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NOVEL POLYCARBOXYBETAINES CONTAINING AMINO ACID RESIDUES: SYNTHESIS, CHARACTERIZATION, STIMULI-SENSITIVITY AND METAL IONS UPTAKE

Novel monomers containing amino acid residues were synthesized by condensation of the acetoacetic ester with glycine, β -alanine and L-lysine in mild conditions. Novel linear and crosslinked polybetaines consisting of in addition to carboxybetaine functionality the amino acid moieties were obtained *via* Michael addition reaction with participation of acrylic acid followed by radical polymerization. The structure of monomers and polymers was analyzed by FTIR, ^1H NMR and UV-Vis spectroscopy. The solution properties of linear polymers were studied by viscometry and GPC. Stimuli-sensitive behavior of modified polycarboxybetaine hydrogels was studied as a function of pH, ionic strength and in water-organic solvent mixtures. The metal ions uptake by linear and crosslinked polycarboxybetaines was investigated by potentiometric titration, swelling-deswelling measurements and atomic emission spectroscopy. It was shown that the selectivity of polymeric adsorbents with respect to metal ions depends on the nature of metal ions and internal structure of polymeric ligands.

Introduction

A renewed interest for polyampholytes is due to appearance of some novel synthetic methods based on the radical and emulsion polymerization of charged anionic and cationic monomers, betaine type (or zwitterionic) monomers together with well-known living polymerization, group transfer polymerization and chemical modification technique [1–4]. Novel approach to design polymeric betaines has been developed recently by several research groups [5–9]. The synthesis of poly(electrolyte-zwitterions) that exhibit simultaneously both polyelectrolyte and polyampholyte character was reported [10–12]. Recently authors [13] described the synthesis and solution properties of new pH-responsive polymers containing amino acid residues.

Stimuli-sensitive behavior of polyampholytes was mostly studied with respect to annealed and quenched polyampholytes [1]. The number of polybetaines that demonstrate the “smart” properties is limited. In our previous publications [14–19] a new pathway of preparation of functional monomers from the acetoacetic ester and various amines was developed. As a result a series of novel water-soluble and water-swelling polycarboxybetaines possessing stimuli-responsive properties were obtained. In the present communication assortment of novel monomers is expanded by modification of the acetoacetic ester by amino acids. Application of Michael addition reaction with acrylic acid resulted in obtaining of novel polycarboxybetaines containing additionally

amine and carboxylic residues. The modified polycarboxybetaines exhibited the stimuli-responsive and metal ions adsorption behavior.

Experimental Part

Materials. Acetoacetic ester (ethyl acetoacetate) (99%), glycine (99%), β -alanine (99%), L-lysine (99%), acrylic acid (99.5% purity), N,N'-methylenebisacrylamide (MBAA) and initiator azoisobutyronitrile (AIBN) were purchased from Aldrich. Acrylic (AA) acid was purified by distillation under the low pressure and kept in refrigerator. Reagent grade solvents acetone and ethanol purchased from Aldrich were used. Metal nitrates of Cu(II), Ni(II), Co(II), Cd(II), Fe(III), Cr(III), Al(III) and Ga(III) were purchased from Junsei Co. (S.Korea). For preparation of aqueous solutions of amino acids and polymers the deionized water was used.

Methods. FT-IR spectra were recorded using a Perkin Elmer Spectrum 2000 series as pellets with KBr. ^1H NMR spectra of monomers in CDCl_3 and polymers in D_2O were recorded at room temperature with Unity Plus 300 MHz FT-NMR Spectrometer (Varian). The viscosity of aqueous solutions of polycarboxybetaines was measured by Ubbelohde viscometer at 25 ± 0.1 °C. The weight-average (M_w) and number-average (M_n) molecular weights of polymers were determined by gel permeation chromatography (GPC) (9200 GPC Youlin Instrument). Ultrahydrogel 500 (Waters, USA) and 0.1N NaNO_3 aqueous solution was used as column and solvent respectively. The column temperature was 45 °C and

flow rate – 1.0 mL/min. The injected volume of sample was 100 μ L. The molecular weights were determined from the calibration curve obtained for pullulan standard set (Shodex, Japan). The running time was 50 min. The refraction index (RI) detector's temperature was kept at 35 °C. The concentration of metal ions was determined by ICP (Inductivity Coupled Plasms) Atomic Emission Spectrometer (ICP-IRIS PA-205, Thermo Jarrell Ash, USA). Electron paramagnetic resonance (EPR) spectra of copper(II) complexes were run on a PS-100X Instrument at 25 °C. Diphenylpicrylhydrazine (DPPH) and Mn²⁺ in MgO were used as the field standards. Polymer-copper(II) complexes were prepared by dissolving of 20 mg of samples in 5 mL of water, adding of 1 mL of 1·10⁻² mol·L⁻¹ Cu(NO₃)₂ and drying the solution in air and vacuum.

