Poly(*N*-phenylmaleimide-*co*-acrylic acid)–Copper(II) and Poly(*N*-phenylmaleimide-*co*-acrylic acid)–Cobalt(II) Complexes: Synthesis, Characterization, and Thermal Behavior

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ABSTRACT: The free-radical copolymerization of *N*-phenylmaleimide (*N*-PhMI) with acrylic acid was studied in the range of 25–75 mol % in the feed. The interactions of these copolymers with Cu(II) and Co(II) ions were investigated as a function of the pH and copolymer composition by the use of the ultrafiltration technique. The maximum retention capacity of the copolymers for Co(II) and Cu(II) ions varied from 200 to 250 mg/g and from 210 to 300 mg/g, respectively. The copolymers and polymer–metal complexes of divalent transition-metal ions were characterized by elemental analysis, Fourier transform infrared, ^{1}H NMR spectroscopy, and cyclic voltammetry. The thermal behavior was investigated with differential scanning calorimetry (DSC) and thermogravimetry (TG). The TG and DSC measurements showed an increase in the glass-transition temperature (T_g) and the thermal stability with an increase in the *N*-PhMI concentration in the copolymers. T_g of poly(*N*-PhMI-*co*-AA) with copolymer composition 46.5:53.5 mol % was found at 251 °C, and it decreased when the complexes of Co(II) and Cu(II) at pHs 3–7 were formed. ○

Keywords: binding properties; hydrophilic polymers; maximum retention capacity; metal-polymer complexes; thermal behavior; thermogravimetric analysis

INTRODUCTION

The copolymerization involving *N*-arylmaleimide has stimulated great interest because of the wide possibilities for the preparation of new materials with improved properties such as flame and heat resistance and thermal and chemical stability.[1,2] The synthesis and some properties of copolymers of alkyl methacrylates with *N*-phenylmaleimide (*N*-PhMI) and its various *p*-substituted phenylmaleimide derivatives have also been reported.[3–7] Our group has previously reported the synthesis, characterization, and thermal behavior of different polymers containing the maleimide moiety.[8–13] We have also recently reported the Cu^{2+}-binding properties of poly(*N*-phenylmaleimide-*co*-β methyl hydrogen

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itaconate) to determine the maximum retention capacity (MRC) at different pHs.

In this article, β-methyl hydrogen itaconate as an electrophilic monomer could be a higher ligand agent than acrylic acid (AA), considered a simple but representative model ligand. In this case, poly(*N*-phenylmaleimide-*co*-acrylic acid) shows a higher MRC than poly(*N*-PhMI-*co*-βMHI), and this finding supports the assumption that the β-carbonyl group cannot interact with the metal because of steric hindrance and can form an unstable polymer–metal complex. It is known that insoluble chelating resins take up transition-metal ions in high yields from aqueous media, but they often adsorb metal ions very slowly because of the lower activity of the ligands placed inside the resin. The metal complexing capacity of the resins depends not only on the nature of the ligand groups but also on their accessibility toward the metal ions. Steric hindrance by the resin matrix and its hydrophobic nature is known to limit the chelating reaction.[15]

The synthesis and polymerization of metal-containing monomers (MCMs) has recently advanced at such a rapid pace because of the efforts of scientists in many countries that a new scientific discipline has been born. It is characterized by novel compositions and unusual properties, which are determined not only by the metals in them but also by the nature of the polymer matrix.[16] Polymeric chains and chelating rings are characteristic of MCMs. The interest in such compounds is primarily due to their wide use as catalysts, antifriction materials, biologically active substances, electrically conductive coatings, and so forth.[17]

Good optical properties and mechanical properties (high tensile strength and impact strength), high softening points, and durability (retention of optical and mechanical properties and abrasion resistance) are some of the requirements for polymers in such applications.[18]

The liquid-phase polymer retention (LPR) technique has important technological applications.[19–22] The LPR technique as an ultrafiltration system (Amicon) was employed to test the coordination properties in the formation of complexes of the copolymers.

