

Preparation, Characterization, and Metal Ion Retention Capacity of Co(II) and Ni(II) from Poly(*p*-HO- and *p*-Cl-phenylmaleimide-*co*-2-hydroxypropylmethacrylate) Using the Ultra Filtration Technique

Guadalupe del C. Pizarro,¹ Oscar G. Marambio,¹ Manuel Jeria-Orell,¹ Diego P. Oyarzún,¹ Bernabé L. Rivas,² Wolf D. Habicher³

¹Department of Chemistry, Technological Metropolitan University, Santiago, Chile

²Polymer Department, Faculty of Chemistry, University of Concepción, Concepción, Chile

³Institute of Organic Chemistry, Dresden University of Technology, 01062 Dresden, Germany

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ABSTRACT: *p*-Chlorophenylmaleimide and *p*-hydroxyphenylmaleimide with 2-hydroxypropyl methacrylate were synthesized by radical polymerization, and the metal ion retention capacity and thermal behavior of the copolymers were evaluated. The copolymers were obtained by solution radical polymerization with a 0.50 : 0.50 feed monomer ratio. The maximum retention capacity (MRC) for the removal of two metal ions, Co(II) and Ni(II) in aqueous phase were determined using the liquid-phase polymer based retention technique. Inorganic ion interactions with the hydrophilic polymer were determined as a function of pH. The metal ion retention capacity does not depend strongly on the pH. Metal ion retention increased with an increase of pH for a copolymer composition 0.50 : 0.50. At different pH, the MRC of the poly(*p*-chlorophenylmaleimide-*co*-2-hydroxypropylmethacrylate) for Co(II) and Ni(II) ions varied from 44.1 to 48.6

mg/g and from 41.5 mg/g to 46.0 mg/g, respectively; while the MRC of poly(*p*-hydroxyphenylmaleimide-*co*-2-hydroxypropyl methacrylate) for Co(II) and Ni(II) ions varied from 28.4 to 35.6 mg/g and from 27.2 to 30.8 mg/g, respectively. The copolymers and copolymer–metal complexes were characterized by elemental analysis, FT-IR, ¹H NMR spectroscopy, and thermal behavior. The thermal behavior of the copolymer and polymer–metal complexes were studied using differential scanning calorimetry and thermogravimetry techniques under nitrogen atmosphere. The thermal decomposition temperature and T_g were influenced by the binding–metal ion on the copolymer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2448–2455, 2007

Key words: radical polymerization; hydrophilic polymer; metal–polymer complexes; thermal behavior

INTRODUCTION

Heavy metal removal using hydrophilic polymers with complexing groups could be of great importance in environmental applications.^{1–9} Maleimide polymers have good thermal stability,^{10–13} and these polymers are increasingly used in outdoor applications where environmental conditions influence their performance. There is a growing interest in the synthesis of new types of polymeric materials as well as in the modification of the polymers' primary structure and its applications.^{14,15} These include a fast complexation of metal ions as well as the reusability of the polychelators.¹⁶ We have recently published

the binding-Cu²⁺ properties for the systems poly(*N*-PhMI-*co*-βMHI)¹⁷ and poly(*N*-PhMI-*co*-AA),^{18,19} and the determination of the maximum retention capacity (MRC) at different pH indicated that the resins' metal complexing capacity depends not only on the ligand groups' nature but also on their accessibility to the metal ions.

The aim of the present article is to synthesize copolymers from Cl-phenylmaleimide (*p*-ClPhMI) and *p*-hydroxyphenylmaleimide (*p*-HO-PhMI) with HPMA by radical polymerization and to study the effect of the chloro- or hydroxyl-aryl group on metal ion retention capacity as well as their binding properties with Co²⁺ and Ni²⁺, using the liquid-phase polymer based retention (LPR) technique, and the effect of metal ion content on the thermal properties.

Poly(*p*-Cl-PhMI-*co*-HPMA) presents a higher MRC than poly(*p*-HO-PhMI-*co*-HPMA). This different result could support the assumption that the hydroxyl-aryl group could prevent the interaction with the metal ions due to steric hindrance and binding hydrogen between OH[−] groups in both monomer units, where it could form an unstable polymer–metal complex.

Correspondence to: G. C. Pizarro (gpizarro@utem.cl or gpizarro2@yahoo.com).

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Steric hindrance by Cl-PhMI units and its hydrophobic nature could limit the chelating reaction, although there is no interaction binding hydrogen as in the case of the HO-PhMI comonomer unit with HPMA.

EXPERIMENTAL

Materials

p-Cl- and *p*-HO-phenylmaleimide were synthesized from maleic anhydride and *p*-chloro or *p*-hydroxy aniline (Merck-Schuchardt, Darmstadt, Germany) in diethyl ether following the published procedure.²⁰ *p*-Chloro aniline (Merck-Schuchardt) was purified by distillation under reduced pressure, and *p*-hydroxyaniline was purified by crystallization. Cl-PhMI and OH-PhMI were purified by recrystallization from cyclohexane. The yield was 87%, m.p. 118–121°C; and 65%, m.p. 155–157°C, respectively.

