# Poly(acrylic acid-*co*-vinylsulfonic acid): Synthesis, Characterization, and Properties as Polychelatogen

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**ABSTRACT:** The synthesis of the water-soluble poly-(acrylic acid-*co*-vinylsulfonic acid) at different feed monomer ratios, while maintaining constant the total number of mol, was carried out by radical polymerization. The copolymers were characterized by FTIR and $^1$H-NMR spectroscopies. The copolymer composition was determined by its sulfur content and by potentiometric titration. The metal ion binding properties for Ni(II) and Cu(II) in the aqueous phase were studied using the liquid-phase polymer-based retention (LPR) technique for two values of ionic strength. For comparison, the retention properties of both homopolymers were included. The complexing ability of the polymer was determined by the relative amount of carboxylic acid groups. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1698–1704, 2003

**Key words:** water-soluble polymers; copolymerization; metal ions; ultrafiltration membranes; polychelatogens

## INTRODUCTION

Water-soluble polymeric supports with complexing and exchange groups are widely studied for the recovery of metal ions from dilute solutions.[1–5] These chelating polymers, termed polychelatogens, were prepared by functionalizing various basic polymers.

Geckeler et al.[6] developed the liquid-phase polymer-based retention (LPR) technique. This method uses solutions of polychelatogens in combination with a filtration membrane, which separates low molecular mass compounds from macromolecular–metal ion complexes. With this technique selective separations of metal ions can be achieved. When solutions of metal ion mixtures are put in contact with the polychelatogen solution, a profile for the retention of the different metal ions during filtration by polychelatogen can be obtained. It is assumed that the only retention mechanism corresponds to the exclusion size.[7]

The LPR technique has important technological applications.[8] It is used in quantitative analysis,[9,10] thus explaining the growing interest to investigate polymers with a higher efficiency and selectivity to remove metal ions.[4,11–15] Different relevant structural characteristics of the polychelatogens have been studied: the nature of the functional groups,[4,11–13] incorporation of spacer groups between the main chain and functional groups, and copolymers that combine different functional groups.[14,15]

Carboxylic and sulfonic acid groups are among the most studied functional groups. The interaction between poly(carboxylic acids) [poly(acrylic acid) (PAA) and poly(methacrylic acid)] and several divalent cations has been basically studied by potentiometric[16–18] and spectroscopic techniques.[19,20] There is strong evidence that the carboxylic acids, as carboxylate groups, coordinate with metal ions. Polymers containing sulfonic acids, as poly(vinylsulfonic acid) (PVSA), do not act as ligands, but the functional group–metal ion interaction is only of the electrostatic type. This was also demonstrated previously by application of the cyclic voltammetric technique.[21]

We recently published[22] a study about the interaction between metal ions with a polymer poly-(methacrylic acid-*co*-2-acrylamido-2-methyl-1-pronanosulfonic acid), which combines carboxylic and sulfonic acid groups in its structure. The metal ion retention properties of the copolymer showed a synergic effect with respect to both homopolymers.

The aim of this study was to further elucidate the nature of the polymer–metal ion interaction. Therefore, poly(acrylic acid-*co*-vinylsulfonic acid) [P(AA-*co*-VSA)] was synthesized where both functional groups are bound directly to the main chain. The metal ion retention properties for Ni(II) and Cu(II) were investigated through the LPR technique.
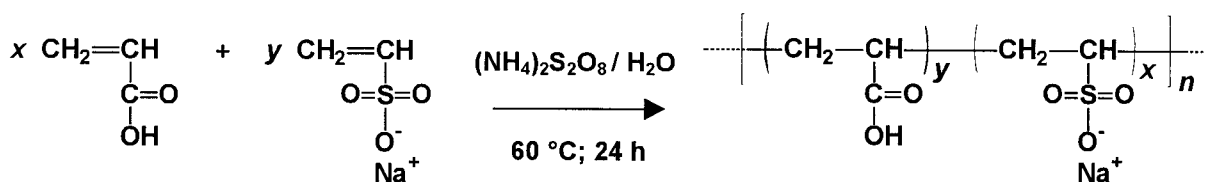
## EXPERIMENTAL

