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Article

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Temperature and Salt Responsivity of Anionic, Cationic and Amphoteric Nanogels Based on N-Isopropylacrylamide, 2-Acrylamido-2-Methyl-1-Propanesulfonic Acid Sodium Salt and (3-Acrylamidopropyl) Trimethylammonium Chloride

Three different nanogels possessing anionic, cationic and amphoteric character were synthesized via conventional redox initiated free radical copolymerization of N-isopropylacrylamide (NIPAM), 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS) and (3-acrylamidopropyl) trimethylammonium chloride (APTAC). The negatively charged [NIPAM]:[AMPS] = 90:10 mol.%, positively charged [NIPAM]:[APTAC] = = 90:10 mol.%, and charge-balanced amphoteric nanogels [NIPAM]:[APTAC]:[AMPS] = 90:5:5 mol.% abbreviated as $NIPAM_{90}$-$AMPS_{10}$, $NIPAM_{90}$-$APTAC_{10}$, and $NIPAM_{90}$-$APTAC_{5}$-$AMPS_{5}$, respectively, were characterized by FTIR spectroscopy, TGA, UV-Vis spectroscopy and DLS measurements. The temperature and salt responsive properties of nanogels in aqueous and aqueous-salt solutions were studied in the temperature range of 25–60 °C and ionic strength (μ) of 0.001–1.0 M NaCl. Anionic $NIPAM_{90}$-$AMPS_{10}$ and cationic $NIPAM_{90}$-$APTAC_{10}$ nanogels, exhibit a pronounced polyelectrolyte effect in aqueous-salt solution due to screening of the negative or positive charges by low-molecular-weight salt. Whereas the charge-balanced amphoteric nanogel $NIPAM_{90}$-$APTAC_{5}$-$AMPS_{5}$ exhibits an antipolyelectrolyte effect due to the screening of electrostatic attraction between opposite charges by low-molecular-weight salt. The difference between the temperature-dependent behaviors of anionic, cationic and amphoteric nanogels is explained by shrinking (polyelectrolyte effect) and expanding (antipolyelectrolyte effect) of macromolecular chains in aqueous-salt solutions.

Keywords: polyampholyte nanogels, poly-N-isopropylacrylamide, ionic monomers, volume phase transition temperature, amphoteric nanogel, anionic nanogel, cationic nanogel.

Introduction

Nanogels are three-dimensional structures that have the properties of both nanomaterials and hydrogels [1]. The main advantages of nanogels are their small size (from 1 to 100 nm), high degree of swelling in water, high stability, biodegradability, adjustable toxicity, stimuli-sensitivity etc. [2–6].

Thermoresponsive nanogels respond to changes in ambient temperature. The temperature at which the nanogel acquires the largest and sharpest change in hydrodynamic diameter due to swelling/deswelling is called the volume phase transition temperature (VPTT). Nanogel swells in water at temperatures below VPTT, and shrinks at temperatures above VPTT [7, 8]. Hydrophobic fragments attached as side chains in the main chain impart thermoresponsive properties to the nanogel [1]. For example, Judah et. al. synthesized nanogels based on NIPAM, N-hydroxyethylacrylamide and N-acryloyl-l-proline by high dilution radical polymerization using DMSO as a solvent. The temperature-responsive properties have been studied in various buffer media and their dependence on the chemical structure of the polymer network has been proven. A slight change in the chemical structure of the side chains of monomers from branched isopropyl groups to linear propyl groups leads to a decrease in the VPTT value by about 10^{o}C [9].

The most common thermoresponsive polymer is poly-N-isopropylacrylamide (PNIPAM), which contains in structure hydrophilic amide and hydrophobic isopropyl groups [10]. NIPAM-based nanogels can be modified by incorporating various comonomers and cross-linking agents, which can reduce or increase VPTT [11]. Copolymerization of NIPAM and various ionic monomers makes it possible to obtain thermoresponsive nanogels with increased VPTT [12, 13]. It is possible to control the VPTT and use the resulting nanogels for controlled drug release by modifying a PNIPAM-based nanogel with different amounts of acrylic acid (AAc) [14]. The PNIPAM-co-AAc nanogels showed two volume phase transitions and the VPTT increased with AAc content.

The authors [15] describe the synthesis of thermoresponsive nanogels based on NIPAM and allylacetic acid (AAA) by radical polymerization. The DLS data at various pH values demonstrate that the phase transition temperature of the microgel shifts towards higher temperatures with an increase in the amount of comonomer AAA.

Zhou et. al. synthesized nanogels based on NIPAM and strongly ionic 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS) by precipitation polymerization in the presence of Fe_3O_4. The resulting nanogels have thermoresponsive and paramagnetic properties, which allows them to be used as draw agents in forward osmosis [16].

In general, despite the progress in the field of synthesis and study of stimuli-responsive polymers, information on comparative study of thermo- and salt responsive polyelectrolyte and polyampholyte nanogels is limited. This article describes the synthesis and characterization of anionic, cationic and amphoteric nanogels based on N-isopropylacrylamide (NIPAM), (3-acrylamidopropyl) trimethylammonium chloride (APTAC) and 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS). The volume phase transition behavior of nanogels was studied in aqueous and aqueous-salt solutions depending on the charge of ionic monomers.

Experimental

Materials

The following chemicals were used: N-isopropylacrylamide (NIPAM, 97 % purity), 2-acrylamido-2-methylpropanesulfonic acid sodium salt (AMPS, 50 wt.%) and (3-acrylamidopropyl) trimethylammonium chloride (APTAC, 75 wt.%) as monomers; ammonium persulfate (APS, 98 % purity) and sodium metabisulfite (SMBS, 97 % purity) as redox initiator; sodium dodecyl sulfate (SDS, 99 % purity) as surfactant; N,N-methylenebis(acrylamide) (MBAA, 99 % purity) as crosslinking agent; sodium chloride (NaCl) and dialysis tubing cellulose membrane (12–14 kDa) as further materials. All chemicals were purchased from Sigma-Aldrich Chemical Co. and used as received.

Methods

Synthesis of nanogels based on NIPAM, APTAC and AMPS

Nanogels NIPAM$_{90}$-APTAC$_{10}$, NIPAM$_{90}$-AMPS$_{10}$ and NIPAM$_{90}$-APTAC$_{5}$-AMPS$_{5}$ were synthesized via conventional redox initiated free radical copolymerization.

