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Synthesis, characterization, and stimuli-sensitive properties of novel polycarbobetaines

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Abstract

Novel monomers bearing propyl and cyclohexyl groups on the side chain were synthesized from the acetoacetic ester and propylamine and cyclohexylamine. Michael addition reaction with acrylic (methacrylic) acid followed by radical polymerization resulted in preparation of both linear and crosslinked betaine type polyampholytes. The polycarbobetaines were characterized by potentiometric titration, viscometry, GPC, FTIR, NMR, and UV–Vis. The ionization constants of acid and base groups were calculated from the Henderson–Hasselbalch equation. Considerable influence of water content on the yield of linear polymers and swelling degree of hydrogels was established. The dependence of swelling degree on the chain length and concentration of crosslinking agents was found. The stimuli-responsive properties of hydrogels were studied in water-organic solvents mixtures and as a function of pH and ionic strength. The adsorption–desorption recycling stages of hydrogels with respect to copper(II) ions were demonstrated.

Keywords: Polycarbobetaines; Hydrogels; Stimuli-responsive properties

1. Introduction

Polyampholytes constantly attract the attention of researchers due to presence of both acidic and basic groups in macromolecular chain [1]. Particularly the protein folding process is closely connected with the ability of polyampholytes to adopt globular, coil and stretched structures as well as to demonstrate phase and volume transitions with respect to environment. Polymeric betaines whose oppositely charged groups remote one from another are displaced on one pendant substituents have less been considered in literature [2,3] in comparison with ‘annealed’ and ‘quenched’ polyampholytes [4,5]. The synthetic strategy of polyampholytes with betaine structure has been outlined in pioneering works of Salamone et al. [6–8]. Polymeric betaines can be synthesized directly by polymerization of betaine monomers [9] or polymer analogous transformation [10–13]. There are several types of polymers with betaine structure: polycarbobetaines, polysulfobetaines and polyphosphobetaines. Poly(*N*-ethyleneglycine), poly[(*N*-3-sulfopropyl)-*N*-methacryloyloxyethyl-*N*,*N*-dimethylammonium betaine] and poly(2-methacryloyloxyethylphosphorylcholine) are typical examples of this kind of betaine polyampholytes.

Recently Laschewsky et al. [14–17] have reported on synthesis and characterization of zwitterionic polysoaps, which combine advantages of the behaviour of polybetaines and micellar polymers. The variation of the polymer geometry produces ‘head-type’, ‘mid-tail type’ and ‘tail-end type’ zwitterionic polysoaps. Authors [18] showed that the addition of acrylic acid to chloroform solution of polyiminoethylene or polyiminohexamethylene produces polyampholyte with more than 90% betaine structure. The specific feature of this reaction is that both a protonation and Michael addition reaction take place simultaneously.

This paper describes the synthesis of novel betaine type monomers and polymers via Michael addition reaction

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followed by radical polymerization, characterization of their structure and studying of the properties of water-soluble and water-swelling polycarbobetaines in aqueous solution and in gel state.

2. Experimental section

2.1. Materials

Acetoacetic ester (ethyl acetoacetate) (99%), propylamine (98%), cyclohexylamine (99%), acrylic acid (99.5% purity), methacrylic acid (98.5% purity), *N*,*N*′-methylenbisacrylamide (MBAA, $M_n = 154$), poly(ethyleneglycol)-dimethacrylate (PEGDMA, $M_n = 330$), poly(ethyleneglycol) diacrylate (PEGDA, $M_n = 700$) and initiator azoisobutyronitrile (AIBN) were purchased from Aldrich. Acrylic and methacrylic acids were purified by distillation under the low pressure and kept in refrigerator. Reagent grade solvents acetone, ethanol, DMF, DMSO purchased from Aldrich were used. Copper (II) nitrate was purchased from Junsei. For preparation of aqueous solutions of polymers the HPLC grade water was used. 0.1 N HCl and 0.084 N NaOH were used for potentiometric titration.

