

Poly(*N,N'*-dimethylacrylamide-*co*-acrylic acid): Synthesis, Characterization, and Application for the Removal and Separation of Inorganic Ions in Aqueous Solution

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ABSTRACT: The synthesis of poly(*N,N'*-dimethylacrylamide-*co*-acrylic acid) under different feed molar ratios was carried out by radical polymerization. Both homopolymers were also synthesized to compare the metal ion binding abilities. All polymers were water-soluble and were characterized by FTIR, ¹H-NMR, ¹³C-NMR, and TGA. The metal complexing properties for the metals Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), Hg(II), Cr(III), and Fe(III) in the aqueous phase were investigated using the liquid-phase polymer-based retention (LPR) method. The metal ion interactions with the hydrophilic polymer were determined as a function of pH and the filtration factor. According to the interaction pattern obtained, the metal ions form the most stable complexes with the copolymer poly(*N,N'*-dimethylacrylamide-*co*-acrylic acid) within the pH range 5–7. Hg(II) was not retained at all the pH ranges investigated. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 93–100, 1998

INTRODUCTION

Polymeric supports with complexing groups are widely investigated and applied for the metal recovery from a dilute solution, such as industrial fluids and waste water. Apart from insoluble, crosslinked polymer reagents containing ligands, e.g., amino, ammonium, phosphoric acid, carboxylic acid, and amidoxime,^{1–8} water-soluble functional polymers have been investigated for the removal of metals in the homogeneous phase.^{5,9–17} These water-soluble chelating polymers, termed polychelators, have been prepared by function-

alizing various basic polymers. By using these polychelators in combination with membrane filtration, higher efficiency and selectivity of membrane separations can be achieved. This method, based on the retention of certain metal ions by a membrane which separates low molar mass compounds from macromolecular complexes of the ions, is called liquid-phase polymer-based retention (LPR).^{18–20}

It is well known that acrylic acid and acrylamide moieties show a complexation ability for metal ions, particularly the former as carboxylic or carboxylate ligand groups. According to that, we had an interest in investigating the complexation properties of poly(acrylic acid-*co*-*N,N'*-dimethylacrylamide) and both homopolymers with a number of metal ions in a homogeneous aqueous phase. The retention as a parameter of interaction was studied in dependence on the filtrate volume and pH.

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Table I Experimental Conditions and Results of the Copolymerization of AA with DMAM and Homopolymerization of AA and DMAM in DMF and 60°C for 6 h

Polymer Sample (No.)	Feed Monomer (mol) DMAM : AA		Yield (%)	$[\eta]$ (dL g ⁻¹)
1	0.020	—	77	0.3487
2	0.015	0.005	66	0.4655
3	0.012	0.008	73	0.3948
4	0.010	0.010	76	0.3177
5	0.008	0.012	66	0.2581
6	0.005	0.015	69	0.2146
7	—	0.020	73	0.2112

EXPERIMENTAL

Reagents

Acrylic acid (AA; Merck) was purified by distillation, and *N,N'*-dimethylacrylamide (DMAM; Fluka) was used as received. 2,2'-Azobis-isobu-

tyronitrile (AIBN; Merck) was recrystallized from methanol. The metal salts (nitrate or chloride) were commercially available and of analytical reagent grade.

Synthesis of Polychelatogenic Polymers

Five monomer ratios of AA and DMAM were used while keeping the total amount constant (0.02) in DMF (12 mL), with AIBN (0.1 mol %) as the initiator, at 60°C for 6 h. The copolymers were precipitated in diethyl ether and purified from low molecular mass compounds by membrane filtration (exclusion rate of 1000 g mol⁻¹). The products were dried under a vacuum up to a constant mass. Both homopolymers, PAA and PAAM, were accordingly synthesized by radical polymerization with 0.1 mol % AIBN and 12 mL DMF at 60°C.

