

Interactions of linear and cross-linked polyacrylic acid with polyvinyl ether of ethyleneglycol in some aliphatic alcohols

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Summary

The interaction of linear and cross-linked polyacrylic acid (PAA) with polyvinyl ether of ethyleneglycol (PVEEG) has been studied in ethanol, isopropanol and their mixture. Formation of interpolymer complexes (IPC) in solutions is accompanied by aggregation of compact particles. Gels of PAA undergo shrinking in solutions of PVEEG.

Introduction

The environmental medium considerably influences the ionic groups in polymers therefore all polyelectrolytes are highly sensitive to small changes of pH, ionic strength, temperature, etc. Usually the changes of environment are accompanied by coil-globule transitions for linear polyelectrolytes and swelling or shrinking for gels [1]. Generally, the behavior of polyelectrolyte gels resembles some properties of linear polyelectrolyte solutions. Different transitions that occurred both in linear and in cross-linked polyelectrolytes have been intensively studied in aqueous media [1, 2]. However, very little is known about the behavior of these systems in polar organic solvents [3, 4].

Interesting changes that occurred with polyelectrolytes can be induced by interactions with complementary non-ionic polymers. In this case the formation of IPC leads to drastic shrinking of macromolecules. Interpolymer reactions in aqueous solutions were the object of intensive research in the seventies and eighties [5-8]. At present the complex formation processes in organic solvents attract considerable attention [9-11]. According to Katime with co-workers [10] 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 classical Tsuchida's works [8] indicate that in protic solvents like alcohols the complexation is strengthened with increasing of dielectric constant. In the present work we observed the complex formation of linear and cross-linked PAA with PVEEG in ethanol, n-propanol, isopropanol and their mixtures. Ethanol, n-propanol, and isopropanol have the next values of dielectric constants at 25 °C: 25.2, 19.7, and 18.3, respectively. Since n-propanol and isopropanol have close values of dielectric constants we selected ethanol, isopropanol and their mixtures in order to study the complexation in alcohols with more wide region of dielectric constants (from 18.3 to 25.2). The second aim of our work was to compare the interpolymer reaction in solution with formation of IPC on the gel-solution boundary.

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Experimental

PVEEG ($M_w=50\div 70\cdot 10^3$) was synthesized by γ -irradiation polymerization, purified and characterized as described in Refs [12, 13]. Linear PAA ($M_w=250\cdot 10^3$) was purchased from Polysciences Corp and used without further purification. Cross-linked PAA was synthesized by three-dimensional radical polymerization in the presence of azoisobutyronitril as initiator and N, N'-methylene-bis-acrylamide as cross-linking agent. 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 a V-630 cathetometer (the accuracy of measurements ± 0.04 mm). Optical density measurements were carried out on KFK-2-UHL-4.2 spectrophotometer (USSR) at the wavelength $\lambda=400$ nm and at room temperature. The starting values of V/V_0 and D at $t=0$ were determined for the gel samples before the interpolymer interaction when they were in pure solvents.

Results and discussion

Recently [14] we studied the complex formation reactions in aqueous and organic solutions. The effect of pH of the solution and low molecular salts addition on the complex formation has been clarified. The stability of interpolymer complexes has been studied. It was found that complexes of PAA with PVEEG are more stable in ethanol and isopropanol than in aqueous solutions.

The complex formation of PAA with PVEEG is accompanied by considerable increase in solution turbidity. The maximum of turbidity corresponds to the equimolar composition of components in IPC (Fig.1). Turbid solutions of IPC are stable to sedimentation during several days and after they began to precipitate. The precipitation process can be accelerated by centrifugation. It should be noted that the maximal turbidity of IPC in isopropanol is higher than in ethanol.

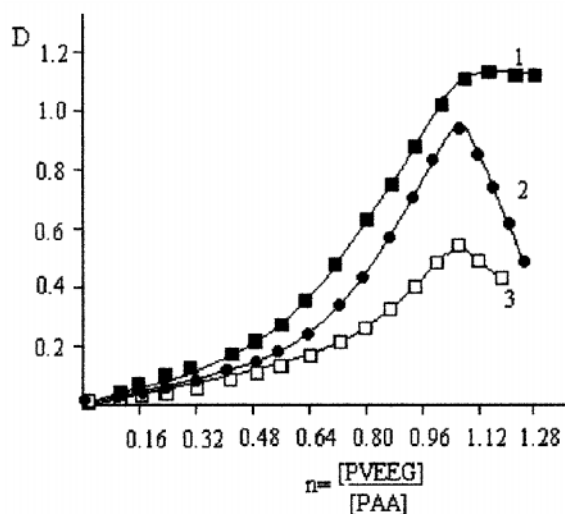


Figure 1. Spectroturbidimetric titration curves of PAA solution by PVEEG in isopropanol (1), isopropanol-ethanol 1:1 mixture (2) and ethanol (3). $[PAA]=[PVEEG]=0.01$ mol. / L.

