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Interpolymer complexes based on N-isopropylacrylamide copolymers and polyacrylic acid

Interpolymer complexes based on N-isopropylacrylamide and 2-hydroxyethylacrylate copolymers (NIPAAm-co-HEA) and polyacrylic acid were investigated by turbidimetric method. The influence of the molecular mass of polyacid, the copolymer composition and the ionic strength of the solution on the critical pH of complexformation was shown. Phase transition behavior of interpolymer complexes in aqueous solutions based on poly(NIPAAm-co-HEA) (for three different compositions) and PAA was investigated. It was revealed that phase transition temperature depends on the initial monomer mixture of poly(NIPAAm-co-HEA) and the composition of interpolymer complexes.

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

Introduction

Among the synthetic polymers characterized by thermosensitive behavior the systems based on N-isopropylacrylamide (NIPAAm) whose homopolymer has a lower critical solution temperature (LCST) in water are the most studied one. PNIPAAm dissolves at temperature below 32°C and precipitates at temperature above LCST [1, 2] due to the presence of the hydrophilic and hydrophobic groups in each monomer unit. Decrease in temperature below LCST is accompanied by the formation of hydrogen bonds between the amide groups of the polymer and water molecules, which significantly facilitates dissolution. At temperature above LCST hydrogen bonds begin to disintegrate. In contrast, hydrophobic interactions are enhanced; as a result the polymer precipitates [3]. Sol-gel transition of PNIPAAm is clearly visible to the naked eye. The results of recent studies using confocal laser microscopy scan have shown that the internal structure of PNIPAAm gel consists of continuous two-sphere structures with dense and sparse zones in the polymer network [4, 5].

Interpolymer reaction of polycarboxylic acids with non-ionic polymers in solution has been attracting close attention of researchers for many years. This is largely due to the fact that the products

of such interactions represent a new class of high-molecular compounds with valuable properties in the scientific and practical terms, significantly different from those of the original polymer components. The formation of polymer-polymer complexes requires a minimum critical content of functional groups in the polymer to provide the desired level of density of hydrogen bonds between the macromolecules. Formation of interpolymer complex in aqueous solution is possible only below critical pH value, because only non-ionized carboxyl groups in the structure of polycarboxylic acids exhibit the ability to form hydrogen bonds [6].

The purpose of this study is to reveal the basic complexation characteristics and phase transition behavior of NIPAAm-co-HEA copolymers with polyacrylic acid. Another important aim is to investigate the influence of the molecular mass of polyacid, the copolymer composition and the ionic strength of the solution on the critical pH of complexformation.

Materials and methods

Materials

N-isopropylacrylamide (97%) (Sigma-Aldrich, USA) was used without further purification.

2-hydroxyethylacrylate (96%, contains 200-650 ppm monomethyl ether hydroquinone as inhibitor) (Sigma-Aldrich, USA) was used without further purification. Ammonium persulfate (Sigma-Aldrich, USA) was used without further purification. N,N-methylene-bis-acrylamide («Reanal», Hungary) was used without further purification. Organic solvents, such as ethyl acetate, hexane, ethanol were used without further purification. Polyacrylic acid (PAA) of different molecular weight - 2000, 250000, 450000 ("Sigma Aldrich", USA) were used without additional purification.

Copolymer synthesis

Synthesis of linear NIPAAm-HEA copolymer. NIPAAm is dissolved in ethanol. Then initiator is also dissolved in solution of NIPAAm ethanol under continuous stirring. HEA is added to solution to form homogeneous blend. 2,2'-Azobisisobutironitrile (AIBN) is used to initiate radical polymerization. The resulting mixture is poured into the glass ampoule and saturated by argon for 10 minutes to remove oxygen. Thus the copolymerization is performed in hermetically sealed glass ampoules at 600C for 40 min. After that obtained copolymer is precipitated in the mixture of hexane and ethylacetate (1:1) twice to remove unreacted monomers and dried at vacuum until it becomes powder.

Methods

Spectro turbidimetric titration of polymer solutions and their complexes with PAA was carried out at $\lambda = 400$ nm using «UV-2401-PC Shimadzu»

(Japan) spectrophotometer, temperature control was performed by thermoelectronic controller of cuvettes "CPS-240A Shimadzu» (Japan).