2.2. Methods

Potentiometric titration of linear polymers was carried out on pH/ISE meters Model 520A equipped with a combined electrodes. 100 mg of polymer was dissolved either in 100 ml NaOH (0.084 N) and then titrated by 0.1 N HCl or dissolved in 100 ml HCl (0.1 N) and then titrated by 0.084 N NaOH. The potentiometric titration curves were plotted in integral and differential forms. Ionization constants of acid and base groups of polyampholytes were determined from the Henderson–Hasselbalch equation. The viscosity of aqueous solutions of polyampholytes was measured by Ubbelohde viscometer at 30 ± 0.1 °C. FT-IR spectra were recorded on a Perkin Elmer IR 2000 series (KBr pellet method). UV–Vis spectra of polymer solutions were recorded on spectrophotometer ‘Perkin–Elmer Lambda 12’ with a scan range of 200–850 nm. ^{1}H NMR spectra were obtained in $CDCl_3$ and D_2O at room temperature with the help of JEOL JNM-LA 300 WB FT-NMR. The molecular weights of samples were determined by GPC (9200 GPC, YonLin Instrument). Ultrahydrogel 500 (Waters, USA) and 0.1 N $NaNO_3$ aqueous solution was used as column and solvent respectively. The column temperature was 45 °C; flow rate −1.0 ml/min. The injected volume of sample was 100 μl. The molecular weights were determined from the calibration curve of pullulan standard set (Shodex, Japan). The running time is 50 min. The refraction index (RI) detectors temperature was kept at 35 °C.

2.3. Monomer synthesis

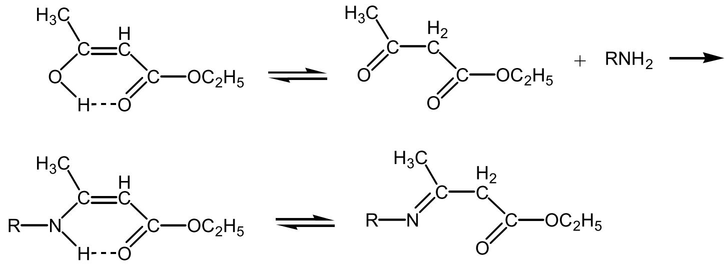
Propylamine (6.5 ml) (or cyclohexylamine, 8.9 ml) was dropwise added to 10 ml of acetoacetic ester (AAE) under the stirring during 3 h at room temperature. After completing the reaction the mixture was left overnight. The organic phase containing the key product was separated from the aqueous phase. The yield of monomers is 98%. The purity of monomers was checked by FTIR. Further the monomers were involved into Michael addition reaction with acrylic or methacrylic acid. Radical polymerization was carried out in bulk and in aqueous solution at 70 °C during 1 h.

2.4. Polymer synthesis

Polymerization reaction was carried out by two ways: with and without addition of initiator. In the latter case the ethyl 3-propylaminocrotonate (2.2 ml) and the acrylic acid (0.8 ml) were mixed and then bubbled by nitrogen gas during 2 min to remove the dissolved oxygen. During the bubbling the mixture started to become turbid due to formation of the first polymer particles and the temperature is gradually increased. The same procedure was used for the polymerization of mixtures of ethyl 3-propylaminocrotonate-acrylic (methacrylic) acid, ethyl 3-cyclohexylaminocrotonate-acrylic (methacrylic) acid. In the presence of initiator, 2–3 mg of AIBN was added to monomer mixtures, and then the mixture was bubbled by nitrogen gas during 2 min and thermostated at 70 °C during 1 h. The radical polymerization of monomers was also carried out in the presence of 5, 10, 15, 25, 35 and 50 vol.% of water. The linear polymers obtained in bulk and in the presence of water were thoroughly washed out by acetone. The samples were dried in vacuo up to constant mass. The crosslinked polymers were synthesized in the presence of crosslinking agents—*N*,*N*′-methylenbisacrylamide (MBAA, $M_n = 154$), poly(ethyleneglycol)dimethacrylate (PEGDMA, $M_n = 330$), and poly(ethyleneglycol)diacrylate (PEGDA, $M_n = 700$). Gel samples were washed by distilled water during 1 week to remove the sol fraction.

2.5. Equilibrium swelling measurements

Equilibrium swollen gels in distilled water were weighed on the analytical balance and then dried up to constant mass. Swelling degree of gels α (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 (g/g) of hydrogels in the mixtures of different solvents (water–ethanol and water–acetone) was determined gravimetrically by measurement of the mass of mixture-swollen and dried gels and calculated according to the formula: $W = (m_{w0} - m_0)/m_0$, (where W is the swelling coefficient, m_{w0} is the mass of gel in water-organic mixtures and m_0 is the mass of dried gel). The swelling degree (g/g)



where R is C_3H_7 or C_6H_{11}

Scheme 1. Formation of alkyl derivatives of ethyl 3-aminocrotonate from the acetoacetic ester and alkylamines.

of hydrogels at different pH and ionic strength was calculated according to procedure described above.