The required amounts of monomers (NIPAM, APTAC and (or) AMPS), MBAA and SDS, listed in Table 1 were dissolved in deionized water with constant stirring. Further, the required amount of APS/SMBS redox system was added to the solution and stirred until complete dissolution. The solution with dissolved monomers, crosslinking agent, surfactant and redox system was transferred to a round bottom flask and heated on a water bath. Free radical copolymerization was carried out at 80 °C for 4 h in an inert atmosphere with constant stirring of the solution. The resulting solutions of nanogels of the indicated compositions were dialyzed against deionized water for 14 days to remove unreacted residues.

Table 1

Ratios of NIPAM, APTAC and AMPS for nanogels synthesis

Nanogel sample	NIPAM, g	APTAC, g	AMPS, g	APS, mg	MBAA, g	SMBS, mg	SDS, g	H_2O, mL	Yield, wt.%
NIPAM$_{90}$-APTAC$_{10}$	0.83	0.225	–	50	0.125	10	0.35	97	90
NIPAM$_{90}$-AMPS$_{10}$	0.815	–	0.367	30	0.123		0.23	97.5	72
NIPAM$_{90}$-APTAC$_{5}$-AMPS$_{5}$	0.735	0.099	0.165	30	0.11		0.23	98.5	70

FTIR spectroscopy. Chemical structure of nanogels was characterized using Cary 660 FTIR spectroscopy (Agilent, USA). Before measurements, nanogels were freeze-dried for 24 h until moisture was removed. The FTIR spectra were measured at room temperature within the 700–4000 cm^{-1} wavenumber range.

TGA analysis. Thermogravimetric analysis of nanogels was carried out using LabSys Evo device (Setaram, France) in the temperature range 25–500 °C (heating rate is 10 $°C \cdot min^{-1}$) in an inert atmosphere. The maximum decomposition temperature of the nanogels was determined from the differential thermal analysis (DTA) curve.

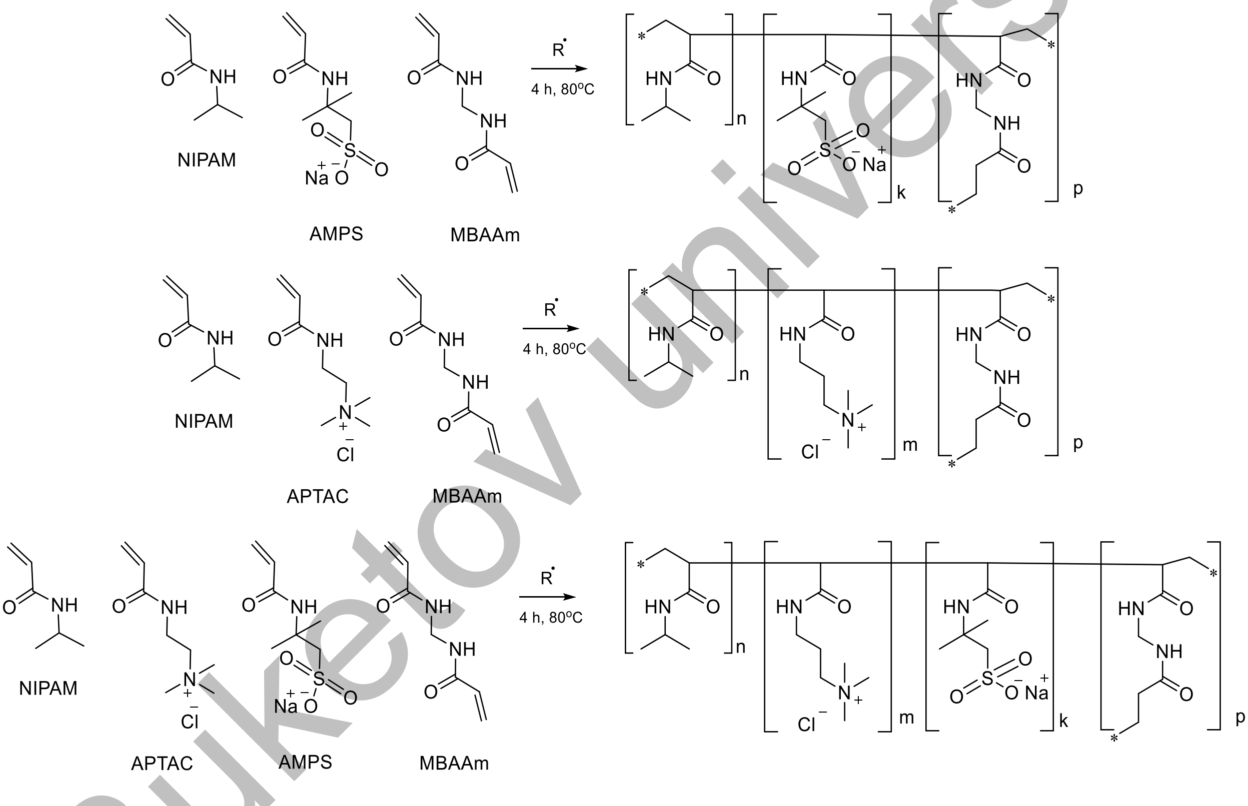
VPTT determination for $NIPAM_{90}$-$APTAC_{10}$, $NIPAM_{90}$-$AMPS_{10}$ and $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ nanogels in aqueous and aqueous-salt solutions. The method for determining the volume phase transition temperature was described in our previous studies [17, 18]. Experiments were carried out at λ = 700 nm at a nanogel concentration of 0.1 wt.%, in the temperature range of 25–60 °C (0.5 $°C{\cdot}min^{-1}$ heating rate). The VPTT of $NIPAM_{90}$-$AMPS_{10}$, $NIPAM_{90}$-$APTAC_{10}$ and $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ nanogels in NaCl solutions with μ = 0.001; 0.01; 0.1; 0.5 and 1 M corresponds to the minimum points on the DTA curves.

DLS measurements. Dynamic Light Scattering (DLS) data were obtained using Zetasizer Nano ZS 90 (Malvern, UK) with a 633 nm laser beam. The mean hydrodynamic radius *(R_h)* was measured in a 0.1 wt.% solution of nanogels in the temperature range from 25 to 60 °C with an interval of 5 °C and at μ = 0.001; 0.1 and 1 M NaCl.

