Polymerization of Olefins with Trialkylboron Catalysts. II. Polymerization of Styrene

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The previous work⁽¹⁾ in these series has shown the polymerization of vinyl chloride and acrylonitrile with trialkylboron catalysts. In the present paper the polymerization of styrene with the same catalysts is studied.

The rate of polymerization of styrene is rather smaller, in bulk system, than that of vinyl chloride or acrylonitrile. But in the emulsion system, the rate of polymerization was large and also the molecular weight of the polymer was very high.

Generally, in the polymerization of vinyl compounds with trialkylboron catalyst, it was considered that the reaction velocity and the yield of the polymer were influenced a good deal by an amount of oxygen in the reaction vessel. The degree of the influence, of course, will vary according to the sort of olefin. In this respect, the influence of oxygen in the polymerization of styrene was considered to be not very large. But, by way of precaution, the experiments in this paper were done under nitrogen stream or in a sealed tube in which the air was replaced by nitrogen. Some properties of the polymer prepared with tri-*iso*-propylboron were studied.

Experimental and Results

Preparation of the catalysts.—In a previous paper⁽¹⁾, the detail of the preparation of triethylboron was reported. Here, the detail of the preparation of tri-*iso*-butylboron is explained chiefly. In the cases of tri-*iso*-butyl- and tri-*iso*-propylboron, the preparations were done according to the general method, i. e., the reaction of Grignard reagent and borontrifluoride, as well as the case of triethylboron.

Triisobutylboron.—To ethereal solution of *iso*-butylmagnesiumbromide prepared by the reaction of 24 g. (1 mol.) of magnesium piece and 137 g. (1 mol.) of *iso*-butylbromide in 500 cc. three necked flask, 40 g. (0.28 mol.) of borontrifluoride etherate was dropped slowly under cooling. After the dropping was over the stirring was continued for twenty minutes.

The ethereal solution was cooled and decanted into a distilling flask. The residue consisting of magnesium halide and unchanged *iso*-butylmagnesiumbromide was treated with unhydrous ether, and the trialkylboron involved was extracted. The ethereal solution was added to the first ethereal solution, and the solvent was distilled off. The distillate of b. p. 188～195°C was collected. Thus, 34 g. of tri-*iso*-butylboron was obtained, corresponding to 56.6% yield from magnesium.

Tri-iso-propylboron. — Tri-*iso*-propylboron was prepared, by the same method, by dropping borontrifluoride etherate to isopropylmagnesiumbromide in ether.

Comparison of the rate of polymerization in bulk- and emulsion system.— The rate of polymerization in bulk- and emulsion system was compared in the following experiments. In these experiments the ratio of catalyst to monomer is constant, that is, 80 g. of monomer, and 0.296 g. of tri-*iso*-butylboron were used. Therefore, the ratio of catalyst to monomer is 0.21%.

The reactions were caused to proceed at 40°C under nitrogen stream which was purified by passing through an aqueous pyrogallol-alkali solution and drying over calcium chloride. A certain weight of monomer or a certain weight of monomer and water, was placed in a four-necked flask which was dipped in a constant-temperature bath.

A stirrer, a stopper, and a passage of nitrogen gas were connected to the flask. When the temperature of the contents reached 40°C, the catalyst was added.

After a certain interval of reaction, 10 g. of the sample was taken out from the reaction vessel, and poured into methanol. And then, the polymer contained in the sample was separated from styrene monomer, filtered, dried under reduced pressure at 50°C, and weighed. In the case of emulsion system, the sample taken out was treated with 5% aqueous sodium chloride solution, and the polymer was separated. Then, the polymer was washed fully with water, dried, and weighed.

Fig. 1 represents the relation between the conversion and the reaction time.

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

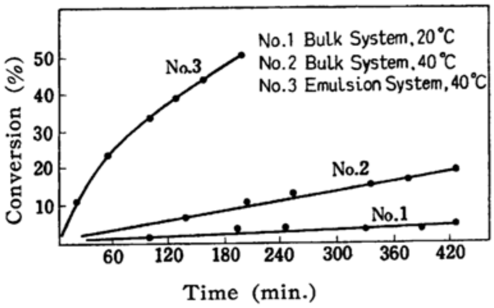

Fig. 1. The rate of polymerization in bulk- and emulsion-system.