2.6. Sorption and desorption of copper(II) ions

Water-swollen gel samples with diameter 2 cm and height 1 cm were placed into the copper(II) solution with concentration 5×10^{-2} mol l^{-1}. The shrinking degree of gels was calculated as m/m_0 (where m and m_0 are the masses of swollen and dried gels). Desorption of copper(II) ions from the gel interior was carried out by soaking of gel in the solution of 0.1 N HCl during 1 day. To recycle the gel sample it was put into distilled water. The volume change of gel during adsorption–desorption process as well as recycling was fixed photographically. The amount of copper(II) absorbed by 1 g of dry gel was determined by UV–Vis, analyzing the supernatant.

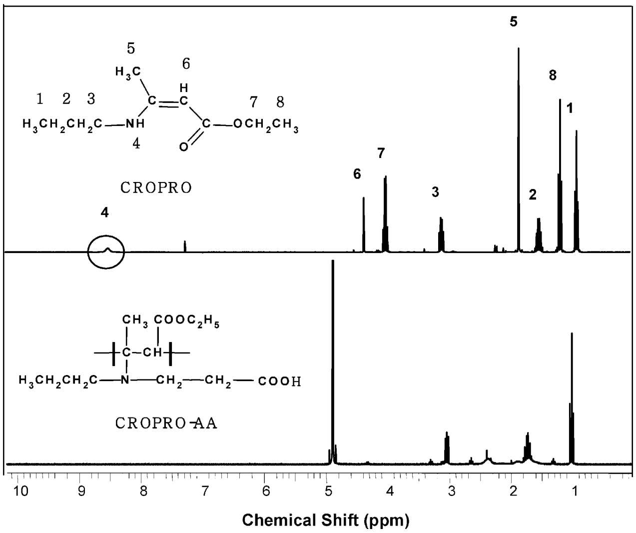
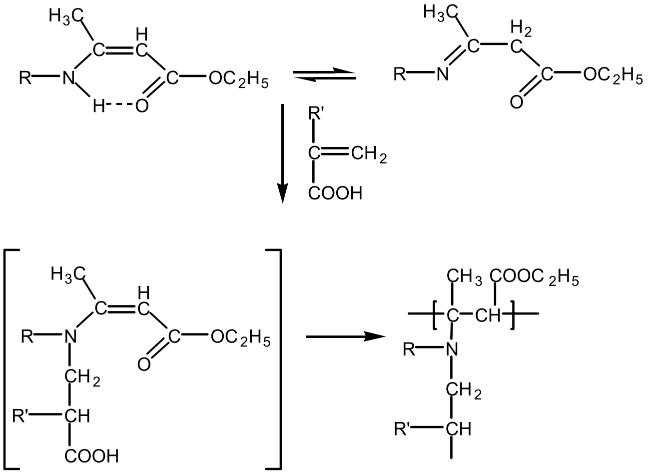


Figure 1. ^1H NMR spectra of CROPRO in $CDCl_3$ and CROPRO-AA in D_2O.

3. Results and discussion

It is well known [19] that acetoacetic ester (AAE) exists



where R is C_3H_7 or C_6H_{11}, Rí is H or CH_3

Scheme 2. Monomer and polymer formation via Michael addition reaction.

Table 1
The influence of water content on the swelling degree of CROCHA-AA and CROPRO-AA

Water content (vol.%)		2	5	10	20	40	60	100	150	200
Swelling degree, g/g	CROCHA-AA	86	127	276	303	503	644	1156	1140	1138
	CROPRO-AA	92	140	286	315	540	680	1200	1188	1180

in keto and enol tautomeric forms. Interaction of AAE with propylamine and cyclohexylamine produces, so called, ethyl 3-propylaminocrotonate (CROPRO) and ethyl 3-cyclohexylaminocrotonate (CROCHA). However both CROPRO and CROCHA analogous to ethyl 3-aminocrotonate (CRO) [20,21] do not polymerize due to formation of π-conjugated enamine and imine tautomeric forms stabilized by intramolecular hydrogen bonds (Scheme 1).