This article reports the solution radical copolymerization of *N*-PhMI with AA, the MRC and binding properties of the synthesized copolymers with Cu(II) and Co(II) at different pHs, and the effect of the incorporation of metal ions into the copolymers on the thermal behavior of these complexes.

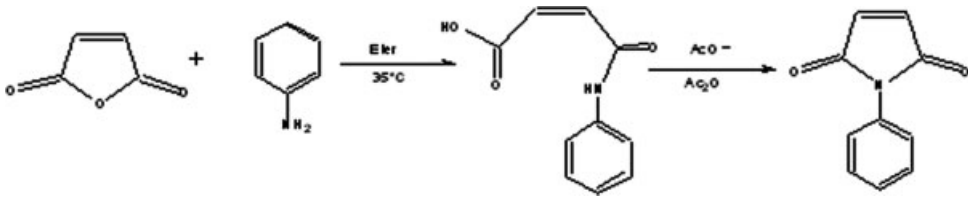
EXPERIMENTAL

Materials

AA (Merck) and aniline (for analysis; Merck) were obtained from commercial sources and purified by distillation under reduced pressure. Dioxane was dried over metallic sodium overnight and then distilled. Benzoyl peroxide (BPO; Fluka) was recrystallized from chloroform and then dried. Ethyl ether was obtained from a commercial source (for analysis; Merck).

Preparation of *N*-PhMI

N-PhMI was synthesized by the reaction of maleic anhydride with aniline in diethyl ether according to a published procedure.[23] The reaction scheme for the preparation of this monomer is shown next:



Preparation of Poly(*N*-PhMI-*co*-AA)

A reaction mixture containing *N*-PhMI and AA as comonomers in different feed molar ratios but with the total amount constant (14 mmol), with 0.6 mg of the initiator (BPO) and 6 mL of dioxane as a solvent, was placed in a copolymerization flask under a nitrogen atmosphere (N_2). This flask was sealed *in vacuo* (10^{-3} mmHg) and was placed in an oil bath at 70 °C for 12 h. The polymer material received was filtered off, washed

with ethyl ether, collected, and dried *in vacuo* up to a constant weight before characterization.

Preparation of the Complexes

The solid complexes were prepared by the addition of an aqueous suspension (2 wt %) of poly(*N*-PhMI-*co*-AA) at pHs 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 a membrane with an exclusion limit of the molecular weight of 10,000 g mol^{-1} (Amicon ultrafiltration equipment) and pressure of 300 kPa. The reservoir contained water at the same pH of the cell solution. Protolysis was employed for the regeneration of the copolymers. Complexes 1–6 were treated with concentrated nitric acid (100 mg mL^{-1}). The metal-ion concentration in the filtrate and in the retentate was determined by atomic absorption spectroscopy. The new complex was dried for further analytical control by thermal analysis and Fourier transform infrared (FTIR).

Characterization of the Copolymers

Measurements

Structural characterization was performed with IR and ^{1}H NMR spectroscopy. FTIR spectra were measured on a Bruker Vector 22 spectrophotometer, and ^{1}H NMR spectra were recorded on a Bruker MSL500 spectrometer (500 MHz) with dimethyl sulfoxide-d_6 (DMSO-d_6; 99.8%) and with tetramethylsilane (TMS) as an internal standard. The elemental analyses were carried out with a CE Fison 1108 analyzer.

Thermal stability studies were performed with a Mettler–Toledo Star System thermogravimetric analyzer at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were carried out with a Mettler–Toledo Star System 822e to determine the glass-transition temperature (T_g) of the copolymer and its complexes (T_g at $\Delta C_p/2$, in the middle of ΔC_p). T_g was measured at a heating rate of 10 °C/min. The determination of the metal-ion concentration in the filtrate was carried out with a PerkinElmer 1100 atomic absorption spectrophotometer. The complexes were dried with Labconco 6L continuous-freeze-drying equipment.