### Materials

Acrylic acid (AA; Merck, Darmstadt, Germany) was purified by distillation under $N_2$. Vinylsulfonic acid

**Scheme 1**

(VSA; Aldrich, Milwaukee, WI) was used as an aqueous solution, 25% w/w, containing 100 ppm of inhibitor MEHQ. Ammonium peroxydisulfate (APS; Merck) was used as received.

The commercial polymers poly(acrylic acid) (PAA) and poly(vinylsulfonic acid) (PVSA), both from Aldrich, were purified and fractionated by ultrafiltration membranes. According to Aldrich, PAA has a weight-average molecular weight of 250,000; therefore the fraction between 100,000 and 1,000,000 Da was studied. The fraction of PVSA between 10,000 and 50,000 Da was studied.

The salts $NaNO_3$, $Cu(NO_3)_2$, and $Ni(NO_3)_2$ (p.a., Merck) were used as received. The solutions were prepared with bidistilled water with conductivity $< 1$ $\mu$S.

## Copolymer synthesis

The copolymer synthesis is shown in **Scheme 1** and the reaction conditions are described as follows. The copolymerization between AA and VSA was carried out in an aqueous medium using APS (5% mol) as initiator. Five feed monomer ratios were studied, keeping constant the total amount of monomers (0.080 mol in 35 mL of solution). The reaction was kept at 60°C under $N_2$ for 24 h. The copolymers were purified and fractionated using an ultrafiltration membrane with an exclusion limit of molecular weight 3000 and 10,000 g mol$^{-1}$. The concentrated copolymer solutions were lyophilized, yielding a white solid, which was dried under vacuum at 40°C until constant weight. Yield: 80–99%.

$^1$H-NMR (D$_2$O): $\delta$ = 1.5–2.6 (CH$_2$); 2.6–2.9 (CH—COOH); 2.6–4.2 (CH—SO$_3$H). FTIR (KBr): 2500–3500 cm$^{-1}$ (st COO—H); 1725 cm$^{-1}$ (st HOC=O); 1452 cm$^{-1}$ (st sym CH$_2$); 1040 cm$^{-1}$ (st sym SO$_2$).

## Characterization

The FTIR (KBr) and $^1$H-NMR (250 MHz, D$_2$O 99.95, 300 K, concentration: 20–40 mg/mL) spectra were recorded with a Magna Nicolet 550 spectrophotometer (Nicolet Analytical Instruments, Madison, WI) and a Bruker AC 250 multinucleus spectrometer (Bruker Instruments, Billerica, MA), respectively. The copolymer composition was determined through two independent methods: determination of the sulfur content (Method 1) and acid–base potentiometric titration (Method 2). The content of sulfur was determined by the Schöniger method.[23] The potentiometric titration was carried out as follows: an amount equivalent to 1.25 meq was dissolved in 30 mL of twice-distilled water. This solution was kept in contact for 2 h with 50 mL of acidified Dowex 50W resin. The solution was filtered and diluted up to 250.0 mL (5 meq/L); 25.0 mL was then titrated with NaOH 0.01063*N*.

The pH was measured with Sensor of pH SenTix 41, WTW, and Inolab pH Level 1, WTW. The compositions (in mol) of the copolymers obtained with both methods are summarized in Table I.

