Novel Hydrogels Based on Itaconic Acid and Citraconic Acid: Synthesis, Metal Ion Binding, and Swelling Behavior

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ABSTRACT: Several copolymer hydrogels were prepared from radical copolymerization of 2-hydroxypropyl methacrylate (HPMA) with itaconic acid (IA) and also with citraconic acid (CA) by using different feed ratios. The copolymers were characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy as well as by thermal analysis. The swelling process of the different hydrogels immersed in water at different pH has been studied, and also the swelling of the hydrogels loaded with metal ions (Pb^{2+}, Cd^{2+}) was investigated. The metal-binding properties were studied by using the liquid-phase polymer-based retention technique, including studies on the influence of pH on the binding process. The efficiency of these hydrogels for the recovery of metal ions in solution was determined by atomic absorption spectroscopic analysis. The thermal characteristics of these copolymers were studied by using differential scanning calorimetry and thermogravimetric analysis in nitrogen atmosphere. Accordingly, the gels loaded with metal ions showed a slight increase of the thermal decomposition temperature when compared with the pristine gels. The copolymer gel HPMA-co-CA showed a single glass transition temperature, whereas for the copolymer systems, HPMA-co-IA, only the copolymers loaded with Cd^{2+} ions showed a glass transition temperature. The morphology of film produced from the copolymers was investigated by scanning electron microscopy, revealing generally smooth surfaces. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 104–111, 2009

Key words: hydrogels; metal ions; swelling behavior; retention capacity; metal–polymer complexes; thermal behavior

INTRODUCTION

Hydrogels have received increasing attention in the last decade because of their significance and applications in areas such as drug delivery, immobilization of enzymes, solute separations, baby diapers, soil for horticulture and agriculture, adsorbent pads, etc.[1–14] Other applications include the recovery of precious metals and metal preconcentration for environmental analysis.[15] The removal of heavy metal ions from industrial wastewater has been given much more attention in the last decade, as heavy metals released into the environment are the environmental pollutants agents most common and difficult to treat, because of their tendency to accumulate in living organisms.[16] The necessity to reduce the amount of heavy metal ions in wastewater streams has led to an increasing interest in selective absorbents polymers or copolymers. Metal-coordinating resins have also been extensively studied.[17–21] Because of the lipophilic character of neutral coordinating resins, the water–resin contact is often weak, thus limiting the accessibility of the ligands and the extraction rate.[22] The water absorption in the hydrophilic polymer network warrants an excellent accessibility of the metal-coordinating moieties, but the swelling variations of the hydrogel as a function of pH and ionic strength must be considered.[23]

This work reports the synthesis of suitable materials for this purpose based on novel copolymers. Thus, hydrogels prepared from copolymers of 2-hydroxypropyl methacrylate (HMPA) with itaconic acid (IA) and with citraconic acid (CA) have been synthesized, and the effect of pH on the swelling behavior and the binding of different heavy metal ions has been studied.

EXPERIMENTAL

Reagents

HPMA (Merck-Schuchardt, Germany), IA (Merck-Schuchardt), and CA (Aldrich CHEMIE, Germany), all analytically pure grade, were used as the monomers. Benzoyl peroxide (BPO; Aldrich CHEMIE)

and ammonium peroxodisulfate (Merck-Schuchardt) were used as the initiators. All chemicals were used as received without further purification. N,N-Methylenebisacrylamide (MBA) (Merck-Schuchardt) was used as the crosslinking agent.

Syntheses of the copolymers

The copolymerizations for HPMA/IA and HPMA/CA were carried out with 1 : 1 feed monomer ratio in solution using 0.5 mol % of BPO as the initiator and MBA (0.5 mol %) as crosslinking agent in dioxane at 70°C and ammonium peroxodisulfate as the initiator, in water at 70°C for 2 h, respectively. The general procedure was as follows: 8 mL of solvent was transferred to septum-copped, nitrogen-purged flasks containing 23 mmol of HPMA, 0.5 mmol % of the initiator, 0.5 mmol % MBA, and 23 mmol of comonomer (IA or CA). The ampoule was degassed with freeze cycles and sealed under high vacuum, and then the copolymerization was carried out. The product was filtered off, washed with diethyl ether, cut into cylinders, and dried *in vacuo* up to a constant mass.

