

Synthesis and Characterization of Poly(hydroxamic acid) Chelating Resin from Poly(methyl acrylate)-Grafted Sago Starch

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Received 26 July 1999; revised 30 April 2000

ABSTRACT: A new chelating ion-exchange resin containing the hydroxamic acid functional group was synthesized from poly(methyl acrylate) (PMA)-grafted sago starch. The PMA grafted copolymer was obtained by a free-radical initiating process in which ceric ammonium nitrate was used as an initiator. Conversion of the ester groups of the PMA-grafted copolymer into hydroxamic acid was carried out by treatment of an ester with hydroxylamine in an alkaline solution. The characterization of the poly(hydroxamic acid) chelating resin was performed by FTIR spectroscopy, TG, and DSC analyses. The hydroxamic acid functional group was identified by infrared spectroscopy. The chelating behavior of the prepared resin toward some metal ions was investigated using a batch technique. The binding capacities of copper, iron, chromium, and nickel were excellent and the copper capacity was maximum (3.46 mmol g^{-1}) at pH 6. The rate of exchange of the copper ion was very fast that is, $t_{1/2} < 5 \text{ min}$. It was also observed that the metal ion-sorption capacities of the resin were pH-dependent and its selectivity toward the metal ions used is in the following order: $\text{Cu}^{2+} > \text{Fe}^{3+} > \text{Cr}^{3+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{As}^{3+} > \text{Pb}^{2+}$. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1256–1264, 2001

Key words: chelating resin; poly(hydroxamic acid); methyl acrylate; sago starch; binding capacity

INTRODUCTION

Polymeric chelating resins containing the hydroxamic acid group are not yet commercially available, but poly(hydroxamic acid) resin seems to have commercial potential, considering that hydroxamic groups can form complexes with a wide range of metals.¹ It has been found to be an effective chelating ligand with the ions such as V^{5+} ,

Fe^{2+} , Fe^{3+} , Cu^{2+} , Cr^{3+} , Zn^{2+} , Au^{3+} , Ag^+ , Co^{2+} , Cd^{2+} , Ni^{2+} , Hg^{2+} , Pb^{2+} , and UO_2^{2+} . Kern and Schulz² synthesized polymeric hydroxamic acid by a reaction with poly(methyl acrylate) (PMA) and hydroxylamine in benzene. Several other resins containing hydroxamic acid groups were prepared from Amberlite IRC-50 by conversion of the carboxylic acid to acid chloride³ or to an ester⁴ and nitrile⁵ followed by treatment with hydroxylamine. Vernon et al.^{6–8} synthesized resins from acrylonitrile–divinylbenzene copolymers and studied their chelating abilities for various metal ions, and they were used for the recovery of metal ions. Wan Yunus⁹ studied the synthesis optimization and application of poly(hydroxamic acid) resin. Much atten-

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Contract grant sponsor: Ministry of Science and Education; contract grant number: 09-04-02-0057.

Journal of Applied Polymer Science, Vol. 79, 1256–1264 (2001)
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tion has been given to the synthesis of these chelating resins and application to the immobilization of enzymes, as well as applications in medicine, agriculture, etc.¹⁰

Ion-exchange resins bearing chelating functional groups have long been of interest for removing specific metals from water. The design of such chelating ligands depends on the stability of the basic macromolecular network and its ability to add the desired chelating functional group, which suits the specific metal. However, this may be the first approach to synthesis of a poly(hydroxamic acid) chelating resin from PMA-grafted sago starch. In this communication, a poly(hydroxamic acid) chelating resin was prepared by a modified method from a cheap starting material and the chelating behavior was examined using some metal ions.

EXPERIMENTAL

Materials

Sago starch was obtained from Tepung Sago Ind. Ltd. (Kuala Lumpur, Malaysia). The methyl acrylate monomer was purchased from Merck (Schuchardt, Germany). To remove the inhibitor, the monomer was passed through a column, which was filled with chromatographic-grade activated alumina. The monomer was stored at -10°C and the purified monomer was used as soon as possible. Ceric ammonium nitrate (BDH, Poole, England), hydroxylamine hydrochloride (Fluka, Messerschittstr, Switzerland), methanol (Beaker, New Jersey, USA), and other chemicals used were analytical reagent grade.

