

Swelling Behavior and Metal Ion Retention from Aqueous Solution of Hydrogels Based on *N*-1-Vinyl-2-Pyrrolidone and *N*-Hydroxymethylacrylamide

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Received 14 April 2008; accepted 21 December 2008

DOI 10.1002/app.29944

Published online 17 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Hydrophilic copolymer gels were prepared by free-radical copolymerization of 1-vinyl-2-pyrrolidone (NVP) and *N*-hydroxymethyl acrylamide (HMAM). The ratios of both monomers and crosslinker agent (CA) were varied, and the effect of external stimuli such as pH of the swelling media and inorganic ion interaction were investigated. The gels showed a pH-responsive behavior. The interactions of inorganic ions with the hydrophilic hydrogels were determined as a function of pH, copolymer composition, and variation of the composition crosslinking degree. Additionally, a decrease of the pH of the solution caused a decrease in the equilibrium degree of swelling of the copolymer gels. The capacity to remove several metal ions such as Cu(II), Cr(III), Co(II), Zn(II), Ni(II), Cd(II), and Fe(III) in the aqueous phase was determined by using the liquid-phase polymer-based retention (LPR) technique. In addition, the copolymers and their

complexes with transition metal ions were characterized by the monomer reactivity ratios by using the Kelen-Tüdös method, elemental analysis, FTIR and ¹H-NMR spectroscopy, differential scanning calorimetry, and thermogravimetric analysis. Based on the results of swelling and retention capacity of metal ions of poly(NVP-*co*-HMAM), it was concluded that the swelling and retention capacity properties of the hydrogels depends on the reaction environment's pH. This is regarded as a functional hydrogel, which could be employed as biodegradable materials for applications in agriculture chemicals and as drug delivery systems. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1792–1802, 2009

Key words: hydrogels; poly(1-vinyl-2-pyrrolidone-*co*-*N*-hydroxymethylacrylamide); monomer reactivity ratios; swelling behavior; retention capacity; metal-polymer complexes; thermal behavior

INTRODUCTION

Interactions between polymers and different metal ions are an interesting field of study because of their potential analytical and technological applicability. Water-insoluble resins have been extensively used to selectively concentrate and separate metal ions from water solutions.^{1,2}

Water-soluble polymers have also been applied to this end, and different techniques such as dialysis^{3,4} and ultrafiltration^{5–15} have been utilized to study the interactions of metal ions with these polymers.

Hydrogels are three-dimensional crosslinked polymeric structures, which are able to swell in an aqueous environment.^{16,17} The hydration power of the

water absorption is one of the most important factors, which is determined by the functionality and quality of hydrogel. Moreover, this feature directly influences the majority of properties. This capacity to imbibe solvent depends on the pH and the ionic composition of the solution containing the hydrogel. These materials are of great interest because of their promising applications for sensors, separation membranes, adsorbents, and materials in medicine and pharmacy such as drug delivery systems.^{18,19}

During the last decade, considerable research has been performed on the characterization and swelling behavior of hydrogels prepared by simultaneous free-radical copolymerization in the presence of an initiator and crosslinking agent (CA).^{20–22} Recently, Katime and Rodríguez²³ synthesized hydrogels from copolymers of acrylic acid and itaconic acid and showed that the hydrogels are potential absorbents of metal ions. The swelling properties of acrylamide (AAM)-based hydrogels have been reported in many studies.^{24–27}

The poly(NVP-*co*-HMAM) showed a LCST around 50°C, which was significantly higher than that of poly(NIPAAm).^{28,29} Furthermore, pH-sensitive hydrogels could be prepared by free-radical

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Contract grant sponsor: Dirección de Investigación de la Universidad Tecnológica Metropolitana; contract grant number: 293/2007.

Contract grant sponsor: Deutsche Akademische Austauschdienst (DAAD).

TABLE I
Experimental Data of the Radical Copolymerization of *N*-1-Vinyl-2-pyrrolidone (NVP) with *N*-Hydroxymethyl acrylamide (HMAM) at 70°C, THF (12 mL), Initiator: 0.5 mol %, Reaction Time: 45 min

| Samples | <i>f</i> | NVP (mol %) | HMAM (mol %) | CA (mol %) | Yield % | Reason molar in feed | Copolymer composition ^a |
|---------|----------|-------------|--------------|------------|---------|----------------------|------------------------------------|
| 1 | 0.861 | 86.1 | 13.9 | | 29.4 | 3.0 : 1.0 | 64.0/36.0 |
| 2 | 0.807 | 80.7 | 19.3 | | 33.7 | 2.0 : 1.0 | 56.3/43.7 |
| 3 | 0.681 | 68.1 | 31.9 | | 55.9 | 1.0 : 1.0 | 51.2/48.8 |
| 4 | 0.510 | 51.0 | 49.0 | | 48.8 | 1.0 : 2.0 | 39.7/60.3 |
| 5 | 0.409 | 40.9 | 59.1 | | 65.5 | 1.0 : 3.0 | 34.7/65.3 |
| 6 | 0.681 | 68.1 | 31.9 | 0.48 | 57.1 | 2.0 : 1.0 | 51.2/48.8 |
| 7 | 0.681 | 68.1 | 31.9 | 0.64 | 81.2 | 2.0 : 1.0 | 51.2/48.8 |
| 8 | 0.681 | 68.1 | 31.9 | 0.79 | 79.5 | 2.0 : 1.0 | 51.2/48.8 |

^a Determined from elemental analyses (in mol %).

copolymerization of 1-vinyl-2-pyrrolidone (NVP) and *N*-hydroxymethyl acrylamide (HMAM) in the presence of *N,N*-methylenebisacrylamide (MBA) as the CA.

The aim of this study was to investigate the swelling properties of HMAM-based hydrogels as a function of pH, copolymer composition, and variation of the composition crosslinking degree. Also, the interactions of inorganic ions with the hydrophilic hydrogels were determined as a function of pH and the filtration factor. The capacity to remove several metal ions in heterogeneous aqueous phase was determined by using the liquid-phase polymer-based retention (LPR) technique. Although the MBA-crosslinked poly(NVP-*co*-HMAM) was essentially insoluble in water, the technique could be employed to this copolymer in the dispersed state, when considering that the rate for changes in the gel volume is inversely proportional to the square of the smallest dimension of the hydrogel. The swelling properties of the hydrogel as dispersed particles was performed by repeated swelling and shrinking procedures.

EXPERIMENTAL

Reagents

The two monomers *N*-hydroxymethyl acrylamide (HMAM) and 1-vinyl-2-pyrrolidone (NVP) were obtained from Merck (Merck-Schuchardt OHG Chemicals, Germany) and were distilled under reduced nitrogen pressure before use. Benzoyl peroxide (BPO) (purchased from Aldrich chemicals, CHEMIE GmbH, Germany) was used as the crosslinker. The other chemicals are of analytical grade and used without further purification. MBA (purchased from Merck-Schuchardt OHG chemicals, Germany) was used as the crosslinker. The solvents were purified in the usual manner before use.

