

## SYNTHESIS OF WATER SOLUBLE COPOLYMERS AND THEIR INTERPOLYMER COMPLEXES WITH POLY(ACRYLIC ACID)

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Received 17 May 2017

Accepted 20 October 2017

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### ABSTRACT

Copolymers are synthesized by free radical copolymerization of *N*-isopropylacrylamide (NIPAAm) with 2-hydroxyethyl acrylate (2HEA). Their interpolymer complexes with poly(acrylic acid) are studied in aqueous solutions by turbidimetric method. The effects of pH, the different molecular mass of polyacid and copolymer composition as well as the ionic strength of the solution on the complexation processes are discussed. The phase transition behavior of interpolymer complexes in aqueous solutions based on a linear copolymer with poly(acrylic acid) is investigated. It is revealed that the phase transition temperature depends on the initial monomer ratio of the copolymer and the interpolymer complexes composition.

**Keywords:** Hydrophilic copolymers, *N*-isopropylacrylamide (NIPAAm), interpolymer complexes, thermosensitive copolymer, 2-hydroxyethylacrylate (HEA), polyacrylic acid.

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### INTRODUCTION

Interpolymer complex (IPC) of poly (carboxylic acid) with different polymers have been the focus of attention for a long time. Comprehensive studies of IPC, their physic-chemical properties and some possible application are presented in refs. [1 - 3]. Several researchers study the effect of the temperature and pH of IPC using different methods. Staikos and coworkers report the effect of temperature on viscometric behavior of complexes between poly(acrylic acid) (PAA) and polyacrylamide as well as PAA with poly(*N*-isopropylacrylamide) (PNIPAAm) in aqueous solutions. They find that the solution viscosity of PAA-PNIPAAm polycomplexes is decreased upon temperature increase, while the opposite trend is observed for complexes of PAA with polyacrylamide [4]. Mun G.A et al. study polycomplexes of polyacrylic acid with Poly(2HEA)

in aqueous solutions and their properties determined by viscometric, turbidimetric, FTIR spectroscopic, and thermogravimetric analysis methods [5].

Interpolymer complexes, which are stabilized by a system of cooperative hydrogen bonds, represent a new class of polymer composite materials. They possess valuable scientific and practical properties that differ from those, characteristic of the original polymer components. Polycarboxylic acid complexes with polyethylene oxide, polyethylene glycol, polyvinylpyrrolidone, polyacrylamide, polyvinyl alcohol and some other water-soluble nonionic polymers are studied in details [6].

Z.S. Nurkeeva et al. [7] study the effect of the polymer concentrations, the molecular weights and the inorganic salts presence on the complexation.

The present study is focused on the effect of the polymer molecular weight and the solution ionic strength on critical pH values of PAA- poly(NIPAAm-2HEA) system.

## EXPERIMENTAL

### Materials and Instrumentation

N-Isopropylacrylamide (NIPAM) was purchased from TCI (Tokyo, Japan) and purified by recrystallization from n-hexane. 2-hydroxyethylacrylate (2-HEA) was purchased from Sigma-Aldrich in the form of 96 % aqueous solution and used as received. 2,2-Azobisisobutyronitrile (AIBN) (Sigma-Aldrich) was doubly recrystallized from ethanol. Polyacrylic acid (PAA) of molecular weights of 2 KDa, 250 KDa and 450 KDa was purchased from Sigma-Aldrich and used as received.

### Turbidometric measurements

The turbidometric titration of the polymer solution was carried out at  $\lambda$  400 nm using «UV-2401-PC» (Shimadzu, Japan) spectrophotometer. The temperature control was performed by the cuvettes thermostatic controller «CPS-240A» (Shimadzu, Japan).

### pH-measurements

pH of solution was determined at 25°C using Ion Meter 3345 (Jenway, UK). The pH value was adjusted by addition of very small amounts of 0,1M solutions of hydrochloric acid or sodium hydroxide to those of the polymers.

