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THE ROLE OF FeSO$_4$ IN THE OBTAINING OF POLYVINYLPIRROLIDONE COPOLYMERS

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Abstract. The proceeding of 2-hydroxyethylmethacrylate grafted polymerization on polyvinylpirrolidone has been examined in the presence of ferrum(II) sulfate. It was observed the formation of crosslinked copolymer capable to be used as a matrix for metal chemical reduction and for metal hydrogel composites obtaining. The effect of Fe^{n+} structure and concentration on the structural parameters of the polymeric network, copolymers composition, efficiency and degree of grafting has been determined. The interaction between the structure of the synthesized copolymers and their thermal and physico-mechanical properties has been established.

Keywords: copolymerization, copolymer, 2-hydroxy-ethylmethacrylate, polyvinylpirrolidone, hydrogel, structure.

1. Introduction

The synthesis of hydrogel composites is one of the topical directions in the chemistry of high-molecular compounds [1]. Hydrogels with metal nano- and microparticles are of special attention [2]. The reason is their unique unity of properties of the polymeric matrix and dispersed phase – metal, for example sharp change of electricoconductivity with the changes in medium moister, temperature, pH, loading, magnetic properties, high thermal conductivity, *etc*. This opens new areas of hydrogels application [3].

The widespread method of metal hydrogels obtaining is the direct filling of polymeric matrix pores by metals obtained *via* their chemical reduction from metal salts. This method is simple from the technological point of view and allows to regulate a content and size of metal particles within a wide range varying the nature and composition of the polymeric matrix as well as operational conditions of reduction.

Polyvinylpirrolidone (PVP) copolymers with mono- and dimethacrylic esters of glycols are promising materials for the composite metal hydrogels because they are highly porous systems. The original porous structure providing copolymers swelling in water and high penetrability for low-molecular compounds are the main factors which allow to use them as the matrices for metal reduction [4].

Recently we have developed the blends based on PVP and 2-hydroxyethylmethacrylate (HEMA) [5, 6]. The blends are hardened in the presence of metal ions with variable oxidation level. The polymerization proceeds with high rate at room temperature, in the air, that allows to simplify and reduce the price of the process, to reduce the process time and thus to expand the areas of its application. Ferrum(II) sulfate was found to be the most effective compound relative to the polymerization rate.

It was approved that hydrogels based on PVP copolymers with HEMA may be used as the matrices for the metal reduction and obtaining of composite hydrogels due to their structural characteristics, ability to absorb water and other solvents, penetration for low-molecular compounds and chemical stability [7]. The nature of metal reduction and properties of composite metal hydrogels mainly depend on the structure and properties of matrix – polymer, because structural characteristics of the polymeric network considerably affect the penetration and sorption ability relative to low-molecular compounds which participate in the redox processes, as well as reduction rate and size of metal particles. In its turn, the polymer structure depends on the choice of the initiating system that affects the structure and properties of the polymeric matrix during its formation [8].

The aim of this work was to investigate the effect of metal salts with variable oxidation level, namely ferrum(II) sulfate, on the formation of HEMA-PVP structure and to establish the correlation between

properties and structure of the synthesized copolymers as the matrices for metal reduction.

2. Experimental

HEMA-PVP blends were the investigation objects. If bulk polymerization took place, $FeSO_4$ would dissolve in HEMA; if it were solution polymerization, ferrum(II) sulfate would dissolve in water. The synthesis was carried out at 298 ± 1 K in the air without additional vacuumization of the initial material. The following components were used: HEMA ($r_{20} = 1079$ kg/m^3, $n_D^{20} = 1.4520$) was purified and distilled under vacuum; PVP with high purity and molecular weight of 28000 was dried at 338 K under vacuum for 2–3 h.

