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Anionic Copolymerization of 2,3-Dimethylbutadiene and 1,1-Diphenylethylene with *n*-Butyllithium in Benzene

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Anionic copolymerization of 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) by *n*-butyllithium (*n*-BuLi) in tetrahydrofuran (THF) has been studied by means of NMR spectroscopy,[1] in which the rates of consumptions of the two monomers were followed. The copolymerization proceeded alternately, when the initial molar ratio of the monomers, $[M_1]_0/[M_2]_0$, was less than unity. In the present study, the copolymerization of the same monomer pair is investigated in benzene at 40°C with *n*-BuLi as an initiator.

Experimental

Meterials. 2,3-Dimethylbutadiene was synthesized by the dehydration of pinacol.[2] The monomer purified by fractional distillation was redistilled *in vacuo* from lithium aluminum hydride. Bp 69°C/760 mmHg, n_D^{20} 1.4360.

1,1-Diphenylethylene prepared from diphenylmethyl carbinol[3] was first treated with a small amount of Na-K alloy and distilled. Bp 115°C/3 mmHg, n_D^{20} 1.6085. Then *n*-BuLi was added to the monomer until the red color of its anion appeared. The monomer was redistilled from the colored mixture *in vacuo*.

Benzene purified by the usual method was redistilled in the presence of a small amount of *n*-BuLi under high vacuum before use.

n-BuLi was prepared in *n*-heptane according to the method of Ziegler.[4]

Polymerization. Copolymerization was carried out in a glass ampoule which had been previously heated with a gas burner *in vacuo*. Benzene and 2,3-dimethylbutadiene were transferred to the ampoule on a vacuum line, and then 1,1-diphenylethylene and *n*-BuLi were added with hypodermic syringes under dry nitrogen. The copolymerization was terminated by adding methanol. The polymer precipitated in methanol was filtrated, washed with methanol, and dried.

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

Results and Discussion

The copolymerization of 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) by *n*-BuLi was followed in benzene at 40°C, the initial molar ratio of M_1 to M_2 being 0.683. The results are shown in Fig. 1. The copolymerization proceeded slowly to reach a constant polymer yield in about 50hr. In this period 2,3-dimethylbutadiene was completely consumed and only unchanged 1,1-diphenylethylene remained in the system. The softening point of the copolymer was about 135°C.

In Fig. 2 the plot of $\log[\eta]$ *vs.* log yield of polymer is shown. The linear relationship suggests that the

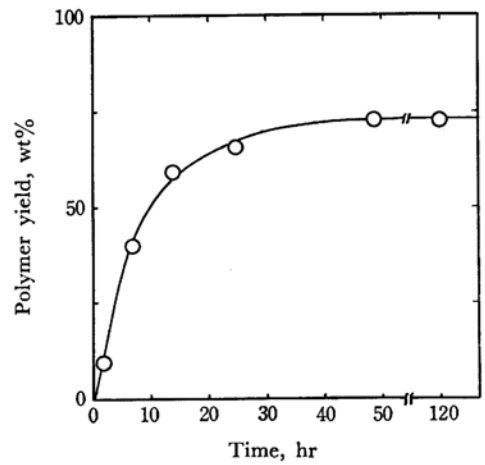

Fig. 1. Anionic copolymerization of 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) in benzene by *n*-BuLi.——Time *vs.* polymer yield. Total monomer: 9.89 mmol, $[M_1]_0/[M_2]_0$: 0.683, benzene: 15.0 ml, *n*-BuLi: 0.090 mmol, temp.: 40°C

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2) C. F. H. Allen and A. Bell, "Organic Syntheses," Coll. Vol. III, p. 312 (1955).
3) C. F. H. Allen and S. Converse, *ibid.*, Coll. Vol. I, p. 226 (1956).
4) K. Ziegler and A. Colonius, *Ann.*, **479**, 135 (1930).

TABLE 1. ANIONIC COPOLYMERIZATION OF 2,3-DIMETHYLBUTADIENE (M_1) AND 1,1-DIPHENYLETHYLENE (M_2) IN BENZENE BY *n*-BuLi

Benzene: 15.0 ml, *n*-BuLi: *ca.* 1 mol% against total monomers, temp., 40°C, time: 96—140 hr.

