

Synthesis and Properties of Photosensitive Rubbers.

III. Synthesis of Chloroacetylated Polybutadiene and its Photosensitivity

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Synopsis

Polymers having chloroacetate groups were prepared by addition reaction of various chloroacetic acids, such as mono-, di-, and trichloroacetic acids, to *cis*-1,4-polybutadiene under nitrogen atmosphere for obtaining photosensitive rubbers. The structure of products obtained was identified as a cyclized polybutadiene having pendent chloroacetate groups. The amount of the incorporated substituent increased up to the maximum of around 20 mol %, and the amount of the residual unsaturated groups in the polymer backbone decreased due to the cyclization of the double bond. Chloroacetylated polybutadiene had higher photocrosslinkability by UV irradiation than chloroacetylated chitosan or PVA owing to the high reactivity of the chloroacetate groups and the double bonds in the polymer. The photosensitivity depends both on the amount of the incorporated chloroacetate groups and the residual double bonds in the polymer and also depends on the glass transition temperature (T_g) of the polymer, and the dependence of the crosslinking reaction on T_g was interpreted to be due to diffusion controlled reaction between excited dichloroacetate groups and olefinic groups in the polymer.

INTRODUCTION

We had found that¹ when a chitosan which can be obtained by the hydrolysis of chitin having *N*-acetylglucosamide units was chloroacetylated, the chitosan could easily be photocrosslinked by UV irradiation. The mechanism of the photocrosslinking reaction was investigated by using isopropyl chloroacetates as model compounds. Moreover, the photosensitive chloroacetate groups were incorporated into poly(vinyl alcohol) for obtaining a new type of photopolymer.²

Poly(vinyl cinnamate)-type photoresists and cyclized polydienes rubbers used together with photocrosslinking reagents, such as bisazides, are already commercialized and are widely used as photoresists.³⁻⁵ It is known that⁶ carboxylic acids add to olefinic compounds to yield the corresponding esters in the presence of acid catalysts, such as *p*-toluenesulfonic acid or perchloric acid. It had been reported that saturated carboxylic acids including acetic acid add to polydienes to yield cyclized polydiene rubbers having pendent carboxylate groups.^{7,8} Therefore, we made an attempt in order to obtain cyclized polydiene rubbers having cinnamate groups by using the reaction of polydienes with cinnamic acid in the presence of acid catalysts, which was reported in a previous paper.⁹

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It is known that^{10,11} the glass transition temperature of photosensitive polymers greatly influences the photosensitivity, because the photocrosslinking reaction takes place in a solid state, where the mobility of the polymer influences the photochemical reaction. We had revealed the dependence of the photosensitivity on the glass-transition temperature of the polymer theoretically and experimentally in the case of the cyclized polydiene rubbers and linear polydiene rubbers having cinnamate groups.¹²⁻¹⁵

This paper describes the synthetic conditions of a new type of photoresist by means of the reaction of polybutadiene and polypentenamer with various chloroacetic acids, and also the influence of the polymer structure on the photosensitivity of chloroacetylated polybutadiene in terms of the glass transition temperature of the polymer.

EXPERIMENTAL

Materials. *cis*-1,4-polybutadiene (*cis*-1,4-BR, $\bar{M}_w = 420,000$) containing 97% *cis*-double bonds was supplied by the Japan Synthetic Rubber Co. Polypentenamer (PP, $\bar{M}_w = 172,000$) containing 82% *trans*- and 17% *cis*-double bonds with less than 1% vinyl side groups was kindly provided by Goodyear Tire and Rubber Co. The polymers were purified by reprecipitation from toluene into methanol. Reagents were used as purchased. Solvents were purified according to conventional methods.

Additional Reaction of Mono-, Di-, Trichloroacetic Acids to *Cis*-1,4-Polybutadiene and Polypentenamer. The addition reaction of mono-, di-, and trichloroacetic acids to *cis*-1,4-polybutadiene and polypentenamer was carried out under various conditions in the presence of *p*-toluenesulfonic acid (*p*-TSH) or perchloric acid (HClO_4) as acid catalysts. A typical example of the procedure is as follows: To a 0.5 g portion of polydiene in 25 cm³ of chlorobenzene containing 0.12 g of *p*-methoxyphenol as a radical scavenger, a 10-g portion of trichloroacetic acid was added at a given temperature with stirring, and then a given amount of *p*-toluenesulfonic acid was added at 80°C. After the reaction was terminated by the addition of 2 mol of triethylamine toward the acid catalyst, the resulting reaction mixture was poured into excess methanol and the precipitated polymer 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 carbon tetrachloride solutions in a refrigerator in darkness.

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 casts of the carbon tetrachloride solution on NaCl plates and using a Hitachi 215 grating infrared spectrophotometer. The amount of various chloroacetate groups in polymers was determined by elemental and NMR analyses.

NMR measurement of samples was carried out on deuterated chloroform or carbon tetrachloride solutions containing tetramethylsiloxane as an internal standard by using a Hitachi Model R-22, 90-MHz Spectrometer. As shown in Figures 1 and 2, 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.¹⁶ The contents of these chloroacetate groups and residual double bonds and the degree of the cyclization in the polymer were estimated by using these equations.