Graft Copolymerization of Methyl Acrylate onto Sago Starch

Exactly 10.00 g of sago starch and 400 mL distilled water were placed into a 1-L flask, which was equipped with a mechanical stirrer and condenser, and immersed in a thermostated water bath. The starch slurry was preheated at 80°C for about 30 min. It was continuously stirred and purged with N_2 gas. After gelatinization, the flask contents was then cooled to 50°C and 8.0 mL diluted sulfuric acid ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}/1 : 1$) was added to the mixture. After 5 min, 40 mL of a 0.1M ceric ammonium nitrate solution was added to the mixture. Exactly 10 min later, 26.0 mL of the methyl acrylate monomer was added and the

mixture was stirred for 1 h. After a complete reaction, the product was cooled under running tap water and poured into 1 L of methanol to induce precipitation. The grafted copolymer was washed several times with methanol : water (4 : 1), and then the product was dried at 50°C to a constant weight.¹¹

After copolymerization, the product was crushed and screened so that the particle size was between 100 and 400 μm . This grafted copolymer was used in the resin preparation.

Preparation of Chelating Resin Containing Hydroxamic Acid Groups

The preparation of a resin containing hydroxamic acid is based on the treatment of poly(acrylate ester) with hydroxylamine.^{12,13}

Preparation of Hydroxylamine (NH_2OH) Solution

Exactly 42.10 g of hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) was dissolved in a 300 mL methanolic solution (methanol : water/5 : 1). The HCl was neutralized by the NaOH solution and the NaCl precipitate was removed by filtration. The pH of the reaction solution was adjusted to pH 13 by addition of the NaOH solution. The reaction medium was maintained at a methanol-to-water ratio of 5 : 1.

The preparation was carried out in a 1-L single-neck flask, which was equipped with a mechanical stirrer and condenser, and immersed in a thermostated water bath. Exactly 20.00 g PMA-grafted sago starch was placed in the flask and the hydroxylamine solution was added to the flask. The reaction was carried out at 72°C for a 2-h duration. After completion of the reaction, the resin was separated from the solution by filtration and washed several times with a methanolic solution (methanol : water/4 : 1). Then, the resin was treated with 200 mL of a methanolic HCl solution (0.2M) for 5 min at least. Finally, the resin was filtered and washed several times with the methanolic solution (methanol : water/4 : 1) and then dried at 50°C to constant weight.

Resin Characterization

Qualitative Test of Hydroxamic Acid Functional Groups

About 0.2 g of the wet resin was shaken with the vanadium (V) ion in a dilute hydrochloric acid solution and a dark purple complexation on the resin beads was observed.

Hydrolysis of Poly(hydroxamic acid) Resin

Exactly 1.00 g of the resin was placed into a 100-mL flask and 50 mL of 1M HCl was added. The flask was fitted with a condenser and immersed in the thermostated water bath. The hydrolysis was carried out at 90°C for reaction periods of 30 and 120 min. After completion of the hydrolysis period, the product was washed thoroughly with a methanol–water solution and dried at 50°C to constant weight.

FTIR Analysis

Infrared spectra of polymer samples as KBr pellets were obtained using an FTIR spectrometer (Perkin–Elmer 1725).

Swelling Study of the Resin

Exactly 0.5000 g of dry resin was soaked in distilled water for 12 h and filtered under slightly reduced pressure. The filtration was continued for exactly 0.5 min after the removal of the surface water. The swollen resin was then pressed lightly between filter papers to remove any remaining surface water and the resin was rapidly weighed.¹⁴

Cation-exchange Capacity

A sample (about 5.0 g) of the ion exchanger was completely converted to the H⁺ form by treatment with a liberal excess of a methanolic solution of HCl (0.2M) in a conical flask using batch equilibration. To remove sorbed HCl, the resin was then washed with methanol–water until the washing solution became free of Cl[−] and the resin was dried at 50°C to a constant weight. The H⁺ form of the resin, 0.2000 g, was weighed into a 250-mL Erlenmeyer flask. Exactly 25 mL of a standard 0.1M NaOH solution was added and the flask was shaken for 4 h. After shaking, 10-mL aliquots of the supernatant solution was back-titrated to the phenolphthalein end point with a standard 0.1M HCl solution.¹⁵

