

Synthesis, Characterization, and Metal Complexation of Poly(*N*-phenylmaleimide-*co*-acrylic acid) and Poly(*N*-phenylmaleimide-*co*-acrylamide) as Polychelatogens in Aqueous Solution

Guadalupe del C. Pizarro,¹ Oscar G. Marambio,¹ Manuel Jeria Orell,¹ Margarita Huerta,¹ Bernabé L. Rivas²

¹Departamento de Química, Universidad Tecnológica Metropolitana, J. P. Alessandri 1242, Santiago de Chile, Chile

²Polymer Department, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile

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ABSTRACT: We carried out the free-radical copolymerization of *N*-phenylmaleimide with acrylic acid and acrylamide with an equimolar feed monomer ratio. We carried out the synthesis of the copolymers in dioxane at 70°C with benzoyl peroxide as the initiator and a total monomer concentration of 2.5M. The copolymer compositions were obtained by elemental analysis and ¹H-NMR spectroscopy. The hydrophilic polymers were characterized by elemental analysis, Fourier transform infrared spectroscopy, ¹H-NMR spectroscopy, and thermal analysis. Additionally, viscosimetric measurements of the copolymers were performed. Hydrophilic poly(*N*-phenylmaleimide-*co*-acrylic acid) and poly(*N*-phenylmaleimide-*co*-acrylamide) were used for the separation of a series of metal ions in the aqueous phase with the liquid-phase polymer-based retention method in the heterogeneous phase. The method is based on the retention of inorganic ions by the polymer in conjunction with

membrane filtration and subsequent separation of low-molecular-mass species from the formed polymer/metal-ion complex. The polymer could bind several metal ions, such as Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III) inorganic ions, in aqueous solution at pH values of 3, 5, and 7. The interaction of the inorganic ions with the hydrophilic polymer was determined as a function of pH and a filtration factor. Hydrophilic polymeric reagents with strong metal-complexing properties were synthesized and used to separate those complexed from noncomplexed ions in the heterogeneous phase. The polymers exhibited a high retention capability at pH values of 5 and 7. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2359–2366, 2006

Key words: membranes; metal–polymer complexes; thermal properties

INTRODUCTION

Polymers of *N*-substituted maleimide derivatives represent a class of highly stable polymers due to the rigid imide rings at the backbone. This provides polymers with higher mechanical and thermal properties. The alternating of copolymers based on *N*-substituted maleimides have been investigated intensively in the field of electrooptical materials.^{1,2}

Metals are among the most commonly encountered and difficult to treat environmental pollutants. They are introduced into the environment during industrial processes, the refining disposal of industrial and domestic waters, and so on. Therefore, the removal of metal ions has attracted considerable

interest for several applications, including improved analyses, the concentration of trace metal ions from dilute solutions, remediation, and a general concern for the elimination of noxious metals from waters that may enter natural waters. In particular, the search for metal-ion-specific polymer reagents has increased.^{3–7}

Polymers as metal-ion-complexing reagents, such as polyethyleneimine, polyvinylpyrrolidone, and polyacrylamide, have been extensively studied and widely applied to the concentration and separation of various elements.^{8–15}

Hydrophilic polymers with complexing groups (polychelatogens) have been tested to show the applicability of the method to the separation of various metal cations and also anionic species for analytical and technological purposes. This method, based on the retention of certain ions by a membrane that separates low-molar-mass compounds from macromolecular metal-ion complexes is called *liquid-phase polymer-based retention* (LPR).^{16–19}

In this study, the interactions of the hydrophilic synthetic polymers with inorganic ions were investi-

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

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TABLE I
Experimental Conditions for the Copolymerization of P(*N*-PhMI-*co*-AA) and P(*N*-PhMI-*co*-AAM) at 12 h of Reaction

<i>N</i> -PhMI		AA or AAm*		Feed molar ratio	Yield (%)	Solvent (mL)	$m_1:m_2$	
mmol/g		mmol	$\text{mL}^{-1} \text{g}^{-1}$				From N/C	From $^1\text{H-NMR}$
10.0	1.73	10.0 ^a	0.69 ^a	1 : 1	36	8	44.1 : 55.9	46.5 : 53.5
10.0	1.73	10.0 ^b	0.71 ^b	1 : 1	38	8	53.5 : 46.5	52.0 : 48.0

Total concentration of monomers = 2.5M. m_1 = copolymer composition of monomer 1 (*N*-PhMI); m_2 = copolymer composition of monomer 2 (AA or AAm; mol %).

^a AA.

^b AAm.

gated in aqueous solution. In addition, thermoanalytical studies of the copolymer and metal complexes at different pH's were performed.

