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ORIGINAL PAPER

Free radical copolymerization of functional water-soluble poly(*N*-maleoylglycine-*co*-crotonic acid): polymer metal ion retention capacity, electrochemical, and thermal behavior

Oscar G. Marambio · Julio Sánchez · Guadalupe del C. Pizarro · Manuel Jeria-Orell · Bernabé L. Rivas

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Abstract In this study, the water-soluble polymers of *N*-maleoyl glycine (MG) with crotonic acid (CA) were copolymerized by free radical polymerization to obtain hydrophilic polymers, in order to study the effect of the functional groups in the copolymers on the metal ion retention capacity, electrochemical and thermal behavior, since that important requirements for their use in technological applications are: high solubility in water, chemical stability, a high affinity for one or more metal ions, and selectivity for the metal ion of interest. The metal complexation properties of poly(MG-*co*-CA) for the metal ions were investigated at pH 3, 5, and 7 in aqueous solution. The metal ion investigated were: Cu(II), Co(II), Cr(III), Ni(II), Cd(II), Zn(II), and Fe(III). The polymeric systems showed high metal ion retention for Zn (II) and Fe(III) at different pH. At different pHs, the MRC of the poly(MG-*co*-CA) for Fe(III) ions varied from 122.1 to 146.2 mg/g and from 120.5 to 133.5 mg/g, (samples 1 and 2 at pH 3 and 7, respectively). The MRC had the highest retention values for both copolymer systems at pH 7. The copolymers presented higher thermal decomposition temperature (TDT) in comparison with copolymer–metal complexes at pH 3 and 5. The cyclic voltammetry (CV) for poly(MG-*co*-CA) (20 mM) was compared with the CV of the [poly(MG-*co*-CA)–Fe(III)] copolymer complex. Moreover, [poly(MG-*co*-CA)–Fe(III)] showed a redox wave difference between +0.25 and +0.50 V possibly due to the presence of metal complexed with the polymer. The electrochemical characterization of the copolymer poly(MG-*co*-AC) shown the reduction of carboxylic acid groups of the

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N-maleoylglycine and crotonic acid moiety to hydroxyl group. The results support the assumption that the copolymer presents convenient electroactivity.

Keywords Radical polymerization · Hydrophilic polymer · Metal–polymer complexes · Electrochemical and thermal behavior

Introduction

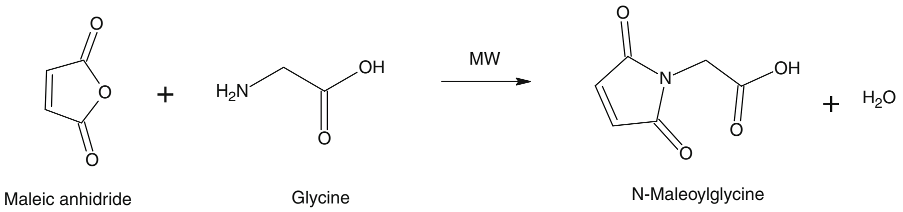
Water-soluble polymers (WSP)s are commercially available and the most important requirements for their use in technological applications are: high solubility in water, easy and inexpensive synthesis, an adequate molecular weight and molecular weight distribution, chemical stability, a high affinity for one or more metal ions, and selectivity for the metal ion of interest [1]. Heavy metal removal using hydrophilic polymers with complexing groups could be of great importance in environmental applications [2–9]. Maleimide polymers have good environmental stability [10–13] and these polymers are increasingly used in outdoor applications where environmental conditions influence their performance. There is a growing interest to synthesize 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 polychelatogens [16]. We have published the binding-metal ion properties for the systems poly(*N*-maleoyl glycine-*co*-itaconic acid) [17], poly(*N*-maleoylglycine-*co*-acrylic acid) [18], and poly(OH-/Cl-phenylmaleimide-*co*-2-hydroxypropylmethacrylate) [19], where the MRC determined at different pH indicated that the resins' metal complexing capacity depends not only on the ligand groups' nature but also on metal ion accessibility.

In this study, we report the synthesis of the water-soluble copolymers of *N*-maleoylglycine (MG) with crotonic acid (CA) by free radical polymerization, commercially available, and a study on their binding properties with different metal ion at different pH and specifically with Fe^{3+}, as well as a study of the effect of metal ion content on electrochemical behavior and thermal properties. The interest to study this water-soluble copolymer is due to important requirements of new materials for technological applications [20, 21].

Experimental

Materials

Maleic anhydride and glycine (purchased from the Merck-Schuchardt OHG chemicals, Germany) were purified by crystallization. Benzoyl peroxide (BPO) was purchased from Aldrich chemicals, CHEMIE GmbH, and Merck-Schuchardt, Germany). Chloroform, tetrahydrofuran (THF), and methanol were used as received, all reagents are analytical pure grade. The metal ions were used from



Scheme 1 Reaction by condensing functionalized amines with maleic anhydride

titrisol ampoules (Merck) as salts: $CrCl_3$, $CdCl_2$, $CoCl_2$, $NiCl_2$, $CuSO_4$, $FeCl_3$, and $ZnCl_2$, as CertiPUR grade. All salts were of analytical grade and used as received. Crotonic acid (CA) was purchased from Sigma.

Maleoyl glycine (MG) was synthesized from maleic anhydride and glycine (Merck-Schuchardt) following the published general microwave procedure [22], illustrated in Scheme 1.

