

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Porous Chelating Resins from Poly(Acrylonitrile-co-Ethyl Acrylate-co-Divinylbenzene)

Taek Seung Lee<sup>a</sup>; Sung Il Hong<sup>a</sup>

<sup>a</sup> Department of Fiber and Polymer Science, College of Engineering, Seoul National University, Seoul, Korea

**To cite this Article** Lee, Taek Seung and Hong, Sung Il(1995) 'Porous Chelating Resins from Poly(Acrylonitrile-co-Ethyl Acrylate-co-Divinylbenzene)', *Journal of Macromolecular Science, Part A*, 32: 3, 379 – 392

**To link to this Article:** DOI: 10.1080/10601329508013670

**URL:** <http://dx.doi.org/10.1080/10601329508013670>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **POROUS CHELATING RESINS FROM POLY(ACRYLONITRILE-*co*-ETHYL ACRYLATE-*co*-DIVINYLBENZENE)**

TAEK SEUNG LEE and SUNG IL HONG

Department of Fiber and Polymer Science  
College of Engineering  
Seoul National University  
Seoul 151-742, Korea

### **ABSTRACT**

Porous chelating resins have been prepared from acrylonitrile-ethyl acrylate-divinylbenzene copolymers by suspension polymerization with inert diluent followed by reaction with hydroxylamine. The porous structure was characterized by scanning electron microscope and varied greatly with the monomer composition and the amount of diluent. The metal binding properties of the chelating resins containing amidoxime and hydroxamic acid ligands derived from the terpolymers were examined with an atomic absorption spectrometer and an inductively coupled plasma spectrometer. This type of chelating resin has some advantages, e.g., ease of preparation (macroreticular) and particular selectivity for metal ions.

### **INTRODUCTION**

Acrylic polymer beads crosslinked with divinylbenzene have been prepared by the suspension polymerization technique from acrylic monomer for various kinds of end-use [1, 2].

Trochimczuk [3] reported that porous copolymers of acrylonitrile and divinylbenzene and terpolymers of acrylonitrile, acrylate, and divinylbenzene could be used as sorbents and the stationary phase of gas chromatography. Also, functional

groups could be introduced to this type of polymer support by various chemical reactions.

Vernon and Eccles [4, 5] obtained chelating resins containing hydroxamic acid from acrylonitrile-divinylbenzene copolymers by the hydrolysis of the copolymers with 50% sulfuric acid followed by reaction with hydroxylamine solution.

Lee and Hong [6] synthesized poly(hydroxamic acid) resins from crosslinked poly(ethyl acrylate) by suspension polymerization. The products had good metal adsorption properties.

Two kinds of chelating ligands, amidoxime and hydroxamic acid, could be obtained by copolymerization of acrylonitrile and acrylate and subsequent reaction with hydroxylamine. Along with this advantage, aliphatic acrylate enhances the segmental motions of chains of vinyl monomers, resulting in a less ordered structure and weaker intermolecular interactions than polyacrylonitrile alone [7-9].

In the present study, porous poly(acrylonitrile-co-ethyl acrylate-co-divinylbenzene) copolymers were prepared and poly(amidoxime-hydroxamic acid) chelating resins could be obtained by reaction of the copolymers and hydroxylamine. The morphological appearance of the resin beads and the metal ion selectivity were investigated in detail.

## EXPERIMENTAL

### Materials and Reagents

Ethyl acrylate (EA) and acrylonitrile (AN) were washed twice with aqueous 5% sodium hydroxide solution to remove inhibitors, then with distilled water several times. After washing, they were dried on calcium chloride for 24 hours.

Divinylbenzene (DVB, 55% mixture with 3- and 4-ethylvinylbenzene), obtained from Aldrich Chemical Co. and used as a crosslinking agent, was technical grade and used as received.

Sodium sulfate (Duksan Pharmaceutical Co.), calcium carbonate (Duksan Pharmaceutical Co.), gelatin (Shinyo Pure Chemicals Co.), 2,2,4-trimethyl pentane (TMP, Junsei Chemical Co.), hydroxylamine hydrochloride (Katayama Chemical), sodium methoxide (Janssen Chimica), metal ion standard solutions (Junsei Chemical Co.), uranyl nitrate hexahydrate (BDH Chemicals), solvents, and other reagents were GR grade and used without further purification.

### Suspension Polymerization of Poly(Acrylonitrile-co-Ethyl Acrylate-co-Divinylbenzene)

The suspension polymerization process was performed in a 1-L round-bottom flask fitted with mechanical stirrer, thermometer, and reflux condenser. A solution of 0.2 g benzoyl peroxide, 40 g of a monomer mixture (acrylonitrile, ethyl acrylate, and divinylbenzene), and a diluent, 2,2,4-trimethyl pentane, was poured slowly into the flask which contained 400 mL water, 30 g sodium sulfate, 5 g calcium carbonate, and 40 mL of 2% gelatin solution. The copolymerization process was carried out at 70°C for 2.5 hours and then at 90°C for 3.5 hours. The resulting copolymer was filtered and washed with 1 N hydrochloric acid solution, distilled water, and metha-

nol. It was then extracted in a Soxhlet apparatus with acetone for 24 hours, air-dried, and dried in vacuo at 40°C for 24 hours.

