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The Mechanism of Reaction between Poly(vinyl Alcohol) and Phosphorous Acid

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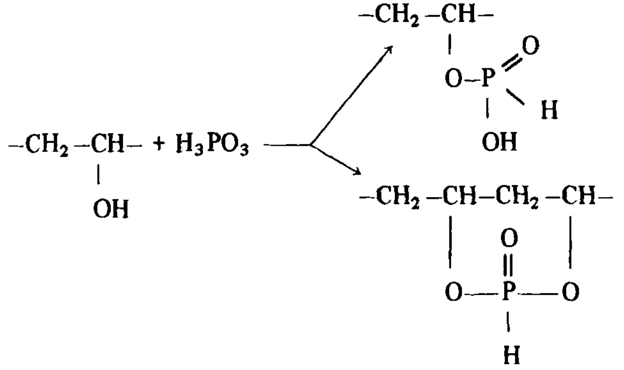
SUMMARY

The reaction mechanism of phosphorous acid and poly(vinyl alcohol) is presented. It has been found that there during this reaction mono- and diesters are formed in which most of the acid radicals are in the phosphonic form. To confirm the presence of this form in the product obtained, reactions with diethyleneamine and chloral have been carried out as characteristic tests for phosphonic groups. The occurrence of C–P bonds resistant to hydrolysis has been also found in the reaction product.

INTRODUCTION

Nifantiev, Fursenko, and Lvov [1] have reported the modification of poly(vinyl alcohol) (PVA) with phosphorous acid in benzene. These authors suggest the course of reaction shown in Eq. (1). This means that mono- and disubstituted esters are formed, and it is possible that disubstituted esters are formed as a result of intermolecular and intramolecular reactions. Such conclusions have been drawn from chromatographic examinations of the product obtained by methanolysis of PVA modified with phosphorous acid. The same reaction mechanism is accepted by Mieos, Volf, and Volgina [2].



Investigations of the hydrolysis of PVA modified with phosphorous acid carried out by the author have shown that in the modification product not all phosphorus undergoes acid hydrolysis or methanolysis. This finding was the basis for the experiments described in the present paper.

EXPERIMENTAL

Hydrolysis of Modified PVA

PVA was modified with phosphorous acid by the author in the manner previously described [3]. Samples of polymer containing about 5% of phosphorus were methanolyzed or acid hydrolyzed. For methanolysis the following procedure was used: 0.1 g sample of PVA esterified with phosphorous acid was heated with 25 ml of anhydrous methanol at 65°C for 25 hr under reflux. Then the sample was extracted with acetone and subjected to phosphorus content determination. Acid hydrolysis was carried out in 0.1 N HCl at 50-60°C for 25 hr. Under these conditions the samples were not dissolved but swollen.

The results of hydrolysis are given in Table 1.

Reaction with Diethyleneamine

2×10^{-2} mole of modified PVA was introduced into a mixture of 1 mole of CCl_4 and 0.5 mole of $(C_2H_5)_2NH$. The mixture was heated at 80°C for 4 hr. The process was carried out for two samples of modified PVA of different phosphorus content: I, 5.61%, II, 10.53%. After the reaction was completed, polymer was extracted with acetone, dried under reduced pressure, and subjected to analysis.

Table 1. Phosphorus Content in Modified PVA after Methanolysis and Acid Hydrolysis

Temperature of heat treatment (°C)	Duration of heat treatment (hr)	Phosphorus content after heat treatment (%)	Phosphorus content after methanolysis (%)	Phosphorus content after acid hydrolysis (%)	Amount of unmethanolyzed phosphorus (%)[a]	Amount of unhydrolyzed phosphorus (%)[a]
60	10	5.02	0.29	0.18	5.79	3.58
100	5	5.04	0.62	0.25	13.31	4.96
120	0.5	5.37	0.88	0.46	16.39	8.58
140	0.5	5.51	1.56	0.63	28.31	11.43
160	0.5	5.79	2.01	0.82	34.71	14.16

[a] Phosphorus content after heat treatment was taken as 100%.

Analysis: I, 3.56% P; 47.18% C; 9.75% H; 0.91% N. II, 5.16% P; 45.84% C; 8.96% H; 1.37% N.