Preparation of polymers

The copolymers were synthesized by free radical polymerization with a 0.50 : 0.50 feed monomer composition in solution using 0.5 mol % of benzoyl peroxide (BPO) as initiator. A typical procedure for the copolymerization reaction was as follows: the mixture of *p*-Chlorophenylmaleimide (*p*-Cl-PhMI)/*p*-HO-PhMI with HPMA (20 mmol) was dissolved in dioxane (7 mL) and BPO as initiator (57.8 μmol). A 2.86 M solution of monomers in dioxane was placed in a copolymerization flask under N₂ and was sealed in vacuum (10⁻³ mmHg), maintaining constant the total amount of comonomers for the different systems. The flask was kept in a controlled temperature oil bath at 70°C for 12 h. The mixture was poured in 50 mL of diethyl ether to precipitate the copolymer. The copolymer was separated by centrifugation, purified by precipitation, and then dried under vacuum until constant weight.

Measurements

FT-IR spectra were recorded on a Bruker Vector 22 (Bruker Optics GmbH, Ettlingen, Germany). The ¹H NMR spectra were recorded in solution at room temperature with a Bruker AC 250 (Bruker, Karlsruhe-Germany) spectrometer using dimethylsulfoxide (DMSO-*d*₆, 99.8%). The concentration of cobalt (II) and nickel (II) ions was determined by atomic absorption spectrometry (Perkin Elmer Model 1100 AAS, Shelton, CT). The elemental analyses were carried out using a Carlo Erba 1106 analyzer (Italy). Molar percentages (mol %) of comonomer units (*m*₁ and *m*₂) for poly(*p*-Cl-PhMI-*co*-HPMA) and poly(*p*-HO-PhMI-*co*-HPMA) were calculated by using elemental analysis data (from the nitrogen content).

Complexation procedure by maximum retention capacity

The solid polymer–metal complexes were prepared by the addition of an aqueous suspension (1 wt %) of copolymer (200 mg) previously adjusted to the corresponding pH by adding dilute nitric acid or sodium hydroxide. The aqueous suspension of polymer and metal chloride (1 wt %) solution were placed into the membrane filtration cell of the ultrafiltration system. The total volume in the cell was kept constant at 20 mL and the contact time was 24 h. The water-containing reservoir was adjusted to the pH of the cell suspension. A membrane with an exclusion limit of 10.000 g/mol (Amicon PM 10 or equivalent, Millipore made in USA) was used. After equilibration, the phases were separated by ultrafiltration. The system was pressurized at 300 kPa, and the cell solution was stirred and then washed with the reservoir fluid at a flow rate of 4–6 mL/min. The filtration fraction (200 mL) was collected and the concentrations of metal ions in the filtrate and in the retentate were determined by atomic absorption spectroscopy. The complex was dried for further analytical control by thermal analyses and FT-IR spectroscopy. Retention values were calculated from the metal ion concentration determinations in the filtrate and in the retentate.

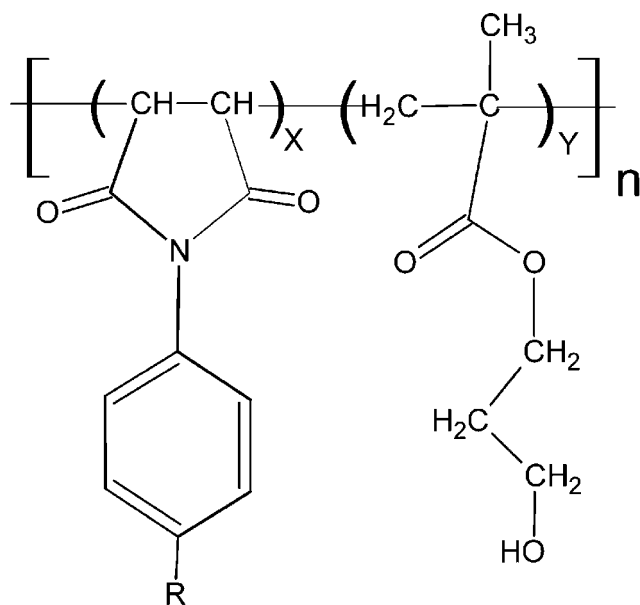
Thermal analysis

The thermal analysis of the copolymers was determined by recording thermogravimetry (TG) and differential scanning calorimetry (DSC) under nitrogen atmosphere (flow rate = 150 and 50 cm³/min, respectively). A mass of 3–4 ± 0.1 mg of the sample was used in each experiment. Thermal stability studies were performed using a Mettler Toledo Star System TG (made in Spain) at a heating rate of 10°C/min. DSC measurements were carried out with a Mettler Toledo Star System 822e to determine the glass transition temperature (*T*_g) of the copolymer. The *T*_g was measured with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Synthesis and characterization

The *p*-Cl-PhMI/*p*-HO-PhMI were copolymerized with HPMA at a 0.50 : 0.50 feed mol ratio. The general structure of the copolymer poly(R-PhMI-*co*-HPMA) is illustrated in Scheme 1. The experimental polymerization conditions and results are shown in Table I. Copolymer composition was determined from elemental analysis data. In general, the copolymers were



R: -OH; -Cl

Scheme 1 General structure of poly(R-PhMI-co-HPMA).

insoluble in water and benzene, and soluble in methanol, dimethylsulfoxide, acetone, and chloroform.