An amount of unbounded PVP was determined using photocolorimetry of water extract [9]. The grafting efficiency (f, %) was calculated as a ratio between grafted PVP (m_1, g) and total amount of PVP in the initial blend (m, g): $f = \dfrac{m_1}{m} \cdot 100$. The grafting degree ($p$, %) – as a ratio between grafted PVP (m_1, g) and total weight of copolymer (M, g): $p = \dfrac{m_1}{M} \cdot 100$. Boundary water absorption (W, wt %) was determined by weight method as the difference between dry (m_2, g) and swelled (m_1, g) samples: $W = \dfrac{m_1 - m_2}{m_1} \cdot 100$. Copolymer swelling factor was determined as a ratio of sizes of dry (d_d, mm) and swelled (d_s, mm) samples: $k = \dfrac{d_s}{d_d}$.

The molecular weight of chain fragment between polymeric network points (M_c, kg/mol) was determined using Flory-Rehner method [10]. The structural parameters of PVP macromolecules – macromolecular swelling factor (a_s); Flory constant (F, m); distance between macromolecule chain ends ($h^{1/2}$); length of the static thermodynamic segment (b, m); number of links in the segment (n_s) – were calculated according to the method [11] using the results of viscosimetric investigations. Thermal stability of copolymers was studied using Paulik-Paulik-Erdey derivatograph. Deformation and elastic characteristics – hardness number (H, MPa); plasticity index (P, %) and elasticity index (E, %) – were determined using hardness meter TShR-320 by measuring the depth of indenter penetration into the sample:

$$H = \frac{0.1F}{p \cdot d \cdot h}; \quad E = \frac{h - h_1}{h} \cdot 100; \quad P = \frac{h}{h_1} \cdot 100$$

where F – applied load, N; d – diameter of indenter ball, mm ($d = 5$ mm); h – depth of ball penetration into the sample under the load F, mm; h_1 – residual deformation after removing the load, mm.

3. Results and Discussion

The investigations results concerning the kinetics of PVP-HEMA copolymerization initiated by metal salts allow to predict the reaction proceeding with the transfer of kinetic chain to PVP macromolecule and formation of grafted crosslinked copolymer [5, 12]. We studied the regularities of bulk copolymerization in the presence of ferrum(II) ions and polymerization in aqueous, organic and water-organic media. The investigated blends have high reactivity and low activation energy. The rate of the reaction in aqueous medium in the presence of $FeSO_4$ is described by the following equation:

$$V = K \cdot [Fe^{2+}]^{0.9} \cdot [HEMA]^{2.0}$$

Rate constants (K) of the reaction at 313, 323 and 33 K are $2.4 \cdot 10^{-4}$; $4.68 \cdot 10^{-4}$ and $6.17 \cdot 10^{-4}$ dm$^3 \cdot$mol$^{-1} \cdot$s^{-1}, respectively. The total activation energy is 37 ± 2 kJ/mol. It is lower than that of the blends initiated by peroxides (cf. $E_a = 57$–68 kJ/mol [12]). The reaction order relative to monomer is 2.0 due to monomer participation in the complex formation. It is noted in [12] that in the presence of Fe^{3+} the polymerization proceeds instantly with uncontrolled rate. To confirm the prediction of grafted copolymer formation we recorded IR-spectra of PVP, polyHEMA, PVP-HEMA mixture and PVP-HEMA copolymer extracted by water till all unreacted PVP was removed. The analysis shows that bands at 650, 1415 and 1480 cm^{-1} typical of PVP are also present in copolymer spectrum. Moreover, the intensity of band at 1320 cm^{-1} corresponding to the deformational vibrations of –CH group of PVP chain is considerably less for copolymer extracted by water compared with the initial PVP in amount commensurable with its content in the copolymer. This fact allows to predict HEMA grafting to PVP with the participation of the mentioned group. At the same time the bathochromic shift of –CH group peak by 5 cm^{-1} is observed. It becomes more intensive with the increase of Fe^{2+} content in the initial blend. The reason is the weakening of C–H bond due to dislodgement of electron density during complex formation:

$$H-\overset{|}{\underset{|}{C}}-\overset{|}{N}-\overset{|}{\underset{|}{C}}=O^{\delta-} \longrightarrow Fe^{n+}$$
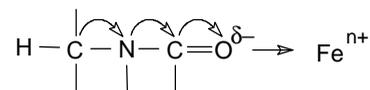
As a result, the chain transfer and grafting reaction proceed easier:
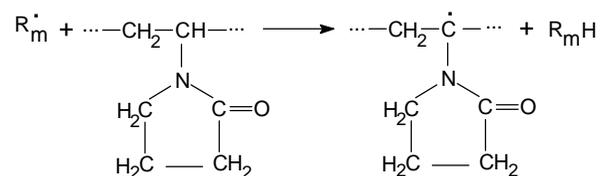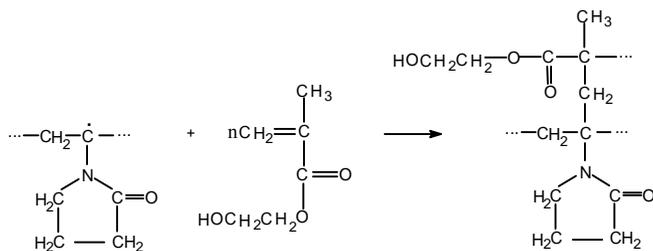
Grafting of HEMA to PVP and effect of copolymer composition on its thermal stability are confirmed by the comparison of thermogravimetric (TG) and differential thermal (DTA) analysis. The results for the mixture (w/w) PVP-polyHEMA = 80:20 (sample 1), copolymer HEMA:PVP = 80:20 obtained *via* polymerization in the presence of ferrum(II) sulfate (sample 2) and copolymer HEMA:PVP = 80:20 obtained *via* polymerization using benzoyl peroxide as the initiator (sample 3) are represented in Fig. 1.

Sample 1 has the lowest thermal stability and decomposes in the area of lower temperatures with maximal exothermal effect at 473 K. The rate constant of destruction (k_{ef}) has the highest value (Table 1).

Thermolysis of the samples is accompanied by the appearance of three effects on DTA curve (Fig. 1b). The first one is exoeffect observed within the range of 420–520 K corresponding to a thermal-oxidation process. The second one is endoeffect (520–570 K) caused by polymer

destruction and formation of decomposition volatile products. The appearance of exoeffect within 570–670 K is caused by thermal-oxidative degradation of the copolymer organic compound followed by the burning of pyrolytic residual at the temperatures above 670 K.

Endoeffect of the sample 2 is more profound compared with that of other samples and shifted toward the area of higher temperatures. At the same time the first exoeffect is minimal. It means the formation of more crosslinked structure with the participation of oxidated –CH groups. For the sample 1 we observe the minimal endoeffect shifted toward the area of lower temperatures (Fig. 1b) and maximal endoeffect indicating the less thermal stability of this sample due to the presence of non-substituted –CH groups in PVP. DTA of the samples 2 and 3 are different due to possible difference in their structures.

At the first stage the destruction of the sample 3 occurs with high rate and value of mass loss is high as well (Fig. 1a, Table 1). So, during HEMA copolymerization with PVP under the influence of Fe^{2+} ions the crosslinked copolymer with high grafting degree is formed. Therefore we can assert that ferrum(II) ions affect the copolymer crosslinking due to the localization of monomer molecules in the field of polarized complex Fe^{2+}-PVP providing the transfer of chain on the polymer.
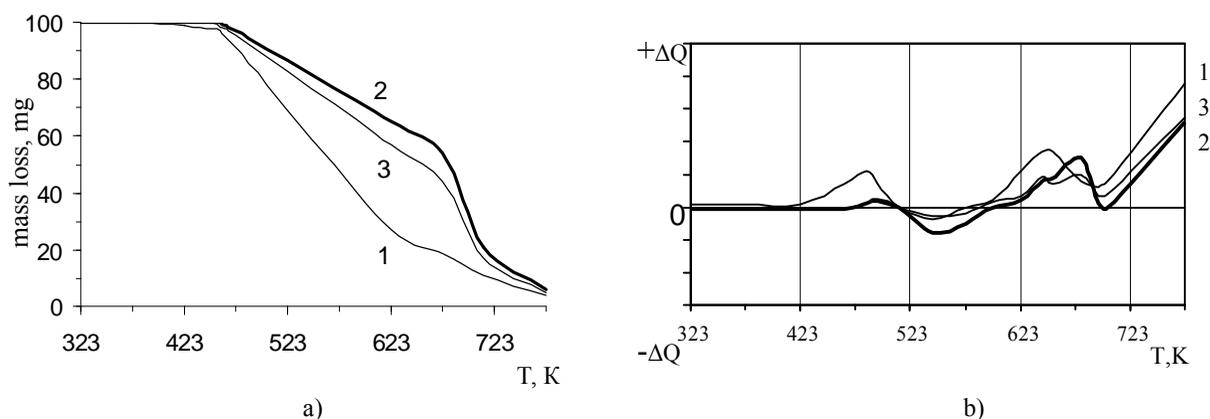
Fig. 1. TG (a) and DTA (b) analysis of copolymers:
1 – PVP-polyHEMA blend (HEMA:PVP (w/w) = 80:20 + FeSO₄);
2 – copolymer HEMA:PVP (HEMA:PVP (w/w) = 80:20 in the presence of FeSO₄)
3 – copolymer HEMA:PVP (HEMA:PVP (w/w) = 80:20 using benzoyl peroxide (BP) as the initiator)