Reaction with Chloral

1×10^{-2} mole of modified PVA was introduced into 0.1 mole of chloral dissolved in 25 ml of n-heptane. The mixture was heated at 50°C for 2 hr. The process was carried out for two samples of various phosphorus content: I, 5.61%, II, 10.53%. After the reaction was completed, polymer was extracted with acetone, dried, and analyzed.

Analysis: I, 3.08% P; 47.51% C; 9.07% H; 1.20% Cl. II, 5.45% P; 44.16% C; 8.58% H; 1.47% Cl.

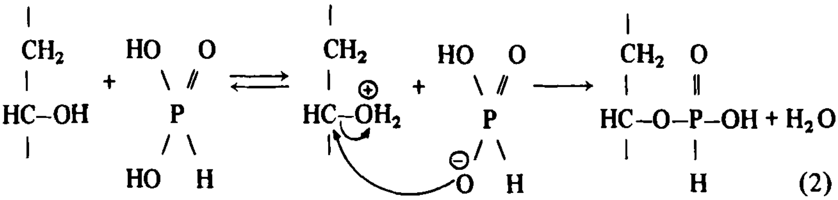
Reaction of H_3PO_3 and Chalcone

1×10^{-2} mole of chalcone was heated in a round-bottom flask with 1×10^{-2} mole of H_3PO_3 at 120°C for 4 hr. Then the mixture was dissolved in benzene. Unreacted H_3PO_3 was washed out with water from the benzene solution. After repeated shaking the benzene solution with water and separation of the mixture in a separatory funnel, the benzene solution was dewatered and benzene evaporated. The dry residue contained 0.48% of phosphorus.

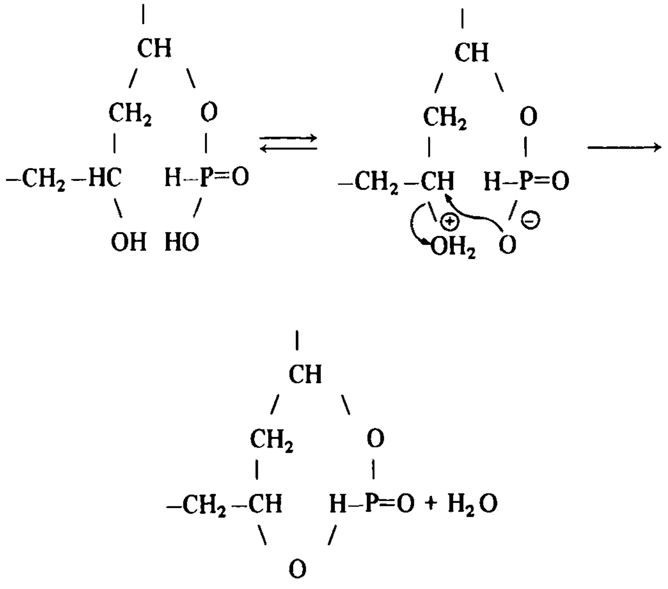
DISCUSSION

The results of phosphorus content determinations in modified PVA (Fig. 1) show the presence of C–P bonds resistant to hydrolysis in the polymer. The percentage content of such bonds depends on the temperature (Fig. 2) of the thermal treatment during which esterification of PVA with H_3PO_3 takes place.

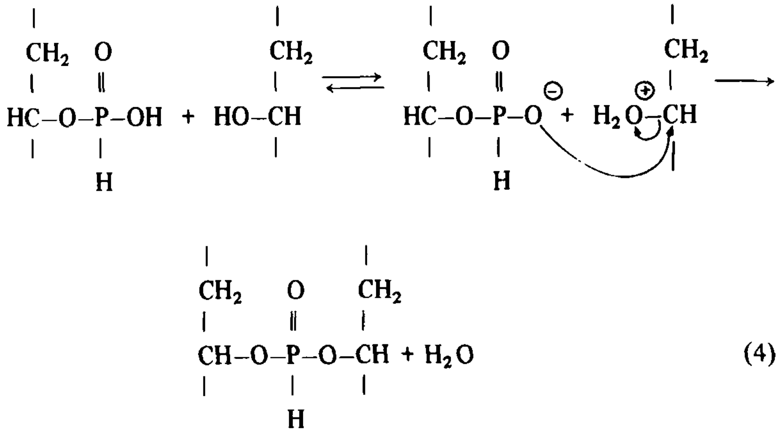
On the basis of experiments the following reaction mechanism of PVA with phosphorous acid is proposed:



