Metal ion retention from aqueous solution using the ultrafiltration technique: preparation, retention capacity of copolymers of *N*-maleimide derivatives with β-methylhydrogen itaconate and metal complexes

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Abstract: Chlorophenylmaleimide (Cl-PhMI) and *N*-maleoylglycine (N-MG) with β-methylhydrogen itaconate (β-MHI) were copolymerized by radical polymerization, and their metal ion retention capacity (MRC) and thermal behavior were studied. The copolymers were obtained by varying the mole fraction of Cl-PhMI or N-MG in the feed from 0.25 to 0.75. The monomer reactivity ratios, r_1 and r_2, were determined using the Kelen–Tüdös method. The molecular weight and polydispersity were also determined. The capacity to remove several metal ions, such as Cu(II), Cr(III), Co(II), Zn(II), Ni(II), Pb(II), and Fe(III), in aqueous phase was determined using the liquid-phase polymer-based retention technique. Inorganic ion interactions with the hydrophilic polymer were determined as a function of pH and the filtration factor. The MRC depends strongly on the pH. Metal ion retention increased with increases in pH and the content of β-MHI units in the macromolecular backbone. The copolymers and polymer–metal complexes of transition metal ions were characterized using elemental analysis, Fourier transform infrared spectroscopy, ^{1}H NMR, and electron paramagnetic resonance spectroscopy. The maximum MRC of Cu(II) ions of poly(Cl-PhMI-*co*-β-MHI) varied from 240 to 260 mg g^{-1}, while the MRC of Cu(II) ions of poly(N-MG-*co*-β-MHI) varied from 270 to 318 mg g^{-1} at pH 5 and pH 7. The thermal behavior of the copolymers and polymer–metal complexes was studied using differential scanning calorimetry and thermogravimetry techniques under nitrogen atmosphere. The copolymers have a lower thermal decomposition temperature than the polymer-metal complex for the same copolymer composition. The thermal behavior may be correlated with the copolymer composition.

Keywords: radical polymerization; maximum retention capacity; metal–polymer complexes; thermal behavior

INTRODUCTION

The copolymerization of alkylmethacrylates with *N*-substituted arylmaleimides using a free radical initiator is well documented.[1–4] Maleimide polymers have good thermal stability with high glass transition temperatures due to their polar five-member imide ring structure.[5] 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 the modification of the primary structure of the polymers.[6–8]

Various techniques to remove heavy metals from wastewaters have been reported, such as precipitation, extraction, membrane filtration, ion exchange, adsorption, and neutralization.[9–11] Heavy metal removal by hydrophilic polymers with complexing groups would be of great importance in environmental applications.[12–20]

There are important approaches that should be considered when designing polymers for metal extraction. These include fast complexation of metal ions as well as the reusability of the polychelatogens.[21]

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We have recently reported the Cu^{2+} binding properties of poly[(*N*-phenylmaleimide)-*co*-(*β*-methyl-hydrogen itaconate)] (poly(N-PhMI-*co*-*β*-MHI))[22] where the copolymer maximum metal ion retention capacity (MRC) for Cu^{2+} ions varied from 296 to 348 mg g^{-1} at pH 5 and pH 7. In the case of poly[N-PhMI-*co*-(acrylic acid)],[23] the maximum retention capacity of the copolymer for Co(II) and Cu(II) ions varied from 200 to 250 mg g^{-1} and 210 to 300 mg g^{-1}, respectively.

These systems were employed to investigate the copolymer coordination properties, determining the MRC at different pH. The binding properties of these copolymers can be compared with the Cu(II) binding properties of a polychelating hydrogel, such as poly[(acrylic acid)-*co*-(itaconic acid)], whose adsorption properties at pH 6.0 were 147 mg of metal ions per gram, and at pH 9 were 320 mg of metal ions per gram of polymer.[24] Other commercial resins, such as poly[(glycidyl methacrylate)-*co*-(ethylene dimethacrylate)] modified with aspartic acid, present a higher MRC value for Cu^{2+} of 24.1 mg g^{-1} at acid pH.[25] The MRC for the copolymers studied is higher than that of resins, indicating that the resins' metal complexing capacity depends not only on the nature of the ligand groups but also on their accessibility towards the metal ions.

In this case, poly(chlorophenylmaleimide-*co*-*β*-MHI) (poly(Cl-PhMI-*co*-*β*-MHI)) presents a lower MRC than poly[(*N*-maleoylglycine)-*co*-*β*-MHI] (poly(N-MG-*co*-*β*-MHI)) and poly(N-PhMI-*co*-*β*-MHI).[22] This result supports the assumption that the chloroaryl group prevents the interaction with the metal by steric hindrance, and that it could form an unstable polymer–metal complex. Steric hindrance by Cl-PhMI units and their hydrophobic nature could limit the chelating reaction.

The aim of the work reported in this paper was to synthesize, by radical polymerization, copolymers of Cl-PhMI and N-MG with *β*-MHI, and to study the coordination properties of the copolymers with various metal ions, such as the study of their MRC and the Cu^{2+} binding properties of these copolymers, using the liquid-phase polymer-based retention (LPR) technique.

EXPERIMENTAL

Materials

Cl-PhMI was synthesized from maleic anhydride (Merck) and *p*-chloroaniline (Merck) in diethyl ether following the published procedure.[26] *p*-Chloroaniline was purified by distillation under reduced pressure. Cl-PhMI was purified by recrystallization from cyclohexane. The yield was 87%, m.p. 118–121 °C, (lit. m.p. 117–118 °C).

N-MG was prepared following a published method[27] by reacting maleic anhydride with glycine in diethyl ether. The yield of N-MG was 38%, m.p. 111–113 °C (lit. m.p. 113–113.5 °C). It was purified by recrystallization from chloroform.

β-MHI was obtained from itaconic acid following Baker and Shoes.[28]

Preparation of polymers

A typical procedure for the copolymerization reaction is the following. The mixture of Cl-PhMI or N-MG with *β*-MHI (20 mmol) was dissolved in dioxane (7 mL) and benzoyl peroxide (BPO) as initiator (57.8 μmol). A 2.86 mol L^{-1} solution of monomers in dioxane was placed in a copolymerization flask under nitrogen, by varying the mole fraction in the feed from 0.25 to 0.75 while maintaining constant the total amount of comonomers. The flask was kept in a controlled temperature oil bath at 70 ± 1 °C for 12 h. To precipitate the copolymer, 50 mL of diethyl ether was poured into the mixture. The copolymer was separated by centrifugation and purified by precipitation, and then dried under vacuum until constant weight.

Measurements

Fourier transform infrared (FTIR) spectra were recorded using a Bruker Vector 22 (Bruker Optics GmbH, Inc., Ettlingen, Germany). ^{1}H NMR spectra were recorded in solution at room temperature using a Bruker AC 250 (Bruker, Karlsruhe, Germany) spectrometer using dimethylsulfoxide (DMSO-d_6, 99.8%). The concentration of Cu(II) ions was determined by atomic absorption spectrometry using a Perkin Elmer model 1100 instrument (Perkin Elmer, Shelton, CT).

