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Solution behavior of quenched or strongly charged polyampholytes in aqueous-salt solutions

Quenched (or strongly charged) polyampholytes based on fully charged anionic monomer — sodium salt of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and cationic monomer — (3-acrylamidopropyl)-trimethylammonium chloride (APTAC) were synthesized by radical copolymerization and their behavior was studied in aqueous-salt solutions. A series of unbalanced (AMPS-25 and AMPS-75) and balanced (AMPS-50) quenched polyampholytes were characterized by 1H NMR, FTIR, GPC, DLS, viscosity, DSC, TGA. It was established that at the isoelectric point (IEP) the quenched polyampholytes in aqueous solutions are stabilized by cooperative intraionic contacts between strong charged anionic and cationic moieties. The conformational state of AMPS-25 and AMPS-75 in aqueous solution is represented as «core» and «shell» structure. The «core» part behaves polyampholyte character (PA region) while the «shell» part exhibits polyelectrolyte effect (PE region). Increasing of the ionic strength tends to shrink the polyelectrolyte «shell» and to swell the polyampholyte «core». In contrast to AMPS-25 and AMPS-75, the hydrodynamic size of balanced polyampholyte AMPS-50 at the IEP increases upon increasing of the ionic strength demonstrating the antipolyelectrolyte behavior. In aqueous solution the isoelectric points of quenched polyampholytes were found to be pH 6.1±0.1. In the presence of KCl the positions of the IEP shifted to pH 6.5–7.0 due to specific binding of chloride ions by quaternary ammonium groups of «quenched» polyampholytes.

Keywords: quenched polyampholytes, isoelectric point, hydrodynamic size, intrapolyelectrolyte complexes, «core-shell» structure, polyampholyte regime, polyelectrolyte regime, ionic strength.

Introduction

Quenched polyampholytes [1–3] are fully charged polyampholytes prepared from the charged cationic and anionic monomers retaining in contrast to annealed polyampholytes their respective charges over a wide range of pH. Typical examples of quenched polyampholytes are copolymers of 2-acrylamido-2-methyl-propanesulfonate sodium salt (AMPS) and 2-acrylamido-2-methylpropyldimethylammonium chloride (AMPDAC) or (3-acrylamidopropyl)trimethylammonium chloride (APTAC) prepared by microemulsion polymerization [4–8]. The precipitation of charged monomer counterions as silver salt was observed for stoichiometric mixture of 2-methacryloyloxyethyltrimethylammonium iodide (METMAI) and silver salt of 2-methcaryloyloxyethanesulfonate (AgMES) [2]. As a result, the AgI as precipitates and the METMA-MES as ion-pair monomers retains in solution. Polymerization of such ion pairs produces equimolar quenched polyampholyte without inorganic counterions. Quenched polyampholytes prepared in solution have a tendency to be alternative because of the strong electrostatic attractive forces acting between the opposite charged monomers.

McCormick and co. [9–13] synthesized a series of low- and high-charge-density ampholytic copolymers of AMPS and AMPDAC and thoroughly studied their solution properties. In studied systems the sulfonate and quaternary ammonium groups are pH insensitive and the charge balance of these terpolymers is exclusively determined by composition of copolymers.

Amphoteric terpolymers consisting of acrylamide, sodium styrene sulfonate, and acryloxyethyl trimethylammonium chloride monomers, demonstrated excellent thermal-resistance and shear-stability in high-salinity solution [14]. Due to remarkable salinity tolerance, temperature resistance, and shear stability they may be widely applied in drilling fluids and oil recovery.

Low and high molecular weight amphoteric random copolymers of AMPS-APTAC with equimolar composition were prepared via reversible addition-fragmentation chain transfer (RAFT) radical polymerization and conventional free-radical polymerization (FRP) [15]. The copolymer prepared by RAFT was soluble in pure water and formed inter-polymer aggregates while the same copolymer prepared by FRP was insoluble in pure water but dissolved in aqueous solutions of NaCl. Such difference in solubility is connected with formation of intra- and inter-chain interactions that enhanced with increasing the molecular weight.

According to literature survey the quenched polyampholytes are less considered subject in comparison with annealed polyampholytes [16–18] and polymeric betaines [19].

In the present paper the solution properties of linear polyampholytes consisting of fully charged anionic AMPS and cationic APTAC monomers are considered together with their behavior at the isoelectric point where the whole macromolecules are quasineutral.

Experimental

Materials

2-Acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS, 98 wt.%) and (3-acrylamidopropyl)-trimethylammonium chloride (APTAC, 75 wt.% in water), and ammonium persulfate (APS, 99 % purity) were purchased from Sigma-Aldrich Chemical Co. used without further purification.

Methods

^{1}H NMR spectra of AMPS-APTAC in D_2O were registered on impulse Fourier NMR spectrometer Bruker 400 MHz (Bruker, Germany). FTIR spectra were recorded on a Cary 660 FTIR (Agilent, USA). The average molecular weights (M_w and M_n) of aqueous solutions of AMPSNa-APTAC were measured by gel-permeable chromatography (GPC) using Viscotek (Malvern) chromatograph equipped with 270 dual detector (Malvern) and VE 3580 RI detector (Malvern). Two 6000M columns (Malvern) were used and DMF was as mobile phase at 0.7 mL/min flow rate. Polystyrene standard samples (PolyCAL™, Malvern) were used in order to plot the calibration curve. The injection volume of sample was equal to 100 µL. The viscosity of polymers was measured on Ubbelohde viscometer at 25±0.1 °C. The average hydrodynamic size and zeta-potential of AMPS-APTAC copolymers were determined with the help of Zetasizer Nano ZS90 (Malvern, UK) at 30 °C. TGA and DSC measurements were performed on «LABSYS evo» (Setaram, France) at heating rate 10 °C/min. Ionic strength of the solution was adjusted by reagent grade KCl. The pH of the solution was regulated by adding of 0.1M HCl or 0.1M NaOH.

