

S. E. KUDAIBERGENOV, V. B. SIGITOV, ZH. E. IBRAEVA, L. A. BIMENDINA

SYNTHESIS AND CHARACTERIZATION OF NOVEL POLYELECTROLYTE GELS BASED ON ETHYL 3-AMINOCROTONATE AND CHARGED MONOMERS

Polyelectrolyte gels based on ethyl 3-aminocrotonate and sodium acrylate (SA), 2-acrylamido-2-methylpropanesulfonic acid (AMPSA) and 2-acrylamido-2-methylpropyltrimethylammonium chloride (AMPTAC) were synthesized *via* Michael-type addition reaction followed by radical polymerization. Hydrogels were characterized by FT-IR. The swelling degree of hydrogels in distilled water varied from 100 to 2000 g/g. The influence of pH, ionic strength and added organic solvents on the swelling-deswelling behavior of hydrogels was studied.

Introduction. Synthesis and characterization of water-swallowable polymeric materials (hydrogels) is important from the theoretical and practical points of view [1]. Recently we have developed new approach to synthesize novel monomers based on acetoacetic ester [2], ethyl 3-aminocrotonate and unsaturated carboxylic acids *via* Michael addition reaction [3-6]. A series of high swellable polyelectrolyte and polybetaine gels were synthesized and characterized. In the present paper we report on synthesis of polybetaine and polyelectrolyte gels with participation of ethyl 3-aminocrotonate and charged monomers such as SA, AMPSA and AMPTAC.

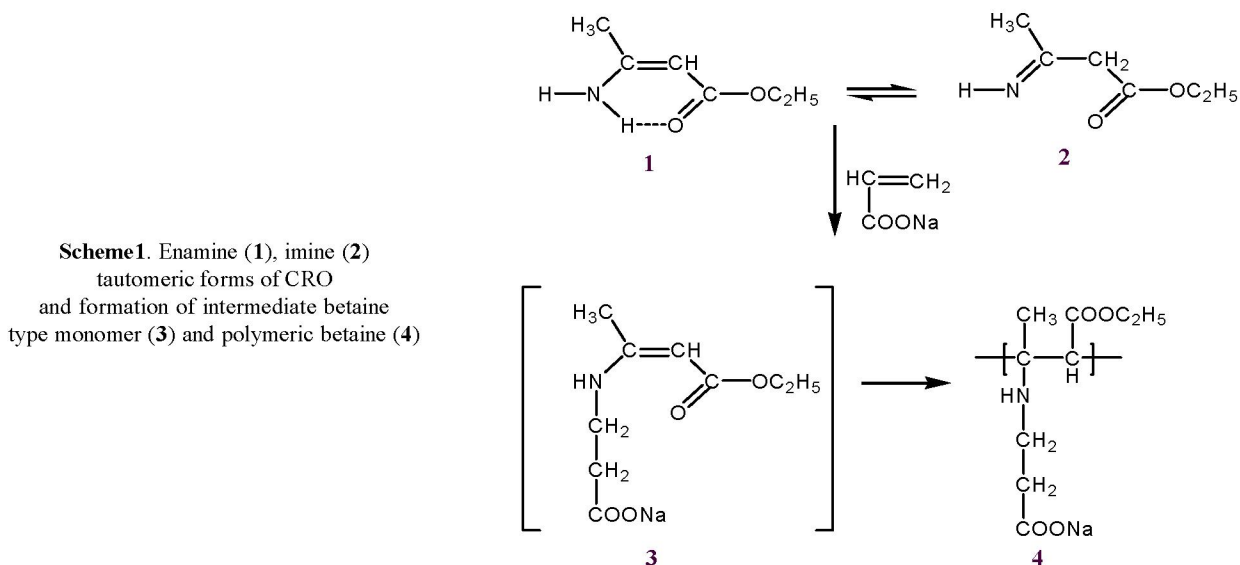
Experimental Part. Materials and Methods. Ethyl 3-aminocrotonate (CRO, 99% purity), sodium acrylate (SA, 99% purity), 2-acrylamido-2-methylpropanesulfonic acid (AMPSA, 99% purity), 2-acrylamido-2-methylpropyltrimethylammonium chloride (AMPTAC, 75% purity), initiator azoisobutyronitrile (AIBN) and crosslinking agent N,N'-methylenebisacrylamide (MBAA) were purchased from Aldrich. Reagent grade solvents acetone, ethanol, and DMF purchased from Aldrich were used. Ionic strength of the solution was adjusted by reagent grade NaCl. FT-IR spectra were recorded using a Perkin Elmer Spectrum GX.