EXPERIMENTAL

Materials

Acrylic acid (AA) and acrylamide (AAm) were obtained from commercial sources and were purified by distillation (AA) and crystallization (AAm) from water. *N*-phenylmaleimide (*N*-PhMI) was prepared according to published procedures.²⁰

Preparation of the copolymers

A volume of dioxane (8 mL) was transferred to septum-capped, nitrogen-purging flasks containing acrylic monomer (10.0 mmol), 15.6 mg of initiator (benzoyl peroxide), and 10.0 mmol of *N*-PhMI previously synthesized. This ampule was sealed *in vacuo* (10^{-3} mmHg), and the copolymerization was carried out at 70°C for 12 h. Polymeric materials were filtered off, washed with diethyl ether, collected, and dried *in vacuo* to a constant weight.

Copolymerization

Poly(*N*-phenylmaleimide-*co*-acrylic acid) [P(*N*-PhMI-*co*-AA)] and poly(*N*-phenylmaleimide-*co*-acrylamide) [P(*N*-PhMI-*co*-AAm)], respectively, were synthesized by radical copolymerization with a 1 : 1 feed monomer molar ratio in solution with 0.5 mol % benzoyl peroxide as the initiator (see Table I).

Copolymer composition

The copolymer composition for P(*N*-PhMI-*co*-AA) and P(*N*-PhMI-*co*-AAm) was calculated in the monomer molar ratio from elemental analysis data (content of N/C) with data according to eqs. (1) and (2), respectively:

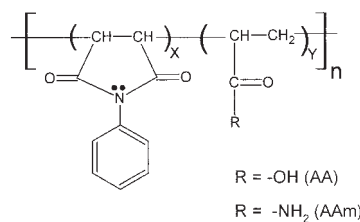
$$X = \frac{N/C_{\text{exp}} \times PF_{\text{CB}}}{PF_{\text{NA}} - N/C_{\text{exp}} \times PF_{\text{CA}}}, Y = 1 \quad (1)$$

$$X = \frac{N/C_{\text{exp}} \times PF_{\text{CB}} - PF_{\text{NB}}}{PF_{\text{NA}} - N/C_{\text{exp}} \times PF_{\text{CA}}}, Y = 1 \quad (2)$$

where X is the copolymer molar ratio for *N*-PhMI, Y is the copolymer molar ratio for AA or AAm, N/C_{exp} is the experimental nitrogen/carbon ratio of both monomer units, PF_{CB} is the formula weight of carbons in monomer B, PF_{NB} is the atom weight of nitrogen in monomer B, PF_{NA} is the atom weight of nitrogen in monomer A, and PF_{CA} is the formula weight of carbon in monomer A for the copolymers *N*-PhMI (monomer A).

Complexation procedure

The solid copolymer/metal complexes were prepared by the addition of a heterogeneous aqueous solution of P(*N*-PhMI-*co*-AA) or P(*N*-PhMI-*co*-AAm) (1 wt %) at pH values of 3, 5, and 7 to an aqueous solution with the metal salts Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III) inorganic ions. The copolymer/metal complexes were placed into the membrane filtration cell and were separated and purified by successive ultrafiltration with a membrane with an exclusion limit of a molecular weight of 10 000 g/mol. The water of the reservoir was adjusted at the same pH as that of the cell solution, and the system was pressurized (300 kPa). The metal-ion concentrations in the filtrate and in the complex were determined by atomic absorption spectroscopy. The new complex was lyophilized for further analytical control by thermal analyses and Fourier transform infrared (FTIR) spectroscopy.



Scheme 1. Structures of P(*N*-PhMI-*co*-AA) and P(*N*-PhMI-*co*-AAm).