Sorption of Metal Ions by Batch Technique

The metal ion binding capacity was measured by a batch equilibration technique for solutions of varying pH (pH 2–6). For the batch technique, the resin (100–200- μ m size) was dried at 50°C to a constant weight. Exactly 0.2000 g of the dry resin was placed into a series of 100-mL polyethylene bottles and the resins were allowed to equil-

ibrate with 25 mL distilled water for at least 10 min. Then, 20 mL of a 0.1M sodium acetate buffer solution at various pH's was added, and 10 min later, 20 mL of a 0.1M metal ion solution was added to each bottle. The mixtures were shaken for 24 h using a rotary shaker. After equilibration was completed, a 5-mL supernatant solution was collected for metal ion determination. The initial and final metal ion concentrations were determined using atomic absorption spectroscopy (GBC-903).

Kinetic Exchange

The rate of exchange of Cu²⁺ in acetate buffer at pH 4 was determined by placing 0.1500 g of resin beads in contact with 10 mL of the 0.1M Cu²⁺ solution for various time intervals. The Cu²⁺ ion concentration was determined as described above. The time required for 50% exchange ($t_{1/2}$) was calculated from the plot of the Cu²⁺ capacity (mmol g^{−1}) versus time.¹⁶

Sorption of Metal Ion with HCl

Exactly 0.1500 g of the resin was placed into a series of polyethylene bottles. Ten milliliters of solutions of various concentrations of HCl ranging from 0.001 to 1M was added. Ten milliliters of a 0.1M metal ion solution was added to each mixture. The mixtures were shaken for 24 h and the metal ion concentrations were analyzed as above.

Thermogravimetric Analysis

Thermogravimetry (TG) experiments were performed using a DuPont thermal analyzer (Model-990). The analyses are carried out in a N₂ atmosphere from room temperature to 1000°C at a heating rate of 10°C min^{−1} with a N₂ flow rate of 50 mL min^{−1}. Primary thermograms were obtained by plotting the percent residual weight against the temperature.

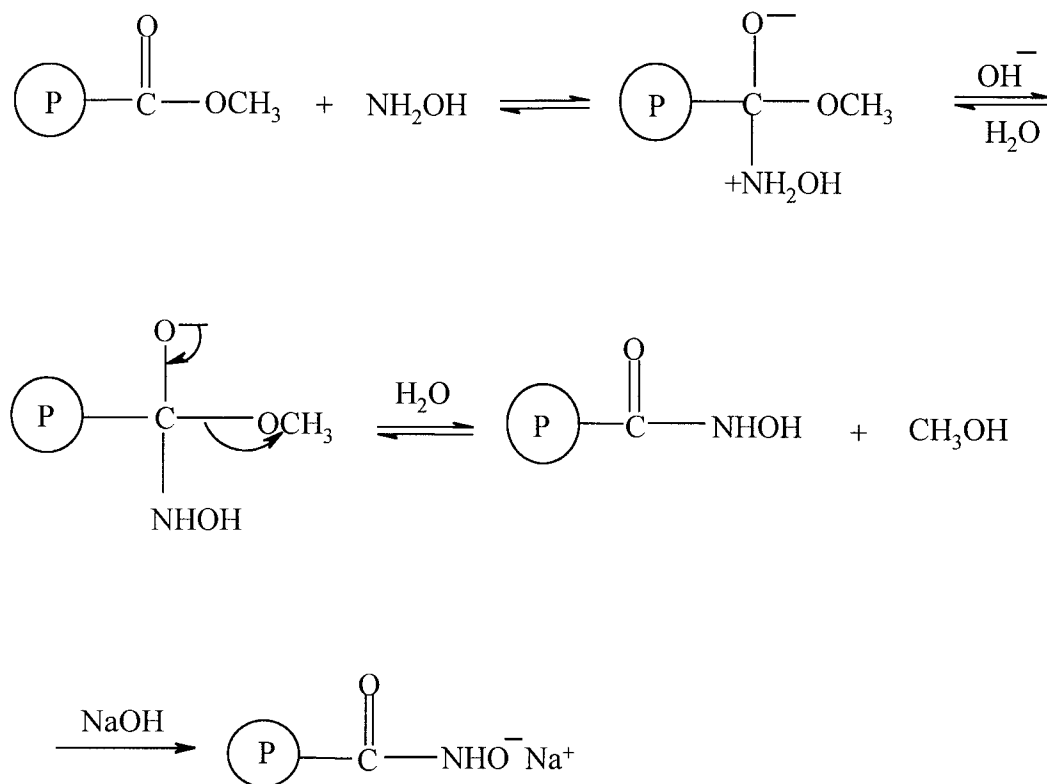
Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) experiments were carried out with a Polymer Laboratories PL-DSC with the N₂ flow rate set at 50 mL min^{−1}. The DSC thermograms were obtained for the PMA-grafted sago starch and poly(hydroxamic acid) resin, which were packed into Al pans, and heated at a rate of 10°C min^{−1}.

