

G. Toleutay^{1,2}, E. Su³, S.E. Kudaibergenov^{1,2}¹*Institute of Polymer Materials and Technology, Almaty, Kazakhstan;*²*Satbayev University, Almaty, Kazakhstan;*³*Istanbul Technical University, Turkey**(E-mail: skudai@mail.ru)*

Swelling and mechanical properties of quenched polyampholyte hydrogels based on 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS) and (3-acrylamidopropyl) trimethylammonium chloride (APTAC)

In our previous paper (Bulletin of the Karaganda University. Chemistry series, 2019, 2(94), P. 35–43) we considered the behavior of quenched (or strongly charged) polyampholytes based on fully charged anionic monomer — 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS) and cationic monomer — (3-acrylamidopropyl) trimethylammonium chloride (APTAC) in aqueous-salt solutions. In the present paper we report the mechanical properties of quenched polyampholyte hydrogels synthesized by free-radical copolymerization of the same monomers in the presence of N,N-methylenebisacrylamide (MBAA) as crosslinking agent. The hydrogel samples in dependence of the molar amount of AMPS were abbreviated as AMPS-75H, AMPS-50H and AMPS-25H. The swelling, rheological, and mechanical properties of quenched polyampholyte hydrogels were evaluated for different compositions of copolymers at fixed initial monomer concentration $C_0 = 0.5$ wt.% and constant amount of [MBAA] = 20 mol.%. The formation of hydrogels in the course of (co)polymerization of oppositely charged monomers in presence of MBAA was monitored by rheometric measurements using oscillatory deformation tests at an angular frequency $\omega = 6.3$ rad·s⁻¹ and strain amplitude $\gamma_0 = 0.01$. The strain-stress curves of as-prepared and swollen polyampholyte gels demonstrate that the highest values of Young's modulus E , fracture stress σ_f and elongation $\varepsilon\%$ are characteristic for as-prepared AMPS-75H and swollen AMPS-50H samples. These results are interpreted in terms of polyelectrolyte and polyampholyte effects.

Keywords: quenched polyampholyte hydrogels, swelling, rheological and mechanical properties, strain-stress, Young's modulus, ionic interactions.

Introduction

Three-dimensional quenched polyampholytes (QPA) can be divided into two categories: chemically and physically crosslinked hydrogels [1, 2]. The long-range Coulombic interactions between opposite charges along the backbone is a governing factor of conformational and volume-phase changes of QPA hydrogels. Swelling ratio at equilibrium Q_e for QPA gels prepared from 2-(methacryloyloxy)ethyltrimethylammonium chloride (MADQUAT) and AMPS was studied in pure water and 2 mol·L⁻¹ NaCl solution [3]. Similar to linear QPA, hydrogels of QPA are in swollen and collapsed states in dependence of the net charges expressed as $\Delta f = f^+ - f^-$ (where f^+ and f^- are the molar ratios of cationic and anionic monomers to the total monomer concentration, respectively). As the concentration of the anionic and cationic parts deviates from the equimolar ones $\Delta f \neq 0$ the swelling ratio increases rapidly. A reasonable explanation of these results are that the number of osmotically active ions in the hydrogel phase increases as the molar ratio of cationic to anionic groups diverges from unity according to Donnan equilibrium. While as the molar ratio of cationic to anionic groups approaches to unity the excess free counterions that are not needed to satisfy the electroneutrality of the chain are effectively «dialyzed» from the hydrogel interior. In 2 mol·L⁻¹ NaCl solution the electrostatic effects are screened and the swelling ratio at equilibrium Q_e levels off and gel behaves as a neutral system. At low ionic strength polyampholyte chains bearing net charges of opposite signs form intraionic complexes leading to a phase separation. At high ionic strength, the gel swells due to screening of electrostatic interactions and such microscale structure dissolves.

QPA hydrogels based on [3-(methacryloylamino)propyl]trimethylammonium chloride (MAPTAC) and 4-vinylbenzenesulfonate (NaSS) P(MAPTAC-co-NaSS) [4] and P(AMPS-APTAC) [5] were compared with polyionic complex (PIC) composed of P(MAPTAC) and P(NaSS) [4]. The main difference between P(MAPTAC-co-NaSS) and P(MAPTAC)-P(NaSS) hydrogels is that the former is composed of oppositely charged monomers, while the latter is the product of matrix polymerization of NaSS on the matrix of

P(MAPTAC). The conformation of P(MAPTAC-*co*-NaSS) can be stabilized by both inter- and intra-ionic interactions, while P(MAPTAC)-P(NaSS) chains are stabilized by interionic salt bonds. The effects of charge ratio and monomer concentrations, the molecular weight of polyelectrolytes on the swelling, toughness, self-healing, and viscoelasticity of QPA and PIC hydrogels were comparatively studied. It was demonstrated that the PIC hydrogels are much tougher than the QPA hydrogels and exhibit better mechanical properties. This is due to structural and morphological differences of two systems. The PIC hydrogel shows a more inhomogeneous, large segregated structure with large pore size ($d = 0.5\text{--}3.0\ \mu\text{m}$), while the QPA hydrogels show more homogeneous structure with diameter of pores $0.1\text{--}0.3\ \mu\text{m}$.

