Synthesis and Properties of Photosensitive Rubbers. I. Direct Addition Reaction of α,β-Unsaturated Carboxylic Acids to Polydienes and Polypentenamer

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Synopsis

The addition reaction of α,β-unsaturated carboxylic acids to polydienes, such as *cis*-1,4-polybutadiene, 1,2-polybutadiene, and polypentenamer, was investigated in the presence of acid catalysts in order to obtain photosensitive rubbers. The structures of products obtained were identified as cyclized polydiene rubbers having pendent α,β-unsaturated carboxylate groups. The amount of the incorporated substrates increased up to the maximum of around 20 mole %, 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 carboxylate groups were located; and a higher one, owing to cyclic segment. These two thermal transitions on the polymer backbone indicate that the cyclic structure exists as a block segment in the polymer and the carboxylate group is incorporated at random in a polydiene structure. The synthetic condition needed to obtain a desired amount of the incorporated substrate and the degree of the cyclization of polydienes and polypentenamer were investigated.

INTRODUCTION

Considerable effort has been devoted to the preparation of new photoresists.[1,2] Among various kinds of photoresists produced, poly(vinyl cinnamate)[3] and cyclized polydiene rubbers[4] used together with photocrosslinking reagents, such as bisazides, are performing a very important role as typical photoresists and are widely in use.

The advantages of poly(vinyl cinnamate)[1] are attributed to long storage stability, high resolving power, and a photosensitivity which does not change even in the presence of oxygen and antioxidants. Furthermore, its photosensitivity can be enhanced by photosensitizers. Its disadvantages are that its thin film tends to have pinholes and that its resistance to etchants, such as hydrogen fluoride, is not satisfactory. Cyclized polydiene rubbers used together with bisazides have advantages in that they have better solubility in organic solvents, which is favorable to developing characteristics, and they also have better adhesiveness to metal plates and silicone wafers.[2] Also fewer pinholes are formed in the thin film, a high resistance to etchants is achieved, and a stable quality of resist is obtained. On the other hand, these photoresists are not stable enough for long storage, and photosensitivity decreases considerably in the presence of oxygen and antioxidants.[1]

If cyclized polydiene rubbers having pendent photosensitive groups, such as

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the cinnamoyl group, can be produced, a new type of photoresist with both the advantages of poly(vinyl cinnamate) and cyclized polydiene rubbers may be prepared.

It is known that carboxylic acids add to olefins to yield the corresponding esters in the presence of acid catalysts[5]:

$$-CH=CH- + RCOOH \xrightarrow[\text{catalyst}]{\text{acid}} -CH_2-\underset{\underset{OCOR}{|}}{CH}-$$
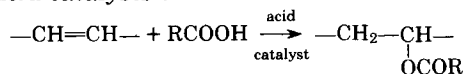
It has been reported that saturated carboxylic acids including acetic acid added to polydienes yield polydienes having pendent carboxylate groups.[6] On the other hand, when a solution of polydienes is treated in the presence of acid catalysts cyclized polydiene rubbers are produced.[7]

Therefore, it is expected that cyclized polydiene rubbers having photosensitive groups including α,β-unsaturated carboxylate groups can be obtained when polydienes are treated with acid catalysts in the presence of α,β-unsaturated carboxylic acids, such as acrylic acid or cinnamic acid.

We have found that α,β-unsaturated carboxylic acids, e.g., acrylic acid and cinnamic acid, add easily to polydienes such as cis-1,4-polybutadiene, 1,2-polybutadiene, and polypentenamer.[8] This article describes the synthetic condition necessary to obtain a desired amount of the incorporated substrate, the desired degree of cyclization of polydienes and polypentenamer, and the properties of the products.

EXPERIMENTAL

Material

cis-1,4-Polybutadiene (cis-1,4-BR) and 1,2-polybutadiene (1,2-BR) were supplied by the Japan Synthetic Rubber Company. cis-1,4-Polybutadiene consists of 97% cis double bonds, and 1,2-polybutadiene consists of 90% 1,2- and 10% cis 1,4-double bonds. The average molecular weight of cis-1,4-polybutadiene was $M_w = 420,000$, and that of 1,2-polybutadiene was $M_n = 150,000$. Polypentenamer (PP) was kindly provided by Goodyear Tire and Rubber Company. It consists of 82% trans and 17% cis double bonds with less than 1% vinyl side groups. The average molecular weight was $M_n = 94,000$ and $M_w = 172,000$. These polydienes and polypentenamer were purified by reprecipitation from toluene into methanol.

Reagents were used as purchased. Solvents were purified according to conventional methods.