$$\mathrm{-CH_2-CH(OH)- + (HO)_2P(=O)H \rightleftharpoons -CH_2-CH(\overset{\oplus}{O}H_2)- + (HO)(\overset{\ominus}{O})P(=O)H \longrightarrow -CH_2-CH(O-P(=O)(OH)H)- + H_2O} \qquad (2)$$



(3)



(4)

In reaction schemes (2)-(4) phosphorous acid is in the phosphonic form, in spite of the fact that two tautomeric forms of this acid are reported in the literature [4, 5] as being in equilibrium:

$$P(OH)_3 \rightleftharpoons HPO(OH)_2$$

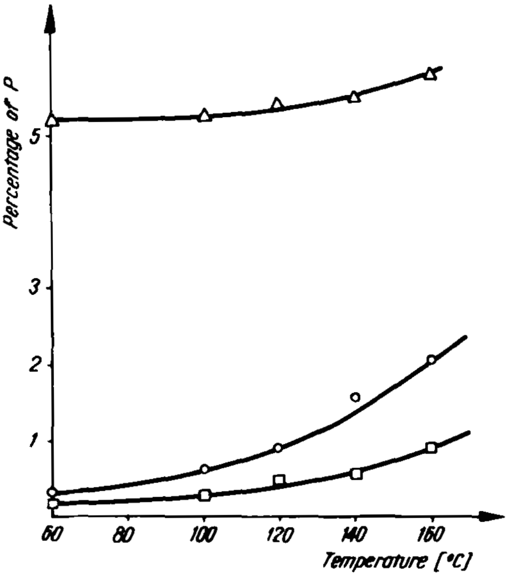


Fig. 1. The effect of reaction temperature on the unhydrolyzed phosphorus content in PVA. △: Phosphorus content before hydrolysis. ○: Phosphorus content after methanolysis. □: Phosphorus content after acid hydrolysis.

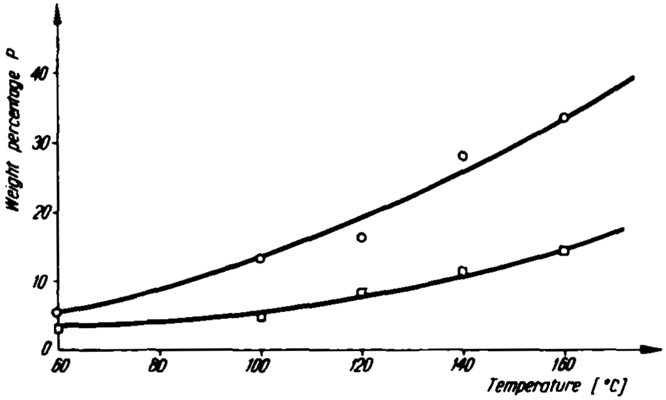


Fig. 2. The effect of reaction temperature on the per cent share of unhydrolyzed phosphorus. ○: In the methanolysis process. □: In the acid hydrolysis process.

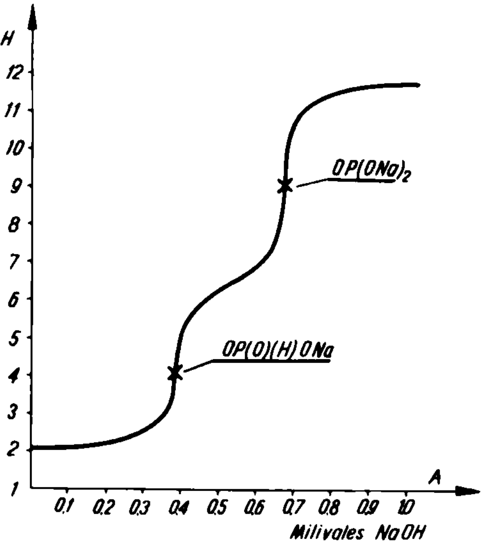
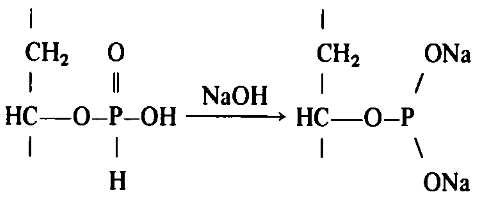