The swelling properties of AMPS-APTAC were evaluated by continuous monitoring of $60\ \mu\text{m}$ sized hydrogels with the help of instrument [6]. It was shown that the charge balanced P(AMPS-APTAC) hydrogel exponentially swells upon ionic strength increases from $5 \cdot 10^{-4}$ to $0.15\ \text{M}$ NaCl exhibiting antipolyelectrolyte effect [7] in response to added salts.

A new class of tough, viscoelastic and self-healing hydrogels was designed by authors [8–11] from supramolecular QPA prepared by random copolymerization of oppositely charged ionic monomers at high monomers concentration and equimolar monomers ratio (charge balance point). These physical gels contain the strong ionic bonds that play the role of permanent crosslink and weak ionic bonds that are responsible for elongation, deformation, twisting, fatigue resistance, internal friction, adhesion, self-healing, shape memory, anti-biofouling and other important functions. In spite of topological difference, the QPA hydrogels are similar to double-network hydrogels [12]. In both cases, the strong bonds form a primary network and the weak bonds — a sacrificial network. The effect of the charge fraction (f) on the swelling volume ratio ($Q_v = V/V_0$, where V and V_0 are the volumes of swollen and as-prepared hydrogels), Young's modulus E , and the compressive fracture stress σ_b of the hydrogels MAPTAC-*co*-NaS) was evaluated. The extremums of curves correspond to the vicinity of charge balance point ($f \approx 0.48\text{--}0.53$) where the Coulomb attraction prevails over the repulsion and polymer chain collapse to globular state. In imbalanced region ($f < 0.48$ and $f > 0.53$) the Coulomb repulsion prevails and polymer segments elongate. The shrinking of the gels near the charge balance point ($f \approx 0.505 \pm 0.025$) is accompanied by dramatic increase in the modulus E and fracture stress σ_b .

A series of experiments were carried out to clarify the effect of specific ions on mechanical and electrical properties of QPA hydrogels on the examples of P(MAPTAC-*co*-NaSS) and various salts [13]. A virgin sample is represented as inhomogeneous medium composed of strong ionic bonds that play the role of permanent crosslink like covalent cross linker and weak ionic bonds that can be ruptured and re-formed. The cut virgin sample contains the ruptured strong and weak ionic bonds. After contacting of the cut surfaces a large number of ionic contacts in the vicinity of surfaces are re-formed across the interface which leads to healing.

Earlier [14] we have studied the swelling properties of a series of QPA hydrogels based on P(AMPS-APTAC) in aqueous-salt solutions. The swelling behavior regardless of hydrogel composition, was followed by Fickian diffusion. The adsorption and desorption ability of QPA hydrogels was evaluated with respect to ionic dyes and surfactants.

In the present paper we report the mechanical properties of QPA hydrogel samples of P(AMPS-APTAC) in dependence of the molar amount of AMPS. The rheological, and mechanical properties of quenched polyampholyte hydrogels were evaluated for different compositions of copolymers at fixed initial monomer concentration $C_0 = 0.5\ \text{wt.}\%$ and constant amount of $[\text{MBAA}] = 20\ \text{mol.}\%$.

Experimental

Materials

Commercially available 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS, 50 wt. % in water), (3-acrylamidopropyl) trimethylammonium chloride (APTAC, 75 wt. % in water), N,N' -methylenebis(acrylamide) (MBAA) purchased from Sigma-Aldrich were used as received. Ammonium persulfate (APS) purchased from Changzhou Qi Di Chemical Co. was used without further purification.

Preparation of polyampholyte hydrogels

Polyampholyte hydrogels were prepared by solution polymerization of the monomers AMPS and APTAC at $60 \pm 2\ ^\circ\text{C}$ in the presence of MBAA as a cross-linker, and $10\ \text{mM}$ APS as an initiator respectively. The molar amount of AMPS in the comonomers feed was varied from 25 to 75 mol.% while initial monomer concentration C_0 and amount of MBAA were fixed at 5 wt.% and 20 mol.%. Further, the QPA hydrogels were coded as AMPS-75H, AMPS-50H and AMPS-25H (where 75, 50 and 25 are the mole percent of AMPS in initial monomer feed). For example, AMPS-50H was prepared from the mixture of 50 mol.%

AMPS and 50 mol.% APTAC in the presence of 20 mol.% MBAA. The synthetic protocol for preparation of AMPS-50H is the following: the mixture AMPS (0.4 g), APTAC (0.2 g), MBAA (0.06) was stirred at room temperature for 15 min to obtain a homogeneous solution. After the addition of APS (30 mg) and stirring for 1–2 min, nitrogen gas was bubbled through the homogeneous solution for 30 min to eliminate oxygen. The solution was then transferred into 1 mL volume syringes, placed into oven and polymerized at 60 °C during 24 h.