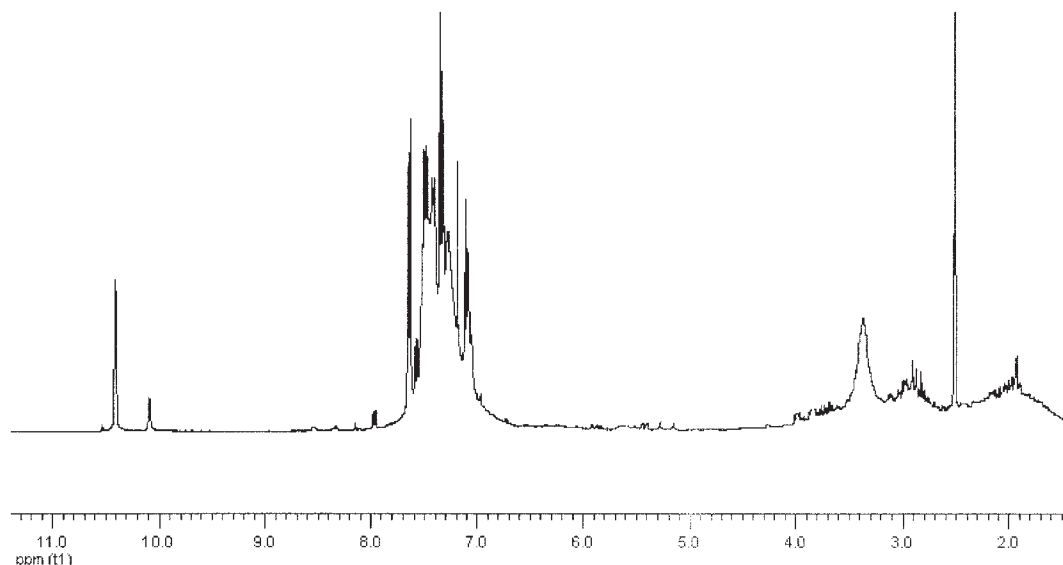


Figure 1 $^1\text{H-NMR}$ spectrum of P(*N*-PhMI-*co*-AAm) (400 MHz in DMSO- d_6 at room temperature with tetramethylsilane as an internal standard).

The aqueous solutions of the polymer (1 wt %) and metal nitrates or chlorides (20 mg/L) were placed into the membrane filtration cell. The total volume in the cell was kept constant at 20 mL. The reservoir contained demineralized water adjusted to the same pH as that of the cell solution. The filtration factors (Z 's = 1–10) were collected, and the concentrations of metal ions in the filtrate and the retentate were determined by atomic absorption spectroscopy. The copolymers were lyophilized for further analytical control. Metal-ion retention values were calculated from the concentration measurements of filtrate.

Equipment

The determination of the metal content was carried out with a PerkinElmer 1100 atomic absorption spectrometer (PerkinElmer, Shelton, CT). For lyophilization, a continuous freeze dryer [LAB CONCO (6 L)] was used. The pH was determined with a Hanna E 211 pH meter (Miami, FL). For the LPR technique, a membrane filtration system was used, as described previously.^{16–19}

Measurements

The elemental analyses were carried out with a Carlo Erba 1106 analyzer (Milano, Italy). FTIR and $^1\text{H-NMR}$ spectra were recorded on a Bruker model vector 22 (Billerica, MA) and a Bruker model Avance 400 spectrometer (Karlsruhe, Germany), respectively. The intrinsic viscosity ($[\eta]$) was measured in dimethyl sulfoxide (DMSO) solutions of the copolymers (0.020–0.040 g/mL) with an Ubbelohde viscosimeter (Merck, Whitehouse Station, NJ) at $30 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

The copolymers P(*N*-PhMI-*co*-AA) and P(*N*-PhMI-*co*-AAm) (see Scheme 1) were obtained from the corresponding monomers by radical solution polymerization. The complexation properties of both copolymers were investigated with the LPR technique at pH values of 3, 5, and 7 for the following seven metals ions: Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III). With this technique, typical retention profiles were obtained that were characteristic for the metal-ion interaction patterns at different pH's.

Synthesis and characterization of the polychelato gens

The copolymerization yields of P(*N*-PhMI-*co*-AA) and P(*N*-PhMI-*co*-AAm) were 36 and 38%, respectively. The copolymers were soluble in DMSO, methanol, and acetone. The copolymers were characterized by elemental analysis, FTIR spectroscopy, $^1\text{H-NMR}$ spectroscopy, $[\eta]$, and thermal analysis.

FTIR spectroscopy

The FTIR spectra of P(*N*-PhMI-*co*-AA) and P(*N*-PhMI-*co*-AAm), respectively, showed the following most characteristic absorption bands (cm^{-1}): 3462.0 (—OH, —COOH, broad band), 2925.8 (CH, CH_2 stretching), 1774.6 (C=O, imide), 1703.0 (C=O, —COOH stretching), 1596.6 (CH, stretching aromatic ring), 1498.6 and 1388.6 (CH_2 bending), 3457.0 (NH—, broad band from amide), 1773.9 (C=O, imide), 1673.0 (C=O, amide stretching), 1585.4 (CH, stretching aromatic ring),

1394.4 (CH₂ bending), and 696.3 and 628.7 (benzene ring and C—N—C bending).

The ¹H-NMR spectrum (DMSO-d₆/tetramethylsilane) of P(*N*-PhMI-*co*-AAm) showed the following signals (δ, ppm): 2.1 and 3.0 (3H, AAm, —CH₂ and —CH—, respectively), 3.5 (2H; —CH— from imide ring), and 6.8–7.9 (5H aromatic ring; see Fig. 1). The relation of the area of aromatic ring protons (5H) with those of AAm protons (3H from the backbone) confirmed the copolymer compositions calculated by elemental analysis. P(*N*-PhMI-*co*-AA) 2.0 and 2.7 (3H, —CH₂— and —CH— from AA, respectively), 3.5 (2H from the imide ring), and 7.0–7.5 (5H aromatic ring). The relation of the area of aromatic ring protons (5H) with those of the AA protons (3H) confirmed the copolymer compositions calculated by elemental analysis.