Copolymer Composition

The molar percentages of the comonomer units (m_1 and m_2) in poly(*N*-PhMI-*co*-AA) were calculated with elemental analysis data (content of nitrogen) according to the following equation:

$$m_1 = \frac{M_2}{[(A_N/B) - \Delta M \times 10^{-2}]}$$

where M_2 is the molecular weight of the AA unit, A_N is the atomic weight of N, B is the concentration of N in the copolymer (%), and ΔM is equal to $M_1 - M_2$. M_1 is the molecular weight of the *N*-PhMI unit (see Tables 1 and 2).

The ^{1}H NMR spectrum (DMSO-d_6/TMS) shows the following signals (δ/ppm): 2.1 (—CH_2—) from the backbone, 2.8–4.0 (2H, imide, and 3H, AA), and 6.6–7.8 (5H, aromatic ring). The relation of the area of the aromatic ring protons (5H) to those of the AA protons (3H) confirms the copolymer compositions calculated by elemental analysis.

The FTIR spectra show the following most typical absorption bands (cm^{-1}) for copolymer 3: 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 (N—C stretching from imide ring) and 1388.6 (CH_2 bending),

Table 1. Elemental Analysis: N/C Relationship and Copolymer Composition Results

	Elemental Analysis [Found (Calculated)]			
Copolymer	N (%)	C (%)	H (%)	N/C Relationship
1	6.9730 (7.0855)	65.9010 (66.9591)	4.1863 (4.2627)	0.10581 (0.10582)
2	6.5520 (6.6096)	65.2440 (65.8202)	4.5210 (4.3521)	0.10042 (0.10042)
3	5.4500 (5.4704)	62.9140 (63.0939)	4.6490 (4.5663)	0.08663 (0.08670)
4	4.1400 (4.1240)	60.1220 (59.8716)	4.1030 (4.8193)	0.06886 (0.06888)
5	3.2090 (3.3436)	55.6230 (58.0039)	4.4820 (4.9660)	0.05769 (0.05764)

Table 2. Experimental Conditions and Yield of the Copolymerization Reaction of *N*-PhMI with AA at 70 °C after 12 h in Dioxane[a]

Copolymer	M_1 [mol % (mmol)]	M_2 [mol % (mmol)]	Initiator (μmol)	Solvent (mL)	Yield (%)	m_1 (mol %)
1	75.0 (10.5)	25.0 (3.5)	7.0	6.0	43.5	74.6
2	66.7 (9.3)	33.3 (4.7)	7.0	6.0	45.0	65.0
3	50.0 (7.0)	50.0 (7.0)	7.0	6.0	46.0	46.5
4	33.3 (4.7)	66.7 (9.3)	7.0	6.0	48.0	30.2
5	25.0 (3.5)	75.0 (10.5)	7.0	6.0	50.0	22.7

[a] M_1 and M_2 are the feed monomer compositions for *N*-PhMI and AA, respectively; m_1 is the copolymer composition of monomer 1.

and 690.5 and 622.9 (monosubstituted benzene ring and C—N—C bending).

Cyclic Voltammetry (CV)

CV was carried out with a Weenking POS 88 instrument with a Kipp Zenen BD93 recorder in dimethyl sulfoxide (DMSO; ca. 1.0×10^{-3} mol dm^{-3}) under a nitrogen atmosphere with tetrabutyl ammonium perclorate (TBAP) (ca. 0.1 mol dm^{-3}) with three-electrode cells. A hanging drop mercury electrode was used as the working electrode, a platinum wire was used as the auxiliary electrode, and a saturated calomel electrode was used as the reference electrode.

Electron Spin Resonance (ESR) Spectroscopy

The ESR spectrum was recorded in the X band (9.85 GHz) with 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.

