Polymerization of Olefins with Trialkylboron Catalysts. I. Polymerization of Vinylchloride and Acrylonitrile

By Nobuyuki ASHIKARI

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Since the discovery of Ziegler's catalyst, organometallic compounds have been studied by many investigators. Recently, Kolesnikov[1] studied the polymerization of acrylonitrile with a mixed catalyst of tributylboron and borontrifluoride. However, there are few studies on the polymerization with trialkylboron catalyst only.

The author studied the polymerization of olefins with trialkylborons, and found that they are excellent catalysts to some olefins such as acrylonitrile, vinylchloride, vinylacetate and styrene.

Reaction mechanism of trialkylalminium catalyst to ethylene has been considered as[2],

$$\mathrm{Ral}+n(\mathrm{CH_2{=}CH_2}) \rightarrow \mathrm{R(CH_2{-}CH_2)}_n\mathrm{{-}al}$$
$$\text{where,} \quad \mathrm{al}=1/3\mathrm{Al}$$

Similarly, in the case of trialkylboron catalyst, an anionic reaction can be considered in some cases. But in other cases, a radical reaction also can be considered.

Experimental and Results

1. On some trialkylborons. — There are several methods of preparation of trialkylboron, and the author adopted the common method, i.e., the reaction of Grignard reagent and borontrifluoride-etherate in ether.

The catalysts prepared in this experiment are triethyl-, tri-*iso*-propyl-, and tri-*iso*-butylboron. Triethylboron was prepared by dropping borontrifluoride-etherate into cooled ether solution of ethylmagnesiumbromide. After the reaction was over, the ether solution was distilled.

Thus, from the Grignard reagent prepared with 24 g. (1 mol.) of magnesium and 40 g. (0.28 mol.) of borontrifluoride-etherate, 22 g. of triethylboron was obtained. The yield to magnesium used was 67%.

Similarly, tri-*iso*-propyl- and tri-*iso*-butylboron were prepared from borontrifluoride-etherate and the corresponding alkylmagnesiumbromide.

Tri-*iso*-butylboron (b. p. 188°C) is very stable even in water, so that it can be used in the emulsion system. Tri-*iso*-propylboron (b. p. 150°C) fumes but does not flame in the air. Triethylboron is very flamable in the air so that it was diluted with hexane or toluene when it was used.

2. Polymerization of vinylchloride.— Vinylchloride has large polarity, and it can be polymerized very easily. The reaction proceeded slowly at −60°C, and rapidly at room temperature. Usually, the product was colorless except in cases when the reaction was carried out in tetrahydrofuran or cyclohexanon.

2.1 Bulk polymerization of vinylchloride.—Since the rate of reaction in the beginning of the polymerization was very great it was easy to obtain up to about 50 per cent. conversion. However, it was fairly difficult to obtain more than 50 per cent. conversion, because the rate of polymerization dropped.

The monomer whose amount is shown in Table I, with 0.1225 g. of triethylboron was sealed in a glass tube under a nitrogen stream. The reaction was carried out at 50°C for five hours. The solution became to solidify within three hours after the reaction occurred. After five hours the sealed tube was opened and the polymer was poured into ethanol, filtered, dried under reduced pressure at 50°C, and weighed. The results are shown in Table I.

TABLE I

BULK POLYMERIZATION OF VINYLCHLORIDE

exp. No.	monomer (g.)	polymer (g.)	Yield (%)
VCB-1	10	2.8795	28.80
VCB-2	15	4.7273	31.52
VCB-3	20	6.9894	34.95
VCB-4	25	8.6975	34.79
VCB-5	30	10.8695	36.23
VCB-6	35	16.8486	48.14

2.2 Solution polymerization.—To look over the rate of polymerization of vinylchloride in alcohol solvent, the author did the following experiment.

Vinylchloride (10 g., 0.16 mol.) was polymerized with 0.148 g. (0.00075 mol.) of tri-*iso*-butylboron catalyst in 30 cc. of ethanol. The reaction was carried out in a sealed tube at 35°C. Each sealed

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1) G. S. Kolesnikov and L. S. Fedorova, *Izv. An. USSR*, No. 2, 236 (1957).

2) K. Ziegler and E. Holzkamp, *Angew. Chem.*, **67**, 543 (1955).

tube was opened after a certain time, and the polymer was separated by filtration. Then, the polymer was dried and weighed. The results are shown in Fig. 1.

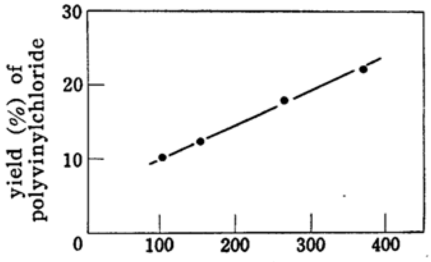

Fig. 1. Relation between the yield and the reaction time.

