AL-FARABI KAZAKH NATIONAL UNIVERSITY

_Faculty of_Chemistry and Chemical Technology faculty

Department _Chemistry and Technology of Organic Materials, Polymers and Natural Componds______________

Confirmed
Dean of the faculty
____________________Ongarbayev Ye.K.

"_______"___________2012 .

Approved by the University scientific-methodical Council meeting
Protocol №_5_ from _22.__05.__ 2011
Vice-Rector for Academic Affairs
___________________Abdibekov U.A.

"__"________ 2012

Educational-methodical complex of the discipline

______ Macromolecules Mechanism Formation
(discipline name)

Speciality Code _ 6M060600 - Chemistry______
(code, speciality)

Education Form full time _________________
(full time, part-time)

Almaty 2012

Educational-methodical complex of the discipline is compiled______
__Grigoriy A. Mun, Deputy of Head of Department _Chemistry and Technology of Organic Materials, Polymers and Natural Componds Department, PhD, Prof.__
(name, position, scientific degree, title of the developer)

On the basis of_Work Education Plan_________________________
(based on what documents)

Considered and recommended at the chair meeting _________________
_____ Department of Colloid and Macromolecular Chemistry

On "__25_" ___May______________ 2012, Protocol №_31___

Head of the Chair _________________________Abilov Zh.A.
(signature)

Recommended at the methodical Council (bureau of the faculty)

On «_25_»____May___ 2012, Protocol №_

Chairman_________________________ Syzdykova
(signature)

Synthesis of polyelectrolites

Novel polycationic and polyampholyte hydrogels were synthesized by gamma-radiation copolymerization of vinyl ethers of monoethanolamine (VEMEA) and ethyleneglycol as well as VEMEA and acrylic acid. The complex formation of the obtained hydrogels with various metal ions and linear polyelecrtrolytes have been studied. The research of interaction with proteins have been started.

Water soluble and crosslinking thermo-sensitive cationic copolymers based on 2-[(methacryloyloxy)ethyl]trimethylammonium chloride and N-isopropylacrylamide (MADQUAT-NIPAAM) were obtained and their interaction with poly(acrylic acid) (PAA) and potassium hexacyanoferrates (II, III) were studied. It was found that the composition of copolymer significantly affects the composition of polyelectrolyte complexes and molecular weight of PAA influences their aggregation stability. The rate of contraction and the final swelling degree of the gel-polymer complexes depends on concentration of PAA in solution and its molecular weight. The hydrogels of copolymers absorb potassium hexacyanoferrates (II, III) and undergo contraction. The sorption ability of hydrogels depends on MADQUAT content in copolymers and is higher with respect to $K_3[Fe(CN)_6]$ than to $K_4[Fe(CN)_6]$. The study of interaction MADQUAT-NIPAAM copolymers with proteins have been started.

Novel non-ionic thermo-sensitive linear and crosslinked polymers have been obtained by gamma-irradiation copolymerisation hydrophilic (of ethylene glycol, 2-hydroxyethylacrylate0 and hydrophobic comomomers (vinyl butyl ethers, vinyl isobutyl ethers, 2-hydroxyethylmethacrylate, butylacrylate). I was found that soluble copolymers are characterized by LCST in water, and polymer hydrogels based this copolymers undergo thermo-induced contraction or collapse. The sorption processes of surfactants by novel thermosnsitive copolymers have been studied.

Stimuli-resposive films were prepared by gamma-radiation cross-linking of the blends based of poly(acrylic acid) and poly(vinyl methyl ether). The environmental pH affects the swelling of the films significantly. In acidic media the films have lower swelling ability because of suppression of carboxylic groups ionisation and formation of additional physical cross-links via interpolymer hydrogen bonding.

Novel polymeric film materials were prepared by radiation grafting of cationic monomer vinyl ether of monoethanolamine on the surface of polyethylene and polypropylene films. The prepared graft copolymers showed a good affinity towards the chelation and/or complexation with different metals investigated here (Pb^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Ag^{+}). Treating of the saturated films with 0.01 HCl at room temperature for one hour easily recover the absorbed metals and accordingly the films can be reused for the resorption of metal ions.

The copolymeric hydrogels based on polyethylene glycol (PEG) and methacrylic acid (MAA) have been synthesized by using γ-irradiation copolymerization. Physical chemical characteristics of obtained networks were studied. The comparative study of uranyl ions adsorption by PEG-MAA and polymethacrylic acid (PMAA) hydrogels was carried out. It was shown that the sorption characteristics depend on pH and ionic strength of solution as well as uranyl ions concentration. The more higher stability in the regeneration processes and possibility of repeated use of copolymeric hydrogel of PEG-MAA for uranyl ions adsorption in comparison to homopolymer PMAA were shown.

1. INTRODUCTION

Among all stimuli-responsive polymers and interpolymer complexes, those demonstrating pH and temperature dependent behaviour attract a great attention from both fundamental and practical points of view. They may find widespread application as sensors, sorbent, actuators, controlled and targeted drug delivery systems, non-viral vectors for gene therapy, attachment/detachment of cultured cells [1,2], etc. Weakly cross-linked macromolecules of hydrophilic polymers loss the ability to dissolve in water but are able to swell and form soft and elastic materials or so-called hydrogels. Hydrogels have very high sorption ability with respect to small- and macromolecules. The main purpose of this research is obtain new stimuli-sensitive polymers, hydrogels and interpolymer complexes for application in separation process

2. MATERIALS AND METHODS

2.1. Materials

Vinyl ether of monoethanolamine (VEMEA), vinyl ether of ethylene glycol (VEEG) and divinyl ether of diethyleneglycol (DVEDEG), vinyl butyl ether

(VBE), vinyl isobutyl ether (ViBE) as the commercial products of Alash Ltd. (Temirtau, Kazakhstan) were used in the present work. They were dried in the presence of dry K_2CO_3 and purified by double distillation.

N-isopropylacrylamide (NIPAAM) was purchased from Japan Co. and purified by triple dissolving in n-hexane at 40°C under stirring followed by precipitation at room temperature. The resulting precipitate was filtered out and dried on open air for 10 hours and then under vacuum for 24 hours.

2-methacryloyloxyethyltrimethylammonium chloride (MADQUAT) was supplied as 75 % aqueous solution (Aldrich). It was purified by precipitation in acetone, dried in a vacuum oven at 45 °C and stored in a dessicator at –5 °C.

Commercial 2-hydroxyethylacrylate (HEA), 2-hydroxyethylmethacrylate (HEMA), butylacrylate (BA) were purchased from Aldrich Chemical Co. HEA, HEMA and BA were purified by vacuum distillation under argon atmosphere.

The polyethylene and polypropylene films classified as "for food packaging" obtained from Munai Plastik Ltd. (Kazakhstan) were used in the study. Before experiments each sample was cleaned by acetone.

The sample of PAA with weight-average molecular weight 250000 Da was purchased from Aldrich and used without further purification.

All the chemicals used in the study were of analytical grade.

2. Methods

The copolymerization was performed in sealed glass ampoules using MRX-γ-25M setup equipped by ^{60}Co source with a dose rate 0.9 Gy/s. Before synthesis the feed mixture was saturated by argon. The synthesized hydrogels were purified by washing them with distilled water during 2 weeks. The composition of copolymers was determined by potentiometric titration.

