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Anionic Copolymerization of Butadiene and 1,1-Diphenylethylene

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The anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene was investigated in tetrahydrofuran (THF) and benzene, using *n*-butyllithium (*n*-BuLi), Na-naphthalene, and Na- and K-dispersions as initiators. An alternating copolymer was formed in THF, where the reaction proceeded without termination and chain-transfer reactions. The monomer reactivity ratios, r_1, were 0.13 (Li^+), 0.09 (Na^+), and 0.09 (K^+) in THF at 0°C. The r_1 values in benzene at 40°C were 54 (Li^+), 0.71 (Na^+), and 0.10 (K^+). The order of rate constants in THF was $k_{12} > k_{11} > k_{21}$; the last of these was $0.27\text{M}^{-1}\ \text{sec}^{-1}$, with *n*-BuLi at 0°C.

In a preceeding paper,[1] the anionic copolymerization of isoprene (M_1) and 1,1-diphenylethylene (M_2) was reported. In the present work, the anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2) was investigated. The results obtained were similar to those of the copolymerization reported in the preceeding paper.

Experimental

Materials. Butadiene (Phillips, polymerization grade) which had been dried over Molecular Sieves was mixed with solvent-free *n*-BuLi just before use; it was then redistilled into a glass ampoule *in vacuo*.

The methods of preparing and purifying the other materials, such as 1,1-diphenylethylene, THF, benzene, and *n*-BuLi, were described in the preceeding paper.[1] The Na- and K-dispersions were prepared in *n*-heptane.

Polymerization. The purified butadiene was first transferred into a known amount of a solvent on a vacuum line, and then the mixture kept under a vacuum was weighed to determine the amount of the monomer transferred. All the mixture was then distilled under a high vacuum into a large amount of the solvent. The solution thus obtained was transferred to glass ampoules with a hypodermic syringe under dry argon. To the ampoules, 1,1-diphenylethylene and initiator were added with syringes. After a given reaction period, the polymerization was terminated by adding a small portion of methanol. The polymer was precipitated in methanol and then filtrated, dried, and weighed. The mother liquor of the polymer precipitation was evaporated at a reduced pressure; the unchanged 1,1-diphenylethylene was thus recovered as a residue. The refractive index and the infrared spectrum of the residue were very similar to those of 1,1-diphenylethylene, indicating that the residue contained a small amount of a compound of a low molecular weight, a compound which was formed by a side reaction.

Electronic Spectrum. The electronic spectrum was taken with a Hitachi 124 Spectrophotometer.

NMR Spectrum. The spectrum of the polymer was measured on a JNM-4H-100 Spectrometer at 100 MHz in a carbon tetrachloride solution at 60°C, using tetramethylsilane as the internal standard.

Molecular Weight. The molecular weight of the polymer was measured in benzene at 37°C with a Mechrolab Vapor Pressure Osmometer, Model 301A.

Viscosity. The solution viscosity of the polymer was taken in toluene at 30.0°C, the concentration of the polymer being 0.5 g/d*l*.

Results

The rate of the copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2) was investigated in THF at 0°C with *n*-BuLi. Figure 1 shows the results. The reaction was completed in 60 min, by which time almost all the butadiene had been consumed. The yield for the alternating copolymerization, which forms a copolymer, $-(M_1M_2)_n-$, is also shown in Fig. 1. This yield reached nearly 100%, indicating that an alternating copolymer was formed.[1] A linear relationship was obtained between the polymer yield (curve B in Fig. 1) and the molecular weight of the polymer, as is shown in Fig. 2. The molecular weight measured nearly agreed with the one calculated for the living polymer system, which proceeds alternatingly. There was also a good linearity between log yield and log$[\eta]$. The relationship between the average molecular weight and intrinsic viscosity was $[\eta] = 4.0\times 10^{-4}\text{M}^{0.60}$ (in toluene at 30°C).

The copolymerizations in THF and in benzene were carried out by using *n*-BuLi, Na-naphthalene, Na- and K-dispersions. All of the copolymers were powders with a softening point of *ca.* 130°C, except for the viscous copolymer obtained in benzene by *n*-BuLi. The copolymer composition, $[m_1]/[m_2]$, was calculated from the polymer yield, as the butadiene was completely incorporated into the copolymer. Some of the results are shown in Table 1. The composition was checked by

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[1] H. Yuki and Y. Okamoto, This Bulletin, **42**, 1644 (1969).