Polymer/metal-ion complexes at pH 5

The FTIR spectrum of P(*N*-PhMI-*co*-AA) showed an important change in the broad signals at 3435.3, 3421.5, and 2925.8 cm⁻¹ (CH, CH₂ stretching) for complexes with metal ions, respectively, in basic media that were attributed to the interaction of the hydroxyl groups predominantly coordinated around the metal ions. The C=O band of carboxylic group at 1703.0 cm⁻¹ decreased in intensity for the complexes with the metal ions [see Fig. 2(A)]. P(*N*-PhMI-*co*-AAm) presented two signals at 3354.0 and 3197.8 cm⁻¹ and 1708.0 and 1667.0 cm⁻¹ [see Fig. 2(B)] that showed important changes in the broadness and intensity of the signal, and this was attributed to the interaction between the carbonyl group of the AAm monomer and the metal ions. In addition, the complexes showed two new absorption bands at 1115.9 and 1256.0 cm⁻¹ due to the coordination of the metal ions with the carboxylate groups with higher intensity. The interaction of the nitrogen atoms from the imide and carboxylic groups could have led to the formation of molecular complexes between the electron-donor nitrogen from imide and the carbonyl groups from AA or AAm.

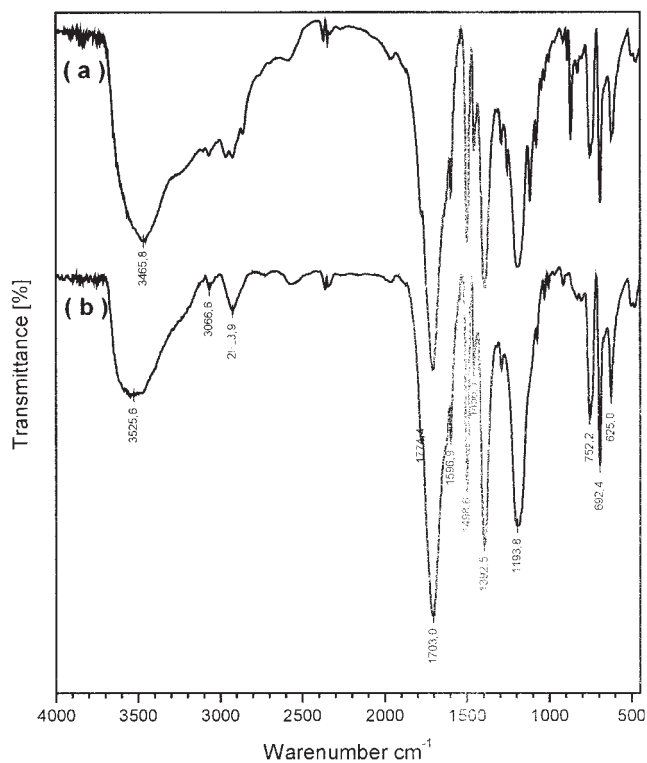
The copolymer composition of P(*N*-PhMI-*co*-AA) and P(*N*-PhMI-*co*-AAm) were determined from elemental analysis (see Table II).

Polymer/metal-ion complexation studies

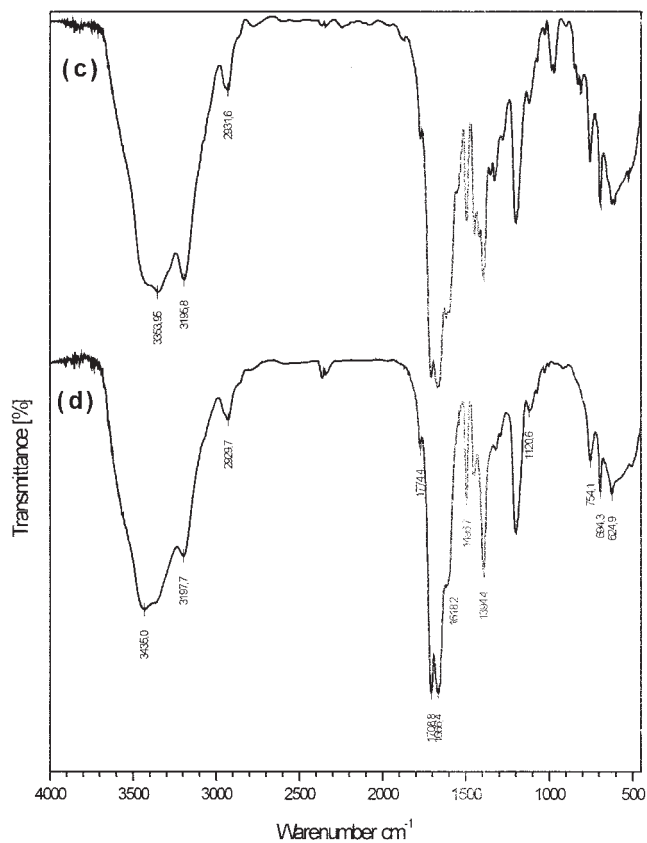
The retention of metal ions in the cell is defined as

$$R = C_r \times C_0^{-1} \times 100(\%)$$

where C_r is the metal-ion concentration in the retentate [the cell solution after a filtrate volume of (V_f) has been passed] and C_0 is the initial metal-ion concentration in the cell. Z , expressed in relative units, is another convenient characteristic of the process:^{16–19}