Interpolymer complex solutions were prepared by mixing solutions of the initial components aiming to determine the critical pH of complexation. The polycomplexes composition was calculated using the formula (1):

$$n = \frac{C_1 V_1}{C_2 V_2} \quad (1)$$

where  $C_1$  was the concentration of PAA solution, 0,01 g/dL,  $V_1$  was the volume of PAA solution which was added to poly(NIPAAm-co-2HEA) solution, mL,  $C_2$  was the concentration of poly(NIPAAm-co-2HEA) solution; 0,01g/dL, while  $V_2$  was the volume of poly(NIPAAm-co-2HEA) solution, 5 mL.

### Synthesis of copolymers

The copolymer of N-isopropylacrylamide (NIPAAm) with 2-hydroxyethyl acrylate (2HEA) was synthesized by the ethanol solution method at 60°C, using Azoisobutyronitrile (AIBN) as an initiator. The resulting mixture was poured into a glass ampoule and

saturated by argon for 10 min to remove the oxygen. Thus, the copolymerization was performed in hermetically sealed glass ampoules at 60°C for 40 min. After that the copolymer obtained was precipitated in a mixture of hexane and ethyl acetate (1:1) twice to remove unreacted monomers and then dried under vacuum until its constant weight was achieved. The copolymer of NIPAAm with 2-HEA of various ratios of the hydrophilic chains ( $M1 = 30:70$ ,  $M2 = 50:50$ ,  $M3 = 70:30$ , respectively) were synthesized by solution polymerization.

## RESULTS AND DISCUSSION

Linear copolymers based on N-isopropylacrylamide (NIPAAm) and 2-hydroxyethylacrylate (HEA) are synthesized by radical copolymerization. The structural formula, the molecular mass and the polydispersity of NIPAAm-HEA copolymers are determined by NMR spectroscopy and gel chromatography. It is revealed that the NIPAAm units increase in the feed composition from 70 % to 90 % leads to molecular mass increase. This is attributed to the fact that NIPAAm unit has a higher reactivity compared to that of HEA [8, 9].

Interpolymer reactions of polycarboxylic acids with non-ionic polymers in solution attract close research attention for many years. This is largely due to the fact that the products of such interactions represent a new class of high-molecular compounds of valuable properties in scientific and practical terms, significantly different from those of the original polymer components.

The complexation of PHEA and PAA in diluted solutions is studied by turbidimetric titration. The effect of the copolymer composition, the ionic strength of the solution, the different molecular mass and pH in the acidic region is followed. Fig. 1 shows the turbidimetric

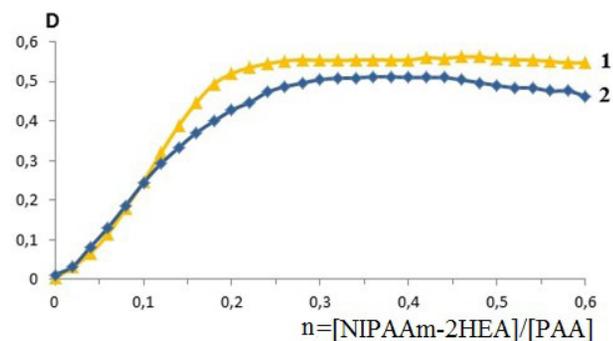


Fig. 1. Turbidimetric titration curves of copolymer with PAA (1:1).  $M_w$  (PAA) = 250KDa, copolymers M3 (1) and M1 (2).

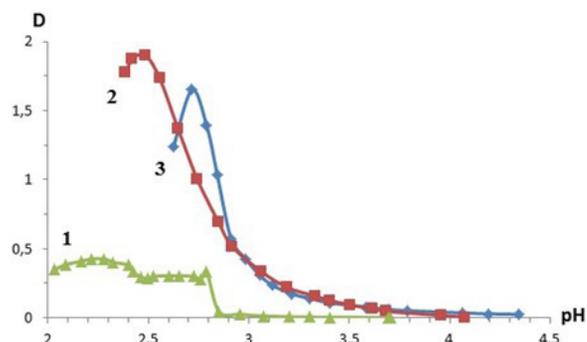


Fig. 2. pH dependence of the turbidity of solutions of copolymer (M2) with PAA mixture (5:1).  $M_w(\text{PAA}) = 2 \text{ kDa}$  (1), 250 kDa (2), 450 kDa (3).

titration curves of NIPAAm-2HEA copolymer aqueous solutions of two compositions using PAA solution. It is seen that an interpolymer complex is formed when the ratio reaches a value of 0.2. The increase of the solution turbidity is an indication of a phase separation in the system due to the formation of a compact IPC structure.