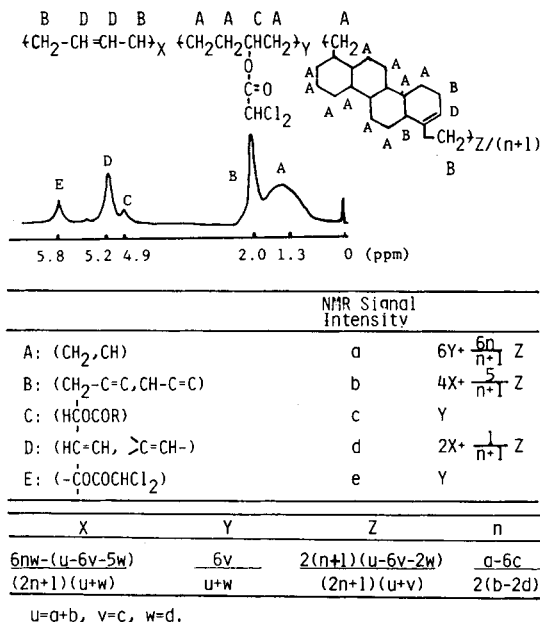


Fig. 1. Relationship between structure of dichloroacetylated *cis*-1,4-BR and NMR spectrum in carbon tetrachloride (90 MHz).

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

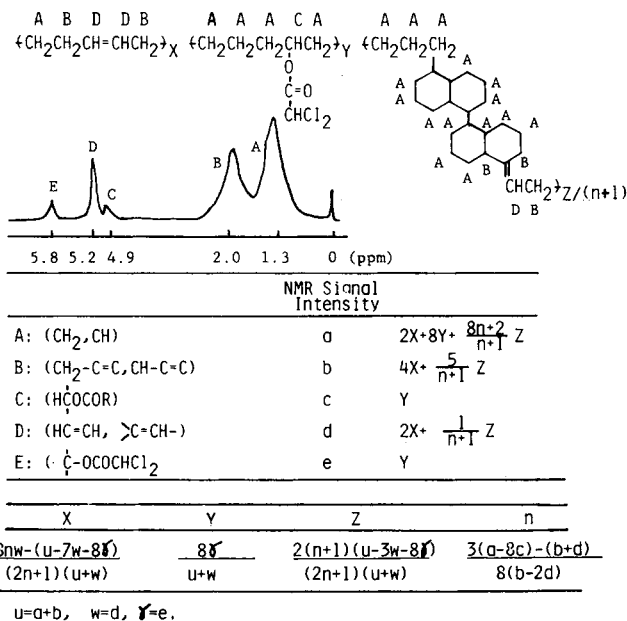


Fig. 2. Relationship between structure of dichloroacetylated PP and NMR spectrum in carbon tetrachloride (90 MHz).

indium was used as a standard. The starting point of the transition temperature was taken to be the transition temperature of the polymers.

Irradiation of Photosensitive Rubbers. A given amount of chloroacetylated *cis*-1,4-polybutadiene was dissolved in carbon tetrachloride. The polymer solution was cast on a flat quartz plate. By evaporation of the solvent under vacuum or heating, a transparent film was obtained. The films were exposed to UV ray from the side of quartz plate at 25°C for a given period at a distance of 45 cm from a 250-W ultra high pressure mercury lamp made by Ushio Denko Co. The irradiated films were immersed in the mixed solvent by xylene and carbon tetrachloride, and the insoluble portion was washed with the mixed solvent and then weighed after drying.

The photosensitivity of dichloroacetylated *cis*-1,4-polybutadiene was also estimated on BR-Cl₂-120 by using minimum UV irradiation time (t) which is necessary to a complete pattern of the thinnest crosslinked film to be formed on a quartz plate after immersion of the UV irradiated film in the mixed solvent of toluene/*n*-hexane (3/1) until the unirradiated film as a control was completely dissolved. The apparent photosensitivity (R_a) was calculated by dividing a molarity (P) of the polymer repeating unit per unit volume (1 cm³) by the minimum UV irradiation time (t), as follows:

$$P = d/U \quad (\text{mol} \cdot \text{cm}^{-3}) \quad (1)$$

$$R_a = P/t \quad (\text{mol} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}) \quad (2)$$

where d and U denote the polymer density regarded as unity and the mass of the polymer repeating unit, respectively.

RESULTS AND DISCUSSION

Characterization

The addition reaction of mono-, di-, and trichloroacetic acids with *cis*-1,4-polybutadiene (*cis*-1,4-BR) and polybutadiene (PP) was carried out under various conditions. Chloroacetic acids added easily to *cis*-1,4-BR and PP in the presence of acid catalysts. The infrared and NMR spectra of the chloroacetylated *cis*-1,4-BR synthesized at 80°C are shown in Figures 1, 2, and 3 where the absorption owing to the chloroacetate groups are discernible. The cyclization of *cis*-1,4-BR and PP was recognized to take place competitively since the amount of the residual double bonds in the polydiene main chain was fairly small compared with that estimated from the amount of the incorporated chloroacetate groups. It is known¹⁶ that the cyclization of polydienes, such as polyisoprene and polybutadiene, by acid catalysts takes place to form six-membered polycyclic 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. Results of the addition reaction of chloroacetic acids to polybutadiene and polybutadiene are summarized in Table I. As shown in Table I, the cyclization of polybutadiene and polybutadiene took place to a similar degree.

The cyclicity (n), which is the number of chain rings, was 1.9 for *cis*-1,4-BR and 1.5 for PP in the presence of dichloroacetic acid, and it was nearly 2 similarly to the case of *cis*-1,4-BR in the presence of *p*-toluenesulfonic acid without