RESULTS AND DISCUSSION

Synthesis and Characterization

N-PhMI was copolymerized with AA in dioxane in the presence of BPO as a radical initiator with different feed molar ratios at a constant total amount of the comonomers. The copolymer composition was determined from the N/C ratio on the basis of elemental analysis data (see Table 1). The relationship of the area of the aromatic ring protons to those of the AA protons confirms the copolymer compositions calculated by elemental analysis.

The experimental copolymerization conditions and results are shown in Table 2. The yields are lower than 50% for all copolymerization reactions. A plot of M_1 (molar fraction of *N*-PhMI in the feed) versus m_1 (molar fraction of *N*-PhMI in the copolymer) is shown in Figure 1. This indicates that the copolymers have a tendency to alternate. The obtained copolymers were soluble in DMSO and insoluble in water, methanol, acetone, and chloroform.

MRC of Poly(*N*-PhMI-*co*-AA) with Cu(II) and Co(II) at Different pHs

The copper- and cobalt-ion binding capacity of copolymer 3 was determined at different pHs (see Table 3). The MRC varied for Co(II) ions from 200 to 250 mg/g and for Cu(II) from 210 to 300 mg/g. The highest retention capacity data were obtained at pH 7. The high coordination capacity of carboxylic groups with divalent cations is well known. Therefore, the higher retention capacity for this copolymer with a 50 mol % concentration

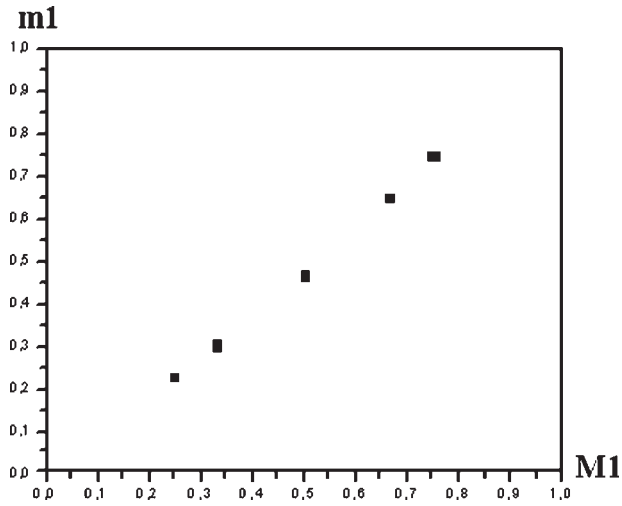


Figure 1. Relationship of the copolymer composition (m_1) and feed monomer ratio (M_1) for the copolymerization of *N*-PhMI with AA.

Table 3. MRC of Copolymer 3 with Co(II) and Cu(II) Ions at Different pHs

Complex	Copolymer 3 pH/Metal Ion	MRC (mg/g)
1	pH 3/Co(II)	200
2	pH 5/Co(II)	240
3	pH 7/Co(II)	250
4	pH 3/Cu(II)	210
5	pH 5/Cu(II)	280
6	pH 7/Cu(II)	300

of AA can be attributed to the carboxylic and carboxylate groups from AA and the nitrogen atom of the maleimide units at different pHs, favoring the arrangement of these groups to coordinate with cobalt and copper ions, particularly at the metal-ion concentration used.

Binding Properties for Complexes of Copolymer 3 with Cu(II) and Co(II) at pH 7

The FTIR spectrum did not show an important change in the broad band at 3436.9 and 3421.5 cm^{-1} for complexes 3 and 6, respectively. It could be attributed to the noninteraction of the hydroxyl groups in the complexes with metal ions. However, the C=O band of the carboxylic group at 1703.0 cm^{-1} decreased in intensity for complexes 3 and 6 (see Fig. 2). This can be attributed to the interaction between the carbonyl group and the metal ions. In addition, the complexes showed new bands at 1560.3 and 1560.0 cm^{-1} for Co(II) and Cu(II), respectively, because of the coordination of the cobalt and copper ions with the carboxylate groups in the last one with higher intensity. In this polymer–metal complex, it is suggested that the metal ion is bound to the nitrogen atom from the imide group, for which the band (sharp) from N—C (stretching) at 1498 cm^{-1} presented a decrease in the intensity of the signal. 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 AA (see Scheme 1).

