

Metal Ion Interaction of Water-Soluble Copolymers Containing Carboxylic Acid Groups in Aqueous Phase by Membrane Filtration Technique

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ABSTRACT: This article reports the synthesis of poly(*N*-maleoylglycine-*co*-itaconic acid) by radical copolymerization under different feed mole ratios and its properties to remove various metal ions, such as Cu(II), Cr(III), Co(II), Zn(II), Ni(II), Pb(II), Cd(II), and Fe(III), in aqueous phase with the liquid-phase polymer-based retention (LPR) technique. The interactions of inorganic ions with the hydrophilic water-soluble polymer were determined as a function of pH and filtration factor. Metal ion retention was found to strongly depend on the pH. Metal ion retention increased as pH and MG content units in the macromolecular backbone increased. The copolymers were characterized by elemental analysis, FTIR, ¹H-NMR, and ¹³C-NMR spectroscopy. Additionally, intrinsic viscosity, molecular weight, and polydispersity have been determined for the copolymers. Copoly-

mer and polymer-metal complex thermal behavior was studied using differential scanning calorimetry (DSC) and thermogravimetry (TG) techniques under nitrogen atmosphere. The thermal decomposition temperatures (TDT) were influenced by the copolymer composition. The copolymers present lower TDT than the polymer-metal complex with the same copolymer composition. All copolymers present a single T_g , indicating the formation of random copolymers. A slight deviation of the T_g for the copolymers and its complexes can be observed. The copolymer T_g is higher than the T_g value for the polymer-metal complexes. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2893–2902, 2007

Key words: hydrophilic polymers; polymer-metal complexes; membranes; thermal properties

INTRODUCTION

Industrial wastewater is the major source of environmental pollution. Heavy metals are among the most dangerous environmental pollutants because they are very toxic, even at low concentrations, because of the possible accumulation at different ecosystem levels. The use of hydrophilic polymers with complexing groups to remove heavy metals could be of great importance in environmental applications.^{1–9} Incorporation of amino acids into polymers has been reported in the literature.^{10–13} Idea of incorporating amino acids as metal chelating ligands is based on their reactivity with different chemical substances, including metal ions, and their high stability. For these reasons, we have focused our attention on the

development of amino acid-based copolymers to obtain hydrophilic polymers of great technological interest.^{14,15}

Metal ion purification and separation is possible in a continuous process homogeneous phase, using the technique called “Liquid-phase polymer based retention” (LPR) based on hydrophilic polymers that act as chelating compounds in liquid phase.^{15–18} The technique is based on the retention of the metal ions of interest, with the formation of a complex in a closed ultrafiltration system. Metal ions are measured using atomic absorption spectrometry through a series of filtrates. On the other hand, polymer-metal complexes are interesting because of the properties that these materials can acquire and their potential technological applications.^{19,20}

In this article, we report the synthesis and characterization of water-soluble poly(*N*-maleoylglycine-*co*-itaconic acid) as well as its binding ability to different metal ions in aqueous solution in conjunction with membrane filtration, by varying the pH and the filtration factor to analyze the copolymer and polymer-metal complexes’ thermal behavior.

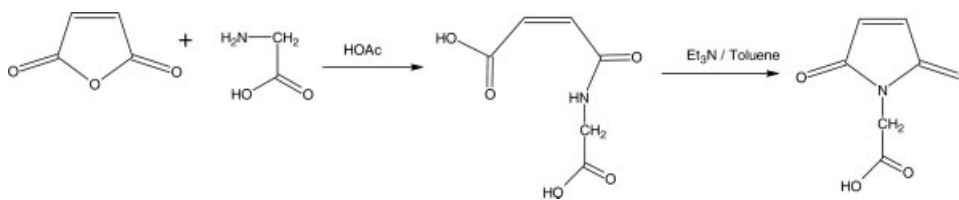
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EXPERIMENTAL

Chemicals

Itaconic acid (IA) (99.8%, Merck) was purified by crystallization. Benzoyl peroxide (BPO, Fluka) was purified by recrystallization from methanol. All salts



Procedure

A solution of maleic anhydride (0.425 mol) in 150 mL of acetic acid (AcOH, p.a., Merck) was placed in a 500-mL round bottom flask and a solution of glycine (0.425 mol) in AcOH (250 mL) was added. The mixture was stirred at room temperature for 3 h. The white precipitate was filtered, washed with cold water (50 mL), and dried until constant weight. The yield was 96.5%. The maleamic acid obtained was suspended in dried toluene (500 mL) and treated with triethylamine (Et_3N , 35.1 mmol). This solution was refluxed under vigorous stirring for 1 h, and the water was removed via a Dean-Stark apparatus (70°C). Toluene was removed by evaporation to produce triethylammonium salt. The solid product was acidified at pH 2 with HCl, extracted with EtAc, and dried with MgSO_4 . The EtAc was removed under vacuum to give *N*-maleoyl glycine. The yield of *N*-maleoyl glycine was 38% and m.p. $111\text{--}113^\circ\text{C}$. It was purified by recrystallization from chloroform.

