Poly(*N*-phenylmaleimide-*co*-*β*-methyl hydrogen itaconate): Synthesis, Characterization, and Copper(II)-Ion-Binding Properties

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ABSTRACT: The radical copolymerization of *N*-phenylmaleimide was carried out with *β*-methyl hydrogen itaconate at 70°C for 12 h. The copolymers were characterized by elemental analysis, thermal analysis, Fourier transform infrared, and ^{1}H-NMR spectroscopy. The monomer reactivity ratios were determined by the Kelen–Tüdös and Fineman–Ross methods. These values demonstrated that the copolymerization reaction produced statistical copolymers with a tendency to alternation. The retention capacity of the copolymers for Cu^{2+} ions varied from 296 to 348 mg/g at pHs 5 and 7. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1361–1367, 2005

Key words: copolymerization; metal-polymer complexes; thermal properties

INTRODUCTION

There is increasing interest in the synthesis of new types of polymeric materials and in the modifications of the primary structures of polymers.[1] The syntheses of poly[(*N*-phenylmaleimide)-*co*-(methyl methacrylate)] and poly[(*N*-tribromophenyl maleimide)-*co*-(methyl methacrylate)] and the phase behaviors of their blends with poly(methyl methacrylate), polycarbonate, poly(maleic anhydride-*alt*-styrene), and poly-(styrene-*alt*-acrylonitrile) have been reported.[2]

The copolymerization reactions involving *N*-phenylmaleimide (*N*-PhMI) have stimulated much interest because of the great potential for the preparation of new materials with improved properties, such as flame and heat resistance and thermal and chemical stability.[3–5] The syntheses and some properties of copolymers of alkyl methacrylates with *N*-PhMI and several N-p-substituted derivatives have also been reported.[6–9] We have previously reported the syntheses, characterizations, and thermal behaviors of different polymers containing the maleimide moiety.[10–14]

The radical copolymerization of *N*-PhMI with styrene, vinyl acetate, and methyl methacrylate has been studied.[15] The copolymerization of *N*-PhMI and styrene yields a copolymer composition close to an alternating distribution, which is independent of the concentration in the monomer feed, whereas the reactions of *N*-PhMI with vinyl acetate and methyl methacrylate form statistical copolymers. There is growing interest in polymers with the ability to remove and concentrate metal ions, particularly those that have an impact on the environmental. One of the most important techniques is liquid-phase polymer-based retention (LPR).[16] This technique combines the use of water-soluble polymers (WSPs) with ultrafiltration membranes; this separates low-molecular-mass species as free ions from high-molecular-mass compounds such as precursor polymers and polymer–metal complexes (PMCs). It is assumed that the only separation mechanism is size exclusion by the ultrafiltration membranes. The LPR technique has important technological applications.[16–22] The projection of its use has the great challenge of increasing the selectivity of the WSP used toward binding specific metal ions. The LPR technique has been demonstrated to be an excellent tool for quantitatively studying polymer/metal-ion interactions.
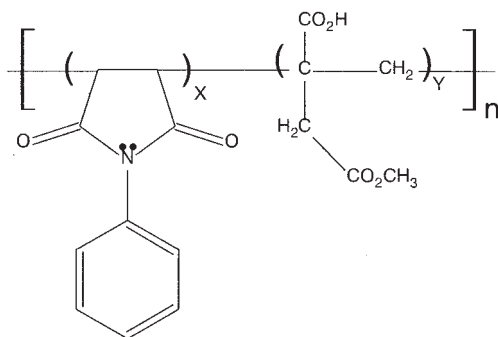
This article describes the synthesis and characterization of poly(*N*-phenylmaleimide-*co*-*β*-methyl hydrogen itaconate) [poly(*N*-PhMI-*co*-*β*-MHI)] and its binding capacity for copper(II) ions at different pHs.

Scheme 1 Structure of poly(*N*-PhMI-*co*-β-MHI).