To characterize the reduction behavior of copolymer 3 and its complexes 3 and 6, CV studies were carried out. CV of *N*-PhMI showed one

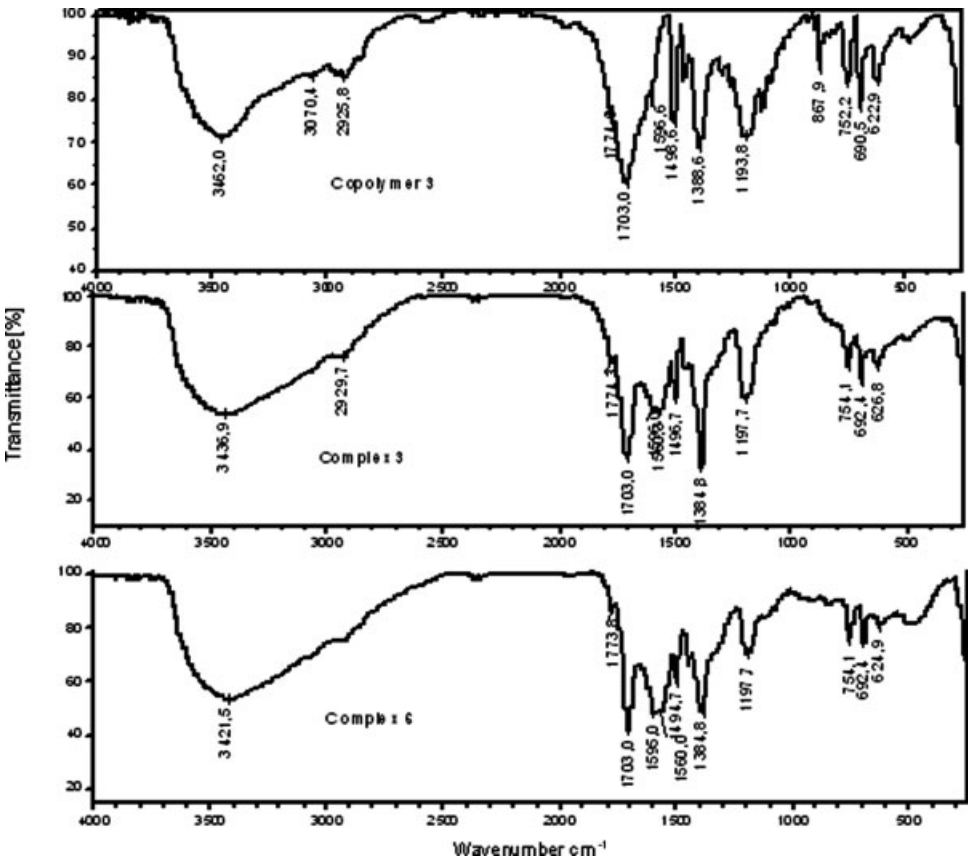
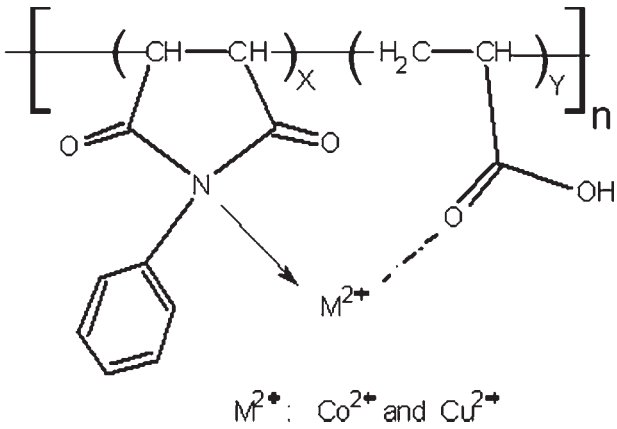


Figure 2. FTIR spectra of copolymer 3 and complexes 3 and 6.



