Water-Soluble Copolymers of 1-Vinyl-2-pyrrolidone and Acrylamide Derivatives: Synthesis, Characterization, and Metal Binding Capability Studied by Liquid-Phase Polymer-Based Retention Technique

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ABSTRACT: Radical copolymerizations of 1-vinyl-2-pyrrolidone with acrylamide and N,N'-dimethylacrylamide at different feed ratios were investigated. The copolymers were characterized by Fourier transform infrared spectroscopy, ¹H NMR, and ¹³C NMR spectroscopy. The copolymer composition was determined from the ¹H NMR spectra and found to be statistical. The metal complexation of poly(acrylamide-co-1-vinyl-2pyrrolidone) and poly(*N*,*N*'-dimethylacrylamide-co-1-vinyl-2-pyrrolidone) for the metal ions Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), Fe(III), and Cr(III) were investigated in an aqueous phase. The liquid-phase polymer-based retention method is based on the retention of inorganic ions by soluble polymers in a membrane filtration cell and subsequent separation of low-molecular compounds from the polymer complex formed. The metal ion interaction with the hydrophilic polymers was determined as a function of the pH and the filtration factor. Poly(N,N-dimethylacrylamide-co-1-vinyl-2-pyrrolidone) showed a higher affinity for the metal ions than poly(acrylamide-co-1-vinyl-2pyrrolidone). According to the interaction pattern obtained, Cr(III) and Cu(II) formed the most stable complexes at pH 7. Pb(II) and Zn(II) were not retained. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 741-750, 1999

Key words: water soluble polymers; polychelatogens; metal ion binding; ultrafiltration membrane.

INTRODUCTION

Membrane filtration processes are among the most promising technologies for enrichment of various species from solutions and for their separation.^{1,2} However to date, membrane separations have seldom been used in analytical chemistry, particularly in inorganic analysis.

The three main membrane types for liquid separation are reverse osmosis, ultrafiltration (UF), and microfiltration. The membranes are usually made of polycarbonate, cellulose (esters), polyamide, polysulfone, etc. Use of inert membranes enables separation to be achieved that cannot be successfully conducted by other means. The possibility of preconcentration and separation of different species without separating agents is another advantage of some membrane techniques.

Membrane separation is most selective, if soluble reagents are added. Hydrophilic polymers with complexing groups, termed polychelatogens,

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Polymer Sample	<i>v v</i>			$\begin{matrix} [\eta]^{\rm b} \\ ({\rm dL}~{\rm g}^{-1}) \end{matrix}$	
1	0.020		95	0.312	
2	_	0.020	37	0.138	
3	0.015	0.005	82	0.395	
4	0.012	0.008	64	0.315	
5	0.010	0.010	65	0.311	
6	0.008	0.012	46	0.395	
7	0.005	0.015	57	0.320	
8	0.020		93	0.349	
9	0.015	0.005	97	0.325	
10	0.012	0.008	87	0.363	
11	0.010	0.010	78	0.350	
12	0.008	0.012	76	0.367	
13	0.005	0.015	55	0.392	

Table I Experimental Conditions and Results of the Copolymerization of Am and DMAm with VPyr in DMF at 60°C for 6 h

^a Samples 1, 2, and 8 correspond to poly(Am), poly(VPyr), and poly(DMAm), respectively, and samples 9 to 13 correspond to DMAm : VPyr.

^b Determined in distilled water at 25°C.

