# *Vinyl-polymerization with Alkylboron Derivatives*

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The outline of alkylboron derivatives as the catalysts for the polymerization of vinyl compounds was previously reported[1]. In the present paper, the preparation of these catalysts, the polymerization rates, the relation between the conversion and the molecular weight, and the influence of oxygen on the polymerization rate are described in detail. The catalysts studied were dialkylboron chloride ($R_2BCl$), dialkylboronous ester ($R_2BOR'$), dialkylborinic acid ($R_2BOH$), and dialkylboron oxide [$(R_2B)_2O$]. Furukawa[2] reported that dialkylboron oxide was a good catalyst. The present investigation shows that the organoboron compounds employed in this experiment are effective for comparatively polar monomers.

## Experimental and Results

**Analytical Methods for Organoboron Compounds.**—The synthesized catalysts were analyzed by the following methods. In the case of $R_2BCl$, hydrogen chloride produced by the decomposition of the sample with water was titrated with sodium hydroxide solution under phenolphthalein indicator. In other cases, quantitative analysis of boron was carried out by the modification of Synder's method[3].

A weighed sample (about 0.2 g.) was taken in a 100 cc. Erlenmeyer flask in which air was previously replaced with nitrogen. After 0.1 N sodium hydroxide solution, the amount of which was nearly equivalent to the theoretical value, was poured into the flask; 30% hydrogen peroxide solution was added slowly to it. The flask was shaken for twenty minutes. Then, the content was transferred into a platinum vessel to be heated gently. After the water was mostly vaporized, the vessel was cooled to room temperature, and the content was poured into a 300 cc. beaker with about 70 cc. of distilled water. To the aqueous solution about 5 cc. of glycerin was added and the titration was carried out with 0.1 N sodium hydroxide solution using phenolphthalein indicator. If the excess of alkaline solution is added at the beginning, the solution containing the sample has to be acidified by the addition of the known volume of hydrochloric acid (0.1 N) before the titration with sodium hydroxide solution is carried out.

**The Monomers and the Treatments of the Polymers.**—The monomers such as styrene (St), methyl methacrylate (MMA), and vinyl acetate (VA) were purified as mentioned below.

St: The "commercial" was washed with 5% alkaline solution, followed by water, dried over calcium chloride, and distilled.

VA: The "commercial" was steam distilled, dried over sodium sulfate, and distilled.

MMA: It was dried with sodium sulfate and distilled.

The distillation of styrene and methyl methacrylate was carried out under reduced pressure. The polymers except for polyvinyl acetate were treated with methanol, filtered, and dried. In the case of polyvinyl acetate, it was separated from its monomer by steam distillation.

**Preparation of the Alkylboron Derivatives.**—*Alkylboron chloride.*—The alkylboron chlorides were prepared according to Booth's method[4], i. e., by passing dry hydrogen chloride into trialkylboron. The reaction proceeds as follows:

$$R_3B + HCl = R_2BCl + RH$$

Using this method, diisopropylboron chloride,

1) N. Ashikari, *J. Polymer Sci.*, **28**, 641 (1958).
2) J. Furukawa, T. Tsuruta et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 733 (1958).
3) H. R. Synder, J. A. Kuck and J. R. Johnson, *J. Am. Chem. Soc.*, **60**, 110 (1938).

diisobutylboron chloride and di-*n*-butylboron chloride were prepared.

To a 100 cc. round bottomed flask, were set an inlet of hydrogen chloride, and a condenser to the top of which a calcium tube was connected. Into this flask 36 g. of triisobutylboron was poured, and hydrogen chloride was introduced. The reaction was continued for 15 hr. at 140°C. Then, the content was distilled under reduced pressure, and the fraction of b. p. $_{31}62\sim65$°C was collected. Thus, 28 g. of diisobutylboron chloride was obtained (87% yield).

