Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Preparation and Characterization of Novel Polymeric Betaines Based on Aminocrotonates

Sarkyt E. Kudaibergenov[ab]; Larisa A. Bimendina[ab]; Marziya G. Yashkarova[b]
[a] Institute of Polymer Materials and Technology, Almaty, Kazakhstan [b] Semipalatinsk State Shakarim University, Semipalatinsk, Kazakhstan

To cite this Article Kudaibergenov, Sarkyt E. , Bimendina, Larisa A. and Yashkarova, Marziya G.(2007) 'Preparation and Characterization of Novel Polymeric Betaines Based on Aminocrotonates', Journal of Macromolecular Science, Part A, 44: 8, 899 — 912
To link to this Article: DOI: 10.1080/10601320701407995
URL: http://dx.doi.org/10.1080/10601320701407995

Journal of Macromolecular Science ®, Part A: Pure and Applied Chemistry (2007) **44**, 899–912

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320701407995

Preparation and Characterization of Novel Polymeric Betaines Based on Aminocrotonates

SARKYT E. KUDAIBERGENOV,[1,2] LARISA. A. BIMENDINA,[1,2] and MARZIYA G. YASHKAROVA[2]

[1]*Institute of Polymer Materials and Technology, Almaty, Kazakhstan*
[2]*Semipalatinsk State Shakarim University, Semipalatinsk, Kazakhstan*

Received October, 2006, Accepted January, 2007

This review summarizes the preparation and physico-chemical properties of novel polymeric betaines based on ethyl 3-aminocrotonate and its N-substituted alkyl derivatives that, in turn, were obtained by condensation of acetoacetic ester with various amines, aminoalcohols, and aminoacids in mild conditions. Stereochemical peculiarities and tautomeric transitions in monomers as well as kinetics and mechanism of formation of linear and crosslinked polybetaines proceeding via Michael addition reaction are outlined. Attention was paid to hydrodynamic, conformational and molecular characteristics of linear and stimuli-sensitive properties of crosslinked systems as a function of pH, ionic strength, thermodynamic quality of solvents and electric field.

Keywords: aminocrotonates; Michael addition reaction; polymeric betaines; hydrodynamic and molecular properties; conformational and volume-phase transitions

1 Introduction

Synthesis and characterization of novel polyampholytes, and especially polymeric betaines, represent a great interest from the theoretical and practical points of view (1–6). Structural and functional similarity of synthetic and natural polyampholytes on the one hand, and the conformational transitions taking place in linear macromolecules and volume-phase transitions that are specific for polymer networks on the other hand, can be of help to model the self-organization, sol-gel and phase transitions in biomacromolecules (7–10). Inclusion of new monomers, namely alkyl 3-aminocrotonates and their N-substituted alkyl derivatives, into polymerization reactions with the aim to obtain novel polymeric betaines is a challenging task. Stereoisomeric forms of alkyl 3-aminocrotonates have sufficiently been studied and the technology of producing anaesthetic drugs on their basis has been developed (11). However there is no available information in the literature on using of aminocrotonates as monomers and involving them polymerization reactions. We have formulated and demonstrated, for the first time, the synthetic pathway to polybetaines through a Michael addition reaction followed by spontaneous or radical polymerization and synthesized, not yet described in the literature, novel betaine type functional polymers (12).

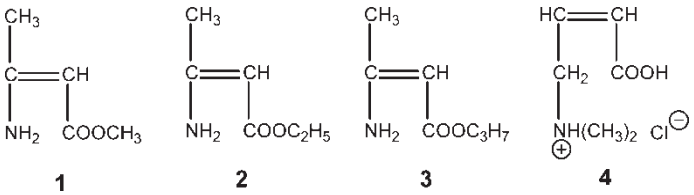
Address correspondence to: Sarkyt E. Kudaibergenov, Institute of Polymer Materials and Technology, Almaty, Kazakhstan and Semipalatinsk State Shakarim University, Semipalatinsk, Kazakhastan. E-mail: ipmt-kau@usa.net or skudai@mail.ru

2 Experimental

2.1 Ethyl 3-Aminocrotonate and its N-Substituted Alkyl Derivatives

2.1.1 Alkyl ethers of 3-aminocrotonate and n-substituted alkyl 3-aminocrotonates

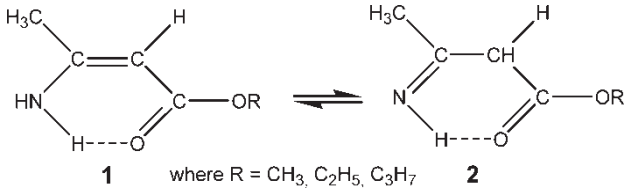
Typical representatives of alkyl esters of 3-aminocrotonates are: methyl 3-aminocrotonate (1), ethyl 3-aminocrotonate (2), isopropyl 3-aminocrotonate (3) and 4-dimethyl aminocrotonic acid (4) in the form of hydrochloride (Scheme 1). They are commercially available products of "ZhongYer Chemicals International Co., Ltd" (P. R. China) and "Anjero-Sudjensk Chemical Pharmaceutical Plant" (Russia). Compounds 1–3 can exist in enamine (E) and imine (I) tautomeric forms stabilized by the system of conjugated and hydrogen bonds (13) (Scheme 2). Compound 4 depending of pH, can exist in anionic, cationic and zwitterionic forms. Tautomeric forms of ethyl 3-aminocrotonate (EAC) in ethanol were studied by spectroscopy, bromometry and refractometry (14). It was found that in ethanol about 80% of enamine and 20% of imine forms exist. Amine groups play a double role: 1) provide imine formation; 2) catalyze proton transformation. According to the literature data (15) and our own quantum chemical calculations (16), the



Sch. 1. Methyl 3-aminocrotonate (1), ethyl 3-aminocrotonate (2), propyl 3-aminocrotonate (3), 4-dimethyl aminocrotonic acid hydrochloride (4).

energetically more favorable state is the trans-conformation and enamine tautomer (Figure 1), because the relative energetic stability of the enamine tautomeric form ($\Delta E = -19.67$ kcal/mol) is lower than the imine tautomeric one ($\Delta E = 0$). According to the author's opinion (17), the transformation of protons from imine to enamine form is the more important stage and proceeds via formation of a dimeric structure (Scheme 3).

The functional groups of EAC were identified by FTIR spectra. They contain adsorption bands at $\nu = 1655$ and a doublet at 1611 and 1619 cm^{-1}, corresponding to C═C and C═N bonds, respectively (Figure 2). Intense peaks at 1286 and 1159 cm^{-1} are attributed to C-O-C bonds of ester groups. The appearance of adsorption bands for C═O at anomalous low frequencies $\nu = 1555$ and 1567 cm^{-1} is probably connected with participation of carbonyl groups in formation of intramolecular hydrogen bonds. Adsorption bands at $\nu = 3230$, 3334 and 3439 cm^{-1} belong to primary aminogroups. Stretching vibrations of CH appear at $\nu = 2980$ cm^{-1}. The intense band at $\nu = 786$ cm^{-1} is attributed to the out-of-plane vibration of pseudo-aromatic rings (Scheme 4, structure 6).



Sch. 2. Enamine (1) and imine (2) tautomeric forms of alkyl 3-aminocrotonates.

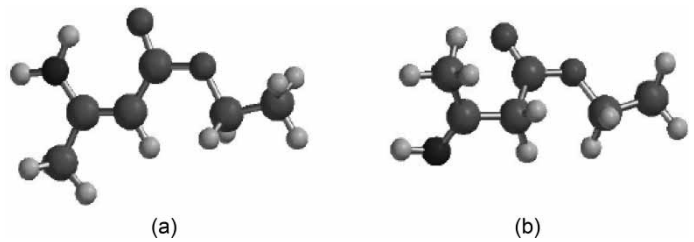
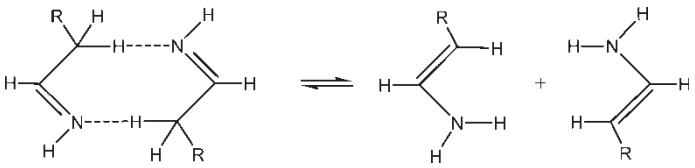


Fig. 1. Molecular model of enamine (1) and imine (2) tautomeric forms of ethyl 3-aminocrotonate.



Sch. 3. Transformation of protons *via* dimeric structure of alkyl 3-aminocrotonates.

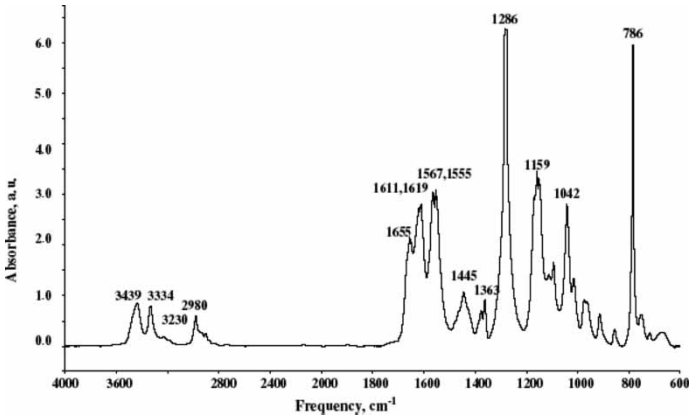
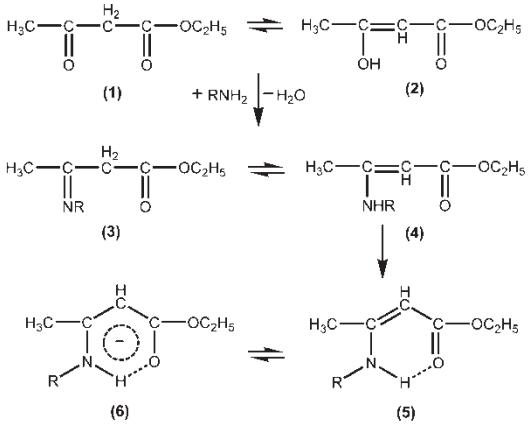


Fig. 2. FTIR spectra of ethyl 3-aminocrotonate.