In order to determine the critical pH of complexation solutions of interpolymer complexes were prepared by mixing the solutions of initial components. Composition of polycomplexes was calculated using the formula:

$$n = \frac{C_1 V_1}{C_2 V_2},$$

C1 – concentration of solution of PAA, 0,01M;
V1 – volume of PAA solution which is added to solution of poly-NIPAAm-co-HEA, mL;

C2 – concentration of solution of poly-NIPAAm-co-HEA; 0,01M;

V2 – volume of solution of poly-NIPAAm-co-HEA, 5 mL.

Results and Discussion

Complexation reactions of temperature sensitive NIPAAm-HEA copolymers with polyacrylic acid

In this study interpolymer complexes based on polyacrylic acid and copolymers were investigated. The influence of the molecular mass of polyacid, the copolymer composition and the ionic strength of the solution on the critical pH of complexformation was shown. Figure 1 shows the turbidimetric titration curves of an aqueous solution of NIPAAm-HEA copolymer of two compositions by PAA solution. It can be seen from the turbidimetry data that when the

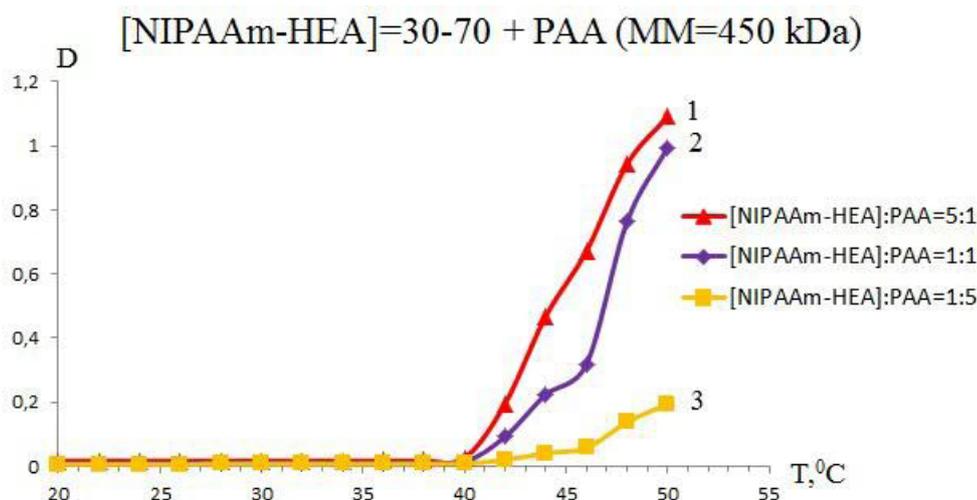


Figure 1 – Turbidimetric titration of NIPAAm-HEA copolymer (30-70; 70-30 mol %) solution by PAA solution.

Note: [NIPAAm-co-HEA]=[PAA]=0,1g/dL; MM(PAA)=250000 Da, pH=2,8

ratio reaches 0.2 (or 1:5 respectively) interpolymer complex is formed. The increase in turbidity of the solution is an indication of the phase separation of the system due to the formation of a compact IPC structure.

The dependence of optical density of the aqueous solutions of equimolar mixtures of NIPAAm-HEA copolymer and PAA on pH of the solution is shown in Figure 2. It is clear from the graph that the rise in molecular mass of polyacid shifts critical pH of complexation to higher values. This is due to the fact that the growth in the length of the macromolecules leads to the decrease in the ionization degree of

polyacid. Consequently, the number of unionized carboxyl groups which are capable of complexation increases. It is necessary to note that IPC practically is not formed at a low molecular mass of polyacrylic acid, in particular 2000 Da.

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

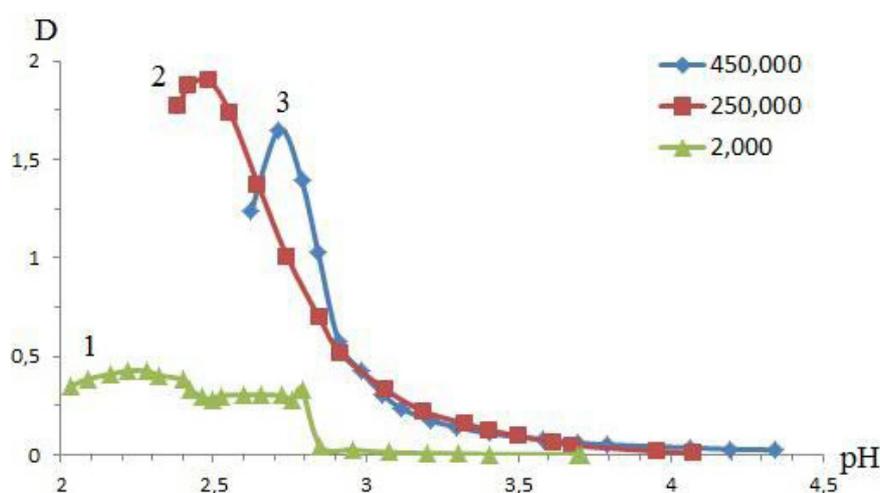


Figure 2 — Dependence of optical density of the mixtures of NIPAAm-co-HEA copolymer solutions with PAA of different molecular weight on pH.