Scheme 1. Structure of the Cu(II) and Co(II) complexes of poly(*N*-PhMI-*co*-AA).

well-defined reduction wave in DMSO (−0.972 V). The wave could correspond to an irreversible two-electron transfer, which could be attributed to the reduction of an imide moiety to 2,5-dihydroxypyrrole derivatives. CV of copolymer 3 displayed two irreversible waves in the whole range of the sweep rates used (50–2000 mV/s). Two peaks appeared at −0763 and −0.985 V (at 2000 mV/s). The first wave was attributed to the reduction of the carbonyl group of the AA moiety. A similar peak was found when the AA monomer was measured in DMSO. The second peak was attributed to the reduction of the imide moiety. Finally, CV of complex 6 showed one peak in the whole range of sweep rates used around −0.750 V, and it was attributed to the reduction of the carbonyl

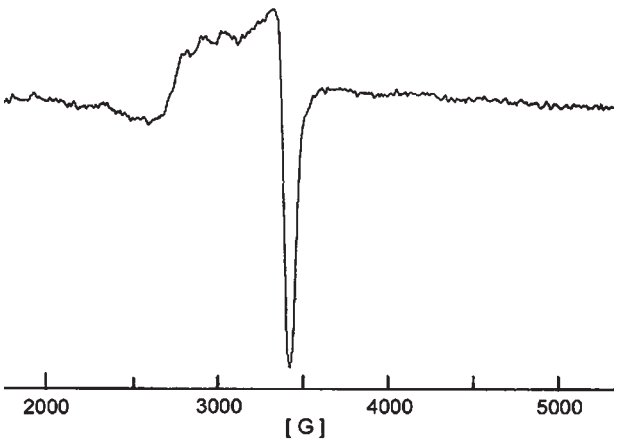


Figure 3. ESR experimental spectrum of complex 6 (spectrometer conditions: microwave frequency = 9.68 GHz, microwave power = 20 mW, modulation amplitude = 0.2 G, scanning rate = 1.25 G/s, and time constant = 0.5 s).

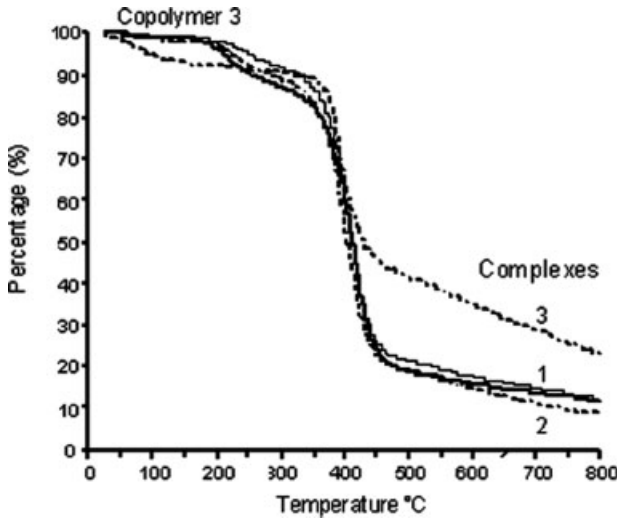


Figure 4. TG thermograms of copolymer 3 and complexes 1–3.

group of the AA moiety. Similar behavior was found for complex 3.