We have found for the first time [22,23] that the addition of electron acceptor monomers such as acrylic or methacrylic acids to CRO breaks the intramolecular hydrogen bonds and via the Michael addition reaction produces the intermediate product, so called betaine monomer (Scheme 2). In case of CROPRO and CROCHA analogous reaction also takes place (Scheme 2).

Formation of intermediate monomer proceeds through the migration of hydrogen atoms from the secondary amine groups to α-carbon atoms of unsaturated carboxylic acids. This is confirmed by disappearance of NH protons of CROPRO and CROCHA (Fig. 1) upon the addition of AA (or MAA).

The specific feature of the system is that the polymerization of monomer mixtures in bulk starts at room temperature even without addition of initiator therefore it is impossible to isolate the intermediate monomer product. Without the initiator the temperature of reaction mixture during 2–3 min increases up to 60 °C (Fig. 2). However, in the absence of initiator the yield of product is low and less than 10%. In the presence of initiator the temperature of reaction mixture increases up to 85 °C, the yield of polymer—up to 30%. AA is more reactive than MAA because the temperature of reaction mixture is 2–3 times higher than in the case of MAA. The mechanism of polymerization of intermediate products in the absence of initiator is probably connected with the migration of hydrogen atoms from enamine to imine tautomeric forms. One can suppose that some monomer molecules capture the 'jumping' hydrogen atoms and consequently produce the free radicals to initiate the polymerization reaction.

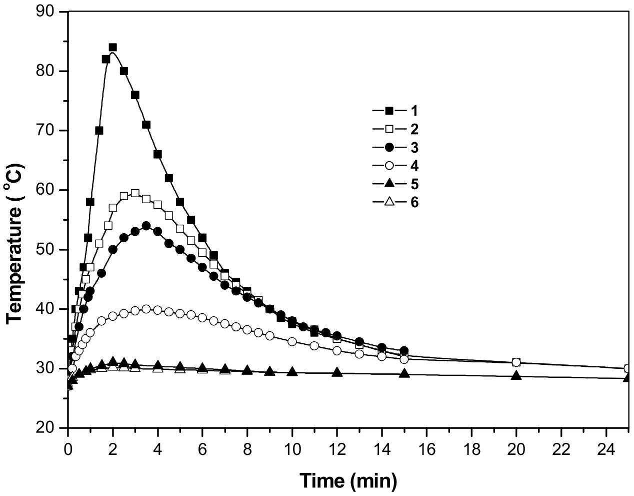


Figure 2. Temperature profile of the polymerization reaction for the equimolar mixture of CROPRO (1, 2), CROCHA (3, 4) with AA and CROCHA with MAA (5, 6) in bulk in the presence (1, 3, 5) and absence (2, 4, 6) of an initiator.

Much influence on the yield of polymers causes the addition of water (Fig. 3). The optimal concentration of water corresponds to 25 vol.%. This is probably accounted for the participation of water molecules in ionization and proton transfer process. In particular it was stated [24] that the hydrogen bonds are able to change significantly the reactivity of monomers and radicals if the heteroatom and the reaction center will participate in formation of unified π-conjugated system.

Addition of water into the reaction mixture considerable increases the swelling degree of hydrogels (Table 1). This is probably due to participation of water molecules in formation of hydrogen bonds with functional groups of monomers in prepolymerization conditions.

The FTIR spectra of CROPRO, CROCHA and polymers synthesized in bulk are shown in Fig. 4. Table 2 represents the identification of functional groups. Disappearance of both C=C and C=N groups and appearance of broadened tertiary amine groups instead of three peaks at 3191, 3281 and 3370 cm^{-1} together with asymmetric (1539–1560 cm^{-1})

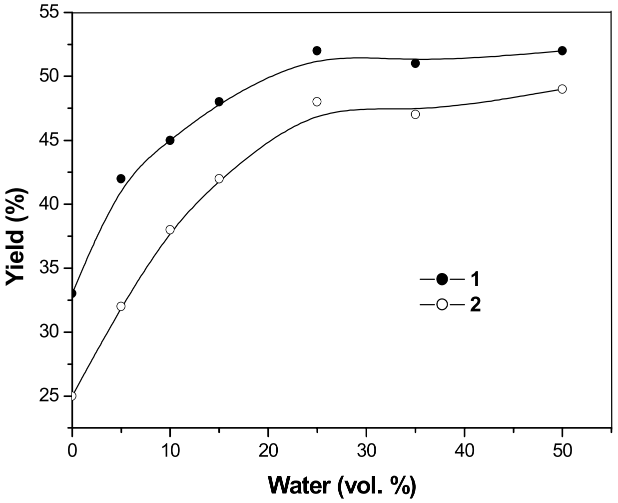


Figure 3. The dependence of the yield on the water concentration for systems CROPRO-MAA (1) and CROCHA-MAA (2).

