

Synthesis and Properties of Photosensitive Rubbers.

IV. Photosensitive Rubbers from Hydroxyethyl Cinnamate and Polyisoprene Modified with Maleic Anhydride

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Synopsis

Polyisoprene in *o*-dichlorobenzene solution were reacted with maleic anhydride at 180°C under nitrogen atmosphere to form modified polyisoprene with α -substituted succinic anhydride groups. These groups were converted by reaction with hydroxyethyl cinnamate in pyridine at 25°C to cinnamate groups. Various amounts of cinnamate groups as photosensitive groups could be easily introduced into polyisoprene up to 75 mol % toward polyisoprene repeating units. Polymer glass transition temperatures of the products rose linearly from -70°C for polyisoprene to 60°C with increasing amounts of the side groups. The solution viscosity of the products in chloroform decreased from 9.34 for polyisoprene to 0.77 with increasing amounts of the side groups. The photosensitivity of the polyisoprene, which is based on the photodimerization of the cinnamate groups, was higher than that of polypentenamer having cinnamate groups due to the interaction by the free carboxylic acids neighboring with the cinnamate groups. The photosensitivity of the cinnamate group was kinetically evaluated in terms of the dependence on the polymer glass transition temperature. The interaction by the free carboxylic acid groups in the polyisoprene reduced the dependence of the photosensitivity on the mobility of the polymer segments. Linear relationship between observed rate constants of the photodimerization and $(T_{UV} - T_g + 50)^{-1}$ was obtained and the slope of the line changed and became very small at higher glass transition temperatures.

INTRODUCTION

Cyclized polydiene rubbers containing photocrosslinking reagents, such as bisazides, are widely used as a typical low-cost photoresist.¹ However, the disadvantages are that these photoresists are not stable enough for long storage and the photosensitivity is subject to decrease considerably in the presence of oxygen and antioxidants. Cinnamate groups have been used in many photoresists such as poly(vinyl cinnamate). The advantages of cinnamate groups are: stability for long storage, a high resolving power, and that the photosensitivity does not change even in the presence of oxygen and antioxidants, and also can be enhanced by photosensitizers.

Therefore, it is desirable to synthesize polydiene rubbers containing cinnamate groups, which may have the advantages of both polydienes and cinnamate groups. An attempt had been made in order to obtain cyclized polydiene rubbers having cinnamate groups by using the addition reaction of polydienes with cinnamic acid in the presence of an acid catalyst.² The structure of the products obtained were cyclized polydiene rubbers having cinnamate groups. The amount of the incorporated cinnamate groups increased up to the maximum of around 20 mol

%, and the amount of the residual unsaturated groups in the polymer backbone decreased because of cyclization of the double bonds.

Maleic anhydride easily adds to polydienes, such as polyisoprene, at high temperatures or in the presence of radical catalysts.^{3,4} Therefore, we have tried to carry out the reaction of polyisoprene with maleic anhydride in *o*-dichlorobenzene at 180°C under nitrogen atmosphere. It was expected that the products would react with hydroxyethyl cinnamate in order to obtain higher amounts of the incorporated cinnamate groups in a polydienes in comparison with the case of the direct addition reaction of cinnamic acid to polydienes in the presence of an acid catalyst. This paper will describe synthetic conditions and the photosensitivity of the polyisoprene having cinnamate groups through the maleic anhydride adduct. The glass transition temperature of photosensitive polymers greatly influences the photosensitivity,^{5,6} because the photocrosslinking reaction takes place in a solid state, where the mobility of the polymer influences the topochemical reaction. We reported the dependence of the photosensitivity on the glass transition temperature of the polymer theoretically and experimentally in the cases of cyclized polydiene rubbers,⁷ linear polydiene rubbers having cinnamate groups,⁸⁻¹⁰ and the cyclized polydiene rubbers having chloroacetyl groups as photosensitive groups.¹¹ Therefore, the photosensitivity of the polyisoprene having cinnamate groups on the influence of the polymer structure was investigated in terms of the role of the glass transition temperature of the polymer. The contribution of the free carboxylic acid groups neighboring the cinnamate groups to photosensitivity was elucidated.

EXPERIMENTAL

Material

Cis-1,4-polyisoprene(IR-2200), supplied by the Japan Synthetic Rubber Co., was purified by reprecipitation from toluene into methanol and dried under vacuum. Reagents were used as purchased. Solvents were purified according to conventional methods.

Synthesis of Hydroxyethyl Cinnamate (CM)¹²

To 37.5 g of ethyleneglycol in 15 mL of pyridine, 50 g of molten cinnamoyl chloride was added dropwise at a temperature below 25°C. After all of the cinnamoyl chloride was added, the reaction was continued for 1 h at 25°C. Then the reaction mixture was poured into water. To the resulting mixture chloroform was added, and the chloroform layer was washed with water, dilute sulfuric acid, and aqueous sodium carbonate. The chloroform solution was dried with anhydrous magnesium sulfate. The identification of the product was carried out by using NMR and IR spectra (Fig. 1). The ester was used without distillation after removing chloroform under reduced pressure.

