Polymer Bulletin 11, 557-560 (1984)

Polymer Bulletin

Complex Formation of Polymethacrylic Acid with Random Copolymer of Vinylpyrrolidone and Vinyl-Amine in Solutions

L. A. Bimendina and A. A. Kurmanbaeva

Institute of Chemical Sciences, Academy of Sciences of the Kazakh SSR, Alma-Ata, USSR

SUMMARY

By IR-spectroscopic, conductometric, potentiometric and viscometric methods the formation of interpolymer complexes in polymethacrylic acid-random copolymer of vinylpyrrolidone and vinylamine (VP/VAm, 88 mol.% of VP) systems in water and methanol have been shown. The properties of copolymer complexes (PMAA-VP/VAm) are compared with ones of homopolymer complexes of polymethacrylic acid-polyvinylpyrrolidone (PMAA-PVP).

INTRODUCTION

The properties of polymethacrylic acid-polyvinylpyrrolidone complexes in solutions have been investigated earlier (I,2). As one can suppose (3) the complex formation in polymer-polymer systems is caused by cooperative interaction of a sufficiently long sequence of functional groups bound into polymer chains.

It should be interesting to investigate the possibility of complex formation in the polymethacrylic acid-random copolymer of vinylpyrrolidone and vinylamine (PMAA-VP/VAm) when the complementarity of reacting macromolecules is disturbed by the presence in copolymer chains of VAm which does not take part in complex formation through H-bonds. Information about interpolymer complexes of random copolymers is very scarce (2).

EXPERIMENTAL

Polymethacrylic acid (PMAA) was obtained by free-radical polymerization in 25% benzene solution at 86°C with 2,2'azoisobutyronitrile as initiator (0.007% of weight monomer) in nitrogen. The PMAA fraction with molecular weight M_v = I35x xIO^3 determined from intrinsic viscosity in methanol by means of: $[\eta]$=24.2xIO^{-4}M$^{0.5I}$(4) was used.

Vinylpyrrolidone and vinylamine copolymer (VP/VAm, 88 mol.% of VP) was obtained from vinylpyrrolidone and vinylphtalimide copolymer by hydrazinolysis (5).

The conductometric and potentiometric measurements were carried out on a "Radelkis"type conductometer OK-IO2 (Hungary) and pH-340 potentiometer (USSR). IR spectra were obtained on a UR-20 (DDR) spectrophotometer using KBr pellets. The viscosity of solutions was measured in an Ubbelohde viscometer.

The polymer complexes were prepared by mixing the solutions of the interacting components. The initial concentrations of polycomplex solutions were about 0.05-0.I0 g/dl.

RESULTS AND DISCUSSION

The composition of polymer complexes was determined by electrochemical methods. Fig.I represents the curves of potentiometric and conductometric titration of 0.0I N PMAA solutions with 0.I N VP/VAm copolymer solutions in water. The bends in the titration curves indicate the complex formation in this system. The composition of PMAA-VP/VAm complexes was determined as the ratio of PMAA (mole) to the average molecular weight of copolymer links, i.e. as the [PMAA] / [VP/VAm] ratio being 2:3 in water.

In IR spectra of the PMAA-VP/VAm complex, in comparison with spectra of individual polymer components (Fig.2) the band of fundamental vibrations of C=O groups of VP-links shifts by 20cm^{-1} to lower frequencies and the outline of this band changes. At the same time the intensity of the band of polyacid C=O group vibrations is increased and shifts to higher frequencies. It notes the destruction of inter- and intramolecular H-bonds in polyacid macromolecules. These changes testify the arising of a H-bonds system between polymer components.

The intrinsic viscosity of PMAA-VP/VAm complexes in water is about 0.I0 dl/g. The complex water solutions display the absence of the concentration dependence of the reduced viscosity as well as the polyelectrolyte anomaly. These data confirm the formation of PMAA-VP/VAm complexes in solution.

One can suppose a considerable role of hydrophobic interactions in the stabilization of the compact structure of complexes in water. It is known that these interactions are weakened at transition to organic solvent. The significant hydrophobization of polymer complex as a consequence of the hydrogen binding of the hydrophilic groups causes a decreased complex solubility in water and the tendency of complex particles to coil up into globules. As can be seen from Fig.3 the compact structure of PMAA-VP/VAm complexes remaines up to ~40 vol.% DMSO content in a water-DMSO mixture. With further increase of the DMSO content a sharp increase of viscosity is observed in a narrow interval of the solvent composition change, i.e. in DMSO probably not only a weakening of hydrophobic interactions takes place but the destruction of hydrogen bonds and hence of the polymer complex occurs. In Fig. 3 the dependence of the intrinsic viscosity [η] on water-DMSO composition for early investigated polymethacrylic acid-polyvinylpyrrolidone complexes (I) is given. The homopolymer PMAA-PVP complexes retain a compact structure up to a high DMSO content in mixture, i.e. they are more stable than copolymer PMAA-VP/VAm complexes.

