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Anionic Copolymerization of Isoprene and 1,1-Diphenylethylene

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Anionic copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2) was carried out in tetrahydrofuran (THF), dioxane, benzene, and *n*-heptane by using *n*-butyllithium (*n*-BuLi), Na-naphthalene, Na- and K-dispersions as initiators. An alternating copolymer was obtained in the copolymerization in THF, which proceeded without a chain transfer and a termination. Monomer reactivity ratios, r_1, obtained by assuming the rate constant $k_{22}=0$, were 0.12 (Li^+), 0.11 (Na^+), and 0.11 (K^+) in THF at 0°C. The r_1 value in benzene at 40°C, however, was affected by the counter ion as follows: 37 (Li^+), 0.38 (Na^+), and 0.05 (K^+). With Li^+ counter ion the values were 0.50 in dioxane at 30°C and 29 in *n*-heptane at 40°C. The order of rate constants in the copolymerization in THF with *n*-BuLi at 0°C, was $k_{12}>k_{11}>k_{21}$, the last of which was 2.64×10^{-3} *l*/mol sec.

Among the anionic copolymerizations of the monomer pairs which copolymerize alternatingly,[1] the results of detailed studies were reported previously on the copolymerizations of 1,1-diphenylethylene and styrene,[2] of 1,1-diphenylethylene and 2,3-dimethylbutadiene,[3] and of *trans*-stilbene and styrene.[4]

In the present study, the copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2) will be investigated under various reaction conditions. The results will be correlated with those of the copolymerization reported previously.

Experimental

Materials. *Isoprene.* The purified monomer (Phillips polymerization grade) was redistilled *in vacuo* from lithium aluminum hydride before use.

1,1-Diphenylethylene. This was first stirred with Na-K alloy under dry nitrogen, and then *n*-butyllithium (*n*-BuLi) in heptane was added to the mixture until a red color due to 1,1-diphenylhexyllithium appeared. The colored solution was carefully distilled *in vacuo* to obtain the pure monomer.

Tetrahydrofuran (THF) and Dioxane. Each of these solvents was refluxed over metallic sodium and then over lithium aluminum hydride, from where it was distilled onto Na-K alloy and naphthalene. From the green solution the solvent was transferred to a reaction vessel on a vacuum system before use.

Benzene and n-Heptane. Each of these solvents purified in the usual manner was distilled under high vacuum in the presence of *n*-BuLi.

n-BuLi. *n*-BuLi was prepared in *n*-heptane and the concentration was determined by double titration.[5]

Na-Naphthalene (Na-Naph.). The concentration of the solution was determined by the titration of a sample solution after hydrolysis by water.[6]

n-Butyl Alcohol. A small amount of metallic sodium was added to the alcohol (spectro grade). The alcohol containing sodium butoxide was then distilled under high vacuum to prepare a standard *n*-butyl alcohol solution in *n*-heptane. The solution was used for the colorimetric titration of a carbanion solution.

Polymerization. The polymerization was carried out in a glass ampoule under dry argon. To the ampoule, isoprene and a solvent were distilled by means of a vacuum line, and then 1,1-diphenylethylene and an initiator were added with hypodermic syringes. The polymerization was terminated after the manner of titration with the *n*-butyl alcohol solution in *n*-heptane to estimate the concentration of living ends.

Electronic Spectrum. The electronic spectrum of a reaction mixture was measured with a Hitachi 124 Spectrophotometer. The sample solution was prepared in a high vacuum system.

NMR Spectrum. The spectrum of the polymer was taken in a carbon tetrachloride solution with a JNM-4H-100 Spectrometer (Japan Electron Optics Laboratory Co., Ltd.) at 60°C.

Molecular Weight. The molecular weight of the polymer was measured on a Mechrolab Vapor Pressure Osmometer, Model 301A, using benzene as a solvent.

Viscosity. The solution viscosity of the polymer in toluene was measured at 30.0°C.

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1) H. Yuki, K. Kosai, S. Murahashi and J. Hotta, *J. Polymer Sci. B*, **2**, 1121 (1964).

2) H. Yuki, J. Hotta, Y. Okamoto and S. Murahashi, This Bulletin, **40**, 2659 (1967).

