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Water soluble copolymers of acrylamide with methylacrylate in reactions of complex formation with polyacrylic acid

In present paper various physical and chemical methods, the interaction of linear copolymers of AA-MA with PAA in aqueous solutions were studied. It was established that copolymers are formed by hydrogen bonds and hydrophobic interactions. Also, it was concluded that with an increasing content of MA in the copolymer, the critical pH of complex formation range increases, as well as the stability of interpolymer complex.

Keywords: interpolymer complex, linear copolymers, hydrogen bonds, hydrophobic interactions.

Introduction

Stimuli - sensitive polymers can significantly change their characteristics for comparatively small variations of thermodynamic variables, as well as under various parameters of the external environment, such as electric or magnetic fields, pH, ionic strength, etc. constitute an important class of smart materials, the application area of which is rapidly expanding.

One of the most promising scientific and practical stimuli - sensitive materials is temperature sensitive polymers that undergo a phase transition at comparatively small variations in temperature. Generally, such polymers are prepared using diphilic soluble monomers. Monomers in their structure simultaneously contain the hydrophilic groups and hydrophobic moieties such as, N-isopropylacrylamide, vinyl methyl ether or N-vinylcaprolactam.

At the department of "Chemistry and technology of organic substances of natural compounds and polymers" of Al-Farabi Kazakh National University, the original approach to synthesis of new thermosensitive polymers, based on the radical copolymerization of hydrophilic and hydrophobic monomers was developed and successfully implemented. It opens possibilities for obtaining soluble and crosslinked polymers with widely adjustable thermo-sensitivity, which have promising applications in electronics and biomedicine.

This is a continuation of research in this area and is devoted to obtaining new temperature-sensitive copolymers based on acrylamide (AA) and methyl acrylate (MA), and to the study of their complexion ability with polyacrylic acid (PAA).

Materials and methods

Linear copolymers of AA and MA were synthesized by the real initiation monomer solutions in a hydro-alcoholic solution. As the initiator was used ammonium persulfate. The synthesis was carried out at 400C in an ampoule from molybdenum glass.

An interpolymer complex of copolymers [AA][MA] with PAA was prepared by mixing solutions of the initial components with concentration 0.01mol / l at a certain ratio.

Interpolymer complexes of copolymers [AA][MA] with PAA at critical pH complexation was obtained by mixing the components of the feed solution with a concentration of 0.01mol/l at a specific ratio, and then added to the solutions of the polycomplexes required amount 0.2 mol/L hydrochloric acid and heated for 5 minutes until equilibrium is reached, after which the measurement was performed.

Results and discussion

It is known that the formation of interpolymer complexes in the system of polycarboxylic acid - a non-ionic polymer is characterized by a number of critical phenomena, which shows strong dependence of system's properties from minor changes in various parameters [50]. Earlier works in collaboration with Tsuchida [51, 52], as well as Nurkeeva ZS co-[53-55] for these systems was the existence of the critical value of pH, at which a sharp increase in the binding component, followed by precipitation of PKI last precipitated. With a decrease in pH increases the number of un-ionized carboxyl groups capable of participating in the formation of hydrogen bonds [53-55].

The complex formation of copolymers [AA] - [MA] with PAA was studied by turbidimetric and pH-metric titration. Turbidimetry method allows fixing solution turbidity as a result of aggregation of the formed particles of polycomplex and rebalancing "connected - proton unbound", respectively. In all cases, in order to establish the composition of the interpolymer, initial solutions of polymers were prepared at a strict pH value by adding small amounts of 0.2M hydrochloric acid and sodium hydroxide. Fixed value of polymers' pH solutions hardly changed during the next 24 hours (±0.05 pH).

Figure 1 shows the turbidimetric titration 0.01M solutions of PAA solution with equimolar concentrations at pH = 4. It has been found that the addition of a copolymer to the solution of PAA leads to a significant increase in the optical density of the polymer solution. Compact polycomplex particles due to their hydrophobic nature begin to aggregate to form larger structures, which is clearly shown by turbidimetric titration curve. At the same time a maximum value of solution turbidity is observed at the above ratio of the interacting components.

Nevertheless, not all ratios of copolymers behave identically. As shown in Figure 1, the relative change in the absorbance of solutions of copolymers observed with increasing content of MA in the copolymer, i.e., the complex forming capacity of the copolymer increases with the content of the hydrophobic copolymer.

