

## Dispersed Homogeneous Polymeric Analogues of Poly-N-Vinyl Pyrrolidone with Organic Acids

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### Abstract

On the basis of the data of IR spectroscopy and X-ray phase analysis, it was established that poly-N-vinyl pyrrolidone enters chemical interaction with organic acids during their joint mechanical activation. The character of this interaction depends on the nature of an acid but does not depend on the type of activator, while the duration of the interaction depends both on the nature of an acid and on the type of activator.

### INTRODUCTION

Among organic polymers, poly-N-vinyl pyrrolidone (PVP) (Scheme 1) is most widely used in pharmacy and in cosmetics. It is applied not only as a binder in manufacturing medical tablets, a thickening agent for creams, in toothpastes and lipsticks, a stabilizing agent in aerosols, but also it possesses the ability to prolong the action of medical preparations; it is used as a basis of blood substitute with disintoxication properties, and in textile industry to enhance dyeability.

Poly-N-vinyl pyrrolidone is a carbon backbone chain linear polymer, it is almost non-toxic, and hygroscopic.

The use of PVP as a filler in mechanocomposites, for example, with biologically active substances (BAS), would allow one not only to

broaden the application range of this polymer but also to obtain new homogeneous dispersed solid-phase materials for pharmacy and cosmetics with the help of a rapid and ecologically safe mechanochemical method.

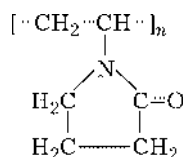
The goal of the present work was to investigate the mechanochemical interaction of PVP with biologically active organic acids of different nature under their joint mechanical activation.

### EXPERIMENTAL

Mechanical activation (MA) of PVP with biologically active organic acids was carried out in a high-energy ball mill of planetary type AGO-2 [1] and in a laboratory ball mill LE-101.

The IR absorption spectra (IRS) were recorded with an infrared spectrometer Specord-75 IR. Before recording, samples were prepared in the form of tablets with calcined KBr. X-ray phase analysis (XPA) was carried out with DRON-3M diffractometer (CuK $\alpha$  radiation).

A polymeric compound poly-N-vinyl pyrrolidone was used in the investigation along with the acids: succinic (CH $_2$ ) $_2$ (COOH) $_2$ , salicylic C $_6$ H $_4$ (OH)COOH, citric (CH $_2$ -COOH) $_2$ C(OH)COOH, and amino acetic (glycine) CH $_2$ NH $_2$ COOH.



Scheme 1.

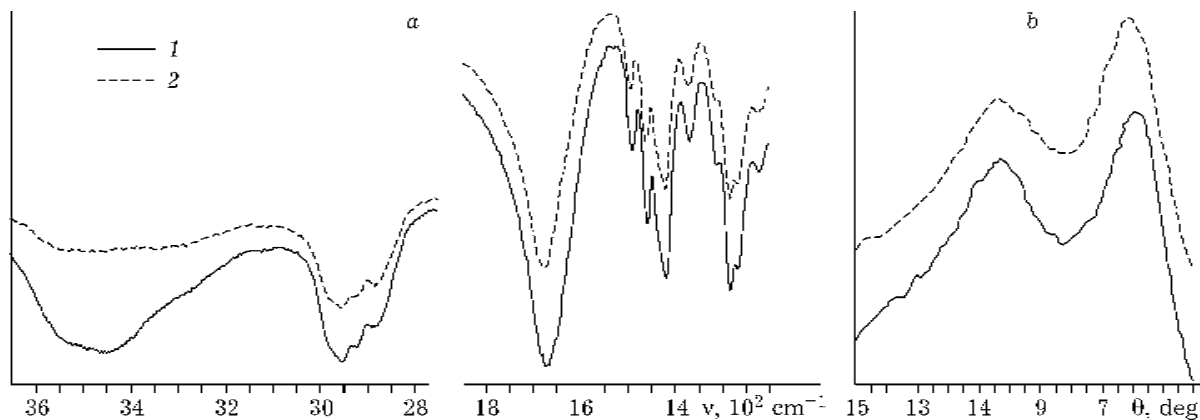


Fig. 1. IR absorption spectrum (a) and diffraction patterns (b) of PVP before (1) and after mechanical activation in AGO-2 mill for 3 min (2).