Addition Reaction of Maleic Anhydride to Polyisoprene (PI-MA)

The addition reaction of maleic anhydride to *cis*-1,4-polyisoprene was carried out in *o*-dichlorobenzene at 180°C under 5 kg·cm⁻² of nitrogen pressure by using

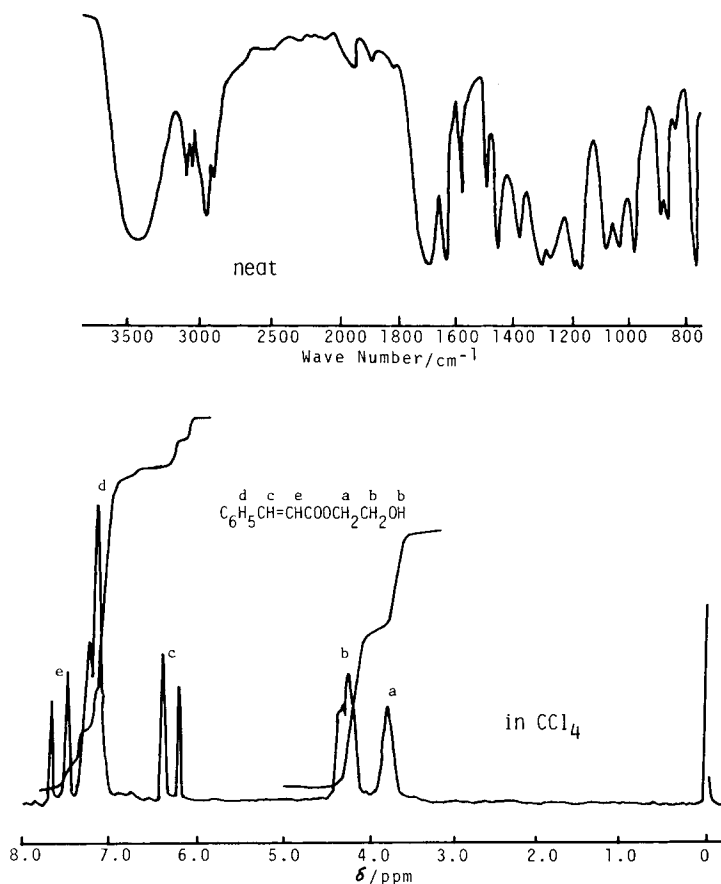


Fig. 1. Infrared and NMR spectra of hydroxyethyl cinnamate.

a pressure-proof glass vessel made by Taiatsu Glass Kogyo Co. To 1 mol-dm⁻³ of *o*-dichlorobenzene solution of polyisoprene, two mol of maleic anhydride per polymer repeating unit were added at 180°C under a nitrogen atmosphere in the presence of an antioxidant. The products having various contents of incorporated anhydride groups were recovered by pouring the resulting mixture into an excess of acetone in the case of the small amount of incorporated anhydride groups of less than 10 mol %, or into an excess of *n*-hexane in the case of the high amount of incorporated anhydride groups of over 16 mol %, at a desired reaction time from 30 min to 6 h. Then, the precipitate was collected by filtration, and the product was dissolved in chloroform. The purification of the products was done by reprecipitation. The product was stored as 1 mol-dm⁻³ of chloroform solution under nitrogen atmosphere in a refrigerator.

Reaction of PI-MA with Hydroxyethyl Cinnamate (PI-MA-CM)

To 1 mol-dm⁻³ pyridine solution of PI-MA, two mol of hydroxyethyl cinnamate per polymer repeating unit of PI-MA were added. The reaction was carried out at 75°C for 21 h. The resulting mixture was poured into methanol-acetone mixture in the case of the amount of incorporated cinnamate groups of less than

16 mol % or into *n*-hexane in the case of higher amount of incorporated cinnamate groups. The photosensitive product was dissolved in chloroform in the case of the amount of incorporated cinnamate groups of less than 16 mol % or in ethyleneglycol monomethylether in the case of a higher amount of incorporated cinnamate. The solution was stored under nitrogen atmosphere in a refrigerator.

Characterization of Products

The products were characterized by elemental, infrared, and NMR analyses. Infrared analyses were carried out on film samples of the polymers, which were prepared by casting the chloroform solution on NaCl plates, using a Hitachi 215 grating infrared spectrophotometer. The amount of various incorporated groups in the polymers were determined by elemental and NMR analyses. NMR measurements of the samples were carried out on deuterated chloroform or carbontetrachloride solutions containing hexamethyl-di-siloxane as an internal standard by using a Hitachi model R-22 (90 MHz) spectrometer.

Solution viscosity of the polymers was measured in chloroform at 30°C. Thermal properties, such as glass transition and melting temperatures, were measured by a differential scanning calorimeter Rigaku Denki Thermoflex 8056 D2 DSC. The scanning speed was 20°C/min in all cases, and indium was used as a standard. The starting point of the transition temperature was accepted as the transition point of the polymers.