The copolymer composition was not determined by elemental analysis, because both monomer units contain hydrogen and carbon atoms. Therefore, it was estimated from the amount of both monomers by assuming a complete reaction, since the yield was high (nearly 100%).

Swelling studies

The studies were carried out at 25°C in buffered solutions; either with $0.01M$ citrate buffer (pH < 7) or phosphate buffer (pH $\geq$ 7). The dried samples of the copolymers were placed in a solution of the defined pH (3, 7, and 10) at 25°C. Every hour, the sample was removed quickly from the solution. The swelling values (S_w) were calculated using the following equation:

$$S_W(\%) = \frac{(W_s - W_d)}{W_d} \times 100$$

where W_s is the weight of the swollen hydrogel at an equilibrium state, and W_d is the weight of the dried hydrogel (Xerogel).

Metal ion absorption studies

The absorption studies for the hydrogels were carried out by placing about 0.5 g of the gel into 20 mL of defined concentration (40 mg L^{-1}) of metal ion solution (Cd^{2+} and Pb^{2+}) and leaving the solution under stirring. After the equilibrium was reached, the liquid-phase polymer-based retention (LPR)

method[24–31] was used to study the retention of metal ions by the hydrogel. Although the MBA-crosslinked poly(HPMA-co-IA) and poly(HPMA-co-AC) were essentially insoluble in water, the retention of metal ions was performed in the aqueous suspension mode, thus allowing the separation of the polymer from the metal ions by continuously washing using the LPR method. This technique uses ultrafiltration membrane to separate low-molecular-mass species such as the free ions from high-molecular-mass compounds such as the polymer–metal complexes. It is assumed that the main separation mechanism is the size exclusion by the ultrafiltration membrane (membranes with a molecular mass exclusion limit of 10,000 g mol^{-1} were used). The metal ion concentration in the retentate was determined by atomic absorption spectroscopy.

Thermal analysis

The thermal analysis of the copolymers was carried out by differential scanning calorimetry (DSC) in a nitrogen atmosphere (flow rate: 150 and 50 cm^3 min^{-1}, respectively), with a Perkin Elmer TGS-1 and Mettler Toledo 822e analyzer. A dry sample size of 3–4 $\pm$ 0.1 mg was used in each experiment.

Measurement

FTIR spectra were recorded on a Bruker Vector 22 (Bruker Optics GmbH, Ettlingen, Germany). The ^{1}H-NMR and ^{13}C-NMR spectra were recorded in solution at room temperature with a Bruker AC 400 (Bruker, Karlsruhe, Germany) spectrometer using deuterated dimethylsulfoxide (DMSO-d_6, 99.8%).

The copolymer morphology was characterized by scanning electron microscopy (SEM). SEM imaging was performed with samples dried under vacuum at 105°C for 24 h by using a SEM (Jeol, GSM-6380LV).

RESULTS AND DISCUSSION

Synthesis and characterization

The radical copolymerizations of HPMA with IA and CA were performed in dioxane and water using several feed monomer compositions. The resulting copolymers were insoluble in solvents such as water, chloroform, ethanol, methanol, pyridine, acetone, and tetrahydrofuran. Reaction conditions and the copolymers yields are shown in Table I. Accordingly, the copolymer HPMA-co-IA reached the highest yield.

The ^{1}H-NMR spectrum (DMSO-d_6) of poly(HPMA-co-IA) exhibits the following signals at δ (in ppm); 0.5–1.6 (—CH$_3$, from HPMA); 1.7–2.2 (—CH$_3$, from the side chain of HPMA); 2.4–2.7 (—CH$_2$, from

TABLE I
Experimental Data for the Radical Copolymerization of 2-Hydroxypropyl Methacrylate (HPMA) with Itaconic Acid (IA) and Citraconic Acid (CA), and MBA (0.5 mol %) at 70°C and 2 h

HPMA mmol (mL)	IA[a]/CA[b] mmol (g)	Molar ratio	Solvent (mL)	Time (h)	Yield (%)
23 (3.22)	23 (2.99)[a]	1 : 1	Dioxane 8	2	92
23 (3.22)	23 (2.99)[b]	1 : 1	Water 8	2	89

[a] In dioxane.
[b] In water.

the backbone of HPMA); 3.1–4.3 (—CH, —CH$_2$ from the side chain of HPMA and —CH$_2$, from the side chain of IA, respectively); 4.3–5.4 (—OH from HPMA) (see Fig. 1).