Results and Discussion

Synthesis and characterization of $NIPAM_{90}$-$AMPS_{10}$, $NIPAM_{90}$-$APTAC_{10}$ and $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ nanogels

The $NIPAM_{90}$-$AMPS_{10}$, $NIPAM_{90}$-$APTAC_{10}$ and $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ nanogels were synthesized *via* conventional redox initiated free radical copolymerization (Scheme 1).



Scheme 1. Nanogels synthesized by free radical copolymerization of NIPAM, APTAC and AMPS monomers in the presence of MBAA

The $NIPAM_{90}$-$AMPS_{10}$ and $NIPAM_{90}$-$APTAC_{10}$ nanogels contain either anionic or cationic monomers; $NIPAM_{90}$-$AMPS_{10}$ is negatively charged, while $NIPAM_{90}$-$APTAC_{10}$ is positively charged. The $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ nanogel has an equal molar ratio of cationic (APTAC) and anionic (AMPS) monomers, therefore, it belongs to charge-balanced nanogel.

FTIR analysis of the $NIPAM_{90}$-$AMPS_{10}$, $NIPAM_{90}$-$APTAC_{10}$ and $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ nanogels

Figure 1 shows the FTIR spectra of the $NIPAM_{90}$-$APTAC_{10}$, $NIPAM_{90}$-$AMPS_{10}$ and $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ nanogels. The broad absorption band in the region of 3290–3500 cm^{-1} corresponds to the secondary and tertiary amine groups, and the absorption bands in the region of 2800–3000 cm^{-1} correspond to the asymmetric and symmetric vibrations of CH groups. Intensive peaks at ν =1640 and 1540 cm^{-1} belong to N-substituted groups (amide I and amide II). The S=O groups containing in AMPS fragments are detected at ν =1040 cm^{-1}.

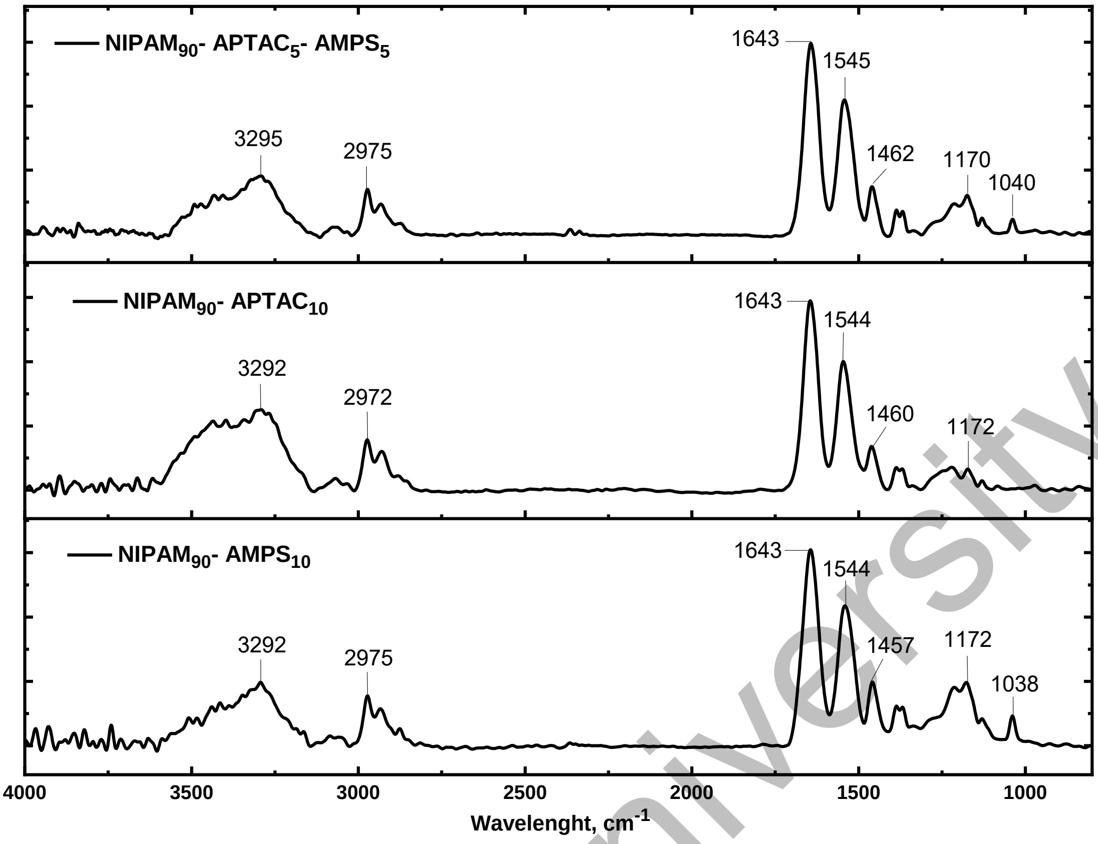


Figure 1. FTIR spectra of the NIPAM$_{90}$-APTAC$_{10}$, NIPAM$_{90}$-AMPS$_{10}$ and NIPAM$_{90}$-APTAC$_5$-AMPS$_5$ nanogels

TGA and DTA data of the NIPAM$_{90}$-AMPS$_{10}$, NIPAM$_{90}$-APTAC$_{10}$ and NIPAM$_{90}$-APTAC$_5$-AMPS$_5$ nanogels

Figure 2 shows the thermogravimetric and differential thermal analysis data for nanogels from which 3 regions can be defined.