Synthesis of the copolymers

The poly(*N*-maleoylglycine-*co*-itaconic acid) P(MG-*co*-IA) was synthesized varying the feed monomer ratio (3 : 1; 2 : 1; 1 : 1; 1 : 2, and 1 : 3), whereas maintaining constant the total amount of mol (0.020), using 0.5 mol % of BPO as the initiator and tetrahydrofuran (THF) as solvent (8 mL). The substances were placed in a copolymerization flask under nitrogen atmosphere (N_2). This flask was vacuum sealed (10^{-3} mmHg) and placed in a temperature-controlled oil bath at 70°C for 2 h. Copolymer yield ranged between 50 and 60%. The copolymers were soluble in water, dimethylsulfoxide, acetone, and chloroform.

Measurements

Metal ion concentration was determined with a Perkin-Elmer 1100 Atomic Absorption Spectrometer (Perkin-Elmer, Shelton, CT). Intrinsic viscosity was

were of analytical grade and used as received and purchased from Fluka and Merck p.a. grade.

N-maleoyl glycine (MG) was prepared following a published method,²¹ reacting maleic anhydride with glycine in diethyl ether. The reaction scheme for monomer preparation is shown below:

determined with an Ostwald viscometer at (30 ± 0.1) $^\circ\text{C}$ using water as solvent (0.1M NaCl).

To dry the samples, a "continuous freeze dryer" (Lab CONCO 6L, Karl-Heinz Müller, Labordedorf GmbH, USA) was used. The pH was determined with a Hanna pH-meter 211 (Miami, USA). For the LPR technique, a membrane filtration system (Amicon, Millipore, USA) was employed to test the coordinating properties of the poly(MG-*co*-IA) as a polychelator. The elemental analyses were performed using an analyzer instrument CE model Fison 1108 (Italy). $^1\text{H-NMR}$ spectra were recorded on a Bruker MSL 500 spectrometer (Bruker; Karlsruhe, Germany) using DMSO-d_6 (99.8%). FTIR spectra were recorded on a Bruker Vector 22 (Bruker Optics, Inc). The number-average (M_n), weight-average molecular weight (M_w), and the molecular weight distribution (polydispersity, M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) under the following conditions: WATERS 600E instrument equipped with UV and RI detectors, using chloroform as solvent (flow rate: 1.0 mL/min). The samples were measured at 30°C with a concentration of 6 mg/mL and calibration was done using poly(methyl methacrylate) (PMMA). Metal ion concentrations were measured on a Perkin-Elmer 3100 Atomic Absorption Spectrophotometer (Perkin-Elmer, Shelton, CT). Thermal stability studies were performed using a Mettler Toledo Star System thermogravimetric analyzer (TGA) at a heating rate of $10^\circ\text{C min}^{-1}$. DSC measurements were carried out with a Mettler Toledo Star System 822e (Spain) to determine the glass transition temperature (T_g) of the copolymer and their polymer-metal ions complexes. The T_g was measured with a heating rate of $10^\circ\text{C min}^{-1}$.

Complexation procedure

For the determination of the complex binding capacity, the copolymer (200 mg) was dissolved in 10 mL water and adjusted to the corresponding pH

TABLE I
Radical Copolymerization of MG (M_1) and IA (M_2)^a at Low Conversion^a

Feed monomer ratio (mol %), copolymers 1-5		Elemental analysis (%)			Copolymer composition (%)		Parameters of KT-equation		Yield (%)
M_1	M_2	C	H	N	m_1	m_2	ε	η	
75	25	46.34	3.79	5.53	58	42	0.987	0.059	51.2
66	34	46.33	3.85	5.09	52	48	0.961	0.021	52.4
50	50	46.29	4.04	3.93	39	61	0.888	-0.250	56.5
34	66	46.25	4.23	2.71	26	74	0.728	-0.804	52.4
25	75	46.23	4.32	2.15	20	80	0.609	-1.215	51.8

^a Reaction conditions: Solvent, dioxane, 70°C ± 1°C, initiator, [BPO] = 1.25 10⁻²M, [M] total = 2.5M.

with the addition of dilute nitric acid or sodium hydroxide. The aqueous solutions of polymer and metal nitrates or chloride (20 mg L⁻¹) were placed into the membrane filtration cell. The total volume in the cell was kept constant at 20 mL. The reservoir contained water adjusted to the cell solution's pH. A membrane with an exclusion limit of 10,000 g mol⁻¹ (Amicon PM 10 or equivalent) 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 metal ion concentrations in the filtrate and the retentate were determined by 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.

RESULTS AND DISCUSSION

Synthesis and characterization of the copolymers and complexes

The *N*-maleoyl glycine (MG) was copolymerized with itaconic acid (IA) in tetrahydrofuran (THF) under several feed-monomer ratios. The results are

summarized in Table I. The copolymers were soluble in water, dimethylsulfoxide, acetone, and chloroform. The poly(MG-co-IA) is a water-soluble copolymer included in the class of synthetic polyelectrolyte (see Fig. 1).