The number-average (M_n) and weight-average (M_w) molecular weights and the molecular weight distribution (polydispersity, M_w/M_n) of the polymers were determined using gel permeation chromatography (GPC). A WATERS 600E instrument was used equipped with UV and RI detectors, using chloroform as solvent (flow rate of 1.0 mL min^{-1}). The samples were measured at 30 °C with a concentration of 6 mg mL^{-1}, and calibration was done using poly(methyl methacrylate) (PMMA).

Electron paramagnetic resonance (EPR) spectroscopy

EPR spectra were recorded in the X band (9.85 GHz) using a Bruker ECS 106 spectrometer with a rectangular cavity and 50 kHz field modulation. The hyperfine splitting constants were estimated to be accurate within 0.05 G.

Copolymer composition

The elemental analyses were performed using a Carlo Erba 1106 analyzer (Italy). Molar percentages (mol%) of comonomer units (m_1 and m_2) for poly(Cl-PhMI-*co*-*β*-MHI) and poly(N-MG-*co*-*β*-MHI) were calculated using elemental analysis data (from the nitrogen content).

Complexation procedure

To determine the complex binding capacity, the copolymer (200 mg) was dissolved in 10 mL water and adjusted to the corresponding pH by adding dilute nitric acid or sodium hydroxide. The aqueous solutions of polymer and metal nitrate or chloride (20 ppm; 2 wt%) solution were placed into the membrane filtration cell. The total volume in the cell was kept constant at 20 mL. The reservoir contained water, and was adjusted to the cell solution's pH. A membrane with an exclusion limit of 10 000 g mol^{-1} (Amicon PM 10 or equivalent, Millipore, USA) was used. The system was pressurized at 300 kPa, the cell solution stirred for 10 min and then washed with the reservoir fluid at a flow rate of 4–6 mL min^{-1}. The filtration fractions ($Z = 1$–10) were collected and the concentrations of metal ions in the filtrate and in the retentate were determined using atomic absorption spectroscopy. The copolymer was dried for further analytical control. Retention values were calculated from the metal ion concentration determinations in the filtrate and in the retentate.

Preparation of complexes by MRC

The solid copolymer–metal complexes were prepared by adding an aqueous solution of poly(Cl-PhMI-*co*-β-MHI) or poly(N-MG-*co*-β-MHI) (2 wt%) at pH 3, pH 5, and pH 7 to an aqueous solution (5 wt%) of the metal salts. The copolymer–metal complexes were placed into the membrane filtration cell and were separated and purified by successive ultrafiltrations, using a membrane with a molecular weight exclusion limit of 10 000 g mol^{-1} (Amicon ultrafiltration equipment, USA). The water-containing reservoir was adjusted to the pH of the cell solution and the system was pressurized (300 kPa). The metal ion concentration in the filtrate and in the complex was determined by atomic absorption spectroscopy. The new complex was dried for further analysis using thermal analyses and FTIR spectroscopy.

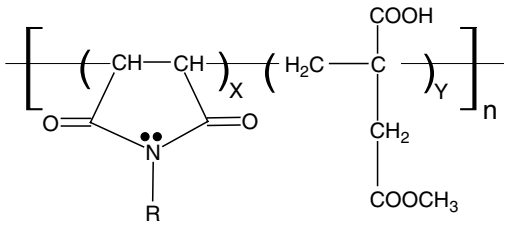
Thermal analysis

The thermal analysis of the copolymers was determined by carrying out TGA and DSC under nitrogen atmosphere (flow rate = 150 and 50 cm^3 min^{-1}, respectively). A sample size of 3–4 ± 0.1 mg was used in each experiment. Thermal stability studies were performed using a Mettler Toledo Star System thermogravimetric analyzer (made in Spain) at a heating rate of 10 °C min^{-1}. DSC measurements were carried out using a Mettler Toledo Star System 822e to determine the glass transition temperature (T_g) of the copolymer. T_g was measured with a heating rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

Synthesis and characterization

The Cl-PhMI or N-MG was copolymerized with β-MHI at different feed mole ratios, while maintaining constant the total amount of monomers. The general structure of the poly(R-MI-*co*-β-MHI) copolymers is illustrated in Scheme 1. The experimental polymerization conditions and results are shown in Table 1. Copolymer composition was determined from elemental analysis data. For the first system, the copolymers are insoluble in water, methanol, and chloroform, and soluble in acetone, dimethylsulfoxide, and dimethylacetamide. Copolymers of the second system are soluble in dimethylacetamide, water, acetone, and chloroform.



R: -CH_2-COOH (MG); -Ar-Cl (Cl-PhMI)

Scheme 1. General structure of poly(R-MI-*co*-β-MHI).

The FTIR spectra (KBr) of poly(Cl-PhMI-*co*-β-MHI) and poly(N-MG-*co*-β-MHI) are shown, respectively, in Fig. 1(a) and 1(b). In Fig. 1(a), the most characteristic absorption bands (in cm^{-1}) are: 3468.8 (OH, –COOH); 2957.2 (CH, CH_2 stretching); 1775.2 and 1740 (C=O imide); 1703.1 (C=O, –COOH stretching); 1673.1 (C=O ester) and 1597.8 (CH– stretching of aromatic ring); 1439 (N–C stretching of imide ring) and 1392 (CH_2 bending); 820 (*para*-substituted phenyl ring, and C–N–C bending).

The FTIR spectrum of P(N-MG-*co*-β-MHI) exhibits an important change in comparison with that of P(Cl-PhMI-*co*-β-MHI). The most characteristic absorption bands (in cm^{-1}) observed are the following: a broad band at 3464.9 (OH, –COOH); 2950.5 (CH, CH_2 stretching), as well as a visible change of those bands of C=O from the imide ring and acid

Table 1. Experimental conditions and results for the copolymerization reaction of Cl-PhMI or N-MG with β-MHI at 70 °C for 12 h in dioxane (7 mL)

Copolymer	f_1	F	M_1 (mmol)	M_2 (mmol)	Initiator BPO (μmol)	Yield (%)
CPhβ-1	0.25	0.228	5.00	15.00	57.8	50.9
CPhβ-2	0.33	0.279	6.67	13.33	57.8	53.4
CPhβ-3	0.50	0.383	10.00	10.00	57.8	37.5
CPhβ-4	0.67	0.543	13.33	6.67	57.8	40.1
CPhβ-5	0.75	0.603	15.00	5.00	57.8	46.8
NMβ-6	0.25	0.249	5.00	15.00	57.8	67.3
NMβ-7	0.33	0.258	6.67	13.33	57.8	59.2
NMβ-8	0.50	0.389	10.00	10.00	57.8	56.3
NMβ-9	0.67	0.488	13.33	6.67	57.8	60.2
NMβ-10	0.75	0.556	15.00	5.00	57.8	56.2
NMβ-11	1.00	–	–	20.00	57.8	80.6

M_1: Cl-PhMI(1–5) or N-MG(6–10); M_2: β-MHI (11) or f_1: feed monomer composition; F: copolymer molar fraction (m_1) mol%, $[M]_{total} = 2.86$ mol L^{-1}.