### **Preparation of Chelating Resin**

To convert these resins into poly(amidoxime-hydroxamic acid) resins, 20.85 g hydroxylamine hydrochloride was placed in a 1-L three-necked flask equipped with mechanical stirrer, reflux condenser, and thermometer, and then dissolved in 300 mL methanol. Sodium methoxide (17.29 g) was put into the solution followed by 10 g of the copolymer beads. This suspended solution was refluxed for 24 hours with slow stirring. After the reaction, the copolymer was filtered and washed with methanol, 1 N hydrochloric acid solution, methanol, deionized water, and methanol. It then was extracted in a Soxhlet apparatus with acetone for 24 hours, air-dried, and dried in vacuo at 40°C for 24 hours.

### **Infrared Spectroscopy**

Infrared spectra were obtained from KBr pellets of various resin beads with an FT-IR spectrometer (Perkin-Elmer 1725X).

### **Nitrogen Analysis**

Acrylonitrile content in the crosslinked resin was derived from nitrogen content determined by the Kjeldahl method [10].

### **Morphological Observation**

The resin surface was coated with gold and observed with a scanning electron microscope (SEM, Philips XL-20).

### **Apparent Density**

The apparent density was determined by the graduated cylinder method [11].

### **Metal Binding Capacity**

A commercially available 1000 ppm metal ion standard solution (except for uranium) was diluted to 100 ppm with deionized distilled water, followed by adjustment to a desirable pH with sodium hydroxide or hydrochloric acid solution. Appropriate quantities of uranyl nitrate were dissolved in 0.1 N nitric acid solution to obtain a 1000-ppm standard solution. The solution was also diluted to 100 ppm with deionized distilled water followed by adjustment of the pH by the same method as described above.

The amount of metal ion was determined with an atomic absorption spectrophotometer (AAS, GBC 904AA). An inductively coupled plasma spectrometer (ICP, Shimadzu ICPQ-1000) was used to determine the amount of such metal ions as vanadium, mercury, and uranium.

## Selectivity

The selectivity of the resin for various metals was measured by a batch method. Resin samples (0.10 g) were equilibrated for 24 hours with 20 mL of mixed metal ion solutions containing 100 ppm each of a specific metal ion pair except for mercury ion which was of 180 ppm.

Selectivity studies were carried out at the pH values listed in Table 1. The pH values applied in these selective studies were settled by means of two factors: a) the metal should not be precipitated under the test conditions; b) the pH should not affect the selective binding in mixed metal solution.

AAS and ICP were used to determine the uncomplexed metal ion concentrations.

## RESULTS AND DISCUSSION

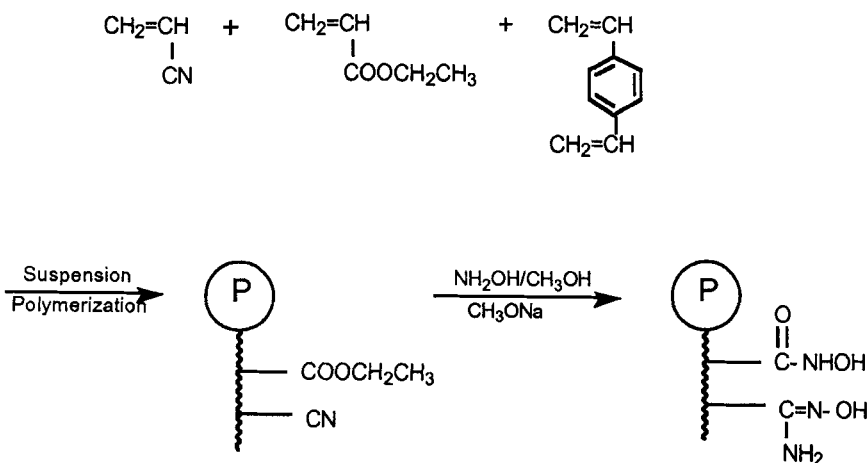
Suspension polymerization may be the most useful method to synthesize cross-linked polymeric beads. The suspension polymerization technique was also applied in this study to prepare crosslinked AN-EA beads. DVB is a crosslinking agent frequently used in polymer supports. Chelating resins prepared with DVB as a crosslinking agent have an effective pore structure (macropore) for the recovery of metals and high physical stability [12, 13].