The equilibrium swelling degree of the hydrogels was determined gravimetrically by the following formula:

$$\alpha = (m-m_{dry})/m_{dry}$$

where m and m_{dry} are the weights of the samples swollen in water and in dry state, respectively.

The swelling ratio V/V_0, where V_0 and V are the volumes of the polymer network immediately after synthesis and in the moment of measurements, respectively, was used for characterization of the hydrogels swelling in dynamics. The diameter of samples was measured using V-630 cathethometer (USSR) with the accuracy of measurements ±0.01 mm.

The grafting was performed in the sealed glass ampoules with polyethylene films immersed in monomer saturated by argon using an MRX-γ-25M setup equipped by ^{60}Co source with a dose rate 0.3 Gy/s. The dose rate was determined by a Fricke dosimeter.

The grafted films were removed and washed in distilled water for 1 day in order to remove unreacted monomer. The removing of impurities from the grafted films was checked gravimetrically.

The grafting degree was determined by gravimetric and potentiometric techniques and calculated by the following formula:

$$GD = [(m_{graft} - m_0)/m_0]\cdot 100\ \% \qquad (1),$$

where m_{graft} and m_0 are the weights of the films after and before grafting, respectively. For potentiometric determinations the grafted films were immersed in excessive amounts of 0.01 M solution of HCl and the excess is titrated by 0.01 M solution of NaOH. The value of m_{graft} was calculated from the titration results.

The water uptake was determined gravimetrically by the following formula:

$$\alpha = (m-m_{dry})/m_{dry} \qquad (2),$$

where m and m_{dry} are the weights of the films swollen in water and in dry state, respectively.

In experiments with copper uptake the samples of the grafted films were soaked into 0.1 M aqueous solutions of $CuCl_2$ for 1 day. The copper uptake was determined gravimetrically by the following formula:

$$\text{Copper uptake} = [(m_{Cu}-m_{graft})/m_{graft}]\cdot 100\ \% \qquad (3)$$

where m_{Cu} and m_{graft} are the weights of the dry films, after and before sorption, respectively.

The potentiometric titration was conducted with a digital ionometer (JenWay, UK).

The FTIR spectra of the films were recorded with the help of FTIR-Satellite spectrophotometer (Mattson, USA).

The synthesis of MADQUAT-NIPAAM copolymers was conducted in 10 % aqueous solutions using ^{60}Co MRX-γ-25 radiation facility with the dose rate 0.3 Gy/s. The hydrogels were synthesized by three-dimensional copolymerization in the presence of $3.84 \cdot 10^{-3}$ g/mL N,N'-methylenebis(acrylamide) as the cross-linking agent.

The compositions of the copolymers were determined by elemental analysis (PERKIN 85 ELMER Series II CHNS/O Analyzer 2400), IR-spectroscopy (FTIR Satellite "Mattson", USA) and ^{1}H and ^{13}C NMR-spectroscopy (Bruker ARX300 spectrometer at 300 and 75 MHz, respectively).

The release of pilocarpine hydrochloride was studied by immersion of dry films saturated with the drug into water and analysing the change in pilocarpine concentration in solution using Shimadzu UV2401PC spectrophotometer (Japan) at the wavelength 215 nm.

3. RESULTS AND DISCUSSION

3.1. Radiation synthesis of cationic and ampholyte hydrogels based on copolymers monoethanolamine and its sorption capability in respect to linear polyelectrolytes and metall ions

Cationic hydrogels have been prepared by copolymerization of vinyl ethers of monoethanolamine (VEMEA) and ethyleneglycol (VEEG) in the presence of divinyl ether of diethyleneglycol (DVEDEG) as a crosslinking agent.

The (co)polymerization of hydrophilic monomers in the presence of bifunctional cross-linkers is one of the methods for preparation of hydrogels. In most cases N, N'-methylene-bis-acrylamide (BAA) is used as a crosslinker for these purposes. However, in the case of vinyl ethers monomers BAA is not suitable because vinyl ethers have very low activity in reactions of radical polymerization and the hydrogels formed have inhomogeneous structure. The mentioned structure can be considered as an interpenetrating network, which incorporates highly cross-linked network composed mostly of BAA and weakly crosslinked network of vinyl ether. In this connection we have used divinyl ether of diethyleneglycol for synthesis of the hydrogels, which reactivity is similar to the reactivity of the monomers used.

The hydrogels were synthesized in the presence of 15 vol. % of water because according to our previous data the addition of water to the feed accelerates the radiation polymerization of the monomers. The main reason of this acceleration is a formation of hydrogen bonds between water and monomer molecules. The effects of absorbed dose and monomer ratio in the feed on the gel and sol fractions as well as the swelling properties of the hydrogels have been studied. It was demonstrated that the gel fraction increases with increase in absorbed dose. At the same time a decrease in sol fraction is observed, which is connected with formation of hydrogel having more cross-linked structure.

Earlier in the study of binary copolymerization of VEEG with VEMEA [3] we have found that the latter monomer is characterized by lower reactivity. By this reason an increase of VEMEA content in the feed mixture leads to a decrease in the gel fraction and increase in the sol fraction. However, the higher content of VEMEA in the feed results in the formation of hydrogels with higher swelling ability due to the ionic contribution of cationic monomer to the total swelling pressure.

The presence of primary amino-groups in VEMEA allows supposing the possible pH-sensitivity of the synthesized hydrogels. In acidic media the hydrogel is characterized by higher swelling ability because of the appearance of additional network charge due to the protonation of amino-groups.

Earlier we studied the interactions of linear copolymers of VEMEA-VEEG with poly(acrylic acid) (PAA) in aqueous solutions [4]. Formation of compact interpolyelectrolyte complexes, which composition depends on pH was shown.

In the present work we have studied the swelling behavior of the synthesized hydrogels in solutions of PAA at different pH (fig.1). It can be seen from the figure that the hydrogel undergoes considerable contraction after immersion into the solution of PAA at pH=2.2 due to the formation of interpolyelectrolyte gel-polymer complex and neutralization of the hydrogel charge. Earlier Kabanov et al.[5] have reported the similar behavior of polyelectrolyte hydrogels in solutions of oppositely charged ionic polymers. However, at higher pH values (pH=8.0) in the first stage of interaction the hydrogel swells additionally then reduces its volume. Probably this unusual behavior is connected with recharging of the gel surface by PAA macromolecules having higher charge density in these pH conditions. Then PAA macromolecules penetrate deeply into the network, the charges are neutralized and the gel volume decreases.

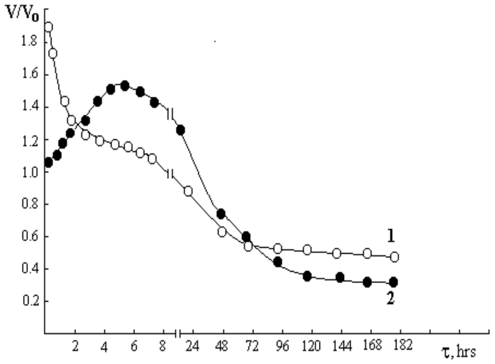


Fig.1. Effect of pH on the swelling kinetics of VEMEA-VEEG (15 : 85 mol.%)

hydrogel in 0.1 M solution of PAA. pH = 2.2 (1), 8.0 (2)

In order to confirm the mechanism of PAA interaction with the hydrogel the FTIR spectra of the starting polymers as well as the gel-polymer complex were recorded. For this purpose the hydrogel as well as the gel-polymer complex were dried and molded. The presence of the bands at 1710 cm^{-1} and 1556 cm^{-1} of unionized and ionized carboxylic groups in the spectrum of gel-polymer complex, respectively, confirms the sorption of PAA by the gel and electrostatic mechanism of this interaction.

