

# A Novel Highly Copper(II)-Selective Chelating Ion Exchanger Based on Poly(Glycidyl Methacrylate-co-Ethylene Dimethacrylate) Beads Modified with Aspartic Acid Derivative

DANIEL HORÁK,<sup>1</sup> MILAN J. BENEŠ,<sup>1</sup> KLARA GUMARGALIEVA,<sup>2</sup> GUENNADI ZAIKOV<sup>2</sup>

<sup>1</sup> Institute of Macromolecular Chemistry, Ac. Sci. of the Czech Republic, Heyrovského Sq. 2, 162 06 Prague 6, Czech Republic

<sup>2</sup> Institute of Biochemical Physics, Rus. Ac. Sci., 4 Kosygin St., Moscow 117334, Russia

Received 9 December 1999; accepted 6 April 2000

**ABSTRACT:** Anchoring the hydroxyaspartic acid onto poly(glycidyl methacrylate-co-ethylene dimethacrylate) (poly(GMA-co-EDMA)) beads or epoxysuccinic acid onto ammonium-modified poly(GMA-co-EDMA) beads resulted in a novel chelating resin, which contained up to 0.37 mmol of the ligand per gram of resin. Batch extraction experiments showed a very high selectivity for Cu<sup>2+</sup> over Zn<sup>2+</sup> and Cd<sup>2+</sup> ions in buffered solutions under competitive conditions. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 913–916, 2001

## INTRODUCTION

The need for more highly specific, metal recovery processes in both hydrometallurgical and environmental applications has led to an increasing interest in selective ion exchange. In particular the search for “ion-specific” resins, which, under proper operating conditions, are selective for only one ionic species,<sup>1,2</sup> has intensified. Important properties of such ion exchangers should include high capacity, high selectivity, and fast kinetics.<sup>3</sup> Most of the commercial resins, when tested in wastewater treatment, show a high capacity, but a very poor selectivity towards different metal ions. In some cases, the kinetics are slow, due to the hydrophobic character of the polymer backbone and chelating groups. Therefore, studies to-

wards the development of resins with improved selectivity and better kinetic performance have been initiated in our laboratory. Recently, some Cu<sup>2+</sup>-selective chelating ion exchangers based on polystyrene<sup>4</sup> or poly(glycidyl methacrylate-co-trimethylpropane trimethacrylate)<sup>2</sup> have been published.

This communication describes the synthesis and metal-ion uptake experiments of a novel, highly Cu<sup>2+</sup>-selective ion exchange resin based on poly(GMA-co-EDMA)-containing derivatives of aspartic acid as the chelating ligand. This ion exchanger combines a high selectivity for Cu<sup>2+</sup> ions with fast exchange kinetics.

## EXPERIMENTAL

### Synthesis of the Sodium Salt of Epoxysuccinic Acid<sup>5</sup>

Five hundred milliliters of aqueous alkaline (pH 4–5.5) maleic acid (116 g, i.e., 1 mol) solution was

Correspondence to: G. E. Zaikov.  
Contract grant sponsor: Grant Agency of the Czech Republic; contract grant number: 203/98/0885.

*Journal of Applied Polymer Science*, Vol. 80, 913–916 (2001)  
© 2001 John Wiley & Sons, Inc.

stirred at 65°C for 1 h with 6.6 g  $\text{Na}_2\text{WO}_4$  (used as the catalyst) and 145.7 g of 28 wt % hydrogen peroxide solution. The volume of the reaction mixture was reduced to 300 mL, and the product was precipitated by acetone, separated, and dried; yield: 178.4 g; the elemental analysis (calculated values in parentheses): C 26.3 (27.3), H 1.2 (1.1).  $^1\text{H-NMR}$  data:  $\delta$  3.6;  $^{13}\text{C-NMR}$  data:  $\delta$  58 (C alif.), 176 (C=O).

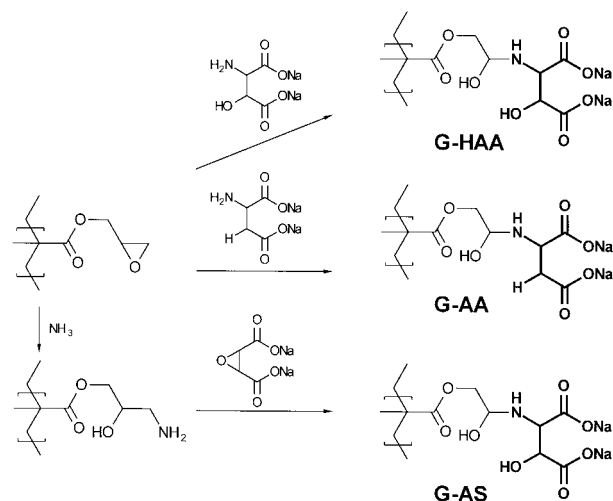
### Synthesis of the Sodium Salt of Hydroxyaspartic Acid<sup>6</sup>