EXPERIMENTAL

Materials

N-PhMI was synthesized from maleic anhydride and aniline in diethyl ether according to a published procedure.[23] It was purified by recrystallization from cyclohexane. The yield of *N*-PhMI was 80%, and its melting point was 88–89°C.

β-Methyl hydrogen itaconate (β-MHI) was obtained from itaconic acid according to Baker and Shoes.[24] The metal salt (sulfate, p.a., for analysis; Merck, Darmstadt, Germany) was analytical-grade and was used as received.

Copolymerization

A typical procedure for the copolymerization was as follows. A mixture of *N*-PhMI and β-MHI (11.56 mmol) was made in dioxane (4 mL) and benzoyl peroxide (BPO), which was used as an initiator (57.8 μmol), and was placed in a copolymerization flask under N$_2$. The flask was kept at 70°C for 12 h. The mixture was poured into 50 mL of diethyl ether to precipitate the copolymer. The copolymer, poly(*N*-PhMI-*co*-β-MHI), was separated by centrifugation, purified by reprecipitation, and dried *in vacuo* until a constant weight was obtained.

Measurements

Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer model 1818 spectrophotometer (Perkin Elmer, Shelton, CT). The ^{1}H-NMR spectra were recorded at room temperature with a Bruker AC 250 (Bruker, Karlsruhe, Germany) with dimethyl sulfoxide-d_6 (DMSO-d_6; 99.8%) and tetramethylsilane (TMS) as an internal standard. The concentration of copper(II) ions was determined with atomic absorption spectrometry.

Copolymer composition

The elemental analyses were carried out with a Carlo Erba 1106 analyzer (Italy). The molar percentages of

the comonomer units (m_1 for *N*-MHI and m_2 for β-MHI) in poly(*N*-PhMI-*co*-β-MHI) were calculated with elemental analysis data (nitrogen concentration):

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

where M_2 is the molecular weight of β-MHI units, A_N is the atomic weight of nitrogen, B is the nitrogen concentration in the copolymers (%), ΔM is the difference between M_1 and M_2, and M_1 is the molecular weight of the *N*-PhMI units.

Preparation of the polychelates

Solid PMCs were prepared by the addition of an aqueous solution of poly(*N*-PhMI-*co*-β-MHI) (2 wt %) at pHs 3, 5, 7, and 9 to aqueous solutions (10 wt %) of the metal salts. The PMCs were separated by decantation and purified by membrane filtration with a membrane with a molecular weight exclusion limit of 10,000 g mol^{-1}.

A reservoir containing water was adjusted to the same pH as that of the cell solution. Protolysis was used for the regeneration of poly(*N*-PhMI-*co*-β-MHI). The copolymer–copper(II) complex was treated with concentrated nitric acid (100 mg mL^{-1}). The copper-ion concentration in the retentate was determined with atomic absorption spectroscopy.

RESULTS AND DISCUSSION

N-PhMI was copolymerized with β-MHI at different feed molar ratios but with the total amount of the comonomers kept constant. The general structure of the copolymers is illustrated in Scheme 1.

The experimental copolymerization conditions and results are shown in Table I.

The copolymer compositions were determined from elemental analysis data (see Table II).

The copolymers were insoluble in water, methanol, and chloroform and soluble in acetone and dimethyl

TABLE I
Experimental Conditions and Results of the Copolymerization of *N*-PhMI with β-MHI at 70°C for 12 h in Dioxane (4 mL)

Copolymer sample	f_1	F	M_1 (mmol)	M_2 (mmol)	Initiator BPO (μmol)	Yield (%)
1	25	25	2.89	8.67	57.6	41.5
2	33	31	3.85	7.71	57.8	36.2
3	50	42	5.78	5.78	57.8	34.4
4	67	55	7.71	3.85	57.8	37.5
5	75	63	8.67	2.89	57.6	36.9

[M]$_{total}$ = 2.89 mol/L.