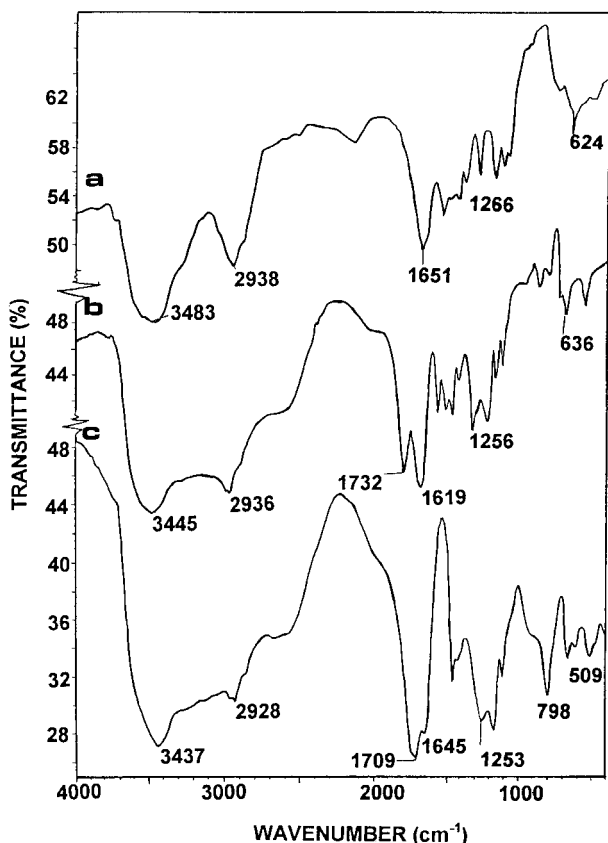


Figure 1 FTIR spectrum of (a) poly(DMAM), (b) poly(DMAM-co-AA), sample 4, and (c) poly(AA).

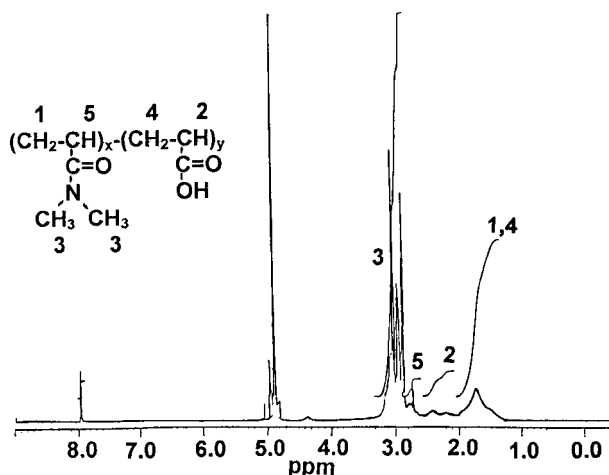


Figure 2 ¹H-NMR spectrum of poly(DMAM-co-AA), sample 4 (250 MHz, D₂O, 29°C, TMS).

Table II Copolymer Compositions of the Different poly(DMAm-co-AA)s Determined from $^1\text{H-NMR}$ Spectra

Polymer Sample (No.)	Feed Monomer Mol Ratio DMAm : AA	Copolymer Composition DMAm : AA
2	1.00 : 0.33	1.00 : 0.03
3	1.00 : 0.66	1.00 : 0.19
4	1.00 : 1.00	1.00 : 0.47
5	1.00 : 1.50	1.00 : 0.64
6	1.00 : 3.00	1.00 : 1.44

Procedure to Investigate the Metal Ion Binding Properties

The membrane filtration [Filtron, 3000 Daltons, poly(ether sulfone)] was carried out in a system as described previously.^{9,11,18-20} For the determination of the complex binding ability, a 2 wt % aqueous solution of each polymer was prepared and adjusted to the corresponding pH by addition of diluted HNO_3 or NaOH . The solutions of polymer and metal nitrates or chlorides (20 mg L^{-1}) were placed into the filtration cell. The total volume in the cell was kept constant at 20 mL. The system was pressurized by nitrogen gas and kept constant at 300 kPa during membrane filtration. A membrane with an exclusion rate of 3000 Daltons was used. The filtration fraction ($Z = 1-10$)

