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Heat-Sensitive Polymers Based on Hexamethylenediamine

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Abstract:

New copolymers of acrylamide with hexcamethylenimine have been synthesized. Their chemical structure has been determined by IR-spectrometry and some other physico-chemical methods. Possibility of obtaining of polymers thermo – and pH sensible polymers has been shown.

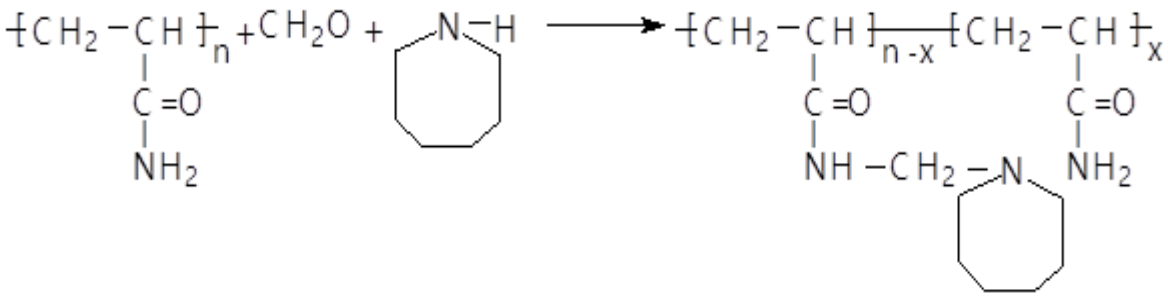
Keywords: polyacrylamid (PAA); hexcamethylenimin (HMI); phormaldehyde (PhA); high critical temperature of mixing (HCTM);low critical temperature of mixing (LCTM).

Introduction: Polyacrylamide (PAA) as a water-soluble industrial polymer has found wide application in various sectors of the national economy. The introduction of various N-substituted organic molecules into its structure gives it pH and thermal sensitivity, the ability to swell and dissolve in organic solvents [1], reversibly and adequately respond to minor changes in its environment (pH, temperature, ionic strength, electric field, etc.). etc.) in a preprogrammed manner.

Previously, by radical polymerization of hexamethylenediamine acrylamide, we obtained polymers with an upper critical mixing temperature (UCST) in isopropyl alcohol, and its copolymers with acrylamide in aqueous solutions had a lower critical mixing temperature (LCST) [2].

The results obtained and their discussion: In this regard, obtaining polymeric derivatives of hexamethylenediamine (HMI) by direct modification of polyacrylamide (PAA) with this imine was interesting.

For the synthesis of a polyacrylamide derivative with hexamethylenediamine (PAA:HMI), the Mannich reaction is used [3], where the interaction of polyacrylamide with formaldehyde (FA) occurs, resulting in the formation of polymethylene acrylamide, then the latter interacts with hexamethylenediamine to form a copolymer of PAA: HMI and water according to the following scheme:



The chemical structure of the synthesized copolymer was identified according to the analysis of IR spectra (Fig. 1).

In the IR spectrum of PAA: HMI, a new absorption band is observed in the region of 1670 cm-1, corresponding to the stretching vibrations of the C=O bond of the N-substituted amide group. Absorption bands with a frequency of 2855 cm-1 and 2926 cm-1 correspond to symmetric and asymmetric vibrations of the CH2 groups of the hexamethylenediamine ring.

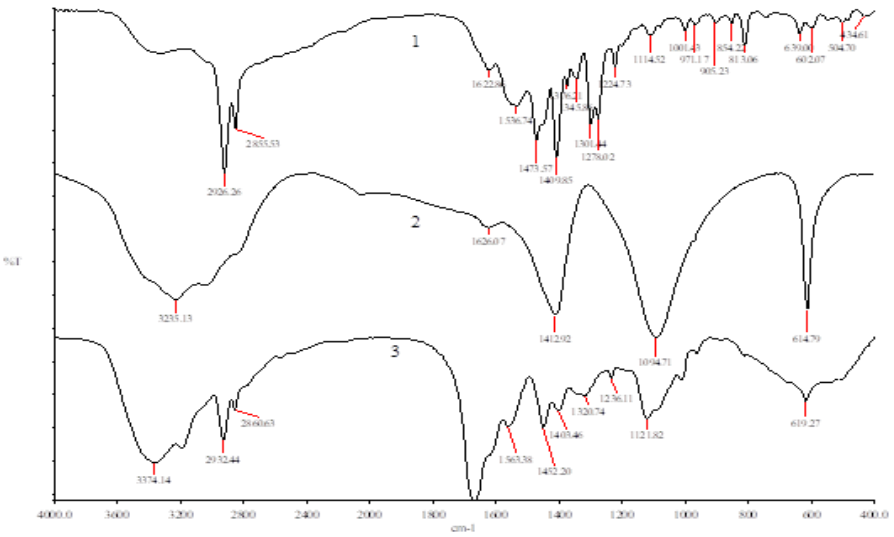
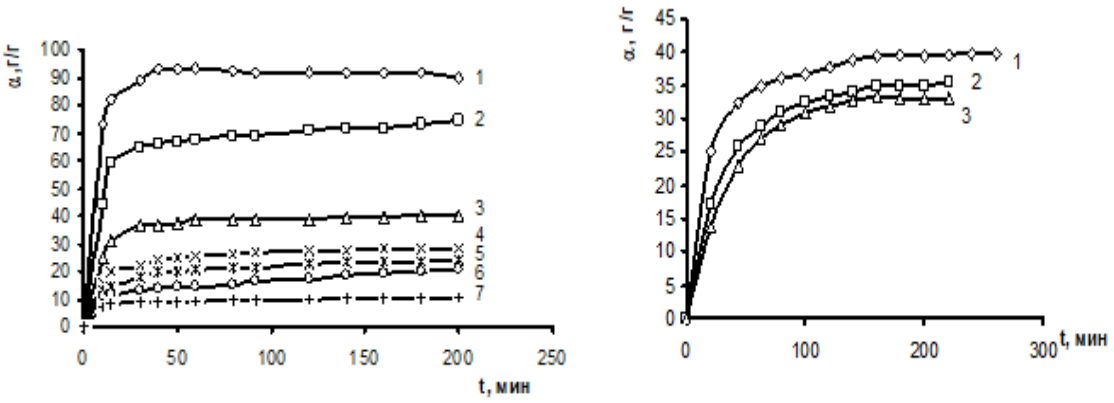