Table 1

Kinetic parameters of thermal destruction (HEMA:PVP = 80:20)

Sample No.	Initiator	Destruction temperature, K	Mass loss, mg	k_{ef}, s⁻¹
1*	–	450–623	70	0.133
2	FeSO₄	450–673	40	0.046
3	BP	450–673	48	0.050

Note: *blend of poly-HEMA, PVP and FeSO₄ (0.05 wt %)

Table 2

Effect of the blend composition on the structural characteristics of the copolymers
($[FeSO_4] = 0.05$ wt %; $T = 298$ K)

Blend composition, mass parts		M_C, kg/mol	n, mol/kg	f, %	p, %	Copolymer composition, mass parts	
HEMA	PVP					polyHEMA	PVP
90	10	9/21	0.11/0.05	88/95	9/10	91/90	9/10
85	15	12	0.09	87	13	87	13
80	20	14/26	0.07/0.04	79/91	16/19	83/82	17/18
75	25	16	0.06	69	17	81	19
70	30	21/28	0.05/0.04	56/81	16/26	81/74	19/26
65	35	27	0.04	37	13	83	17

Notes: numerator – values of block-copolymers; denominator – values of copolymers synthesized in water (H_2O:blend = 1:1 w/w); M_c – molecular weight of the chain fragment between polymeric network points; n – network density; f – grafting efficiency; p – grafting degree

Table 3

Effect of $FeSO_4$ concentration on the grafting efficiency, grafting degree
and copolymers composition ($T = 298$ K; HEMA:PVP = 80:20 w/w)

$[FeSO_4]$, wt %	M_C, kg/mol	n, mol/kg	f, %	p, %	Copolymer composition, wt %	
					polyHEMA	PVP
0.01	15.8	0.063	76/91	15/19	84/82	16/18
0.03	14.8	0.067	77/67	15/14	84/86	16/14
0.05	13.6	0.074	79/59	16/13	83/87	17/13
0.07	13.2	0.076	82/37	17/8	83/92	17/8

Notes: numerator – values of block-copolymers; denominator – values of copolymers synthesized in water (H_2O:blend = 1:1 w/w); M_c – molecular weight of the chain fragment between polymeric network points; n – network density; f – grafting efficiency; p – grafting degree

Table 4

Effect of $FeSO_4$ on the intrinsic viscosity $[\eta]$ of PVP solutions and structural parameters of PVP macromolecules
($T = 296$ K; PVP molecular weight $36 \cdot 10^4$)

$[FeSO_4]$, %	$[\eta]$	a_s	$F \cdot 10^{-21}$, m	$(h^2)^{1/2} \cdot 10^8$, m	$b \cdot 10^9$, m	n_S
0	0.72	0.97	2.14	4.95	6.01	24.03
0.01	0.94	1.066	2.01	5.52	7.48	29.95
0.05	0.92	1.059	2.02	5.48	7.36	29.44
0.1	0.91	1.056	2.02	5.45	7.30	29.20