Results and Discussion

Synthesis and characterization of AMPS-APTAC copolymers

Quenched polyampholytes based on AMPS and APTAC were synthesized by free radical (co)polymerization in the presence of APS at 60 °C during 4 h at various molar ratio of initial monomers [AMPS]:[APTAC] = 75:25, 50:50 and 25:75 mol/mol. Further in dependence of molar fraction of AMPS they are abbreviated as AMPS-25, AMPS-50 and AMPS-75 (Fig. 1).

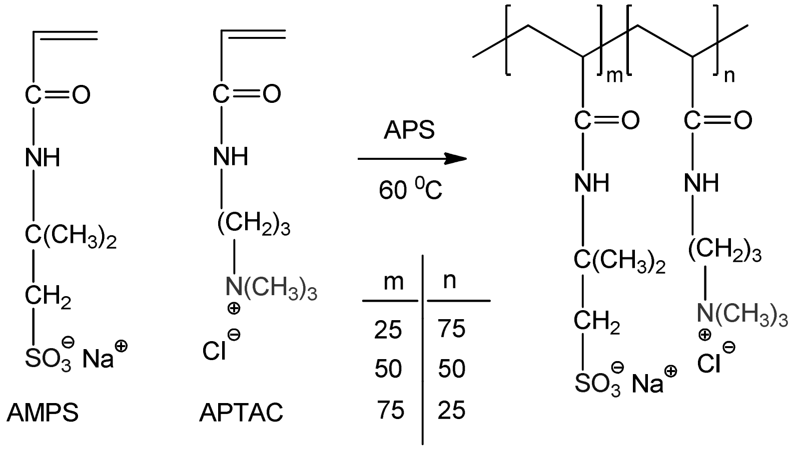


Figure 1. Polymerization protocol of AMPS and APTAC

The obtained copolymers were dissolved in distilled water, dialyzed against deionized water and freeze-dried. ^{1}H NMR spectra of AMPS-75, AMPS-50 and AMPS-25 in D_2O are shown in Figure 2.

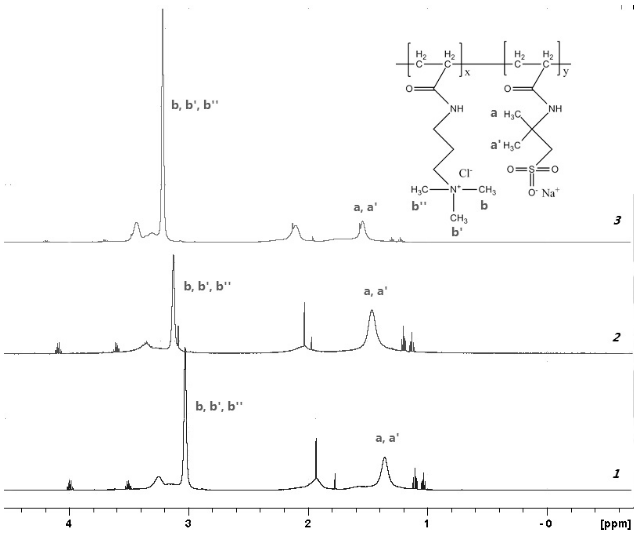


Figure 2. ^{1}H NMR spectra of AMPS-50 (1), AMPS-75 (2) and AMPS-25 (3), in D_2O

The molar composition of AMPS-APTAC copolymers was estimated from the integral peaks of methyl groups (a, a’ and b, b’, b’’) that belong to each monomer as shown in Table 1.

Table 1

Theoretical and experimentally found molar composition of AMPS-APTAC copolymers

No. samples	Molar composition of [AMPS]:[APTAC], mol/mol	
	Theoretically prescribed	Experimentally found from ^{1}H NMR spectra
1	75:25	72:28
2	50:50	53:47
3	25:75	25:75

FTIR spectrum of AMPS-50 together with identification of characteristic bands of functional groups of AMPS-25 and AMPS-75 are presented in Figure 3 and Table 2.