Fig.1. IR spectra of the obtained compounds: 1 - GMI, 2 - PAA,3 - PAA: GMI.

The resulting polymers are white powdery substances that swell well but are insoluble in water. The insolubility of this polymer is apparently due to the partial crosslinking of polymer macromolecules under the influence of formalin, which is confirmed by studying the swelling kinetics of the resulting modified polymers under various conditions. It has been shown that polymer hydrogels (PHs) obtained in this way, depending on the conditions of their preparation, exhibit different water-absorbing abilities. An increase in the crosslinking agent (SA) concentration during synthesis leads to a decrease in the degree of equilibrium swelling of the samples (Fig. 2).

It can be seen (Fig. 2) that an increase in the concentration of HMI: FA in the reaction mixture leads to a decrease in the degree of swelling, which is associated with an increase in the number of cross-links between macro chains.

The study of the effect of temperature on the degree of swelling of polymers (Fig. 3) showed an anomalous phenomenon, i.e. with increasing temperature, the swelling weakens, which indicates the thermal sensitivity of polymers [3].



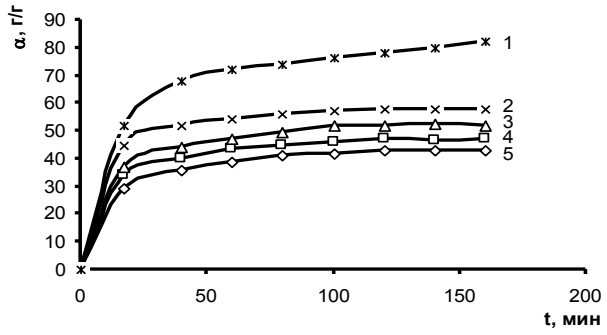


Figure. 2. Swelling kinetics of polymers with different SA content in water. The initial ratio of PAA:GMI: FA polymers.

The numbers on the curves correspond to: 1:0.5:0.5 (1); 1:0.75:0.75 (2); 1:1:1 (3); 1:1.5:1.5 (4); 1:2:2 (5); 1:2.5:2.5 (6); 1:3:3 (7). T=25oC. Figure. 3. Kinetics of polymer swelling in water at temperatures of 25 (1); 30(2); and 35^{0}C (3).

The presence of ionogenic groups in the polymer is confirmed by studying the dependence of the degree of swelling of polymers on the ionic strength of the solution. The effect of ionic strength on the swelling kinetics of samples was studied in aqueous solutions of KCI with different concentrations (ionic strength μ) (Fig. 4).

Fig. 4. Dependence of the degree of swelling on time at different ionic strengths of the KCI solution (1-0.15; 2-0.3; 3 - 0.45; 4 - 0.6; 5 - 0.75·10-2 mol ion / l.). T=25oC.

The data shown in Fig. 4 show that with an increase in the ionic strength of the solution, the degree of swelling of the polymer decreases. This phenomenon confirms the fact that the decrease in the swelling of gels is due to the screening of the charged groups of the PAA: HMI macromolecule by the ions of the low molecular weight salt.

The main advantage of hydrogels with ionogenic functional groups is their sensitivity to pH. The influence of the pH value of the medium on the swelling kinetics of polymers was studied by adding certain amounts of NaOH and HCl to water.

The study of the influence of the pH medium on the degree of swelling of the modified polymer equilibrium swollen in water showed (Fig. 5) that a sharply induced collapse is observed in the studied samples with a decrease in the pH medium, i.e. with a decrease in the pH value of the solution, a decrease in the degree of swelling of the polymer sample is observed. This is because with a decrease in the pH value of the medium, water becomes a “bad” solvent for the GMI-based polymer.

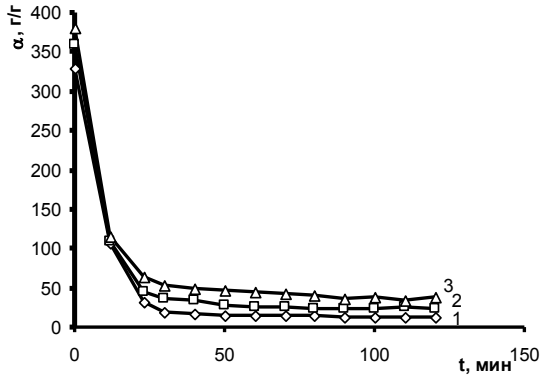


Fig.5. Kinetics of the collapse of an equilibrium swollen modified polymer at various pH values of the solution. 1, 2, 3, respectively pH=1; 2; 3. T=25^{o}C

Conclusion: Thus, the obtained data on the synthesis and study of the physicochemical properties of polyacrylamide modified with hexamethylenediamine show that the degree and rate of water absorption of the studied polymers are significantly affected by the conditions for their preparation, as well as the medium of absorbed water. These data indicate that the variation of the above factors makes it possible to control the process of swelling of hydrogels, which leads to the production of polymers with thermo- and pH-sensitive properties.

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