Metal Ion Retention Using the Ultrafiltration Technique: Preparation, Characterization of the Water-Soluble Poly(1-vinyl-2-pyrrolidone-*co*-itaconic acid) and Its Metal Complexes in Aqueous Solutions

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ABSTRACT: Radical copolymerization of 1-vinyl-2-pyrrolidone with itaconic acid at different feed monomer ratios (75–25 mol %) were investigated. The copolymers were characterized by elemental analysis, Fourier transform infrared (FTIR), ^{1}H and ^{13}C NMR spectroscopy. The copolymer composition was determined from elemental analysis and found to be statistical copolymers. Additionally, viscosimetric measurements, molecular weight, and polydispersity have been determined. The metal complexation of poly(1-vinyl-2-pyrrolidone-*co*-itaconic acid) for the metal ions such as Cr(III), Co (II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III) were investigated at pH 3, 5, and 7 in aqueous solution. The metal ion interaction with hydrophilic polymers was determined as a function of the pH and filtration factor. Poly(1-vinyl-2-pyrrolidone-*co*-itaconic acid) showed a high affinity for the metal ions at pH 5 and 7. The poly(NVP-*co*-IA), with a copolymer composition of 29 : 71 mol % (PVA-3), presented the highest metal ion retention values, particularly at higher pHs, at which the carboxylic acid groups are nonprotonated and could easily coordinate with the metal ions. According to the interaction pattern obtained, Cr(II), Zn(II), Pb(II), and Ni(II) formed the most stable complexes at pH 7. The thermal behaviors of the copolymer and polymer metal complex were characterized using differential scanning calorimetry (DSC) and thermogravimetry techniques under nitrogen atmosphere. The copolymers present high thermal stability and do not present glass transition in DSC curves between 25 and 500°C. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3982–3989, 2008

Key words: hydrophilic copolymer; radical copolymerization; metal complexation; polychelatogen; thermal behavior

INTRODUCTION

Water-soluble polymers are commercially available and the most important requirements for the technological applications of these polymers are high solubility in water, easy and inexpensive synthesis, adequate molecular weight and molecular weight distribution, chemical stability, high affinity for one or more metal ions, and selectivity for the metal ion of interest.[1] Poly(1-vinyl-2-pyrrolidone) (PVP) is a nonionogenic synthetic polymer which possesses a number of unique properties. Because of its hydrophilicity and nontoxicity, it is widely used in various industrial fields.[2] In particular, the preparation of soluble polymeric chelating agents has received attention for its use in recovering metals from dilute solutions,[3–8] especially heavy metals in relatively low concentrations. A number of approaches have been suggested to remove metal ions from aqueous solution.[9–11] Polymers as metal ion-complexing agents have been extensively studied and widely applied to the concentration and separation of various elements.[12–22] Hydrophilic polymers with complexing groups, termed polychelatogens, have been tested to show the applicability of the method to the separation of various metal ion species for analytical and technical purposes, such as separation and measurement of binding properties of metal ions. The liquid-phase polymer retention (LPR) technique as an ultrafiltration system was employed to test the coordination properties in the formation of complexes of the copolymers.[12–22] This method is based on the retention of certain ions by a membrane which separates low molar mass compounds from macromolecular complexes.

In our previous work we reported on poly(1-vinyl-2-pyrrolidone-*co*-2-hydroxyethyl methacrylate). In this study we report on the retention percentages of metal ions applicability of these copolymers at various pH values. The copolymer contains hydroxyl group as chelating properties which are well known by their weak capability to bind metal ion. Therefore, for this copolymer a cooperative effect of different functional groups facilitating interactions with the metal ion is suggested.[23]

In this article, the synthesis of poly(1-vinyl-2-pyrrolidone-*co*-itaconic acid) with two varied feed mole ratio and their binding ability with inorganic ions in aqueous solution like Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III) were investigated at different pH, and the filtration factor was reported, as well as the thermal behavior of the copolymers and copolymer–metal ion complexes.

EXPERIMENTAL

Reagents

1-Vinyl 2-pyrrolidone (Merck-Schuchardt, Germany) and itaconic acid (Merck-Schuchardt) were purified by distillation and recrystallization, respectively. All the other reagents were used as received. The metal ions were used from titrisol ampoules (Merck) as salts: $CrCl_3$, $CdCl_2$, $CoCl_2$, $NiCl_2$, $CuSO_4$, $FeCl_3$, $ZnCl_2$, as CertiPUR grade. All salts were of analytical grade and used as received.