Irradiation of Photosensitive Rubbers

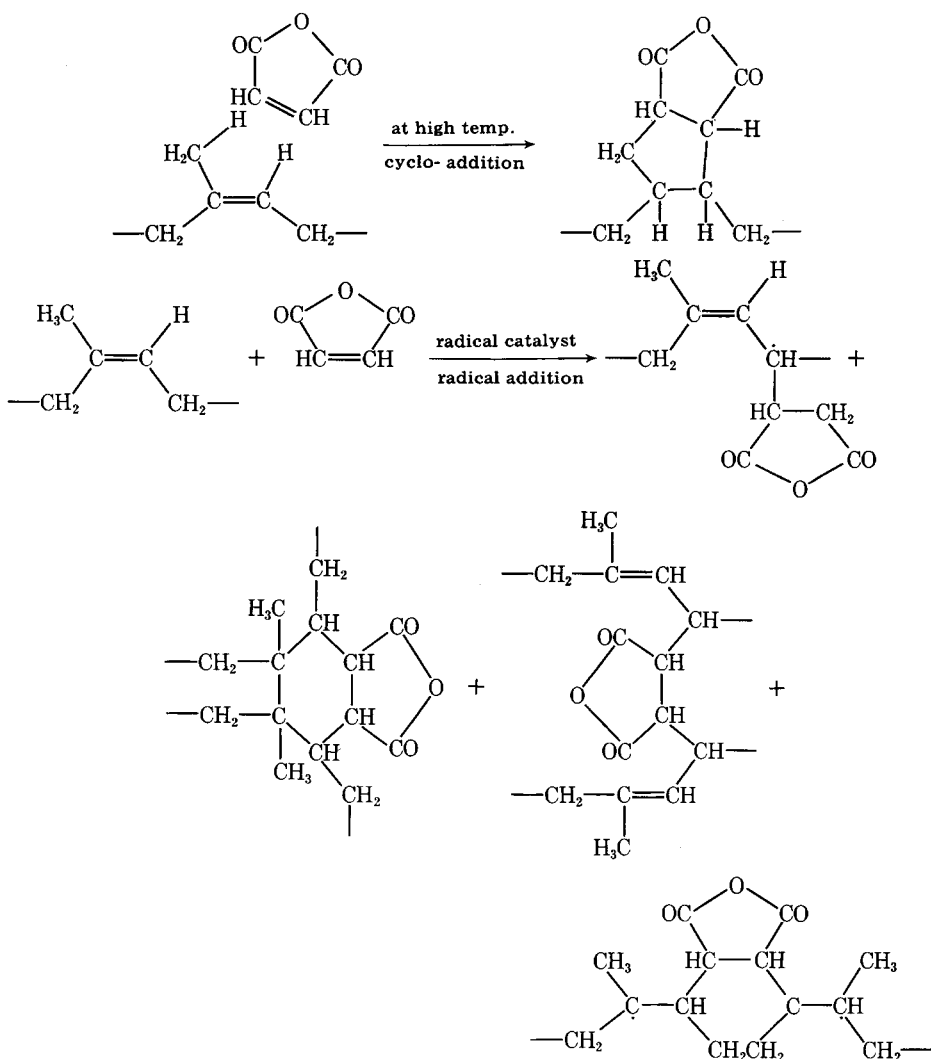
Film specimens for UV irradiation were prepared by casting the chloroform solution on NaCl plates for infrared analyses. Their film thickness used was about 5×10^{-3} cm, which was measured by using the standard calibration curve of 1375 cm^{-1} absorption intensity in infrared spectra, and the film thickness was 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 an ultrahigh pressure mercury lamp (250 W) made by Ushio Denki Co, where the incident light intensity was measured to be $11.5 \text{ W}\cdot\text{cm}^{-2}$ by using a photometer for 254 nm. The photodimerization rate of cinnamate groups was determined by the intensity change of the infrared absorption at 1637 cm^{-1} due to the carbon-carbon double bond of cinnamate groups by using Hitachi 215 grating infrared spectrophotometer.

RESULTS AND DISCUSSION

Addition Reaction of Maleic Anhydride to Polyisoprene (PI-MA)

Maleic anhydride easily adds to polyisoprene at high temperature³ or in the presence of radical catalysts. The reaction can be illustrated in the following scheme to take place by the *ens cyclo-* addition reaction at high temperatures in the absence of radical catalysts and by a hydrogen abstraction reaction on

α -CH₂ toward the double bond in polydienes in the presence of radical catalysts:



The radical addition reaction yielded products which had many complicated structures and the large portion of the products became insoluble.³ Therefore, the reaction was carried out at a high temperature (180°C) in *o*-dichlorobenzene in the absence of radical catalysts under a pressure of nitrogen (5 kg·cm⁻²). The IR and NMR spectra of the products (PI-MA) are shown in Figures 2 and 3, where the absorptions due to the α -substituted succinic anhydride group are discernible. The intensity of the absorption due to methyl group in polyisoprene moiety was observed to decrease in the IR and NMR spectra, and an absorption at 910 cm⁻¹ due to a terminal double bond (CH₂=C<) appeared. The products were soluble, and no insoluble product was obtained. Therefore, the structure of the products was identified to be the one due to the dipole addition reaction as indicated in the scheme.

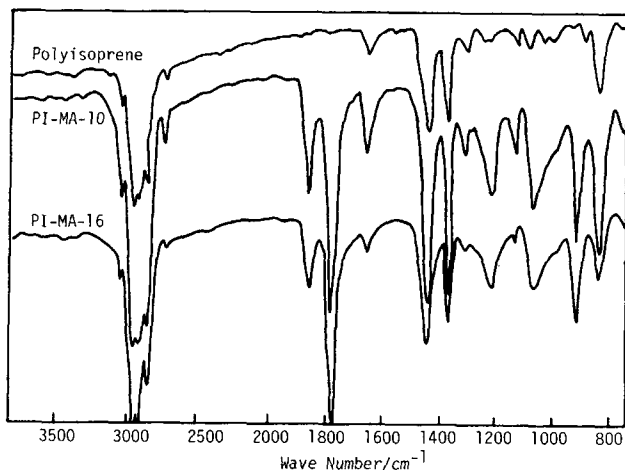


Fig. 2. Infrared Spectra of PI-MA films.