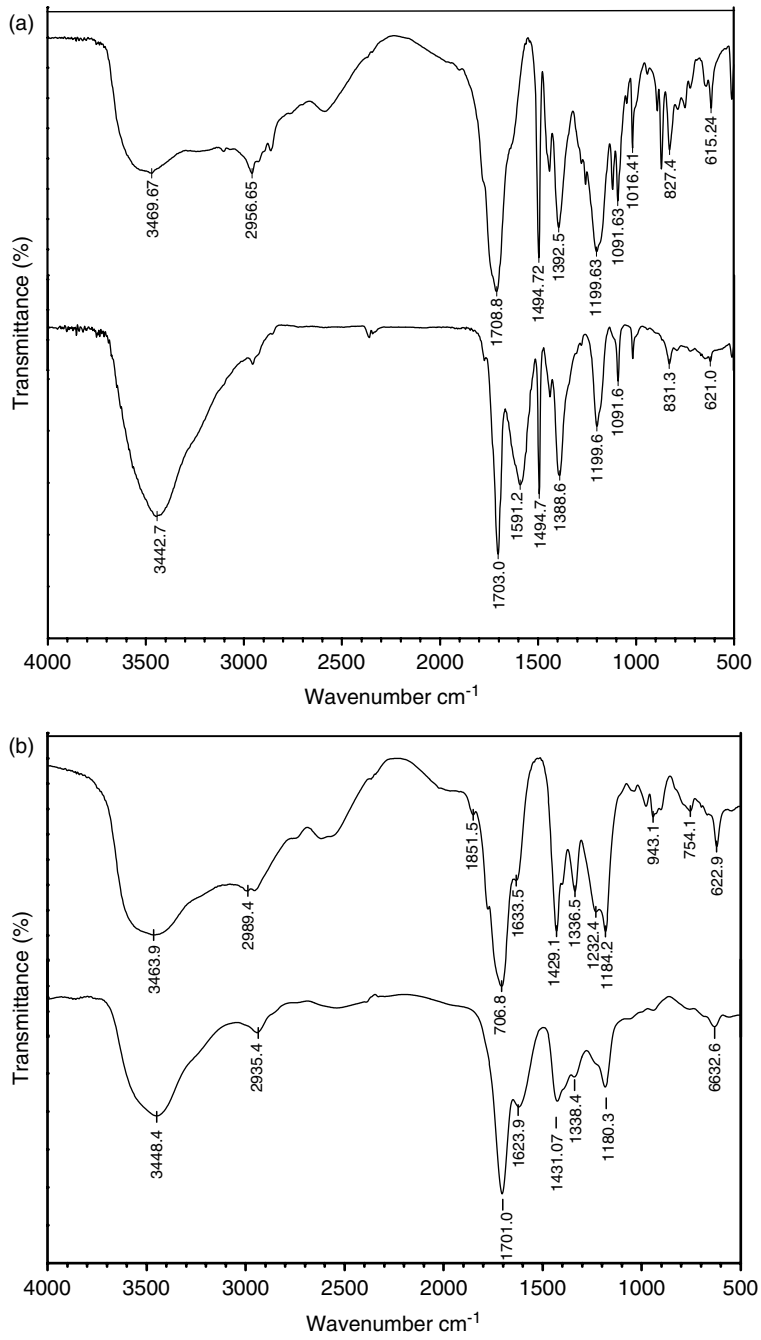


Figure 1. FTIR spectra of (a) CPhβ-3 and polymer–metal complexes CPhβi-37, and (b) NMβ-8 and polymer–metal complexes NMβi-87.

groups at 1777.5, 1706.9, and 1635.2 from the ester group.

The ^{1}H NMR spectra of (a) P(Cl-PhMI-*co*-β-MHI) in DMSO-d_6 and (b) P(N-MG-*co*-β-MHI) in D_2O show the following signals (δ, ppm): (a) 2.2 (–C–CH_2) from the backbone, 2.6 (–CH_2, CH_2COO), 2.8–3.8 (–CH–, from imide and CH_3 from OCH_3), and 7.0–7.8 (–CH=, aromatic ring); (b) 2.4 (3H, –CH_3); 3.0 (2H, –CH_2) from the backbone, and (2H, –CH from imide ring), 3.5 (2H, –CH_2COO from β-MHI), 4.0 (2H, –CH_2COOH), and 4.7 solvent (D_2O). These signals are broad due to the presence of various types of protons with similar chemical shifts (Fig. 2).

The GPC results (Table 2) indicate that NMβ-8- and CPhβ-3-supported polymers have relatively high polydispersity values, PD = 2.01 and 2.12, respectively.

EPR

The EPR spectra were recorded for different copolymer compositions and pH valuess. No well-resolved

Table 2. The molar mass distributions for the copolymers from GPC curves

Sample	$M_{w(GPC)}$ (g mol^{-1})	$M_{n(GPC)}$ (g mol^{-1})	PD (M_w/M_n)
CPhβ-3	3.095×10^4	1.46×10^4	2.12
NMβ-8	2.759×10^4	1.37×10^4	2.01

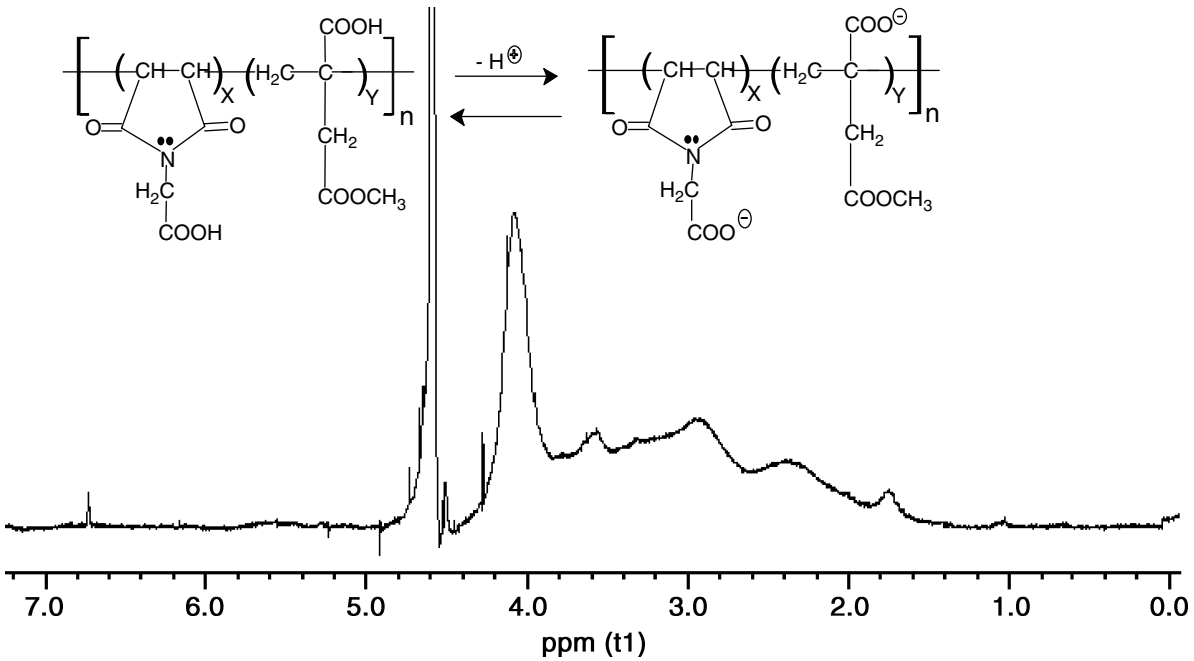


Figure 2. ^{1}H NMR (250 MHz, DMSO-d_6, room temperature) spectrum of NMβ-8.