The possibility of complex formation in PMAA-VP/VAm-methanol systems was investigated. Titration curves in methanol exhibit a typical inflection point terminating I:I complex

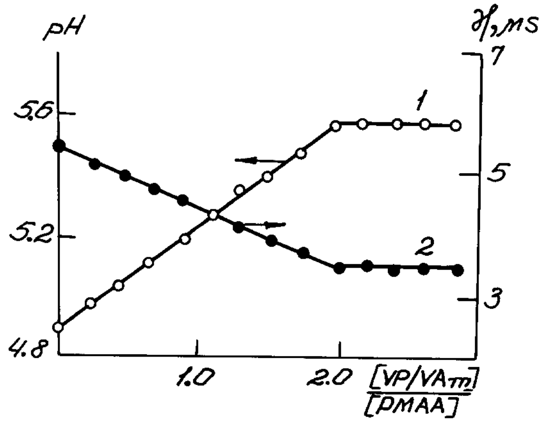

Fig.I.Curves of potentiometric (I) and conductometric (2) titration in the PMAA-VP/VAm-water system. ($\varkappa$ is the specific electroconductivity in millisimenses, I $\mu s=10^{-6}om^{-1}cm^{-1}$).

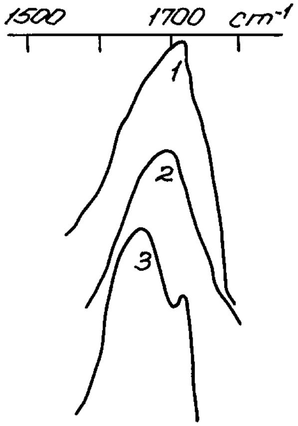

Fig.2.IR spectra of PMAA (I), VP/VAm (2), PMAA-VP/VAm complex (3).

formation. Viscometric behaviour of PMAA-VP/VAm complexes in methanol displays the typical properties of complex water solutions.

PMAA-VP/VAm complexes forming in methanol are less stable than ones in water and decompose at a much lower DMSO content in methanol-DMSO mixtures (Fig.3). The complex compact structure in non-aqueous media apparently is in addition stabilized by liophobic interactions of"nonsoluble parts" of reacting macromolecules (6).

PMAA-VP/VAm complexes are stable to thermal action the intrinsic viscosity does not change and is low both in water (I5-80°C) and methanol (I5-40°C). At the ionization of the polyelectrolyte component of the PMAA-VP/VAm complex the stabilization of the complex compact structure is observed up to a degree of neutralization of about α =0.03; thereafter the complex decomposes and the system behaves as a ty-

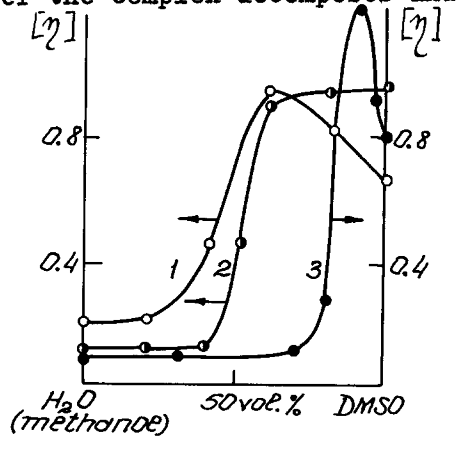

Fig.3. Dependence of intrinsic viscosity of PMAA -VP/VAm (I,2) and PMAA-PVP (3) complexes on methanol-DMSO (I) and water-DMSO (2,3) mixed solvent composition.

pical polyelectrolyte during ionization. Compact complexes forming in methanol already decompose at insignificant quantities of added alkali and viscosity sharply increases with increase of degree of neutralization. Thus, PMAA-VP/VAm complexes forming in methanol are less stable than the same complexes forming in water to the action of organic solvent (DMSO) and ionization.

The formation of interpolymer complexes in polymethacrylic acid-random copolymer of vinylpyrrolidone and vinylamine system was thus shown. Forming copolymer complexes are less stable in comparison with homopolymer complexes to action of organic solvent and ionization.

REFERENCES

I. L.A.Bimendina, V.V.Roganov and E.A.Bekturov, J.Polym.Sci., Symp., N44, 65 (I974)
2. E.A.Bekturov and L.A.Bimendina, Adv.Polym.Sci., 4I, 99 (I98I)
3. A.D.Antipina, I.M.Papisov and V.A.Kabanov, Vysokomol.Soedin., Ser.B, I2, 329 (I970)
4. N.M.Wiederhorn and A.R.Brown, J.Polym.Sci., 8, 652 (I952)
5. E.Ph.Panarin and S.N.Ushakov, Chem.Pharm.J., N5, 28 (I968)
6. S.Ya.Frenkel, in "Vvedenie v statisticheskuyu teoriyu polimerizatsii", Nauka, Moscow-Leningrad (I965)

Accepted May 3, 1984