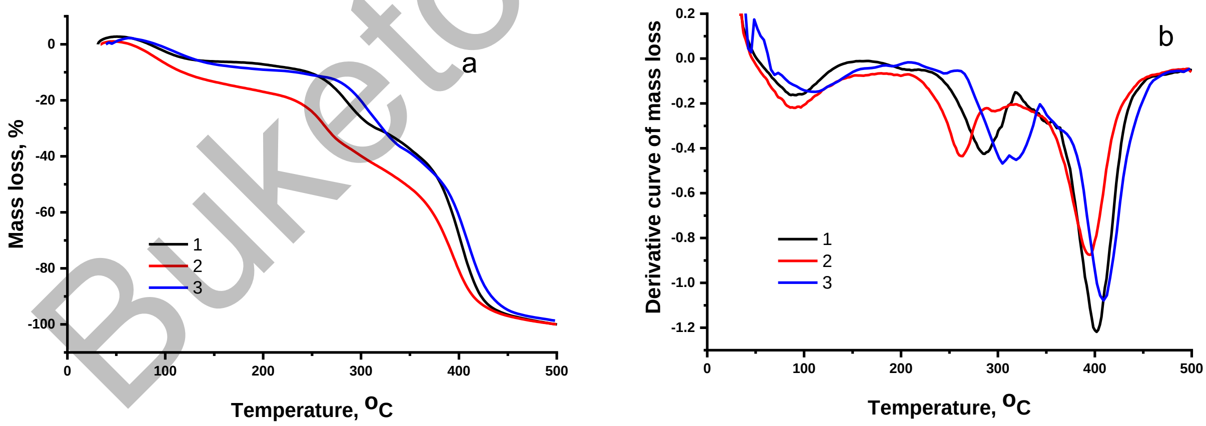


Figure 2. (a) TGA and (b) DTA curves of (1) NIPAM$_{90}$-AMPS$_{10}$; (2) NIPAM$_{90}$-APTAC$_{10}$;
(3) NIPAM$_{90}$-APTAC$_5$-AMPS$_5$ nanogels

The sample mass is lost at >100 °C, probably due to the evaporation of physically adsorbed moisture. The weight loss between 250–300 °C is probably due to the decomposition of NIPAM fragments. Complete thermal decomposition of nanogels occurs in the temperature range of 410–420 °C. The thermal stability of nanogels changes in the following order: NIPAM$_{90}$-APTAC$_5$-AMPS$_5$ > NIPAM$_{90}$-AMPS$_{10}$ > NIPAM$_{90}$-APTAC$_{10}$. This demonstrates that the charge-balanced nanogel is more stable than the anionic and cationic ones.

Volume Phase Transition Behavior (VPTB) of NIPAM$_{90}$-AMPS$_{10}$ and NIPAM$_{90}$-APTAC$_{10}$ nanogels in aqueous and aqueous-salt solutions

Figures 3, 4 show the effect of temperature and salt additive on the phase behavior of the anionic NIPAM$_{90}$-AMPS$_{10}$ and cationic NIPAM$_{90}$-APTAC$_{10}$ nanogels. Since the NIPAM$_{90}$-AMPS$_{10}$ and NIPAM$_{90}$-APTAC$_{10}$ nanogels are anionic and cationic polyelectrolytes, the addition of a salt leads to the screening of electrostatic repulsion between uniformly charged groups respectively. As a result, the macromolecular chains tend to shrink. However, there are no changes in the phase behavior of the NIPAM$_{90}$-AMPS$_{10}$ nanogel and the transmittance remain constant at ionic strengths μ = 0.001–0.01 M. Only starting from μ = 0.1 M NaCl the polyelectrolyte effect is suppressed and the value of VPTT is equal to 42.1 °C (Fig. 3, Table 2). As a further increase in the ionic strength to μ = 0.5 and 1 M NaCl, the VPTT values of NIPAM$_{90}$-AMPS$_{10}$ decrease and amount to 36.2 and 31.3 °C, respectively. The VPTT value at μ = 1 M is less than the LCST of pure PNIPAM, which is ~33 °C. It is likely that, at high NaCl concentrations, the screening of electrostatic repulsion between negatively charged AMPS groups is so effective that the phase behavior and solubility of NIPAM$_{90}$-AMPS$_{10}$ nanogel is determined by NIPAM$_{90}$ fragments. In case of NIPAM$_{90}$-APTAC$_{10}$ nanogel the ionic strength in the range of μ = 0.001–0.1 M NaCl does not significantly change the phase behavior of the NIPAM$_{90}$-APTAC$_{10}$ nanogel and the values of VPTT are equal to 46.4, 47.7, and 45.2 °C, respectively (Fig. 4, Table 2). Even further increase of the ionic strength up to μ = 0.5 and 1 M slightly changes the solubility and phase behavior of the NIPAM$_{90}$-APTAC$_{10}$ nanogel. This is probably due to the stronger polyelectrolyte character of NIPAM$_{90}$-APTAC$_{10}$ nanogel compared to NIPAM$_{90}$-AMPS$_{10}$ and its less salt-sensitivity. An increase in temperature enhances inter- and intramolecular hydrophobic interactions between NIPAM$_{90}$ fragments, thereby causing a shift in the VPTT towards lower temperatures, that are equal to 41.8 and 35.9 °C, respectively.

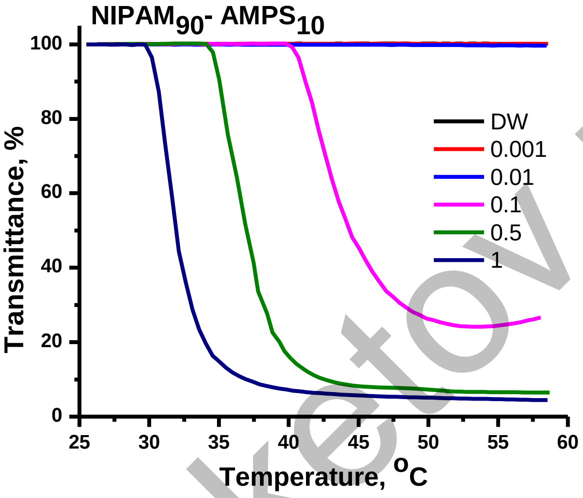


Figure 3. Effect of temperature and ionic strength (μ) on transmittance of NIPAM$_{90}$-AMPS$_{10}$ nanogel

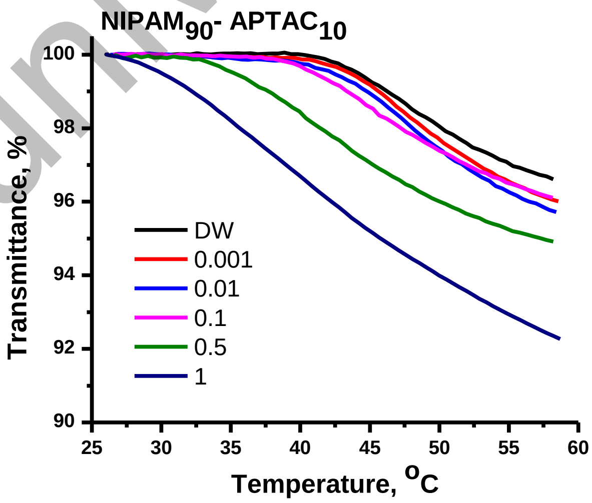


Figure 4. Effect of temperature and ionic strength (μ) on transmittance of NIPAM$_{90}$-APTAC$_{10}$ nanogel