The FTIR spectra of the different copolymers show similar characteristic signals of the different functional groups.

The FTIR spectra (KBr, cm^{-1}) of the poly(*p*-Cl-PhMI-co-HPMA) (a) and their copolymer metal ion complexes with Co(II) at pH 3, 5, and 7 (b, c, and d) are presented, respectively in Figure 1, in which the most characteristic absorption bands (in cm^{-1}) are: 3445.9 (OH, $-\text{COOH}$), 2928.9 (CH, CH_2 stretching), 1740.1 and 1711.1 (C=O imide), and 1633.7 (C=O, ester stretching), 1494.8 (N—C stretching of imide ring), and 1392 (CH_2 , bending); 820 (*p*-substituted phenyl ring).

The FT-IR spectrum of the poly(*p*-Cl-PhMI-co-HPMA)-metal (II) ion complexes, [see Figs. 1(b-d)] presents an important change in the intensity of the

TABLE I
Experimental Conditions and Results of the Copolymerization Reaction of Cl-PhMI/HO-PhMI with HPMA at 70 °C by 12 h in Dioxane

Copolymer	f_1	F_1	M_1 (mmol)	Yield (%)	Elemental analysis (%)		
					C	N	H
Cl-PhMI-co-HPMA	0.50	0.43	7.2	63	57.03	3.52	6.27
HO-PhMI-co-HPMA	0.50	0.56	7.2	66	61.14	3.13	7.70

$$[M]_{\text{total}} = 2.86 \text{ mol/L.}$$

absorption signs in comparison with the copolymer's FT-IR spectra. The most characteristic absorption bands (in cm^{-1}) observed were the following: a broad band at 3445.9 of the hydroxyl group maintains its intensity, but a slightly sharper sign is observed; 2928.9 of the CH, CH_2 stretching, decreased in intensity as well as a visible change of those bands of C=O from imide ring at 1711.1, which decreased in intensity for the complexes with Co(II) and Ni(II), and at 1633.7 of the ester group, which increased in intensity and this effect is slightly increased at higher pH (5 and 7). This result could be attributed to the interaction of the C=O band of the ester group at 1633.7, which increased in intensity because of the coordination of the metal ions with this functional group. In this polymer-metal complex, it is suggested that the metal ions is bound to the nitrogen atom from imide group, for which the band (sharp) from N—C (stretching) at 1498 presented a decrease in signal intensity. The FTIR spectrum for the system of poly(HO-PhMI-co-HPMA) with Co(II) and Ni(II) presents similar absorption signals.

The ^1H NMR spectra in $\text{DMSO}-d_6$ of poly(*p*-Cl-PhMI-co-HPMA) and poly(*p*-HO-PhMI-co-HPMA) do not present important signal changes. The first sys-

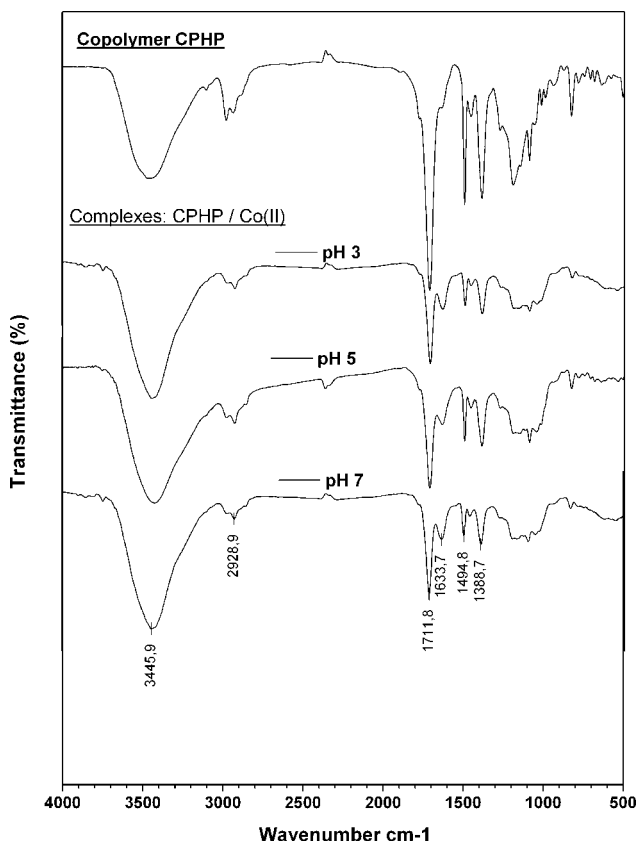


Figure 1 FT-IR spectra of CPHP and polymer-metal complexes CPHP/Co(II), respectively.