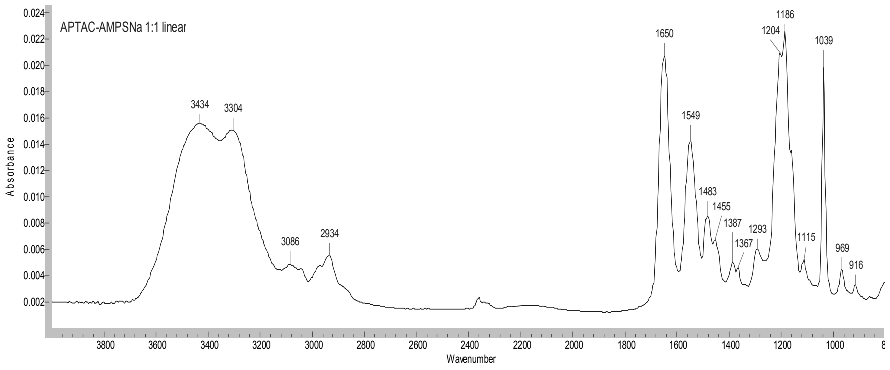


Figure 3. FTIR spectrum of AMPS-50

Table 2

Identification of FTIR spectra of AMPS-25, AMPS-50 and AMPS-75

Functional groups	ν(NH)	ν(CH)	ν(CONH) Amide I,	ν(CONH) Amide II,	δ(CH)	ν(S=O)
Band assignments, cm^{-1}	3434, 3304	2934	1650	1548	1186, 1204	1039

Thus, both ^{1}H NMR and FTIR spectra confirm the compositional closeness of copolymers to that of the monomer feed indicating the formation of homogeneous AMPS-APTAC copolymers in the course of radical polymerization. The conversion of AMPS-APTAC copolymers found from ^{1}H NMR spectra exceeded 80 %. The weight-average molecular weight (M_w), the number-average molecular weight (M_n), and z-average molecular weight (M_z) together with polydispersity index (PDI) of the AMPS-APTAC copolymers according to GPC measurements are summarized in Table 3.

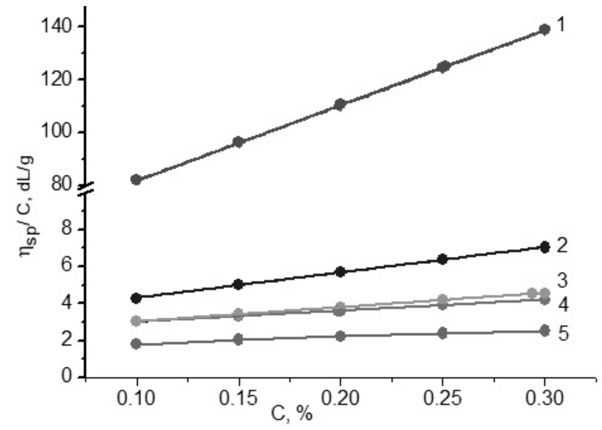
Table 3

The molecular weights and PDI of AMPS-APTAC copolymers

Copolymers	$M_w \cdot 10^{-5}$	$M_n \cdot 10^{-5}$	$M_z \cdot 10^{-5}$	PDI
AMPS-75	6.40	6.37	6.50	1.01
AMPS-50	3.31	2.01	5.11	1.65

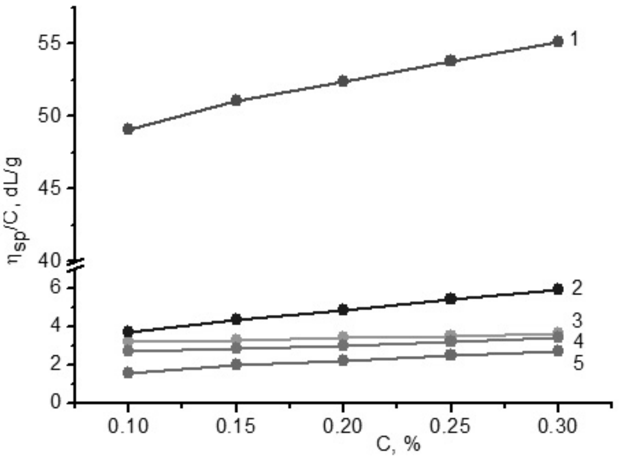
Solution properties of AMPS-APTAC copolymers

Concentration dependence of the reduced viscosity of AMPS-APTAC at different ionic strengths of the solution (μ) expressed as mol·L^{-1} of KCl is demonstrated in Figures 4–6.



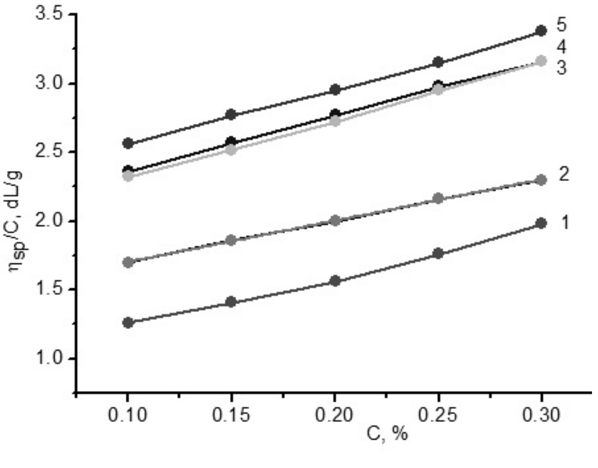
μ (mol·L^{-1}): *1* — 0; *2* — 0.1; *3* — 0.5; *4* — 0.75; *5* — 1.0