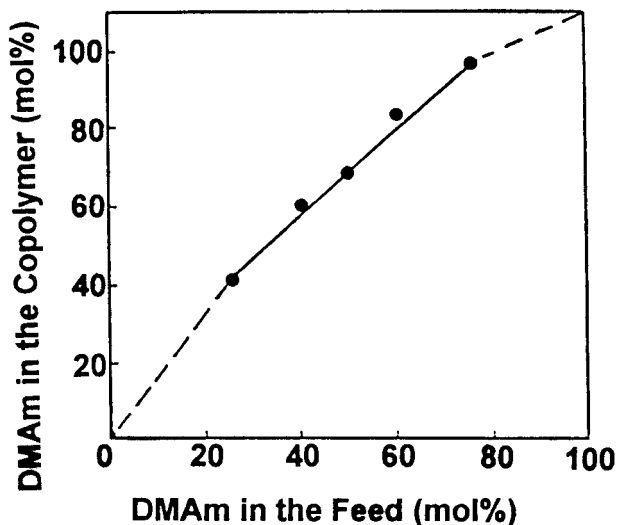


Figure 3 Relationship of the feed monomer ratio and copolymer composition for the copolymerization of DMAm and AA (60°C , 6 h, DMF).

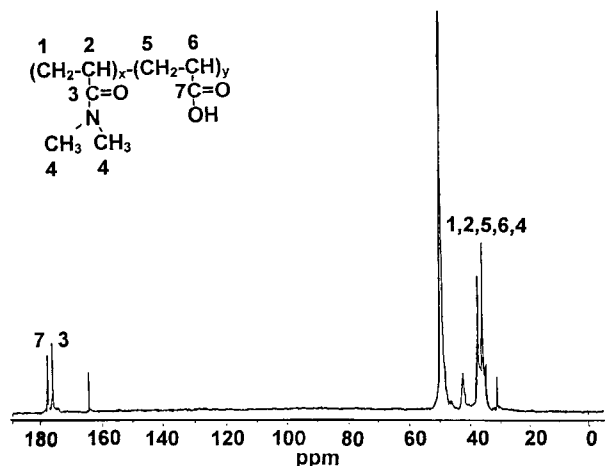


Figure 4 $^{13}\text{C-NMR}$ spectrum of poly(DMAm-co-AA), sample 4 (62.9 MHz, MeOD, 29°C , TMS).

was recollected and the concentration of metal ions in the filtrate were determined by atomic absorption spectroscopy. Z is defined as the ratio of the volume in the filtrate (V_f) and the volume of the cell solution (V_0).

Characterization

FTIR spectra were recorded on a Magna Nicolet 550 spectrophotometer. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Bruker AC 250 spectrometer. The viscosities of the polymers were determined with an Ostwald viscometer at $30.0 \pm 0.1^\circ\text{C}$ using water as a solvent. Dynamic ther-

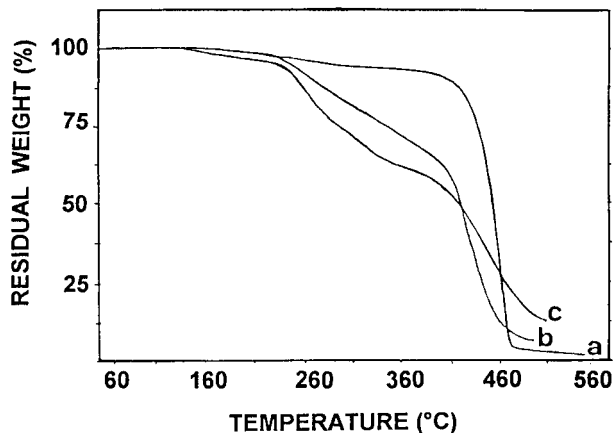


Figure 5 Thermal behavior of the polymers: (a) DMAm, (b) poly(DMAm-co-AA), sample 4; (c) poly(AA) (heating rate: $10^\circ\text{C min}^{-1}$ under N_2).