The ^{13}C-NMR spectrum (in DMSO-d_6, in the gel state) of poly(HPMA-*co*-IA) shows the following signals at δ (in ppm): between 18 and 22 (—CH$_3$, methyl carbon groups of HPMA; —CH$_3$ from the side chain and —CH$_2$ from the backbone of HPMA); 35–45 (—CH$_2$— from the backbone of IA and HPMA, respectively); 65–70 (—CH$_2$—CH— from the side chain of HPMA); 165–175 (—C=O) from HPMA and IA (see Fig. 1).

The ^{1}H-NMR spectra in DMSO-d_6 in the gel state of poly(HPMA-*co*-CA): The system shows the following signals at δ (in ppm): 0.4–1.6 (—CH$_3$, from HPMA and CA); 1.7–2.3 (—CH$_3$, from the side chain of HPMA); 2.3–2.7 (—CH$_2$, from the backbone of HPMA); 3.1–4.2 (—CH, from the backbone of CA and —CH, —CH$_2$ from the side chain of HPMA, respectively); 4.7–5.2 (—OH from HPMA) (see Fig. 2).

The ^{13}C-NMR spectrum (in DMSO-d_6 in the gel state) of poly(HPMA-*co*-CA) shows the following signals at δ (in ppm): between 18 and 22 (—CH$_3$, methyl carbon groups of HPMA and CA; —CH$_3$ from the side chain and —CH$_2$ from the backbone of HPMA); 45 (—CH— from the backbone of CA); 65–70 (—CH$_2$—CH— from the side chain of HPMA); 175–180 (—C=O) from HPMA and CA (see Fig. 2).

FTIR spectroscopic studies

The FTIR spectra of both unloaded gels showed the following signals: the absence of the absorption band at 1640 cm^{-1}, characteristic for the carbon–carbon double bond, in the two investigated materials
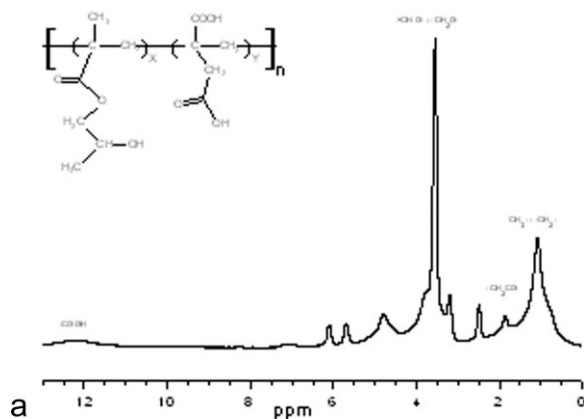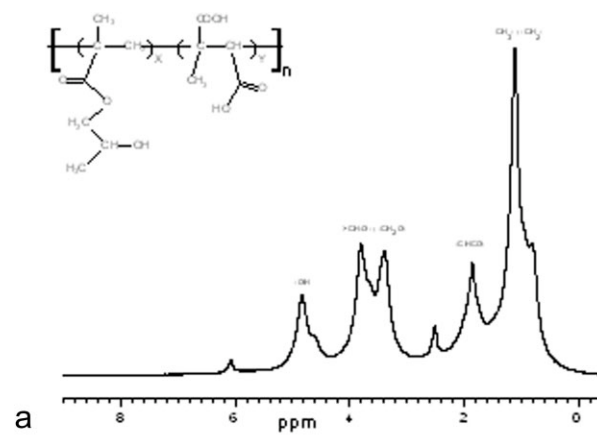

Figure 1 ^{1}H-NMR and ^{13}C-NMR spectra of poly(HPMA-*co*-IA) (400 MHz and 69.2 MHz, respectively, in DMSO-d_6; room temperature in gel state).