Monomer synthesis. The aqueous solutions of selected amino acids were dropwise added to 10 mL of acetoacetic ester (AAE) during 3h under the stirring at room temperature till the molar ratio of AAE and amino acids reached 1:1 mol/mol. After completion of the reaction some amount of NaCl was added to saturate the water phase by salt, the mixture was additionally stirred during 30 min and left overnight. The organic phase was separated from the water one with the yield 96-98%. Monomers obtained by condensation of AAE and aminoacids were abbreviated as CROGly, CROAla and CROLys (Table 1). The purity of monomers was checked by ¹H NMR spectroscopy.

Table 1. Survey of monomers obtained by condensation of AAE* and amino acids

Amino acid	Quantity (mL)	Monomer abbreviation	Yield (%)	End or side group
Glycine (25% aq.)	5.89	CROGly	98	Carboxyl
β-Alanine (10% aq.)	7.00	CROAla	96	Carboxyl
L-Lysine (40% aq.)	11.47	CROLys	97	Amino carboxyl

* The quantity of AAE is 10 ml

Synthesis of linear and crosslinked polybetaines. Equimolar amount CROGly (or CROAla, CROLys) and AA was mixed then the AIBN (1-2 mg) was added. The mixture was bubbled by nitrogen during 5-7 min and thermostated at 70 °C for 1 h.

Table 2. Polymerization of equimolar mixture of monomers and AA

Polymer	Monomer (mL)	AA (mL)	Yield (%)
CROGly-AA	3.24	1.26	33
CROAla-AA	2.20	0.80	31
CROLys-AA	4.60	1.40	33

Table 2 shows the polymerization conditions of amino acid derivatives of ethyl 3-aminocrotonate (CRO). The linear polymers obtained in bulk were thoroughly washed out by acetone, dried and dissolved in water. They were purified by ultrafiltration using the cellulose membrane with pore size 5 kD and freeze-dried. To synthesize the gel samples the equimolar mixture of monomers, 1 mg of AIBN and 2-3 mg of MBAA were mixed, bubbled by nitrogen gas during 5-7 minutes and then placed into the oven heated up to 70 °C for 1 h. The obtained gels were placed into the deionized water to swell and during 1-2 weeks periodically washed out to remove the sol fractions.

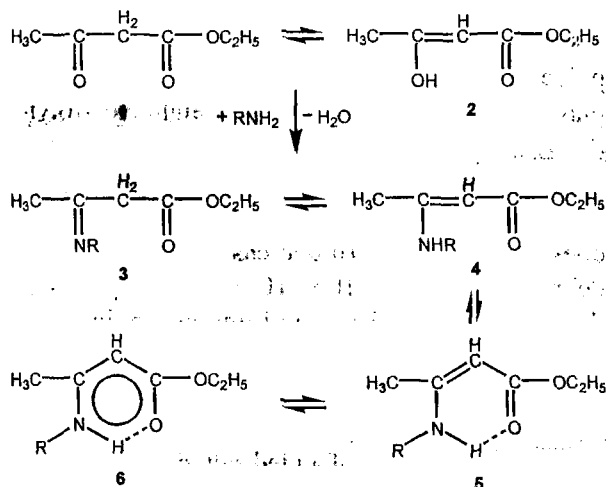
Equilibrium swelling measurements. Equilibrium-swollen in distilled water gels were weighed on the analytical balance and then dried at 60 °C up to constant mass. Swelling degree (α) of gels (in g/g) was calculated according to the formula: $\alpha = m - m_0 / m_0$ (where m and m_0 are the masses of swollen and dried gels, respectively). The swelling degree of CROGly-AA, CROAla-AA and CROLys-AA in water was equal to 25, 26 and 670 g/g respectively. The swelling degree of hydrogels in the mixtures of different solvents (water-ethanol, water-acetone) was determined gravimetrically by measurement of the mass of water-swollen (m_{ws}) and mixture-swollen (m_{ms}) gels and calculated in percentage $(m_{ms} / m_{ws}) \times 100\%$. To study the pH sensitivity of hydrogels, the gel samples swollen in water ($m = 2 \pm 0.1$ g) were placed into aqueous solutions, pH of which were preliminary adjusted by adding HCl or NaOH. The pH-sensitivity of gels was determined according to $(m_{pH} / m_w) \times 100\%$ (where m_{pH} is the gel mass at definite pH, m_w is the mass of gel swollen in water, respectively). Influence of the ionic strength (μ) on the swelling-shrinking behavior of hydrogels was studied by comparing the swelling degree of gel samples at different salt concentration value ($\mu = 10^{-5}$ – 10^{-1} mol·L⁻¹ NaCl). After equilibration of samples the swelling degree was determined as described above.