Table III Thermal Decomposition Temperature (TDT) and Activation Energy of Polymers

Polymer Sample (No.)	Copolymer Composition DMAm : AA	TDT _{10%} ^a (K)	TDT _{50%} ^b (K)	<i>E_a</i> (kJ mol ⁻¹)	
				1st Decomposition	2nd Decomposition
1	—	681.15	730.15	203.27	—
2	1.00 : 0.03	558.35	710.15	46.23	86.57
3	1.00 : 0.19	543.15	696.15	57.34	62.95
4	1.00 : 0.47	538.35	694.15	14.55	15.70
5	1.00 : 0.64	538.35	694.15	10.50	14.64
6	1.00 : 1.44	536.35	690.15	16.88	11.42
7	—	523.35	681.78	16.39	6.31

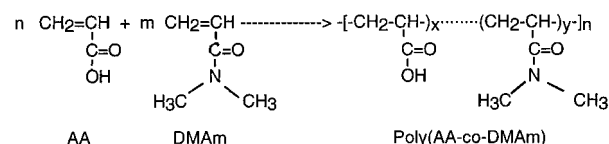
^{a,b} Temperatures that occur at 10 and 50% of weight loss, respectively.

mogravimetric analyses were carried out in a Polymer Laboratories STA-625 thermobalance. Samples (1–3 mg) were placed in the Pt sample holder, and the thermal degradation measurements were carried out between 25 and 500°C at a 10°C min⁻¹ heating rate under N₂.

RESULTS AND DISCUSSION

Synthesis and Characterization

The five copolymerizations were carried out in DMF at different feed compositions, while keeping constant the total amount of comonomers (0.02 mol) (see Table I):



All the copolymers are white solids and water-soluble. The yield ranged between 66 and 76%, the last value corresponding to a 1 : 1 feed ratio. The intrinsic viscosity decreases as the DMAm content decreases in the copolymer composition ranging between 0.4655 and 0.2146 (dL g⁻¹).

The FTIR spectrum of polymer 4 is shown in Figure 1. All the copolymer spectra show the presence of $\nu\text{C}=\text{O}$ (tertiary amide) at 1619.5 cm⁻¹ with variable intensity. Other important absorption signals correspond to νOH at 3445.8 cm⁻¹ and $\nu\text{C}-\text{H}$ at 2935.8 cm⁻¹. The 250 MHz ¹H-

NMR spectrum shows the disappearance of olefinic protons as well as all the signals corresponding to the protons coming from both monomers (see Fig. 2). For all copolymers, the intensity of each peak varied according to the copolymer composition. The signal at 4.9 ppm corresponds to D₂O (99.9%).

The copolymer composition was calculated from these spectra by comparison of the integration area of 1 H belonging to DMAm with the other one belonging to AA. Thus, the signals between 2.0 and 2.6 ppm were employed. The results are summarized in Table II. Nevertheless, the integration areas are small, and the copolymer composition values are in agreement with those determined from the elemental analysis (C, H, N). The copolymer composition depends on the feed monomer ratio giving statistical copolymers. The DMAm radical shows a higher tendency to homopropagate than to copolymerize (see Fig. 3). Due to the high conversion, it was not possible to determine the copolymerization parameters r_1 and r_2 either by the Fineman–Ross or by the Kelen–Tüdös methods.

The copolymer structure was confirmed also by ¹³C-NMR spectroscopy (see Fig. 4). The signals attributed to methyl, methylene, and methyne carbons coming from both monomers are placed between 30 and 48 ppm. At low field (177–180 ppm), both carbonyl carbons are absorbed. The signal at the lower field was assigned to carbonyl moieties from carboxylic acid.

