

# Interpolymer complexes of poly(vinyl ether) of ethylene glycol with poly(carboxylic acids) in aqueous, alcohol and mixed solutions

Z.S. Nurkeeva\*, G.A. Mun, V.V. Khutoryanskiy, A.A. Zotov, R.A. Mangazbaeva

*Kazak State National University, Department of High Molecular Compounds, Karasai Batyra 95, 480012 Almaty, Kazakhstan*

Received 15 November 1999; received in revised form 24 January 2000; accepted 7 February 2000

## Abstract

The effect of polymer concentrations, pH, nature and molecular weight of polyacid and nature of solvent on the complex formation of poly(carboxylic acids) with poly(vinyl ether) of ethylene glycol has been studied. The role of hydrophobic interactions and ionization of polyacid in the stabilization of interpolymer complexes in aqueous solutions has been clarified. It has been shown that an increase of polymer concentrations and the hydrophobicity of polyacid shifts the critical pH values to the higher region. The competition between polymer–solvent and polymer–polymer interactions governs the complex formation processes. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Interpolymer complexes; Hydrophobic interactions; Ionization

## 1. Introduction

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) [1], poly(ethoxyethyl vinyl ether) [2], poly(ethylene glycol vinyl ether) and poly(diethylene glycol vinyl ether) [3].

Poly(ethylene glycol vinyl ether) or poly(vinyl ether of ethylene glycol) (PVEEG) is a water-soluble polymer with a structure that is similar to poly(vinyl alcohol) (PVA) on the one side (hydroxyl groups) and possessing some properties of poly(oxyethylene) (POE) (oxyethylene pendant groups) on the other.

It is well known that PVA as well as POE form interpolymer complexes (IPC) with poly(carboxylic acids) due to the formation of cooperative hydrogen bonds in aqueous and organic solutions. In aqueous solutions these complexes are additionally stabilized by hydrophobic interactions. The influence of the nature and molecular weight of the interacting polymers as well as the parameters of the environment (nature of solvent, pH and ionic strength of solution, temperature) on complexation of POE and PVA with poly(carboxylic acids) has been studied in detail by different authors [4–13].

However, very little is known about the complexation of

polymers of vinyl ethers with poly(acrylic acids) (PAA) and poly(methacrylic acid) (PMAA), except for some works of Cowie et al. [14] and Staikos et al. [15].

Earlier we demonstrated the complexation of PVEEG with PAA in aqueous and alcohol (ethanol and isopropanol) solutions [16]. The influence of pH, ionic strength and the nature of the solvent on the complexation process have been studied. It was shown that an increase of hydrophobicity of macromolecules by copolymerization with hydrophobic monomers enhances the hydrophobic interactions and leads to additional stabilization of the IPC [17–19].

The aim of the present work is to examine the influence of polymer concentrations, the nature of the polyacid, the molecular weight of PAA and the nature of the solvent on the stability of the IPC formed in aqueous and isopropanol solutions.

## 2. Experimental section

PVEEG was synthesized by  $\gamma$ -irradiation polymerization of the monomer in mass with the help of  $^{60}\text{Co}$  “MRX- $\gamma$ -25M” at an irradiation dose rate of 90 rad/s for 9 h [20]. The synthesized polymer was purified by a three-fold precipitation from ethanol to diethyl ether and dried in a vacuum desiccator at 30°C until constant weight was achieved. The average-viscosity molecular weight ( $M_v$ ) of PVEEG in water calculated from the equation [3]:

$$[\eta] = 8.8 \times 10^{-4} M^{0.50}$$

\* Corresponding author.

E-mail address: khutor@nursat.kz (Z.S. Nurkeeva).

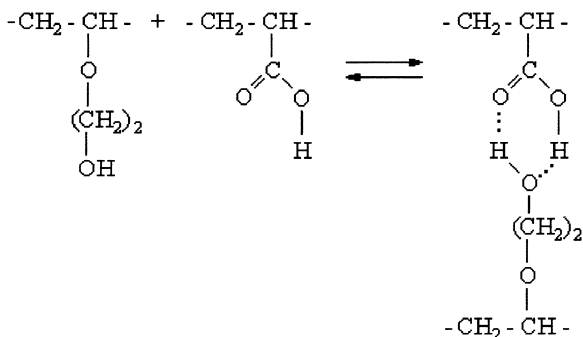


Fig. 1. Postulated mechanism of complex formation between PVEEG and PAA.

corresponds to  $50 \times 10^3$ . PAA ( $M_w = 250 \times 10^3$  and  $750 \times 10^3$ ) was purchased from Aldrich Chem. Comp. Inc., and was used without further purification. PMAA ( $M_v = 1.5 \times 10^6$ ) was synthesized by radical polymerization in the presence of azoisobutyronitril, purified and characterized as described in Ref. [17].

