Polymerization of Olefins with Trialkylboron Catalyst. III. Copolymerization of Butadiene, Isobutylene and 1-Phenylbutadiene

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As is well known, the monomers having comparatively large polarity easily polymerize with alkylboron catalyst, but those having small polarity do not. The polymerizations of the monomers which polymerize alone, and the copolymerizations of those monomers have already been reported[1,2]. In this paper, the copolymerizations of some monomers which exhibit no tendency to polymerize alone, such as butadiene, isobutylene, and 1-phenylbutadiene were studied. In every pair of the monomers treated in this paper, the copolymerization rates were very small. Particularly, the reaction rate of 1-phenylbutadiene with another monomer was so small that the relative reactivity could not be obtained. The relative reactivities of such pairs as isobutylene-acrylonitrile, butadiene-styrene and butadiene-acrylonitrile were obtained.

Experimental and Results

1. Monomers.—*1*) *Isobutylene and butadiene.*—Isobutylene[3] was prepared by dehydration of *tert*-butanol with anhydrous oxalic acid at about 90°C, dried over calcium chloride, and redistilled. Butadiene was prepared according to Blatt's method[4], i. e., thermal decomposition of cyclohexene, dried over calcium chloride, and redistilled.

2) *Acrylonitrile, styrene and methyl methacrylate.*—The commercial substances were dried and distilled just before use.

3) *1-Phenylbutadiene.* — This was synthesized

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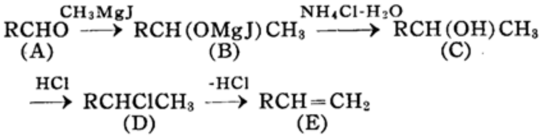
[1] N. Ashikari, This Bulletin, **31**, 229 (1958).

[2] N. Ashikari, *J. Polymer Sci.*, **31**, 249 (1958).

[3] N. Daidan et al., *J. Electrochem. Soc. Japan* (*Denki Kagaku*), **13**, 27 (1945).

[4] A. H. Blatt et al., "Organic Syntheses", Col. Vol. II, John Wiley & Sons, Inc., New York (1943) p. 655.

from cinnamic aldehyde by the following method[5,6]:



$$\underset{(A)}{RCHO} \xrightarrow{CH_3MgJ} \underset{(B)}{RCH(OMgJ)CH_3} \xrightarrow{NH_4Cl\text{-}H_2O} \underset{(C)}{RCH(OH)CH_3} \xrightarrow{HCl} \underset{(D)}{RCHClCH_3} \xrightarrow{-HCl} \underset{(E)}{RCH=CH_2}$$

Where, R is $C_6H_5CH=CH-$.

D was prepared by treating C with dry hydrogen chloride at 0°C, and E was prepared by heating D in pyridin solvent for about one hour. After the reaction was over, unchanged pyridin was distilled off, and the product was washed thoroughly with water to remove the complex of pyridin-hydrogen chloride. Then, the product was dried over calcium chloride and distilled. The yield of pure 1-phenylbutadiene boiling at 56~57°C/3 mmHg was 17~20% of the theoretical amount for cinnamic aldehyde.

II. Procedure of the Copolymerization and the Treatment of the Polymer.—In a polymerization tube, a certain amount of high-boiling monomer such as styrene or acrylonitrile was placed, and the tube was cooled in dry ice-methanol. After the content was thoroughly cooled, the tube was placed on a balance, and a certain amount of second monomer, liquefied by cooling, such as isobutylene or butadiene was poured into the tube. Then, the catalyst, triisobutylboron was added to the tube under nitrogen stream, and the tube was sealed.

The reaction was stopped by cooling the tube in dry ice-methanol. After the tube was opened, the polymer was precipitated by adding the content of the tube into methanol, filtered, dried under reduced pressure at 50°C, and weighed. If the copolymerization was carried out in emulsion system, the polymer was taken out by treating the content with hot water (about 90°C) containing 5% sodium chloride. Thus, the polymer isolated was washed thoroughly with hot water, followed with methanol, dried and weighed.