The yield of poly (MG-co-IA) ranged between 50 and 60%. The FTIR spectra of copolymers show basically the absorption bands at 3464 cm⁻¹ (-OH; -COOH, broad band); 2988 cm⁻¹ (-CH, -CH₂ stretching); 1777 cm⁻¹ (C=O, imide, stretching); 1703.0 cm⁻¹ (C=O, -COOH stretching from IA), 1498.6 cm⁻¹ (N-C stretching from imide ring). The FTIR spectra of the polymer metal complexes show an important change of the broad band at 3446.5 cm⁻¹ (-OH; -COOH, broad band) and 2951.2 cm⁻¹ (-CH, -CH₂ stretching), which could be attributed to the interaction of this carboxylic acid groups with the metal ions. The absorption band at 1772.4 cm⁻¹ (C=O, imide, stretching) decreased in intensity for the complexes; 1698.7 cm⁻¹ (C=O, -COOH stretching from IA). This result indicates that this function is also involved in the polymer-metal ion interaction. The polymer-metal complexes showed two new absorption bands at 1605.9 and 1385.8 cm⁻¹ with higher intensity. This should be because of the coordination of the metal ions with the carboxylate groups from IA units and the nitro-

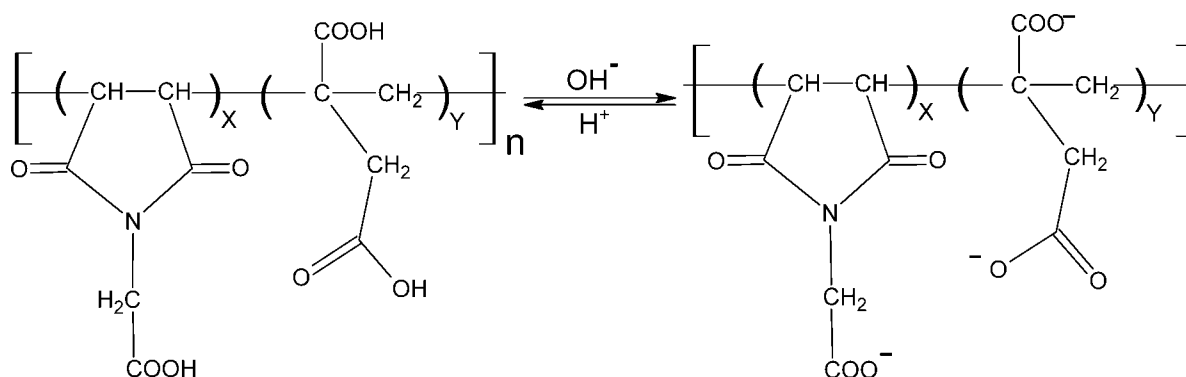


Figure 1 Acid-base equilibrium for the copolymer poly(*N*-maleoylglycine-co-itaconic acid) poly(MG-co-IA)-3.

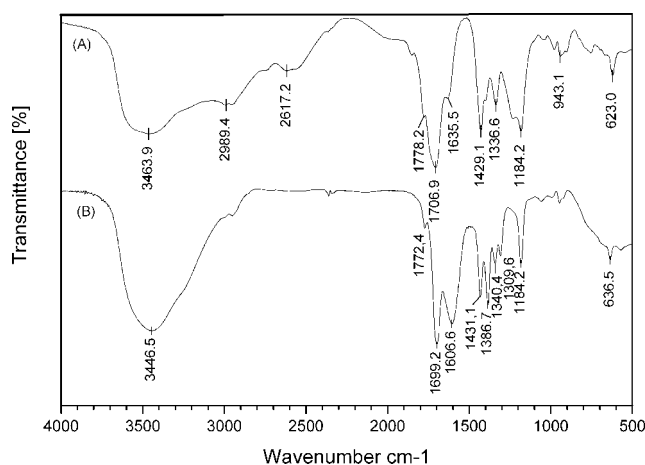


Figure 2 FTIR spectra of A: poly(*N*-maleoylglycine-*co*-itaconic acid), poly(MG-*co*-IA)-3; B: polymer-metal complex at pH 7.

gen atom from imide at higher pH, which can lead to the formation of molecular complexes between the imide's electron donor nitrogen and the itaconic acid's carbonyl groups [see Fig. 2(A,B)].

The $^1\text{H-NMR}$ spectra for the copolymers present the following signals (δ in ppm): 2.3 [2H, CH_2 —] from the backbone, 2.6–3.5 [2H, —CH—] of imide, 3.5–3.9 [2H, — CH_2 —COOH] from IA and 3.8–4.3 [2H, — CH_2 COOH] of MG; the signal at 4.7 ppm corresponds to the solvent. For all copolymers, the intensity of each peak varied according to the copolymer composition (see Fig. 3).

The copolymer structure was also confirmed by $^{13}\text{C-NMR}$ spectra, which presented the following signals (δ in ppm): 25 and 30 [— CH_2 — of backbone]; 40–42 [— CH_2 COOH] of IA; 68 [—CH—] of imide groups, and at 70 [— CH_2 —COOH] of the monomer MG, 170–190 were assigned [—C=O] from imide and [—COOH] of the IA, respectively.

The copolymer composition of poly(MG-*co*-IA) was determined from the N/C ratio on the basis of elemental analysis data for the copolymers 1–5 (see Table I).

