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# Interpolymer Complex Formation Between Linear and Crosslinked Poly(acrylic acid) and Poly(vinyl ether of ethyleneglycol)

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## Abstract

The formation of H-bonded interpolymer complexes between linear and cross-linked poly(acrylic acid) and poly(vinyl ether of ethyleneglycol) is considered. The effects of pH and concentrations of polymers solution as well as the nature of the solvent on the complexation processes are discussed. It was found that the complexes are formed in aqueous solutions only below some critical pH value, which depends on the concentration of polymers and ionic strength of the solution. The interaction between gel of poly(acrylic acid) swollen in alcohol with solution of linear poly(vinyl ether of ethyleneglycol) is accompanied by formation of turbid layer of polycomplex and contraction of gel.

## Introduction

Interaction between two different macromolecular species may lead to the formation of an interpolymer complex (IPC), which essentially possesses properties entirely different from those of the component polymers. Many biological macromolecules may give such complexes in aqueous solutions. This phenomenon is due to the existence of several types of interactions between the polymer chains: electrostatic attractions, hydrogen bonds, hydrophobic interactions, double or triple helix formation, etc. Numerous reports are devoted to the interpolymer complexes stabilized by hydrogen bonds. Most of them are based on poly(carboxylic acids) and nonionic macromolecules [1-4].

Recently considerable attention has been paid to a new family of water-soluble polymers based on vinyl ethers containing different oxyethylene pendant groups such as poly(methyl triethylene glycol vinyl ether) [5], poly(ethoxyethyl vinyl ether) [6], poly(vinyl ether of ethyleneglycol) [7] and poly(vinyl ether of diethyleneglycol) [7].

Poly(vinyl ether of ethyleneglycol) (PVEEG) is a water-soluble polymer with a structure that is similar to polyvinyl alcohol (PVA) on the one side (hydroxyl groups) and possessing some properties of polyoxyethylene (POE) (oxyethylene pendant groups) on the other. The complexes between poly(acrylic acid) (PAA) and PVA or POE are well known from the literature [1–4]. However, the information about the complexation behavior of PVEEG is quite insufficient.

In the present paper we will consider the complex formation processes between linear and crosslinked PAA and PVEEG.

## Experimental

PVEEG was synthesized by γ-irradiation polymerization as described in refs [7, 8]. Polyacrylic acid of molecular weight 250000 was purchased from Aldrich Chem.Corp.Inc and used without further purification.

The viscosity measurement were carried out in an Ubbelohde viscometer at 298 ± 0.1 K. Turbidimetric measurements were carried out with the help of the spectrophotometer KFK–2–UHL–4.2 (USSR) at the wavelength $\lambda = 400$ nm and at room temperature. The pH of solutions was adjusted with a very small amount of 0.1 M HCl and determined using an EV pH-meter (USSR). Low molecular salt (NaCl) was analytical grade and used without further purification.

The degree of PAA gels swelling was measured by the $V/V_0$ ratio, where $V_0$ and V are the volumes of the polymer network after synthesis and in the state of equilibrium swelling, respectively. The diameter of the cross-linked PAA samples was determined with

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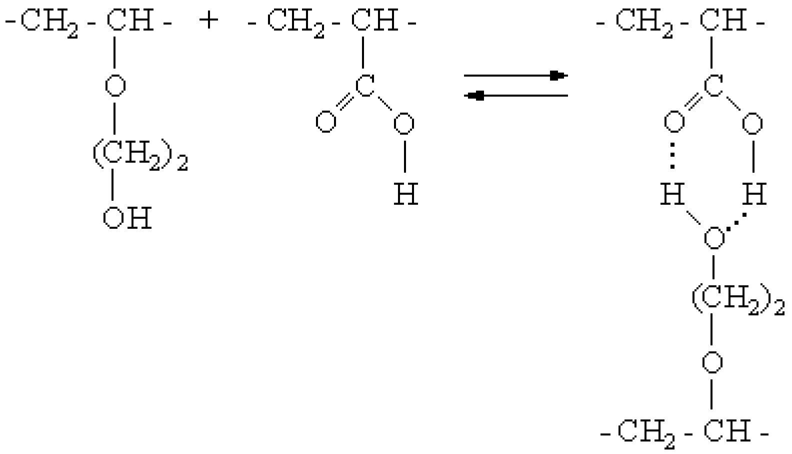
*corresponding author. E-mail: khutor@nursat.kz a V–630 cathetometer (the accuracy of measurements ± 0.04 mm).