Fig. 3. Plot of pH titration of 0.5 g PAV modified with H_3PO_3. Phosphorus content, 5.59%.

Reaction (2) is the main one and takes place over a wide range of temperatures (Table 1). Such a reaction is supported by the fact that a diagram characteristic of dibasic acid is obtained (Fig. 3) during titration of the product with sodium hydroxide solution which is a result of the shift of equilibrium towards the phosphite form in alkaline medium (Eq. 5).



$$\underset{|}{\overset{\overset{|}{CH_2}}{\overset{|}{HC}}}-O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-OH \xrightarrow{NaOH} \underset{|}{\overset{\overset{|}{CH_2}}{\overset{|}{HC}}}-O-P\begin{matrix}\diagup ONa\\ \diagdown ONa\end{matrix} \qquad (5)$$

The yield of Reaction (2) is about 96% at 60°C. Figure 4 shows the dependence of the content of hydroxyl groups linked to phosphorus on the temperature. The plot was based on the results of titration of modified PVA with 0.1 N NaOH. The pH measurements were made at 20°C using 0.5 g of polymer. The results confirm the assumption that some of the hydroxyl groups participate in intra- and intermolecular reactions (Eqs. 3

and 4). This finding was confirmed by an increase in the viscosity of the solutions (Fig. 4). A rapid increase of the reduced viscosity for 0.5% of the polymer solutions subjected to heat treatment above 100°C is probably due to the corss-linking of phosphonic groups in the polymer above this temperature.

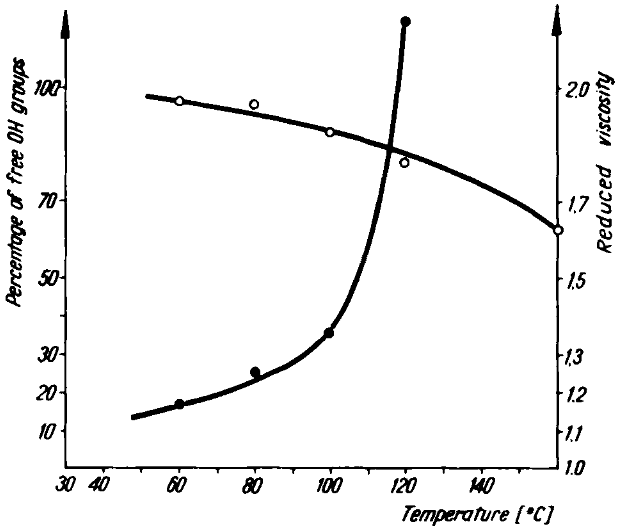


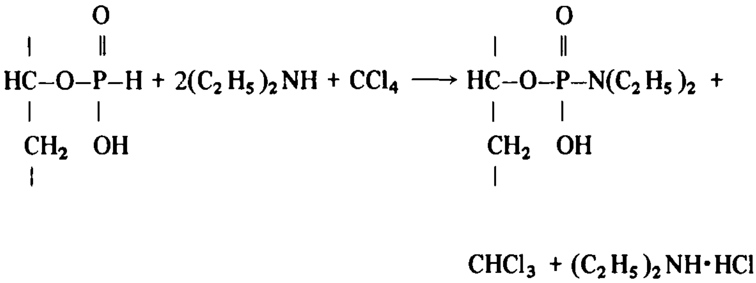
Fig. 4. The effect of the reaction temperature. ●: On reduced viscosity of modified PAV for 0.5% solutions. ○: On the content of hydroxyl group combined with phosphorus atoms. Reaction time, 0.5 hr. Concentration of H_3PO_3 solution used for swelling, 10%.