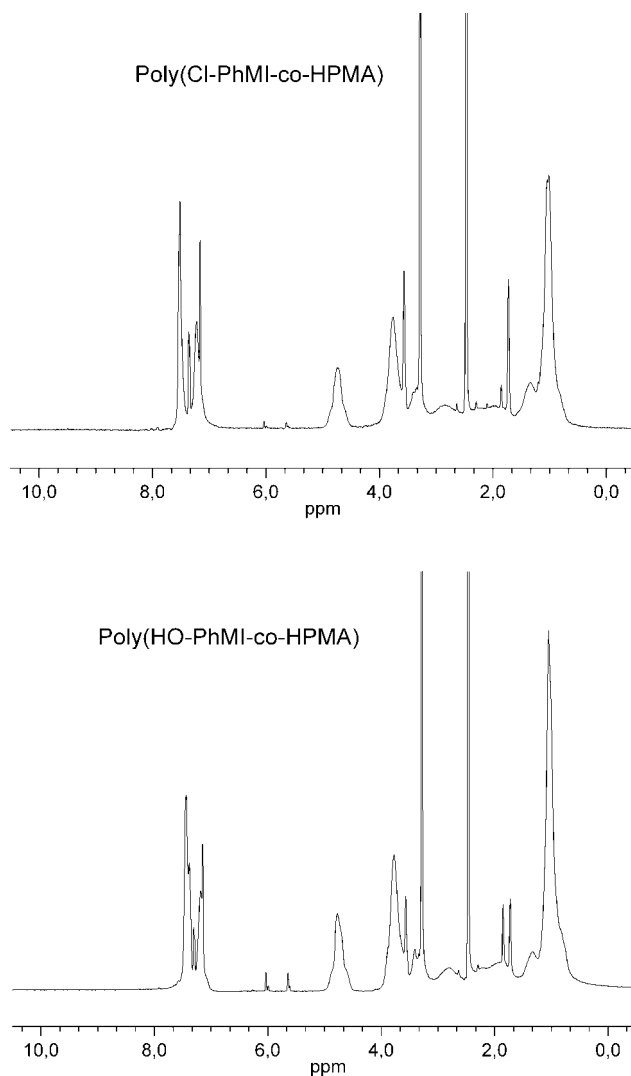


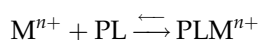
Figure 2 ^1H NMR (250 MHz, $\text{DMSO-}d_6$), room temperature, for CPHP and OPHP.

tem presents the following signals at δ (in ppm): (a) 0.9–1.7 ($-\text{CH}_3$); 1.8–3.6 ($-\text{CH}_2$, HPMA and $-\text{CH}$, from imide) from the backbone, 3.6–4.0, ($-\text{CH}_2-$, from side chain), 4.7 ($-\text{OH}$ from HPMA), and 7.0–7.8 ($-\text{CH}=\text{}$, aromatic ring) (see Fig. 2).

Complexing properties of copolymers

The copolymers' metal ion complexing properties were studied by using liquid-phase polymer based retention (LPR) technique at pH 3, 5, and 7 with two metals ions (see Fig. 3).

Retention depends on polymer complex dissociation, which is generally described by a reversible reaction^{21–26}:



where, PL = poly(CI-PhMI-co-HPMA) or poly(HO-PhMI-co-HPMA) with pendant ligand L at the

chain; M^{n+} , metal ion; PLM^{n+} , polymer–metal complexes.

Poly(CI-PhMI-co-HPMA) and poly(HO-PhMI-co-HPMA) showed higher complexing properties at higher pH (see Table II).

In general, a high metal ion retention with both systems takes place with Co(II) and Ni(II) at different pH. At pH 7, poly(CI-PhMI-co-HPMA) metal retention for Co(II) and Ni(II) ions varied from 44.1 to 48.6 mg/g and from 41.5 to 46.0 mg/g, respectively; while poly(*p*-HO-PhMI-co-HPMA) retention for Co(II) and Ni(II) ions varied from 28.4 to 35.6 mg/g and from 27.2 to 30.8 mg/g, respectively, at different pH. Therefore, metal ion retention increases slightly with an increase in pH for all copolymers, observing a slight pH influence.

Thus, poly(CI-PhMI-co-HPMA) and poly(HO-PhMI-co-HPMA) are effective reagents for separation of various metal ions at different pH. At pH 3, this copolymer shows a slightly lower metal ion affinity, and the copolymers presented lower retention values for Co(II) and Ni(II) ions in comparison with retention at pH 5 and pH 7.

