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Radiation grafting of vinyl ether of monoethanolamine on polypropylene films for application in waste water treatment†

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The radiation-chemical grafting of the vinyl ether of monoethanolamine as a cationic monomer on polypropylene films has been studied. Water uptake and degree of grafting were determined gravimetrically and using FTIR methods. The dependence of the grafting process on water and hexane addition to the monomer mixture has been investigated. The prepared graft copolymers of different grafting degrees and with cationic character were investigated for their properties in removing heavy toxic metals, such as Pb^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+} and Ag^{+}, from waste water. The kinetics of the sorption/desorption process for Cu^{2+}, Ni^{2+} and Co^{2+}, and factors affecting the metals treatment process, like the pH of the metal solution and the degree of grafting, have been studied.

Introduction

Radiation-induced graft polymerization is one of the best methods for obtaining materials with new properties. Radiation grafting of various monomers on plastic films can successfully solve the problem of preparation of polyfunctional sorbents and membranes.[1–3] The obtained materials are convenient for waste water treatment applications, since they are able to absorb various impurities very fast due to their chelation and/or complexation abilities through their reactive groups, such as carboxylic acid, amine, amide, nitrile, oxime groups, *etc.* In addition, these materials can be reused without lose of their sorption characteristics.[1]

One of the advantages of the radiation grafting technique is the possibility of polymerization of monomers which cannot be polymerized using a substantial initiation and, accordingly, introduction of such functional groups in the polymeric materials. The vinyl ether of monoethanolamine (VEMEA) is one of the monomers which can be polymerized to form high molecular weight polymers using radiation initiation.[4] Polymers of VEMEA can be used as anion-exchange resins, complexing agents, sorbents, floatation reagents, flocculants, *etc.*[5,6]

In our previous work[7] we have studied the preparation of polyethylene (PE) films grafted with the vinyl ether of monoethanolamine (VEMEA) using a gamma-irradiation technique. The obtained materials demonstrated high affinity in respect to Cu^{2+} ions. However, the grafting degree of VEMEA on PE was relatively low (up to 19%, even at very high absorbed doses). In the present work, we have attempted to prepare better materials by grafting of VEMEA on polypropylene (PP) films. The influence of grafting conditions, such as variation of monomer concentration by addition of water or hexane, was determined. On the other hand, the swelling behavior of graft copolymers was investigated and also the possibility of their practical uses in waste water treatment for removal, separation and purification of metal ions such as Pb^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Ag^{+}, *etc.* The effect of pH of the waste feed solution and the grafting degree of films on the treatment process has been studied.

Experimental

Materials

VEMEA used in the present work was a commercial product of Alash Ltd. (Temirtau, Kazakhstan). It was dried in the presence of dry K_2CO_3 and purified by double distillation under an argon atmosphere by the methodology described in ref. 4 Polypropylene film classified as "for food packaging", obtained from Munai Plastik Ltd. (Kazakhstan), was used in this study. Before each experiment, the samples were washed with acetone.

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

Methods and techniques

Radiation grafting copolymerization. The grafting was performed in sealed glass ampoules with PP films immersed in monomer saturated by argon using an MRX-γ-25 M setup equipped with a ^{60}Co source giving a dose rate of 0.3 Gy s^{-1}. The dose rate was determined by a Fricke dosimeter.

The grafted films were removed and washed thoroughly with distilled water and then soaked in distilled water for 1 day in order to remove unreacted monomer. The removal of impurities from the grafted films was checked by ascertaining whether the sample had reached a constant weight after one day of immersion. The covalent grafting was also confirmed by testing for a constant weight, even after boiling the films in water for several hours. The grafted films were dried in a vacuum oven at 40 °C for 2 h, and then weighed.

The grafting degree (GD) was determined by calculating the

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†Electronic supplementary information (ESI) available: figures showing the dependence of the extent of grafting and water uptake on hexane content in the feed mixture at different absorbed doses. See http://www.rsc.org/suppdata/jm/b2/b202689a/

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percentage increase in weight using eqn. 1

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

where m_0 and m_{graft} are the weights of the films before and after grafting, respectively.

Swelling measurements. Cleaned, dried and weighed films were immersed in distilled water at 25 °C for 1 day and then removed, blotted quickly with absorbent paper and weighed. The water uptake (α) was determined gravimetrically from eqn. 2

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

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

Metal ion uptake measurements

In experiments with metal uptake, samples of the grafted films of known weight were soaked into 0.01 M aqueous solutions of metal for 1 day until equilibrium was reached. The films were removed, dried in vacuum and then weighed. The metal uptake, expressed in mmol g^{-1} was determined by measuring the increase in weight of the samples.