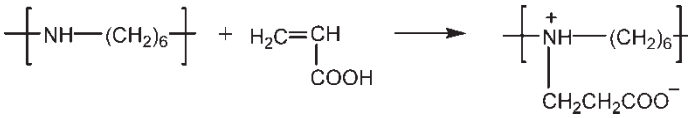
^{1}H-NMR spectrum of EAC in $CDCl_3$ contains a singlet of olefin protons with chemical shift at 4.5 ppm and doublets of methylene protons at 5.8 ppm. Broadened signals of NH_2 protons participating in formation of intramolecular hydrogen bonds appeared at 7.91 ppm. (11).

Interaction of acetoacetic ester (AAE) in enol tautomeric form (2) with ammonia leads to formation of ethyl 3-aminocrotonate (EAC) while condensation of AAE with primary



where R–H, CH_3, C_2H_5, C_3H_7, *iso*-C_3H_7, *diiso*-C_3H_7, C_6H_{11}, $C_{12}H_{25}$, C_2H_4OH, C_2H_4COOH, $CH(CH_3)COOH$, phosphatidylethanolamine

Sch. 4. Ketone (1) and enol (2) tautomeric forms of acetoacetic ester and imine (3) and enamine (4) tautomeric forms of N-substituted ethyl 3-aminocrotonates stabilized by intramolecular hydrogen bonds (5), and formation of pseudo-aromatic ring (6).



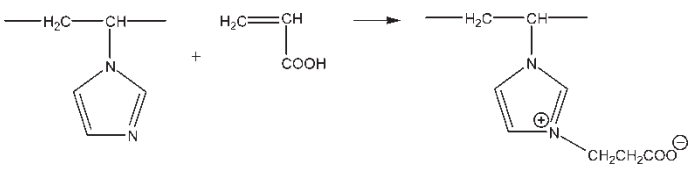
Sch. 5. Binding of aminogroup protons of polyaminoethylene to α-carbon atoms of acrylic acid *via* Michael addition reaction.

and secondary alkylamines, aminoalcohols (ethanolamine, phosphatidylethanolamine), aminoacids (glycine, β-alanin, L-lysine) produces a series of N-substituted aminocrotonates, which can exist in imine (3) and enamine (4) tautomeric forms (Scheme 4) (18). In turn, the enamine tautomeric form is additionally stabilized by intramolecular hydrogen bonds (5), leading to formation of pseudo-aromatic rings (6) as a result of conjugation of C═C and C═O bonds with participation of lone electron pairs of nitrogen atoms (Scheme 4). One can suggest that, in the case of N-substituted ethyl 3-aminocrotonates, the lengthening of alkyl radicals promotes shifting of the tautomeric equilibrium to the energetically more favorable enamine form.

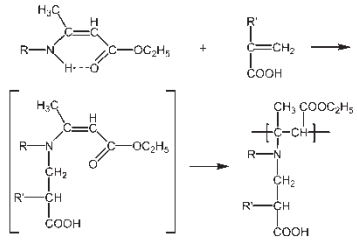
2.2. Synthesis of Aminocrotonate Based Polybetaines Via Michael Addition Reaction

The authors of Reference (19) showed that the addition of acrylic acid (AA) to a chloroform solution of polyaminoethylene and polyiminohexamethylene produces a polybetaine with more than 90% zwitterions structure due to binding of aminogroup protons to α-carbon atoms of AA *via* Michael addition reaction (Scheme 5). Another example of polycarboxybetaine formation by Michael reaction is interaction of poly(N-vinylimidazole) with AA (20) (Scheme 6). Polymerization of 2-hydroxyethylacrylate *via* a Michael-type addition of hydroxyl groups to methacrylate carbon-carbon double bonds was studied by the authors of Reference (21).

Ethyl 3-aminocrotonate (EAC) and its N-substituted alkyl derivatives, in spite of the presence of labile double bonds, do not polymerize themselves due to the formation of π-conjugated systems stabilized by intramolecular hydrogen bonds. The addition of unsaturated carboxylic acids to AAE, EAC (or to its N-substituted alkyl derivatives) breaks the intramolecular hydrogen bonds and, *via* the Michael addition reaction, produces the intermediate products which are able to be polymerized spontaneously or in the presence of initiators (22–29) (Scheme 7). The mechanism of



Sch. 6. Interaction of poly(N-vinylimidazole) with acrylic acid leading to formation of polycarboxybetaine.



where R=H, CH_3, C_2H_5, C_3H_7, *iso*-C_3H_7, *diiso*-C_3H_7, C_6H_{11}, $C_{12}H_{25}$, C_2H_4OH, C_2H_4COOH, $CH(CH_3)COOH$, phosphatidylethanolamine; R' – H or CH_3.

Sch. 7. Migration of enamine protons to unsaturated carboxylic acids and formation of intermediate carboxybetaine and final polycarboxybetaine products.

formation of intermediate betaine monomers includes the migration of the labile enamine protons to α-carbon atoms of unsaturated carboxylic acids. This is confirmed by the disappearance of NH protons at $\delta = 8.5$ ppm (Figure 3). Binding of NH protons to α-carbon atoms of AA shifts the methylene protons of the propyl radicals. The main difference between the ethyl 3-(propyl)aminocrotonate (EPAC) and poly[carboxyethyl 3-(propyl)aminocrotonate] (PCEPAC) is the appearance, in the polymer product, of two new peaks at 1.8 and 2.6 ppm which belong to methylene groups situated near the tertiary amine and carboxylic groups. Saturation of C═CH bonds is accompanied by shifting of CH protons from 4.3 to 3.9 ppm. The betaine structure of the formed polymers is also confirmed by FTIR spectra (Table 1). Disappearance of both C═C and C═N bonds and appearance of broadened asymmetric COO^- vibrations confirms the formation of polymers with betaine structure. Gradually decreasing and disappearance of the out-of-plane vibration (at $\nu = 786\ cm^{-1}$), that is specific for the pseudoaromatic ring, confirms the proceeding of the Michael addition reaction (see Scheme 4, structure 6).

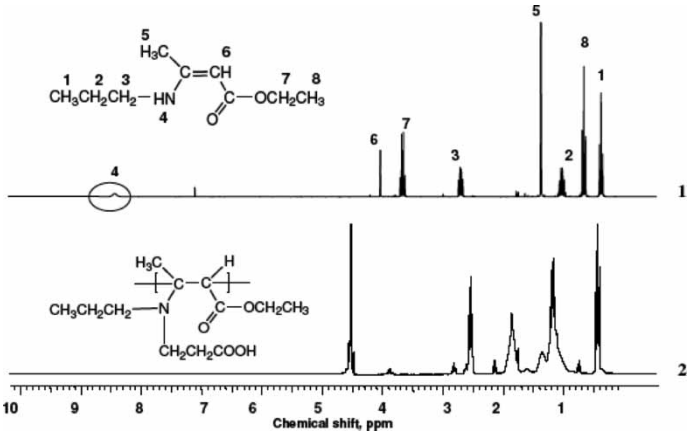


Fig. 3. ^{1}H-NMR spectra of ethyl 3-(propyl)aminocrotonate (1) in $CDCl_3$ and poly[carboxyethyl 3-(propyl)aminocrotonate] (2) in D_2O.

Table 1. Characteristic bands of functional groups of AA, EAC, poly(carboxyethyl 3-aminocrotonate) (PCEAC) and poly[carboxyethyl 3-(propyl)aminocrotonate] (PCEPAC).

Functional groups	Frequency, cm^{-1}			
	AA	EAC	PCEAC	PCEPAC
ν (NH)	—	3230, 3334, 3439	3421	3430
ν (CH)	2987	2958	2959	2980
ν (C═O)	1704	1555, 1566	1707	1702
ν (C═C)	1634	1655	—	—
ν (C═N)	—	1621	—	—
ν_{as} (COO^-)	—	—	1559	1550
δ(C═C)	—	786	—	—

The specific feature of the systems consisting of aminocrotonates and unsaturated carboxylic acids is fast, spontaneous polymerization of equimolar monomer mixtures in bulk (Figure 4). Since the polymerization process starts immediately at room temperature, and even without addition of initiator, it is difficult to isolate the intermediate monomer products.

Figure 5 shows the kinetics of polymerization of an equimolar mixture of EAC and AA in bulk without added initiator at various temperatures. The gradual diminishing of band intensity at $\nu = 786\ cm^{-1}$ and simultaneous increasing of the viscosity of the mixture shows the proceeding of polymerization reaction. The increasing of temperature enhances the reaction rate. The activation energy of the polymerization process found from the Arrhenius plot is equal to $60.8\ kJ \cdot mol^{-1}$.

The mechanism of spontaneous polymerization, that is accompanied by heating of the system, can probably be explained by the initiation of reactions by protons which are generated as a result of transformation of labile protons from one tautomeric form into another (Scheme 8). Shuttling-protons migrating from the enamine to imine form (or *vice versa*) may attack the C═C bonds and initiate the formation of active radicals that participate in chain growth. In favor of polymerization reaction by proton transfer serves the fact that the model mixtures of EAC and acetic acid (model of AA) and AA with primary amines (model of EAC) do not polymerize in the absence of initiator. Previously, polymerization of α-aminomethacrylate by the proton transfer mechanism was marked by the authors of Reference (30).