Procedure

Equimolar amounts of maleic anhydride and glycine were placed in an Erlenmeyer flask with a loose small beaker cap and irradiated by setting the power range to medium high (70% of total power) in a domestic microwave oven for 2.5 min. The reaction mixture turned red. After irradiation, the reaction mixtures were cooled and extracted with methanol and absorbed in a small amount of silica gel column. Then, to remove the solvents, they were placed in a rotatory evaporator under reduced pressure until obtaining a fine powder. The fine powder was placed on top of the column of absorbent (silica gel column) and purified using a mixture solvent (5:95 methanol/chloroform). The maleimide was analyzed by TLC (with internal standard). Yield 40.0% of ***N***-maleoylglycine.

Preparation of polymers

The copolymers were synthesized by free radical polymerization with a 0.75:0.25 and 0.50:0.50 feed monomer composition in solution (THF) using 0.5 mol% of benzoyl peroxide (BPO) as initiator. A typical procedure for the copolymerization reaction was as follows: the mixture of MG with CA (20 mmol) was dissolved in THF (7 mL) and BPO as initiator (57.8 μmol). A 2.86 M solution of monomers in THF was placed in a copolymerization flask under N_2 and was sealed in vacuum (10^{-3} mmHg), maintaining constant the total amount of comonomers in the different systems. The flask was kept in a controlled temperature oil bath at 70 °C for 16 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, Inc., Ettlingen, Germany). The ^{1}H-NMR spectra were recorded in solution at room temperature with a Bruker AC 250 (Bruker, Karlsruhe-Germany) spectrometer using (D_2O, 99.8%). The concentration of the metal 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(MG-*co*-CA) were calculated by using elemental analysis data (from the nitrogen content). The number-average (M_n) and weight-average (M_w) for molecular weight and the molecular weight distribution (polydispersity, M_w/M_n) of the polymers were determined by size-exclusion chromatography (SEC), under the following conditions: WATERS 600E instrument equipped with UV and RI detectors, using THF 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 performed using poly(styrene) (PSt).

Complexation procedure

The polymer–metal complexes were prepared by adding an aqueous solution (2 wt%) of the copolymer (200 mg) previously adjusted to the corresponding pH by adding dilute nitric acid or sodium hydroxide. The aqueous solution of polymer and metal chlorides (20 mg L^{-1}) solution were placed into the membrane filtration cell of the ultrafiltration system. 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^{-1}. 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 solution. A membrane with an exclusion limit of 10.000 g mol^{-1} (Amicon PM 10 or equivalent, Millipore made in USA) was used. After equilibration, the phases were separated by ultrafiltration. The filtration fraction (200 mL) was collected and the concentration of metal ions in the filtrate and retentate were determined by atomic absorption spectroscopy (AAS). 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.

Maximum retention capacity (MRC)

The complexes were prepared by the addition of an aqueous solution (2 wt%) of the copolymer at pH 3, 5, and 7. This copolymer solution was saturated with an aqueous solution (10 wt%) of the metal salts until its MRC. The copolymer–metal complexes already formed were placed in the membrane filtration cell and were separated and purified by successive ultrafiltration procedures with an exclusion limit of the molecular weight of 10.000 g mol^{-1} (Amicon ultrafiltration equipment) and pressure of 300 kPa. The filtration fraction (200 mL) was collected and the concentration of metal ions in the filtrate and retentate were determined by AAS. The complex was dried for further analytical control.

Cyclic voltammetry

Cyclic voltammetry was carried out using a potentiostat/galvanostat CV-Bas 50 W in water with 0.1 M Na_2SO_4 using three-electrode cells. A platinum electrode was used as the working electrode, a platinum wire as the auxiliary electrode, and saturated calomel electrode (SCE) (Ag/AgCl) as the reference electrode. A solution of 0.1 M Na_2SO_4 was the electrolyte support employed. The experiments were carried out in argon atmosphere at room temperature for the entire range of the sweep rates.

Thermal analysis

The thermal analysis of the copolymers was performed by recording TG and DSC under nitrogen atmosphere (flow rate = 150 and 50 $cm^3\ min^{-1}$, 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 thermogravimetric analyzer (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^{-1}.

Results and discussion

Synthesis and characterization

The MG was copolymerized with CA at 0.50:0.50 (sample 1) and 0.75:0.50 (sample 2) feed mol ratios. The general structure of the copolymer poly(MG-*co*-CA) is illustrated in Scheme 2. The experimental polymerization conditions and results are shown in Table 1. Copolymer composition was determined from elemental analysis data. In general, the copolymers were water-soluble.

