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# Organoboron Compounds. XI.* The Polymerization of Vinylboronic Acid

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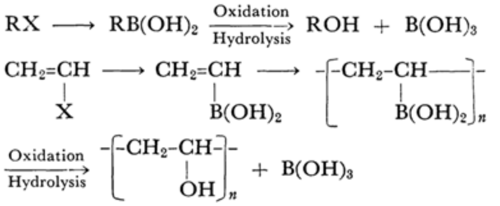
It has been found that potassium persulfate is a good initiator for the polymerization of vinylboronic acid. With this initiator the polymerization has been studied in acidic as well as in basic medium, and the best conditions for the polymerization have been established with the help of molecular weight determination of the products. The highest molecular weight has been observed in basic medium to be about 7000. A mixed solvent (1 : 1) of ether and acetone has been used as the precipitant. The variation in the rate of polymerization and the boron content has been investigated in a narrow range of pH, from 6 to 8.

In the course of our investigation of some boronic acids we observed that boronic acids with an alkyl or an aryl group attached to the boron atom can be converted, on oxidation and hydrolysis, into the corresponding alcohol and boric acid. In the case of vinylboronic acid, where a vinyl group is linked with the boron atom, it is to be expected that polyvinyl alcohol may eventually be produced by its polymerization, oxidation and hydrolysis, as is formulated below:

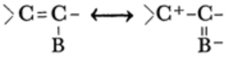


$$RX \longrightarrow RB(OH)_2 \xrightarrow[\text{Hydrolysis}]{\text{Oxidation}} ROH + B(OH)_3$$

$$\underset{\displaystyle X}{CH_2{=}CH} \longrightarrow \underset{\displaystyle B(OH)_2}{CH_2{=}CH} \longrightarrow -\left[CH_2-\underset{\displaystyle B(OH)_2}{CH}-\right]_n-$$

$$\xrightarrow[\text{Hydrolysis}]{\text{Oxidation}} -\left[CH_2-\underset{\displaystyle OH}{CH}-\right]_n- + B(OH)_3$$

Ritter et al.[1,2] and Matteson[3] have, however, pointed out that a resonance stabilization of the intermediate radical would result from the carbon-boron $\pi$-bonding when the vinyl group is one of the three groups bonded to the boron atom:



$$\rangle C{=}\underset{\displaystyle B}{C}- \longleftrightarrow \rangle C^{+}-\underset{\displaystyle \overset{\|}{B^{-}}}{C}-$$

In general, there are two processes in the vinyl-type polymerization, namely, ionic and radical polymerization. As a result of the mesomeric effect described above, and as a result of the great difficulty encountered in removing the free water from vinylboronic acid, it is probable that no ionic initiator has any influence on opening the vinyl group. In fact, no polymerization was effected when a solution of vinylboronic acid was treated with ionic initiators, but radical polymerization really occurred when potassium persulfate was used as an initiator.

Vinylboronic acid and its butyl ester were prepared by Normant[4] and by Matteson[5], who reported that polymerization readily set in during the synthesis. The present paper will deal with more detailed experiments carried out on the polymerizing factor of vinylboronic acid; the results of these experiments are shown in Tables I—IV.

As regards the polymerization in an aqueous solution, some instances have been known, such as those of itaconic acid[6] and acrylic acid, both of which use potassium persulfate as the initiator. On the other hand, *p*-vinylbenzeneboronic acid has been found to enter into polymerization by the same initiator in *t*-butyl alcohol.[7] Vinylboronic acid can be polymerized to higher-molecular substances in a dilute solution of sodium hydroxide rather than in a dilute solution of hydrochloric acid.

The polyvinylboronic acids of higher degrees of polymerization are soluble in water, and the lower polymers are soluble in an extremely dilute alkaline solution. All of them are insoluble in common organic solvents with the exception of tetrahydrofuran.

It has been established experimentally that the best conditions for polymerization are when the concentration of the medium is 0.11 N alkali, the concentration of the initiator is 4% (weight percent based on the monomer), and the temperature is 50°C. The rate of polymerization and the boron content were investigated in a narrow pH range, from 6 to 8, with the specimens of polyvinylboronic acids obtained under the conditions described above. The results are shown in Fig. 1.

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* Part X: This Bulletin, **39**, 1582 (1966).

** Died April 9, 1965.

[1] T. D. Parsons, M. B. Silverman and D. M. Ritter, *J. Am. Chem. Soc.*, **79**, 5091 (1957).

[2] T. D. Parsons and D. M. Ritter, ibid., **76**, 1710 (1954).

[3] D. S. Matteson, ibid., **81**, 5004 (1959).

[4] H. Normant, *Compt. rend.*, **248**, 828 (1959).

[5] D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960).

[6] C. S. Marvel and T. H. Shepherd, *J. Org. Chem.*, **24**, 599 (1959).