Addition Reaction of α,β-Unsaturated Carboxylic Acids to Polydienes and Polypentenamer

The addition reaction of α,β-unsaturated carboxylic acids, e.g., acrylic acid and cinnamic acid, to polydienes and polypentenamer was carried out under various conditions using p-toluenesulfonic acid or sulfuric acid as acid catalysts. A typical example of the procedure is as follows: To a 0.5-g portion of polydiene in 25 cm^3 chlorobenzene containing 0.12 g p-methoxyphenol as radical scavenger, a 10-g portion of cinnamic acid or acrylic acid was added at a given temperature with stirring, and then a 1.2-g portion of p-toluenesulfonic acid was added. After

the reaction was terminated by a small amount of triethylamine, the resulting reaction mixture was poured into excess methanol and the precipitate was obtained as a product. The product was purified by reprecipitation from chloroform into methanol and dried at room temperature *in vacuo.* The products were stored under nitrogen as xylene solution containing antioxidants in a refrigerator in darkness.

Characterization of Products

The samples 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 an NaCl plate and by using a Hitachi 215 grating infrared spectrophotometer. The amount of α,β-unsaturated carboxylate groups in the polymers and residual double bonds in the polydienes and polypentenamer were determined on the basis of the absorption intensity at 1720 (CH_2=CH$\underline{C}$OO—) or 1700 cm^{-1} (PhCH=CH$\underline{C}$OO—), 1450 (—$\underline{CH_2}$—) or 1380 cm^{-1}, ($\underline{CH_3}$—), and 970 (*trans*-CH=$\underline{CH}$—) or 910 cm^{-1} ($\underline{CH_2}$=CH—), or 730 cm^{-1} *cis*-$\underline{CH}$=CH—) by using standard calibration procedures combined with NMR data. NMR measurements of the samples were carried out on deuterated chloroform or carbon tetrachloride solutions containing hexamethyldisiloxane as an internal standard by using a Hitachi model R-22 (90 MHz) spectrometer. As shown in Figures 1, 2, and 3, the NMR spectra of the products were assigned by a method similar to that in the case of cyclized polybutadiene which has been reported by Tanaka and Gonzalez.[9] The relationship among the degree of the cyclization, the incorporated cinnamic acid, and the signal intensity is summarized in Table I. The contents of these carboxylates and residual double bonds, and the degree of the cyclization and cyclicity in the polymers were estimated by using these equations.

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 10°C/min in all cases, and indium was used as a standard. The starting point of the transition temperature was taken to be the transition point of the polymer.

RESULTS AND DISCUSSION

Characterization

The addition reaction of α,β-unsaturated carboxylic acids, such as acrylic acid and cinnamic acid, with polydienes and polypentenamer was carried out under various conditions. Acrylic acid and cinnamic acid added easily to polydienes and polypentenamer in the presence of acid catalysts. The infrared and NMR spectra for the cinnamoylated *cis*-1,4-BR, 1,2-BR, and PP obtained from the reaction, carried out at 97°C, are shown in Figures 1, 2, 3, and 4, where the absorption owing to the cinnamoyl group is discernible in these spectra. The cyclization of polydienes and polypentenamer was recognized to take place competitively since the amount of the residual double bond on the polydiene main
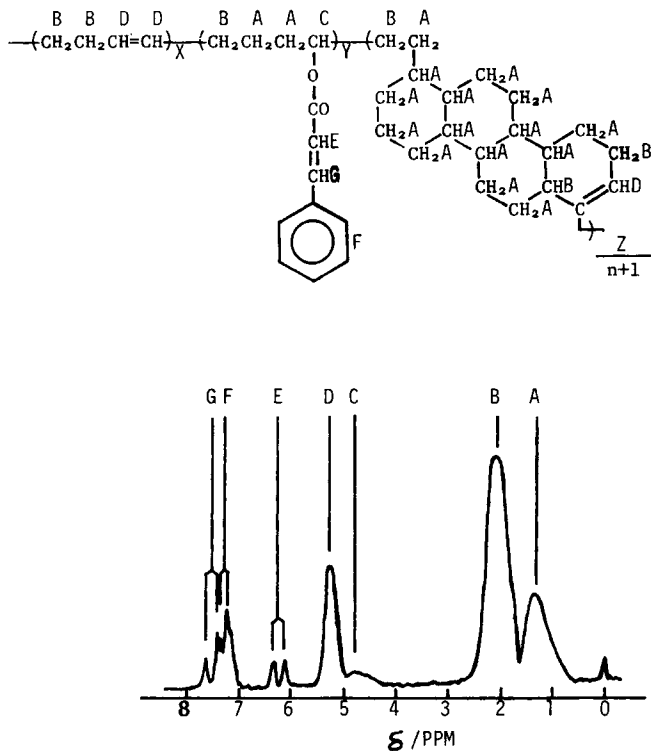
Fig. 1. Relationship between structure of cyclized cis-1,4-polybutadiene having cinnamoyl group and NMR spectrum in deuterated chloroform at 30°C (90 MHz).

chain was fairly small compared with that estimated from the amount of the cinnamoyl group added to the polymer.