3) H. Yuki, K. Hatada and T. Inoue, *J. Polymer Sci. A-1*, **6**, 3333 (1968); H. Yuki, Y. Okamoto and K. Sadamoto, This Bulletin, **42**, (1969).

4) H. Yuki, M. Kato and Y. Okamoto, This Bulletin, **41**, 1940 (1968).

5) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

6) G. M. Burnett and R. N. Young, *Europ. Polym. J.*, **2**, 329 (1966).

Results

The copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2) in THF at 0°C was carried out with *n*-BuLi as an initiator, the initial molar ratio of monomers, $[M_1]_0/[M_2]_0$, being 0.650. The results are shown in Fig. 1. The reaction proceeded so slowly that it took 80 hr to be completed, when unchanged 1,1-diphenylethylene remained in the system, but isoprene was completely consumed. Since 1,1-diphenylethylene can not be homopolymerized, the yield of the copolymer is maximum when the two monomers copolymerize alternatingly, if $[M_1]_0/[M_2]_0<1$. In Fig. 1, the yield against the theoretical amount of the alternating copolymer is also shown. It reaches 100%, indicating the formation of the alternating copolymer in the system. It was observed that the concentration of the living ends titrated by *n*-butyl alcohol was constant regardless of the reaction time and was nearly equal to the concentration of the initiator used.

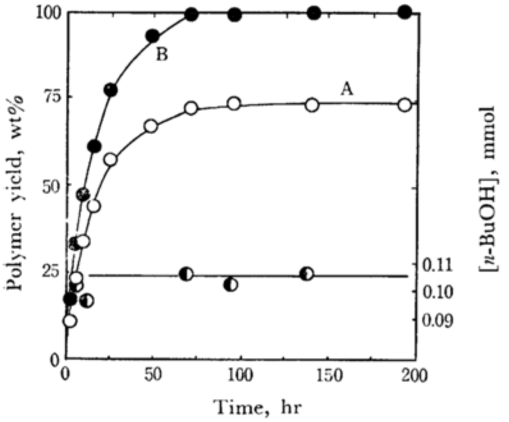

Fig. 1. Anionic copolymerization of isoprene and 1,1-diphenylethylene. —— Time *vs*. polymer yield (THF)

A: Polymer yield against total monomers
B: Polymer yield as alternating copolymerization
◐: *n*-Butyl alcohol required for terminating copolymerization
$[M_1]_0$: 6.48 mmol, $[M_2]_0$: 9.97 mmol,
[*n*-BuLi]: 0.107 mmol, THF: 15 m*l*, temp.: 0°C

The relationship between the polymer yield (curve B in Fig. 1) and the polymer molecular weight is shown in Fig. 2. A linear relationship was found between the two and the line almost agreed with the theoretical line for the living polymer produced by alternating copolymerization. There was also a linearity between log Yield and log $[\eta]$.

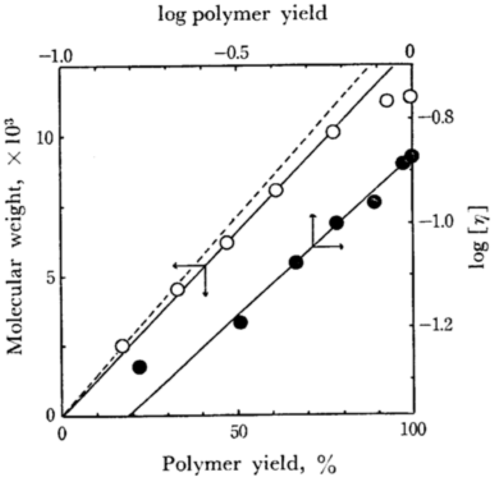

Fig. 2. Anionic copolymerization of isoprene and 1,1-diphenylethylene. —— Relationship between polymer yield and molecular weight

Dotted line: Molecular weight calculated as living polymer
$[M_1]_0$: 6.48 mmol, $[M_2]_0$: 9.97 mmol,
[*n*-BuLi]: 0.107 mmol, THF: 15.0 m*l*,
temp.: 0°C

The material balance after the prolonged copolymerization reaction was examined. A part of the results is listed in Table 1. As isoprene was completely incorporated into the copolymer, the copolymer composition, $[m_1]/[m_2]$, was calculated from the polymer yield and the initial monomer concentrations.[3,4] The $[m_1]/[m_2]$ ratio in the copolymer obtained in THF slightly exceeded unity with increasing the $[M_1]_0/[M_2]_0$ ratio from 0.6 to 0.9. The alternating copolymer was powder. On the other hand, the copolymer obtained in benzene was viscous and contained a great deal of isoprene, even at $[M_1]_0/[M_2]_0=0.6$.