RESULTS AND DISCUSSION

Grafted Copolymers

The PMA-grafted sago starch was obtained by a free-radical initiating process. The optimum reac-



Scheme 1 Reaction mechanism of converting poly(acrylate ester) into poly(hydroxamic acid) via treatment with hydroxylamine in an alkaline medium.

tion conditions used for obtaining the PMA-grafted copolymer at the concentration of ceric ammonium nitrate, methyl acrylate, sulfuric acid, and sago starch (expressed as an anhydroglucose unit) were 8.77×10^{-3} , 0.803, 0.175, and 0.135 mol L⁻¹, respectively. The reaction temperature and period were 50°C and 60 min, respectively.

Poly(hydroxamic acid) Resin

The common method of hydroxamic acid preparation is the reaction between an ester and hydroxylamine in an alkaline medium. The optimum experimental parameters such as the PMA-grafted copolymer–hydroxylamine ratio, 1 : 1; reaction period, 2 h; temperature, 72°C; reaction medium methanol–water ratio, 5 : 1; and pH, 13, of the reaction medium were determined and used.

The mechanism of grafting methyl acrylate onto sago starch by ceric initiation was presented elsewhere.¹⁷ Here, the mechanism of the reaction of poly(acrylate ester) with hydroxylamine, giving the conversion to poly(hydroxamic acid), is shown in Scheme 1. This mechanism is based on the mechanism suggested by Domb et al.¹⁰

Qualitative Test for Hydroxamic Acid Functional Groups

The qualitative test for the hydroxamic acid group in the resin can be performed by a visual color test.^{4,9} The presence of hydroxamic acid groups on the resin was confirmed by the formation of a dark purple color with vanadium ions. The purple color was not observed when PMA-grafted sago starch was reacted with the vanadium under similar conditions.

It was also observed that when a solution of Fe^{3+} or Cu^{2+} was added to the hydrated resin the swollen resin turned deep brown or blue–green, respectively, which also supports the presence of the hydroxamic acid group on the prepared resin. It was also observed that the resin, when it was in the metal complex form, shrank significantly. This behavior provides additional evidence for a significant concentration of hydroxamic acid groups on the polymer backbone.¹⁰

Analysis of FTIR Spectra

The FTIR spectrum of sago starch showed the characteristic absorption bands at 3402 and 2930