It is known that the cyclization of polydienes such as polyisoprene and polybutadiene by acid catalysts takes place to form poly-six-member cyclic structures and that the cyclization is terminated by the elimination of a proton. In the case of polybutadiene a trisubstituted double bond is formed on the ring.[7,9,10]

When solutions of cis-1,4-BR, 1,2-BR, and PP were treated in the presence of p-toluenesulfonic acid or perchloric acid as acid catalysts, the solution viscosity and the content of the double bond of the product decreased with reaction time, and the absorption at 820 cm^{-1} owing to trisubstituted double bonds[11] was recognized in the infrared spectra of these products, which indicated that the cyclization of these polydienes and polypentenamer took place in the same fashion as in the case of polybutadiene.[9,10] Also, it was confirmed that cinnamic acid did not add to these trisubstituted double bonds on the rings.

Therefore, it is concluded that cinnamic acid adds to only the original double bond of the polydienes and polypentenamer and the structure consists of the three components as indicated in Figures 1, 2, and 3. Results of the addition reaction of α,β-unsaturated carboxylic acids to polydienes and polypentenamer are summarized in Table II. As shown in Table II, the cyclization of polydienes and polypentenamer took place in the following order:
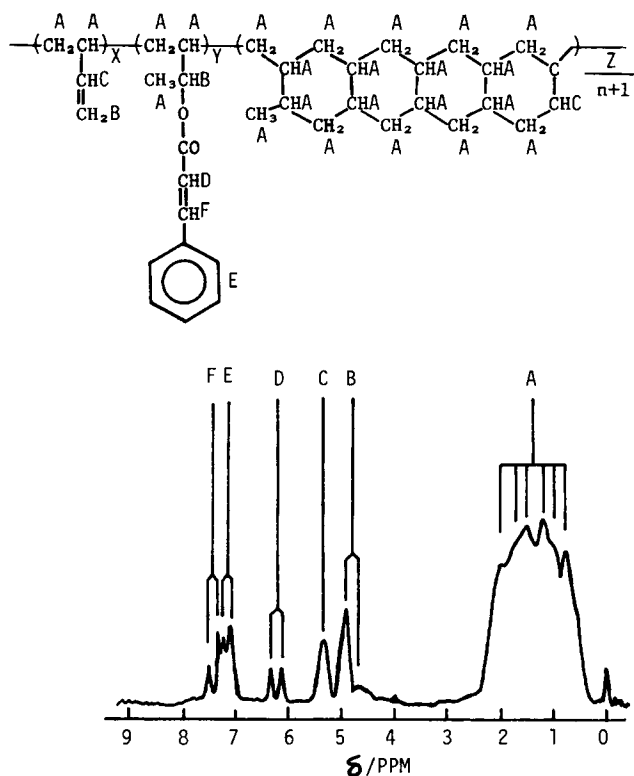
1,2-BR $\gg$ cis-1,4-BR > PP

Fig. 2. Relationship between structure of cyclized 1,2-polybutadiene having cinnamoyl group and NMR spectrum in deuterated chloroform at 30°C (90 MHz).

The cyclicity, n, which is the number of chain rings, was nearly 2 for cis-1,4-BR and PP and nearly 3 for 1,2-BR in the presence of cinnamic acid, and it was almost the same as in the absence of cinnamic acid.