Metal ion interaction of the copolymer

The metal ion retention results for all the studied copolymers show that both comonomer units have approximately the same metal ion affinity. The retention behavior can be attributed to that the copolymer P(MG-*co*-IA) has two ionic monomer units with different carboxylic acid functional groups in the side chain of its structure. These ionic monomer units can exhibit strong metal ion binding attraction forces as ionic polymers or polyelectrolytes, characteristics that also depend on the pH. Additionally, an interaction could exist between the nitrogen atom from imide and carboxylic groups and from IA unit, possibly

leading to the formation of molecular complexes.²² 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. The interaction of the nitrogen atom from MG and carboxylic groups can lead to the formation of molecular complexes between the electron donor nitrogen from MG and the carbonyl or carboxylate groups from IA at different pH (see Scheme 1).

The FTIR spectra of the copolymer-metal complexes show an important change of the broad band at 3446.5 and 2989.4 cm^{-1} , respectively, which could be attributed to the interaction of the hydroxyl groups from carboxylic acid groups in the complexes. The C=O band of imide and carboxylic group at 1778.2 and 1706.9 cm^{-1} were increased in the intensity for the complexes with the metal ion respectively, and a displacement of the signs is also observed. This is attributed to the interaction between the carboxylate groups and the metal ions at higher pH. In addition, the complexes at pH 5 and 7 show a new band at 1606.6 and 1386.7 cm^{-1} because of the coordination of the metal ions with the carboxylate and nitrogen of the imide group, respectively. In the last one with higher intensity, the interaction of the nitrogen atom from imide and carboxylate groups can lead to the formation of molecular complexes between the electron donor nitrogen from imide and the carbonyl or carboxylate groups from itaconic acid (see Scheme 1). At pH 3, the FTIR spectra show change in the intensity and broadening of the sings at band at 3446.5 and 2989.4 cm^{-1} and at 1706.9 cm^{-1} , respectively, for the complexes with the metal ion. A slight displacement of the signs is also observed, and this could be mean that those functional groups have a participation in the complex-formation.

Monomer reactivity ratios

The monomer reactivity ratio values for the copolymerization of MG and IA were determined from the

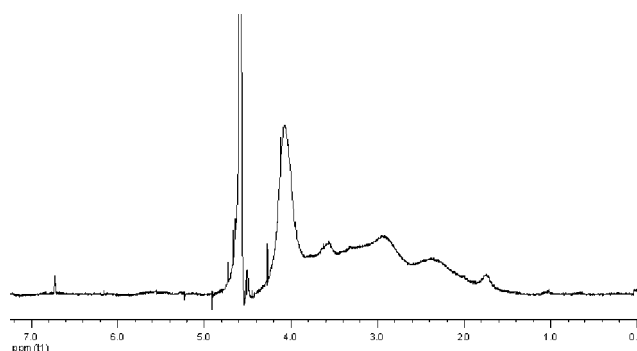
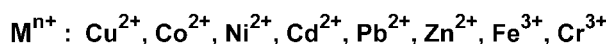
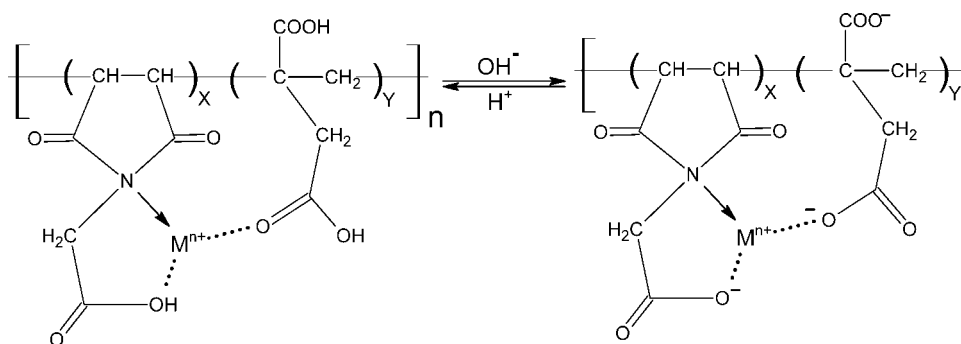


Figure 3 $^1\text{H-NMR}$ spectrum of poly(*N*-maleoylglycine-*co*-itaconic acid), poly(MG-*co*-IA)-3.



Scheme 1 Interaction poly(MG-co-IA) with metal ions.

copolymer composition. Monomer reactivity ratios for the system were calculated using the low-conversion method reported by Kelen Tüdös²³ (see Table I). System behavior was evaluated with a plot of the copolymer composition (F) versus feed composition (f) (see Fig. 4). The incorporation ratios were calculated from elemental analysis, giving best values and yielded reactivity ratios for $r_1 = 0.130$ (MG) and $r_2 = 1.13$ (IA), respectively, and $r_1 \times r_2 = 0.15$. The resulting values r_1 and r_2 upon applying the Kelen Tüdös method to the data for all copolymerization systems indicate that the monomers MG present a different reactivity toward the other comonomer, where IA has a strong tendency toward homodyad formation.

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

The GPC results in Table II show that the copolymers 1, 3, and 5 resulted in polymers with relatively high polydispersity values (PD = 1.59–1.70).

