

# Synthesis and Chelating Properties of Some Poly(amidoxime-hydroxamic acid) Resins Toward Some Trivalent Lanthanide Metal Ions

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**ABSTRACT:** The chelation properties of the addition-type polymers poly(amidoxime-hydroxamic acid) and poly(*N*-methyl amidoxime-*N*-methyl hydroxamic acid) toward some trivalent lanthanide metal ions [La(III), Nd(III), Sm(III), Gd(III), and Tb(III)] were studied by a batch equilibration technique as a function of contact time, pH, and

counterion. The effect of the crosslinker, divinylbenzene, was also studied. The selectivity and binding capacity of the resins toward various lanthanide metal ions are discussed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 691–696, 2005

**Key words:** copolymerization; crosslinking; resins; synthesis

## INTRODUCTION

Chelate-forming polymers have been studied extensively by many authors and research groups.<sup>1–24</sup> In addition, the role played by toxic heavy metals in the aquatic environment<sup>5–7</sup> has stimulated considerable activity and interest<sup>1–14</sup> in the development of metal chelating polymers, which have found widespread use in the separation and monitoring of trace heavy metal ions, including lanthanides, from aqueous solutions.<sup>1,2,12–17</sup> Moreover, interest in chelating polymers also stems from the need to separate precious metals from aqueous solutions.<sup>8–11</sup> Vernon<sup>22</sup> summarized the desirable properties of a chelating polymer, which include a high capacity, a high selectivity, fast kinetics of metal-ion uptake, and a high mechanical strength and durability.

A variety of methods are known for the preparation of hydroxamic acids;<sup>2,25–31</sup> perhaps the most common methods involve the acylation of an acid derivative, such as an ester or acid chloride, with hydroxylamine and its derivatives. The syntheses of poly(hydroxamic acid) ion-exchange resins have been achieved through the treatment of copoly(acrylamide-divinylbenzene) with hydroxylamine hydrochloride in the presence of KOH and from the reaction between acryl hydroxamic acid with divinylbenzene by a free-radical solution polymerization.<sup>32</sup> Poly(hydroxamic acid) resins have also prepared from crosslinked poly(methyl methac-

rylate) beads; this resin exhibited a high affinity toward Fe(III) and Pb(II) ions, and its capacity was pH dependent.<sup>33</sup> Recently, Haron et al.<sup>34</sup> synthesized and characterized a poly(*N*-methyl hydroxamic acid) resin from poly(*N*-methyl-divinylbenzene) beads and discovered that the resin was efficient in the separation of some rare earth ions in solution mixtures with HCl as the eluent at pH 2.

Several experimental and commercial oxime-containing polymers have been described in the literature.<sup>14,15,35–39</sup> The incorporation of oxime groups in chelate-forming polymers has been achieved through a variety of reaction schemes. Walsh et al.<sup>40</sup> achieved the incorporation of hydroxyoxime groups into a substituted phenylacrylate polymer via the Fries rearrangement. Recently, Coutinhom et al.<sup>41</sup> synthesized chelating resins with amidoxime groups through the suspension polymerization of acrylonitrile and divinylbenzene and the subsequent chemical modification of cyano groups by a reaction with hydroxylamine; they studied the effect of divinylbenzene and the level of dilution on the complexation capacity of the resin for copper ions.

In connection with our recent work on the chelating properties of chelate-forming polymers toward some divalent and trivalent metal ions,<sup>12–17</sup> we present in this article results pertaining to the sorption properties of polymers that had two kinds of chelating ligands, amidoxime and hydroxamic acids, toward some trivalent lanthanide metal ions [La(III), Nd(III), Sm(III), Gd(III), and Tb(III)] in aqueous solutions; these polymers were obtained by the copolymerization of acrylonitrile and ethylacrylate and a subsequent reaction with hydroxylamine.