III. Copolymerization Rates of Butadiene-acrylonitrile in the Bulk and Emulsion Systems.—The copolymerization rate of butadiene-acrylonitrile in emulsion system was compared with that in bulk system.

Generally, the polymerization rate in emulsion system is larger than that in bulk system. In this experiment, the same results were obtained. Moreover, in emulsion system, fairly strong copolymer was obtained.

The total weight of the two monomers in each pair was 11.3 g., and the volume of the catalyst was 0.1 cc. in each experiment. In emulsion system, 12 cc. of distilled water containing 5% emulsifier was used. Each reaction was carried out in a sealed tube at 40°C for five hours. The relation between the conversion and the mole fraction of butadiene in the monomer mixture is shown in Fig. 1.

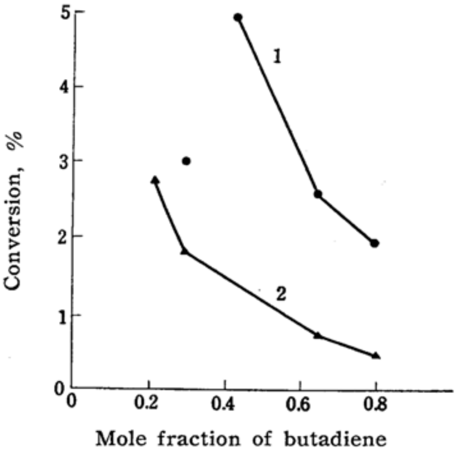


Fig. 1. Copolymerization rates of butadiene-styrene in bulk and emulsion system.
(1) emulsion system
(2) bulk system

IV. Monomer Reactivity Ratios.—The relative reactivities (r_1, r_2) of such pairs as isobutylene-acrylonitrile, butadiene-styrene, and butadiene-acrylonitrile were evaluated graphically using the following equation[7]:

$$r_2 = \frac{\log([M_2]_0/[M_2]) - \frac{1}{p}\log\frac{1-p[M_1]/[M_2]}{1-p[M_1]_0/[M_2]_0}}{\log([M_1]_0/[M_1]) + \log\frac{1-p[M_1]/[M_2]}{1-p[M_1]_0/[M_{02}]}}$$

where $p=(1-r_1)/(1-r_2)$, $[M]_0$ and $[M]$ represent the monomer concentration in the intitial and final states of polymerization, respectively,

TABLE I. ISOBUTYLENE-ACRYLONITRILE

No.	$[M_1]_0$	$[M_2]_0$	Conversion	N%	$[M_1]$	$[M_2]$
1	0.179	0.02	3.44	13.8	0.1757	0.0163
2	0.166	0.04	3.72	14.6	0.1626	0.0356
3	0.179	0.06	3.96	15.2	0.1750	0.0543
4	0.125	0.08	4.77	17.6	0.1218	0.0733
5	0.100	0.10	5.53	18.0	0.0966	0.0923
6	0.116	0.12	5.54	18.7	0.1123	0.1105
7	0.061	0.14	9.02	21.1	0.0575	0.1253
8	0.054	0.18	8.26	21.9	0.0509	0.1638

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[5] E. C. Coyner and G. A. Ropp, *J. Am. Chem. Soc.*, **69**, 2231 (1947).

[6] A. Klages, *Ber.*, **35**, 2650 (1902).

[7] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 207 (1950).

TABLE II. BUTADIENE-ACRYLONITRILE

No.	$[M_1]_0$	$[M_2]_0$	Conversion	N%	$[M_1]$	$[M_2]$
1	0.0500	0.4490	4.45	15.46	0.04094	0.43599
2	0.1000	0.4000	3.81	13.57	0.09088	0.39019
3	0.0759	0.1755	3.82	12.73	0.07101	0.17084
4	0.1000	0.1509	0.64	11.98	0.09914	0.15017
5	0.2000	0.2000	2.26	11.18	0.19484	0.19614
6	0.2000	0.0509	1.78	8.06	0.19691	0.04951

TABLE III. BUTADIENE-STYRENE

No.	$[M_1]_0$	$[M_2]_0$	Conversion	C%	$[M_1]$	$[M_2]$
1	0.0315	0.200	4.28	90.96	0.02447	0.19439
2	0.0472	0.175	2.99	91.14	0.04512	0.17107
3	0.0631	0.150	2.32	90.78	0.05925	0.14770
4	0.1000	0.100	1.45	89.04	0.09607	0.09983
5	0.0944	0.100	2.01	89.68	0.08996	0.09931
6	0.2202	0.150	1.34	89.20	0.21399	0.14968

and subscripts 1 and 2 mean that the corresponding quantities are concerned with components 1 and 2, respectively.