The existence of some critical pH of the complex formation with the participation of poly (carboxylic acid) and nonionic polymer systems is shown by Tsuchida [10]

In this study, the influence of different factors on  $\text{pH}_{\text{critical}}$  of copolymer-PAA system is evaluated. The dependence of the optical density of NIPAAm-2HEA copolymer and PAA equimolar mixtures on pH of the solution is shown in Fig. 2. It is evident that the aqueous solution is transparent in a certain pH range, but as it reaches a critical value the solution turns opaque. The change in turbidity is explained with the cooperative interaction in the system. It is clear from the graph that the polyacid molecular mass increase shifts the critical pH of complexation to higher values. This is due to the fact that the growth of the macromolecules length leads to a decrease in the ionization degree of the polyacid. Consequently, the number of unionized carboxyl groups which are capable of complexation increases. It is necessary to note that IPC is practically not formed at a low molecular mass of polyacrylic acid, in particular 2kDa.

Fig. 3 shows data on the influence of the copolymer composition on the complexation with polyacrylic acid in an aqueous solution. It is found that the hydrophobic units increase in the copolymer composition brings about a shift in critical pH to higher values. This is explained by the fact that the hydrophobic interactions contribute

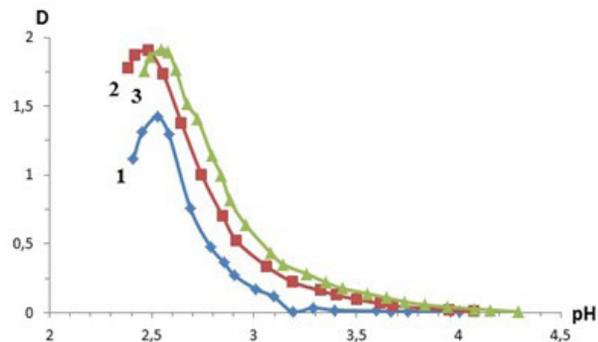


Fig. 3. pH dependence of turbidity of solutions of PAA mixture (5:1) with a copolymer (M1 (1), M2 (2) and M3 (3)) ( $M_w(\text{PAA}) = 250 \text{ kDa}$ ).

to the stabilization of the interpolymer complexes based on NIPAAm-HEA copolymers and polyacrylic acid.

Copolymers of a varying ionic strength are studied to follow the complexing ability of NIPAAm-HEA. Fig. 4. displays the data obtained. It is obvious that the increase of the ionic strength of the solution results in critical pH value increase. This indicates that the presence of low molecular mass salts is the factor that promotes IPC formation resulting from the decline of the thermodynamic quality of the solvent and the surge in macromolecules interaction.

The temperature affects the phase transition behavior of the interpolymer complexes based on copolymers with polyacrylic acid. The phase transition behavior of aqueous mixtures based on copolymers (M1, M2, M3) and PAA of 450 kDa molecular mass is investigated by the turbidimetric method. It is seen from Figs. 5 - 7 that the temperature increase leads to solution turbidity

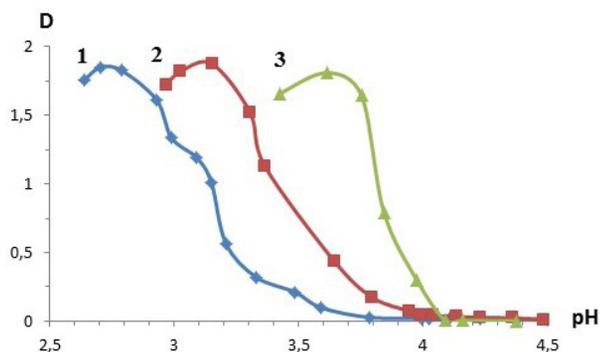


Fig. 4. pH dependence of the turbidity of solutions of copolymer (M2) with PAA mixture (5:1).  $M_w(\text{PAA}) = 250 \text{ kDa}$ ,  $[\text{NaCl}] = 0,002$  (1); 0,005 (2); 0,01 (3) mol/L.

increase. This is due to the destruction of the hydrogen bonds between water and the copolymer molecules and the enhancement of the hydrophobic interactions.