Table 2

The effect of the ionic strength on the volume phase transition temperature of NIPAM$_{90}$-AMPS$_{10}$, NIPAM$_{90}$-APTAC$_{10}$ and NIPAM$_{90}$-APTAC$_{5}$-AMPS$_{5}$ nanogels

Nanogel	Ionic strength, μ, mol·L^{-1} (NaCl)					
	0	0.001	0.01	0.1	0.5	1.0
	Volume phase transition temperature, VPTT, °C					
NIPAM$_{90}$-AMPS$_{10}$	–	–	–	42.1	36.2	31.3
NIPAM$_{90}$-APTAC$_{10}$	48	46.4	47.7	45.2	41.8	35.9
NIPAM$_{90}$-APTAC$_{5}$-AMPS$_{5}$	40.4	39.2	40.4	47.8	45.1	38.3

Thus, $NIPAM_{90}$-$AMPS_{10}$ and $NIPAM_{90}$-$APTAC_{10}$ nanogels exhibit a strong polyelectrolyte effect and only at higher ionic strength $\mu > 0.1$ M NaCl the polyelectrolyte effect is suppressed due to screening of the electrostatic repulsion between uniformly charged groups by low-molecular-weight electrolytes.

Volume Phase Transition Behavior (VPTT) of charge-balanced $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ *nanogel in aqueous-salt solutions*

Figure 5 shows the effect of temperature and ionic strength on the phase behavior of the charge-balanced $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ nanogel. At ionic strengths equal to $\mu = 0.001$ and 0.01, the phase transition temperatures are equal to 39.2 °C and 40.4 °C and shift towards higher temperatures, respectively. The reason for this phenomenon is the demonstration of the antipolyelectrolyte effect, in which there is a gradual destruction of ionic contacts between the APTAC and AMPS monomers due to the screening of the electrostatic attraction between oppositely charged fragments by low-molecular-weight salts. The antipolyelectrolyte effect is characterized by the unfolding (swelling) of macromolecules of charge-balanced polyampholytes in a quasi-neutral state in a low-molecular-weight salt solution due to screening of the electrostatic attraction of oppositely charged fragments.

A further increase in ionic strength shifts the VPTT to maximal value 47.8 °C at $\mu = 0.1$ M. The VPTT values decrease to 45.1 and 38.3 °C at $\mu = 0.5$ and 1 M respectively. At extremely high ionic strengths ($\mu = 0.5$ and 1 M), the charged macromolecules approach neutrality due to a sufficient number of counterions, therefore, complete screening of opposite charges. In addition, probably there is a “salting out” effect of ionic groups, which leads to a decrease of VPTT. Under these conditions, $NIPAM_{90}$ fragments determine the solubility and phase behavior of the charge-balanced $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ nanogel.

It should be noted that at $\mu > 0.1$ M, a smaller change in the turbidity of the $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ solution observed than when the nanogel is in solutions with a lower concentration of salt. This is due to the dependence of light scattering on the size, density of individual particles and the increase in temperature at which particles stick together, hence the change in transmittance.

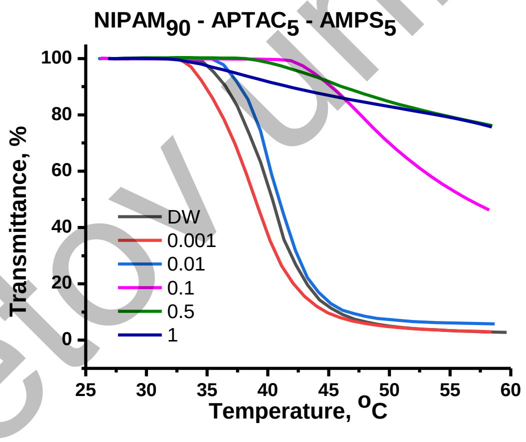


Figure 5. Effect of temperature and ionic strength (μ) on transmittance of the nanogel $NIPAM_{90}$-$APTAC_5$-$AMPS_5$

Thus, the addition of a low-molecular-weight salt promotes an increase in the hydrophilicity of ionic groups of the charge-balanced $NIPAM_{90}$-$APTAC_5$-$AMPS_5$ nanogel due to the antipolyelectrolyte effect, as well as an increase in the hydrophobicity of NIPAM due to enhancement of inter- and intramolecular hydrophobic interactions. An increase in temperature reduces the quality of water in relation to $NIPAM_{90}$ fragments, causing phase separation.

The mean hydrodynamic radius (R_h) *of* $NIPAM_{90}$-$AMPS_{10}$ *and* $NIPAM_{90}$-$APTAC_{10}$ *nanogels in aqueous-salt solutions*

The mean hydrodynamic radius was measured in a 0.1 wt.% solution of $NIPAM_{90}$-$AMPS_{10}$ and $NIPAM_{90}$-$APTAC_{10}$ nanogels in the temperature range from 25 to 50 °C with an interval of 5 °C in *deionized* water and in NaCl solutions with $\mu = 0.001$; 0.1 and 1 M.

The dependence of the average hydrodynamic particle size of the $NIPAM_{90}$-$AMPS_{10}$ nanogel on temperature and ionic strength is shown in Figure 6. It was previously described that the ionic strength equal to $\mu = 0.001$ M does not affect the phase behavior of the nanogel, the transmittance remains constant (Fig. 3). Therefore, an increase of temperature does not affect the nanogel particle size, in the temperature range of

25–50 °C in 0.001 M NaCl solution R_h is ~10–20(±1) nm (Fig. 6*a*). At $\mu = 0.1$ M and temperatures of 25–35 °C, there are particles with sizes of ~12(±0.5), 60(±1) and 100(±5) nm (Fig. 6*b*). The VPTT of the nanogel in a 0.1 M NaCl solution is 42.1 °C (Table 2); upon reaching 40 °C, in addition to particles with a size of ~12(±0.5) nm, the aggregation of nanogel particles is observed and R_h increases up to 300(±5) nm. At 45 and 50 °C, the R_h particle size is ~250(±2) and 300(±5) nm, respectively.