The kinetics of the sorption/desorption processes of Cu^{2+}, Ni^{2+} and Co^{2+} ions were studied by photometric measurements at the wavelengths 240, 237 and 243 nm, respectively, using a Shimadzu UV2401PC spectrophotometer.

The FTIR spectra of the films were recorded with a Mattson FTIR-Satellite spectrophotometer.

Results and discussion

Radiation grafting of monoethanolamine on polypropylene films

In our previous study[7] we could not achieve the high grafting degree of VEMEA on polyethylene. For this reason, we selected polypropylene as a new substrate for grafting because its structure may afford a higher reactivity with respect to irradiation.

The low reactivity of VEMEA in polymerization reactions requires considerable absorbed doses to prepare polymers. Polypropylene films were immersed in VEMEA and irradiated over a wide range of absorbed doses. The grafting degree of VEMEA on PP as a function of absorbed dose is summarized in Table 1. An increase of the grafting degree is observed in the whole range 54–432 kGy. The grafting of VEMEA species onto PP films causes an increase in water uptake by the prepared material because of the hydrophilization of its surface (Table 1). It can be seen that, unlike active monomers (*e.g.* acrylic acid[1]), the grafting of VEMEA requires considerable absorbed doses, and even under these conditions, the grafting degree values are comparatively low. Besides, the grafting process is not very effective and is always accompanied by formation of PVEMEA homopolymer.

Table 1 Dependence of grafting degree and water uptake[a] of grafted films on absorbed dose

Absorbed dose/kGy	Grafting degree (%)	Water uptake/g g^{-1}
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

[a] Water uptake is measured in g water per g PP + VEMEA.

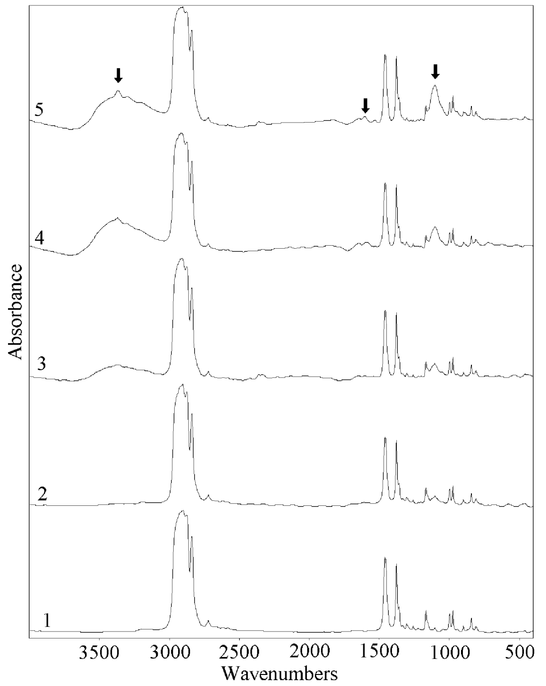


Fig. 1 FTIR spectra of pure polypropylene film (1) and grafted films with grafting degrees of 4.41 (2), 8.13 (3), 18 (4), 25.7% (5).

In order to characterize the obtained materials, as well as to confirm the grafting, we have recorded the FTIR spectra of the films (Fig. 1). In the spectrum of the starting polypropylene, the most intense bands appear at 2902, 2879, 2840, 1459, 2376, 1166, 997, 971 and 884 cm^{-1}, resulting from the valent and deformation vibrations of the CH, CH_2 and CH_3 groups. New bands at 1103 cm^{-1}, a vibration characteristic of VEMEA ether groups, 1602–1646, 3301 and 3301 cm^{-1}, due to deformation and valent vibrations of VEMEA primary amino groups, appear in the spectra of grafted films. The presence of these new bands in the spectra confirms that the grafting process has taken place. Moreover, increasing the absorbed dose leads to an increase in the intensity of these bands.

It is well known that additives affecting the swelling of the substrate film can allow more effective grafting of the monomers.[8] We have checked the effect of hexane addition on the grafting degree as well as on water uptake by the prepared material (see ESI). The addition of small amounts of hexane (up to 5 vol.%) increases slightly the grafting degree and water uptake values, but further addition leads to lowering of these values, which is probably connected to dilution of the monomer.

Previously,[7] we found that the addition of water to the monomer mixture enhances the grafting of VEMEA on PE. The effect of water addition on the grafting degree and water uptake of the grafted PP films is shown in Fig. 2(a) and (b), respectively. A considerable increase in these parameters is observed upon addition of 10 vol.% of water. Thus, films with a grafting degree of more than 90% can be obtained, and they show water uptake of up to 11 g per gram of dry polymer. Actually, this very high grafting degree corresponds to the formation of a thin gel layer on the surface of the polymeric material.