Figure 2 ^{1}H-NMR and ^{13}C-NMR spectra (in gel state) of poly(HPMA-*co*-CA) (400 MHz and 69.2 MHz, respectively, in DMSO-d_6; room temperature in gel state).

clearly indicates that a copolymer was formed in both cases. The absorption band at 1726.3 shows the carbonyl group stretching vibration of the HPMA-IA copolymer. The absorption band at 1782.2 cm^{-1} indicates the carbonyl group stretching vibration of the HPMA-CA copolymer. On the other hand, the bands that appear at 3439.1 and 3436.2 cm^{-1} are assigned to the OH stretching of the carboxylic groups of IA and CA, respectively. The bands ranging from 2982.9 to -2981.0 cm^{-1} in both FTIR spectra indicate the aliphatic C—H stretching vibration.

Swelling studies in pure water: Influence of the pH

The swelling behavior of poly(HPMA-co-IA) and poly(HPMA-co-CA) was investigated as a function of pH by immersion of the gels in buffered solutions at pH = 3, 7, and 10 at room temperature (25°C). Figure 3(a,b) shows the swelling behavior of the copolymers poly(HPMA-co-IA) and poly(HPMA-co-CA) after different swelling times. The swelling of
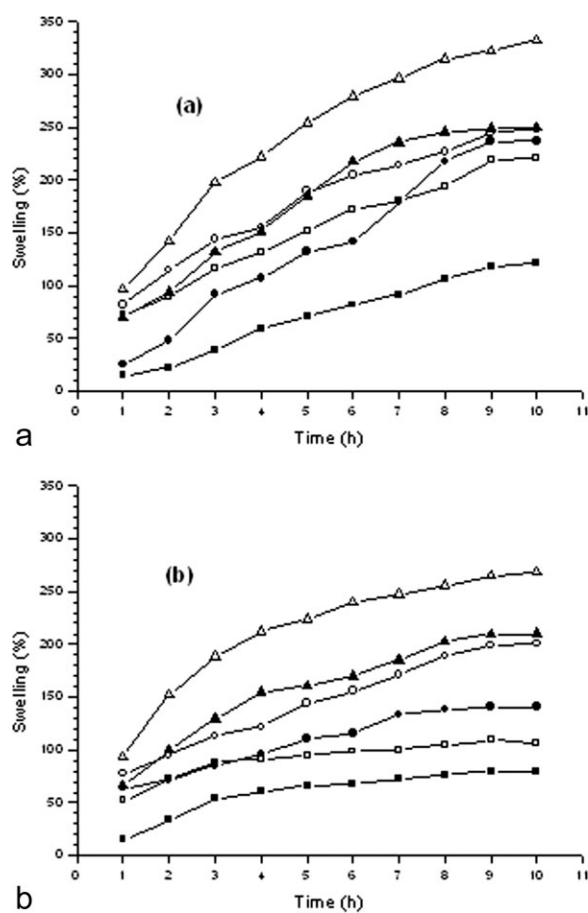

a

b

Figure 3 Swelling isotherms of (a) poly(HPMA-co-IA) and (b) poly(HPMA-co-CA) in water (□, pH = 3; ○, pH = 7; Δ, pH = 10) and metal ion solution (□, pH = 3; ●, pH = 7; ▲, pH = 10) as a function of pH (buffered solutions, at 25°C, period of 10 h).

the hydrogels increased at the pH range of 7–10, where the maximum swelling could be observed. This could be attributed to the complete dissociation of the acid groups of IA and CA at this pH range. The first and second dissociation constants of IA were $pKa_1 = 3.85$ and $pKa_2 = 5.44$, and for CA, $pKa_1 = 2.29$ and $pKa_2 = 6.15$.[32] Therefore, the behavior observed is the consequence of the ionizable groups of the polymer, which enhances the repulsive forces of the carboxylic groups with the neighboring chains. Moreover, the swelling increased with time; however, after some time, it leveled off. This value of swelling may be named as the equilibrium swelling percentage.

Swelling and metal ion binding studies

The effect of metal ions present in the solution on the equilibrium swelling degree of HPMA-IA and HPMA-CA copolymers was investigated at 25°C. The results are given in Figure 4(a,b). The hydrogels were immersed in solutions of the metal ions (Cd^{2+} and Pb^{2+}) at a defined concentration (40 mg L^{-1}). The pH of the solution was adjusted to pH = 3, 7, and 10 to study the effect of the metal ions. As shown in Figure 4(a,b), when the solution is loaded with the metal ions, the equilibrium swelling degree values show a decrease in all cases.