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## EXPERIMENTAL

## Materials

Unless otherwise indicated, all chemicals were obtained from commercial sources and were used as received; acrylonitrile, 2,2,4-trimethyl pentane, gelatin, and sodium perchlorate (98%) were obtained from BDH Chemicals, Ltd. (Poole, England); benzoyl peroxide, and ethylacrylate were purchased from Fluka (Buchs, Switzerland); divinylbenzene was received from Merck (Darmstadt, Germany); hydroxylamine hydrochloride and *N*-methyl hydroxylamine hydrochloride were received from Aldrich (Milwaukee, WI) and from GCC Clwyd, England), respectively. The following lanthanide salts were also used as received without further purification:  $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  from Aldrich and  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  from K&K Laboratories, Inc. (Jamaica, NY).

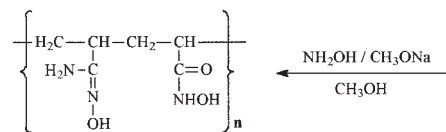
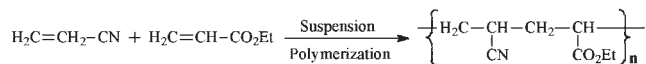
## Instrumentation and measurements

The IR spectra of the polymers and their monomers were recorded with the aid of a Nicolet Impact 400 (Madison, WI) Fourier transform infrared spectrophotometer from 400 to 4000  $\text{cm}^{-1}$ . KBr discs were used for all solid samples by the mixture about 1.0 mg of the sample with about 100 mg of KBr. Complexometric titrations were performed with a Metrohm 655 Dosimat titrator (Switzerland). Samples were shaken with a GFL-1083 shaker with a thermostated water bath maintained at 25°C. The water regain parameter ( $\alpha$ ;  $\text{gg}^{-1}$ ) of the polymers was determined with the procedure of Sugii et al.<sup>36</sup> as follows: samples of dry polymers were suspended in water and left for 2 and 24 h. The resins were centrifuged, weighed, dried at 80°C, and reweighed.  $\alpha$  was calculated with the following equation:

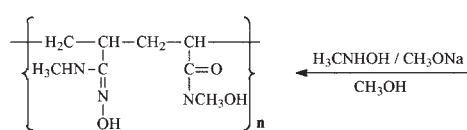
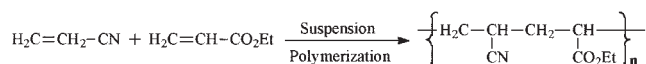
$$\alpha = \frac{\text{Mass of polymer-bound water (g)}}{\text{Mass of dry polymer (g)}}$$

Preparation of poly(acrylonitrile-*co*-ethylacrylate)

This copolymer was synthesized according to the following general procedure (Scheme 1).<sup>31</sup> A solution of 10.01 g of ethylacrylate (0.10 mol), 21.22 g of acrylonitrile (0.40 mol), 4 mol % divinylbenzene (0.02 mol, 2.60 g) as a crosslinker (with respect to both monomers), and 0.15 g of benzoyl peroxide in 50 mL of 2,2,4-trimethylpentane was poured slowly into a 1-L three-necked flask fitted with a reflux condenser, a thermometer, and a dropping funnel containing a solution of 25.0 g of sodium sulfate (0.176 mol), 4.0 g of calcium carbonate (0.04 mol), and 30 mL of a 2% gelatin solution in 300 mL of water. The mixture was



Polymer I (poly amidoxime-hydroxamic acid polymer)

Polymer II (poly *N*-methyl amidoxime-*N*-methyl hydroxamic acid polymer).

Scheme 1

heated at 70°C with stirring for 2.5 h and was then heated at 90°C for 3.5 h. The resulting copolymer was filtered and washed with a 1M hydrochloric acid solution, distilled water, and methanol. After Soxhlet extraction with acetone for 24 h, the solid copolymer was dried *in vacuo* at 40°C for 24 h.