Polymer Synthesis. Equimolar mixture of CRO (0.5 mol, 1.8 mL) and SA (0.5 mol, 1.2 mL) containing $5 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ AIBN and $5 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ MBAA was bubbled by nitrogen gas during 5 min to remove the dissolved oxygen. The polymerization reaction in the bulk was carried out at 70 °C during 1 h. The crosslinked polymers of CRO-AMPSA and CRO-AMPTAC were synthesized in the same conditions at the molar ratio of monomers in the feed 1:1. Gel samples were washed by distilled water during 1 week to remove the sol fractions. A pieces of equilibrium swollen gels in distilled

water were weighed on the analytical balance and then dried up to constant mass. Swelling degree (in g/g) of gels in pure water was calculated according to $(m - m_0)/m_0$, where m and m_0 are the masses of swollen and dried gels respectively. To study the pH sensitivity of hydrogels, the gel samples were placed into aqueous solutions, pH of which were kept by adding 0.1M HCl or NaOH. The pH-sensitivity of gels was determined according to $(m_{\text{pH}} - m_0)/m_0$ (where m_{pH} is the gel mass at chosen pH, m_0 is the mass of dry gel respectively). Swelling-shrinking behavior of hydrogels as a function of the ionic strength μ adjusted by NaCl was determined according to $(m_{\mu} - m_0)/m_0$ (where m_{μ} is the gel mass at chosen ionic strength, m_0 is the mass of dry gel respectively). The swelling degree of hydrogels in the mixtures of different solvents (water-ethanol, water-acetone, water-DMF and water-DMSO) was determined gravimetrically by measurement of the mass of mixture-swollen and dried gels and calculated according to $(m_{\text{wo}} - m_0)/m_0$, (where m_{wo} is the mass of gel in water-organic solvent mixtures and m_0 is the mass of dried gel).

RESULTS AND DISCUSSION. It is well known [7-9] that ethyl 3-aminocrotonate (CRO) belongs to low active compound due to existing in enamine (1) and imine (2) tautomeric forms (Scheme 1).

The specific property of CRO is the conjugation of C=C and C=O (or C=N and C=O) bonds and additional stabilization of enamine tautomeric forms via formation of intramolecular hydrogen bonds or else pseudo-aromatic cycle. Transformation of protons from imine to enamine tautomeric forms is important stage and proceeds via formation of the dimeric structure [10]. According to [7-9] at room temperature the enamine form is more stable than imine one. Our results on molecular modeling also confirm more energetically stable state of enamine form [5].



The relative energetic stability of enamine tautomeric form ($\Delta E = -19.67 \text{ kcal}\cdot\text{mol}^{-1}$) is lower than imine one ($\Delta E = 0$) therefore in the course of enamine consumption the enamine \leftrightarrow imine equilibrium is shifted to left side. Besides for N-substituted imines the increasing of nitrogen charge [11] and bulky substitution [12] causes decreasing of imine portion in favor of enamine form. Recently [3-6] we have found that CRO can form intermediate betaine type monomers with unsaturated carboxylic acids *via* Michael-type addition reaction and be further polymerized. It is known [13] that polycarboxybetaines with more than 90% zwitterionic structure are formed in the course of carboxyethylation of polyiminoethylene or polyiminohexamethylene by adding of acrylic acid *via* Michael-type addition reaction. Poly(N-vinylimidazole) based poly(carboxybetaine) with two methylene groups between the opposite charges was achieved by the nucleophilic addition reaction of the mentioned polymer to the carbon-carbon double bond of acrylic acid [14]. Polymerization of 2-hydroxyethylacrylate *via* Michael-type addition of hydroxyl groups to methacrylate carbon-carbon double bonds was studied by authors [15]. In this communication our earlier developed approach [2-6] was extended to synthesize novel polycarboxybetaine, polysulfobetaine and polycationic gels based on CRO and SA (AMPSA and AMPTAC). As seen from Scheme 1 the addition of SA to CRO leads to formation of intermediate monomer **3** that is further polymerized to final polymer product **4**. Formation of intermediate monomer **3** is confirmed by disappearance of intensive band of **1** at 789 cm^{-1} that represents the out-of-plane vibration of pseudo-aromatic

cycle of CRO. Identification of FTIR spectra of SA, CRO and **4** is given in Table 1, while FTIR spectra of CRO-SA, CRO-AMPSA and CRO-AMPTAC are summarized in Fig. 1.