EPR spectra were registered at pH below 7; however, the EPR spectrum at pH higher than 5 showed a well-resolved hyperfine pattern (Fig. 3), which could correspond to a typical square planar or tetragonal Cu(II) coordination geometry, with $g_{||} = 2.22$ G, $g_{\perp} = 2.08$, and $A_{||} = 150$ G. No well-resolved hyperfine pattern for other complexes could be found, indicating that the metal retention capacity decreases at pH below 7.

Monomer reactivity ratios

The monomer reactivity ratio (MRR) values for both systems were determined from the monomer feed ratios and the copolymer composition obtained at relatively high conversions, according to the low-conversion Kelen–Tüdös (K-T) method.[29] The K-T equation is symmetrically transformed into

$$G = r_1 \times F - r_2 \qquad (1)$$

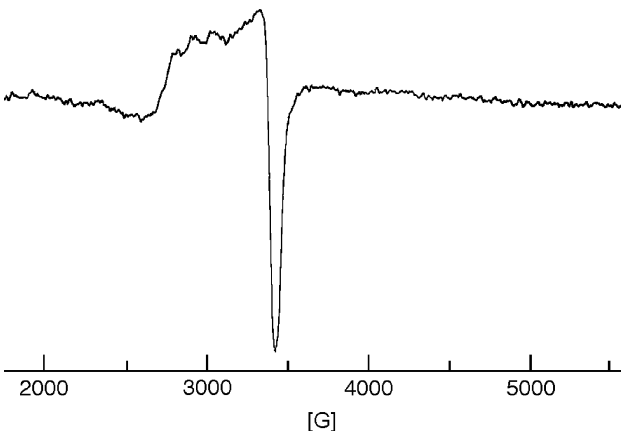


Figure 3. ESR experimental spectrum of complex CPhβi-37. Spectrometer conditions: microwave frequency, 9.68 GHz; microwave power, 20 mW; modulation amplitude, 0.2 G; scan rate, 1.25 G s^{-1}; time constant, 0.5 s.

by introducing the new parameters ξ, η, and $\alpha = (F_{\min} \times F_{\max})^{0.5}$, where $F_{\min}$ and $F_{\max}$ correspond to the smallest and largest fraction calculated in the copolymer (F), respectively (Table 3).

The transformed variables are defined as

$$\eta = G/(r_1 + r_2/\alpha);\ \xi = F/(\alpha + F)$$

The r_1 and r_2 values were also calculated according to

$$\eta = (r_1 + r_2/\alpha)\xi \qquad (2)$$

where η and ξ are mathematical functions of the monomer molar ratios in the feed and in the copolymer, respectively, and α is an arbitrary denominator with any positive value, which produces a more homogeneous distribution of data along η-ξ axes.

Where these parameters ξ, η and α, have been previously defined: $G = (m_1/m_2 - 1)/z$ and $F = (m_1/m_2)/z^2$; $z = \log 1 - \delta_1)/\log(1 - \delta_2)$; $\delta_1 = \delta_2 y/X_o$; $\delta_2 = \text{wt\%}(\mu + X_o)/(\mu + y)/100$; $\mu = \mu_2/\mu_1$; $y = m_1/m_2$; $X_o = M_1/M_2$; wt% = conversion; μ_1 and μ_2 are the molecular weights of monomers 1 and 2, respectively; M_1 and M_2 = initial composition of monomers in mol, M_1 represents Cl-PhMI or N-MG and M_2 represents β-MHI; m_1 and m_2 correspond to the monomer composition in the copolymer for each monomer.

The variable ξ can take any possible value in the interval 0 to 1. A plot of η *versus* ξ gives a straight line, which on extrapolation to $\xi = 0$ and 1 gives $-r_2/\alpha$ and r_1, respectively.

According to these values, the MRRs for poly(Cl-PhMI-*co*-β-MHI) are $r_1 = 0.292$ and $r_2 = 0.54$ ($r_1 \times r_2 = 0.16$) and for poly(N-MG-*co*-β-MHI) are $r_1 = 0.595$ and $r_2 = 0.618$ ($r_1 \times r_2 = 0.3675$). In general, these results suggest that the chain-growth reactions

proceed predominantly by the addition of acrylic monomers to the –N–MI• macroradical, producing statistical copolymers with more incorporated β-MHI units. We have previously published the MMRs for the poly(MG-*co*-AA), poly(MG-*co*-AAm),[30] and poly(N-PhMI-*co*-β-MHI) systems,[22] which indicated

Table 3. Copolymerization data for Cl-PhMI or N-MG with β-MHI to determine r_1 and r_2 using the Kelen–Tüdös method ($\alpha = 1.33$, $\mu = 0.694$; $\alpha = 2.17$, $\mu = 0.627$, respectively)

Feed monomer ratio (mol%)			Elemental analysis (%)			Copolymer composition		K-T equation parameters	
$[M_1]$	$[M_2]$	Yield (%)	C	H	N	m_1	m_2	ε	η
25	75	41.5	51.79	5.39	2.46	29.3	77.2	0.140	–0.274
33	67	36.2	52.02	5.07	2.81	34.0	72.1	0.260	–0.256
50	50	34.4	52.51	4.65	3.54	45.1	61.7	0.505	–0.085
67	33	37.5	54.34	4.32	4.46	58.8	45.7	0.727	0.138
75	25	36.9	55.03	4.00	4.84	64.7	39.7	0.860	0.185
25	75	51.3	52.33	4.76	2.01	24.9	75.1	[a]	[a]
33	67	46.2	52.79	4.60	2.41	25.8	74.2	0.415	–0.395
50	50	38.9	53.70	4.29	3.19	38.9	61.1	0.644	–0.004
67	33	31.6	54.93	3.87	4.25	48.8	51.2	0.843	0.256
75	25	34.2	55.37	3.73	4.63	55.6	44.4	0.875	0.448

[a] Values outside range; conversion $\leq$20%.