## RESULTS AND DISCUSSION

### Mechanical activation of initial compounds

It was established by us previously that MA of the organic acids involved in the experiment, carried out in a high-energy mill for  $\tau_a \leq 10$  min, does not result in any substantial distortions of their structure [2–4].

The IR spectrum of PVP (Fig. 1, a) corresponds to the IR spectrum of the standard sample [5]: all the bands of the spectrum are distinct and intensive. The band in the region  $3700\text{--}3250 \text{ cm}^{-1}$  relates to the stretching vibrations of absorption water [6]. The diffraction patterns of PVP (see Fig. 1, b) have two halos within the small angle region. The data of IR spectroscopy and XPA provide evidence of the X-ray amorphous structure of PVP.

The IR spectra and diffraction patterns of PVP before and after activation for 3 min are almost identical. Therefore, MA does not cause essential distortions of the structure of the initial polymer.

### Mechanical activation of the mixtures of the polymer with acids

Analysis of the IR spectra and diffraction patterns of two-component mixtures of PVP with organic acids before and after activation showed that the polymer interacts mechanochemically with succinic, citric and salicylic acids forming mechanocomposites.

Indeed, in the IR spectra of a mixture of PVP with succinic acid (at the mass ratio of

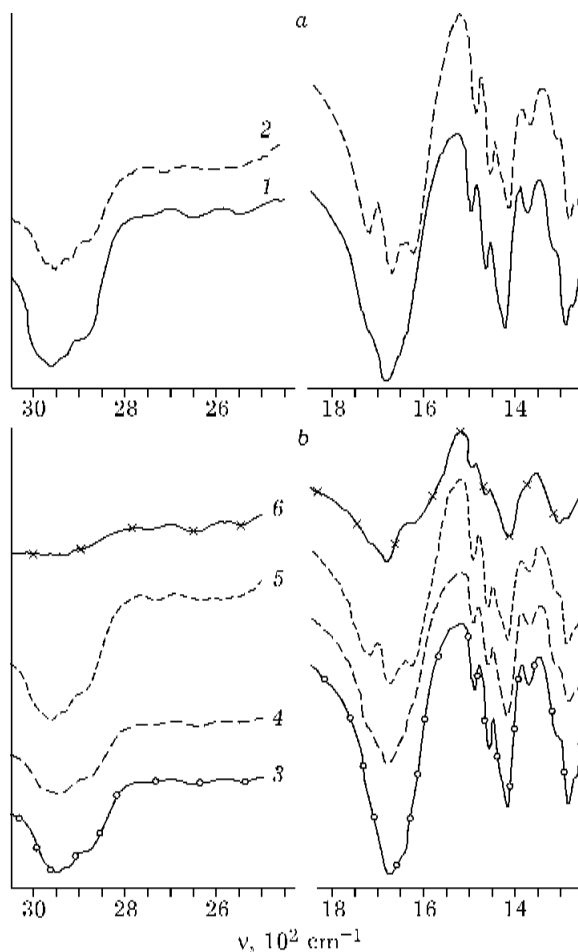
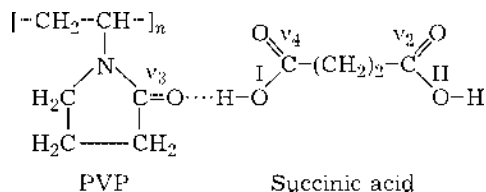


Fig. 2. IR absorption spectra of PVP mixtures with succinic acid: initial (1) and activated in high-energy (a) and usual (b) ball mills. Activation time: 2 – 10 s, 3 – 10 min, 4 – 10 min with the addition of 0.5 ml of water, 5 – 10 min + exposure for 5 days after activation, 6 – 60 min + exposure for 3.5 months; mass ratio polymer : acid = 5 : 1 (1–5), 1.5 : 1 (6).