(a)



(b)

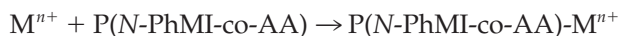
Figure 2 FTIR spectra of (a) P(*N*-PhMI-*co*-AA) and (b) its complex with metal ions and (c) P(*N*-PhMI-*co*-AAm) and (d) its complex with metal ions.

TABLE II
Elemental Analysis Data of P(N-PhMI-co-AA) and P(N-PhMI-co-AAm)

Copolymer	C		H		N		O		N/C	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
P(N-PhMI-co-AA)	63.67	62.99	4.49	5.61	5.71	5.30	26.1	26.6	0.0897	0.0841
P(N-PhMI-co-AAm)	63.93	60.70	4.92	5.27	11.5	10.5	19.7	23.6	0.1799	0.1730

$$Z = V_f \times V_c^{-1}$$

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



where R is the polymer backbone, $R(LH)_p$ is the acid chelating groups, MX_n is the salt, and M^{n+} represents Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III) as inorganic ions.

In systems in which the concentration of inorganic ions was small relative to the polymer concentration, only the formation of $R(LH)_{p-n}(ML)_n$ could be taken into account. The concentration of elements noncomplexed by the polymer in the volume (V_c) was determined by two processes: (1) before the reaction and (2) by the irreversible transfer of the metal ion across the membrane.

Typical retention profiles of P(N-PhMI-co-AA) and P(N-PhMI-co-AAm) are shown in Figures 3 and 4. In general, strong complexation with both systems took place with all metal ions at pH values 3, 5, and 7. At pH 3 and pH 5, where all metal retention values were approximately between 60 and 99%, except for Ni(II) (0.00 and 48.5% and 23.5 and 26.5%), respectively. These values increased at pH 7 and were higher for P(N-PhMI-co-AA) (78.0%) than for P(N-PhMI-co-AAm) (59.5%; see Table IV).

A predominant influence of the comonomer AAm with respect to the AA comonomer units in the complex formation at pH 5 and pH 7 was observed, and the retention values for both systems slightly increased from pH 3 to pH 7. All the other metal ions showed a strong dependence on the pH 3, pH

5, and 7. For example, for both systems at pH 3, Co(II) and Fe(III) showed a retention value over 90%; in contrast, Cr(III) and Ni(II) had a retention value of 67.0%; the retention values were 0 and 61.0% for P(N-PhMI-co-AA), and 23.5% for P(N-PhMI-co-AAm), respectively, for $Z = 10$. The highest value for Ni(II) was found to be 78.0% at pH 7 with AA as the comonomer unit. At pH values of 5 and 7, all the retention values were over 74.5%, except for Ni(II) with values of 48.5 and 26.5% at pH 5 and 78.0 and 59.5% at pH 7 for both systems, respectively. Thus, P(N-PhMI-co-AA) and P(N-PhMI-co-AAm) were shown to be effective reagents for the separation of various metal ions, including Ni(II) at pH values of 5 and 7 (see Table IV).

The existence of differences in the complexing ability of the copolymers may be attributed primarily to the structural difference in the repetitive units of the copolymers and acrylic co-units.

According to the most probable interaction mechanism of the intramolecular complexation of the metal ions by the copolymer, the corresponding parts of the copolymer chains are arranged around the metal ions. This variation of the molecular shape leads to an alteration of the viscosity.²¹

The retention of inorganic ions by the LPR method is influenced by the pH of the solution. This factor affects both the formation complex reaction and the flow rate through the membrane. It is known that the flow rate also decreases with the polymer concentration, but on the other hand, the last factor generally increases the retention due to the better complexing ability of the polymer reagent. $[\eta]$ increased in the presence of inorganic ions, with higher values found at pH 5 (Table III). This behavior was attributed to a progressive breakup of the intramolecular hydrogen binding in the chain, which should have been produced by the forming complex. This produces an increase of $[\eta]$ due to an increase of the hydrodynamic volume.