Vinylchloride also polymerized in tetrahydrofuran or cyclohexanon. In these solvents the product was colored. On account of the reaction system being homogenious, in tetrahydrofuran, the reaction proceeded smoothly.

The monomer (25 g.) was polymerized with 0.1225 g. of triethylboron in 25 g. of tetrahydrofuran at 50°C, for eight hours, and 12.444 g. of the polymer was obtained. The yield was 49.78%.

2.3 Emulsion polymerization.—In emulsion polymerization of vinylchloride the reaction proceeded rapidly. Of course, the rate of polymerization is varied by the concentration of catalyst. Fig. 2 represents the relation between the yield and the concentration of catalyst.

In this experiment, the monomer (20 g.) was polymerized with a certain weight of tri-*iso*-butylboron catalyst in 20 g. of aqueous solution containing 1 g. of emulsifier at 40°C in a sealed tube. After four hours, each sealed tube was opened and the solution was treated with five per cent. aqueous sodium chloride solution. Then the polymer was separated, filtered, washed throughly with water, dried and weighed.

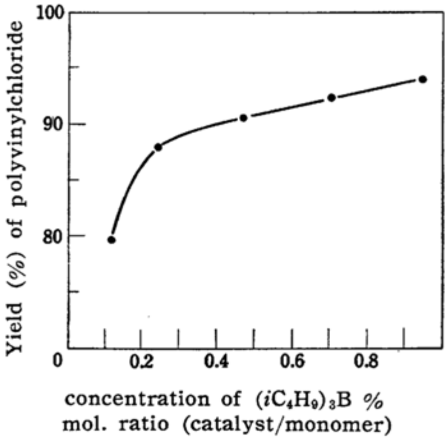

Fig. 2. Relation between the yield and the concentration of catalyst.

2.4 Influence of addition of titaniumtetrachloride.—As is well known, in the polymerization of ethylen, the mixed catalyst of trialkylaluminum and titaniumtetrachloride is used.

Similarly, an experiment using the mixted catalyst of trialkylboron and titaniumtetrachloride for the polymerization of vinylchloride was done, i.e., the monomer (20 g.) and the mixed catalyst consisting of 0.07 g. of tri-*iso*-butylboron and 0.05 g. of titaniumtetrachloride were sealed and maintained at 30°C. After one month, only 7.4 g. of polymer was obtained. Therefore, it is considered that the addition of titaniumtetrachloride to trialkylboron drops the rate of polymerization.

2.5 Measurement of molecular weight of polyvinylchloride.—Each sample got in the experiments of Table I was dissolved in cyclohexanon and the viscosity was measured at 30°C with Ubbelohde viscometer. The specific viscosity by concentration (η_{sp}/C) is represented in Fig. 3.

From Fig. 3, the intrinsic viscosity is 0.275–0.620. Therefore, the weight-average molecular weight calculated from Nakajima's equation[3] $M=313\times10^2\left(\log^{-1}\frac{[\eta]}{2}-1\right)$

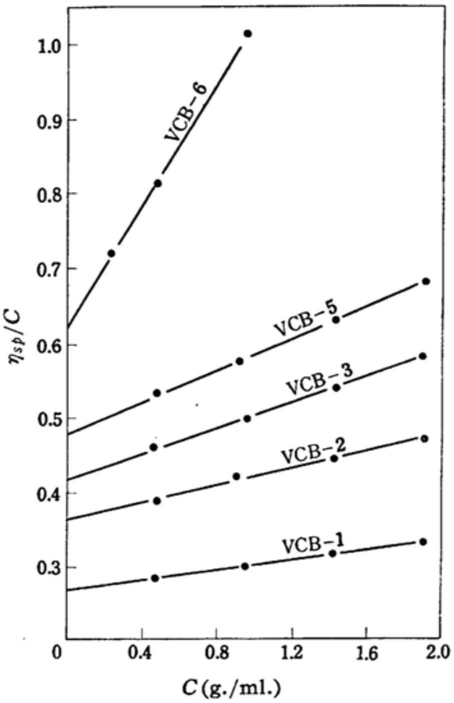

Fig. 3. Intrinsic viscosity of polyvinylchloride.

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[3] A. Nakajima, ***Chemistry of High Polymers, Japan, Kôbunshi Kagagu*, 7**, 309 (1950).

is 11675–32615. The molecular weight of the polymer prepared in emulsion system, is 40500 (exp. No. VCH–4).

The condition of polymerization of exp. No. VCH-4 is as follows: monomer, 20 g.; aqueous solution containing five per cent. sodium lauryl sulfate, 20 g.; tri-*iso*-butylboron, 0.148 g.; temperature, 40°C; reaction time, four hours.