The study of the binding capacity was carried out with five copolymers at different copolymer compositions. Those with feed monomer ratios of 3:1, 2:1, 1:1, 1:2, and 1:3 showed no important differences at the same pH. The MRC of the Cu(II) and Co(II) complexes showed a slight increase when the content of AA in the backbone chain was increased. The highest MRC values were found at pHs 5 and 7, and these were related to the copolymer composition when the content of AA was increased. The MRC values for the polymer–metal complex can

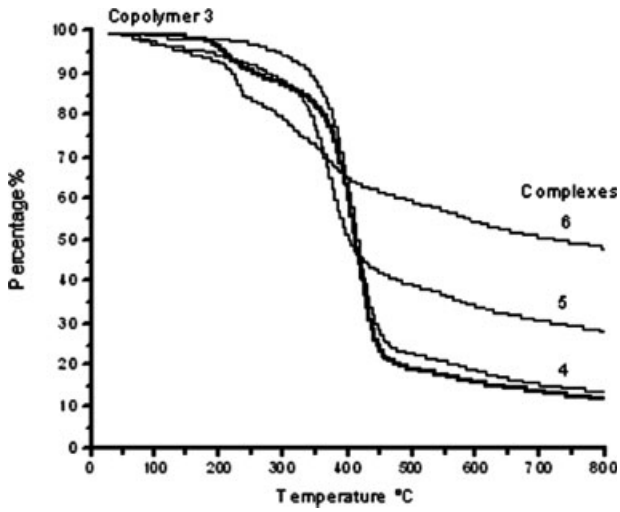


Figure 5. TG thermograms of copolymer 3 and complexes 4–6.

Table 4. Weight Loss as a Function of the Final Thermal Decomposition Temperature of Copolymer 3 and Its Complexes 1–6

		Weight Losses (%) at Different Temperatures (°C)						
Sample	TDTe (°C)	200	300	400	500	600	700	800
Copolymer 3	350.4	2.4	11.4	35.6	81.0	82.8	84.8	86.8
Complex 1	372.8	0.4	6.5	35.3	77.0	80.6	83.5	85.8
Complex 2	370.0	0.8	8.8	44.2	79.0	83.2	86.8	89.1
Complex 3	373.2	0.7	1.9	26.8	51.4	57.6	63.8	69.7
Complex 4	357.9	0.3	3.6	34.1	75.7	79.6	82.9	84.5
Complex 5	331.6	1.6	7.5	45.2	56.7	61.6	65.2	67.8
Complex 6	215.0	2.3	15.7	30.1	35.7	40.6	44.2	46.5

be compared with the binding properties for Cu(II) of a polychelating hydrogel such as poly (acrylic acid-*co*-itaconic acid); their adsorption properties at pH 6.0 were 147 mg of metal ions/g and at pH 9 were 320 mg of metal ions/g of polymer.[24] Other commercial resins such as poly (glycidyl methacrylate-*co*-ethylene dimethacrylate) modified with aspartic acid, despite the highest values of MRC of Cu^{2+}, of 24.1 mg/g at pH acid.[25] The MRC for poly(*N*-PhMI-*co*-AA) is higher than the MRC of these resins.

To characterize complex 6, ESR studies were performed. The ESR spectrum was recorded at different copolymer compositions and pHs. Complex 6 showed a well-defined ESR spectrum at pH 7 (see Fig. 3). The ESR pattern corresponded to a typical square planar or tetragonal Cu(II) coordination geometry, with $g_{\|} = 2.18$ (value parallel), $g_{\perp} = 2.05$ (value perpendicular), and $A_{\|} = 107$ (parallel hyperfine constant).

Thermal Behavior

Thermogravimetric Analysis

Increasing the *N*-PhMI content in the copolymer led to a slight increase in the onset temperature decomposition. The thermogravimetry (TG) of copolymer 3 and its complexes 1–6 is plotted in Figures 4 and 5, and the data derived from them are collected in Table 4.

Copolymer 3 degraded in a one-step process. After the first elimination of water, monomer residue, and other low-molecular-weight impurities, the resulting material had an extrapolated thermal decomposition temperature (TDTe) of 350 °C.