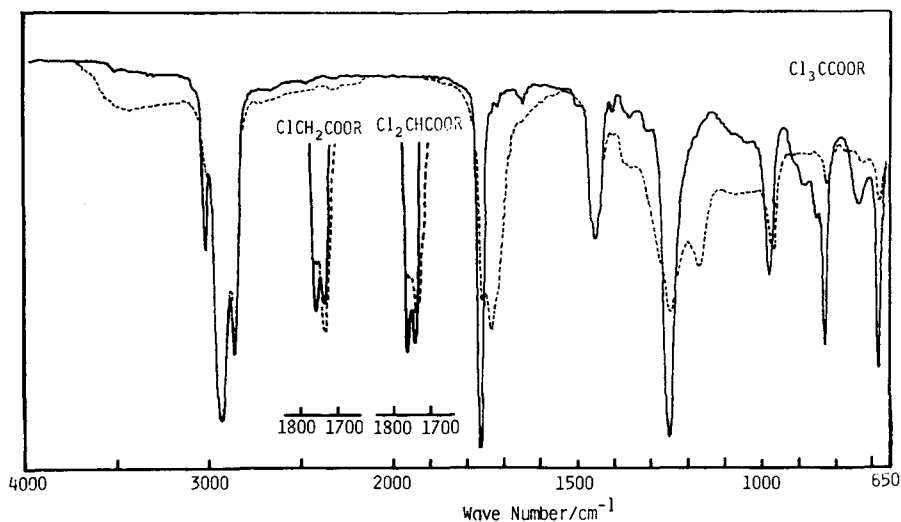


Fig. 3. IR spectra of chloroacetylated *cis*-1,4-BR (film): (—) before UV irradiation; (- - -) after UV irradiation.

chloroacetic acids.⁹ Consequently, the structures of the resulting polymers are characterized, as shown in Scheme 1.

Synthetic Conditions

The addition reaction of chloroacetic acids to *cis*-1,4-BR or PP was carried out in the presence of *p*-toluenesulfonic acid (*p*-TSH) or perchloric acid (HClO₄) as shown in Table I. In the case of *cis*-1,4-BR, HClO₄ has higher catalysis than *p*-TSH, as shown by lack of residual double bonds after reaction for 6 h, compared to 29 mol % with *p*-TSH. Table II shows the solvent effect on this reaction. As the dielectric constant of the solvent increased, the reaction was accelerated. However, solvent with too much polarity, such as 1,2-dichloroethane, caused by

TABLE I
Cationic Modification of PP and *Cis*-1,4-BR with Chloroacetic Acids^a

| Polymer | Substrate S | Catalyst | Time (h) | Content (mol %) | | | <i>n</i> ^e |
|--------------------|------------------------|----------------------------|--------------------------------|-----------------|------------------|---------------------|-----------------------|
| | | | | S ^b | C=C ^c | Cyclic ^d | |
| PP | Cl ₂ CHCOOH | <i>p</i> -TSH ^f | 3 | 15 | 22 | 66 | 1.5 |
| | | | 9 | 22 | 8 | 70 | |
| <i>Cis</i> -1,4-BR | | | 3 | 14 | 40 | 46 | 1.9 |
| | | | 9 | 19 | 2 | 79 | |
| <i>Cis</i> -1,4-BR | Cl ₃ CCOOH | <i>p</i> -TSH ^g | 6 | 15 | 29 | 56 | |
| | | | HClO ₄ ^g | 6 | 12 | 0 | |

^a PP and *cis*-1,4-BR: 0.5 g; S: 10 g; chlorobenzene: 25 cm³; *p*-methoxyphenol: 0.12 g; temp: 80°C.

^b Incorporated chloroacetate groups.

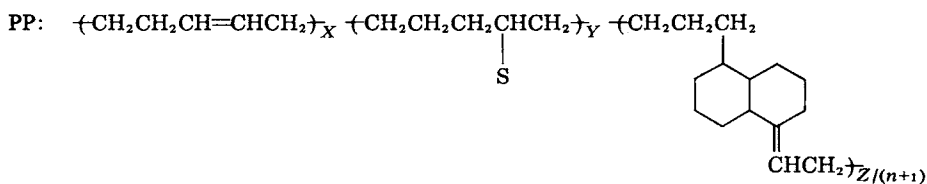
^c Residual double bonds of PP and *cis*-1,4-BR.

^d Degree of cyclization.

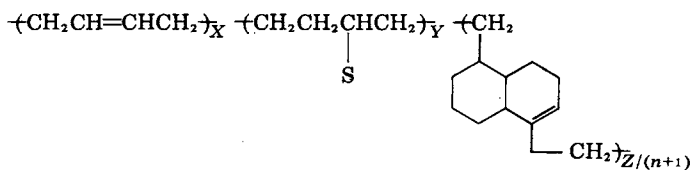
^e Cyclicity.

^f 10 mol %.

^g 1.0 mol %.



cis-1,4-BR:



S: Chloroacetate group

Scheme 1

cyclization reaction exclusively. The solution viscosity of the products decreased with long reaction time because of the cyclization reaction of polydienes.

The time conversion of the addition reaction of dichloroacetic acid to *cis*-1,4-BR or BP in the presence of *p*-TSH is shown in Figure 4. The rate of the addition reaction and the amount of the residual double bonds were almost similar degree for both *cis*-1,4-BR and PP, as shown in Figure 4. The addition reaction of various chloroacetic acids to *cis*-1,4-BR took place with the following order of the rate of the reaction, as indicated in Figure 5: trichloroacetic acid > dichloroacetic acid > monochloroacetic acid.

The addition reaction of monochloroacetic acid to *cis*-1,4-BR took place more slowly than the other chloroacetic acids, and the consumption of the double bond in the polymer reached at a steady state after 10 hr in the presence of 10 mol % of *p*-TSH.