The primary thermograms of all polymers have a typical sigmoidal shape. All the copoly-

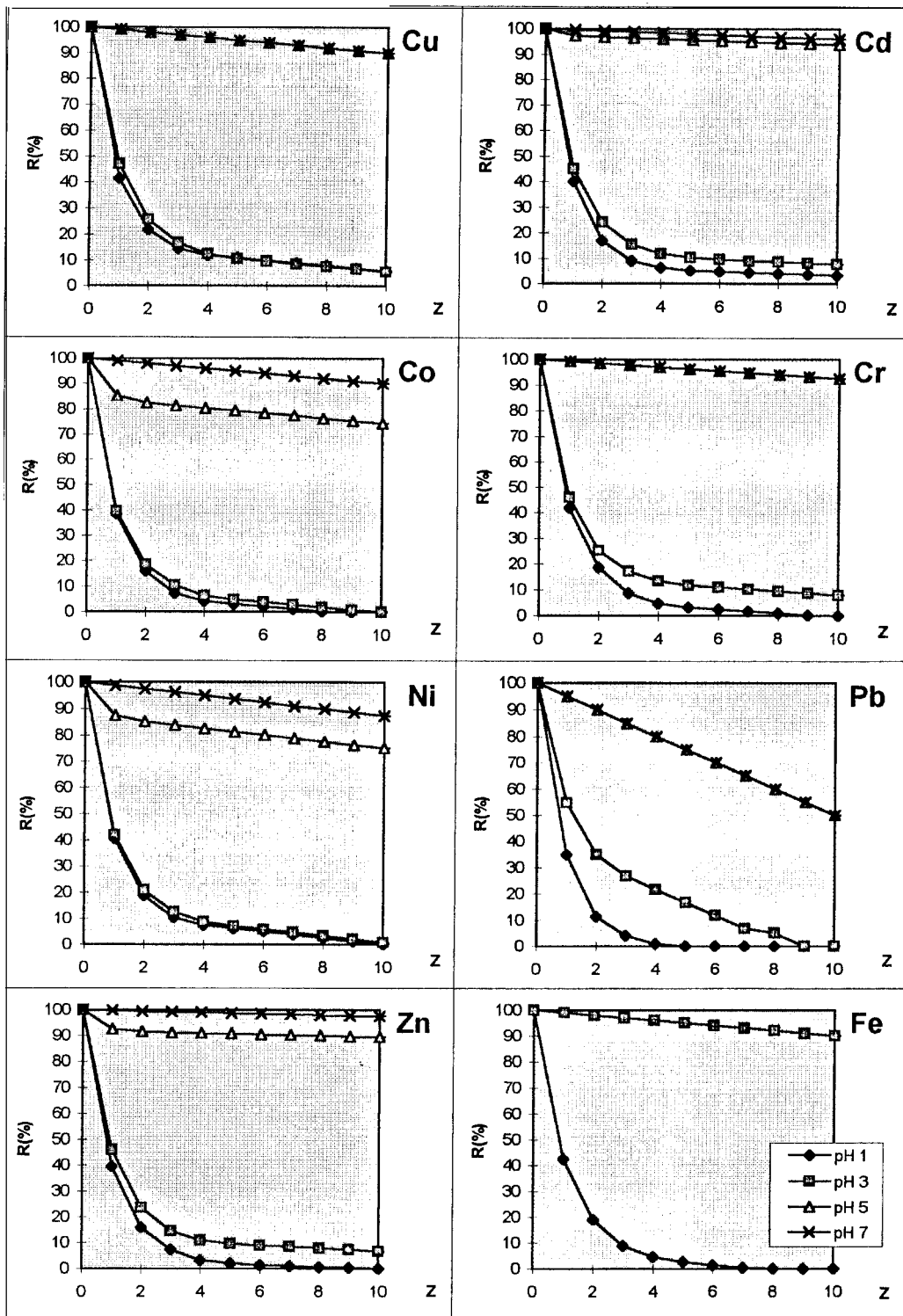


Figure 6 Retention of metal ions by an aqueous solution of 2 wt % poly(DMAm-co-AA), sample 4, as a function of the ratio of filtrate volume to cell solution volume (Z) at different pH.