Synthesis of the copolymer

P(NVP-*co*-IA) was synthesized in solution (dioxane) by free radical copolymerization with 3 : 1, 1 : 1, and 1 : 3 feed monomer ratio and using 0.5 mol % of benzoyl peroxide as the initiator (acronym of the copolymers: PVA-2, PVA-1, PVA-3, respectively). Prior to the polymer–metal interaction studies, the polymers were dissolved in water and purified by membrane filtration with an exclusion limit of a molecular weight of 10,000 g/mol, using the polymer fraction over 10,000 g/mol. The yield of the copolymers was higher than 70%.

Measurements

The elemental analyses were carried out using a Carlo Erba 1106 analyzer (Italy). Fourier transform infrared (FTIR) spectra were recorded on a Bruker model vector 22 Spectrophotometer (Bruker Optics). The ^1H NMR spectra were recorded in solution at room temperature with a Bruker AC 250 (Bruker, Karlsruhe, Germany) spectrometer using deuterated dimethylsulfoxide (DMSO-d_6, 99.8%). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and the molecular weight distri-

bution (polydispersity, M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) under the following conditions: WATERS 600E instrument equipped with UV and RI detectors with THF as solvent (flow rate: 1.0 mL/min). The samples were measured at 30°C with a concentration of 6 mg/mL, and the calibration was performed using poly(methyl methacrylate).

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 coordinating properties of the polychelatogen P(NVP-*co*-IA). Details have been previously described.[15–17]

Copolymer composition

Molar percentages (mol %) of comonomer units (m_1 and m_2) in poly(NVP-*co*-IA) using elemental analysis data (content of nitrogen) were calculated. Elemental analysis (*found*): Poly(NVP-*co*-IA): C, 50.60; N, 5.49; H, 7.31 for a copolymer composition of 55 : 45 mol %.

C, 46.81; N, 2.98; H, 5.67 for a copolymer composition of 29 : 71 mol %.

Intrinsic viscosity [η]

The intrinsic viscosity was determined experimentally by measurement of flow times of solvent (to) and a series of dilute polymer solutions of known concentration (c) in a standard suspended level capillary viscometer. The specific viscosity (η_{sp}) was calculated from the following equation.

$$\eta_{sp} = \frac{\eta_c - \eta_o}{\eta_o} = \frac{t_c - t_o}{t_o}$$

The intrinsic viscosity was obtained by plotting η_{sp}/c versus c and extrapolating to zero concentration.

Viscosity measurements were carried out using an Ubbelohde viscometer at 30°C ± 0.1°C (manual for relative measurement) in aqueous solutions of copolymers (0.020–0.040 g/mL) at different pH (3, 5, and 7) unbuffered (0.1M NaCl). The intrinsic viscosity of aqueous solutions (0.1M NaCl) of the copolymer in the presence of the metal ions Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III) (20 mg/L each) were measurement at different pH.

Complexation procedure

To determine the metal binding capacity of the copolymer, 200 mg of the sample was dissolved in water, and the solution was adjusted to the corresponding pH by adding diluted nitric acid or so-

TABLE I
Experimental Conditions and Results for the Copolymerization of Poly(1-vinyl-2-pyrrolidone-*co*-itaconic acid)

Sample abbreviation	NVP (mmol)	IA (mmol)	Feed mole ratio	Yield (%)	Time (h)	Solvent (mL)	Copolymer composition (mol %) from EA
PVA-2	30 (3.21)[a]	10 [1.30][b]	3 : 1	76	2	15	72 : 28
PVA-1	20 (2.14)	20 [2.60]	1 : 1	75	2	15	55 : 45
PVA-3	10 (1.07)	30 [3.90]	1 : 3	69	2	15	29 : 71

Total monomer concentration = $2.67M$.
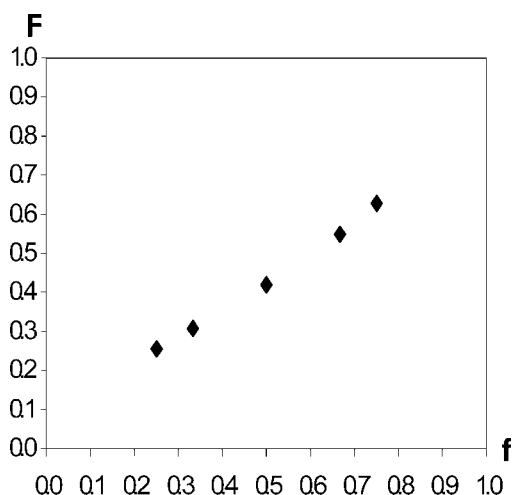[a] Values in parentheses are concentration of NVP (mL).
[b] Values in square brackets are concentration of IA (g).