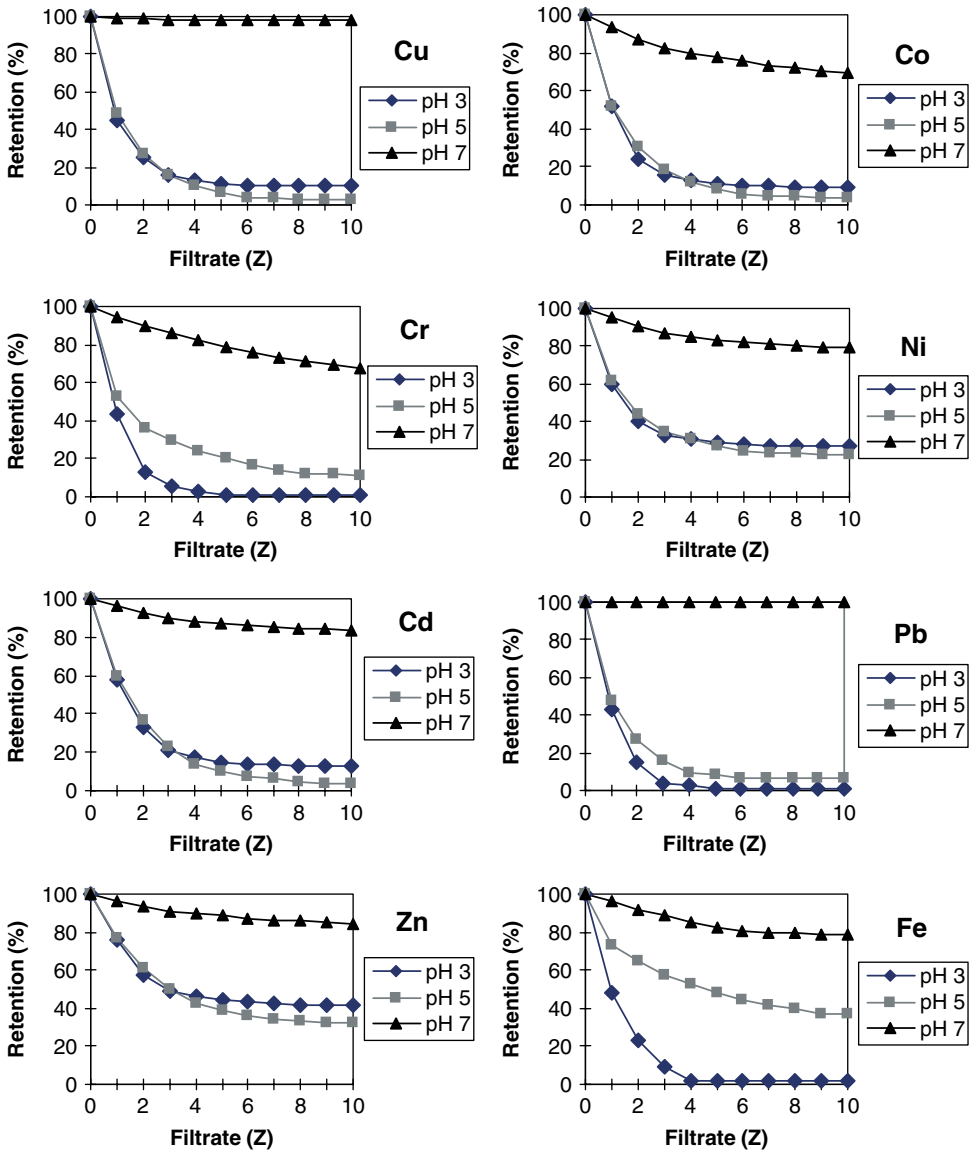


Figure 4. Typical metal ion retention profiles for CPhβi-33, CPhβi-35, and CPhβi-37.

that the acrylic monomers possess a similar chain incorporation tendency.

Properties as polychelatogens of poly(Cl-PhMI-co-β-MHI) and poly(N-MG-co-β-MHI)

The metal ion complexing properties of poly(Cl-PhMI-*co*-β-MHI) and poly(MG-*co*-β-MHI) were investigated using the LPR technique at pH = 3, 5, and 7 with eight metal ions (Figs 4 and 5). For the washing and enrichment methods, the metal ion retention in the cell solution is defined as

$$R = \frac{C_r}{C_o} \times 100\%$$

where C_r is the metal ion concentration in the retentate and C_o is the initial metal ion concentration in the cell. The filtration factor Z, expressed in relative units, is another useful characteristic of the process:[31–35]

$$Z = \frac{V_f}{V_c}$$

where V_c is the cell solution volume and V_f is the filtrate volume.

Retention depends on polymer complex dissociation, which is generally described by a reversible reaction:

$$M^{n+} + PL \Leftrightarrow PLM^{n+}$$

where PL = poly(Cl-PhMI-*co*-β-MHI) or poly(MG-*co*-β-MHI) with pendant ligand L at the chain; M^{n+} is the metal ion; and PLM^{n+} is the polymer–metal complex.

Poly(Cl-PhMI-*co*-β-MHI) presented higher complexing properties at basic pH (Table 4). In general for poly(Cl-PhMI-*co*-β-MHI), there is high metal ion retention for all metal ions at pH 7. At pH 3 and 5, the copolymer presents lower metal ion retention. These values increased at pH 7 and when the copolymers were richest in β-MHI monomer units, indicating a predominant influence of the pH and copolymer composition. At pH 7, all the retention values are higher than that 75%, except for Co(II) and Cr(III) (62