Note: [NIPAAm-co-HEA]:PAA=5:1; pH=2,8; [NIPAAm-co-HEA]=[PAA]=0,1 g/dL; IMM [NIPAAm-HEA]=50-50 mol %; MM(PAA)=2000 Da (1), 250000 Da (2), 450000 Da (3)

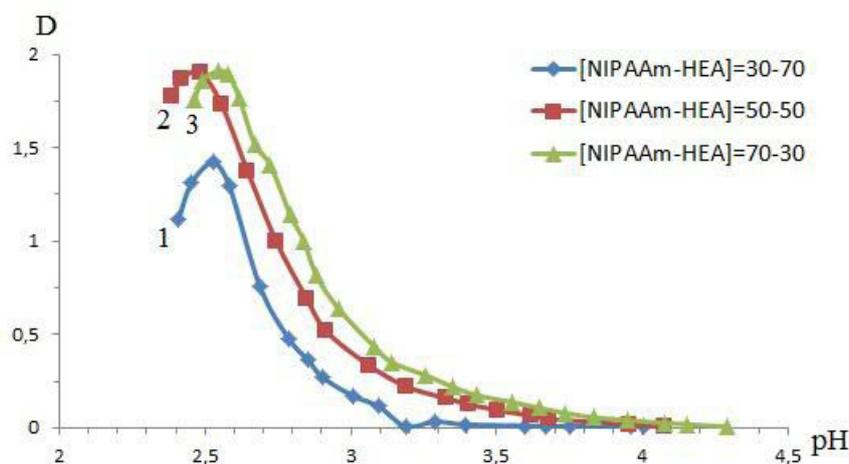


Figure 3 — Dependence of optical density of the mixtures of NIPAAm-HEA copolymer solutions of various compositions with PAA on pH.

Note: [NIPAAm-co-HEA]:PAA=5:1; pH=2,8; [NIPAAm-co-HEA]=[PAA]=0,1 g/dL; MM(PAA)=250000 Da; IMM [NIPAAm-HEA]= 30-70 (1); 50-50 (2); 70-30 (3) %.

Figure 4 displays the data on the determination of the effect of ionic strength of the medium on the complexation process. It is obvious that the increase in the ionic strength of the solution results in the rise in critical pH value. This indicates that the presence of low molecular mass salts is the factor that promotes the IPC formation. This is the result of the decline in the thermodynamic quality of solvent.

The temperature effect on phase transition behavior of interpolymer complexes based on NIPAAm-HEA copolymers with polyacrylic acid.

Phase transition behavior of interpolymer complexes in aqueous solutions based on poly(NIPAAm-co-HEA) (for three different compositions, namely 30-70, 50-50, 70-30 mol %) and PAA of 450 kDa molecular mass was investigated by turbidimetric method. It can be seen from Figures 5-7 that the increase in the temperature leads to the rise in solution turbidity. This is due to the destruction of hydrogen bonds between water and copolymer molecules and the enhancement in hydrophobic interactions.

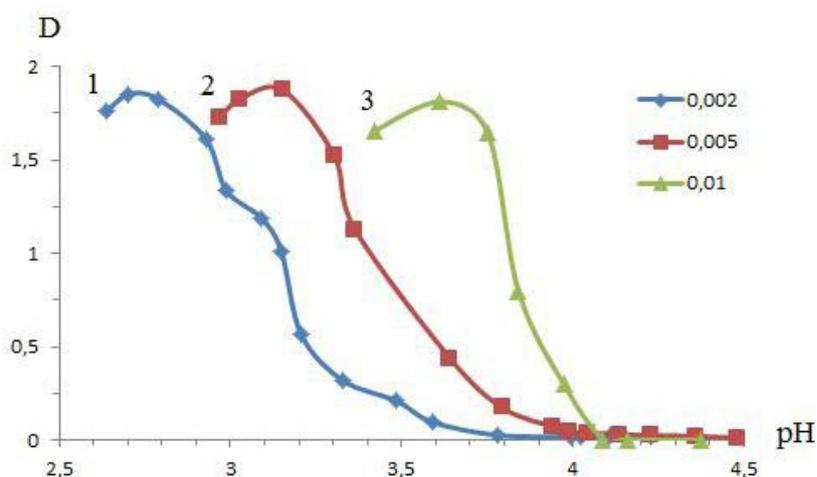


Figure 4 – Dependence of optical density of the mixtures of NIPAAm-HEA copolymer solutions with PAA on pH at various ionic strength of medium.