Methods

Rheological measurements

The rheological measurements were conducted on a Bohlin Gemini 150 rheometer system (Malvern Instruments, UK) equipped with a Peltier device for temperature control. Hydrogel samples were prepared between rheometer plates at 60 °C for monitoring gelation. The frequency sweep tests were carried out over the frequency range of 0.1 to 100 rad·s⁻¹ placing the gel samples between the cone and plates (diameter 40 mm) at the constant distance between them 150 μm. The frequency-sweep tests at strain amplitude $\gamma_0 = 0.01$ were carried out at 25 °C.

Swelling tests

Hydrogels taken out of the syringes after 24 h reaction time were cut into small pieces of about 1 cm in length, and immersed in an excess of water. After reaching an equilibrium degree of swelling, which was monitored by recording the mass and diameter of gel specimen, the samples were taken out of water and freeze-dried (Christ Alpha 2–4 LDplus). The fraction of the monomers converted into a water-insoluble polymer, that is, the gel fraction W_g was calculated by formula:

$$W_g = \frac{m_{dry}}{C_0 \times m_0}, \quad (1)$$

where m_{dry} and m_0 are the weights of the gel specimens in dried and as-prepared states, respectively, and C_0 is the monomer concentration (wt.%) in the initial reaction mixture.

The relative weight (m_{rel}) and volume (V_{rel}) swelling ratios of as-prepared gels were determined by formulas:

$$m_{rel} = \frac{m_{swl}}{m_0}; \quad (2)$$

$$V_{rel} = \left(\frac{d_{swl}}{d_0} \right)^3, \quad (3)$$

where d_0 and d_{swl} are the diameters of as-prepared and swollen specimen respectively, m_{swl} is the weight of swollen gel specimen.

Mechanical tests

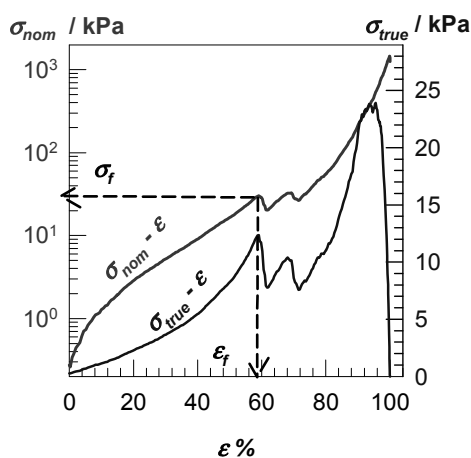


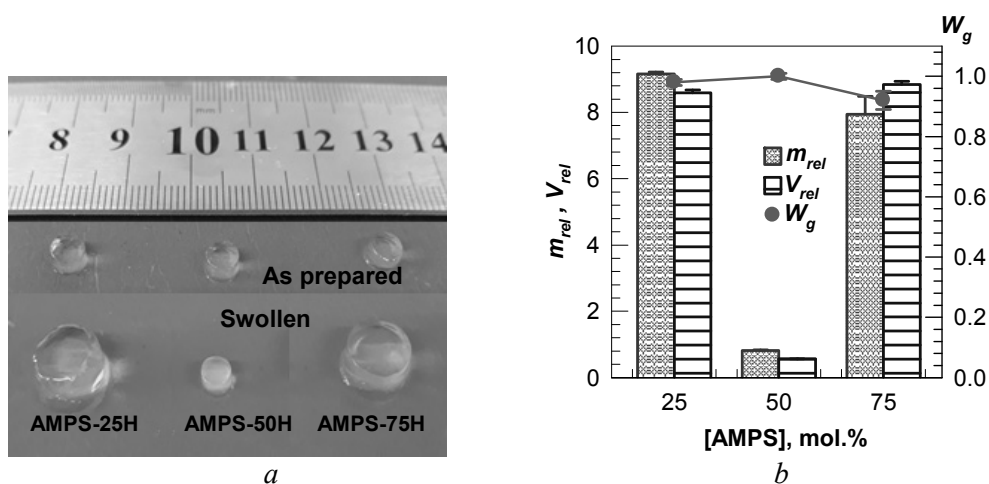
Figure 1. Typical stress-strain curves of under compression where the nominal stress σ_{nom} (red curve) and true stress σ_{true} (blue curve) are plotted against the compressive strain ε . Dashed lines represent calculations of the fracture stress σ_f and fracture strain ε_f from the maximum in the $\sigma_{true}-\varepsilon$ curve

The compression tests were performed at room temperature on Zwick Roell test machine using 500 N load cell. Initial compressive contact to 0.05 N was applied to ensure complete contact between the sample and the surface. Load and displacement data were collected during the experiments at a constant crosshead speed of 3 mm·min⁻¹. Compressive stress was presented by its nominal σ_{nom} and true values σ_{true} , which are the force per cross-sectional area of the undeformed and deformed specimen, respectively. Assuming the sample volume remains constant during deformation, the true stress σ_{true} was calculated as $\sigma_{true} = \lambda\sigma_{nom}$, where λ is the deformation ratio (deformed length/original length). The compressive strain is given by the compression ratio ε which is the change in the sample length relative to its initial length, i.e., $\varepsilon = 1 - \lambda$. Figure 1 shows the typical stress-strain curves of AMPS-50H, where the σ_{nom} and σ_{true} are plotted against the strain ε .