## Preparation of the polymers

Poly(amidoxime-hydroxamic acid) (I), was synthesized by adding 15.16 g of sodium methoxide (0.28 mol), followed by 10 g of the copolymer, poly(acrylonitrile-*co*-ethylacrylate), to a solution of 20.85 g of hydroxylamine hydrochloride (0.30 mol) in 300 mL of methanol. The suspended solution was refluxed for 24 h with slow stirring. The resulting polymer was filtered and washed with methanol, a 1M hydrochloric acid solution, deionized water, and methanol. After Soxhlet extraction with acetone for 24 h, the polymer was dried *in vacuo* at 40°C for 24 h, crushed, and sieved through a mesh size of 35–60 (0.25–0.5 mm). The resulting solid polymer was white with a decomposition point greater than 220°C.

Poly(*N*-methylamidoxime-*N*-methylhydroxamic acids) (II and III)

II and III were synthesized according to the same general procedure, with 10.43 g of hydroxylamine hydrochloride (0.15 mol) and 12.53 g of *N*-methyl hy-

droxylamine hydrochloride (0.15 mol) for **II** and with 25.06 g of *N*-methyl hydroxylamine hydrochloride (0.30 mol) for **III**. **II** was pale yellow with a decomposition point greater than 240°C, and **III** was deep yellow with a decomposition point greater than 260°C.

#### Preparation of IV–VI

The same general procedure used for the synthesis of **I** was also used for the preparation of **IV–VI** by the addition of a certain amount of the crosslinker, divinylbenzene, to the reaction mixture. The following molar percentages of divinylbenzene, with respect to both monomers, were used: 12 (0.06 mol, 7.80 g), 16 (0.08 mol, 10.40 g), and 20 (0.10 mol, 13.0 g) for **IV**, **V**, and **VI**, respectively. The resulting solid polymers were off-white with a decomposition point greater than 230°C.

#### Sorption of metal ions on the polymers

A batch equilibrium method was used to study the metal chelation characteristics of the polymers for each metal ion. Duplicate experiments involving 0.10 g of dry, 35–60-mesh-size resin samples were suspended with 15.0 mL of acetate–acetic acid buffer solution at pH 7.0 and with a total ionic strength of 0.10M (with sodium perchlorate) for 2 h to equilibrate. To this mixture, 10.0 mL of metal-ion solution containing a total of 15.0 mg of metal ion was added. After it was shaken for a definite period of time at 25°C, the mixture was filtered, and the amount of metal ion remaining in the filtrate was determined by complexometric titration with a standard ethylenediaminetetraacetic acid (EDTA) solution and xylenol orange solution as the indicator.<sup>16</sup>

The extent of metal-ion uptake was studied under similar experimental conditions, where the contact time was varied from 0.25 to 24 h after the solution was equilibrated with distilled water. Similar experiments were also carried out in buffered solutions, in which the pH was varied between 4.0 and 7.5 for a fixed contact time of 6 h and an ionic strength of 0.1M. The effect of counterion on the metal-ion uptake of the resins was investigated by experiments with a fixed contact time of 6 h at 25°C and pH 7.0 with different counterions to adjust the ionic strength to 0.1 (0.02 buffer and 0.08 counterion).

#### Metal-ion desorption

Desorption experiments on trivalent lanthanide chelates of the polymers were performed by batch processes under continuous stirring. In these experiments, samples of lanthanide-chelated polymer were suspended in 20.0 mL of 3.0M HCl. After it was shaken for 6.0 h, the mixture was filtered and neutral-

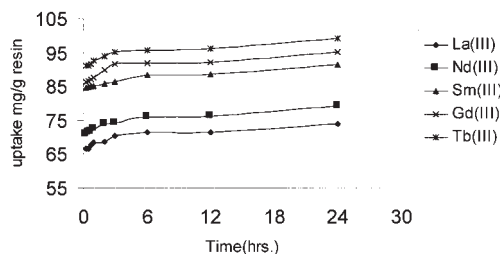


Figure 1 Ln(III) uptake by **I** as a function of contact time.

ized with a 3.0M NaOH solution, and the amount of metal ion eluted in the filtrate was determined by complexometric titration with standard EDTA solution and xylenol orange solution as the indicator.