PAA and VEEG-VEMEA are weak anionic and cationic polyelectrolytes, respectively. Therefore pH should affect considerably on their ionization degree and hence on the swelling behavior of gel-polymer complex. In this connection we studied the effect of pH on the swelling behavior of gel-polymer complex. For this purpose the sample of VEEG-VEMEA gel was immersed into 0.1 mol/L solution of PAA for 10 days. Then the gel-polymer complex obtained was immersed into solitions with different pH. The gel-polymer complex is characterized by extreme swelling behavior in the media with different pH. The observed dependence of equilibrium swelling degree on pH is typical for polymers having polyampholyte properties. In acidic media the additional protonation of primary amino-groups is occurred resulting in an increase of the hydrogel charge and additional swelling. In basic region the part of unbound carboxylic groups of PAA are ionized and hydrogel attains the negative charge, which leads to its swelling. The pH value (pH=5.4), at which the hydrogel is characterized by minimal swelling degree, can be considered as the isoelectric point of the gel-polymer complex. In this point the negatively charged PAA groups neutralize the positively charged groups of VEMEA and the structure of the gel-polymer complex is relatively compact.

The interaction of copolymers VEMEA-VEEG hydrogels with transition metal ions and gold ions at varying conditions (pH, ionic strength, initial concentration of salt solution) have been investigated. For example it was shown that samples of equilibrium swollen VEMEA-VEEG hydrogel in water solution of

$CuCl_2$ become deep blue and solution is decolorized. The observed phenomenon is connected with the complex fomation between copper ions and VEMEA-VEEG hydrogel. that polymer network undergo nonmonotonous alteration of volume in the complexation process: contraction of the gel appear at the initial stage of complexation and then gel significantly swells. This unusual phenomenon of repeated swelling is obviously caused by additional cross-linking of the network by formation of coordination bound at the complexation and appearance of additional charge on the surface of hydrogel. Hydrogel can swell or contract depending on which factor dominates. It was shown that VEMEA-VEEG hydrogels undergo monotonous contraction in KCl solution (0,05 mol/L) because of repression of polyelectrolyte effect in the presence of low molecular weight salt concerning the absence complexation in the system KCl – cationic gel.

Varying of pH in the range from 2 to 6 leads to contraction of hydrogel network in acid media, but no complexation is observed. Apparently, it is caused by competition of protons with metal ions and increasing of ionic strength due to presence of $CuCl_2$ salt ions of external solution. Sorption process goes more intensively at increasing pH and phenomenon of repeated swelling even at initial stage of the process.

Desorption of Cu^{2+} ions from hydrogel polymer matrix ([VEMEA]:[VEEG]= 13:87 mol.%) readily undergoes in acid media (pH=2,2). During this process hydrogel swells and loses blue colour, and external solution is significantly coloured. Sorption – desorption processes can be multiple reproduced concerning possibility of using VEMEA-co-VEEG hydrogels as sorbents of transitional metals.

It was found also good sorption capability of VEMEA-co-VEEG hydrogels in respect to gold ions.

3.2. Complex formation of temperature-responsive cationic linear copolymers and hydrogels based on [2-(methacryloyloxy)ethyl]trimethylammonium chloride and N-isopropylacrylamide with potassium hexacyanoferrates (II, III) and acrylic acid

Water-soluble and weakly cross-linked cationic polyelectrolytes have attracted considerable attention of researchers because of their ability to form polycomplexes with various large and small molecules. These complex formation reactions can be successfully utilized in purification of wastewater and enrichment technologies.

Complexation of polymers with inorganic ions occurs due to two possible mechanisms – donor-acceptor bonding and electrostatic interactions. The first kind of polycomplexes is formed between polymers having electron-donating groups and transition metal ions. The second kind of interactions is realized, when the polyelectrolyte and inorganic ions are oppositely charged. In some cases the binding of inorganic ions by polyelectrolytes occurs by two mechanisms simultaneously.

Some industrial processes involving application of iron-cyanide complexes have led to contamination of soil and ground water with wastes which are potentially hazardous, because they can be converted to extremely toxic free cyanides (CN^-, HCN) in the presence of UV-light. Different sorbents of inorganic and organic nature were suggested to remove these contaminations. The ability of hecaxyanoferrates to form complexes with some polymers can be used for development of decontamination technologies.

In the present work the temperature-responsive cationic polyelectrolytes were synthesized by copolymerization of 2-(methacryloyloxy)ethyltrimethylammonium chloride (MADQUAT) with N-isopropylacrylamide (NIPAAM) and the water-soluble copolymers and hydrogels obtained were studied as complex forming reagents in respect to potassium hexacyanoferrates (II, III).

Complex formation of linear MADQUAT-NIPAAM copolymers with potassium hexacyanoferrates (II, III) was studied in aqueous solutions by viscometric and turbidimetric methods. It was found that an addition of $K_3[Fe(CN)_6]$ solution to the solution of the copolymer is accompanied by drastic decrease in viscosity caused by compaction of macromolecules in course of complex formation reaction. The same phenomenon is observed upon addition of $K_4[Fe(CN)_6]$. However, unlike homopolymer PMADQUAT the mixing of the copolymers with potassium hexacyanoferrates (II, III) in dilute solutions (0.001 M) is not accompanied by phase separation. The appearance of the turbidity becomes seen in more concentrated solutions (0.01 M). Such difference between complexation behavior of PMADQUAT and the copolymers synthesized can be explained by the presence of NIPAAM units, which do not complex with $K_3[Fe(CN)_6]$ or $K_4[Fe(CN)_6]$ and provide higher solubility of polycomplexes in water. However, since the copolymers of MADQUAT and NIPAAM undergo separation upon heating the polycomplexes can precipitate forming yellow sediments at higher temperatures.

The behavior of polycomplexes in solutions was studied in a wide temperature interva. It was shown that the polycomplexes aggregate and loose solubility at lower temperatures in comparison with starting polymer. The aggregation of polycomplexes is due to the presence of NIPAAM in copolymer as well as additional hydrophobization caused by complexation.

The hydrogels MADQUAT-NIPAAM have been synthesized and characterized. We studied the complexation of these hydrogels with potassium hexacyanoferrates (II, III). It was found that the volume ratio V/V_0 of the starting hydrogels depends strongly on the composition of copolymers. An increase in MADQUAT content increases the swelling ability of the samples due to ionic contribution to the total swelling pressure. The gel samples immersed in aqueous solutions of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ undergo contraction and acquire greenyellow color, which is caused by complexation. The amplitude of contraction depends on MADQUAT content in copolymers and is maximal for hydrogels with highest MADQUAT content.

The contraction curves of the samples also depend on MADQUAT content in copolymers. The higher the NIPAAM content the higher the final DS of the hydrogels saturated by potassium hexacyanoferrates (II, III) because NIPAAM does not participate in complexation and remains relatively hydrophilic after the process. In addition an increase in NIPAAM content in the hydrogels shifts the saturation point to the lower relative concentration of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$.

