

Nonionic Water-Soluble Polymer: Preparation, Characterization, and Application of Poly(1-vinyl-2-pyrrolidone-*co*-hydroxyethylmethacrylate) as a Polychelatogen

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ABSTRACT: The free-radical copolymerization of water-soluble poly(1-vinyl-2-pyrrolidone-*co*-hydroxyethylmethacrylate) was carried out with a feed monomer ratio of 75:25 mol %, and the total monomer concentration was 2.67M. The synthesis of the copolymer was carried out in dioxane at 70°C with benzoyl peroxide as the initiator. The copolymer composition was obtained with elemental analysis and ¹H-NMR spectroscopy. The water-soluble polymer was characterized with elemental analysis, Fourier transform infrared, ¹H- and ¹³C-NMR spectroscopy, and thermal analysis. Additionally, viscosimetric measurements of the copolymer were performed. The thermal behavior of the copolymer and its complexes were investigated with differential scanning calorimetry (DSC) and thermogravimetry techniques under a nitrogen atmosphere. The copolymer showed high thermal stability and a glass transition in the DSC curves. The separation of various metal ions by the water-soluble poly(1-vinyl-2-pyrrolidone-*co*-hydroxyethylmethacrylate) reagent

in the aqueous phase with liquid-phase polymer-based retention was investigated. The method was based on the retention of inorganic ions by this polymer in a membrane filtration cell and subsequent separation of low-molar-mass species from the polymer/metal-ion complex formed. Poly(1-vinyl-2-pyrrolidone-*co*-hydroxyethylmethacrylate) could bind metal ions such as Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III) in aqueous solutions at pHs 3, 5, and 7. The retention percentage for all the metal ions in the polymer was increased at pH 7, at which the maximum retention capacity could be observed. The interaction of inorganic ions with the hydrophilic polymer was determined as a function of the pH and filtration factor. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 178–185, 2006

Key words: radical polymerization; hydrophilic polymers; metal-polymer complexes; differential scanning calorimetry (DSC); thermogravimetric analysis (TGA)

INTRODUCTION

Poly(1-vinyl-2-pyrrolidone) (PVPD) is a nonionogenic synthetic polymer that possesses a number of unique properties. Thus, despite the apparent hydrophobicity of its monomeric units, being similar in chemical composition to the units of polyleucine, a typical hydrophobic peptide, PVPD is rather hygroscopic and readily soluble in water. Because of its hydrophilicity and nontoxicity, it is widely used in medicine as a blood plasma substitute, for prolonging the action of drugs, and in various industrial fields.¹

Soluble polymeric supports have been developed for the complexation of various metals. In particular,

the preparation of soluble polymeric chelating agents has received attention for applications to metal recovery from dilute solutions.^{2–11}

Polymers as metal-ion-complexing agents have been extensively studied and widely applied to the concentration and separation of various elements.^{12–20}

The aim of this article is to study in conjunction with membrane filtration the metal-ion interactions of a nonionic water-soluble synthetic polymer with inorganic ions in aqueous solutions, such as Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III), at different pH values because of their environmental and analytical interest as well as the thermal behavior of the copolymer and polymer/metal-ion complexes.

EXPERIMENTAL

Reagents

1-Vinyl-2-pyrrolidone (NVP; Merck, Stuttgart, Germany) and hydroxyethylmethacrylate (HEMA; Merck) were purified by distillation. All the other reagents were used as received.

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TABLE I
Experimental Conditions for the Copolymerization of P(NVP-co-HEMA)

NVP		HEMA		Feed molar ratio	Yield(%)	Time (h)	Solvent (mL)	Copolymer composition from H-NMR
mmol	mL	mmol	mL					
30	3.21	10	1.22	3 : 1	72	2	15	54 : 46

Total concentration of monomers = 2.67M.

The metal ions were used from Titrisol ampules (Merck) as salts: CrCl₃, CdCl₂, CoCl₂, NiCl₂, CuSO₄, FeCl₃, and ZnCl₂ (CertiPUR-grade).

Synthesis of the copolymer

Poly(1-vinyl-2-pyrrolidone-co-hydroxyethylmethacrylate) [P(NVP-co-HEMA)] was synthesized by radical copolymerization with a 3 : 1 feed monomer ratio in solution with 0.5 mol % benzoyl peroxide as the initiator.¹⁵ Before the interaction studies, the polymer with the 3 : 1 feed monomer composition was dissolved in water and purified by membrane filtration with a membrane with an exclusion limit of a molecular weight of 10,000 g/mol. In this study, the fraction of the polymer over 10,000 g/mol was used. The yield of the copolymer was higher than 72%. All salts were analytical-grade and were used as received.

Measurements

The elemental analyses were carried out with a Carlo Erba 1106 analyzer (Italy). Fourier transform infrared (FTIR) and ¹H-NMR spectra were recorded on a Bruker Vector 22 (Bruker Optics, Inc., Billerica, MA) and Bruker Avance 400 spectrometer (Karlsruhe, Germany), respectively. The intrinsic viscosity was measured in water solutions of copolymers (0.020–0.040 g/mL) with an Ubbelohde viscometer (Merck) at 30 ± 0.1°C.