dium hydroxide ($0.1N$). The aqueous solutions of polymer and metal ions [sulfates, nitrates, or chlorides of Cr(III), Co (II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III), 20 mg/L] were placed into the membrane filtration cell with a solution concentration of 1 wt % of polymer. The total volume in the cell was kept constant at 20 mL. The reservoir contained water adjusted to the cell solution's pH. A membrane with an exclusion limit of 10,000 g/mol (AMICON PM 10 or equivalent) was used. In a pressurized system (300 kPa), the cell solution was stirred for 10 min and then washed with the reservoir fluid at a flow rate of 3–6 mL/min. The filtration fractions ($Z = 1$–10) were collected and the metal ion concentrations in the filtrate and the retentate were determined by atomic absorption spectroscopy. The copolymer was dried for further analytical control. Retention values were calculated from the concentration measurements of filtrate and retentate.

RESULTS AND DISCUSSION

Characterization of poly(NVP-*co*-IA) at different feed monomer ratios

Reaction conditions and copolymer compositions are shown in Table I. Copolymers PVA-1 and PVA-3 are
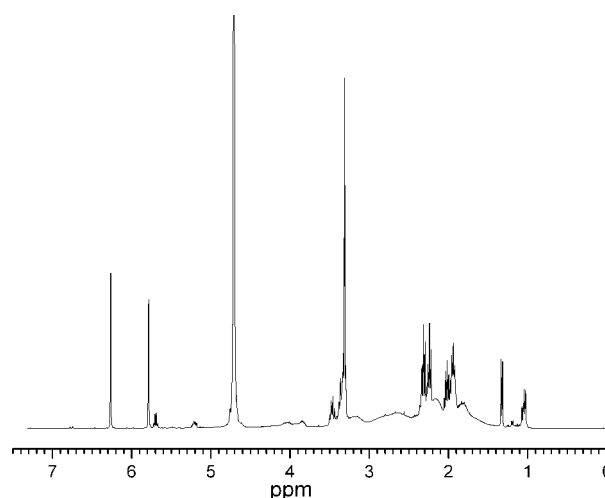
soluble in water, dimethylsulfoxide, acetone, and chloroform.

The copolymer poly(NVP-*co*-IA) was synthesized by free radical solution polymerization. The weight ratios of 1-vinyl-2-pyrrolidone with itaconic acid in the copolymers were determined from N/C weight-percent ratio by elemental analysis. The highest yield value corresponds to the copolymer PVA-2 (76%) in a copolymer composition 72 : 28 mol % for the copolymer richest in the NVP monomer. The copolymer composition depends on the feed monomer ratio giving statistical copolymers incorporating higher amounts of IA because of the higher reactivity of the radical species of this comonomer unit (see Fig. 1).

The ^1H NMR spectrum shows the following signals (δ in ppm): 1.4–1.8 [—CH_2] from NVP; 1.8–2.2 [—CH_2] from the backbone of IA monomer units; 2.2–2.6 [—CH_2COOH], [—CH_2] from the backbone NVP; and [—CH_2] in ring from NVP; 3.2–4.3 [—CH_2N and —CHN]; 4.7 was assigned to the solvent (see Fig. 2).

The ^{13}C NMR spectrum shows the following signals (δ in ppm): between 15 and 20 [—CH_2—] groups of NVP, 32 [—CH_2—COOH]; 33 [—CH_2—] at the chain; 39 and 46 [—CH_2—N], [—CH_2—],

**Figure 1** Relationship of the monomer ratio (*F*) and copolymer composition (*f*) for the copolymerization of NVP.

Figure 2 ^1H NMR spectrum for the copolymer poly(1-vinyl-2-pyrrolidone-co-itaconic acid) (PVA-3) (400 MHz, in D_2O, room temperature).

