

Oleh Suberlyak, Oleksandr Grytsenko, Krystyna Hischak and Natalia Hnatchuk

RESEARCH OF INFLUENCE OF THE METAL NATURE ON THE MECHANISM OF POLYVINYLPIRROLIDONE METAL COPOLYMERS SYNTHESIS

*Lviv Polytechnic National University,
12, St. Bandera str., 79013 Lviv, Ukraine; ogrytsenko@polynet.lviv.ua*

Received: October 29, 2012 / Revised: December 03, 2012 / Accepted: February 18, 2013

© Suberlyak O., Grytsenko O., Hischak K., Hnatchuk N., 2013

Abstract. The influence of the metal fine filler nature on the polymerization mechanism of polyvinylpyrrolidone-methacrylate compositions in the presence and without iron(II) sulphate has been determined. The catalysis mechanism has been confirmed *via* complexation with charge transfer between the initial composition components. The metal activating effect increases with the increase of its negative electrochemical potential.

Keywords: polyvinylpyrrolidone, kinetics, complexation, catalysis, metal-hydrogels.

1. Introduction

Nowadays polymerization in the presence of inorganic compounds, which are the catalysts for polymer forming reactions, on the one hand, and fillers of formed composite materials, on the other hand, is a relatively new area in polymer chemistry. The polymer hydrogels are of special interest. By introduction of fillers different by their nature to the hydrogel material we can get new materials – composite hydrogels – with a new set of properties depending on the filler nature. The synthesis with simultaneous filling enables to distribute filler in a polymer volume and obtain composite materials with isotropic properties, which mainly depend on the polymerization kinetics. Knowing the peculiarities of filling influence on the polymer forming processes we can widely change both the structure and properties of polymers.

The authors established previously the possibility of composite polymer materials obtaining on the basis of polyvinylpyrrolidone (PVP) with 2-hydroxyethyl methacrylate (HEMA) copolymers in the presence of metal salts with variable oxidation rate *via* polymerization and simultaneous filling by fine fillers of different nature – some metal powders (magnetic and conductive), their

oxides, graphite and aerosil [1]. Using initiating complex system PVP-Meⁿ⁺ allows to synthesize the copolymers at room temperature in air at high rate (hardening time is from 10 s to 30 min) [2]. The obtained new hydrogel composite materials combine mechanical, conductive and sorption properties, which can widely vary depending on the initial compositions structure, content and nature of the metal, temperature and moisture during operation.

The purpose of the present work is to investigate the influence of metal fine powders nature on the polymerization mechanism of polyvinylpyrrolidone-methacrylate compositions in the presence and without iron(II) sulphate. Therefore we investigated the effect of metal nature on the polymerization kinetics of HEMA-PVP compositions and the structure of obtained compositional materials.

2. Experimental

Using the results of the previous researches [2], for the synthesis of filled hydrogels we selected polymerization in a block of the HEMA:PVP = 80:20 (wt %) composition in the presence of 0.05 % FeSO₄. The composition was experimentally selected taking into account the dependence of the polymerization rate on PVP and FeSO₄ content, as well as the analysis of viscosity, based on the sedimentation conditions of the filler particles and the necessity of highly productive process. For the synthesis we used 2-hydroxyethyl methacrylate ($r_{20} = 1079 \text{ kg/m}^3$, $n_D^{20} = 1.4520$), which was purified and distilled under vacuum (residual pressure of 14 N/m^2 , boiling point 351 K), the content of residual ethyleneglycol dimethacrylate was not more than 0.15 %. PVP with $MW = 12000$ and 28000 of high purification was dried under vacuum at 338 K for 2–3 h before use. Fine powders of Zn, Co, Ni, Fe, Cu, Ag metals and FeCo

alloy with particles size within 0.05–50 μm were used. The polymerization was carried out at 293 K, outdoors, in daylight. The polymerization kinetics was controlled by the change in volume of the reaction mixture during the monomer polymerization using the dilatometer method [3]. The polymerization rate was calculated at monomer conversion of 5 % using the method described in [4]. Spectroscopic studies were performed on a spectrometer Perkin Elmer PARAGON 1000 PC, using pressed tablets of copolymer powder and KBr. The amount of unbound PVP was determined by photocalorimetry of water extract [5]. The grafting efficiency (f , %) was calculated as the ratio between grafted PVP and the total amount of PVP in the initial composition, degree of grafting (p , %) – as a ratio between grafted PVP and the copolymer total weight. Structural parameters of polymer network were evaluated on the basis of M_S – average molecular weight of the segment based on the investigations results of a swelling, using Flory method [6]. The degree of swelling was determined using weight method as a difference between masses of polymer sample.