Results and Discussion

Swelling characteristics of QPA hydrogels

Photos of as-prepared and swollen (immersed into water and equilibrated) as well as the relative weight m_{rel} , volume V_{rel} , and gel fraction W_g of QPA hydrogels calculated by formulas 1–3 are shown in Figure 2. As prepared (or initial) hydrogel samples have the same size. After immersing and equilibration in aqueous solution the QPA hydrogels of AMPS-75H and AMPS-25H are transparent and in swollen state, while AMPS-50H is cloudy and in shrunken state. These results are explained by Donnan effect. In case AMPS-25H and AMPS-75H, due to excess of positive and negative charges in hydrogel network the number of osmotically active ions in the hydrogel phase increases leading to swelling of hydrogels. In case of AMPS-50H, the equimolar amount of cationic and anionic charges compensate each other and the excess free counterions (Na^+ and Cl^-) that are no more needed to satisfy the electroneutrality of the chains are effectively released from the hydrogel interior.

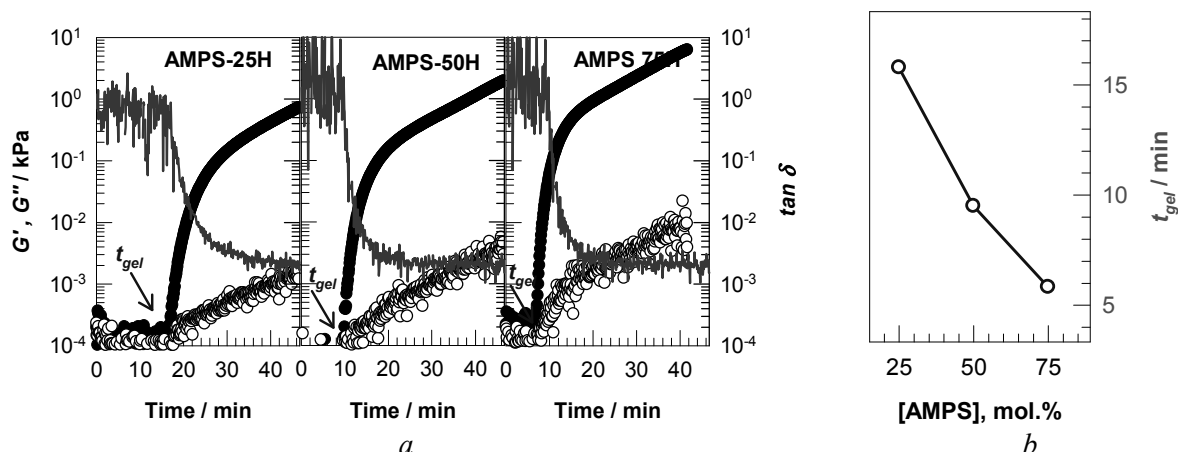


a — Images of as-prepared (top) and swollen (bottom) QPA hydrogels in water;
b — the relative weight m_{rel} (red bars), volume V_{rel} (blue bars), and gel fraction W_g (green symbol) of polyampholyte hydrogels as a function of AMPS in the feed

Figure 2

Gelation

The dynamics of gel formation was monitored by rheometric measurement using the oscillatory deformation tests at an angular frequency ω of 6.3 rad·s⁻¹ and strain amplitude γ_0 of 0.01. Figures 3a, b show the loss G'' and storage modulus G' of the reaction solutions plotted vs the reaction time together with the loss factor $\tan\delta$ (G''/G') of the reaction system. As seen from Figure 3b the gelation time decreases with increasing of AMPS content in reaction mixture. This is probably accounted for higher reactivity of AMPS ($r_{AMPS} = 0.62$) in comparison with APTAC ($r_{APTAC} = 0.36$) that is responsible for decreasing of gelation time [15–17].



a — Storage G' (filled symbols), loss modulus G'' (open symbols) and loss factor $\tan \delta$ (red lines) of the reaction mixture as a function of reaction time. $\omega = 6.3 \text{ rad}\cdot\text{s}^{-1}$. $T = 60 \text{ }^\circ\text{C}$. Blue arrows show the gelation point of the system;
b — Gel points t_{gel} ($\tan \delta = 1$, open symbols) are plotted as a function of AMPS content in reaction mixture.
 Error bars are smaller than the symbols where the bars are not shown

Figure 3

Mechanical and rheological properties

Table represents the mechanical characteristics of QPA hydrogels with different AMPS content. With increasing of AMPS content the mechanical strength (E_c) increases 3 times and fracture stress (σ_f) increases 2 times.

Table

Swelling and compressive mechanical properties of QPA hydrogels. [MBAA] = 20 mol. %, [APS] = 10 mM

Code	m_{rel}	$\text{H}_2\text{O wt.}\%$	W_g	As-prepared gel		Swollen gel	
				E/kPa	σ_f/kPa	E/kPa	σ_f/kPa
AMPS-25H	9.2 ± 0.1	99.4	0.98	5.2 (0.4)	24 (1)	11.2 (0.7)	6.0 (0.8)
AMPS-50H	0.82 ± 0.02	99.5	1.00	12 (1)	30 (2)	23 (2)	147 (12)
AMPS-75H	7.9 ± 0.5	93.8	0.92	19 (4)	55 (3)	33 (1)	27 (3)

Figure 4 shows the results of rheological measurements: storage G' , loss modulus G'' and loss factor $\tan \delta$ of as-prepared QPA hydrogels. It is seen that AMPS-75H demonstrates stronger mechanical properties but exhibits the brittleness (lines on the third graph are approximated). These results are in good agreement with the loss factor $\tan \delta$ (G''/G') of the reaction system.