Figure 4. Concentration dependence of the reduced viscosity of AMPS-25



μ (mol·L^{-1}): *1* — 0; *2* — 0.1; *3* — 0.5; *4* — 0.75; *5* — 1.0

Figure 5. Concentration dependence of the reduced viscosity of AMPS-75



μ (mol·L^{-1}): *1* — 0.05; *2* — 0.1; *3* — 0.75; *4* — 1.0; *5* — 0.5

Figure 6. Concentration dependence of the reduced viscosity of AMPS-50

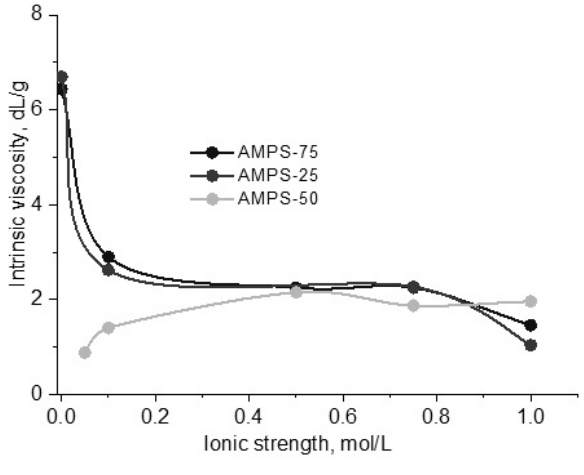


Figure 7. Dependence of the intrinsic viscosity of AMPSNa-APTAC copolymers on the ionic strength of the solution adjusted by KCl

The unbalanced AMPS-APTAC polyampholytes, to whom belong AMPS-25 and AMPS-75, can be considered as a combination of polyampholyte and polyelectrolyte regimes because the charge imbalance causes the increasing of net charge of macromolecules. In that case, the conformational state of AMPS-25 and AMPS-75 in aqueous solution can be represented similar to «core» and «shell» structure. The «core» part containing the equal amount of positive (25 mol.%) and negative (25 mol.%) charges that are mutually compensated can belong to polyampholyte region. The «shell» part of AMPS-25 and AMPS-75 containing the excess of either positive or negative charges is responsible for water solubility and should give to macromolecules polyelectrolyte character. Since the «core» part of AMPS-50 comprising of equal number of positive and negative charges (balanced polyampholyte) has no excess of positive and negative charges in «shell» part, it forms a fine suspension in water but is soluble in salt solution. Surprisingly in pure water AMPS-25 and AMPS-75 do not exhibit polyelectrolyte effect in spite of the excess of positive (Z = +50 mV) and negative (Z = –40 mV) charges. Concentration dependence of the reduced viscosity has a linear character (Figs. 4 and 5). Decreasing of the reduced viscosity upon dilution is probably connected with domination of polyampholyte effect over polyelectrolyte effect. Intramolecular salt bonds (50 mol.%) formed between 25 mol.% positive and 25 mol.% negative charges (polyampholyte effect) prevail the electrostatic repulsion of similar charges (polyelectrolyte effect) in macromolecular chains. In other words, due to counteracting of polyampholyte and polyelectrolyte effects the conformation of macromolecules remains unchanged (or slightly changed) upon dilution in spite of the excess of positive or negative charges. As seen from Figures 4 and 5 the reduced viscosity of AMPS-25 and AMPS-75 decreases with increasing of the ionic strength. In contrast, the reduced viscosity of AMPS-50 increases upon addition of KCl demonstrating antipolyelectrolyte behavior (Figs. 6 and 7). Since AMPS-25 and AMPS-75 contain an excess of positive and negative charges and behave polyelectrolyte character, addition of low-molecular-weight salts shields the electrostatic repulsions. In its turn, addition of low-molecular-weight salts to AMPS-50 shields the electrostatic attraction between the oppositely charges and results in increasing the reduced viscosity. In case of AMPS-25 and AMPS-75 it is expected the simultaneous realization of both polyelectrolyte and polyampholyte behavior. Screening of similar charged monomers by low-molecular-weight salts tends to shrink the «shell» (polyelectrolyte part) while surrounding of oppositely charged monomers by low-molecular-weight salts tends to swell the «core» (polyampholyte part). Such antagonism between polyelectrolyte and polyampholyte effects may cause not dramatically decreasing of the intrinsic viscosity upon increasing of the ionic strength. The plateau observed at $\mu > 0.1$ is likely due to opposite actions of polyelectrolyte and polyampholyte effects. Analogous behavior was observed for AMPS-MADQUAT copolymers with the excess of AMPS monomers at $\mu = 0.5 — 2.0$ [20].

Behavior of AMPS-APTAC at the IEP

In pure water the isoelectric points (IEP) of AMPS-APTAC copolymers corresponding to zero net charge (quasi-electroneutral) of macromolecules are around of pH 6.1±0.1 (Fig. 8). At the IEP the average hydrodynamic size of quenched polyampholytes is minimal due to strong electrostatic attraction of oppositely charged monomers. Increasing of the average hydrodynamic size of amphoteric macromolecules from both sides of the IEP is interpreted in terms of expanding of macromolecular chains due to strong electrostatic repulsion of anionic or cationic groups respectively [16–18].