Turbidimetric measurements were carried out with the help of the spectrophotometer “KFK-2-UHL-4.2” (USSR) at wavelength  $\lambda = 400$  nm and at room temperature.

The pH of the solutions was adjusted with a very small amount of 0.1 M HCl. It was determined using an EV-74 pH-meter.

IPCs in isopropanol were prepared by mixing of the initial component solutions in equimolar proportion. It is known [21,22] that there is some influence of mixing order of the initial components on the turbidity of the IPC solutions. We also observed this influence for our systems; therefore, the order of mixing was always the same: 1 ml 0.01 M PAA, 3 ml isopropanol and finally 1 ml 0.01 M PVEEG. Aqueous solutions of the IPC were prepared by mixing of the initial components in equimolar proportion and acidifying up to pH = 2.6. After preparing the samples, they were shaken vigorously and left for 30 s before the determination of their stability.

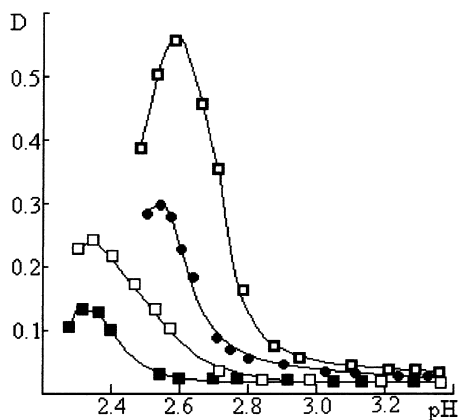


Fig. 2. Dependence of solution turbidity of PVEEG–PAA mixtures on pH. [PVEEG] = [PAA] = 0.005 M (■), 0.01 M (□), 0.05 M (●), 0.1 M (◻).

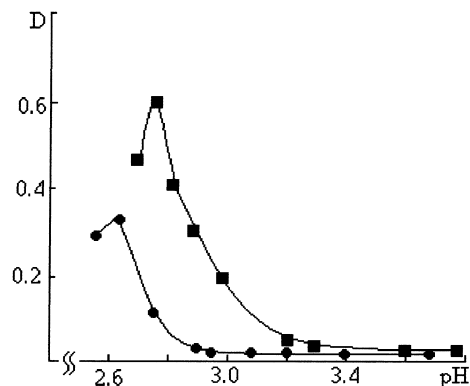


Fig. 3. Dependence of solution turbidity of PVEEG–PMAA (1:1) mixtures on pH. [PVEEG] = [PMAA] = 0.01 M (●), 0.05 M (■).

### 3. Results and discussion

PVEEG forms stoichiometric IPCs (1:1) with PAA in aqueous and alcohol solutions [16] according to the next-postulated mechanism (Fig. 1). In aqueous solutions the complexation occurs only below some critical pH value. We have studied the influence of polymer concentrations and the molecular weight of PAA on the critical pH values for PVEEG–PAA complexes. Fig. 2 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 in the PAA ionization with an increase in its concentration in the solution.

The molecular weight of PAA, which ranged between 250 and  $750 \times 10^3$ , does not affect the critical pH value for the PVEEG–PAA system. The authors [5] demonstrated the existence of a certain range of chain length in which the perfect complex formation is possible. Inside of this range the properties of the IPC composed of polymers with varied molecular weights are similar. Probably, in our case, the molecular weight of PAA ( $250\text{--}750 \times 10^3$ ) is ranged between the lower and the upper critical molecular weights; the properties of these IPCs are similar.

It is known that the hydrophobicity of the interacting polymers plays an important role in the additional stabilization of the IPC by the hydrophobic interactions in the aqueous solutions. Tsuchida et al. [23] and Kabanov et al. [24,25] showed that the complexes of PMAA with PEO are more stable than the complexes of PAA with PEO due to the additional hydrophobic stabilization of the IPC by methyl groups of PMAA. In order to compare the complexes of PVEEG–PAA and PVEEG–PMAA we have determined the critical pH values at two different concentrations. Unfortunately, the solubility of PMAA in water was limited;