The osmotic swelling pressure of the mobile ions inside the poly(HPMA-co-IA) and poly(HPMA-co-CA) hydrogels having carboxylic groups fixed in the hydrogel network is decreasing, so that they can substantially act like weak acid-type cation exchange polymers. When immersed in electrolyte solutions, the ion exchange takes place during the swelling process, having a considerable effect on the water absorption.[33]

Because of the high content of carboxyl groups per repeat unit of IA and CA, the observed metal ion binding capacity is a result of the higher number of ionizable groups on both copolymers. Hereby, the metal ions binding is in agreement with the exchange between the metal ion in the external solution and the hydrogen ions from the carboxylic groups in the copolymer chains.

The metal ion binding capacity was determined at different pH (see Table II) and it is pH-dependent in agreement with the carboxylic proton–metal ion exchange process. At pH = 3.0, the metal ion uptake is very low due to the small ionization degree. Increasing the pH (= 7 and 10), increases the ionization of the carboxylic groups of the comonomers, and the high values of the metal ion uptake are reached. The highest retention values (higher than 94%) were obtained at pH = 10 for both.

The metal ion retention results for both copolymers show that the IA and CA comonomer units
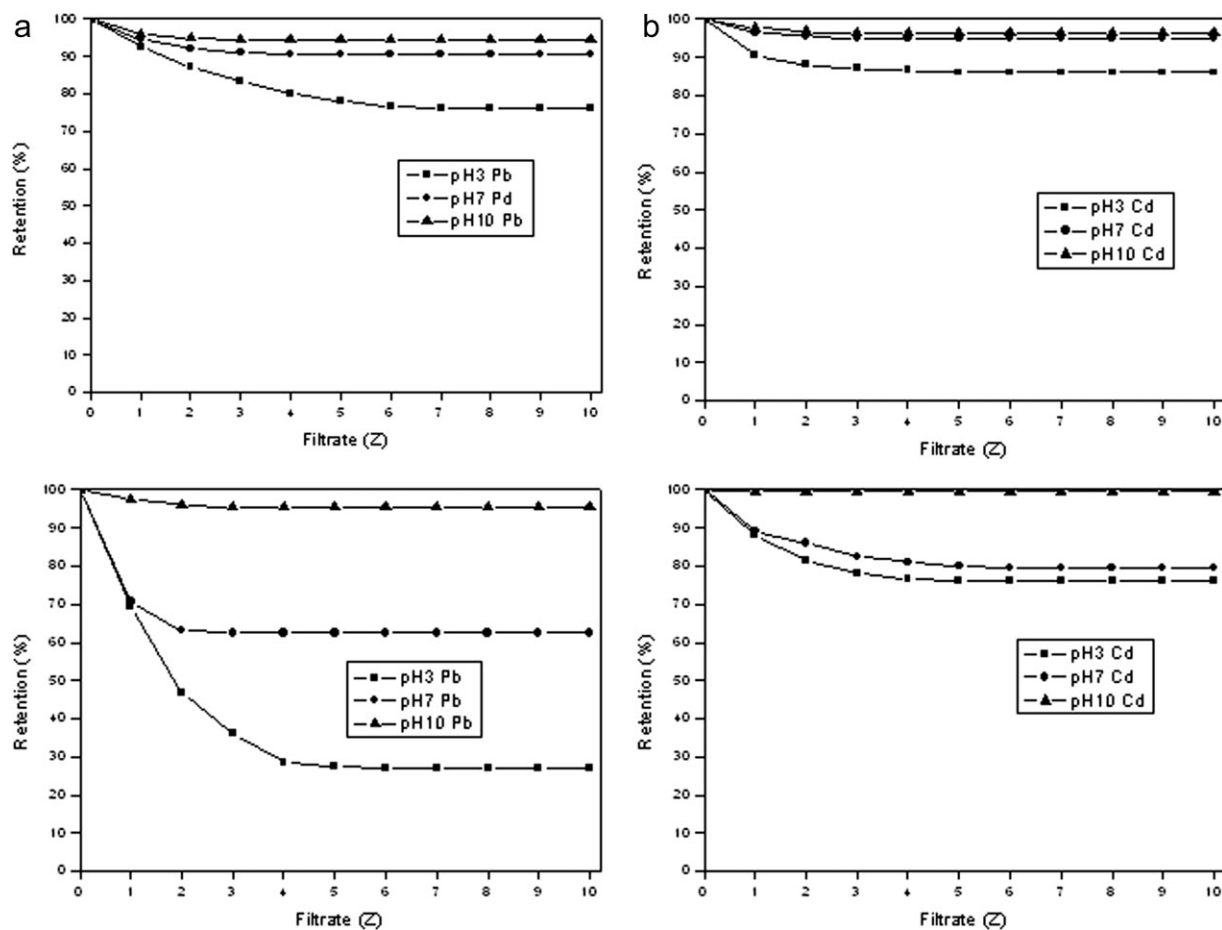
Figure 4 Metal ion retention profiles of poly(HPMA-*co*-IA) and poly(HPMA-*co*-CA), respectively: (a) Pb^{2+}; b) Cd^{2+}, respectively, as a function of pH ($\square$, pH = 3; $\bullet$, pH = 7; $\blacktriangle$, pH = 10) (buffered metal ion solution, at 25°C).