Trichloroacetic acid could add to polybutadiene even in the absence of a cat-

TABLE II
Solvent Effect on the Addition Reaction of Dichloroacetic Acid to *Cis*-1,4-BR^a

| Solvent | Dielectric constant | Time (h) | Content (mol %) | | | η_{sp}/c^e (dL/g) |
|--------------------|---------------------|----------|-----------------|------------------|---------------------|------------------------|
| | | | S ^b | C=C ^c | Cyclic ^d | |
| Toluene | 2.38 ^f | 3 | 10.8 | 52.2 | 36.9 | 2.36 |
| | | 6 | 16.0 | 36.3 | 47.7 | 1.47 |
| Chlorobenzene | 5.71 ^g | 3 | 12.4 | 42.9 | 44.7 | 1.98 |
| | | 6 | 19.7 | 17.2 | 63.1 | 1.72 |
| 1,2-Dichloroethane | 10.65 ^g | 3 | 11.2 | 30.0 | 58.8 | 1.42 |
| | | 6 | 14.9 | 0 | 85.1 | 0.59 |

^a *Cis*-1,4-BR: 0.5 g; dichloroacetic acid: 10 g; solvent: 25 cm³; *p*-TSH: 10 mol %; *p*-methoxyphenol: 0.12 g; temp: 80°C.

^b Incorporated dichloroacetate groups.

^c Residual double bonds.

^d Degree of cyclization.

^e In carbon tetrachloride at 30°C.

^f At 25°C.

^g At 20°C.

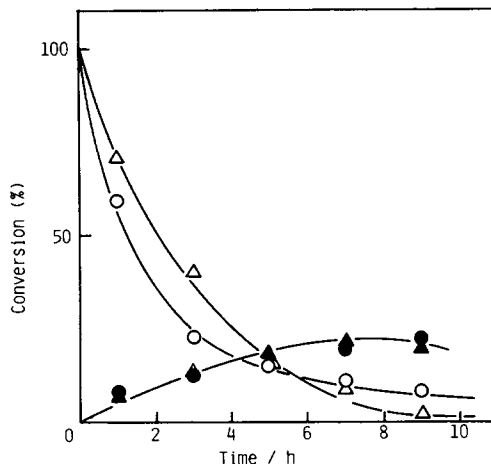


Fig. 4. Addition reaction of dichloroacetic acid to PP and *cis*-1,4-BR. Residual double bond: (○) PP; (△) *cis*-1,4-BR. Incorporated dichloroacetate group: (●) PP, (▲) *cis*-1,4-BR. Catalyst: *p*-TSH (10 mol %).

alyst due to its high acidity, as shown in Figure 6. However, higher amounts of the incorporated chloroacetate groups were obtained by using large amounts of *p*-TSH, though cyclization increased with increasing amounts of *p*-TSH. Consequently, the amount of the catalysts should be as small as possible for retention of the amount of the residual double bond in the polymer.

The influence of the reaction temperature was investigated, as shown in Figure 7. The reaction time bearing the maximum yield of the incorporated dichloroacetate groups was observed to become shorter with increasing reaction temperature from 80°C to 120°C. However, the maximum yield of the incorporated dichloroacetate groups did not change with reaction temperature. On the other hand, the cyclization reaction became faster with increasing reaction temperature.

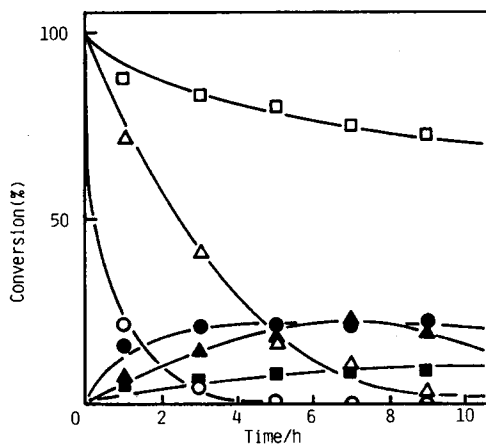


Fig. 5. Addition reaction of chloroacetic acids to *cis*-1,4-BR. Residual double bond: (□) mono-, (△) di-, and (○) trichloroacetic acid. Incorporated chloroacetate group: (■) mono-, (▲) di-, and (●) trichloroacetate. Catalyst: *p*-TSH (10 mol %).

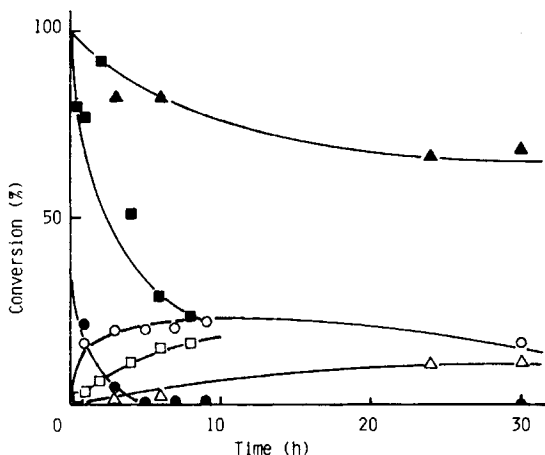


Fig. 6. Addition reaction of trichloroacetic acid to *cis*-1,4-BR. Residual double bond: (▲) noncatalyst; (■) *p*-TSH (1 mol %); (●) *p*-TSH (10 mol %). Incorporated trichloroacetate group: (△) noncatalyst; (□) *p*-TSH (1 mol %); (○) *p*-TSH (10 mol %).

Photosensitivity of Chloroacetylated *Cis*-1,4-BR

We had reported that the photocrosslinking reaction of chloroacetylated chitosan¹ and PVA² is initiated by excitation of the chloroacetate groups and followed by hydrogen abstraction from the polymers. Figure 1 indicates that the absorption due to chloro group at 730 cm^{-1} and 640 cm^{-1} in the infrared spectrum decreased and the absorption due to ester group of trichloroacetylated *cis*-1,4-BR at 1760 cm^{-1} shifted to 1720 cm^{-1} due to mono- and dichloroacetate groups after UV irradiation, as was the case of chloroacetylated chitosan and PVA. Hydrogen chloride was observed to be generated during UV irradiation.