The results of the addition reaction are summarized in Table I. The amount of the incorporated α -substituted succinic anhydride groups increased up to 75 mol % toward polymer repeating unit with a longer reaction time, although the values scattered due to the difference of reaction batches where the reaction

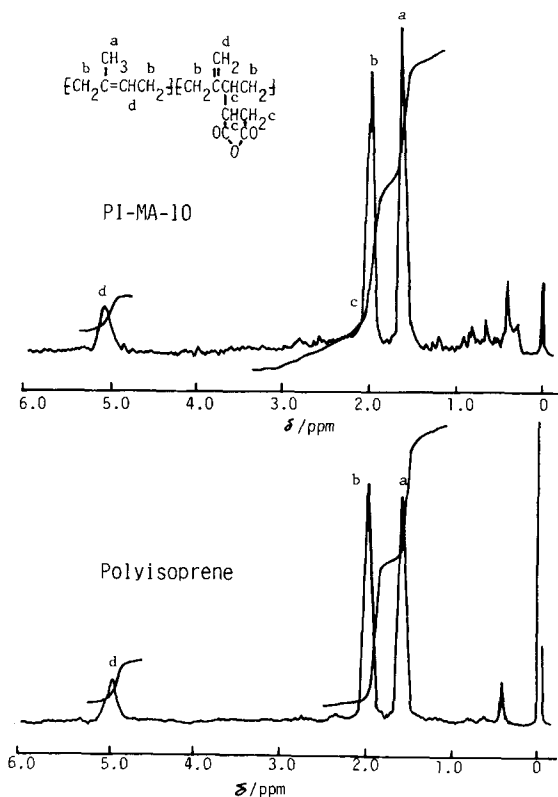


Fig. 3. NMR spectra of PI-MA-10 and polyisoprene in CCl_4 .

TABLE I
 Addition Reaction of Maleic Anhydride to Polyisoprene^a

No. ^b	Polymer ^c	Time ^d (h)	Incorporated ^e substrate (mol %)	T_g^f (°C)	η_{sp}/C^g	Nonsolvent ^h
<i>cis</i> -1,4-polyisoprene				-70	9.34	Acetone
1	PI-MA-3	0.5	3.0	-68	12.2	Acetone
	-10	1.0	10	-61	9.09	Acetone
	-16	2.0	16	-54	3.14	<i>n</i> -Hexane
2	PI-MA-26	1.0	26	-35	0.87	<i>n</i> -Hexane
	-47	2.0	47	-27	0.47	<i>n</i> -Hexane
	-54	3.0	54	-10/15	0.35	<i>n</i> -Hexane
	-63	4.0	63	46	0.50	<i>n</i> -Hexane
3	PI-MA-75	6.0	75	64	1.6	<i>n</i> -Hexane

^a 1 mol/dm³ of *cis*-1,4-polyisoprene in *o*-dichlorobenzene solution, *cis*-1,4-polyisoprene/maleic anhydride = 1/2, reaction temperature = 180°C.

^b Reaction batch number.

^c Abbreviation of the products.

^d Reaction time.

^e The amount of incorporated maleic anhydride (mol %) toward polymer repeating unit.

^f Glass transition temperature of the products measured by DSC.

^g 0.05 g/10 cm³ in chloroform at 30°C, g/100 cm³.

^h Nonsolvent for precipitation of the products.

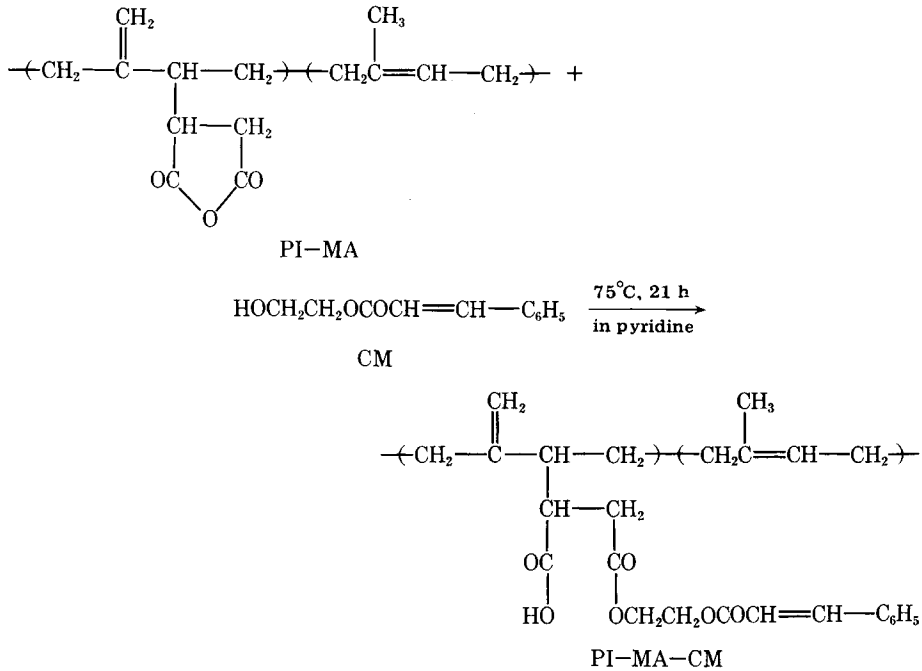
temperatures were a little different. The glass transition temperature (T_g) of PI-MA rose from -70°C of polyisoprene to 64°C of PI-MA having 75 mol % of α -substituted succinic anhydride groups.

