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Abstract

Full Text

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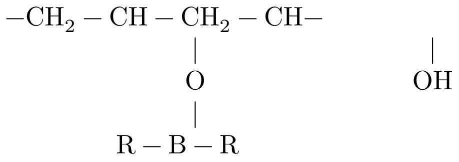
ON THE SYNTHESIS OF BORON DERIVATIVES OF POLYVINYL ALCOHOL

The presence of reactive hydroxyl groups ($\sim 38.64\%$) in the molecule of polyvinyl alcohol creates the possibility of carrying out numerous transformation reactions in its chain. For example, individual representatives have been obtained that contain titanium, copper, phosphorus, sulfur, boron, and other elements in their molecule. In the USSR, research in this field was begun by one of us jointly with K. V. Belogorodskaya (^{1}). The present work is a continuation of studies on the synthesis of derivatives of polyvinyl alcohol with organoelement radicals in the side chain. Until now, esters of polyvinyl alcohol with boric acid have been known; recently a paper was published (^{2}) on the preparation of an ester of polyvinyl alcohol with mono-*n*-butylboric acid.

For modifying the properties of polyvinyl alcohol, the preparation of esters of polyvinyl alcohol with disubstituted organoboronic acids is also of interest. There are no reports in the literature on the preparation of esters of polyhydric alcohols, including polyvinyl alcohol, with disubstituted organoboronic acids.

We investigated the conditions for preparing esters of polyvinyl alcohol with disubstituted organoboronic acids of the general formula:

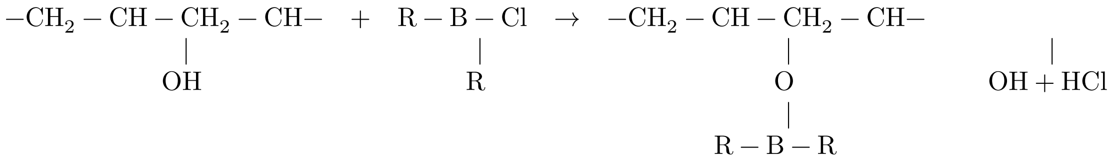


$$\begin{array}{ccccccc} -CH_2 - & CH & - CH_2 - & CH- & & & \\ & | & & & & & | \\ & O & & & & & OH \\ & | & & & & & \\ R - & B & - R & & & & \end{array}$$

where R is aryl or alkyl.

For this purpose the following routes were used:

1. Interaction of partially saponified polyvinyl acetate with acid chlorides of disubstituted organoboronic acids.
2. Interaction of polyvinyl alcohol with acid chlorides of disubstituted organoboronic acids according to the following scheme:



$$\underset{\substack{| \\ \mathrm{OH}}}{-\mathrm{CH_2}-\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH}- \;+\; \mathrm{R}-\underset{\substack{| \\ \mathrm{R}}}{\mathrm{B}}-\mathrm{Cl} \;\rightarrow\; -\mathrm{CH_2}-\mathrm{CH}-\underset{\substack{| \\ \mathrm{O} \\ | \\ \mathrm{R-B-R}}}{\mathrm{CH_2}}-\mathrm{CH}- \quad \underset{\substack{| \\ \mathrm{OH}}}{} + \mathrm{HCl}$$

where $R = \mathrm{C_6H_5}$ or $\mathrm{C_4H_9}$.

The present work reports the synthesis and properties of the ester of polyvinyl alcohol and diphenylboronic acid.

When the reaction was carried out with partially saponified polyvinyl acetate, containing $\sim$ 10 mol.% hydroxyl groups, with an excess of diphenylboron chloride in the presence of magnesium carbonate in a nonpolar solvent medium (benzene), no positive results could be obtained.