Equipment

The determination of the metal-ion concentrations was carried out with a PerkinElmer 1100 atomic absorption spectrometer (PerkinElmer, Shelton, CT). For lyophilization, a Lab Conco 6L continuous freeze dryer (Karl-Heinz Müller, Laborbedorf GmbH) was used. The pH was determined with a Hanna 211 pH-meter (Miami, FL). For the liquid-phase polymer-based retention (LPR) technique, a membrane filtration system was employed to test the coordinating properties of the polychelator P(NVP-co-HEMA). Details have been previously described.^{15–17}

Copolymer composition

The molar percentages of the comonomer units (m_1 and m_2) in P(NVP-co-HEMA) with elemental analysis

data (concentration of N) were calculated 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 HEMA units, A_N is the atom weight of N, B is the concentration of N in the copolymers (%), and ΔM is equal to $M_1 - M_2$. M_1 is the molecular weight of the NVP unit.

ANAL. Found for P(NVP-co-HEMA): C, 56.58%; N, 6.2%; H, 7.845%.

Complexation procedure

For the determination of the complex binding capacity, the copolymer (1 wt %, 200 mg) was dissolved in water (10 mL) and adjusted to the corresponding pH by the addition of diluted nitric acid or sodium hydroxide. The aqueous solutions of the polymer and metal, sulfates, nitrates, or chlorides (20 ppm) were placed in the membrane filtration cell. The total volume in the cell was kept constant at 20 mL. The reservoir contained water adjusted to the same pH as that of the cell solution. A membrane with an exclusion limit of 10,000 g/mol (Amicon PM 10 or the equivalent, Millipore, Bedford, USA) was used. The system was pressurized (300 kPa), and the cell solution was stirred for 10 min and then washed with the reservoir fluid at a flow rate of 4–6 mL/min. The filtration fractions ($Z = 1-10$) were collected, and the concentrations of the metal ions in the filtrate and the retentate were determined by atomic absorption spectroscopy. The copolymer was lyophilized for further analytical control. Retention values were calculated from the concentration measurements of the filtrate and retentate.

RESULTS AND DISCUSSION

Synthesis and characterization of P(NVP-co-HEMA)

The copolymer was soluble in water, dimethyl sulfoxide, acetone, and chloroform. The reaction conditions and copolymer compositions are shown in Table I.

The copolymer P(NVP-co-HEMA) was synthesized by radical solution polymerization. The weight ratios of NVP to HEMA in the copolymer were calculated

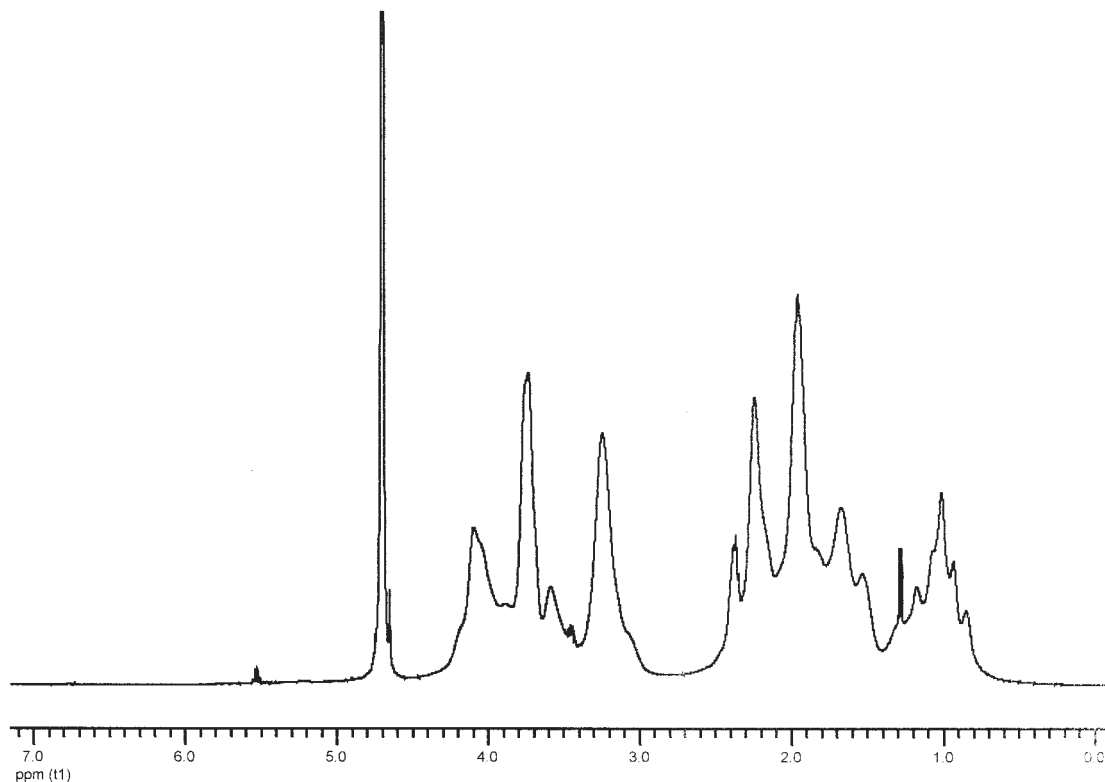


Figure 1 ^1H -NMR spectrum of P(NVP-co-HEMA) (400 MHz, in D_2O at room temperature).

from the N/C weight percentage ratio determined by elemental analysis and ^1H -NMR spectroscopy.

