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Synthesis, Characterization and Stimuli-Sensitive Properties of Novel Linear and Crosslinked Polybetaines Based on Acrylic Acid and Ethyl 3-Aminocrotonate

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Summary: Novel linear and crosslinked polybetaines based on acrylic acid (AA) and ethyl 3-aminocrotonate (CRO) have been synthesized by a Michael addition reaction followed by radical polymerization. The polymerization of AA and CRO was carried out in bulk, water and organic solvents. The dependence of polymer yield on the molar ratio of monomers and water content was found. Primary attention was paid to linear and crosslinked polybetaines synthesized at equimolar ratio of monomers in the feed. The composition and structure of linear polybetaines was determined by elemental analysis, potentiometric titration, FTIR and NMR spectroscopy. The isoelectric points of linear and crosslinked polybetaines determined by electrophoresis, viscometry and swelling experiments corresponded to pH 2.0-2.2. The stimuli-sensitive properties of amphoteric gels were studied as a function of pH, ionic strength, water-organic solvent mixture, electric, and combined electric and magnetic fields. Appearance of pH gradient within the polyampholyte gel matrix under the externally imposed DC electric field was observed.

Introduction

A number of studies on the volume phase transition of anionic, cationic and nonionic hydrogels has been reviewed in refs.[1-3] Little attention, however, has been paid to amphoteric polyelectrolyte hydrogels.[4,5] In contrast to uniformed polyelectrolytes the behavior of polyampholytes depends on the concentration of the constituent ionic groups and the pH of the external solution.[6-10] Polyampholyte gels also show a reentrant

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volume transition in response to pH [11,12] and are useful to design artificial muscles, chemo-mechanical, [13] and biochemo-mechanical[14] systems. Polymeric betaines, whose oppositely charged groups are remote one from another and are displaced on pendant substituents have less been considered in literature,[15,16] in comparison to "annealed" and "quenched" polyampholytes.[17-19]

The synthetic strategy for polyampholytes with betaine structure has been outlined in the pioneering work of Salamone et al.[20-22] Polymeric betaines can be synthesized directly by polymerization of betaine monomers[23] or polymer analogous reaction.[24-27] It was shown that polyampholytes could also be synthesized by hydrogen transfer polyaddition[28] or Michael addition reaction.[29] Previously[30,31] we succeeded in synthesizing novel polybetaines based on ethyl 3-aminocrotonate and acrylic acid using the Michael addition reaction followed by radical polymerization. In the present communication we describe, in more detail, the influence of monomer feeds and solvent nature on the conversion and composition of linear polybetaines derived from the acrylic acid and ethyl 3-aminocrotonate. The acid-base properties, viscosity and electrophoretic mobility of linear polybetaines are considered. The effects of pH, ionic strength, water-organic solvent mixtures, and combined electric and magnetic fields on the behavior of novel polybetaine gels, are also described.

Materials

Ethyl 3-aminocrotonate (CRO, 99% purity), acrylic acid (AA, 99% purity), azoisobutyronitrile (AIBN), N,N'-methylenbisacrylamide (MBAA) and the reagent grade solvents acetone, benzene, ethanol, chloroform, DMF, DMSO, hexane were purchased from Aldrich. AA and CRO were purified by distillation under the low pressure and kept in refrigerator. Reagent-grade NaCl and standard titration solutions of 0.1N HCl and NaOH were used.

Methods

FT-IR spectra were recorded using a Perkin Elmer Spectrum 2000 series as pellets with KBr. ^{1}H NMR spectra of monomers and polymers were obtained in $CDCl_3$ and D_2O at room temperature with the help of JROL JNM-LA 300 WB FT-NMR. Molecular modeling was performed with the help of the Single Point Energy calculation method with Hartree-Fock 3-21G*.

Synthesis of linear and crosslinked polybetaines

Polymerization of AA and CRO was carried out in bulk, water and organic solvents. The mixture of CRO and AA containing 2 mg of AIBN was bubbled by nitrogen gas during 2-3 min. to remove the dissolved oxygen and thermostated at 70 °C during 1 h. The total amount of monomer mixture was always 1.5 mL. Polymerization of equimolar mixtures of monomers in water and organic solvents was also carried out in the presence of AIBN (2 mg) at 70 °C. The volume ratio of solvents and monomer mixture was 1:1 vol/vol. Radical polymerization of equimolar mixtures of monomers was also carried out in the presence of various amounts of water at identical conditions described above. Linear polymers obtained in bulk, water and organic solvents were thoroughly washed out by acetone. Samples were dried *in vacuo* to constant mass. Crosslinked polymers were synthesized as justdescribed, but in the presence of MBAA (2 mg). Gel samples were washed in distilled water for 2-3 weeks to remove the sol fraction.