[—CH—] groups at the chain; 132 and 135 [—C—CH$_2$—] from IA; a group of signals from low to high field at 172 and 177 were assigned to [—COOH]; 180 [—C=O] from NVP (see Fig. 3).
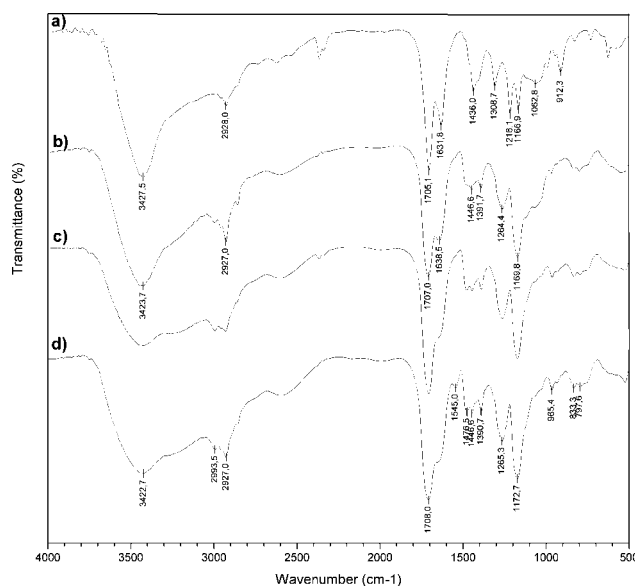
The FTIR spectra (KBr, cm^{-1}) for the copolymer indicate the presence of the following most characteristic absorption bands: 3427.5 ν(OH); 2928.0 ν(CH, CH$_2$); 1705.1 ν(C=O, acid); and 1631 ν(C=O from NVP) [see Fig. 4(a)].

Interactions with metal ions at different pH

The FTIR spectra (KBr, cm^{-1}) of the complexes at pH 3, 5, and 7 [see Figs. 4(b), 4(c), and 4(d), respectively] presented important changes of the bands at 2928.0 ν(CH), and 1705.1 ν(C=O), acid groups and 1631.8 from carbonyl group from NVP) for complexes with Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III) ions in mixture. This result could be attributed to an interaction of carboxyl groups in the complexes. The characteristic absorption bands at 3427.5 cm^{-1} ν(HO; —COOH) presented an important change at higher pH (5 and 7, broad band), although no important change was observed at pH 3. The intensity of the absorption band of carboxylic acid groups from IA at 1705.1 cm^{-1} ν(C=O) increased for the copolymer metal complexes with metal ions at pH 5 and 7 because of metal ion coordination with the carboxylic acid group from IA. The absorption band at 2928.0 cm^{-1} ν(CH, CH$_2$) increased, a result which can be attributed to the interaction of the —CH group bound to the nitrogen atom [—CHN] of NVP [see Fig. 4(b–d)]. The interaction of the nitrogen atom of NVP and carboxylic groups of IA can lead to the formation of molecular complexes between the electron donor nitrogen of NVP and the carboxyl groups IA. The polymer–metal complexes presented new absorption bands, at
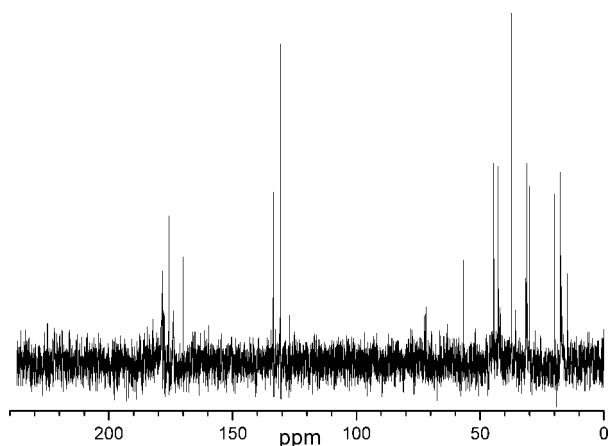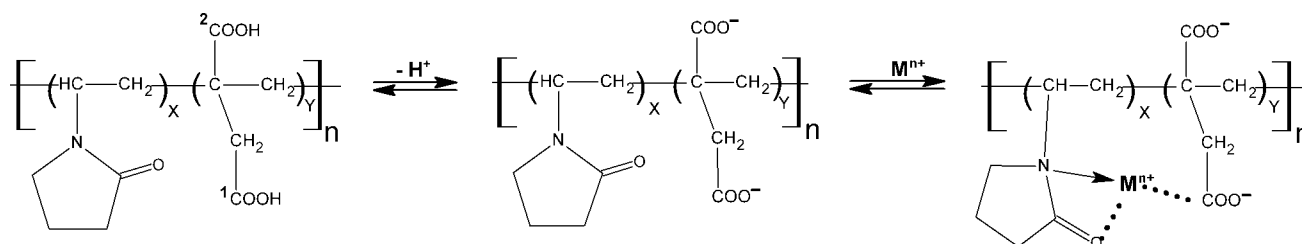

Figure 4 FTIR spectrum for (a) poly(1-vinyl-2-pyrrolidone-*co*-itaconic acid) (PVA-3) and (b–d) polymer–metal complex at pH 3, 5, and 7, respectively.