One hundred sixty milliliters of 25 wt % aqueous ammonia was stirred at 50°C for 32 h with 11 g of sodium salt of epoxysuccinic acid. The volume of the reaction mixture was reduced until the crystallization of the product. Yield: 11.3 g; the elemental analysis (calculated values for 0.8-*M* hydrate in parenthesis): C 21.7 (21.7), H 3.0 (3.0), N 6.1 (6.3);  $^1\text{H-NMR}$  data:  $\delta$  3.8 (CH—NH<sub>2</sub>), 4.4 (CH—OH);  $^{13}\text{C-NMR}$  data: 60 (CH—NH<sub>2</sub>), 75 (CH—OH), 175 and 179 (C=O).

Poly(GMA-*co*-EDMA) beads were prepared by suspension polymerization using a mixture of glycidyl methacrylate (GMA) and ethylene dimethacrylate (EDMA) (3 : 2 v/v) with a mixture of cyclohexanol and 1-dodecanol (9 : 1 v/v) as a porogen (monomers : porogens 2 : 3 v/v) as described earlier.<sup>7</sup> Bead size fraction 12–20  $\mu\text{m}$  was used for further reactions. The BET surface area of the beads in the dry state was 69  $\text{m}^2/\text{g}$  and the pore volume was 1.4  $\text{cm}^3/\text{g}$ .

The resin G-A was prepared from poly(GMA-*co*-EDMA) beads (50 g) by heating them in an excess (400 mL) of 25 wt % ammonia at 50°C for 28 h. The resulting product was washed in a column with water until pH 7, followed with 200 mL of methanol, 200 mL of acetone, dried in vacuum over  $\text{P}_2\text{O}_5$ . The elemental analysis (calculated values in parenthesis are for 60% conversion of oxirane to amino groups): C 57.1 (57.7), H 7.3 (7.4), N 2.95 (2.96).

The resins G-HAA, G-AA, or G-AS were prepared according to Scheme 1. A mixture of 5 g of poly(GMA-*co*-EDMA) suspended in 28 mL of water for 16 h and sodium salt of hydroxyaspartic acid (8.15 g, i.e., two molar excess with regard to oxirane groups), or sodium salt of aspartic acid (5.62 g, i.e., two molar excess with regard to oxirane groups), and 35 mg of cetyltrimethylammonium bromide used as a catalyst was heated at 90°C for 1, 2, 5, 10, and 21 h. The resin was filtered and purified in a column by thorough



**Scheme 1** Immobilization of chelating ligands on poly(GMA-*co*-EDMA) beads.

washing with water, followed by conditioning with 0.5 *N*-HCl. The resin was washed with water until neutral pH and dried in vacuum for 48 h. The reaction of the aminoderivative of poly(GMA-*co*-EDMA) (sample G-A) with sodium salt of epoxysuccinic acid was performed under the same conditions as described above, resulting in G-AS resin. The resulting resins were characterized by elemental analysis, and the degree of conversion of the oxirane (or amino) groups was determined as a best fit between the results of elemental analysis and those calculated from chemical formulas corresponding to various reaction conversions.

Batch metal-uptake experiments with resins under competitive and noncompetitive conditions were performed with standard 0.2 *M*- $\text{CuSO}_4$  solution and with standard 0.2 *M*-metal chloride solutions of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  in buffer solution NaOAc–HOAc (pH 5) at room temperature for 24 h. For the competitive experiments, batches of 0.2 g of resin in  $\text{H}^+$  form were used, together with a mixture of 60 mL of buffer and 60 mL of standard  $\text{MCl}_2$  solution. Samples for metal analysis were prepared by elution of the loaded resin in column with 0.5 *N*-HCl. The metal contents of the resulting solutions were determined by AAS spectroscopy in acetylene–air flame using Varian SpectraAA apparatus. For the noncompetitive experiments, batches of 0.2 g of resin in its  $\text{H}^+$  form were contacted with an aqueous solution containing 20 mL of each of the standard  $\text{MCl}_2$  solution and 60 mL of buffer. The resin was transferred into a column, washed with an excess of water,