The copolymers were characterized by TF-IR, ^1H NMR spectroscopy, size-exclusion chromatography (SEC), as well as by thermal analysis through

Scheme 2 General structure of poly(MG-*co*-CA)

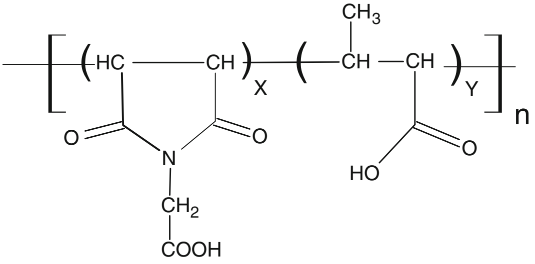


Table 1 Experimental conditions and results of the copolymerization of MG with CA, at 70 °C by 16 h in tetrahydrofuran (THF)

Poly(MG-*co*-CA) acronym	f_1	F_1	M_1/M_2 (mmol) (g)	Yield (%)	Elemental analysis (%) exp(calc)		
					C	N	H
Sample 1	0.75	0.87	12.0 (1.860)/4.0 (0.344)	63	44.00 (47.16)	7.79 (8.35)	3.88 (3.53)
Sample 2	0.50	0.85	10.0 (1.550)/10.0 (0.860)	66	43.73 (47.29)	7.13 (8.22)	3.93 (3.59)

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

f_1 monomer feed (mol%), F_1 copolymer composition (mol%)

termogravimetric analyzer (TG) and differential scanning calorimetry (DSC). A number-average (M_n) and weight-average (M_w) for molecular weight and the molecular weight distribution (polydispersity, M_w/M_n) of 22.210 and 22.450 Daltons and PD = 1.011 and 1.024, respectively, were determined. The FT-IR spectra of the different copolymers show similar characteristic signals coming of different functional groups.

The FT-IR spectra (KBr, cm^{-1}) of the poly(MG-*co*-CA) (a) and their copolymer–metal ion complexes with the metal ion at pH 3, 5, and 7 (b, c, d, and e) are presented, respectively, in Fig. 2. The most characteristic absorption bands (in cm^{-1}) are: 3428.5 (OH, –COOH), 2927.0 (CH, CH_2 stretching), 1778.1 and 1771.1 (C=O imide), and 1704.1 (C=O, carboxylic acid stretching), 1494.8 (N–C stretching of imide ring), and 1428.3 and 1334.8 (CH, CH_3, bending).

The FT-IR spectra of the copolymer and poly(MG-*co*-CA)–metal ion complexes obtained in the maximum retention capacity (MRC) studies, are given in Fig. 1a, b. An important change in the absorption signal at 1,706 cm^{-1} was observed, the C=O band of the carboxylic group, additionally showed a new band at 1626.6 cm^{-1}, because of the coordination of metal ions with the carboxylate groups, in the last one with higher intensity.

The ^{1}H-NMR spectra in D_2O of poly(MG-*co*-CA) presents the following signals at δ (in ppm): 0.7–1.2 (H_c, –CH_3 and H_d, CH– from crotonic acid); 1.7–2.1 (H_e, CH, form crotonic acid), 3.0–3.9, (H_a,–CH, from imide ring), 3.9–4.4 (–CH_2, side chain) (see Fig. 2).

Complexing properties of copolymers

The copolymers' metal ion complexing properties were studied by using LPR technique at pH 3, 5, and 7 with seven metals ions, M^{n+} = Cu(II), Co(II), Cr(III), Ni(II), Cd(II), Zn(II), and Fe(III), at low concentration (20 mg L^{-1}) (see Figs. 3, 4).

Metal ion retention depends on polymer complex dissociation, which is generally described by a reversible reaction [23–28].

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

where PL = poly(MG-*co*-CA) (sample 1) and poly(MG-*co*-CA) (sample 2), (see Table 2) with pendant ligand L at the chain; M^{n+}, metal ion; PLM^{n+}, polymer–metal complexes.

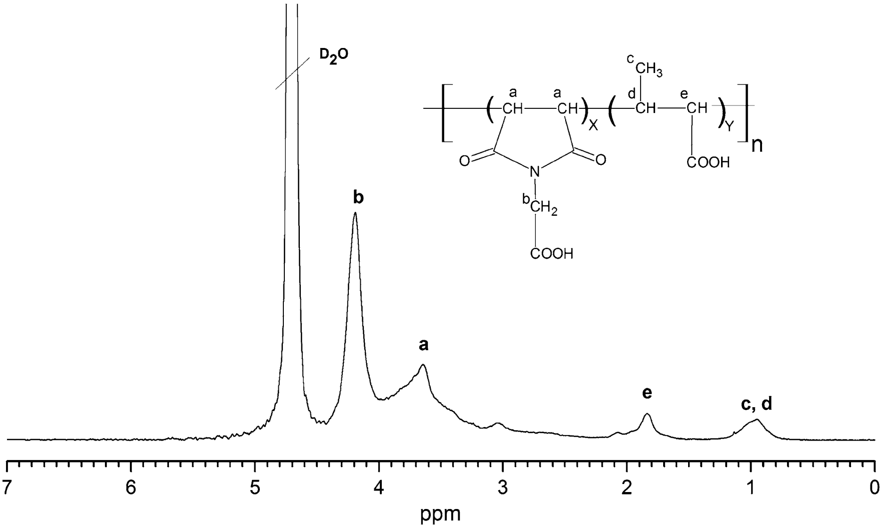


Fig. 1 ^{1}H-NMR (250 MHz, D_2O) at room temperature for poly(MG-*co*-CA) (sample 1)

Poly(MG-*co*-CA) (sample 1) showed higher complexing properties at higher pH (see Table 2). In general, using the LPR technique, both polymeric systems showed high metal ion retention for Fe(III) at different pH. At pH 7, metal retention of poly(MG-*co*-CA) (samples 1/pH 7 and 2/pH 7) for Fe(III) ions varied from 79 to 57% ($Z = 10$), respectively. Therefore, metal ion retention increases strongly with an increase of pH for poly(MG-*co*-CA) (sample 2) copolymers, observing a lower pH influence for retention of the other metal ions.