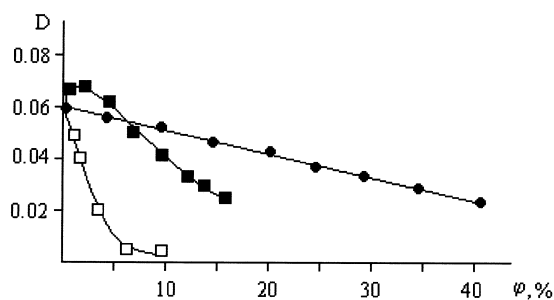


Fig. 4. Dependence of turbidity of PVEEG–PAA complexes formed in water (pH = 2.6) on the concentration of added water (●), isopropanol (■) and DMF (□). [PAA] = [PVEEG] = 0.01 M.

therefore, we could not determine the critical pH values at concentrations higher than 0.5 M. Fig. 3 shows that the critical pH values of the PVEEG–PMAA complexes are higher than that of the PVEEG–PAA complexes. Hence, the hydrophobic interactions increase the critical pH values and stabilize the IPC compact structure.

According to Jiang and co-workers [13,26,27] 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 the IPC. We checked the effect of addition of different solvents such as DMF, water and isopropanol into the solutions of the IPC formed in water and isopropanol. We selected DMF as the complex-breaking solvent because it is a non-complexing medium for the PVEEG–PAA system [16]. Water and isopropanol are complexing solvents for PVEEG–PAA. By using different combinations of these solvents we could elucidate how the mixing of the complexing solvent with non-complexing one, and the complexing solvent with another complexing one as well as simple dilution influences the IPC stability.

The addition of water (pH = 2.6) into the PVEEG–PAA aqueous solution is accompanied by a linear decrease of optical density according to Bouguer–Lambert–Beer's law.

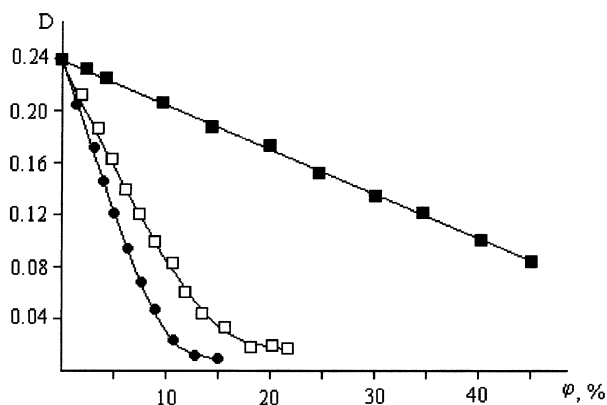


Fig. 5. Dependence of turbidity of PVEEG–PAA complexes formed in isopropanol on the concentration of added isopropanol (■), water (□) and DMF (●). [PAA] = [PVEEG] = 0.01 M.

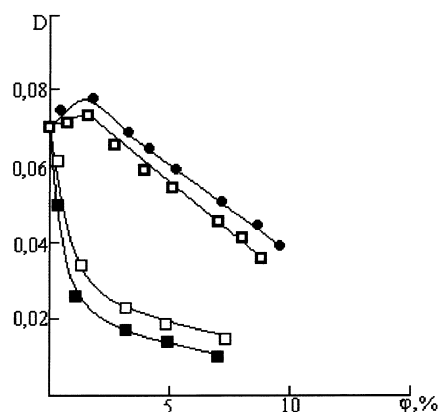


Fig. 6. Dependence of turbidity of PVEEG–PAA complexes formed in water (pH = 2.6) on the concentration of added isopropanol (●, ■) and DMF (□, ■).  $M_w$  = (PAA) =  $250 \times 10^3$  (□, ■);  $750 \times 10^3$  (●, □). [PAA] = [PVEEG] = 0.01 M.

In these conditions the addition of water into the IPC aqueous solutions at constant pH = 2.6 does not lead to a destruction of the complexes (Fig. 4). 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 a 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.

In the case of the PVEEG–PAA complexes formed in isopropanol the addition of water and DMF destroys the IPC less intensively (Fig. 5). 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 Bouguer–Lambert–Beer's law. Hence, the complexes of PVEEG–PAA formed in isopropanol are more stable than those of formed in aqueous solutions. DMF is a strong proton-accepting solvent that destroys complexes both in aqueous and organic solutions. The dilution of the IPC solutions does not destroy the complexes.

In order to confirm that the molecular weight of PAA, ranged at the interval  $250$ – $750 \times 10^3$  does not influence the properties of the IPC we have compared the stability of the PVEEG–PAA complexes with different molecular weights of PAA in aqueous solutions to the addition of isopropanol and DMF (Fig. 6). It is seen from the figure that the IPCs are destroyed at practically the same content of isopropanol and DMF added to the complexes. Thus, the stability of the IPC composed of PAA with different molecular weights is practically the same.