TABLE II
Data from the Copolymerization of N-PhMI with β-MHI Used to Determine r_1 and r_2 by the K–T Method

Feed monomer ratio (mol %)		Yield (%)	Elemental analysis (%)			Copolymer composition		K–T equation parameter	
M_1	M_2		C	H	N	m_1	m_2	ε	η
25	75	41.5	55.41	5.32	2.35	25	75	0.865	0.13
33	67	36.2	55.37	5.23	2.81	31	69	0.736	0.06
50	50	34.4	56.58	4.87	3.76	42	58	0.455	−0.11
67	33	37.5	60.49	4.75	4.80	55	45	0.226	−0.24
75	25	36.9	62.09	4.59	5.42	63	37	0.135	−0.27

sulfoxide (DMSO). The yield was lower than 43% for all the copolymerization reactions, and there was not an important effect of the monomer feed composition (f_1) on the yield.

The FTIR spectrum (KBr, cm^{-1}) of poly(N-PhMI-co-β-MHI) is shown in Figure 1. The most characteristic absorption bands can be observed: 3467.6 (OH, —COOH), 2956.9 (CH, CH_2 stretching), 1775.2 (C═O imide), 1740 (C═O ester), 1703.1 (C═O, —COOH stretching), 1597.8 (CH— stretching aro-

matic ring), 1439 and 1396 (CH_2, bending), and 694 and 626 cm^{-1} (monosubstituted benzene ring, C—N—C bending).

Copolymer/Cu(II)-ion complexes in a basic medium

The FTIR spectra of the complexes showed an important change in the broad band at 3448.9 (OH—, —COOH) and 2954.5 cm^{-1} (CH, CH_2 stretching) and