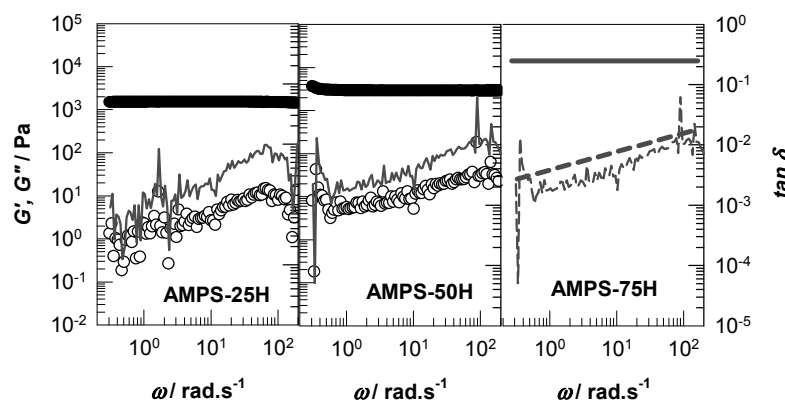
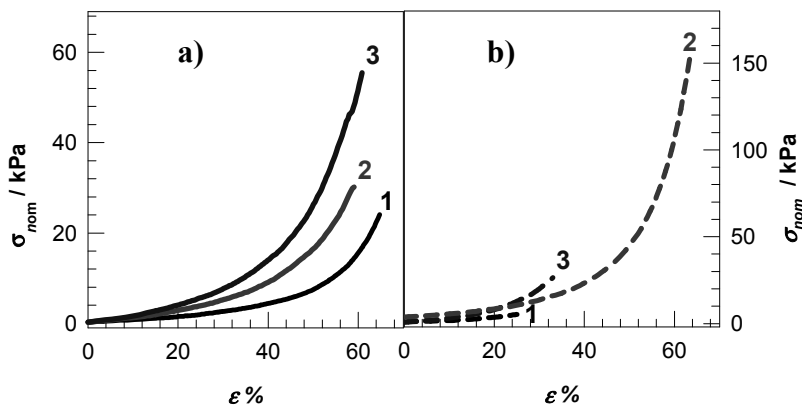


Figure 4. Storage G' (filled symbols), loss modulus G'' (open symbols) and loss factor $\tan \delta$ (red lines) of QPA hydrogels prepared between rheometer plates at $60 \text{ }^\circ\text{C}$ for 1 h at $25 \text{ }^\circ\text{C}$. $\gamma_0 = 0.01$. Hydrogel codes are indicated in the graphs. Note that the green lines are approximated data for AMPS-75H

The corrected strain-stress curves of as-prepared and swollen QPA hydrogels at various AMPS concentration are shown in Figures 5*a, b*. The Young's modulus E , fracture stress σ_f and fracture strain $\varepsilon\%$ (or elongation) of QPA hydrogels as a function of AMPS content are represented in Figures 6*a, b*. The highest values of Young's modulus E and fracture stress σ_f exhibit as-prepared AMPS-75H sample. However, in swollen state the AMPS-50H shows significantly improved mechanical characteristics. It should be noted that dialysis of as-prepared hydrogel samples in pure water plays the crucial role in enhancing the ionic bond formation whereupon the polymer concentration governs the competition between intra-chain and inter-chain complexation to form a tough hydrogel [11]. In case of equimolar AMPS-50H hydrogel, the formation of intra-ionic contacts between oppositely charged monomers leads to toughening of hydrogel sample (Figs. 5*b* and 6*b*). Compression tests of swollen hydrogel samples are shown in Figure 7.



MBAA = 20 mol.%; $R = 3 \text{ mm} \cdot \text{min}^{-1}$. 1 — AMPS-25H; 2 — AMPS-50H; 3 — AMPS-75H

Figure 5. Compressive stress-strain curves of as-prepared (*a*) and dialyzed (*b*) QPA hydrogels

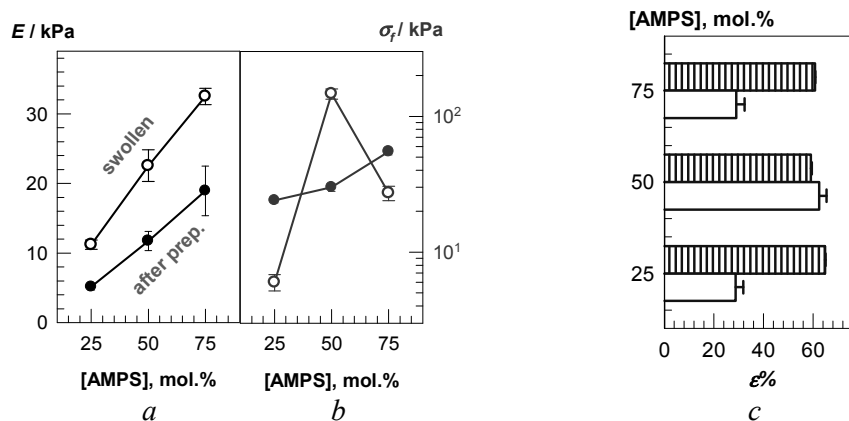


Figure 6. The compressive moduli E_c (*a*), fracture stress σ_f (*b*) and fracture strain $\varepsilon\%$ (*c*) of as-prepared (filled symbols and bars) and swollen QPA hydrogels (open symbols and bars) as a function of AMPS content in the feed