Sorption of transition metals by grafted films

Polymer–metal ion complexation is an attractive approach for preparation of functional sorbents for waste water treatment. The presence of electron-donating primary amino and ether groups in VEMEA gives its polymers the ability to form

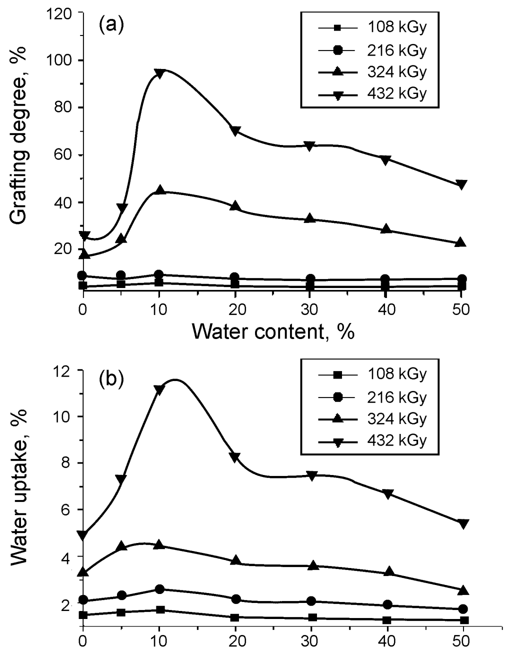
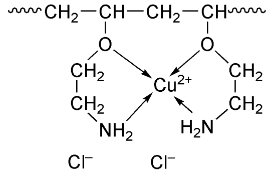


Fig. 2 Dependence of the grafting degree (a) and water uptake (b) on water content in the feed mixture at different absorbed doses.



Scheme 1

polycomplexes with Cu^{2+} ions, according to Scheme 1:[9] We have studied the ability of the grafted films to absorb various heavy metals in order to evaluate the possibility of their use in waste water treatment. A diagram showing the capacity of the grafted films for metal uptake is shown in Fig. 3. It can be seen that the films with a higher grafting degree are characterized by a considerably greater binding ability with respect to heavy metals. The nature of the metal ion also has great importance in the amount binding to the polymeric material. The affinity of metal ions to VEMEA decreases in the following series: $Cu^{2+} > Zn^{2+} > Ni^{2+} > Fe^{3+} > Co^{2+} > Ag^{+} > Cd^{2+} > Pb^{2+}$.

A similar trend was observed for binding of Zn^{2+}, Co^{2+}, Cd^{2+} and Hg^{2+} to gelatin,[10] and is in accordance with Pearson's principle,[10,11] that is, soft acids prefer to bind soft bases and hard bases prefer to bind hard bases.

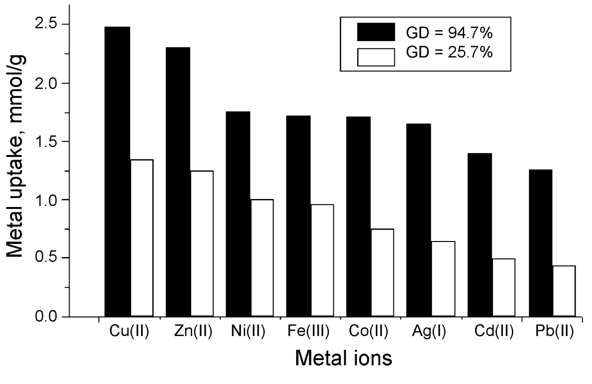


Fig. 3 Sorption of different metals by the grafted films.

Thus, the maximum metal uptake is very dependent on the type of metal ion and its coordination, as well as the ionic size of the metal, all of 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 ion with the lowest ionic radius, Cu^{2+}, showed the highest metal uptake.[12]

The possibility of using the obtained materials repeatedly was evaluated over several sorption–desorption cycles. The kinetics of sorption/desorption of metal ions could not be followed by gravimetric studies because that requires removal and drying of the samples periodically, which affects the accuracy of the results. Thus, a spectrophotometric technique was applied. With this technique it is easy to determine the desorbed/absorbed amounts of metal ions without removing and drying the samples. As the grafted film is immersed into a metal salt solution, it starts to absorb metal ions, therefore, the concentration of metal ions in solution decreases with the sorption process and this decrease was monitored using a spectrophotometer. The metal sorption increases with time and reaches a maximum after about 2 h (Fig. 4), when the chelating sites of the film are saturated. The maximum amount of absorbed metal salt, which was determined spectrophotometricaly and expressed in mmol g^{-1}, coincides well with the metal uptake obtained by the gravimetric technique.