[7] J. Pellon, L. H. Schwind, M. J. Guinard and W. M. Thomas, *J. Polymer Sci.*, **55**, 161 (1961).

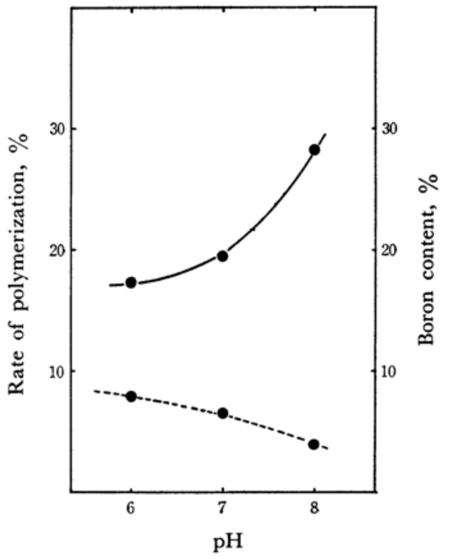

Fig. 1. The rate of polymerization and the boron content of the products in the range of pH 6—8.
—— rate of polymerization, ---- born content

The rate of polymerization becomes higher with an increase in the pH value, but the boron content decreases. This may show that the cleavage of the carbon-boron bond has really occurred.

The infrared spectra of the products obtained in an acidic medium show absorptions of 3500 $cm^{-1}$ (O–H), 1300—1400 $cm^{-1}$ (B–O), 1000—1100 $cm^{-1}$ (B–C) and 2900 $cm^{-1}$ ($CH$, $CH_2$), while those of the products obtained in a basic medium resemble the spectra of polyvinyl alcohol.

Since their structure is similar to that of polyvinyl alcohol, the average molecular weight was roughly estimated from the following equation (I), using the constants of polyvinyl alcohol ($K = 8.5\times 10^{-4}$ and $\alpha = 0.62$ at 20°C),[8] the molecular weight being about 7000 (maximum) in a basic medium and from 500 to 1000 in an acidic medium:

$$[\eta] = KM^{\alpha} \qquad \text{(I)}$$

The intrinsic viscosity was measured in water and found to be in the range from 0.04 to 0.2 at 20°C, so the products should be called "oligomers" rather than "polymers."

## Experimental Results

**The Preparation of Vinylboronic Acid.**—The method used here was practically identical with that of Matteson,[4] who prepared vinylboronic acid from vinylmagnesium bromide and trimethyl borate, but the procedure of crystallization was somewhat modified. After acidifing the solution of vinylboronic acid sodium salt with phosphoric acid, and extracting it with ether, the ethereal solution was concentrated. The vinylboronic acid was then precipitated by pouring a concentrated ethereal solution of it into a large quantity of *n*-hexane before using it; it was dried in a vacuum oven within five minutes, m. p. 83°C. Yield 35%.

**Selection of Initiator.**—The initiators used in the experiments are listed in Table I. A solution of 2 g. of the monomer in 10 ml. of the solvent was prepared. This solution was then introduced in seven 20-ml. sealed tubes, each containing 0.05 g. of the initiator. All the tubes were deaerated and sealed under reduced presure. Samples 1—3 were kept at a constant temperature of 80°C for 24 hr., and samples 4—7, at −70°C in a dry ice - acetone bath for 48 hr. From sample 3 a polymer was isolated by adding a mixed ether-acetone solvent (1 : 1 by volume), while no polymer was obtained from the others with any kind of precipitating reagent.

TABLE I. INITIATORS AND SOLVENTS OF POLYMERIZATION

| No. | Initiator | Solvent | Type of polymerization |
|---|---|---|---|
| 1 | Benzoic peroxide | *t*-Butylalcohol | Radical |
| 2 | Azobisisobutylonitrile | *t*-Butylalcohol | Radical |
| 3 | Potassium persulfate | Water | Radical |
| 4 | Sodium naphthalene | Glycoldimethyl ether | Ionic |
| 5 | Ethyllithium | Ethyl ether | Ionic |
| 6 | Sodium cyanide | Dimethylformamide | Ionic |
| 7 | Sodium triphenylmethane | Ethyl ether | Ionic |

**Polymerization of Vinylboronic Acid.**—Further polymerization experiments employing potassium persulfate initiation were carried out both in basic medium of an aqueous solution of sodium hydroxide and in acidic medium of an aqueous solution of hydrochloric acid.