1446.6 cm^{-1} and 1391.7 cm^{-1}, with a slightly lower intensity and other at 1264.4 cm^{-1} and 1169.8 cm^{-1} with higher intensity. This result could be due to metal ion coordination with the carboxylate groups from the IA units and the nitrogen or carbonyl atoms from NVP at higher pH, possibly leading to the formation of molecular complexes between the electro-donor nitrogen or carbonyl groups from NVP which are able to form donor–acceptor bonds with metal ions and itaconic acid that has two carboxylic groups which potentially can interact with metal ions. The difference in pK_a (pK_{a_1} = 3.85; pK_{a_2} = 5.44)[24] of carboxylic groups of itaconic acid may have a crucial role in the complexation reaction (see Scheme 1). In this connection the amount of both carboxylic groups ionized at pH 7 was determined (PVA-3, 88.2%; PVA-1, 80%) to clarify the amount of involved carboxylate-metal ions into complexation reaction. In the process of complexation it is not possible to discard the formation of intermacromolecular polymer–metal complexes.

Copolymer behavior as a polychelatogen

P(NVP-*co*-IA) has the characteristic of an electrolyte and presents three potential ligand groups in its structure. The complexation properties of PVA-3 and PVA-1 with a copolymer composition of 29 : 71 mol % and 55 : 45 mol % were determined. The metal ion retention properties of these polymers were compared using LPR technique at pH 3, 5, and 7, depending on the washing behavior. In the washing and enrichment methods, the metal ion retention in the cell solution is defined as

Figure 3 ^{13}C NMR spectrum for the copolymer poly(1-vinyl-2-pyrrolidone-*co*-itaconic acid) (PVA-3) (62.9 MHz, in D$_2$O, room temperature).

Scheme 1 Interaction of poly(NVP-*co*-IA) with metal ions at different pH.

$$R = (C_r/C_o) \times 100 \ (\%)$$
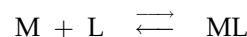
where C_r is the metal ion concentration in the retentate (the cell solution volume, V_c, after a filtrate volume of V_f has been passed) and C_o is the initial metal ion concentration in the cell. The filtration factor Z, expressed in relative units, is another convenient characteristic of the process.[19–23,25]

$$Z = V_f/V_c$$

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

$$M + L \ \rightleftharpoons \ ML$$

In systems with inorganic ion concentrations that are relatively small with respect to the polymer concentration, only the formation of ML may be taken into account. The concentration of the elements that do not form complexes is determined through measurements before and after the contact process.