Copolymers of AN and DVB prepared in the presence of inert diluents form porous structures because of the additional crosslinking with strong intermolecular interactions. Therefore, these interactions increase the difficulties in chemical modification of the polymers. The introduction of EA was aimed at obtaining internal plasticization of the copolymer. Scheme 1 shows the preparation method for poly(amidoxime-hydroxamic acid) resins.

EA was assumed to convert hydroxamic acid and AN was assumed to convert hydroxamic acid and amidoxime groups with the relative proportion of the latter [14]. In this study, EA content was fixed at 20 mol%. Some of the nitrile and ester groups in the crosslinked resin could be hydrolyzed and converted to carboxylic acid by reaction with hydroxylamine. Egawa [12] evaluated the content of amidoxime and carboxylic acid groups introduced to the resin with a hydrophilic crosslinker from the anion- and cation-exchange capacity. The cation-exchange capacities (the content of the amidoxime and the other acidic groups) were higher than the anion-exchange capacities (the content of amidoxime group) of the resins. Thus, Egawa

TABLE 1. pH Values of Selectivity Studies

Pair	Cu	Fe	Co	Ni	V
Fe	2.0	—	—	—	—
Co	4.5	2.5	—	—	—
Ni	4.2	2.5	4.5	—	—
V	4.2	2.0	4.3	4.5	—
Hg	4.6	2.5	4.5	4.5	4.5



SCHEME 1. Preparation of poly(amidoxime-hydroxamic acid) chelating resin.

thought that the acidic groups, such as hydroxamic acid and carboxylic acid groups, were formed in the course of the reaction. However, the difference between anion- and cation-exchange capacity is too small to evaluate the content of the acidic groups on the resin. According to Yunus [15], poly(carboxylic acid) obtained from the hydrolysis of polyacrylate showed some metal sorption capacity only at high pH. Thus it would be concluded that the carboxylic acid groups could be introduced to the resin in the process of synthesis. The amount of the carboxylic acid groups, however, was not important in this system, and the metal binding capacity depended strongly on two ligands, amidoxime and hydroxamic acids, rather than on carboxylic acid.

Figure 1 shows the AN content derived from Kjeldahl's nitrogen analysis in the crosslinked copolymer resins. The AN content in the resin decreased with an increase in the crosslinking ratio and with a decrease in the AN content fed. The AN content was also affected by the amount of diluent in the polymerization process when TMP was used as the precipitating diluent because it is a good solvent for the monomer AN but a precipitant for the polymer. Thus, discrete phase separation or precipitation occurred during the polymerization process along with competition for EA monomers (reactivity ratio [3]:  $r_{AN}$  0.356;  $r_{EA}$  1.075). It is possible that this precipitation and the lower reactivity of AN compared to EA suppressed the growth of AN monomers in the polymeric chain, resulting in the lower AN content in crosslinked resins obtained from higher dilution.

The infrared spectrum of the AN-EA-DVB copolymer (Fig. 2a) shows the characteristic nitrile stretch absorption band at  $2225\text{ cm}^{-1}$ . The characteristic absorptions of amidoximes are shown in Fig. 2(b). The amine stretching absorption appears at  $3400\text{ cm}^{-1}$ , the broad absorption of the  $\text{-OH}$  stretch at  $3325\text{ cm}^{-1}$ , and the broad absorption at  $1650\text{ cm}^{-1}$  from the  $\text{C}=\text{N}$  stretch of the oxime group. The absorption band at  $900\text{ cm}^{-1}$  has been assigned to the  $\text{N-O}$  stretch of oximes. Absorption at  $2225\text{ cm}^{-1}$  in Fig. 2(b) indicates the presence of unreacted nitrile

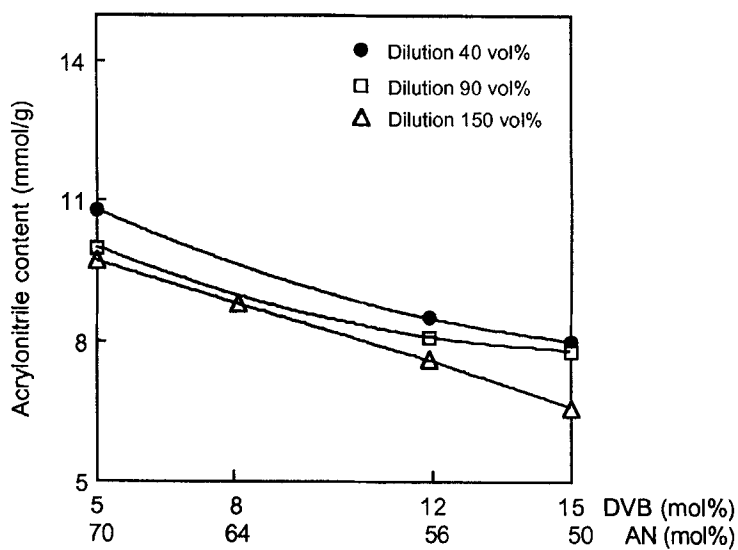


FIG. 1. Acrylonitrile content in copolymers (EA feed 20 mol%).