## Results and discussion

### *Interactions in aqueous solutions*

It is known that intermolecular hydrogen bonds are formed only with participation of unionized COOH of carboxylic acids [1–4]. Therefor the decreasing of pH of the solution should be favorable for complex formation. As it was found earlier [9, 10] the addition of aqueous solution of PVEEG to aqueous solution of PAA in weakly acidic media (pH = 4÷5) does not lead to the formation of IPC and is accompanied by a marked increase of the intrinsic viscosity. Apparently, this can be attributed to the presence of the polyelectrolyte effect. However, in acidic media (pH = 2.0) the viscometric and turbidimetric curves are characterized by corresponding minimum and maximum due to the formation of IPC with stoichiometric composition [11]. One can suppose that a complexation process takes place according to the next scheme:



The existence of some critical pH of complex formation for poly(carboxylic acid)–nonionic polymer systems was shown earlier by Tsuchida and Abe [3]. In our opinion, the critical pH value can be considered as some criterion of ability to form IPC for any interacting system consisting of poly(carboxylic acid) and nonionic polymer in aqueous solutions [12]. We have determined the critical pH values for PVEEG-PAA complexes at different polymers concentrations in solution [13]. Fig. 1 shows the dependence of solution turbidity of the PVEEG-PAA mixtures on pH at different polymer concentrations. A sharp increase of turbidity at a narrow range of pH corresponds to the critical pH value. Below this value the mixture of polymers became turbid and the complexes precipitate from the solution. It is seen from the figure that an increase of polymer concentrations shifts the critical pH values to the higher pH region. Probably, this dependence can be explained by a decrease of the PAA ionization with an increase of its concentration in the solution.

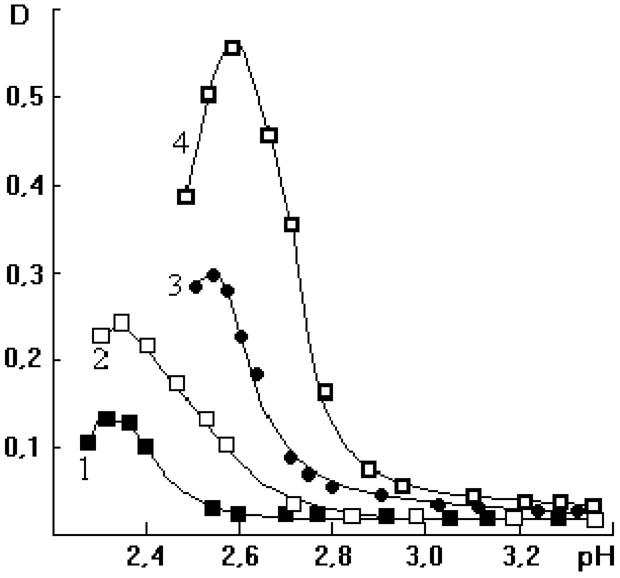


Fig.1. Dependence of solution turbidity of PVEEG-PAA mixtures (1:1) on pH. [PVEEG] = [PAA] = 0.005 M (1), 0.01 M (2), 0.05 M (3), 0.1 M (4)

The information about the influence of ionic strength on the complexation due to H-bonds formation is insufficient and contradictory. Recently Frenkel's group have reported that increasing of ionic strength depresses the complexation of PAA with poly(vinyl alcohol) [14] and oxyethylcellulose [15]. But according to Iliopoulos et al [16] and Staikos et al [17] the increase of ionic strength is favorable for complex formation. We have checked the influence of ionic strength on the complex formation of PAA and PVEEG [11]. In the presence of NaCl in solution the turbidimetric curve and characteristic composition of IPC considerably deviates from the curve obtained without the salt. Moreover, the yield of IPC increases in the presence of NaCl. The increase of ionic strength also shifts the critical pH value of complexation to the higher pH region promoting the complexation (Fig.2).