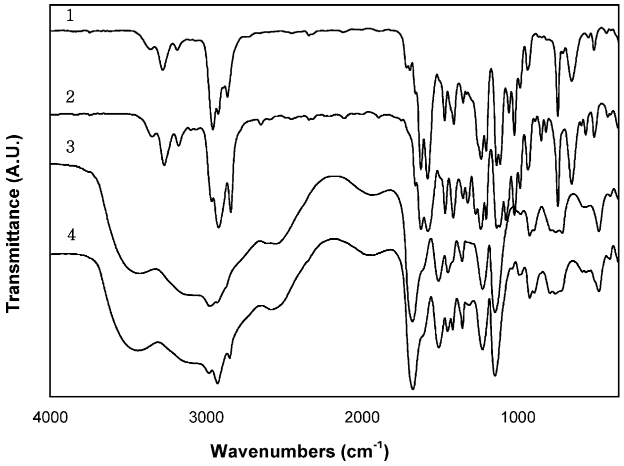


Figure 4. FTIR spectra of CROPRO (1), CROCHA (2), CROPRO-MAA (3) and CROCHA-MAA (4).

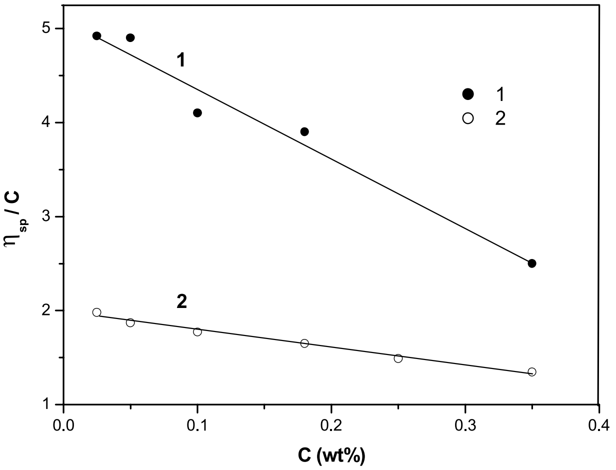


Figure 5. Dependencies of the reduced viscosity of CROPRO-MAA (1) and CROPRO-AA (2) on polymer concentration.

and symmetric (1449 cm^{-1}) COO^{-} vibrations from the acidic monomers confirms the formation of polymers with betaine structure. Aqueous solutions of CROCHA-AA and CROCHA-MAA exhibit the absorbance peaks at 300 and 250 nm that are also specific for carboxylic and amine groups respectively.

The molar ratio of amine and carboxylic groups found from the back potentiometric titration is equal to 1:1. This confirms the betaine structure of synthesized polymers. The acidic ionization constants (pK_a) of COOH and NH^{+} groups found from the Henderson–Hasselbalch equation are equal to 6.0 and 7.6 for CROPRO-AA and 5.4 and 7.6 for CROCHA-AA.

The results of viscometric measurements are shown in Fig. 5. The increasing in reduced viscosity upon dilution is specific for polyelectrolytes. The molecular weights of polymers estimated from the GPC experiments are about 4×10^{6} Da.

Table 3 summarizes the swelling degree of crosslinked samples in water and organic solvents. The swelling degree of CROPRO-AA and CROCHA-AA increases with lengthening of the crosslinkers. But, it decreases with increasing in the concentration of crosslinker as shown in Fig. 6. In polar solvents the swelling degree of hydrogels changes in the following order: water $\gg$ DMSO $\gg$ DMF $>$ ethanol $>$ acetone. Significantly collapsing of hydrogels in ethanol and acetone is connected with poor thermodynamic quality of solvents with respect to hydrophilic groups of polymers. Discontinuous and continuous collapsing of hydrogels takes place correspondingly between 80–90 vol.% of acetone and 40 vol.% of ethanol in water–acetone and water–ethanol mixtures (Fig. 7). These results confirm the universal behavior of hydrogels with respect to thermodynamic quality of solvents. pH-dependent behavior of gel samples is bell-shape (Fig. 8). Significant swelling of hydrogels between pH 3–8 is due to ionization of carboxylic 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. Swelling–shrinking behavior of hydrogels as a function of NaCl concentration is illustrated on Fig. 9. Sharp decrease in the swelling degree at $\mu=10^{-4}$–10^{-2} is