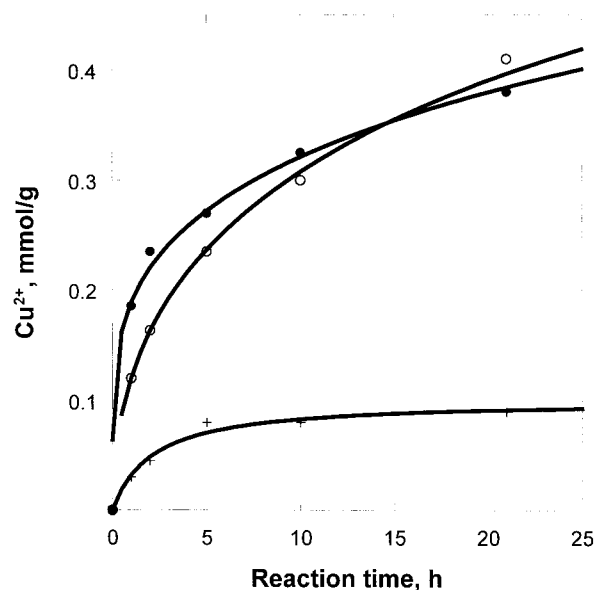
and the metal ion was eluted with 0.1 *N*-HCl. The eluent was treated with ammonia until formation of ammine complex  $[\text{Cu}(\text{HN}_3)_x]^{2+}$ , and the amount of metal ion in solution was determined by titration with chelator 3 using a murexide indicator for the determination of  $\text{Cu}^{2+}$ , and using an eriochrome black T indicator for  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ .

## RESULTS AND DISCUSSION

The chelating ion-exchange resins were synthesized from poly(GMA-*co*-EDMA) beads according to Scheme 1 in the presence of cetyltrimethylammonium bromide phase-transfer catalyst. Unlike classical tridentate iminodiacetic acid ligand (N,O,O), G-HAA and G-AS resins contain a tetradentate ligand (N,O,O,O). The degree of conversion of oxirane groups after reaction with hydroxyaspartic acid for 21 h was calculated to be 14%, corresponding to a ligand concentration of 0.37 mmol/g of G-HAA resin. Slightly lower conversion (10%) was achieved in the reaction of poly(GMA-*co*-EDMA) with aspartic acid resulting in G-AA resin. In G-AS resin, the monitoring of the reaction conversion was somewhat complicated by the fact that the starting G-A resin, in contrast to poly(GMA-*co*-EDMA), contained nitrogen. Nevertheless, the reaction conversion of amino to succinic acid groups was estimated to 30%. It is interesting to note that in the absence of a catalyst the reactions proceeded only slowly and with very low conversion. Such behavior is often observed in crosslinked resins, where solvent that is very favorable for a given reaction may be essentially nonsolvent for the polymeric matrix.<sup>8</sup> In the case of poly(GMA-*co*-EDMA), the reaction proceeded in water, which is a poor solvent for the matrix.

As shown in Figure 1, the uptake of copper by chelating resins increased with reaction time. Because  $\text{Cu}^{2+}$  uptake did not significantly change after a 21-h reaction, in the following the data for resins synthesized only at this reaction time are discussed. Relatively slow kinetics compared with ion-exchange is typical of all complex-forming resins.<sup>9,10</sup> Hydrophilization of the carrier skeleton could improve the kinetics.

Table I shows the metal-ion uptake capacities of the resins under both noncompetitive and competitive conditions. Uptake experiments with metal ions of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$  were performed in buffered solutions. The behavior of G-A, G-AS, and G-HAA resins showed that under both conditions the uptake of  $\text{Cu}^{2+}$  was highest of all



**Figure 1** Effect of reaction time on the uptake of copper(II) ions: ○ G-AS; ● G-HAA; × G-AA.

three metal ions. Only G-HAA resin retains under noncompetitive conditions the  $\text{Zn}^{2+}$  ions. The lowest metal uptake capacity (not exceeding 0.10 mmol  $\text{Cu}^{2+}$ /g) was found in the G-AA resin. The G-A, G-AS, and G-HAA resins retained ca. 0.4–0.5 mmol  $\text{Cu}^{2+}$ /g under noncompetitive conditions and 0.3–0.4 mmol  $\text{Cu}^{2+}$ /g under competitive conditions. The maximum uptake capacity for  $\text{Cu}^{2+}$  found in G-A resin for noncompetitive conditions was 0.53 mmol/g. The uptake capacity of G-HAA resin for  $\text{Cu}^{2+}$  under the same conditions was 0.38 mmol/g, which indicates that all of the ligands are chelating.