The highest yield value (72%) corresponded to a copolymer composition of 54 : 46 mol % for the copolymer richest in the NVP monomer.

The ^1H -NMR spectrum (in D_2O) showed the following signals (δ): 0.5–1.3 ($-\text{CH}_3$), 1.4–2.6 ($-\text{CH}_2$ from the backbone of both monomer units and $-\text{CH}_2\text{CH}_2\text{CO}$ from NVP), and 2.9–4.5 ppm ($-\text{CH}_2\text{N}$ and $-\text{CHN}$, and $-\text{CH}_2\text{CH}_2-\text{OH}$). The signal at 4.7 ppm was assigned to the solvent (see Fig. 1).

The relationship of the area corresponding to $-\text{CH}_2\text{N}$ (2H) of ring protons from NVP with those

methyl protons (3H) coming from the HEMA unit confirmed the copolymer composition calculated by elemental analysis.

The ^{13}C -NMR spectrum (in D_2O) showed the following signals (δ): 15–20 ($-\text{CH}_3$, CH_2- groups of NVP), 32 ($-\text{CH}_2-\text{CO}$), 32–38 ($-\text{CH}_2-$ at the chain), 40–50 ($-\text{CH}_2-\text{N}$, $-\text{CH}_2-$, and $-\text{CH}-$ groups at the chain), 66–67 ($-\text{CH}_2-\text{CH}_2\text{OH}$), and 110 ppm ($-\text{C}-\text{CH}_2-$ from HEMA). A group of signals from a low field to a high field at 165 ppm was assigned to $-\text{COOH}$; there were also signals at 175–180 ($-\text{C}=\text{O}$ from NVP) and 210 ppm ($-\text{COO}-$ from HEMA; see Fig. 2).

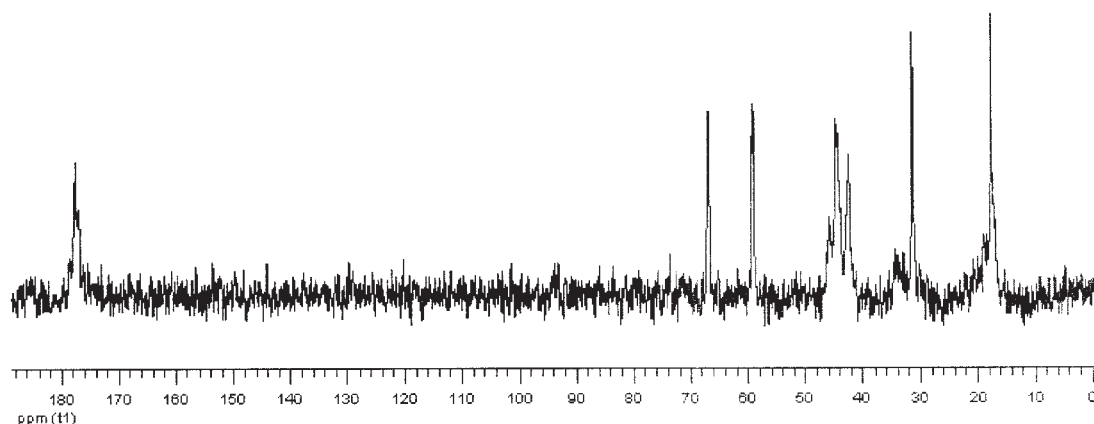


Figure 2 ^{13}C -NMR spectrum of P(NVP-co-HEMA) (62.9 MHz, in D_2O at room temperature).