Potentiometric titration

Potentiometric titration of linear polymers was carried out on a 2-point calibrated "CORNING pH meter 240", equipped with combined electrodes. Direct and back potentiometric titration was carried out as follows. 50 mg of polymer samples were dissolved in either 20 mL of water or 0.1N NaCl and titrated by 0.1N NaOH. For back titration 170 mg of polymer samples were dissolved either in 100 mL of 0.1N NaOH and titrated by 0.1N HCl or dissolved in 100 mL of 0.1N NaOH and titrated by 0.1N HCl. Potentiometric titration curves were plotted in integral and differential forms. The acid-base ratio of functional groups was calculated from the inflection points and differential peaks. The ionization constants of acid and base groups were determined from the Henderson-Hasselbalch equation.

Measurement of the isoelectric point (IEP)

In order to determine the isoelectric point (IEP), the dependence of the reduced viscosity on pH was measured using an Ubbelohde viscometer at 25±0.1 °C. Polymer solutions were filtered through the 0.45µm filter and adjusted to different pH by addition of 0.5N NaOH or HCl, with the concentration of polymer held constant. Then these solutions were stirred and the values of viscosity were measured. Electrophoretic mobility of polybetaine was measured by Doppler electrophoretic light scattering with the help of the Coulter DELSA 440SX. Electrophoretic light scattering was carried out at 25±0.1 °C at four angles (8.9, 17.6, 26.3, 35,2°). The electric field was applied at a constant current of 8-14 mA. The electrophoretic cell had a rectangular cross section connecting the hemispherical cavities in each electrode. The total sample volume was about 1 mL. pH of the polymer solutions was adjusted by 0.5N NaOH or HCl. After adjusting pH and stirring about 30 min the solution was injected into the cell through the 0.45μm filter. The measured electrophoretic mobility, U, was the average value at the upper stationary layer for the four scattering angles. The value of pH at U = 0 was adopted as the IEP.

Equilibrium swelling measurements

Gels, swollen to equilibrium in distilled water, were weighed on an analytical balance and then dried. The swelling degree of the 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 influence of pH on the swelling behavior of hydrogels was studied by comparing the swelling degree of gel samples at various pH. Gel samples were placed in water solutions, the pH values of which were adjusted by adding 0.1N NaOH or HCl. Since mineral acids and bases have low buffer capacity, the pH of gel-containing aqueous solutions was maintained by adding of appropriate amount of acid or base. After equilibration the preliminary weighed gels were dried up to constant mass and the swelling degree was determined. The swelling degree of hydrogels at different ionic strengths, adjusted by NaCl, and in the mixtures of different solvents (water–ethanol, water-acetone, water-N,N-dimethylformamide), was also determined gravimetrically as described above.

Effect of externally imposed electric and magnetic fields

The equipment and measurement technique concerning the influence of externally imposed DC electric field and combined electric and magnetic fields on the behavior of gels was studied as described in.[32-34]

RESULTS AND DISCUSSION

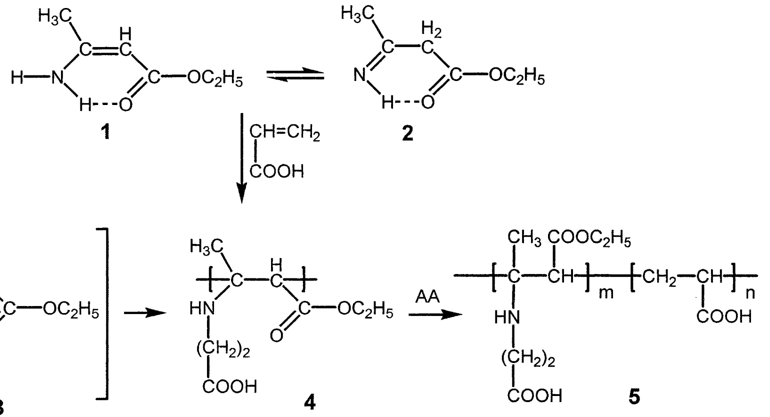
Polymerization of CRO and AA via Michael addition reaction

It is well known that ethyl 3-aminocrotonate (CRO) exists in the enamine (**1**) and imine (**2**) tautomeric forms and in spite of the presence of C=C and C=N double bonds, it does not polymerize.[35,36] The reason is that the C=C and C=O (or C=N and C=O) bonds are conjugated and additionally stabilized via intramolecular hydrogen bonds. According to literature data [36] at room temperature the enamine form is more stable than the imine form. In particular it was found[35] that in ethanol there are 80% enamine and 20% imine isomers. Our results on molecular modeling also confirm the more energetically stable state of the enamine form. The relative energetic stability of enamine tautomeric form (ΔE = -19.67 kcal·mol^{-1}) is lower than that of the imine (ΔE = 0). Therefore the enamine form is preferentially involved in the Michael reaction with AA, and in the course of enamine consumption the enamine↔imine equilibrium is shifted to left side. Recently [30,31] we have shown for the first time that upon the addition of unsaturated carboxylic acids, the intramolecular hydrogen bonds of CRO are disrupted, the hydrogen atoms of primary amine groups migrate to the double bonds of AA, and via the Michael addition reaction the intermediate product, **3**, the so-called betaine monomer, is produced (Scheme 1). It was demonstrated that the polymerization reaction is spontaneous, exothermic and even can start at room temperature without addition of initiator. The spontaneous polymerization of zwitterionic monomers was also observed by the authors.[37] It was shown[29] 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 was that both a protonation and Michael addition reaction take place simultaneously.