Table 1. Identification of FTIR spectra of SA, CRO and **4**

Functional groups	Frequency, cm^{-1}		
	SA	CRO	4
$\nu(\text{NH})$	–	3440, 3334	3376
$\nu(\text{CH})$	3045	2979	2938
$\nu(\text{C=O})$	1704	1742, 1716	1675
$\nu(\text{C=C})$	1640	1659	–
$\nu(\text{C=N})$	–	1622	–
$\nu_{\text{as}}(\text{COO}^-)$	1556	–	1562
$\nu_{\text{s}}(\text{COO}^-)$	1448	–	1409
$\delta(\text{C=C})$	–	789	–
out-of-plane	–	789	–

Disappearance of intensive peaks at $\nu = 1659, 1622$ and 1640 cm^{-1} that belong to C=C and C=N of CRO and C=C of SA, broadening and shifting of intensive lines of primary amine groups of CRO at $\nu = 3440$ and 3334 cm^{-1} up to 3376 cm^{-1} confirms the formation of polymer product. Anti-symmetric vibrations of carboxylate ions in SA and **4** appear at $\nu = 1556$ and 1562 cm^{-1} .

Analysis of FTIR spectra of monomers and polymers shows that for mixture of CRO and AMPSA (AMPTAC) the reaction takes place analogous to Michael-type addition reaction with formation of polysulfobetaine CRO-AMPSA and cationic polyelectrolyte CRO-AMPTAC respectively (Scheme 2). For CRO-AMPSA additional intensive peaks of SO_3^- appear at 1186 and 1036 cm^{-1} [16].

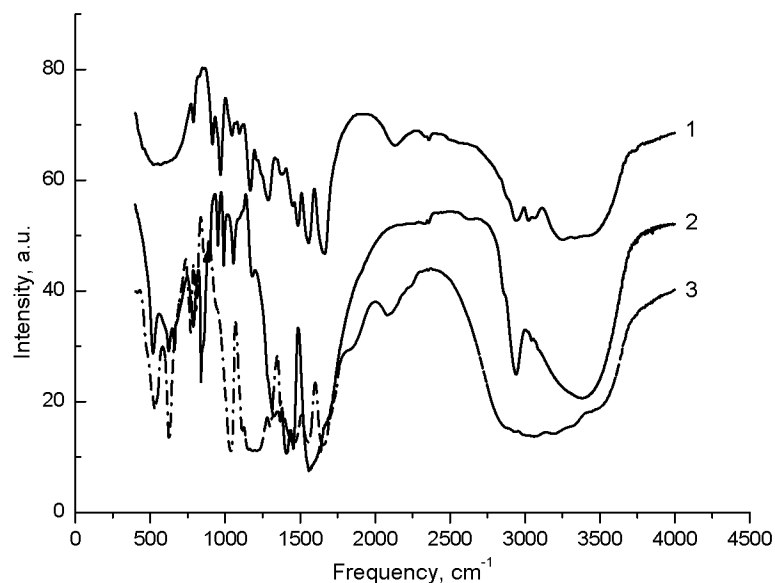
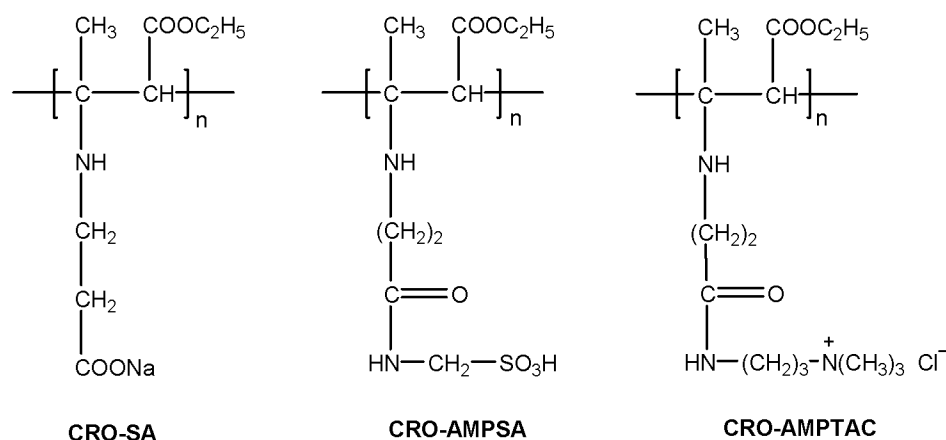


Figure 1.
FT-IR spectra of CRO-AMPTAC (1),
CRO-SA (2) and CRO-AMPSA (3)



Scheme 2. Repeating monomeric units of CRO-SA, CRO-AMPSA and CRO-AMPTAC hydrogels

The swelling degree of CRO-AMPSA, CRO-SA and CRO-AMPTAC in pure water was found to be 100, 160 and 2100 g/g respectively. Extremely high swelling ability of CRO-AMPTAC is probably explained by strong polyelectrolyte character of the network.