The solution viscosity of PI-MA in chloroform increased in the case of a lower level of functionalization; then it decreased with high degree of functionalization. Moreover, the viscosity started to increase again with a higher degree of functionalization, as shown in PI-MA-63 and -75. These viscosity observations may not result from degradation of the polymer main chain, but rather from a change in the degree of polymer-polymer interaction as the substitution changes. In addition, with the change in the functionalization of polyisoprene, the solubility of the particular polymer changed dramatically in such a way that PI-MA having less than 10 mol % of the incorporated groups was soluble in *n*-hexane and insoluble in acetone. Their properties were almost the same as the virgin polyisoprene. However, PI-MA having over 16 mol % of the incorporated succinic anhydride groups was insoluble in *n*-hexane and soluble in acetone. Their properties were different from the virgin polyisoprene due to the incorporated succinic anhydride groups.

Reaction of PI-MA with Hydroxyethyl Cinnamate (PI-MA-CM)

The reaction was carried out according to the procedure described in the experimental section. Succinic anhydride groups in PI-MA were apparently converted (Figs. 4 and 5) to mono(β -cinnamoyloxyethyl)succinate groups in PI-MA-CM since at 1637 cm⁻¹ they disappeared by UV irradiation. Therefore, it was confirmed that the succinic anhydride group in PI-MA was completely converted to the cinnamate group by the reaction with hydroxyethyl cinnamate,

and the cinnamate groups were dimerized by UV irradiation:



Properties of PI-MA-CM

The properties of PI-MA-CM are summarized in Table II. The glass transition temperature (T_g) and the solution viscosity of PI-MA-CM were almost the same as the one of PI-MA. The relationship between the glass transition temperature (T_g) of PI-MA-CM and the concentration of the cinnamate group ([C]) is shown in Figure 6. T_g of PI-MA-CM did not change at the low concentration of less than 10 mol % of the incorporated side groups, while at the

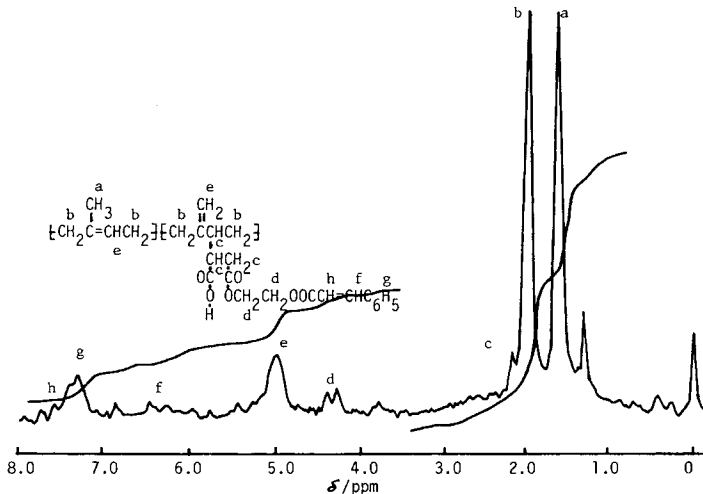


Fig. 4. NMR spectrum of PI-MA-CM-16 in CCl_4 .

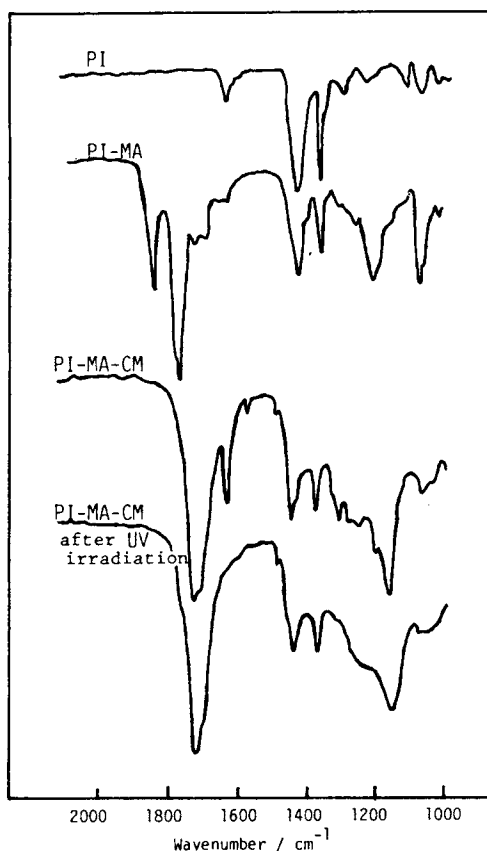


Fig. 5. IR spectra of polyisoprene, PI-MA, PI-MA-CM, and UV-irradiated PI-MA-CM.