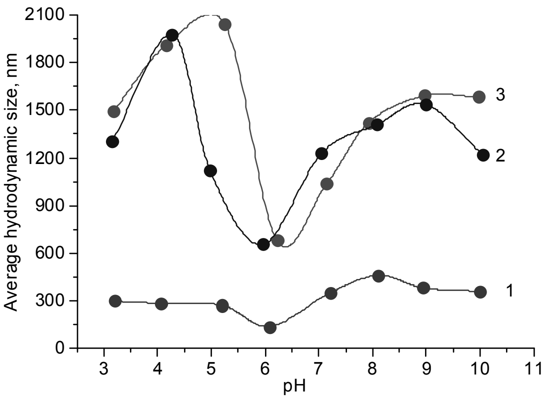


Figure 8. pH dependent average hydrodynamic size of AMPS-50 (1), AMPS-75 (2) and AMPS-25 (3) in aqueous solution

In the presence of KCl the position of the IEP shifts to higher values of pH up to 6.5–7.0. It is connected with specific binding of chloride ions by quaternary ammonium groups that diminishes the amount of positive charges (leading to apparent change of copolymer composition) and increases the value of the IEP in comparison with the nonsalted solution [21].

Different behavior of unbalanced (AMPS-25 and AMPS-75) and balanced (AMPS-50) polyampholytes upon increasing of the ionic strength is illustrated in Figure 9. In aqueous solution AMPS-25 and AMPS-75 have an excess of positive (Z = +50) and negative (Z = –40) charges while AMPS-50 is in electroneutral state (Z = 0).

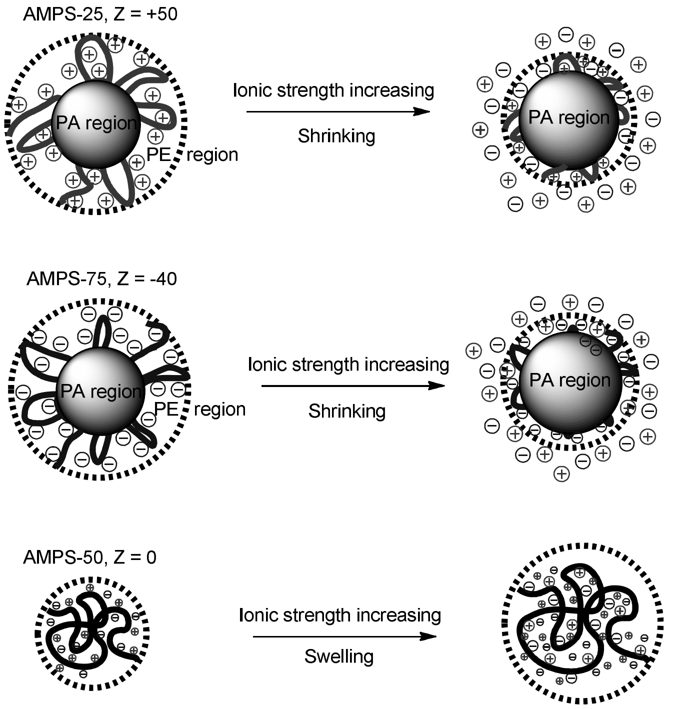


Figure 9. Schematic representation of «core-shell» structure and behavior of AMPS-25, AMPS-50 and AMPS-75 in aqueous-salt solution

Increasing of the ionic strength screens the electrostatic repulsion between uniformly charged groups, if polyelectrolyte effect dominates and shields the electrostatic attraction between oppositely charged monomers, if polyampholyte effect prevails (Table 4). In former case, the macromolecular chain diminishes, whereas in the latter case it expands.

Table 4

Intrinsic viscosities of AMPS-APTAC copolymers in dependence of the ionic strength

Copolymers	Intrinsic viscosity, dL·g^{-1}					
	Ionic strength, KCl mol·L^{-1}					
	0	0.05	0.1	0.5	0.75	1.0
AMPS-25	46.4	-	2.68	-	2.32	1.12
AMPS-50	-	0.88	1.40	2.15	1.90	1.96
AMPS-75	53.8	-	2.93	-	2.42	1.47

The viscometric data reveal that in aqueous solutions of KCl the intrinsic viscosities of AMPS-25 and AMPS-75 decrease while the intrinsic viscosity of AMPS-50 increases demonstrating antipolyelectrolyte behavior. In aqueous solution the conformation of AMPS-25 and AMPS-75 can be considered as «core» and «shell» structure where the «core» part exists in polyampholyte regime, the «shell» part represents a polyelectrolyte regime. Addition of low-molecular-weight salts tends to shrink the «shell» part (polyelectrolyte region) and to swell the «core» part (polyampholyte region). Such antagonism between polyelectrolyte («shell») and polyampholyte («core») effects may cause gradual decreasing of the intrinsic viscosity at relatively high ionic strengths.

According to Lifshiz et al [22] the globular structure of macromolecules can be considered as dense three-dimensional nucleation, consisting of a dense «core» surrounded by loose and open surface or hydrophilic «edge». In our mind, such globular structure can exist at the IEP of quenched polyampholytes as represented schematically in Figure 10. Imaginative structure of «core» consists of 1) high dense globule ($r = \sim 5–10$ nm), 2) low-dense globule ($r = \sim 25–50$ nm), 3) dense coil ($r = \sim 100$ nm), and 4) low-dense coil ($r = \sim 200–500$ nm). Radial distribution of macromolecular chains may have whole-number values $r_1{:}r_2{:}r_3{:}r_4 = a{:}b{:}c{:}d$. Formation of spherical globules with an ~5 nm diameter was directly visualized by Field Emission Scanning Electron Microscope (FE-SEM) images for charge-balanced polyampholyte chains made of sodium 4-vinylbenzenesulfonate (NaSS) and [3-(methacryloylamino)propyl]trimethylammonium chloride (MPTC) denoted as poly(NaSS-*co*-MPTC) [23] (Fig. 11).