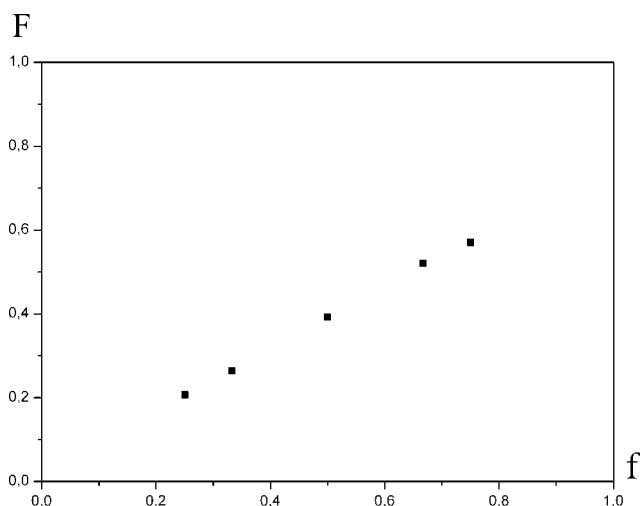


Figure 4 Copolymer composition (F) versus feed monomer composition (f).

Interactions with metal ions of poly(P(MG-co-IA) at different pH

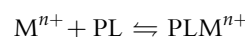
The P(MG-co-IA) copolymers are obtained from counts present in the macromolecule with electrolyte, MG, and IA characteristics. P(MG-co-IA)'s metal ion complexing properties were investigated using the LPR technique at pH 3, 5, and 7 with eight metal ions. For the washing and enrichment methods, metal 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 (the cell solution volume, V_c after a filtrate volume V_f has been passed), is another convenient characteristic of the process.^{24,25}

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

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



where, PL = poly(MG-co-IA) with pendant ligand L at the chain; M^{n+} , metal ion; PLM^{n+} , polymer-metal complexes.

TABLE II
The Molar Mass Distributions of Copolymers by GPC Curves

Sample designation	$M_{w, \text{GPC}} \times 10^4$ (g/mol)	$M_{n, \text{GPC}} \times 10^4$ (g/mol)	PD (M_w/M_n)
Copolymer-1	3.305	1.94	1.70
Copolymer-2	3.510	2.10	1.67
Copolymer-3	3.195	2.0	1.59