3. Results and Discussion

Metal fine powders of different nature with different properties (electrochemical and magnetic) were used during polymerization as a filler in the presence of small amounts of FeSO_4 (Fig. 1a) and the same metal powders without the addition of Fe(II) salt to the system (Fig. 1b). In the presence of powdered Fe, Co, Ni, Zn, and FeCo the polymerization proceeds with a higher rate than that under the influence of FeSO_4 (Figs. 1, 2). Moreover, Zn has the most active surface. Cu and Ag powders retard the process. The polymerization rate increases with the increase of metal filler content in the initial composition (Fig. 1b).

In all cases the process is exothermic (except for the compositions containing copper and silver) and is accompanied by a gel-effect, taking place both in the presence and absence of Fe(II) salts. For the compositions with zinc the polymerization with self-acceleration is observed after a short induction period, and the highest conversion is achieved (Fig. 2).

The analysis of the kinetic dependences shows that metals with negative electrochemical potential are the catalysts of polymerization. The higher electrochemical potential of the metal, the higher the rate of such polymerization. Moreover, the presence of Fe^{2+} ion in the reaction volume does not change this relationship, indicating that powder metal surface is actively involved in the initiating of the electrochemical polymerization.

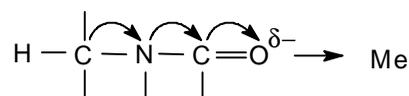
In order to determine the effect of PVP on HEMA polymerization in the presence of metal surfaces we

investigated the process kinetics at different weight ratio of HEMA:PVP = (100:0)–(60:40). Dependence of polymer yield on the polymerization time for the compositions with different PVP content and equal content of metal powder are represented in Fig. 3.

HEMA homopolymerization is slow in the absence of PVP. The introduction of PVP into the composition increases the polymerization rate proportionally to the increase of PVP content, whereas the induction period is not observed. Thus, the matrix effect and the role of charge transfer complex between HEMA and PVP are confirmed [7]. The complexation in the HEMA-PVP-metal system is confirmed by the results of quantum mechanical calculations performed using the software package Chem3D. Taking into account covalent, torsion and electrostatic interactions the structural formulas of PVP-(meth)acrylates and their complexes with metals were obtained, interatomic spacing, charges on atoms and energy parameters were defined. In the presence of zinc the nitrogen atom of PVP pyrrolidone cycle changes its sign to the opposite one (from +0.35 to -0.26 eV) and the negative charge of oxygen increases almost twice. The charges change of carbon atoms with double bond was observed on the oxygen of HEMA carbonyl group as well. Such redistribution of charges is a proof of complex formation with charge transfer involving metal.

Kinetic parameters of metal-methacrylate compositions polymerization showed high reactivity of PVP monomer-metal system. The results of IR-spectroscopy confirm the presence of PVP-metal complex. The obtained IR-spectra of metal-polymers are identical by their nature, though shift and splitting of some peaks are observed caused by the influence of metal surface. The absorption bands typical of PVP and HEMA which are present in both spectra of metal-polymers and copolymer+metal mixtures were selected for the comparison. The band characterizing the -OH group of HEMA becomes more asymmetric and broader than that in HEMA-PVP copolymer, indicating the formation of hydrogen link involving OH groups. The difference of the obtained spectra is the shift of vibration frequency of C=O typical bands for hydroxyethyl-1 from 1727 to 1714–1721 cm^{-1} (depending on metal nature) and their splitting.