Measurements

FTIR spectra were recorded on a Bruker model vector 22 Spectrophotometer (Bruker Optics, USA). The ¹H-NMR spectra were recorded in solution at room temperature with a Bruker AC 250 (Bruker, Karlsruhe, Germany) spectrometer using DMSO-*d*₆ (99.8%). The elemental analyses were carried out using a Carlo Erba 1106 analyzer (Italy).

The metal ion concentrations were measured with a Perkin-Elmer 1100 Atomic Absorption Spectrometer (Perkin Elmer, Shelton, CT). For dried samples, a continuous freeze dryer (LAB CONCO 6L, Karl-Heinz Müller, Laborbedorf GmbH, USA) was used. The pH was determined with a pH-meter Hanna 211 (Miami, USA). For the LPR technique, a membrane filtration system was employed (Millipore, Amicon, USA) to test the metal-complexing properties of the poly(NVP-*co*-HMAM). Details have been previously described.⁵⁻¹⁵

Syntheses of the copolymers

The copolymerization of P(NVP-*co*-HMAM) was carried out using several feed compositions of both monomers from 25 to 75 mol %. The following general procedure was used: 12 mL of tetrahydrofuran (THF) were transferred to a septum-capped, nitrogen-purged ampoule containing 26.6 mmol of HMAM, 0.5 mmol % of BPO, and 26.6 mmol of NVP. The ampoule was degassed with several freeze cycles and sealed under vacuum (1.33×10^{-4} kPa). The copolymerization was carried out at 70°C for 45 min. The copolymer material was filtered off, washed with ether, collected, and dried under vacuum up to constant mass.

Syntheses of the hydrogels

Crosslinked P(VNP-*co*-HMAM) hydrogels (Samples 6, 7, and 8, respectively, see Table I) contained

68.1 mol % of NVP and 31.9 mol % of HMAM as feed mole ratios and 0.48, 0.64, and 0.79 mol % of MBA, respectively. The hydrogels were prepared by solution free-radical polymerization. NVP, HMAM, and BPO (0.5 mol %) as initiator were dissolved in THF, and the reaction solution was heated and polymerized for 45 min at 70°C in a glass tube. The product was dried until constant weight. Finally, the dried product was characterized and the swelling properties were determined.

The degree of crosslinking of the copolymer was not determined by elemental analysis, as both monomer units and the CA possess nitrogen and carbon atoms. Therefore, the crosslinking degree was estimated from the amount of CAs by assuming a complete gelation reaction.

Compositions of the copolymers

The copolymers, obtained in the form of long cylinders, were cut into pieces (4- to 5-mm long) and dried in a vacuum oven for 48 h to constant mass. The copolymer composition was determined from the elemental analysis data (nitrogen content).

Swelling studies

The swelling studies were carried out at 25°C in buffered solutions, either 0.01M citrate buffer (pH < 7) or phosphate buffer (pH > 7) was used. The dried samples of copolymers were placed in a solution of the defined pH (2–9) at 25°C. Each sample was removed every hour from the solution and was weighed after a period of 44 h. The swelling values (S_w) were calculated using the following equation:

$$S_w = (W_s - W_d)/W_d,$$

where W_s is the weight of the swollen hydrogel at an equilibrium state, and W_d is the weight of the dried hydrogel.

Complexation procedure

This technique uses ultrafiltration membrane to separate low-molecular-mass species such as the free ions from high-molecular-mass compounds such as the polymer–metal complexes. It is assumed that the main separation mechanism is the size exclusion by the ultrafiltration membrane (membranes with a molecular mass exclusion limit of 10,000 g mol⁻¹ were used). To determine the complexing capacity, the copolymer (200 mg) was suspended in 10 mL water and adjusted to the corresponding pH by adding dilute nitric acid or sodium hydroxide. The aqueous solutions of polymer and metal nitrate or chloride (20 ppm) (2 wt %) solution were placed into the

membrane filtration cell. The total volume in the cell was kept constant at 20 mL. The reservoir contained water and was adjusted to the pH of the cell solution. A membrane with a nominal exclusion limit of 10 kg mol⁻¹ (Amicon PM 10, or equivalent Millipore) was used. The system was pressurized at 300 kPa, the cell solution stirred for 10 min, and then washed with the reservoir fluid at a flow rate of 4–6 mL min⁻¹. The filtration fractions ($Z = 1–10$) were collected and the concentrations of metal ions in the filtrate and in the retentate were determined by atomic absorption spectroscopy. The copolymer was dried for further analytical control by thermal analyses and FTIR spectroscopy. Retention values were calculated from the metal ion concentration determinations in the filtrate and in the retentate.

Thermal analysis

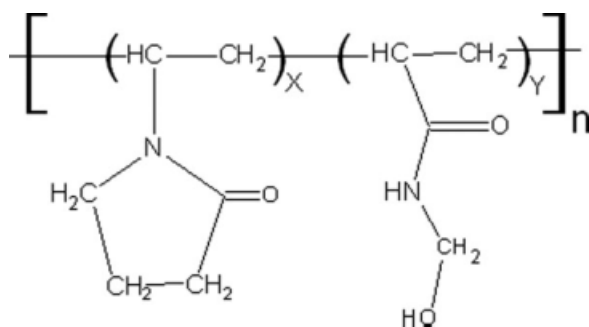
The thermal analysis of the copolymers was determined by recording thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere (flow rate = 150 and 50 cm³ min⁻¹, respectively). A sample size of 3–4 ± 0.1 mg was used in each experiment. Thermal stability studies were performed using a Mettler Toledo Star System TGA (made in Spain) at a heating rate of 10°C min⁻¹. 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.

The LCST of the hydrogels were observed by DSC, temperature range: 20–80°C. The rates of heating of the samples were adjusted at 5°C min⁻¹. The hydration of the aqueous copolymer solutions of varying composition was observed by DSC. The concentration of the hydrogels were varied in a range 50–60 mg mL⁻¹ (5–6 wt %).

RESULTS AND DISCUSSION

Synthesis and characterization of the copolymers

The radical copolymerization of NVP with HMAM were conducted in tetrahydrofuran using several feed monomer compositions. The resulting copolymers were insoluble in solvents such as chloroform, acetone, ethanol, methanol, pyridine, tetrahydrofuran, dimethylsulfoxide, and water. The weight ratios of NVP and HMAM in the copolymers were calculated from the C/N mass percent ratio determined by elemental analysis. The general structure of the copolymers P(NVP-co-HMAM) is illustrated in Scheme 1. The experimental polymerization conditions and results (summarized in Tables I and II) show that for the NVP/HMAM system, the



Scheme 1 Structure of poly(NVP-co-HMAm).

copolymer contained 51.2 mol % NVP while using an initial monomer feed ratio of 2 : 1. The yield of copolymers increased when the monomer feed ratio NVP/HMAm decreased (see Table I). These results were correlated well with the values of r_2 obtained for HMAm.