Due to the fact that swollen AMPS-25H contains the excess of cationic monomer — APTAC and absorbs much water in comparison with AMPS-50H hydrogel, the former is mechanically stable while the latter is ruptured under compression. However, the fracture stress (σ_f) of swollen AMPS-50H is 6 times higher than as-prepared state. The elongation (ε) values of as-prepared hydrogels are in the same level (62 ± 2), but for swollen AMPS-50 the value of ε (in %) is much higher than that of AMPS-25H and AMPS-75H (Fig. 6*c*). Thus both the fracture stress (σ_f) and fracture strain (ε) of swollen AMPS-50H are much higher in comparison with swollen AMPS-25H and AMPS-75H (Fig. 6*b, c*). The reasonable explanation of this phenomenon is that the opposite charges within AMPS-50H stabilized by intra- or interionic contacts act as physical crosslinks. Such globular conformation of AMPS-50H is unfolded and extended upon stretching.

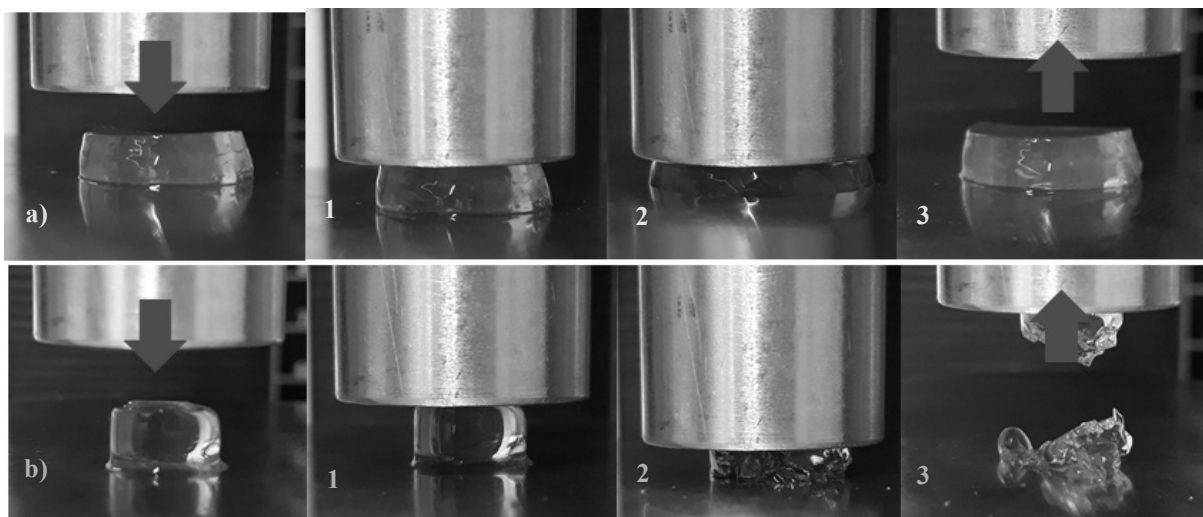


Figure 7. Photographs of swollen AMPS-25H (a) and AMPS-50H (b) hydrogel samples during the compression tests. Images a1–a3 show during uniaxial compression up to a strain ε of 40 %. The images b1–b3 show the rupture of hydrogel specimen upon compression

Our data are in good agreement with results of authors [11] who studied the effect of the charge fraction on the swelling degree, Young's modulus E , elongation ε , and the compressive fracture stress σ_f for QPA hydrogels based on [3-(methacryloylamino)propyl]trimethylammonium chloride-*co*-sodium 4-vinylbenzenesulfonate.

Conclusion

Three samples of quenched (or high-charge-density) polyampholyte hydrogels were prepared from anionic AMPS and cationic APTAC monomers in the presence of MBAA. They were characterized by swelling measurements, rheological experiments, and mechanical tests. The swelling and mechanical properties of as-prepared and equilibrated QPA hydrogels are different due to excess or equal numbers of anionic and cationic monomers. In dependence of composition they behave as polyelectrolyte and polyampholyte hydrogels. The shrinking of the AMPS-50H gels is accompanied by dramatic increase in the fracture stress σ_b and fracture strain ε , %. It is outlined that dialysis of as-prepared hydrogel samples in pure water plays the crucial role in competition between repulsive polyelectrolyte effect for AMPS-25H and AMPS-75H, and attractive polyampholyte effect AMPS-50H due to intra-ionic complexation between oppositely charged monomers. Both the fracture stress (σ_f) and fracture strain ($\varepsilon\%$) of swollen AMPS-50H are much higher than AMPS-25H and AMPS-75H. This is explained by globular structure of AMPS-50H stabilized by ionic bonds between oppositely charged monomers. Upon stretching the globular parts unfold and extend exhibiting improved mechanical properties. Supramolecular QPA prepared by random copolymerization of oppositely charged ionic monomers at relatively high monomers concentration and equimolar monomers ratio represents a new class of hydrogels containing both strong and weak ionic bonds. The former serves as permanent crosslinks to maintain the shape of the gel the latter as sacrificial network is responsible for elongation, deformation, adhesion, self-healing, shape memory, and other important functions.