have been tested to show the applicability of the method to the separation of various metal cations and anionic species for analytical and technological purposes, such as the treatment of wastewater, groundwater, and seawater; separation of radionuclides and measurement of binding properties of metal ions.^{3–18} The ligands and their metal complexes can be retained by an ultrafilter, whereas the free metal ions pass through the filtration membrane. This method is called liquidphase polymer-based retention.^{11,19,20} A series of polymers have been designed and investigated with respect to the analytical determination of metal ions. Among these, phosphorous-containing polymers based on poly(vinyl alcohol) were applied to separate actinides.¹³ Poly(ethyleneimine)-based reagents have been used in many studies as complexing ligands, as well as a versatile source of chelating derivatives for removing metal ions from aqueous solutions by means of complexation-UF.^{11,15-18,21} Thus, poly(ethyleneimine)-methyl phosphonic acid was tested as a macromolecular reagent to the isolation and analysis of plutonium in contaminated waters from the area near to the Chernobyl nuclear power plant.²² Reagents were also used that had typical acidic chelating groups, 8-quinolinol and iminodiacetic groups, neutral thiourea groups, and trimethylammonium-based anion-exchange groups.²³ Introduction of strong chelating groups into the basic polymer backbone results in a more effective retention of metals. Poly(acrylic acid) and copolymers with acrylamides (Am's)^{24,25} and *N*-maleyl glycine,²⁶ as well mixtures of two polychelatogens²⁷ were investigated in their ability to bind di- and trivalent cations. The advantages of this method are the high selectivity of the separation, owing to the use of a selective binding, and the low energy requirements involved in UF. In this article, the synthesis of poly(Am-co-1-vinyl-2-pyrrolidone)s and poly(*N*,*N*'-dimethylacrylamide-co-

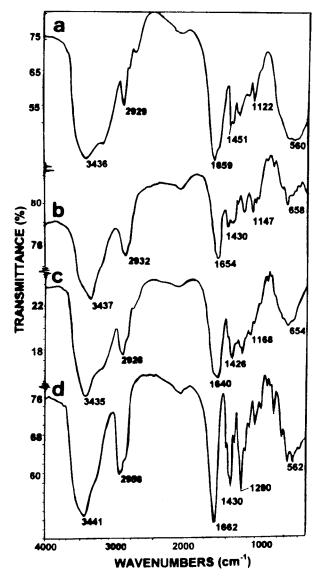


Figure 1 FTIR spectra (a) poly(DMAm), (b) poly(D-MAm-co-VPyr) sample **11**, (c) poly(Am-co-VPyr), sample **5**, and (d) poly(VPyr).

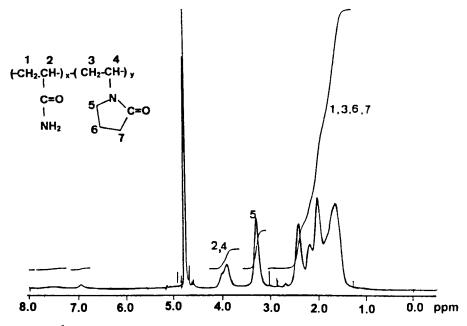


Figure 2 1 H NMR spectrum of poly(Am-co-VPyr), sample 5 (250 MHz, D₂O, 29°C, trimethylsilane).

1-vinyl-2-pyrrolidone)s with varied feed mole ratio, and their metal ion binding ability investigated at different pH and filtration factor, is reported.

EXPERIMENTAL

Reagents

Am (Merck), N,N'-dimethylacrylamide (DMAm; Fluka) were used as received. 1-Vinyl-2-pyrrolidone (VPyr; Merck) was purified by distillation under nitrogen. 2,2'-Azobis-isobutyronitrile (AIBN; Merck) was recrystallized from methanol. Metal salt standard solutions of 1000 ppm (Merck) were used to prepare the metal ion solutions.

Synthesis of the Polychelatogens

Five copolymers of Am with VPyr and DMAm with VPyr were synthesized keeping constant the total amount of mol (0.020) in dimethylformamide (DMF) (10 mL), with AIBN as the initiator (0.1 mol %) at 60°C for 6 h. The copolymers were precipitated in diethyl ether (100 mL) and purified from low-molecular mass compounds by membrane filtration (exclusion rate of 1000 g mol⁻¹). Products were dried under vacuum until constant weight. Copolymers are white solids

and soluble in water. Three homopolymers poly(Am), poly(DMAm), and poly(VPyr)—were also synthesized by radical polymerization under the same conditions of the copolymers, in DMF (10 mL) with AIBN (0.1 mol %) at 60°C for 6 h.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Magna Nicolet 550 spectrophotom-

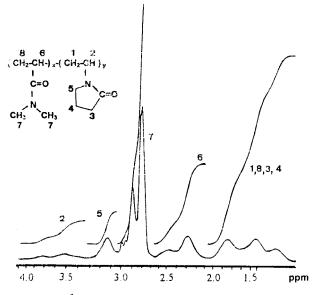


Figure 3 ¹H NMR spectrum of poly(DMAm-*co*-VPyr), sample **11** (250 MHz, D₂O, 29°C, trimethylsilane).