Scheme 2.

5 : 1) activated for 10 s in a high-energy or for 10 min in a ball mill (exposure: 5 days), instead of one band with the maximum at  $1675\text{ cm}^{-1}$  related to the stretching vibrations of carbonyl groups  $\nu_1$  C=O of the initial polymer and dimers of succinic acid, we observed in fact three bands with the maxima at  $1675$ ,  $1730$  and  $1630\text{ cm}^{-1}$  (Fig. 2, curves 1, 2 and 5). It is likely that MA of the mixture causes rupture of hydrogen bonds in the associates of acids, while active centres, namely active oxygen atoms, appear on the polymer surface [7]; these atoms are able to form hydrogen bonds, due to the unshared electron pair, with the monomers of the carboxylic acid.

According to Scheme 2, the above-indicated bands can be related to the stretching vibrations of C=O bonds in the following groups:  $\nu_1$  – unreacted (initial) associates of the acid and PVP,  $\nu_2$  – carboxylic groups II of the monomers of succinic acid [8],  $\nu_3$  – PVP bound through hydrogen bonds with carboxylic groups I of succinic acid,  $\nu_4$  – carboxylic groups I of acid monomers, respectively.

Hydrogen bonds between the acid and the polymer are stronger than those in acid associates because  $(\nu_2 - \nu_3) \gg (\nu_2 - \nu_1)$  [6].

Due to redistribution of electron density in carboxylic groups I of the acid, forming strong hydrogen bonds with the polymer,  $\nu_4 \neq \nu_2$  and  $\nu_4 < \nu_2$ . It is possible that  $\nu_4 \approx \nu_3$ .

It follows from Fig. 2 (curves 2 and 5) that the character of interaction is independent of activator type. However, in the case of high-energy mill AGO-2, the interaction proceeds almost from the very beginning of activation within 10–30 s. Further increase in activation time causes amorphization of the reaction products. For activation in a usual ball mill, mechanochemical interaction of PVP with succinic acid taken in the same mass ratio is only slightly noticeable at  $\tau_a = 10$  min (see Fig. 2, b, curve 3). An increase in the time of activation of the

mixture and addition of water in the amount of 0.5–1.0 ml (in order to increase the efficiency of interaction due to enhancement of the dissociation of the acid [9]) have no substantial effect on the process (see Fig. 2, curve 4). The results of interaction are clearly exhibited only after the activated samples are kept for 5–7 days. The sample activated in a usual ball mill for 10 min and stored for 5 days is almost identical with the sample activated in a high-energy mill for 10 s (see Fig. 2, curves 2 and 5).

In the IR spectra of mechano-composites, absorption in the region  $2800\text{--}2400\text{ cm}^{-1}$  which is characteristic of the stretching and combined vibrations of OH group [8] becomes diffuse, the main maximum at  $\sim 2650\text{ cm}^{-1}$  disappears, which can be the evidence of the presence of strong hydrogen bonds of PVP with succinic acid in the mechano-composite [6, 8].

It follows from the diffraction patterns of activated mixtures of PVP with succinic acid (Fig. 3) that the ratio of intensities of the halos related to the polymer changes with an increase in activation time. The position of the