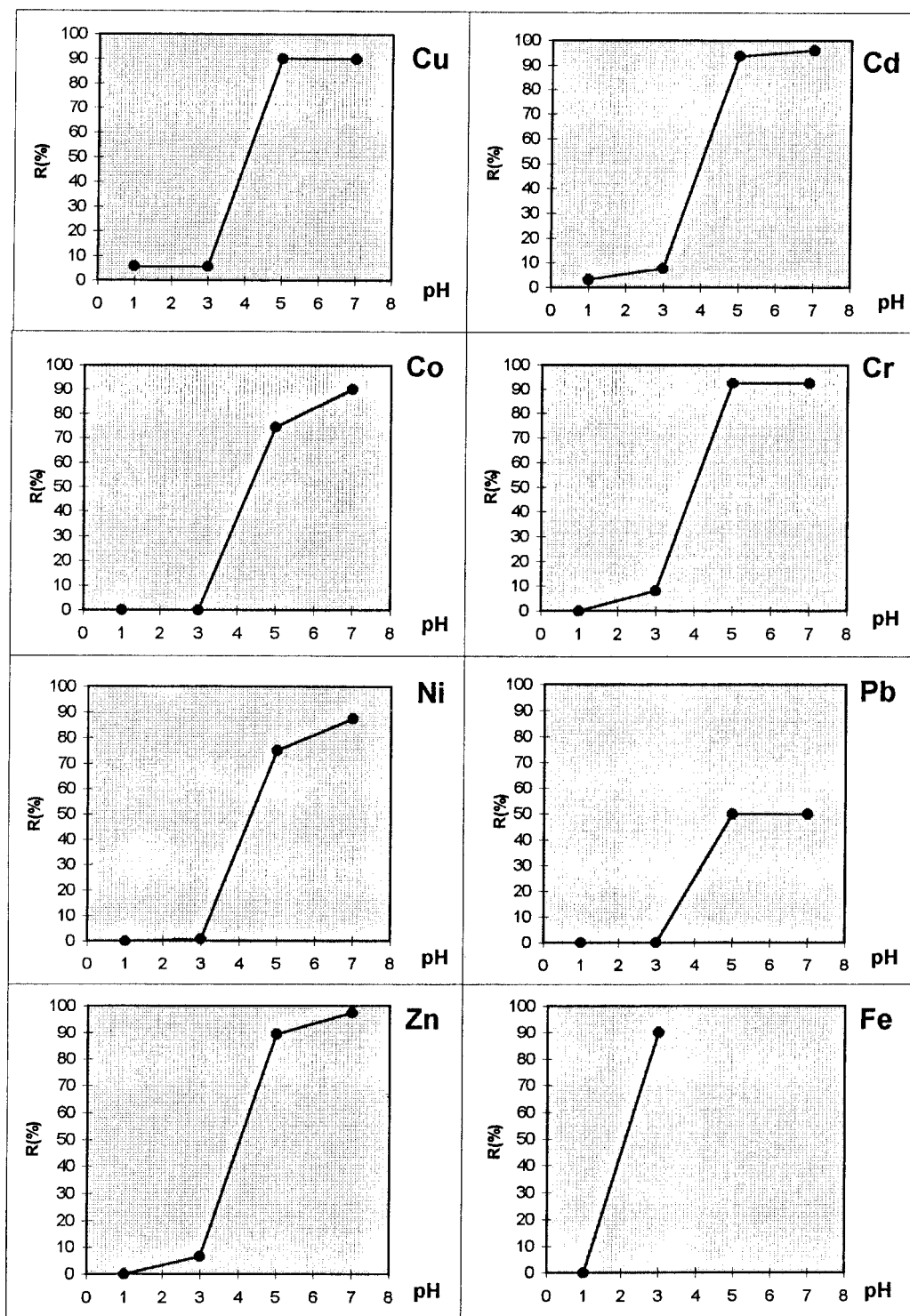


Figure 7 Effect of the pH at $Z = 10$ on the retention of metal in an aqueous solution of 2 wt % of poly(DMAM-co-AA), sample 4.