Thus, poly(MG-*co*-CA) (sample 1) is an effective reagent for separation of various metal ions at pH 7. At pH 3, (sample 1/pH 3) this copolymer shows a slightly lower metal ion affinity, and presented lower retention values, except for Fe(III) ions, when comparing with retention at pH 7. The differences in the complexing ability of the copolymer respect to Fe(III), may be attributed primarily to structural moieties, a large ratio of surface area to volume can contribute to some of the unique properties of the complex metal ions, and a high stability of the copolymer complex forming with Fe(III). The interconnected carboxylic acid/carboxylate groups containing domains are highly polar and can be swollen by water. Therefore, the interconnected functional groups containing domains can provide a good diffusion path for Fe(III) through the matrix polymeric. The retention of the Zn(II) is slightly higher than that of Cu(II). The modification of the polymers' primary structure in its application indicates that the polymer metal complexing capacity depends not only on the ligand groups' nature but also on metal ion accessibility and stability of the copolymer complex.

Poly(MG-*co*-CA), compared with previous study, presents a lower MRC than that of poly(*N*-maleoyl glycine-*co*-itaconic acid) [17], and poly(*N*-maleoylglycine-*co*-acrylic acid) [18], but higher than that of poly(OH, Cl-phenylmaleimide-*co*-2-hydroxypropylmethacrylate) [19]. This different results could support the assumption

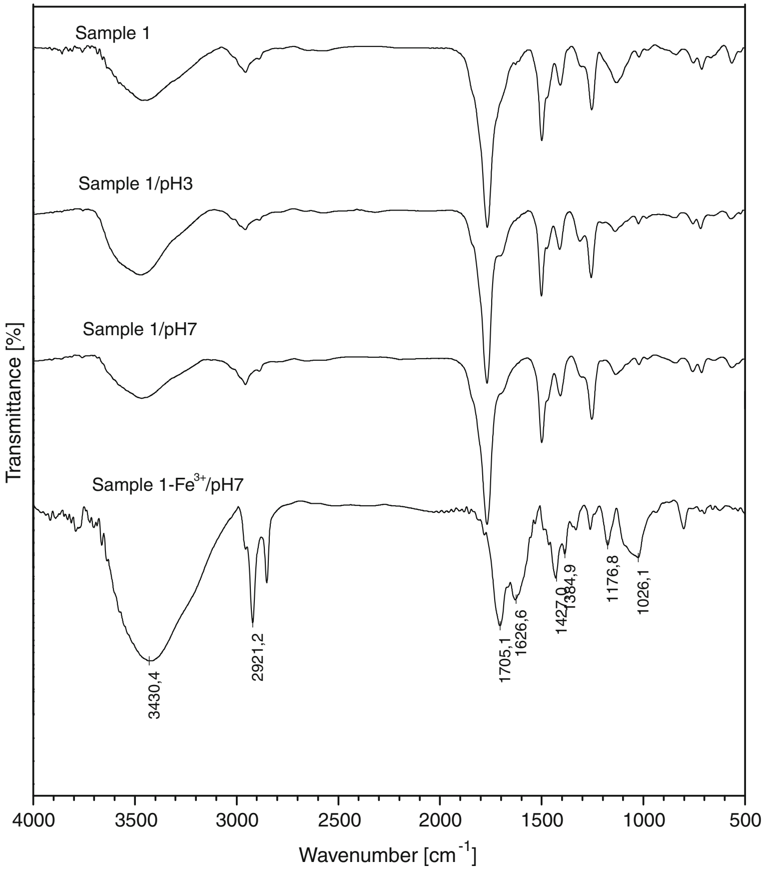


Fig. 2 FT-IR spectra of poly(MG-*co*-CA) and polymer–metal complexes at different pH (5, 7) respectively

that the carboxylic acid group could prevent the interaction with the metal ions due to binding hydrogen between –COOH groups in both monomer units, where it could form stable hydrogen-binding inter/intra macromolecular complexes.

The metal ion retention values for the copolymers show that both co-monomer units possess functional groups with a low metal ion affinity. This retention behavior can be attributed to that the copolymer poly(MG-*co*-CA) has hydrophilic monomer units with two carboxylic acid functional groups in the side chain and that it can exhibit strong and stable hydrogen-binding inter/intra macromolecular attraction forces that also depend on pH [29]. Additionally, an interaction of the nitrogen atom from an imide group unit could exist, resulting 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 1,498 cm^{-1} presented a light decrease (see Fig. 2). The interaction of the imide and carboxylic acid groups with