In general, a high complexation with P(NVP-*co*-IA) and metal ions was observed. Typical P(NVP-*co*-IA) retention profiles are shown in Figure 5. The copolymer's retention percentage occurring with all
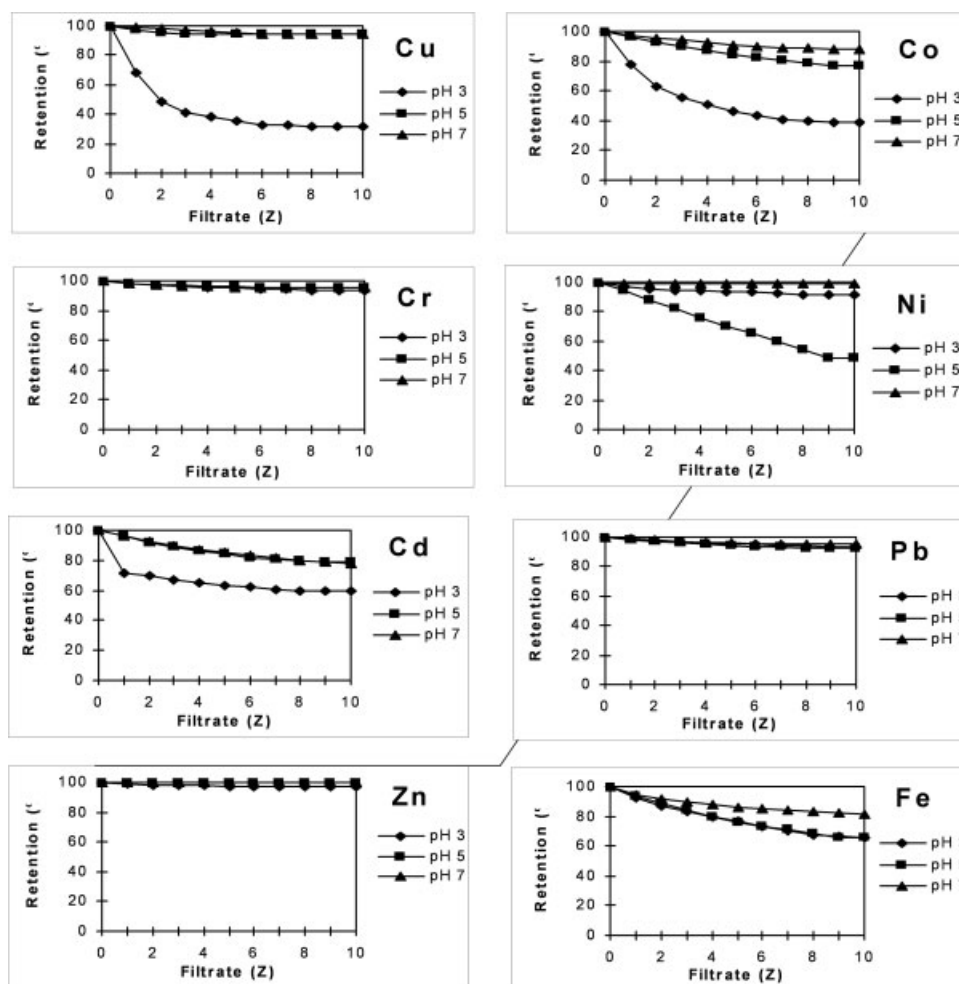
Figure 5 Retention profiles for different metal ions in an aqueous solution (1 wt %) of copolymer PVA-1 at different pH.

TABLE II
Retention Percentage for Seven Metal Ions by P(NVP-*co*-IA) at pH 3, 5, and 7

Sample abbreviation	pH	Retention percentage of metal ion (%)							
		Cu(II)	Co(II)	Cr(III)	Fe(III)	Cd(II)	Pb(II)	Zn(II)	Ni(II)
PVA-1	3	62	69	94	66	60	94	97	89
	5	94	77	96	66	79	93	99	92
	7	95	88	95	85	79	95	99	99
PVA-3	3	70	74	97	70	74	96	98	95
	5	82	88	95	72	75	96	98	96
	7	90	89	95	87	75	97	99	99

metal ions increased at pH 7. For example, the copolymers present lower retention values at pH 3 than at pH 5 and 7 for a filtration factor of $Z = 10$ for Cu(II), Co(II), Cd(II), and Fe(III) with retention values for copolymer VPA-1 between 60 and 69% and for VPA-3 between 70 and 74%. The highest values were found for Cr(III), Zn(II), Ni(II), and Pb(II) at $Z = 10$ (see Table II). At pH 7, all the retention values are higher, except for Cd(II) where copolymer PVA-1 retained 78% and PVA-3 retained 73%. Therefore, retention values of metal ions increase significantly, particularly for Fe(III), Co(II), and Cu(II), with an increase of the pH (see Table II). This result may be due to the formation and rearrangement of different complexes of the copolymer with some of the metal ions studied. A higher complexation for Cr(III), Pb(II), Ni(II), and Zn(II) were observed at all pH under study. At pH 3 for Cu(II), Cd(II), and Co(II), the retention values are lower than 70%, except for Cd(II) which showed slight increase between pH 3 and 7 for VPA-3. Some influence of the complexing comonomer unit was observed at pH 5 and 7 for all the metal ions, and particularly for Cu(II) and Co(II).

The retention percentage values indicate that the copolymer possesses approximately the same reactivity toward all the metal ions, except for Cu(II), Co(II), Cd(II), and Fe(III) at pH 3 when important differences in the copolymer's complexing ability was observed. It is likely that this is due to intramolecular hydrogen bonding attraction forces of the chains and the complexing process which is not in a fast equilibrium. The groups that participate in this process are mainly the carboxylic acid groups from IA comonomer unit and the nitrogen atom from NVP moiety. The percentage retention values would

indicate that the polymer–metal ion interaction was basically through electrostatic forces. An increase in the pH of media results in an increased number of deprotonated carboxylic acid groups along the polymeric chains, thus increasing the possibility of these groups to form a complex with the same metal ion. In this case, the higher stability of copolymer metal complex results in favorable energy because the formation of complexes are also characterized by a more uniform distribution of chelating sites.[25]

The GPC results in Table III indicate that PVA-2, PVA-1, and PVA-3 resulted in polymers with relatively high polydispersities (PD = 1.38, 1.32, and 1.39, respectively).