We carried out and studied the reaction of interaction of diphenylboron chloride and its complexes—with polyvinyl alcohol—in an elec-

of proton-donor polar solvents according to the following schemes:

$$\begin{gathered}-\mathrm{CH_2{-}CH(OH){-}CH_2{-}CH(OH)}- + \mathrm{Ph_2BCl{:}NC_5H_5} \longrightarrow \\ -\mathrm{CH_2{-}CH(O{-}BPh_2){-}CH_2{-}CH(OH)}- + \mathrm{C_5H_5NH^+Cl^-}\end{gathered}$$

$$\begin{gathered}-\mathrm{CH_2{-}CH(OH){-}CH_2{-}CH(OH)}- + \mathrm{Ph_2BCl{:}O{=}CH{-}N(CH_3)_2} \longrightarrow \\ -\mathrm{CH_2{-}CH(O{-}BPh_2){-}CH_2{-}CH(OH)}- + \left[\mathrm{H{-}C(OH){=}N(CH_3)_2}\right]^+ \mathrm{Cl^-}\end{gathered}$$

$$\begin{gathered}-\mathrm{CH_2{-}CH(OH){-}CH_2{-}CH(OH)}- + \mathrm{Ph_2BCl{:}O{=}S(CH_3)_2} \longrightarrow \\ -\mathrm{CH_2{-}CH(O{-}BPh_2){-}CH_2{-}CH(OH)}- + \mathrm{(CH_3)_2SOH^+Cl^-}\end{gathered}$$

Polyvinyl alcohol with $M = 48\,000$ and 1.62 mol.% residual acetate groups was used in the work. Diphenylboron chloride and its complexes with pyridine and dimethylformamide, synthesized by us ([3,4]), were used as esterifying agents. Diphenylboron chloride had the following characteristics: b.p. 119–120°/3 mm, d_4^{20} 1.1091 and n_D^{20} 1.6075. Electron-donor solvents were used as the reaction medium: pyridine, dimethylformamide, and dimethyl sulfoxide. In the case of pyridine, the polyvinyl alcohol was subjected to preliminary activation in order to increase its reactivity; this was carried out by two methods: swelling in a mixture of 90% pyridine and 10% water for 48 hours and treatment several times with dry pyridine, or heating at 100° for 4 hours. In experiments in dimethylformamide medium, the polyvinyl alcohol was also heated before the reaction at 100°. In dimethyl sulfoxide, polyvinyl alcohol dissolves at 50–60° over 30 min, giving a clear solution stable at room temperature. The reaction products were isolated from the reaction mixture by precipitation in methanol, purified by two repeated precipitations, washed, and dried in vacuum at room temperature to constant weight. The content of OH groups was determined by acetylation according to Verley, and the elemental composition (carbon, hydrogen, and boron content) by Korshun' s rapid combustion method. Subsequent pro-

verification of the results was carried out by the Wittig method ([5]), for the simultaneous determination of boron and phenyl groups by decomposition with chloric mercury.

A study of the reaction of polyvinyl alcohol with diphenylboron chloride showed that at 20° esterification does not proceed in pyridine, but with an increase in temperature above 60° the reaction rate increases, so that at 80° a fairly high degree of substitution is obtained. For complete homogenization of the reaction mixture, chloroform was added. The reaction rate increases when the excess of diphenylboron chloride is increased. For example, in experiments carried out in pyridine, at a molar ratio of 1 : 1 the degree of substitution was 42.2 mole %, whereas at 2 : 1 it was 81.9 mole % in 24 hours. As the duration of the reaction increases, the degree of substitution increases. In dimethylformamide the reaction is homogeneous from the very beginning, proceeds more uniformly and intensively than in pyridine, so that in 10 hours the degree of substitution reaches ∼ 61 mole %, and in 24 hours ∼ 96 mole %. In dimethyl sulfoxide, at a lower temperature (50°), in 5 hours the degree of substitution reaches ∼ 15 mole %, and in 12 hours ∼ 37 mole %. Thus, the greater the ionizing ability of the solvent, the higher the rate of the esterification reaction of polyvinyl alcohol.

For the polymers obtained, an IR absorption spectrum was recorded, which confirmed the presence in the polymer of new groups in comparison with polyvinyl alcohol: the band at 1270 cm^{-1} may be assigned to the vibration of the B–C bond

in the grouping –B [[unclear: structural formula]] according to the literature data ([6],[7]), and the band

at 1350 cm^{-1} to the vibration of the B–O bond, characteristic of esters of diphenylboric acid ([6],[8]). The absorption band of OH groups, very strong in the spectrum of polyvinyl alcohol in the region ∼ 3340 cm^{-1}, in the spectrum of the ester of polyvinyl alcohol with diphenylboric acid is very weak at ∼ 3580 cm^{-1}.