Table III summarizes characteristics of *cis*-1,4-BR having chloroacetate groups

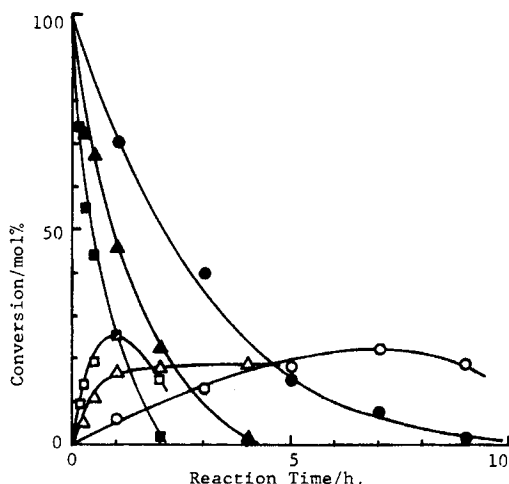


Fig. 7. Addition reaction of dichloroacetic acid to *cis*-1,4-BR at various reaction temperatures. Residual double bond: (○) 80°C ; (△) 100°C ; (□) 120°C . Incorporated dichloroacetate group: (●) 80°C ; (▲) 100°C ; (■) 120°C . Reaction condition: Similar to the one in Table II.

TABLE III
 Characteristics of *cis*-1,4-BR with Pendent Chloroacetate Groups Used for UV Irradiation^a

| Substrate S | Catalyst | Time (h) | S ^b (mol %) | C=C ^c (mol %) | Cyclized ^d (mol %) | T _g ^e (°C) | Remarks |
|------------------------|-------------------------------|-------------|---------------------------|-----------------------------|----------------------------------|-------------------------------------|---------------------------|
| ClCH ₂ COOH | <i>p</i> -TSH (2 mol %) | 40 | 3.5 | 82 | 15 | -114 | BR-Cl ₁ -no. 1 |
| | <i>p</i> -TSH (10 mol %) | 40 | 14 | 54 | 32 | -74 | BR-Cl ₁ -no. 2 |
| | HClO ₄ (2 mol %) | 5 | 4.1 | 79 | 17 | -114 | BR-Cl ₁ -no. 3 |
| Cl ₂ CHCOOH | <i>p</i> -TSH (10 mol %) | 1 | 4.0 | 71 | 25 | -95 | BR-Cl ₂ -no. 1 |
| | <i>p</i> -TSH (10 mol %) | 7 | 22 | 3.0 | 75 | -14 | BR-Cl ₂ -no. 2 |
| | HClO ₄ (1 mol %) | 5.5 | 15 | 1.6 | 83 | -2 | BR-Cl ₂ -no. 3 |
| Cl ₃ CCOOH | HClO ₄ (1 mol %) | 4 | 11 | 26 | 63 | -14 | BR-Cl ₂ -no. 4 |
| | <i>p</i> -TSH (1 mol %) | 6 | 15 | 29 | 56 | | BR-Cl ₃ -no. 1 |
| | HClO ₄ (0.5 mol %) | 4.4 | 11 | 1.7 | 87 | | BR-Cl ₃ -no. 2 |

^a *Cis*-1,4-BR: 0.5 g; S: 10 g; chlorobenzene: 25 cm³; *p*-methoxyphenol: 0.12 g; temperature 80°C.

^b Incorporated chloroacetate groups.

^c Residual double bonds.

^d Degree of cyclization.

^e Measured by DSC.

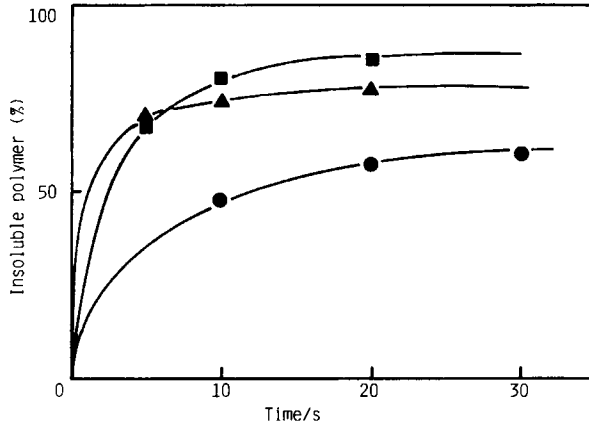


Fig. 8. Photosensitivity of dichloroacetylated *cis*-1,4-BR by UV irradiation. (■) BR-Cl₂-No. 1, $l = 1.4 \times 10^{-3}$ cm; (▲) BR-Cl₂-no. 2, $l = 1.2 \times 10^{-3}$ cm; (●) BR-Cl₂-no. 3, $l = 1.6 \times 10^{-3}$ cm.

used for UV irradiation. Although trichloroacetylated *cis*-1,4-BR seemed to have the highest photosensitivity among the chloroacetylated polybutadienes, the polymer tended to crosslink during evaporation of casting solvents. Therefore, the photosensitivity was estimated on the dichloroacetylated *cis*-1,4-BR.

The photosensitivity of dichloroacetylated *cis*-1,4-BR is shown in Figure 8. The highly cyclized *cis*-1,4-BR (BR-Cl₂-no. 3) having 15 mol % of dichloroacetate groups in the polymer repeating unit, crosslinked more slowly than BR-Cl₂-no. 1 or -no. 2. The photocrosslinking reaction took place in seconds and was considerably faster than that of chloroacetylated chitosan and PVA.