It is also revealed that the phase transition temperature depends on the feed composition of poly(NIPAAm-co-2HEA) and the mixtures composition. The increase of 2HEA units in the copolymer brings about a shift in LCST to higher values. For instance, LCST is about 32°C-35°C for M1 and M3 copolymers, whereas its value is around 40°C - 42°C for copolymer of M2 [8]. IPCs of poly(NIPAAm-co-2HEA):PAA=5:1; 1:1 compositions show a higher amplitude of the optical density in 20°C - 50°C range when compared to that of IPCs of [NIPAAm-2HEA]:PAA=1:5 composition. This is attributed to the larger number of NIPAAm-2HEA copolymer macromolecules in IPC as a result of system's hydrophobicity increase.

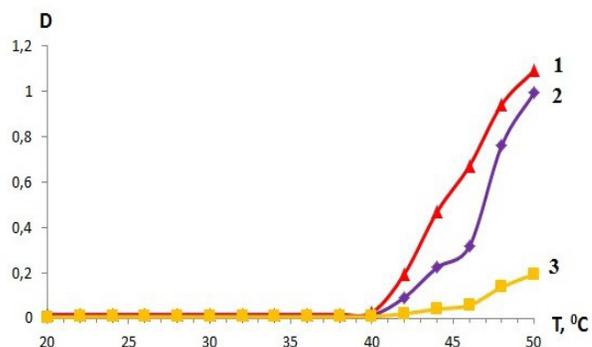


Fig. 5. Temperature effect on the turbidity of copolymer (M1) with PAA complexes.  $M_w$  (PAA) = 450 kDa; poly(NIPAAm-co-HEA):PAA = 5:1 (1); 1:1 (2); 1:5 (3).

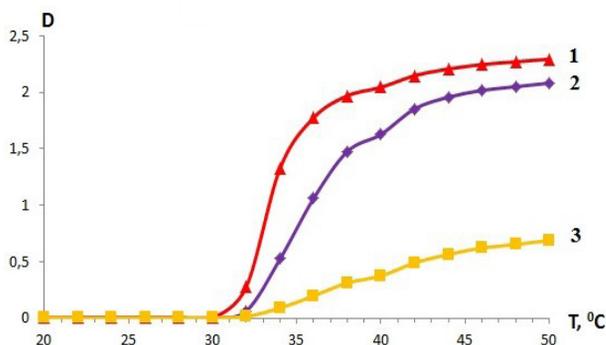


Fig. 6. Temperature effect on the turbidity of copolymer (M2) with PAA complexes.  $M_w$  (PAA) = 450 kDa; poly(NIPAAm-co-2HEA):PAA = 5:1 (1); 1:1 (2); 1:5 (3).

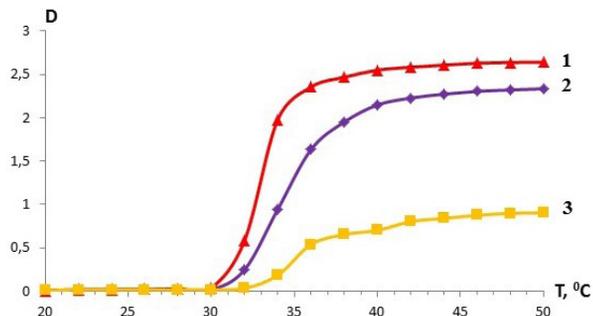


Fig. 7. Temperature effect on the turbidity of copolymer (M3) with PAA complexes.  $M_w$  (PAA) = 450 kDa; Copolymer:PAA = 5:1 (1); 1:1 (2); 1:5 (3).