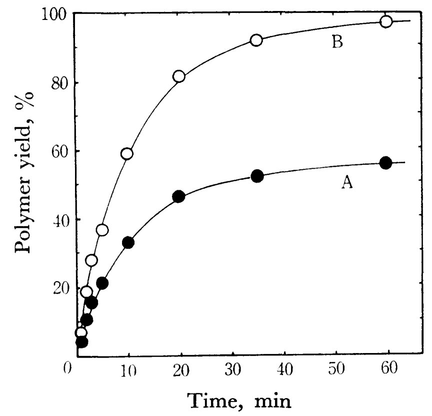

Fig. 1. Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2)——Time *vs.* polymer yield.
A: Polymer yield based on total monomers.
B: Polymer yield based on an alternating copolymerization.
$[M_1]_0=5.74$ mmol; $[M_2]_0=11.39$ mmol; [*n*-BuLi]=0.11 mmol; THF=15.0 m*l*; temp., 0°C

TABLE 1. ANIONIC COPOLYMERIZATION OF BUTADIENE (M_1) AND 1,1-DIPHENYLETHYLENE (M_2)—MATERIAL BALANCE
M_1, 0.302 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	24	0.949	1.07	1.182	0.064	1.15
THF	48	1.009	1.00	1.226	0.096	1.09
THF	48	1.328	0.758	1.254	0.382	1.06
Benzene	96	0.596	1.68	0.344	0.534	23.2
Benzene	120	0.924	1.08	0.372	0.826	14.2
Benzene	96	1.348	0.744	0.394	1.242	10.8

a) Contained *ca.* 7 mg of lithium compounds.
b) Copolymer composition.

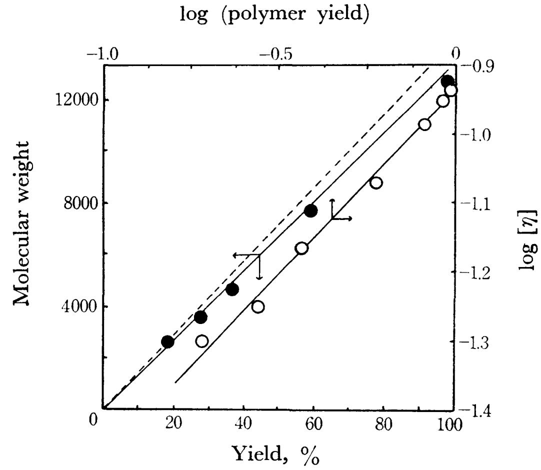

Fig. 2. Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2).
Relationships between polymer yield and molecular weight, and between polymer yield and intrinsic viscosity.
Dotted line: Molecular weight calculated for living polymerization.
Reaction conditions are shown in Fig. 1.

elementary analysis and NMR spectroscopy. The results are listed in Table 2. The data supported the composition shown in Table 1. The monomer reactivity ratio, r_1, was calculated by means of the integrated Mayo-Lewis copolymer composition equation.[2] The r_1 values are shown in Tables 3 and 4. In THF at 0°C, the values were almost constant, regardless of the initiators used. Although it has been shown that $NaB(Ph)_4$ depresses the dissociation of an ion to free ions,[3] the r_1 value was not affected by the presence of $NaB(Ph)_4$ in the copolymerization initiated by Na-naphthalene in THF. In benzene at 40°C, however, the values were 54, 0.71, and 0.10 with *n*-BuLi, Na-, and K-dispersions respectively. The copolymerization carried out in benzene without an initiator gave

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

Solvent 15 m*l*	Initiator	$[m_1]/[m_2]$[a]	Elementary analysis Calcd[b] C,%	Calcd[b] H,%	Found C,%	Found H,%	NMR $[m_1]/[m_2]$
THF	*n*-BuLi	1.00	92.26	7.74	92.00	7.70	0.97
Benzene	K-dispersion	1.08	92.20	7.80	92.03	7.69	1.05
Benzene	Na-dispersion	1.50	91.98	8.02	91.75	7.85	1.40
Benzene	*n*-BuLi	10.8	89.80	10.20	89.60	9.82	9.50

a) Copolymer composition calculated from polymer yield.
b) Based on the copolymer composition.
c) Copolymer composition obtained from NMR spectrum.

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

3) D. N. Bhattacharyya, C. L. Lee, J. Smid and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965); H. Hostalka and G. V. Schulz, *J. Polym. Sci.*, **B3**, 175 (1965).