TABLE III
[η] of P(N-PhMI-co-AA) and P(N-PhMI-co-AAm)
at 30°C in DMSO

Sample	[η] (dL/g)
P(N-PhMI-co-AA)	0.240
P(N-PhMI-co-AA)- M^{n+} at pH 5	0.265
P(N-PhMI-co-AAm)	0.250
P(N-PhMI-co-AAm)- M^{n+} at pH 5	0.280

Thermal behavior

Thermogravimetric analysis (TGA)

The TGAs of copolymers and their complexes (M^{n+}) are plotted in Figure 5, and data derived from the analyses are collected in Table V. At less than 200°C, the weight loss was not significant and was attributed

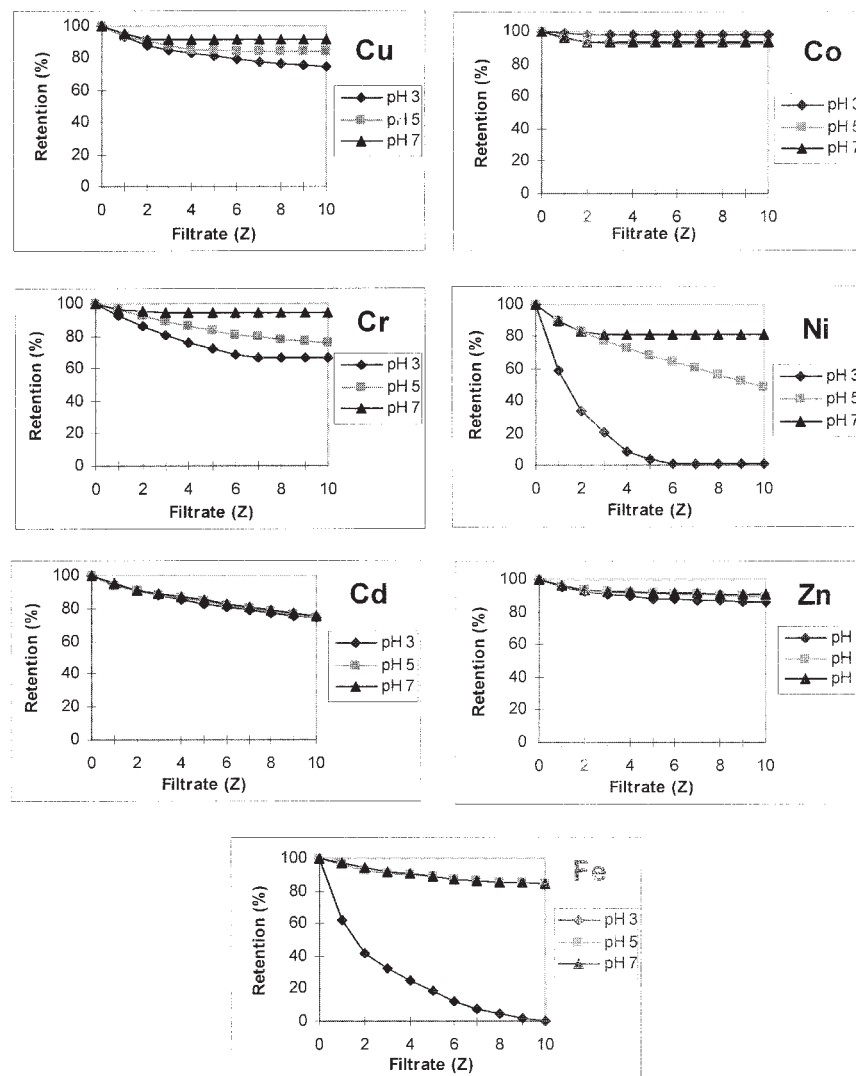


Figure 3 Retention profiles for different metal ions by an aqueous solution (1 wt %) of P(N-PhMI-co-AA) at different pH values.

to the loss of solvent and a small amount of monomer residue in the complexes and the copolymers.

The thermal behaviors of the P(N-PhMI-co-AA) and P(N-PhMI-co-AAm) copolymers were examined by TGA under nitrogen at a heating rate of 10°C/min, and the thermograms of P(N-PhMI-co-AA) and P(N-PhMI-co-AAm) were recorded under dynamic conditions. The plot showed that the copolymers degraded continuously in a one-stage process. As shown in Figure 5, the copolymers were stable up to 300 and 360°C, respectively. At pH 5, the complex exhibited a slight higher stability, obviously because of the complexing process of the metal-polymer support. For example, the copolymers had mass losses of 2.4 and 9.5% at 200°C, and for the polymer/metal complex, the mass losses were 3.7 and 7.3%, respectively (see Table V).

As expected, the copolymer P(N-PhMI-co-AA) showed a higher stability than P(N-PhMI-co-AAm). For example, P(N-PhMI-co-AA) had a mass loss 2.4% at 200°C and 11.4% at 300°C compared with the values

of 9.5% at 200°C and 19.9% at 300°C for P(N-PhMI-co-AAm). The copolymers with a composition of approximately 54 : 46 mol % at different pH values of contact with metal ions presented a higher thermal decomposition temperature (TDT) than that of P(N-PhMI-co-AA) or P(N-PhMI-co-AA). The data are summarized in Table V. The main reason for this was attributed to the formation and rearrangement of different complexes of the copolymer with some of the metal ions studied.