Polymer Sample ^a	Feed Monomer Ratio Am or DMAm : VPyr	Copolymer Composition Am or DMAm : VPyr
3	3.00:1.00	4.71:1.00
4	1.50:1.00	3.00:1.00
5	1.00:1.00	2.60:1.00
6	0.66:1.00	2.34:1.00
7	0.33:1.00	1.54:1.00
9	3.00:1.00	3.73:1.00
10	1.50:1.00	2.50:1.00
11	1.00:1.00	1.80:1.00
12	0.66:1.00	1.81:1.00
13	0.33:1.00	0.92:1.00

Table IICopolymer Composition of poly(Am-co-VPyr)sand poly(DMAm-co-VPyr)sDetermined from ¹H NMR Spectra

 $^{\rm a}$ Copolymers **3–7** and **9–13** correspond to poly (Am-co-VPyr)s and poly (DMAm-co-VPyr)s, respectively.

eter. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AC 250 spectrometer. The viscosities of the polychelatogens were determined with an Ostwald viscometer at 25.0 \pm 0.1°C using water as solvent. The viscosimetric molecular weight, M_v for the homopolymers [poly(Am), poly(DMAm), and poly(VPyr)] were 41,500, 8,400, and 15,800, respectively.

Metal ion concentrations were measured by atomic absorption spectroscopy on a Perkin– Elmer 3100 spectrometer. pH was controlled on a pH meter (H. Jürgens & Co.) Dynamic thermo-

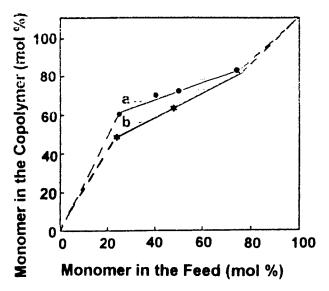


Figure 4 Relationship of the feed monomer ratio and copolymer composition for the copolymerizations of Am (a) and DMAm (b), with VPyr (60°C, 6 h, DMF).

gravimetric analyses were conducted in a Polymer Laboratories STA -625 thermobalance.

Metal Ion Binding Capability Study of the Polychelatogens by the Liquid-Phase Polymer-Based Retention Technique

For the determination of the metal complex binding capacity, polymer (2 wt %) solutions were adjusted to the corresponding pH by the addition of a small amount of diluted nitric acid or sodium hydroxide. Solutions of polymer and metal nitrate or chloride (20 mg L^{-1}) were placed into the membrane filtration cell. The pH of the cell and the reservoir solutions were adjusted at the same pH. Total volume in the cell was kept constant (20 mL). The system was pressurized under nitrogen (300 kPa) during membrane filtration. Filtration runs were conducted over membranes with an exclusion limit rating of $10,000 \text{ g mol}^{-1}$. Filtration fractions (Z = 1-10) were collected, and metal ion concentrations in the filtrate were determined by atomic absorption spectroscopy. Metal ions studied were Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), and Cr(III).

RESULTS AND DISCUSSION

Synthesis and Characterization of the Polychelatogens

The 10 copolymerizations were conducted in DMF at different feed mole ratios, whereas keeping constant the total mole number of comonomers

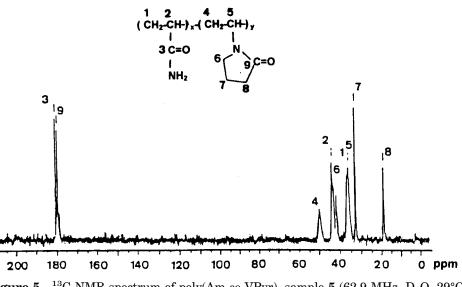
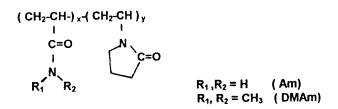


Figure 5 13 C NMR spectrum of poly(Am-co-VPyr), sample 5 (62.9 MHz, D₂O, 29°C, trimethylsilane).