The $^1\text{H-NMR}$ spectrum shows the following signals (δ in ppm): 1.0–2.7 ($-\text{CH}_2$ in ring from NVP); ($-\text{CH}_2$) from the backbone of both monomer units; 2.8–4.3 ($-\text{CH}_2\text{NHCO}$ of HMAm), NVP; 3.2–4.3 ($-\text{CH}_2\text{N}$ and $-\text{CHN}$); 4.1–4.9 (HOCH_2NH from side chain); 5.0–5.9 ($-\text{OH}$ from HMAm); 7.8–8.6 ($-\text{HNCO}$ from HMAm) (see Fig. 1).

The FTIR spectra of copolymers investigated are presented in Figure 2. The absence of the absorption band at 1640 cm^{-1} , characteristic for the carbon-carbon double bond, in the two investigated systems clearly indicates that a true copolymer is formed in both cases. In Figure 2, the absorption bands at 1655.9 cm^{-1} stem from the carbonyl group and that at 1015.8 cm^{-1} the N–H stretching vibration of the HMAm in the copolymer. On the other hand, the bands that appear at 3418.9 cm^{-1} are assigned to

the OH stretching. The bands in the range of 2930.9 in the FTIR spectra indicate the aliphatic C–H stretching vibration.

Monomer reactivity ratios

The copolymer compositions were determined from the elemental analysis data (see Table II). To determine the monomer reactivity ratios, a plot of the monomer feed composition (M_1) versus the monomer composition in the copolymer (m_1) (mol %) for NVP is shown in Figure 3 for P(NVP-co-HMAm). The $r_{1(\text{NVP})}$ and $r_{2(\text{HMAm})}$ monomer reactivity ratio values were determined from the monomer feed ratios and copolymer compositions obtained at low conversions using the Kelen Tüdös (K-T) method.³⁰ The K-T equation (1) is symmetrically transformed into

$$\eta = G/(\alpha + F) \quad \xi = F/(\alpha + F) \quad (1)$$

by introducing the new parameters ξ , η , and $\alpha = (F_{\min} \times F_{\max})^{0.5}$, where F_{\min} and F_{\max} correspond to the smallest and largest fraction in the copolymer (F) that are calculated, respectively.

The $r_{1(\text{NVP})}$ and $r_{2(\text{HMAm})}$ values were also determined according to eq. (2):

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

where η and ξ are mathematical functions of the monomer molar ratios in the feed and in the copolymer, respectively, α is an arbitrary denominator with any positive value, which produces a more homogeneous distribution of data along $\eta - \xi$ axes.

By introducing the parameters ξ , η , and α , where $G = (m_1/m_2 - 1)/z$ and $F = (m_1/m_2)/z^2$; $z = \log(1 - \delta_1)/\log(1 - \delta_2)$; $\delta_1 = \delta_2 y/X_0$; $\delta_2 = \text{wt \% } (\mu + X_0)/(\mu + y)/100$; $\mu = \mu_2/\mu_1$; $y = m_1/m_2$; $X_0 = M_1/M_2$; $\text{wt \%} = \text{conversion}$; μ_1 and μ_2 are the molecular

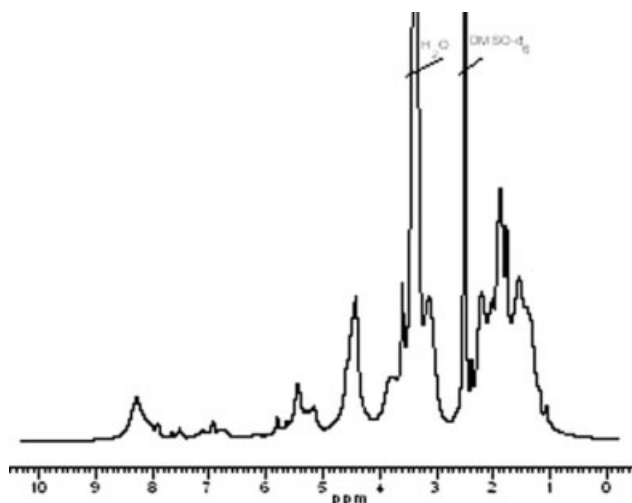


Figure 1 $^1\text{H-NMR}$ spectrum of the copolymer P(1-vinyl-2-pyrrolidone-co-N-hydroxymethyl acrylamide) (400 MHz, in $\text{DMSO-}d_6$, room temperature).

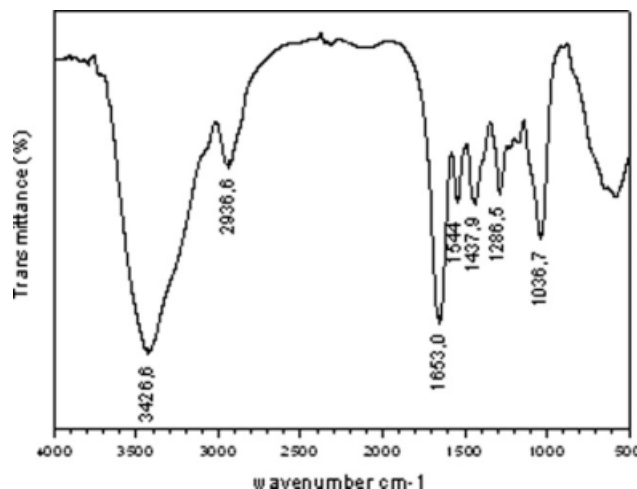


Figure 2 FTIR spectrum of P(1-vinyl-2-pyrrolidone-co-N-hydroxymethyl acrylamide).

TABLE II
Elemental Analysis, N/C Ratio, and Copolymer Composition

| Samples | Elemental analysis (calculated values) | | | Composition (mol %) ^a | |
|---------|----------------------------------------|---------------|-------------|----------------------------------|-------|
| | N | C | H | M_1 | m_1 |
| 1 | 11.53 (13.03) | 52.18 (58.98) | 7.80 (7.76) | 86.1 | 64.0 |
| 2 | 11.68 (13.12) | 51.34 (58.98) | 7.56 (7.67) | 80.7 | 56.3 |
| 3 | 11.76 (13.18) | 50.68 (58.98) | 7.69 (7.61) | 68.1 | 51.2 |
| 4 | 12.03 (13.33) | 49.43 (58.98) | 7.53 (7.48) | 51.0 | 39.7 |
| 5 | 12.00 (13.39) | 48.30 (58.98) | 7.45 (7.41) | 40.9 | 34.7 |

^a Determined from elemental analyses in mol %.

masses of the monomers 1 and 2, respectively; M_1 and M_2 = initial composition of monomers in mol; m_1 and m_2 correspond to the monomer composition in the copolymer for each monomer.