Metal ions uptake experiments. Aqueous solutions of CROGly-AA, CROAla-AA and CROLys-AA

(0.1 wt.%) were titrated by $5 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ metal solutions. The adsorbed amount of metal ions was calculated from the bends of potentiometric titration curves. Gel samples with diameter 20 mm, height 5 mm were immersed for 1 day in 50 mL of Cu(II), Ni(II), Co(II), Cd(II), Fe(III), Cr(III), Al(III) and Ga(III) solutions of definite concentration. The concentration of adsorbed metal ions (C_{Me}) was calculated as: $C_{\text{Me}} = C_0 - C_s$ (where C_0 is the initial concentration of metal ions, C_s is the concentration of metal ions in supernatant). Determination of the shrinking degree of gels in the course of metal uptake was also performed. Water swollen gel samples with diameter 20 mm and height 5 mm were placed into the metal ions solution ($C_{\text{Me}} = 1 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$). The shrinking degree of gels as a function of time was calculated as V_t/V_0 (where V_t and V_0 are the volumes of shrunken at definite time t , and initially swollen gels at $t = 0$). Desorption of metal ions within gel volume was carried out by soaking of gel samples in 0.1N HCl. For recycling of gel samples they were periodically washed out by distilled water. The change of gel volume during the adsorption-desorption experiments as well as recycling process was fixed photographically.

Results and Discussion

Analogous to ammonia, primary and secondary amines, amino acids (glycine, β -alanine, L-lysine) are also able to interact with keto (1) and enol (2) tautomeric forms of AAE and to produce the N-substituted ethyl 3-aminocrotonates (CRO) (5) which also exists in imine (3) and enamine (4) tautomeric forms (Scheme 1).



Scheme 1. Formation of amino acid derivatives of ethyl 3-aminocrotonate (CRO)

In its turn the 5 is additionally stabilized via formation of hydrogen bonds. The conjugation of C=C and C=O bonds leads to formation of pseudo-aromatic cycle (6) the activity of which is extremely low. Therefore analogous to CRO [20] the 5 is not involved into polymerization reaction. In FTIR spectra the characteristic bands for CROGly, CROAla and CROLys appear at 1644 cm^{-1} (C=C) and $1728\text{--}1754 \text{ cm}^{-1}$ (C=O). UV spectra of CROGly, CROAla and CROLys show a specific absorption bands at 295, 299 and 310 nm that belong to carboxylic groups of amino-acids. Addition of AA to CROGly, CROAla and CROLys leads to destabilization of the structure 5 due to transfer of the labile hydrogen atoms of the secondary amine groups to α -carbon atoms of unsaturated carboxylic acids *via* Michael addition reaction. Earlier [18] the migration of hydrogen atoms from the secondary amine groups to α -carbon atoms of unsaturated carboxylic acids was confirmed for ethyl 3-propylaminocrotonate and ethyl 3-cyclohexylaminocrotonate. Authors [21] showed that the addition of acrylic acid to chloroform solution of polyiminoethylene or polyiminohexamethylene yields a polybetaine with more than 90% zwitterion structure *via* Michael addition reaction. Poly(N-vinylimidazole) based poly(carboxybetaine) with two methylene groups between the opposite charges was achieved by the Michael addition reaction of the mentioned polymer to the carbon-carbon double bond of acrylic acid [22]. Polymerization of 2-hydroxyethylacrylate *via* Michael-type addition of hydroxyl groups to methacrylate carbon-carbon double bonds was studied by authors [23].

Equimolar mixture of AA and CROGly (CROAla and CROLys) was involved directly into radical polymerization without isolation of intermediate product because sometimes it exhibits high activity and is able to spontaneous polymerization [14–18]. FTIR spectra of CROGly-AA, CROAla-AA and CROLys-AA are summarized in Table 3. Disappearance of C=C absorption bands at 1644 cm^{-1} confirms the involvement of double bonds into the polymerization reaction. In addition the bands of carbonyl group, symmetric and asymmetric carboxylate ions are appeared. In comparison with monomers the FTIR spectra of polymers are broad and smooth. UV spectra of polymers have absorbance peak at 287 nm that belong to carboxylic groups.