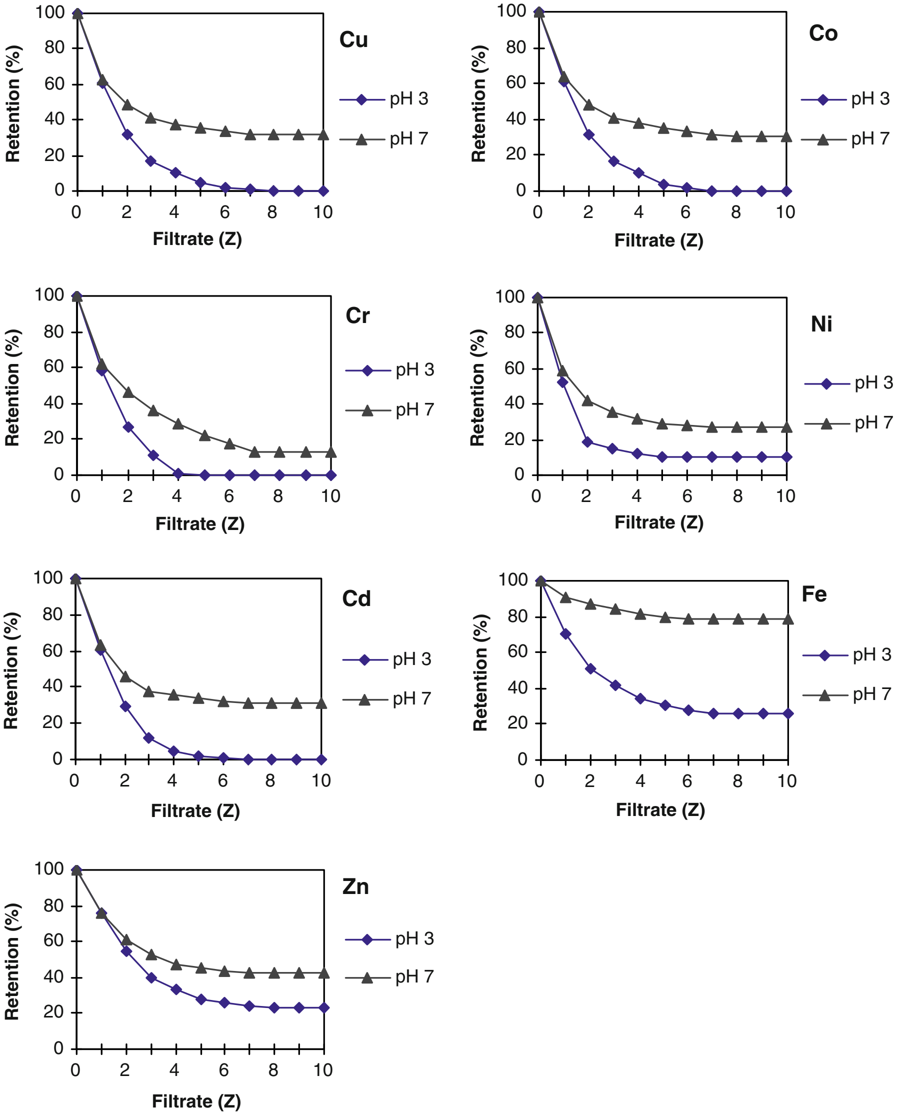


Fig. 3 Typical metal ion retention profiles for poly(MG-*co*-CA), (sample 1), at different pH

metal ions can lead to the formation of inter/intra macromolecular complexes between the electron donor nitrogen of the imide and the carboxylic acid groups. In this case, a different complex formation may occur at different pH when the nitrogen atom from the imide and the carboxylic acid groups from the side chains may participate as donor groups in the complex formation as occurs in some biological system [30], see Scheme 3.

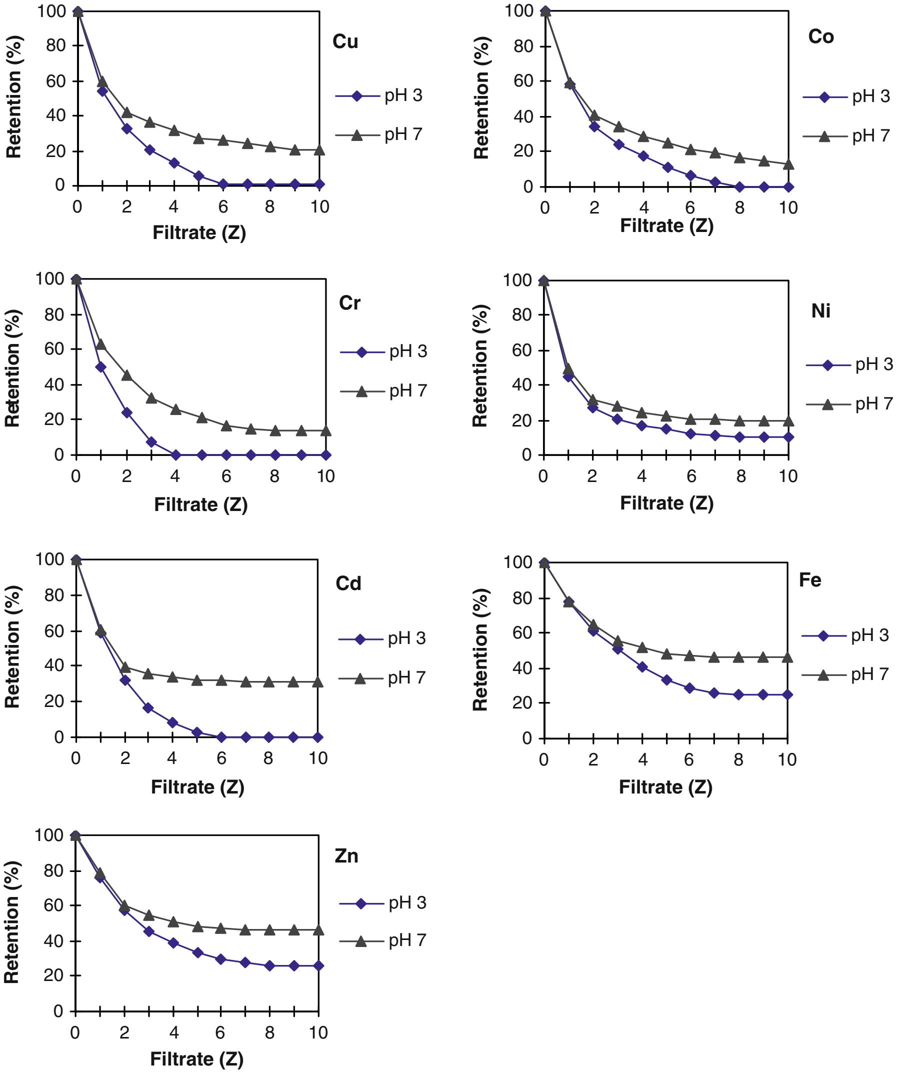
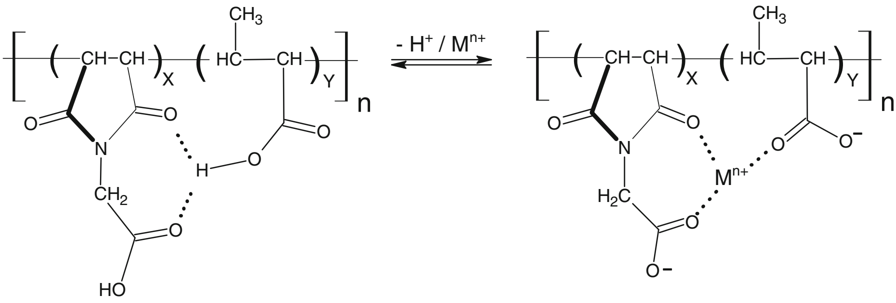