　　The products had two or three thermal transitions on DSC analysis, as shown in Table II. Figures 5, 6, and 7 show the relationships between the T_g and the amount of the residual double bonds or the degree of the cyclization or the amount of the incorporated cinnamoyl group in the polymer. As shown in these figures, the lower thermal transition (T_{g_1}) and the higher one (T_{g_2}) were correlated with the amount of residual double bond and the degree of the cyclization, while a clear relationship between T_{g_1} or T_{g_2} and the amount of the incorporated cinnamoyl group was not observed. It is presumed that the lower thermal transition (T_{g_1}) is ascribed to the glass transition owing to the original polydiene segment, and the higher one (T_{g_2}), to the glass transition owing to the cyclic segment formed. These thermal transitions on a polymer backbone indicate that the cyclic structure exists as a block segment in the polymer and the carboxylate group is incorporated at random in a polydiene structure, because T_{g_1} changed drastically by crosslinking cinnamoyl groups with UV irradiation and T_{g_2} did not change to the same extent, as shown in Table III. Consequently, the
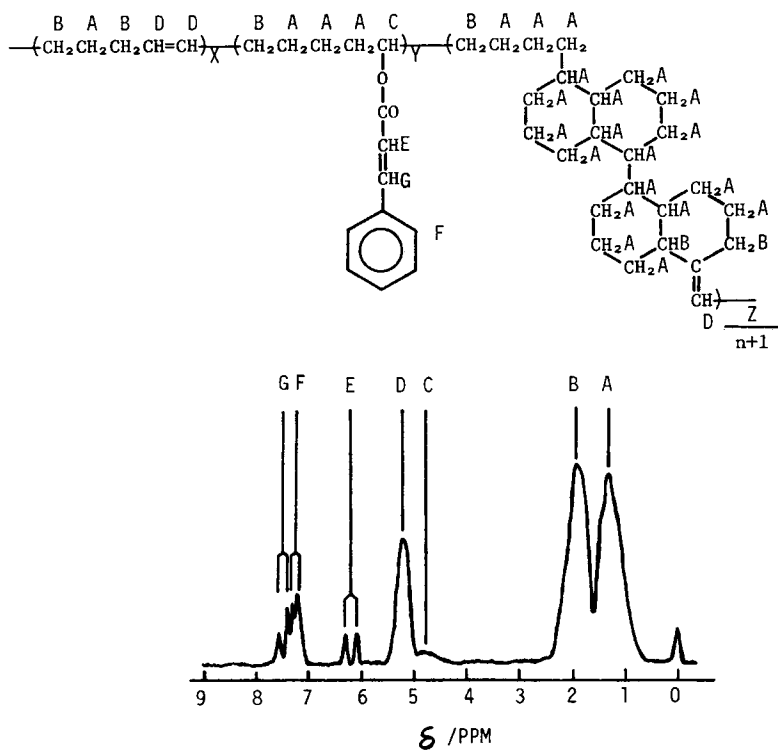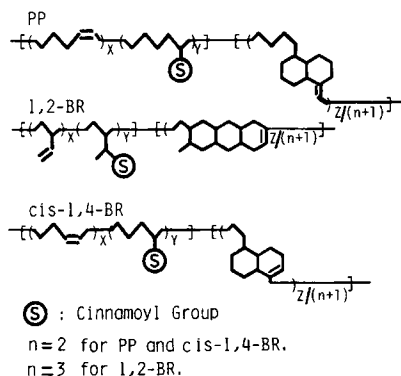
Fig. 3. Relationship between structure of cyclized polypentenamer having cinnamoyl group and NMR spectrum in deuterated chloroform at 30°C (90 MHz).

structures of the products are characterized as shown in Scheme 1.

Scheme 1.   Structure of cyclized polydienes and polypentenamer having cinnamoyl group.

Synthetic Condition

The reaction of polypentenamer with acrylic acid at 70°C resulted in a cross-linked product, while the reaction at 30°C in the presence of perchloric acid as catalyst yielded a soluble product containing 20 mole % of incorporated acrylate

TABLE I
Relationship between Degree of Cyclization and Incorporated Ester and NMR Signal Intensity

NMR signal intensity		Polymer		
		cis-1,4-BR	1,2-BR	PP
A	a	$4Y + \dfrac{6n}{n+1}Z$	$3X + 6Y + \dfrac{6n+5}{n+1}Z$	$2X + 6Y + \dfrac{8n+2}{n+1}Z$
B	b	$4X + 2Y + \dfrac{5}{n+1}Z$	$2X + Y$	$4X + 2Y + \dfrac{5}{n+1}Z$
C	c	Y	$X + \dfrac{1}{n+1}Z$	Y
D	d	$2X + \dfrac{1}{n+1}Z$	Y	$2X + \dfrac{1}{n+1}Z$
E	e	Y	$5Y$	Y
F	f	$5Y$	Y	$5Y$
G	g	Y		Y
Cyclicity n		$\dfrac{a - 4e}{2(b - 2d - 2e)}$	$\dfrac{a + b - 5c - 7d}{-3(b - 2c - d)}$	$\dfrac{3a - b - d - 16e}{8(b - 2d - 2e)}$
$X + Y + Z = 1$				

groups, as shown in Table II. The crosslinking seems to be caused by the reaction among acrylate groups at high temperature. At 3°C, only a small amount of the addition reaction of acrylic acid to polypentenamer took place, but the cyclization was almost the same as that at 30°C, as shown in Figure 8.

The reaction with cinnamic acid proceeded in such a way that the amount of the incorporated substrate increased up to a maximum of around 15 mole % and the amount of the residual double bond in the polydienes and polypentenamer decreased. Solution viscosities of the products in chloroform decreased, and the products became more soluble in chloroform. The decreases in both solution viscosities and the amount of the residual double bond are due to the cyclization of polydienes and polypentenamer. The cyclization of polydienes and poly-pentenamer took place in competition with the addition reaction of carboxylic acids in the following order:

$$1,2\text{-BR} \gg cis\text{-1,4-BR} > \text{PP}$$

Catalysts affected the reaction rate as indicated in Table IV. In the case of super acids, such as perchloric acid and trifluoromethanesulfonic acid, the reaction was completed very quickly. However, in the case of these super acids, particularly in the case of sulfuric acid which is a dibasic acid, the products tended to be insoluble owing to crosslinking. Therefore, the amount of the catalyst should be as small as possible.