Note: [NIPAAm-co-HEA]:PAA=5:1; [NIPAAm-co-HEA]=[PAA]=0,1 g/dL; pH=2,8; MM(PAA)=250000 Da; IMM [NIPAAm-HEA]=50-50 mol %; [NaCl]=0,002 (1); 0,005 (2); 0,01 (3) mol/L

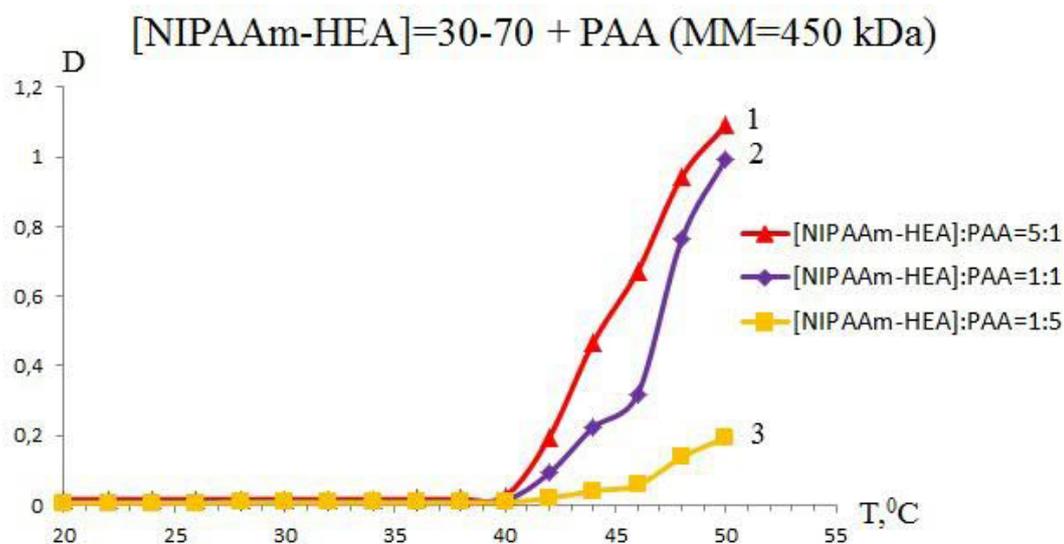


Figure 5 – Dependence of turbidity of the mixtures of NIPAAm-HEA copolymer solutions with PAA on temperature. Note: [NIPAAm-co-HEA]=[PAA]=0,1 g/dL; IMM[NIPAAm-HEA]=30-70 mol %; MM(PAA)=450000 Da; [NIPAAm-co-HEA]:PAA=5:1 (1); 1:1 (2); 1:5 (3).

It was also revealed that the temperature at which phase transition occurs was dependent on the initial monomer mixture of poly(NIPAAm-co-HEA) and the composition of interpolymer complexes. The increase in HEA units in the copolymer brings about the shift in LCST to higher values. IPCs of [NIPAAm-

co-HEA]:PAA=5:1; 1:1 compositions shows higher amplitude of optical density in 20-50°C range comparing to IPCs of [NIPAAm-co-HEA]:PAA=1:5 composition. This is attributed to larger number of NIPAAm-HEA copolymer macromolecules in IPC, as a result the growth in system's hydrophobicity.