At 25 °C and ionic strength $\mu = 1$ M, the particle size is ~15(±1) nm (Fig. 6*c*). Raising the temperature to 30 °C causes the aggregation of nanoparticles and their size R_h is 240(±5) nm. The VPTT of the NIPAM$_{90}$-AMPS$_{10}$ nanogel in 1 M NaCl is 31.3 °C (Table 2), therefore, an increase in size up to ~550(±10) nm at 35–40 °C is observed. A further increase in temperature to 45–50 °C leads to a decrease in the particle size to 310–420(±5) nm; probably, the formed nanogel aggregates begin to shrink.

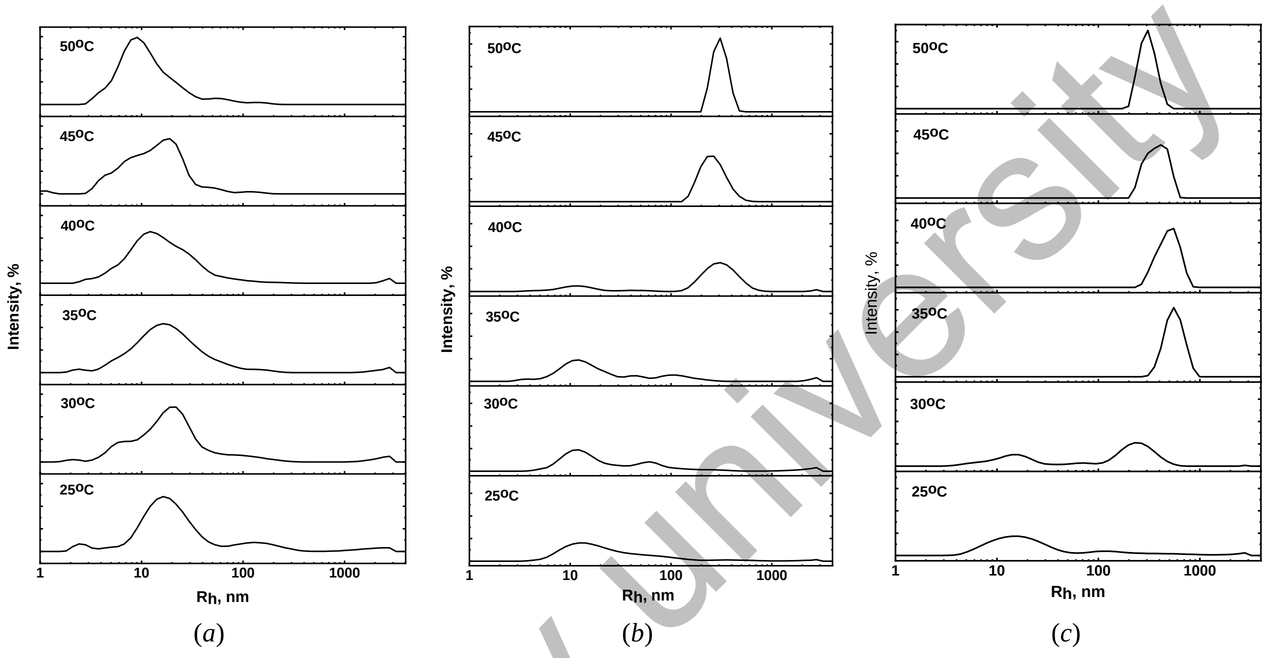


Figure 6. Effect of temperature and ionic strength (μ) on the mean hydrodynamic radius (R_h) of NIPAM$_{90}$-AMPS$_{10}$ at μ = (*a*) 0.001, (*b*) 0.1 and (*c*) 1.0