Table V shows the solvent effect on the reaction. As the dielectric constant of the solvent increased, the reaction was accelerated. However, solvents with too much polarity, such as nitrobenzene and 1,2-dichloroethane, caused cross-linking of the products, because in such polar solvents polydienes and polypen-tenamer were isolated from the solution as soon as the catalysts were added. Therefore, chlorobenzene seems to be a suitable solvent for the reaction.

Cinnamic acid is slightly soluble in chlorobenzene, toluene, and xylene below
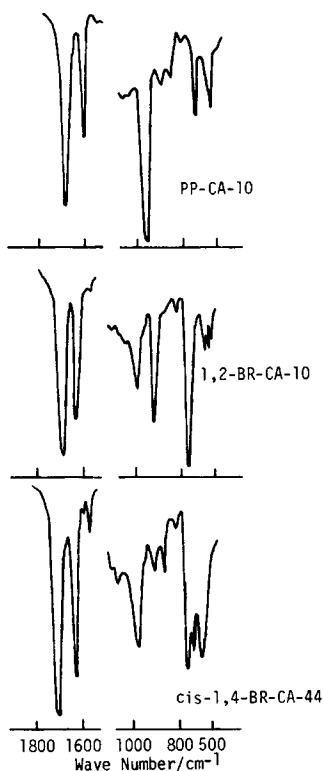
Fig. 4. Infrared spectra of cyclized polydienes and polypentenamer having cinnamoyl group (film).

60°C. Consequently, the influence of the reaction temperature was investigated over 60°C. Figure 9 shows the time conversion on the amounts of the residual double bond and the incorporated cinnamoyl group. A point where the maximum yield of the incorporated cinnamoyl group was attained existed in the course of the reaction. As shown in Figures 9 and 10, the higher reaction temperature increased both apparent rates of the cyclization reaction and the addition reaction of carboxylic acids to polydienes and polypentenamer, but decreased the maximum yield of the incorporated cinnamoyl groups. The cyclization reaction of
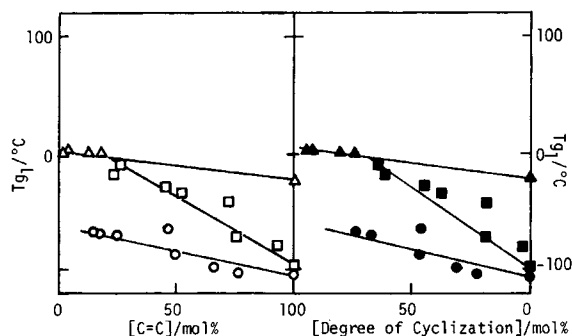

Fig. 5. Relationships between T_{g1} and residual double bond and degree of cyclization in polymers: (O, ●) cis-1,4-BR; (△, ▲) 1,2-BR; (□, ■) PP.

TABLE II
Cationic Modification of Polydienes and Polypentenamer with α,β-Unsaturated Carboxylic Acids[a]

Polymer	Substrate S	Temp., °C	Time, hr	S[b] mole %	C=C[c] mole %	Cyclic[d] mole %	n[e]	η_{sp}/C[f] dl/g	DSC, °C[g] T_1	T_2	T_3	Remarks
PP	CH₂=CHCOOH	60	5	0.5	—	—	—	Ins[h]				
		70	24	3.0	—	—		Ins[h]				
		70	48	20	—	—		Ins[h]				
		110	22	20	—	—		Ins[h]				
		30[i]	44	20	15	65	1.79	Sol[h]				
	Ph—CH=CHCOOH	80	40	4.3	92.3	3.4		3.43	−79	(−45)		PP-CA -10
		97	10	6.5	74.9	18.6		3.95	−72			-20
		97	20	9.0	72.1	18.9		1.89	−43	22		-40
		97	40	10.8	51.7	37.5		1.73	−35	80		
		97	66	10.1	45.3	44.6		1.39	−28	70	110	
		110	40	9.7	26.1	64.2		0.54	−10	80	112	PP-CA-110-40
		104[i]	0.5	14.7	23.5	61.8		1.00	−19	80	115	PA-CA-2-20-79
		80[i]	5	12.3	18.5	69.2						
cis-1,4-BR	Ph—CH=CHCOOH	98	6	1.7	76.0	22.3	2.25	3.18	−103	−72, −20[j]	(112)	cis-1,4-BR-CA -6
		98	12	3.0	66.1	30.9		3.02	−98	−65, −20[j]	(125)	-12
		98	20	4.1	49.7	46.2		2.21	−87	−16	(120)	-20
		98	44	7.2	46.7	46.1		0.95	−66	−33	(122)	-44
		105[i]	0.75	8.2	24.7	67.1		1.90	−72	−35	(123)	cis-1,4-BR-CA -No. 1
		105[i]	1.5	8.5	17.0	74.5		0.96	−71	−24		-No. 2
		105[i]	2.3	10.2	15.3	74.5		0.73	−68	−3		-No. 3
1,2-BR	Ph—CH=COOH	97	10	7.2	17.8	75.0	2.85	0.46	0	75		1,2-BR-CA -10
		97	20	6.5	12.6	80.9		0.36	1	80		-20
		97	40	3.9	3.7	92.5		0.27	2	90	113	-40
		104[i]	0.5	3.9	1.4	94.8		0.20	0	86		1,2-BR-CA-2-20-79