TABLE 3. ANIONIC COPOLYMERIZATION OF BUTADIENE (M_1) AND 1,1-DIPHENYLETHYLENE (M_2)—MONOMER REACTIVITY RATIO, r_1, DETERMINED WITH *n*-BuLi IN THF AT 0°C (A) AND WITH Na-DISPERSION IN BENZENE AT 4 C (B)[a)]

Run No.	$[M_1]_0/[M_2]_0$	Time hr	Yield mol%	$[m_1]/[m_2]$[b)]	η_{sp}/C	r_1
A	1.065	24	96.4	1.15	—	0.17
A	1.000	48	94.1	1.09	—	0.17
A	0.833	24	88.7	1.05	—	0.10
A	0.758	48	83.9	1.06	—	0.12
A	0.731	24	82.3	1.05	—	0.11
A	0.508	18	66.1	1.04	—	0.10
					Average	0.13
B	1.046	187	85.2	1.50	0.50	0.79
B	0.961	187	83.3	1.42	0.52	0.70
B	0.929	187	83.2	1.38	0.74	0.71
B	0.814	187	78.2	1.35	0.42	0.75
B	0.724	187	75.7	1.25	0.68	0.61
					Average	0.71
B[c)]	0.976	187	0	—	—	—

a) $[M_1]_0$, 5.6 mmol; solvent, 15 m*l*; *n*-BuLi, 0.11 mmol; Na-dispersion, *ca.* 0.5×10^{-3} atom; temp, 0°C
b) Copolymer composition
c) Without initiator

TABLE 4. ANIONIC COPOLYMERIZATION OF BUTADIENE (M_1) AND 1,1-DIPHENYLETHYLENE (M_2)—MONOMER REACTIVITY RATIO, r_1

Solvent	Initiator	Temp. °C	Run of experiment	r_1
THF	*n*-BuLi	0	6	0.13
THF	Na-naph.	0	6	0.09
THF	K-dispersion	0	5	0.09
Benzene	*n*-BuLi	40	5	54
Benzene	Na-dispersion	40	5	0.71
Benzene	K-dispersion	40	5	0.10

no polymer, even after 187 hr at 40°C (Table 3). With Li^+ as a counter ion, the r_1 value was strongly influenced by the solvent; with Na^+ and K^+, less influence of the solvent was observed (Table 4).

The microstructures of butadiene in the homopolymer and in the alternating copolymer were investigated by NMR spectroscopy. Figure 3 shows the spectrum of the alternating copolymer obtained with *n*-BuLi in THF. The polybutadiene obtained by *n*-BuLi in THF had 82% 1,2- and 18% 1,4-structures, while the alternating copolymer had 30% 1,2- and 70% 1,4-structures.

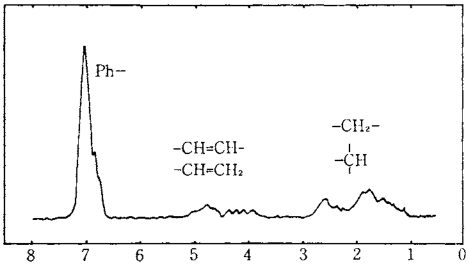

Fig. 3. NMR spectrum of the alternating copolymer of butadiene and 1,1-diphenylethylene. (in CCl_4 at 60°C)

The copolymerization in THF at 0°C was followed spectrophotometrically. As soon as *n*-BuLi was added to a monomer solution at $[M_1]_0/[M_2]_0=0.53$, an absorption maximum due to a diphenylethylene anion appeared at 496 mμ. Its optical density had been almost constant for 5 hr, in which time the polymerization had been completed. The molar extinction coefficient was 1.7×10^4; this agrees the value found in the copolymerization of isoprene and 1,1-diphenylethylene.[1)] These results suggest that almost all of the living ends in the system were 1,1-diphenylethylene anions.

Discussion

The results of the copolymerization investigated in this work were very similar to those found in the copolymerization of isoprene and 1,1-diphenylethylene.[1)] Both the copolymerizations in THF proceeded in living systems to give alternating copolymers, and all the r_1 values determined under the same reaction conditions were very similar. The rate of the consumption of butadiene was first-order with respect to its own concentration, as is shown in Fig. 4; this figure was obtained by analyzing the results in Fig. 1. This means that the reverse reaction between the 1,1-diphenylethylene anion and butadiene can be disregarded.[1)]

$$\sim\sim M_2^- + M_1 \underset{k_{-21}}{\overset{k_{21}}{\rightleftarrows}} \sim\sim M_1^-$$

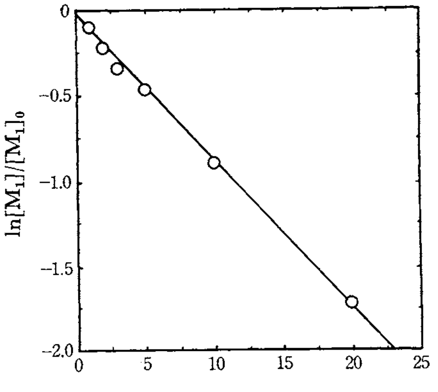

Fig. 4. Anionic copolymerization of butadiene (M_1) and 1,1-diphenylethylene (M_2)—First order plot. Reaction conditions are shown in Fig. 1.