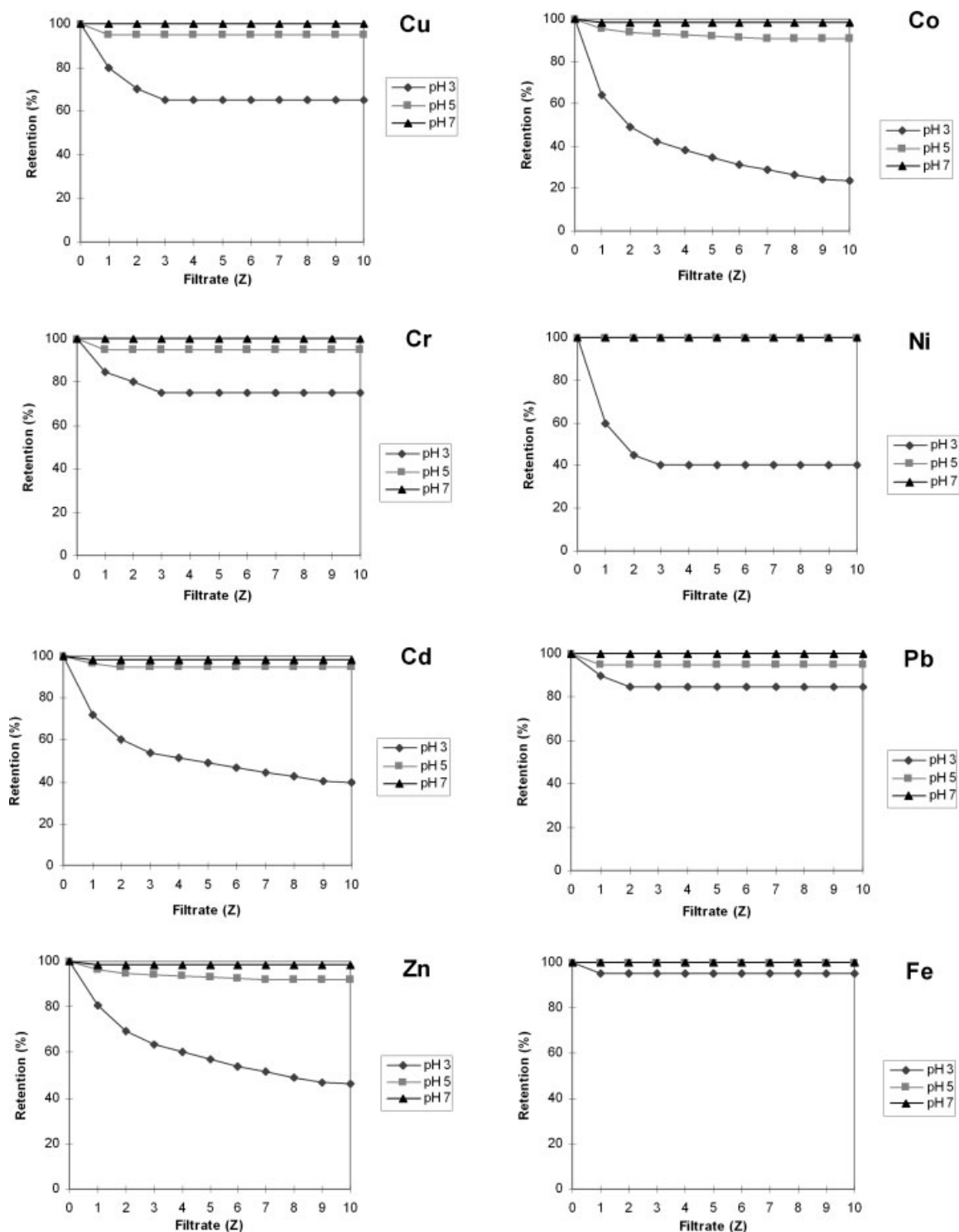


Figure 5 Typical metal-ion retention profiles of poly(*N*-maleoylglycine-*co*-itaconic acid), P(MG-*co*-IA)-2.

In systems with a lower inorganic ion concentration in comparison with the polymer, only the formation of PLM^{n+} may be taken into account. The concentration of metal ions that does not form complexes with the polymer is determined in the volume V_c by two processes: the previous reaction and the irreversible transfer of M^{n+} through the membrane.

Typical retention profiles for P(MG-*co*-IA) is shown in Figure 5. Poly(*N*-maleoylglycine-*co*-itaconic acid) presented higher complexing properties than poly(MG),¹⁴ which is an effective reagent for the separation of various metal ions. The carboxylic acids from IA as electrophilic monomer with two electron donating groups should be a better ligand group

TABLE III
Metal-Ion Retention (R%) of Poly(MG-co-IA)1-5 for Different Copolymer Compositions

Copolymer composition MG/IA, m_1/m_2	Metal ions								
	pH	Cu(II)	Co(II)	Cr(III)	Ni(II)	Cd(II)	Pb(II)	Zn(II)	Fe(III)
Copolymer 1, 57/43	3	78	24	95	25	57	89	56	99
	5	99	95	99	99	99	94	99	99
	7	99	98	99	99	99	98	99	99
Copolymer 2, 52/48	3	65	24	75	40	40	85	46	95
	5	95	91	95	99	95	95	92	99
	7	99	99	99	99	98	99	99	99
Copolymer 3, 39/61	3	68	45	24	10	10	90	10	93
	5	99	99	99	99	99	87	99	99
	7	94	91	86	93	94	96	95	92
Copolymer 4, 26/74	3	75	16	45	20	28	60	45	95
	5	95	92	95	95	96	95	92	95
	7	95	92	90	95	95	99	96	95
Copolymer 5, 20/80	3	71	45	71	20	29	84	23	98
	5	99	97	99	99	99	95	99	99
	7	99	99	99	99	99	97	99	99

reagent than MG when it exhibits only one carboxylic acid group. The copolymer contains carboxylic acid and imide as potential ligand groups with well-known chelating properties. Consequently, a cooperative effect between the different functional groups facilitating interactions with the metal ions is likely in this polymer.

In general, a high complexation with P(MG-co-IA) (copolymers 1-5) takes place with all metal ions at pH 5 and 7. At pH 3, the retention is lower than that at a higher pH, except for Fe(III) and Pb(II), Cr(III), and Cu(II). At pH 3, the copolymers 1-3 present a lower retention for the metal ions, for example copolymer 1, for Co(II) (24%) and Ni(II) (25%), copolymer-2 for Co(II) 24% and higher percentage for Ni(II) (over 40%) (see Fig. 5). Copolymer-3 presented low retention values for all metal ions, for example Ni(II) (10%) and Cd(III) (10%), except for Fe(III), Pb(II), and Cu(II) 93, 90, and 68% respectively. These values increased at pH 5 and 7 (see Table III) when the copolymers were rich in both unit monomers because of the more pronounced ionic interaction as

the pH was increased. Therefore, a predominant influence is observed at pH 5 and 7.

For example at pH 3 and factor of filtration $Z = 10$, copolymer-4 presented a low retention value for all metal ions including Cr(III) (45.0%) and Pb(II) (60.0%), whereas the highest value found corresponds to Fe(III) (95%) at $Z = 10$. At pH 5 and 7, all the retention values are higher than 90%. Therefore, metal ion retention increases significantly, particularly for Ni(II), Cd(III), Co(II), and Zn(II) with a pH increase for all the different copolymer composition. Thus, P(MG-co-IA) is an effective reagent for the separation of various metal ions. In general, only high complexation with P(MG-co-IA) takes place, except for a low metal ion affinity demonstrated by Co(II), Ni(II), and Cd(II) at pH 3.