## RESULTS AND DISCUSSION

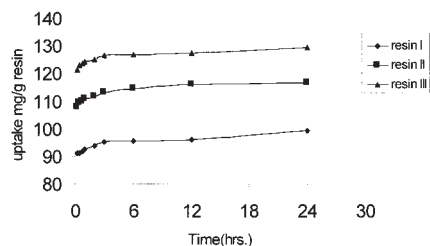
#### Characterization of the polymers and their chelates

The IR spectra of the polymers and their chelates were consistent with the structures assigned to them. The typical structures of these polymers are depicted in Scheme 1. The IR spectrum of poly(acrylonitrile-co-ethylacrylate) shows the characteristic nitrile stretching absorption band at 2240  $\text{cm}^{-1}$ . Absorption bands at about 3420  $\text{cm}^{-1}$ , found in the polymers and their metal chelates, were assigned to N–H stretching. The broad absorption bands observed at about 3235  $\text{cm}^{-1}$  and the broad bands at 1650  $\text{cm}^{-1}$  were attributed, respectively, to the –OH and C=N stretching of the oxim group. The strong bands in the 1580–1670- $\text{cm}^{-1}$  region were due to the hydroxamate stretching vibrations; these bands overlapped with the C=N bands.

$\alpha$  provides an indirect measurement of the hydrophilic character of the polymer.<sup>36</sup> A high  $\alpha$  may indicate the presence of microporous hydrophilic sites, which provide the water-transport channels required for the effective sorption of metal ions from aqueous solutions. The experimental values were 4.78, 6.06, 7.20, 4.49, 4.40, and 3.87  $\text{gg}^{-1}$  for **I**, **II**, **III**, **IV**, **V**, and **VI**, respectively.

#### Rate of metal-ion uptake as a function of contact time

The rate of metal-ion uptake by the polymers as a function of contact time was investigated by a batch equilibrium technique. Figure 1 shows a typical dependence of metal-ion uptake on contact time. The results indicate fast rates of equilibration; about 90% metal-ion uptake was achieved after 2–3 h, and uptake reached a steady state after 5–6 h. The metal-ion uptake capacities of the polymers toward the investigated lanthanide metal ions ( $\text{Ln}^{3+}$ ) increased with decreasing ionic radii of the lanthanide ions and followed the order  $\text{Tb}^{3+} > \text{Gd}^{3+} > \text{Sm}^{3+} > \text{Nd}^{3+}$