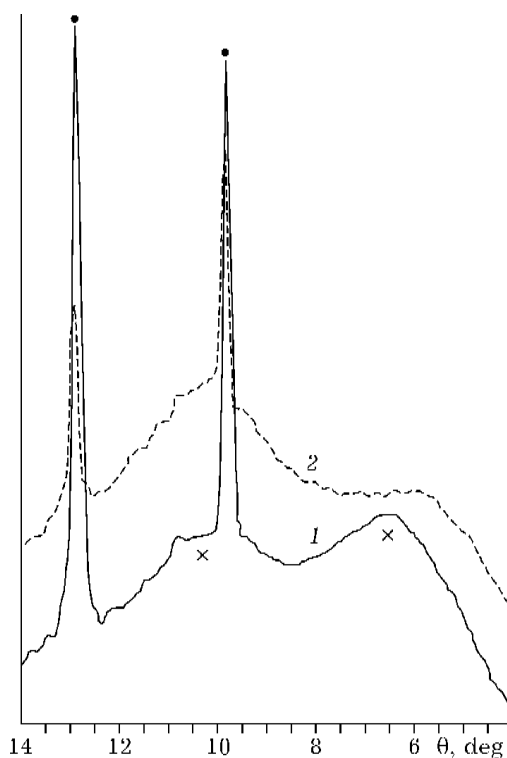


Fig. 3. Diffraction patterns of the mixtures of PVP with succinic acid activated for 3 (1) and 10 min (2). Mass ratio polymer : acid = 5 : 1. • Succinic acid, × PVP.

halo  $d = 7.375 \text{ \AA}$  (see Fig. 1, *b*, curve 1 and Fig. 3, curve 2) shifts to smaller values by 8 %. These changes are likely to be connected with the appearance of active oxygen atoms on the polymer surface; these atoms form strong hydrogen bonds with the acid, which disturbs the electron sextet in five-membered heterocycles of the polymer. However, the framework structure of the main carbon chain is conserved because any noticeable changes of the parameters of characteristic bands belonging to the vibrations of  $\text{CH}_2$  and  $\text{CH}$  groups in the regions  $3000\text{--}2850$ ,  $1500\text{--}1400$  and  $1350\text{--}1250 \text{ cm}^{-1}$  are absent from the IR spectrum of the mechano-composite, that is, a polymer-analogous transformation with the formation of mechano-composite, *i.e.* a polymer-analogue, takes place [5, 7].

The structure of succinic acid in the mechano-composite is not disturbed to a substantial extent because changes in the positions of reflections of the acid in the diffraction patterns of the mechano-composite do not exceed 1.5–2.0 % (see Fig. 3). Therefore, it may be assumed that H bonds of succinic acid monomers with PVP, similarly to H bonds of succinic acid in associates, lie in (1–001) plane [10]. During the mechanochemical interaction of the acid with PVP, the acid reflections broaden with time, their intensities decrease, and the ratio of intensities changes. After the mechanochemical interaction is over, the intensity of  $d = 3.44 \text{ \AA}$  ( $I/I_s = 100$ ) reflection is substantially smaller than that of reflection  $d = 4.41 \text{ \AA}$  ( $I/I_s = 90$ ). It may be assumed that the rupture of H bonds in the associates of the acid and the formation of stronger H bonds between the acid and the polymer in the same plane result in a more substantial decrease in the amplitude of  $F_{hkl}$  wave [11] scattered by the elementary cell in the direction determined by the position of these H bonds than that observed for other directions. Because of this, the intensity of the corresponding reflection decreases to a more substantial extent than the intensities of other reflections.

The mass ratio (m. r.) polymer : acid = 5 : 1 for the mechanochemical interaction between PVP and succinic acid is likely to be optimal from the viewpoint of completeness of reaction. Indeed, for example, the most intensive

band in the IR spectrum of the mixture with m. r. 1.5 : 1 after MA in a usual ball mill for  $\tau_a > 40$  min and exposure for 3.5 months is that of the stretching vibration of  $\text{C}=\text{O}$  groups of the initial components ( $\nu_1 \text{ C}=\text{O}$ ), while  $\nu_3 \text{ C}=\text{O}$  (PVP bound with succinic acid) is exhibited only as a shoulder (see Fig. 2, *b*, curve 6).