higher concentration of over 16 mol % T_g rose linearly with increasing the amount of the cinnamate groups from -70°C of polyisoprene to 60°C of PI-MA-CM having 75 mol % of the cinnamate side groups. The solubility of PI-MA-CM also depended on the amount of the incorporated cinnamate groups. In the case

TABLE II
Properties of PI-MA-CM^a

Polymer	C^b (mol %)	T_g^c ($^\circ\text{C}$)	η_{sp}/C^d	Density ($\text{g}\cdot\text{cm}^{-3}$)
PI ^e		-70	9.34	
PI-MA-CM-3	3.0	-68	2.93	1.01
-10	10	-63	2.44	1.08
-16	16	-45	0.92	1.03
-26	26	-8	0.60	1.12
-54	54	35	0.77	1.12
-63	63	50	0.77	1.16
-75	75	60	1.33	1.12

^a Abbreviation of the products from the reaction of hydroxyethyl cinnamate and polyisoprene modified with maleic anhydride (PI-MA).

^b The amount of incorporated cinnamate groups (mol %) toward polymer repeating unit.

^c Glass transition temperature of the products measured by DSC.

^d $0.05 \text{ g}/10 \text{ cm}^3$ in chloroform at 30°C , $\text{g}/100 \text{ cm}^3$.

^e *cis*-1,4-polyisoprene.

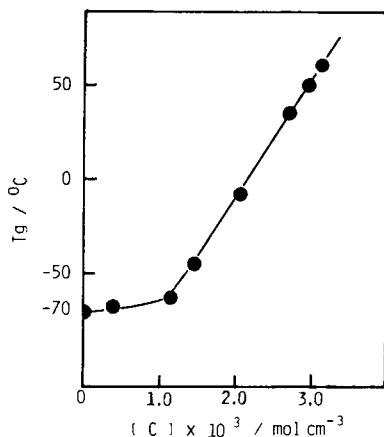


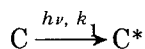
Fig. 6. Relationship between $[C]$ and T_g of PI-MA-CM.

of PI-MA-CM having over 16 mol % of the cinnamate group, *n*-hexane was a poor solvent and acetone was a good solvent, and PI-MA-CM having over 50 mol % of the side groups was soluble in an aqueous alkaline solution due to free carboxylic acid groups neighboring with the cinnamate groups.

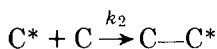
Photosensitivity of PI-MA-CM

The photosensitivity of PI-MA-CM, which is due to the photodimerization of the cinnamate groups in PI-MA-CM, was estimated by using the observed rate constants of the photodimerization. The photodimerization of cinnamate groups can be expressed by the following four basic reaction equations¹³:

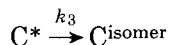
I. Excitation:



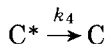
II. Dimerization:



III. Isomerization:



IV. Deactivation:



Here C and C^* denote the cinnamate groups at the ground singlet state and the lowest excited state consisting of the singlet or or triplet state, respectively. The kinetic equation for the photodimerization of the cinnamate groups can be derived by using the previous four basic reaction equations and by assuming the steady state of the excited species and the isomerization reaction of the cinnamate groups does not take place in a solid film, as follows:

$$\begin{aligned} -d[C]/dt &= 2d[C-C]/dt \\ &= 2\alpha I_{\text{abs}} k_2 [C] / k_4 \end{aligned} \quad (1)$$

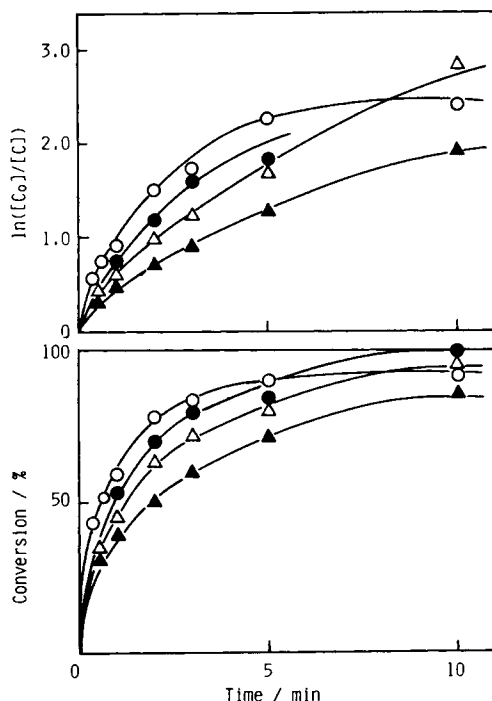


Fig. 7. Conversion of cinnamate groups and the relationship between $\ln([C_0]/[C])$ and UV-irradiation time: (O) PI-MA-CM-10 ($l = 0.91 \times 10^{-3}$ cm); (●) PI-MA-CM-26 ($l = 1.02 \times 10^{-3}$ cm); (Δ) PI-MA-CM-54 ($l = 0.95 \times 10^{-3}$ cm); (\blacktriangle) PI-MA-CM-63 ($l = 1.14 \times 10^{-3}$ cm).