The mechanism of spontaneous polymerization of CRO upon addition of AA is complicated and not clear yet. Probably the hydrogen atoms shuttling from the enamine, **1,** to the imine, **2,** tautomeric forms are responsible for initiation and spontaneous polymerization. In the latter case some monomer molecules can capture the migrating hydrogen atoms and produce the free radicals to initiate the polymerization reaction. It is supposed that the high reactivity of the intermediate product **3,** is such that it can be involved into homopolymerization and copolymerization reactions with either AA or CRO, and as a result the polybetaine **4** and betaine containing copolymer **5** can be formed (Scheme 1).

It should be noted that the mixtures of CRO and acetic acid as well as the mixtures of AA and primary (or secondary) amines are not able to polymerize spontaneously. This favors the proceeding of polymerization via Michael reaction.

Fig 1 shows the conversion of CRO, AA and mixture of CRO-AA at identical polymerization conditions, e.g. when the amount of both AA and CRO taken for polymerization is equal to those in CRO-AA mixture. As seen from Fig.1, CRO itself does not polymerize in the presence of initiator, while the yield of PAA is approximately 50-60%, independent of amount. The conversion of CRO-AA increases exponentially with increase of added AA. The data of elemental analysis show that when the CRO is in excess the main product is polybetaine **4** (Table 1), while the excess of AA in the monomer feed leads to formation of copolymer **5** containing betaine **3** and AA. Due to the very low reactivity of CRO, its copolymerization with **3** is less probable.



Scheme 1. Polymerization protocol of CRO and AA via Michael addition reaction

This statement is also confirmed by direct and back potentiometric titration of CRO-AA (Table 1, Fig. 2). The content of acidic and basic groups is close to equimolar for polymers synthesized at [CRO]:[AA] = 90:10, 80:20, 70:30, 60:40 and 50:50 mol% in the feed. In the course of back potentiometric titration of [CRO]:[AA] = 50:50 mol%, three well defined peaks are distinguished. The first peak corresponds to titration of the excess of mineral acid or base. The rest two peaks are responsible for successive titration of COOH and NH_2^+ as well as NH and COO^-. The amount of COOH and NH_2^+ calculated from the potentiometric back titration corresponds to 54.5 and 45.5 mol% respectively. The amount of NH and COO^- determined from the potentiometric data is equal to 40 and 60 mol% respectively. Thus the content of acid and base groups calculated from the back potentiometric titration is (45±5 mol.%) and coincides well with direct potentiometric titration data. Ionization constants of carboxylic and secondary amine groups determined from the Henderson-Hasselbalch equation are equal

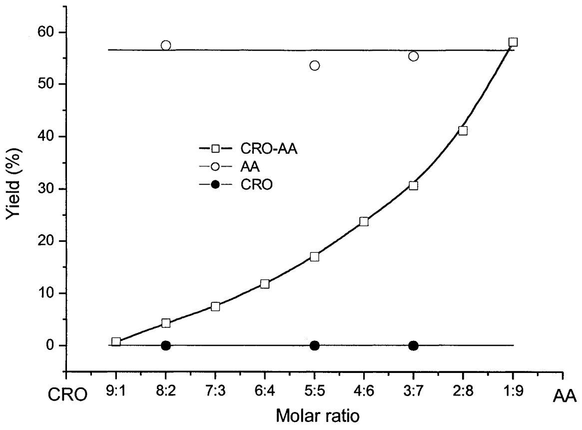


Figure 1. Yield of polymer products on the molar ratio of AA and CRO in bulk. Total volume of monomer mixture is 1.5 mL, [AIBN] = 2 mg. Polymerization time is 1 h. T = 70 °C.

Table 1. Acid-base contents of copolymers found by elemental analysis and potentiometric titration

Monomer ratio in the feed, mol%		Data of elemental analysis, % N		Acid-base contents found from the elemental analysis, mol%		Acid-base contents found from the potentiometric titration curves, mol%	
CRO	AA	Calcd	Found	Carboxylic	Amine	Carboxylic	Amine
10	90					91	9
20	80					77	23
30	70	5.75	5.73	63	37	72	28
40	60					69	31
50	50	6.96	7.18	45	55	59	41
50*	50					54.5	45.5
50**	50					46	54
60	40					46	54
70	30					60	40
80	20					50	50
90	10					43	57

*Found from the back potentiometric titration.