M_1 g	M_2 g	$[M_1]_0/[M_2]_0$ mol/mol	Polymer g	Yield mol%	Unchanged M_2, g	$[m_1]/[m_2]$[a] mol/mol	r_1
0.405	0.873	1.017	1.150	92.7	0.127	1.19	0.25
0.335	0.776	0.960	0.978	91.8	0.210	1.14	0.21
0.405	0.960	0.925	1.081	90.0	0.284	1.18	0.27
0.405	0.976	0.910	1.099	89.3	0.189	1.14	0.22
0.405	1.057	0.840	1.190	85.8	0.265	1.14	0.23
0.269	0.848	0.694	0.810	76.1	0.178	1.09	0.18

a) Molar ratio of monomers in the copolymer. Average 0.23

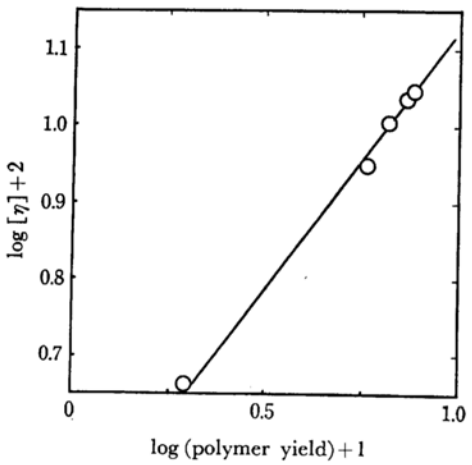

Fig. 2. Anionic copolymerization of 2,3-dimethylbutadiene (M_1) and 1,1-diphenylethylene (M_2) in benzene by *n*-BuLi.——Relationship between polymer yield and viscosity of polymer.

copolymerization proceeded without a termination and a chain transfer, probably to give a living polymer.

The copolymerization was carried out for a prolonged time and the material balance was checked in order to confirm the complete consumption of the M_1 monomer. The results are listed in Table 1. It was found that the total amount of the monomers charged, M_1+M_2 (g), was substantially equal to the sum of the polymer obtained and the unchanged M_2 monomer recovered from the mother liquor of the polymer precipitation. This fact means that 2,3-dimethylbutadiene was completely incorporated into the copolymer. The molar ratio of the monomers in the copolymer, $[m_1]/[m_2]$, can then be calculated from the polymer yield. The $[m_1]/[m_2]$ ratio decreased with a decrease in the ratio of the charged monomers, $[M_1]_0/[M_2]_0$.

The monomer reactivity ratio, r_1, is obtained by means of the integrated copolymer composition equation, assuming that the M_2 monomer does not homopolymerize and the M_1 monomer has been completely consumed.[5] The r_1 values are shown in Table 1. As a mean value, 0.23 was obtained. This indicated that 1,1-diphenylethylene is more reactive to 2, 3-dimethylbutadienyl anion than 2,3-dimethylbutadiene. In the copolymerization in THF, the r_1 value was almost zero and an alternating copolymer was obtained, when the $[M_1]_0/[M_2]_0$ ratio was less than unity.

In the copolymerizations of styrene and butadiene,[6] styrene and isoprene,[7] and 1,1-diphenylethylene (M_2) and isoprene (M_1)[8] by lithium catalysts, greater relative reactivities of conjugated dienes than the comonomers have been found in a nonpolar solvent, contrary to the less reactivities in a polar solvent. In the last pair of monomers, the r_1 values were 0.13 in THF and 37 in benzene. The relative reactivities of the two monomers against isoprene anion reversed in these two solvents. In the copolymerization of 2,3-dimethylbutadiene and 1, 1-diphenylethylene, the latter was always more reactive in both THF and benzene.

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6) I. Kuntz, *J. Polymer Sci.*, **54**, 569 (1961).
7) A. V. Tobolsky and C. E. Rogers, *ibid.*, **38**, 205 (1959).
8) H. Yuki and Y. Okamoto, This Bulletin, **42**, 1644 (1969).