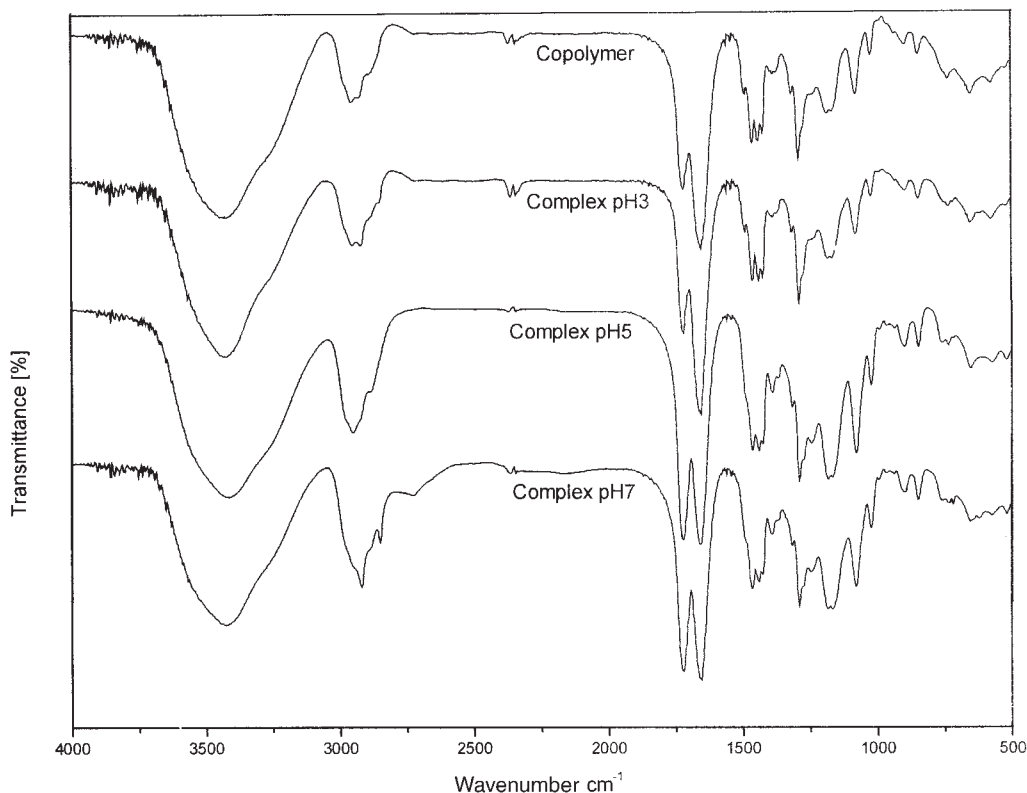


Figure 3 FTIR spectrum of P(NVP-*co*-HEMA) and the complexes.

The FTIR spectra (KBr) for the copolymer showed the presence of the following most characteristic absorption bands: 3421.9 [$\nu(\text{OH})$], 2900 [$\nu(\text{CH}, \text{CH}_2)$], 1710 [$\nu(\text{C}=\text{O}, \text{ester})$], and 1655 cm^{-1} [$\nu(\text{C}=\text{O} \text{ amide})$]; see Fig. 3].

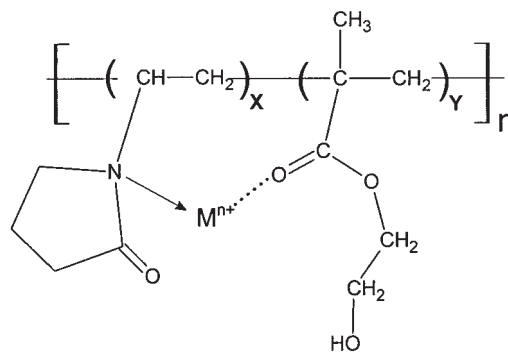
Interactions with metal ions of P(NVP-*co*-HEMA) at different pHs

The FTIR spectra (KBr) of the complexes showed an important change in the absorption band at 2956.4 [$\nu(\text{CH})$] and 1719.3 cm^{-1} [$\nu(\text{C}=\text{O}, \text{ester})$] for complexes with metal ions, which could be attributed to the stronger interaction through the ester and amide groups but not in the important way of the hydroxyl groups. The characteristic absorption bands at 3421.9 cm^{-1} [$\nu(\text{OH})$] showed an important change at a basic pH (5 and 7, broad band); at pH 3, the band did not show an important change, except that it was sharp. The intensity of the absorption band of the carboxylic group from HEMA at 1719.3 cm^{-1} [$\nu(\text{C}=\text{O}, \text{ester})$] increased for the complexes with metal ions at pHs 5 and 7 because of the coordination of the metal ions with the carboxyl group from HEMA. The absorption band at 2956.4 cm^{-1} [$\nu(\text{CH}, \text{CH}_2)$] increased, and that could be attributed to the interaction of the $-\text{CH}$ group bound to the nitrogen atom ($-\text{CHN}$) from NVP (see Fig. 3). The interaction of the nitrogen atom from NVP and carboxylic groups could lead to the forma-

tion of molecular complexes between the electron-donor nitrogen from NVP and the carbonyl groups from HEMA (see Scheme 1). At pH 3, the FTIR spectra did not show any change.

Behavior of the copolymer as a polychelator

P(NVP-*co*-HEMA) has the characteristics of a nonelectrolyte. The complexation properties of P(NVP-*co*-HEMA) with a copolymer composition of 54 : 46 mol % and its interaction with seven metal ions were investigated with the LPR technique at pHs 3, 5, and 7 according to the washing behavior. The copolymer



Scheme 1 Interaction of P(NVP-*co*-HEMA) with metal ions.