** Found from the direct potentiometric titration in the presence of 0.1N NaCl.

to 6.2 and 9.5 respectively. The higher pK_a of carboxylic groups in comparison with poly(acrylic acid) (pK_a=4.3) may be connected with the nearest-neighbor effect.[38]

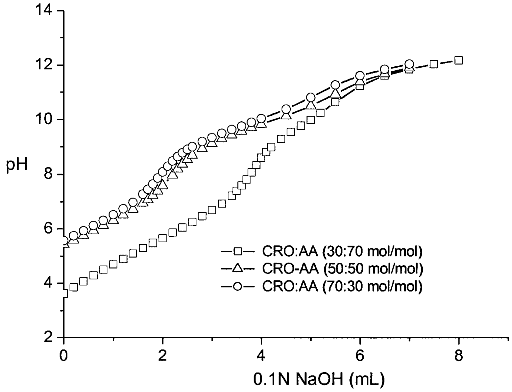


Figure 2. Potentiometric titration curves of CRO-AA synthesized at various molar ratio of monomers in the feed.

Thus, depending on the AA content in the monomer feed, either betaine type polyampholyte **4** or poly(betaine-electrolyte) **5** can be formed. Unique properties of poly(ampholyte-electrolyte) were recently outlined by authors.[39,40]

It is interesting to follow by the influence of solvent nature on the yield and acid/base molar ratio of final products. As seen from Fig. 3, the polymer yield increases according to relative dielectric permittivity of solvents. This is probably explained by active participation of polar solvents in the hydrogen-transfer process. Table 2 presents the content of acid and base groups found from the potentiometric titration data. In water, ethanol, water-ethanol mixture, DMF and benzene the content of carboxylic groups is 50±5 mol% and probably the main product is polybetaine **4,** while in hexane and chloroform the polybetaine **4** is enriched by AA and the structure **5** is formed.

We have found a drastic influence of water content on the conversion of CRO-AA (Fig. 4). Addition of 15-100 vol% of water into the equimolar monomer mixture of CRO and AA increases the yield of polymer 3-4 times in comparison with the bulk (16%). This is probably connected with participation of water molecules in proton transfer process. In particular, it was stated[41] that hydrogen bonds are able to change significantly the reactivity of monomers and radicals if the heteroatom and the reaction center participate in the formation of a unified π-conjugated system.

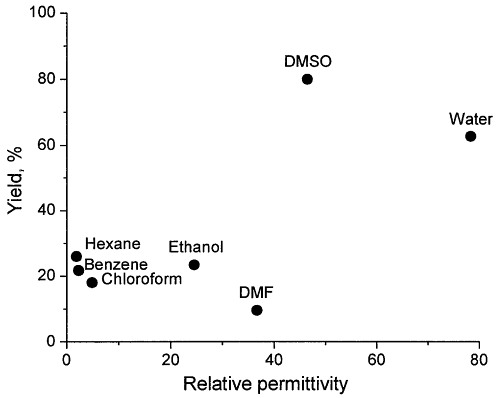


Figure 3. Dependence of the yield of equimolar mixture of CRO-AA on relative permittivity of solvents. The volume ratio of monomer mixture and solvents is 50:50 vol/vol.

Table 2. Acid-base contents of polymer products synthesized in various solvents. The molar ratio of CRO:AA in the monomer feed is 50:50 mol/mol. The volume ratio of solvent and monomer mixture is 50:50 vol/vol.

Solvent	Water	Ethanol	Water/ethanol (50:50 vol/vol)	DMF	Benzene	Hexane	Chloroform
[COOH], mol.%	59	51	48	55	57	69	62
[NH], mol.%	41	49	52	45	43	31	38

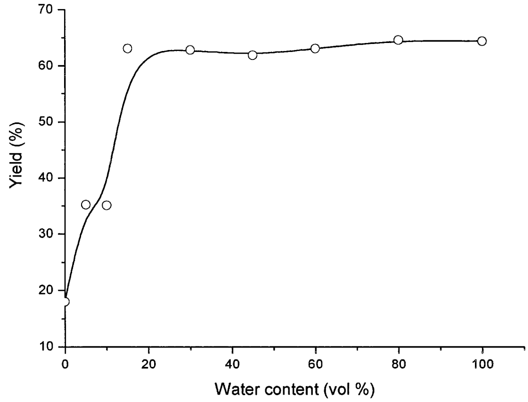


Figure 4. Influence of water content on the yield of the equimolar mixture of CRO-AA.

The structures of formed polymers were identified by FTIR and ^{1}H NMR spectroscopy. FTIR spectra of CRO, AA and CRO-AA (50:50 mol.%) are shown in Fig. 5. Disappearance of intensive peaks of monomers at ν = 1659, 1622 and 1634 cm^{-1} that belong to C=C and C=N of CRO and C=C of AA, and broadening and shifting of intensive lines of primary amine groups of CRO at ν = 3230, 3334 and 3440 cm^{-1} up to 3157 and 3421 cm^{-1} clearly show the formation of polymer product. Stretching vibrations of CH and C=O as well as the symmetric and asymmetric vibrations of carboxylate ions appear respectively at ν = 2958, 1707, 1559 and 1450 cm^{-1}. Besides the intensive rocking vibration of C=C at ν = 789 cm^{-1} from CRO, a diminished but very small shoulder is still seen in the spectrum of polymer. The very small peak at ν = 1632 cm^{-1}, attributed to C=C of AA, indicates the latter's presence in the final product. The admixtures of AA and CRO in the polymer product may be connected with formation of salt bonds between the secondary amine groups of **4** and AA as well as between the carboxylic groups of **4** and amine groups of CRO. Thus analysis of FTIR spectra reveals that the main product of polymerization of CRO and AA is **4,** containing insignificant additives of monomers (AA and CRO). However from the FTIR spectra it is difficult to identify the structure of copolymer **5**.