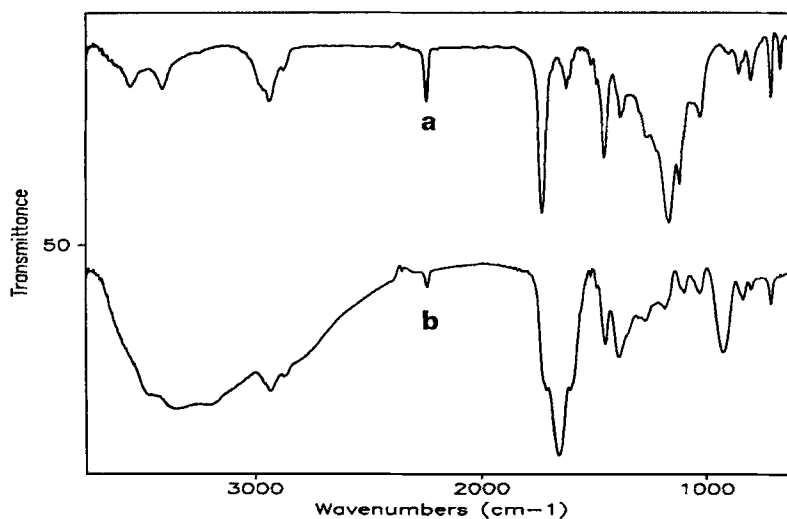


FIG. 2. Infrared spectra of AN/EA/DVB copolymer: (a) before and (b) after amidoximation and hydroxamation.

groups which are probably dispersed randomly throughout the resin as are the amidoxime groups.

Trochimczuk [3] proposed that the terpolymers containing up to 55 mol% EA units still have porous structures although the pore volume gets smaller and smaller. The terpolymers with an acrylate content exceeding these values have a so-called "expanded structure" and their porosity may change upon treatment in broad ranges. AN monomer, like TMP, cannot dissolve the resulting polyacrylonitrile during suspension polymerization, acting as a precipitant to polymeric growing chains. Thus macroreticular resins could be obtained at various polymerization conditions showing a large, definitive, and permanent internal porous structure with an effective surface area. In general, there are three methods to prepare porous matrices: (a) by addition of a solvating diluent; (b) by addition of a nonsolvating diluent; (c) by addition of a linear polymer [16]. By far the most important method is the incorporation of inert solvents or diluents into a polymerization mixture [17]. The growing chains remain fully solvated and do not collapse as the comonomers are consumed during suspension polymerization in good solvents. The product is, therefore, similar to a gel-type resin, but it remains in a fully expanded form. Sudden collapse is caused by removal of the diluent after isolation of the beads, and as a result a corrugated effect is shown. This is in contrast to the relatively smooth surface of a corresponding gel-type resin, where the contraction is slow and progressive during polymerization. The products are called *macroporous*. With the macroporous product, even when all the diluent is removed and the nuclei are aggregated, significant porosity can remain as a result of the much larger expansion of the solvated network during polymerization. The resulting materials are translucent and will readily absorb varying quantities of a good solvent. When the solvent employed during polymerization is a good solvent for the monomer but a precipitant for the polymer, the term *macroreticular* is generally used to describe the product. Polymerization is complicated by the occurrence of discrete phase separation or precipitation, during which macromolecular chains tend to aggregate into tangled glass-like masses, leaving a network of large, diluent-filled voids or pores within each suspension droplet. The final product is an opaque material with a characteristic mat appearance in the dry state. It has a definitive and permanent internal porous structure with a well-defined internal surface, and pore diameters can be as high as several thousand angstroms.

Table 2 illustrates the morphological appearance of the bead surface in this system. Powdery resin bead did not appear in this system, implying that suspension copolymerization of AN/EA/DVB was easier than any other system. In spite of using a nonsolvating diluent, the morphologies of all the resins are not macroreticular. This means that crosslinking ratio and degree of dilution in the polymerization process is more important than the solvation behavior of the diluent. Gel-type resins were observed in highly crosslinked systems regardless of the degree of dilution. Macroreticular, gel, and macroporous resins are shown in Fig. 3(a), (b), and (c), respectively. In general, the whole structure is not susceptible to the dramatic changes observed with gel-type when the nature of the surrounding medium is changed. The dimensional stability of macroreticular resins makes them resistant to high pressure in column applications where better solvent flow rates can be achieved than in the case of gel polymers [18]. Macroreticular resins usually display a negligible change in volume during use.