where l and I_{abs} denote film thickness of a specimen and light intensity absorbed by a specimen, and α denotes the reciprocal of an Einstein:

$$\alpha = (6.023 \times 10^{23} h\nu)^{-1} \quad (2)$$

When film specimens of PI-MA-CM were 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, (Fig. 5). Therefore, the consumption of the cinnamate groups was estimated by using the IR spectral change at 1637 cm^{-1} . In this case, film specimens used for irradiation showed a large UV absorption around 300 nm, which is an effective wavelength for the dimerization of cinnamate groups.¹⁴ That is, the absorbed light intensity I_{abs} is nearly equal to the incident light intensity I_0 . Consequently, the photodimerization rate can be represented as a pseudo first-order reaction rate equation,⁷⁻¹⁰ as follows:

$$-d[C]/dt = 2\alpha I_0 k_2 [C]/lk_4 \quad (3)$$

$$\ln([C_0]/[C]) = k_{\text{obs}} t \quad (4)$$

$$\begin{aligned} k_{\text{obs}} &= 2\alpha I_0 k_2 / lk_4 \\ &= k_{\text{obs}}^u / l \end{aligned} \quad (5)$$

where $[C_0]$ denotes the initial concentration of the cinnamate group. Therefore, the observed rate constant on the unit film thickness (k_{obs}^u) was used for a comparison of the photosensitivity of PI-MA-CM.

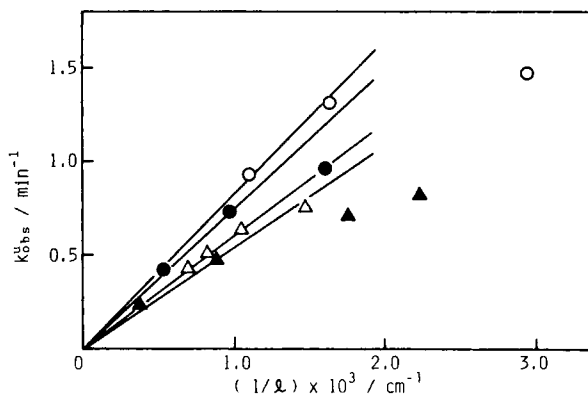


Fig. 8. Relationship between k_{obs}^0 and $1/l$ of PI-MA-CM: (○) PI-MA-CM-10; (●) PI-MA-CM-26; (△) PI-MA-CM-54; (▲) PI-MA-CM-63.

The time conversion of the cinnamate group in PI-MA-CM and its pseudo first-order kinetics are shown in Figure 7. The rate of the conversion was observed to decrease with increasing the amount of the cinnamate group by comparison with them on a similar film thickness. The observed rate constant was obtained as the initial slope of the pseudo first-order kinetics, which was dependent on the film thickness⁷⁻¹⁰ (Fig. 8). The slope of the line approached zero on very thin films due to the influence of absorbed light intensity so that the initial slope of the line was taken as the observed rate constant on the unit film thickness in order to compare the photosensitivity of PI-MA-CM. The photosensitivity of PI-MA-CM slightly decreased with increasing the amount of the incorporated cinnamate groups, and the photosensitivities of PI-MA-CM-54 and -63 were almost equal.

Photodimerization Rate Constant and Glass Transition Temperature

The glass transition temperature of photopolymers greatly influences^{5,6} its photosensitivity because the photocrosslinking reaction takes place in a solid state, where the mobility of the polymer influences the topochemical reaction. We had revealed the dependence of the photosensitivity on the glass transition temperature of the polymer, theoretically⁹ and experimentally.^{7,8,10}

The rate constant of the photodimerization of cinnamate groups is diffusion controlled, and the rate constant is proportional to the reciprocal of the viscosity of the system where reactive sites are located. The viscosity can be expressed by using the polymer viscosity, which is also described by using the polymer glass transition (T_g), as shown in the following equation:

$$\eta_{\text{polymer}} = X \cdot \exp[4.0 \times 10^3/R(T - T_g + 50)] \quad (6)$$

where η_{polymer} , X , and T denote the polymer viscosity, a preexponential term, and UV-irradiation temperature, respectively. However, the viscosity could not be exactly the same as the real polymer viscosity because of the entanglement of polymer chains, the excluded volume of side chains where reactive sites are located and the interaction between reactive sites, such as hydrogen bonding or charge transfer interactions. Therefore, a parameter (μ) which indicates a correlation between the viscosity of the system where reactive sites are located

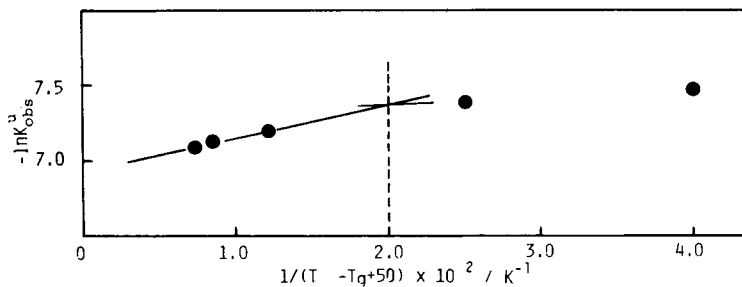


Fig. 9. Relationship between $-\ln(k_{\text{obs}}^u)$ and $(T - T_g + 50)^{-1}$ of PI-MA-CM.

and the polymer viscosity estimated by using the polymer glass transition temperature should be introduced into the viscosity term, as follows:

$$\eta_{\text{reactive site}} = X' \cdot \exp[4.0 \times 10^3 \mu / R(T - T_g + 50)] \quad (7)$$

