

Hydrogels based on acrylic acid-co-vinyl-isobutyl ether and their complex formation properties

Nam I.K., Mun G.A., Kurbanova G.K., Urkimbaeva P.I., Nurkeeva Z.S.

Abstract

Nowadays the hydrophilic polymeric networks (polymer hydrogels) due to the complex of benefit physico-chemical properties attract a wide attention of specialists working in various fields of science, medicine and technology. The special attention of chemists is aimed on so-called stimuli-sensitive or intelligent hydrogels, which can undergo a volume phase transition in response to change in environmental parameters such as temperature, pH, solvent composition, etc [1]. Scientific group of Kazak State National University, Department of Macromolecular Chemistry works in this field [2-5]. Here we report about our achievements on pH-sensitive hydrogels.

1. Synthesis of new pH-sensitive polymeric hydrogels

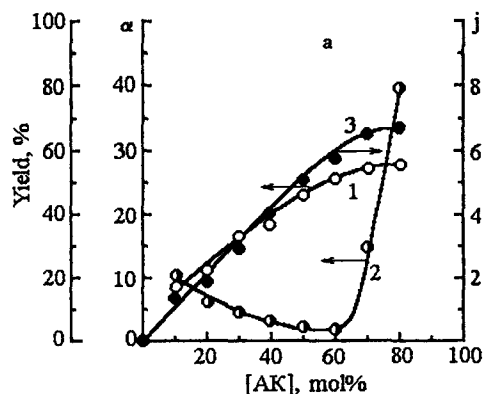
Novel pH-sensitive anionic polymers were synthesized by-initiated radical copolymerization of AA vinyl ethers vinyl alkyl ethers (VBE and VIBE) of hydrophobic nature. The relative activity of vinyl ethers and AA has been determined via the binary copolymerization investigation of at low conversion degree in aqueous solutions. It has been found that vinyl ethers are considerably less active in comparison with AA [6]:

$$r_1(\text{AA})=5.4 \quad r_2(\text{VBE})=0.01$$

$$r_1(\text{AA})=5.6 \quad r_2(\text{VIBE})=0.01$$

The copolymerization rate depends on active acrylic comonomer concentration in a feed. With conversion and enriching of reaction mixture by low active acrylic monomer the copolymerization rate is decreased, AA units content in polymer composition is decreased and composition inhomogeneity is appeared. Similar regularities were observed for three-dimensional copolymerization of vinyl

alkyl ethers (VBE and VIBE) with AA in the presence of divinyl ether of diethyleneglycol (DVEDEG) as cross-agent. An increasing of acrylic co-monomer concentration in the feed increases the rate and yield of sol and gel fractions and decreases the AA content in cross-linked copolymers. It causes the significant appearance of composition inhomogeneity for cross-linked copolymers (fig.1).



Al-Farabi Kazak State National University
Chemistry Faculty, Department of Macromolecular
Chemistry Karasai Batyr Str. 95, Almaty 480012,
Republic of Kazakstan

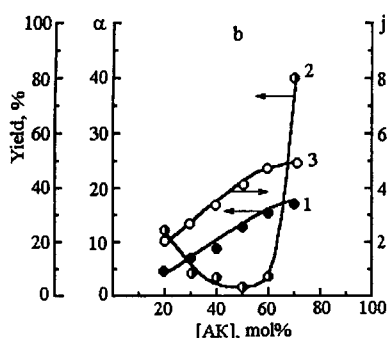


Fig.1. The influence of feed composition on yield of gel-fraction (1), swelling degree (2) and cross-linking density j (3) of copolymeric AA-VBE (a) and AA-VIBE (b). [CA]=4mol%; D=102,1 kGy; alcohol 50 vol.% in the feed.

As it is well known for polyelectrolyte gels the high equilibrium swelling degrees (α) are reached due to the ionic contribution of ionic groups into whole swelling pressure of polymeric network. But the swelling degree pass through minimum and gel-fraction yield increases during the increasing of irradiation dose. It can be supposed that the reason of observed effects is the peculiarities of three-dimensional radical copolymerization in the system VEEG-BAA with significant difference in monomer and CA activities. BAA as a more reactive agent is consumed at initial conversion degrees. It is accompanied by the formation of high-density network (low and high nc). It depresses the effects concerned with increasing of network charge. So then, the significant difference between the monomer and CA activities is accompanied by more inhomogeneous network formation with low and high cross-linking density phases in comparison with systems in which co-monomer activities are similar.