From Fig. 4, we can get $k_{21}=0.27\text{M}^{-1}\text{sec}^{-1}$. Various rate constants determined in the copolymerizations in THF employing methyl derivatives of butadiene as a component are collected in Table 5. The reactivities (k_{21}) of the dienes decreased with an increase in the methyl group. The retarding effect of the group, however, was different for two living ends, the styryl anion and the diphenylethylene anion, indicating that the steric effect also affects the reactivities of the dienes. As to the reactivity of the anion (k_{12}), the isoprenyl anion should be more reactive as a result of the electron-donating effect of the methyl group. However, the butadienyl anion was more reactive to 1,1-diphenylethylene than the isoprenyl anion. This must also be caused by the steric factor. Similar results were reported in the addition reactions of styrene to styryl and α-methylstyryl anions, in which the styryl anion was more reactive.[9)]

TABLE 5. RATE CONSTANT IN THF

Diene	k_{11} $\text{M}^{-1}\text{sec}^{-1}$	k_{21}, $\text{M}^{-1}\text{sec}^{-1}$		k_{12}[e)] $\text{M}^{-1}\cdot\text{sec}^{-1}$
		M_2=DPE	M_2=Styrene	
Butadiene	0.59[a)]	0.27[b)]	3.27×10[d)]	4.5
Isoprene	3.8×10^{-2} [a)]	2.6×10^{-3} [b)]	1.7×10[d)]	0.35
2,3-Dimethyl-butadiene	1.4×10^{-3} [c)]	1.6×10^{-3} [c)]	4.8×10^{-1} [d)]	—

a) Li, 0°C, Refs. 7 and 8.
b) Li, 0°C, this work and Ref. 1.
c) Li, 22°C, Ref. 4.
d) Na, 25°C, Ref. 6.
e) This was obtained from r_1 in Table 6 and k_{11}.

The monomer reactivity ratios, r_1, obtained in the copolymerizations of 1,1-diphenylethylene (M_2) and conjugated dienes (M_1) by means of *n*-BuLi are summarized in Table 6. In THF, 1,1-diphenylethylene is more reactive to the M_1 anion than the corresponding M_1 monomer. In benzene, however, isoprene and butadiene are more reactive than 1,1-diphenylethylene. The effects of the solvent and initiator in Tables 4 and 6 suggest that the r_1 value may increase with a decrease in the polarity of the carbon-metal bond.

TABLE 6. MONOMER REACTIVITY RATIO, r_1, IN THE COPOLYMERIZATIONS OF 1,1- DIPHENYLETHYLENE (M_2) AND DIENES (M_1) BY *n*-BuLi

M_1	THF[a)]	Benzene[b)]	Ref.
Butadiene	0.13	54	This work
Isoprene	0.11	37	1
2,3-Dimethylbutadiene	~0[c)]	0.23	4,5

a) at 0°C b) at 40°C c) at 22°C

The microstructures of butadiene, isoprene, and 2,3-dimethylbutadiene in the homopolymers and in the alternating copolymers with 1,1-diphenylethylene are summarized in Table 7; all of the polymers were formed in THF by means of *n*-BuLi. The 1,4-structure was greater in the alternating copolymer than in the homopolymers, and the order of the content of the 1,4-structure was 2,3-dimethylbutadiene>isoprene>butadiene. In the alternating copolymer of 2,3-dimethylbutadiene and 1,1-diphenylethylene, no 1,2-structure was present because of its big steric hindrance. However, in the case of the butadiene-diphenylethylene alternating copolymer, the 1,2-structure existed because of its lower steric hindrance. These results suggest that the microstructure of the dienes in the alternating copolymer is controlled strongly by the steric effect. In orther words, the effect must affect the rate constant, k_{12}, as has been described above.

TABLE 7. MICROSTRUCTURES OF THE DIENES IN THE HOMOPOLYMERS AND THE ALTERNATING COPOLYMERS OBTAINED IN THE POLYMERIZATION BY *n*-BuLi IN THF

Diene	Homopolymer, %			Alternating oopolymer, %		
	1,2-	1,4-	3,4-	1,2-	1,4-	3,4-
Butadiene	82	18	—	30	70	—
Isoprene	29	~0	71	~0	83	17
2,3-Dimethylbutadiene	49	51	—	0	100	—

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