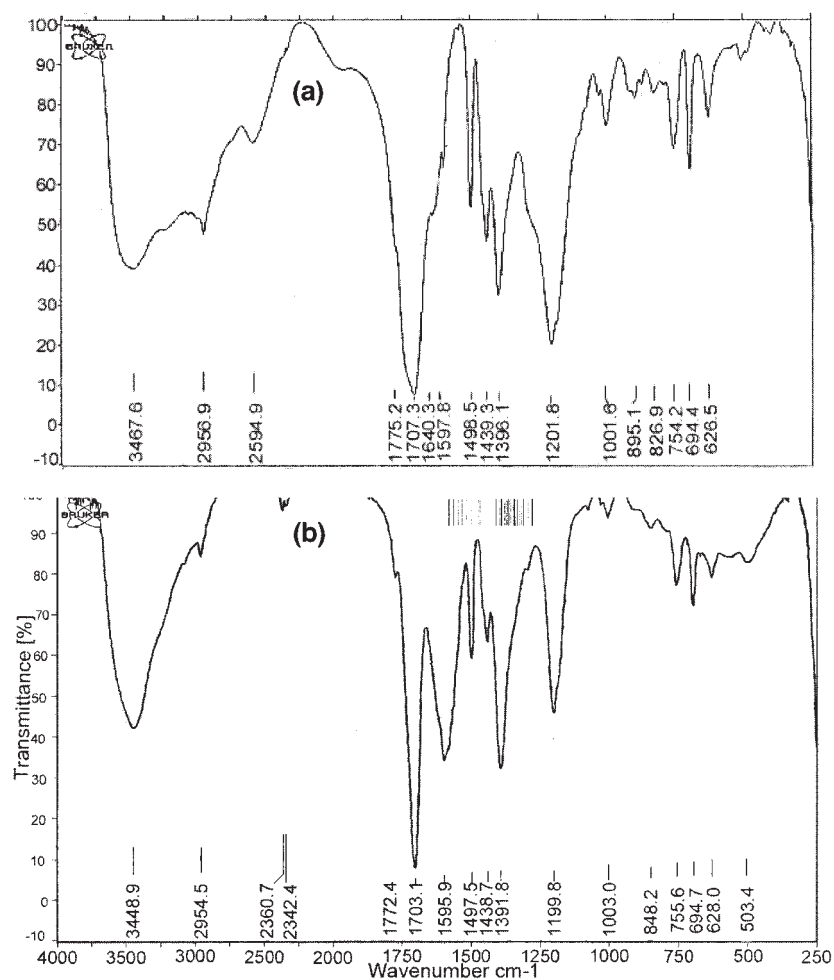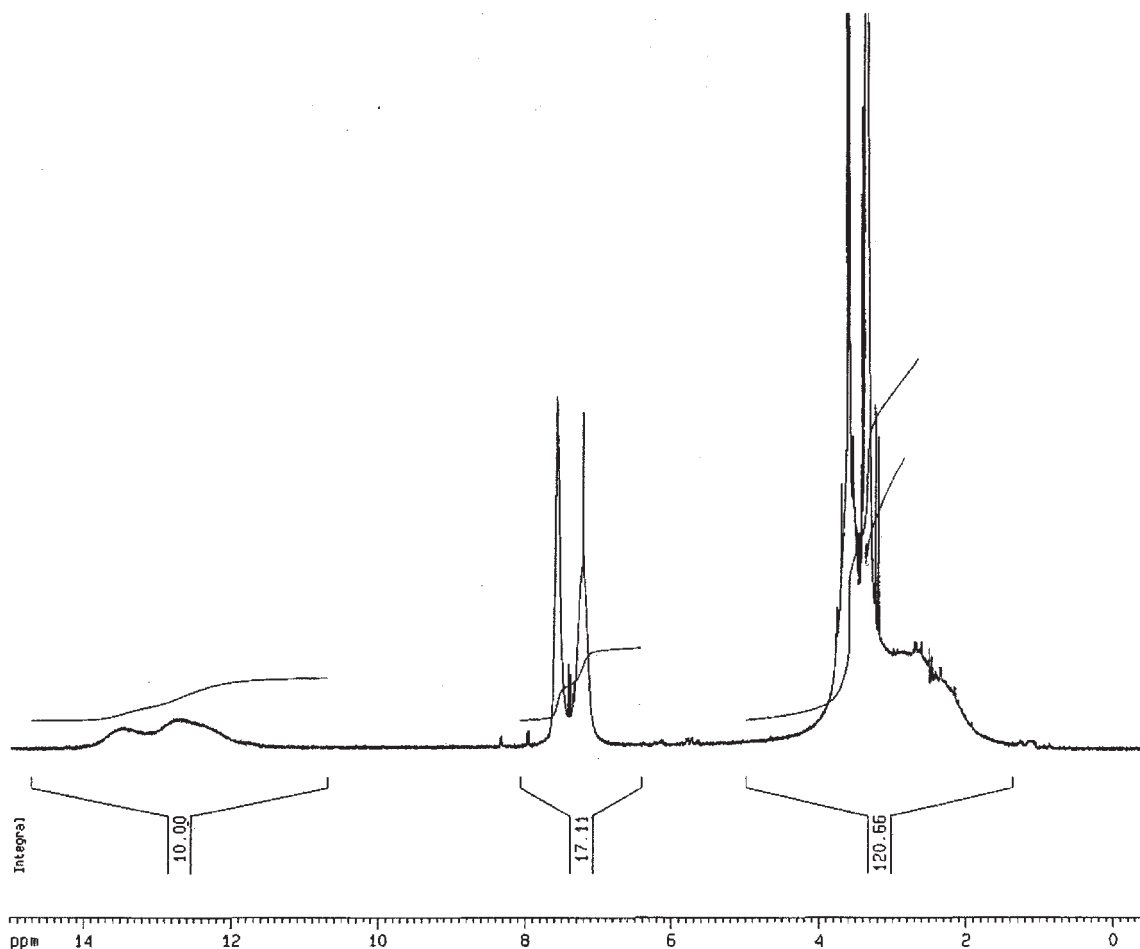**Figure 1** FTIR spectra of (a) poly(N-PhMI-co-β-MHI) and (b) the poly(N-PhMI-co-β-MHI)-Cu(II) complex.