Figures 4 and 5 shows the $\eta - \xi$ plots according to the K-T method, from which the monomer reactivity ratios were determined for both copolymers system (see Table III).

The variable ξ can take any possible value in the 0 to 1 interval. A plot of η vs. ξ gives a straight line, which on extrapolation to $\xi = 0$ and $\xi = 1$ gives $-r_2/\alpha$ and r_1 , respectively. The data base included in Table IV, yielded the reactivity ratios for P(NVP-co-HMAm) of $r_1 = 0.075$ (NVP) and $r_2 = 0.85$ (HMAm). The reactivity ratios obtained indicate that the systems of P(NVP-co-HMAm) can be considered as a random-alternating incorporation, NVP tends to copolymerization, whereas HMAm tends to homopolymerization.

Degree of swelling

Crosslinked P(VNP-co-HMAm) hydrogels containing 68.1 mol % of NVP and 31.9 mol % of HMAm as monomer units, and 0.48; 0.64, and 0.79 mol % of MBA as cross-linker (see samples 6, 7, and 8, respec-

tively, Table, I). The swelling behavior of P(NVP-co-HMAm) was also investigated as a function of pH at different mol % of MBA at room temperature (25°C). Figure 5(a,b) shows the swelling behavior of P(NVP-co-HMAm) after different swelling times at different MBA compositions and pH. The swelling of the hydrogel increased at a pH range of 3–7, where the maximum swelling could be observed at pH 7. Moreover, the swelling increased with time, but after a certain period (30 h), it levels off. This value of swelling may be named equilibrium swelling percentage. The gels were swollen in buffered media with $I = 0.05M$. From this data, it was observed that the swelling decreased as the content of MBA increased. A very low percentage of CA yield gels with high retention capacity. Moreover, the swelling of the hydrogels increased with a decreasing pH to 0.48 mol % of MBA, which could be attributed to the high attraction forces due to the hydrogen binding at pH 3. For all compositions of MBA, the maximum swelling occurred at the pH range of 3–7, except to the lower percentages of MBA studied. The P(NVP-co-HMAm) gel (Sample 7) swells 400% more at pH 7 when compared with the P(NVP-co-HMAm) gel (Sample 8). A plausible explanation for

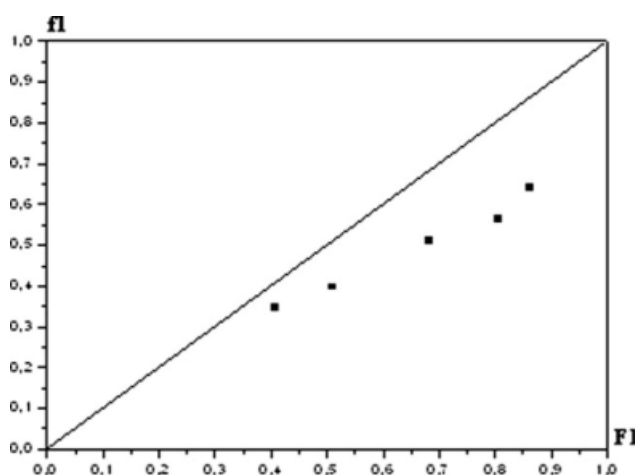


Figure 3 Relationship of the monomer ratio (F) and copolymer composition (f) for the copolymerization of NVP.

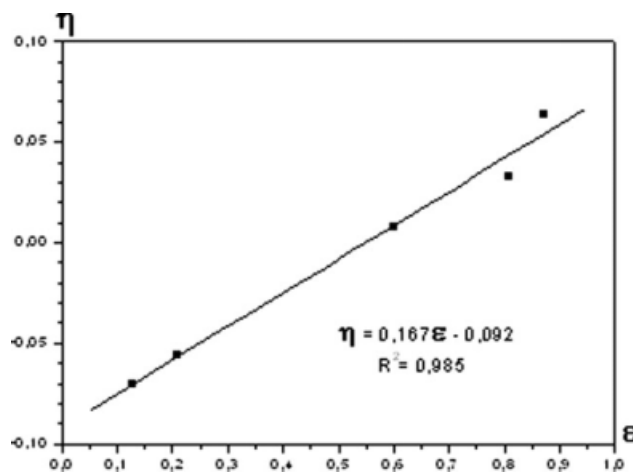


Figure 4 η vs. ϵ representation of the copolymerization parameters according to the K-T method for the polymerization for poly(NVP-co-HMAm).

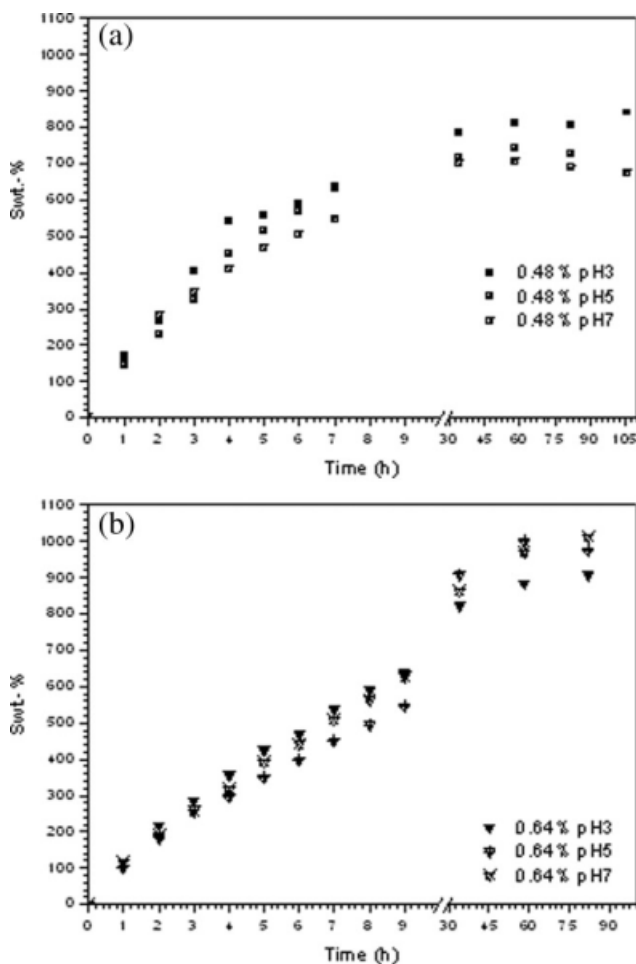


Figure 5 Swelling isotherm of poly(NVP-co-HMAm) at different CA compositions: (a) CA 0.48 mol % (□); (b) CA 0.64 mol % (▼), respectively, as a function of time, in buffered solutions at pH 3, 5, and 7 at 25°C.

this difference in the swelling may be found when considering the chemical nature of the two hydrogels. Thus, the higher percentage of MBA in the network copolymer could lead to a reduction of the hydrostatic pressure inside of the network, and, consequently, the hydrodynamic volume of the hydrogels decreases.