However, in the absence of initiator, the yield of polymer product does not exceed ~10%, therefore the further

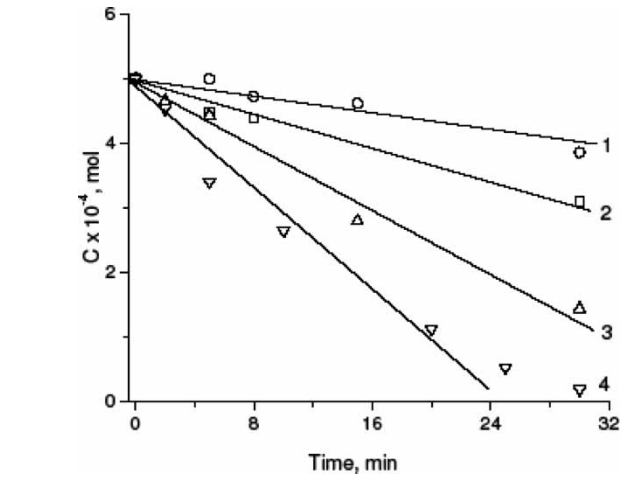


Fig. 5. Decrease of the concentration of EAC with reaction time at T = 293 (1), 303 (2), 313 (3) and 323 K (4) in the absence of initiator.

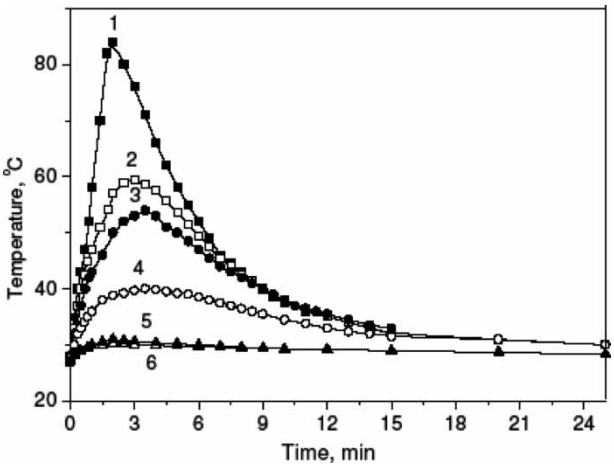
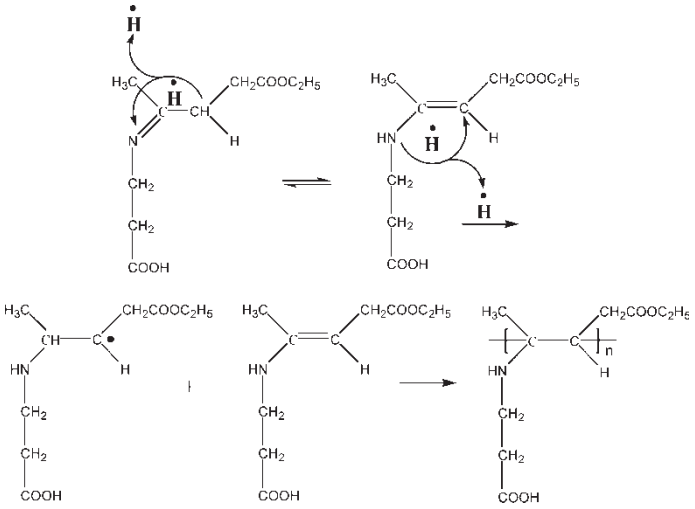
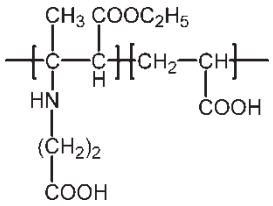


Fig. 4. Temperature profile of the polymerization reaction for the equimolar mixture of ethyl 3-(propyl)aminocrotonate (curves 1 and 2), ethyl 3-(cyclohexyl)aminocrotonate (curves 3 and 4) with AA and ethyl 3-(cyclohexyl)aminocrotonate with MMA (curves 5 and 6) in bulk in the presence (1,3,5) and absence (2,4,6) of an initiator.



Sch. 8. Initiation of polymerization reaction of carboxyethyl 3-aminocrotonate by shuttling-protons generated as a result of transformation of labile protons from one tautomeric form into another.



Sch. 9. Structure of copolymer of ethyl 3-aminocrotonate and acrylic acid.

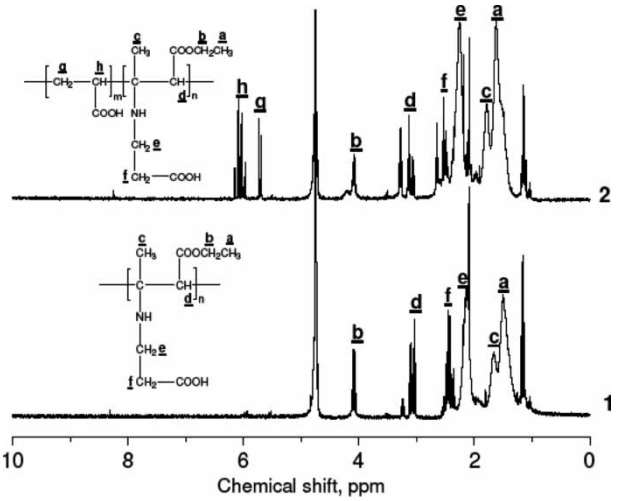


Fig. 6. ^{1}H-NMR spectra of poly(carboxyethyl 3-aminocrotonate) (1) and copolymer of carboxyethyl 3-aminocrotonate with AA (2).

polymerization reaction is preferential to carry out in the presence of initiator. The influence of the feed composition on the composition and structure of polymers was carefully studied for various mixtures of EAC and AA (31). The data of elemental analysis and potentiometric titration reveal that, when the EAC is in excess, the final product is poly(carboxyethyl 3-aminocrotonate), while an excess of AA leads to formation of copolymers containing both carboxybetaine and AA fragments (Scheme 9). This is confirmed by the appearance of AA proton signals in copolymers (Figure 6). As seen from Table 2, for polymers obtained at the ratio of monomer mixture [EAC]:[AA] = 90:10, 80:20, 70:30, 60:40 and 50:50 mol%, the content of acidic and basic groups is close to equimolar. Potentiometric titration curves show that the composition of polybetaines synthesized at molar ratios of [EAC]:[AA] = 70:30 and 50:50 mol%, is equimolar (Figure 7, curves 1 and 2). In contrast, the composition of polybetaine synthesized with excess of AA, when [EAC]:[AA] = 30:70 mol%, is enriched by AA due to copolymer formation (Figure 7, curve 3).

The influence of solvent nature, length of alkyl substitutes and of initiator concentration on the yield of polybetaines was studied. As seen from Figure 8, in dependence on solvent nature, the yield of PCEAC increases in the order: DMSO > water > ethanol > benzene > chloroform. This is probably due to active participation of polar solvents in the process of proton transfer which is responsible for chain growth. The content and ionization constants of acid and base groups of PCEAC synthesized in various solvents are given in Table 3. In water, ethanol, water-ethanol and DMF the content of carboxylic groups is equal to 50 ± 5 mol%, while the polymers synthesized in hexane and chloroform contain an excess of AA. The values of ionization constants (pK_a) of carboxylic and amine groups are replaced at the interval of 5.35–5.87 and 9.50–9.75, respectively.

The yield of PCEAC strongly depends on water content added to equimolar mixtures of EAC and AA (Figure 9). It is 3–4 times higher than the polymer yield obtained in bulk. The same regularity is observed for poly[carboxyethyl 3-(propyl)aminocrotonate] (PCEPAC) and poly[carboxyethyl

Table 2. The content of acidic and basic groups in polymeric betaines determined by elemental analysis and potentiometric titration

Feed composition, mol%		Elemental analysis, %N		Acid and base contents determined by elemental analysis, mol%		Acid and base contents determined by potentiometric titration, mol%	
EAC	AA	Calc.	Found	COOH	NH	COOH	NH
10	90					91,0	9,0
20	80					77,0	23,0
30	70	5,75	5,73	63	37	72,0	28,0
40	60					69,0	31,0
50	50	6,96	7,18	45	55	54,7	45,3
50[a]	50					54,5	45,5
50[b]	50					54,5	45,5
60	40					46,0	54,0
70	30					45,0	55,0
80	20					50,0	50,0
90	10					45,2	54,8

[a]Determined by direct potentiometric titration in the presence of 0,1 N NaCl.
[b]Determined by back potentiometric titration.

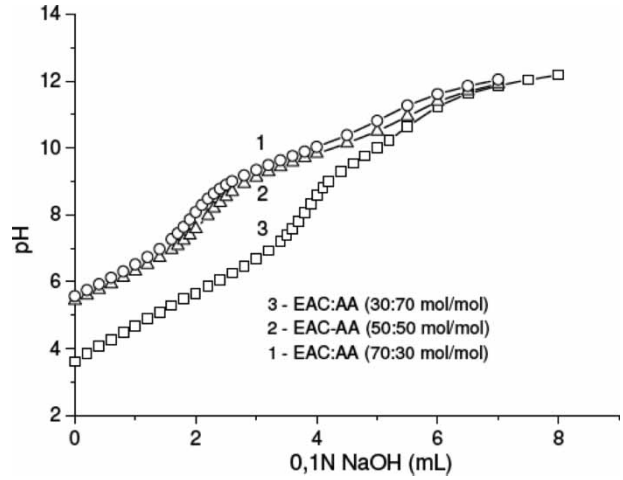


Fig. 7. Potentiometric titration curves of polymers synthesized at various composition of monomers in the feed.

Table 3. Acid-base content and ionization constants of PCEAC synthesized in various solvents[a]

Solvent	[COOH], mol%	[NH], mol%	pK_a (COOH)	pK_a (NH)
Water	59	41	5.44	9.50
Ethanol	51	49	—	—
Water-Ethanol (1:1 vol/vol)	48	52	—	—
DMF	55	45	5.87	9.62
Hexane	68	32	5.35	9.65
Chloroform	62	38	5.65	9.75

[a]The feed composition is 50:50 mol%. The volume ratio of solvent and monomer mixture is 1:1 vol/vol.