All the polymers are not wetted by and are not soluble in water, even on heating, nor in alcohols, acetone, or ethyl acetate. Polymers of all degrees of substitution dissolve in strongly polar solvents: pyridine, dimethylformamide, and dimethyl sulfoxide, with the solubility increasing as the degree of substitution increases. All these polymers readily dissolve in benzyl alcohol, which apparently is explained by the high affinity of the phenyl groups present in the side chain for the solvent molecules. In dioxane, in the cold, most of the polymers swell, and on heating they dissolve.

The results of a study of the viscosity of solutions of the starting polyvinyl alcohol ($[\eta] = 0.798$), of polyvinyl alcohol after heating in pyridine at 100° for 24 hours ($[\eta] = 0.794$), and of esters of polyvinyl alcohol and diphenylboric acid of various degrees of substitution (for example, $[\eta] = 0.799$ with 72.74 mole % ester units) showed that no appreciable destruction of the chains occurs. Thus, it may be assumed that, using polyvinyl alcohol of various molecular weights as the starting material, one can obtain its esters with chain lengths close in magnitude, owing to insignificant destruction even under prolonged heating (100°).

The experimental data showed that the polymers obtained, unlike low-molecular compounds analogous in structure, are resistant to the action of water. They do not hydrolyze even on boiling in water for 8-10 hours. The resistance of the B—O—C bond of the polymers to the action of water is apparently explained by the shielding effect, on the one hand, of the phenyl radicals attached to the boron atom and, on the other hand, of the polymeric carbon-carbon chain. Steric hindrances impede attack of the boron atom by water molecules. The greater the degree of sub—

Table 1

Glass-transition temperature and electrical properties of esters of polyvinyl alcohol and diphenylboric acid

No.	Polymer name	Degree of substitution, mol. %	Glass-transition temperature, °C	ρ_v, ohm · cm	tg δ	E
1	Polyvinyl alcohol	–	80	$1 \cdot 10^{11}$	3	3.5
2	Ester of polyvinyl alcohol and diphenylboric acid	14.4	106.5	–	–	–
3	Same	36.6	135	–	–	–
4	» »	42.2	–	$9 \cdot 10^{14}$	0.021	3.3
5	» »	80.6	136	$1 \cdot 10^{15}$	0.018	–
6	» »	91.3	–	$7.5 \cdot 10^{14}$	0.015	3.3

···of the ether, the lower the probability of approach and penetration of water molecules to the B—O—C bond, and the lower the degree of hydrolysis of the ether. The polymers obtained, when heated for several hours in the presence of alkalis and ammonia, undergo partial hydrolysis. Hydrolysis of these polymers with an aqueous ammonia solution (25%) proceeds faster than hydrolysis with caustic soda (25%).

To determine the glass-transition temperature, tablets were pressed from the products obtained. The glass-transition temperature was determined from the thermomechanical curve obtained on Kargin dynamometric balances. As can be seen from Table 1, the introduction of diphenylboroxy groups has a strong effect on the glass-transition temperature (T_c), which, with increasing degree of substitution, increases to a certain value in comparison with T_c of the initial polyvinyl alcohol. Thus, if for polyvinyl alcohol $T_c = 80°$, then for the ester containing 14.4 mol.% of such groups, $T_c = 106°$, while polymers containing 37 mol.% of diphenylboroxy groups have $T_c = 135°$. The increase in the glass-transition temperature upon introduction of diphenylboroxy groups is a very noteworthy property of these polyvinyl alcohol derivatives and, apparently, should be explained mainly by the rigidity of the phenyl rings. The interaction between polymer chains is increased due to the van der Waals forces of the phenyl radicals, which leads to an increase in the glass-transition temperature.

To determine the electrical properties, films were cast from 3-5% solutions in dioxane onto the surface of mercury. Some indices of the electrical properties of the polymers are given in Table 1. These data show that, upon introduction of diphenylboroxy groups, the electrical-insulating properties of the polymers improve in comparison with the initial polyvinyl alcohol.

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Note: Figure translations are in progress. See original paper for figures.