(0.02) (Table I). All copolymers are white solids and water-soluble.



Yields varied between 46 and 97%, the last value corresponding to copolymer **9**, which has a higher

content of DMAm (0.015 mol) in the feed. The poly(DMAm-*co*-VPyr)s show higher yields than the poly(Am-*co*-VPyr)s due to the electronic effect of the methyl groups. As the content of VPyr increased in the feed, the yield decreased due to the homopropagation reaction of VPyr is not favored. The other comonomer is the responsible of the higher yield and viscosity of the copolymers. The intrinsic viscosity ranged between 0.315 and 0.395 (dL g⁻¹).

All the FTIR spectra show basically the same absorption bands corroborating the presence of

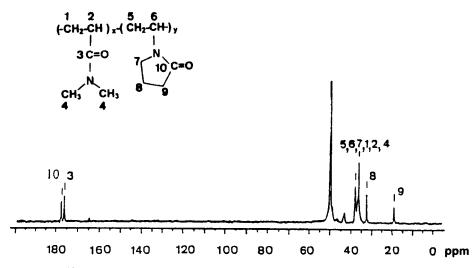


Figure 6 ¹³C NMR spectrum of poly(DMAm-co-VPyr), sample **11** (62.9 MHz, D₂O, 29°C, trimethylsilane).

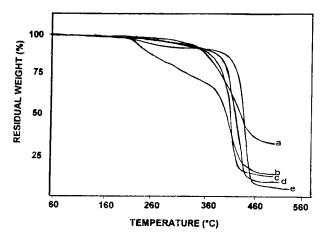


Figure 7 Thermal behavior of the polymers: (a) poly(Am), (b) poly(Am-*co*-VPyr) sample **5**, (c) poly(D-MAm), (d) poly(DMAm-*co*-VPyr) sample **11**, and (e) poly(Pyr) (heating rate: 10°C min⁻¹) under nitrogen.

 $\nu_{\rm C=O}$ (amide) at 1662 cm⁻¹ with varied intensity. Other important absorption signals correspond to $\nu_{\rm C=H}$ at 2958 cm⁻¹ and between 1400 and 1450 cm⁻¹ that was associated with $\nu_{\rm C=N}$ (amide) (Fig. 1).

The ¹H NMR spectra show the disappearance of olefinic protons, as well as the signals corresponding to the characteristic protons coming from the both monomers (Figs. 2 and 3). For all copolymers, the intensity of each peak varied according to the copolymer composition. The signal at 4.9 ppm corresponded to D_2O (99.9%).

Copolymer composition was calculated from these spectra by comparison of the integration area of one proton belonging to each comonomer. Thus, for VPyr, the signals placed between 3.2 and 3.4 ppm attributed to methylene protons placed in position 5 of the ring and the methyl proton signal placed between 2.9 and 3.1 ppm (DMAm) were used.

Results are summarized in Table II. These values are in agreement with those determined by elemental analysis.

The copolymer composition depends on the feed monomer ratio giving statistical copolymers incorporating in higher amounts the Am and DMAm monomers respect to VPyr due to the higher reactivity of the radical species of the former (Fig. 4). Copolymers with a copolymer composition closer to an alternating one was observed to those with the lowest content of the Am and DMAm in the feed, copolymer 7 (1.54 : 1.00) and copolymer 13 (0.92 : 1.00), respectively.

The copolymer structure was also confirmed by 13 C NMR (Figs. 5 and 6). At low fields (~ 180 ppm) appear two signals assigned to both carbonyl carbons coming from the Am or DMAm and VPyr moieties. Signals corresponding to methyl, methylene, and methylene carbons are placed between 20 and 49 ppm.