The recovery and separation of absorbed metals can be easily carried out by treating the films with 0.01 M HCl for 1 h. Fig. 5 shows the kinetics of the desorption process for Cu^{2+}, Ni^{2+} and Co^{2+} ions. The desorbed metal ion concentration increases in HCl solution with time and then reaches a maximum when the desorption process is complete. The regenerated films are once again effective for resorption of

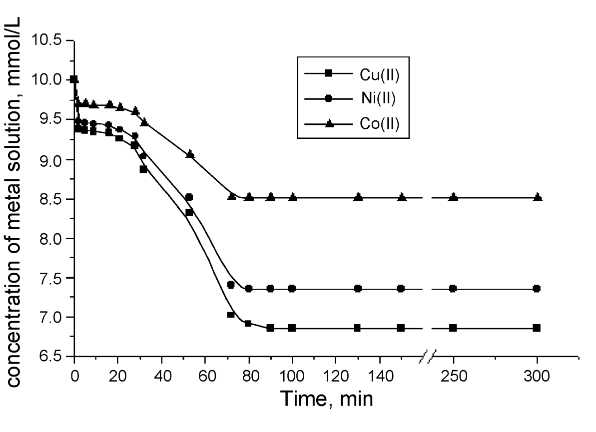


Fig. 4 Kinetics of the sorption process for Cu^{2+}, Ni^{2+} and Co^{2+} ions by the grafted films (GD = 94.7%).

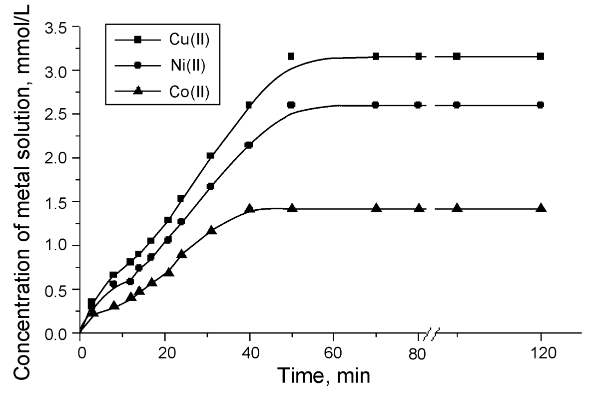


Fig. 5 Kinetics of desorption process for Cu^{2+}, Ni^{2+} and Co^{2+} ions by the grafted films (GD = 94.7%).

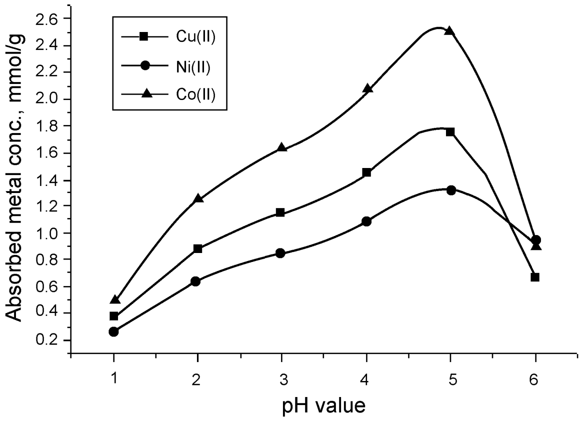


Fig. 6 Dependence of metal sorption by the grafted films on pH (GD = 94.7%).

metal ions with the same efficiency, as checked for our films over 5 cycles.

Studies on the effect of pH on the sorption characteristics of the grafted films were carried out *via* metal uptake measurements over a pH range from 1 to 6 (Fig. 6). It was found that the metal sorption process increases with increasing pH for Cu^{2+}, Ni^{2+} and Co^{2+}, reaching a maximum at pH = 5, then decreases. In acidic solutions, the metal uptake decreases due to competition with the 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 maximum sorption.

Conclusions

Novel polymeric materials were prepared by radiation grafting of the cationic monomer of vinyl ether of monoethanolamine on the suface of polypropylene. The grafting degree and water uptake of the films are functions of absorbed dose. The addition of water to the feed mixture up to 10% increases the grafting degree and water uptake, as does the addition of 5% hexane. The prepared graft copolymers showed a good affinity towards chelation and/or complexation with different metals investigated here (Pb^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Ag^{+}). Maximum sorption for Cu^{2+}, Ni^{2+} and Co^{2+} is achieved after a treatment time of 2 h in a feed solution of pH 5. Treating the saturated films with 0.01 M HCl at room temperature for 1 h allows easy recovery of the absorbed metals and, accordingly, the films can be reused for the resorption of metal ions.

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