[a] Polydienes and polypentenamer, 0.5 g; S, 10 g; chlorobenzene, 25 cm³; p-toluenesulfonic acid, 1.2 g; p-methoxyphenol, 0.12 g.
[b] Incorporated substrate.
[c] Residual double bond of polydienes and polypentenamer.
[d] Degree of cyclization.
[e] Cyclicity.
[f] In chloroform at 30°C.
[g] Thermal transition of the products measured by DSC.
[h] Ins, insoluble in chloroform; sol, soluble in chloroform.
[i] Catalyst, perchloric acid (70 wt %) 0.05 cm³.
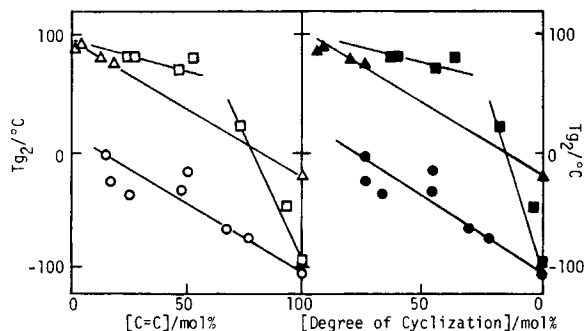[j] Melting temperature.

Fig. 6. Relationship among T_{g2} and residual double bond and degree of cyclization in polymers: (O, ●) cis-1,4-BR; (△, ▲) 1,2-BR; (□, ■) PP.

polydienes and polypentenamer, which is an intramolecular and irreversible reaction, was much faster than the addition reaction of carboxylic acids. On the other hand, the addition reaction of carboxylic acids to polydienes and polypentenamer is a reversible reaction. High reaction temperatures are not suitable for the addition reaction.

At low reaction temperature, an induction period of the reaction was observed, which might be caused by p-methoxyphenol added as a radical scavenger to prevent the products from crosslinking between cinnamoyl groups in the reaction. When p-methoxyphenol was added to the reaction system, the reaction was retarded, as shown in Table VI.
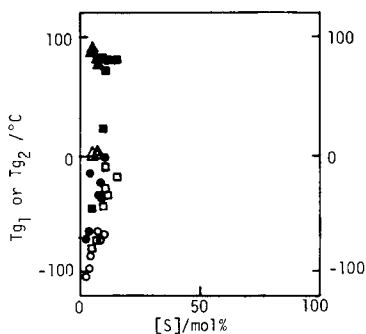

Fig. 7. Relationships between T_g and cinnamoyl group concentration in polymers. T_{g1}, (O) cis-1,4-BR; (△) 1,2-BR; (□) PP. T_{g2}, (●) cis-1,4-BR; (▲) 1,2-BR; (■) PP.

TABLE III
Changes of Thermal Transition Temperature of Cyclized Polydienes and Polypentenamer
Having Cinnamoyl Group by UV Irradiation

cis-1,4-BR-CA-No. 1			1,2-BR-CA-2-20-79			PP-CA-2-20-79		
Conversion,[a]			Conversion,[a]			Conversion,[a]		
%	T_{g1},°C	T_{g2},°C	%	T_{g1}, °C	T_{g2}, °C	%	T_{g1}, °C	T_{g2}, °C
0	−72	−35	0	0	86	0	−19	80
34.2	—[b]	−30	22.3	2	78	14.4	−9	70
49.3	—[b]	−26	35.7	7	51	29.8	−4	70
70.6	—[b]	−20	90	—[b]	58	44	−3	70

[a] Conversion of cinnamoyl group by UV irradiation.
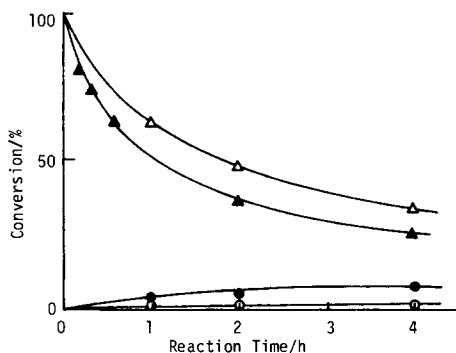[b] T_g disappeared.