Fig. 4 Typical metal ion retention profiles for poly(MG-*co*-CA), (sample 2), at different pH

Table 2 Retention (%) properties of poly(MG-*co*-CA) for seven metal ions at pH 3 and 7

Poly(MG-*co*-CA) acronym	pH	Retention of metal ion (%)						
		Cu(II)	Co(II)	Cr(III)	Ni(II)	Cd(II)	Zn(II)	Fe(III)
Sample 1/pH 3	3	10	13	5	10	0	28	36
Sample 1/pH 7	7	32	31	13	27	32	43	79
Sample 2/pH 3	3	0	0	0	11	0	26	35
Sample 2/pH 7	7	22	13	14	20	32	46	57



Scheme 3 Interaction of the carboxylic acid groups from both monomer units

Maximum retention capacity (MRC) of the copolymers for Fe(III) ions

The MRC had the highest retention values for both copolymer systems at pH 7, and this result is related to the copolymers' nature. The interaction of both units can lead to the formation of molecular complexes with electron donor nitrogen from imide and carboxylic acid or carboxylate groups at higher pH (intramolecular complexes). The highest maximum retention capacity values for Fe(III) ions was found at pH 7. The binding capacity for the Fe(III) ion varied from 133.5 to 146.2 mg/g for poly(MG-*co*-CA)(sample 1—Fe^{3+}/pH 3 and pH 7 and sample 2—Fe^{3+}/pH 3 and pH 7) (see Table 3).

Cyclic voltammetry

The CV showed one well-defined reduction wave in water between −0.4 and −0.6 V (at 50 mV/s). The process could correspond to a quasi-reversible step of electron transfer, which can be attributed to the reduction of an imide moiety to 2,5-dihydroxypyrrole derivatives.

The electrochemical characterization of the copolymer poly(MG-*co*-CA) (sample 1) showed the reduction of carboxylic acid groups of the *N*-maleoylglycine and crotonic acid moiety to hydroxyl group is shown in Fig. 5. The signal could include both processes.

Figure 6 shows the CV of the poly(MG-*co*-CA) (sample 1) using for different polymer concentrations (10, 20, 30, and 51 mM) at 50 mV/s. The voltammogram shows the linear increasing reduction wave when polymer concentration increases.

Table 3 Maximum retention capacity (MRC) for the copolymers-metal complex at different pH

Poly(MG-*co*-CA)-Fe^{3+} Acronym	m_1:m_2 (Copolymer comp.) (mol%)	pH	V (mL) 1 wt%	Retentate (mg/g)
Sample 1—Fe^{3+}/pH 3	87:13	3	1.0	122.1
Sample 1—Fe^{3+}/pH 7	87:13	7	1.0	146.2
Sample 2—Fe^{3+}/pH 3	85:15	3	1.0	120.6
Sample 2—Fe^{3+}/pH 7	85:15	7	1.0	133.5

