New Thermo-Sensitive Hydrogel Based on Copolymer of 2-hydroxyethyl Acrylate and Ethyl Acrylate

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Nomenclature

HEA – 2-hydroxyethyl acrylate EA – ethyl acrylate LCST – lower critical solution temperature BAA – N,N'-methylene-bis-acrylamide DSC – differential scanning calorimetry TGA – thermal gravimetric analysis IMM – initial monomer mixture CPB – cationcetylpyridinium bromide SDS – sodium dodecyl sulfate CPB - cetylpyridinium bromide CPL - copolymers CA – crosslinking agent SDS – sodium dodecyl sulfate PVP – polyvinylpyrrolidone Surfactants – surface-active substances Surfactants – surface active agents FTIR - Fourier transform infrared spectrometer

1. Introduction

Stimuli-responsive materials have attracted significant attention in the past two decades due to their diverse applications. In particular, water-sol-

Abstract

In this work firstly the thermo-sensitive polymer hydrogels were obtained by three-dimensional radical copolymerization of water-soluble HEA and hydrophobic monomer ethyl acrylate (EA) in the presence of crosslinking agent N,N'-methylenebisacrylamide (BAA). The hydrogels with certain copolymer compositions showed thermo-sensitive behavior in aqueous solutions. The regularity of complex formation of cross-linked copolymer HEA-EA with anionic and cationic surface-active substances have been studied. The swelling behavior of the hydrogels in cetylpyridinium bromide aqueous solutions was studied. Increased swelling of the hydrogels was observed in the surfactant solutions. The increased swelling was more prominent for the hydrogels with a higher content of the hydrophobic moiety in the copolymer composition and with the higher surfactant concentration. The reason for the observed phenomenon is discussed.

> uble polymers exhibiting lower critical solution temperature (LCST) are among the most interesting stimuli-sensitive materials due to numerous potential applications in controlled release systems [1], biotechnology [2], separation and enrichment technologies [3], and stabilization of colloids [4]. Pursuing these applications requires precise control over the properties of stimuli-responsive materials. Here we show that the magnitude of thermal response can be tuned in a broad range. This tunable thermosensitivity is integrated with adjustable LCST and the ability to form controlled assemblies in the 5–250 nm range.

> Sensitivity of hydrophilic polymers to changes in the temperature of environment can be observed when macromolecules have a proper hydrophilic-hydrophobic balance, as demonstrated for a few water-soluble polymers with LCST. In solutions, these polymers undergo phase separation upon heating and their cross-linked analogs (hydrogels) experience sharp contraction or collapse. N-isopropylacrylamide (NIPAAM) is one of the most

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studied monomers for the preparation of temperature-responsive polymers [5]. The cloud point of homopolymer of NIPAAM is around 32 °C, and copolymerization of NIPAAM with different anionic [6], cationic [7], and non-ionic [8] monomers can significantly change this value. The other temperature-sensitive polymers, which are not based on NIPAAM, include polymers based on N-vinylcaprolactame, 2-ethyl-2-oxazoline, N,N-diethylacrylamide (DEAM), methylvinylether (MVE), and N-vinylcaprolactam (NVCl) [9]. A copolymer produced by a combination of a thermo-responsive monomer, such as NIPAAM, with a pH-responsive monomer yields double-responsive copolymers.

All above mentioned thermosensitive polymers were obtained by homo- or copolymerization of amphiphilic monomers that have both hydrophilic and hydrophobic moieties in their structure. In our work we used another approach for synthesis of series new thermosensitive polymers of linear and cross-linked structure. This approach includes radical copolymerization of hydrophilic monomers with hydrophobic ones. An advantage of this approach is the flexibility of variations of properties using a small set of inexpensive components. The resulting polymers would have a tunable hydrophilic-hydrophobic balance and exhibit temperature-induced phase separation. This approach was demonstrated in several published studies, where thermosensitive polymers were synthesized by free radical copolymerization of the following monomeric pairs: vinyl ether of ethyleneglycol (VEEG)-vinyl butyl (VBE), VEEG-vinyl isobutyl ether [10], vinyl ether of diethyleneglycol-VBE [11], 2-hydroxyethylacrylate (HEA) – VBE [12], HEA – butylacrylate [13], hydroxyethylacrylate (HEA)-hydroxyethylmethacrylate [14] and N-vinylpyrrolidone – vinyl propyl ether [15].