The number-average molecular weight (M_n), weight-average molecular weight (M_w), the Z and

Table 3. FTIR spectroscopic data of polycarboxybetaines modified by amino acids

Functional groups	Wavenumber, cm ⁻¹		
	CROGly-AA	CROAla-AA	CROLys-AA
ν(OH)	3471	3490	3500
ν(CH)	2966	2960	2970
ν(C=O)	1719	1711	1711
ν _{as} (COO ⁻)	1560	1564	1568
ν _s (COO ⁻)	1399	1400	1410
ν(C-N)	1170	1167	1172
ν(C-O-C)	1040	1048	1050

Z+1 average molecular weights (M_z and M_{z+1}) of CROGly-AA, CROAla-AA and CROLYs-AA were derived from the gel permeation chromatograms (GPC). As seen from Table 4 the molecular weights of modified polycarboxybetaines are high and the polydispersity index is very broad. This is probably connected with highly associated *via* ionic and hydrogen bonds of macromolecules. The GPC data are consistent with viscometric measurements. The reduced viscosity of CROGly-AA and CROLys-AA in water is equal to 3.2 and 13.4 dL·g⁻¹ (C = 0.2%). Increasing of the reduced viscosity with dilution is specific for polyelectrolyte effect, e.g. expansion of macromolecular chains is due to electrostatic repulsion of charged groups. The viscosity of CROLys-AA is much higher than those of CROGly-AA and coincides well with more than 2 times higher molecular weight of CROLys-AA.

Table 4. The average molecular weights and the polydispersity of the modified polycarboxybetaines

Polycarboxybetaines	The average molecular weight				Polydispersity, M_w/M_n
	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-5}$	$M_z \cdot 10^{-6}$	$M_{z+1} \cdot 10^{-6}$	
CROGly-AA	25.0	7.24	2.8	5.16	28.94
CROAla-AA	29.0	8.01	2.76	5.01	27.74
CROLys-AA	187.6	16.0	3.53	5.15	8.44

The stimuli-responsive properties of crosslinked CROLys-AA were studied with respect to pH, ionic strength, and solvent nature. pH-dependent behavior of gel sample is bell-shape (Fig.2). Contraction of hydrogels in strong acidic region is explained by suppression of ionization degree of carboxylic groups by mineral acid. Considerable swelling of hydrogel at pH > 3 is accounted for the partial ionization of carboxylic groups that causes the electrostatic repulsion of negative charges. Significant swelling of

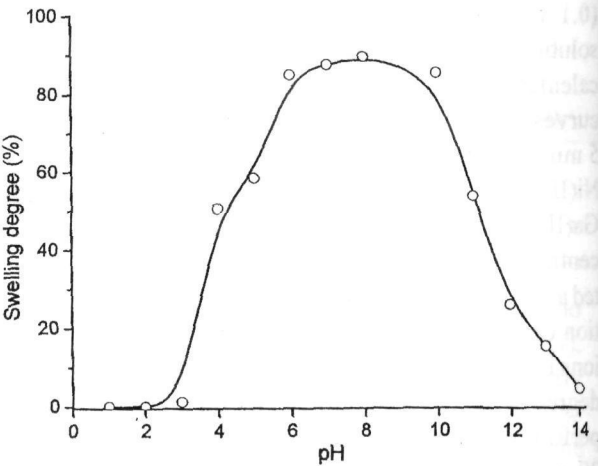


Figure 1. pH-dependent swelling of CROLys-AA

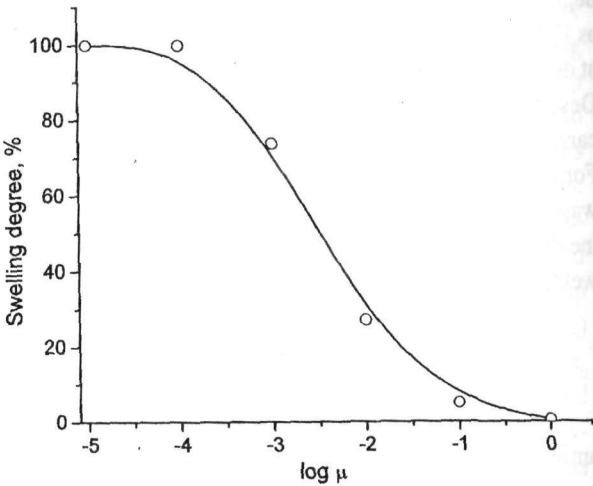


Figure 2. The effect of salt concentration on the swelling-deswelling behavior of CROLys-AA gel

hydrogels between pH 6-10 is the result of ionization of both carboxylic groups. Shrinking of gel specimen at pH > 10 is probably accounted for suppression of polyelectrolyte affect by the excess of NaOH that plays the role of low-molecular-weight electrolyte.