The values of $[M_1]$, $[M_2]$, conversion, etc., are shown in Tables I—III.

The relative reactivities (r_1, r_2) are shown in Table IV. Table V shows the values in the case of radical type determined by other investigators[8].

TABLE IV. RELATIVE REACTIVITIES

	iB-AN	Bd-AN	Bd-St
r_1	0.02±0.02	0.40±0.02	1.30±0.1
r_2	1.8 ±0.2	0.04±0.01	0.01±0.01
T	50	50	43

iB: isobutylene, AN: acrylonitrile,
Bd: butadiene, T: reaction temp. (°C)

TABLE V. THE VALUES OF (r_1, r_2) REPORTED ON EARLIER PAPER

	Bd-AN	Bd-St
r_1	0.35±0.01	1.48±0.08
r_2	0.05±0.01	0.23±0.07
T	50	50

V. Infrared Spectra and Turbidity Measurement of 1-Phenylbutadiene—Methyl Methacrylate Copolymer.—It had not been clear whether 1-phenylbutadiene enters into a copolymerization reaction or not. In this respect, the copolymerization of this monomer with methyl methacrylate was carried out to make this point clear. As previously mentioned, 1-phenylbutadiene does not polymerize alone with organo boron catalyst, but does thermally. Therefore, even if the two components are present in the product, it does not always mean a copolymer. For the purpose of looking over the product, infrared spectra and turbidity measurement of the product were employed.

V-1) Copolymerization of 1-phenylbutadiene with methyl methacrylate.—The monomer mixture (feed 1 : 1) consisted of 1-phenylbutadiene and methyl methacrylate (0.0237 mol.) was polymerized with 0.1 cc. of triisobutylboron catalyst in a sealed tube at 50°C for 15 hr. The product precipitated with methanol was redissolved in benzene and precipitated with methanol two times. Thus, 0.0702 g. of the polymer was obtained (conversion: 1.3%).

V-2) Infrared spectra.—The infrared spectrum of the sample obtained above was observed in

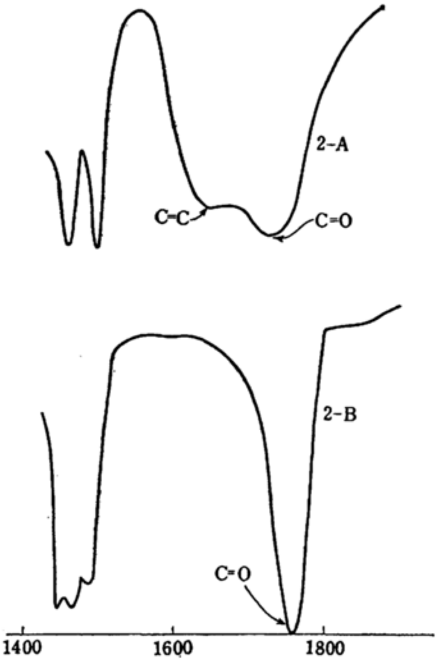

Fig. 2. Infrared spectra of phenylbutadiene-methyl methacrylate copolymer and polymethyl methacrylate.
A, 1-Phenylbutadiene—methyl methacrylate copolymer
B, Polymethyl methacrylate

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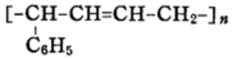
[8] T. Alfrey, J. J. Bohrer and H. Mark, "High Polymers", Vol. VIII, "Copolymerization" Interscience Publishers, Inc., New York (1952), p. 32, 44.

order to confirm the presence of the two components. Fig. 2-A is the spectrum of the sample, and Fig. 2-B is that of polymethyl methacrylate prepared with alkylboron catalyst.