In this work firstly the thermosensitive polymer hydrogels were obtained by three-dimensional radical copolymerization of water-soluble HEA and hydrophobic monomer ethyl acrylate (EA) in the presence of crosslinking agent N,N'-methylenebisacrylamide (BAA).

2. Experimental

2-hydroxyethyl acrylate (HEA) and ethyl acrylate (EA) ("AldriCh", USA), are purified by double vacuum distillation. The amount N,N'-methylene-bis-acrylamide of basic substance is 96%. (MBAA) ("Reanal", Hungary) were used without additional purifying grade (p.a.). Ammonium persulfate were used without additional purifying grade (puriss.). Surface active agents (surfactants), sodium dodecyl sulfate (SDS) (Altey-Analityc, Kazakhstan) and cetylpyridinium bromide (CPB) (Vekton, Kazakhstan) were used without further purification.

Stitched hydrogels based on HEA and EA were obtained through radical polymerization by chemical initiation. They were used as the initiator of ammonium persulfate and as the sutured agent of N, N'-methylene-bis-acrylamide.

The experience was performed in hermetically sealed ampoules made of synthesized molybdenum glass in a water solution at the temperature of 60 °C. The ampoules were purged with argon for 10–15 min to separate the oxygen from the reaction mixture. Purification was performed 21 days in the distilled water then with ethanol. After purification, we left uniformly swollen samples in distilled water.

In order to study the influence of HEA-EA cross-linked reticulated copolymers (CPL) on the temperature, we put the uniformly swollen hydrogels in the form of tablets in special thermostatic cells. The relative change in the volume of the polymeric hydrogel in the cathetometer B-630 (Russia) we evaluated as the change in the ratio of V/V_0 with increasing temperature. Here, V_0 and V – volume of the samples in the synthesis and in the uniform swelling.

In order to investigate complexing of crosslinked reticulated copolymers with surfactants, samples of uniformly swollen hydrogels in the form of tablets in a certain concentration of surfactants were set and the volume change of the polymeric hydrogel in a cathetometer (ratio of V/V_0) was estimated.

During the investigation, we omitted them into the distilled water to extract the excessive amount of surfactant which was out of intermolecular reactions of CPL/surfactant polycomplex obtained on the basis of HEA-EA cross-linked reticulated copolymers. Effect of gel on the temperature we investigated by relative volume change in the cathetometer B-360.

Sorption and desorption properties of surfactant and HEA-EA cross-linked reticulated copolymers were tested for wavelength $\lambda = 260$ nm on the spectrophotometer "UV-2401-PC Shimadzu" (Japan).

The weighted amount of polymer is kept in a solvent until it got balanced swelling to determine a balanced swelling reaction of polymeric hydrogel. The amount of solvent in the film is calculated by the following formula: here: m - mass of equally swelled polymer sample; $m_0 - mass$ of dry polymer sample.

Rank of balanced swelling has been measured several times and average value was chosen.

The dry sample's mass is detected by drying the sample in the vacuum cabinet till the constant mass. ISO 9001 Sartorius (Germany) scales were used in measurement. The average value of swelling rank is determined by several experiments performed in parallel.

Gel-sol fraction flow of investigated gels is defined by the following formula:

 $G = m_0/m_{synth} * 100\%$

G – flow of gel fraction, %

 m_0 – mass of dry gel, g

 m_{synth} – mass of synthesized gel, g

S = 100 - G

S – flow of sol fraction, %.

The IR spectra of film are recorded in the range of 4000–400 cm⁻¹ on the spectrometer "Satellite FTIR Mattson" (USA).

3. Results and Discussion

Currently, the relevance of the new direction of creation and research of intelligent materials design, responding by schedule, to the impact of the environment on the basis of sciences polymers in chemistry, physics, medicine, biology and biotechnology has not lost its significance. From the science and practical point intelligent materials based on water-soluble polymers are of great interest. Special features such as diphilic, thermosensitivity in the macromolecules of stimulus-sensitive polymers gave intensive development in the field of modern chemistry and polymer technology [16–18].