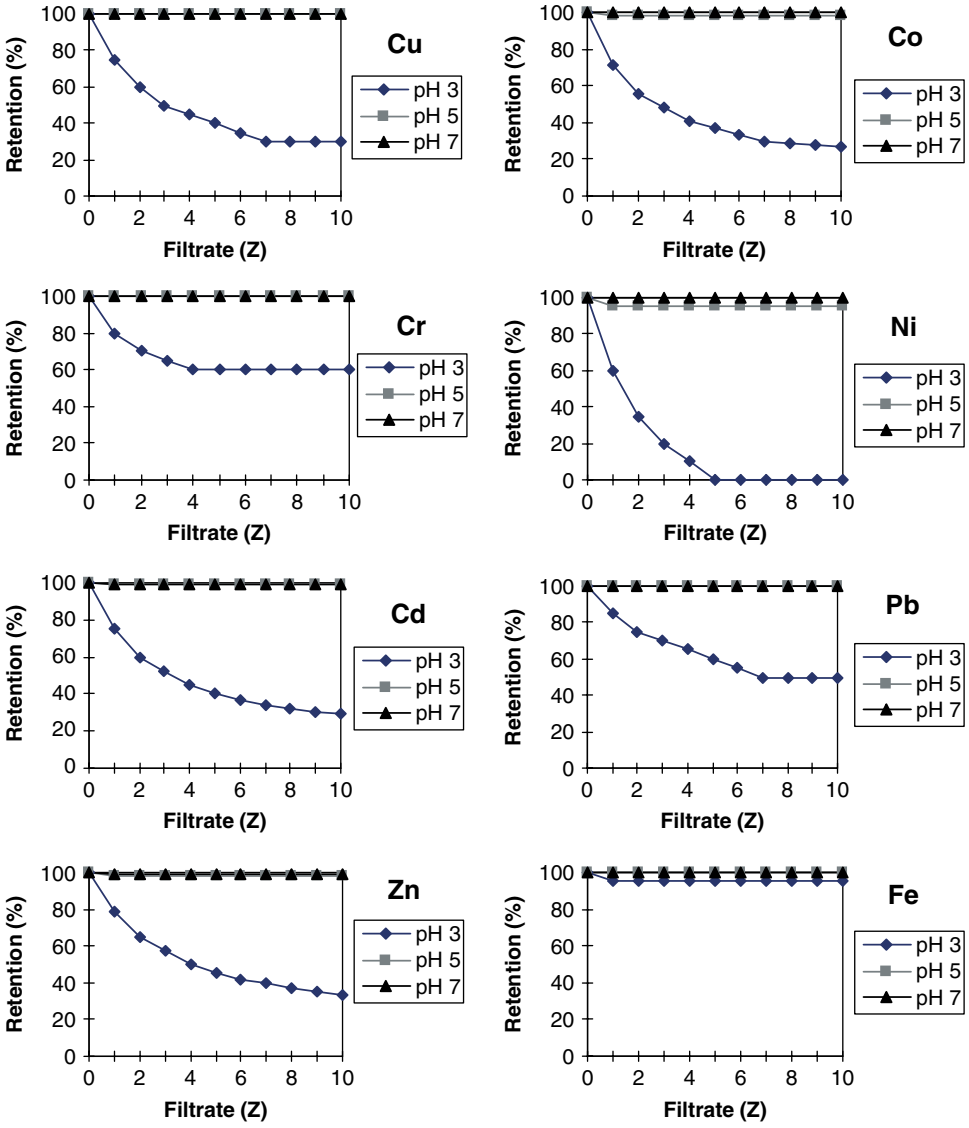


Figure 5. Typical metal ion retention profiles for NMβi-83, NMβi-85, and NMβi-87.

Table 4. Metal ion retention capacity (MRC) for poly(Cl-PhMI-*co*-β-MHI) and poly(N-MG-*co*-β-MHI) at different copolymer compositions

Copolymer–metal ion complex	pH	Metal ion retention (%)							
		Cu(II)	Co (II)	Cr(III)	Ni(II)	Cd(III)	Pb(II)	Zn(II)	Fe(III)
CPhβi-13	3	15.3	2.0	7.0	20.0	21.5	15.0	26.0	28.0
CPhβi-15	5	20.0	24.2	21.0	45.0	38.5	26.0	34.5	32.0
CPhβi-17	7	90.0	79	75.0	85.0	89.5	81.0	88.5	90.0
CPhβi-33	3	10.0	9.5	1.5	17.0	13.0	8.7	14.4	15.9
CPhβi-35	5	23.0	14.5	11.5	32.0	23.5	16.8	32.3	37.5
CPhβi-37	7	88.5	69.5	67.5	79.5	83.5	80.0	84.3	78.5
CPhβi-53	3	0.0	2.5	0.0	12.0	4.0	4.0	4.5	9.0
CPhβi-55	5	15.0	10.5	10.2	25.0	22.0	15.0	21.5	25.0
CPhβi-57	7	65.0	62.5	70.0	80.0	81.0	70.0	72.0	75.0
NMβi-63	3	45	29	70	0.0	41.5	35.0	42.0	80
NMβi-65	5	100	97	100	95.0	98.5	100	94.5	100
NMβi-67	7	100	99	100	95.0	99.5	100	98.5	100
NMβi-83	3	30.5	26.5	60.0	0.0	29.5	50.5	33.5	95.0
NMβi-85	5	100	98.0	100	95.0	99.5	100	98.0	100
NMβi-87	7	100	100	100	100	99.5	100	99.5	100
NMβi-103	3	0.0	10.5	40.0	0.0	24.0	10.0	24.5	90
NMβi-105	5	95	90.5	100	90.0	92.0	95.0	91.5	95
NMβi-107	7	95	92.5	90.0	90.0	91.0	90.0	100	95

and 68%, respectively) when the copolymer is richest in Cl-PhMI units. Therefore, metal ion retention increases significantly, particularly for Cu(II), Co(II), Cd(II), Pb(II), Zn(II), and Fe(III), with an increase in pH for all the copolymer compositions. Thus, poly(Cl-PhMI-*co*-β-MHI) is an effective reagent for the separation of various metal ions at basic pH. At pH 3, this copolymer shows a low metal ion affinity, and the copolymers presented low retention values for all metal ions at the various copolymer compositions.

The metal ion retention values for all copolymers indicate that both comonomer units possess functional groups with metal ion affinity. This retention behavior can be attributed to two characteristics: the copolymer poly(Cl-PhMI-*co*-β-MHI) has one ionic monomer unit with different carboxylic acid functional groups in the side chain of its structure and it can exhibit strong metal ion binding attraction forces as an ionic polymer that also depend on the pH. Additionally, an interaction of the nitrogen atom from the imide group unit could occur, and could result in molecular complex formation. For this polymer–metal complex, the results suggest that the metal ion is bound to the nitrogen atom from the imide group, in which the absorption band (sharp) from N–C (stretching) at 1498 cm^{-1} shows an intensity decrease. The interaction of the imide and carboxylic groups with metal ions can lead to the formation of molecular complexes between the electron donor nitrogen of the imide and the carbonyl groups of the β-MHI.

Binding properties as a polychelatogen of poly(N-MG-co-β-MHI)

Poly(N-MG-*co*-β-MHI) presented better complexing properties than poly(Cl-PhMI-*co*-β-MHI), indicating that it is an effective reagent for separating various metal ions. In general, high complexation with poly(N-MG-*co*-β-MHI) takes place with all metal ions at pH 5 and 7. At pH 3, the copolymer has lower metal ion retention, except for Fe(III) (over 95%) (Table 4). These values increase at pH 5 and 7, when the copolymers are richest in N-MG monomer units, indicating a predominant pH influence. At pH 5 and 7, all the retention values are higher than 90%, indicating that metal ion retention increases significantly, particularly for Ni(II), Cd(III), Co(II), and Zn(II), with a pH increase for all the copolymer compositions. Thus, poly(N-MG-*co*-β-MHI) is an effective reagent for separating these metal ions and it shows better complexing properties than poly(N-MG).[35] In general for poly(N-MG-*co*-β-MHI), only high complexation takes place, except for Co(II), Ni(II), and Cd(II) at pH 3 when it presents a low metal ion affinity. At pH 3, the copolymers show low retention values for all metal ions except for Fe(III), Pb(II), and Cr(III) with values of 95, 50, and 60%, respectively.

The metal ion retention results for all copolymers show that both comonomer units possess approximately the same affinity towards the metal ions. The retention behavior can be attributed to the fact that poly(N-MG-*co*-β-MHI) has two ionic monomer units with different carboxylic functional groups in the side chain of its structure, and these can exhibit strong metal ion binding attraction forces, as ionic polymers or polyelectrolytes, which also depend on the pH. Additionally, an interaction of the nitrogen atom from the imide and carboxylic groups could occur to form a β-MHI unit, which can lead to molecular complex formation. According to the probable intramolecular complexation of the metal ions by the copolymer,

the corresponding functional groups of the copolymer chains are arranged around the metal ions.

MRC of polymer–Cu(II) ion complexes in basic medium

Copolymer–metal complexes with metal ion binding for both systems were investigated as a function of pH. The MRC of the copolymers at different copolymer composition presented no important differences. The MRC was highest for both copolymer systems at pH 5 and 7, and this result is related to the copolymer composition.