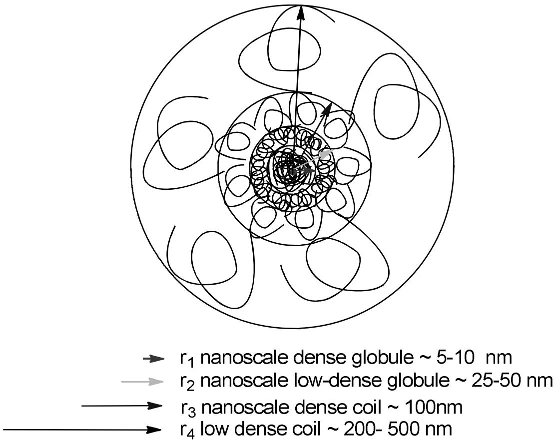


Figure 10. Proposed structure and proposed size of quenched polyampholytes in aqueous solution at the isoelectric point (IEP)

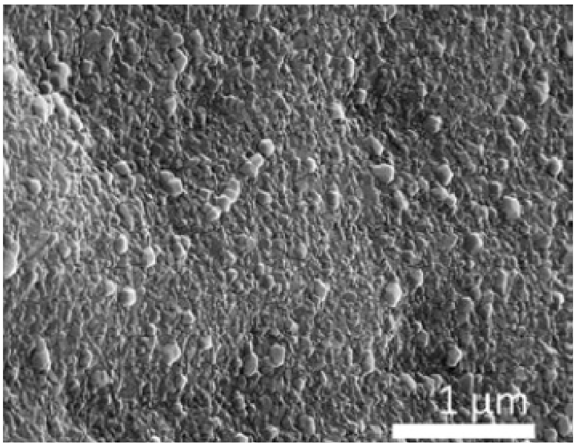


Figure 11. Cross-sectional FE-SEM image of poly(NaSS-*co*-MPTC) at 20 ºC [23]

Thermal properties of solid AMPS-APTAC copolymers

The results of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of quenched polyampholytes are shown in Figure 11. An initial decreasing of sample mass at the interval of temperature 65–120 ºC is due to loosing of the humidity. Intensive mass loose of samples starts at the interval of temperature 308–332 ºC. It is connected with thermal decomposition of polymers.

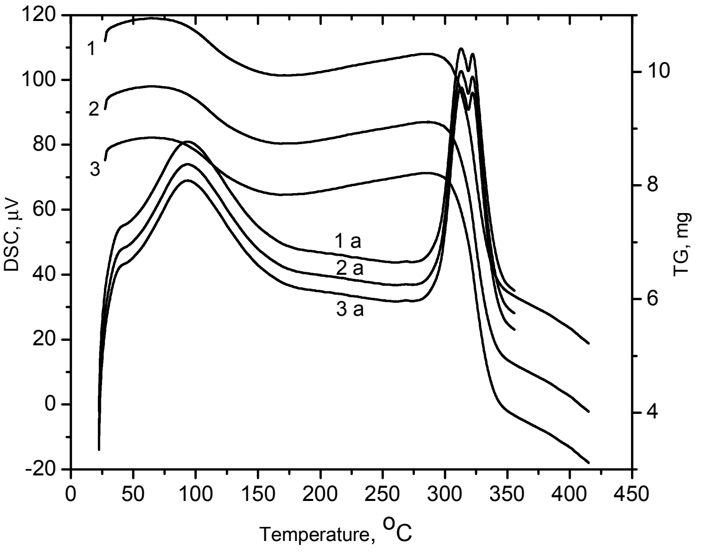


Figure 11. TG (1–3) and DSC (1a-3a) curves of AMPS-50 (1), AMPS-75 (2), AMPS-25 (3)

Conclusions

Quenched (or high-charge-density) polyampholytes were prepared from anionic AMPS and cationic APTAC monomer pairs. Copolymers with large charge asymmetries (AMPS-25 and AMPS-75) exhibited a good solubility in water. Equimolar polyampholyte (AMPS-50) was dispersed in water but soluble in aqueous solutions of KCl. Polyampholytes with excess of anionic (AMPS-75) or cationic (AMPS-25) charges behave as neutral polymers, e.g. at concentration range of 0.05–03 g·dL^{-1} the reduced viscosity linearly diminishes upon dilution. The viscometric data reveal that in aqueous solutions of KCl the intrinsic viscosities of AMPS-25 and AMPS-75 decrease while the intrinsic viscosity of AMPS-50 increases demonstrating *antipolyelectrolyte* behavior. In aqueous solution the conformation of AMPS-25 and AMPS-75 can be considered as «core» and «shell» structure where the «core» part exists in polyampholyte regime, the «shell» part represents a polyelectrolyte regime. Addition of low-molecular-weight salts tends to shrink the «shell» part (polyelectrolyte region) and to swell the «core» part (polyampholyte region). Such antagonism between polyelectrolyte («shell») and polyampholyte («core») effects may cause not dramatically decreasing of the intrinsic viscosity at relatively high ionic strengths. In aqueous solution the positions of the isoelectric points of strongly charged polyampholytes determined by DLS experiments are around of pH 6.3±0.2. In the presence of KCl the position of the IEP shifts to pH 6.5–7.0 due to specific binding of chloride ions by quaternary ammonium groups of APTAC. Imaginative structure of polyampholyte «core» at the IEP consisting of high dense globule, low-dense globule, dense coil, and low-dense coil is suggested. Quenched polyampholytes exhibit thermostability up to 300 ºC.