The metal ion retention values for the copolymers show that both comonomer units possess functional groups with metal ion affinity. This retention behavior can be attributed to that the copolymer poly(R-PhMI-co-HPMA) has one hydrophilic monomer unit with a carbonyl functional groups in the side chain of its structure and that it can exhibit strong metal ion binding attraction forces that also depend on pH. Additionally, an interaction of the nitrogen atom from an imide group unit could exist, and could result in molecular complex formation. In this polymer–metal complex, the results suggest that the metal ion is bound to the nitrogen atom from the imide group, where the absorption band (sharp) from N–C (stretching) at 1498 cm^{-1} presented an important decrease. The interaction of the imide and carbonyl groups with metal ions can lead to the forma-

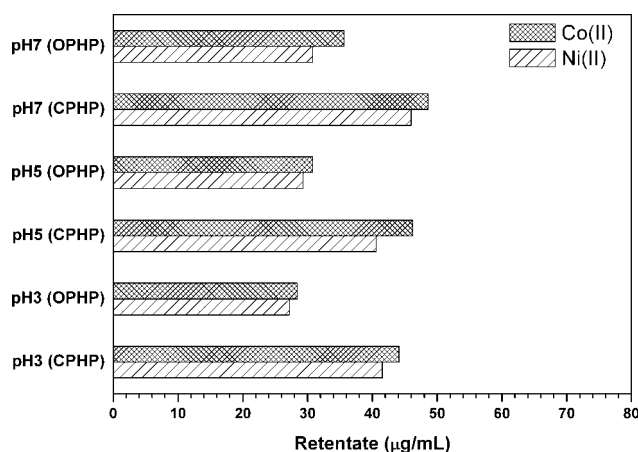


Figure 3 Typical metal ion retention profiles for CPHP/Ni(II), CPHP/Co(II), and CPHP/Co(II) and OPHP/Ni(II).

TABLE II
Maximum Retention Capacity (MRC) for the Copolymers-Co(II) and Ni(II)
Ion at Different pH

Copolymer–metal ion complex (acronym)	$m_1 : m_2$ (mol %)	pH	V (mL) (1 wt %)	Retentate ($\mu\text{g}/\text{mL}$)
CPHP-3/Co ²⁺	43 : 57	3	1.0	44.1
CPHP-5/Co ²⁺	43 : 57	5	1.0	46.2
CPHP-7/Co ²⁺	43 : 57	7	1.0	48.6
CPHP-3/Ni ²⁺	43 : 57	3	1.0	41.5
CPHP-5/Ni ²⁺	43 : 57	5	1.0	40.6
CPHP-7/Ni ²⁺	43 : 57	7	1.0	46.0
OPHP-3/Co ²⁺	56 : 44	3	1.0	28.4
OPHP-5/Co ²⁺	56 : 44	5	1.0	30.8
OPHP-7/Co ²⁺	56 : 44	7	1.0	35.6
OPHP-3/Ni ²⁺	56 : 44	3	1.0	27.2
OPHP-5/Ni ²⁺	56 : 44	5	1.0	29.3
OPHP-7/Ni ²⁺	56 : 44	7	1.0	30.8

tion of molecular complexes between the electron donor nitrogen of the imide and the carbonyl groups of the HPMA.

A predominant influence of the pH in the complex formation is reported²⁷ and it was established that different types of complexes were successively formed when the pH was increased.

In this case, different complex formation may occur at different pH when the nitrogen atom from imide, the carbonyl and hydroxyl groups from HPMA side chains may participate as donor groups in the complex formation as occurs in some biological system.²⁷ In this complex, the composition of the copolymer unit-metal complexes is practically 1 : 1, indicating that the metal can be bound to two ligands from copolymer unit and the other coordination sites could be occupied by hydroxyl or by water molecules although this was not clear from FTIR spectroscopic measurements. Nevertheless, this kind interaction usually occurs when the six coordination sites of metal are not occupied by copolymer ligands. If two copolymer ligands are involved in coordination, then an interaction with the hydroxyl group in the plane of metal is also possible.

Poly(Cl-PhMI-co-HPMA) presented higher complexing properties than that poly(HO-PhMI-co-HPMA), indicating that it is an effective reagent to separate metal ions. At pH 5 and 7, all the retention values for Co(II) ion are higher than 46.2 $\mu\text{g}/\text{g}$ and 30.8 $\mu\text{g}/\text{g}$ for poly(Cl-PhMI-co-HPMA) and poly(HO-PhMI-co-HPMA), respectively; while the retention values for Ni(II) ion are higher than 40.6 $\mu\text{g}/\text{g}$ and 29.3 $\mu\text{g}/\text{g}$ for poly(Cl-PhMI-co-HPMA) and poly(HO-PhMI-co-HPMA), respectively.

Maximum retention capacity of the copolymers for Co(II) and Ni(II) ions

The maximum retention capacity (MRC) had the highest retention values for both copolymer systems

at pH 5 and 7, and this result is related to the copolymers' nature.