Sorption ability of copolymeric hydrogels was evaluated by spectrophotometric method. We listed the data on the weight of absorbed salt per 1 gram of dry gels and also indicated the results in mol of the salt per mol of MADQUAT unit in the network in parentheses. The hydrogels bind more amount of $K_3[Fe(CN)_6]$ than $K_4[Fe(CN)_6]$ because every coordination ion $[Fe(CN)_6]^{3-}$ interacts with three units of MADQUAT but the ion $[Fe(CN)_6]^{4-}$ requires four MADQUAT units for binding. It can be seen that the higher MADQUAT content in copolymers leads to a greater sorption ability. Besides the amount of the salt absorbed by hydrogel containing 1 mol of MADQUAT units is not constant and depends on the composition of copolymers.

The polycomplexes of gels with the coordination compounds were thoroughly washed by distilled water, dried and analyzed by FTIR spectroscopy. The appearance of the band at 2117 cm^{-1} resulting from the vibrations of -CN groups in the coordination compound in the spectrum of polycomplex confirms the presence of $K_3[Fe(CN)_6]$ inside the gel.

In the present work we have studied also the interaction between hydrogels of MADQUAT-NIPAAM (26:74 mol.%) and linear PAA with different molecular weights (2000, 250000, 450000, 750000 Da). Fig.2 shows the dependence of the relative volume of the gel samples immersed in aqueous solutions of PAA on time. It can be seen that the hydrogel sample immersed into solution of PAA with lowest molecular weight (2000 Da) undergo contraction with the highest rate. The sample reaches the equilibrium for 40-60 mins. The gel samples immersed into PAA solutions with 250000 and 450000 Da also reduce their volume gradually but their final equilibrium swelling is much higher. The PAA with the highest molecular weight 750000 Da also causes the volume changes of the gel sample. However in the first stage of interaction (first ten minutes) the gel sample increases its swelling degree slightly. Then the gel begins to contract reaching the equilibrium during 60-70 mins. In summary, the molecular weight of linear PAA strongly affects the interaction. The higher the molecular weight of PAA the lower the amplitude of hydrogel contraction as a result of interpolyelectrolyte interaction. This trend can be explained by decrease in penetration ability of linear macromolecules through the network. A slight increase in the first 10 mins of interaction observed for PAA with 750000 Da can be explained by temporary increase in the hydrogel surface charge density caused by local contraction of the surface. After the macromolecules penetrate deeper they neutralize the inner part of the gel charge and the sample undergo contraction.

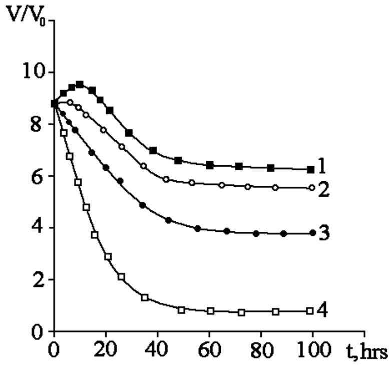


Fig.2. Swelling behavior of MAD-NIPAAM hydrogels in PAA aqueous solutions. C_{PAA}=0.01M; [MAD]:[NIPAAM]= 26:74 mol.%; M_W=750000 (1); 450000 (2); 250000(3) 2000 (1).

The effect of polymer concentration on the kinetics of hydrogel contraction was studied for PAA with the lowest molecular weight 2000 Da. It was found that if the concentration of PAA is very low (0.001 M) the contraction of the gel sample is slower. However there is practically no difference in contraction kinetics for 0.01 M and 0.1 M solutions of PAA. It is likely that above 0.01 M concentration there is saturation, i.e. it is more than enough macromolecules of PAA in solution, which can interact with the sample.

The effect of environmental pH at constant ionic strength μon the gel contraction kinetics as a result of interpolyelectrolyte reaction have been studied. An increase in solution pH accelerates the contraction process. Such a trend can be explained by dissociation of carboxylic groups of PAA. At low pH value (pH 2.8) the dissociation of carboxylic groups of PAA is completely suppressed, hence the linear polymer interacts with NIPAAM units of hydrogel mainly through hydrogen bonding. The MADQUAT units do not participate in this interaction and remain charged, which leads to a relatively higher swelling degree of the sample. At higher pH (pH 6.7 and 8.4) the ionisation of carboxylic groups is very high and they are able to interact with MADQUAT units of hydrogel and reduce the gel volume very efficiently.

3. 3. Hydrophilic stimuli-responsive films based on poly(acrylic acid)-poly(vinyl methyl ether) blends cross-linked by gamma-radiation

Poly(vinyl methyl ether) (PVME) is a non-ionic water-soluble polymer with unique ability to loose its solubility in water at higher temperatures. This property has attracted attention of different researchers and a lot of studies have been performed on temperature-induced phase separation in PVME-water system recently.

In the present work we have prepared PAA-PVME cross-linked films, studied their swelling properties in solutions with different pH and the possibility of their use as drug delivery system..

PVME as well as copolymers of vinyl methyl ether with maleic anhydride are important components of pharmaceutical formulations for controlled release of some drugs. The low value of glass transition temperature of PVME provides materials containing this polymer softness, elasticity and high adhesiveness, which is very important for their application as biomaterials. However the high adhesive ability of PVME is one of the difficulties in preparation of polymeric films by casting because of difficult detachment of these materials from the casting surface. In this connection the blending of PVME with other polymers is of considerable interest.

It is known that the mixing of aqueous solutions of PVME and PAA is accompanied by appearance of turbidity and precipitation of interpolymer complex (IPC), stabilized by hydrogen bonds, which disturbs the homogenous film formation. There are two possibilities to prevent the complex formation between PVME and PAA. The first one includes the neutralization of PAA by addition of some strong base. In these conditions the IPC will not be formed because the hydrogen bonding is possible with participation of unionised groups only and the mixture of solutions will not undergo phase separation. However, the films prepared by this technique would not be homogenous because of the complete immiscibility of the polymers. The second possibility is addition of organic solvents, which can prevent complexation because of their strong hydrogen bonding ability with respect to polymers. In the present work we have used dimethylformamide (DMF) as an additive, which prevents complexation. The films based on compositions with 10 and 20 mol.% of PVME were cast from 0.3 M aqueous solutions of polymers containing 30 vol.% DMF. The blends with higher PVME content could not be prepared because they were very adhesive and could not be detached from the surface of a Petri dish. After evaporation of the solvent the films obtained were homogenous and very elastic.

In order to prepare cross-linked materials the films were subjected to gamma-irradiation. It was shown that an addition of PVME to the composition increases the gel fraction considerably. It is well known that the gelation dose is inversely proportional to the molecular weight of a polymer, i.e. the higher the molecular weight of the polymer the lower the gelation dose. However, in our case an addition of lower molecular PVME to the mixture enhances the gelation. Cowie et al /6/ have reported that the blends of PAA with PVME are characterized by lower glass transition temperature (T_g) than pure PAA. It is likely that a decrease in

T_g favours the formation of the gel at lower doses because of the higher flexibility of the composition.

The cross-linked PAA-PVME blend films are able to swell in water and form hydrogels. It was found an increase in absorbed dose decreases the swelling ability of the materials considerably, which is connected with increase in cross-linking degree. An addition of PVME to the composition also decreases the swelling ability of the films because of its higher hydrophobicity and more ability for cross-linking.