Fig. 8. Addition reaction of acrylic acid to polypentenamer. PP, 0.5 g; acrylic acid, 10 g; chlorobenzene, 25 cm³; catalyst, HClO₄ 100 mole % toward polymer; p-methoxyphenol, 0.12 g. Residual double bond, (△) at 0°C; (▲) at 30°C. Incorporated acryloyl group, (○) at 0°C; (●) at 30°C.

The influence of the amount of cinnamic acid on the reaction is shown in Figure 11. When the amount of cinnamic acid in the reaction mixture was increased, the amount of catalysts had to be decreased, because increasing the amount of catalysts and cinnamic acid increases the ion strength in the solution to precipitate polydienes and polypentenamer. The amount of the incorporated cinnamoyl group increased slightly with increasing the amount of cinnamic acid added. However, the cyclicities n were nearly 2 for cis-1,4-BR and PP and nearly 3 for 1,2-BR in either the presence or absence of cinnamic acid.

The termination of the reaction was carried out by the addition of bases such as triethylamine and pyridine to prevent the products from cationic crosslinking during the precipitation. Triethylamine did not influence the reaction; the amount of the incorporated cinnamoyl group was decreased slightly by the addition of triethylamine.

As mentioned above, optimum reaction temperature and time should be selected in order to obtain a proper amount of the incorporated substrate and the degree of the cyclization of polydienes and polypentenamer. For example, cyclized polydienes and polypentenamer, which have various degrees of cyclization and the highest amount of the incorporated cinnamoyl group, can be synthesized under the following reaction condition: (1) The mole ratio of cinnamic acid

TABLE IV
Effect of Catalysts on the Addition Reaction of Cinnamic Acid to Polypentenamer[a]

Catalyst	S,[b] mole %	C=C,[c] mole %	Cyclic,[d] mole %	η_{sp}/C,[e] dl/g
p-TsOH	5.7	94.3	0	3.30
TiCl₄	4.2	52.7	43.1	crosslinked
BF₃OEt₂	2.8	8.0	89.2	0.28
CF₃SO₃H	1.9	5.1	93.0	0.16
HClO₄	2.0	2.4	95.6	0.30
H₂SO₄	—	—	—	crosslinked

[a] Polypentenamer, 0.5 g; cinnamic acid, 10 g; chlorobenzene, 25 cm³; catalyst, 100 mol % toward polymer; reaction temp., 98°C; time, 6 hr; p-Methoxyphenol, 0.12 g.

[b] Incorporated cinnamoyl group.

[c] Residual double bond of polypentenamer.

[d] Degree of cyclization.

[e] In chloroform at 30°C.

TABLE V
Solvent Effect on the Addition Reaction of Cinnamic Acid to Polypentenamer[a]

Solvent	Dielectric constant	Time,[b] hr	S,[c] mole %	C=C,[d] mole %	Cyclic,[e] mole %	η_{sp}/C,[f] dl/g
Toluene	2.38[h]	6	4.9	95.1	0	4.99
		12	5.4	84.7	9.9	4.50
Chlorobenzene	5.71[i]	6	5.7	94.3	0	3.30
		12	6.5	74.9	18.6	3.95
1,2-Dichloroethane	10.65[j]	6	4.4	90.7	4.9	Crosslinked
		12	5.8	83.6	10.6	Crosslinked
1,2-Dichloroethane/nitrobenzene[g]	34.82[k]	6	6.2	83.7	10.1	3.01
		12	8.5	56.2	35.3	Crosslinked

[a] Polypentenamer, 0.5 g; cinnamic acid, 10 g, solvent, 25 cm³; p-TsOH, 1.2 g; p-methoxyphenyl, 0.12 g; reaction temp., 98°C.
[b] Reaction time.
[c] Incorporated cinnamoyl group.
[d] Residual double bond.
[e] Degree of cyclization.
[f] In chloroform at 30°C.
[g] Mixture, 1 v/v.
[h] At 25°C.
[i] At 20°C.
[j] At 20°C.
[k] At 25°C for nitrobenzene.

versus polydienes or polypentenamer unit is over 10.   (2) An antioxidant, such as t-butylphenol or p-methoxyphenol, is added at a mole ratio of 0.2 per polymer unit to prevent oxidation and crosslinking of the polymers, and the reaction
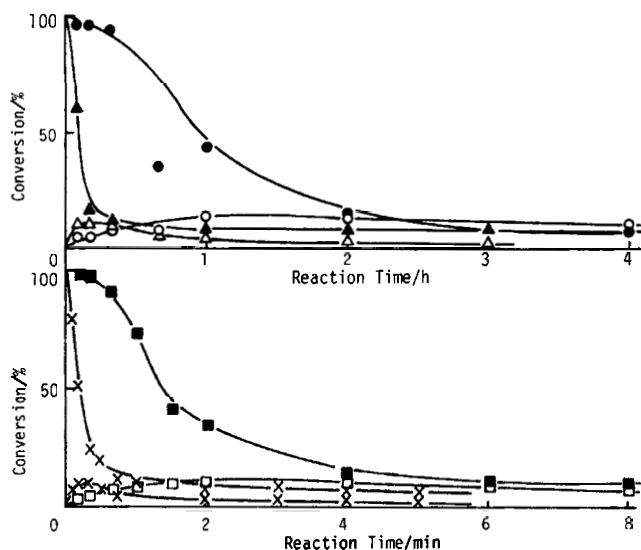