Swelling-deswelling behavior of ionic gels was studied in dependence on pH, ionic strength and water-organic solvent mixtures. In acidic region the CRO-SA and CRO-AMPSA hydrogels are in shrunken state due to suppression of the ionization degree of carboxylic and sulfonic groups (Fig. 2).

At higher pH the polymer chain expands because of the electrostatic repulsion of the ionized groups. Shrinking of gel specimen at pH > 8 is probably accounted for suppression of polyelectrolyte effect by the excess of NaOH that plays the role of low-molecular-weight electrolyte. Sharp decreasing of the swelling

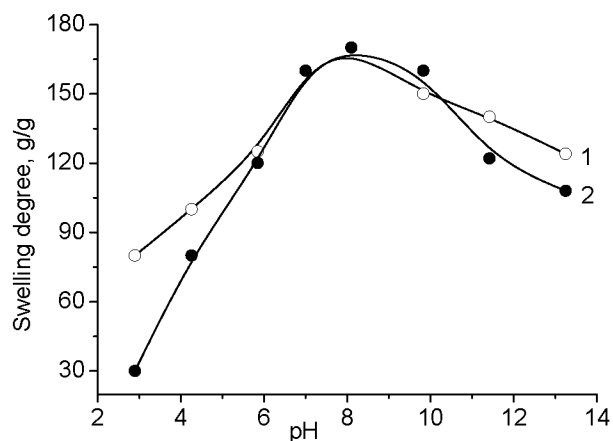


Figure 2. Dependence of the swelling degree of CRO-SA (1) and CRO-AMPSA (2) on pH

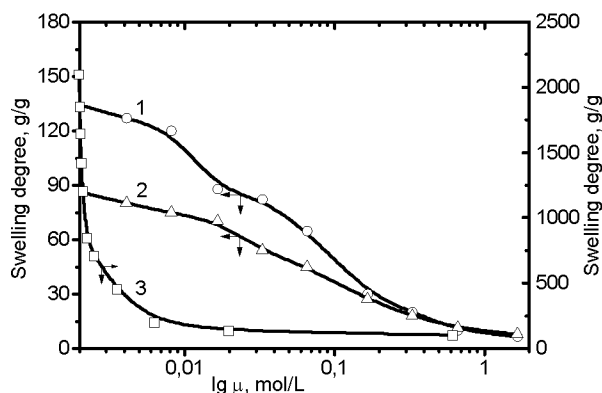


Figure 3. Dependence of the swelling degree of CRO-SA (1), CRO-AMPSA (2) and CRO-AMPTAC (3) on the ionic strength

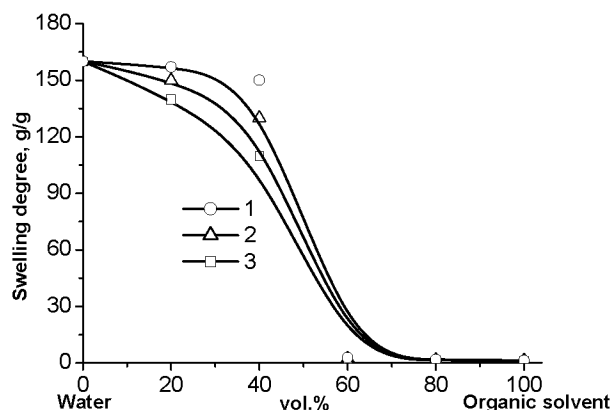


Figure 4. Swelling-deswelling of CRO-SA in water-acetone (1), water-ethanol (2) and water-DMF (3) mixtures

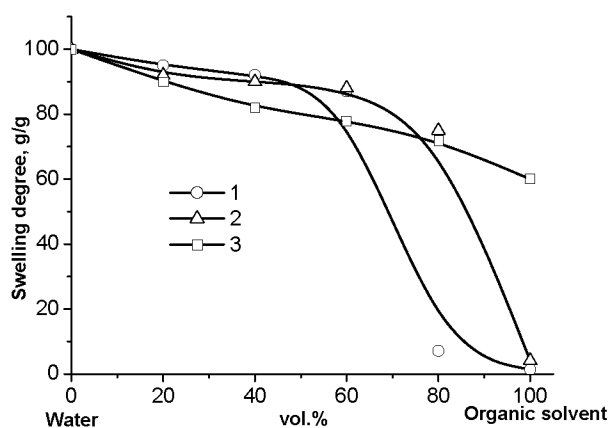


Figure 5. Swelling-deswelling of CRO-AMPSA in water-acetone (1), water-ethanol (2) and water-DMF (3) mixtures