In this paper, for the first time by the method of radical copolymerization new copolymers on the basis of 2-hydroxyethyl acrylate and ethyl acrylate from the initial monomer mixture (IMM) of different units ([HEA-EA] = 30-70; 50-50; 70-30 mol.%) were synthesized. The crosslinking agent (CA) -N, N'-methylene-bis-acrylamide (BAA) and as the initiator- ammonium persulfate were used. The basic laws of the three-dimensional copolymerization were studied by the method of sol-gel analysis. In the main monomer mixture an impact of the EA amount to the flow of the gel fraction and swelling uniformity in the water of the HEA-EA reticulated copolymers is shown in the Table 1. It has been identified that in the initial monomer mixture with the increase of EA grade the rank of HEA-EA



Fig. 1. Influence of the temperature on the HEA-EA copolymer networks: LMW [HEA-EA] = 30-70(1); 50-50(2); 70-30 mol.%(3).

copolymer hydrogels swelling uniformity in the water rises. The increase of HEA-EA copolymer hydrogels swelling rank can be explained by the decrease of cross linking rank with an increase in monomer concentration of low-active EA.

 Table 1

 Gel and sol fraction of the HEA-EA copolymers

LMW compound [HEA]:[EA], mole. %	Cross- linking agent, %	Gel- fraction, %	Sol- fraction, %	$A_{\rm water}, g/g$
70:30	0.1	60.13	39.87	07.81
50:50	0.1	56.80	43.20	10.45
30:70	0.1	45.26	54.74	12.76

In this paper, thermosensitive properties of new reticulated copolymers are studied (Fig. 1). To do this samples, uniformly swollen in the water, of polymeric hydrogels are placed in the thermostatic cells, then the change of ratio of relative swelling values (V/V_0) in accordance with the temperature is investigated. From the obtained data revealed that thermo-induced collapse is essential for the HEA-EA copolymer hydrogels and when an environmental temperature rises the amplitude ratio of the relative swelling of hydrogel decreases (Fig. 1). As shown in Fig. 1, an increase in molar concentration of the EA leads to a slight change in polymers thermosensitive property, that is, when the temperature of the polymeric hydrogel rises collapsing enhances. By the increase of the EA unit in the compound of initial monomer hydrophobic interactions accelerate, therefore breakdown of hydrogen compound in the hydrogel-water system occurs and the relative volume of the network slightly reduces.

This paper also determines that with the increase of EA monomer units the phase transition zone, i.e. the comparative volume compression of the network runs at the high amplitude. An explanation to this fact is the results gained above (Table 1) and the value of the degree of swelling of the network.

In this paper, in order to regulate the phase transition temperature of copolymers based HEA and using suggested hydrogel as depot of drug carriers, their interaction with surface-active substances (surfactants) in the aqueous medium have been studied. Used surfactant has been proposed as a drug model. The anion sodium dodecyl sulfate (SDS) and cationcetylpyridinium bromide (CPB) were used as surfactants.

Quite known from that basically link between diphilic ions of surface-active substances (surfactant) and matrices without ionic polymers passes through hydrophobic interactions and close to the polymer chain in comparison with the solution volume the local concentration of surfactant increases, in some cases, it provides polymers with new properties. In the paper authors found that from the result of sodium dodecyl sulfates interaction with polyvinylpyrrolidone (PVP), the last one acquires polyelectrolyte properties and clusters NaSDS similar to micelle formed by 4 times lower concentration than the critical micellization concentration [19].

In this work, in order to regulate the phase transition temperature included in the basis of HEA, their interaction with surface-active substances (surfactants) in the aqueous medium have been studied.

To investigate the interaction between HEA-EA cross-linked copolymer and surfactant, we put the samples of polymeric hydrogels, equally swollen in the water, into the water solution with varying concentration of NaSDS, and it was placed under surveillance for changes in their swelling ratios (V/V_0) with respect to time. Figure 2 (a, b, c) below shows the concentration of HEA-EA copolymers with various initial monomer structure, changed curves in swelling parameters of various solutions of NaSDS. According to reports, it was observed additional swelling of hydrogel samples upon formation of complex with NaSDS. It is found that at



Fig. 2. Swelling of HEA-EA copolymeric hydrogels in the water solution of SDS: LMW [HEA-EA] = 30-70 (1); 50-50 (2); 70-30 mol.% (3); [NaSDS] = $2 \cdot 10^{-5}$ (a); $8 \cdot 10^{-4}$ (b); $5 \cdot 10^{-5}$ (c) mol/l.