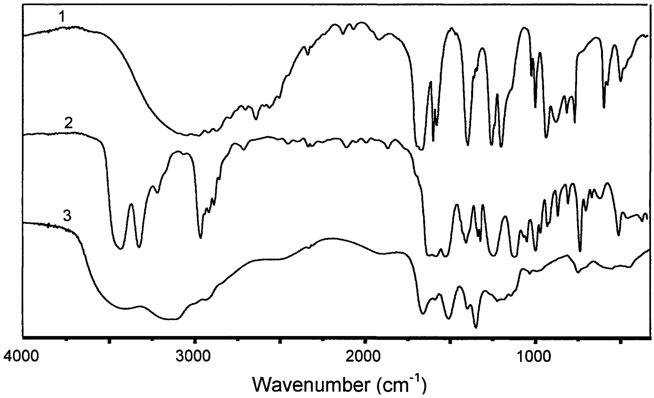


Figure 5. FTIR spectra of AA (1), CRO (2), and CRO-AA (50:50 mol.%) (3).

^{1}H NMR spectra of CRO-AA shown in Fig. 6 coincide well with the results of elemental analysis and potentiometric titration. NMR spectra of CRO-AA (80:20 and 50:50 mol.%) are identical showing that the main polymer is polybetaine **4**. Appearance of additional proton signals from the AA when the molar ratio of CRO-AA is 20:80 testifies to the formation of polymer structure **5**. Thus NMR spectra are in good agreement with elemental analysis and potentiometric titration and show on the formation of **4** and **5**, depending on polymerization conditions.

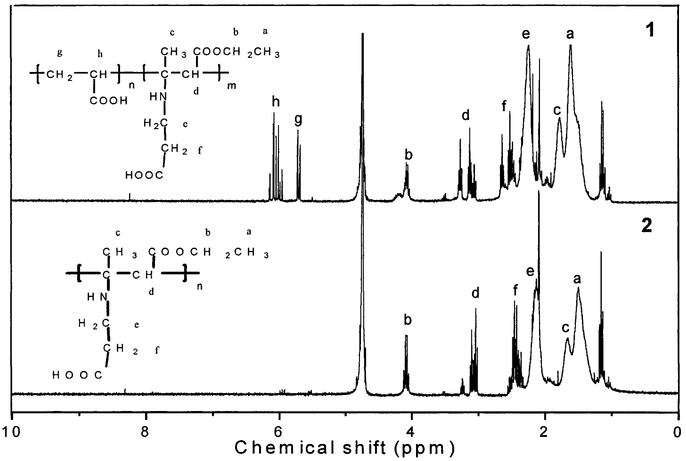


Figure 6. ^{1}H NMR spectra of poly(betaine-acrylic acid) (1) and polybetaine (2).

The properties of linear and crosslinked polybetaines in aqueous and aqueous-salt solutions were studied for samples synthesized at equimolar ratio of AA and CRO in

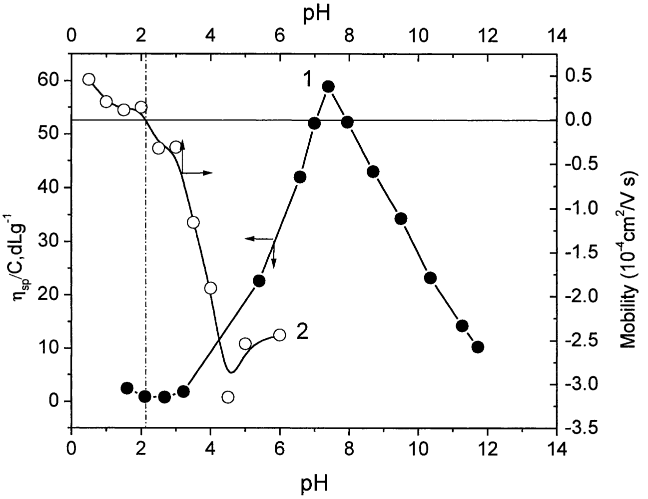


Figure 7. Reduced viscosity (curve 1) and electrophoretic mobility (curve 2) of the polybetaine **4** vs. pH of the solution.

bulk. Fig. 7 shows the influence of pH on the viscosity and electrophoretic mobility of CRO-AA.