*Analysis.*—A weighing bottle containing 0.3116 g. of the sample was put in a 300 cc. flask containing 100 cc. of distilled water. The weighing bottle was tied with wire to the rubber stopper of the flask as shown in Fig. 1. After the rubber

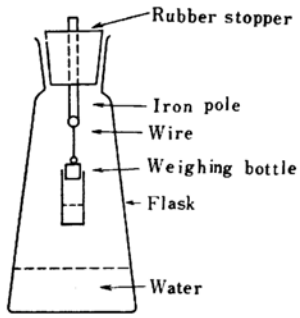


Fig. 1. The vessel for the decomposition of $R_2BCl$.

stopper was closed, the flask was shaken vigorously to open the stopper of the weighing bottle. The rubber stopper was taken off, and the titration was carried out. The amount of the spent sodium hydroxide solution (0.1 N) was 21.6 cc.

*Anal.* Found: Cl, 22.42. Calcd. for $(C_4H_9)_2BCl$: Cl, 22.12%.

Similarly, other dialkylboron chlorides were analyzed. The conditions of the preparation and the yields are shown in Table I.

TABLE I. ALKYLBORON CHLORIDE

| R in $R_2BCl$ | Temp. °C[a] | Time hr. | b. p. °C | Yield % |
|---|---|---|---|---|
| iso-$C_3H_7$ | 120 | 15 | 125 | 88 |
| *n*-$C_4H_9$ | 140 | 15 | 67/18 mmHg[b] | 82 |

a) Reaction temperature
b) Booth's value is 173°C[4].

Generally, dialkylboron chloride is rather more unstable to oxygen than the corresponding trialkylboron. For example, diisopropylboron chloride is inflammable in contact with air, but triisopropylboron is not so.

*Dialkylboronous ester.*—This is easily prepared by the reaction between dialkylboron chloride and alcohol[5]. The reaction formula is as follows:

$$R_2BCl + R'OH = R_2BOR' + HCl$$

Using this method various dialkylboronous esters were prepared. When alcohol was dropped slowly into dialkylboron chloride under nitrogen stream, the reaction took place at once.

The product consisted of two layers. The upper layer was colorless and the lower one, the amount of which was small, was slightly colored. The upper layer was separated from the lower one and distilled. Few studies on the esters of such type as $(iso\text{-}C_3H_7)_2BOR$ have been performed. The yields and the boiling points of these derivatives are shown in Table II.

TABLE II. THE YIELD AND THE BOILING POINT OF $(iso\text{-}C_3H_7)BOR$

| R in $(iso\text{-}C_3H_7)_2BOR$ | ROH(g.) added | Yield % | b. p. °C |
|---|---|---|---|
| $CH_3$ | 3 | 91.1 | 117 |
| $C_2H_5$ | 4 | 80.0 | 132 |
| iso-$C_3H_7$ | 5 | 80.7 | 51(32 mmHg) |
| iso-$C_4H_9$ | 6 | 70.1 | 70(32 mmHg) |
| *tert*-$C_4H_9$ | 6 | 35.5 | 92(30 mmHg) |

In Table II, the weigt of the diisopropylboron chloride used was 10 g. in each experiment. Moreover, diisobutylboron isobutyl ester was prepared. This boiled at 97°C/27 mmHg. The yield was 92%.

Analysis of $(iso\text{-}C_3H_7)_2BO(iso\text{-}C_3H_7)$
Sample: 0.1935 g., alkali added: 12.7 cc.
Found B, 7.25%, Calcd. B, 7.05%

*Dialkylborinic acid and dialkylboron oxide.*—Dialkylborinic acid was prepared according to Eq. 1, but was not always isolated purely because of decomposition by distillation.

$$R_2BCl + H_2O = R_2BOH + HCl \quad (1)$$

Dialkylboron oxide was prepared purely by distillation of the product from dialkylboron chloride and equivalent water. To 28.5 g. of di-*n*-butylboron chloride was added 3.2 g. of pure water under nitrogen stream, and the product was distilled. Thus, 18.5 g. of the product which boiled at 90~92°C/1 mmHg (reported value[6], 136°C/12 mmHg) was obtained (78.3% yield, calculated from di-*n*-butylboron chloride).