The primary thermograms of all polymers have a typical sigmoidal shape (Fig. 7). All the copolymers degrade in one step except of copolymer **3**, which is the richest in Am. Copolymers are stable

			$E_a \; (\text{kJ mol}^{-1})$		
Polymer Sample	TDT _{10%} (K)	TDT _{50%} (K)	1st Decomposition	2nd Decomposition	
1	506.2	671.2	66.7	59.4	
2	599.2	701.5	158.4		
3	528.2	688.2	43.9	44.8	
4	598.2	697.2	70.1		
5	648.2	а	61.2		
6	631.2	699.7	75.2		
7	598.2	703.7	82.2		
8	681.2	730.2	203.2		
9	603.9	681.2	142.1		
10	568.4	683.2	120.4		
11	633.4	688.2	146.4		
12	618.3	678.5	148.4		
13	653.3	689.2	129.9	_	

Table III Thermal Decomposition (TDT) and Activation Energy of the Polychelatogens

 a It decomposes over 773 K. $TDT_{10\%}$ and $TDT_{50\%}$ correspond to the temperatures at which 10 and 50% of weight is lost.

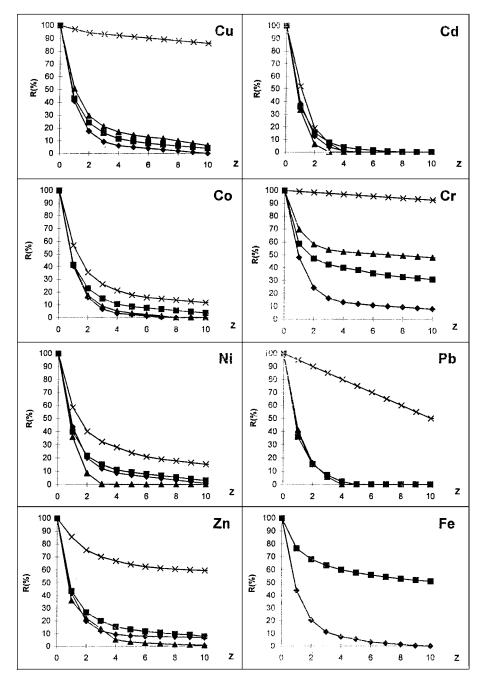


Figure 8 Retention of metal ions by poly(Am-*co*-VPyr) sample **5** (2 wt %) at pH 1 (\blacklozenge), pH 3 (**I**), pH 5 (\blacktriangle), and pH 7 (\times) in the presence of 0.15*M* NaNO₃ as a function of the ratio filtrate volume-to-cell solution volume (*Z*).

up to 200°C, and then they lose weight by evolution of CO_2 and NH_3 , depending on copolymer composition. By increasing the content of VPyr, thermal stability increased due to a higher rigidity of the heterocyclic ring.

Thermal stability and activation energy in the degradation process (E_a) was determined accord-

ing to Wen and Lin.²⁸ It increased for the copolymers with a higher content of the more stable unit, VPyr (Table III).

Polychelatogens-Metal Ion Interactions Study

The metal ion complexing ability of Am^{25} and VPyr moieties to form metal ions complexes in

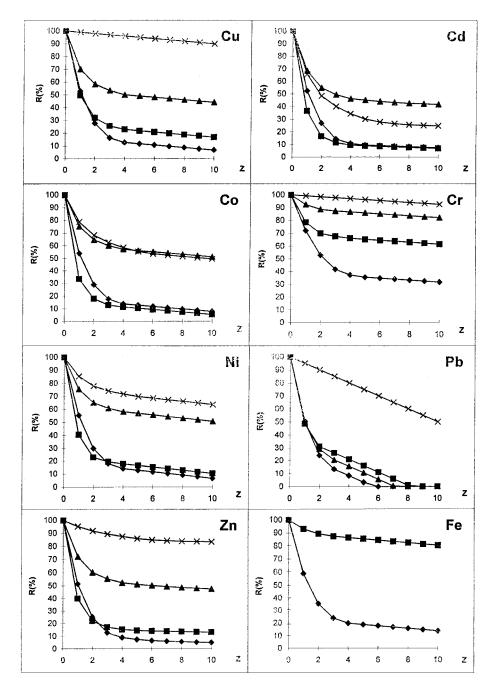


Figure 9 Retention of metal ions by poly(DMAm-*co*-VPyr), sample **11** (2 wt %) at pH 1 (\blacklozenge), pH 3 (\blacksquare), pH 5 (\blacktriangle), and pH 7 (\times) in the presence of 0.15*M* NaNO₃ as a function of the ratio of filtrate volume-to-cell solution volume (*Z*).

aqueous solutions are well known, particularly the last one that is highly selective for gold.⁸

The homopolymers [poly(Am), poly(DMAm), and poly(VPyr)] were also synthesized by radical polymerization to compare their polychelatogenic properties with those of the copolymers poly(Am*co*-VPyr) and poly(DMAm-*co*-VPyr). Copolymers with an equimolar mixture of both monomer units in the feed were selected to study the ability properties to bind metal ions.