The minimal viscosity and the zero mobility are observed near of pH 2.1-2.2 that corresponds to the isoelectric point (IEP). The sharp increase of the reduced viscosity in the pH range 3-7.5 is due to ionization of carboxylic groups. The decrease in viscosity in the basic region is probably accounted for suppression of polyelectrolyte effect by the excess of NaOH that plays the role of low-molecular-weight electrolyte. At pH < 2 a slight increase of the viscosity as a result of protonation of nitrogen atoms is observed. The "asymmetric" character of chain stretching and "anomalous" low magnitude of the IEP ($pH_{IEP} \approx 2.0$-2.1) may be the result of different accessibility of carboxylic and secondary amine groups to ionization. Carboxylic groups replaced far from the main chain can be ionized more easily than the secondary amine groups that are near of the main chain and in a hydrophobic environment. Therefore ionization of carboxylic groups more effectively unfolds the macromolecule than the ionized nitrogen atoms located close to the main chain. Since the requirement of the IEP is the overall electroneutrality of macromolecular chain, the added mineral acid at first suppresses the ionization of carboxylic groups decreasing the negative charges of the whole macromolecules.

At lower pH, however, some parts of the secondary amine groups can also be ionized. These results are in good agreement with the electrophoretic data, e.g. the amount of negative charges on macromolecules is significantly higher at pH>2 than the amount of positive charges at pH<2. Also, the specific binding of Cl^- diminishes the amount of positively charged groups and shifts the IEP to the acidic region. Taking into account that the value of pK_b of secondary amine groups is equal to 4.5 the ionized amount of amine groups at pH = 2.0 was calculated from the Henderson-Hasselbalch equation. It is proved that at the IEP only 3% of secondary amine groups are ionized to make the macromolecules overall electroneutral.

It should be mentioned that the acid/base properties of betaine type polyampholytes are quite different from those of "annealed" polyampholytes.[19] The position of the IEP of "annealed" polyampholytes depends strongly on the molar ratio of acid-base monomers in copolymers. A very low isoelectric state ($pH_{IEP} = 2$-3) is observed for amphoteric copolymers containing up to 90-95 mol.% of acidic monomers. In contrast to "annealed" polyampholytes and polycarboxybetaines, polysulfobetaines at low pH exhibit neither increasing viscosity nor existence of an IEP, due to strong acidity of the sulfonate groups.[42,43]

As seen in Fig. 8, the pH-dependent behavior of polybetaine gel synthesized at the same conditions is also in good agreement with the linear analogue. The swelling degree of polybetaine gel is minimal around the IEP ($pH_{IEP} \approx 2.0$).

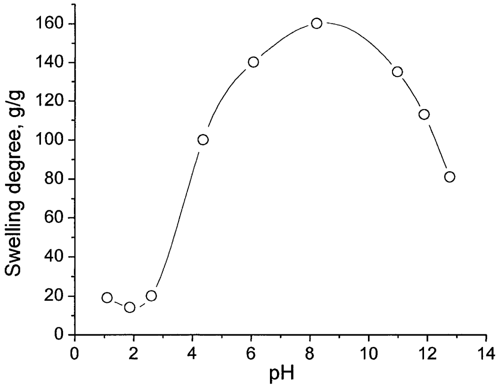


Figure 8. Dependence of the swelling degree of polybetaine gel on pH.

The viscosity of polybetaines is extremely high in aqueous solution. This may be due to intermolecular association of macromolecules via formation of ionic and hydrogen bonds. The value of the intrinsic viscosity determined in $2 \cdot 10^{-3}$ mol·L^{-1} HCl is equal to 26.0 dL·g^{-1}.

Effect of the ionic strength

Changes in of the reduced viscosity of linear polybetaines and the swelling degree of crosslinked polybetaines in the presence of salt are shown in Figures 9 and 10. As the ionic strength increases both the reduced viscosity and swelling degree at first sharply decreases, reaches a minimum, and then slightly increases. To interpret these results the ability of polymeric betaines to form intraionic and interionic associates should be taken into account.[44] Probably small amount of added NaCl at first disrupts the interionic aggregates. Further increasing of the ionic strength destroys intraionic contacts allowing minor expansion of the polymer coil.[45] These results are in qualitative agreement with the theoretical[46] and experimental[47] data that show the collapsing of balanced polyampholytes at low salt and swelling at high salt concentrations.

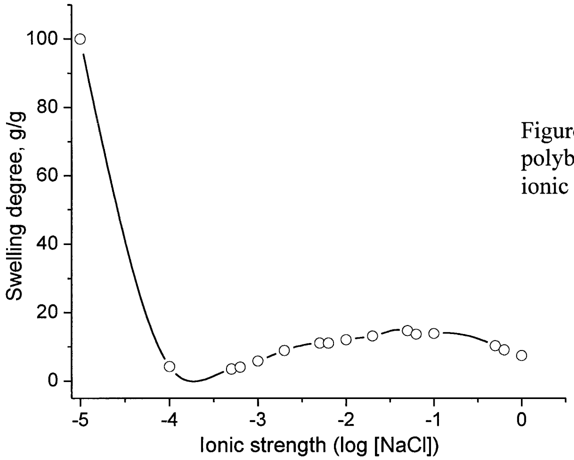


Figure 9. Shrinking of the polybetaine gel as a function of ionic strength.