In Fig. 1, No. 1 and No. 2 are the cases of bulk-system and No. 3 is the case of emulsion system. From Fig. 1, it is clear that the rate of polymerization in emulsion system is larger than that in bulk system. Especially, in No. 3, 80 g. of aqueous solution which contained 5% of emulsifier was used, so that the ratio of catalyst to the whole solution was very small.

The relation between the conversion and the concentration of catalyst.— A certain weight of monomer (18 g.) and a certain weight of tri-*iso*-propylboron were sealed in a nitrogen-replaced tube, and the polymerization was caused to proceed at 40°C. After ten hours reaction, each sealed tube was opened and the contents were poured into methanol. Thus, the polymer contained was separated from the monomer, filtered, dried under reduced pressure at 50°C, and weighed. The results are shown in Table 1.

TABLE I

THE RELATION BETWEEN THE CONVERSION AND THE CONCENTRATION OF CATALYST

Expt. No.	4	5	6	7	8
catalyst (%)[a]	0.0835	0.1670	0.2505	0.3340	0.4175
polymer (g.)	3.553	4.245	4.540	4.712	4.500
conversion (%)	19.74	23.58	25.22	26.18	25.00

a: catalyst/monomer mol ratio.

Molecular weight of polystyrene.— Each sample in Table 1 was dissolved in pure toluene and the viscosity was measured at 30°C with Ubbelohde viscometer. The intrinsic viscosity, $[\eta]$, was obtained from Fig. 2, in which is plotted η_{sp}/C against concentration (C), where η_{sp} represents a specific viscosity.

The molecular weight was calculated from the intrinsic viscosity with Alfrey's equation[2]; $[\eta]=0.55\times10^{-4}M^{0.81}$. The intrinsic viscosities and the molecular weight of the samples polymerized in bulk- and emulsion system were shown in Table II.

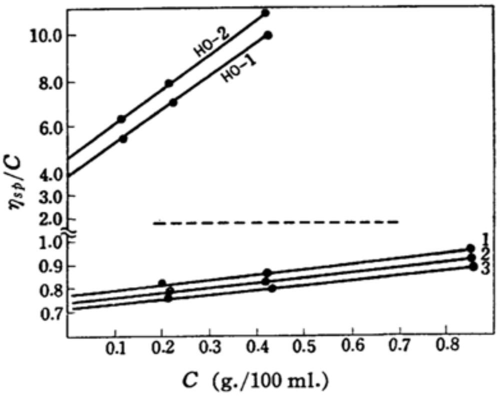

Fig. 2. Viscosity η_{sp}/C vs. C curves for polystyrene

TABLE II

THE INTRINSIC VISCOSITY AND MOLECULAR WEIGHT OF POLYSTYRENE

Exp. No.	4	5	6	HO-1	HO-2
intrinsic viscosity	0.78	0.75	0.72	3.75	4.50
mol. wt. ($\times10^{-3}$)	133	127	121	927	1160

In Fig. 2, the samples of HO-1 and HO-2 were prepared in the emulsion system. In the case of HO-1, 18 g. of monomer, 0.07 g. of tri-*iso*-butylboron, and 18 g. of aqueous solution containing 5% emulsifier were sealed in a glass tube. The reaction was caused to proceed at 40°C for five hours. The polymer was treated by the same method as mentioned on p. 540. Thus, 14 g. of the polymer was obtained. The conversion is 77%.

Similarly, in the case of HO-2, 25 g. of monomer, 0.1 g. of tri-*iso*-butylboron, and 25 g. of aqueous solution containing 5% emulsifier were used. Other conditions, i. e., temperature, time, and treatment of the polymer, were the same as in the case of HO-1. Thus, 18 g. of the polymer was obtained (72% conversion).

Generally, the molecular weight of the polymer prepared in a bulk system was $1\sim2\times10^5$, and in the case of emulsion system, the molecular weight was $1\sim2\times10^6$.

Properties of polystyrene polymerized with tri-*iso*-propylboron in bulk system.

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[2] T. Alfrey and A. Bartovics, *J. Am. Chem. Soc.*, **65**, 2319 (1943).

