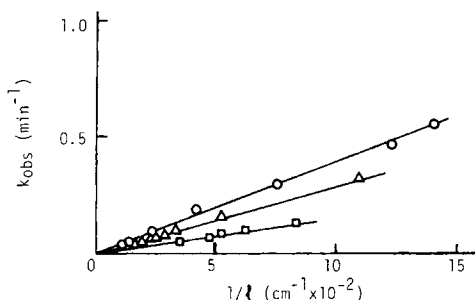
Fig. 4. Relationship between k_{obs} and reciprocal of film thickness $(1/l)$: (O) cis-1,4-BR-CA-No. 1; ($\triangle$) 1,2-BR-CA-2-20-79; ($\square$) PP-CA-2-20-79.

ization can be treated as first-order kinetics with respect to the concentration of the cinnamate group. The slopes gave the observed rate constants on the unit film thickness (k_{obs}^u) in order to compare the photosensitivity of the polymers. Table II summarizes the observed rate constants and the overall rate of the photodimerization with the glass transition temperatures of the polymers incorporating the cinnamate groups, where the observed rate constant decreased in the following tendency: cis-1,4-BR-CA > PP-CA > 1,2-BR-CA. This tendency corresponds to that of the glass transition temperature, which correlates to the mobility of the cinnamate group.

Photodimerization Rate Constant and Glass Transition Temperature[6,7]

The observed rate constant for unit film thickness (k_{obs}^u) can be expressed by eq. (10) as follows:

$$k_{obs}^u = \frac{2\beta k_2}{k_4} \tag{12}$$

$$\beta = \alpha I_0$$

The photodimerization reaction can be considered as a diffusion-controlled reaction, and the rate constant (k_2) can be represented by Smoluchowski's equation and Einstein-Stokes' equation,[12,13] as follows:

$$k_2 = \frac{8\delta KT}{3\eta} \tag{13}$$

where K, δ, and η denote Boltzmann constant, steric factor and a viscosity of the system. The rate constant for the deactivation (k_4) can be considered as a constant at a definite irradiation temperature. Consequently, the observed rate constant for unit film thickness (k_{obs}^u) can be represented as a function of a viscosity of the system,

$$k_{obs}^u = \frac{16\beta\delta KT}{3k_4\eta}$$

$$= \frac{\beta\zeta}{\eta} \tag{14}$$

$$\zeta = \frac{16\delta KT}{3k_4} \tag{15}$$

TABLE II
Photodimerization of Cyclized Polydienes and Polypentenamer with Pendent Cinnamate Groups

Polymer	Y, mol %	$[C_0]$, mol/cm³	k^u_{obs} min⁻¹ × 10³ᵃ	$\ln k^u_{obs}$	$R_p = \frac{1}{2}k^u_{obs}[C_0]$, (mol cm⁻³ min⁻¹) × 10⁷	$\ln R_p$	T_{g1}, °C	$1/(T_{uv} - T_{g1} + 50)$, K⁻¹ × 10³ ᵇ
cis-1,4-BR-CA-6	1.7	3.01 × 10⁻⁴	1.28	-6.66	1.93	-15.46	-103	5.62
-12	3.0	5.13 × 10⁻⁴	0.975	-6.93	2.50	-15.20	-98	5.78
-20	4.1	6.83 × 10⁻⁴	0.644	-7.35	2.20	-15.33	-87	6.17
-44	7.2	1.11 × 10⁻³	0.238	-8.34	1.32	-15.84	-66	7.09
-No.1	8.2	1.23 × 10⁻³	0.315	-8.06	1.94	-15.46	-72	6.80
1,2-BR-CA-10	7.2	1.11 × 10⁻³	0.193	-8.55	1.07	-16.05	0	13.33
-20	6.5	1.02 × 10⁻³	0.143	-8.85	0.729	-16.43	1	13.51
-40	3.9	6.52 × 10⁻⁴	0.081	-9.42	0.264	-17.45	2	13.70
-2-20-79	3.9	6.52 × 10⁻⁴	0.275	-8.20	0.897	-16.23	0	13.33
PP-CA-10	6.5	8.37 × 10⁻⁴	0.588	-7.44	2.46	-15.22	-72	6.80
-20	9.0	1.11 × 10⁻³	0.336	-8.00	1.86	-15.50	-43	8.47
-40	10.8	1.29 × 10⁻³	0.270	-8.22	1.74	-15.56	-35	9.09
-110-40	9.7	1.18 × 10⁻³	0.072	-9.54	0.425	-16.99	-10	11.76
-2-20-79	14.7	1.64 × 10⁻³	0.138	-8.89	1.13	-16.00	-19	10.64