The formation of polycomplexes involving weak polyelectrolytes typically affects the pH of aqueous solutions. Previously, critical pH of complexion (pHcrit.) was accepted as a criterion for the ability of polymers to form complexes. System with a high of complexion ability is characterized by a large value pHcrit. Mixing of PAA with nonionic polymers at pH below pHcrit leads to the formation of hydrophobic particles IPC with compact conformation. In this case, the system exhibits phase separation and the appearance of turbidity [53-55].

In the work by titration of an aqueous solution of a polyacid copolymer solution pH increase is not observed as in the case of pH-sensitive copolymers. Data definition of pHcrit copolymers aqueous solutions are shown in Figure 2. As can be seen from the figure, the highest value corresponds to pHcrit copolymer [AA]: [MA] with composition [50]:[50].

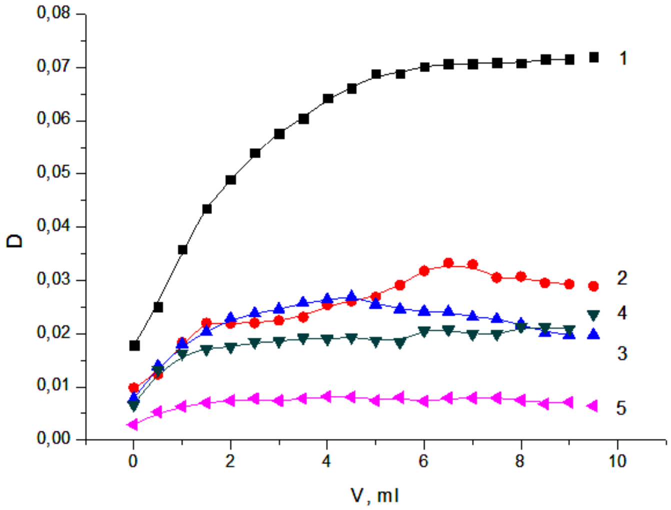


Figure 1 - The turbidimetric titration curves of solutions of PAA with solutions AA-MA.
Note: [AA]:[MA] = 50:50 (1); 60:40 (2); 70:30 (3); 80:20 (4); 90:10 мол.% (5),
[copolymer]=[PAA]=0,01 M; Mr (PAA)= 250 000; pH=4.

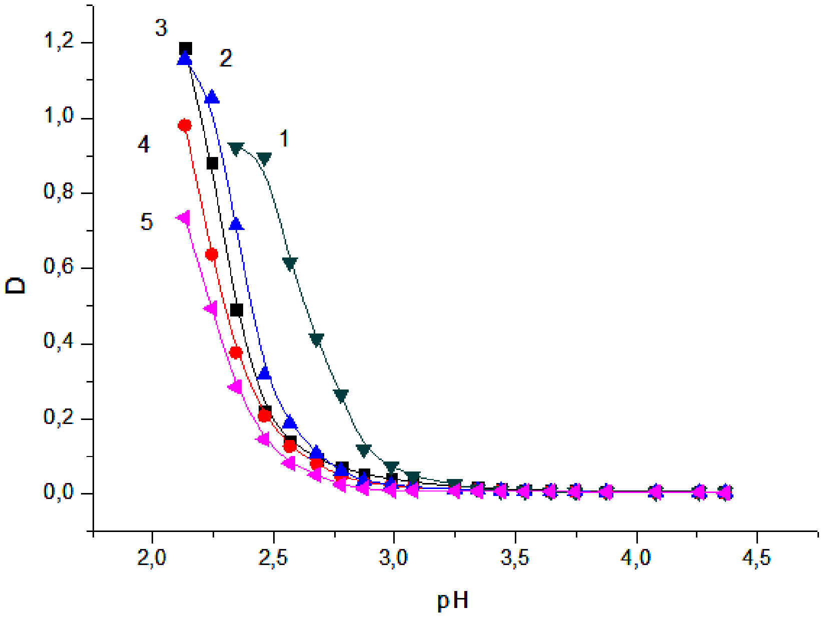


Figure 2 - Critical pH formation of complexes of polyacrylic acid copolymers with different AA-MA composition.