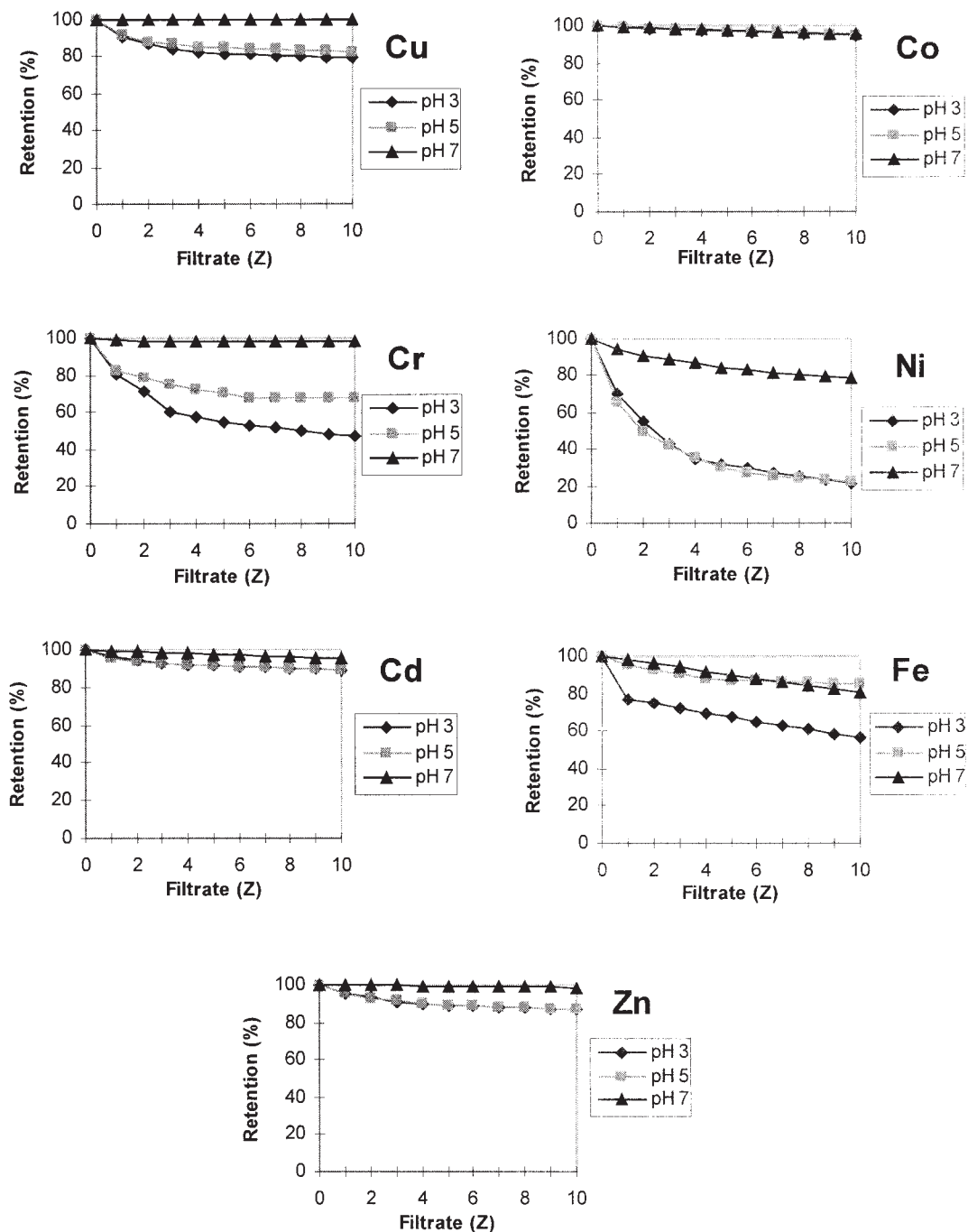


Figure 4 Retention profiles for different metal ions with an aqueous solution (1 wt %) of P(NVP-co-HEMA) at different pHs.

contains hydroxyl, amide, and ester as potential ligand groups. The chelating properties of the amide groups for some metal ions are well known, as well as the weak capability to bind metal ions of the hydroxyl group. Ester groups are not usually used as ligand groups. Therefore, for this polymer, a cooperative effect of different functional groups facilitating interactions with the metal ions is suggested.

In the washing and enrichment methods, the retention of metal ions (R) in the cell solution is defined as follows:

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

where C_r is the metal-ion concentration in the retentate (the cell solution after a filtrate volume of V_f has been passed) and C_0 is the initial metal-ion concentration in the cell. Z , expressed in relative units, is another convenient characteristic of the process:¹⁹⁻²⁴

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

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

pH	Metal ion						
	Cu(II)	Co(II)	Cr(III)	Ni(II)	Cd(II)	Fe(III)	Zn(II)
3	79.0	94.5	47.0	21.5	89.0	56.7	87.0
5	82.5	94.5	67.7	22.0	89.0	85.0	86.6
7	100.0	95.0	98.5	78.5	95.0	80.5	98.5

where V_c is the volume of the cell solution. The retention depends on polymer complex dissociation, which is generally described by a reversible reaction:



where M is the metal ion and L is the polymer with complexing groups (ligands). 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.