TABLE II. RATE OF POLYMERIZATION AND NORMALITY OF MEDIUM[a)]

| Acidic medium[b)] | | | Basic medium[c)] | | | |
|---|---|---|---|---|---|---|
| No. | Normality of HCl | Pr % | No. | Normality of NaOH | Pr % | Pd % |
| 1 | 0.25 | 3.2 | 1 | 0.065 | 62.5 | 14 |
| 2 | 0.05 | 4.5 | 2 | 0.11 | 64.5 | 77 |
| 3 | 0.0025 | 8.5 | 3 | 0.55 | —* | — |
| 4 | 0.0005 | 16.0 | 4 | 1.11 | — | — |

a) All sealed tubes were kept at 50°C in a bath for 48 hr.
b) Monomer (1.25 g.) was introduced each in four sealed tubes each with 10 ml. of water containing hydrochloric acid of the specified normal concentration and with 0.05 g. of initiator.
c) Monomer concentration was 0.8 g. per 10 ml. of water containing sodium hydroxide of the specified normal concentration. Initiator (0.016 g.) was added.
* Not precipitated in a mixture of ether-acetone (1: 1 by volume).

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8) H. Staudinger and H. Warth, *J. prakt. Chem.*, **155**, 261 (1940).

TABLE III. RATE OF POLYMERIZATION AND CONCENTRATION OF INITIATOR[a]

| Acidic medium[b] | | | Basic medium[c] | | | |
|---|---|---|---|---|---|---|
| No. | Quantity of initiator[d] % | Pr % | No. | Quantity of initiator[d] % | Pr % | Pd % |
| 1 | 0.5 | 5.0 | 1 | 1.0 | 64.0 | 93 |
| 2 | 1.0 | 6.5 | 2 | 2.0 | 64.5 | 77 |
| 3 | 2.0 | 10.5 | 3 | 4.0 | 65.8 | 54 |
| 4 | 4.0 | 16.0 | 4 | 8.0 | 53.3 | 40 |

a) All sealed tubes were kept at 50°C in a bath for 48 hr.

b) A stock solution of the monomer was prepared, which contained 1.25 g. of the sample in 10 ml. of hydrochloric acid of concentration $5\times10^{-4}$ N.

c) Solvent was a sodium hydroxide solution of 0.11 N. A solution of the monomer was of the concentration corresponding to the acidic medium.

d) Expressed by the number of grams per 100 g. of vinylboronic acid taken.

The relations of the rate of polymerization to the normality of the medium, the concentration of the initiator, and the temperature of polymerization were investigated. The experimental methods employed were described below each of Tables II—IV. All the tubes used in the experiments were dearated and sealed under a vaccum. A tetrahydrofuran solution of the polymer was precipitated and purified in a mixed solvent of ether and acetone (1 : 1 by volume). The rate of polymerization was determined by weight percent based on the monomer. The polymerization degree was measured at 20°C using a dilute-type Ubbelohde viscosimeter. The symbols used in Tables II—IV are as follows: (Pr)—the rate of polymerization, and (Pd)—the degree of polymerization.

TABLE IV. RATE OF POLYMERIZATION AT VARIOUS TEMPERATURES

| Acidic medium[a] | | | Basic medium[b] | | | |
|---|---|---|---|---|---|---|
| No. | Temp. °C | Pr % | No. | Temp. °C | Pr % | Pd % |
| 1 | 0 | 10.0 | 1 | 0 | 10.0 | —* |
| 2 | 15 | 12.0 | 2 | 20 | 35.0 | 78 |
| 3 | 30 | 16.0 | 3 | 30 | 62.0 | 77 |
| 4 | 50 | 16.5 | 4 | 50 | 69.0 | 99 |

a) Monomer (1.25 g.) was placed in each tube with 10 ml. of $5\times10^{-4}$ N of hydrochloric acid and with 0.05 g. of potassium persulfate.

b) Monomer solution consists of 0.8 g. per 10 ml. of water containing 0.11 N of sodium hydroxide. Concentration of initiator was fixed at 2%, namely 2 g. per 100 g. vinylboronic acid taken.

* Not precipitated in a mixture of ether-acetone (1 : 1 by volume).

**Determination of Boron.**—Although a number of methods have been proposed for the analysis of boron, they are for the most part troublesome. Our modification of the method of Martin[9] has been proved to be easier and more practical.

The sample is refluxed with a sodium peroxide solution for several hours until it is dissolved. The solution is then exactly neutralized to pH 6.9 with hydrochloric acid by the help of a pH-meter; when mannitol is added, the solution is titrated back with a standard solution of sodium hydroxide until the pH-meter indicates 6.9 exactly. The boron content (%) is given by the following equation (II):

$$B\% = \frac{10.8}{W} \times \frac{NV}{V_t} \qquad \text{(II)}$$

where $N$ and $V$ are the normality and the used volume of a standard solution of sodium hydroxide respectively, where $V_t$ is the final volume of the solution of the sample, and where $W$ is the number of grams of the weighed sample.

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[9] J. R. Martin, *Anal. Chem.*, **24**, 182 (1952).