possess approximately the same affinity toward the metal ions. The retention behavior can be attributed to the fact that both polymers have two ionizable carboxylic-functional groups per repeat unit. These can exhibit strong metal ion binding attraction forces, similar to ionic polymers or polyelectrolytes, which also depend on the pH.

Thermal behavior

The TG results for poly(HPMA-*co*-IA) and poly (HPMA-*co*-CA) are summarized in Table III. The copolymers from both systems presented two-step degradation, after first eliminating water or mono-mer residue as well as other low-molecular-weight impurities (see Fig. 5). For the poly(HPMA-*co*-IA), the resulting material had two extrapolated thermal decomposition temperatures with TDT_1 at 159.2°C and TDT_2 at 347.5°C. The poly(HPMA-*co*-IA) copoly-mer–metal ion complexes with Cd(II) and Pb(II) show a slight increase of the TDT and higher mass loss values than the respective copolymer gels. This

could be attributed to the interaction or bonding between the polymer ligands and the metal ion.

The poly(HPMA-*co*-CA) exhibited a two-step deg-radation with TDT_1 at 154.3°C and TDT_2 at 345.3°C, respectively. The TDT of the copolymer–metal com-plexes were also higher than for the copolymers, exceptionally for the poly(HPMA-*co*-CA) metal complex Pb/Cd(II) at pH 7. The thermal stability of poly(HPMA-*co*-CA)-Cd(II) complexes was higher (TDT_1 = 315.0°C) than for the polymer-Pb(II) (TDT_1 = 261.5°C) complexes. The greatest weight

TABLE II
Metal Ion Retention Capacity for Poly(HPMA-*co*-IA) and Poly(HPMA-*co*-CA) at pH = 3, 7, and 10

Copolymer–metal ion complex	pH	Metal ion retention (%)	
		Cd(II)	Pb(II)
Poly(HPMA-*co*-IA)	3	86.0	76.0
	7	95.0	90.5
	10	96.5	94.5
Poly(HPMA-*co*-CA)	3	76.0	27.0
	7	79.5	62.5
	10	99.5	95.5

TABLE III
Thermal Decomposition Temperatures and Mass Loss (%) at Different Temperatures and Copolymer–Metal Ion Complexes at pH = 10

	TDTe	100°	200°	300°	400°	500°	550°
Poly(HPMA-co-IA)	159.2	3.4	19.2	33.1	68.8	94.2	94.6
	347.5						
Poly(HPMA-co-IA)-Pb	348.8	0.4	2.9	11.3	73.3	92.4	93.0
Poly(HPMA-co-IA)-Cd	309.1	4.4	10.6	26.6	59.9	75.3	76.5
Poly(HPMA-co-CA)	154.3	1.4	15.4	32.9	64.3	83.4	84.6
	345.3						
Poly(HPMA-co-CA)-Pb	261.5	1.6	9.8	25.3	54.0	74.0	75.5
Poly(HPMA-co-CA)-Cd	315.0	4.3	14.9	27.3	61.5	80.2	81.1

loss for the copolymer and the complexes occurs between 300 and 400°C (see Table III). At pH 3, 5, and 7, the complexes' higher residual mass percentage may be attributed to the percentage of metal incorporated at this pH. The incorporation of the copolymer of IA monomer decreased the TDTe values in the copolymers in comparison with P(HPMA-co-CA) probably due to the hydrogen binding interaction that could be forming an unstable polymer–metal complex.