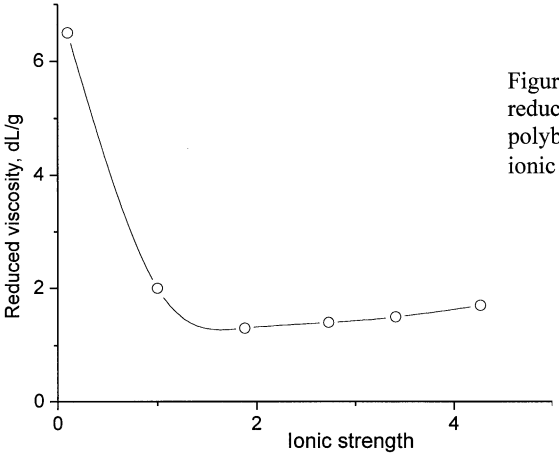


Figure 10. Changes in the reduced viscosity of linear polybetaine as a function of the ionic strength. C = 0.5 g·dL^{-1}.

Effect of binary solvents

Polybetaine gels shrink in water-acetone, water-alcohol and water-DMF mixtures (Fig. 11). Addition of organic solvents causes gradual deswelling of gel samples, the effectiveness of which changes in the order DMF > acetone > ethanol. This ordering is due to decreasing of dielectric permittivity of the medium, which enhances the condensation of counterions on the macroions. The latter leads to decreasing osmotic pressure within the gel. In organic solvents, macromolecular chains are in the collapsed state due to suppression of ionization. These results confirm the universal behavior of polyelectrolyte gels with respect to the thermodynamic quality of solvents.

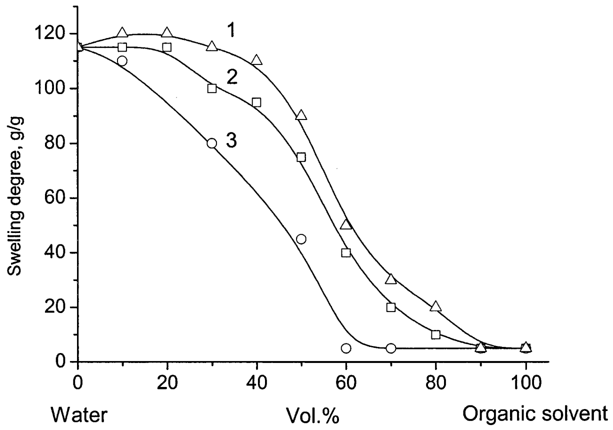


Figure 11. Deswelling of polybetaine gel in water-ethanol (1), water-acetone (2), and water-DMF (3) mixtures.

Effect of combined electric and magnetic fields

Previous work has shown the influence of electric[48] and combined electric and magnetic fields[32, 49] on the behavior of polyampholyte and polyelectrolyte gels. Fig. 12 demonstrates the kinetics of polybetaine gel contraction under the imposed DC electric field and cross-combined electric and magnetic fields. Increasing the electric current leads to enhancement of the gel's contraction rate; the values of $\Delta m/m_0$ are increased linearly, reaching the constant state. Application of a constant magnetic field accelerates gel contraction. Apparently the magnetic field distorts paths of charge carriers and the

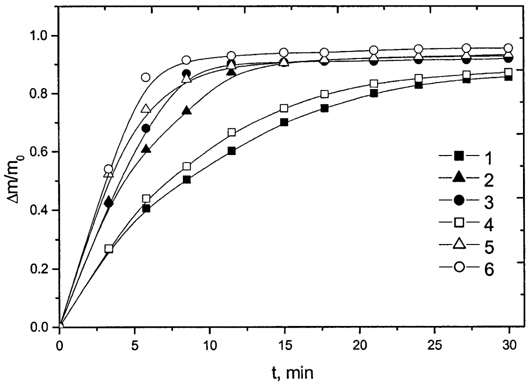


Figure 12. Kinetics of gel contraction under the influence of DC electric field (curves 1-3) and combined electric and magnetic fields (curves 4-6) at E=10 (curves 1,4), 20 (curves 2,5), 30 (curves 3,6) V. Magnetic field is constant and equal to 100 G.

specimen is additionally polarized in the direction perpendicular to the vector of electric current. Consequently the opposite sides of the specimen bear non-zero charge. As a result these charged areas are attracted to oppositely charged electrodes, and the contraction rate increases.

Formation of pH-gradient

Previously[33,34] the formation of a pH-gradient within polyampholyte gel matrix under the externally imposed DC electric field was observed for "annealed" amphoteric gels based on vinyl-2-aminoethyl ether and acrylic acid. Fig. 13 shows the time dependence of pH change within polybetaine gel volume. The applied DC electric field causes a sharp appearance of pH gradient during 1-2 min that is fully stabilized after 5 min. When the electrical stimulus was removed, pH quickly adopted the initial value. The values of $\Delta pH = pH_0 - pH_{t\rightarrow 0}$ (where pH_0 is the initial pH, $pH_{t\rightarrow 0}$ is the pH value extrapolated to zero time $pH_{t\rightarrow 0}$) are a function of DC electric field.