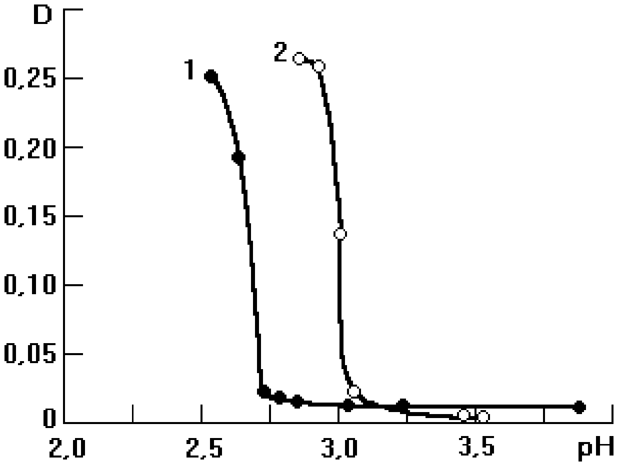


Fig.2. Dependence of solution turbidity of PVEEG-PAA mixtures (1:1) on pH. [NaCl]: 0 (1) and 0.1 mol×L$^{-1}$ (2). Concentration of polymers is 0.01 M

According to Jiang and co-workers [4] the competition between polymer-polymer interactions and polymer-solvent interactions is the decisive factor governing the complexation in solutions. This competition can be better demonstrated by adding some strong proton-accepting solvents into the solutions of IPC. We checked the effect of addition of different solvents such as dimethylformamide (DMF), water and isopropanol into the solutions of the IPC formed in water. The addition of water (pH = 2.6) into the PVEEG-PAA aqueous solution is accompanied by linear decrease of optical density according to Bouger-Lambert-Beer's law. In this conditions the addition of water into the IPC aqueous solutions at constant pH = 2.6 does not lead to a destruction of the complexes. Small amounts of isopropanol added to the solution of the IPC stabilize the complex. Then, the further addition of isopropanol leads to the IPC destruction. The addition of DMF leads to a considerable non-linear decrease of solution turbidity caused by the IPC destruction. Thus, in mixture of solvents the IPC particles began to destroy at about 5 vol.% of DMF and 13–15 vol.% of isopropanol. Hence, DMF possess higher destruction ability than isopropanol.

## *Formation of interpolymer complexes in organic and mixed solutions*

In recent years there is an increased interest of researchers to the processes of complex formation in organic solvents [4]. The transition from aqueous solutions to organic ones let us not only regulate the intensity of complex formation but also use novel water-insoluble polymers to prepare complexes.

According to Katime with co-workers [18] strong donor or acceptor solvents (such as amides, sulfoxides, organic acids, etc.) can prevent interaction, owing to their competing ability with the interacting sites in polymers. But, in solvents with weaker competing ability (such as alcohols, ethers, ketones, etc.) complexation can occur depending on the complexing character of the solvent and solvophobic interactions.

The complex formation of PAA with PVEEG in ethanol, isopropanol and their mixture (1:1) is accompanied by considerable increase in solution turbidity [13]. The maximum of turbidity corresponds to the equimolar composition of components in IPC (Fig. 3).

We have studied the kinetics of solution turbidity increase after the mixing of ethanol and isopropanol solutions of initial reagents. At concentrations of initial components lower than 0.001 M in ethanol and 0.00025 M in isopropanol the appearance of turbidity is not observed. If the polymers concentrations are higher than these critical value then the size of IPC aggregates increases very significantly with time. The obtained experimental results indicate that isopropanol is more favorable solvent for complexation than ethanol, because of the less solvating ability of the former in respect to polymers [13].

However in water-alcohol mixtures (1:1) the formation of IPC is not observed. It is known [14] that in mixtures of selective solvents of certain composition the formation of the most unfolded conformations of amphiphilic macromolecules takes place because of the strengthening of the polymer-solvent interactions.

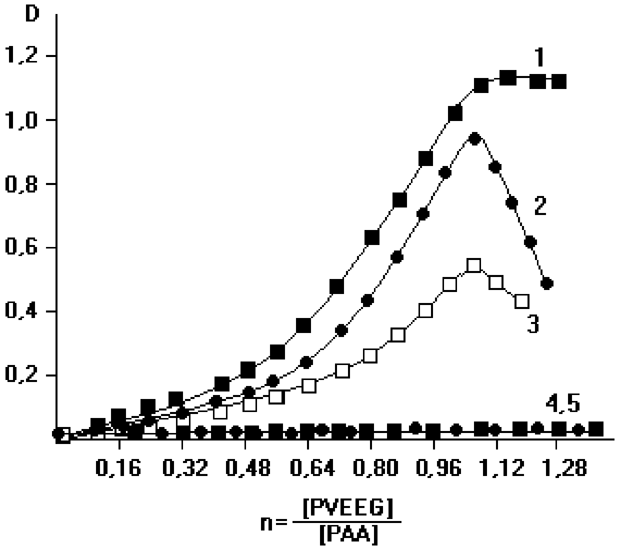


Fig.3. Turbidimetric titration curves of PAA by PVEEG solutions in isopropanol (1), 1:1 isopropanol-ethanol mixture (2), ethanol (3), 1:1 ethanol-water mixture (4), 1:1 isopropanol-water mixture (5). Concentration of polymers is 0.01 M