The thermal stability of polymer–metal complexes is known to be affected primarily by the nature of the polymer and microenvironmental conditions such as additional coordination bonds. According to the literature, the thermal stability of functional polymers with metals will generally be enhanced. When the polymer interacts with metal ions, the thermal energy supplied to the polymer–metal complex may result in a catalytic role of metal ion to the thermal decomposition of the polymer–metal complex.[34]

Glass transition temperature (T_g)

The T_g was estimated from the second DSC run with a heating rate of 10°C min^{-1}. DSC thermograms of poly(HPMA-co-IA) ($T_g = 170$°C) and poly(HPMA-co-CA) ($T_g = 185$°C) and its metal complexes at pH 7
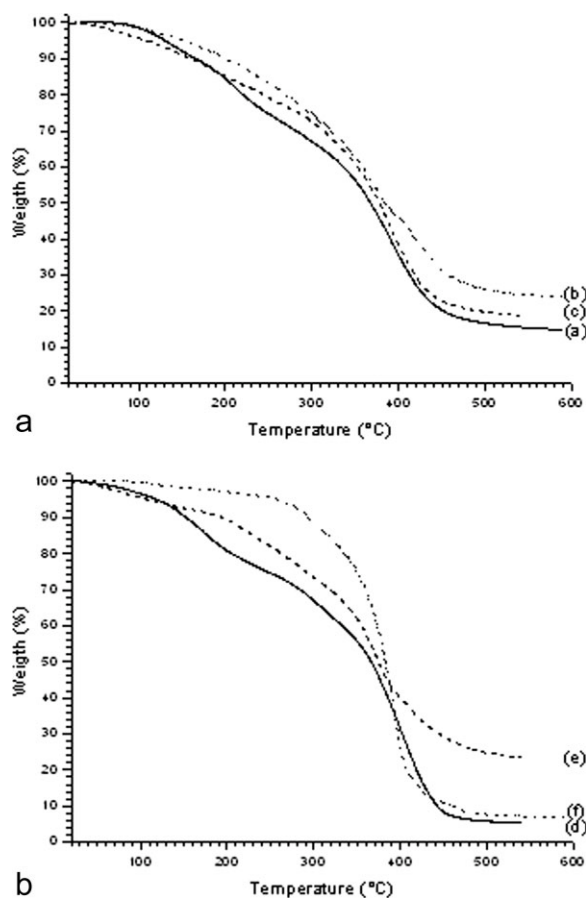
Figure 5 Thermograms of (a) poly(HPMA-co-IA) and its (b) Pb^{2+} complex and (c) Cd^{2+} complex at pH = 10; (d) poly(HPMA-co-CA) and its (e) Pb^{2+} complex and (f) Cd^{2+} complex at pH = 10.
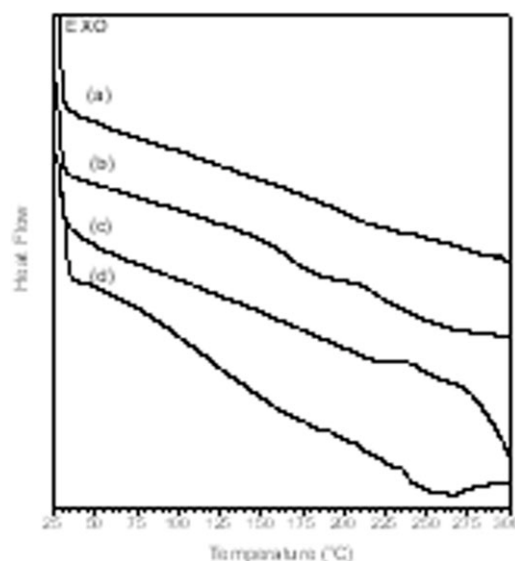
Figure 6 DSC thermograms of (a) poly(HPMA-co-IA) and (b) its Cd^{2+} complex at pH = 10; (c) poly(HPMA-co-CA) and (d) its Cd^{2+} complex at pH = 10.
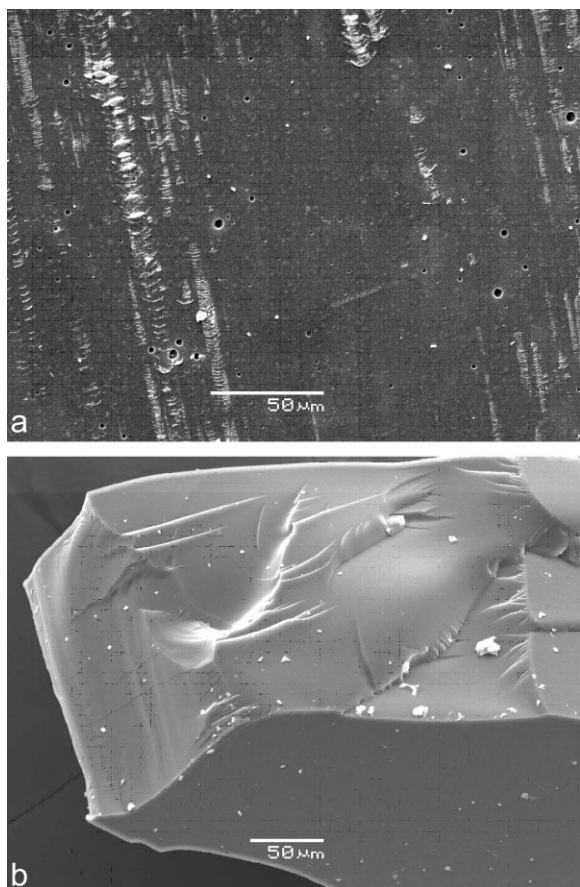
Figure 7 SEM micrographs of films of the (a) hydrogels and (b) poly(HPMA-*co*-CA) showing smooth surfaces of the films.