In this case, poly(HO-PhMI-co-HPMA) presents a lower MRC than found for poly(Cl-PhMI-co-HPMA). This result supports the assumption that the hydroxyl aryl group could prevent the interaction with the metal because of steric hindrance and hydrogen binding interaction that could be forming an unstable polymer–metal complex. The copolymers' metal ion complexing capacity depends not only on the nature of the ligand groups, but also on their accessibility to the metal ions. Steric hindrance by Cl-PhMI and HO-PhMI units and a hydrophobic nature are known to limit the complexing reaction. Additionally, the hydrogen binding interaction of the hydroxyl groups of HO-PhMI and HO— from the HPMA monomer can lead to an unstable polymer–metal complex. The interaction of both units can lead to the formation of molecular complexes with electron donor nitrogen from imide and carboxyl groups from HPMA at higher pH (intramolecular complexes). The absorption bands at 1633.7 cm^{-1} (C=O from ester group) and at 1389.5 cm^{-1} (C–N stretching) predominantly coordinated around the cobalt or nickel ions.

The highest maximum retention capacity values for Co(II) ions were found at pH 5 and 7. The binding capacity for the Co(II) ion varied from 44 to 48 mg/g for poly(Cl-PhMI-co-HPMA) and from 28 to 35 mg/g for poly(HO-PhMI-co-HPMA), while the binding capacity for Ni(II) ion varied from 41.5 to 46 mg/g for poly(Cl-PhMI-co-HPMA) and from 27.2 to 30.8 mg/g for poly(HO-PhMI-co-HPMA) (see Table II).

Thermal behavior

Glass transition temperature of copolymer and metal complexes

The glass transition temperature (T_g) was estimated from the second DSC run. DSC thermograms of poly(Cl-PhMI-co-HPMA), CPHP; poly(HO-PhMI-co-

HPMA); OPHP and its metal complexes at pH 3, 5, and 7 are illustrated in Figures 4 and 5 ($T_g = 165.1$ and 146.8°C , respectively). The T_g for CPHP decreases as the pH increased in the presence of the metal ions Co(II) and Ni(II), except for CPHP/Ni(II) at pH 7 when a slight increase was observed. The main explication can be attributed to a consequence of a lower percentage of intramolecular crosslinking reaction. The T_g for OPHP decreases as the pH increased, although an increase was observed in the presence of the metal ions Co(II) and Ni(II) (see Table III). All synthesized copolymers presented a single T_g , indicating the formation of copolymers with a tendency to alternancy. In the range of pH 3–7, the T_g of the copolymer–metal complexes CPHP/Co(II) and OPHP/Co(II) varied from 160 to 158.7°C and from 163.8 to 161.5°C , respectively; while the T_g for the copolymer metal complexes CPHP/(Ni(II) and OPHP/Ni(II) varied from 146.4 to 167.0°C and from 158.3 to 153.2°C , respectively.

The TG results for poly(Cl-PhMI-co-HPMA) and poly(HO-PhMI-co-HPMA) are summarized in Table IV. The copolymers from both systems presented single-step degradation, after first eliminating water or monomer residue as well as other low molecular weight impurities (see Figs. 6 and 7). The resulting material has an extrapolated thermal decomposition temperature (TDT) of about 350°C . The TDT of the copolymer metal complexes were also lower than for the copolymers, except for the copolymer metal complex OPHP/Co(II) and OPHP/Ni(II) at pH 3. The thermal stability of polymer–metal complexes is known to be affected primarily by the nature of the polymer and microenvironmental conditions such as

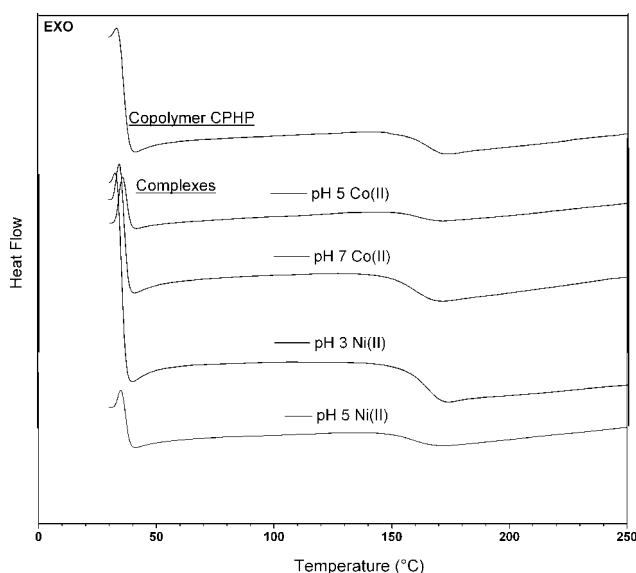


Figure 4 DSC thermograms of CPHP and polymer–metal complexes CPHP/Co(II) and CPHP/Ni(II). Heating rate: $10^\circ\text{C}/\text{min}$.