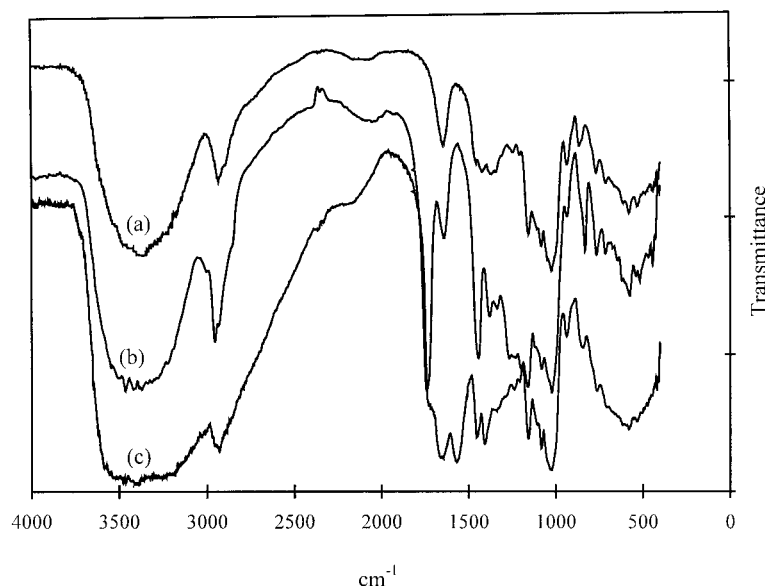


Figure 1 FTIR spectrum of (a) sago starch, (b) PMA-grafted sago starch, and (c) poly(hydroxamic acid) resin.

cm^{-1} due to O—H and C—H stretching modes, respectively, and other absorption bands at 1646 and 1024 cm^{-1} for O—H and C—H bending, respectively, as shown in Figure 1(a). The FTIR spectrum of purified PMA-grafted sago starch shows a new absorption band characteristic of an ester at 1741 cm^{-1} (C=O stretching mode) in addition to the same absorption bands of sago starch as shown in Figure 1(b). Figure 1(c), the C=O band of 1741 cm^{-1} had disappeared and a new band associated with hydroxamic acid (C=O at 1646 cm^{-1}) and an amide II band (N—H at 1568 cm^{-1}) appeared. These new bands suggest that the material is poly(hydroxamic acid) from PMA-grafted sago starch.

Hydrolysis of Hydroxamic Acid by Hydrochloric Acid

Hydrolysis of hydroxamic acid to convert it into carboxylic acids and hydroxylamines can be carried out in both acidic and alkaline conditions.¹⁸ In this study, two samples of hydroxamic acid were separately hydrolyzed in a 1M HCl solution for 30 and 120 min. After the hydrolysis, the FTIR spectra of both products were taken. These are presented in Figure 2(b,c). In both cases, the carbonyl band of hydroxamic acid shown in Figure 2(a) at 1646 cm^{-1} disappeared and a new band corresponding to the carboxylic acid at 1714 cm^{-1} was produced as given in Figure 2(b,c). These

provide strong evidence for the presence of hydroxamic acid groups in the grafted copolymer product.

Sorption of Metal Ions by Batch Method

The sorption behavior of the poly(hydroxamic acid) resin toward metal ions was investigated by the study of resin binding of Cu^{2+} , Fe^{3+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cr^{3+} , As^{3+} , and Pb^{2+} ions in aqueous solutions. The study was carried out in a sodium acetate buffer solution from pH 2 to 6. From the results, one can infer that the relative amount of metal ion taken up by the resin increases steadily with increase of the pH of the medium (Fig. 3). This resin exhibits high affinity for copper, iron, chromium, and nickel. The binding capacities of Cu, Fe, Cr, and Ni were 3.46, 2.45, 2.43, and 2.34 mmol g^{-1} , respectively, at pH 6. Although the binding capacity of copper is the highest, other metal ions also have significant sorption capacity. The sorption capacities of Cu, Fe, Cr, Ni, Co, Zn, Cd, As, and Pb ions were pH-dependent and its selectivity toward these metal ions is in the following order: $\text{Cu}^{2+} > \text{Fe}^{3+} > \text{Cr}^{3+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{As}^{3+} > \text{Pb}^{2+}$. The complexation of hydroxamic acid with a bivalent metal ion is shown in Scheme 2.