3-(cyclohexyl)aminocrotonate] (PCECHAC). This is probably due to participation of water molecules in proton transport *via* hydrogen bonds as was shown in particular by the authors (32).

The addition of water into the reaction mixture considerably increases the degree of swelling of hydrogels (Table 4). This is probably due to participation of water molecules in formation of hydrogen bonds with functional groups of monomers in prepolymerization conditions.

The yield of polycarboxybetaines synthesized in bulk is a function of alkyl chain length and increases in the following order: carboxyethyl 3-(diisopropyl)aminocrotonate (CEDIPAC) > carboxyethyl 3-(isopropyl)aminocrotonate (CEIPAC) > carboxyethyl 3-(propyl)aminocrotonate> carboxyethyl 3-(cyclohexyl)aminocrotonate (CECHAC) > carboxyethyl 3-(methyl)aminocrotonate (CEMAC) > carboxyethyl 3-aminocrotonate (CEAC) (Table 5). Such tendency is probably connected with bulky alkyl groups, which stabilizes the more reactive *trans*-conformation of monomers.

Increasing the hydrophobicity influences the equilibrium between zwitterionic (charged) and molecular (uncharged) forms. For example, PCEAC preferentially exists in zwitterionic form (a) while substitution of hydrogen by bulky disiopropyl moieties stabilizes the molecular state (b) (Scheme 10).

Figure 10 represents the dependence of PCEAC yield on initiator concentration. The optimal concentration of initiator is found to be 1 wt% from the monomer mass.

Linear and crosslinked polymers containing carboxybetaine (1), sulfobetaine (2) and quaternary ammonium (3) groups were also synthesized by a Michael addition reaction (Scheme 11) (33). The structure of the macromolecules was established by FTIR spectroscopy. Disappearance of intense peaks at $\nu = 1659, 1622, 1640\ cm^{-1}$, which belong to C═C and C═N bonds of EAC and C═C bonds of sodium acrylate and broadening and shifting of intense lines of primary amine groups of EAC at $\nu = 3440, 3334\ cm^{-1}$ and $3376\ cm^{-1}$ confirms the formation of a polymer product.

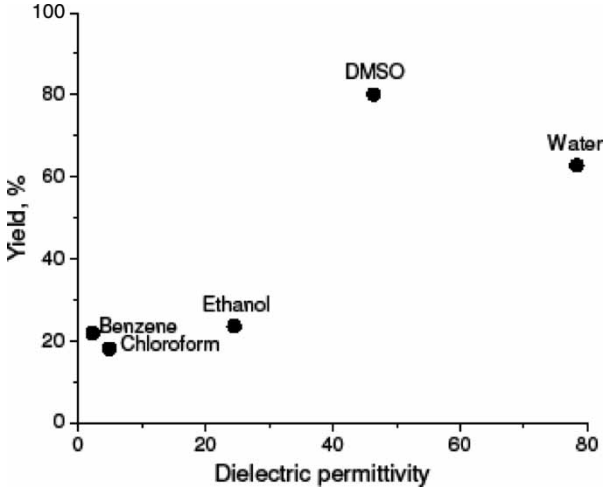


Fig. 8. Yield dependence of PCEAC on dielectric permittivity of solvents.

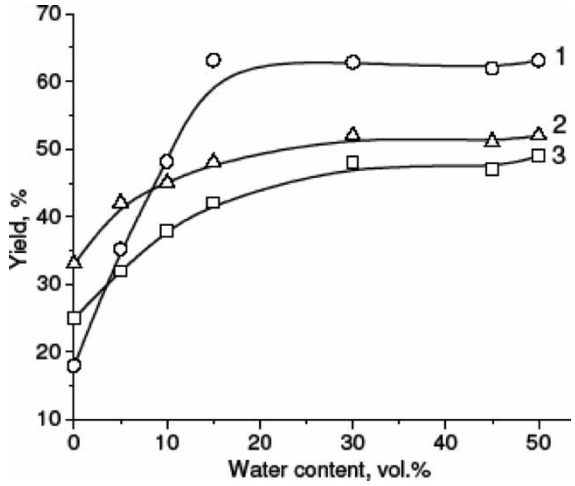


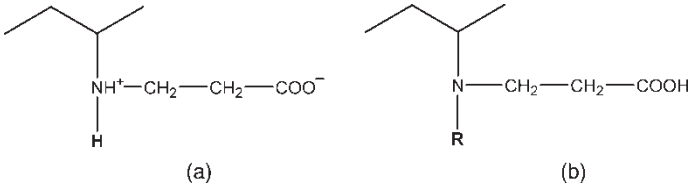
Fig. 9. Influence of water content on the yield of PCEAC (1), PCEPAC (2) and PCECAC (3).

Table 4. The influence of water content on the swelling degree of PCEPAC and PCECHAC

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

Table 5. The yield of polycarboxybetaines in bulk derived from the N-substituted ethyl 3-aminocrotonates

Monomers	CEDIPAC	CEIPAC	CEPAC	CECHAC	CEMAC	CEAC
Yield of polymer, %	56	40	33	25	22	18



Sch. 10. Zwitterionic (a) and molecular (b) forms of poly(carboxyethyl 3-aminocrotonate) (a) and poly[carboxyethyl 3-(diisopropyl)aminocrotonate] (b).

Asymmetric vibrations of carboxylate-ions appear at $\nu = 1556$ and 1562 cm^{-1}. Intense bands at $\nu = 1186$ and 1036 cm^{-1} are specific for SO_3^- groups.

By condensation of acetoacetic ester with aminoalcohols and aminoacids, followed by *via* Michael addition reaction, a series of polymeric betaines modified by ethanolamine (PCEAC-Ea), glycine (PCEAC-Gly), β-alanin (PCEAC-Ala), and L-lysine (PCEAC-Lys) were synthesized and their structures were identified by ^{1}H-NMR spectroscopy (34) (Scheme 12). Phosphatidylethanolamine-containing

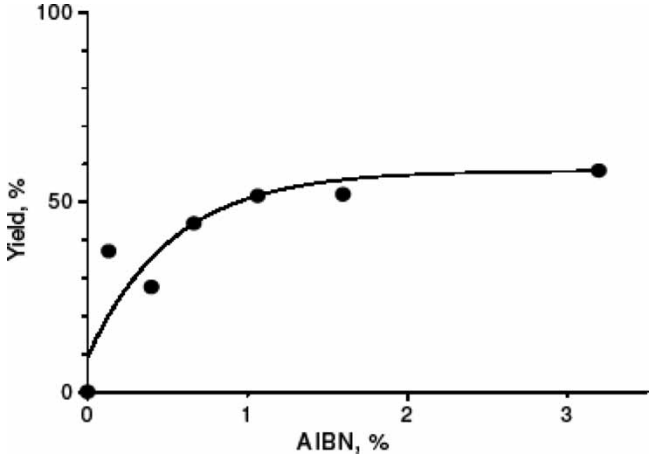
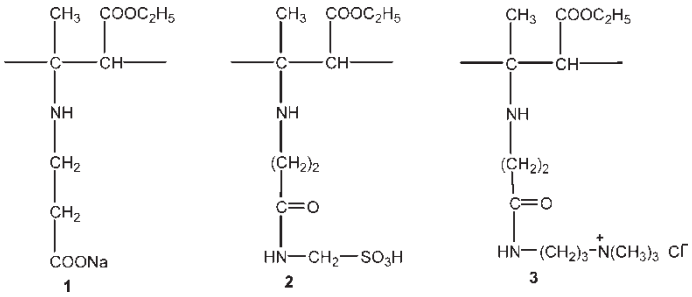
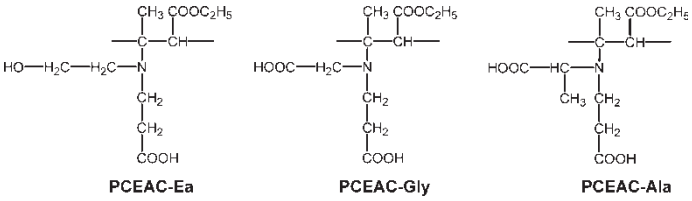


Fig. 10. Influence of initiator concentration on the yield of PCEAC.

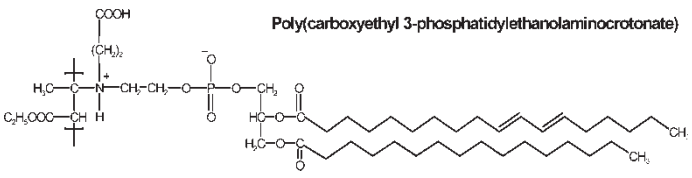


Sch. 11. Structural formulas of aminocrotonate polymers containing carboxybetaine (1), sulfobetaine (2) and quaternary ammonium (3) groups.

monomers and polymers were also synthesized in bulk, chloroform and ethanol (35–37) (Scheme 13). These polymers contain the hydrophobic "tails" and hydrophilic (or zwitterionic) "heads" and are able to undergo



Sch. 12. Poly(carboxyethyl 3-aminocrotonate) modified by ethanolamine (PCEAC-Ea), glycine (PCEAC-Gly), and β-alanin (PCEAC-Ala).



Sch. 13. Phosphatidylethanolamine-containing poly(carboxyethyl 3-aminocrotonate).