Notes: a_s – macromolecule swelling factor; F – Flory constant; $(h^2)^{1/2}$ – distance between macrochain ends; b – length of the static thermodynamic segment; n_s – number of links in the segment

a)   b)
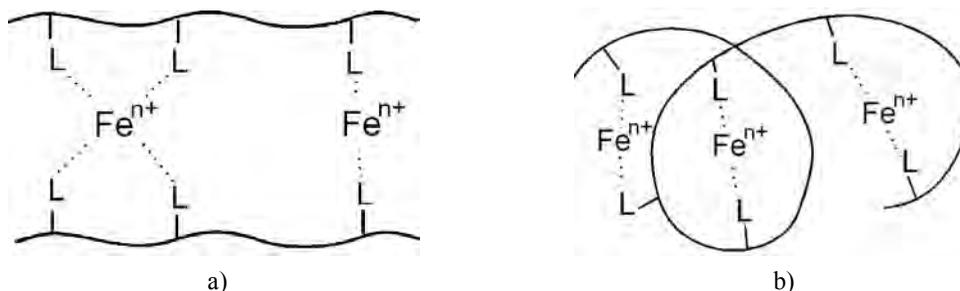
Fig. 3. Formation of intermolecular (a) and intramolecular (b) interaction between metal ions
and PVP macromolecules

During HEMA polymerization on PVP matrix in the presence of transition metal ions the dynamic and structural effects occur. The dynamic effect develops high polymerization rate and structural one affects the formation of copolymer structure through Me^{n+}.

We investigated the effect of polymerization type (block or solution polymerization) and ratio between the initial components on the copolymers composition, efficiency, degree of PVP grafting and structural parameters of the polymeric network to form the polymeric hydrogels with given characteristics providing optimal mechanical properties.

The presence of PVP in the copolymers increases their hydrophilicity, thermal stability and improves their mechanical properties compared with homopolymers [8]. However, only part of polyvinylpirrolidone participates in the grafted polymerization. Unreacted PVP may be washed out during hydration that affects physico-mechanical properties of copolymers. Therefore from the scientific and practical points of view it is interesting to determine the amount of reacted PVP. One can see from Table 2 that copolymer composition depends on the ratio between initial components of the blend. The increase in PVP amount decreases the grafting efficiency f and increases the grafting degree p. Moreover these values are higher for the copolymers obtained *via* solution polymerization compared with those obtained *via* block polymerization. There is also a difference between structural characteristics of the polymers network (molecular weight of the chain fragment between polymeric network points and network density) though general tendency to the decrease of network density is the same. The reason is that PVP macromolecules act such network fluffer. A part of PVP which does not participate in the grafting process is washed out during hydration and thus increases the free volume in the copolymer structure.

The increase in FeSO₄ concentration within 0.01–0.07 wt % has different influence on the grafting efficiency and grafting degree of the copolymers obtained *via* different types of polymerization (Table 3).

For the copolymers synthesized in the solution the increase in FeSO₄ concentration decreases both efficiency and degree of grafting from 91 to 37 % and from 19 to 8 %, respectively.

In the case of block-polymers the values f and p increase and the copolymer with a higher degree of crosslinking is obtained. It is connected with the effect of ferrum(II) ions on the PVP conformation at the initial stage of polymerization. The obtained results are in agreement with extreme dependence of polymerization rate on $[Fe^{2+}]$ in the solution [5, 12].

The effect of ferrum(II) ions on the PVP conformation in aqueous solutions is confirmed by the change of viscosity and structural parameters (Table 4). The small concentrations of FeSO₄ (till 0.01 wt %) essentially increase the intrinsic viscosity, the distance between macrochain ends and the length of the static thermodynamic segment. The further increase in Fe^{2+} concentration slightly decreases mentioned parameters. The possible reasons are curling of PVP macromolecules, the increase in balls size, the decrease in macrochains flexibility and mobility due to the intermolecular interaction between metal ions and PVP macromolecules (Fig. 3a).