Acknowledgements

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References

1 Salamone, J.C., Tsai, C.C., Watterson, A.C., & Olson, A.P. (1980). Novel ampholytic polymers. A new class of ionomer, in: *Polymeric Amine and Ammonium Salts*. Oxford: Pergamon Press, 105–112.

2 Salamone, J.C., & Rice, W.C. (1987). Polyampholytes. In: *Encycl. of Polym. Sci. Eng*. Edited by H.F. Mark, N.M. Bikales, C.G. Overberger, and G. Menges. New York: Wiley, 514–530.

3 Salamone, J.C., Watterson, A.C., Hsu, T.D., Tsai, C.C., & Mahmud, M.U. (1977). Polymerization of vinylpyridinium salts. IX. Preparation of monomeric salt pairs. *J. Polym. Sci. Polym. Lett. Ed*., *15*, 487–491.

4 Candau, F., & Joanny, J.F. (1996). Polyampholytes (Properties in aqueous solution). In: *Polymeric Materials Encyclopedia*. Edited by J.C. Salamone. New York: CRC Press Boca Raton, 5476–5488.

5 Corpart, J.M., & Candau, F. (1993). Formulation and polymerization of microemulsions containing a mixture of cationic and anionic monomers. *Colloid Polym. Sci*., *271*, 1055–1067.

6 Corpart, J.M., & Candau, F. (1993). Characterization of high charge density ampholytic copolymers prepared by microemulsion polymerization. *Polymer, 34*, 3873–3886.

7 Candau, F. (1995). Recent developments in microemulsion copolymerization. *Macromol. Symp., 92*, 169–178.

8 Ohlemacher, A., Candau, F., Munch, J.P., & Candau, S.J. (1996). Aqueous solution properties of polyampholytes: Effect of net charge distribution. *J. Polym. Sci. Part B: Polym. Phys*., *34*, 2747–2757.

9 McCormick, C.L., & Johnson, C.B. (1998). Water-soluble polymers 28. Ampholytic copolymers of sodium 2-acrylamido-2-methylpropanesulfonate with (2-acrylamido-2-methylpropyl)dimethylammonium chloride: synthesis and characterization. *Macromolecules*, *21*, 686–693.

10 Lowe, A.B., & McCormick, C.L. (2002). Synthesis and solution properties of zwitterionic polymers. *Chem. Rev*., *102*, 4177–4189.

11 McCormick, C.L., & Salazar, L.C. (2010). Water-soluble copolymers: 44. Ampholytic terpolymers of acrylamide with sodium 2-acrylamido-2-methylpropanesulphonate and 2-acrylamido-2-methylpropanetrimethyl-ammonium chloride. *J. Appl. Polym. Sci*., *48*, 1115–1120.

12 Fevola, M.J., Bridges, J.K., Kellum, M.G., Hester, R.D., & McCormick, C.L. (2004). pH-responsive ampholytic terpolymers of acrylamide, sodium 3-acrylamido-3-methylbutanoate and (3-acrylamidopropyl)trimethylammonium chloride. I. Synthesis and characterization. *J. Appl. Polym. Sci*., *42*, 3236–3251.

13 Fevola, M.J., Kellum, M.G., Hester, R.D., & McCormick, C.L. (2004). pH-responsive ampholytic terpolymers of acrylamide, sodium 3-acrylamido-3-methylbutanoate and (3-acrylamidopropyl)trimethylammonium chloride. II. Solution properties. *J. Appl. Polym. Sci*., *42*, 3252–3270.

14 Dai, C., Xu, Zh., Wu, Y., Zou, Ch., Wu, X., & Wang, T., et all (2017). Design and Study of a Novel Thermal-Resistant and Shear-Stable Amphoteric Polyacrylamide in High-Salinity Solution. *Polymers*, *9*, 296. DOI:10.3390/polym9070296.

15 Nakahata, R., & Yusa, S. (2018). Solution Properties of Amphoteric Random Copolymers Bearing Pendant Sulfonate and Quaternary Ammonium Groups with Controlled Structures. *Langmuir*. DOI: 10.1021/acs.langmuir.7b03785.

16 Kudaibergenov, S.E. (1999). Recent advances in studying of synthetic polyampholytes in solutions. *Adv. Polym. Sci.*, *144*, 115–197.

17 Kudaibergenov, S.E. (2002). Polyampholytes: Synthesis, Characterization and Application. New York: Kluwer Academic/Plenum Publishers.

18 Kudaibergenov, S.E. (2008). Polyampholytes. In *Encyclopedia of Polymer Science and Technology*. John Wiley Interscience: Hoboken, NJ, USA, 1–30.

19 Kudaibergenov, S., Jaeger, W., & Laschewsky, A. (2006). Polymeric betaines: Synthesis, characterization and application. *Advances in Polymer Science, 201*, 157–224.

20 Corpart, J.M., & Candau, F. (1993). Aqueous solution properties of ampholytic copolymers prepared in microemulsions. *Macromolecules, 26*, 1333–1343.