TABLE 2. Morphological Appearance of Various AN/EA/DVB Copolymers

Degree of dilution, vol%	EA 20 <sup>a</sup>			
	AN 70/DVB 5	AN 64/DVB 8	AN 56/DVB 12	AN 50/DVB 15
40	G	G	G	G
60	MP	MP	MP	G
90	MR	MP	MP	G
120	MR	MR	MP	G
150	MR	MR	MP	MP

<sup>a</sup>G = gel-type resin. MP = macroporous resin. MR = macroreticular resin.

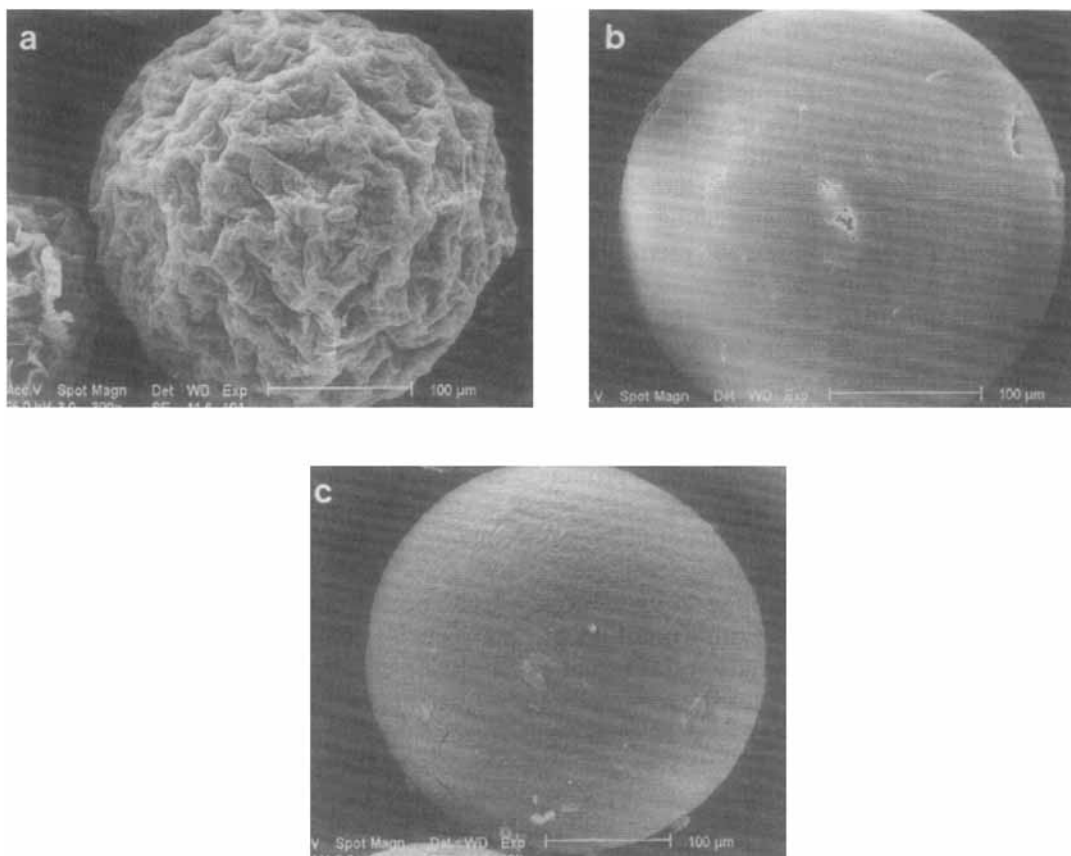


FIG. 3. SEM photographs of crosslinked resins: (a) AN 70 mol%, DVB 5 mol%, dilution 120 vol%; (b) AN 64 mol%, DVB 8 mol%, dilution 40 vol%; (c) AN 56 mol%, DVB 12 mol%, dilution 60 vol%.

TABLE 3. Effects of Crosslinking Ratio and Degree of Dilution on the Apparent Density of Poly(Amidoxime-Hydroxamic Acid)s from AN/EA/DVB Copolymers

Degree of dilution, vol%	EA 20			
	AN 70/DVB 5	AN 64/DVB 8	AN 56/DVB 12	AN 50/DVB 15
40	0.74	0.73	0.62	0.44
90	0.46	0.46	0.18	0.22
120	0.39	0.39	0.16	0.20
150	0.34	0.17	0.16	0.13

TABLE 4. Copper Ion Adsorption Capacity of Various Poly(Amidoxime-Hydroxamic Acid)s from AN/EA/DVB Copolymers