Analysis of $[(n\text{-}C_4H_9)_2B]_2O$
Sample: 0.1419 g., alkali added: 10.8 cc.
Found B, 8.41%, Calcd. B, 8.27%

**The Rate of the Polymerization of Styrene with these Derivatives.**—By observing the polymerization rates, the activities of these catalysts were compared. The catalysts employed in this experiment were isopropylboron derivatives. In

TABLE III. THE SORT AND WEIGHT OF THE CATALYST IN THE POLYMERIZATION OF STYRENE

| Catalyst type | Weight, g. | Wt. of St, g. |
|---|---|---|
| $R_2BOR$ | 0.3681 | 130 |
| $R_2BCl$ | 0.3562 | 148 |
| $(R_2B)_2O$ | 0.4022 | 106 |

Where, R is iso-$C_3H_7$.

4) R. B. Booth and C. A. Craus, ibid., **74**, 1415 (1952).
5) M. F. Lappert, *Chem. Revs.*, **56**, 1015 (1956).
6) J. R. Johnson, H. R. Synder and M. G. Van Campen, Jr., *J. Am. Chem. Soc.*, **60**, 115 (1938).

TABLE IV. THE CONDITION OF THE POLYMERIZATION FOR INVESTIGATING THE RELATION BETWEEN THE CONVERSION AND THE INTRINSIC VISCOSITY

| Monomer | Temp., °C | Vessel | Cat.[a]/monomer wt. % | $O_2$ mol. ($\times 10^5$) |
|---|---|---|---|---|
| MMA | 50 | flask | 0.296 | $N_2$ stream |
| St | 50 | flask | 0.379 | $N_2$ stream |
| VA | 50 | ampoule | 0.414 | 5.0 |

a) The catalyst is diisopropylboron oxide.

every case, the value of catalyst/monomer was 0.188 in mol. %. The weights of the catalysts and the monomer were shown in Table III.

Each reaction was carried out at 50°C under nitrogen stream in a four necked flask to which a stirrer, an inlet of nitrogen, and a thermometer were connected.

At a certain interval of reaction, 10 g. portions of the sample were taken out and poured into methanol. Then, the polymer was filtered, dried, and weighed. These results were represented in Fig. 2.

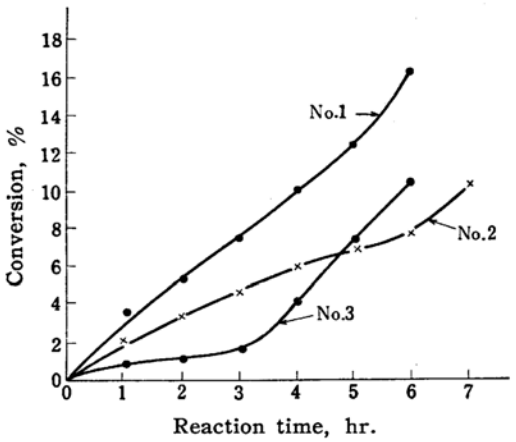


Fig. 2. Polymerization rates of styrene with three types of alkylboron.
No. 1, $(R_2B)_2O$: No. 2, $R_2BOR$: No. 3, $R_2BCl$, where, R is iso-$C_3H_7$.

Usually, in the polymerization with these catalysts, the polymerization rate increased rapidly after a certain reaction time (as shown in Fig. 2).

**Relation between the Conversion and the Molecular Weight.**—In usual "radical polymerization", the molecular weight is expected to have no relation with the conversion. However, in high conversion, many examples[7] have shown the fact that the former depends on the latter. The same phenomenon was observed, even in low conversion, in the case of the polymerization with alkylboron catalyst. Methyl methacrylate, styrene and vinyl acetate were polymerized in the following conditions (Table IV).

When the reaction was carried out in an ampoule, the apparatus shown in Fig. 4 was used. When a flask was used as a reaction vessel, the reaction was carried out under nitrogen stream, and the sample was taken out after a certain interval of reaction. The relation between the conversion and the intrinsic viscosity was represented in Fig. 3.

In this case, the viscosity of each polymer was measured in the following condition (Table V).