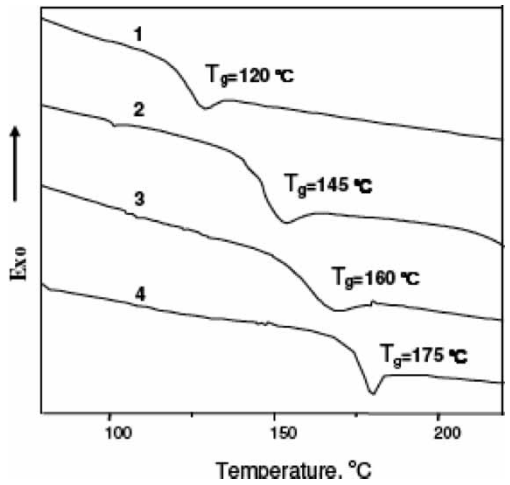


Fig. 11. DSC curves of PCEAC (1), poly[carboxyethyl 3-(methyl) aminocrotonate] (PCEMAC) (2), PCEPAC (3) and PCECHAC (4).

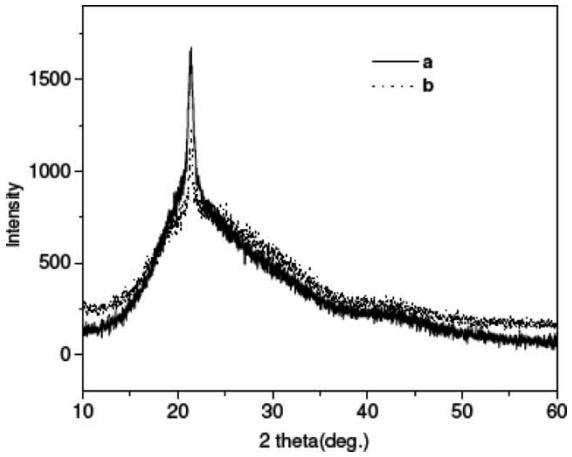


Fig. 13. X-ray diffractogram of carboxyethyl 3- phosphatidylethanolaminocrotonate (a) and poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) (b).

conformational transition from a compact polysoap-like conformation to an expanded polyelectrolyte-like state.

3 Results and Discussion

3.1 Physico-Chemical Characteristics of Linear and Crosslinked Polybetaines

3.1.1 Properties of Some Linear Polybetaines in Condensed State

Figure 11 shows the results of DSC for a series of polybetaines that differ each other by N-alkyl substitutes (18). The glass transition temperatures T_g of polycarboxybetaines synthesized in bulk are shifted to a high temperature region in the following order: PCECHAC > PCEPAC > PCEMAC > PCEAC. The influence of solvent nature on the T_g of PCEAC synthesized in various solvents was also studied. The results show that the dependence on solvent nature of the T_g of PCEAC arrange as follows: water (214°C) ≈ ethanol (213°C) > chloroform (205°C) > hexane (190°C) > benzene (180°C). This sequence is in good agreement with the relative dielectric permittivity of the solvents.

DSC curves of the carboxyethyl 3-phosphatidylethanolaminocrotonate and poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) are shown in Figure 12 (36, 37). For the carboxyethyl 3-phosphatidylethanolaminocrotonate, the transition from the liquid crystalline mesophase to isotropic state takes place at 265°C while for poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) it corresponds to 270°C. XRD spectra of carboxyethyl 3-phosphatidylethanolaminocrotonate and poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) show the appearance of crystalline reflections at $2\theta = 21.4^\circ$ (Figure 13). This is probably connected with highly ordered phosphatidyl "tails", which are closely packed into a crystalline structure.

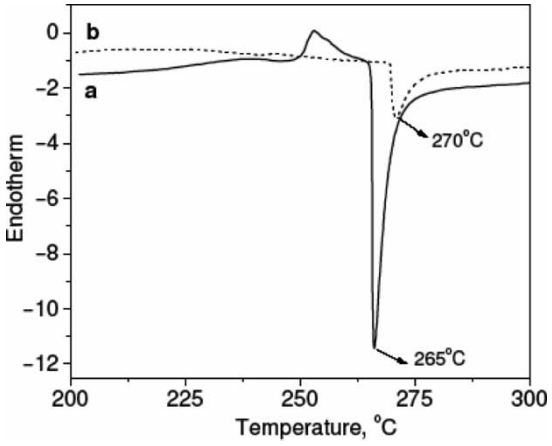


Fig. 12. DSC curves of carboxyethyl 3-phosphatidylethanolaminocrotonate (a) and poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) (b).

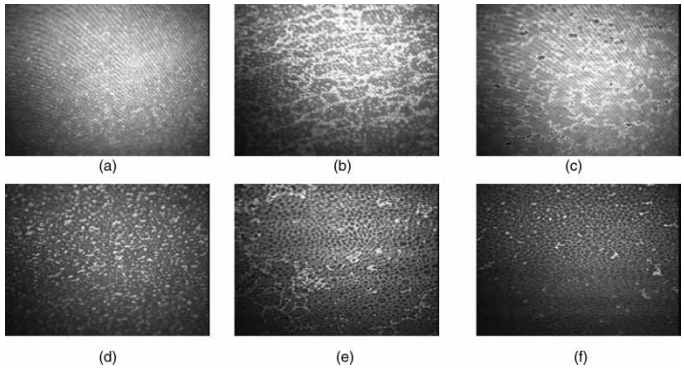


Fig. 14. TEM images of poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) at 210 (a), 330 (b), 450 (c), 510 (d), 580 (e) and 640 $Å^2$/molecule (f).

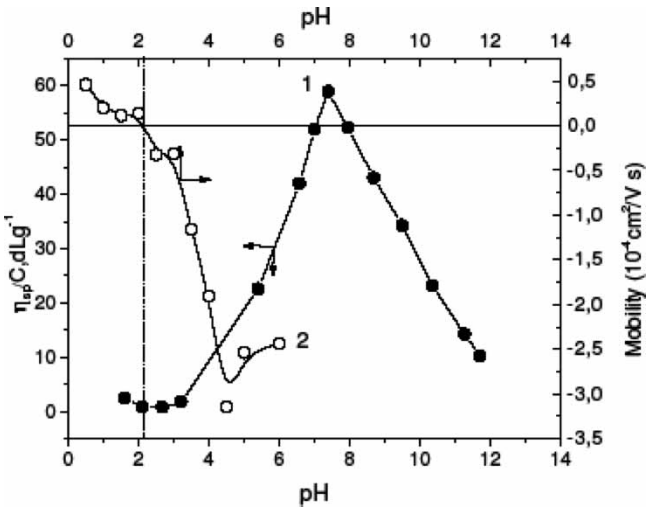


Fig. 15. Reduced viscosity (curve 1) and electrophoretic mobility (curve 2) of the PCEAC vs. pH of the solution.

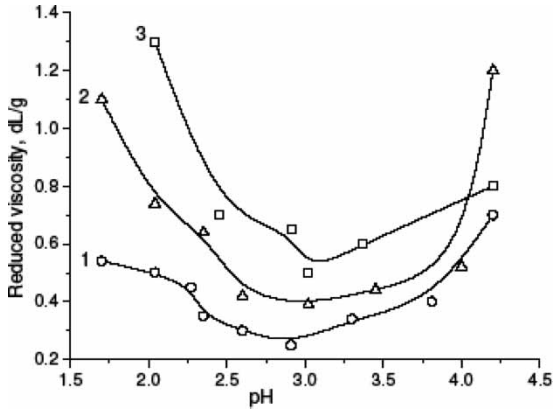


Fig. 16. pH dependencies of the reduced viscosities of the PCEMAC (1), PCEEAC (2) and PCEPAC (3) in water.

Langmuir-Blodgett multilayers of poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) were assembled to construct a model of a biomembrane system by LB technique (38). Figure 14 shows the TEM images from which the surface pressure (π) – area (A) isotherm for poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) was determined. The area extrapolated to $\pi = 0$ is equal to 310 Å^2/molecule.

Table 7. The average molecular weights, the intrinsic viscosities and the PDI of polycarboxybetaines

Polybetaines	$M_n \cdot 10^{-4}$	$M_w \cdot 10^{-5}$	$[\eta]$, dL · g^{-1}	PDI
PCECHAC	7.2	3.5	19.4	4.9
PCPPAC	3.4	3.7	10.5	10.9
PCPCHAC	7.8	4.8	4.0	6.2

3.2 Behavior of Linear Polybetaines in Solutions

The influence of pH on the viscosity and electrophoretic mobility of PCEAC was studied (22, 31, 39). The minimal viscosity and the zero mobility are observed near of pH 2.1–2.2 that corresponds to the isoelectric point (IEP) (Figure 15). 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 by suppression of the 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 ($pH_{IEP} \approx 2.1$) may be the result of different accessibility of carboxylic and secondary amine groups to ionization. Carboxylic groups disposed far from the main chain can be ionized more easily than the secondary amine groups that are near the main chain and in a hydrophobic environment. Therefore, ionization of carboxylic groups more effectively unfolds the macromolecule than the ionization of 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.

Increasing the hydrophobicity of polybetaines increases the pH values of the IEP in the following order: PCEPAC (3.1) > PCEEAC (2.9) > PCEMAC (2.7) > PCEAC (2.1) (Figure 16).

The hydrodynamic parameters of poly(carboxyethyl 3-aminocrotonate) (PCEAC) in dependence on pH are shown in Table 6 (40). A small radius of gyration R_g, not defined with the wavelength of the incident light source used, the negative value of the second virial coefficient A_2, and the low value of the reduced viscosity η_{sp}/C at

Table 6. The hydrodynamic parameters of PCEAC in aqueous solution at different pH and $\mu = 0.1$

Polymer	pH	M_n[a]	PDI[a]	M_w	R_g, nm	η_{sp}/C, dL · g^{-1}	$A_2 \times 10^{-4}$, cm^3 · mol · g^{-2}	Mean[b] d_h, nm	Peak[b] d_h, nm
PCEAC	2.1	—	—	44000	undefined	0.5	−38.8	40	18
	7.0	31000	2.15	96000	32	60.0	18.9	191	16

[a]Results are obtained using SEC.
[b]DLS results are obtained at fixed polymer concentration and 90° scattering angle.