The results indicate that the copolymers obtained are stimuli-responsive hydrogels that change their volume and elasticity depending on the amount of crosslinker and on the pH of the liquid phase.

A water absorption of 1000% per g xerogel for the copolymer 2 : 1 was obtained, having the highest content of NVP and 0.64 mol % of crosslinker. This copolymer was also very stable with regard to time, and the optimum pH was 7.

This result can be explained by the gradual diffusion of water molecules into the network of the hydrogel and the complete filling or occupation of the preexisting or dynamically formed spaces in the polymer chains. Nevertheless, the monomer ratio feed of 2 : 1 with 0.64 mol % MBA provides suitable properties of the hydrogel.

The hydrogel as a polychelator

The P(NVP-co-HMAm) hydrogel features three potential ligand groups. Thus, the complexation properties of the P(NVP-co-HMAm) hydrogel (Samples 1–8) at different copolymer compositions were determined. The metal ion retention properties of these polymers were compared using the LPR technique at different pH (3, 5, and 7).^{31,32} In the washing and enrichment methods, the metal ion retention in the cell solution is defined as follows:

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

where C_r is the metal ion concentration in the retentate (the cell solution volume, V_{cr} after a filtrate volume, V_f has been passed), and C_0 is the initial metal ion concentration in the cell. The filtration factor Z , expressed in relative units, is another convenient characteristic of the process.

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

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

TABLE III
Data for the Determination of the Reactivity Ratios for P(1-Vinyl-2-pyrrolidone-co-N-hydroxymethyl acrylamide) Using the Kelen-Tüdös Method

| Monomer feed (mol%) | | Parameters | | | Copolymer composition (mol%) | | wt % | K-T equation | |
|---------------------|--------------|------------|----------|-------|------------------------------|-------|------|--------------|--------|
| M_1 (NVP) | M_2 (HMAM) | X_0 | γ | F | M_1 | m_1 | | ξ | η |
| 86.1 | 13.9 | 6.21 | 1.79 | 63.6 | 81.8 | 18.2 | 29.4 | 0.873 | 0.064 |
| 80.7 | 19.3 | 4.18 | 1.29 | 39.0 | 76.2 | 23.8 | 33.7 | 0.808 | 0.033 |
| 68.1 | 31.9 | 2.14 | 1.05 | 13.97 | 61.5 | 38.5 | 55.9 | 0.601 | 0.008 |
| 51.0 | 49.0 | 1.04 | 0.66 | 2.438 | 50.0 | 50.0 | 48.8 | 0.208 | -0.056 |
| 40.9 | 59.1 | 0.69 | 0.53 | 1.351 | 35.7 | 64.3 | 65.5 | 0.272 | -0.070 |

η vs. ϵ ; $\mu = 0.9098$; $\alpha = 9.2716$.

TABLE IV
Retention Values (%) of Seven Metal Ions for the Copolymer P(NVP-co-HMAm) at pH = 3, 5, and 7

| Sample | pH | Retention (%) of metal ion | | | | | | |
|--------|----|----------------------------|--------|---------|---------|--------|--------|--------|
| | | Cu(II) | Co(II) | Cr(III) | Fe(III) | Cd(II) | Ni(II) | Zn(II) |
| 1a | 3 | 0.0 | 0.0 | 0.0 | 0.0 | 15.5 | 0.0 | 8.0 |
| 1b | 5 | 0.0 | 0.0 | 0.0 | 7.5 | 13.0 | 0.0 | 19.5 |
| 1c | 7 | 95.0 | 10.0 | 51.5 | 98.0 | 19.0 | 67.5 | 21.0 |
| 3a | 3 | 0.0 | 0.0 | 0.0 | 18.5 | 3.5 | 0.0 | 5.5 |
| 3b | 5 | 19.5 | 0.0 | 14.5 | 96.5 | 7.0 | 0.0 | 27.5 |
| 3c | 7 | 94.0 | 53.0 | 66.5 | 97.0 | 49.5 | 69.0 | 21.0 |
| 5a | 3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 6.5 |
| 5b | 5 | 10.5 | 11.0 | 0.0 | 82.5 | 26.0 | 0.0 | 3.5 |
| 5c | 7 | 89.0 | 36.5 | 54.5 | 98.0 | 39.0 | 58.5 | 9.0 |
| 6a | 3 | 4.0 | 6.5 | 0.0 | 5.0 | 15.0 | 0.0 | 10.0 |
| 6b | 5 | 9.0 | 15.0 | 0.0 | 75.5 | 21.0 | 0.0 | 17.5 |
| 6c | 7 | 88.0 | 16.0 | 55.5 | 98.0 | 31.0 | 67.0 | 28.0 |
| 7a | 3 | 8.0 | 6.5 | 3.0 | 25.0 | 28.0 | 0.0 | 20.0 |
| 7b | 5 | 18.0 | 25.0 | 25.0 | 85.5 | 42.0 | 5.0 | 37.5 |
| 7c | 7 | 98.0 | 26.0 | 55.5 | 98.0 | 64.0 | 87.0 | 38.0 |

