# *Organoboron Compounds. I. On the Reaction of n-Butylboronic Acid with Polyvinylalcohol*

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(Received October 17, 1960)

It is well-known that boric acid reacts with various diols and sugars, giving more acidic complexes, and thus boric acid can be titrated with standard sodium hydroxide in the presence of mannitol. One of the authors[1] previously studied the reactions polarimetrically and showed that the formation of the complexes is a reaction of ionic nature. Boric acid, reacting with polyvinylalcohol, also forms polyvinyl borate ester. Owing to this reaction a remarkable change is observed on the viscosity of aqueous polyvinylalcohol on the addition of boric acid, hence boric acid is available as a modification agent of the viscosity of aqueous polyvinylalcohol when filaments are spum from it. In a similar manner esters of boronic acid with polyols can be formed, which have been known as arneboronates. Kuivila[2] prepared

1) Y. Tsuzuki, This Bulletin, **16**, 23 (1941).

2) H. Kuivila, *J. Org. Chem.*, **19**, 780 (1954).

them by the reaction of some arylboronic acid with numerous diols and sugars.

The present paper deals with the reaction of *n*-butylboronic acid with polyvinylalcohol, and discusses the experimental method, esterification grade, and some properties of the products.

## Experimental

**Preparation of *n*-Butylboronic Acid.** — *n*-Butylboronic acid was prepared in an atmosphere of nitrogen, practically according to Johonson's method[3], in the following way:

$$n\text{-Bu-MgBr} + B(OCH_3)_3 \rightarrow n\text{-Bu-B}(OCH_3)_2 + MgBrOCH_3$$

$$n\text{-Bu-B}(OCH_3)_2 + H_2O \rightarrow n\text{-Bu-B}(OH)_2 + CH_3OH$$

From 80.6 g. (0.50 mol.) of *n*-butylmagnesiumbromide and the equivalent quantity of methylborate (52 g.) was obtained *n*-butylboronic acid as fine crystals, m. p. 92~94°C, yield ca. 50 g. (ca. 50% of the theory).

**Esterification of Polyvinylalcohol with *n*-Butylboronic Acid.** — Purified polyvinylalcohol (PVA) which has the polymerization grade of about 1500 and was reprecipitated by the usual method is dissolved in water, the concentration of which is always kept constant (2.5%). The concentration of boronic acid solutions varied from experiment to experiment. The solution of boronic acid is placed in a 500 ml. four-necked flask with a reflux condenser, and a 2.5% solution of PVA is dropped from a separating funnel at a temperature from 40 to 70°C during one hour, and stirring is continued for one more hour. An insoluble product appears as a white emulsion. On salting out this emulsion, a gum-like material is produced. This product is dried in vacuo and reprecipitated from benzene solution into cold methanol for purification.

**Determination of Boron.**—Although a number of methods for the analysis of boron have been proposed, they are for the most part troublesome. The present authors have modified the method of Martin in the following way[4], which is 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 exactly neutralized to pH 6.9 with hydrochloric acid by the help of a pH-meter and on adding mannitol the solution is titrated back until the pH-meter exactly indicates the mark of 6.9. The content of boron can be estimated from the data*.

**Infrared Spectra.** — *n*-Butylboronate ester is dissolved in carbon tetrachloride and a thin film is made on a mercury dish. The thickness was about 0.03 mm. The apparatus used was a Hitachi spectrophotometer EPI-2.

## Results and Discussion

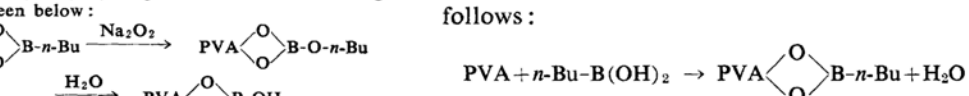
Polyvinylalcohol (PVA) reacts with *n*-butylboronic acid instantly in aqueous solution. The product is obtained in a state of emulsion, but after salting out, it can be obtained as a solid. If the concentration of *n*-butylboronic acid is varied against the constant concentration of PVA, the products are varied in form from gum-like to transparent white hard solids. The materials obtained are all insoluble in water, but dissolve in many organic solvents. These differences chiefly depend upon the boron content of the products. The solubility of the products increases with the increasing boron content. Table I shows the solubility in several organic solvents, of the product which contains the highest quantity of boron.

TABLE I. THE SOLUBILITY OF PVA-*n*-BUTYLBORONATE

| Solvent | Solubility | Solvent | Solubilty |
|---|---|---|---|
| Methanol (in hot) | s | Chloroform | ss |
| Ethanol | s | Benzene | ss |
| Buthanol | s | Toluene | ss |
| Ether | ss | Nitrobenzene | sw |
| Tetrahydrofuran | ss | Phenol | sw |
| Petroleum-ether | sw | Chlorobenzene | s |
| Acetone | sw | Aniline | is |
| Ethylacetate | s | Pyridine | s |
| Carbon disulfide | ss | Formic acid | is |
| Carbon tetrachloride | ss | Acetic acid | sw |