## Properties as polychelatogen

For the determination of the complex binding ability, 50 mL of a 5.0 meq/L aqueous solution of the polychelatogens were prepared and adjusted to pH 5.0 by the addition of HNO$_3$ or NaOH. The metal nitrate (0.10 m*M*) and the polymer solution were placed into the filtration cell. The experiments were carried out in

**TABLE I**
**Experimental Conditions and Results of Copolymerization**

| Sample no. | Feed monomer ratio (VSA : AA) | Yield (%) | | S (%) | Copolymer composition (VSA : AA) | |
|---|---|---|---|---|---|---|
| | | >10 kDa | 3–10 kDa | | Method 1 | Method 2 |
| 1 | 0.5 : 1.0 | 95.5 | — | 8.38 | 0.29 : 1.00 | 0.31 : 1.00 |
| 2 | 1.0 : 1.0 | 92.9 | — | 14.36 | 0.77 : 1.00 | 0.78 : 1.00 |
| 3 | 2.0 : 1.0 | 79.0 | — | 17.34 | 1.32 : 1.00 | 1.50 : 1.00 |
| 4 | 4.0 : 1.0 | 87.3 | — | 19.24 | 2.00 : 1.00 | 1.85 : 1.00 |
| 5 | 9.0 : 1.0 | 45.7 | 46.4 | 20.67 | 2.91 : 1.00 | 2.78 : 1.00 |
| PVSA | 1.0 : / | 19.6 | 80.4 | 23.70 | — | — |

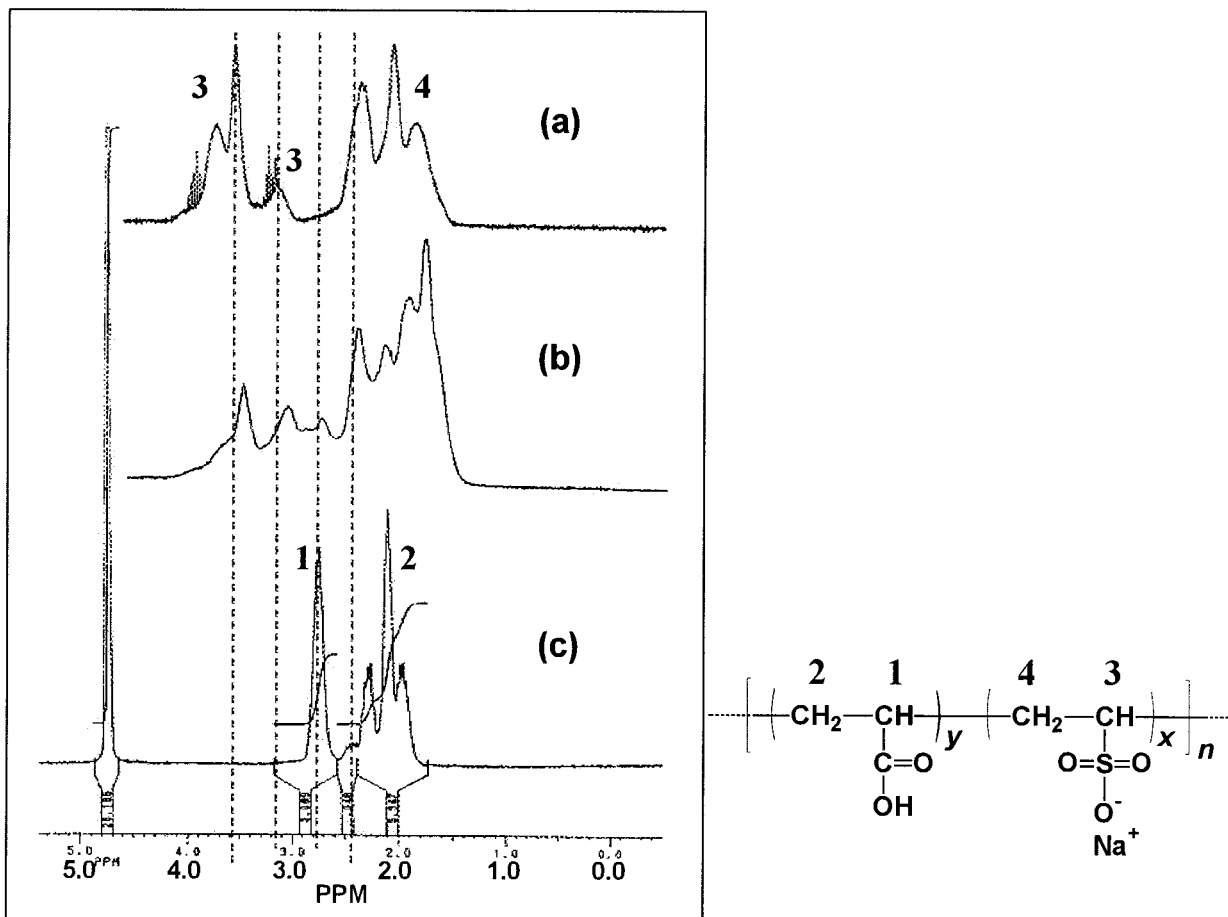**Figure 1**    $^1$H-NMR spectra of (a) PVSA, (b) P(AA-*co*-VSA) (sample 3), and (c) PAA.