TABLE V. THE CONDITION OF MEASUREMENT OF THE VISCOSITY

| Polymer | Solvent | Temp., °C |
|---|---|---|
| PMMA | toluene | 30 |
| PSt | toluene | 30 |
| PVA | benzene | 30 |

Where, "P" means a polymer.

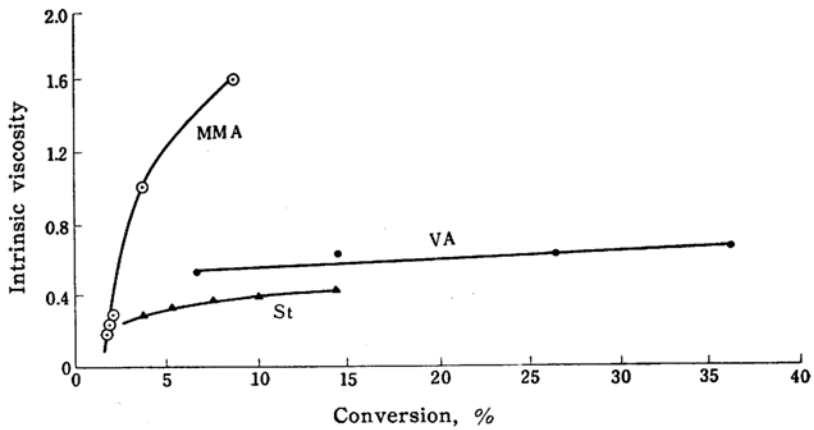


Fig. 3. Relation between the conversion and the intrinsic viscosity.

7) M. Ōiwa, *Chemistry and Chem. Ind.* (*Kagaku to Kogyo*), **11**, 792 (1958).

TABLE VI. POLYMERIZATION CONDITIONS FOR INVESTIGATING THE INFLUENCE OF OXYGEN

| Monomer | Time, hr. | Temp., °C | Catalyst | Catalyst/monomer, wt. % | Cat., wt. |
|---|---|---|---|---|---|
| St | 5 | 40 | $R_2BO\cdot iso\text{-}C_3H_7$ | 0.42 | 0.0754 |
| MMA | 1 | 40 | $R_2BO\cdot iso\text{-}C_3H_7$ | 0.40 | 0.0754 |
| VA | 0.5 | 41 | $R_2BO\cdot iso\text{-}C_4H_9$ | 0.41 | 0.0766 |

Where, R is iso-$C_3H_7$.

TABLE VII. MEASUREMENT OF THE VISCOSITIES AND THE EQUATIONS FOR CALCULATING THE MOLECULAR WEIGHT

| Polymer | Solvent | Temp., °C | Eq. ($[\eta]=$ ) | Reference |
|---|---|---|---|---|
| PSt | toluene | 30 | $0.55\times10^{-4}M^{0.81}$ | 8 |
| PMMA | toluene | 25 | $0.71\times10^{-4}M^{0.73}$ | 9 |
| PVA | benzene | 30 | $5.63\times10^{-4}M^{0.62}$ | 10 |

**Influence of Oxygen on the Polymerization Rate.**—To observe the influence of oxygen on the polymerization rate some monomers were polymerized in the following apparatus (Fig. 4).

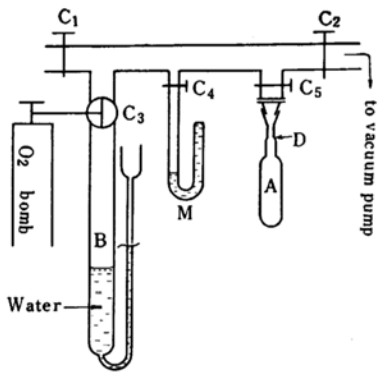


Fig. 4. Apparatus for investigating the influence of oxygen.
M: Manometer
B: Gas burette
A: Polymerization tube

**The Explanation of the Apparatus and the Procedure.**—The volume of the space enclosed by stopcocks $C_1$-$C_5$ is 136 cc., and that of A, polymerization tube, is 70 cc. The volume from $C_5$ to D is 5 cc.