Fig. 3. Swelling properties of HEA-EA copolymer hydrogels in the CPB water solution: LMW [HEA-EA] = 30-70 (1); 50-50 (2); 70-30 mol.% (3); [CPB] = $2 \cdot 10^{-3}$ (a); 6,2 $\cdot 10^{-4}$ (b); $5 \cdot 10^{-5}$ (c) mol/l.

the critical and low micellization concentration of NaSDS the amplitude of network swelling significantly reduced. Charged by ionized groups during the formation of micelles in a higher concentration $(2*10^{-3} \text{ mol/l})$ (higher than micellization concentration of NaSDS) of HEA-EA copolymeric hydrogels, which leads to additional swelling hydrogels initial network. Also, it was found that an increase in EA monomeric units included in the initial monomeric mixture comprising at all concentrations NaSDS the swelling amplitude of networks has significantly increased. The reason for the penetration of low molecular weight NaSDS inside the network is that alkyl group in copolymers responsible for the hydrophobicity is compressed from the surface side of hydrogels. The degree of crosslinking of polymers is also important.

To investigate the interaction between the HEA-EA copolymer hydrogels and cationcetylpyridinium bromide (CPB), we put the samples of network polymers, equally swollen in the water, into the CPB water solution and with respect to time we investigated their relative volume (V/V_0). Figure 3 (a, b, c) shows how the complex formation between HEA-EA copolymeric hydrogels and CPB passes through additional swelling. It is worth to note that in comparison with the cationic CPB complex composition of HEA-EA copolymeric hydrogels goes well with the anionic SDS concentration of which is $2*10^{-3}$ (Figs. 2a and 3a). It is obvious that the complex formed by the interaction of alkyl groups and CPB and SDS and hydrophobic units of EA. And, ion free network of HEA-EA copolymers under the influence of ionic groups of surfactants gets charge, and it is timely, after the repulsion of like charges of ionic components affects the additional swelling of the original network.

Based on the literature review, thermosensitive gels are divided into three here types: 1) the gels swelling at high temperatures; 2) the gels getting compressed at a high temperature (gels drawn to collapse); 3) at increasing temperature swelling, compressing and re-swelling gels or compressing, swelling and re-swelling (swelling-collapse – swelling, collapse – swelling-collapse), that is, it was found that these types of gels tend to "oscillation characteristics". During the experiment, it was investigated the effect of temperature on the HEA-EA reticulated copolymers (Figs. 4 and 5) and their integrated framework. Every time when the temperature increases V/V₀ volume of hydrogels (V₀ and V – volume of sample upon synthesis

and in the state of equilibrium swelling under given conditions) monotonously decreases. Interaction of polymer network of copolymers with ionic surfactant leads to modification of thermosensitive properties of polymeric hydrogels. It was determined that the resulting transition temperature of complexes CPL/surfactant was conducted at a higher temperature zone than the pure copolymer networks.

It is found that in case of decrease in mole percent of EA, which is in the initial monomer composition of copolymers, in the composite based HEA-EA hydrogels from 70 to 30 (Fig. 4), the interphase transition zone of network moves into the high temperature zone. This is explained by the fact that the copolymers, which includes the alkyl group responsible for the hydrophobicity have decreased.

It is found that during the study the comparative volume of CPL (HEA-EA)/SDS composite (Fig. 5 curve 2) is changed at the high temperature zone and an interphase transition of CPL (HEA-EA)/CPB composite (Fig. 5 curve 3) runs in low temperature zones.

These results are consistent with earlier findings [1], that is, the phenomenon is due to the clenching of copolymers, which includes the alkyl group responsible for the hydrophobicity and pyridine group. The main reason that the comparative volume, interphase transition of CPL (HEA-EA)/SDS composite passes through the high temperature zones is that the like charges of SDS included in the hydrogels repel each other, from the expansion of the macromolecules and respectively upon formation of "polyelectrolyte swelling" the force opposite to thermo sensitivity is generated.