mers as well as poly(AA) degrade in two steps (see Fig. 5). The thermal stability and the activation energy involved in the degradation pro-

cess (E_a) determined according to Wen and Lin²¹ increase as the content of the more stable moiety, DMAM, increases (see Table III). The

Table IV Retention (%) of the Seven Metal Ions by the Three Polymers Based on DMAM and AA for $Z = 10$ at pH 7.0

Polymer	Metal Ion						
	Cu(II)	Co(II)	Ni(II)	Cd(II)	Cr(III)	Zn(II)	Pb(II)
Poly(DMAM)	61	21	35	13	93	15	42
Poly(AA)	71	75	77	75	71	69	50
Poly(DMAM-co-AA)	90	90	88	97	93	97	50

most probable products of thermal degradation are CO_2 and NH_3 .

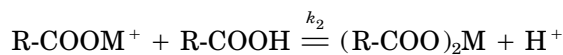
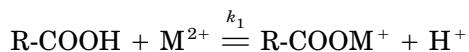
Complexation Properties

The complexing properties of water-soluble poly(DMAM-co-AA), sample 4, poly(AA), and poly(DMAM) for several metal ions were investigated using the LPR method.^{18–20} The complexation abilities are documented in the retention profiles which are plots of the retention R vs. the filtration factor Z . Z is defined as the ratio of the volume of the filtrate (V_f) and the volume of the cell solution (V_0). The retention of metal ions in the cell solution by a polymeric reagent can be conveniently calculated as follows:

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

where C_r is the metal 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. Typical retention profiles are shown in Figures 6 and 7. In general, only a slight complexation with the hydrophilic polymer takes place for all metals at pH 1 and 3 except for Fe(III) at pH 3. That allows the separation of Fe(III) from the other metals. The complexation capability of poly(DMAM-co-AA) and poly(AA) increases as the pH increases, with a sharp change of the complexation behavior at pH 3, particularly for Cu(II), Zn(II), Cd(II), Cu(II), Co(II), Ni(II), and Cr(III). At pH 5, most of the carboxylic groups exist as carboxylate groups, and the tertiary amide, as unprotonated groups.

Assuming that the carboxylic acid moiety interacts stronger than does the tertiary amide moiety, each divalent metal ion such as the Cu(II) ion interacts with one, two, or four carboxyls:



The products of the composition 2 : 1 are presumably formed. This may be achieved either by interaction with two carboxyls of the same polymer chain (intramolecular interaction) or by a different one (intermolecular interaction).²² At pH 7 and $Z = 10$, poly(DMAM-co-AA) forms stronger metal complexes than do both homopolymers, poly(DMAM) and poly(AA), except for Cr(III), which was strongly complexed with poly(DMAM) (92.5%). In general, it may be due to the cooperative interactions between both ligand groups with the corresponding metal ions, which would be favored at pH 7.0 where the groups are basically free amide and carboxylate groups.²³ The values for Cu(II), Co(II), Ni(II), Cd(II), and Zn(II) were higher: 87% (see Table IV). Hg(II) was not complexed at all the pH investigated. This may be attributed to the higher ion radius and different electronegativity.

CONCLUSIONS

The radical copolymerization of DMAM with AA gave statistical copolymers whose copolymer composition depended on the feed molar ratio. The thermal stability of the copolymer was higher than that of poly(AA) but lower than that of poly(DMAM).