Glass transition

The glass transition was estimated from the trace of this second run. In all cases, to determine the glass-transition temperature (T_g) of the samples, the criterion of T_g at $\Delta C_p/2$ was adopted (where C_p is heat capacity).

DSC thermograms of P(N-PhMI-co-AA) and P(N-PhMI-co-AAm) and the copolymer/metal ion complexes [Fig. 6(a-d)] are illustrated in Figure 6. As shown by these

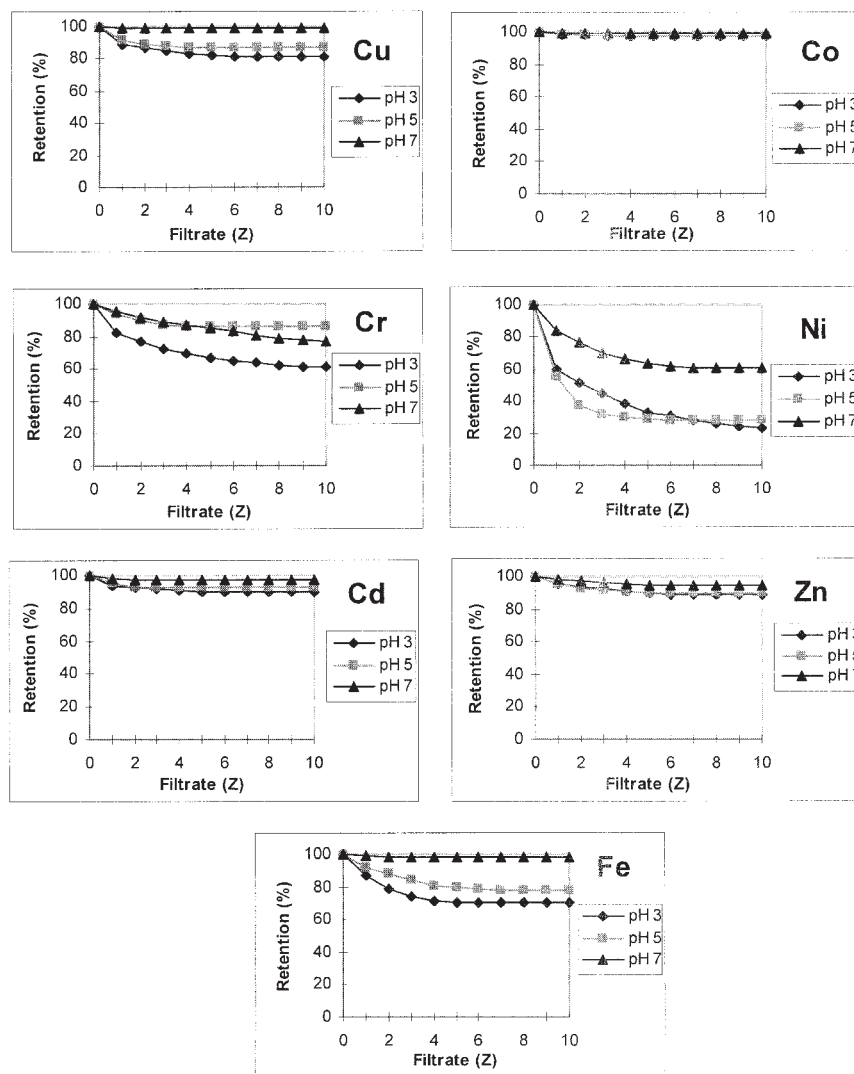


Figure 4 Retention profiles for different metal ions by an aqueous solution (1 wt %) of P(N-PhMI-co-AAm) at different pH values.

curves, T_g (220–260°C) decreased when the copolymer presented in its structure a high percentage of metal-ion bonding to the comonomer units (see Table VI).

The initial deflection was proportional to the sample heat capacity. The T_g was around 230°C for

TABLE IV
Retention Values of Seven Metal Ions for P(N-PhMI-co-AA) and P(N-PhMI-co-AAm) at Different pH's

pH	Metal ion						
	Cu(II)	Cd(II)	Co(II)	Cr(III)	Ni(II)	Fe(III)	Zn(II)
P(N-PhMI-co-AA)							
3	75.0	73.5	94.5	67.0	0.00	98.7	85.9
5	82.5	74.5	89.5	76.0	48.5	98.8	89.8
7	91.5	74.5	93.5	94.5	78.0	81.0	90.7
P(N-PhMI-co-AAm)							
3	79.5	87.5	94.0	61.0	23.5	80.5	87.8
5	84.0	89.0	94.0	86.0	26.5	86.0	88.2
7	95.0	90.0	95.0	87.0	59.5	84.5	92.6