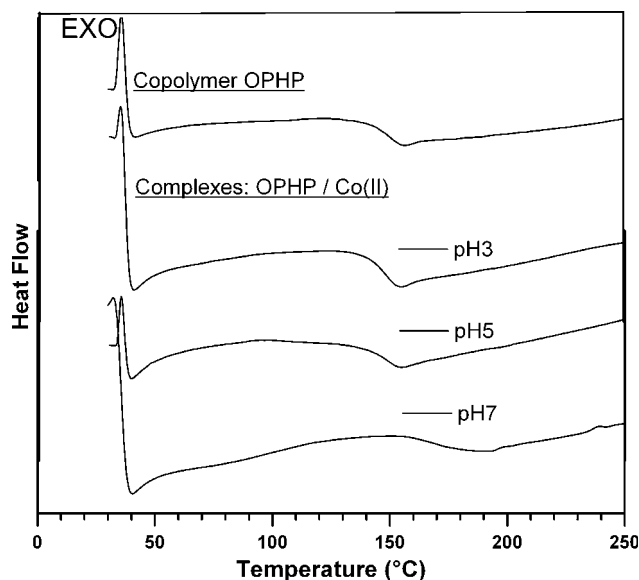


Figure 5 DSC thermograms OPHP and polymer–metal complexes OPHP/Co(II) and OPHP/Ni(II). Heating rate: $10^\circ\text{C}/\text{min}$.

additional coordination bonds. According to the literature, the thermal stability of functional polymers with metal will generally be enhanced. Some recent reports, however, support these TGA results. 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.²⁸

The greatest weight loss for the copolymer and the complexes occurs between 400°C and 550°C (see Table IV). At pH 3, 5, and 7, the complexes' higher residual mass percentage may be attributed to the

TABLE III
 T_g of Poly(Cl-PhMI-co-HEMA)(1) and Poly(HO-PhMI-co-HEMA)(6–10) and Their Polymer–Metal Ion Complexes at pH 3, 5, and 7

Copolymer	T_g ($^\circ\text{C}$)
Polymer- Co^{2+} complexes at pH 3, 5, and 7	
CPHP	165.1
OPHP	146.8
CPHP-3	160.2
CPHP-5	162.1
CPHP-7	158.7
OPHP-3	163.8
OPHP-5	160.5
OPHP-7	161.5
Polymer- Ni^{2+} complexes at pH 3, 5, and 7	
CPHP	165.1
OPHP	146.8
CPHP-3	146.4
CPHP-5	147.5
CPHP-7	167.0
OPHP-3	158.3
OPHP-5	155.3
OPHP-7	153.2

TABLE IV
Thermal Decomposition Temperature and Weight Loss at Different Temperatures for the Cl-PhMI/HPMA and HO-PhMI/HPMA and Their Copolymer–Metal Ion Complexes

Sample acronym	Copolymer composition	TDT (°C)	Weight loss (%) at different temperatures (°C)					
			100	200	300	400	500	550
CPHP	43 : 57	365.4	0.3	2.5	5.3	55.0	91.5	92.7
CPHP-3/Co ²⁺	43 : 57	350.0	0.9	3.4	3.5	60.7	85.2	81.1
CPHP-5/Co ²⁺	43 : 57	361.0	0.1	3.2	5.7	62.0	89.5	91.5
CPHP-7/Co ²⁺	43 : 57	361.0	1.3	4.7	8.0	63.9	88.9	91.7
CPHP-3/Ni ²⁺	43 : 57	360.0	0.6	3.0	6.0	41.4	88.6	90.4
CPHP-5/Ni ²⁺	43 : 57	363.0	1.1	3.5	6.5	44.7	85.5	87.5
CPHP-7/Ni ²⁺	43 : 57	363.0	2.0	3.2	7.8	48.9	81.3	89.8
OPHP	56 : 44	359.3	1.8	4.3	8.8	63.8	95.0	96.1
OPHP-3/Co ²⁺	56 : 44	361.4	1.2	2.3	5.8	70.6	90.3	92.6
OPHP-5/Co ²⁺	56 : 44	354.5	0.2	1.1	2.6	66.4	89.8	92.1
OPHP-7/Co ²⁺	56 : 44	343.0	0.2	2.7	8.7	67.8	80.3	85.2
OPHP-3/Ni ²⁺	56 : 44	363.4	1.0	2.5	5.5	70.0	89.3	90.6
OPHP-5/Ni ²⁺	56 : 44	358.5	0.3	1.3	2.8	68.0	90.8	94.3
OPHP-7/Ni ²⁺	56 : 44	353.0	0.2	2.0	5.7	69.0	80.9	95.2

M_1 = Cl-PhMI(1–7) or HO-PhMI(8–14); M_2 = HEMA.

percentage of metal incorporated at this pH. The copolymer–metal complexes OPHP/Co(II)-Ni(II) present a lower TDT than CPHP/Co(II)-Ni(II) for the