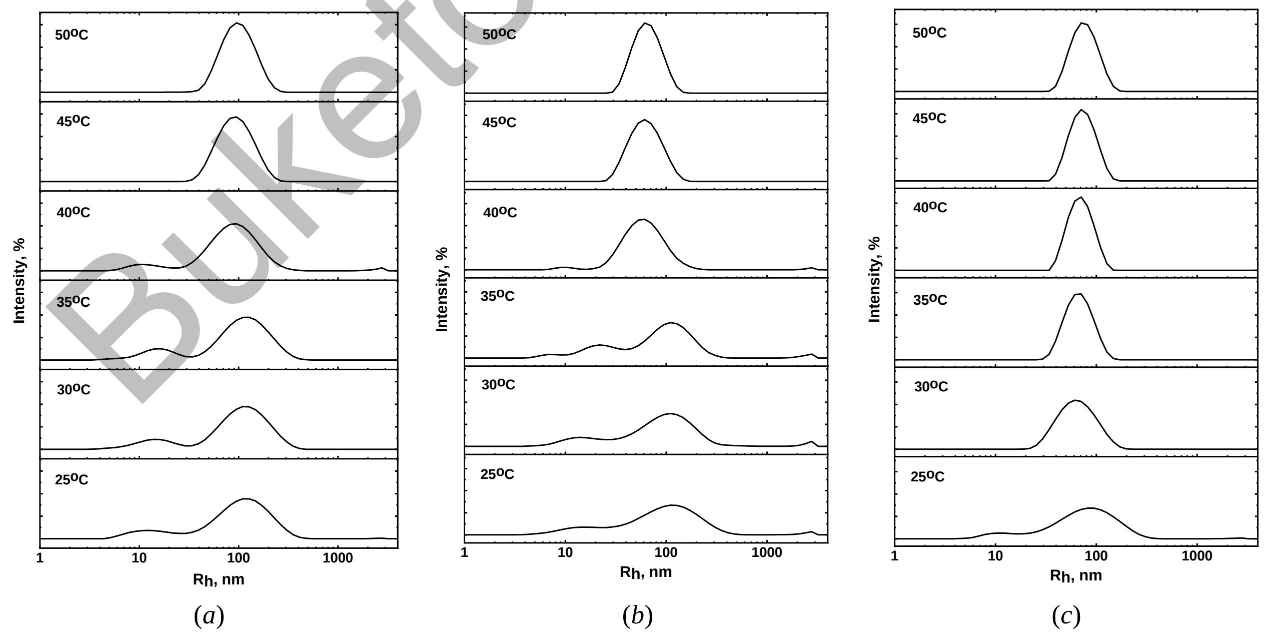


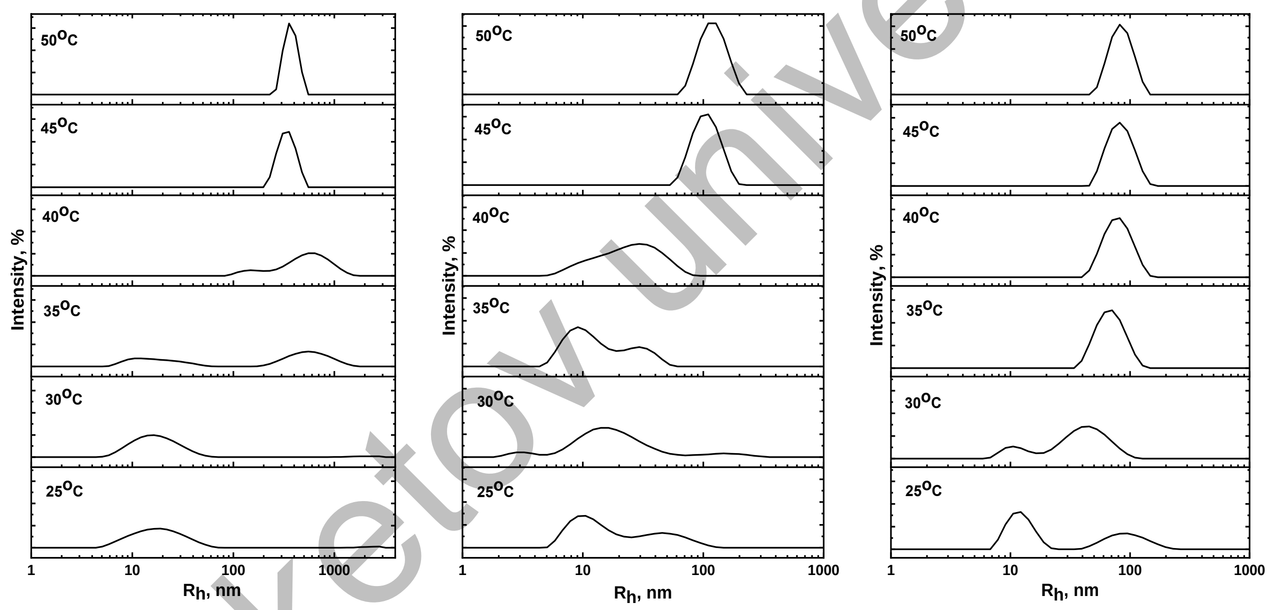
Figure 7. Effect of temperature and ionic strength (μ) on the mean hydrodynamic radius (R_h) of NIPAM$_{90}$-APTAC$_{10}$ at μ = (*a*) 0.001, (*b*) 0.1 and (*c*) 1.0

The effect of temperature and salt additive on the average hydrodynamic particle size of the NIPAM$_{90}$-APTAC$_{10}$ nanogel is shown in Figure 7. At ionic strength $\mu = 0.001$ and 0.1 M and in the temperature range of 25–35 °C, the particle size R$_h$ is ~15(±2), 115(±5) nm (Fig. 7*a*, 7*b*). An increase of temperature to 40 °C leads to a decrease in the size of R$_h$ particles to ~10(±0.5) and 60(±5) nm. At 45 and 50 °C, temperatures close to VPTT (Table 2), the particle size distribution becomes monomodal and have values ~ 95(±1) nm in 0.001 M NaCl solution and ~ 60(±1) nm in 0.01 M. In solutions with ionic strength $\mu = 1$ M at room temperature, the R$_h$ is ~10(±0.5) and 90(±0.5) nm (Fig. 7*c*). With a further increase in temperature from 30 to 50 °C, the average R$_h$ values are in the range of 60–70 (±5) nm; therefore, at temperatures close to the VPTT, no significant changes in size occur.

The mean hydrodynamic radius (R$_h$) of NIPAM$_{90}$-APTAC$_5$-AMPS$_5$ nanogel in aqueous and aqueous-salt solutions

The mean hydrodynamic size of NIPAM$_{90}$-APTAC$_5$-AMPS$_5$ was measured in a 0.1 wt.% solution of nanogel in the temperature range from 25 to 50 °C with an interval of 5 °C in *deionized* water and in NaCl solutions with $\mu = 0.001$; 0.1 and 1 M (Fig. 8).

A particle size of ~ 18(±1) nm is observed in solution with an ionic strength of $\mu = 0.001$ M at 25 °C (Fig. 8*a*). An increase in the ionic strength to $\mu = 0.1$ and 1 M leads to the appearance of particles with sizes of ~10, 45 and 90 (±1) nm. Most likely, the appearance of large particles leads to the determination of the antipolyelectrolyte effect, due to unfolding of macromolecules and the aggregation of nanogel particles occurs.



(*a*) (*b*) (*c*)

Figure 8. Effect of temperature and ionic strength (μ) on the mean hydrodynamic radius (R$_h$) of NIPAM90-APTAC5-AMPS5: μ = (*a*) 0.001, (*b*) 0.1 and (*c*) 1.0

An increase in temperature promotes the aggregation of nanogels. Aggregates with R$_h$~560–600 (±10) nm formed in 0.001 M NaCl solution at 35 and 40 °C. Under these conditions, the hydrophobicity of the NIPAM regions prevails over the antipolyelectrolyte effect. In a 0.1 M salt solution at 47.8 °C, a bulk phase transition observed (Fig. 8*b*). An increase of temperature directly proportionally affects the aggregation of nanogel particles, reaching a maximum at 45.1 °C. A further increase in temperature does not affect the size and structure of nanogel particles. As the ionic strength increases, the opposing AMPS and APTAC blocks electrostatically screened. A bulk phase transition observed by NIPAM fragments at $\mu = 1$ M, since the antipolyelectrolyte effect is suppressed (Fig. 8*c*). The increase in nanogel particles size remained colloidal stable above the VPTT.

Conclusions

Polyelectrolyte NIPAM$_{90}$-AMPS$_{10}$, NIPAM$_{90}$-APTAC$_{10}$ and polyampholyte NIPAM$_{90}$-APTAC$_{5}$-AMPS$_{5}$ nanogels were obtained *via* conventional redox initiated free radical copolymerization with N,N-methylene-bis(acrylamide) (MBAA) as a crosslinking agent.