the presence of $0.010M$ and with $0.10M$ $NaNO_3$ as external salt. The system was pressurized using nitrogen gas at a constant 300 kPa during membrane filtration. The filtration fractions ($F = 0.2$–7) were collected and the concentration of metal ions in the filtrate was determined by atomic absorption spectrometry. $F$ is defined as the ratio between the volume in the filtrate ($V_f$) and the volume of the cell solution ($V_0$). $V_0$ was kept constant during the experiment.

## RESULTS AND DISCUSSION

To study the effect of an intrinsic property of a polychelatogen—the presence of a strong and a weak acid group on at the same chain—on the metal ion retention capacity, copolymers of AA and VSA were synthesized by radical polymerization. Five feed mol ratios were used, keeping constant the total amount of monomers (see **Scheme 1**).

Table I shows the copolymerization yield as a function of the feed monomer ratio. As the content of VSA monomer unit increases, the yield above 10 kDa decreases. The FTIR spectra of the copolymers show the characteristic absorption bands at $1040 \ cm^{-1}$ (symmet-

ric stretching of $SO_2$) from VSA units, and at 1726 $cm^{-1}$ (stretching C=O) from AA units. A very good correlation was observed between the relative intensities and the copolymer compositions. Figure 1 shows the $^1$H-NMR spectra of one copolymer (sample 3). For comparison, the spectra of both homopolymers are included. The absorption signals correspond to all the expected ones, confirming that copolymerization occurred. For the copolymer, it was not possible to integrate the signals because of their overlapping. Hence, it was not possible to determine the copolymer composition from the $^1$H-NMR spectra.