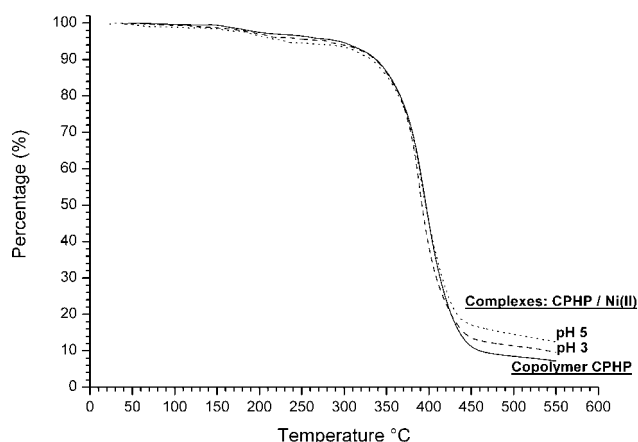
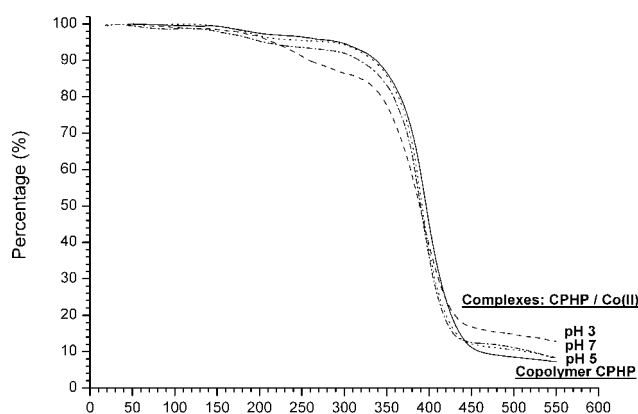


Figure 6 TGA thermograms CPHP and polymer–metal complexes CPHP/Co(II) and CPHP/Ni(II). Heating rate: 10°C/min.

same copolymer composition (see Figs. 6 and 7). The incorporation of the hydroxyl group in arylmaleimide monomers decreased the TDT values in the copolymers in comparison with P(Cl-PhMI-co-HPMA) due to steric hindrance and the hydrogen binding interaction that could be forming an unstable polymer–metal complex.

CONCLUSIONS

Complexes of P(HO-PhMI-co-HPMA) and P(Cl-PhMI-co-HPMA) with Ni(II) and Co(II) were synthesized and investigated as a function of the pH. The liquid phase polymer retention (LPR) technique has important technological applications. LPR technique as ultrafiltration system was employed to test the coordination properties in the formation of com-

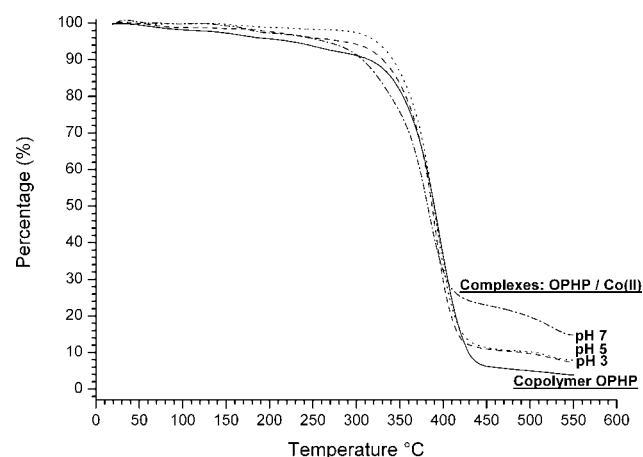


Figure 7 TGA thermograms OPHP and polymer–metal complexes CPHP/Co(II). Heating rate: 10°C/min.

plexes of the copolymers, P(CI-PhMI-*co*-HPMA) and P(HO-PhMI-*co*-HPMA) in aqueous suspension, 2 wt %).

The MRC for the copolymers at different pH (3, 5, and 7) and metal ions showed no important differences. The MRC had the highest retention values for both copolymer systems at pH 5 and pH 7, and this result is related to the copolymer composition. In this case, the poly(HO-PhMI-*co*-HPMA) presents a lower MRC than poly(CI-PhMI-*co*-HPMA).

The MRC for Ni(II) and Co(II) varied from 44 to 48 mg/g and 41.5 to 46 mg/g, respectively, for poly(CI-PhMI-*co*-HPMA); and from 28 to 35 mg/g, and 27.2 mg/g to 30.8 mg/g, respectively, for poly(HO-PhMI-*co*-HPMA). The copolymer P(CI-PhMI-*co*-HPMA) and P(HO-PhMI-*co*-HPMA) presented higher TDT in comparison with copolymer metal complexes CPHP and OPHP/Co(II), -Ni(II) at pH 3 and 5. All copolymers synthesized presented a single T_g indicating the formation of copolymers with a tendency to alternancy.

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