Figure 2 ^{1}H-NMR spectrum (250 MHz, DMSO-d_6, room temperature, TMS as an internal standard) of poly(N-PhMI-co-β-MHI).

at those bands of C=O from ester and COOH at 1740.3 and 1707 cm^{-1}, respectively. The most characteristic absorption bands were observed at 3448 (OH—, —COOH, sharp), 1703 (C=O from imide, COO$^-$ from the ionization of COOH and ester groups), 1585 (C=O from carboxylic acid predominantly coordinated around the copper ions), and 1394 cm^{-1} (CH$_2$, bending). The interaction of the units could lead to the formation of molecular complexes with electron-donating nitrogen from imide and carboxylate groups from COOH at a basic pH (intramolecular complexes).

The ^{1}H-NMR spectrum (DMSO-d_6/TMS; N-PhMI-co-β-MHI) showed the following signals at δ (ppm): 2.2 (—C—CH$_2$) from the backbone, 2.6 (—CH$_2$, CH$_2$COO), 2.8–3.8 (—CH— from imide, CH$_3$ from OCH$_3$), and 7.0–7.7 (—CH—, aromatic ring). They were broad because of the presence of various types of protons with similar chemical shifts (see Fig. 2).

Monomer reactivity ratios

To determine the monomer reactivity ratios, the monomer feed composition (f) was plotted against the

monomer composition in the copolymer (F; mol %) for N-PhMI (Fig. 3).

The monomer reactivity ratios for N-PhMI and β-MHI were determined from the monomer feed ratios and the copolymer compositions obtained at relatively high conversions according to the high-conversion Kelen–Tüdös (K–T) method.[25] The K–T equation symmetrically was transformed into
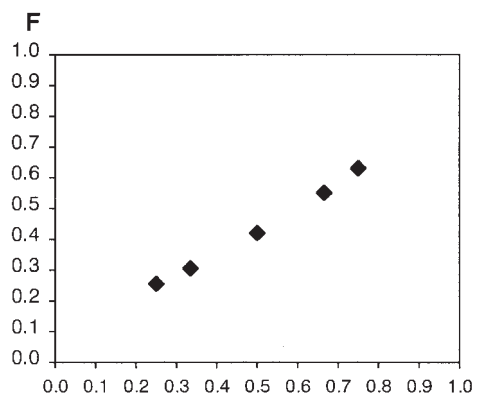
Figure 3 Relationship between f and F for N-PhMI.
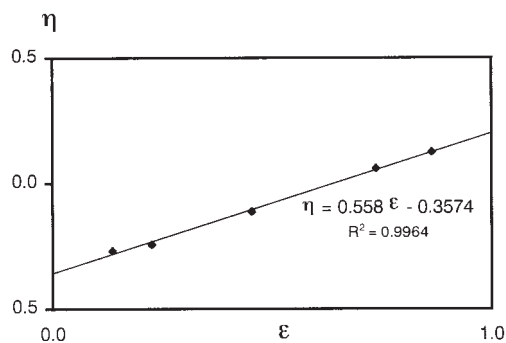
Figure 4 η–ε representation of the copolymerization parameters according to the K–T method for the polymerization of N-PhMI with β-MHI.

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

with the addition of the new parameters ξ, η, and $\alpha = (F_{min} \times F_{max})^{0.5}$. F is the copolymer molar fraction, and F_{min} and F_{max} are the smallest and largest copolymer fractions, respectively (see Table II).