ᵃ Apparent rate constant for 1 cm of film thickness.
ᵇ T_{uv} = UV irradiation temperature, 25°C.

where T is irradiation temperature and ζ can be considered as a constant at a definite temperature.

The viscosity of the system can be represented by Doolittle's equation,[14] as follows:

$$\ln\eta = \ln X + \frac{Bv_0}{v_f} \tag{16}$$

where B and X are constants and v_0 and v_f denote occupied volume and free volume of the system, respectively. The free volume of a polymer can be represented by using an equation of state about one mole of a system under a condition in which a temperature of the system (T) is higher than the glass transition temperature (T_g), as follows:

$$Pv_f = SR(T - T_0) \qquad T \geq T_g \tag{17}$$

where P, SR, R, and T_0 denote inner pressure, entropy of the system, gas constant, and apparent temperature at which the free volume of the system can be assumed to be zero, respectively. The apparent temperature (T_0)[15] is known to be $T_g - 51.6$, or $T_g - 55$ by Williams, Landel, and Ferry's equation[16] or by calculation of the entropy,[17] respectively. Therefore, T_0 can be estimated to be $T_g - 50$, as follows:

$$T_0 \doteq T_g - 50 \tag{18}$$

From eqs. (16) and (17), the viscosity of a polymer system can be expressed in the following equation, which is similar to Vogel's equation:

$$\ln \eta = \ln X + \frac{BPv_0}{SR(T - T_0)} \tag{19}$$

$$\text{Vogel's equation:} \quad \ln \eta = \ln X + \frac{BPv_0}{R(T - T_0)}$$

where B is usually unity and BPv_0/S can be considered to be the apparent activation energy of flow (E_{vis}). Consequently, the viscosity of the system and the observed rate constant can be represented by the following equations:

$$\eta = X \exp\left[\frac{E_{vis}}{R(T - T_0)}\right] \tag{20}$$

$$k_{obs}^u = \beta A \exp\left[\frac{-E_{vis}}{R(T - T_0)}\right] \tag{21}$$

$$A = \frac{\zeta}{X}$$

Moreover, the observed rate constant can be rewritten by eq. (18) to a function of the glass transition temperature as follows:

$$k_{obs}^u = \beta A \exp\left[\frac{-E_{vis}}{R(T - T_g + 50)}\right] \tag{22}$$

According to Williams, Landel and Ferry's equation, the specific free volume in polymer liquids is known to be 0.025 at the glass transition temperature[14,16]:

$$\frac{v_f}{v_0 + v_f} = 0.025 \tag{23}$$

The free volume is much smaller than the occupied volume so that eq. (23) can be rewritten to the following equation:

$$\frac{v_f}{v_0} \doteq 0.025 \qquad (24)$$

From eqs. (17) and (18), eq. (24) can be rewritten as follows:

$$\frac{50SR}{Pv_0} = 0.025 \qquad (25)$$

Therefore, the activation energy of flow (E_{vis}) can be obtained as a constant from eq. (25) as follows:

$$E_{vis} = \frac{BPv_0}{S}$$

$$= 2 \times 10^3 R \qquad (\because B \doteq 1) \qquad (26)$$

$$= 3.97 \times 10^3 \text{ cal/mol}$$

Figure 5 shows the relationship between the observed rate constant (k^u_{obs}) and the glass transition temperature of the polymer, where the close agreement with eq. (22) was observed. The apparent activation energies obtained were as follows: PP-CA, 830 cal/mol; cis-1,4-BR-CA, 2210 cal/mol; and 1,2-BR-CA, 4970 cal/mol.