The complexation ability of the hydrophilic polymers depended on the pH and on the filtration factor. Poly(DMAM) forms stable and selectively complexes with Fe(III) at pH 3. The copolymeric and the carboxylic acid moieties interacted more strongly with the metal ions than did the tertiary amide moiety, particularly at pH 5 and 7.

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REFERENCES

1. P. M. Berkel, W. L. Driessen, J. Reedijk, D. C. Sherrington, and A. Zitsmanis, *React. Funct. Polym.*, **27**, 15 (1995).
2. Y. Ito and T. Saegusa, *J. Macromol. Sci. Chem. A*, **13**, 523 (1979).
3. G. V. Myasoedova and S. B. Savrin, *CRC Crit. Rev. Anal. Chem.*, **17**, 1 (1986).
4. B. L. Rivas, in *The Polymeric Material Encyclopedia: Synthesis, Properties and Applications*, J. C. Salamone, Ed., CRC Press, Boca Raton, FL, 1996.
5. B. L. Rivas and K. E. Geckeler, *Adv. Polym. Sci.*, **102**, 171 (1992).
6. B. L. Rivas, H. A. Maturana, R. E. Catalán, and I. M. Peric, *J. Appl. Polym. Sci.*, **38**, 801 (1989).
7. B. L. Rivas, H. A. Maturana, X. Ocampo, and I. M. Peric, *J. Appl. Polym. Sci.*, **58**, 2201 (1995).
8. B. L. Rivas, E. Pereira, and P. Reyes, *Bol. Soc. Chil. Quím.*, **40**, 441 (1995).
9. K. E. Geckeler, G. Lange, H. Eberhardt, and E. Bayer, *Pure Appl. Chem.*, **52**, 1883 (1980).
10. E. Bayer, B. Ya. Spivakov, and K. Geckeler, *Polym. Bull. (Berl.)*, **13**, 307 (1985).
11. K. E. Geckeler, E. Bayer, B. Ya. Spivakov, V. M. Shkinev, and G. A. Vorobeva, *Anal. Chim. Acta*, **189**, 285 (1986).
12. K. E. Geckeler, E. Bayer, V. M. Shkinev, and B. Ya. Spivakov, *Naturwissenschaften*, **75**, 198 (1988).
13. B. Ya. Spivakov, V. M. Shkinev, V. I. Golovanov, E. Bayer, and K. E. Geckeler, *Macromol. Theory Simul.*, **5**, 357 (1996).
14. K. E. Geckeler, R. Zhou, A. Fink, and B. L. Rivas, *J. Appl. Polym. Sci.*, **60**, 2191 (1996).
15. G. del C. Pizarro, B. L. Rivas, and K. E. Geckeler, *Polym. Bull. (Berl.)*, **37**, 525 (1996).
16. K. E. Geckeler, R. Zhou, and B. L. Rivas, *Angew. Makromol. Chem.*, **197**, 107 (1992).
17. K. E. Geckeler, B. L. Rivas, and R. Zhov, *Angew. Makromol. Chem.*, **193**, 195 (1993).
18. B. Ya. Spivakov, K. E. Geckeler, and E. Bayer, *Nature (Lond.)*, **315**, 313 (1985).
19. K. E. Geckeler, V. M. Shkinev, and B. Ya. Spivakov, *Sep. Purif. Methods*, **17**, 105 (1988).
20. B. Ya. Spivakov, V. M. Shkinev, and K. E. Geckeler, *Pure Appl. Chem.*, **66**, 631 (1994).
21. W. Y. Wen and J. W. Lin, *J. Appl. Polym. Sci.*, **22**, 2285 (1978).
22. A. O. Pomogailo and D. Wöhrle, in *Macromolecule–Metal Complexes*, F. Ciardelli, E. Tsuchida, and D. Wöhrle, Eds., Springer-Verlag, Berlin, 1989.
23. B. L. Rivas, S. A. Pooley, M. Soto, and K. E. Geckeler, *J. Polym. Sci. Part A Polym. Chem.*, **35**, 2461 (1997).