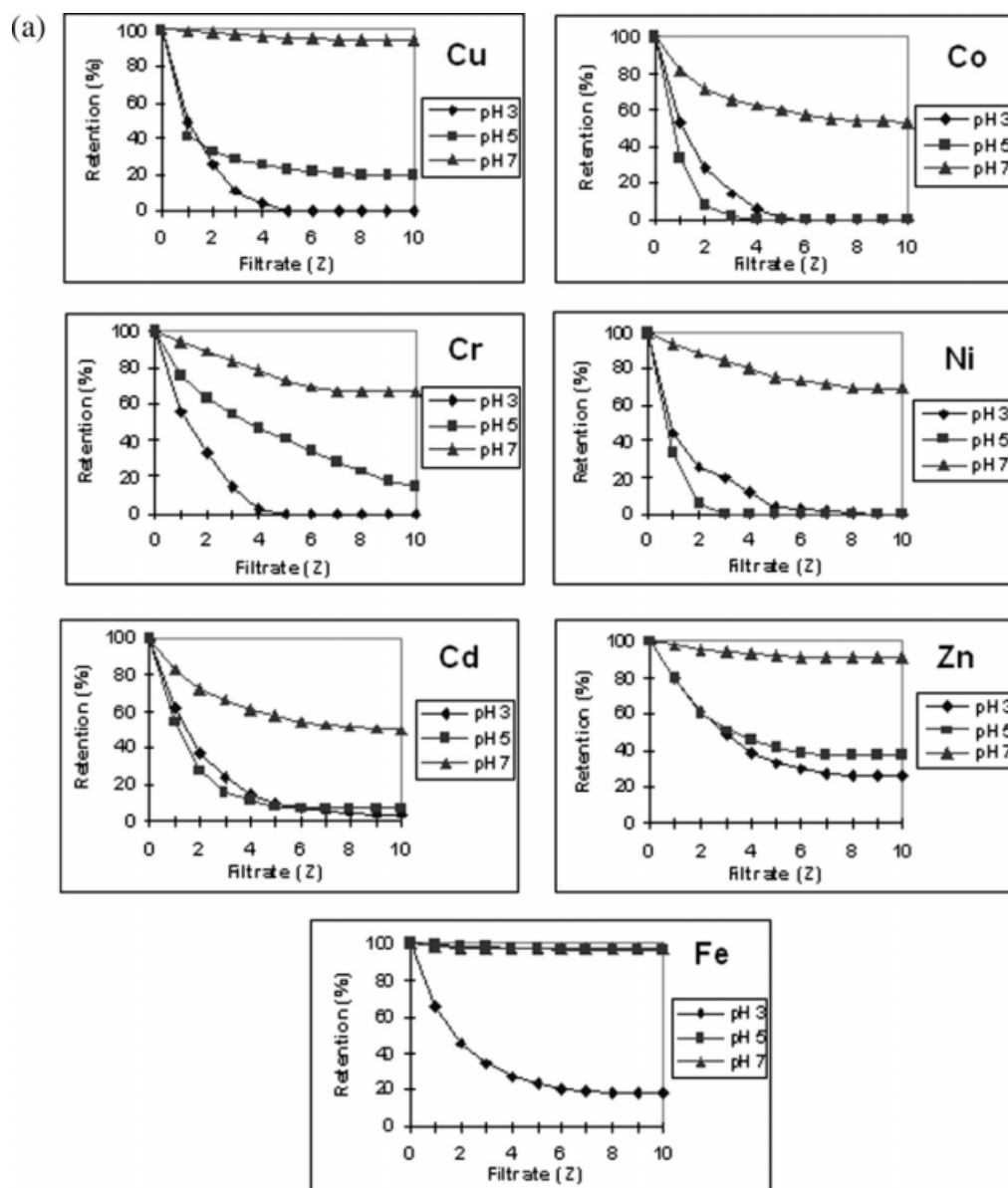


Figure 6 Retention profiles of different metal ions in aqueous solution (1 wt %) for poly(NVP-co-HMAm): (a) Sample 3 and (b) poly(NVP-co-HMAm) with CA, Sample 6, at different pH.

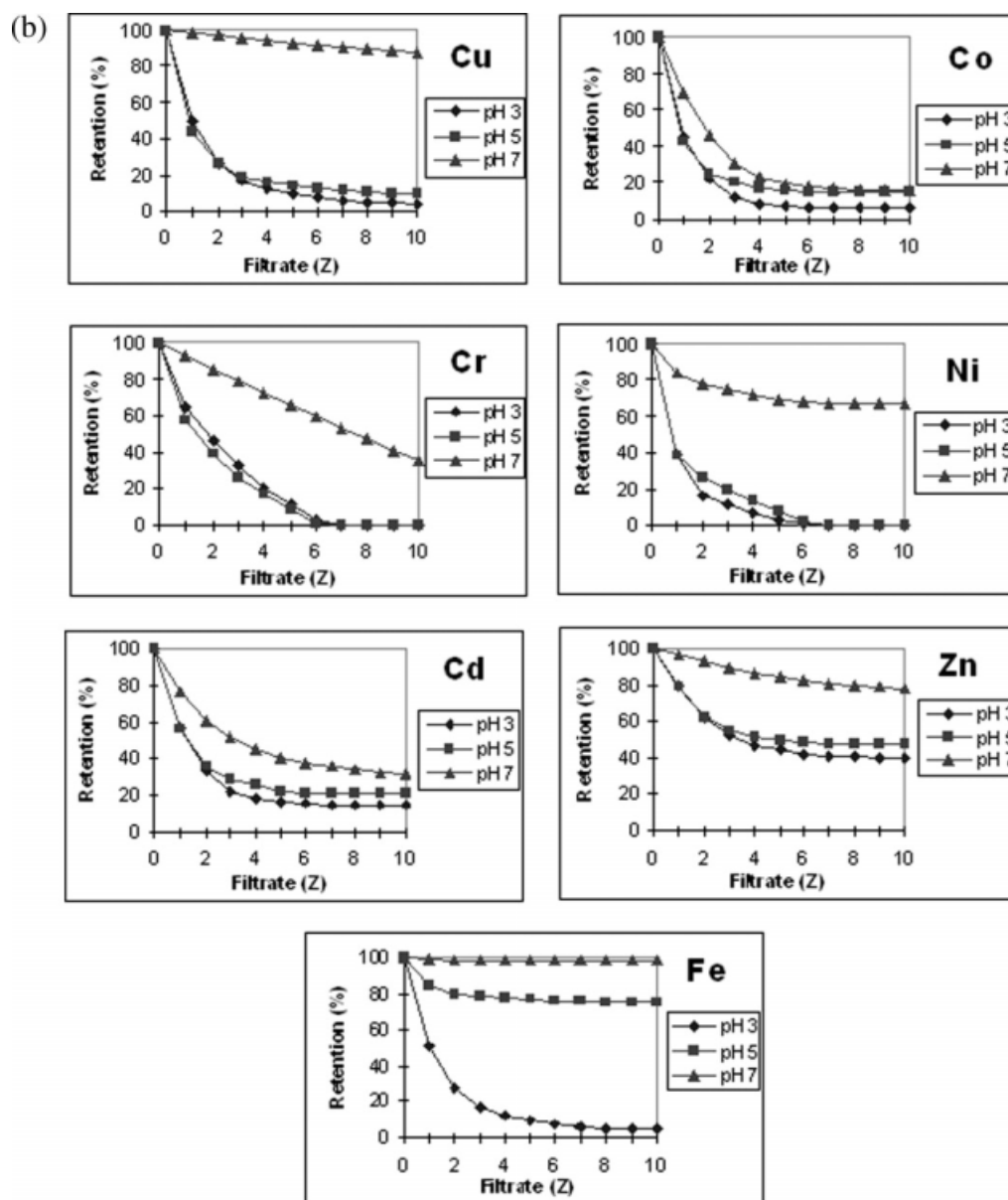
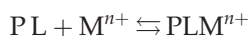


Figure 6 (Continued from the previous page)



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

Typical retention profiles of P(NVP-co-HMAm) as a function of the pH are shown in Figure 6(a,b). In general, a high complexation with P(NVP-co-HMAm) and metal ions was observed. The copolymer's retention percentage occurring with all metal ions increased at pH 7. For example, the copolymers showed lower retention values at pH 3 and 5 than those at 7 for a filtration factor of $Z = 10$.