Figure 9 shows the relationship between the rate of the photocrosslinking reaction (R_p) and the reciprocal of the film thickness (l), where the rate was observed to increase linearly with increasing the reciprocal of the film thickness

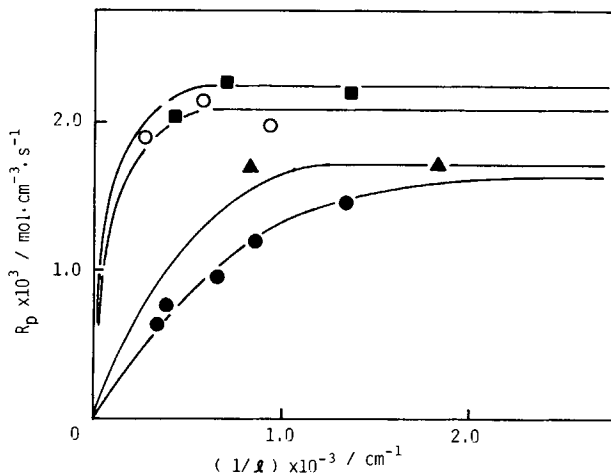


Fig. 9. Relationship between R_p and $1/l$ of dichloroacetylated *cis*-1,4-BR. (■) BR-Cl₂-no. 1; (▲) BR-Cl₂-2; (●) BR-Cl₂-no. 3; (○) BR-Cl₂-no. 4.

up to a point, at which UV ray could pass through the film, that is, at which the crosslinking reaction by UV light seems to occur in a homogeneous condition in terms of photons.

Although very thin film was needed for avoidance of the influence of the film thickness on UV irradiation, it was difficult to weigh correctly thin and light crosslinked films at an early stage of the reaction. Therefore, the photosensitivity of the dichloroacetylated *cis*-1,4-BR was estimated by using the minimum UV irradiation time (t) which is necessary to a complete pattern of the thinnest crosslinked film to be formed on a quartz plate, as described in experimental part. The apparent photosensitivity (R_a), which was obtained by dividing a molarity (P) of the polymer repeating unit per unit volume (1 cm^3) by the minimum irradiation time, could be considered to be proportional to the rate of the crosslinking reaction of the polymer ($d[\text{cross}]/dt$) because the R_a value is proportional to the yield of the crosslinked polymer in polymer repeating unit mole per unit volume (1 cm^3) and per unit reaction time (s) and the yield per second ($d[P]/dt$) should be proportional to the rate of the crosslinking reaction per unit volume ($d[\text{cross}]/dt$). Table IV summarizes the result of UV irradiation on BR-Cl₂-120, which was synthesized at 120°C, with the characteristics. The minimum UV irradiation time was observed to increase with decreasing amounts of residual double bonds, and with increasing amounts of dichloroacetate groups. This tendency agreed with the result shown in Figures 8 and 9. The apparent order of the photocrosslinking reaction was proportional to both first order on the concentration of dichloroacetate groups and second order on the concentration of residual double bonds, as indicated in Figure 10.

$$R_a = k(S)(M)^2 \propto d[\text{cross}]dt \quad (3)$$

where S and M denote dichloroacetate group and residual double bond, respectively.

Mechanism of Photocrosslinking

It was found that mobility of reactive groups is very important in diffusion controlled reactions in polymer solids, such as the photodimerization of anthryl groups¹¹ or cinnamoyl groups¹² and glass transition temperature (T_g) of polymers is important in terms of the mobility. As shown in Table IV, T_g of dichloroa-

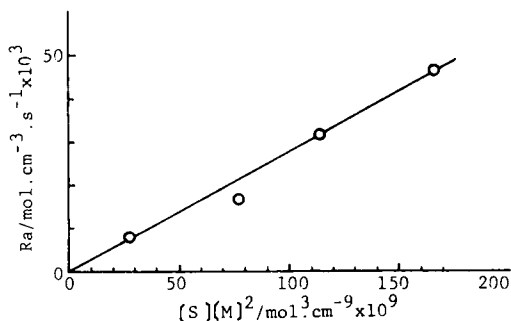


Fig. 10. Relationship between $[M][S]^2$ and apparent photosensitivity (R_a) of dichloroacetylated *cis*-1,4-BR (BR-Cl₂-120). S: dichloroacetate group; M: residual double bond.

TABLE IV
Photosensitivity of *Cis*-1,4-Polybutadiene with Pendent Dichloroacetate Groups

| Polymer ^a BR-Cl ₂ -120 | Content ^b | | Concentration ^c | | T_g (°C) | Temp ^d $(T - T_g + 50)^{-1}$ (K ⁻¹ × 10 ³) | Time ^e | | Photosensitivity ^f $R_c = [P]/t_{av}$ (mol·cm ⁻³ ·s ⁻¹ × 10 ³) |
|---|----------------------|----------------|--|--|---------------|--|-------------------|------------|---|
| | S (mol %) | C=C (mol %) | [S] (mol·cm ⁻³ × 10 ³) | [M] (mol·cm ⁻³ × 10 ³) | | | [P] | t (s) | |
| 1 | 9.0 | 72 | 1.37 | 11.0 | 15.3 | 5.95 | 0.3 | 0.33 | 46.4 |
| 2 | 14 | 55 | 1.95 | 7.65 | 13.9 | 6.85 | 0.2 | 0.45 | 30.9 |
| 3 | 19 | 44 | 2.43 | 5.62 | 12.8 | 8.70 | 0.4 | 0.73 | 17.5 |
| 4 | 24 | 26 | 2.83 | 3.07 | 11.8 | 9.62 | 1.7 | 1.45 | 8.14 |

^a Polymers were synthesized at 120°C.

^b S and C=C denote incorporated dichloroacetate groups and residual double bonds, respectively.

^c Concentration of dichloroacetate groups: [S]; residual double bonds: [M]; and polymer repeating unit: [P].

^d T_g and T denote glass transition temperature and UV irradiation temperature (20°C).