A typical retention profile shows the metal ion retention (R) versus filtration factor (Z). Z is defined as the ratio of volume of the filtrate (V_f) versus the volume in the cell (V_0) , and R is the

Polychelatogen	Cu(II)	Co(II)	Ni(II)	Zn(II)	Pb(II)	Cd(II)	Cr(III)
Poly(Am)	90	8	5	37	50	3	93
Poly(DMAm)	61	21	35	15	42	13	93
Poly(VPyr)	37	13	15	34	50	49	89
Poly(Am-co-VPyr)	86	12	15	59	50	0	89
Poly(DMAm-co-VPyr)	90	50	64	83	50	25	93

Table IV Retention % of Different Metal Ions by the Five Polychelatogens for Z = 10 and pH 7

fraction per unit of metal ions remaining in the cell. R is normally expressed in %. At high Z values, it is frequently found that a remaining residue of metal ions cannot be eluted by filtration at the same pH.

Figure 8 and 9 show the retention profiles of poly(Am-*co*-VPyr) and poly(DMAm-*co*-VPyr), respectively, for different metal ions as a function of pH. In general, the metal ion retention increased as the pH increased, with the highest values corresponding to pH 7.0.

Poly(Am-co-VPyr) shows the highest affinity for Cu(II) and Cr(III) at pH 7.0 remaining above 86% and 93% at Z = 10, respectively. Complexes with Cd(II), Co(II), and Ni(II) were almost completely destroyed at the same pH and Z. On the other hand, Pb(II) and Zn(II) show an intermediate behavior staying 50% and 60% at Z = 10, respectively. Fe(III) was significantly retained at pH 3 and was not investigated at higher pH due to the presence of colloidal gels. At pH 3, only the trivalent cations, Fe(III) and Cr(III), were retained in 50%. Accordingly, a selective separation of these metal ions depending on the pH should be possible.

In general, at a lower pH, the poly(DMAm-co-VPyr) showed a higher affinity to the different metal ions than poly(Am-co-VPyr), particularly at pH 3 for Ni(II), Cu(II), and Zn(II). At pH 7, a similar capability to bind metal ions Pb(II), Cu(II), and Cr(III) is shown. In general, it may be due to the cooperative interactions between the ligand groups with the corresponding metal ions, which would be favored at pH 7.

Table IV shows the retention ability of the five polychelatogens for the seven metal ions at pH 7 and Z = 10. All the polymers show a high affinity for Cr(III) and Cu(II), except poly(VPyr) (37%). The Am moiety increased the retention capacity for Zn(II), and the tertiary amide groups of poly-(DMAm) increased the retention of Zn(II) at pH 7 and Z = 10. Thus, the retention values (in mg L^{-1} g of polymer) for the five polychelatogens are the following: poly(Am), 18.3; poly(DMAm), 7.65; poly(VPyr), 16.7; poly(Am-co-VPyr), 29.7; poly(D-MAm-co-VPyr), 41.6.

CONCLUSIONS

The radical polymerization of VPyr with Am and DMAm gave statistical copolymers whose copolymer composition depended on the feed molar ratio. Thermal stability depended on the copolymer composition, and copolymers were very stable up to 200°C.

The affinity of the polychelatogens to metal ions depended on the pH and filtration factor Z. The tertiary amide groups of the DMAm moiety interacted more strongly than the amide group of Am moiety with the metal ions, particularly at pH 3. Poly(DMAm-co-VPyr) also formed stable complexes at pH 7 with Cr(III) and Zn(II) and with Fe(III) at pH 3. At pH 1 and pH 3, Pb(II) and Cd(II) were not retained.

It would be possible to separate Cu(II) and Cr(III) at pH 7 and Z = 10 from an aqueous solution containing metal ions, such as Ni(II), Co(II), Cd(II), and Zn(II).

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