Table 2
Identification of FTIR spectra of monomers and polymers

Functional groups	Frequency (cm^{-1})					
	Monomer		Polymer			
	CROPRO	CROCHA	CROPRO-AA	CROPRO-MAA	CROCHA-AA	CROCHA-MAA
ν(NH)	3370	3354	–	–	–	–
	3281	3278	–	–	–	–
	3191	3180	–	–	–	–
ν(OH)	–	–	3458	3433	3451	3445
ν(CH)	2969	2936	2972	2988	2942	2942
ν(C=O)	1688	1682	1715	1702	1711	1704
ν(C=C)	1654	1655	–	–	–	–
ν(C=N)	1606	1600	–	–	–	–
$\nu_{as}(\mathrm{COO}^{-})$	–	–	1557	1544	1560	1539
$\nu_{s}(\mathrm{COO}^{-})$	–	–	1398	1398	1449	1449
ν_{ω} C=C)	780	780	–	–	–	–

Table 3
Swelling degree of hydrogel in the presence of various crosslinkers and in organic solvents medium

Solvent	Crosslinker	Swelling degree (g/g)	
		CROPRO-AA	CROCHA-AA
Water	MBAA	250	244
	PEGDMA	420	310
	PEGDA	510	356
DMSO	MBAA	100	79
DMF		10	9
Ethanol		5	3
Acetone		2.5	2.5

probably attributed to screening of charged groups of polyelectrolyte gel by low-molecular-weight ions.

The formation of five- or six membered chelate ‘bridge’ where one copper(II) ion binds two monomeric units is specific for polycarbobetaines [25,26]. Therefore, in case of CROPRO-AA and CROCHA-AA gels one can assume the involvement of both carboxylate and amine groups into coordination sphere of copper(II) ions and formation of six membered chelate cycle with one or two betaine units. The ability of betaine type hydrogels to absorb and desorb copper(II) ions is shown on Fig. 10. At first the thin colored layer is formed on the gel surface that is accompanied by simultaneously shrinking of gel specimen. Then the shell layer gradually moves into the gel interior. 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 (Scheme 3). The chelate formation of the betaine units and copper ions suppresses the facile mobilization of metal ions into the gel matrix. In our experiments the gel specimen is completely loaded by copper(II) ions during 7 h.

Desorption of copper(II) ions from the gel interior takes place in the medium of 0.1 N HCl due to destruction of ligand-metal complexes and replacement of metal ions by

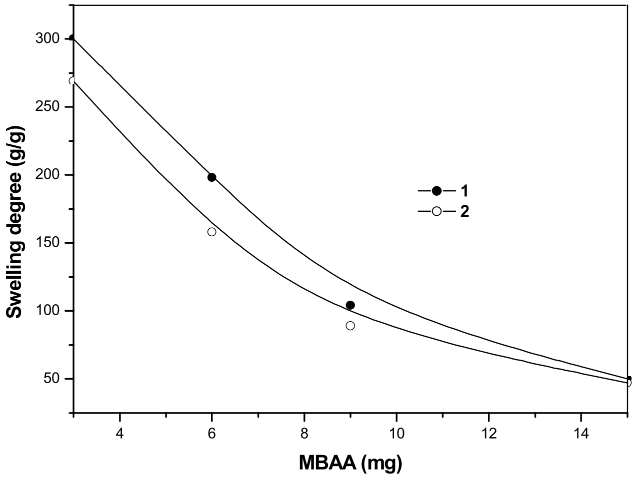


Figure 6. Dependence of the swelling degree of CROPRO-AA (1) and CROCHA-AA (2) on the concentration of crosslinking agent.