Typical retention profiles of P(NVP-*co*-HEMA) are shown in Figure 4. In general, high complexation with P(NVP-*co*-HEMA) and metal ions was observed. The percentage of retention for the copolymer that took place with all metal ions was increased at pH 7. For example, the copolymer presented low retention values at pH 3 for $Z = 10$, except for Cu(II), Zn(II), Cd(II), and Co(II), which showed retention values between 79 and 94.5%; the highest value was for Co(II) at $Z = 10$ (see Table II). At pH 7, all the retention values were higher. Therefore, the retention of metal ions increased significantly, particularly for Fe(III), Cr(III), and Ni(II) by an increase in the pH (see Table II). This may be due to the formation and rearrangement of different complexes of the copolymer with some of the metal ions studied.

Higher complexation for Co(II), Cu(II), Cd(II), and Zn(II) was observed at all pHs under study. At pH 3 for Ni(II), Cr(III), and Fe(III), the retention values were lower than 60% and increased, except for Ni(II), for which they lightly increased from pHs 3 to 5. These values increased at pHs 5 and 7 (see Table II). Some influence of the complexing comonomer unit at pHs 5 and 7 was observed for all the metal ions.

The retention percentage of the copolymer showed that it possessed approximately the same reactivity toward all the metal ions, except for Ni(II), Cr(III), and Fe(III) at pH 3, at which significant differences in the complexing ability of the copolymer were observed. This behavior could probably be attributed to intramolecular hydrogen-bonding attraction forces of the chains and the equilibrium complexes process, which were not in a quick equilibrium. The groups

TABLE III
Intrinsic Viscosity (dL/g) of P(NVP-*co*-HEMA) and its Complexes with Cr(III), Cu(II), Zn(II), Co(II), Ni(II), Fe(III), and Co(II)^a

pH	P(NVP- <i>co</i> -HEMA)	P(NVP- <i>co</i> -HEMA)-M ⁿ⁺
3	0.130	0.260
5	0.160	0.275
7	0.180	0.375

^a At 30°C, in water, and with 20 mg/L metal ions.

that participated in this process were mainly the carbonyl groups from HEMA monomer units and the nitrogen atom from NVP. The carboxyl group at the lateral chain from HEMA and the nitrogen atom and carboxyl group from NVP could exhibit relative weakening of the intramolecular binding attraction forces of the chains in comparison with the ionic polymer polyelectrolyte.^{15-17,22} The retention percentage values indicated that the polymer/metal-ion interaction was basically through electrostatic forces. Complex formation was strongly dependent on the pH; the differences in the electron spin resonance spectra of three complexes observed for Cu²⁺ with polyethyleneimine at different pHs confirmed this suggestion.^{25,26} The complexes were not in a fast equilibrium, and this allowed them to be identified separately. An increase in the pH of the medium increased the number of deprotonated amino groups along the polymeric chains, thus increasing the possibility of amino groups interacting with the same metal ion.

The intrinsic viscosity of aqueous solutions of the copolymer depended on the pH and on the presence of the metal ions (see Table III). At different pHs, the intrinsic viscosity of the copolymer increased in the presence of the metal ions. This behavior could be attributed to a weakening of the intramolecular hy-

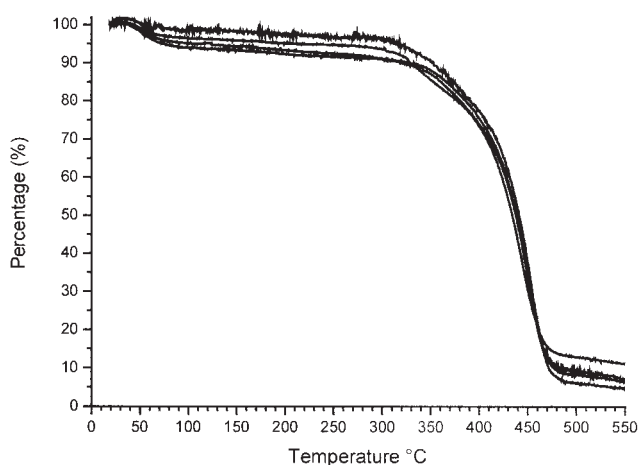


Figure 5 Thermograms of the copolymer and metal complexes of P(NVP-*co*-HEMA) and metal ions at different pHs. The heating rate was 10°C/min under a nitrogen atmosphere.

TABLE IV
Thermal Behavior and TDT of the Copolymer and its Complexes at Different pH Values (Initial Mass = 4.2–6.0 mg)

Temperature (°C)	Weight loss (%) at different temperatures (°C)					TDT
	150	250	350	450	550	
P(NVP- <i>co</i> -HEMA)	6.7	8.4	11.9	64.3	95.3	308
P(NVP- <i>co</i> -HEMA)-M ⁿ⁺ at pH 3	5.7	7.6	13.0	66.4	93.6	308
P(NVP- <i>co</i> -HEMA)-M ⁿ⁺ at pH 5	1.8	3.2	9.7	62.7	93.1	309
P(NVP- <i>co</i> -HEMA)-M ⁿ⁺ at pH 7	4.1	5.4	14.6	69.7	88.9	298

drogen-bonding attraction forces in the chains, which was caused by an increase in the charges along the macromolecules during the complexing process.