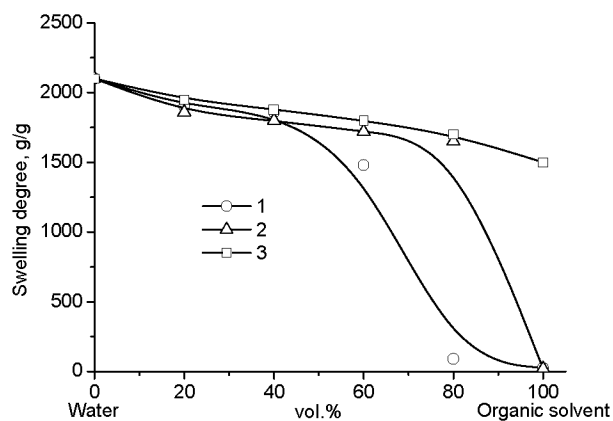


Figure 6. Swelling-deswelling behavior of CRO-AMPTAC in water-acetone (1), water-ethanol (2) and water-DMF (3) mixtures

degree of polycationic gel CRO-AMPTAC upon addition of neutral salt is the result of screening of electrostatic repulsion of ionic groups by low-molecular-weight ions (Fig. 3).

Gradually shrinking of CRO-SA and CRO-AMPSA with increasing of the ionic strength may be due to zwitterionic character of macromolecular chains. Polybetaine and polyelectrolyte gels shrink in water-acetone, water-ethanol and water-DMF mixtures (Figs. 4-6).

This is due to decreasing of the dielectric permittivity of medium that enhances the condensation of counterions to macroions. It leads to decreasing of the osmotic pressure within gel volume. Discontinuous gel collapsing is observed for CRO-SA in water-acetone (ethanol, DMF) mixtures starting at 60 vol.% of organic solvents. CRO-AMPSA and CRO-AMPTAC gels collapse at 80 vol.% of acetone and in pure ethanol. Continuous shrinking of hydrogels is observed for

CRO-AMPSA and CRO-AMPTAC in water-DMF mixture. These results confirm the universal behavior of polyelectrolyte gels with respect to thermodynamic quality of solvents.

Conclusions. Addition of sodium acrylate, 2-acrylamido-2-methylpropanesulfonic acid and 2-acrylamido-2-methylpropyltrimethylammonium chloride to ethyl 3-aminocrotonate leads to formation of monomer products *via* Michael-type addition reaction due to migration of hydrogen atoms from the enamine tautomeric form to α -carbon atoms of monomers. FT-IR spectra confirm the formation of novel polymers. Polybetainic and polycationic gels show stimuli-responsive behavior in dependence of pH, ionic strength and water-organic solvent mixtures.

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Резюме

Этил-3-аминкродонат пен натрий акрилаты (НА), 2-акриламид-2-метилпропансульфон қышқылы (АМПСК) және 2-акриламид-2-метилпропил үшметиламмоний хлорид (АМПҰ-АХ) негізіндегі полиэлектролиттік гидрогельдер Михаэль қосылу реакциясы бойынша, әрі қарай радикалдык синтезделді. Гидрогельдер ИҚ-Фурье спектроскопиясы арқылы сипатталды. Дистилденген суда гидрогельдердің ісіну дәрежесі 100-ден 2000 г/г дейін өзгереді. Гидрогельдердің ісінігіштік-сығылғыштық қасиеттеріне орта рН-ы мен иондық күшінің және органикалық еріткіштердің әсері зерттелді.

Резюме

Полиэлектролитные гели на основе этил-3-аминокродоната и акрилата натрия (АН), 2-акриламидо-2-метилпропансульфоновой кислоты (АМПСК) и 2-акриламидо-2-метилпропилтриметиламмоний хлорида (АМПТАХ) были синтезированы по реакции присоединения Михаэля с последующей радикальной полимеризацией. Гидрогели были охарактеризованы ИК-фурье спектроскопией. Степень набухания гидрогелей в дистиллированной воде варьируется от 100 до 2000 г/г. Изучено влияние рН, ионной силы среды и добавки органических растворителей на набухающе-сжимающее поведение гидрогелей.

*Institute of Polymer Materials
and Technology, Almaty*

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