It has been shown earlier [14] that IPC do not formed in mixtures of water with alcohols by the reason of considerable increase in thermodynamic quality of mixed solvent and strengthening of polymer-solvent interactions. Unlike of water-alcohol mixtures the mixture ethanol-isopropanol (1:1 by volume) is more favorable medium for the

formation of IPC. Probably ethanol and isopropanol possess similar solvating ability in respect to corresponding groups of polymers and the selective solvation of different groups of polymers does not occurred in their mixture.

It has been reported by Maunu et al [15] that the complexation between complementary macromolecules occurs instantly after the mixing of the solutions. Then the fast complexation is followed by the aggregation of the complexes, the rate of which is strongly dependent on conditions like temperature, concentration and pH. In order to clarify the influence of solvent nature and polymer concentration on the aggregation of IPC we have studied the kinetics of solution turbidity increase after the mixing of ethanol and isopropanol solutions of initial reagents (fig. 2, 3). At concentrations of initial components lower than 0.001 M in ethanol and 0.00025 M in isopropanol the aggregation of IPC is not observed. If the polymers concentrations are higher than these critical values then the size of IPC aggregates increases very significantly with time. As it is seen from the figures the increase in turbidity of IPC solutions is more significant in isopropanol. Moreover, the lower critical polymers concentration in ethanol is higher than the corresponding value in isopropanol. This lower critical polymers concentration can be considered as some criterion of complexation ability of the system. Hence, isopropanol is more favorable solvent for complex formation than ethanol because of the less solvating ability of former in respect to polymers.

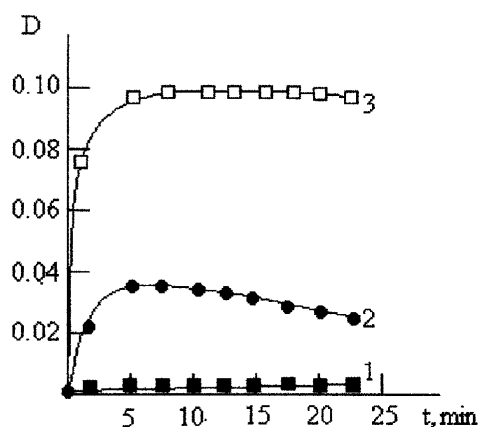


Figure 2. Kinetics of aggregation of PAA-PVEEG complex in ethanol. $[PVEEG]=[PAA]=0.001$ M (1), 0.005 M (2), 0.01 M (3).

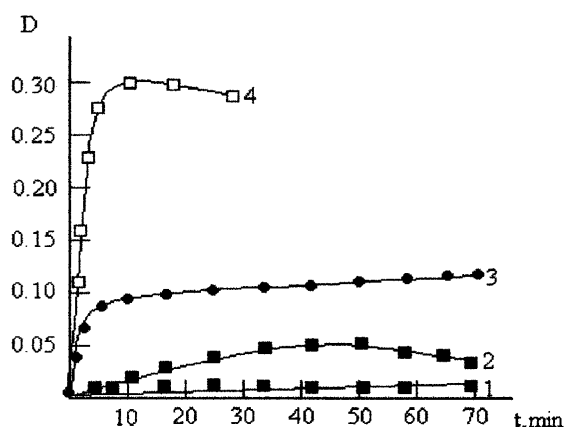


Figure 3. Kinetics of aggregation of PAA-PVEEG complex in isopropanol. $[PVEEG]=[PAA]=0.00025$ M (1), 0.001 M (2), 0.005 (3), 0.01 (4).

The complex formation of linear non-ionic polymers with gels of polycarboxylic acids has been considered earlier by Osada et al [16], Starodubtzev et al [17, 18], Frenkel et al [19], Tanaka et al [20], and in our previous work [21]. Khokhlov and Kramarenko [22] 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. However, they have considered formation of IPC only in aqueous media.

Earlier [21] 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 [19] taking into

consideration the state of double electric layer on gel-solution boundary, in particular the density of surface charge of hydrogel.

The complexation between gel and linear polymers in organic media has not been considered before. However, in organic media the ionization of carboxylic groups is depressed. Therefore, the influence of thermodynamic quality of solvent should be predominant in this case.

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. We have studied the influence of polymers concentration on the formation of muddy IPC layer on the hydrogel solution boundary (fig. 4, 5). It is seen from the figures that the higher the concentration of polymers, the faster the increase of gel turbidity is observed. Besides 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. This layer of complex generally determines the turbidity of the gel. 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 6). The process of diffusion of PVEEG into the gel requires considerable period time up to 50 hours.