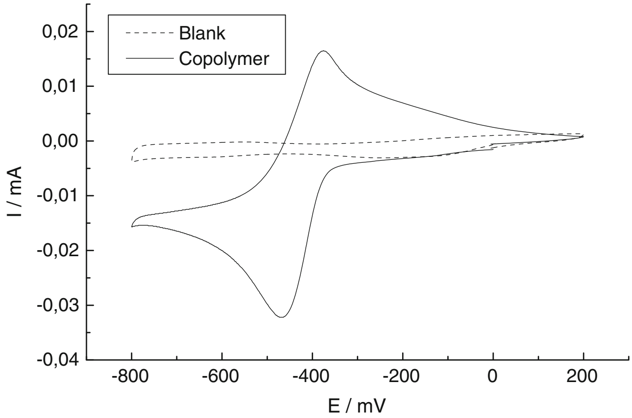


Fig. 5 Plot of current (mA) vs. potential (mV). Cyclic voltammograms (CV) of the copolymer P(MG-*co*-CA) 30 mM (sample 1) at 50 mV/s

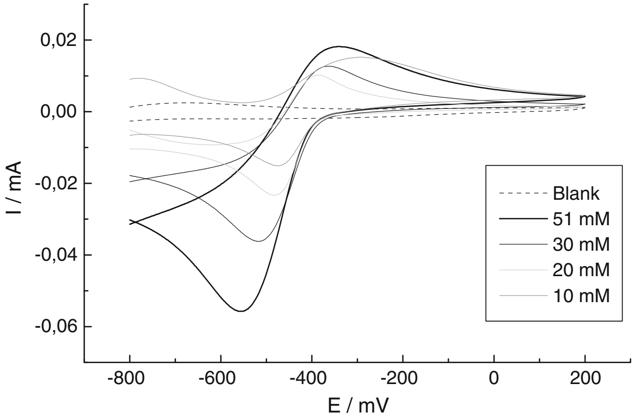


Fig. 6 Plot of current (mA) vs. potential (mV). Cyclic voltammograms (CV) of the copolymer (MG-*co*-CA) (sample 1) in different concentration (10, 20, 30, 51 mM) at 50 mV/s

The copolymers show a linear relationship when the slope of these curves indicated that the copolymer presents convenient electroactivity and indicating that the control of the reaction is by diffusion.

The cyclic voltammetry of copolymer poly(MG-*co*-CA) (sample 1) (30 mM) was compared with the CV of the copolymer previously complexed with Fe(III) (approx. 0.26 mM of Fe(III) complexed in the polymer) [poly(MG-*co*-CA)–Fe(III)] (see Fig. 7). These voltammograms showed a decreasing reduction signal in the case of iron-complex polymer in comparison with the polymer without metal. This behavior could be due to that the polymer's carboxylic acid groups are ligands and form the metal-complex polymer, therefore, these moieties are fewer

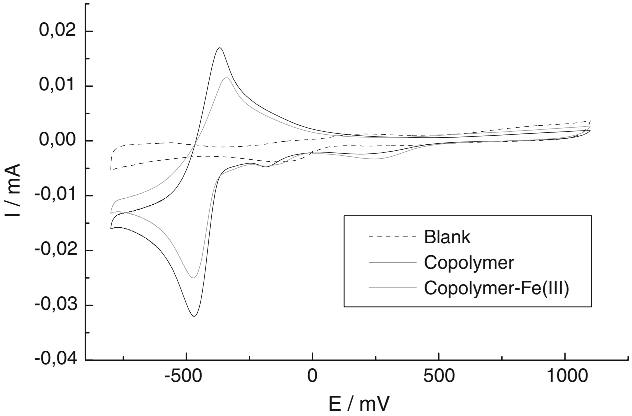


Fig. 7 Plot of current (mA) vs. potential (mV). Cyclic voltammograms (CV) of the copolymer (MG-*co*-CA) (sample 1) 30 mM at 50 mV/s. and iron-complex copolymer 30 mM [poly(MG-*co*-CA)–Fe(III)] with approx.0.26 mM of Fe(III) complexed

in the reduction process. Moreover, [poly (MG-*co*-CA)–Fe(III)] showed a redox wave between +0.25 and +0.5 V, which possibly is due to the presence of metal in the polymer.

Thermal behavior

The TG results for poly(MG-*co*-CA) are summarized in Table 4. 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 Fig. 8). The resulting material has an extrapolated thermal decomposition temperature (TDT) of about 340 °C. The TDT of the copolymer–metal complexes were also lower than for the copolymers, especially at pH 3. The thermal stability of polymer–metal complexes is known to be affected primarily by the nature of the polymer and micro-environmental conditions such as additional coordination bonds. According to the literature, the thermal stability of functional polymers with metal will generally be enhanced. When the polymer interacts with metal ions, the thermal energy supplied to the polymer–metal complex may result in a catalytic role of metal ion in the thermal decomposition of the polymer–metal complex [19, 31].

The highest weight loss for the copolymer and the complexes occurs between 400 and 500 °C (see Table 4). At pH 3, and 7, the complexes' lower residual mass percentage may be attributed to the percentage of metal incorporated at this pH.

Glass transition temperature

The glass transition temperature (T_g) was analyzed from 20 to 500 °C. The DSC thermograms do not show T_g for poly(MG-*co*-CA) and poly(MG-*co*-CA)-M_n^{n+}.