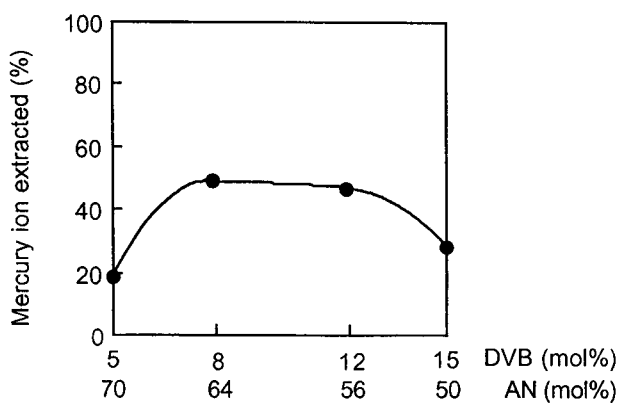
Degree of dilution, vol%	EA 20			
	AN 70/DVB 5	AN 64/DVB 8	AN 56/DVB 12	AN 50/DVB 15
40	94.3 <sup>a</sup>	87.7	64.4	14.6
60	68.4	95.2	80.3	43.2
90	74.8	45.8	29.8	53.5
120	90.6	94.2	43.5	48.9
150	81.6	98.9	37.8	40.1

<sup>a</sup>Copper ion extracted (%) in 100 ppm 20 mL (pH 4) copper solution by the resin (0.10 g).

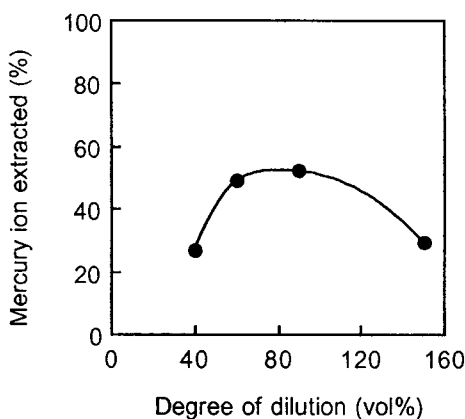
TABLE 5. Iron Ion Adsorption Capacity of Various Poly(Amidoxime-Hydroxamic Acid)s from AN/EA/DVB Copolymers

Degree of dilution, vol%	EA 20			
	AN 70/DVB 5	AN 64/DVB 8	AN 56/DVB 12	AN 50/DVB 15
40	19.2 <sup>a</sup>	10.7	15.6	29.4
60	32.8	6.1	17.0	22.7
90	37.6	4.7	11.1	5.2
120	26.7	16.2	34.6	10.3
150	19.9	34.5	21.9	18.3

<sup>a</sup>Iron ion extracted (%) in 100 ppm 20 mL (pH 2.5) iron solution by the resin (0.10 g).



(a)

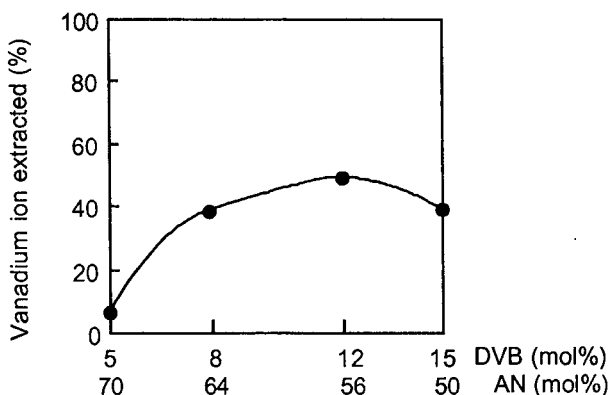


(b)

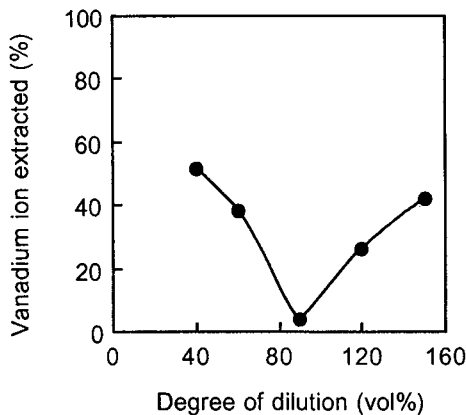
FIG. 4. Effects of the crosslinking ratio and degree of dilution on mercury ion binding capacity of various poly(amidoxime-hydroxamic acid)s from AN/EA/DVB copolymers. Resin: 0.10 g in 100 ppm, 20 mL mercury solution (pH 3). Resin: (a) dilution 60 vol%; (b) crosslinking 8 mol%.

Table 3 shows the effects of crosslinking ratio and degree of dilution on the apparent densities of the resins. The apparent density did not vary greatly at 90, 120, and 150 vol% dilution, but at 40% dilution the monomer AN and diluent TMP, acting as precipitants, and the other monomer, EA, acting as a good solvent of the resulting polymer chain, behave in a more complicated manner in the polymerization system. Because their behaviors are contrary to each other, various apparent densities result.