Acknowledgments

This research was funded by the Ministry of Education and Science of the Republic of Kazakhstan (IRN AP05131003, 2018–2020). E.S. thanks TUBITAK-BIDEB for a Ph.D. scholarship. G.T. thanks Prof. O. Okay from Istanbul Technical University (Turkey) for giving the possibility to perform experiments.

References

- 1 Kudaibergenov, S.E. (2002). *Polyampholytes: Synthesis, Characterization and Application*. New York: Kluwer Academic/Plenum Publishers.
- 2 Su, E., & Okay, O. (2017). Polyampholyte hydrogels formed via electrostatic and hydrophobic interactions. *Eur. Polym. J.*, 88, 191–204.

- 3 Nisato, G., Munch, J.P., & Candau, S.J. (1999). Swelling, structure, and elasticity of polyampholyte hydrogels. *Langmuir*, 15, 4236–4244.
- 4 Luo, F., Sun, T.L., Nakajima, T., King, D.R., Kurokawa, T., & Zhao, et al. (2016). Strong and tough polyion-complex hydrogels from oppositely charged polyelectrolytes: A comparative study with polyampholyte hydrogels. *Macromolecules*, 49, 2750–2760.
- 5 Gao, M., Gawel, K., & Stokke, B.T. (2014). Polyelectrolyte and antipolyelectrolyte effects in swelling of polyampholyte and polyzwitterionic charge balanced and charge offset hydrogels. *Eur. Polym. J.*, 53, 65–74.
- 6 Tierney, S., Hjelme, D.R., & Stokke, B.T. (2008). Determination of swelling of responsive gels with nanometer resolution. Fiber-optic based platform for hydrogels as signal transducers. *Anal. Chem.*, 80, 5086–5093.
- 7 Wang, F., Yang, J. F., & Zhao, J. (2015). Understanding anti-polyelectrolyte behavior of a well-defined polyzwitterion at the single-chain level. *Polym. Intern.*, 64, 999–1005.
- 8 Sun, T.L., Luo, F., Kurokawa, T., Karobi, S.N., Nakajima, T., & Gong, J.P. (2015). Molecular structure of self-healing polyampholyte hydrogels analyzed from tensile behaviors. *Soft Matter*, 11, 9355–9366.
- 9 Sun, T.L., Luo, F., Hong, W., Cui, K.P., Huang, Y.W., & Zhang H.J., et al. (2017). Bulk energy dissipation mechanism for the fracture of tough and self-healing hydrogels. *Macromolecules*, 50, 2923–2931.
- 10 Bin, Ihsan A., Sun, T.L., Kurokawa, T., Karobi, S.N., Nakajima, T., & Nonoyama, T., et al. (2016). Self-healing behaviors of tough polyampholyte hydrogels. *Macromolecules*, 49, 4245–4252.
- 11 Sun, T.L., Kurokawa, T., Kuroda, S., Bin, Ihsan A., Akasaki, T., & Sato, K., et al. (2013). Physical hydrogels composed of polyampholytes demonstrate high toughness and viscoelasticity. *Nature Materials*, 12, 932–937.
- 12 Gong, J.P. (2010). Why are double network hydrogels so tough? *Soft Matter*, 6, 2583–2590.
- 13 Charaya, H., Li, X.D., Jen, N., & Chung H.J. (2019). Specific ion effects in polyampholyte hydrogels dialyzed in aqueous electrolytic solutions. *Langmuir*, 35, 1526–1533.
- 14 Toleutay, G., Dauletbekova, M., Shakhvorostov, A., & Kudaibergenov, S.E. (2019). Quenched polyampholyte hydrogels based on (3-acrylamidopropyl)trimethyl ammonium chloride and sodium salt of 2-acrylamido-2-methyl-1-propanesulfonic acid. *Macromol. Symp.* DOI: 10.1002/masy.201800160.
- 15 Zheng, H.L., Feng, L., Gao, B.Y., Zhou, Y.H., Zhang, S.X., & Xu, B.C. (2017). Effect of the cationic block structure on the characteristics of sludge flocs formed by charge neutralization and patching. *Materials*. DOI: 10.3390/ma10050487
- 16 Travas-Sejdic, J., & Easteal, A. (2000). Study of free-radical copolymerization of acrylamide with 2-acrylamido-2-methyl-1-propane sulfonic acid. *J. Appl. Polym. Sci.*, 75, 619–628.
- 17 Zhang, C., & Easteal, A.J. (2003). Study of poly(acrylamide-co-2-acrylamido-2-methylpropane sulfonic acid) hydrogels made using gamma radiation initiation. *J. Appl. Polym. Sci.*, 89, 1322–1330.