The metal-ion uptake experiments conducted under competitive conditions indicated that the resins were highly selective for  $\text{Cu}^{2+}$  over the other metal ions (Table I). Despite the highest capacity of the G-A resin for  $\text{Cu}^{2+}$  (0.38 mmol/g), the selectivity of this resin was lower than the selectivity of G-AS and G-HAA resin. The uptake capacity for  $\text{Cu}^{2+}$  in G-AS and G-HAA resin was ca. 0.33 mmol/g. The uptake capacities for  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  at pH 6 were very much lower, i.e., ca. 0.003 and 0.005 mmol/g, respectively. The selectivities for  $\text{Cu}^{2+}$  over  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  were thus very high at pH 6, and were higher than that have been found for polyGMA-bimam<sup>2</sup> and other types of ion exchangers, viz. those with polystyrene or silica backbones.<sup>4,11</sup>

The lower selectivity of G-A resin found in metal uptake experiments indicated the impor-

**Table I Metal Uptake by the Chelating Ion Exchange Resins**

Sample	Degree of Conversion %	Ligand mmol/g	Noncompetitive Conditions			Competitive Conditions		
			Cu <sup>2+</sup> mmol/g	Zn <sup>2+</sup> mmol/g	Cd <sup>2+</sup> mmol/g	Cu <sup>2+</sup> mmol/g	Zn <sup>2+</sup> mmol/g	Cd <sup>2+</sup> mmol/g
G-A	60	2.11	0.53	0.01	0	0.38	0.001	0.001
G-AS	30	0.18 <sup>a</sup>	0.41	0.03	0.03	0.33	0.0002	0.00005
G-HAA	14	0.37	0.38	0.21	0.02	0.32	0.0003	0.00004
G-AA	10	0.31	0.09	0.05	0.03	0.10	0.0003	0.00003

<sup>a</sup> Succinic acid groups.

tance of the hydroxyl group of G-AS and G-HAA resins for the formation of metal–ligand complexes. The overall metal-uptake capacity of the resin G-HAA at pH 6 under competitive conditions was 0.32 mmol/g, which indicated that 86% of the ligands in the resin were occupied by metal Cu<sup>2+</sup> ions, in good agreement with the results obtained in the noncompetitive uptake experiments. The high ligand occupation for Cu<sup>2+</sup> found in these experiments most probably indicates the formation of 1 : 1 Cu<sup>2+</sup>–ligand complex on the polymer. In these complexes the aspartic ligand probably acts as a tetradentate donor ligand.

The loading capacity of the ion-exchange resins G-HAA for Cu<sup>2+</sup> remained the same after several cycles of consecutive loading with the 0.2 M–CuSO<sub>4</sub> stock solution at pH 6 and stripping with 0.1 M–HCl, indicating that the resin structure, backbone with ligand, is chemically and mechanically stable when treated with strong acid.

In summary, we have demonstrated that the novel chelating ion-exchange resin poly(GMA-co-EDMA) modified with hydroxyaspartic acid has a very high selectivity towards Cu<sup>2+</sup> ions in the presence of other divalent transition metal ions.

Financial support by grant No. 203/98/0885 of the Grant Agency of the Czech Republic is gratefully acknowledged.

## REFERENCES

1. Sarzanini, C.; Mentasti, E.; Porta, V. In *Ion Exchange for Industry*; Sreat, M., Ed.; Ellis Horwood: Chichester, UK, 1988, p. 189.
2. van Berkel, P. M.; Driessen, W. L.; Koolhaas, G. J. A. A.; Reedijk, J.; Sherrington, D. C. *J Chem Soc Chem Commun* 1995, 147.
3. Slater, M. J., Ed. *Ion Exchange Advances*; Elsevier: London, UK, 1992.
4. Sahni, S. K.; Driessen, W. L.; Reedijk, J. *Inorg Chim Acta* 1988, 154, 141.
5. Payne, G. B.; Williams, P. H. *J Org Chem* 1959, 24, 54.
6. Kaneko, T.; Katsura, H. *Bull Chem Soc Jpn* 1963, 36, 899.
7. Horák, D.; Pelzbauer, Z.; Bleha, M.; Ilavský, M.; Švec, F.; Kálal, J. *J Appl Polym Sci* 1981, 26, 411.
8. Sherrington, D. C. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Bikales, N. M.; Overberger, Ch. G.; Mendes, G., Eds.; Wiley: New York, 1988, p. 133, vol. 14.
9. Warshavsky, A. In *Syntheses and Separations Using Functional Polymers*; Sherrington, D. C.; Hodge, P., Eds.; Wiley: Chichester, UK, 1988, p. 325.
10. van Berkel, P. M.; Punt, M.; Koolhaas, G. J. A. A.; Driessen, W. L.; Reedijk, J.; Sherrington, D. C. *React Funct Polym* 1997, 32, 139.
11. van Berkel, P. M.; Verweij, P. D.; Driessen, W. L.; Reedijk, J. *Eur Polym J* 1992, 28, 747.