The copolymer composition was also examined by other methods as shown in Table 2. The elementary analyses of the copolymer are well consistent with the calculations based on the copolymer compositions derived from the polymer yields. The copolymer compositions obtained from the ratios of aromatic to aliphatic protons in their NMR spectra are also in accord with the above compositions within analytical errors.

The monomer reactivity ratio, r_1, was obtained from the integrated Mayo-Lewis copolymer composition equation, assuming $k_{22}=0$.[2] The r_1 values thus obtained are listed in Tables 3—5. In the copolymerizations in THF at 0°C using *n*-BuLi, Na-naphthalene, and K-dispersion as initiators, the r_1 values were almost constant (0.11—0.12). In benzene at 40°C, however, the values were 37, 0.38, and 0.05 with *n*-BuLi, Na-dispersion, and K-dispersion respectively. With *n*-BuLi in dioxane at 30°C and in *n*-heptane at 40°C, the values were 0.50 and 29 respectively. The r_1 value at 25°C in THF seemed to be smaller than that at 0°C. The copolymerization carried out in benzene without an initiator gave no polymer even after 216 hr at 40°C

TABLE 1. ANIONIC COPOLYMERIZATION OF ISOPRENE (M_1) AND 1,1-DIPHENYLETHYLENE (M_2)
MATERIAL BALANCE

M_1: 0.442 g, initiator: *n*-BuLi 0.11 mmol, temp.: 0°C in THF, 40°C in benzene

Solvent 15.0 m*l*	Time hr	M_2 g	$[M_1]_0/[M_2]_0$ mol/mol	Polymer g	Unchanged[a] M_2, g	$[m_1]/[m_2]$[b] mol/mol
THF	96	1.293	0.904	1.544	0.187	1.06
THF	96	1.522	0.770	1.589	0.370	1.02
THF	96	1.797	0.607	1.625	0.630	1.00
Benzene	120	0.506	2.32	0.494	0.440	24.8
Benzene	120	1.162	1.01	0.562	1.042	9.87
Benzene	120	1.733	0.653	0.600	1.554	7.47

a) Contained *ca.* 7 mg of Li-compounds.
b) Molar ratio of monomers in copolymer.

TABLE 2. ANIONIC COPOLYMERIZATION OF ISOPRENE (M_1) AND 1,1-DIPHENYLETHYLENE (M_2)
COPOLYMER COMPOSITION

Initiator: *n*-BuLi

Solvent 15.0 m*l*	Yield wt%	$[m_1]/[m_2]$[a]	Elementary analysis Calcd[b] C%	H%	Found C%	H%	NMR $[m_1]/[m_2]$[c]
THF	11.1	1.00	91.76	8.24	91.95	8.20	—
THF	23.4	1.00	91.86	8.14	91.86	8.07	—
THF	72.6	1.00	91.88	8.12	92.00	8.11	0.96
Dioxane	78.7	1.23	91.56	8.44	91.23	8.23	1.27
Dioxane	97.4	2.34	90.88	9.12	90.98	8.98	2.40
Benzene	27.9	7.47	89.16	10.50	89.16	10.41	7.10
Benzene	43.6	13.9	88.98	11.02	88.93	10.89	—

a) Copolymer composition calculated from polymer yield.
b) Based on the copolymer composition. Correction was done for end group of low molecular weight polymer.
c) Copolymer composition obtained from NMR spectrum.