The P(NVP-co-HMAm) exhibited higher complexing properties at higher pH (see Table IV). In gen-

eral with P(NVP-co-HMAm), there is high metal ion retention for all metal ions at pH 7. At pH 3 and 5, the copolymer presents lower metal ion retention. These values increased at pH 7 when the copolymers were rich in HMAm unit monomer, indicating a predominant influence of the pH and copolymer composition. At pH 7, for some metal ions, the retention values are higher than that 75%, for example Cu(II), Zn(II), and Fe(III), when the copolymer has the highest content of HMAm units. Therefore, the metal ion retention increased, particularly for Co(II), Cr(III), Ni(II), and Cd(II) for copolymer compositions rich in HMAm units (Samples 3–7, Table IV). Thus, the P(NVP-co-HMAm) is an effective reagent for the separation of various metal ions at

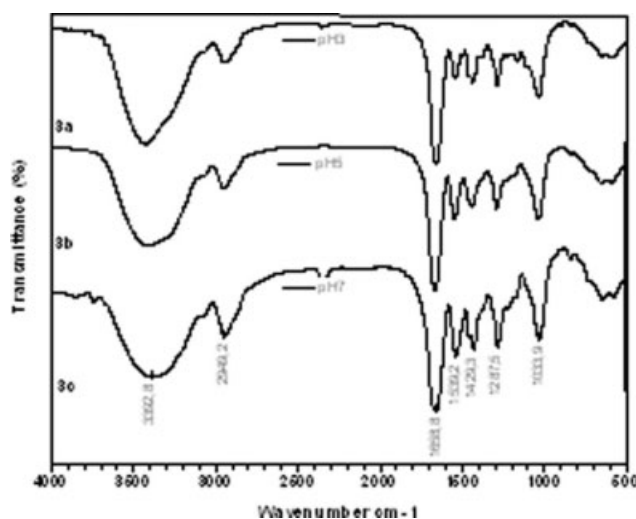


Figure 7 FTIR spectra for the poly(NVP-co-HMAM)-metal complex (a-c) at pH = 3, 5, and 7, respectively.

pH 7. At pH 3 and 5, the copolymers showed a low metal ion affinity, and the copolymers presented low retention values for all metal ions at different copolymer compositions.

The metal ion retention values for all copolymers indicate that both comonomer units possess functional groups with metal ion affinity at pH 7. This retention behavior can be attributed to two characteristics: the copolymer P(NVP-co-HMAM) having two nonionic monomer units with carbonyl groups from amide and hydroxy-functional groups in the side chains of the HMAM structure. Therefore, it can show that metal-binding forces as ionic polymers also depend on the pH. Additionally, an interaction of the nitrogen atom from the amide group could exist and result in a molecular complex formation. In this polymer-metal complex, the results suggest that the metal ion is bound to the nitrogen atom from amide group, in which the absorption band (sharp) from N-C (stretching) at 1539.2 and 1498 cm^{-1} showed an intensity decrease, and the hydroxyl group, in which the absorption band (sharp) from OH (stretching) at 3392.8 cm^{-1} , showed an intensity decrease and a broad band (Fig. 7).

Thermal behavior

The thermal behavior of the P(NVP-co-HMAM) was examined by TGA and DSC under nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$.

The TGA of the copolymers and their polymer-metal complexes with the seven metal ions in the mixture have been plotted in Figure 8, and the derived data are shown in Table V. The plot shows that the copolymer degraded continuously in a two-stage process. As shown in Figure 8, the copolymers

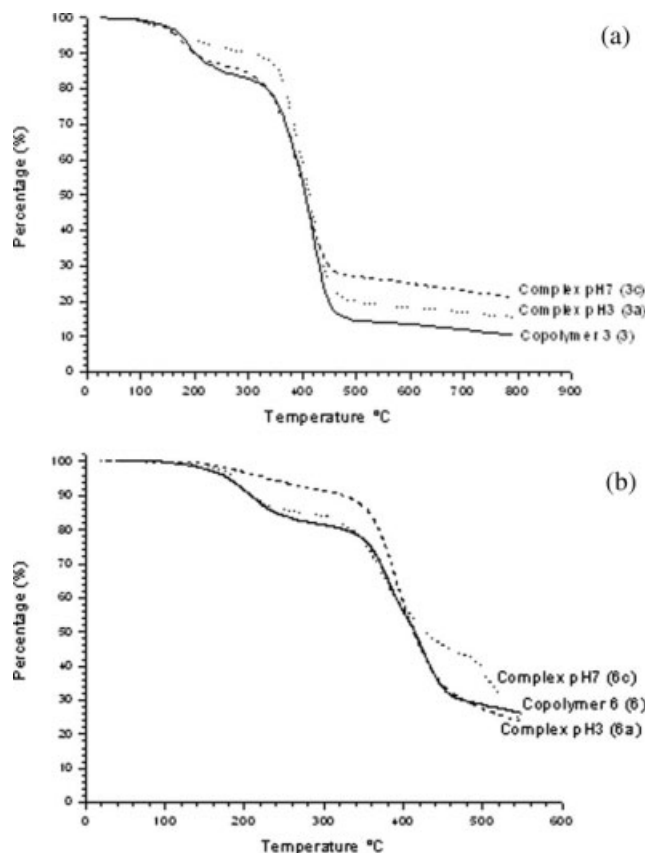


Figure 8 TGA thermograms of poly(NVP-co-HMAM): (a) Sample 3 a-c and (b) Sample 6 a-c with CA at different pH. Heating rate: 10°C/min ; copolymer composition: 51.2 : 48.8 mol %.

were stable up to 320°C . At 150°C , the weight loss is significant (around 15%) and is attributed to the loss of water and a small amount of monomer residue in the copolymer-metal complexes and crosslinking copolymers. At pH 7, the complex exhibited a lower