Intrinsic viscosity

The variation of the molecular shape leads to an alteration of the viscosity,²⁶ where the viscosity behavior of poly(MG-co-IA) in water can be studied

TABLE IV
Intrinsic Viscosity for the Copolymers and Copolymer-Metal Complexes

pH	Copolymer (1, 3, 5), [η] (g dL ⁻¹)	Copolymer metal-complexes		Copolymer composition (mol %)
		Sample designation	[η] g dL ⁻¹	
3	0.080	1.3	0.150	58 : 42
5	0.110	1.5	0.240	
7	0.130	1.7	0.210	
3	0.080	3.3	0.090	39 : 61
5	0.120	3.5	0.150	
7	0.130	3.7	0.180	
3	0.090	5.3	0.140	20 : 80
5	0.100	5.5	0.180	
7	0.100	5.7	0.210	

TABLE V
Thermal Decomposition Temperature and Weight Loss at 800 °C for Poly(MG-co-IA) and the Copolymer–Metal-Ion Complexes at Different pHs

Sample designation	TDTe (°C)	Weight loss (%) at 800 (°C)
Copolymer 1	297.4	72.6
Complex 1.3	305.7	77.0
Complex 1.7	320.5	66.9
Copolymer 3	288.0	76.8
Complex 3.3	294.8	80.6
Complex 3.7	326.9	64.5
Copolymer 5	164.2	46.2
Complex 5.3	164.1	78.3
Complex 5.7	189.6	61.2

TDTe, extrapolated thermal decomposition temperature.

from the plot η_{sp}/C in function of C by extrapolation to infinite dilution. To verify the differences among the hydrodynamic volumes of the copolymer and the polymer–metal complex, the intrinsic viscosity is determined at different pHs and copolymer compositions. The intrinsic viscosity of the solutions with a defined ionic strength (0.1M NaCl) and the copolymer–metal ion was measured at pH 3, 5, and 7 (see Table IV). The results show that the intrinsic viscosity of the solutions depends on the pH and the high-

est value was found at pH 7. In both cases, it increased in the presence of the metal ions. At pH 5 and 7, the intrinsic viscosity of the copolymers is generally increased in the presence of the metal ions. This behavior can be attributed to a weakening of the chains' intramolecular hydrogen bonding attraction because of an increase of the degree of ionization of the copolymer at higher pH (5 and 7), where these corresponding carboxylate as functional groups present ionic interaction with the metal ions that can be intramolecular or intermolecular of the copolymer chains and these are arranged around the metal ions, causing a variation of the molecular shape that leads to an alteration of the viscosity.

Thermal behavior

The incorporation of MG into the copolymer increased the thermal decomposition temperature (TDT) values. The thermal stability increases with increased MG content in the copolymer, which could be because of the maleimide polymers that have good thermal stability because of the polar five-member imide ring structure²⁷ In this case, copolymers 1 and 3 show a higher TDT than copolymer 5. Increasing the MG content increases the onset decomposition temperatures.