The significant downward deviation of band vibration frequencies (from 1286 to 1260 cm^{-1}) is characteristic of -C=N- group of pyrrolidone cycle confirming its direct physical interaction with the metal. This change indicates the weakening of C-H bond due to the strengthening of mesomeric effect by metal:



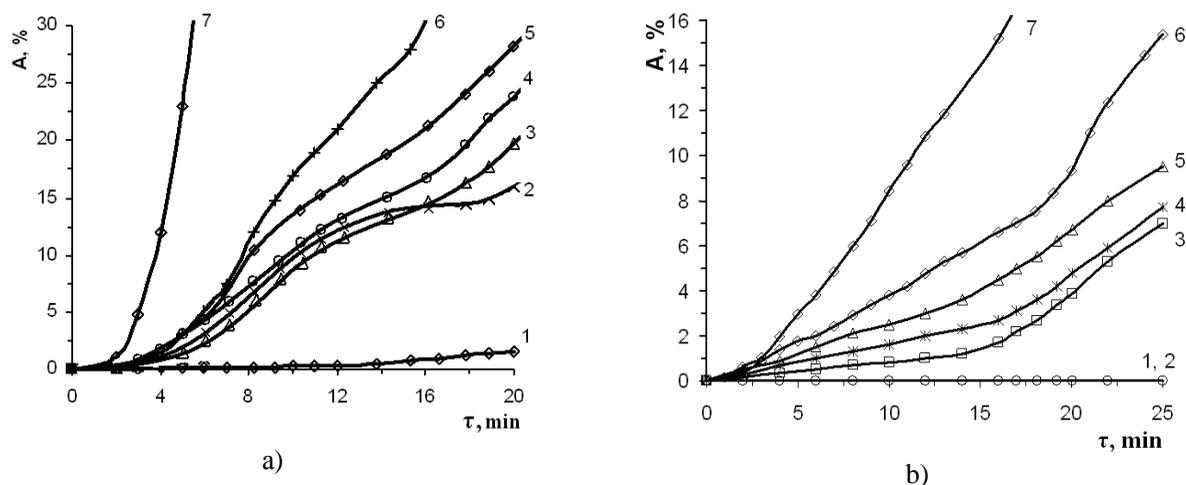


Fig. 1. Influence of the metal nature on the polymer yield. For (a): $[\text{FeSO}_4] = 0.05 \text{ wt } \%$; Cu (1); without metal (2); Ni (3); Co (4); FeCo (5); Fe (6) and Zn (7). For (b): Cu (1); Ag (2); Ni (3); Co (4); Fe (5); Zn (6) and Zn (20 wt %) (7)
 HEMA: PVP = 80:20; $MW_{\text{PVP}} = 12 \cdot 10^3$; $[\text{Me}] = 10 \text{ wt } \%$; $T = 298 \text{ K}$

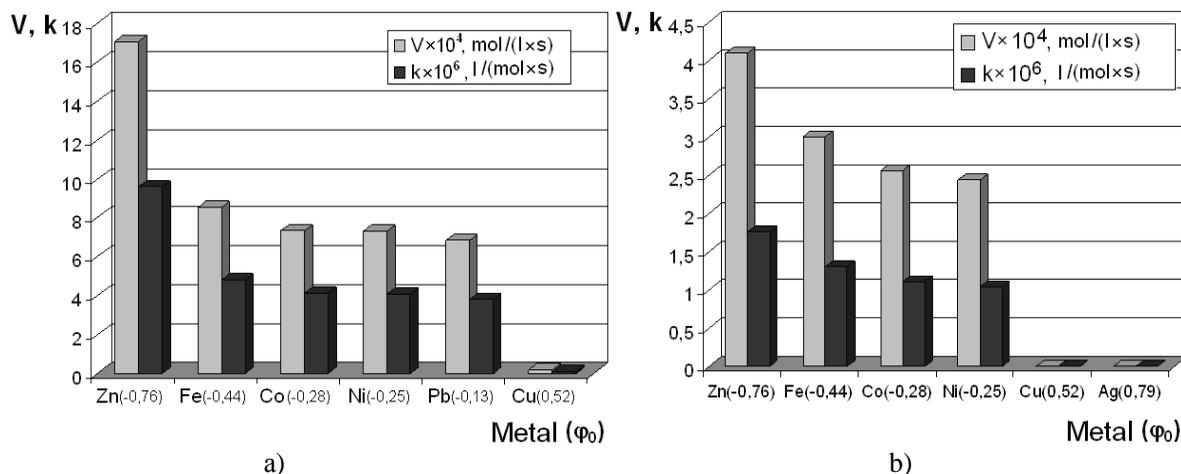


Fig. 2. Dependence of the polymerization initial rate (V) and polymerization effective constant (k) on the metal nature (standard electrochemical potential, j_0): in the presence of $0.05 \text{ wt } \%$ FeSO_4 (a) and without FeSO_4 (b).
 HEMA: PVP = 80:20; $MW_{\text{PVP}} = 12 \cdot 10^3$; $[\text{Me}] = 10 \text{ wt } \%$; $T = 298 \text{ K}$