TABLE 3. ANIONIC COPOLYMERIZATION OF ISOPRENE (M_1) AND 1,1-DIPHENYLETHYLENE (M_2)
MONOMER REACTIVITY RATIO, r_1 (THF)

$[M_1]_0$: 6.53—6.62 mmol, solvent: 15.0 m*l*, temp.: 0°C

Initiator 0.11 mmol	$[M_1]_0/[M_2]_0$	Time hr	Yield mol%	$[m_1]/[m_2]$[a]	η_{sp}/C d*l*/g	r_1
Na-Naph.	1.07	96	96.9	1.15	0.190	0.16
Na-Naph.	1.00	96	94.7	1.11	0.211	0.15
Na-Naph.	0.962	96	94.3	1.09	0.200	0.11
Na-Naph.	0.852	96	90.8	1.03	0.204	0.05
Na-Naph.[b]	0.997	96	95.2	1.10	0.213	0.13
					<Average	0.12>
K-disp.	1.00	96	94.0	1.14	—	0.17
K-disp.	0.906	123	86.5	1.11	—	0.15
K-disp.	0.830	144	85.4	1.03	—	0.05
K-disp.	0.781	144	81.3	1.03	—	0.06
					<Average	0.11>

a) Molar ratio of monomers in copolymer.
b) Contained 0.50 mmol of $NaB(Ph)_4$.

TABLE 4. ANIONIC COPOLYMERIZATION OF ISOPRENE (M_1) AND 1,1-DIPHENYLETHYLENE (M_2) MONOMER REACTIVITY RATIO, r_1 (BENZENE, *n*-BuLi)

$[M_1]_0$: 6.51–6.57 mmol, solvent: 15.0 m*l*, initiator: 0.12 mmol, temp.: 40°C

$[M_1]_0/[M_2]_0$	Time hr	Yield mol%	$[m_1]/[m_2]$[a)]	η_{sp}/C d*l*/g	r_1
2.32	120	72.8	24.8	0.122	47.4
1.53	120	64.8	13.9	0.120	34.7
1.01	120	55.3	9.87	0.122	33.5
1.00	72	54.7	10.7	0.115	37.5
0.654	120	45.8	7.47	0.123	31.7
				<Average	36.8>
1.00[b)]	216	0	—	—	—

a) Molar ratio of monomers in copolymer.
b) Without initiator.

TABLE 5. ANIONIC COPOLYMERIZATION OF ISOPRENE (M_1) AND 1,1-DIPHENYLETHYLENE (M_2) MONOMER REACTIVITY RATIO, r_1

Solvent	Initiator	Temp. °C	Number of experiment	r_1
THF	*n*-BuLi	0	5	0.11
THF	*n*-BuLi	25	2	0.04
THF	Na-Naph.	0	4	0.12
THF	K-disp.	0	4	0.11
Dioxane	*n*-BuLi	30	6	0.50
Benzene	*n*-BuLi	40	5	37
Benzene	Na-disp.	40	5	0.38
Benzene	K-disp.	40	4	0.05
n-Heptane	*n*-BuLi	40	4	29

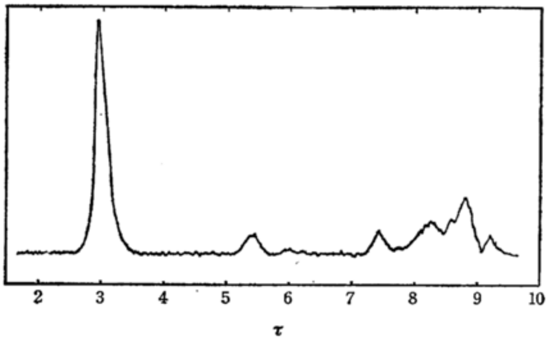

Fig. 3. NMR spectrum of the alternating copolymer of isoprene and 1,1-diphenylethylene in carbon tetrachloride at 60°C.

(Table 5), suggesting that no polymerization occurred by free radical mechanism under the reaction conditions employed.

The NMR spectrum of the alternating copolymer obtained with *n*-BuLi in THF is shown in Fig. 3. The homopolymerization of isoprene by *n*-BuLi in the same solvent yielded a polymer with 29% 1,2-, 71% 3,4- and ~0% 1,4-structures. The analysis was done with NMR spectrum according to the method of Chen.[7)] The alternating copolymer showed no peak in its NMR spectrum at the same position as that of the polyisoprene. On the other hand, in the IR spectrum of the copolymer, an absorption due to the vinyl group was found at 910 cm^{-1}, but very weak suggesting that there was little 1,2-structure in the copolymer. Therefore, assuming that the isoprene was incorporated in the copolymer through 3,4- and 1,4-additions, the ratio of 3,4- to 1,4-addition was 17:83, on the basis of the NMR spectrum.