It is interesting to note that the shrunken in PVEEG solutions gels placed into the pure solvents maintain their shrunken state during the long time. It is indicated that the IPC are stable to dilution and interpolymer reactions between gels and linear polymers are irreversible. This is in good agreement with our previous results on stability of polycomplexes formed from linear polymers [14].

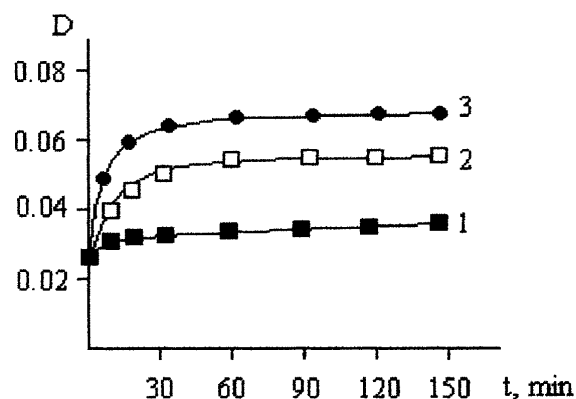


Figure 4. Kinetics of optical density increase for PAA gels immersed into ethanol solution of PVEEG. [PVEEG] = 0,01 (1), 0,05 (2), 0,1 (3) mol / L.

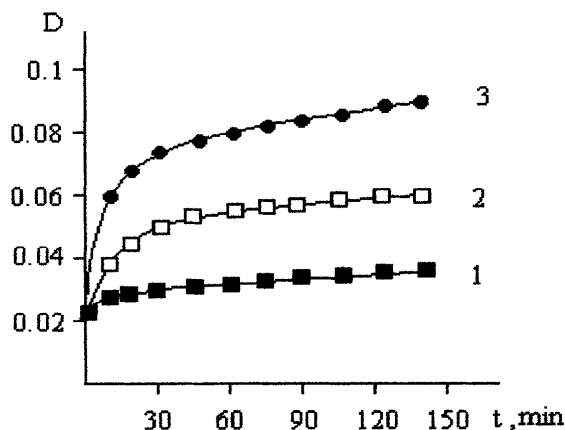


Figure 5. Kinetics of optical density increase for PAA gels immersed into isopropanol solution of PVEEG. [PVEEG] = 0,01 (1), 0,05 (2), 0,1 (3) mol / L.

The obtained results about the influence of dielectric constant of solvent on the complexation are in disagreement with Tsuchida's with co-workers findings [8]. In our case the decrease of dielectric constant of alcohol from ethanol to isopropanol increases the complexation of polymers. The similar influence of dielectric constants of solvents was also observed by Baranovsky with co-workers [23] and in our previous work [24]. Probably the effect of the solvent dielectric constant on complexation should be

considered from the position of competition between polymer-polymer and polymer-solvents interactions. If the decrease of dielectric constant decreases the polymer-solvent interactions then it should favor the complexation, and vice versa.

The results on gel contraction and increase of turbidity are in good agreement with interaction of linear macromolecules in solutions. Unlike of aqueous solutions [21] the swelling behavior of PAA gels in alcohol solutions of PVEEG generally depends on the thermodynamical quality of the solvent therefore the complex formation of PAA gels with organic solutions of PAA in all cases is accompanied by contraction of networks.

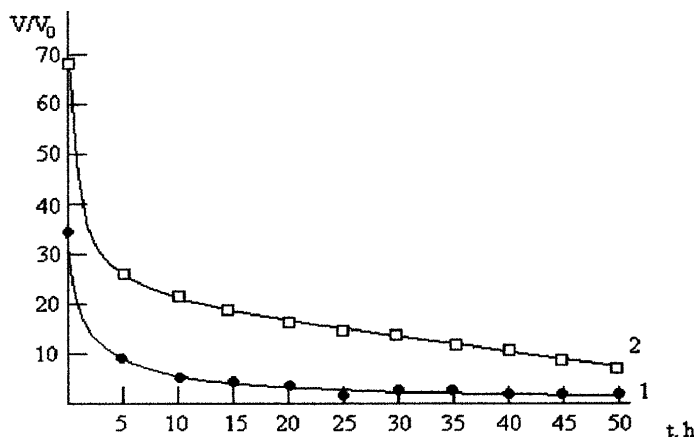


Figure 6. Contraction of PAA gels in 0.01 M solutions of PVEEG in isopropanol (1) and ethanol (2)

Conclusions

The formation of IPC in solutions as well as on gel-solution boundary strongly depends on the nature of a solvent. The deterioration of thermodynamic quality of a solvent is favorable for complex formation due to the decrease of polymer-solvent interactions. Phenomena observed during the complex formation of gel and linear polymer resembles interpolymer reactions that occurred between linear macromolecules. In both cases the increase of turbidity as well as the decrease of macromolecules (gels) size can be observed.

Acknowledgments

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