In this case, poly(Cl-PhMI-*co*-β-MHI) presents a lower MRC than poly(N-MG-*co*-β-MHI). This result supports the assumption that the chloroaryl group prevents the interaction with the metal by steric hindrance, and that it could form 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 toward the metal ions. Steric hindrance by Cl-PhMI units and the hydrophobic nature is known to limit the chelating reaction. The FTIR spectra of the complexes present an important change in the broad bands with respect to the copolymer: at 3447.3 cm^{-1} (OH–, –COOH); at 1772.4, 1703.2, and 1590.9 cm^{-1} in the C=O bands of the imide ring, the C=O from COO^- (ionization of COOH), and ester groups; and a change of these bands was observed at 1494.5, 1438.5, and 1389.5 cm^{-1} (C–N stretching). The interaction of both units can lead to the formation of molecular complexes with electron donor nitrogen from imide and carboxylate groups from COOH at basic pH (intramolecular complexes). The absorption bands at 1590.9 cm^{-1} (C=O from carboxylic acid) and at 1389.5 cm^{-1} (C–N stretching) predominantly coordinated around the Cu ions. The highest MRC for Cu(II) ions values were found at pH 5 and 7. The binding capacity for Cu(II) ions varied from 240 to 318 mg g^{-1}. The highest retention values for poly(N-MG-*co*-β-MHI) are obtained at pH 5 and 7 and are related to the copolymer composition (Table 5).

Table 5. Maximum retention capacity for poly(Cl-PhMI-*co*-β-MHI) and poly(N-MG-*co*-β-MHI) for Cu(II) ions at different pH

Copolymer–metal ion complex	m_1:m_2 (mol%)	pH	V (mL), 5 wt%	Cu^{2+} (mg) retentate	Binding capacity (mg g^{-1})
CPhβi-13	23:77	3	1.70	48.0	240.1
CPhβi-15	23:77	5	1.65	52.6	260.2
CPhβi-17	23:77	7	1.60	56.2	280.6
CPhβi-33	38:62	3	1.60	44.5	220.5
CPhβi-35	38:62	5	1.65	48.1	240.6
CPhβi-37	38:62	7	1.75	52.6	260.0
CPhβi-53	60:40	3	1.70	47.6	238.0
CPhβi-55	60:40	5	1.60	50.0	250.0
CPhβi-57	60:40	7	1.70	52.1	260.6
NMβi-63	25:75	3	1.65	54.0	270.2
NMβi-65	25:75	5	1.60	58.2	290.3
NMβi-67	25:75	7	1.65	60.1	300.3
NMβi-83	39:61	3	1.70	56.3	280.4
NMβi-85	39:61	5	1.65	60.1	300.4
NMβi-87	39:61	7	1.65	62.2	310.8
NMβi-103	56:44	3	1.60	58.1	290.0
NMβi-105	56:44	5	1.55	59.3	296.5
NMβi-107	56:44	7	1.55	63.8	318.8

Thermal behavior

The TGA results for poly(N-MG-*co*-β-MHI) and poly(Cl-PhMI-*co*-β-MHI) and their copolymer–metal ion complexes are summarized in Table 6. The copolymers of both systems presented single-step degradation, after first eliminating water or monomer residue as well as other low-molecular-weight impurities (Fig. 6). The resulting material has an extrapolated thermal decomposition temperature (TDTe) of about 280 °C. The poly(N-MG-*co*-β-MHI) copolymers present a lower TDTe than poly(Cl-PhMI-*co*-β-MHI) for the same copolymer composition (Table 6). For example, copolymer CPhβ-3 with a 50:50 (mol%) composition presents a TDTe higher than NMβ-8 for the same composition. Degradation at a lower temperature could be attributed to the increased number of end groups in low-molecular-weight polymers that act as initiating sites for degradation. The incorporation of a chloride group in arylmaleimide monomers decreased the TDTe values in the copolymers in comparison with poly(N-PhMI-*co*-β-MHI) previously published.[22]

Table 6. Thermal decomposition temperature and weight loss for copolymers and copolymer–metal ion complexes at different temperatures

Sample	pH	TDTe (°C)	Weight loss (%) at different temperatures						
			100 °C	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C
CPhβ-3		337	0.0	3.0	25.0	42.2	50.0	62.2	70.4
CPhβi-33	3	300	0.0	1.0	4.0	18.0	26.0	27.0	29.0
CPhβi-35	5	300	0.0	1.0	2.5	13.1	16.6	19.8	21.0
CPhβi-37	7	300	0.0	2.0	4.0	25.2	40.4	52.0	54.0
NMβ-8		283	2.0	13.2	27.8	48.9	61.3	69.8	74.7
NMβi-83	3	281	1.6	3.6	19.5	42.7	57.6	64.3	68.5
NMβi-85	5	290	1.9	4.2	26.1	54.1	65.5	76.4	83.4
NMβi-87	7	316	2.5	4.5	19.8	40.7	51.3	57.7	63.9

M_1 = Cl-PhMI or N-MG; M_2 = β-MHI; copolymer composition 50:50 of the copolymer CPhβ-3 and NMβ-8.

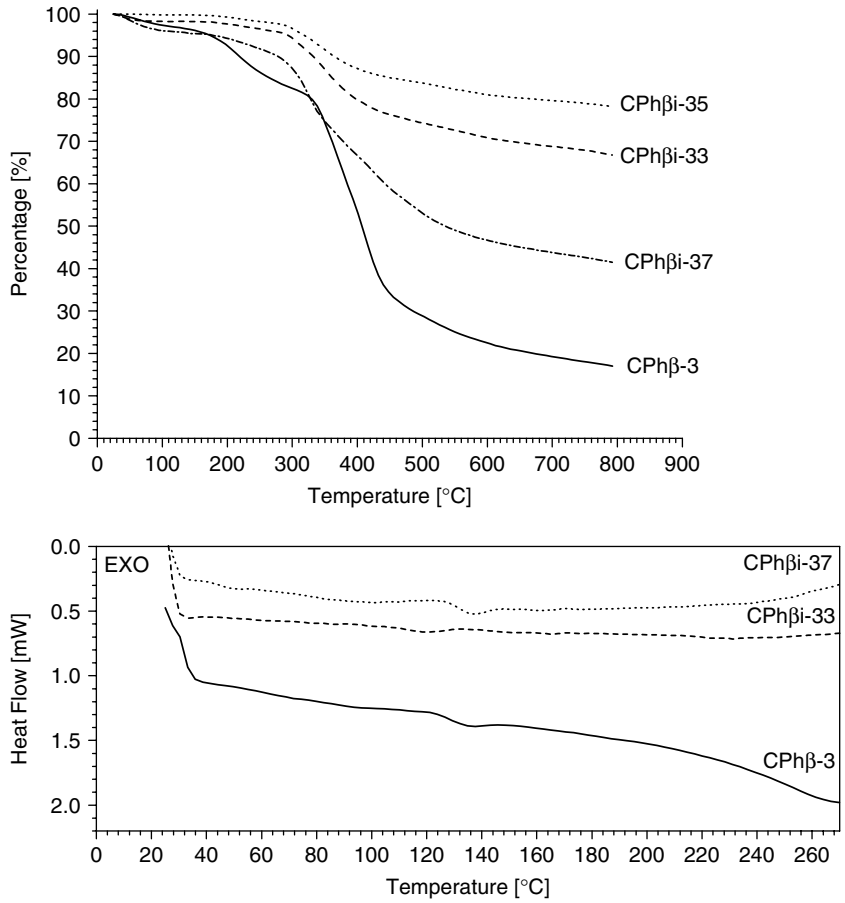


Figure 6. TGA/DSC thermograms of CPhβ-3 and polymer–metal complexes CPhβi-33, CPhβi-35, and CPhβi-37 at different pH. Heating rate: 10 °C min^{-1}.