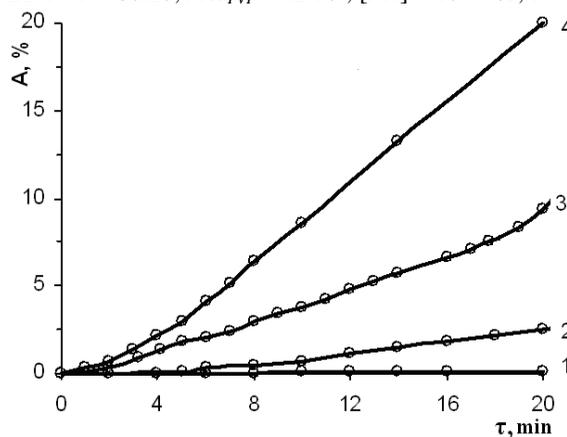


Fig. 3. Dependence of polymer yield on HEMA:PVP weight ratio: 100:0 (1); 90:10 (2); 80:20 (3) and 70:30 (4).
 $T = 298 \text{ K}$; $[\text{Zn}] = 10 \text{ wt } \%$; $MW_{\text{PVP}} = 12 \cdot 10^3$

The weakening of the bond between hydrogen and tertiary carbon atom of the PVP main chain promotes grafted polymerization due to the chain transfer to PVP. The additional confirmation is a decrease of the peak in the area of 1320 cm^{-1} , typical of C–H bond in the presence of metals, compared with pure PVP taken in an amount commensurate with its content in the copolymer (Fig. 4). The sharp decrease of the peak intensity occurs in a row $\text{Ni} > \text{Zn} > \text{Co}$.

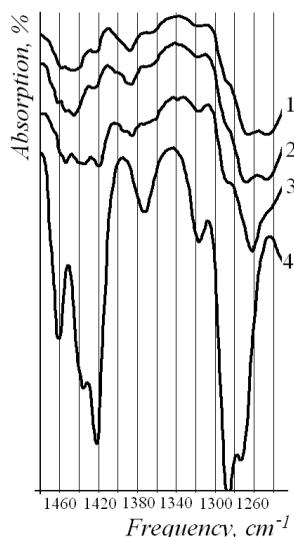


Fig. 4. IR-spectra of metal-contained copolymers: Co (1); Zn (2); Ni (3) and PVP (4). HEMA: PVP = 80:20; metal content is 10 %

The additional evidence of grafted polymer forming is the amount of grafted PVP in the final copolymer. One can see from Table 1, the efficiency of PVP grafting (f) increases with the increase of metal activity in the initiating polymerization.

Table 1

Influence of metal nature on the efficiency (f), grafting degree (P) and copolymers composition

HEMA: PVP = 80:20 wt %; $[\text{Me}] = 10\text{ wt \%}$; $T = 298\text{K}$;
 $MW_{\text{PVP}} = 28 \cdot 10^3$

Metal	f , %	P , %	M_s^* , kg/mol	Composition of copolymer, %	
				polyHEMA	PVP
Ni	24	9	8.60	91	9
Fe	70	15	9.8	85	15
Zn	74	16	10.27	84	16
Co	87	18	4.80	82	18

Note: $*M_s$ – molecular weight of polymer network interstitial segment

At the same time the inversely proportional dependence of the crosslinking degree on the metal activity is observed. At the highest Me activity the polymer with a minimum crosslinking degree (the highest

M_s) is formed. Obviously, the obtained results may be explained by the difference in rate and nature of copolymer structure forming on the surface and inside the composition volume. The dynamic thermo-mechanical analysis (DTMA) confirms this phenomenon.