The transformed variables are defined as follows:

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

The monomer reactivity ratios (r_1 and r_2) were also determined according to eq. (2):

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

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

In addition, G is equal to $(m_1/m_2 - 1)/z$, and F is equal to $(m_1/m_2)/z^2$. z is equal to $\log(1 - \delta_1)/\log(1 - \delta_2)$; δ_1 is equal to $\delta_2 y/X_0$, and δ_2 is equal to wt % $(\mu + X_0)/(\mu + y)/100$. μ is equal to μ_2/μ_1, y is equal to m_1/m_2, X_0 is equal to M_1/M_2, and wt % is the conversion; μ_1 and μ_2 are the molecular weights of monomer 1 and 2, respectively.

ξ can take any possible value between 0 and 1. A plot of η versus ξ gives a straight line, which upon extrapolation to $\xi = 0$ and $\xi = 1$ gives $-r_2/\alpha$ and r_1, respectively (see Fig. 4).

According to these values, the monomer reactivity ratios were as follows: $r_1 = 0.2$ and $r_2 = 0.74$, ($r_1 \times r_2 = 0.148$). For comparison, the Fineman–Ross method[26] was used, and the values were $r_1 = 0.24$ and $r_2 = 0.78$ ($r_1 \times r_2 = 0.187$), which demonstrated very good agreement with those determined by the K–T method.

In general, these results suggest that the chain growth reactions proceeded predominantly by the addition of acrylic monomers to the ~N-PhMI · macro-

radical, producing statistical copolymers with more β-MHI units incorporated. We previously published the reactivity monomer ratios for poly(N-maleoylglycine-co-acrylic acid) [poly(MG-co-AA)] and poly(N-maleoylglycine-co-acrylamide) [poly(MG-co-AAm)][27] and showed that the two acrylic monomers possessed a similar tendency of incorporation into the chain, although the acrylamide presented a greater tendency to homopropagation. The results of the copolymerizations yielding poly(MG-co-AA) and poly(MG-co-AAm) showed that acrylic acid and acrylamide possessed approximately the same reactivity toward N-maleoylglycine and had a strong tendency toward alternation.

Hocking et al.[28] applied the K–T method to poly-[(sodium N-sulfophenyl)maleimide)] with acrylamide and determined the monomer reactivity ratios ($r_1 = 0.31$ and $r_2 = 0.55$).

TABLE III
Binding Capacity of Poly(N-PhMI-co-β-MHI) for the Cu(II) Ion at Different pH Values

m_1/m_2 (mol %)	pH	Volume (mL; 10 wt %)	Cu^{2+} retentate (mg)	Binding capacity (mg/g)
25:75	3	1.70	52.8	264.1
25:75	5	1.65	65.6	328.2
25:75	7	1.60	60.2	300.6
25:75	9	1.60	58.5	290.5
42:58	3	1.65	44.1	220.6
42:58	5	1.75	69.6	348.0
42:58	7	1.70	67.6	338.0
42:58	9	1.60	60.0	300.0
63:37	3	1.70	40.1	200.6
63:37	5	1.60	63.6	318.0
63:37	7	1.55	59.3	296.5
63:37	9	1.55	58.2	290.8