Mechanochemical interaction of PVP with salicylic and citric acids proceeds in a similar manner (Fig. 4, *a*, *b*). Thus, in addition to the band  $\nu \text{ C}=\text{O}$  ( $1700 \text{ cm}^{-1}$ ) of unreacted citric acid and PVP, a weak shoulder is observed at  $\sim 1630 \text{ cm}^{-1}$  in the IR spectrum of a mixture of PVP with citric acid (m. r. 1 : 1.5) activated in a ball mill for 45 min; after MA for 2 h, a band with the maximum at  $1625 \text{ cm}^{-1}$  appears (see Fig. 4, curve 3) which relates to  $\nu$

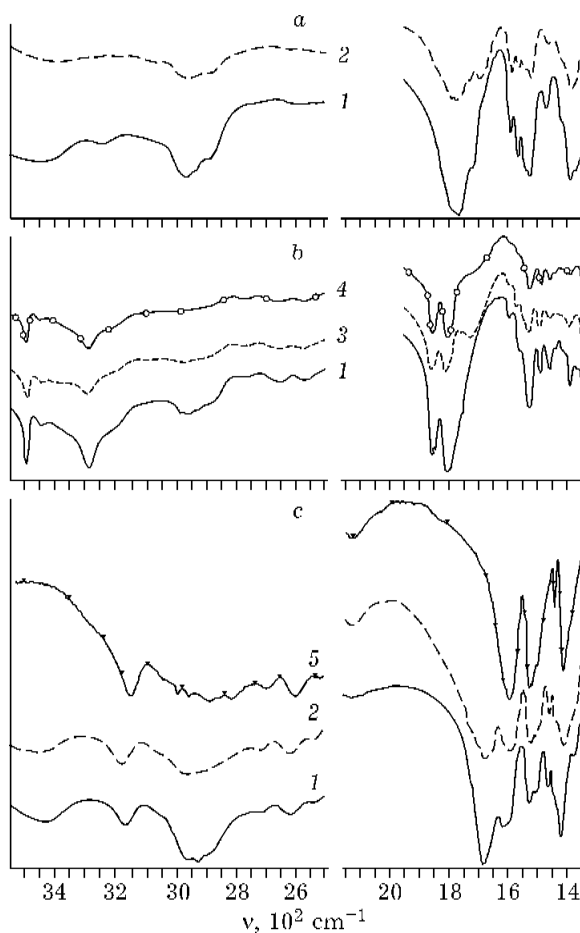


Fig. 4. IR absorption spectra of the mixtures of PVP with salicylic (*a*), citric (*b*) and aminoacetic (*c*) acids: *a*, *c* – AGO-2 mill, *b* – ball mill; m. r. polymer : acid = 2.5 : 1 (*a*, *c*), 1 : 1.5 (*b*, curves 1, 3, 4); activation time: 1 – initial, 2 – 1 min, 3 – 120 min, 4 – 45 min + exposure for 45 days, 5 – aminoacetic acid activated for 1 min.

C=O vibrations of PVP in the mechano-composite with citric acid. Exposure of samples at any stage of activation does not cause noticeable changes of their IR spectra (curve 4). Therefore, the interaction of citric acid with PVP, unlike for the interaction with succinic acid, proceeds directly in the ball mill during MA.

According to XPA data for the activated mixtures of citric acid with PVP, the reflections of citric acid broaden, their intensities decrease, the ratio of their intensities changes. However, the positions of reflections of citric acid, similarly to those of succinic acid, remains almost unchanged during MA with PVP ( $\Delta d \leq 2\%$ ) [12]. So, it may be assumed that the rupture of H bonds in the associates of citric acid and the formation of new strong H bonds during MA do not cause essential changes in the structure of the acid. The observed change in reflection intensity ratio is likely to be due to redistribution of electron density in the carboxylic groups of the acid during the formation of H bonds with the polymer; this may change the amplitude of  $F_{hkl}$  waves scattered by the unit cell of the acid in the directions determined by the position of new H bonds with the polymer.

According to the data of IR spectroscopy, no interaction of citric acid with PVP occurs in the case of higher content of the polymer; steric hindrance seems to be a possible reason.