The reason why the observed activation energies of flow are different from the value obtained by eq. (26) can be that the microbrownian mobility of a polymer segment (internal viscosity) estimated by the polymer glass transition temperature cannot be directly considered as the local viscosity of the photo-reactive site because of the entanglement of polymer chains and the excluded volume of the side chains between polymer main chains and photoreactive groups.[18] Moreover, the observed activation energy of flow, obtained by the photodimerization reaction of the cinnamate groups, includes a factor of interaction, such as hydrogen bonding and electrostatic or charge transfer interaction, due to neighboring groups of reactive sites.[19,20] Such interaction could make reactive groups more reactive or less reactive in locations.

Therefore, the apparent viscosity of a local reactive site should be represented
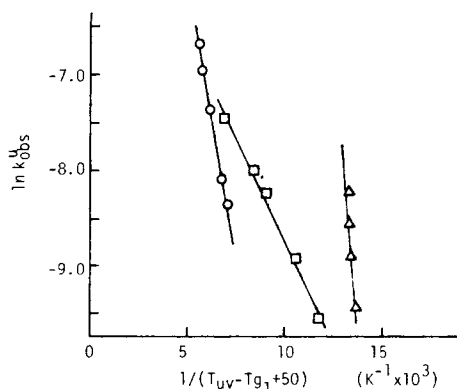

Fig. 5. Relationship between ln k^u_{obs} and $1/(T_{uv} - T_{g1} + 50)$; T_{uv} = UV irradiation temperature, 25°C; (O) cis-1,4-BR-CA; (△) 1,2-BR-CA; (□) PP-CA.

by parameters related to the dependence on the internal viscosity estimated by the glass transition temperature of a polymer segment, as follows:

$$\eta_{\text{local}} = X' \exp \left[\frac{\mu B v_0}{v_f} \right]$$

$$= X' \exp \left[\frac{\mu B P v_0}{SR(T - T_0)} \right] \tag{27}$$

where X' and μ are parameters related to the dependence of the apparent viscosity of a local reactive site on the internal viscosity; μ is a parameter of the dependence on the glass transition temperature of a polymer segment. Equation (21) can be rewritten by eqs. (26) and (27), as follows:

$$k_{\text{obs}}^u = \beta A' \exp \left[\frac{3.97 \times 10^3 \mu}{R(T - T_0)} \right] \tag{28}$$

The observed activation energy of flow, which varies with the dependence of the photodimerization of the cinnamate groups on the glass transition temperature of polymers, can be represented in the following equation:

$$E_{\text{vis}} = 3.97 \times 10^3 \mu$$

$$\doteqdot 4.0 \times 10^3 \mu \tag{29}$$

The μ values, which indicate the dependence of the reaction on the glass transition temperature of polymers, were as follows: PP-CA, 0.21; cis-1,4-BR-CA, 0.55; 1,2-BR-CA, 1.2. These results indicate that μ increases with increase in the side chain length and with decrease in the carbon number of a polymer repeating unit in a polymer main chain. A long side chain may increase the excluded volume of side chains. The increase in the excluded volume may increase additional energy for reactive groups to transfer and encounter. On the other hand, a long side chain may make the preexponential term of eq. (28) on the observed rate constant large, as shown in the high photosensitivity of 1,2-BR-CA in spite of its high glass transition temperature. The same effect of side chain length on the reactivity of cinnamate groups was observed in the case of uncyclized polypentenamer having pendent cinnamate groups.[7] Moreover, the increase in the number of carbons in the polymer repeating unit in a polymer main chain may enhance the orientation of reactive groups because of the increase in its flexibility.