Table 4 displays the copper binding capacity of this type of resin which has good capacity below 8% crosslinking (high AN content). The hydroxamic acid



(a)

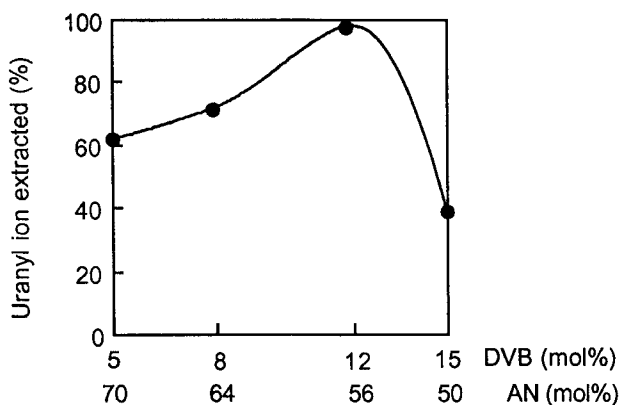


(b)

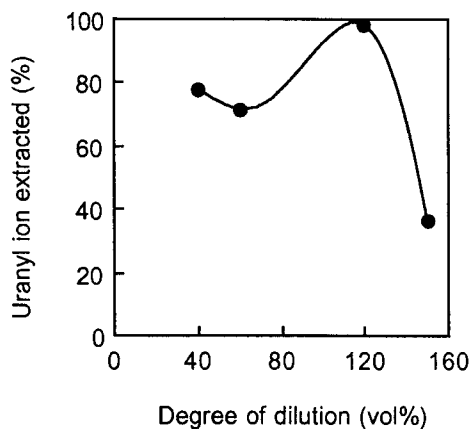
FIG. 5. Effects of the crosslinking ratio and degree of dilution on vanadium ion binding capacity of various poly(amidoxime-hydroxamic acid)s from AN/EA/DVB copolymers. Resin: 0.10 g in 100 ppm, 20 mL vanadium solution (pH 3). Resin: (a) dilution 60 vol%; (b) crosslinking 8 mol%.

group as well as the amidoxime group are well-known for their chelating ability with copper ion. Thus it is presumed that the copper binding capacity is more influenced by the crosslinking ratio than by the AN content. However, amidoxime ligand is not suitable for binding of iron ion as shown in Table 5. Mercury and vanadium ions were extracted fairly well by this type resin as displayed in Figs. 4 and 5. With vanadium, that resin prepared with 8 mol% crosslinking and 90 vol% dilution showed the lowest binding capacity. Uranyl ion binding capacity, shown in Fig. 6, was more influenced by the degree of dilution and the crosslinking ratio.

In general, binding capacities of poly(amidoxime-hydroxamic acid) resins were lower than those of poly(hydroxamic acid) resins, presumable because the



(a)



(b)

FIG. 6. Effects of the crosslinking ratio and degree of dilution on uranyl ion binding capacity of various poly(amidoxime-hydroxamic acid)s from AN/EA/DVB copolymers. Resin: 0.10 g in 100 ppm, 20 mL uranium solution (pH 3). Resin: (a) dilution 60 vol%; (b) crosslinking 8 mol%.

mixed ligand distorts the chain conformation of the macromolecular complex, thereby allowing chelation with metals and resulting in the formation of unstable chelates. Thus large metals such as the uranyl ion are bound much more by this type of resin than by small ones.

Poly(amidoxime-hydroxamic acid) shows a very particular selectivity for metal ions (Tables 6 and 7). First of all, copper and iron are preferentially complexed over every metal ion except vanadium regardless of the crosslinking ratio and the AN content in the resin. Although the selectivity for vanadium is very high in most metal pairs by poly(amidoxime-hydroxamic acid), it is more influenced by DVB and AN content than any other metal.

TABLE 6. Selective Binding of Metal by Poly(Amidoxime-Hydroxamic Acid) from AN 70 mol%, DVB 5 mol% (dilution 60 vol%)

Metal pair	Alone, mmol/g	Mixed, mmol/g	Relative % difference
Cu/Fe	0.22/0.10	0.22/0.07	0/ - 30
Cu/Co	0.22/0.02	0.26/0	+ 118/
Cu/Ni	0.22/0.04	0.21/0.02	- 5/ - 50
Cu/V	0.22/0.03	0.11/0.26	- 50/ + 867
Cu/Hg	0.22/0.02	0.24/0.13	+ 109/ + 650
Fe/Co	0.10/0.02	0.33/0.03	+ 330/ + 150
Fe/Ni	0.10/0.04	0.39/0.04	+ 390/0
Fe/V	0.10/0.03	0/0.13	/ + 433
Fe/Hg	0.10/0.02	0.28/0.10	+ 280/ + 500
Co/Ni	0.02/0.04	0.04/0.06	+ 200/ + 150
Co/V	0.02/0.03	0.04/0.25	+ 200/ + 833
Co/Hg	0.02/0.02	0.03/0.03	+ 150/ + 150
Ni/V	0.04/0.03	0.03/0.25	- 25/ + 833
Ni/Hg	0.04/0.02	0.04/0.10	0/ + 500
V/Hg	0.03/0.02	0.26/0	+ 867/