The effect of ionic strength (μ) on the swelling-deswelling behavior of CROLys-AA gel is shown in Fig.3. At the interval of $\mu = 1 \cdot 10^{-5} - 1 \cdot 10^{-4}$ mol·L⁻¹ gel does not shrink. Sharp decreasing of the swelling degree starts at [NaCl] > 110⁻³ mol·L⁻¹. To interpret these results the existence of intragroup, intra- and intermolecular associates should be taken into account [24]. Small amount of added salt probably disrupts the intragroup and intrachain associates. At higher concentration of added salt, due to screening of the charged groups of polyelectrolyte chains by low-molecular-weight electrolytes, the gel collapses.

Figure 3. The effect of water-ethanol (1) and water-acetone (2) mixtures on the swelling-deswelling behavior of CROlys-AA gel

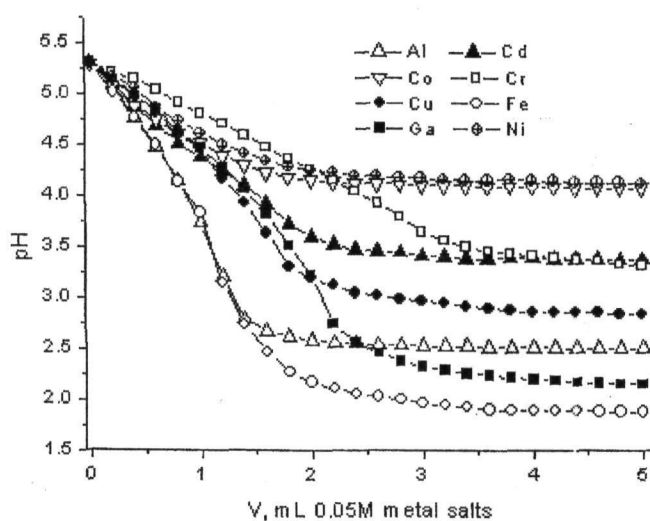
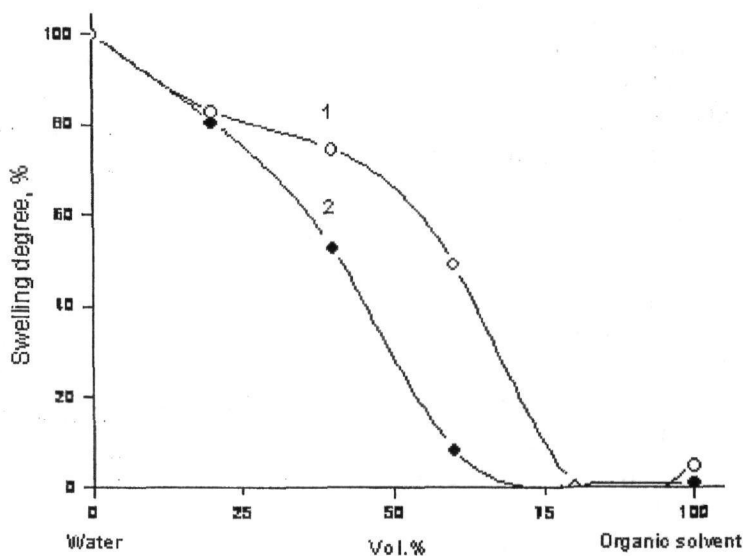


Figure 4. Potentiometric titration of linear CROAla-AA by 0.05M metal salts. [CROAla-AA] = 0.1 wt. %

Drastically shrinking of GROLys-AA gel takes place at 20 vol.% of ethanol and 40 vol.% of acetone (Fig. 3). This is due to decreasing of the dielectric constant of medium that enhances the condensation of counterions to macroions. The latter leads to decreasing of the osmotic pressure within the gel volume. In pure ethanol and acetone the gel network is in collapsed state due to significant suppression of ionization and poor thermodynamic quality of solvents with respect to ionizable groups of polyelectrolytes.

The metal ion binding ability of linear polymers was studied by potentiometric titration. As seen from Fig. 4 adding of metal salts to aqueous solutions of linear polymers leads to overall acidification of the medium. This is connected with replacement of protons by metal ions. Due to formation of intra- or inter-macromolecular ionic and coordination bonds the polymer-metal complexes are precipitated. Addition of the excess of metal salts slightly changes pH.

The metal binding capacity calculated from the potentiometric titration curves is shown in Table 5.

Table 5. Metal ions binding capacity of linear CROGly-AA, CROAla-AA and CROLys-AA

Polymer	Amount of metal ions (mg) adsorbed by 1 g of linear polymers							
	Al(III)	Cd(II)	Co(II)	Cr(III)	Cu(II)	Fe(III)	Ga(III)	Ni(II)
CROGly-AA	153	984	345	791	600	373	726	366
CROAla-AA	164	1007	408	732	560	400	711	391
CROLys-AA	126	609	345	465	475	385	633	293

The effectiveness of linear polymers to bind metal ions arranges as following:

CROGly-AA: $\text{Cd(II)} > \text{Cr(III)} > \text{Ga(III)} > \text{Cu(II)} > \text{Fe(III)} \approx \text{Ni(II)} > \text{Co(II)} > \text{Al(III)}$.