Binding capacity of poly(N-PhMI-co-β-MHI) for Cu(II) at different pHs

The copper-ion-binding capacity was determined at different pHs (see Table III).
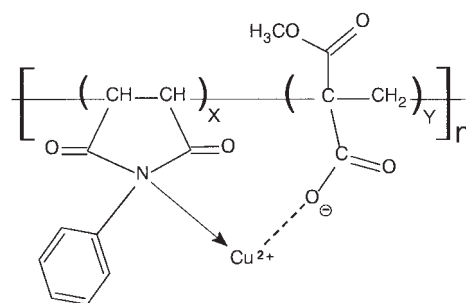
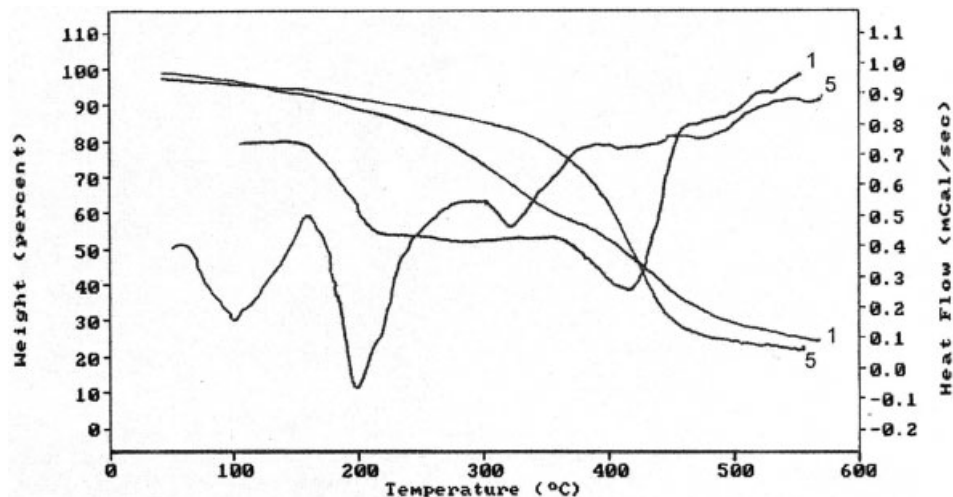**Scheme 2** Structure of the poly(N-PhMI-co-β-MHI)–copper(II) ion complex.

Figure 5 TGA/DSC thermograms of poly(*N*-PhMI-*co*-β-MHI) at a heating rate of 10°C/min.

This study was carried out with three copolymers. Those with monomer feed compositions of 2:1 and 1:2 were not included because 3:1 and 1:3 showed no important differences. The maximum retention capacity for copper(II) ions was very low at pH 3, and the values at pHs 7 and 9 were very similar.

At pHs 5 and 7, the highest retention values were found. The binding capacity for Cu(II) varied from 290 to 348 mg/g. The highest retention values were obtained at pH 5 and were related to the copolymer composition.

Carboxylic acid has a high capacity to coordinate with divalent cations, and so the higher retention capacity for the copolymers with a high concentration of the β-MHI moiety could be attributed to the carboxylic and carboxylate groups from β-MHI favoring the arrangement of these groups to coordinate with copper ions, particularly at this metal-ion concentration (see Scheme 2).

Copolymer composition/thermal behavior relationship

Differential scanning calorimetry (DSC) thermograms of poly(*N*-PhMI-*co*-β-MHI)s of different compositions (curves 1 and 5) are illustrated in Figures 5 and 6. The melting temperature (130–280°C) increased when the copolymers were richest in the *N*-PhMI moiety.

The thermogravimetric analysis (TGA)/DSC results for poly(*N*-PhMI-*co*-β-MHI) are summarized in Table IV. Figure 5 shows the DSC curves of some copolymers with the characteristic endothermic and exothermic peaks. The initial deflection was proportional to the sample heat capacity. The copolymers showed an endothermic transition due to the melting process between 130 and 280°C. This behavior may be correlated to the copolymer composition; it increased when the content of *N*-PhMI increased. Other endothermic peaks were characterized as a decomposition process beyond 250°C.
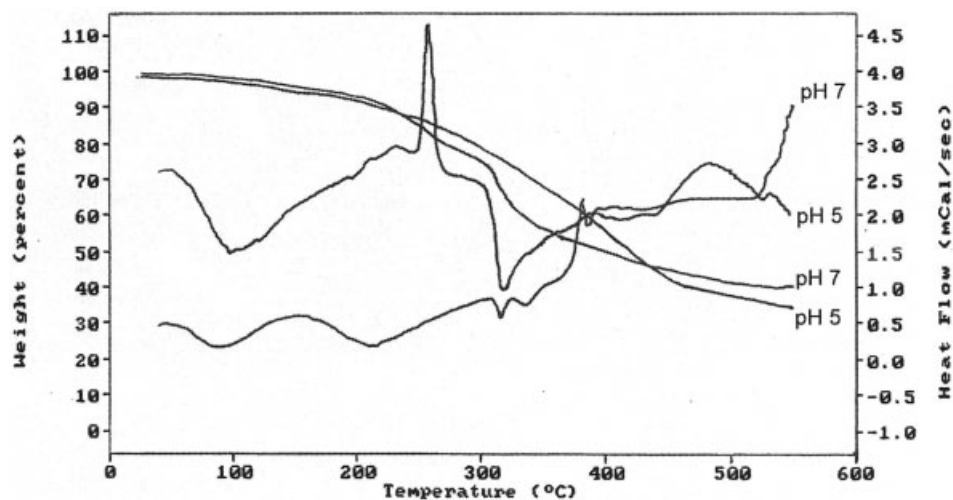