It is known that the hydrodynamic behavior of both PAA [28] and PVEEG [3,29] in the water–DMF mixtures is characterized by the unfolding of macromolecules with an increase of the DMF content. The maximal hydrodynamic volume is realized in pure DMF. Hence, the polymer–solvent

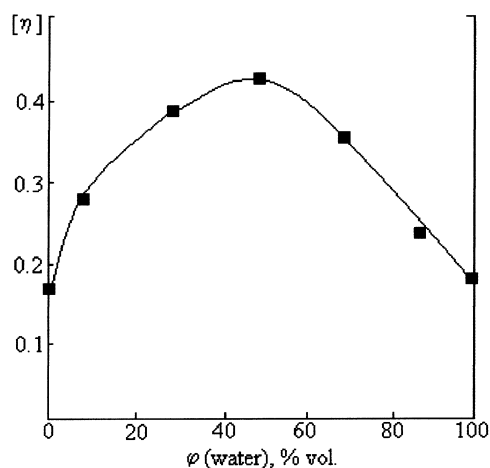


Fig. 7. Dependence of intrinsic viscosity of PVEEG (dl/g) on the composition of isopropanol–water mixture.

interactions in DMF are always stronger than the polymer–polymer interactions. Therefore, the complexes of PVEEG–PAA do not form in DMF, and the addition of DMF destroys the complexes formed in water.

Earlier [14] we demonstrated that the PVEEG–PAA complexes do not form in the water–isopropanol mixture (1:1). By comparing the stability of IPC formed in water and isopropanol we can determine the stability region of the complex and conclude that the IPC exists only in pure solvents, or their mixtures with high content of one of the components. If the content of isopropanol is higher than 13–15 vol.% or lower than 85 vol.% complexes do not form.

In the water–alcohol mixtures the conformation of PAA macromolecules is characterized by a complex dependence on the composition of solvent mixtures [28]. The maximal hydrodynamic volume of the macromolecules corresponds to the mixed solvent of a certain composition. The same situation is realized for the behavior of PVEEG in the water–alcohol mixtures (Fig. 7). Probably, in aqueous solutions, the conformation of amphiphilic macromolecules is stabilized by the hydrophobic interactions of non-polar groups (Fig. 8(a)). In alcohol solutions the hydrophilic fragments are linked by intermolecular hydrogen bonds, and the alcohol molecules solvate the organophilic parts of the polymer (Fig. 8(b)). In mixed water–alcohol solution the simultaneous solvation of hydrophilic groups by water and that of the organophilic ones by alcohol leads to the unfolding of the macromolecules (Fig. 8(c)). Therefore, we can observe the complexation in water as well as in isopropanol. In mixed solvents of a certain composition, the complexes do not formed because the polymer–solvent interactions are stronger than the polymer–polymer ones.

#### 4. Conclusion

The complex formation between poly(carboxylic

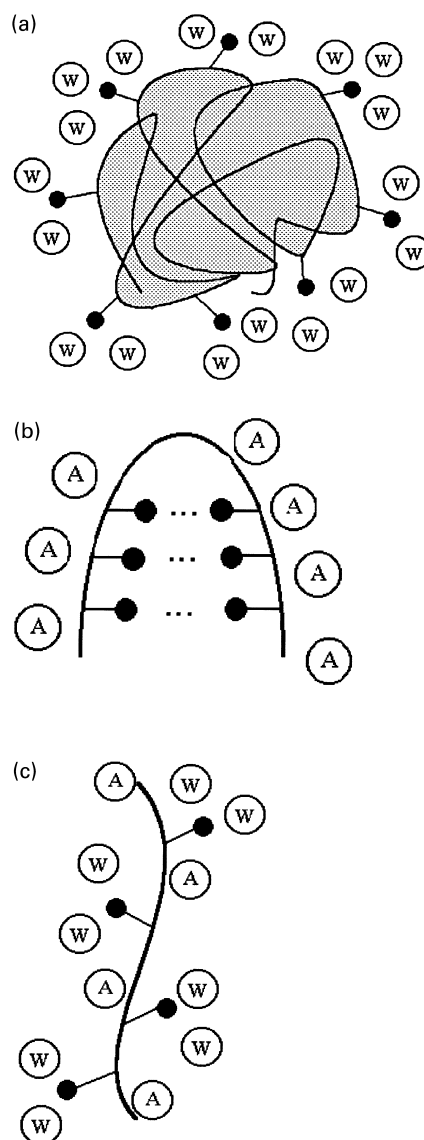


Fig. 8. Possible structures of amphiphilic macromolecules in water (a), alcohol (b) and their mixture (c). Molecules of water and alcohol are indicated as W and A, respectively. Black circles indicate the hydrophilic groups. The filled area indicates the hydrophobic interactions (a).