CROAla-AA: $\text{Cd(II)} > \text{Cr(III)} > \text{Ga(III)} > \text{Cu(II)} > \text{Co(II)} > \text{Fe(III)} > \text{Ni(II)} > \text{Al(III)}$.

CROLys-AA: $\text{Ga(III)} > \text{Cd(II)} > \text{Cu(II)} > \text{Cr(III)} > \text{Fe(III)} > \text{Co(II)} > \text{Ni(II)} > \text{Al(III)}$.

The metal ions adsorption capacity of linear polymers is in the order: CROGly-AA > CROAla-AA > CROLys-AA. Affinity of linear polymers is very high for Cd(II), Cr(III) and Ga(III) but lowest for Al(III) ions. The is connected with poor ability of Al(III) to form chelate complexes.

The EPR parameters of CROGly-AA/Cu(II) with $g_{\perp} = 2.053$, $g_{\parallel} = 2.324$ and $A_{\parallel} = 132.8$ are very close to those for PAA-Cu(II) but the spectra represent a superposition of two individual spectra where one of them is specific for binuclear copper(II) complexes stabilized by OH⁻ bridges [25]. In the case of CROGly-AA/Cu(II) one can propose that the carboxylic groups from both glycine and acrylic acid

are involved into coordination sphere of copper(II) ions and bridged by additional copper(II) ions forming binuclear complexes. It is not excluded that the coordination bonds between nitrogen atoms and copper(II) ions may additionally stabilize such structure.

It is interesting to note that the aqueous solution of CROGly-AA/Cu(II) complex at first is light-blue. However after some time the color is deepened, and it becomes dark-blue. This is probably connected with involvement into the coordination sphere of copper(II) at first only carboxylic groups of glycine and acrylic acid (light blue). However the stability of 9-membered cyclic structure is very low therefore after some time the tertiary amine groups are probably involved into complexation reaction and more stable mixed 5- and 6-membered chelate complex is formed (dark blue). The structure of this complex is more or less repeats the structure of EDTA complex of copper(II).

Interaction of hydrogels with metal ions is accompanied by contraction and colorization of samples (Fig.5a-d). At first the thin colored layer on the gel surface is formed and it gradually moves into the

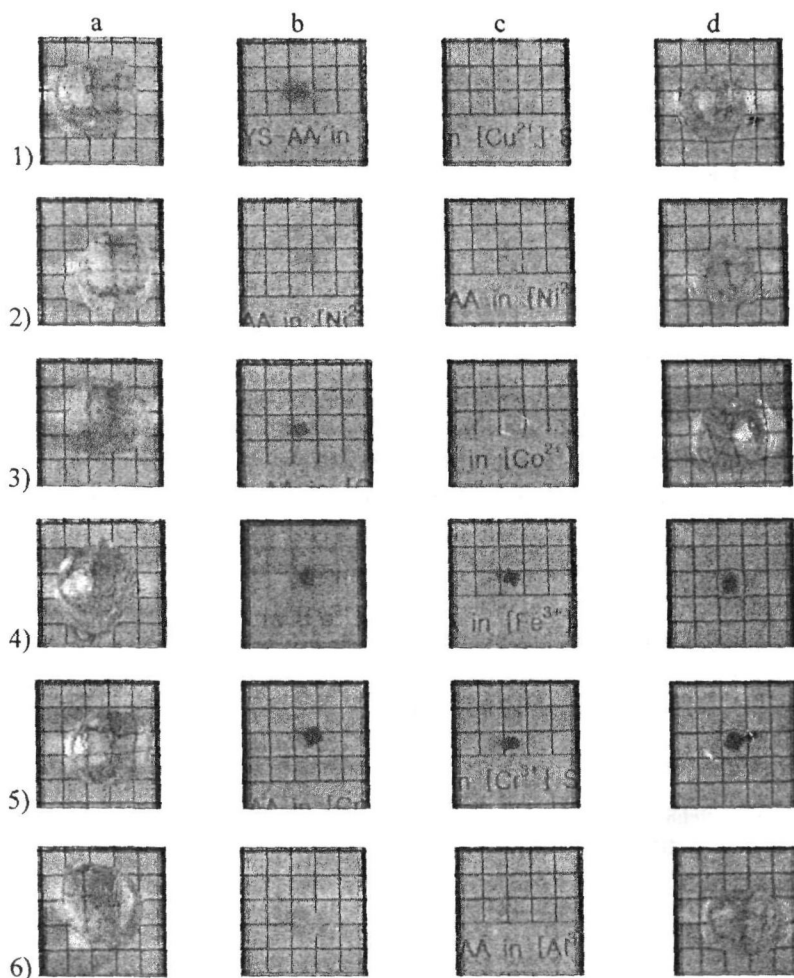


Figure 5. Adsorption-desorption and recycling stages for CROLys-AA gel complexes with Cu(II) (1), Ni(II) (2), Co(II) (3), Fe(III) (4), Cr(III) (5) and Al(III) (6).
a - initially swollen gel,
b - complexed gel,
c - after gel soaking in 0.1N HCl for 1 day, d - after gel soaking in water for 1 week