—Some properties of polystyrene polymerized with tri-*iso*-propylboron were studied.

The infrared spectra. — The infra-red spectrum of the polymer was compared with that of a polymer prepared with the ordinary catalyst such as radical type. Each film of which the thickness was about 0.01 mm. was prepared by evaporation of toluene used as a solvent of the polymer on a glass plate floated on mercury. The infrared spectrum of the polymer prepared with this catalyst almost exactly resembles that of ordinary polymer, so that only one spectrum is shown in Fig. 3.

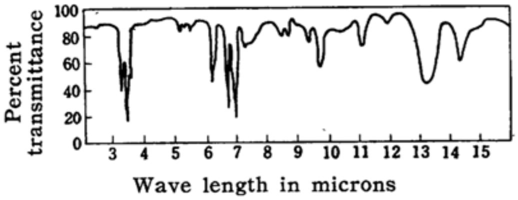

Fig. 3. Infrared spectrum of polystyrene prepared with tri-*iso*-propylboron in bulk system.

X-ray diffraction patterns.—The X-ray diffraction patterns of two samples, i. e., the ordinary polymer and the polymer prepared with this catalyst, were compared as well as the case of infra-red spectra. The specimens having 3 mm. of thickness were made by press at 150°C for ten minutes. Fig. 4-1 is a pattern of ordinary polymer and Fig 4-2 is that of the polymer described in this paper.

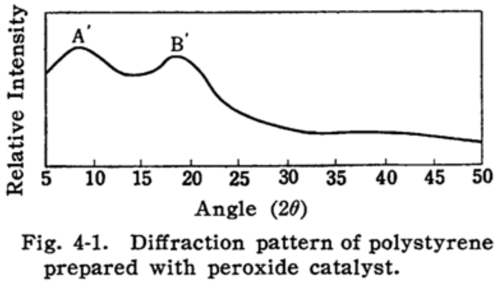

Fig. 4-1. Diffraction pattern of polystyrene prepared with peroxide catalyst.

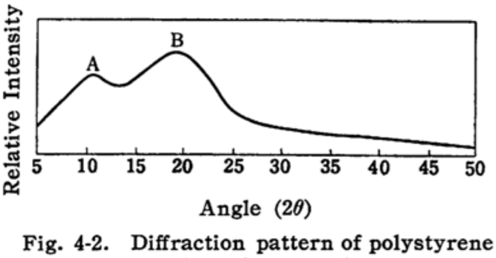

Fig. 4-2. Diffraction pattern of polystyrene prepared with tri-*iso*-propylboron.

Figs. 4-1 and 4-2 represent relative values. From these patterns, it is obvious that the relative intensities between peak A and B in Fig. 4-2 differ from those of peak A' and B' in Fig. 4-1.

Solubility in methyl-ethyl-ketone. — The polymer whose molecular weight was 1.2×10^5 was treated with methyl ethyl ketone for two days at room temperature. The polymer perfectly dissolved in this solvent. If the polymer is a crystalline one, it must be insoluble3).

Softening point.—The softening point of the polymer which was the same kind as the sample used above was measured similarly by the measuring the melting point. In this case, a small piece whose size was about 0.5 mm.×1 mm.×20 mm. was used instead of powder in a case measuring melting point, and the temperature of deformation of the piece was observed. The softening point was about 100°C.

Summary

Styrene was polymerized with tri-*iso*-propylboron and tri-*iso*-butylboron prepared by the reaction of Grignard reagents and borontrifluorides. In regard to the rate of polymerization in bulk- and emulsion system, that in the latter was much larger than that in the former. Moreover, in the emulsion system, a very highly polymerized product was easily obtained.

Some properties of the polymer prepared with tri-*iso*-propylboron were studied in comparison with ordinary polymer. The solubility in methyl-ethyl-ketone and the infrared spectrum closely resembled those of ordinary polymers. On the X-ray diffraction pattern, a little difference was observed. But, it is not evident whether the crystalline structure exists or not.

I wish to express my sincere thanks to Mr. H. Matsuo in this laboratory who observed the infrared spectra, and to Mr. S. Ōwaki who observed the X-ray patterns.

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3) F. Danusso and G. Moraglis, *J. Polymer Sci.*, **24**, 161 (1957)