In this case macromolecules can more easily interact with the solvent than with each other and complexes do not formed.

We have studied the stability of PVEEG-PAA complexes formed in isopropanol to the addition of isopropanol, water and DMF [13]. Complexes began to destroy at 10 vol.% of DMF and 15 vol.% of water. The dilution of the IPC solution by isopropanol does not lead to its destruction, and is also accompanied by a linear decrease of turbidity according to Bouger-Lambert-Beer's law. Hence, the complexes of PVEEG-PAA formed in isopropanol are more stable than those of formed in aqueous solutions.

## *Complex formation of polyacrylic acid gels with linear polyvinyl ether of ethyleneglycol*

The complex formation of linear non-ionic polymers with gels of polycarboxylic acids has been considered earlier by Osada et al [19], Starodubtzev et al [20,21], Frenkel et al [22], Tanaka et al [23], and Mun et al [24]. Khokhlov and Kramarenko [25] have developed some theoretical representations on this subject. The influence of solvent quality on the collapse of polymer gels induced by complex formation with linear polymers was shown.

Earlier [24] we demonstrated that depending on the pH medium the complex formation in the hydrogel-linear polymer aqueous solution system is accompanied either by additional swelling or contraction of the network. This phenomenon was explained from Frenkel's diffusion approach point of view [22] taking into consideration the state of double electric layer on gel-solution boundary, in particular the density of surface charge of hydrogel.

The interaction of cross-linked PAA with solution of PVEEG in ethanol and isopropanol is accompanied by formation of muddy layer on gel-solution boundary [26]. The higher the concentration of linear polymer in solution, the faster the of gel turbidity is observed. In isopropanol solution of PVEEG an increase of turbidity is more significant. One can suppose that in the first stage of interaction the macromolecules of linear polymer attack the surface of gel and form the muddy layer of interpolymer complex. Then in the second stage the macromolecules of PVEEG penetrate through the complex layer into the gel and form complexes inside the network. The formation of IPC inside the gel is accompanied by contraction of the network (Fig. 4)

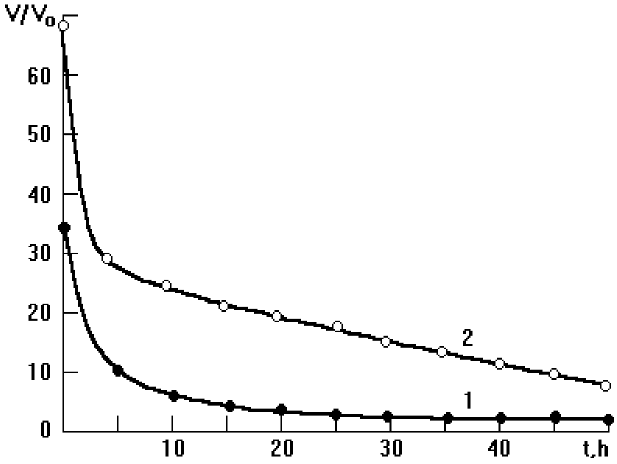


Fig.4. Contraction of PAA gels in 0.01 M solutions of PVEEG in isopropanol (1) and ethanol (2)

## Conclusions

The interpolymer reactions between linear PVEEG and PAA have been studied in aqueous and organic solutions. The critical pH of complexation was used as criterion of complex forming ability of the polymers in aqueous solutions. It was found that the increase of polymers concentration and ionic strength of the solution increases their ability to form complexes. The stability of complexes to addition of different solvents was evaluated. The PVEEG-PAA complexes are more stable in organic solvents (ethanol and isopropanol) than in water.

Gels of PAA immersed in PVEEG solutions became turbid and undergo contraction because of the complex formation between gel and linear polymer.

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