The kinetics of hydrogels swelling is a parameter, which is very important for application of these films as biomaterials. We have studied the swelling kinetics of cross-linked films in solutions of different pH. In acidic medium (pH 2.2) the films achieve its equilibrium swelling for 20-30 min but the values of their water sorption capacity are relatively low. The equilibrium swelling degree (α) of pure PAA film is 6.6 g/g but the compositions containing PVME are characterized by even lower values of α. These low α values are caused not only by higher hydrophobicity of these blends but also by the possibility of interpolymer complex formation between unionised carboxylic groups of PAA and ether groups of PVME via hydrogen bonding and appearance of additional physical cross-links.

In solutions with higher pH the films swell to a significantly higher extent. In this case the swelling degree of the hydrogel films is due to dissociation of carboxylic groups of PAA and appearance of the network charge. Besides the interpolymer hydrogen bonding is not possible in these conditions.

The structure of the films purified from linear un-cross-linked polymers was evaluated by FTIR spectroscopy. The spectrum of PAA is characterized by the presence of the band at 1711 cm^{-1}, which is typical for carbonyl stretching of COOH-groups. The bands at 1111 and 1086 cm^{-1} observed in the spectrum of PVME are related to vibrations of ether groups. The same bands are observed in the spectrum of PAA-PVME film confirming that both polymers are cross-linked within one network. Some broadening of these bands is likely related to the hydrogen bonding between COOH-groups of PAA and ether-groups of PVME.

Soft and elastic consistency of PAA-PVME films in dry and in swollen state is an important property, which is typical for blends of PAA with poly(vinyl ethers).

The materials obtained in the present work can be used as bioadhesive films in ophthalmic applications, where the high elasticity of a polymer is required. Pilocarpine hydrochloride is an effective drug, which is widely used in human and veterinary medicine for treatment of glaucoma. The films containing pilocarpine hydrochloride were obtained in the present work by immersion of the dry cross-linked samples into 1 % aqueous solutions of pilocarpine for several days. Then the films were removed and dried. The release of the drug from the films into water was studied by UV-spectroscopy at the wavelength 215 nm. It was found that the amount of the drug released as well as the release rate are strongly dependent on the content of PVME in the film. An increase in PVME content in the film decreases these release parameters considerably. There are several possible reasons responsible for this regularity. First, the films containing higher amount PVME exhibit less swelling degree, which can delay the release of the drug from the polymer blend. Second, the films containing lower amount of PAA can absorb less amount of pilocarpine hydrochloride since the drug strongly interacts with carboxylic groups of polyacid via electrostatic contacts. Taking into account the specific interaction between the drug molecules and PAA one can suppose that even after 300-400 mins of release a significant amount of the drug is still retained in the polymeric matrix.

3.4 Radiation grafting of vinyl ether of monoethanolamine on polyolefine films

The use of ionizing radiation is preferred for grafting of polymers on different surfaces. The advantages of radiation technique include the possibility to regulate the grafting process and in some cases to initiate the polymerization of monomers, which cannot be prepared by other ways.

In recent years, there has been an increasing interest of researchers to the radiation grafting of functional polymers on different surfaces. This technique can be successfully utilized for preparation of selective sorbents, hydrophilization of surfaces, modification of membrane properties of different materials, enhancing the biocompatibility of medical devices.

The irradiation of polyethylene films immersed into the monomer results in the grafting of VEMEA. In order to characterize the obtained materials as well as to confirm grafting we have recorded the FTIR spectra of the films. In the spectrum of the starting polyethylene there are bands 2915, 2848, 1463 and 719 cm^{-1}, responsible for valent and deformation vibrations of CH-groups. New bands in the area 1089-1110 cm^{-1}, characteristic for vibrations of ether groups of VEMEA, 1576-1595, 3368 and 3300 cm^{-1}, responsible for deformation and valent vibrations of VEMEA primary amino-groups, are appeared in the spectra of grafted films. The presence of these new bands in the spectra confirms the grafting process. Moreover, an increase of absorbed dose leads to the increasing of the intensity of these bands.

The grafting degree of VEMEA as a function of the absorbed dose has been determined by two different methods – gravimetric and potentiometric ones. The results are summarized in table 1. The gravimetric and potentiometric data are in close agreement. It can be seen that unlike of active monomers the grafting of VEMEA required considerably higher values of absorbed doses and even in these conditions the grafting degree values are comparatively low. In addition the appearance of grafted species on polyethylene films requires some minimal dose, which is within 54-108 kGy. This "inhibition period" is caused by the low activity of VEMEA in radiation polymerization. Besides the grafting process is not very effective and is always accompanied by the formation of PVEMEA homopolymer.

Table 1. Dependence of grafting degree and water uptake of grafted films on absorbed dose

Absorbed	Grafting degree, %	Water uptake, g/g

dose, kGy	Gravimetric data	Potentiometric data	
54	0	0	0
108	0.75	0.6	0.75
162	4.35	4	1.32
270	9.4	8.1	2,73
324	11.4	12.5	3,05
378	12.8	14	3,75
432	18.1	16.9	4

The grafting of hydrophilic monomer of a hydrophobic polyethylene surface results in the enhancing ability to absorb water. Thus, the values of water uptake by the grafted films reach 4 g per 1 g of dry material. It should be noted that the formation of a hydrogel layer on a surface of polyethylene is observed at doses higher than 400-450 kGy.

In order to increase the efficiency of grafting we have studied the effect of water addition to the monomer taking into account the following: first; it was shown that the water added to the feed mixture accelerates the radiation polymerization of VEMEA, second; the presence of water in monomer should increase the number of active radicals in the system because of the radiolysis of water .

The dependences of grafting degree on the water content in the feed at various absorbed doses have been studied. It is obvious that the presence of 10 vol. % of water in the feed increases the grafting degree to reach maximum value. However, the further addition of water from 10 to 50 vol.% leads to a decrease in the grafting degree value to reach a lower one than without water addition. This dependence can be explained by the action of two factors: first is the favourable effect of water, second is the dilution of the feed or enhancing the formation of homopolymer. The similar trends are also observed for the values of water-uptake by the grafted films. The addition of 10 vol.% of water to the feed results in the growth of water uptake, and then it decreases with increasing of water percentage because of dilution of the feed.

As a weak cationic polyelectrolyte the PVEMEA demonstrates the ability for reversible conformation transitions in respond to the change of pH. The water uptake of the grafted films was studied as a function of pH medium. It was found that from the figure that the water uptake is increased upon shifting to the acidic pH region due to the protonation of primary amino-groups and appearance of the additional positive charge on the surface.

In order to increase the grafting degree of VEMEA on a polymeric surface we selected polypropylene as a new substrate for grafting because its structure affords to suppose the higher reaction ability in respect to irradiation.

Polypropylene films were immersed in VEMEA and irradiated in a wide range of the absorbed dose. The grafting degree of VEMEA on PP as a function of absorbed dose is summarized in table 2. An increase of the grafting degree is observed in the whole range 54-432 kGy. The appearance of VEMEA species on PP film causes the increase in water uptake by the prepared material because of the hydrophilization of its surface (table 2).

An increase of the grafting degree is observed in the whole range 54-432 kGy. The grafting of VEMEA onto polympropylene is more effective than onto polyethylene. Polymer –metal ions complexation is attractive approach for preparation of functional sorbents for waste water treatment. The presence of electron-donating primary amino- and ether-groups in VEMEA provides the ability of its polymers to form polycomplexes with various metal ions.