TABLE V
Thermal Behavior and Thermal Decomposition Temperatures for the Copolymer and Its Copolymer-Metal Complexes at Different pH (Initial Mass 2.2–4.0 mg)

| Sample | Mass loss (%) at different temperatures ($^\circ\text{C}$) | | | | | |
|--------|--------------------------------------------------------------|------|------|------|------|-------|
| | 150 | 250 | 350 | 450 | 550 | TDT |
| 1 | 2.4 | 30.3 | 50.2 | 64.3 | 73.6 | 157.2 |
| 1a | 3.7 | 27.6 | 43.0 | 66.4 | 70.6 | 160.3 |
| 1b | 5.0 | 11.3 | 23.6 | 40.0 | 60.7 | 170.6 |
| 1c | 4.0 | 10.0 | 22.3 | 38.5 | 58.3 | 175.5 |
| 3 | 1.1 | 44.7 | 69.6 | 78.2 | 85.0 | 155.3 |
| 3a | 4.0 | 40.0 | 65.0 | 74.0 | 80.0 | 160.4 |
| 3b | 8.1 | 17.7 | 31.1 | 44.2 | 64.6 | 183.4 |
| 3c | 6.1 | 15.4 | 28.6 | 42.7 | 60.9 | 198.2 |

Metal ions in the mixture: M^{n+} : Cu^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Fe^{3+} , Cr^{3+} ; TDT, thermal decomposition temperature.

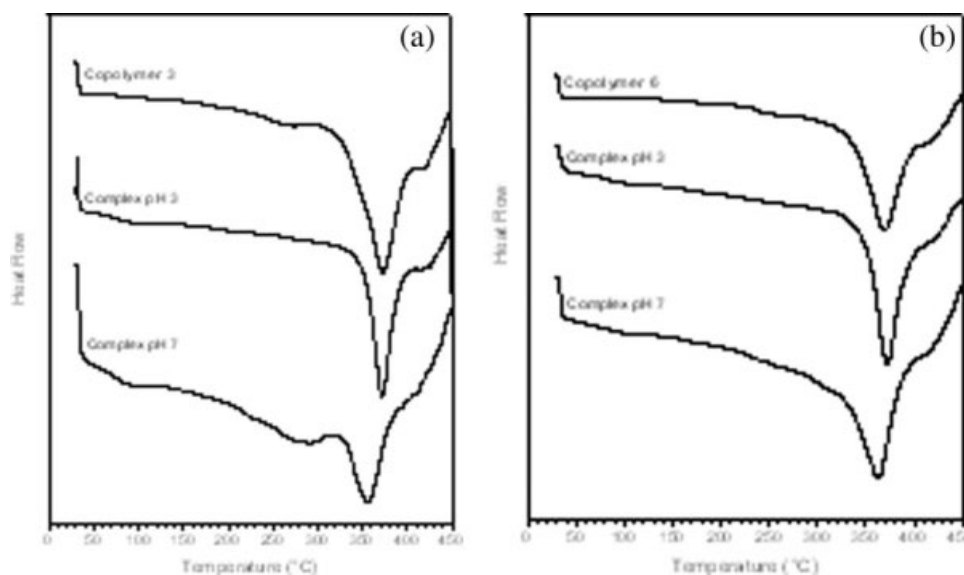


Figure 9 DSC thermograms of poly(NVP-*co*-HMAM): (a) Sample 3 and complex at different pH (3 a–c) and (b) Sample 6 and complex at different pH (6 a–c). Heating rate: 10°C/min.

stability, obviously due to the complexing process of the metal–polymer support. For example, the P(NVP-*co*-HMAM) (Sample 6 a–c) had a mass loss of 2.4% at 150°C and for the complexes it was 5.0% at pH 5. This may be due to the formation and rearrangement of different complexes of the copolymer with some of the metal ions studied.

The copolymer metal complexes with a composition approximately 50 : 50 mol % (Sample 3) at different pH (Sample 3 a–c) exhibits a lower thermal degradation temperature (TDT) than the copolymer (Sample 3). The data are summarized in Table V. The residual mass for complexes at pH = 3, 5, and 7 was higher than that of the copolymer, which can be principally attributed to the fact that the linear P(NVP-*co*-HMAM) exhibits in its structure a high percentage of intramolecularly bonded metal ions.

Glass transition temperature

The glass transition temperature (T_g) was analyzed in the second run. The apparent glass transition was found to be approximately at 90°C. Another significant peak, a broad endothermic transition, was observed and can be attributed to the decomposition reaction in the temperature range of 300–400°C [Fig. 9(a,b)]. The copolymer shows a single T_g , indicating the formation of random copolymers.

Low critical solution temperature

The pH-sensitive hydrogels could be prepared by the free-radical copolymerization of NVP and HMAM in the presence of the crosslinker MBA. The

P(NVP-*co*-HMAM) showed a LCST around 50°C (Sample 3a, 50.3°C and 3b, 51°C) which was significantly higher than P(NIPAAm).²⁸ Several studies have been performed to investigate the temperature collapse in P(NIPAAm) hydrogels.^{28–33} It was reported that when a hydrophilic moiety is incorporated into the hydrogel, the hydrophilic/hydrophobic balance is shifted toward a more hydrophilic nature, and its LCST is shifted to a higher temperature. It was concluded that the swelling and retention capacity properties of the hydrogels depends on the reaction environment's pH. This is regarded as a functional hydrogel that could be employed as biodegradable materials for applications in agriculture chemicals and as drug delivery systems.

CONCLUSIONS

The copolymer gels P(NVP-*co*-HMAM) were prepared by free-radical copolymerization. All polymers obtained were insoluble in water and in some common organic solvents.

The reactivity ratios obtained indicate that the system P(NVP-*co*-HMAM) can be considered as a random-alternating copolymer, being much closer to alternating than to random. The radical polymerization of NVP with HMAM exhibited random copolymer structure, whose copolymer composition depended on the feed molar ratio.

The swelling characteristics of the copolymer gels showed an increase at a pH range of 3–7, where the swelling maximum was observed at pH 7. The copolymer composition has a significant impact on the equilibrium degree of the swelling behavior of both copolymer gels.

A change in the CA of the hydrogel from 0.48 to 0.79 mol % caused a decrease in the equilibrium degree of swelling. The copolymer composition and the pH are the basic parameters affecting the equilibrium degree of swelling of the P(NVP-co-HMAM) gels.

The separation of various metal ions by the P(NVP-co-HMAM) hydrogels to metal ions depended on the pH and filtration factor Z. It is shown that P(NVP-co-HMAM) can bind metal ions like Co(II), Zn(II), Ni(II), and Fe(III) in aqueous solution at pH 5 and 7. At pH 7, most metal ions showed retention values higher than 50%, except for Co(II), Zn(II), and Cd(II). Thus, P(NVP-co-HMAM) is an effective reagent for the separation of metal ions because of the high content of metal ions at pH 7. This behavior can probably be attributed to the chains' intramolecular attraction forces.

A higher stability of the polymer-metal complexes was found at pH 5 and 7, with the thermal decomposition temperature up to 160°C.

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