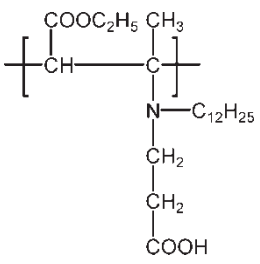
Table 8. The average molecular weights and the PDI of PCEAC modified by aminoacids

Polybetaines	The average molecular weight				η_{sp}/C, $dL \cdot g^{-1}$	PDI
	$M_n \cdot 10^{-4}$	$M_w \cdot 10^{-5}$	$M_z \cdot 10^{-6}$	$M_{z+1} \cdot 10^{-6}$		
PCEAC-Gly	2.5	7.24	2.8	5.16	3.2 (C = 0.2%)	28.94
PCEAC-Ala	2.9	8.01	2.76	5.01	—	27.74
PCEAC-Lys	18.7	16.0	3.53	5.15	13.4 (C = 0.2%)	8.44

pH = 2.1 confirm a very compact conformation of polymer particles at the IEP. The values of R_g, A_2, and η_{sp}/C of the PCEAC at pH = 7.0 correspond to the expanded state of macromolecules and correlate well with the data of Figure 15.

Table 7 represents the average number molecular weight (M_n), the average weight molecular weight (M_w), the intrinsic viscosity ([η]) and polydispersity index (PDI) of poly[carboxyethyl 3-(cyclohexyl)aminocrotonate] (PCECHAC), poly[carboxypropyl 3-(propyl)aminocrotonate] (PCPPAC) and poly[carboxypropyl 3-(cyclohexyl)aminocrotonate] (PCPCHAC) (40). The molecular weights and PDI of poly(carboxyethyl 3-aminocrotonate) (PCEAC) modified by glycine (PCEAC-Gly), β-alanine (PCEAC-Ala), and L-lysine (PCEAC-Lys) derived from the gel permeation chromatograms are given in Table 8 (34). The specific peculiarity of polycarboxybetaines modified by aminoacids is the high viscosity and PDI. This is probably accounted for by existence of intermacromolecular associates stabilized by ionic and hydrogen bonds.

Hydrophobically modified polybetaines, namely poly (carboxyethyl 3-phosphatidylethanolaminocrotonate) (see Scheme 13) and poly[carboxyethyl 3-(dodecyl)aminocrotonate] (Scheme 14) combine the behavior of zwitterionic and amphiphilic polymers (36), (37, 41). Due to the superposition of hydrophobic and ionic interactions, they favor the formation of self-organized and (micro)phase-separated systems in solution, at interfaces as well as in the bulk phase. The dependence of pK_a on ionization degree (α) for poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) exhibits the nonmonotonic changing of pK_a (Figure 17). The values of pK_a increase with α and show a maximum at $\alpha \approx 0.4$. This is attributed to the change of poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) from a compact polysoap-like conformation to an expanded polyelectrolyte-like state.



Sch. 14. Structural formula of poly[carboxyethyl 3-(dodecyl) aminocrotonate].

The electrostatic Gibbs energy (G_{el}) that corresponds to the additional work required to remove the protons from the macromolecule was calculated according to the equation: $\Delta G_{el} = 2.303\ RT \cdot A$ (where R is Boltzman's constant, T is absolute temperature, A is area of conformational change corresponding to shaded region in Figure 17) is equal to 45.72 $kJ \cdot mol^{-1}$. This value of ΔG_{el} found for poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) is much higher than that of ΔG_{el} for PMAA (42) and hydrophobically modified polyelectrolytes (43). This is accounted for by the more stable, compact conformation of poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) due to stabilization of its globular structure by hydrophobic interactions of phosphatidyl "tails" that need more electrostatic force to disrupt. The apparent ionization constants (pK_a) of OPOH, COOH and NH^+ groups, found from the Henderson-Hasselbalch equation, are equal to 2.57, 4.75 and 7.08 respectively, and these values coincide well with the acidic strength of phosphoric, carboxylic and amine groups (Figure 17). Increasing of the reduced viscosity of poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) with decreasing of concentration is due to electrostatic repulsion of charged (phospho- and carboxylic) groups (Figure 18).

Figure 19 illustrates the changes of the intrinsic viscosity and of the swelling degree of linear and crosslinked poly[carboxyethyl 3-(dodecyl)aminocrotonate] (PCEDDAC) in

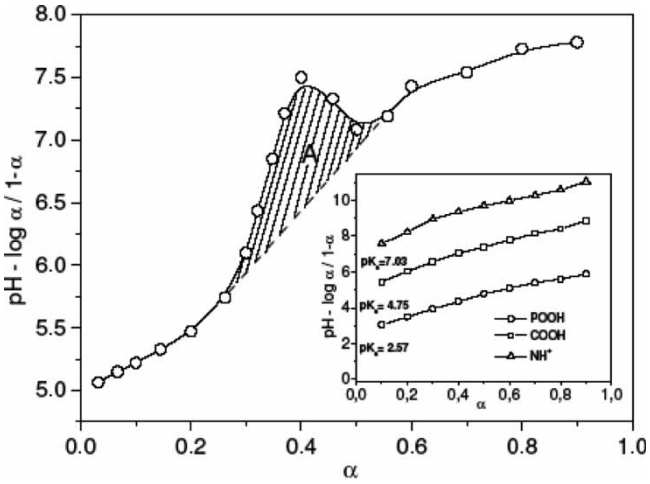


Fig. 17. Potentiometric titration curve of poly(carboxyethyl 3-phosphatidylethanolaminocrotonate) and the values of apparent ionization constants of its functional groups.

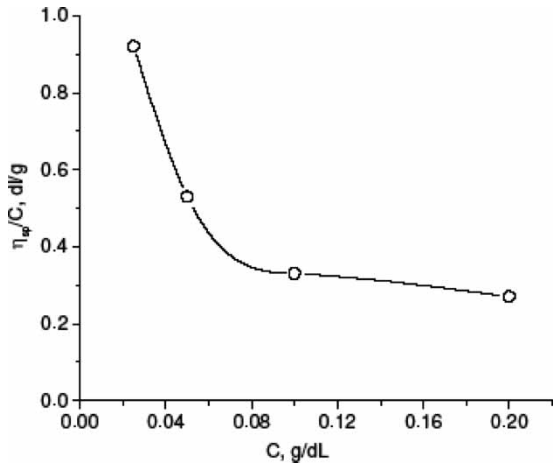


Fig. 18. Dependence of the reduced viscosity of poly(carboxyethyl 3-phosphatidylethaminocrotonate) on its concentration.

water-DMSO mixtures (41). The insoluble betaine parts of PCEDDAC tend to aggregate in pure DMSO and form intra- or interchain associates surrounded by a hydrophobic corona. Addition of 10 vol% of water to DMSO increases considerably both the swelling degree and the intrinsic viscosity. A reasonable explanation of this phenomenon may be the unfolding of the macromolecules due to the preferential solvation of the betaine fragments of PCEDDAC by water, and of the dodecyl chains by the organic solvent. However, a further enrichment of the solvent mixture by water causes the shrinking of the macromolecules, due to reversible micelle formation stabilized by hydrophobic interactions of the long alkyl chains. The insolubility of PCEDDAC at more than 30 vol% of water is probably connected with a strong compaction of the polymer particles. A hypothetical structure of PCEDDAC in DMSO, water-DMSO, and water environments is presented in Scheme 15.

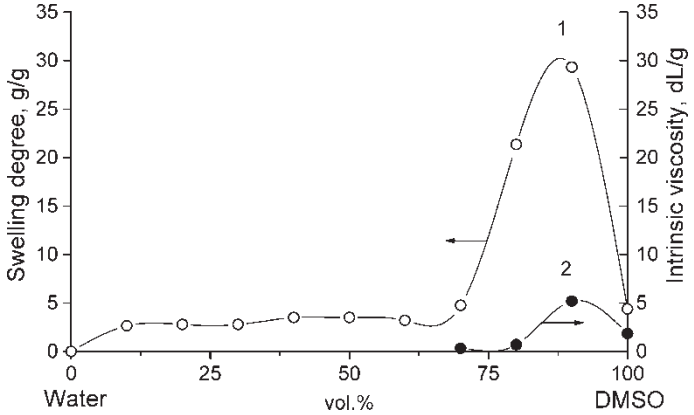
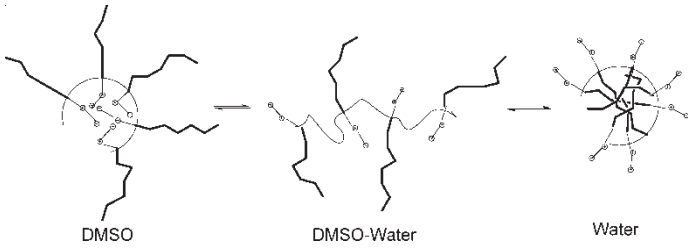


Fig. 19. Dependence of the swelling degree (curve 1) and the intrinsic viscosity (curve 2) of PCEDDAC in water-DMSO mixture.



Sch. 15. Conformation of linear poly[carboxyethyl 3-(dodecyl) aminocrotonate] in DMSO, DMSO-water and water solutions.

3.3 Volume-Phase Transitions in Polybetaine Gels

Table 9 summarizes the swelling degree of crosslinked betaines in water and organic solvents (44). In polar solvents, the swelling degree of hydrogels changes in the following order: water >>DMSO >>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.