As a result of Reactions (2), (3), and (4), mono- and diesters of phosphorous acid are formed, the acid radical being in the phosphonic form. This is supported by reactions characteristic of the phosphonic form with diethyleneamine and chloral (Eqs. 6 and 7).

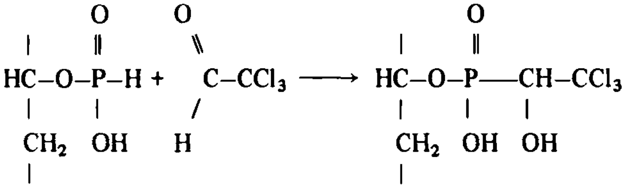
Such reactions have been reported in the literature for low-molecular weight compounds [8-10] and cellulose [11].

Poly(vinyl alcohol) is dehydrated already at 70°C (Reaction 8).

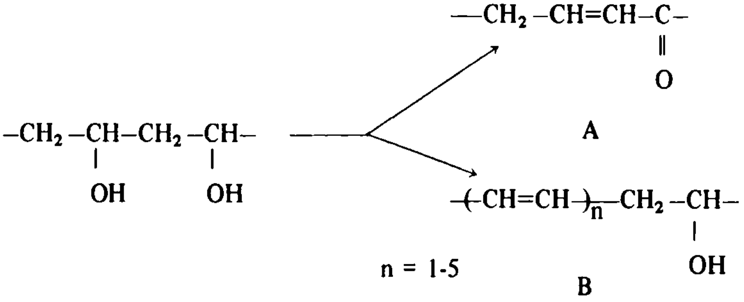
As a result of dehydration, PVA segments of conjugated double bonds and carbonyl groups are formed in macromolecules [6, 7]. Phosphorous acid is a dehydrating agent and its acid radicals linked to the polymer favor the dehydration process. This process takes place both in the presence and absence of oxygen.



$$\overset{|}{\underset{\underset{|}{CH_2}}{\underset{|}{HC}}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-H + 2(C_2H_5)_2NH + CCl_4 \longrightarrow \overset{|}{\underset{\underset{|}{CH_2}}{\underset{|}{HC}}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-N(C_2H_5)_2 + CHCl_3 + (C_2H_5)_2NH{\cdot}HCl \quad (6)$$



$$\overset{|}{\underset{\underset{|}{CH_2}}{\underset{|}{HC}}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-H + \overset{\overset{O}{\backslash\backslash}}{\underset{\underset{H}{/}}{C}}-CCl_3 \longrightarrow \overset{|}{\underset{\underset{|}{CH_2}}{\underset{|}{HC}}}-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-\underset{\underset{OH}{|}}{CH}-CCl_3 \quad (7)$$

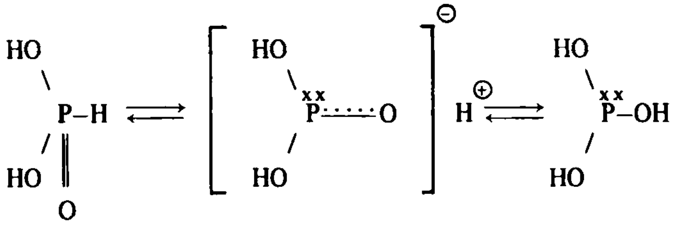


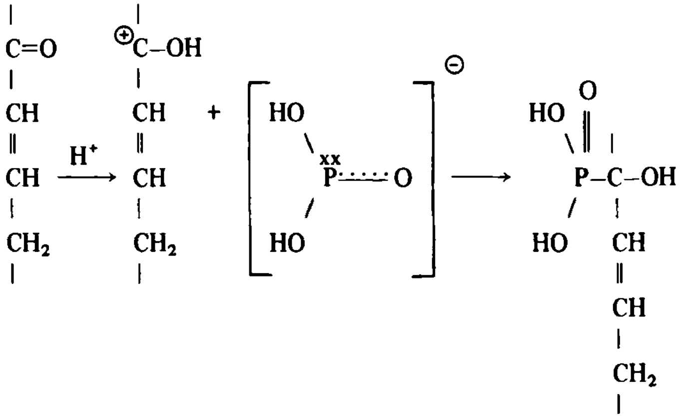
(8)

In samples of polymer of higher phosphorus content dehydration proceeds at a higher rate and at a lower temperature (Fig. 5).