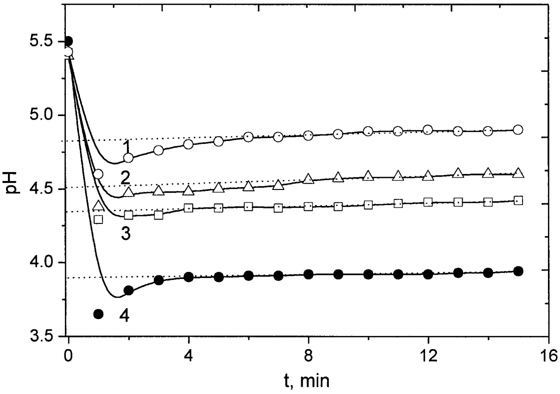


Figure 13. Change in pH with time in the gel near the anode (1), in the center (2,3) and near the cathode (4), with E=10V. The dotted lines indicate on the extrapolation of pH to $pH_{t\rightarrow 0}$.

Fig. 14 represents the dependence of pH on distance ± *l* when the glass electrode is placed on cathode or anode sides of gel specimen in comparison with its central section where *l*=0.

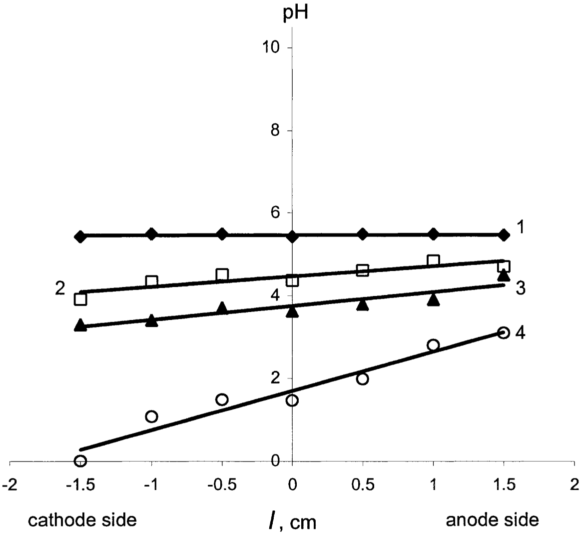


Figure 14. The dependence of pH gradient on distance *l* without the imposed DC electric field (1) and with applied D.C. voltages E=5V (2), 10V (3) and 15V(4).

Without the applied DC electric field, the pH is uniform and equal to 5.46. Increasing of the electric field shifts the pH gradient in the acidic direction. The dependence of pH gradient on *l* has linear character, and the slope of the line is proportional to the strength of applied DC electric field. In order to interpret these data the distribution of fixed network charges and counterions within the gel specimen should be considered. The externally imposed potential across the gel causes the polarization of network charges and counterions. The latter are produced by water electrolysis. Negative fixed charges (COO^-) and mobile ions (OH^-) accumulate at the anodal side (zone **A**) while the accumulation of positive fixed charges (NH_2^+) and mobile ions (H^+) takes place at the cathodal side (zone **C**). The intermediate zone **B** is relatively electroneutral with respect to zones **A** and **C**. Increasing of the DC electric current leads to overall acidification of the gel sample due to enhanced ionization of carboxylic groups (see Fig.14, curve 4). As a result the zones **B** and **C** become narrower, and the zone **A** expands. It should be noted that the existence of a pH gradient is specific only for amphoteric gels and was not detected for uniformly charged polyacid or polybase gels.[19]

Conclusion

Novel linear and crosslinked betaine type polyampholytes were synthesized from the ethyl 3-aminocrotonate and acrylic acid via Michael addition reaction followed by radical polymerization. Polymerization mechanism is probably connected with migration of hydrogen atoms from enamine to imine tautomeric forms. Molecular modeling shows that the enamine tautomeric form is more energetically stable and preferentially involved into Michael addition reaction. The influence of the monomers ratio in the feed and solvent nature on the conversion and composition of polymer products was established. Considerable increasing of the yield of linear polybetaines upon addition of water into the reaction mixture is connected with participation of water molecules in proton transfer process. Elemental analysis together with potentiometric titration, FTIR and NMR data confirm the formation of polybetaine structure and copolymers of betaine with AA, depending on the molar ratio of monomers in the feed. The isoelectric points of linear and crosslinked polybetaines determined by combination of viscometric and electrophoretic methods and from the equilibrium swelling measurements arrange at pH=2.0-2.1. Anomalous low values of the IEP polybetaines are accounted for low ionization degree of secondary amine moieties displaced near of the main chain surrounded by hydrophobic groups. The behavior of linear and crosslinked polyampholytes with respect to ionic strength is explained by destruction of intraionic and interionic associations. Shrinking of polybetaine gel in water-organic solvents mixtures is explained by decreasing of the dielectric permittivity of medium that leads to condensation of counterions to macroions. The combined electric and magnetic fields enhances the gel collapse due to additional polarization of gel specimen. Appearance of pH gradient within the gel volume under imposed externally DC electric field is connected with polarization of network charges and counterions.

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