The intrinsic viscosity of the copolymer's aqueous solutions depended on the pH and metal ion presence (see Table IV). At different pH, the intrinsic viscosity of copolymer PVA-1 increased with metal ion presence. For example, when this copolymer had a copolymer composition of 55 : 45 mol %, the intrinsic viscosity increased when the pH increased. This behavior can be attributed to a weakening of the intramolecular hydrogen bonding attraction forces in the chains. When the copolymer PVA-3 was rich in the IA comonomer unit, having a copolymer composition of 29 : 71 mol %, it presents a decreasing intrinsic viscosity due to metal ion presence. This behavior can be attributed to an increase in the intramolecular hydrogen bonding attraction forces in the chains, which is caused by an increase in the charges

TABLE III
The Copolymer's Molar Mass Distributions for GPC Curves

Copolymer abbreviation	$M_{w(GPC)}$ ($\times 10^3$ g/mol)	$M_{n(GPC)}$ ($\times 10^3$ g/mol)	PD (M_w/M_n)
PVA-2	2.205	1.594	1.38
PVA-1	2.110	1.604	1.32
PVA-3	2.495	1.788	1.39

TABLE IV
Intrinsic Viscosity [η] (dL/g) for Poly(NVP-*co*-IA) and Its Copolymer–Metal Complexes at Different pH (at 30°C, in Water, 20 mg/L Metal Ions)

Sample abbreviation	pH	[η] (dL/g)
PVA-1	Copolymer-1	0.1037
PVA-1/pH3	Complex 1/pH 3	0.1342
PVA-1/pH5	Complex1/pH 5	0.1837
PVA-1/pH 7	Complex1/pH 7	0.2292
PVA-3	Copolymer -3	0.0926
PVA-3/pH 3	Complex 3/pH 3	0.0978
PVA-3/pH 5	Complex 3/pH 5	0.1683
PVA-3/pH 7	Complex 3/pH 7	0.1876

Metal ions in mixture, M^{n+}: Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Cr^{3+}.
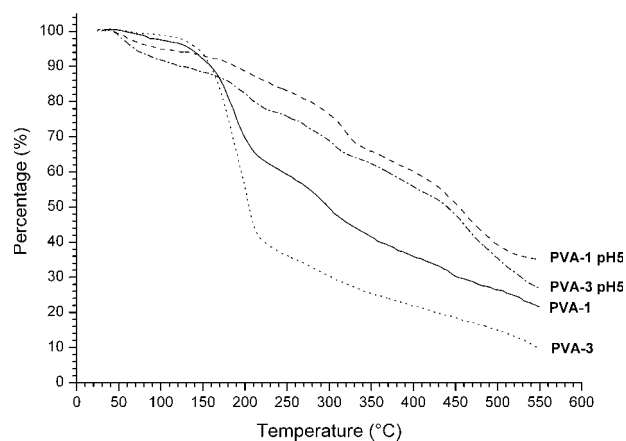
Figure 6 Copolymer and copolymer–metal complex thermograms for poly(1-vinyl-2-pyrrolidone-*co*-itaconic acid) (PVA-1, PVA-3) at pH 5. Heating rate: 10°C/min, under nitrogen atmosphere.

Figure 7 DSC of poly(1-vinyl-2-pyrrolidone-*co*-itaconic acid) (PVA-1). Heating rate: 10°C/min, in nitrogen atmosphere.
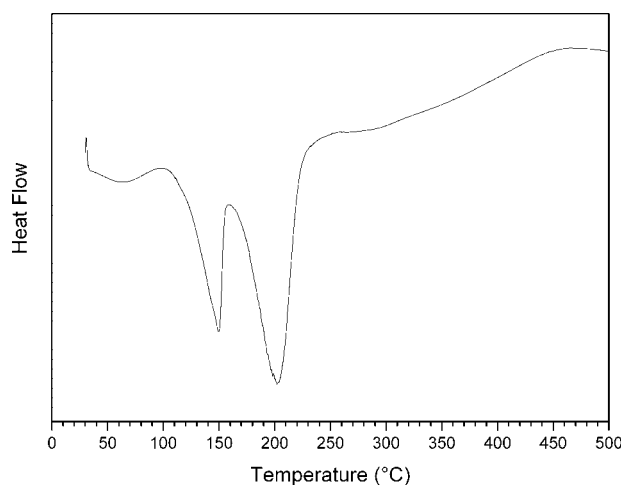
Thermal behavior

The thermal behavior of the poly(NVP-*co*-IA) copolymers were examined by thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) under nitrogen, at a heating rate of 10°C/min. The TGA of the copolymers and their polymer–metal complexes with the metal ions in mixture have been plotted in Figure 6 and the derived data are given in Table V.