Table 2. Dependence of grafting degree and water uptake of grafted polypropylene films on absorbed dose

Absorbed dose, kGy	Grafting degree, %	Water uptake, g/g
54	3.00	0.50
108	4.41	1.52
162	6.80	2.00
216	8.13	2.12
270	14.11	2.60
324	18.00	3.31
378	19.20	4.00
432	25.70	4.98

We have studied the ability of the grafted films to absorb various heavy metals in order to evaluate the possibility of their uses in waste water treatment. The diagram showing the ability of the grafted films for metals uptake is shown in fig.3. It can be seen that the films with a higher grafting degree are characterized by considerable higher binding ability in respect to heavy metals. The nature of metal ion also has a great importance in the binding to the polymeric material. The affinity of the metal ions to VEMEA is decreased in the following direction:

$$Cu^{2+} > Zn^{2+} > Ni^{2+} > Fe^{3+} > Co^{2+} > Ag^{+} > Cd^{2+} > Pb^{2+}.$$

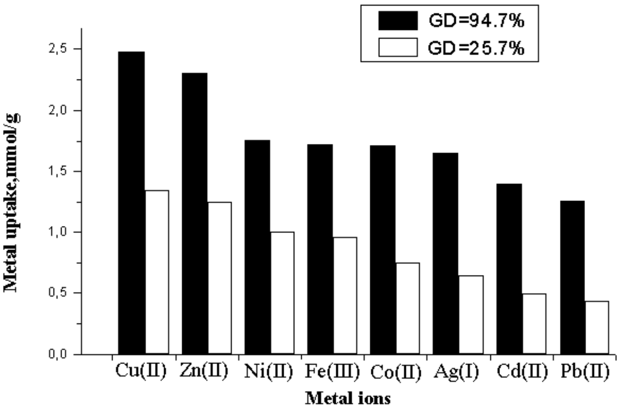


Fig.3. Sorption of metal ions by grafted films

Thus, the maximum value of metal uptake is very dependent on the type of metal ions and its coordination as well as the ionic size of the metal, which affect the permeability and diffusion of these metals through the porous ionic films. The latter parameter is mainly dependent on the polarity, electronic configuration and ionic radii of these metal ions.

The possibility to use the obtained materials repeatedly was evaluated in the several sorption-desorption cycles. The kinetics of sorption/desorption of metal ions could not be followed by gravimetric studies because it requires removing and drying the samples periodically that affects the accuracy of results. So, the spectrophotometric technique is applied. In this technique it is easy to determine the desorbed/absorbed amounts of metal ions without removing and drying the samples. The grafted film immersed into metal salt solution starts to absorb metal ions. Therefore the concentration of metal ions in solution decreases with sorption process and this decrease was monitored using spectrophotometer. The metal sorption increases with time and reaches the maximum after about 2 hours, when the chelating sites of the film are saturated. The maximal amount of absorbed metal salt, which was determined spectrophotometricaly and expressed in mmol/g units, coincides well with the metal uptake obtained by gravimetric technique.

The recovery and separation of absorbed metals can be easily carried out by treating the films with 0.01 M HCl for one hour. Desorbed metal ion concentration increases in solution of HCl with time and then reaches the maximum when desorption process is completely done. The regenerated films are again effective for resorption of metal ions with the same efficiency as checked for our films for 5 times.

Studies on the effect of pH on sorption characteristics of grafted film were carried out by metal uptake measurements over pH that ranged from 1 to 6. It was found that the metal sorption process increases with increasing of pH for Cu^{2+}, Ni^{2+}, Co^{2+} and reaches the maximum at pH=5 then decreases. In acidic solutions, the metal uptake decreases due to the competition with protonation reaction. On the other hand, at pH higher than 5 the metal uptake decreases due to the precipitation of hydroxides. Generally each metal ion has its own pH at which it shows maximal sorption.

One of the approaches that can be used to enhance the radiation grafting of VEMEA is to perform the process in the presence of more active monomer. In this work we have studied the preparation of novel materials by γ-initiated radiation grafting of cationic monomer VEMEA from its mixtures with vinyl ether of ethyleneglycol (VEEG) onto polyolefin films. We studied the effect of VEEG addition on the grafting of VEMEA onto polyethylene films. Table 2 presents the data on total grafting degree GD_{total} of VEMEA and VEEG at different absorbed doses and monomer ratios. It can be seen that an increase of absorbed dose considerably increases the total grafting degree. A significant increase in grafting is observed with addition of VEEG to the commoner mixture. Thus, the grafting degree, which is observed at 216 kGy for pure VEMEA, is 7.9 %. However, in the presence of 50 mol.% of VEEG the value of GD_{total} is increased to 258.5 %. Such a considerable enhancement is likely to be due to higher reactivity of VEEG in copolymerization.

Table 3. Data on total grafting degree GD_{total} of VEMEA and VEEG at different absorbed doses and monomer ratios.

Absorbed dose, kGy	Total grafting degree, %			
	100 mol. % VEMEA	90 mol. % VEMEA 10 mol. % VEEG	70 mol. % VEMEA 30 mol. % VEEG	50 mol. % VEMEA 50 mol. % VEEG
54	0	2.0	4.1	4.7
108	0.8	3.9	6.0	33.9
162	4.4	9.3	19.6	58.7
216	7.9	12.6	78.6	258.5

FTIR spectra of virgin polyethylene (PE) film, PE grafted with VEEG, PE grafted with VEMEA as well as the film grafted with mixture of the two monomers were recorded in order to characterize the materials obtained. PE film shows several distinct bands at 2908, 2869, 1464, 1376 and 723 cm^{-1}, responsible for valent and deformation vibrations of CH-groups. Grafting of VEMEA onto PE is accompanied by appearance of the new bands at 3367 and 1579 cm^{-1}, responsible for stretching and bending of primary amino groups, and the band at 1108 cm^{-1}, typical for vibrations of ether groups.

The spectrum of VEEG grafted material has very broad new absorption band centred at 3366 cm^{-1}, characteristic for hydrogen-bonded hydroxyl groups' vibrations, new bands at 1095 and 1072 cm^{1}, responsible for symmetric and asymmetric vibrations of ether groups.

The spectrum of the materials obtained by grafting from binary monomer mixtures shows the presence of amino groups in the sample (1557 cm^{-1}), confirming the grafting of VEMEA. The new characteristic bands are observed at 3361 cm^{-1} (hydroxyl- and primary amino-groups) and 1107 cm^{-1} (ether bonds), which can be characteristic for both monomers.

Using a combination of gravimetric technique for determination of the total grafting degree and potentiometric titration method for determination of ionic monomer VEMEA grafting degree we have determined the grafting degrees of individual monomers in the graft copolymer (Table 4).

As in the case of conventional copolymerization VEEG has higher reactivity in grafting than VEMEA. For all absorbed doses (162 and 216 kGy) an increase of VEEG content in the feed mixture leads to an increase in the grafting degree of both monomers VEEG and VEMEA.

Such behaviour can be attributed to the increasing of the copolymerization rate with addition of VEEG, which in turn increases the grafting of both monomers and the total grafting degree.

It can be said that the presence of more active monomer in the feed mixture enhances the grafting of the less active monomer due to the significant increase in total grafting degree resulting from the increasing of copolymerization rate.

Table 4. Dependence of grafting degree of VEEG and VEMEA on the feed mixture composition.