The copolymer composition was determined by means of two independent methods: determination of the sulfur content (Method 1) and acid–base potentiometric titration (Method 2). The principle of the second method is that the titration curve of the copolymers should present two equivalent points. Table I shows the results for Method 1. Figure 2 shows the titration curves of two homopolymers and one copolymer (sample 2). The plots on the right show the first derivate of the corresponding titration curves. In the case of the homopolymers, the results are in agreement with those previously reported.[24,25] The titration
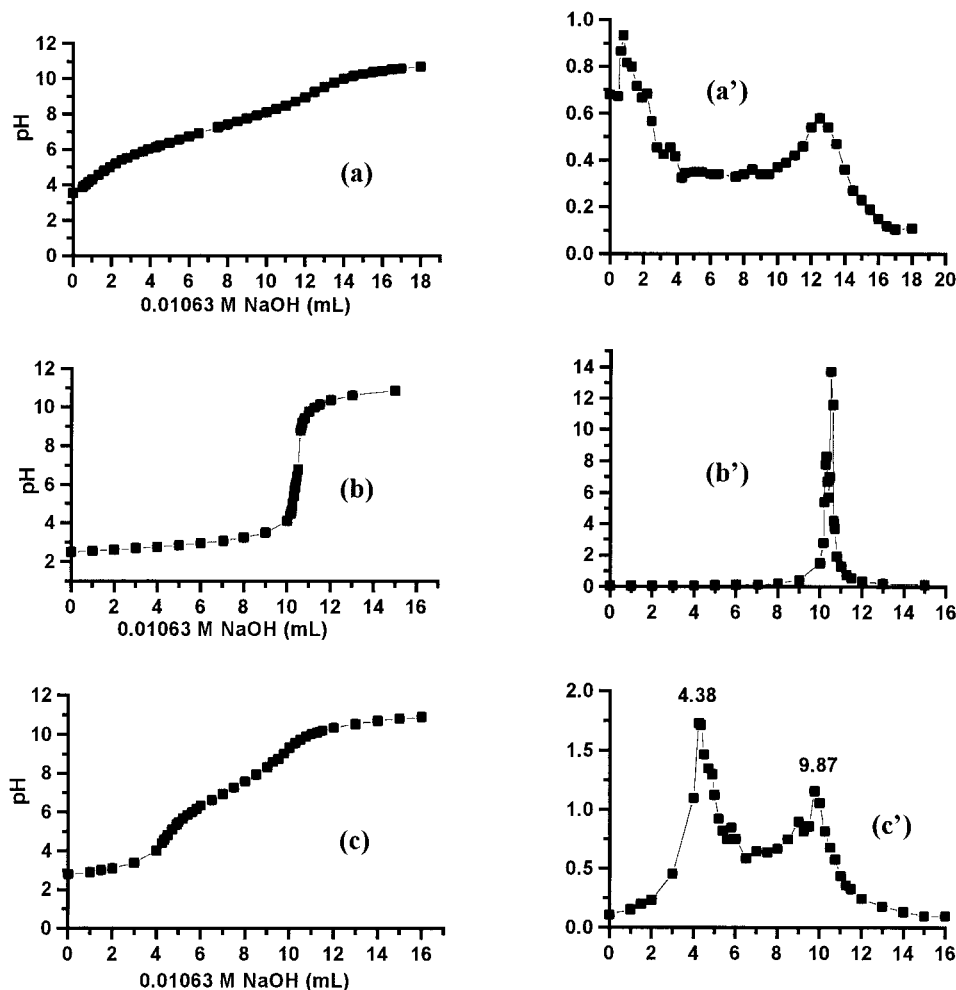
**Figure 2** Acid–base potentiometric titrations of polychelatogens: (a) PAA, (b) PVSA, (c) P(AA-*co*-VSA) (sample 2). First derivates: (a'), (b'), and (c').

of copolymers showed two equivalent points. The first equivalent point was attributed to the sulfonic acid group and the second to the carboxylic acid groups. The copolymer composition was determined according to the following expression:

$$(VSA/AA) = V_1/(V_2 - V_1)$$

where $V_1$ and $V_2$ correspond to the necessary NaOH volume to achieve the first and second equivalent points. The results are summarized in Table I.

Two statistical tools were applied to see whether the results obtained by the two methods differed: paired *t*-test and use of regression lines for comparing analytical methods.[26] The former was applied to calculate the differences between the pairs of values. These differences have a mean $d = -0.014$ and a standard deviation $s_d = 0.137$. Substituting in equation $t = d \cdot n^{1/2}/s_d$, with $n = 5$, gives $t = -0.237$. The critical value is $t_4 = 2.78$ ($p = 0.05$). Because the calculated value of $|t|$ is less than this value, the following conclusion is reached: the methods do not give signifi-

cantly different results for the copolymer composition. Figure 3 shows the comparison of two analytical methods and the regression line calculated. Its intercept is $-0.086$, with upper and lower confidence limits of $-0.469$ and $+0.296$: this range includes the ideal value of zero. The slope of the graph is 1.070, with a 95% confidence interval of 0.842–1.298: again, this range includes the model value, in this case, 1.0. Therefore, this test leads to the same conclusion as the paired *t*-test.