The thermal stability increases on increasing the content of maleimide derivatives, and Cl-PhMI > N-MG, in the copolymers, which is due to the good thermal stability of maleimide polymers attributed to the polar five-member imide ring structure.[36]

The DSC thermograms for NMβ-8 and CPhβ-3 and their metal complexes at pH 3, 5, and 7 show T_g of 130–135 and 110–115 °C, respectively, which increases as the pH increases. The copolymer–metal complexes of CPhβ-3 presented a lower TDT in comparison with copolymer and NMβ-8 at pH 3 and 5, but not at pH 7. The highest weight loss for the copolymer CPhβ-3 and the complexes occurs between 350 and 500 °C (Table 6).

All copolymers synthesized presented a single T_g value indicating the formation of copolymers with a random tendency. A slight deviation of T_g for CPhβ-3 and the complexes can be observed (Fig. 6). The T_g values of all the complexes are higher than those of the copolymers, except for CPhβi-43.

CONCLUSIONS

Poly(Cl-PhMI-*co*-β-MHI) and poly(N-MG-*co*-β-MHI) were soluble in dimethylsulfoxide and acetone, and poly(N-MG-*co*-β-MHI) was soluble in water. The experimental data indicate that poly(Cl-PhMI-*co*-β-MHI) and poly(N-MG-*co*-β-MHI) can be considered as statistical copolymers with some tendency to alternation. The GPC results showed that both systems have a high polydispersity.

In general, poly(Cl-PhMI-*co*-β-MHI) and poly(N-MG-*co*-β-MHI) show a high metal ion retention for all metal ions at pH 7. At pH 3 and 5, the copolymer has a lower retention for the metal ions. These values increased at pH 7 where the copolymers were richest in β-MHI monomer units, indicating a predominant influence of the pH.

The highest MRC for Cu(II) ions was found at pH 5 and 7. The capacity to bind Cu(II) ions varied from 240 to 318 mg g^{-1}. The highest retention values for poly(N-MG-*co*-β-MHI) are obtained at pH 5 and 7 and are related to the copolymer composition.

The copolymer composition influenced both systems' TDT. Maleimide incorporation increases TDT and T_g values. The copolymer–metal complexes presented higher TDT than the copolymer.

The complexes' residue mass may be attributed to a higher percentage of metal incorporated at this pH. All synthesized copolymers present a single T_g value, indicating the formation of statistical copolymers.

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REFERENCES

1 Bharel R, Choudhary V, Varna IK and Wang FW, *J Appl Polym Sci* **49**:31 (1993).
2 Bharel R, Choudhary V, Varna IK and Wang FW, *J Appl Polym Sci* **54**:2165 (1994).
3 Bharel R, Choudhary V, Varna IK and Wang FW, *J Appl Polym Sci* **57**:767 (1995).
4 Choudhary V and Mishra A, *J Appl Polym Sci* **62**:707 (1996).
5 Rzaev ZMO, *Progr Polym Sci* **25**:163 (2000).
6 Morlay C, Cromer M, Mouginot M and Vittori O, *Talanta* **48**:1159 (1999).
7 Morlay C, Cromer M and Vittori O, *Water Res* **34**:455 (2000).
8 Mouginot Y, Morlay C, Cromer M and Vittori O, *Anal Chim Acta* **407**:337 (2000).
9 Ripperger KP and Alexandratos SD, *Stud Surf Sci Catal B* **120**:473 (1999).
10 Rivas BL, Pooley SA, Maturana HA and Villegas S, *Macromol Chem Phys* **202**:443 (2001).
11 George B, Pillai VNR and Mathew BJ, *J Appl Polym Sci* **74**:3432 (1999).
12 Beatty ST, Fischer RJ, Hagers DL and Rosenberg E, *Ind Eng Chem Res* **38**:4402 (1999).
13 Li W, Zhao H, Teasdale PR, John R and Zhang S, *React Funct Polym* **52**:31 (2002).
14 Denizli A, Kesenci K, Salih B, Senel S and Piskin E, *J Appl Polym Sci* **71**:1397 (1999).
15 Denizli A, Say R and Arica MY, *J Macromol Sci Pure Appl Chem* **37**:343 (2000).
16 Wang CC, Chang CY and Chen CY, *Macromol Chem Phys* **202**:882 (2001).
17 Saglam A, Bektas S, Patir S, Genc Ö and Denizli A, *React Funct Polym* **47**:185 (2001).
18 Chanda M and Rempel GL, *React Funct Polym* **35**:197 (1997).
19 Deng YL, Fan XD and Waterhouse J, *J Appl Polym Sci* **73**:1081 (1999).
20 Arvanitoyannis I, Nikolaou E and Yamamoto N, *Macromol Chem Phys* **196**:1129 (1995).
21 Disbudak A, Bektas S, Patir S, Genc Ö and Denizli A, *Sep Purif Technol* **26**:273 (2002).
22 Pizarro G del C, Marambio OG, Jeria-Orell M, Huerta MR and Rivas BL, *J Appl Polym Sci* **95**:1361 (2005).
23 Marambio OG, Pizarro G del C, Jeria-Orell M, Huerta MR, Olea-Azar C and Habicher WD, *J Polym Sci A: Polym Chem* **43**:4933 (2005).
24 Katime I and Rodríguez E, *J Macromol Sci Pure Appl Chem* **A38**:543 (2001).
25 Horak D, Benes MJ, Gumargalieva K and Zaikov G, *J Appl Polym Sci* **80**:913 (2001).
26 Cava M, Deano H and Muth K, *Org Synth* **41**:93 (1961).
27 Pizarro G del C, Rivas BL and Geckeler KE, *Bol Soc Chil Quim* **41**:181 (1996).
28 Baker RB and Shoes RE, *J Org Chem* **17**:297 (1974).
29 Tüdös F, Kelen T and Turcsanyi B, *J Polym Sci Polym Chem Ed* **15**:3047 (1977).
30 Pizarro G del C, Rivas BL and Geckeler KE, *J Macromol Sci Pure Appl Chem* **A34**:855 (1997).
31 Moreno-Villoslada I and Rivas BL, *J Membrane Sci* **215**:195 (2003).
32 Rivas BL, Schiappacasse LN, Pereira E and Moreno-Villoslada I, *J Chil Chem Soc* **49**:345 (2004).
33 Pizarro G del C, Rivas BL and Geckeler KE, *J Macromol Sci Pure Appl Chem* **A34**:1483 (1997).
34 Rivas BL, Pooley SA and Luna M, *J Appl Polym Sci* **83**:2556 (2002).
35 Pizarro G del C, Rivas BL and Geckeler KE, *Polym Bull* **37**:525 (1996).
36 Senel S, Rzaev ZMO and Piskin E, *Polym Int* **52**:713 (2003).