At $[M_1]_0/[M_2]_0=0.650$, the copolymerization by *n*-BuLi carried out in THF at 0°C was followed spectrophotometrically. As soon as *n*-BuLi was added, the reaction mixture showed an absorption maximum at 496 mμ due to the diphenylethylene anion; its optical density had been constant during 150 hr at least. The molar extinction coefficient[*1] was 1.7×10^4, which agrees closely with 1.8×10^4 of 1,1-diphenylhexyllithium anion.[8)] These results apparently indicate that the most of the living ends present in the system were 1,1-diphenylethylene anion.

Discussion

The copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2) initiated by *n*-BuLi in THF under a condition of $[M_1]_0/[M_2]_0<1$ proceeded without a termination and a chain transfer to give an alternating copolymer. Among the rate constants of the propagation reactions, k_{22} must be zero and k_{12} must be greater than k_{11} in such a copolymerization reaction.

$$\sim\!\sim M_1^- + M_1 \xrightarrow{k_{11}} \sim\!\sim M_1^- \quad (1)$$

$$\sim\!\sim M_1^- + M_2 \xrightarrow{k_{12}} \sim\!\sim M_2^- \quad (2)$$

$$\sim\!\sim M_2^- + M_1 \xrightarrow{k_{21}} \sim\!\sim M_1^- \quad (3)$$

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7) H. Y. Chen, *Anal. Chem.*, **34**, 1793 (1962).

[*1] Calculated for the initiator concentration assuming the living polymer system.

8) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).

$$\sim\!\sim M_2^- + M_2 \xrightarrow{k_{22}} \sim\!\sim M_2^- \tag{4}$$

The sum of the concentrations of the living ends, $[M_1^-]+[M_2^-]$, should be equal to that of the initiator, $[C]_0$.

$$[M_1^-] + [M_2^-] = [C]_0 \tag{5}$$

In Eq. (5), $[M_1^-]$ is negligible because the anion existing in the system was mostly M_2^-, which must be far more stable than the M_1 anion owing to the conjugation with its two benzene rings. So we can assume $k_{12} \gg k_{21}$ and get[3]

$$-\frac{d[M_1]}{dt} = k_{21}[C]_0[M_1] \tag{6}$$

The equation shows that process (3) is the rate determining step in the copolymerization.

Recently, Ureta *et al.*[9] have reported the anionic copolymerization of styrene (M_1) and 1,1-diphenylethylene (M_2), in which they found that process (3) was a reversible reaction as follows:

$$\sim\!\sim M_2^- + M_1 \underset{k_{-21}}{\overset{k_{21}}{\rightleftarrows}} \sim\!\sim M_2M_1^- \tag{7}$$

If so in the present copolymerization, Eq. (6) must be rewritten as

$$-\frac{d[M_1]}{dt} = k_{21}[M_2^-][M_1] \times \frac{k_{12}[M_2]}{k_{-21}+k_{12}[M_2]} \tag{8}$$

The analysis of the results in Fig. 1 gave a linear relationship between log $[M_1]$ and t as is shown in Fig. 4, indicating that the rate of the consumption of isoprene is first order with respect to its own concentration as represented by Eq. (6). Consequently, there must be $k_{12}[M_2] \gg k_{-21}$ in Eq. (8) and the reversible reaction (7) may be neglected. From Fig. 4, we can get $k_{21}=2.64\times10^{-3}$ l/mol sec in THF at 0°C. Taking into account the difference of the reaction temperature, the above value seems to be greater than $k_{21}=1.3$—1.8×10^{-3} l/mol sec found in the copolymerization of 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) by means of *n*-BuLi at 22°C. The values indicate that isoprene is sterically and electronically more reactive than 2,3-dimethylbutadiene because the latter has one more methyl group.

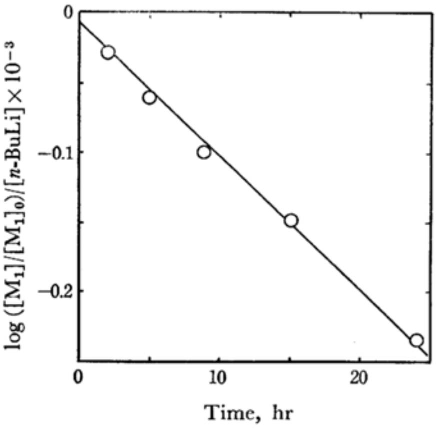

Fig. 4. Anionic copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2).—First order plot $[M_1]_0$: 6.48 mmol, $[M_2]_0$: 9.97 mmol, [*n*-BuLi]: 0.107 mmol, THF: 15.0 ml, temp.: 0°C.