21 Alfrey, T., Morawetz, H., Fitzgerald, E.B., & Fuoss. R.M. (1950). Synthetic electrical analog of proteins. *J. Am. Chem. Soc.*, *72*, 1864.

22 Lifshits, I.M., Grosberg, A.Y., & Khokhlov, A.R. (1979). Volume interactions in the statistical physics of polymer macromolecule. *Sov. Phys. Rev.*, *22*, 123–142.

23 Li, X., Charaya, H., Bernard, G.M., Elliott, J.A.W., Michaelis, V.K., Lee, B., & Chung, H-J. (2018). Low-temperature ionic conductivity enhanced by disrupted ice formation in polyampholyte hydrogels. *Macromolecules*, *51*, 2723–2731.

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Quenched, немесе күшті зарядталған, полиамфолиттердің сулы-тұзды ерітіндідегі қасиеті

Радикалды сополимерлеу әдісі көмегімен оң және теріс зарядталған мономерлер натрий 2-акриламид-2-метил-1-пропансульфон қышқылы (AMPS) және (3-акриламидопропил)үшметиламмоний хлориді (APTAC) негізінде сызықты полиамфолиттер синтезделіп, олардың сулы-тұзды ерітіндідегі физика-химиялық қасиеті зерттелді. Тең емес (AMPS-25 және AMPS-75) және тең (AMPS-50) қатынаста алынған quenched полиамфолиттер ^{1}H ЯМР- және ИҚ-спектроскопия, термогравиметриялық талдау, дифференциалды-сканирлеуші калориметрия әдістерімен сипатталып, олардың тутқырлықтары анықталды. Quenched полиамфолиттер изоэлектрлік нүкте (ИЭН) жағдайында күшті зарядталған анионды және катионды фрагменттер арасындағы ионаралық байланыс көмегімен тұрақталатындығы зерттелді. Сулы ерітіндідегі AMPS-25 және AMPS-75 конформациялық жағдайы «ядро» және «қабық» құрылымынан тұрады. Бұнда «ядро» қабатшасы полиамфолиттік сипатта (ПА аймақ) болса, «қабық» қабатшасы полиэлектролиттік эффект (ПЭ аймақ) көрсететіні белгілі болды. Ертіндінің иондық күшін арттыру полиэлектролиттік «қабық» қабатшасының қысылуына, ал «ядро» қабатшасының ісінуіне әкелетіндігі анықталды. Зарядтары тең емес AMPS-25 және AMPS-75-ке қарағанда, зарядтары тең қатынастағы полиамфолит AMPS-50-тің ИЭН-дегі гидродинамикалық өлшемі ертіндінің иондық күшін арттырғанда өсіп, антиполиэлектролиттік сипатқа ие болады. Сулы ертіндідегі quenched полиамфолиттің ИЭН-сі pH=6,1±0,1 тең. KCl қатысында ИЭН quenched полиамфолиттегі төрттік аммоний тобының хлорид иондарды байлануы нәтижесінде pH=6,5–7,0 аралығына ығысатындығы белгілі болды.

Кілт сөздер: quenched полиамфолиттер, изоэлектрлік нүкте, гидродинамикалық өлшем, полиэлектролитішілік кешен, «ядро-қабық» құрылым, полиамфолиттік жағдай, полиэлектролиттік жағдай, иондық күш.

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Поведение quenched, или сильно заряженных, полиамфолитов в водно-солевых растворах

Методом свободно-радикальной сополимеризации синтезированы quenched (или сильно заряженные) линейные полиамфолиты на основе отрицательно и положительно заряженных мономеров — натриевой соли 2-акриламидо-2-метил-1-пропансульфоновой кислота (AMPS) и (3-акриламидопропил)триметиламмоний хлорида (APTAC) и исследованы их физико-химические свойства в водно-солевых растворах. Ряд несбалансированных (AMPS-25 и AMPS-75) и сбалансированных (AMPS-50) quenched полиамфолитов охарактеризованы методами ^{1}H ЯМР- и ИК-спектроскопии, термогравиметрического анализа и дифференциально-сканирующей калориметрии, а также изучена их вязкость. Установлено, что в изоэлектрической точке (ИЭТ) quenched полиамфолиты стабилизируются с помощью внутриионных контактов между сильно заряженными анионными и катионными фрагментами. Конформационное состояние AMPS-25 и AMPS-75 в водном растворе представлено как структура «ядро» и «оболочка». При этом «ядро» имеет полиамфолитный характер (ПА область), а «оболочка» проявляет полиэлектролитный эффект (ПЭ область). Повышение ионной силы раствора приводит к сжатию «оболочки» полиэлектролита и набуханию «ядра» полиамфолита. В отличие от AMPS-25 и AMPS-75, гидродинамические размеры сбалансированного полиамфолита AMPS-50 в ИЭТ увеличиваются при повышении ионной силы раствора, демонстрируя *антиполиэлектролитный* характер. Установлено, что в водном растворе ИЭТ quenched полиамфолитов имеют pH=6,1±0,1. В присутствии KCl положение ИЭТ смещается до pH=6,5–7,0 из-за специфического связывания хлорид-ионов четвертичными аммониевыми группами quenched полиамфолитов.

Ключевые слова: quenched полиамфолиты, изоэлектрическая точка, гидродинамический размер, внутриполиэлектролитные комплексы, структура «ядро-оболочка», полиамфолитный режим, полиэлектролитный режим, ионная сила.