Dose, kGy	Feed mixture composition, mol.%		Total grafting degree, %	Grafting degree of VEMEA, %	Grafting degree of VEEG, %
	VEMEA	VEEG			
162	90	10	9.3	1.1	8.2
	70	30	16.9	1.4	18.2
	50	50	58.7	9.4	49.3
216	90	10	12.6	1.6	11
	70	30	78.6	7.2	71.4
	30	50	258.5	26.7	231.8

The presence of amino- and hydroxyl-groups will modify the hydrophilic properties of the graft copolymer. The obtained materials were evaluated for their sorption ability in respect to water and cooper (II) ions.

Table 5 presents the data on water and copper (II) ions uptake by the films obtained at different monomer ratios in the feed mixture. It is clearly seen that an increase of VEEG content in the feed leads to the higher value of water uptake, i.e. the film becomes more hydrophilic.

The uptake of copper (II) ions was controlled by two different methods - gravimetric measurements of the dry film weight increase after sorption and spectrophotometric monitoring of residual copper (II) ions in solution.

The results obtained by two methods are in good agreement and indicate the higher copper (II) uptake for films prepared from the mixtures of higher VEEG content.

Table 5. Dependence of water and copper (II) ions uptake by the grafted films on

the composition of feed mixture at absorbed dose 216 kGy.

Feed mixture composition, mol. %		Water uptake, g/g	Copper (II) ions uptake, %	
VEMEA	VEEG		Gravimetric determination	Spectrophotometric determination
100	0	1.48	0.25	0.21
90	10	2.30	1.20	1.12
70	30	75.00	19.00	18.32
50	50	103.00	23.50	22.76

In order to clarify the mechanism of copper (II) binding by the grafted films we have studied the effect of pH on absorption (Fig. 2).

It was shown from the figure that the uptake of copper (II) ions increases with increasing pH, reaching a maximum at pH 5.0, then decreases. In acidic solutions, the uptake is low due to competition with the protonation reaction. On the other hand, at pH higher than 5.0, the metal uptake decreases due to the precipitation of copper (II) hydroxide.
on the pH.

This result is in good agreement with that obtained in our previous work and confirms that the binding of copper (II) ions by VEMEA-VEEG grafted film takes place mainly due to donor-acceptor interaction with unprotonated amino-groups of VEMEA.

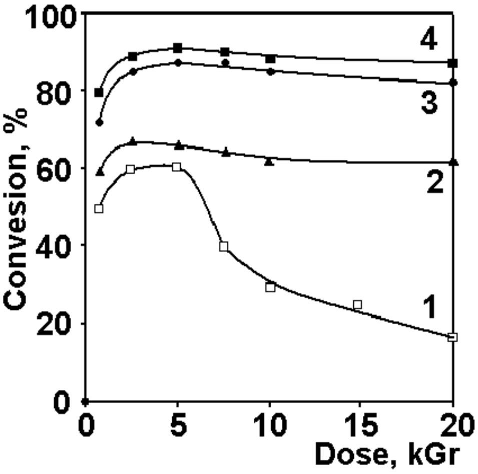
3.5. Synthesis and characterization of hydrogels based on copolymers of polyethylene glycol and methacrylic acid as sorbent of uranyl ions

The using of high energies irradiation for synthesis of polymers has a number of advantages in comparison to other methods of synthesis: obtaining of polymers free of initiators, easy control of irradiation process and carrying out of polymerization at low temperatures. In the present work the copolymeric hydrogels were synthesized by γ-irradiation of water-ethanol of polyethylene glycol and methacrylic acid (PEG-MAA) in presence of crosslinking agent threethyleneglycol dimethacrylate (TEGDMA) and physical chemical characteristics were studied. The comparative study of uranyl ions adsorption by PEG-MAA and polymethacrylic acid (PMAA) hydrogels was carried out using UV-, FTIR spectroscopy methods.

From the structural point of view, in the obtained PEG-MAA hydrogels the one end of PEG chain probably is bound or grafted to the PMAA chain. Such assumption about the structure of polymer network was done because in absence of crosslinking agent obtaining of hydrogels was not possible.

Figure 3 shows the change of gel-fraction yield (CR (%)) of hydrogels with irradiation dose (from 1.4 to 20 kGr), composition of feed monomer mixture and molecular weight of PEG. It can be seen, that highest yield of copolymers is achieved at dose 5 kGr. The following small decrease of CR (%) can be attributed to the scission of methacrylic acid chains. It is known from the literature that polymers, containing quarter carbon atom in its structure under ionizing irradiation undergo to destruction processes and the sharp decrease of the yield of PMAA hydrogel after irradiation dose 5 kGr confirm this supposition. Also it should be noticed that decreasing of CR (%) for copolymeric hydrogels PEG-MAA is less pronounced then for PMAA what is probably due to the template mechanism of copolymerization of the last. As a result, additional physical crosslinks appear in the system because of the formation of interpolymer complexes of hydrogen bonds.

Also from the presented Figure 3 it can be seen that in case of copolymers the increasing of concentration of MAA in the feed monomer mixture results in increase of their yield. There is two possible reason of it, the first one is due to enhance of the template copolymerization and the second is because crosslinking of PEG chains at such conditions of experiment was not observed, increasing of PEG content in the feed monomer mixture decrease conversion of PEG-MAA.



[PEG]:[MAA] = 0:100 (1); 64.7:35.3 (2); 50:50 (3); 40:60 (4), mol %

Figure 3. Conversion (yield of gel-fraction) of PEG-MAA hydrogels of different composition irradiated to various dose.

The swelling characteristics of PEG-MAA networks with different molecular weight of PEG were studied in the present work. It has been found that hydrogel samples with the smallest PEG chain length have the highest swelling degree. Obtained results can be attributed to decrease of the amount of hydrogen bonds between PEG ether oxygen and PMAA carboxylic groups which play role of additional crosslinks in the network structure.

Polymeric hydrogels containing ionic functional groups are widely used materials for different metal ions adsorption due to high adsorption ability, possibility of regeneration and repeated use.

The present work is devoted to comparative study of uranyl ions sorption by PEG-MAA and PMAA hydrogels. The structural feature of hydrogels based on PEG-MAA copolymers is the possibility of specific interactions between unionised carboxylic groups of MAA and ether oxygen of PEG via hydrogen bonding at low pH values. Taking into account the possibility of interpolymer complex formation within the network of PEG-MAA the sorption of uranyl ions by these hydrogels and pure poly(methacrylic acid) (PMAA) were studied additionally as a control network without interpolymer interaction.

Figure 4 shows adsorption isotherms of hydrogels of PEG-MAA and PMAA network obtained by plotting its adsorption capacities versus equilibrium UO_2^{+2} ions concentration. The sorption of uranyl ions by hydrogels is accompanied by acquiring of yellow colour by the samples. It can be seen from figures that adsorption becomes more pronounced at higher concentration of the uranyl ions. Besides, composition of copolymers does not affect significantly on its adsorption capacity. It can be seen from the figure that both hydrogels adsorb almost the same amount at low concentration of uranyl ions (100-200 ppm) in spite of the lower content of carboxylic groups of MAA in copolymer then that is in PMAA hydrogel. It can be attributed to conformational peculiarities of the first network. Besides the coordination binding interaction of ether oxygen with UO_2^{+2} can play some role in adsorption.