Thermal Behavior

Thermogravimetric analysis (TGA)

TGA thermograms of the copolymers and their complexes are plotted in Figure 5, and the data derived from them are collected in Table IV. Under 200°C, the weight loss was not significant and was attributed to the loss of solvent and a small amount of monomer residue in the complexes and copolymers.

The thermal behavior of the P(NVP-*co*-HEMA) copolymer was examined by TGA under nitrogen at a heating rate of 10°C/min (Fig. 5). The plot shows that the copolymer degraded continuously in a one-stage process. As shown in Figure 5, the copolymer was stable up to 308°C. At pH 5, the complex exhibited a slightly higher stability, obviously because of the complexing process of the metal-polymer support. For example, the copolymer had a mass loss of 6.7% at 150°C, and for the complexes, it was 5.7, 1.8, and 4.1% at pHs 3, 5, and 7, respectively (see Table IV). 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 P(NVP-*co*-HEMA) was less stable than the complexes. For example, P(NVP-*co*-HEMA) had a mass loss of 8.4% at 250°C and 11.9% at 350°C, in comparison with values of 3.2% at 250°C and 9.7% at 350°C for the complex at pH 5.

The copolymer with a composition of approximately 56:46 mol % at different pHs in contact with metal ions presented a thermal decomposition temperature (TDT) similar to that of P(NVP-*co*-HEMA).

TABLE V
 T_g and ΔC_p for P(NVP-*co*-HEMA) and its Complex at Different pH Values

	P(NVP- <i>co</i> -HEMA)	Polymer/metal-ion complex		
		pH 3	pH 5	pH 7
T_g (°C)	135	115	120	124
ΔC_p (J g ⁻¹ K ⁻¹)	0.276	0.134	0.163	0.183

The data are summarized in Table V. The residual mass for complexes at pHs 3, 5, and 7 was higher than that for the copolymer. The main reason could be attributed to the fact that the linear P(NVP-*co*-HEMA) presented 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.

Glass-transition temperature (T_g)

T_g was estimated from the trace of this second run. In all cases, to determine T_g of the samples, the criterion of T_g at $\Delta C_p/2$, where ΔC_p is heat capacity, was adopted.

Differential scanning calorimetry (DSC) thermograms of P(NVP-*co*-HEMA) (curve a) and copolymer/metal ion complexes (curves b–d) are illustrated in Figure 6. T_g for the polymer-metal complexes showed a decrease with respect to the T_g value of the copolymer (135°C). The same behavior for $\Delta C_p/2$ was observed in both polymer-metal complexes.

The initial deflection was proportional to the sample heat capacity. T_g of P(NVP-*co*-HEMA) was around 135°C, and T_g for the complexes was between 115 and 124°C. The copolymer showed a single T_g , which indicated the formation of random copolymers.

CONCLUSIONS

The copolymer was soluble in water, dimethyl sulfoxide, acetone, and chloroform. The separation of various metal ions by the water-soluble P(NVP-*co*-HEMA) reagent in an aqueous phase with LPR was investigated. P(NVP-*co*-HEMA) could bind metal ions such as Cr(III), Co(II), Zn(II), Ni(II), Cu(II), Cd(II), and Fe(III) in aqueous solutions at pHs 3, 5, and 7. At pHs 5 and 7, most metal ions showed retention values over 80%, except for Ni(II). At pH 7, most metal ions showed retention values higher than 95%, except for Ni(II) and Fe(III). Thus, P(NVP-*co*-HEMA) is an effective reagent for the separation of metal ions because of the high concentration of metal ions at pHs 5 and 7. In general, only slight complexation of Ni(II) and Cr(III) with P(NVP-*co*-HEMA) took place at pH 3. This behavior can probably be attributed to intramolecular hydrogen-bonding attraction forces of the chains. It was not possible to establish a general behavior

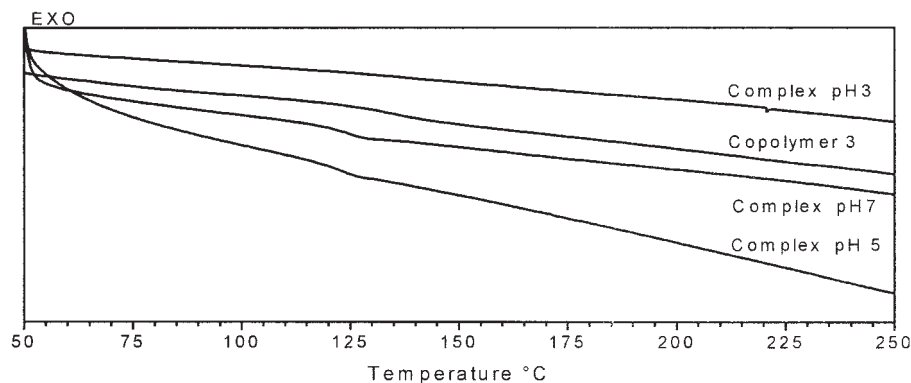


Figure 6 DSC of P(NVP-co-HEMA) and polymer-metal complexes at different pHs. The heating rate was 10°C/min under a nitrogen atmosphere.

based on the ionic radius and the hard-soft acid-base principle.