The Co(II) and Cu(II) complexes showed higher TDTe values than copolymer 3, except for complexes 5 and 6 at pHs 5 and 7. The major weight loss for copolymer 3 and its complexes occurred between 400 and 500 °C, except for

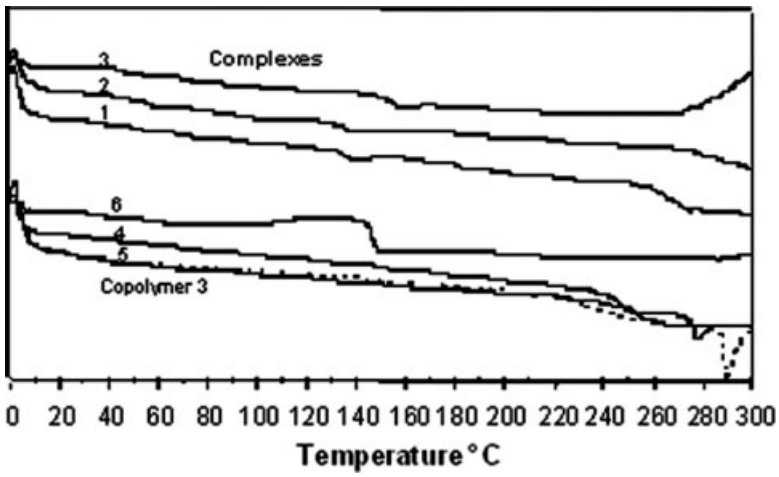


Figure 6. DSC thermograms for copolymer 3 and complexes 1–6.

Table 5. T_g and ΔC_p for Copolymer 3 and Its Complexes 1–6

		Complexes					
	Copolymer 3	1	2	3	4	5	6
T_g (°C)	251.0	246.0	231.2	146.2	135.0 258.7	133.0	151.8
$\Delta C_p/2$ (J g^{-1} K^{-1})	0.465	0.451	0.354	0.631	0.117 0.377	0.146	0.159

complex 6; this showed 45.6% decomposition at 600 °C and increased up to 51.5% at 800 °C (see Table 4). The residue mass of complex 6 may be attributed to a higher percentage of metal incorporated at this pH. Under 200 °C, the weight loss was not significant and was attributed to the loss of the solvent and small amounts of monomer residues in copolymer 3.

T_g

T_g was estimated from the second DSC run. To determine the T_g values of the samples, the criterion of T_g at $\Delta C_p/2$ was used in all cases.

The T_g values of the copolymer and its complexes 1–6 are presented in Figure 6 as a function of the different metal-ion contents.

All the synthesized copolymers showed a single T_g, which indicated the formation of random copolymers. The T_g values of copolymers 1–5 varied from 190 to 250 °C and increased with a higher *N*-PhMI concentration in the copolymer. A great deviation of T_g of copolymer 3 and its complexes can be observed. The T_g values of all the complexes were lower than the T_g value for copolymer 3. The T_g values for the copper(II) complexes showed a decrease from pH 3 to pH 7 (see Table 5 and Fig. 6).Two T_g's for complex 4 were detected. The higher T_g should be attributed to the copolymer fraction without metal ion incorporated because of polymer–polymer interactions (hydrogen-bond interactions in the copolymer).

CONCLUSIONS

Complexes of poly(*N*-PhMI-*co*-AA) with Cu(II) and Co(II) were synthesized and investigated as a function of the pH. The MRCs for the copolymers at different copolymer compositions showed no important differences. The MRCs for Cu(II) and Co(II) varied from 210 to 300 mg/g and from 200–250 mg/g, respectively, at pH 5, and a slight increase was observed when the content of AA in the backbone chain was increased. At pHs 5 and 7, the highest retention values were found, and these were related to the copolymer composition.

The ESR studies indicated that complex 6 corresponded to a typical square planar or tetragonal Cu(II) coordination geometry.

The thermal behavior in TG for all the complexes was not significantly different, except for complex 3, with Co(II) at pH 7, which showed a higher TDTe.

Complex 4, with Cu(II) at pH 3, showed a small increase in TDTe. The increase in the *N*-PhMI unit in the copolymers at the same time increased T_g and the thermal stability of the copolymers.

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