The plot shows that the copolymer degraded continuously at various stages of the process, except for PVA-3 at one stage. As shown in Figures 6 and 7 the copolymers were stable up to 150°C. At 150°C, the weight loss was not significant and was attributed to the loss of solvent and a small amount of monomer

residue in the copolymer metal complexes and copolymers. At pH 5 and 7, the complex exhibited a higher stability, obviously because of the complexing process of the metal–polymer support. For example, the copolymer PVA-1 had a mass loss of 2.4% at 150°C and for the complexes it was of 5.0% at pH 5 (see Table V). This may be due to the formation and rearrangement of different complexes of the copolymer with some of the metal ions studied.

As expected, the copolymer with a composition of $\sim$ 55: 45 mol % (PVA-1) was less stable than the other complexes. For example, PVA-1 had a mass loss of 30.3% at 250°C and 50.2% at 350°C, but dropped to 11.3% at 250°C and 23.6% at 350°C at pH 5.

The copolymer metal complex with a composition of $\sim$ 55 : 45 mol % at different pH presents a higher thermal degradation temperature than PVA-1. The data are summarized in Table V. The residual mass for complexes at pH 3, 5, and 7 is higher than that of the copolymer, which can be principally attributed to the lineal poly(NVP-*co*-IA) present in its structure with a high percentage of intramolecular bonding-metal ions.

Glass transition temperature

The glass transition temperature (T_g) was analyzed in the second run. The DSC thermograms do not show T_g for poly(NVP-*co*-IA) from 20 to 500°C.

CONCLUSIONS

The radical polymerization of NVP with IA gave statistical copolymers whose copolymer composition depends on the feed molar ratio.

The separation of various metal ions by the poly(1-vinyl-2-pyrrolidone-*co*-itaconic acid) reagent

TABLE V
Thermal Behavior and Thermal Decomposition Temperatures (TDT) for the Copolymer and Its Copolymer–Metal Complexes at Different pH (Initial Mass 4.2–6.0 mg)

Sample abbreviation	Weight-loss (%) at different temperatures (°C)					
	150	250	350	450	550	TDT
PVA-1	2.4	30.3	50.2	64.3	73.6	157.2
PVA-1/pH 3	3.7	27.6	43.0	66.4	70.6	160.3
PVA-1/pH 5	5.0	11.3	23.6	40.0	60.7	170.6
PVA-1/pH 7	4.0	10.0	22.3	38.5	58.3	175.5
PVA-3	1.1	44.7	69.6	78.2	85.0	155.3
PVA-3/pH 3	4.0	40.0	65.0	74.0	80.0	160.4
PVA-3/pH 5	8.1	17.7	31.1	44.2	64.6	183.4
PVA-3/pH 7	6.1	15.4	28.6	42.7	60.9	198.2

Metal ions in mixture, M^{n+}: Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Cr^{3+}.

depended on the pH and filtration factor Z. It is shown that poly(NVP-*co*-IA) can bind metal ions like Cr(III), Zn(II), Ni(II), and Pb(II) in aqueous solution at pH 3, 5, and 7. At pH 7, most metal ions showed retention values higher than 80%, except for Cd(II) (78%). Thus, P(NVP-*co*-IA) is an effective reagent for the separation of metal ions because of the high content of metal ions at pH 5 and 7. In general, a lower complexation of Co(II), Cu(II), Cd(II), and Fe(III) with P(NVP-*co*-IA) took place at pH 3 with values higher than 60%. This behavior can probably be attributed to the chains' intramolecular hydrogen bonding attraction forces.

The intrinsic viscosity increased in the presence of metal ions depending on the pH and copolymer composition, with higher values found at pH 5 and 7.

A higher stability of the polymer–metal complexes was found at pH 5 and 7, with the thermal decomposition temperature up to 180°C. This result may be due to the formation and rearrangement of different copolymer complexes with some of the metal ions studied.

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