The stimuli-responsive properties of polybetaine gels were studied with respect to pH, ionic strength, and solvent nature (45–47). pH-dependent behavior of gel sample is bell-shaped (Figure 20). Contraction of hydrogels in strong acidic region is explained by suppression of ionization degree of carboxylic groups by mineral acid. Considerable swelling of hydrogels at pH$\sim$8 is the result of ionization of carboxylic groups. Shrinking of gel specimen at pH > 8 is probably accounted for suppression of polyelectrolyte affect by the excess of NaOH that plays the role of low-molecular-weight electrolyte. These results are in good agreement with SEM data obtained at pH = 1.1, 7.0 and 12.4, when conformation of macromolecules is in collapsed, swollen and shrunken states. In acidic region the pore size of PCECAC is in the range of 15–20 μm. In a neutral region, the pores increase up to 80–100 μm, and in a strong base region they decrease up to 40–50 μm. A sharp decrease of the swelling degree and pore size of PCEPAC and PCECAC at $\mu = 10^{-4} - 10^{-2}$ is connected by screening of macromolecules

Table 9. Swelling degree of hydrogels in the presence of various crosslinkers and in organic solvents medium

		Swelling degree, g/g	
Solvent	Crosslinker	PCEPAC	PCECHAC
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

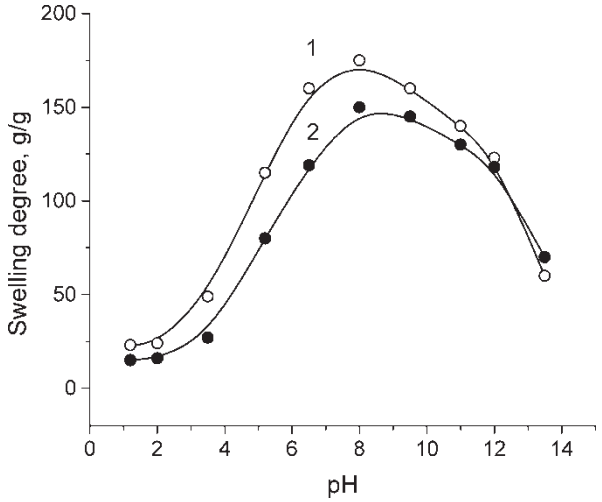


Fig. 20. pH dependent swelling of PCEPAC (1) and PCECHAC (2).

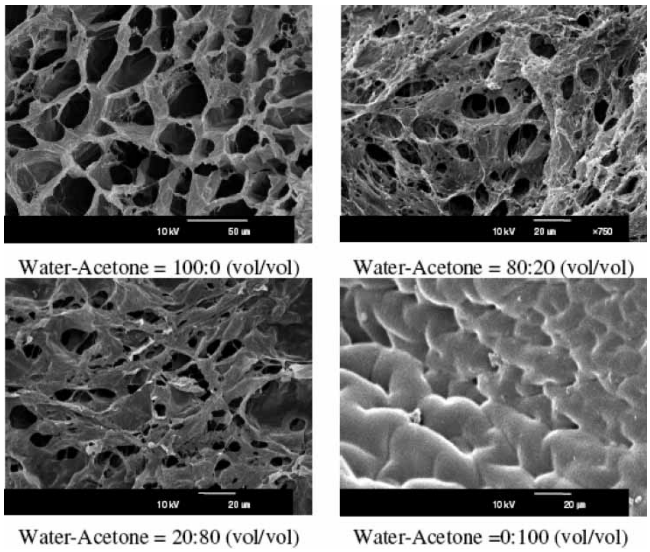


Fig. 22. SEM pictures of PCECHAC gel in water, acetone and water-acetone mixtures.

charges by low-molecular-weight electrolytes. In pure ethanol and acetone, the gel network is in a collapsed state due to the significant suppression of ionization and poor thermodynamic quality of solvents with respect to ionizable groups of polyelectrolytes (Figure 21).

SEM pictures of PCECAC taken in water-acetone mixtures are also in good agreement with swelling-deswelling behavior of such hydrogels (Figure 22). The average pore size of PCECAC gel in pure water is 30–40 μm. Increasing the acetone content in the water-acetone solvent mixture results in a decrease of the gel pore size down to 15–20 μm. In pure acetone, the gel sample is in collapsed state with pore size of 1–2 μm.

It is well known that polyelectrolyte gels swell, shrink, or bend when an external electric current is applied (48). The bending behavior of PCEPAC gels was studied under an externally imposed DC electric field (49–51). A gel rod placed parallel to the electrodes bends to the cathode side. If the electric stimulus is removed, the gel gradually returns to the original position. When the polarity of the electrodes is altered, the gel bends toward the opposite direction. The bending angle increases with increasing voltage across the gel. The driving force of the bending toward the negative electrode is the swelling of the gel on the anode, and the shrinking on the cathode side induced by the osmotic pressure difference. If the gel rod is placed perpendicular to the electrodes, the applied DC electric field causes a sharp appearance of pH gradient during 1–2 min. After 5 min, the pH value becomes stable. The magnitude of the pH in the gel volume returns quickly to the initial state if the electricity is switched off. Figure 23 presents the dependence of the pH on the distance $\pm L$ when the glass electrode is placed on the cathode or anode side of a gel specimen in comparison with its central section where $L = 0$. Without an applied DC electric field, the pH gradient along the sample is uniform and equal to 5.46. An increase of the electric field shifts the pH gradient to the more acidic region. The dependence of the pH gradient on L is linear, but the slopes of the straight lines differ and depend on the value of the applied DC electric field. Appearance of pH gradient is interpreted as follows: the externally imposed potential across the gel causes the accumulation of negative fixed charges (COO^-) and mobile ions (OH^-) on the anodic side (zone A), while the accumulation of positive fixed charges (NH_2^+) and mobile ions (H^+) takes place on the cathodic side (zone C). Zone B probably contains an equal number of positive and negative charges. As a result, zones A, B, and C have comparatively a basic, neutral, and acidic character, respectively. Increasing the DC electric current leads to

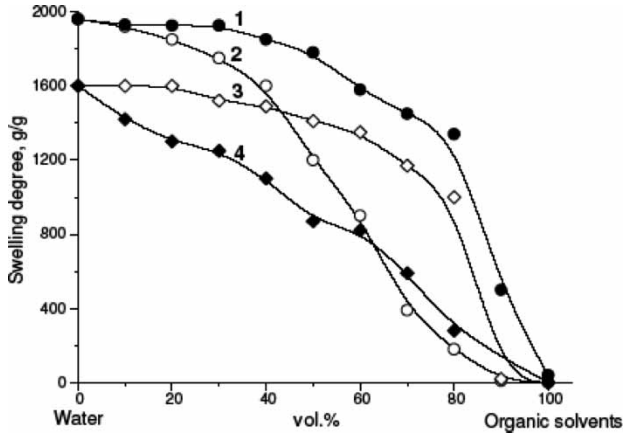


Fig. 21. Swelling-deswelling behavior of crosslinked PCEPAC (1,2) and PCECHAC (3,4) in water-acetone (1,3) and water-ethanol (2,4) mixtures.

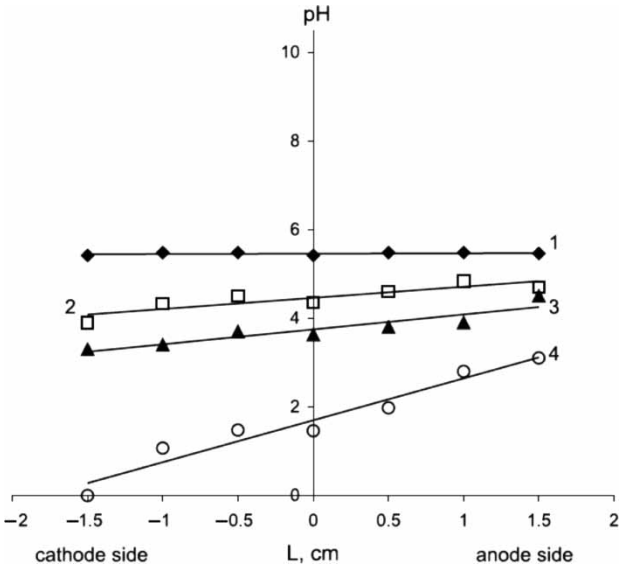


Fig. 23. Dependence of pH gradient on distance L without the imposed DC electric field (1) and at E = 5 (2), 10 (3) and 15 volts (4).

the overall acidifcation of the gel sample (Figure 23, curve 4) due to the easy ionization of the acidic groups. Consequently, this narrows the zones B and C and expands zone A.

4 Conclusions

The synthetic strategy, solution properties, conformational and volume-phase transitions of linear and crosslinked polymeric betaines based on ethyl 3-aminocrotonate and its N-substituted alkyl derivatives are outlined in this review. The specific peculiarity of aminocroronates is enamine-imine tautomerism and their ability to spontaneous polymerization in bulk in the presence of unsaturated carboxylic acids proceeding *via* the Michael addition reaction. The mechanism of spontaneous polymerization can probably be explained by initiation of reactions with the help of «shuttling protons» migrating from the enamine to imine form (or *vice versa*). The addition of water into the reaction mixture considerable increases the yield of linear polybetaines and swelling degree of betaine type hydrogels due to participation of water molecules in proton transformation process and formation of hydrogen bonds with functional groups of monomers in prepolymerization conditions. Anomalous low values of the isoelectric points of polybetaines are explained by different accessibility of carboxylic and secondary amine groups to ionization. Hydrophobically modified polybetaines in solid state exhibit the phase transition from the liquid crystalline to isotropic state, while in aqueous solution they demonstrate the conformational transition from the coiled to expanded structure. Volume transition of polybetaine gels in response to pH, ionic strength, solvent quality and DC electric field is interpreted in the light of ionization state of functional groups, screening of electrostatic interactions, condensation of charged network with counterions, and migration of hydrated ions and water molecules within network. Appearance of pH gradient along the gel specimen is accounted for polarization of network under the applied externally DC electric field. The accumulated knowledge on synthesis-structure-property relationships is effective tool for development of wastewater purification technology, protein separation principle, drug delivery system, soil structuring agent, pour point depressants etc.