DTMA is particularly relevant for the filled materials, since it shows the influence of filler on the change of macromolecules mobility in the boundary surface layers. It is known that at the interface with a solid the relaxation processes nature is changed [8] because the application of solids as a filler in the boundary layers of filled polymer systems changes the molecular mobility of both components at the interface. The obtained dependence (Fig. 5) allows to compare the change of accumulation modulus (Fig. 5a) and mechanical loss tangent (Fig. 5b) of polymers between each other and to conclude that metal nature affects the polymer network formation. Glass transition temperature (T_g) indicating a significant change in the structure phase, may vary under the internal stresses not only due to the changes in supermolecular structure, but also due to the changes in intermolecular distances and intermolecular interactions, correspondingly. The peak on the $tg\delta = f(T)$ curve corresponds to the T_g value. The structural changes stimulating an increased flexibility of macromolecules (the increase of accumulation modulus G'), usually contribute to the decrease of the glass transition temperature.

Chemical structure of the chains causes a significant impact on their flexibility and energy of intermolecular interaction, *i.e.* on the number and type of connections of fluctuation nets, and respectively on T_g . Thus, the increase of T_g indicates the growth of crosslinking density in the polymer network. The presence of two peaks in the graphical dependence of the mechanical loss tangent on the temperature is a peculiarity indicating the presence of areas with different crosslinking degrees in the structure of obtained copolymers. Moreover, it is an evidence that copolymer with different structures is formed both in the interfacial layer over the metal particle surface and in the volume (Fig. 5, curves 2-4). High activity of zinc and PVP complexation ability is a reason of physical interaction between them, which promotes the grafting reaction and formation of more crosslinked polymer over the metal surface. Due to PVP local concentration over the metal surface and monomer remoteness from the active centers in the composite volume the copolymer with a polymer network of lower density is formed. In the case of Co and Ni, whose activity is lower than that of Zn, the PVP concentration over the metal surface and in the composite volume is more uniform, which contributes to a less defective structure formation.

Boundary layer over the metal surface can be formed by intermolecular physical and chemical links. The magnitude of surface interactions is estimated by thickness of the composition surface layer (determined by

the difference between the masses of pure metal plate and plate after its immersion in composition, taking into account the plate physical sizes) as well as by the change of wetting contact angle and surface electrical resistance (Table 2) over the metal surface.

The iron surface has the highest adsorption activity, since a layer with the largest thickness is formed over it from the composition components solutions and composition as itself. The polymer adsorption layer is formed due to the physical interaction, as it was confirmed

by the change of metals surface resistance after adsorption (Table 2). As a result of PVP and HEMA adsorption and physical interaction with the metal surface the surface hydrophilicity varies depending on interaction nature. The change of wetting contact angle (Table 2) testifies to this.

Absence of chemical bond between polymer and metal surface is confirmed by morphological researches of metal-hydrogel based on HEMA-PVP copolymers (Fig. 6). We observe a separation of the polymer from the metal surface after swelling in water.

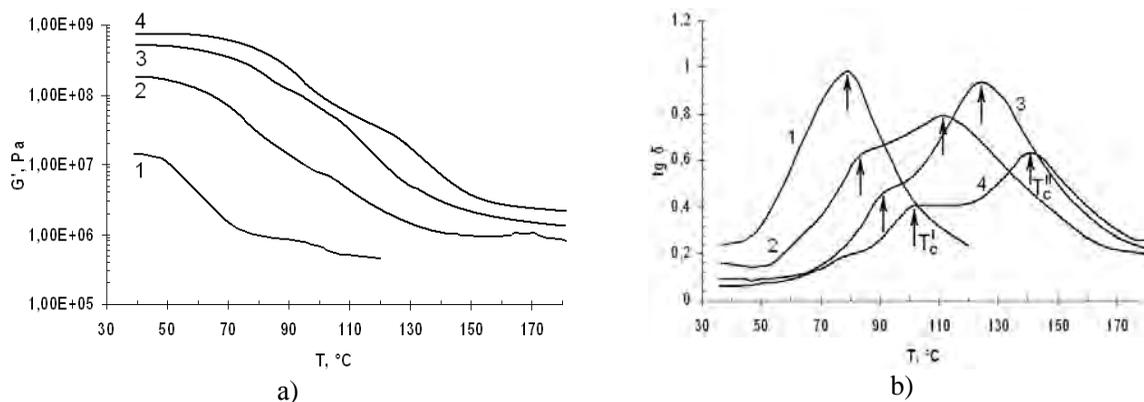


Fig. 5. Dependence of HEMA-PVP copolymers storage modulus G' (a) and mechanical losses tangent $\lg \delta$ (b) on the metal nature: without metal (1); Zn (2); Co (3) and Ni (4).