The origin of such interaction is accompanied by changing internal mobility of polymeric chains. Loose polymeric coil of PVP is easily penetrated for monomer molecules and in such a case the grafting is maximum (Table 3). With increasing concentration of ions in solution the most part of them gets into the macromolecule coil and due to the high complexing ability of both Fe^{2+} and PVP the interaction between them occurs, which is a result of coil compression (Fig. 3b).

With the increase of $[Fe^{2+}]$ the coil is packed and centers, where grafting takes place, become less accessible for monomer molecules, resulting in reduced grafting efficiency. During block polymerization the macromolecules of PVP become straighter and local concentration of HEMA in the area of PVP-Fe^{2+} complex occurs favoring the grafting. The obtained data for block-copolymers correlate with above-mentioned results of IR-spectroscopic and derivatographic investigations.

Table 5

Dependence of physico-mechanical properties of copolymers obtained in solution on the blend composition ($T = 298$ К, [FeSO₄] = 0.01 %; blend:H₂O = 1:1)

Blend composition, mass parts		H, MPa	P, %	E, %	W, %	k
HEMA	PVP					
90	10	0.101	11	89	48	1.19
80	20	0.099	13	87	52	1.28
70	30	0.082	15	85	63	1.34
60	40	0.079	18	82	69	1.35
50	50	0.050	21	79	76	1.36

Notes: H – hardness number; E – elasticity index; P – plasticity index; W – water content; k – hydrogel swelling factor

Since polymeric hydrogels are mainly used in swelled form, we investigated the physico-mechanical properties of copolymers obtained after swelling in water and their dependence on water content and swelling factor (Table 5). To combine the stages of hydrophilic polymer synthesis and its further swell in a solvent, we carried out HEMA copolymerization with PVP in aqueous solution in the presence of metal ions. The increase in PVP content leads to the decrease in hardness and elasticity of hydrogel. The reason is PVP wash-out during copolymer hydration and increase of free volume. As a result, the increase in the amount of unbounded PVP macromolecules in the polymer volume decreases the network density and increases polymer looseness.

The increase of PVP concentration leads to the increase in water content and swelling factor. The reasons are network hydrophysics due to introducing chemically bounded hydrophilic chains of PVP and the increase in intermacromolecular free volume due to partial wash-out of unreacted PVP. Thus hydrogel plasticity increases.

4. Conclusions

We examined $FeSO_4$ influence on the structure formation and properties of HEMA-PVP copolymers which may be used as matrices for the production of metal hydrogel *via* chemical reduction of metals in the polymeric network. The fact of HEMA grafted polymerization with PVP and formation of crosslinked copolymer under the influence of Fe^{2+} salts was established. As a result, formed copolymers have a higher crosslinking degree compared with those obtained *via* polymerization initiated by benzoyl peroxide. The relation between physico-chemical properties and the structure of the synthesized copolymers was studied. So, the synthesis of grafted copolymers with necessary crosslinking degree and definite complex of physico-mechanical properties is possible and may be controlled.

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РОЛЬ FeSO₄ В ПРОЦЕСАХ ОДЕРЖАННЯ КОПОЛІМЕРІВ ПОЛІВІНІЛПІРОЛІДОНУ

Анотація. *Підтверджено перебіг прищепленої полімеризації 2-гідроксіетилметакрилату на полівініл-піролідоні в присутності сульфату заліза (II) з утворенням сітчастого кополімеру, придатного для використання як матриці для хімічного відновлення металів та одержання на його основі композиційних металогідрогелів. Встановлено вплив композиційного складу і концентрації Fe^{n+} на структурні параметри полімерної сітки, склад кополімерів, ефективність та ступінь прищеплення. Встановлено взаємозв'язок структури синтезованих кополімерів з їх температурними та фізико-механічними властивостями.*

Ключові слова: *кополімеризація, кополімер, 2-гідроксіетилметакрилат, полівінілпіролідон, гідрогель, структура.*