Table 6. Metal ions binding capacity of crosslinked CROGly-AA, CROAla-AA and CROLys-AA

Polymer	Amount of metal ions (mg) adsorbed by 1 g of dry hydrogels							
	Al(III)	Cd(II)	Co(II)	Cr(III)	Cu(II)	Fe(III)	Ga(III)	Ni(II)
CROGly-AA	79	469	156	337	260	200	306	164
CROAla-AA	130	703	350	685	491	452	482	305
CROLys-AA	136	650	380	512	516	402	676	305

gel volume. The driving force of this process is "ion-hopping transportation" of metal ions through intra- and intermolecular chelate formation, e.g. constant migration of metal ions deeply into the gel volume by exchanging of free ligand vacancies. The gel-metal complexes of Cu(II), Ni(II), Co(II), Fe(III) and Cr(III) ions are colored excepting for Al(III), Ga(III) and Cd(II) that are colorless.

Metal sorption ability of hydrogels expressed as V/V_0 is shown in Fig. 6. The effectiveness of metal ions to shrink CROLys-AA gel is arranged as follows: Cu(II) > Fe(III) > Ga(III) > Al(III) > Co(II) \approx Ni(II) > Cd(II). Table 6 summarizes the adsorbed amount of Cu(II), Ni(II), Co(II), Cd(II), Fe(III), Cr(III), Ga(III) and Al(III) ions by 1 g of dry gels.

The adsorption capacity of gels changes as follows:

CROAla-AA: Cd(II) > Cr(III) > Cu(II) > Ga(III) > Fe(III) > Co(II) > Ni(II) > Al(III).

CROGly-AA: Cd(II) > Cr(III) > Ga(III) > Cu(II) > Fe(III) > Ni(II) > Co(II) > Al(III).

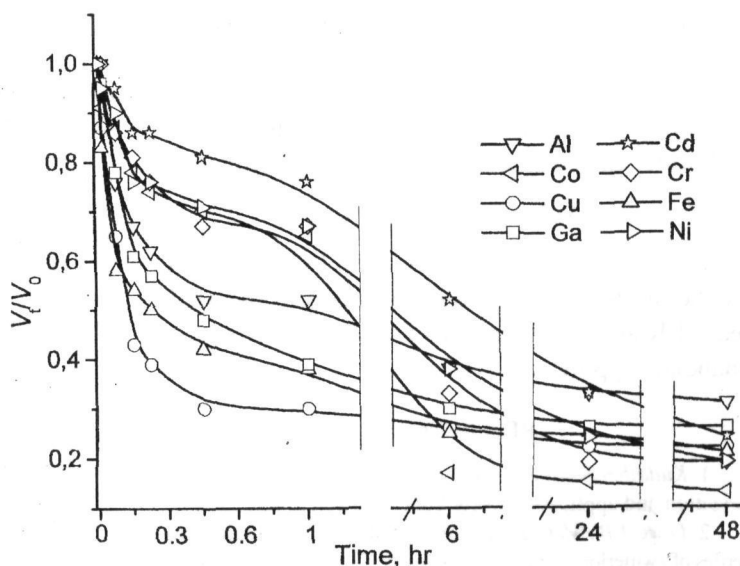
CROLys-AA: Ga(III) > Cd(II) > Cu(II) \approx Cr(III) > Fe(III) > Co(II) > Ni(II) > Al(III).

This order coincides well with the sequence of linear polymers found from the potentiometric

titration curves. The metal uptake behavior of gels is lower than the linear analogues excepting for CROLys-AA. The latter is probably due to participation of two amine and two carboxylic groups of CROLys-AA in metal binding process. In contrast to linear polymers, the complexation ability of gels is arranged in the following order: CROLys-AA \geq CROAla-AA > CROGly-AA. This may be connected with different swelling ability of hydrogels and accessibility of ligand groups for metal binding.