Table 4 Thermal decomposition temperature for the poly(MG-*co*-CA) and their copolymer–metal ion complexes

Sample acronym	TDT (°C)	Weight loss (%) at different temperatures (°C)					
		100	200	300	400	500	550
Poly(MG-*co*-CA) Sample 1	337.7	7.4	7.6	8.4	43.3	58.3	62.8
Poly(MG-*co*-CA)–Mn^{n+} Sample 1/pH 3	303.5	6.0	7.4	13.4	48.1	74.7	89.4
Poly(MG-*co*-CA)–Mn^{n+} Sample 1/pH 7	326.8	6.4	7.7	9.5	43.8	87.7	94.3
Poly(MG-*co*-CA) Sample 2	341.2	10.0	10.0	11.1	44.6	60.0	64.3
Poly(MG-*co*-CA)–Mn^{n+} Sample 2/pH 3	303.6	4.6	6.0	10.0	46.4	71.2	87.4
Poly(MG-*co*-CA)–Mn^{n+} Sample 2/pH 7	318.6	5.5	6.4	8.6	44.2	83.0	93.8

TDT thermal decomposition temperature

Conclusions

Complexes of the poly(*N*-maleoylglycine-*co*-crotonic acid) with metal ions were synthesized and investigated as a function of pH. The poly(MG-*co*-CA) are high solubility in water, easy and inexpensive synthesis, and had an adequate molecular weight and molecular weight distribution, chemical stability, a relatively high affinity for Fe(III).

The LPR technique as ultrafiltration system was employed to test the coordination properties in the formation of copolymer complexes, in aqueous solution (2 wt%). The MRC had the highest retention values for both copolymer systems at pH 7, and this result is related to the copolymer composition. The MRC for Fe(III) varied from 122 to 146 mg/g (sample 1/Fe^{3+}) and 120.5 to 133.5 mg/g (sample 2/Fe^{3+}) for poly(MG-*co*-CA). Poly(MG-*co*-CA) presented higher TDT in comparison with copolymer–metal complexes at pH 3 and 5.

The electrochemical characterization of the copolymer poly(MG-*co*-CA) shown the reduction of carboxylic acid groups of the *N*-maleoylglycine and crotonic acid moiety to hydroxyl group. The signal could include both processes. The cyclic voltammetry of copolymer poly(MG-*co*-CA) (30 mM) was compared with the CV of the copolymer previously complexed with Fe(III). These voltammograms showed a decreasing redox signal in the case of iron-complex polymer compared with the polymer without metal. This behavior could be attributed to the carboxylic group since the copolymer are ligands and form the metal-complex polymer. Therefore, these moieties are fewer in the reduction process. Poly(MG-*co*-AC)–Fe(III) showed a redox wave between +0.25 to +0.50 V possibly due to the presence of metal complexed with the polymer. The copolymers show a linear relationship when the

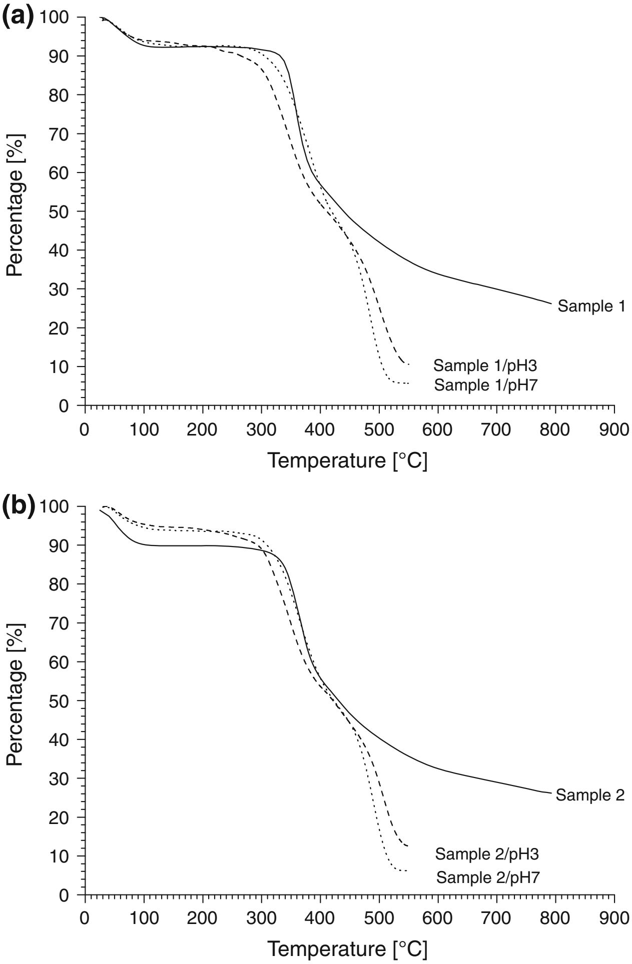


Fig. 8 **a** TGA thermograms of *a* poly(MG-*co*-CA) (sample 1) and polymer–metal complexes (samples 1/pH 3 and pH 7). **b** Poly(MG-*co*-CA) (sample 2) and polymer–metal complexes (samples 2/pH 3 and pH 7). Heating rate: 10 °C/min

slope of these curves indicated that the copolymer presents convenient electroactivity and indicating that the control of the reaction is by diffusion.

The resulting material has an extrapolated thermal decomposition temperature (TDT) of about 340 °C. The TDT of the copolymer–metal complexes were also lower than that for the copolymers, especially at pH 3.

The implications of the results presented for these copolymers are good for the water technology, but in view of the results presented, we could explore some other areas of applications, especially for Fe(III) and Zn(II), due to their good electrochemical and thermal stability properties, because there exists a tremendous interest in use of conducting polymers in electronics applications.

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