Composition, wt %: HEMA:PVP = 80:20; $MW_{PVP} = 28 \cdot 10^3$; $[Me] = 10$ wt %.

T_g' is a glass transition temperature in the volume, T_g'' is the same temperature at the boundary phase

Table 2

Characteristics of the surface layers depending on the metal nature

Metal	HEMA			PVP			HEMA-PVP			HEMA-PVP-H ₂ O		
	$h, \mu\text{m}$	$\theta, ^\circ$	$\rho \times 10^{-5}, \Omega$	$h, \mu\text{m}$	$\theta, ^\circ$	$\rho \times 10^{-5}, \Omega$	$h, \mu\text{m}$	$\theta, ^\circ$	$\rho \times 10^{-5}, \Omega$	$h, \mu\text{m}$	$\theta, ^\circ$	$\rho \times 10^{-5}, \Omega$
Zn	0.5	38	3.6	1.9	62	5.5	8.6	5	9.4	6.0	70	7.5
Fe	1.4	68	0.4	4.0	18	98	10.0	10	160	8.0	16	10.2
Cu	0.1	56	3.0	0.7	66	3.5	2.5	7	2.0	2.1	75	4.2

Notes: h – thickness of the surface layer; θ – wetting angle; ρ – surface electrical resistance.

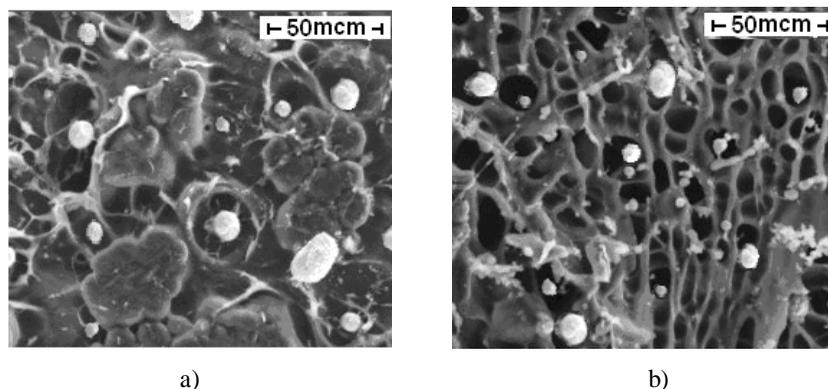


Fig. 6. Photos of surface of hydrogel based on HEMA-PVP copolymers: HEMA:PVP:H₂O = 80:20:0 (wt %); $[Zn] = 5$ wt % (a) and HEMA:PVP:H₂O = 80:20:50 (wt %); $[Zn] = 5$ wt % (b)

Investigation of the swelling nature of copolymer allows to suggest that polymer-metal interaction is broken under the solvent action. In a case of links complete cleavage at polymer-metal interface the swelling of filled sample is determined as:

$$Q = V = (V_2^{-1} - \Phi)/(1 - \Phi) \quad (1)$$

where Q – the degree of swelling; Φ – volume part of the filler; V – theoretical volume part of polymer in the swollen sample; V_2 – the true value of the volume part of polymer in the swollen sample.

The value of the interaction between the polymer and the metal surface may be determined according to the dependence of $V_2/V = f[\Phi(1-\Phi)]$. In our case this dependence is a linear one and V_2/V value decreases with the increase of $[\Phi(1-\Phi)]$ (Fig. 7).

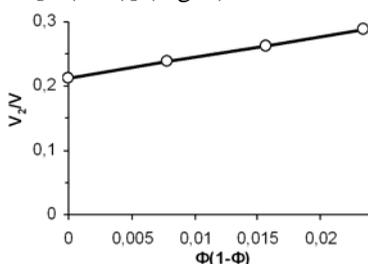


Fig. 7. Dependence of V_2/V on $[\Phi(1-\Phi)]$ for metal-polymers HEMA-PVP with different concentration of zinc

The dependence indicates a physical interaction between polymer and metal in the studied system, since the increase of filler content increases the volume part of swollen polymer.