Figure 4 shows the relationship between the feed monomer ratio and the copolymer composition. For all feed ratios, AA showed a higher degree of incorporation than that of VSA. This was explained by the effect of the side substituents. The electronegativity of the sulfonic group is higher than that of the carboxylic group; it decreases the density of $\pi$-electrons on the sulfonic acid with respect to that of the carboxylic acid. Hence, the reactivity of the former is lower than the second. Moreover, because of the same inductive effect, the reactivity of the carboxylic acid radical AA· is lower than that of the VSA·. Therefore, when the AA
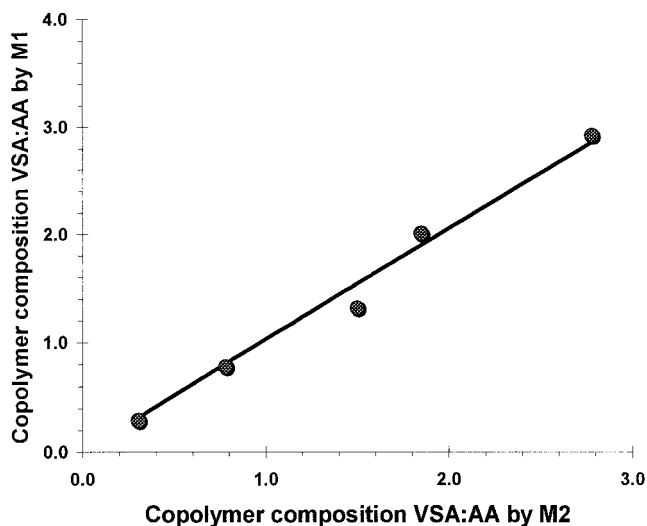
**Figure 3** Comparison of methods to determine the copolymer compositions.

is incorporated into the chain, the macroradical obtained does not have enough reactivity to attack the less reactive VSA.

The properties of polychelatogen were studied by the LPR technique. The retention profile gives the metal ion retained in the polychelatogen solution as a function of the filtration factor $F$. To compare the results, the amount of metal ion is expressed as the ratio (%) between the metal ion mass retained in the cell at a given $F$ and the initial metal ion mass.

Regarding the experimental conditions detailed in the experimental section, it is necessary to mention the following: (1) The criterion to define the polymer concentration was to minimize the interactions between the chains that favored the intrapolymer polychelates[27]; (2) the ratio between the functional group concentration and the metal ion concentration was 25 : 1; hence, it is possible to assume that the interaction of Ni(II) ions with the chains will not be affected by the presence of the Cu(II) ions; (3) the pH 5 was adjusted to make compatible the high degree of ionization with the nonformation of the insoluble hydroxides; (4) the effect of the ionic strength was studied with two concentrations of $NaNO_3$ for the washing solution. The $NaNO_3$ was selected with respect to NaCl to avoid the competition with the $Cl^-$ ions in the complexing reactions, especially for Cu(II) ions.

Figure 5 shows the retention profiles of Ni(II) and Cu(II) for the PAA, PVSA, and P(AA-*co*-VS). Sample 2 was selected because its copolymer composition is close to 1 : 1. The continuous line corresponds to the blank experiment (in the absence of polychelatogen). The ultrafiltration membrane contributes slightly to the metal ion retention value. At high ionic strength [see Fig. 5(a), (c)], for both Ni(II) and Cu(II), the polychelatogens show a low retention capacity. This can be