Fig. 9. Addition reaction of cinnamic acid to polypentenamer.   PP, 0.5 g; cinnamic acid, 10 g; chlorobenzene, 25 cm³; catalyst, HClO₄ 100 mole % toward polymer; p-methoxyphenol, 0.12 g. Residual double bond, (●) at 60°C; (▲) at 83°C; (■) at 100°C; (×) at 130°C.   Incorporated, cinnamoyl group, (○) at 60°C; (△) at 83°C; (□) at 100°C; (×) at 130°C.
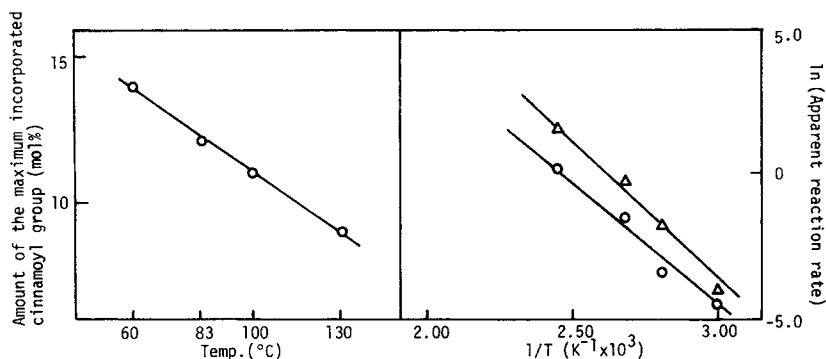
Fig. 10. Influence of reaction temperature on the amount of incorporated cinnamoyl group and the apparent reaction rates of addition reaction of cinnamic acid and cyclization reaction of polypentenamer. (O) Addition reaction of cinnamic acid; (△) cyclization reaction.

should be carried out under nitrogen atmosphere. (3) The volume of chlorobenzene as a solvent is 50 cm³/1 g polymer. (4) As little perchloric acid (70 wt %) as possible should be added as a catalyst, and a relatively low reaction temperature around 80°C should be selected. (5) When the amount of the incorporated cinnamoyl group in the polymer has reached a maximum of 15–20 mole
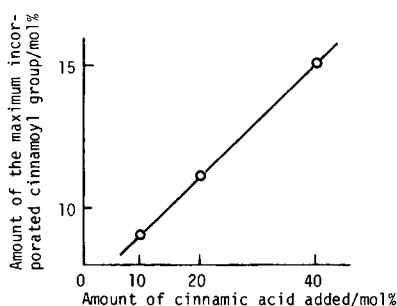

Fig. 11. Influence of the amount of cinnamic acid added on the addition reaction of cinnamic acid to polypentenamer. PP, 0.5 g; chlorobenzene, 25 cm³; catalyst, $HClO_4$ 100 mole % toward polymer; p-methoxyphenol, 0.12 g; reaction temp., 130°C.

TABLE VI

Influence of p-Methoxyphenol on the Addition Reaction of Cinnamic Acid to cis-1,4-Polybutadiene[a]

Amount of p-methoxyphenol, g	Time,[b] sec	S,[c] mole %	C=C,[d] mole %	Cyclic,[e] mole %
0	30	6.1	22.0	71.8
	60	6.1	8.0	85.9
0.175	30	4.9	47.0	48.1
	60	6.3	13.0	80.7

[a] cis-1,4-Polybutadiene, 0.5 g; cinnamic acid, 40 g; chlorobenzene, 25 cm³; perchloric acid, 0.5 cm³; reaction temp., 130°C.

[b] Reaction time.

[c] Incorporated cinnamoyl group.

[d] Residual double bond.

[e] Degree of cyclization.

% per polymer unit, the reaction temperature is lowered to 0°C or room temperature to maintain the highest amount of incorporated cinnamoyl group. The reaction is continued at the temperature to obtain various degrees of cyclization since at room temperature or below the amount of the incorporated cinnamoyl group did not decrease and only the degree of the cyclization increased with reaction time. (6) Finally, the reaction is terminated by pyridine or triethylamine and the products are recovered by pouring the resulting reaction mixture into excess methanol.

The investigation in terms of the relationship between the polymer structure and its photosensitivity will be presented separately in another paper.

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