5 References

1. Candau, F. and Joanny, J.F. *Polymeric Materials Encyclopedia*; Salamone, J.C. (ed.); CRS Press: Boca Raton, 5476–5488, 1996.
2. Kudaibergenov, S.E. (1999) *Adv. Polym. Sci.*, **144**, 115–197.
3. Kudaibergenov, S.E. *Polyampholytes: Synthesis, Characterization and Application*; Kluwer Academic/Plenum Publishers: New York, 2002.
4. Lowe, A.B. and McCormick, C.L. (2002) *Chem Rev.*, **102**, 4177–4189.
5. Dobrynin, A.V., Colby, R.H. and Rubinstein, M. (2004) *J. Polym. Sci. Part B: Polym. Phys.*, **42**, 3513–3538.
6. Kudaibergenov, S.E., Jaeger, W. and Laschewsky, A. (2006) *Adv. Polym. Sci.*, **201**, 157–224.
7. Bekturov, E.A. and Kudaibergenov, S.E. (1986) *J. Macromol. Sci. Phys.*, **B25**, 133–151.
8. Bekturov, E.A. and Kudaibergenov, S.E. (1989) *Makromol. Chem. Macromol. Symp.*, **26**, 281–295.
9. Bekturov, E.A., Kudaibergenov, S.E. and Rafikov, S.R. (1990) *J. Macromol. Sci. Rev.*, **C30**, 233–303.
10. Bekturov, E.A., Kudaibergenov, S.E. and Rafikov, S.R. (1991) *Uspekhi Khimii (Adv. Chem.)*, **60**, 835–851.
11. Murzagulova, K.B. Doctoral Thesis; Almaty, Kazakhstan, 1999; Vol. 58.
12. Kudaibergenov, S.E., Bimendina, L.A., Yashkarova, M.G., Orazzhanova, L.K. and Sigitov, V.B. *Sintez, Issledovanie i Primenenie Polimernykh Betainov na Osnove Aminokrotonatov*; Semipalatinsk State Shakarim University: Semipalatinsk, 2006.
13. Freimans, Ya.F. *Khimiya Enaminoketonov, Enaminoiminov, Enaminotionov*; Zinatne: Riga, 1974.
14. Seher, A. (1951) *Arch. Pharm.*, **284**, 371.
15. Lammertsma, K. and Prasad, B.V. (1994) *J. Am. Chem. Soc.*, **116**, 642.
16. Koizhaiganova, R.B., Bimendina, L.A. and Kudaibergenov, S.E. (2004) Second Intern. Scientific-Practical Conference, Karaganda, Kazakhstan, March, 22–24, 2004.
17. Kerselidze, D.A., Zarkua, T.Sh., Kikalishvili, T.D., Churguliya, E.D. and Makaridze, M.C. (2002) *Uspekhi Khimii (Adv. Chem.)*, **71**, 1120.
18. Kudaibergenov, S.E., Kozhabekov, D.B., and Geckeler, K.E, (2002) *Kazakhstan Patent*, No. 14007.
19. Schulz, R.C., Schmidt, M., Schwarzenbach, E. and Zoller, E.J. (1989) *Macromol. Chem. Macromol. Symp.*, **26**, 221.
20. Luca, C., Mihailescu, S. and Popa, M. (2002) *Eur. Polym. J.*, **38**, 1501.

21. Gibas, M. and Korytkowska-Walach, A. (2003) *Polym. Bull.*, **51**, 17–22.
22. Koizhaiganova, R.B., Kudaibergenov, S.E. and Geckeler, K.E. (2002) *Macromol. Rapid. Commun.*, **23**, 1041–1044.
23. Huyghe, G., Koizhaiganova, R., Kudaibergenov, S. and Geckeler, K. (2002) *Proc. of International monitoring conference* "*Development of Rehabilitation Methodology of Environment of the Semipalatinsk Region Polluted by Nuclear Tests*" Semipalatinsk, September, 22–24.
24. Noh, J.G., Sung, Y.J., Kudaibergenov, S.E. and Geckeler, K.E.Abstracts of the 2nd K-JIST/NAIST Joint Symposium on Advanced Materials, Nara, Japan, 2002.
25. Kudaibergenov, S.E. *Intern. Symp. on Polyelectrolytes*. Sweden, Lund University. (2002) Koizhaiganova, R.B., Bimendina, L.A., and Kudaibergenov, S.E. *Abstr. of Intern. Symp. on Polyelectrolytes*, Massachusetts, Amherst, 2004.
26. Koizhaiganova, R.B. (2004) *Vestnik Natl. Acad. Nauk Republic of Kazakhstan*, **2**, 157–162.
27. Koizhaiganova, R.B., Bimendina, L.A. and Kudaibergenov, S.E. (2004) *Poisk*, **4**, 9–14.
28. Koizhaiganova, R.B., Sigitov, V.B., Bimendina, L.A. and Kudaibergenov, S.E. (2005) *Polym. Bull.*, **53**, 161–168.
29. Noh, J.-G., Sung, Y.-Ju., Geckeler, K.E. and Kudaibergenov, S.E. (2005) *Polymer*, **46**, 2183–2190.
30. Baraki, H., Habaue, S. and Okamoto, Y. (1999) *Polym. Prepr.*, **40**(**2**), 807.
31. Kudaibergenov, S.E., Didukh, A.G., Zhumadilova, G.T., Koizhaiganova, R.B., Bimendina, L.A., Noh, J.-G. and Geckeler, K.E. (2004) *Macromol. Chem. Macromol. Symp.*, **207**, 153–171.
32. Kabanov, V.A., Zubov, V.P. and Semchikov, Yu.D. Kompleksno-radikal'naya Polimerizatsiya Khimiya: Moscow, 1987.
33. Kudaibergenov, S.E., Ibraeva, Zh.E., Bimendina, L.A. and Sigitov, V.B. (2006) *Doklady Natl. Acad. Nauk Republic of Kazakhstan*, **4**, 40–44.
34. Kudaibergenov, S.E., Sigitov, V.B., Choi, S.-H. and Geckeler, K.E. (2006) *Doklady Natl. Acad. Nauk Republic of Kazakhstan*, **5**, 41–51 (in English).
35. Nepal, D., Kudaibergenov, S.E. and Geckeler, K.E. *Korea Polymer Science Meeting*; Seoul, 2003.
36. Ibraeva, Zh.E., Nepal, D., Geckeler, K.E., Bimendina, L.A. and Kudaibergenov, S.E. (2004) *Doklady Acad. Nauk Republic of Kazakhstan*, **3**, 25–34 (in English).
37. Kudaibergenov, S.E., Ibraeva, Zh.E., Nepal, D., Geckeler, K.E. and Bimendina, L.A. (2004) *Vestnik of Kazakh Natl. Univ. Ser. Khim.*, **4**(36), 483–487 (in English).
38. Kudaibergenov, S.E., Ibraeva, Zh.E., Bimendina, L.A., Hahn, M., Jaeger, W., Laschewsky, A., Yeroshina, S. and Ibraev, N. *Materials of the European Polymer Congress*, Moscow, June 27-July 1, 2005.
39. Didukh, A.G., Makysh, G.Sh., Bimendina, L.A. and Kudaibergenov, S.E. *Advanced Macro- and Supramolecular Materials and Processes*; Geckeler, K.E. (ed.); Kluwer Academic/Plenum Publishers: New York, 2002, 139–153.
40. Didukh, A.G., Koizhaiganova, R.B., Bimendina, L.A., Geckeler, K.E. and Kudaibergenov, S.E. (2005) *Izv. Akad. Nauk Republic of Kazakhstan, Ser. Khim.*, **2**, 95–105 (in English).
41. Didukh, A.G., Koizhaiganova, R.B., Bimendina, L.A. and Kudaibergenov, S.E. (2003) *J. Appl. Polym. Sci.*, **92**, 1042–1048.
42. Bekturov, E.A. and Bakauova, Z.Kh. Synthetic Water-Soluble Polymers in Solutions; Huthig & Wepf: Heidelberg, 1986.
43. Wang, C., Tam, K.C. and Jenkins, R.D. (2002) *J. Phys. Chem.*, **106**, 1195.
44. Didukh, A.G., Koizhaiganova, R.B., Khamitzhanova, G., Bimendina, L.A. and Kudaibergenov, S.E. (2003) *Polym. Intern.*, **52**, 883–891.
45. Choi, S.H., Geckeler, K.E., Didukh, A.G. and Kudaibergenov, S.E. *Abstr. Intern. Symp. on Frontiers in Molecular Science 2002*, Quindao, P. R. China, 2002; 15.
46. Didukh, A.G., Sigitov, V.B., Bimendina, L.A., Kudaibergenov, S.E., Noh, J.G. and Sung, Y.J. (2004) *Izv. Acad. Nauk Republic of Kazakhstan, Ser. Khim.*, **1**, 96–105.
47. Koizhaiganova, R.B., Bimendina, L.A. and Kudaibergenov, S.E. (2004) *Kazakhstani Science News*, **4**(**82**), 9–14.
48. Osada, Y. and Gong, J-P. (1998) *Adv. Mater.*, **10**, 827–837.
49. Kudaibergenov, S.E., Sigitov, V.B., Didukh, A.G. and Moldakarimov, S.B. (2002) *Polym. Prepr.*, **41**(**1**), 724–725.
50. Kudaibergenov, S.E., Didukh, A.G. and Moldakarimov, S.B. *ACS Symposium Series 833 Polymer Gels. Fundamentals and Applications*; Bohidar, H.B., Dubin, P. and Osada, Y. (eds.); ACS: Washington, DC, 149–162, 2002.
51. Didukh, A.G., Sigitov, V.B. and Kudaibergenov, S.E. (2004) *Vestnik Kazakh Natl, Univ. Ser. Khim.*, **3**(**35**), 168–172.