explained by the shielding effect of the single electrolyte (in excess) on the charge of the polyion. The retention profiles of PAA and P(AA-*co*-VSA) are practically the same. By decreasing the single electrolyte concentration, the behavior changes sharply [see Fig. 5(b), (d)]. The retention profiles are almost linear. For each metal ion, the retention profiles of the polycarboxylates (PAA and copolymers) are similar, differing from the profile corresponding to PVSA. For Cu(II), the net retention of the polymers containing carboxylate units is about 90% for $F = 5.5$ (see Fig. 6), indicating the complex formation. PVSA shows a similar retention for both metal ions, demonstrating that the interaction would be electrostatic. The sulfonate group–Ni(II) interactions are stronger than the carboxylate group–Ni(II) interactions. It is not possible to give a definite explanation for this result. It could be that a hypothesis of the experimental design is not satisfied: the interaction between Ni(II) and the polycarboxylate may be affected by the presence of Cu(II).

Finally, no synergic effect for the copolymer was observed. This behavior would be determined, basically, by the relative amount of the carboxylate groups in the chain.

## CONCLUSIONS

The copolymers synthesized by radical polymerization are soluble in water. The acrylic acid monomer unit is characterized by a higher degree of incorporation. The copolymer composition values determined by sulfur content and potentiometric titration are in agreement.

The metal ion retention for Cu(II) and Ni(II) studied by the LPR technique was strongly dependent on the ionic strength. At high ionic strength no important differences between the polychelatogenic properties
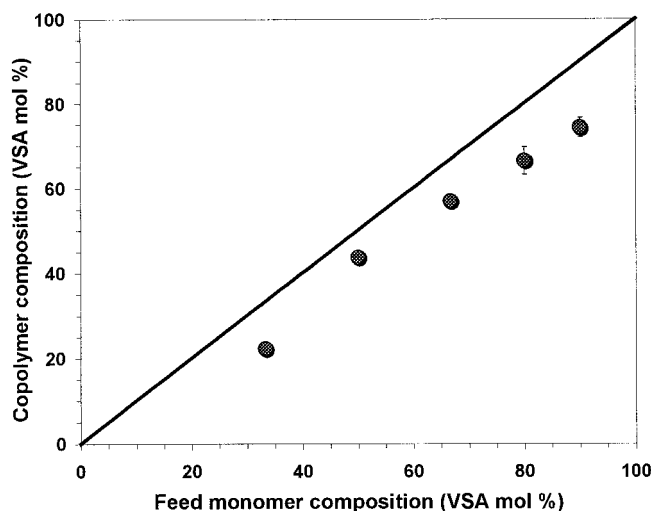