Consequently, the observed rate constant of the photodimerization (k_{obs}^u) can be expressed by using T_g ⁷ as follows:

$$\begin{aligned} k_{\text{obs}}^u &= \beta \zeta / \eta_{\text{reactive site}} \\ &= \beta A \cdot \exp[-4.0 \times 10^3 \mu / R(T - T_g + 50)] \\ \beta &= \alpha I_0, \quad A = \zeta / X', \quad \text{and} \quad \zeta = 16KT\delta / 3k_4 \end{aligned} \quad (8)$$

where β and A are constant at a constant temperature (T), and K and δ denote the Boltzman constant and the steric factor of diffusion, respectively. 4.0×10^3 is an apparent activation energy of the flow for the reaction system estimated by T_g , and μ indicates the dependence of the reaction on the glass transition temperature of the polymers:

$$E_{\text{vis}} = 4.0 \times 10^3 \mu \quad (\text{cal/mol}) \quad (9)$$

The relationship between the observed rate constant and the glass transition temperature of the polymer is shown in Figure 9. A linear relationship between $\ln(k_{\text{obs}}^u)$ and $(T - T_g + 50)^{-1}$ was observed under the condition in which the polymer glass transition temperature was below the UV-irradiation temperature ($T \gtrsim T_g$). Moreover, the linear relation was turned down at $2 \times 10^{-2} \text{K}^{-1}$, where T_g was equal to the UV-irradiation temperature. The linear relation was turned down at the point because the motion of the reactive sites may be frozen at the temperatures below the glass transition temperature, and the photosensitivity increases when lowering the glass transition temperature.

The apparent activation energy of the flow and the parameter (μ) for the reaction were 45.5 and 0.011 cal/mol, respectively. In spite of the expectation that the long and big-size side chains of PI-MA-CM seem to cause the large dependence of the reaction on the glass transition temperature due to the excluded volume of the side chains,^{7,10} the parameter obtained is much smaller than that of cyclized⁷ or linear polydienes⁸⁻¹⁰ having cinnamate groups. The photosensitivity of PI-MA-CM was higher than that of cyclized or linear polydienes having cinnamate groups. This phenomenon may be due to the interaction of free carboxylic acid groups with neighboring cinnamate groups in PI-MA-CM. Free carboxylic acid groups could interact by hydrogen bonding forces to form an aggregation of cinnamate groups so that the dependence of the photodimerization of PI-MA-CM on the glass transition temperature decreases.

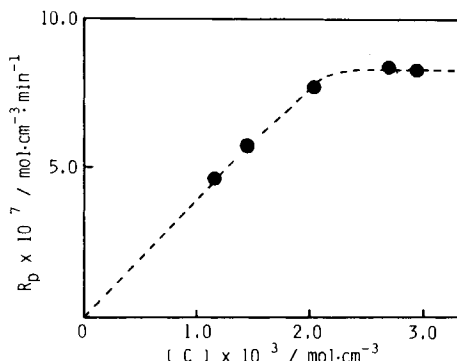


Fig. 10. Relationship between R_p and $[C]$: (---) Theoretical curve calculated by $R_p = \beta \cdot A \cdot [C] \cdot \exp[-E_{\text{vis}}/R(T - T_{g0} - \gamma[C] + 50)]$.

Overall Rate of Photodimerization

The relationship between the overall rate of the photodimerization (R_p) and the concentration of the cinnamate group ($[C]$) is shown in Figure 10. The overall rate increased with increasing the concentration of the cinnamate groups and reached to a plateau. The glass transition temperature of polymers is dependent on the amount of the cinnamate group and the glass transition temperature (T_g) can be represented in a linear relation, as follows:

$$T_g = T_{g0} + \gamma[C] \quad (10)$$

where T_{g0} denotes the glass transition temperature of the virgin polymer; the overall rate of the photodimerization can be expressed in the following equation⁷⁻¹⁰:

$$R_p = \beta A \cdot [C] \cdot \exp[-E_{\text{vis}}/R(T - T_{g0} - \gamma[C] + 50)] \quad (11)$$

where the maximum rate could be observed at a certain amount of the cinnamate group, as indicated in the following equation:

$$[C]_{R_p \text{max}} = (T - T_{g0} + 50)/\gamma + [E_{\text{vis}} - \sqrt{4R \cdot E_{\text{vis}}(T - T_{g0} + 50) + E_{\text{vis}}^2}]/2\gamma R \quad (12)$$

However, no maximum or plateau were observed, as shown in Figure 10, because of the small dependence of the photodimerization on the glass transition temperature. Therefore, the overall rate increases linearly with increasing amounts of cinnamate groups when the photodimerization does not depend on the polymer glass transition temperature.

In conclusion, the linear relationship between observed rate constants of the photodimerization and $(T - T_g + 50)^{-1}$ was obtained. The slope of the line became very flat in the case of the polymers having higher glass transition temperatures than the UV-irradiation temperature. The photosensitivity of PI-MA-CM was higher than that of cyclized or linear polydienes having cinnamate groups due to the interaction by the free carboxylic acid groups neighboring with the cinnamate groups. The interaction by free carboxylic acid groups in PI-MA-CM reduced the dependence of the photodimerization on the mobility of the polymer segments. The neutralization of the carboxylic acid groups would give rise to a large amount of ionic agglomeration in accord with our proposed

mechanisms and further enhanced the photosensitivity of the resulting polymers.

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