The effect of ionic monomers on the volume phase transition behavior of nanogels based on the results of UV-Vis and DLS measurements was studied. Negatively and positively charged nanogels NIPAM$_{90}$-AMPS$_{10}$ and NIPAM$_{90}$-APTAC$_{10}$ demonstrate a volume phase transition at ionic strengths equal to or higher than 0.1 M NaCl due to the presence of polyelectrolyte effect. The volume phase transition temperature (VPTT) of the amphoteric nanogel NIPAM$_{90}$-APTAC$_{5}$-AMPS$_{5}$ increases with the addition of salt, which can be explained by the antipolyelectrolyte effect. With an increase in ionic strength, the general hydrophobization of macromolecular chains occurs and, as a result, the VPTT of NIPAM$_{90}$-APTAC$_{5}$-AMPS$_{5}$ decreases.

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N-изопропилакриламид, 2-акриламидо-2-метил-1-пропансульфон қышқылы натрий тұзы және (3-акриламидопропил)триметиламмоний хлориді негізіндегі анионды, катионды және амфотерлі наногельдердің температураға және тұзға сезімталдығы

N-изопропилакриламид (НИПАМ), 2-акриламидо-2-метилпропансульфонат натрий тұзы (АМПС) және 3-акриламидопропилтриметиламмоний хлориді (АПТАХ) негізінде бос радикалды сополимерлеу арқылы аниондық, катиондық және амфотерлік сипаттағы үш түрлі наногельдер синтезделді. Теріс зарядталған [НИПАМ]:[АМПС] = 90:10 моль.%, оң зарядталған [НИПАМ]:[АПТАХ] = 90:10 моль.% және амфотерлік заряд теңестірілген [НИПАМ]:[АПТАХ]:[АМПС] = 90:5:5 моль.%, тиісінше NIPAM$_{90}$-AMPS$_{10}$, NIPAM$_{90}$-APTAC$_{10}$ және NIPAM$_{90}$-APTAC$_{5}$-AMPS$_{5}$ деп қысқартылған наногельдері ИК спектроскопиясы, ТГА, УФ-көрінетін спектроскопиясы және ДЛС өлшемдерімен сипатталды. Наногельдердің су және тұз ерітінділеріндегі температура мен тұзға сезімталдық қасиеттері 25–60 °C температура диапазонында және иондық күші (μ) 0.001–1.0 M NaCl аралығында зерттелді. Аниондық NIPAM$_{90}$-AMPS$_{10}$ және катиондық NIPAM$_{90}$-APTAC$_{10}$ наногельдері төмен молекулалық салмақ тұзымен теріс немесе оң зарядты скринингке байланысты тұз ерітіндісінде айқын полиэлектролиттік әсер көрсетеді. Зарядпен теңестірілген амфотерлік наногель NIPAM$_{90}$-APTAC$_{5}$-AMPS$_{5}$ төмен молекулалық салмақты тұзбен қарама-қарсы зарядтар арасындағы электростатикалық тартылысты қорғауға байланысты антиполиэлектролит әсерін көрсетеді. Аниондық, катиондық және амфотерлік наногельдердің температураға тәуелді әрекетінің айырмашылығы тұз ерітінділеріндегі макромолекулярлық тізбектердің қысылуымен (полиэлектролиттік әсер) және кеңеюімен (антиполиэлектролиттік әсер) түсіндіріледі.

Кілт сөздер: полиамфолит наногельдер, поли-N-изопропилакриламид, иондық мономерлер, көлемдік фазалық ауысу температурасы, амфотерлік наногель, анионды наногель, катионды наногель.

А.Е. Аязбаева, А.В. Шахворостов, С.Е. Кудайбергенов

Температурная и солевая чувствительность анионного, катионного и амфотерного наногелей на основе N-изопропилакриламида, натриевой соли 2-акриламидо-2-метил-1-пропансульфоновой кислоты и (3-акриламидопропил)триметиламмоний хлорида

Три различных наногеля, обладающих анионным, катионным и амфотерным характером, были синтезированы с помощью обычной свободнорадикальной сополимеризации N-изопропилакриламида (НИПАМ), натриевой соли 2-акриламидо-2-метил-1-пропансульфоновой кислоты (АМПС) и (3-акриламидопропила) триметиламмоний хлорида (АПТАХ). Отрицательно заряженный [НИПАМ]:[АМПС] = 90:10 мол.%, положительно заряженный [НИПАМ]:[АПТАХ] = 90:10 мол.% и амфотерный со сбалансированным зарядом [НИПАМ]:[АПТАХ]:[АМПС] = 90:5:5 мол.% наногели, сокращенно NIPAM$_{90}$-AMPS$_{10}$, NIPAM$_{90}$-APTAC$_{10}$ и NIPAM$_{90}$-APTAC$_{5}$-AMPS$_{5}$, соответственно, были охарактеризованы с помощью ИК-спектроскопии, ТГА, УФ-видимой спектроскопии и измерений ДЛС. Температурные и солечувствительные свойства наногелей в водных и водно-солевых растворах изучали в интервале температур 25–60 °C и ионной силы (μ) 0.001–1.0 M NaCl. Анионный НИПАМ$_{90}$-АМПС$_{10}$ и катионный НИПАМ$_{90}$-АПТАХ$_{10}$ наногели проявляют выраженный полиэлектролитный эффект в водно-солевом растворе за счет экранирования отрицательного или положительного заряда низкомолекулярной солью. В то время как заряд-сбалансированный амфотерный наногель NIPAM$_{90}$-APTAC$_{5}$-AMPS$_{5}$ проявляет антиполиэлектролитный эффект за счет экранирования электростатического притяжения между противоположными зарядами низкомолекулярной солью. Различие в температурно-зависимом поведении анионного, катионного и амфотерного наногелей объясняется сжатием (полиэлектролитный эффект) и расширением (антиполиэлектролитный эффект) макромолекулярных цепей в водно-солевых растворах.

Ключевые слова: полиамфолитные наногели, поли-N-изопропилакриламид, ионные мономеры, температура объемно-фазового перехода, амфотерный наногель, анионный наногель, катионный наногель.

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