**Figure 4** Relationship between the copolymer composition of P(AA-*co*-VSA) and the feed monomer ratio.
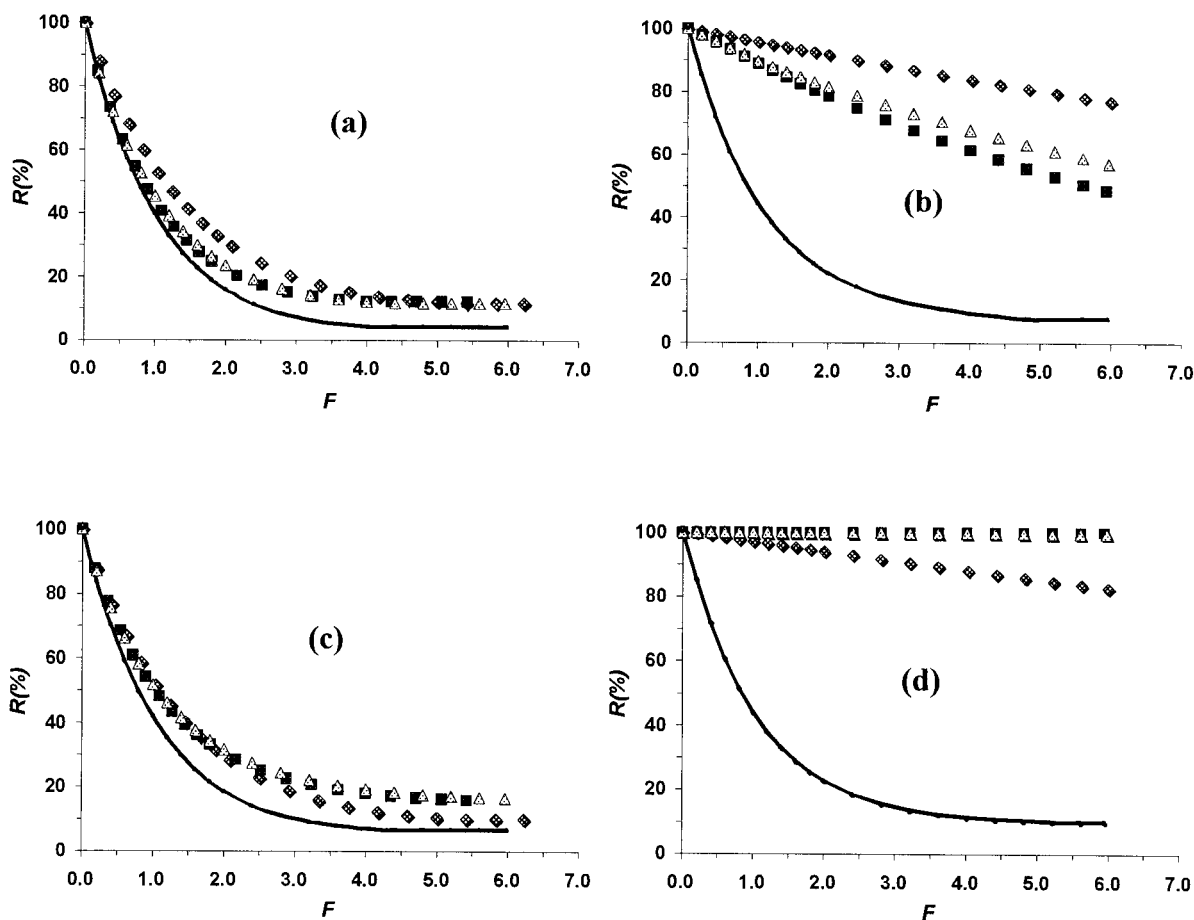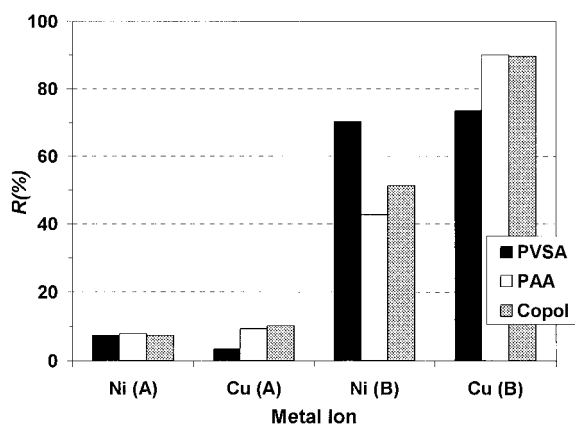
**Figure 5** Retention profiles of (a) Ni(II), 0.10*M* NaNO$_3$; (b) Ni(II), 0.010*M* NaNO$_3$; (c) Cu(II), 0.10*M* NaNO$_3$; (d) Cu(II), 0.010*M* NaNO$_3$ by the polymers PAA (■), PVS (◆), and P(AA-*co*-VSA), sample 2 (▲).

were observed as a result of the shielding of charges of the polyion caused by the excess of the single salt. The metal ion interaction between PVSA and the metal ions is basically electrostatic and the interactions between the carboxylate groups and the Cu(II) ions involve a complex formation.



**Figure 6** Comparison of the metal ion retention at different ionic strengths: (A) 0.10*M* NaNO$_3$; (B) 0.010*M* NaNO$_3$. *F* = 5.5.

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