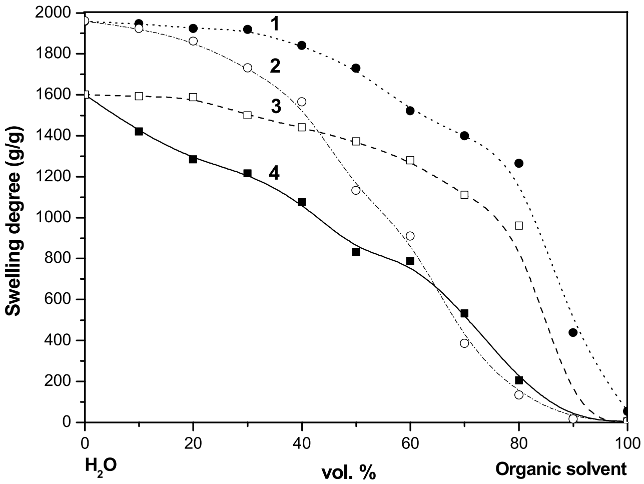


Figure 7. Swelling–deswelling behavior of CROPRO-AA (1,2) and CROCHA-AA (3, 4) in water–acetone (1, 3) and water–ethanol (2, 4) mixtures.

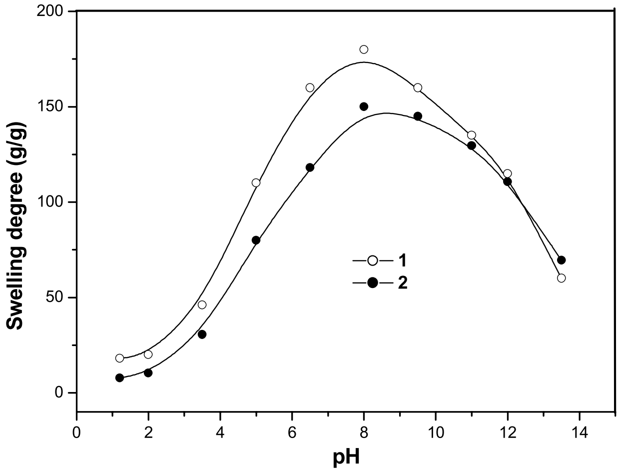


Figure 8. Dependence of the swelling degree of CROPRO-AA (1) and CROCHA-AA (2) on pH.

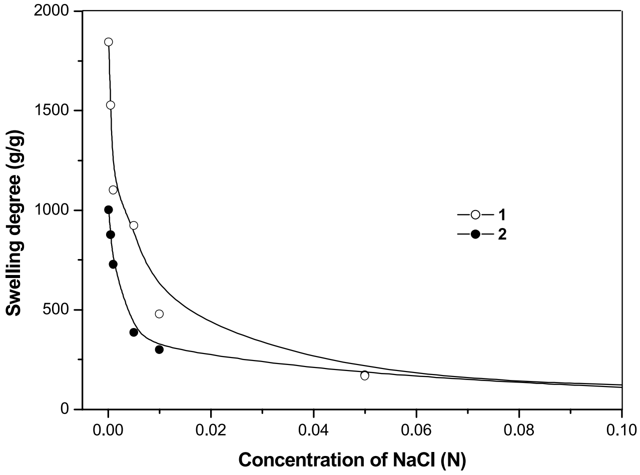


Figure 9. Dependence of the swelling degree of CROPRO-AA (1) and CROCHA-AA (2) on the ionic strength.