Figure 6 TGA/DSC thermograms of the poly(*N*-PhMI-*co*-β-MHI)–copper(II) complex at a heating rate of 10°C/min.

Sample no.	Copolymer composition (*N*-PhMI/β-MHI)	Temperature melting range (°C)	TDT (°C)	Weight loss (%) at different temperatures (°C)				
				100	200	300	400	500
1	25:75	130–220	250	4.0	13.0	33.0	53.8	71.6
2	33:67	150–230	270	4.0	12.0	30.2	51.1	70.6
3	50:50	170–250	300	3.1	8.1	20.9	44.2	64.4
4	67:33	170–260	320	2.5	3.6	12.8	37.3	73.2
5	75:25	180–280	350	1.4	4.4	7.0	38.6	73.9
6	0:100	100–210	170	0.0	27.0	46.0	60.0	76.5

The thermal stability increased as the *N*-PhMI concentration increased in the copolymer, and this occurred because the maleimide polymers had good thermal stability on account of the polar five-member imide ring structure[28] In this case, copolymers 1 and 2 presented a higher melting point range. Increasing the *N*-PhMI content led to higher onset temperatures of decomposition.

Copolymer 3, with a 50:50 (mol/mol) composition at different pHs, in contact with copper(II) ions, presented a lower thermal decomposition temperature (TDT) than poly(*N*-PhMI-*co*-β-MHI). The data are summarized in Table V and Figure 6. The incorporation of copper(II) ions into the copolymer reduced the TDT values.

The copolymers had a higher TDT than the complex for the same copolymer composition (300°C; see Table IV). The main reason was that linear poly(*N*-PhMI-*co*-β-MHI) had in its structure a high percentage of intramolecular and intermolecular bonding metal reactions because of a higher percentage of metal-ion bonding to comonomer units.

CONCLUSIONS

All obtained polymers were soluble in DMSO and acetone and insoluble in water.

The experimental data indicated that poly(*N*-PhMI-*co*-β-MHI) could be considered a statistical copolymer with some tendency to alternation ($r_1 \times r_2 = 0.140$).

The thermal stability decreased with an increasing concentration of β-MHI in the copolymer, and this was due to the lower percentage of crystallization or higher percentage of intramolecular crosslinking reactions.

Increasing the *N*-PhMI concentration led to increases in the onset decomposition temperatures. The TDTs of poly(*N*-PhMI-*co*-β-MHI) were influenced by the composition of the copolymer. The incorporation of *N*-PhMI increased the TDTs. The kinetic parameters showed the same trend and one-order kinetics.

The binding capacity for Cu(II) ions varied from 290 to 347 mg/g. The highest retention values were obtained at pH 5 and were related to the copolymer composition.

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TABLE V
TDT and Weight Loss Values at Different Temperatures for Poly(*N*-PhMI-*co*-β-MHI)–Copper(II) 50:50 mol %)

pH	Weight loss (%) at different temperatures (°C)					TDT (°C)
	100	200	300	400	500	
3	3.0	5.0	20.0	33.8	44.0	220
5	3.0	5.0	26.0	43.9	54.0	252
7	3.0	5.0	29.0	53.2	61.0	239