Amino acid molecules are bipolar ions, so mechanochemical interaction with PVP similar with the above-considered interaction of PVP with the acids is impossible for them. The product of MA of a mixture of glycine with the polymer in a high-energy mill is a dispersed homogeneous mixture of the initial components (compare curves 1 and 2 in Fig. 4, c). The IR spectrum of this mixture contains the bands of the initial acid activated for 1 min (see Fig. 4, c, curve 5) and the polymer (see Fig. 1, a, curve 2). The use of the usual ball mill does not change the situation. An increase in activation time causes amorphization of the components. At the same time, the data of the analysis of IR spectra of three-component mixtures of PVP, for example with aminoacetic and succinic acids at definite m. r., provide evidence that mechanochemical interaction proceeds in the mixture during MA; it differs from the in-

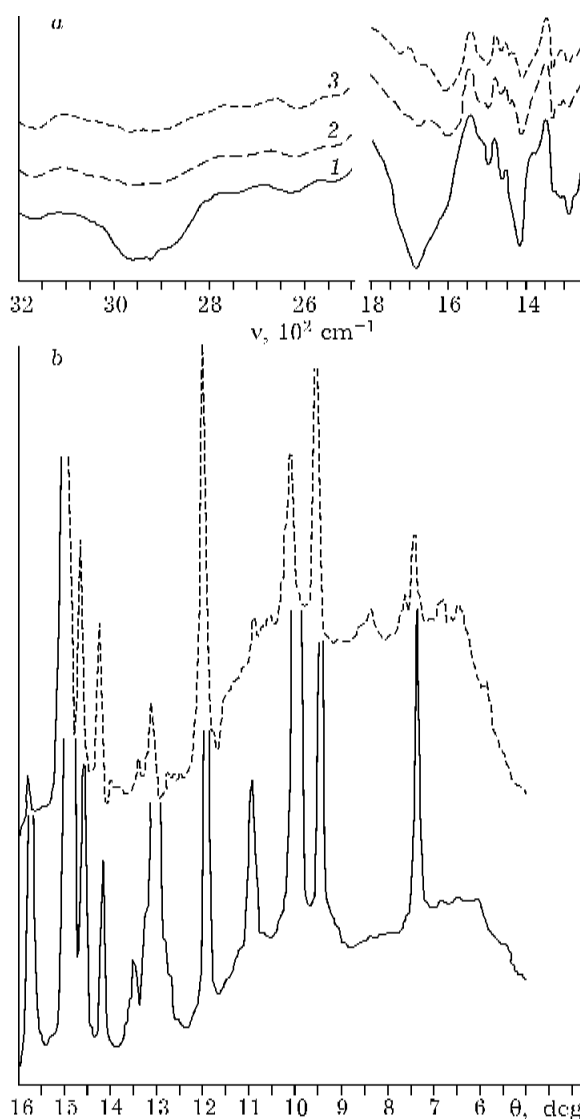
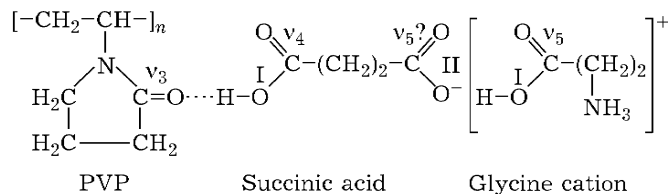


Fig. 5. IR absorption spectrum (a) and diffraction patterns (b) of the mixture of PVP with succinic and aminoacetic acids. Time of activation in ball mill, min: 0 (1), 30 (2), 30 + exposure for 35 days (3).

teraction of PVP with succinic acid (compare Fig. 5, a, curve 2, and Fig. 2, b, curve 2).

It is known that bipolar ions of amino acids are transformed into ammonium cations in the acid medium ( $\text{pH} < 7$ ). Taking into account the data, as well as the presence of a substantial amount of water in the system under investigation, due to the hygroscopic properties of PVP, one may assume that the acidity of the reaction medium is characterized by  $\text{pH} < 7$  as a result of dissociation of succinic acid during MA. Therefore, during MA of the three-component mixture of PVP with succinic and aminoacetic acids, the interaction of glycine with



Scheme 3.

carboxylic groups II of succinic acid is possible; glycine cations are formed in this process.