## CONCLUSIONS

Interpolymer complexes based on polyacrylic acid and NIPAAm-2HEA copolymers were investigated. The influence of the polyacid molecular mass, the copolymer composition and the ionic strength of the solution on the critical pH of the complex formation was determined. It was revealed that the polyacid molecular mass increase shifted the critical pH of complexation to higher values. It was also found that the increase of the hydrophobic units in the copolymer composition brought about a shift in critical pH to higher values. The increase of the ionic strength of the solution also resulted in critical pH value increase.

The phase transition behavior in aqueous solutions of interpolymer complexes based on poly(NIPAAm-co-2HEA) (for three different compositions) and PAA of a varying molecular mass was investigated by turbidimetric method. It was found that the temperature increase lead to solution turbidity increase. It was also revealed that the phase transition temperature depended on feed composition of poly(NIPAAm-co-2HEA) and the composition of the interpolymer complexes. The increase of 2HEA units in the copolymer brought about a shift in LCST to higher values. IPCs of a higher copolymer content showed a more significant amplitude of the optical density comparing to IPCs of copolymer:PAA = 1:5 composition.

## REFERENCES

1. Z.S. Nurkeeva, G.A. Mun, V.V. Khutoryanskiy, Interpolymer Complexes of water-soluble nonionic polysaccharides with polycarboxylic acids and their applications, *Macromol. Biosci.*, 3, 2003, 283-295.

2. J. Wu, B. Zhou, Z. Hu, Phase Behavior of Thermally Responsive Microgel Colloids, *Physical Review Letters*, 90, 2003, 48304.
3. B.R. Saunders, B. Vincent, Colloidal copolymer microgels of *N*-isopropylacrylamide and acrylic acid: pH, ionic strength and temperature effects, *J. Chem. Soc., Faraday Trans.*, 92, 1996, 5013-5016.
4. G. Staikos, Georges Bokias, K. Karayanni, Interpolymer Complexes of Poly(acrylamide) and Poly(Nisopropylacrylamide) with Poly(acrylic acid): a Comparative Study *Polymer International* 41, 1996, 345-350.
5. G.A. Mun, V.V. Khutoryansky, S.N. Shmakov, Z.S. Nurkeeva, Kinam Park, Interpolymer complexes of poly(acrylic acid) with poly(2-hydroxyethyl acrylate) in aqueous solutions, *J. Colloid Polym. Sci.*, 283, 2004, 174-181.
6. Zauresh S. Nurkeeva, Vitaliy V. Khutoryansky, Grigoriy A. Mun, Interpolymer complexes of poly(acrylic acid) nanogels with some non-ionic polymers in aqueous solutions, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 236, 2004, 141-146.
7. Z.S. Nurkeeva, G.A. Mun, V.V. Khutoryanskiya, A.B. Bitekenova, A.V. Dubolazov, S.Zh. Esirkegenova, pH effects in the formation of interpolymer complexes between poly (N-vinylpyrrolidone) and poly (acrylic acid) in aqueous solutions, *The European Physical Journal*, E 10, 2003, 65-68.
8. U. Nakan, R.K. Rahmetullaeva, G.A. Mun, E.M. Shaihtudinov, G.Zh. Yeligbaeva, El-Sayed Moussa Negim, Linear copolymer of N-isopropylacrylamide and 2-hydroxyethylacrylate: synthesis, characterization and monomer reactivity ratios, *Oriental Journal of Chemistry*, 5, 32, 2016, 2347-2354.
9. U. Nakan, R.K. Rahmetullaeva, G.A. Mun, E.M. Shaihtudinov, El-Sayed Negim, Muhammad Idris Saleh, Synthesis and characterization of hydrophilic copolymers, *International Journal of Biology and Chemistry*, 3, 2013, 58-62.
10. E. Tsuchida, K. Abe, Interactions between macromolecules in solution and intermacromolecular complexes, *Adv. Polym. Sci.*, 45, 1982.