Fig. 4. Effect of the temperature on the composites based HEA-EA hydrogels: LMW [HEA-EA] = 30-70(1); 50-50(2); 70-30(3) mol.%; CPL (HEA-EA)/CPB composites; [CPB], mol/l = $2 \cdot 10^{-3}$.



Fig. 5. Effect of the temperature on the HEA-EA hydrogel and composites based on them: LMW [HEA-EA] = 30:70 (1) mol.%; CPL (HEA-EA)/SDS (2); CPL (HEA-EA)/CPB (3); [Surfactant], mol/l = $2 \cdot 10^{-3}$.



Fig. 6. Desorption kinetics of HEA-EA hydrogels in the SDS water solution: LMW [HEA]:[EA] = 30:70 (3); 50:50 (2); 70:30 (1) mol. %; [SDS]* 10^{-3} mol/l = 0.05.



Fig. 7. Desorption kinetics of HEA-EA hydrogels in the SDS water solution: LMW [HEA]:[EA] = 30.70 mol. %; [SDS]* $10^{-3} \text{ mol/l: } 2,0 (1); 0,8 (2); 0,05 (3).$

It was determined that the obtained transition temperature of CPL/CPB complexes is conducted at a higher temperature zone than pure reticulated copolymers.

In order to use hydrogels as carriers or adsorbents in medicine, it is necessary to determine how they adsorb surfactants. Thereby, SDS sorption laws by dint of HEA-EA hydrogels has been studied by UV spectroscopy, at the wavelength of $\lambda = 260$ nm. Subsequently for 26 h the equilibrium concentration of SDS is reduced and then stabilized. Desorption results of different composition of graft copolymers (Fig. 6) and various concentrations of surfactants (Fig. 7) were shown. With the reduction of the fragments with the lowest activity of HEA, part of the network, the immobility of surfactant volume increases. Given data is well combined with the contents of V/V₀ change of HEA-EA hydrogels in surfactant solutions.

Table 2 shows the volume of SDS set in HEA-EA hydrogels estimated for 1 gram of dry polymer. With the reduction of HEA units content in the initial monomer mixture compound and with the increased concentration of SDS in the surrounding mixture introduced volume of SDS rises.

Table 2

Amount of SDS immobilized with HEA-EA gels

LMW In the solutions Amount of [SDS] compound [SDS], in the polymer [HEA]:[EA], mol/l network, for dry mol. % polymers mol/g 0.1904*10-3 70:30 2*10-3 2*10-3 0.2469*10-3 50:50 $2*10^{-3}$ 30:70 0.2898*10-3 30:70 8*10-4 $0.0311*10^{-4}$ 0.0245*10-5 30:70 5*10-5

HEA-EA copolymers and CPL (HEA-EA)/surfactant composites within their framework were recorded by ATR/FTIR spectrometer containing infrared spectra with Fourier transform (Fig. 8). All spectra were taken in the range of 4000–500 cm⁻¹ at the room temperature. As indicated in Fig. 8, CPL (HEA-EA)/surfactant composites in comparison with the initial mixture, it was stated that it is characterized by an absorption band 1022.1 cm⁻¹ corresponding to the stretching vibrations of sulfa group of sodium dodecyl sulfate (SDS). Growth of absorption bands in the zone 2925.3 cm⁻¹, attributed to the methylene group fraction of the hydrophobic part of the surfactant.



Fig. 8. IR spectra of HEA-EA hydrogels and composites within their framework: LMW [HEA-EA] = 30:70 (1) mol.%; CPL (HEA-EA)/SDS (2); CPL (HEA-EA)/CPB (3); [Surfactant], mol/l = $2 \cdot 10^{-3}$.

Method of analysis by differential scanning calorimetry (DSC) gives a chance for the implementation of the thermal analysis of thermosetting compositions and preparations. For example, the temperature change, the beginning and the end of the process, the glass transition temperature of polymers, melting point and heat, the specific heat, the temperature of crystallization and etc. can be determined [20].