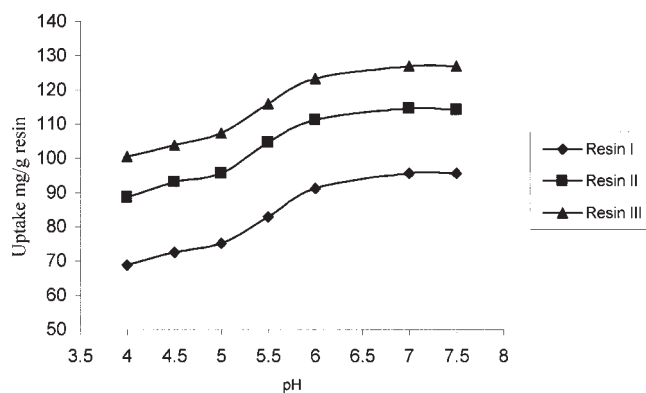


**Figure 2** Rate of Tb(III) uptake as a function of contact time for I–III.

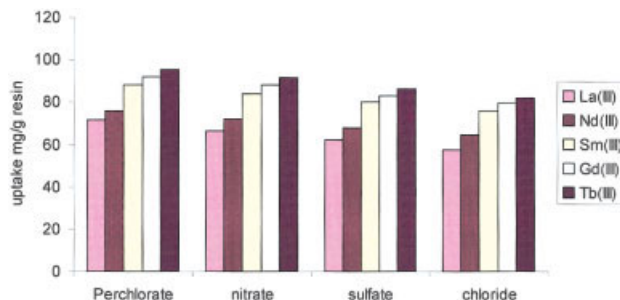
$> \text{La}^{3+}$ ; this was consistent with earlier investigations.<sup>7,36</sup> The results also show that the extent of metal-ion uptake by I–III followed the order  $\text{III} > \text{II} > \text{I}$ , as displayed in Figure 2. This trend could be explained by the stability constant between the monomers of the polymeric ligand and the lanthanide ions  $\text{Ln}^{3+}$ ; the electron-donating ability of the methyl group could have stabilized the polymeric ligand (hydroxamate group) and, thus, increased the stability constant with the lanthanide ions. For I–VI, the results also indicate fast rates of equilibration; about 90% metal-ion uptake was achieved after 2–3 h, and uptake reached a steady state after 5–6 h. The uptake also increased as the ionic radii of the lanthanide ion ( $\text{Ln}^{3+}$ ) decreased; this was due to the higher stability of the formed complex between the polymeric ligand and the metal ion.<sup>42</sup> The extent of metal-ion uptake followed the order  $\text{Tb}^{3+} > \text{Gd}^{3+} > \text{Sm}^{3+} > \text{Nd}^{3+} > \text{La}^{3+}$ .

### pH dependence of the metal-ion uptake

The binding capacities of I, II, and III toward  $\text{Ln}^{3+}$  were investigated in the pH range 4.0–7.5 under continuous shaking for a fixed contact time of 6 h at 25°C and at an ionic strength of 0.10M. Typical pH-binding capacity profiles are illustrated in Figure 3 for I, II, and III. The results reveal that metal-ion uptake increased with the pH of the medium and approached a steady state at about pH 7.0. This behavior could be ex-



**Figure 3** Tb(III) uptake as a function of the pH of I–III.



**Figure 4** Counterion effects for I. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

plained by the nature of the chelating agent; the hydroxyl group ( $-\text{OH}$ ) existed in equilibrium, involving the protonated and unprotonated forms in the investigated pH range. Therefore, at higher pH values,  $\text{Ln}^{3+}$  ions competed favorably toward donor sites compared with hydrogen ions, in accordance with our recent work.<sup>13,16</sup>

### Effect of counterions on the sorption of lanthanide metal ions

The effect of counterions on the chelation properties of the polymers was studied by the determination of the metal-ion uptake as a function of the counterion at 25°C and in an acetate–acetic acid buffer at pH 7.0 and for a fixed contact time of 6.0 h. Ionic strength was maintained at 0.10M with different types of salts, including  $\text{NaClO}_4$ ,  $\text{NaCl}$ ,  $\text{NaNO}_3$ , and  $\text{Na}_2\text{SO}_4$ . The average of two duplicate runs was used, and typical results are displayed in Figure 4 for I for  $\text{La}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Tb}^{3+}$ . The observed metal-ion uptake with chloride, nitrate, perchlorate, and sulfate as counterions followed the order  $\text{Tb}^{3+} > \text{Gd}^{3+} > \text{Sm}^{3+} > \text{Nd}^{3+} > \text{La}^{3+}$ . This trend was observed in an earlier investigation<sup>16</sup> and followed the increase in the hydrated ionic radius in going from  $\text{Tb}^{3+}$  to  $\text{La}^{3+}$ .

The results of these experiments for the three polymers also show that the rate of metal-ion uptake increased in the order  $\text{ClO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ . This order may have been related to the free energy of hydration of the anion<sup>13,16</sup> and could also be explained in terms of the stability constants of complexes of  $\text{Ln}^{3+}$  with the anions.<sup>42,43</sup> For example, perchlorate has the lowest binding capacity or stability constant with  $\text{Ln}^{3+}$  ions; the metal-ion uptake in the presence of perchlorate ion, as an anionic strength adjuster, was higher than in the presence of other electrolytes that had relatively higher binding capacities with  $\text{Ln}^{3+}$ . In other words, the ligand with the higher stability constant with metal ions screened the metal ions from the polymeric ligand, so the metal uptake by these polymeric ligands decreased.