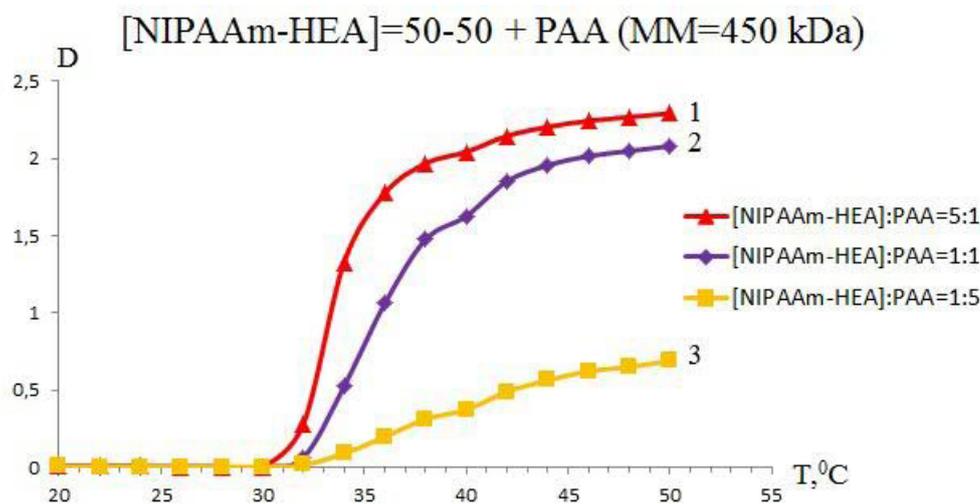


Figure 6 — Dependence of turbidity of the mixtures of NIPAAm-HEA copolymer solutions with PAA on temperature. Note: [NIPAAm-co-HEA]=[PAA]=0,1 g/dL; IMM[NIPAAm-HEA]=50-50 mol %; MM(PAA)=450000 Da; [NIPAAm-co-HEA]:PAA=5:1 (1); 1:1 (2); 1:5 (3)

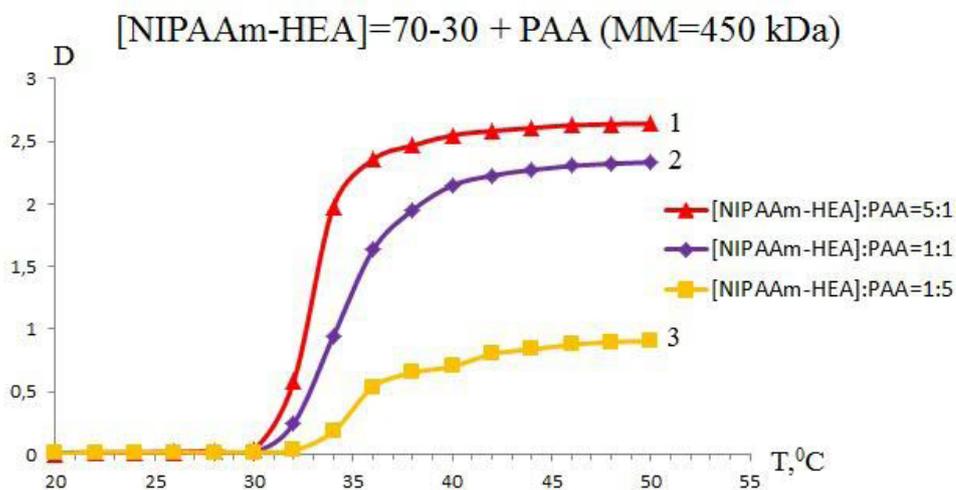


Figure 7 — Dependence of turbidity of the mixtures of NIPAAm-HEA copolymer solutions with PAA on temperature. Note: [NIPAAm-co-HEA]=[PAA]=0,1 g/dL; IMM[NIPAAm-HEA]=70-30 mol %; MM(PAA)=450000 Da; [NIPAAm-co-HEA]:PAA=5:1 (1); 1:1 (2); 1:5 (3)

Conclusion

Interpolymer complexes based on polyacrylic acid and NIPAAm-HEA copolymers were investigated. The influence of the molecular mass of polyacid, the copolymer composition and the ionic strength of the solution on the critical pH of

complexformation was shown. It was revealed that the rise in molecular mass of polyacid shifts critical pH of complexation to higher values. It was found that the increase in hydrophobic units in the copolymer composition brings about the shift in critical pH to higher values. The increase in the

ionic strength of the solution also results in the rise in critical pH value.

Phase transition behavior of interpolymer complexes in aqueous solutions based on poly(NIPAAm-co-HEA) (for three different compositions, namely 30-70, 50-50, 70-30 mol %) and PAA of 450 kDa molecular mass was investigated by turbidimetric method. It was found that the increase in the temperature leads to the rise in solution turbidity. It was also revealed that the temperature at which phase transition occurs was dependent on the initial monomer mixture of poly(NIPAAm-co-HEA) and the composition of interpolymer complexes. The increase in HEA units in the copolymer brings about the shift in LCST to higher values. IPCs of [NIPAAm-HEA]:PAA=5:1; 1:1 compositions shows more significant amplitude of optical density comparing to IPCs of [NIPAAm-HEA]:PAA=1:5 composition.

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