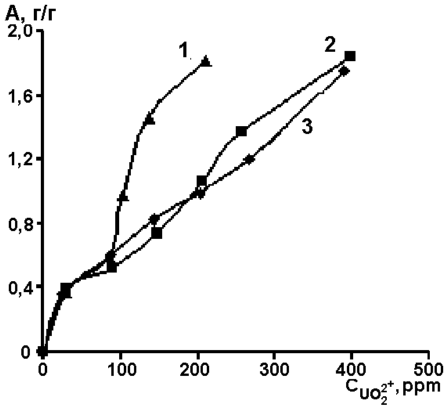


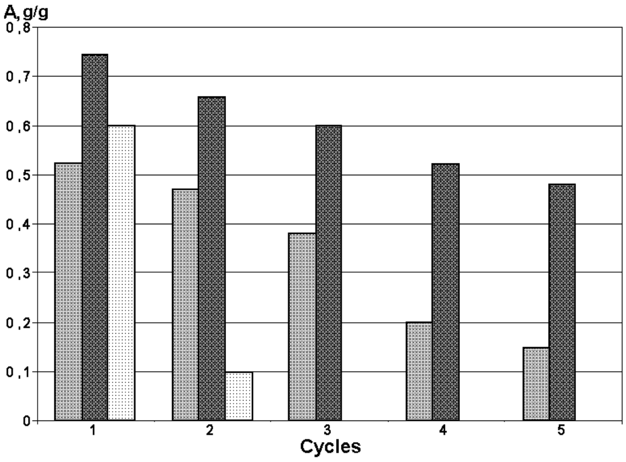
Figure 4. Adsorption isotherms of UO^{2}_{2+} ions adsorption onto PMAA (1)

and PEG-MAA (2,3) hydrogels.

[PEG]:[MAA] = 50:50 (2); 40:60 (3)

The sorption of uranyl ions by the hydrogels can be followed by FTIR spectroscopic analysis of dried samples. It was shown that the FTIR spectra of initial PMAA and PEG-MAA hydrogels as well as of samples after sorption from solutions with different uranyl ions concentration. The appearance of new band at 1539 cm^{-1} and 1532 cm^{-1} in the spectra of PMAA and PEG-MAA hydrogels saturated by UO_2^{+2} ions, respectively, responsible for asymmetric vibration signals of carboxylate anions indicates the ionisation of carboxylic groups caused by formation of ionic bonds with uranyl ions. Also a new band in the spectra of hydrogels after sorption of uranyl ions at 937 cm^{-1} belongs to uranyl nitrate hexahydrate.

The stability of PEG-MAA and PMAA hydrogels in regeneration processes for repeated using in adsorption processes was studied (Fig. 5). For desorption of urany ions from hydrogels the 0.1 M solution of HCl acid was used. It was found that PMAA network undergo to destruction after the second cycle of regeneration and became not suitable for adsorption purposes. At the same time, copolymeric hydrogels PEG-MAA can be used in sorption-desorption processes more then 5 times. The stability of copolymers to desorption processes in comparison to PMAA is probably attributed to the formation of interpolymer complexes between COOH groups of PMAA and ether oxygen of PEG which enhance the mechanical strength of hydrogel.



PEG-MAA - ■ (200 ppm); ▩ (100 ppm); PMAA - □ (100 ppm)

[PEG]:[MAA]=40:60 mol %

Figure 5. Adsorption capability of PEG-MAA hydrogels in the sorption-desorption processes

4. CONCLUSIONS

Novel cationic and ampholyte hydrogels were synthesized by gamma-radiation copolymerization of vinyl ethers of monoethanolamine and ethyleneglycol in the presence of cross-linking agent. The cationic hydrogels are able to bind various metal ions and poly(acrylic acid) to form interpolyelectrolyte complexes having swelling properties typical for polyampholytes. The interactions of the synthesized polyampholyte hydrogels and linear poly(acrylic acid) or poly(vinyl ether of monoethanolamine) are accompanied by contraction of the networks independently on pH. However the mechanism of interpolyelectrolyte interactions can be different at different pH.

Temperature-responsive complex forming linear polyelectrolytes of high molecular weight and their hydrogels were synthesized by γ-irradiation copolymerization of MADQUAT and NIPAAM. It was shown that the linear copolymers are able to form polycomplexes with potassium hecacyanoferrates (II, III), which solubility greatly depends on concentration of the reagents and temperature. Using the temperature-sensitivity of the copolymers it is possible to regulate the solubility of polycomplexes. The hydrogels of copolymers absorb potassium hexacyanoferrates (II, III) and undergo contraction. The sorption ability of hydrogels depends on MADQUAT content in copolymers and is higher with respect to $K_3[Fe(CN)_6]$ than to $K_4[Fe(CN)_6]$. Water-soluble copolymers as well as hydrogels based on MADQUAT and NIPAAM are able to interact with linear PAA and form polycomplexes. The nature of interaction is different at different pH. In acidic media the polycomplexes are stabilized by hydrogen bonds but at higher pH the electrostatic forces play the major role. The molecular weight of PAA as well as the composition of copolymers affects the aggregation stability of polycomplexes and their composition.

Stimuli-resposive hydrogel films were prepared by gamma-radiation cross-linking of the blends based of poly(acrylic acid) and poly(vinyl methyl ether). The films containing higher amount of poly(vinyl methyl ether) are easier cross-linked and have lower swelling ability. The environmental pH affects the swelling of the films significantly. In acidic media the films have lower swelling ability because of suppression of carboxylic groups ionisation and formation of additional physical cross-links via interpolymer hydrogen bonding. The possibility for application of the films as drug delivery systems is demonstrated with anti-glaucoma medicine pilocarpine hydrochloride.

- Novel polymeric materials were prepared by radiation grafting of cationic monomer vinyl ether of monoethanolamine on the suface of polyethylene and polypropylene. The grafting degree and water uptake of films are function of absorbed dose. The addition of water to feed mixture up to 10% increases the grafting degrees and water uptake as well as addition of 5% hexane did the same trend. The prepared graft copolymers showed a good affinity towards the chelation and/or complexation with different metals investigated here (Pb^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Ag^{+}). Maximal sorption for Cu^{2+}, Ni^{2+}, Co^{2+} is achieved after treating time 2 hours in feed solution of pH 5. Treating of the saturated films with 0.01 HCl at room temperature for one hour easily recover the absorbed metals and accordingly the films can be reused for the resorption of metal ions.

Novel non-ionic thermo-sensitive linear and crosslinked polymers have been obtained by gamma-irradiation copolymerisation hydrophilic (of ethylene glycol, 2-hydroxyethylacrylate0 and hydrophobic comomomers (vinyl butyl ethers, vinyl isobutyl ethers, 2-hydroxyethylmethacrylate, butylacrylate). I was found that soluble copolymers are characterized by LCST in water, and polymer hydrogels based this copolymers undergo thermo-induced contraction or collapse. The sorption processes of surfactants by novel thermosnsitive copolymers have been studied.

The copolymeric hydrogels based on PEG and MAA were synthesized by using γ-irradiation method in presence of crosslinking agent threethyleneglycol dimethacrylate. Physical chemical characteristics of obtained networks were studied. It was found that the swelling and structural characteristics of PEG-MAA hydrogels depend on composition of reaction mixture, PEG molecular weight and pH of solution. The comparative study of uranyl ions adsorption by PEG-MAA and polymethacrylic acid (PMAA) hydrogels was carried out using UV-, FTIR, TGA spectroscopy methods. It was shown that the sorption characteristics depend on pH and ionic strength of solution as well as uranyl ions concentration. The higher stability in the regeneration processes and possibility of repeated use of copolymeric hydrogel of PEG-MAA for uranyl ions adsorption in comparison to homopolymer PMAA were shown.

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