Desorption of metal ions in the medium of 0.1N HCl starts from the gel surface and moves into the volume. This process at first is accompanied by the further gel collapsing, because in the acidic region it is in shrunken state. However after leaching out of metal ions the slightly swelling of gel samples is observed. This is explained by ionization of amine groups. It should be marked that trivalent ions Fe(III) and Cr(III) are not completely desorbed from the gel interior by 0.1N HCl even during one week (see Fig. 5b-d). This is probably accounted for realization of 6 coordination bonds and participation of 3 amine and 3 carboxylate groups in coordination sphere of Fe(III) and Cr(III) ions.

Figure 6. Time-dependent contraction of CROLys-AA gel in aqueous solutions of metal salts



The gel samples can easily be regenerated by periodically washing out with distilled water (see Fig.5d). These experiments clearly demonstrate the applicability of hydrogels to adsorb and desorb some metal ions several times.

Conclusion

Novel linear and crosslinked polycarboxybetaines were synthesized for the first time from the acetoacetic ester and amino acids followed by Michael reaction with acrylic acid and radical polymerization. It was shown that the molecular weights of polycarboxybetaines are very high and arrange between $(7-16) \cdot 10^5$. This is probably due to highly associated *via* ionic and hydrogen bonds macromolecular aggregates. Swelling-collapsing properties of hydrogels under the externally imposed stimuli are connected with ionization of functional groups, electrostatic effects and changing of the thermodynamic quality of solvents. Both linear and crosslinked polybetaines exhibit the complexation ability with respect to metal ions (Cu(II), Ni(II), Co(II), Cd(II), Fe(III), Al(III), Ga(III)). The driving force of this process is the formation intra- and intermolecular chelate bridge that is accompanied by precipitation of linear polymers and shrinking of hydrogels. For CROGly-AA/Cu(II) system the formation of binuclear complexes is proposed. Linear polymers showed the maximal metal-binding capacity for Cd(II), Cr(III) and Ga(III) ions. The metal uptake capacity of crosslinked gel samples was lower, but for the most of metal ions it was possible to provide the recycling stage, e.g. leaching out of adsorbed metals by 0.1N HCl. Only Fe(III) and Cr(III) ions were not desorbed from the gel volume probably due to formation of a very stable 6 coordination bonds with amine and carboxylic groups of amino acid residues. The ability of recycled polybetaine gels to swell in fresh water and be applied several times is proposed.

Acknowledgements

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Резюме

Құрамында амин қышқылдары бар жаңа мономерлер, жұмсақ жағдайларда ацетосірке эфирінің глицинмен, β-аланинмен және L-лизинмен конденсациялануы нәтижесінде синтезделді. Құрамында карбоксибетанин топтарымен қатар амин қышқыл қалдығы бар жаңа сызықтық және тігілген полибетаиндер, акрил қышқылы қатысуында Михаэль қосылу реакциясы арқылы, әрі қарай радикалдық полимерленумен алынды. Мономерлер мен полимерлердің құрылымдары ИК-фурье-, ¹H ЯМР-, УК-көрінетін спектроскопия әдістерімен талданды. Сызықтық полимерлер ерітінділерінің қасиеттері вискозиметрия және ГПХ әдістерімен зерттелді. Поликарбоксибетанин гидрогельдерінің ынталандыру сезгіштік қасиеті рН-тан, иондық күштен және сулы-органикалық

еріткіштен тәуелді зерттелді. Металдар иондарының сызықтық және тігілген поликарбоксибетанинмен сорбциялануы потенциометрлік титрлеумен, ісіну-сығылуды өлшеумен және атомды-эмиссиондық спектроскопиямен зерттелді. Полимерлік сорбенттердің металдар иондарына қатысты талғамдығы, олардың табиғаты мен полимерлік лигандтардың ішкі құрылымына тәуелді екендігі көрсетілді.

Резюме

Новые мономеры, содержащие аминокислоты, синтезированы конденсацией ацетоуксусного эфира с глицином, β-аланином и L-лизинном в мягких условиях. Новые линейные и сшитые полибетаины, содержащие наряду с карбоксибетановыми группами аминокислотные остатки, получены через реакцию присоединения Михаэля с участием акриловой кислоты с последующей радикальной полимеризацией. Структура мономеров и полимеров проанализировали методами ИК-фурье-, ¹H ЯМР – УФ-видимой спектроскопии. Свойства растворов линейных полимеров изучены методами вискозиметрии и ГПХ. Стимулчувствительное поведение поликарбоксибетановых гидрогелей было изучено в зависимости от pH, ионной силы и состава водно-органической смеси. Сорбция ионов металлов линейными и сшитыми поликарбоксибетанами была изучена потенциометрическим титрованием, измерением набухания-сжатия и атомно-эмиссионной спектроскопией. Показано, что селективность полимерных сорбентов в отношении ионов металлов зависит от природы ионов металлов и внутренней структуры полимерных лигандов

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