The comparative analysis of the data on the synthesis of copolymers of vinyl alkyl ethers with acrylic acid showed, that the values of gel-fraction yield and cross-linking density are higher and the equilibrium swelling degrees are lower for VBE-AA system than for VIBE-AA one. Thus, the equilibrium swelling of hydrogels in water can be regulated not only by an increase of hydrophilic fragments concentration in the network but, by changing of

the structure of vinyl alkyl ether. Namely, the transition from VBE to VIBE in the line of cases is accompanied by an increase of α in approximately two times at the same synthesis conditions.

2. Swelling behavior of pH-sensitive copolymers VAE-AA

The behavior of copolymer VAE-AA contained both ionic pH-sensitive carboxylic groups and hydrophobic VAE units has been studied in wide interval of pH medium.

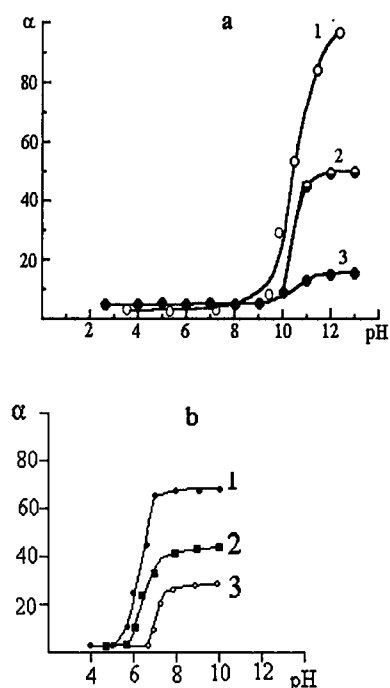


Fig.2. The dependence of swelling degree on pH of media for hydrogels AA-VBE (a) and AA-VIBE (b).

- a) $\mu=0,01$; [VBE]:[AA], mol%: 1 - 10,9:89,1; 2 - 17,5:82,5; 3 - 28,2:71,8;
 b) $\mu=0,05$; [VIBE]:[AA], mol%: 1 - 9,8:90,2; 2 - 15,1:84,9; 3 - 27,7:72,3.

It is seen that polymeric networks based on copolymers VAE-AA characterized by pH-induced collapse (the equilibrium swelling degree of hydrogels abruptly decreases at narrow range of pH). The

value of pH transition for VBE-AA hydrogels is located in alkaline area and practically independent on their composition. An increase of VBE content in cross-linked copolymer is accompanied only by a decrease of transition amplitude. In contrast to VBE-AA the pH of transition of VIBE-AA hydrogels is located in acidic area and an increase of VIBE content in copolymers shifts the transition pH to the higher values. The observed different behavior of networks is caused by more intensive hydrophobic interactions for hydrogels of copolymers VBE-AA. The additional ionization of carboxylic groups is required to overcome the hydrophobic interactions in VBE-AA, therefore the transition of these gels in alkaline pH region. The dependence of swelling degree of cross-linked VBE-AA and VIBE-AA copolymers as the function of ionic strength (μ) looks like one for polyelectrolyte hydrogels. An increase of low molecular weight salt concentration in solution up to 0, 1 mol/l leads to the noticeable decrease of values. It is connected with the depressing of polyelectrolyte swelling. The further increase of ionic strength does not influence the value that is determined by only network swelling in these conditions. Besides an increase of ionic strength of the solutions shifts the pH transition of hydrogels of copolymers VIBE-AA to the higher values region and decreases the collapse amplitude.

Thus, the change of pH from neutral to more acidic region depresses the ionization of carboxylic groups and decreases the electrostatic repulsion of macrochains for novel synthesized anionic networks. It favors the formation of more compact conformations of macromolecules. The interval of pH with abrupt changing of value governs by variation of copolymer composition as well as by structure of VAE.

3. Interactions of AA-VIBE hydrogels with linear polymers.

Interactions of hydrogels with linear polymers represent interesting opportunity of modification the properties of polymeric networks. Usually they are accompanied by the changing of swelling behavior of hydrogels. The response of hydrogels to the complex formation with linear polymers

strongly depends on the nature of interaction, molecular weight and concentration of linear polymer, pH and ionic strength of the solution, nature of the solvent, and temperature [28].

We studied the interactions of hydrogels based on PAA and VIBE-AA with linear PVEEG in aqueous and organic solutions varying different factors such as pH, concentration of linear polymer in solution, and nature of solvent [7]. Depending on the pH of an aqueous medium the complex formation in the hydrogellinear polymer solution system is accompanied either by swelling or contraction of the network. An increase of PVEEG concentration decreases the value of additional swelling of hydrogels (fig.3). At some concentration of PVEEG the hydrogel does not change its volume in course of interpolymer reaction. The further increase of PVEEG concentration leads to the contraction of the network.