Note: [AA]:[MA] =50:50 (1); 60:40 (2); 70:30 (3); 80:20 (4); 90:10 (5) мол.%

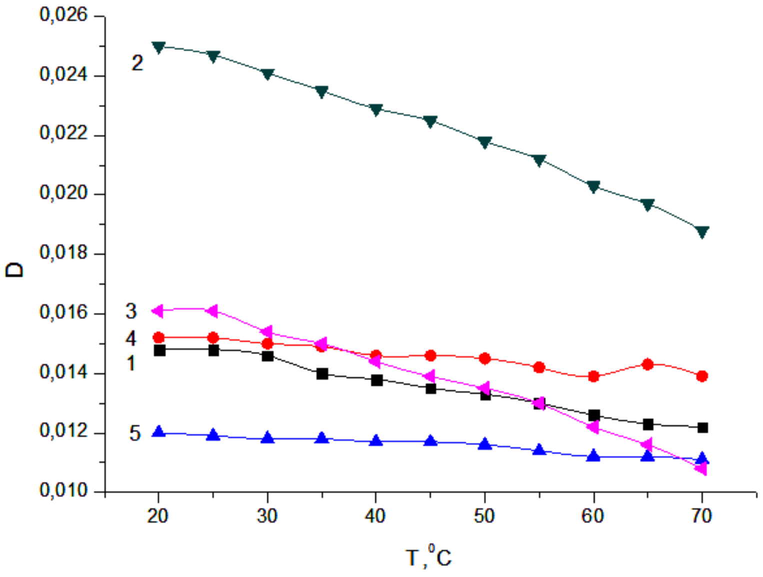
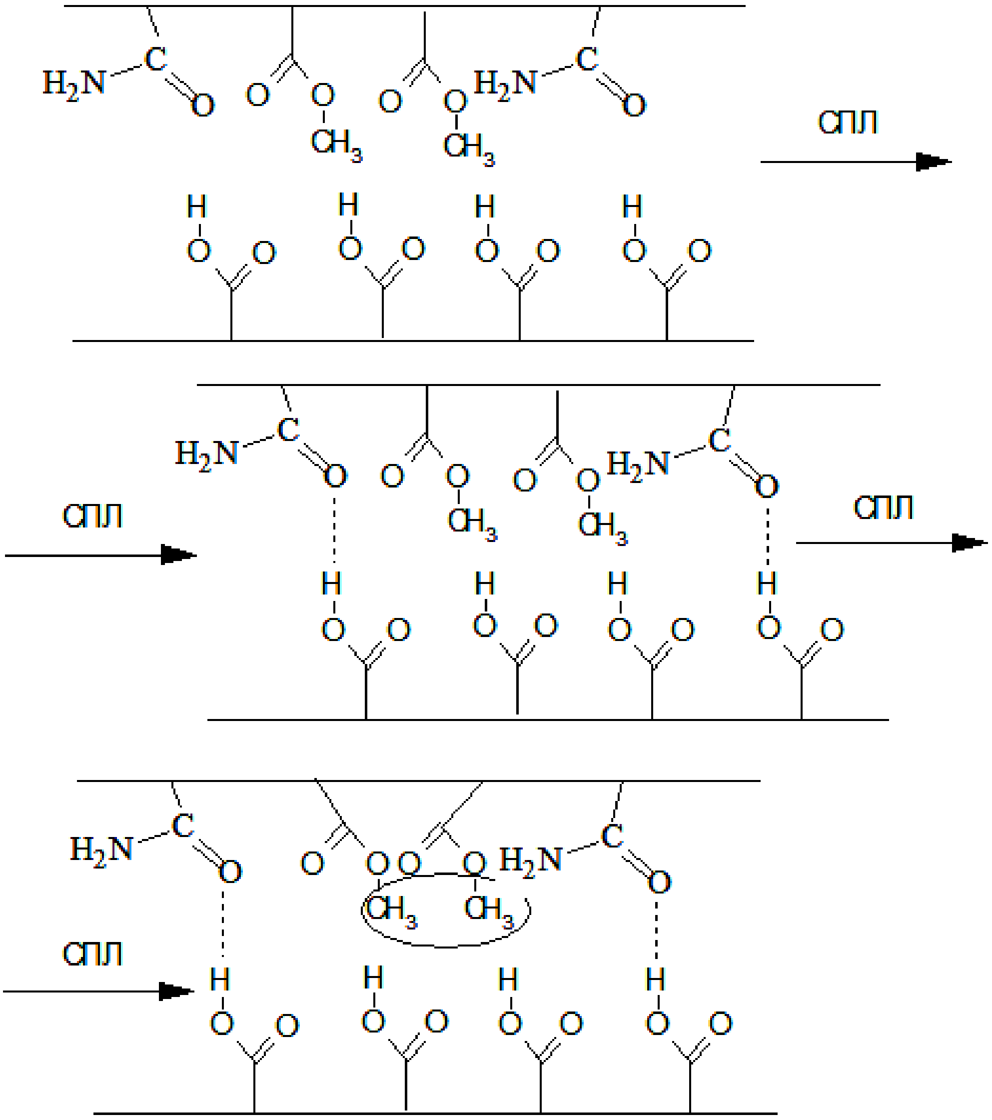