Comparing A with B, it is clear that the product obtained in paragraph V-1 is not identical with polymethyl methacrylate. In Fig. 2-A, the absorption band at about 1650 cm^{-1} owes to C=C, and the band at about 1740 cm^{-1} owes to C=O of methyl methacrylate. Of course, the absorption band of C=C indicates the existence of poly-(1-phenylbutadiene) shown below.

poly(1-phenylbutadiene):



$$[\text{-}\underset{\displaystyle C_6H_5}{CH}\text{-}CH{=}CH\text{-}CH_2\text{-}]_n$$

V-3) *Measurement of turbidity.* — The sample obtained in paragraph V-1 was dissolved in 200 cc. of acetone and the turbidity was measured utilizing a nephelo-titrator. The same measurements were carried out with thermally polymerized 1-phenylbutadiene and polymethyl methacrylate prepared with alkylboron catalyst.

In every case, the condition of the measurement was as follows: solvent, acetone; nonsolvent, distilled water; concentration, 0.0070%; temperature, 25°C. These results are represented in Fig. 3.

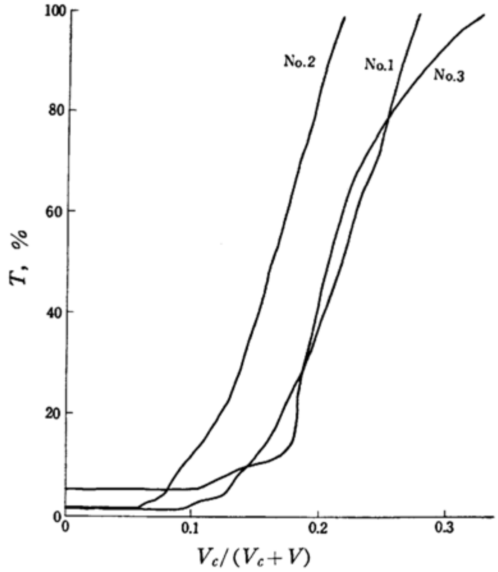


Fig. 3. Diagram of $T-V_c/(V_c+V)$.
T: turbidity, V_c: volume of water,
V: volume of acetone.
No. 1, Copolymer
No. 2, Phenylbutadiene
No. 3, Methyl methacrylate

Comparing No. 1 with No. 2 and 3 in Fig. 3, it may be considered that 1-phenylbutadiene copolymerizes with methyl methacrylate.

Discussion

Diagram of $T-V_c/(V_c+V)$.—If the product (1-phenylbutadiene-methyl methacrylate) is a mixture of the two components, the influence of 1-phenylbutadiene must be more striking around the bottom of No. 1 in Fig. 3. Moreover, the product is a low polymer, so that when it contains the greater part of polymethyl methacrylate, the bottom of No. 1 must be situated on the right side of No. 3. From the viewpoint mentioned above, the product obtained in paragraph V-1 may be considered as a copolymer.

The Relative Reactivities.—The following methods have been employed for obtaining the composition in a copolymer which consists of C and H atoms:

a) from analytical value of C atoms,
b) from refractive index,
c) from ultraviolet absorption.

Any method will contain more or less errors. In this respect, a) is, particularly, apt to contain an error.

Therefore, some questions will be present in the relative reactivity in the copolymerization of butadiene-styrene, reported in this paper. In this respect, the other methods will be employed to the butadiene-styrene copolymer.

As is well known, the mechanism of the polymerization with alkylboron catalyst is a radical type. The propriety of the mechanism is proved in this paper also, comparing the values of the relative reactivities obtained in this experiment with those in the copolymerization with peroxide catalyst.

Summary

The relative reactivities in the copolymerization of some monomers which do not polymerize alone with alkylboron catalyst, with those which polymerize alone, were obtained. The copolymerization rate of 1-phenylbutadiene with another monomer was so small that the relative reactivity could not be obtained. But, from the studies on the reaction product of 1-phenylbutadiene and methyl methacrylate, it was considered that the former copolymerized with the latter.

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