The monomer reactivity ratios, r_1, obtained in the copolymerizations of 1,1-diphenylethylene (M_2) with three comonomers (M_1) by *n*-BuLi are summarized in Table 6. 1,1-Diphenylethylene was always more reactive to the M_1 anion than the corresponding M_1 monomer in THF. In benzene, 1,1-diphenylethylene was more reactive when the comonomer was styrene or 2,3-dimethylbutadiene, while less reactive when isoprene was the comonomer. In the copolymerization of isoprene and 1,1-diphenylethylene with *n*-BuLi, the monomer reactivity ratio was strongly influenced by the solvent (Table 5). The r_1 value in hydrocarbon solvent was larger than unity, while in dioxane and THF, the value approached zero with the increasing polarity of the solvent. No effect of the initiator on the r_1 value was observed in the copolymerization in THF, but in benzene the value varied in the order of $Li^+ \gg Na^+ > K^+$. When the counter ion was either Na^+ or K^+, a small influence of the solvent was observed on the r_1 value. These tendencies suggest that the r_1 value may decrease with an increase in the ionic character of the carbon - metal bond. Similar results have been reported in the anionic copolymerizations of butadiene and styrene,[10] and of isoprene and styrene.[11] The high reactivity of the dienes observed in these copolymerizations was explained by preferential absorption of the dienes at the active center.[*2] Such an absorption may be excluded for 2,3-dimethylbutadiene because of its steric hindrance.

TABLE 6. MONOMER REACTIVITY RATIO, r_1, IN ANIONIC COPOLYMERIZATION OF 1,1-DIPHENYLETHYLENE AND OTHER MONOMERS BY *n*-BuLi

M_1 monomer	M_2 monomer 1,1-Diphenylethylene in THF	in Benzene
Isoprene	0.11	37
2,3-Dimethylbutadiene	0	0.23
Styrene	0.13	0.71

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[9] E. Ureta, J. Smid and M. Szwarc, *J. Polymer Sci. A-1*, **4**, 2216 (1966).

[10] I. Kuntz, *J. Polymer Sci.*, **54**, 569 (1961).

[11] A. V. Tobolsky and C. E. Rogers, *ibid.*, **38**, 205 (1959).

[*2] Worsfold denied the above explanation from the result of the kinetic study of the copolymerization of styrene and isoprene. D. J. Worsfold, *J. Polymer Sci. A-1*, **5**, 2783 (1967).

It is well known that $NaB(Ph)_4$ depresses the dissociation of an ion pair to free ions in the anionic polymerization of styrene.$^{12)}$ The presence of $NaB(Ph)_4$ of the present copolymerization with Na^+ counter ion in THF had no influence on the r_1 value as is shown in Table 3. The fact demonstrates that, if the copolymerization may involve two kinds of propagating species, a free ion and an ion pair, the r_1 values for these two species will be very similar.

The alternating copolymer consisted of isoprene unit having 83% of 1,4-structure, in comparison with ~0% in the polyisoprene polymerized under the same conditions. In the copolymerization isoprene adds to the bulky 1,1-diphenylethylene anion at the sterically less hindered 4-position, and then the resulting isoprenyl anion adds to 1,1-diphenylethylene at the less hindered 1-position than the 3-position. A similar result was observed in the alternating copolymer of 2,3-dimethylbutadiene and 1,1-diphenylethylene,$^{3)}$ in which the microstructure of 2,3-dimethylbutadiene was only 1,4 addition. A small portion of the 3,4-addition appeared in the copolymer of isoprene and 1,1-diphenylethylene may be attributed to the less steric hindrance than that of 2,3-dimethylbutadiene.

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12) D. N. Bhattacharyya, C. L. Lee, J. Smid and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965); H. Hostalka and G. V. Schulz, *J. Polymer Sci. B*, **3**, 175 (1965).