3 Polymerization of acrylonitrile.—Acrylonitrile was very easily polymerized by trialkylboron catalyst. Generally, a white polymer was obtained except for such case as those in which the reaction was very vigorous or polymerization proceeds in dimethylformamide.

3.1 Relation between the yield and the reaction time.—Each sealed tube which contained 12 g. of monomer, 20 cc. of *n*-hexane, and 0.693 g. of triethylboron, was set at 50°C. After certain intervals of time, the polymer was taken out from the sealed tube, treated with ethanol, dried, and weighed. The yield is shown in Table II.

TABLE II

RELATION BETWEEN THE YIELD AND THE REACTION TIME

exp. No.	time (hr.)	polymer (g.)	yield (%)
A-1	1	1.6757	13.8
A-2	3	5.7621	48.0
A-3	5	10.2811	85.0
A-4	7	10.6320	88.6

Proceeding of polymerization in ethanol with tri-*iso*-butylboron catalyst was slower than that of polymerization in hexane, and usually a white product was obtained. For example, when the polymerization of 20 g. of monomer was carried out with 0.396 g. (0.0015 mol.) of tri-*iso*-butylboron, in 25 cc. of ethanol, at 50°C for seven hours, 13.674 g. of polymer was obtained. The yield is 70%.

3.2 Influence of concentration of catalyst on the yield of polymer.—The result of polymerization that was carried out at 50°C, for five hours, with triethylboron catalyst is shown in Table III. In this case, the amount of catalyst is constant (0.0693 g.), and that of monomer is varied.

TABLE III

RELATION BETWEEN THE YIELD AND THE CONCENTRATION OF CATALYST

exp. No.	monomer (g.)	catalyst*	polymer (g.)	yield (%)
B-1	8.06	0.4602	7.66	94
B-2	12.09	0.3068	11.49	95
B-3	16.16	0.2301	15.12	94
B-4	20.15	0.1841	19.14	90
B-5	24.18	0.1534	20.55	85

* catalyst/monomer, mol. %

3.3 Relation between the intrinsic viscosity and the concentration of catalyst.—The same sample in Table III was dissolved in dimethylformamide and the viscosity measured at 25°C. The intrinsic viscosity was calculated from specific viscosity by the following equation;

$$[\eta]=[(1-4k'\eta_{sp})^{1/2}-1]/2k'C \qquad (1)$$

where, $k'=0.33$[4].

The relation between $[\eta]$ and the concentration of catalyst is represented in Fig. 4.

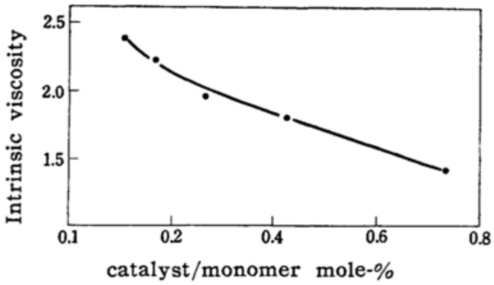

Fig. 4. Relation between the intrinsic viscosity and concentration of catalyst (triethylboron).

3.4 The molecular weight of polyacrylonitrile.—The value of intrinsic viscosity calculated from equation (1) is slightly greater than that extrapolated in Fig. 5. The molecular weight calculated from Stockmayer's equation[5], $[\eta]=2.43\times10^{-4}M^{0.75}$, is 100,000—200,000.

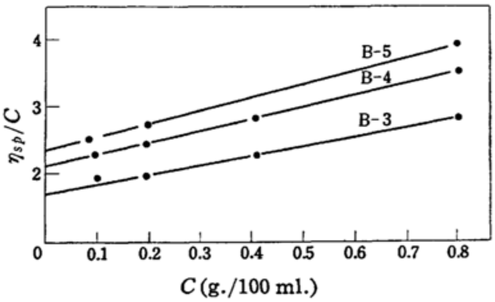

Fig. 5. Intrinsic viscosity of polyacrylonitrile.

Summary

It was found that trialkylboron is an excellent catalyst for the polymerization to some olefins which have comparatively large polarities. Vinylchloride and acrylonitrile were polymerized with this catalyst at a comparatively low temperature, and

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[4] R. Clealand and W. Stockmayer, *J. Polymer Sci.*, **17**, 473 (1955).

[5] B. Cleland and W. Stockmayer, ibid., **17**, 476 (1955).

white polymers were usually obtained.

Vinylchloride was polymerized in bulk-, solution- and emulsion-system, and the rate of polymerization or the relation between the yield and the concentration of catalyst was investigated. Generally, the molecular weight of the polyvinylchloride was small (less than 50,000).

The polymerization of acrylonitrile was studied chiefly in a solution system. Usually, the molecular weight of polyacrylonitrile was fairly large.

Electrical Communication Laboratory
Nippon Telegraph and Telephone
Public Corporation, Musashino
Tokyo