Figure 3 – Temperature dependence of the optical density of aqueous solutions of [AA]: [MA] = 50:50, copolymer and PAA.

Note: [AA]:[MA]=50:50 : [ПАК]=1:1 (1), 1:2 (2), 1:4 (3), 2:1 (4), 4:1 (5).

As seen in Figure 3 at given pH = 4 thermosensitive interaction with PAA copolymer leads to a decrease of thermosensitivity at any copolymer ratio: PAA. Summarizing the results of this work [68] it can be suggested that in these conditions the interaction of copolymers



with PAA is carried by hydrogen bonds to form a hydrophilic associates, which reduces thermosensitivity.

The approximate scheme of complex formation in the system of copolymer with PAA can be represented as follows:

In present work, to examine the ability of polymers to form a complex while changing their ionic strength was used low molecular weight salt of NaCl, presence of which can differently affect complex formation in the «non-ionic polymeric polycarboxylic acid» system.

Figure 4 shows the data on the influence of a low molecular weight on phase behavior of salt in aqueous solution with PAA copolymer mixture of different composition at pH of 4. As seen from the figure in the absence of a given low molecular weight salts at pH, the complex formation is not noticed (optical density is close to 0). At the same time by adding NaCl to the system the separation by phases can be seen, and as the concentration of NaCl increases, the tubidity of the solution increases as well. This indicates the formation of a relative hydrophobic interpolymer complex, which precipitates in the presence of NaCl.

Consequently, for this system increase of ionic strength promotes increase in the system's ability to form the interpolymer complex formed by hydrogen bonds. At the same time, with increasing content of

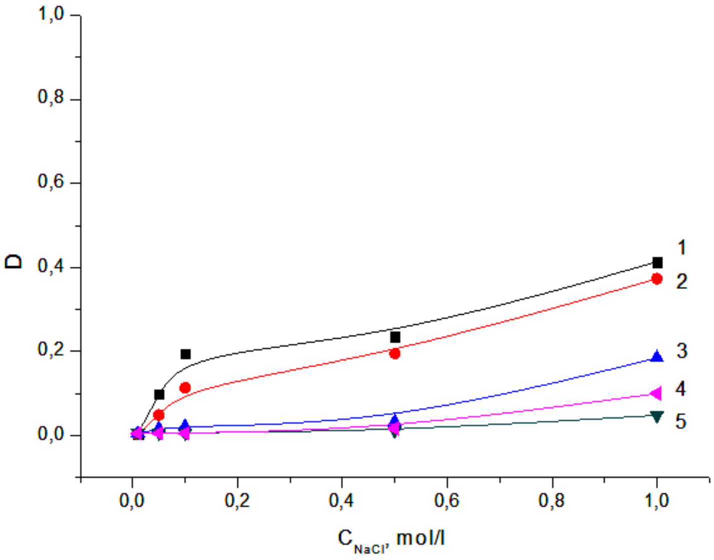


Figure 4 - Influence of NaCl concentration on optical density of the copolymer aqueous solutions with PAA.

Note: [AA]:[MA] = 50:50 (1); 60:40 (2); 70:30 (3); 80:20 (4); 90:10 мол.% (5)
Mw (PAA) = 250 000, [AA-MA] = [PAA] = 0,01 M.

the hydrophobic component of copolymer effects on NaCl complexation process becomes more significant.

Thus, the interaction of linear copolymers of AA-MA with PAA in aqueous solutions was studied with the various physical and chemical methods. It was established that the binding polymers were made by hydrogen bonds and hydrophobic interactions. With an increasing content of MA in the copolymer, the critical pH of complex formation range increases, however, at the same time the stability of interpolymer complex increases as well.

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