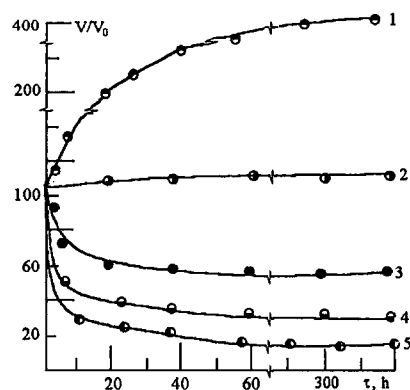


Fig.3. The kinetics of swelling ratio changes of VIBE-AA hydrogels in water solution of PVEEG. VIBE : AA = 9.8 : 90.2 mol%; PVEEG, mol/l: 1-0,1 2-0,3 3-0,6; 4-1,0; 5-2,0.

The interval of PVEEG concentration, which characterized by additional swelling of the hydrogels, increases for copolymers containing higher AA units. The swelling behavior of the hydrogels in PVEEG solutions can be interpreted from the diffusion theory point of view for polyelectrolyte hydrogels [8]. The complexation of the hydrogels AA-VIBE with PVEEG is more effective at low

values of pH and at high ionic strength. The interactions between AA-VIBE hydrogels and PVEEG in ethanol-water mixed solvent are accompanied by their dramatic contraction. The amplitude of contraction in course of the complexation as much as higher organic co-solvent content in the mixture.

4. Interactions of AA-VIBE hydrogels with copper (II) ions.

Interactions of the AA-VIBE hydrogels with copper (II) ions was investigated. The polymer metal complexes were formed with participation of carboxyl group of AA. It is accompanied by dramatic collapse of the hydrogels (fig.4).

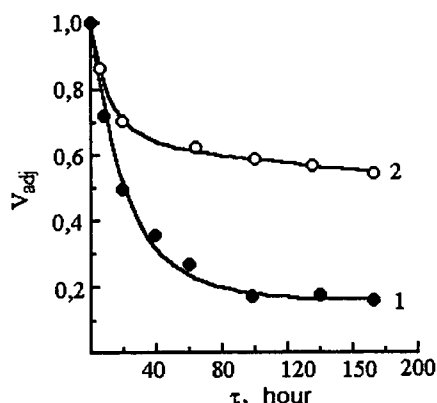


Fig.4. The kinetics of adjusted volume change of PAA (1) and copolymeric AA-VIBE (2) hydrogels in the presence of Cu^{2+} .

$V_{\text{adj}} = V/V_B$, where V - volume of hydrogel at the time moment τ , V_w volume of hydrogel in water. $[\text{AA}] : [\text{VIBE}] = 95, 4 : 4, 6 \text{ mol. \%}$; $[\text{Cu}^{2+}] = 1 \cdot 10^{-4} \text{ mol/l}$.

Swelling behavior of the copolymeric hydrogels and hydrogels of homopolyacrylic acid in the course of complex formation with Cu^{2+} was investigated. The noticeable differences were observed. As it is seen from fig.4, in the presence metal ions the amplitude of collapse of AA-VIBE hydrogels is much higher than in the case of PAA hydrogel.

Besides, AA-VIBE hydrogels are characterized by higher sorption ability of metal ions in comparison with PAA gel (fig.5).

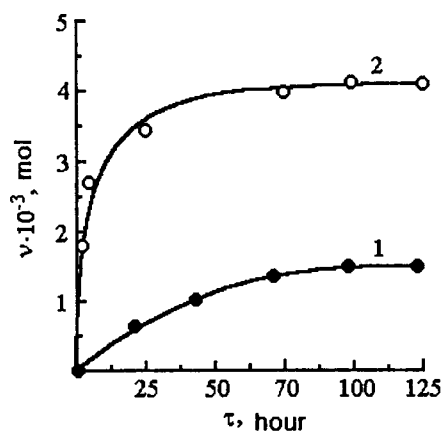


Fig 5. The kinetics of sorption of Cu^{2+} ions by the hydrogels PAA (1) and copolymeric AA-VIBE (2). $[\text{AA}]:[\text{VIBE}] = 95,4:4,6 \text{ mol/\%}$; $[\text{Cu}^{2+}] = 1 \cdot 10^{-4} \text{ mol/l}$.

They can absorb up to 100 % copper ions from the solutions with the concentration $1 \cdot 10^{-4} \text{ mol/l}$ while gel PAA only sorbs less than 10 % at the same conditions. The complex $[\text{Cu}^{2+}]:[\text{polymer}]$ composition obtained in copper ions excess is 1:4 and 1:1, 4 for PAA and copolymer AA-VIBE respectively. Apparently, these peculiarities are due to the presence of hydrophobic units in copolymeric gel and compact conformation of macromolecules. In accordance with literature data, these conditions are conducive for easier coordination of metal ion with carboxylic groups with participation remote along the macrochains functional groups.