An additional proof of the dehydration process during modification of PVA with phosphorous acid is the fact that samples of polymer swollen with phosphorous acid and heated grow dark, becoming brown in color at 100°C and brown-black over 140°C. This is due to the presence of high chromophoric group content which results from the dehydration of PVA.

Thus, the occurrence of carbonyl groups and conjugated double bonds [6] in modified PVA leads presumably to Reaction (9) which is responsible for the presence of C–P bonds resistant to hydrolysis in the modified polymer.





(9)

Reaction (9) presumably proceeds according to the ionic mechanism in an analogous way in the reaction of phosphorous acid or hypophosphorous acid with ketones catalyzed by acids [15].

In agreement with the literature [12, 17], both tautomeric forms of phosphorous acid can form a shared ion which enters into reaction with the electrophilic carbon atom of the carbonyl group (Reaction 9).

To obtain additional proof for the course of Reaction (9), a modification of polybutadiene was carried out with phosphorous acid. A purified sample of polybutadiene was swollen in 20% phosphorous acid and heated to 140°C. Analytical examination showed the absence of phosphorus in the polymer, and this excludes the attachment of phosphorous acid to the double bond nonactivated by carbonyl group (15) or by a free radical mechanism [16].

It is hardly probable, on this basis, for phosphorous acid to attach to conjugated double bonds (Product 8B) during modification of PVA. The literature [13, 14] has reported many addition reactions of phosphorous acid to double bonds activated by the adjacent carbonyl group. Reactions of this type are catalyzed by alcoholate. In such cases phosphorus

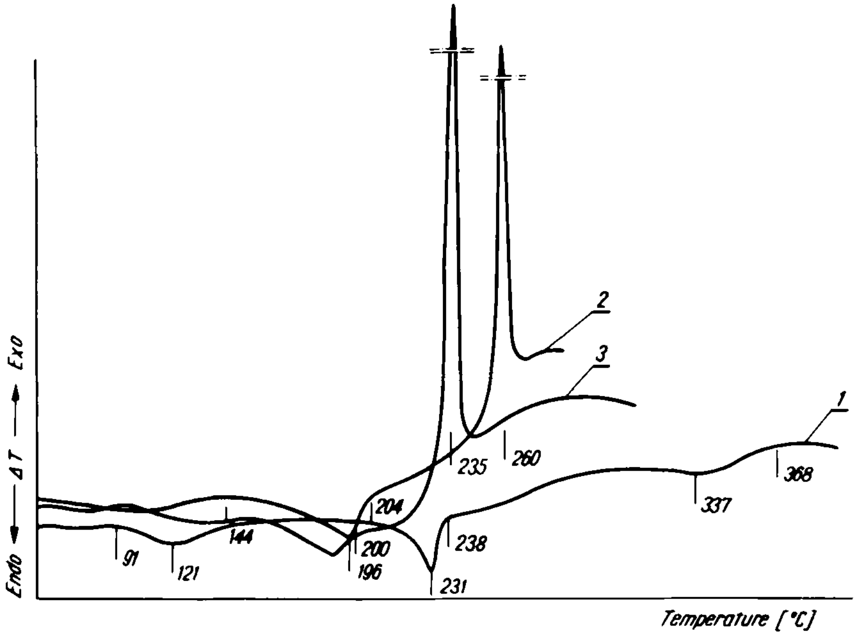


Fig. 5. Programmed DTA for PAV in air. 1: Unmodified PVA. 2: Modified PVA; phosphorus content, 1.76%. 3: Modified PVA; phosphorus content, 5.59%.

substitution takes place at the carbon atom in the β-position to carbonyl group, but in the case of acid catalysis the substitution proceeds at the carbon of the carbonyl group [15] and this is in agreement with the proposed mechanism of PVA modification with the aid of phosphorous acid (Reactions 2-4, 8, 9). This mechanism is also confirmed by the reaction of H_3PO_3 with chalcone.

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