Overall Rate of Photodimerization

The overall rate of the photodimerization (R_p) on the unit film thickness can be rewritten by eqs. (9), (10), (18), (28), and (29), as follows:

$$R_p = \frac{k_{\text{obs}}^u [C]}{2}$$

$$= \frac{\beta A'[C]}{2} \exp \left[\frac{-E_{\text{vis}}}{R(T - T_g + 50)} \right]$$

$$= \frac{\beta A'[C]}{2} \exp \left[\frac{-4.0 \times 10^3 \mu}{R(T - T_g + 50)} \right] \tag{30}$$

When the glass transition temperature is dependent on the amount of the cinnamate groups, the glass transition temperature (T_g) can be expressed as follows:

$$T_g = T_{g0} + \gamma [C] \tag{31}$$

where T_{g0}, γ, and [C] denote the glass transition temperature of virgin polymer, a coefficient, and the concentration of the cinnamate group, respectively. Therefore, the overall rate of the photodimerization can be represented[6,7] as follows:

$$R_p = \frac{\beta A'[C]}{2} \exp \left[\frac{-E_{\text{vis}}}{R(T - T_{g0} - \gamma [C] + 50)} \right] \tag{32}$$

where the maximum rate can be observed at a certain amount of the cinnamate groups, as shown in the following equation:

$$[C]_{R_p\text{max}} = \frac{T - T_{g0} + 50}{\gamma} + \frac{E_{\text{vis}} - \sqrt{4RE_{\text{vis}}(T - T_{g0} + 50) + E_{\text{vis}}^2}}{2\gamma R} \tag{33}$$

Figure 6 shows the relationship between $\ln R_p$ and $1/(T - T_{g1} + 50)$, where the overall rate of the photodimerization decreases with an increase in the glass transition temperature, although the overall rate is dependent on both the concentration of the cinnamate groups and the glass transition temperature. The linear relationship was particularly observed in 1,2-BR-CA and PP-CA, because the amounts of the cinnamate groups in the polymers are small and almost constant (Table I). Figure 7 indicates no linear correlation between the overall rate of the photodimerization and the amount of the cinnamate groups, because the glass transition temperature is independent of the amount of the cinnamate groups and increases with increasing amount of cyclized units.

In conclusion, the photosensitivity of the cyclized rubber having cinnamate groups decreased with an increase in the amount of the cyclized unit in the polymer owing to the rise in the glass transition temperature. No linear relationship between the overall rate of the photodimerization and the amount of the incorporated cinnamate groups was observed. Moreover, the observed activation energy of flow represented a dependence of the reaction on the glass transition temperature of polymer segments, and its dependence increased with
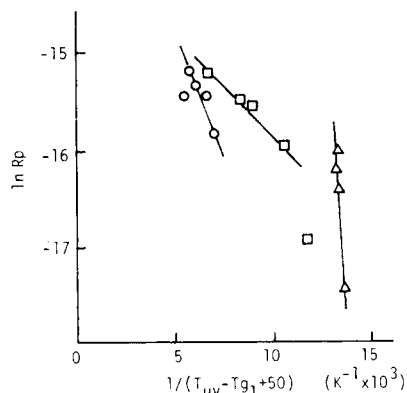

Fig. 6. Relationship between $\ln R_p$ and $1/(T_{uv} - T_{g1} + 50)$; T_{uv} = UV irradiation temperature, 25°C; (O) cis-1,4-BR-CA; (△) 1,2-BR-CA; (□) PP-CA.
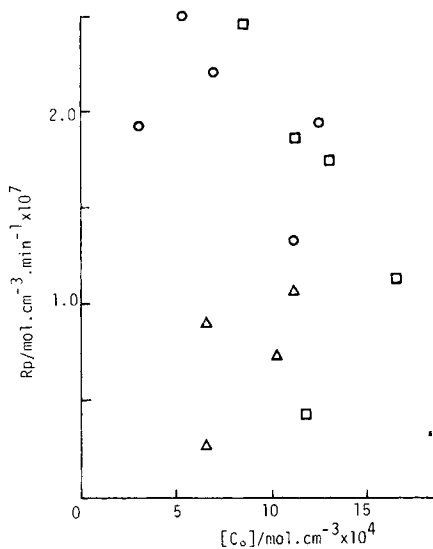
Fig. 7. Relationship between R_p and cinnamate group concentration [C_0] in polymers: (O) *cis*-1,4-BR-CA; (△) 1,2-BR-CA; (□) PP-CA.

an increase in the side chain length and with a decrease in the number of carbons in the polymer repeating unit in the polymer main chain.

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