The increase of metal ion concentration in external solution leads to more effective collapse of AA-VIBE hydrogels. The amplitude and speed of the hydrogels swelling ratio changes increase in more concentrated solutions as well as in the order $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$.

The desorption processes of Cu^{2+} ions from complexes with hydrogels were investigated. It was found that complex is very stable in water and buffer solution with alkaline pH value, and metal ions practically are not delivered from the complexes. The optimal conditions for full extraction of Cu^{2+} ions and regeneration of the hydrogels were found. It is necessary to treat the hydrogel

complexes with strong acidic medium for ionic change. Then hydrogels were immersed in water, where they swell to initial state. It is accompanied with intensive extraction of copper (II) ions up to 80%. At water replacement the full extraction of metal ions can be reached.

5. Immobilization of drugs into the AA-VIBE polymeric hydrogel matrixes.

Due to their hydrophilic and ionic properties the AA-VIBE hydrogels can be considered as perspective drug carriers. The immobilization of dimedrol into the hydrogels and drug release processes were investigated. It was found that AA-VIBE copolymeric hydrogels are undergone the contraction caused by the complex formation via ionic binding carboxylate anions and positively charged molecules of dimedrol. The amplitude and speed of the contraction as well as the drug abundance in the gels increase versus the concentration of dimedrol in the initial solution. The composition of the complex was calculated from the kinetical curves of drug absorption by hydrogels. It was equal to the ratio 1:2 of drug to AA units in the gel composition. Obviously, the reason is that the participation of ether oxygen in dimedrol molecule to form hydrogen bonds or structure hindrances. Dimedrol-hydrogel complexes obtained are very stable in pure water, but destroyed in isotonic solution (0,9% NaCl) modeling human organism medium. At these conditions intensive drug delivery is observed with high yield (more than 85%).

Conclusions

Thus, the complex formation of new hydrogel based on AA and VIBE with polyvinyl ether of ethylene glycol, Cu^{2+} ions and dimedrol was investigated. The possibility to regulate the absorption and desorption processes through the changes of the environmental parameters has been shown.

References

1. Y. Osada, S.B. Ross-Murphy, *Intelligent Gels*, J. Scientific American, vol. 268, N5, 1993. P. 82-87
2. S.E. Kudaibergenov, Z.S. Nurkeeva, G.A. Mun, B.B. Ermukhambetova, I.K. Nam. Temperature-responsive swelling and deswelling hydrogels of the copolymers from vinyl ether of ethylene glycol and butyl vinyl ether, *Macromol. Rapid Commun.*, Vol.16, 1995. P. 855-860.
3. S.E. Kudaibergenov, Z.S. Nurkeeva, G.A. Mun, I.K. Nam, V.A. Kan, V.V. Khutoryanskii, Design of "intelligent" polymer materials based on vinyl ethers, *Proc. of Int. Conf. on Advanced sciences and technologies*, Korea, June 12-16, 1998. P.473-475.
4. G.A. Mun, Z.S. Nurkeeva, B.B. Ermukhambetova, I.K. Nam, V.A. Kan, S.E. Kudaibergenov, Thermo- and pH-sensitive amphiphilic gels of copolymers of vinyl ether of ethylene glycol, *Polym. Adv. Technol.*, Vol.10, 1999. P. 151-156.
5. G.A. Mun, I.E. Suleimenov, Z.S. Nurkeeva, S. E. Kudaibergenov, I.K. Nam, V.A. Kan, Effect of the structural inhomogeneity of polyelectrolyte gels on their thermal sensitivity, *Polymer Science*, Vol. 40A, 1998. P. 433-440.
6. G.A. Mun, Z.S. Nurkeeva, I.K. Nam, Synthesis and properties of new pH-sensitive copolymers of vinyl alkyl ethers and acrylic acids, *Vestnik KazGU*, N. 12(4). P.43-49.
7. G.A. Mun, V.V. Khutoryanskii, I.K. Nam, Z.S. Nurkeeva, S.E. Kudaibergenov, Complex formation between linear and cross-linked vinyl isobutyl ether-acrylic acid copolymers and poly(ethyleneglycol vinyl ether), *Polymer Science*, vol. 40B, N7-8, 1998. P. 290-293.
8. T.V. Budtova, I.E. Suleimenov, S.Ya. Frenkel About the swelling of polyelectrolyte hydrogels in linear polymer solutions, *Vysokomol. Soed.A.*, Vol. 35, N.11, 1993. P.93-96.