In this paper by dint of analyzing method DSC the glass transition temperature of new copolymers were determined (Fig. 9). It has been determined, the more increases in monomer units of ethyl acrylate contained in the initial monomer mixture (IMM) of copolymer, the more the glass transition temperature increases. This is due to the fact that ethyl acrylate and hydroxyethyl acrylate as the part of the copolymer give polymers elasticity, i.e. with an increase of these units within the initial monomer compound leads to an acceleration of the segments activity. Also, when the molar percentage of HEA varies from 70 to 30 in the initial monomer mixture of copolymers, the glass transition temperature of copolymers switches to the high temperature zone, and therefore when the initial monomer volume of HEA-EA is 70:30 percent in the copolymer compound, it is determined that the copolymers at the molecular level monotonous. According to the published reports it is known that the glass transition temperature of homo-HEA

is -15 °C and poly-EA 21 °C. With DSC you can identify the strong intermolecular interactions. The combination of copolymers with IMM in the case of 70-30 mole percent, can be explained by the fact that the EA are adapted to interact with macromolecules dimmers associates of HEA gradually crumble, it also points to the instability of the copolymers. Also, for copolymers, the connection between the hydrophilic HEA and hydrophobic EA, compared to their initial homopolymer has a high T_g, that is compared with the theoretical essence calculated on the basis of linear additively rule has a low T_g . This representation of T_g value reduces segments of macromolecules and explains interactions between the polymers as affecting the physical crosslinking (Table 3).

 Table 3

 Glass transition temperature of polymers

Initial monomer mixture, [HEA-EA] mol.%	Glass transition temperature T _g , °C
30:70	135.3
70:30	102.7
70:30(SDS)	111.1
70:30 (CPB)	120.6

During operation, also the temperature of the HEA-EA/surfactant composites taken on the basis of HEA-EA was determined. As shown in Table 3, it was determined that copolymers based on HEA-EA track to the glass transition temperature, i.e. to its high temperature zone.

Thermal gravimetric analysis (TGA) of the copolymers indicated in the Fig. 9 by differential charts. As seen in Fig. 9, when the mole percentage of HEA is 30 in the initial monomer mixture of HEA-EA copolymer, it was found that at temperatures above 160 °C immediately undergoes degradation and indicates that its polymeric degradation passes through only one-step. By the volume in-



Fig. 9. DSC and TG study for copolymers on the basis of HEA-EA, Initial monomer mixture [HEA]:[EA] = 30:70 mol.%.

crease of EA in the IMM compound an grid connection is quickly formed, it was determined, that the copolymers immediately subjected to degradation, and this is because the EA in the copolymer compound forms a large structure from molecules (Table 4).

4. Conclusions

For the first time via radical copolymerization which underlies 2-hydroxyethyl acrylate (HEA) and ethyl acrylate (EA), units of various new reticulated structures of copolymers of the initial monomer mixture (IMM) were synthesized. It has been determined, that for the obtained new HEA-EA copolymer the low critical solution temperature (LCST) is characterized. Complexing surface active agents of copolymer taken based on HEA-EA was investigated by exchange reaction between the anionic sodium dodecyl sulfates and cationic cetylpyridinium bromide. It was found

Table 4
Mass indications of HEA-EA copolymers subjected to degradation
(LMW [HEA-EA] = 30:70 mol.%).

Temperature range	(90–140) °C	(140–190) °C	(190–350) °C	(350–398) °C
Mass elimination	-7.00 %	-24.27 %	-16.43 %	-60.45%
stages	or	or	or	or
-	-0.65 mg	-2.125 mg	-3.1 mg	-3.875 mg
Residual mass	93 %	75.73 %	83.57%	39.55%
	or	or	or	or
	1.0948 mg	3.7958 mg	2.5696 mg	9.4543 mg

that compared to HEA-EA copolymeric hydrogels, thermosensitive properties of HEA-EA/surfactant composite containing surface active agents somewhat modified and hydrogel-surfactant complexes as compared to HEA-EA gels also pass through an extensive phase transition zone. To study the physical and mechanical properties of the new linear copolymer thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were conducted. As a result, it was determined that with the growth in units of EA the glass transition temperature is increased. This is due to the increase in the EA structure (more molecules) in copolymers.

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