To tube A in which nitrogen had replaced air, 20 cc. of monomer was introduced and the tube was cooled in dry-ice methanol. After the catalyst, the amount of which was shown in Table VI, was added under a nitrogen stream, the tube was connected to the apparatus. The gas involved in tube A and other spaces enclosed by stopcocks $C_1$-$C_4$ was removed by a vacuum pump. After a certain amount of oxygen contained in burette B was introduced to the tube, it was sealed. The sealed tube was transferred into a constant temperature bath. The reaction temperature, the reaction time, etc., were shown in Table VI.

Thus, from the yield obtained after the same reaction time, the influence of oxygen on the polymerization rate was compared. The relation between the amount of oxygen and the conversion was represented in Fig. 5.

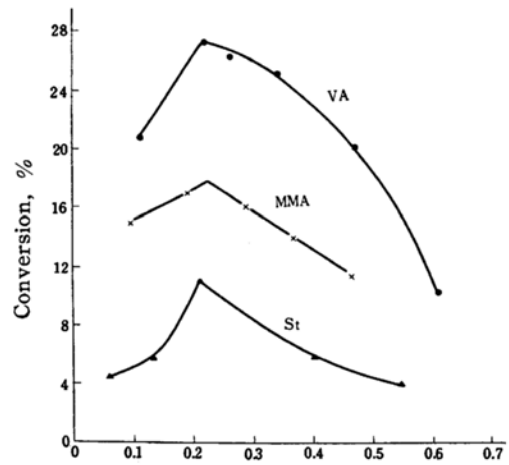


Fig. 5. Diagram of conversion—$O_2$/catalyst. The influence of oxygen on the polymerization rate.

The viscosity of each sample shown in Fig. 5 was measured to obtain the relation between the molecular weight and the value of $O_2$/catalyst in mole ratio. These results are represented in Fig. 6. The conditions of measurement of the viscosity and the equations for calculation of the molecular weight are shown in Table VII.

From Fig. 5, it is clear that the polymerization rate is the largest when the value of $O_2$/catalyst in mole ratio is 0.22. In regard to the molecular weight, the molecular weight at the maximum point of the polymerization rate is minimum except in the case of polyvinyl acetate. The reason why the curve of the molecular weight of PVA against the mole ratio of $O_2$/catalyst differed from those of polymethyl methacrylate and polystyrene is not clear.

8) T. Alfrey and Batovics, *J. Am. Chem. Soc.*, **65**, 2319 (1943).
9) S. Chinai, J. Matlack and A. Resnick, *J. Polymer Sci.*, **17**, 391 (1955).
10) A. Nakajima, *Chemistry of High Polymers (Kobunshi Kagaku)*, **11**, 142 (1954).

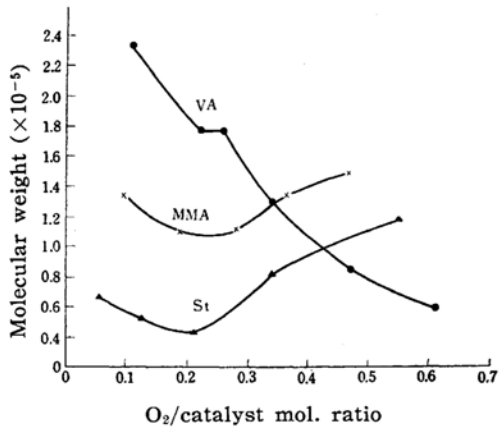


Fig. 6. Relation between the molecular weight and $O_2$/catalyst mol.-ratio.

## Summary

Such alkylboron derivatives as dialkylboron chloride, dialkylborinic acid, dialkylboronous ester, and dialkylboron oxide as the catalysts for the polymerization of vinyl compounds were studied. Although dialkylborinic acid was a good catalyst, it was pretty difficult to isolate it purely, therefore, only a brief description was made in this paper. Of course, some dialkylborinic acids can be isolated purely under suitable conditions. In regard to this, further investigation will be performed.

The polymerization rates of styrene with these catalysts, the relation between the conversion and the intrinsic viscosity, and the influence of oxygen on the polymerization rate were studied. The polymerization rate of some monomers with dialkylboronous ester is maximum when $O_2$/catalyst in mole ratio is 0.22.

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