Г. Төлеутай, Э. Су, С.Е. Кұдайбергенов

Анион мономері акриламид-2-метил-1-пропансульфон қышқылы натрий тұзы (AMPS) және катион мономері 3-акриламидопропил-триметиламмоний хлориді (АРТАС) негізінде жоғары зарядталған полиамфолитті гидрогельдердің механикалық және ісіну қасиеттері

Біздің алдыңғы жұмыста (Қарағанды университетінің хабаршысы. Химия сериясы, 2019, № 2(94), 35–43 бет) біз толық зарядталған анион-мономер акриламид-2-метил-1-пропансульфон қышқылы натрий тұзы (AMPS) және катион мономері 3-акриламидопропил-триметиламмоний хлориді (АРТАС) негізінде полиамфолиттердің су-тұз ерітінділерінде әрекетін қарастырдық. Бұл мақалада N,N-метилден бисакриламидінің (МВАА) байланыстырушы агент ретінде қатысуымен ескерілген мономерлердің еркін радикалды сополимеризациясы арқылы синтезделген жоғары зарядталған полиамфолитті гидрогельдердің механикалық қасиеттері туралы баяндаймыз. AMPS молярлық мөлшеріне байланысты гидрогель үлгілері AMPS-75Н, AMPS-50Н және AMPS-25Н ретінде қысқартылды. Жоғары зарядталған полиамфолитті гидрогельдердің реологиялық және механикалық қасиеттері әртүрлі сополимерлі композициялар үшін тұрақты бастапқы мономер концентрациясы $C_0 = 0,5$ мас.% және тұрақты мөлшері $[МВАА] = 20$ моль% алынды. Қарама-қарсы зарядталған мономерлердің сополимеризациясы кезінде гидрогельдердің түзілуі МВАА қатысуымен $\omega = 6,3$ рад·с⁻¹ және кернеудің амплитудасы $\gamma_0 = 0,01$ болғанда тербелмелі деформация тесттерін қолданып, реометриялық өлшеулер көмегімен бақыланды. Постинтезделген және ісінген полиамфолитикалық гелдерге арналған кернеудің қисық сызықтары синтезделген AMPS-75Н үлгілері сондай-ақ AMPS-50Н ісінген күйінде ең жоғары механикалық қасиеттерін көрсетті. Бұл нәтижелер полиэлектролит пен полиамфолиттің әсері тұрғысынан түсіндіріледі.

Кілт сөздер: күшті зарядталған полиамфолиттер, ісіну, реологиялық және механикалық қасиеттері, кернеу-деформация, Юнг модулі, иондық өзара әрекеттесу.

Г. Толеутай, Э. Су, С.Е. Кудайбергенов

Механические и набухающие свойства сильнозаряженных полиамфолитных гидрогелей на основе анионного мономера 2-акриламид-2-метил-1-пропансульфоновой кислоты (AMPS) и катионного мономера — 3-акриламидопропилтриметиламмоний хлорида (APTAC)

В нашей предыдущей работе (Вестник Карагандинского университета. Сер. Химия, 2019, 2(94), с. 35–43) мы рассмотрели поведение «quenched» (или сильно заряженных) полиамфолитов на основе полностью заряженного анионного мономера — 2-акриламид-2-метил-1-пропансульфоновой кислоты (AMPS) и катионного мономера — 3-акриламидопропилтриметиламмоний хлорида (APTAC) в водно-солевых растворах. В настоящей статье сообщаем о механических свойствах сильно заряженных полиамфолитных гидрогелей, синтезированных путем свободнорадикальной сополимеризации тех же мономеров в присутствии N,N-метиленбисакриламида (МВАА) в качестве сшивающего агента. Образцы гидрогеля в зависимости от молярного количества AMPS были сокращенно обозначены как AMPS-75Н, AMPS-50Н и AMPS-25Н. Реологические и механические свойства сильно заряженных полиамфолитных гидрогелей были оценены для различных составов сополимеров при фиксированной начальной концентрации мономера $C_0 = 0,5$ мас.% и постоянном количестве [МВАА] = 20 мол.%. Образование гидрогелей в ходе сополимеризации противоположно заряженных мономеров в присутствии МВАА контролировали с помощью реометрических измерений с использованием тестов колебательной деформации при угловой частоте $\omega = 6,3$ рад·с⁻¹ и амплитуде деформации $\gamma_0 = 0,01$. Кривые напряжения-деформации для свежесинтезированных и набухших полиамфолитных гелей показывают, что самые высокие значения модуля Юнга E , степень разрушения σ_f и относительного удлинения характерны для синтезированных образцов AMPS-75Н и в набухом состоянии AMPS-50Н. Эти результаты интерпретируются с точки зрения эффектов полиэлектролита и полиамфолита.

Ключевые слова: сильнозаряженные полиамфолиты, набухание, реологические и механические свойства, напряжение-деформация, модуль Юнга, ионные взаимодействия.