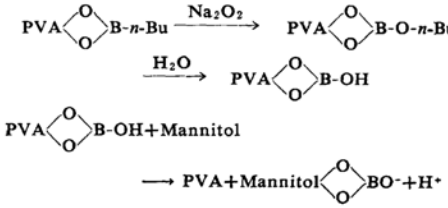
Note, s: soluble ss: very soluble
is: insoluble sw: swelling

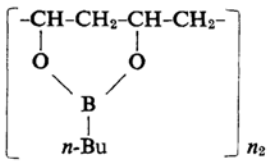
It has been known that in acetalization of PVA, the product acetalized dissolves in various organic solvents, and that the solubility increases with the acetalization grade. In view of these phenomena, the authors have estimated the esterification grade of PVA-boronates by determining the boron content of the products, the formation of which is formulated as follows:



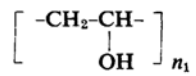
In the above reaction PVA is partially esterified with boronic acid; hence the product may be represented as consisting of the following two parts:

3) J. R. Johnson et al., *J. Am. Chem. Soc.*, **60**, 115 (1938).
4) J. R. Martin, *Anal. Chem.*, **24**, 182 (1952).
* While PVA-borate is produced as the result of oxidation and hydrolysis, it gives free PVA on adding mannitol as seen below:





Mol. wt. = 153.8



Mol. wt. = 44

Then,

$$N = 2n_2 + n_1$$

where $N$ is the polymerization grade of PVA, and

$$B\% = (10.8\, n_2)/(153.8\, n_2 + 44\, n_1) \times 100$$

$$E_g = 2n_2/N \times 100$$

where $E_g$ is the esterification grade.

From the above three equations, it follows that

$$E_g = (133.74 \times B\%)/(16.41 - B\%)$$

Flory[5] has shown from the statistical theory that the maximum grade of acetalization is 86.47%; that is to say, 13.53% of the hydroxyl groups in PVA remains unreacted. While Noma and his coworkers[6] obtained experimentally the maximum value of acetalization, they used the reaction of PVA with diethylchloroacetal, and by determining the chlorine content by the Carius method, they found that the acetalization grade is not affected by the concentration of diethylchloroacetal, and the maximum value is in reality less than 85%. As to the reaction of PVA with *n*-butylboronic acid, the esterification grade $E_g$ increases with concentration of the latter. Table II shows the relation between the concentration of *n*-butylboronic acid and $E_g$, where the concentration of PVA is fixed to be 2.5%.

Table II. Relation between concentration of reactant and $E_g$

| No. | *n*-Butylboronic acid | Molar ratio | B% | $E_g$, % |
|---|---|---|---|---|
| B-1 | 1.25 | 1/2 | —* | — |
| B-2 | 2.50 | 1 | 5.97 | 75.4 |
| B-3 | 5.00 | 2 | 6.17 | 80.6 |
| B-4 | 7.50 | 3 | 6.31 | 83.6 |
| B-5 | 10.00 | 4 | 6.39 | 85.6 |

* Not salted out.

As seen from Table II the molar ratio of PVA to *n*-butylboronic acid is varied from one half to four. Above this concentration *n*-butylboronic acid dissolves incompletely, and hence the reaction does not proceed normally.

It is, however, to be remarked that the maximum value of $E_g$ agrees with the values obtained by Flory[5] and Noma[6]. The structure of PVA has been studied by many authors[7] and is generally considered to be of 1, 3-glycol form, but in the above equations the forms of 1, 2- and 1, 4-glycol, are not effective in estimating the value of $E_g$, because the molecular weight of the unit is equal.

Observing the fact that these esters in benzene as well as carbon tetrachloride can be spun into poor solvents and that the esters are very soluble in various solvents it may be considered that PVA reacts with boronic acid to form no didiol complexes II of so-called network structure but yields a monodiol I. This presumption is supported by the investigations of PVA-borate by Irany[8] and by Deuel[9]. Sakurada and Okada[10] previously reported on the reaction of PVA with boric acid, showing the structure of the product by means of X-ray diffraction, that the trivalent hydroxyl groups in boric acid form a cyclic structure such as III and when the relative concentration of boric acid to PVA becomes higher, a didiol structure II should also be taken into consideration.

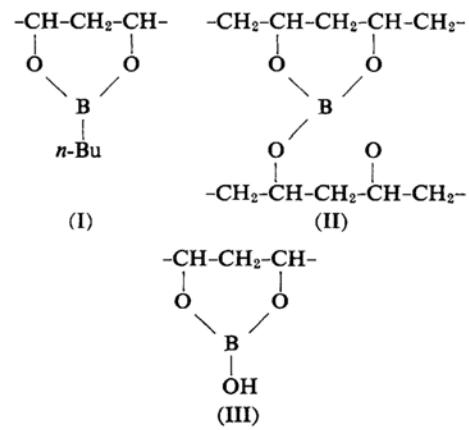


Fig. 1

In the case of *n*-butylboronic acid, however, a structure as II is not conceivable, for boronic acid is of divalent character and the boron atom is sterically hindered by the *n*-butyl group greater than the hydroxyl of boric acid.