are illustrated in Figure 6. The synthesized copolymers presented a single T_g, indicating the formation of random copolymers. The T_g for poly(HPMA-*co*-IA) and poly(HPMA-*co*-CA) decreases as the pH increased in the presence of the metal ions Pb(II) and Cd(II). The main explication can be attributed to a consequence of a lower percentage of intramolecular crosslinking reaction. In the range of pH 3–7, the T_g of the poly(HPMA-*co*-IA)-Cd^{2+} complexes varied from 165 to 150°C, and for the poly(HPMA-*co*-CA)-Cd^{2+} complexes, from 178.8 to 171.5°C, respectively.

Scanning electron microscopy

The typical microphotographs from SEM of the poly(HPMA-*co*-IA) and poly(HPMA-*co*-CA) samples are shown in Figures 7(a,b). The SEM microphotographs in Figure 7(a,b) show that the top surfaces of the samples were generally smooth.

CONCLUSIONS

Copolymer gels of poly(HPMA-*co*-IA) and poly (HPMA-*co*-CA) were prepared by radical copolymer-

ization. All obtained polymers were insoluble in water and in some common organic solvents.

The swelling characteristics of both copolymer gels showed an increase in the pH range of 7–10, where the swelling maximum was observed. Hydrogel swelling decreases when the gel is loaded by metal ions.

Metal absorption increases as the pH of external solution increased. The study showed that poly (HPMA-*co*-IA) and poly(HPMA-*co*-CA) could be used as metal absorbents (Cd^{2+}, Pb^{2+}) and are expected to be applicable to absorption of other ions.

The poly(HPMA-*co*-IA) and poly(HPMA-*co*-CA) showed a two-step degradation. Both copolymer–metal ion complexes with Cd(II) and Pb(II) showed a slight increase of TDT, but a exceptionally higher for the poly(HPMA-*co*-CA) metal complex Pb/Cd(II) at pH 7 and higher weight loss values than respective copolymer gels.

The microphotographs of the film's surfaces show that the top surfaces of the film were generally smooth.

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