The intrinsic viscosity increased in the presence of the metal ions, depending on the pH, with higher values found at pHs 5 and 7. A higher stability of the polymer-metal complexes was found with TGA. This may be due to the formation and rearrangement of different complexes of the copolymer with some of the metal ions studied. The copolymer with a composition of approximately 56:46 mol % at different pHs in contact with metal ions presented a TDT similar to that of P(NVP-co-HEMA). The residual mass for complexes at pHs 3, 5, and 7 was higher than that for the copolymer. The copolymer showed a single T_g , which indicated the formation of random copolymers. T_g for the polymer-metal complexes decreased with respect to the T_g value of the copolymer (135°C).

References

- Sidelkovskaya, F. P. *Khimiya N-Vinylpyrrolidona I Ego Polimerov*; Nauka: Moscow, 1970; p 117.
- Geckeler, K. E.; Pillai, V. N. R.; Mutter, M. *Adv Polym Sci* 1981, 39, 65.
- Spivakov, B. Y.; Geckeler, K. E.; Bayer, E. *Nature* 1985, 315, 313.
- Spivakov, B. Y.; Shkinev, V. M.; Vorob'eva, G. A. *Anal Chim Acta* 1986, 189, 285.
- Rivas, B. L.; Pereira, E. D.; Moreno-Villoslada, I. *Prog Polym Sci* 2003, 28, 173.
- del C. Pizarro, G.; Rivas, B. L.; Geckeler, K. E. *Pure Appl Chem* 1997, 34, 855.
- Moreno-Villoslada, I.; Miranda, V.; Oyarzún, F.; Hess, S.; Luna, M.; Rivas, B. L. *J Chil Chem Soc* 2004, 49, 121.
- Rivas, B. L.; Schiappacasse, L. N.; Pereira, E.; Moreno-Villoslada, I. *J Chil Chem Soc* 2004, 49, 345.
- Champ, S.; Xue, W.; Huglin, M. B. *Macromol Chem Phys* 2000, 201, 931.
- del C. Pizarro, G.; Rivas, B. L.; Geckeler, K. E. *J Macromol Pure Appl Chem* 1997, 34, 855.
- Dan, Y.; Chen, S. Y.; Zhang, Y. F.; Xiang, F. R. *J Polym Sci Part B: Polym Phys* 2000, 38, 1069.
- Bekturov, E. A.; Kudaibergenov, S. E.; Rafikov, S. R. *Russ Chem Rev* 1991, 60, 410.
- Spivakov, B. Y.; Shkinev, V. M.; Geckeler, K. E. *Pure Appl Chem* 1994, 66, 631.
- Spivakov, B. Y.; Shkinev, V. M.; Golovanov, V. I.; Bayer, E.; Geckeler, K. E. *Macromol Theory Simul* 1996, 5, 357.
- del C. Pizarro, G.; Rivas, B. L.; Geckeler, K. E. *J Chil Chem Soc* 1996, 41, 181.
- del C. Pizarro, G.; Rivas, B. L.; Geckeler, K. E. *J Macromol Sci Pure Appl Chem* 1997, 34, 681.
- del C. Pizarro, G.; Rivas, B. L.; Geckeler, K. E. *J Macromol Sci Pure Appl Chem* 1997, 34, 1483.
- del C. Pizarro, G.; Marambio, O. G.; Rivas, B. L.; Geckeler, K. E. *Polym Bull* 1998, 41, 687.
- Rivas, B. L.; Maturana, H. A.; Villegas, S.; Pereira, E. *J Appl Polym Sci* 2000, 77, 1994.
- Rivas, B. L.; Pooley, S. A.; Soto, M.; Geckeler, K. E. *J Appl Polym Sci* 1999, 72, 741.
- Rivas, B. L.; Pooley, S. A.; Maturana, H. A.; Villegas, S. *Macromol Chem Phys* 2001, 202, 4432.
- del C. Pizarro, G.; Marambio, O. G.; Jeria, M.; Geckeler, K. E. *Macromol Chem Phys* 2003, 204, 922.
- Marambio, O. G.; del C. Pizarro, G.; Jeria, M.; Huerta, M. *J Chil Chem Soc* 2003, 48, 41.
- Rivas, B. L.; Pooley, S. A.; Luna, M. *J Appl Polym Sci* 2002, 83, 2556.
- Kavanov, V. A.; Molochnikov, L. S.; Babkin, O. H.; Sultanov, J. M.; Orudzhev, D. D.; Efendiev, A. A. *Polym Sci USSR A* 1986, 28, 2736.
- Molochnikov, L. S.; Radionov, B. K. *Russ J Phys Chem* 1995, 69, 768.