**The Effect of Catalyst and Temerature.** — While in acetalization of PVA, an acid catalyst is fundamental for determining the reaction velocity[11], but the reaction of this esterification

5) P. J. Flory, *J. Am. Chem. Soc.*, **61**, 1518 (1939).
6) K. Noma et al., *High Polymer Chem.* (*Kobunshi Kagaku*), **6**, 439 (1939).
7) C. S. Marvell and C. E. Denoon, *J. Am. Chem. Soc.*, **60**, 1045 (1938).
8) E. P. Irany, *Ind. Eng. Chem.*, **35**, 1290 (1943).
9) H. Deuel und H. Neukom, *Makromol. Chem.*, **3**, 13 (1949).
10) I. Sakurada and A. Okada, *High Polymer Chem.*, (*Kobunshi kagaku*), **15**, 491 (1958).
11) G. Smets and B. Pett, *Makromol. Chem.*, **33**, 41 (1959). Y. Ogata et al., *J. Am. Chem. Soc.*, **78**, 2962 (1956).

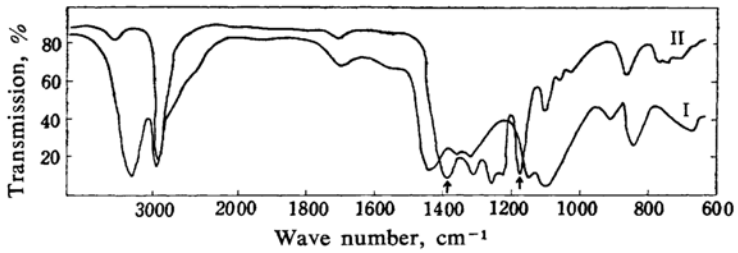



Fig. 2. Infrared spectra of polyvinylalcohol (I) and polyvinyl *n*-butylboronate (II).

proceeds instantly, and the determination of $E_g$ showed that the influence of $H^+$ on the reaction was not noticeable. Of course in alkaline solution, esterification does not proceed; the ester, if produced, may be saponified as soon as it is formed.

**The Effect of Temperature.** — The effect of temperature on $E_g$ is remarkable. In the range of 40 to 70°C, the values of $E_g$ rise as the temperature is raised, as shown in Table III.

TABLE III

| Temp., °C | 40 | 50 | 60 | 70 |
|---|---|---|---|---|
| $E_g$, % | 69.3 | 71.9 | 80.3 | 85.6 |

**Infrared Spectra.** — In order to study the structure of the esterification products, deeper infrared spectra were taken in the form of films prepared from carbon tetrachloride solutions of the esters on a mercury dish, the results of the observation being shown in Fig. 2.

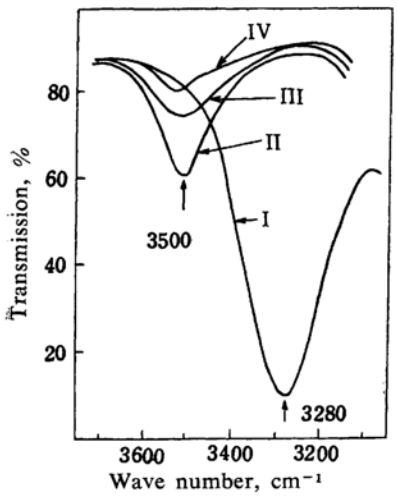



Fig. 3. Shifts of OH absorption band.
I: PVA II: B-2 III: B-4 IV: B-5

Curve I in Fig. 2 shows the spectrum of PVA unreacted. On treating with *n*-butylboronic acid it shows new absorption bands in the region of 1000 to 1500 $cm^{-1}$. In this region 1190 and 1390 $cm^{-1}$ can be assigned respectively to -B-C and -B-O bonds[12-14]. At the same time the OH stretching absorption band at 3280 $cm^{-1}$ of PVA shifts to a higher frequency by treatment with boronic acid and decreases in intensity with the increasing value of $E_g$ as shown in Fig. 3.

As seen in Fig. 3, it is observed that the decrease in intensity is related to $E_g$ qualitatively, and quantitative treatments will be reported in a later paper.

## Summary and Conclusion

It has been shown that PVA is partially esterified with *n*-butylboronic acid, giving products of the form of PVA  B-*n*-Bu.

The esterification grade, $E_g$, of the products is estimated from the boron content. $E_g$ increases with the increasing concentration of *n*-butylboronic acid used, the maximum $E_g$ being 85.6%. $E_g$ rises from 69.3 to 85.6% as the reaction temperature is elevated from 40 to 70°C.

On treating with *n*-butylboronic acid PVA shows new absorption bands 1190 and 1390 $cm^{-1}$ in deeper infrared spectra, which are assigned respectively to -B-C and -B-O bonds. At the same time the OH stretching absorption band at 3280 $cm^{-1}$ of PVA shifts to a higher frequency, and decreases in intensity with the increasing $E_g$.

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12) W. J. Lehmann, *J. Chem. Phys.*, **28**, 777 (1958).
13) Jeo Cazes, *Compt. rend.*, **247**, 2019 (1958).
14) H. R. Snyder et al., *J. Am. Chem. Soc.*, **80**, 3612 (1958).