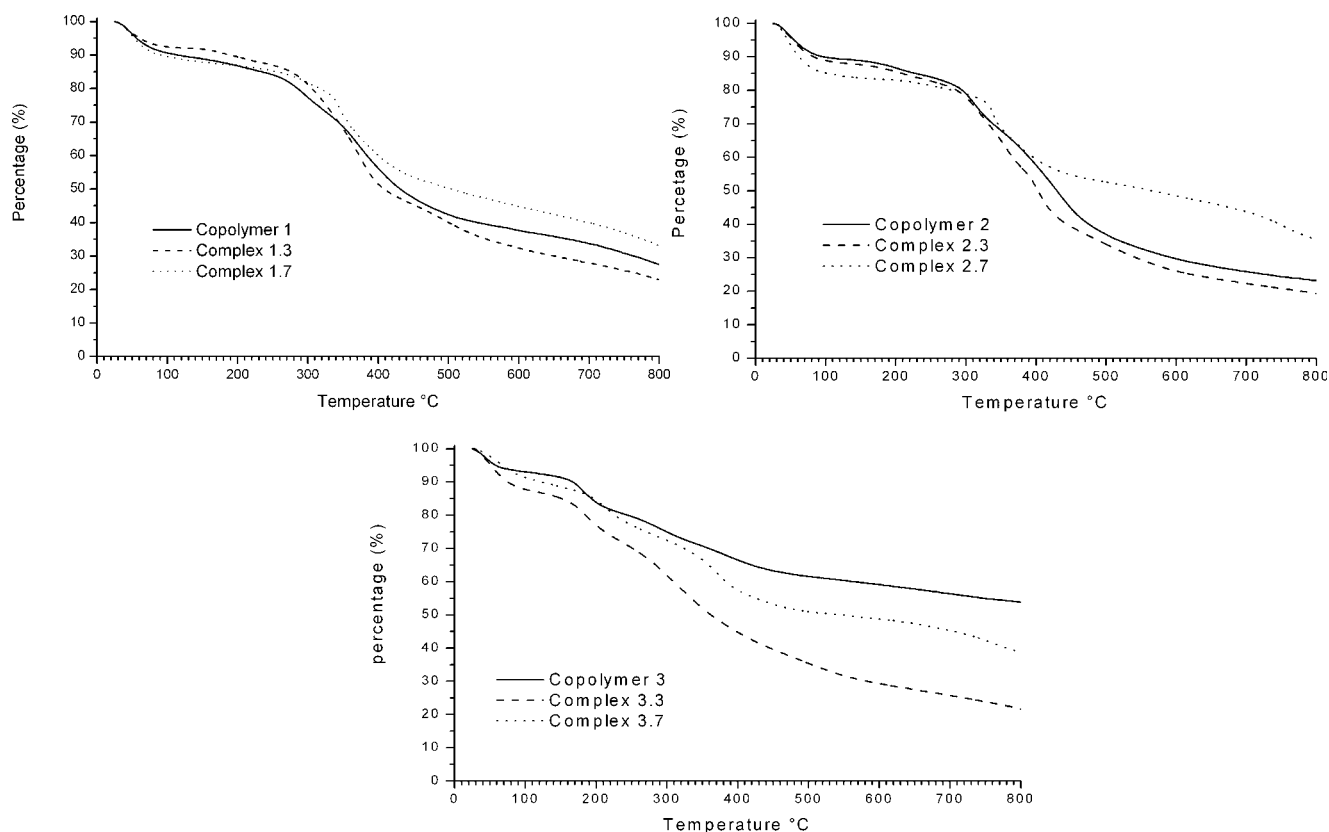


Figure 6 Thermograms for copolymers 1–3 and their complexes at pH 3 and 7. Heating rate $10^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere.

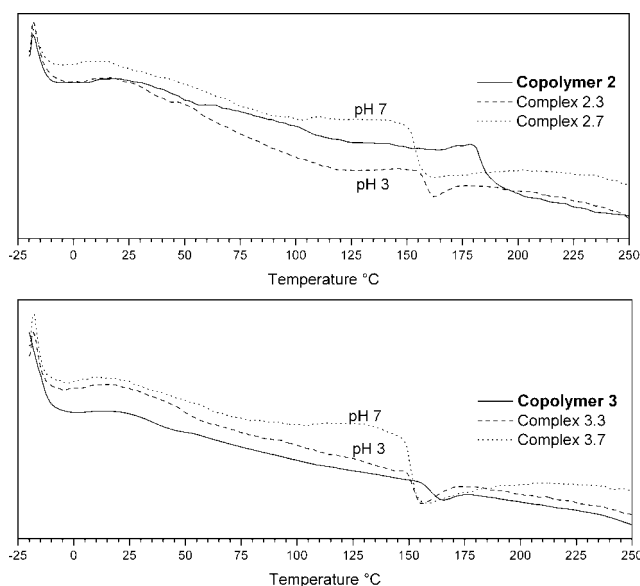


Figure 7 DSC thermograms for copolymers 2 and 3 and their polymer-metal complexes at pH 3 and 7, glass transition temperature (T_g). Heating rate $10^\circ\text{C min}^{-1}$ in nitrogen atmosphere.

The copolymers show lower TDT than for a complex with the same copolymer composition (Table V summarizes and Figure 6 shows the data). This result can be attributed to that the lineal poly(MG-co-IA), which presents in its structure a high percentage of an intra- and intermolecular bonding-metal reactions because of a higher percentage of metal ion bonding to comonomer units.

Copolymer 3, with a copolymer composition 39 : 61 mol %, shows a lower TDT than that of copolymers 1 and 2. Additionally, at a different pH and in contact with metal ions, it presents a TDT higher (at pH 7) or similar (at pH 3) to the TDTs for a copolymer without metal ions.

Glass transition temperature

The glass transition temperature (T_g) was estimated from the second DSC run. The T_g values for copolymers 2 and 3 and their polymer-metal complexes formed at different pH are shown in Figure 7.

All copolymers show a single T_g , indicating the formation of random copolymers. The T_g of the copolymers 1–5 varied from 150 to 180°C , and it decreases with increasing IA content in the copolymer. A slight deviation of the T_g for the copolymers 2 and 3 and its complexes can be observed. The T_g of copolymer 2 is higher than the T_g value for the polymer-metal complexes. The T_g for these complexes presents a slight decrease in the T_g value from pH 3 to pH 7.

CONCLUSIONS

P(MG-co-IA) is an effective reagent for separating various metal ions. In general, only high complexation with P(MG-co-IA) takes place, except for Co(II), Ni(II), and Cd(II) at pH 3 when it shows a low metal ion affinity. Its metal ion affinity has a strong dependency on the pH since when the pH is increased, metal ion affinity also increased. Only a slight influence was observed because of copolymer composition.

Intrinsic viscosity increased in the presence of metal ions and also depends on the pH with the highest value of retention capacity being found at pH 7. This behavior can be attributed to a weakening of the hydrogen binding attraction forces of the intramolecular chain and because of the formation of the carboxylate groups.

Thermal stability increases as the MG content in the copolymer increases. Increasing the MG content leads to an increase in the onset decomposition temperatures. The thermal decomposition temperatures of poly(MG-co-IA) were influenced by the copolymer composition. At different pHs, the copolymers showed lower TDT than the complex ones for the same copolymer composition.

All copolymers showed a single T_g . The T_g of the copolymers 1–5 varied between 150 and 180°C and decreased with increasing IA concentration in the copolymer.

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