^e Minimum UV irradiation time which is necessary to a complete pattern of the thinnest crosslinked film to be formed on a quartz plate; t_{av} denotes the average.

^f Apparent photosensitivity.

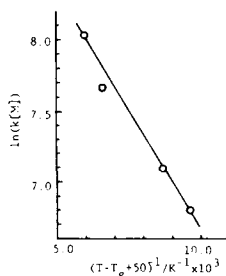


Fig. 11. Relationship between $\ln(k[M])$ and $(T - T_g + 50)^{-1}$ on dichloroacetylated *cis*-1,4-BR (BR-Cl₂-120). T : UV irradiation temperature (20°C); T_g = glass transition temperature of polymer.

cetylated *cis*-1,4-BR increased with decreasing amounts of residual double bonds. Therefore, we assumed that the second order of the crosslinking reaction on the concentration of residual double bonds might be related to both the concentration itself and T_g . Linear relationship between $\ln(k[M])$ and $(T - T_g + 50)^{-1}$ was observed in Figure 11, as indicated in the following equation:

$$\ln(k[M]) = C_1 - C_2(T - T_g + 50)^{-1} \quad (4)$$

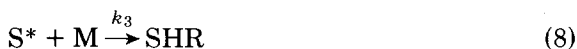
where C_1 , C_2 , and T denote constants and irradiation temperature (20°C). Therefore, the rate of the crosslinking reaction can be expressed as follows:

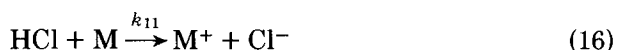
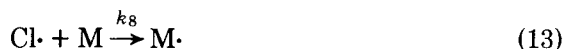
$$d[\text{cross}]/dt = \{\exp[C_1 - C_2/(T - T_g + 50)]\}[S][M] \quad (5)$$

The order of the crosslinking reaction can be considered to be first order on both the concentration of dichloroacetate groups and residual double bonds.

In the case of EPDM modified by grafting of benzoin derivatives containing chlorines, the crosslinking reaction of the elastmer film was reported to take place to bear 40 crosslinks/2 mol photosensitizer in a polymer chain, and to be due to action of the unsaturations in the polymer as crosslinking centers.¹⁷ The crosslinking reaction of dichloroacetylated *cis*-1,4-BR took place much faster than that of chloroacetylated chitosan and PVA, so that the crosslinking reaction of dichloroacetylated *cis*-1,4-BR could be considered to be due to the chain addition reaction of residual double bonds.

When the initial stage of the reaction is considered to be due to hydrogen abstraction reaction by an excited dichloroacetate group, similarly to the case of chloroacetylated chitosan¹ and PVA,² the reaction can be expressed as follows:





where simplification of reactions is done by consideration of most probable reactions and by application of kinetic treatment for polymerization reaction in order to avoid complicated kinetics. A carbonyl group of excited dichloroacetate group ($\text{S}^* = \text{CHCl}_2\text{CO}^*\text{O}-$) abstracts a hydrogen from a methylene group of an olefinic group ($\text{M} = -\text{CH}_2\text{CH}=\text{CHCH}_2-$) to form a hydrogenated dichloroacetate radical [$\text{SH}\cdot = \text{CHCl}_2\dot{\text{C}}(\text{OH})\text{O}-$] and an allyl-type radical ($\text{R}\cdot = -\text{CH}_2\text{CH}=\text{CH}\dot{\text{C}}\text{H}-$) which is too stable to initiate chain addition reaction of olefinic groups, as shown in eqs. (6) and (7). Formation of hydroxyl groups during UV irradiation was observed as shown in the IR spectra of Figure 3, which suggests that $\text{SH}\cdot$ and $\text{R}\cdot$ radicals may combine together by cage effect in polymer solids to bear a SHR bond having a hydroxyl group [$\text{SHR} = \text{CHCl}_2\text{C}(\text{OH})-(\text{O}-)(-\text{CHCH}=\text{CHCH}_2-)$] with crosslinking reaction, as described in eq. (8). The hydrogenated dichloroacetate radical ($\text{SH}\cdot$) generates a chloro radical ($\text{Cl}\cdot$) or adds to an olefinic group to initiate radical chain addition reaction of olefinic groups, as shown in eqs. (9) and (12). The chloro radical ($\text{Cl}\cdot$) reacts with the allyl-type radical ($\text{R}\cdot$) to form hydrogen chloride (HCl) by hydrogen abstraction reaction or to form a chlorinated hydrocarbon (RCl) or the chloro radical adds to olefinic groups to initiate radical chain addition reaction of olefinic groups, as indicated in eqs. (10), (11), and (13). Propagating crosslinking radicals ($\text{M}_n\cdot$) may be terminated by olefinic groups to form allyl type radicals ($\text{R}\cdot$), as shown in eq. (15), because the combination reaction of radicals, which are far apart from each other, is difficult in polymer solids. Since hydrogen chloride was observed to be generated during UV irradiation and the crosslinking reaction of dichloroacetylated *cis*-1,4-BR was not initiated with heating in the presence of azobisisobutyronitrile (AIBN), hydrogen chloride may initiate cationic chain addition reaction of olefinic groups. Some olefinic monomers, such as isobutene, are known to act as a terminator of cationic polymerization by hydrogen transfer

reaction from monomer to form an allyl-type stable cation.¹⁸ Therefore, the termination reaction of the cationic crosslinking reaction may be due to hydrogen transfer reaction from an olefinic group with formation of an allyl-type stable cation ($R^+ = -CH_2CH=CHC^+H-$).