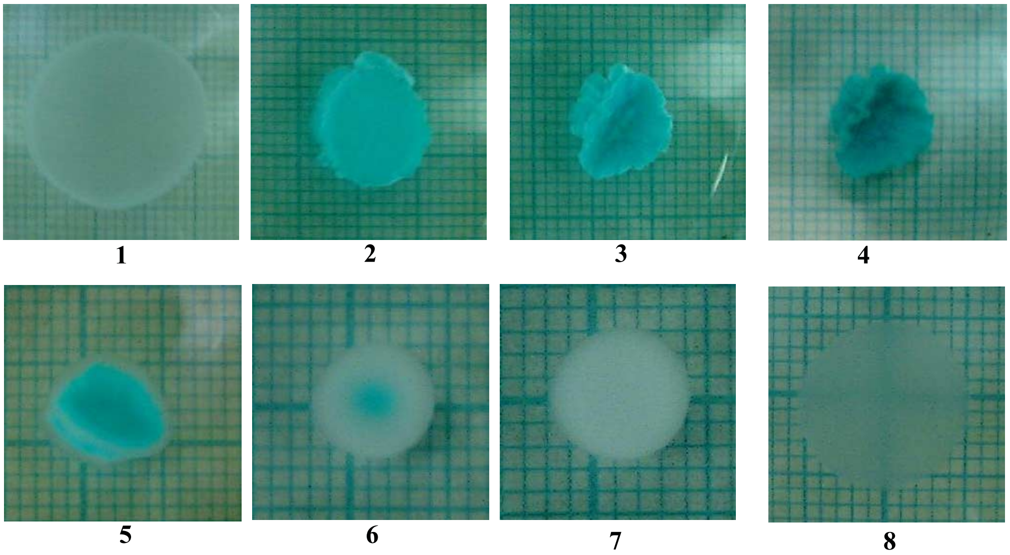


Figure 10. Adsorption (1–4) and desorption (5–7) of copper(II) ions by CROPRO-AA gel and washing of gel by water (8) as a function of time. Initial state (1), after 30 min (2), 1 h (3), 7 h (4), 3 min (5), 15 min (6), 1 h (7), 2 days (8).

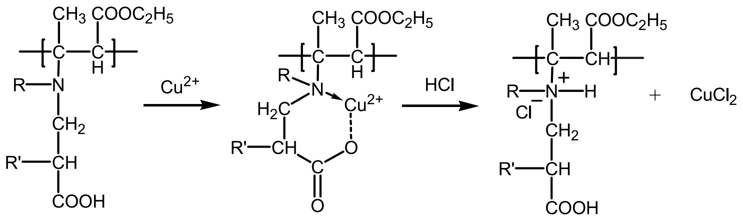
protons as shown in Scheme 3. According to UV–Vis measurements up to 90% of copper(II) ions release from the gel volume during 2 h.

Regeneration of gel sample can be realized in fresh water. As seen from Fig. 10 the gel sample gradually returns to initial state after 2 days.

Adsorption and desorption of copper(II) ions followed by gel regeneration were repeated 10 times without the loss of gel capacity, durability and reusability. Thus the advantage of betaine type gels developed in this work is: (i) high adsorption capacity (1 g of dry gel adsorbs up to 500 mg of copper(II) ions); (ii) easy and fast desorption of metal ions by mineral acid (for instance, by 0.1 N HCl); (iii) durability of hydrogel materials (10 times repeatable use of the adsorbent); (iv) good mechanical stability (preservation of gel shape without cracks). Therefore, one can conclude that betaine type hydrogels have potential application for removal and recovery of metal ions from wastewater.

4. Conclusion

Novel ethyl 3-alkylaminocrotonates containing the propylamine and cyclohexylamine groups have been synthesized from the acetoacetic ester and appropriate amines in the mild conditions with high yield 95–98%. They were involved into Michael addition reaction with unsaturated carboxylic acids followed by radical polymerization. The exothermic character of polymerization process with and without addition of initiator was marked. In the absence of initiator the possible mechanism of formation of polymeric betaines is the participation of migrating hydrogen atoms from enamine to imine tautomeric forms in polymerization process. The disappearance of C=C and C=N bonds in monomers and appearance of COO^- groups testify the formation of polymers. The structure of monomers and polymers were evaluated from FTIR and NMR spectroscopy. TGA and DSC results show the thermal stability of polymers as well as increasing in glass transition temperatures with increasing in the hydrophobicity of macromolecules. The dependence of the yield of linear polymers and the swelling degree of hydrogels on the concentration of water was established. The equimolar amount of amine and carboxylic groups found from the back potentiometric titration reveals the betaine structure of polymers. The ionization constants of acid and base groups were found from the Henderson–Hasselbalch equation. The swelling degree of hydrogels increases with lengthening of the crosslinkers, but decreases with increasing in the concentration of crosslinker. In water-organic solvent



Scheme 3. Sorption and desorption of copper(II) ions by betaine gels.

mixtures the swelling degree of hydrogels changes in the following order: water ≫ DMSO ≫ DMF > ethanol > acetone. Drastically collapsing of hydrogels at 90 vol.% of acetone was found. The response of hydrogels with respect to pH and ionic strength is explained by ionization of functional groups and suppression of the electrostatic repulsion between the charged groups by low-molecular-weight counterions.

Complexation of hydrogels with copper(II) ions through intra- and intermolecular chelate formation causes the shrinking of gel specimen. Desorption of metal ions from the gel interior is provided in acidic region due to replacement of ligand-metal bonds by ligand-proton ones. The recycling of gels in fresh water was shown.

Acknowledgements

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