TABLE 7. Selective Binding of Metal by Poly(Amidoxime-Hydroxamic Acid) from AN 50 mol%, DVB 15 mol% (dilution 60 vol%)

Metal pair	Alone, mmol/g	Mixed, mmol/g	Relative % difference
Cu/Fe	0.14/0.08	0.06/0.07	- 57/ - 13
Cu/Co	0.14/0.04	0.18/0	+ 129/
Cu/Ni	0.14/0.03	0.16/0	+ 114/
Cu/V	0.14/0.16	0.14/0.16	0/0
Cu/Hg	0.14/0.04	0.76/0	+ 543/
Fe/Co	0.08/0.04	0.16/0.04	+ 200/0
Fe/Ni	0.08/0.03	0.20/0.07	+ 250/ + 233
Fe/V	0.08/0.16	0.05/0	- 36/
Fe/Hg	0.08/0.04	0.12/0	+ 150/
Co/Ni	0.04/0.03	0.02/0.07	- 50/ + 233
Co/V	0.04/0.16	0.02/0.16	- 50/0
Co/Hg	0.04/0.02	0.02/0	- 50/
Ni/V	0.03/0.16	0/0.17	/ + 106
Ni/Hg	0.03/0.04	0.04/0	+ 133/
V/Hg	0.16/0.04	0.18/0	+ 113/

## CONCLUSIONS

Porous poly(amidoxime-hydroxamic acid) chelating resins were prepared by suspension polymerization with a diluent, 2,2,4-trimethyl pentane, followed by reaction with hydroxylamine. The resulting resin beads showed various morphological appearances (macroreticular, macroporous, and gel-type) with variation of the crosslinking ratio and the degree of dilution. This type of chelating resin has a good adsorption capacity toward copper and uranyl ions, but is poor for the iron ion. This resin also showed a very particular selectivity for metal ions. Copper and iron were preferentially adsorbed over every metal ion except vanadium regardless of the crosslinking ratio.

## REFERENCES

- [1] M. H. Skovby and J. Kops, *J. Appl. Polym. Sci.*, **39**, 169 (1990).
- [2] M. Hassanein, A. Alkelah, A. Selim, and H. El Hamshary, *Eur. Polym. J.*, **25**, 1083 (1989).
- [3] B. N. Kolarz, M. Wojaczyńska, A. Trochimczuk, and J. Łuczyński, *Polymer*, **29**, 1137 (1988).
- [4] F. Vernon and H. Eccles, *Anal. Chim. Acta*, **82**, 369 (1976).
- [5] F. Vernon and H. Eccles, *Ibid.*, **83**, 187 (1976).
- [6] T. S. Lee and S. I. Hong, *Polym. Bull.*, **32**, 273 (1994).
- [7] J. Grobelny, P. Takely, and E. Turska, *Polymer*, **22**, 1649 (1981).
- [8] A. K. Gupta and R. P. Singhal, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2243 (1983).
- [9] A. K. Gupta, V. K. Singhal, and J. Agarval, *J. Appl. Polym. Sci.*, **26**, 3599 (1981).
- [10] G. H. Jeffery, J. Basett, J. Mendham, and R. C. Denney, *Textbook of Quantitative Chemical Analysis*, 5th ed., Longman Scientific & Technical, 1989, p. 302.
- [11] A. Krause, A. Langa, and M. Ezrin, *Plastics Analysis Guide*, Hanser Publishers, 1983, p. 16.
- [12] H. Egawa, M. Nakayama, T. Nonaka, and E. Sugihara, *J. Appl. Polym. Sci.*, **33**, 1993 (1987).
- [13] H. Egawa, M. Nakayama, T. Nonaka, and E. Sugihara, *J. Macromol. Sci. - Chem.*, **A25**, 1407 (1988).
- [14] A. L. Crumbliss, J. M. Garrison, C. R. Bock, A. Schaaf, C. J. Bonaventura, and J. Bonaventura, *Inorg. Chim. Acta*, **133**, 281 (1987).
- [15] W. Yunus and Z. Ahmad, *Pertanika*, **11**, 255 (1988).
- [16] J. Seidl, J. Marinsky, K. Dusek, and W. Heitz, *Adv. Polym. Sci.*, **5**, 113 (1967).
- [17] P. Hodge and R. C. Sherrington, *Polymer-Supported Reactions in Organic Synthesis*, Wiley, New York, 1980, p. 13.
- [18] A. Alkelah and A. Moet, *Functionalized Polymers and Their Applications*, Chapman & Hall, 1990, p. 33.

Received March 2, 1994

Revision received June 8, 1994