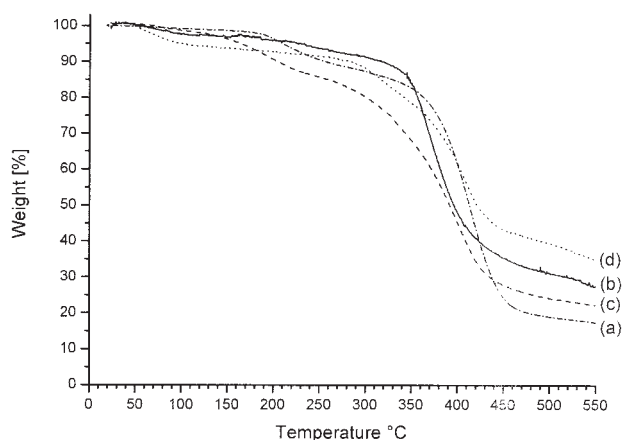


Figure 5 Thermograms for (a) P(N-PhMI-co-AA) and (b) its metal complexes at pH 5 and (c) P(N-PhMI-co-AAm) and (d) its metal complexes at pH 5 (heating rate = 10°C/min in a nitrogen atmosphere).

TABLE V
Thermal Behaviors and TDTs of the Copolymer and its Complexes at pH 5

	Temperature (°C)				TDT (°C)
	200	300	400	500	
<i>N</i> -PhMI- <i>co</i> -AA	2.4	11.4	35.6	79.6	377
<i>N</i> -PhMI- <i>co</i> -AAm	9.5	19.9	54.9	75.8	340
(<i>N</i> -PhMI- <i>co</i> -AA)-M ⁿ⁺ at pH 5	3.7	8.3	52.1	68.6	346
(<i>N</i> -PhMI- <i>co</i> -AAm)-M ⁿ⁺ at pH 5	7.3	12.0	38.2	60.6	347

P(*N*-PhMI-*co*-AA) and 240°C for P(*N*-PhMI-*co*-AAm). The copolymer showed a single T_g , which indicated an alternating character of the copolymers. A slight deviation of the T_g from the copolymer with the complex could be appreciated. T_g for the complexes showed an increase from the T_g value for the copolymers. The same behavior for $\Delta C_p/2$ was observed in both complexes.

CONCLUSIONS

The copolymers P(*N*-PhMI-*co*-AA) and P(*N*-PhMI-*co*-AAm) were synthesized by radical copolymerization and characterized. Their interactions with seven metal ions were investigated in heterogeneous aqueous solutions at different pH values with the LPR technique. At pH 5 and pH 7, most metal ions showed retention values over 70%, except for Ni(II). $[\eta]$ increased in the presence of the metal ions depending on the pH, with the highest values at pH 5 and pH 7. A lower stability of the polymer/metal complexes was found by TGA. For example, the copolymer showed a mass loss between 82.8 and 68.8% at 600°C, and the polymer/

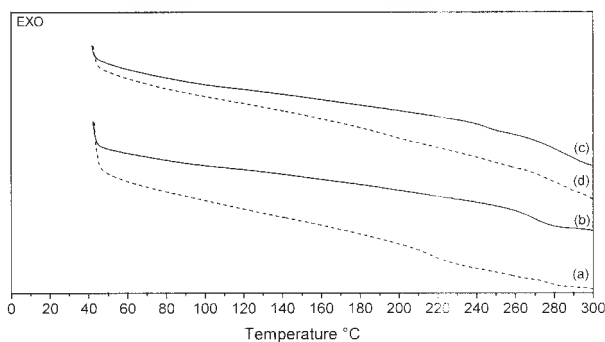


Figure 6 DSC for (a) P(*N*-PhMI-*co*-AA) and (b) its metal complexes at pH 5 and (c) P(*N*-PhMI-*co*-AAm) and (d) its metal complexes at pH 5 (heating rate = 10°C/min in a nitrogen atmosphere).

TABLE VI
 T_g and ΔC_p for P(*N*-PhMI-*co*-AA) and P(*N*-PhMI-*co*-AAm) at pH 5 with Metal Ions

	P(<i>N</i> -PhMI- <i>co</i> -AA)	Complex at pH 5	P(<i>N</i> -PhMI- <i>co</i> -AAm)	Complex at pH 5
T_g (°C)	220	260	240	257
$\Delta C_p/2$ (J g ⁻¹ K ⁻¹)	0.354	0.465	0.318	0.471

metal-ion complex showed a mass loss between 68.8 and 60.0%, respectively. This could be attributed to the formation and rearrangement of different complexes of the copolymer with some metal ions studied.

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