acids) and PVEEG has been studied. The effect of polymer concentrations, pH and molecular weight of PAA on the complexation has been clarified. The general regularities of complex formation with the participation of PVEEG resemble the complexes of PVA and PEO. However, the higher stability of the PVEEG–PAA complexes in isopropanol, than in water, makes them different from PVA–PAA and PEO–PAA because the latter are less stable in organic solutions [5]. Probably, the difference between them can be explained by a specific structure of the PVEEG macromolecules that represent a combination of properties of both PVA and PEO.

## References

- [1] Forder C, Patrickios CS, Armes SP, Billingham NC. *Macromolecules* 1997;30:5758.
- [2] Horinaka J, Matsumura Y, Yamamoto M, Aoshima S, Kobayashi K. *Polym Bull* 1997;42:85.
- [3] Nurkeeva ZS, Kasaikin VA, Ivleva EM, Daurenbekova GB, Legkumetz RE, Sigotov VB, Ergozhin EE. *Vysokomolek Soed* 1990;31B:415.
- [4] Kabanov VA, Papisov IM. *Vysokomolek Soed A* 1979;21:243.
- [5] Bekturov EA, Bimendina LA. *Adv Polym Sci* 1981;41:99.
- [6] Tsuchida E, Abe K. *Adv Polym Sci* 1982;45:1.
- [7] Bailey FE, Lundberg RD, Callard RW. *J Polym Sci* 1964;2A:845.
- [8] Iliopoulos I, Audebert R. *Polym Bull* 1985;13:171.
- [9] Maunu SL, Kopri T, Lindberg JJ. *Polym Bull* 1989;19:171.
- [10] Oyama HT, Hemker DJ, Frank CW. *Macromolecules* 1989;22:1255.
- [11] Soutar I, Swanson L. *Macromolecules* 1990;23:5170.
- [12] Staikos G, Bokias G. *Makromol Chem* 1991;192:2649.
- [13] Jiang M, Li M, Xiang M, Zhou H. *Adv Polym Sci* 1999;146:121.
- [14] Cowie JMG, Garay MT, Lath D, McEwen IJ. *Br Polym J* 1989;21:81.
- [15] Koussathana M, Lianos P, Staikos G. *Macromolecules* 1997;30:7798.
- [16] Mun GA, Nurkeeva ZS, Khutoryanskiy VV. *Macromol Chem Phys* 1999;200:2136.
- [17] Kudaibergenov SE, Nurkeeva ZS, Mun GA, Ermukhambetova BB, Akbauova AT. *Macromol Chem Phys* 1995;196:2203.
- [18] Mun GA, Khutoryanskiy VV, Nam IK, Nurkeeva ZS, Kudaibergenov SE. *Polym Sci* 1998;40:290.
- [19] Khutoryanskiy VV, Mun GA, Nurkeeva ZS. In: *Proceedings of the Fifth International Symposium on Polymers and Polymer Composites*. Almaty, 1999. p. 105.
- [20] Nurkeeva ZS, Shaikhutdinov EM, Seitov AZ, Saikieva SKh. *Vysokomolek Soed* 1987;29A:932.
- [21] Perez-Dorado A, Pierola IF, Baselga J, Gargallo L, Radic D. *Makromol Chem* 1989;190:2975.
- [22] Perez-Dorado A, Pierola IF, Baselga J, Gargallo L, Radic D. *Makromol Chem* 1990;191:2905.
- [23] Ikawa T, Abe K, Honda K, Tsuchida E. *J Polym Sci Polym Chem Ed* 1975;13:1505.
- [24] Antipina AD, Baranovsky VYu, Papisov IM, Kabanov VA. *Vysokomolek Soed* 1972;14:941.
- [25] Papisov IM, Baranovsky VYu, Sergieva EI, Antipina AD, Kabanov VA. *Vysokomolek Soed* 1974;16:1133.
- [26] Xiang M, Jiang M, Zhang Y, Wu C. *Macromolecules* 1997;30:5339.
- [27] Zhang Y, Xiang M, Jiang M, Wu C. *Macromolecules* 1997;30:6084.
- [28] Bekturov EA, Bakauova ZKh. *Synthetic water soluble polymers in solutions*. Basel: Huthig-Wepf, 1986.
- [29] Nurkeeva ZS, Legkumetz RE, Ergozhin EE, Daurenbekova GB. *Vysokomolek Soed* 1986;28B:649.