### Effect of crosslinker on metal-ion uptake

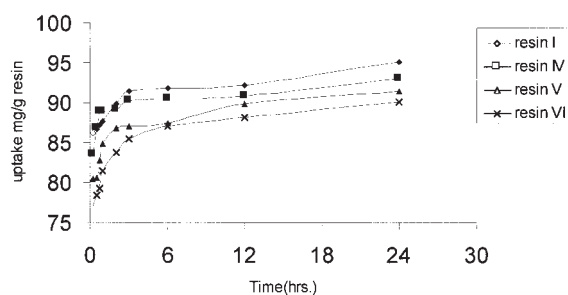
The effect of crosslinker on the sorption properties of the polymers containing amidoxime groups was investigated by the preparation of polymers containing various amounts of the crosslinker, divinylbenzene. When we compared the metal-ion uptake capacities of I and IV–VI, we observed that the extent of metal-ion uptake by these polymers followed the order I (4% crosslinking) > IV (12% crosslinking) > V (16% crosslinking) > VI (20% crosslinking). These results are displayed in Figure 5. The results reveal that the sorption process of the polymers was highly affected by the relative amount of the crosslinker; I (4% crosslinked) displayed the highest metal-ion uptake capacity. The decrease in the metal-ion uptake by crosslinking may be explained by the presence of steric hindrance of the divinylbenzene crosslinker, which hindered complete coordination with metal ions. This behavior was observed in an earlier investigation in our laboratory.<sup>13</sup>

### Metal-ion desorption

The desorption of chelated metal ions from a chelating polymer can be achieved by mineral acids such as HCl or HNO<sub>3</sub>. The desorption behavior of the investigated Ln<sup>3+</sup> ions from the polymers was examined by batch processes with 3M HCl as the eluent at 25°C with continuous shaking for 6.0 h. The results of desorption are shown in Table I. The results show that the binding capacities of Ln<sup>3+</sup> ions with various resins fell in the order Tb<sup>3+</sup> > Gd<sup>3+</sup> > Sm<sup>3+</sup> > Nd<sup>3+</sup> > La<sup>3+</sup>, which was in good agreement with the stability constants of the formed complexes.

## CONCLUSIONS

In this study, we focused on the preparation and chelating properties of some addition polymers. The polymers were characterized by IR spectroscopy. The chelating properties of these polymers toward some trivalent lanthanide ions (La<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>,



**Figure 5** Rate of Gd(III) uptake as a function of contact time for I, IV, V, and VI.

**TABLE I**  
Desorption of Chelated Lanthanide Metal Ions  
by 3M HCl

	Recovery (%)				
	La(III)	Nd(III)	Sm(III)	Gd(III)	Tb(III)
<b>I</b>	70.6	67.6	61.9	51.3	48.3
<b>II</b>	60.4	55.2	48.4	42.6	38.4
<b>III</b>	51.6	44.3	38.2	32.7	28.5
<b>IV</b>	81.7	74.5	70.1	57.5	56.1
<b>V</b>	86.6	79.6	73.1	59.5	58.8
<b>VI</b>	91.8	89.4	82.3	74.7	72.3

Temperature = 25°C; shaking time = 6 h.

and Tb<sup>3+</sup>) were investigated by a batch equilibration method. The results indicate that III had the highest metal-ion uptake capacity, and the extent of metal-ion uptake followed the order Tb<sup>3+</sup> > Gd<sup>3+</sup> > Sm<sup>3+</sup> > Nd<sup>3+</sup> > La<sup>3+</sup>.

The effect of exposure time on the metal-ion uptake was also investigated. The results reveal that a time of 6 h was enough to achieve maximum metal-ion sorption. The pH-binding capacity profiles showed that the metal-ion uptake of the resins increased with increasing pH and reached a maximum at pH 7.0. Variable amounts of divinylbenzene as a crosslinker were introduced in the preparation of I. The results indicate that the uptake decreased as the amount of crosslinker increased. The effect of counterions on the sorption properties was also studied, and the results indicate that metal uptake was highest among the perchlorate anions; also, the uptake increased as the concentration of perchlorate anions increased.

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