Thus, the specific character of HEMA-PVP copolymerization mechanism over the metal surface lies in the fact that among all elementary reactions of the polymerization process (initiation, growth and break of the chain) the can metal play role only in initiation. Therefore, we suggest the following scheme for the formation of HEMA-PVP copolymers with the participation of metal surfaces (Fig. 8).

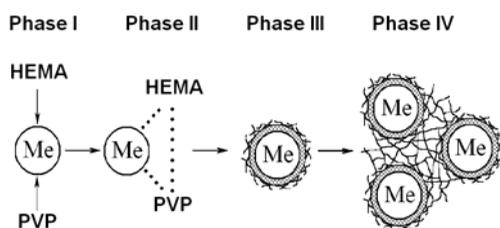


Fig. 8. Possible scheme of HEMA-PVP copolymers formation with metal surfaces participation

At first the diffusion of HEMA and PVP components to the metal surface (Phase I) and physical adsorption take place due to the formation of complexes between metal, HEMA and PVP (Phase II). Simultaneous complex formation of HEMA with PVP and metal weakens and breaks double bond, which is a factor of

polymerization initiation over metal surface (Phase III). The next stage (Phase IV) is polymerization propagation in the reaction medium from the metal particles surface.

4. Conclusions

Metal-containing copolymers were synthesized on the basis of quick-hardening PVP-containing monomers *via* polymerization in the presence of metal fine fillers and metal ions with alternating oxidation rate as well as without them. It was found that the metals with negative electrochemical potential and their alloys are catalysts for HEMA polymerization in the presence of PVP. The metal activating effect increases with the increase of its electrochemical potential. We established the polymerization regularities of polyvinylpyrrolidone-methacrylate compositions over metal surface at room temperature in the presence of oxygen. The catalysis mechanism was confirmed *via* complexation with charge transfer between the components of the initial composition and metal filler. The filler surface affects the thermo-mechanical properties of the copolymers (accumulation modulus and mechanical loss tangent).

References

- [1] Grytsenko O., Orlova A. and Skorokhoda V.: *Visnyk Nats. Univ. "Lvivska Polytechnika"*, 2003, **488**, 300.
- [2] Suberlyak O., Skorokhoda V. and Grytsenko O.: *Vopr. Khimii i Khim. Techn.*, 2000, **1**, 236.
- [3] Toroptseva A., Belohorodskaya K. and Bondarenko V.: *Laboratornyi Prakticum po Khimii i Tekhnologii VMS. Khimiya, Leningrad* 1972.
- [4] Kabanov V.: *Practicum po VMS. Khimiya, Moskva* 1985.
- [5] Suberlyak O., Skorokhoda V. and Thir I.: *Vysokomol. Soed.*, 1989, **3**, 336.
- [6] Savchenko M., Baranova A. and Ullberh Z.: *Dop. Akad. Nauk Ukr.*, 1992, **2**, 108.
- [7] Skorokhoda V.: *Chem. & Chem. Techn.*, 2010, **4**, 191.
- [8] Lipatov Yu.: *Phisyykokhimiya Mnogokomponentnyh Polymernyh System. Naukova dumka, Kyiv* 1986.

ДОСЛІДЖЕННЯ ВПЛИВУ ПРИРОДИ МЕТАЛУ НА ЗАКОНОМІРНОСТІ СИНТЕЗУ МЕТАЛОНАПОВНЕНИХ КОПОЛІМЕРІВ ПОЛІВІНІЛПІРОЛІДОНУ

Анотація. Встановлено вплив природи металевого дисперсного наповнювача на закономірності полімеризації полівінілпіролідон-метакрилатних композицій в присутності і без домішок сульфату заліза (II). Підтверджено механізм каталізу через комплексоутворення з перенесенням заряду між компонентами вихідної композиції. Встановлена зростаюча активуюча дія металу із зростанням його від'ємного електрохімічного потенціалу.

Ключові слова: полівінілпіролідон, кінетика, комплексоутворення, каталіз, металогідрогелі.