When a steady state on active species and equilibrium on excited dichloroacetate groups are assumed, and also initiator efficiency of $SH\cdot$, $Cl\cdot$, and HCl toward the chain addition reaction of olefinic groups are expressed by f_s , f_c , and f_{HCl} , respectively, the concentration of each species can be obtained as follows:

$$[S^*] = K[S] \quad (19)$$

$$\frac{k_7[SH\cdot][M]}{k_2[S^*][M]} = f_s, \quad \frac{k_8[Cl\cdot][M]}{k_4[SH\cdot]} = f_c, \quad \frac{k_{11}[HCl][M]}{k_5[Cl\cdot][R\cdot]} = f_{HCl} \quad (20)$$

$$d[SH\cdot]/dt = 0, \quad k_2[S^*][M] - k_4[SH\cdot] - k_7[SH\cdot][M] = 0$$

From eqs. (19) and (20), the concentration of $SH\cdot$ is expressed as follows:

$$\begin{aligned} [SH\cdot] &= (1 - f_s)k_2[S^*][M]/k_4 \\ &= (1 - f_s)k_2K[S][M]/k_4 \end{aligned} \quad (21)$$

$$d[M_n\cdot]/dt = 0, \quad k_7[SH\cdot][M] + k_8[Cl\cdot][M] - k_{10}[M_n\cdot][M] = 0$$

From eqs. (18)–(21), the concentration of $M_n\cdot$ can be expressed as follows:

$$[M_n\cdot] = k_2(f_s + f_c - f_{sf_c})K[S]/k_{10} \quad (22)$$

$$d[R\cdot]/dt = 0, \quad k_2[S^*][M] + k_{10}[M_n\cdot][M] - (k_5 + k_6)[Cl\cdot][R\cdot] = 0$$

$$[Cl\cdot][R\cdot] = (k_2[S^*][M] + k_{10}[M_n\cdot][M])/(k_5 + k_6) \quad (23)$$

From eqs. (19)–(21), the concentration of HCl can be expressed as follows:

$$\begin{aligned} [HCl] &= k_5f_{HCl}[Cl\cdot][R\cdot]/k_{11}[M] \\ &= k_2k_5f_{HCl}K(1 + f_s + f_c - f_{sf_c})[S]/(k_5 + k_6)k_{11} \end{aligned} \quad (24)$$

$$d[M_n^+]/dt = 0, \quad k_{11}[HCl][M] - k_{13}[M_n^+][M] = 0$$

From eq. (24), the concentration of M_n^+ can be expressed as follows:

$$\begin{aligned} [M_n^+] &= k_{11}[HCl]/k_{13} \\ &= k_2k_5f_{HCl}K(1 + f_s + f_c - f_{sf_c})[S]/(k_5 + k_6)k_{13} \end{aligned} \quad (25)$$

The rate of the crosslinking reaction can be considered as the sum of those due to the reactions indicated in Eqs. (8), (12), (14) and (17) as follows:

$$d[\text{cross}]/dt = k_3[S^*][M] + k_7[SH\cdot][M] + k_9[M_n\cdot][M] + k_{12}[M_n^+][M]$$

Finally, the rate can be expressed by eqs. (19), (21), (22), and (25) as follows:

$$d[\text{cross}]/dt = k'[S][M] \quad (26)$$

where

$$\begin{aligned} k' &= \{k_3 + k_2f_s + k_2k_9(f_s + f_c - f_{sf_c})/k_{10} \\ &\quad + k_2k_5k_{12}f_{HCl}(1 + f_s + f_c - f_{sf_c})/(k_5 + k_6)k_{13}\}K \end{aligned} \quad (27)$$

Eq. (26) agrees with the experimental result.

The apparent rate constant (k') in aspect of diffusion controlled reaction is related to the rate constants k_2 and k_3 which have the same dependence on diffusion, because k_9/k_{10} , f_{HCl} , $(f_s + f_c - f_{sf_c})$, K , and $k_5 k_{12}/(k_5 + k_6)k_{13}$ can be regarded as functions which are independent on diffusion controlled reactions, as indicated in eq. (27). Therefore, the dependence of the crosslinking reaction on the glass transition temperature of the polymer may be interpreted to be due to the diffusion controlled reaction of excited dichloroacetate groups and olefinic groups.

When we considered the initial stage of the crosslinking reaction due to homolytic dissociation of excited dichloroacetate groups as follows: $S^* \rightarrow S + \text{Cl}\cdot$; the kinetic equation on the rate of the crosslinking reaction was obtained to be proportional only to the first order on the concentration of dichloroacetate groups.

CONCLUSION

The addition reaction of chloroacetic acids to olefinic groups in *cis*-1,4-polybutadiene and polypentenamer was carried out. These chloroacetylated polymers were easily obtained with around 20 mol % of pendent chloroacetate groups and with cyclization of polymer backbone. Dichloroacetylated *cis*-1,4-polybutadiene showed much higher photosensitivity than chloroacetylated chitosan and PVA. The kinetic order of the crosslinking reaction was obtained experimentally to be proportional to both the first order on the concentration of dichloroacetate groups and the second order on the concentration of olefinic groups. However, the order of the crosslinking reaction on the concentration of olefinic groups could be regarded as the first order by the consideration of relationship between glass transition temperature (T_g) of the polymer and the concentration of olefinic groups in the polymer. The mechanism of the crosslinking reaction was interpreted by kinetic investigation as follows: The crosslinking reaction may be initiated by excited dichloroacetate groups to abstract hydrogen from olefinic groups, similarly to the case of chloroacetylated chitosan and PVA; then the crosslinking reaction may proceed with both radical chain and cationic chain addition reaction of olefinic groups. The termination of the crosslinking reaction may be due to the formation of allyl type stable radicals or cations by hydrogen transfer from olefinic groups to propagating active species. The dependence of the crosslinking reaction on T_g of the polymer may be related to the reaction of excited dichloroacetate groups and olefinic groups.

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