Redistribution of electron density in the carboxylic group II of succinic acid during such an interaction should result in a decrease in the force constant  $K$  of  $\nu_2$  C=O bond (see Scheme 2), and consequent decrease in the frequency of the stretching vibration of this bond, so that  $\nu_5$  C=O <  $\nu_2$  C=O (see Schemes 2, 3). Indeed, the IR spectrum of the three-component mixture of PVP with succinic and aminoacetic acids (m. r. = 3 : 1 : 1) exhibits a sharp decrease in the intensity of the band related to the stretching vibrations of carboxylic groups II of succinic acid ( $\nu_2$  C=O) at  $1730\text{ cm}^{-1}$  (see Fig. 5, *a*, curve 2).

At the same time, a new band  $\nu_5$  C=O with the maximum at  $1605\text{ cm}^{-1}$  appears, and its intensity increases. In the IR spectrum of the mixture activated for 30 min and stored for 35 days (see Fig. 5, *a*, curve 3), the  $\nu_2$  C=O band is very weak while  $\nu_5$  C=O is the most intensive one; it is broad and asymmetric. The intensity of  $\nu_1$  C=O band at  $1675\text{ cm}^{-1}$  related to unreacted PVP and succinic acid sharply decreases, too. The  $\nu_5$  C=O band belongs to the stretching vibrations  $\nu_{as}$  COOH of glycine cation and possible to  $\nu$  C=O of the carboxylic group II of succinic acid. The bipolar structure of aminoacetic acid is not distorted because all the bands characteristic of this structure are present in the IR spectrum of the product of mechanochemical interaction of the components:  $\delta$   $\text{NH}_3^+$   $1550\text{--}1470\text{ cm}^{-1}$ ,  $\nu$   $\text{NH}(\text{NH}_3^+)$   $3150$  and  $2115\text{ cm}^{-1}$  [8]. At the same time, the intensity of the maximum at  $1310\text{ cm}^{-1}$  of the band in the region  $1350\text{--}1250\text{ cm}^{-1}$  decreases sharply; this peak is related to  $\nu$  C–O +  $\delta$ OH vibrations of succinic acid and is characteristic of the IR spectrum of the acid [8]. In the IR spectrum of the product of the mechanochemical interaction of PVP with suc-

cinic acid, the intensity of the maximum at  $1310\text{ cm}^{-1}$  exhibits no substantial changes (see Fig. 2, *a*, curves 1 and 2). This fact may be the evidence of the differences in the mechanochemical interaction of carboxylic groups of succinic acid with PVP and aminoacetic acid, and is an indirect confirmation of the formation of glycine cation.

The diffraction patterns of the considered three-component mixture after MA contain relatively broadened reflections of glycine and very weak reflections of succinic acid (see Fig. 5, *b*). The contours of PVP halo are conserved. The shift of reflections related to acids is not more than 2 %, which is an evidence of the absence of any substantial changes in the structures of acids in the mechanocomposite with PVP. Unlike for succinic acid and the case with two-component systems, the ratio of reflection intensities after MA for glycine is not changed. Therefore, a part of carboxylic groups of succinic acid interacts with PVP during MA of the three-component mixture; the interaction results in the formation of strong hydrogen bonds with active oxygen atoms on the polymer surface, while the rest carboxylic groups interact with bipolar glycine ions forming glycine cations.

## CONCLUSIONS

1. Mechanical activation of the mixtures of PVP with biologically active organic acids except aminoacetic acid results in the fixation of an acid on the polymer surface and in the formation of a composite, which is a polymer analogue of PVP.

2. In high-energy AGO-2 mill, the interaction of the polymer with an acid occurs directly during activation.

3. In a ball mill, the interaction of the polymer with an acid occurs either during MA (cit-

ric) or after MA (succinic), depending on the strength of hydrogen bonds in the associates of the acids.

4. Aminoacetic acid does not interact directly with the polymer. In three-component mixtures PVP–succinic acid–aminoacetic acid at definite mass ratios glycine (in the form of cation) interacts mechanochemically with succinic acid; thus it can be fixed on the polymer, too.

5. The optimal mass ratio of polymer to acid for which the interaction of the polymer with the acid proceeds most completely for the investigated acids depends on the structure of the acid.

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