Most hydroxamic acid complexes with transition metal salts are highly colored. It has been observed that complex formation requires the hy-

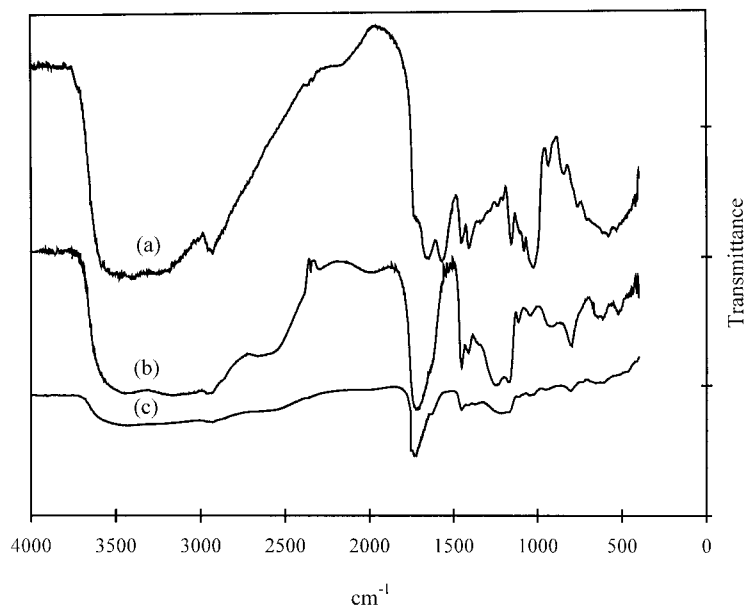


Figure 2 FTIR spectrum of (a) poly(hydroxamic acid) resin, (b) 30-min hydrolysis of resin, and (c) 120-min hydrolysis of resin.

droxylamine oxygen to be unsubstituted, although the nitrogen may bear a substituent.¹⁹ Much evidence is now accumulated that indicates that the hydroxamate anion is a bidentate ligand and forms a complex in which the metal ion is bound to both oxygen atoms.^{1,2,18,19}

The sorption rate study of the Cu^{2+} ion was also carried out in a buffer solution at pH 4. The sorption rate of the Cu^{2+} ion under these conditions was very fast, that is, $t_{1/2} < 5$ min (Fig. 4). The resin has the advantage of a fast rate of equilibrium and a negligible affinity toward alkali metal ions.

The poly(hydroxamic acid) resin was soaked in distilled water and swelling of the resin was observed. Maximum absorption was $90 \text{ g water g}^{-1}$. High water regain may allow better interaction with metal ions and is favorable for the kinetics of extraction.⁶ High water regain was presumably a result of the high hydrophilicity of the acrylate and hydroxamic acid groups,¹⁰ in addition to the presence of OH groups in the starch sample.

The cation-exchange capacity of the poly(hydroxamic acid) resin was determined based on the amount of sodium hydroxide reacted with the H^+ form resin. The resin was reacted with a specific amount of a $0.1M$ NaOH solution and the excess sodium hydroxide was measured by back titration to the phenolphthalein end point with a standard HCl solution.¹⁵ The cation-exchange capacity and

other physical and chemical properties of the resin are presented in Table I.

The sorption capacities of some metal ions using this poly(hydroxamic acid) resin are comparable to other research reported.^{7,9,12} An extensive study on poly(hydroxamic acid) resin containing crosslinked divinylbenzene was undertaken by Vernon and Eccles.⁶ They thoroughly studied the chelating abilities for various metal ions and significant sorption capacities of copper, iron, uranium, silver, and gold were obtained. However, they found that the rate of sorption was not rapid, that is, $t_{1/2}$ is 43 min. Wan Yunus⁹ studied metal capacities using the poly(hydroxamic acid) resin and also used divinylbenzene as a crosslinker. Metal capacities were high and the kinetics of the metal ion exchange were much improved ($t_{1/2} = 8$ min) in comparison with the earlier poly(hydroxamic acid) resin. He also evaluated the resin in terms of its ability to remove uranium from seawater. Poly(hydroxamic acid) in gel or water-soluble form was prepared from polyacrylamide by Domb et al.¹⁰ and this polymer exhibited high affinity to iron and copper and binding of 3.0 mmol g^{-1} for both metals was achieved. Takahiro et al.²⁰ prepared a chelating resin bearing dihydroxamic acid groups and the absorptive ability for uranium in seawater was described as $40 \mu\text{g uranium g}^{-1}$. However, although the overall metal ion capacities of our poly(hydroxamic acid)

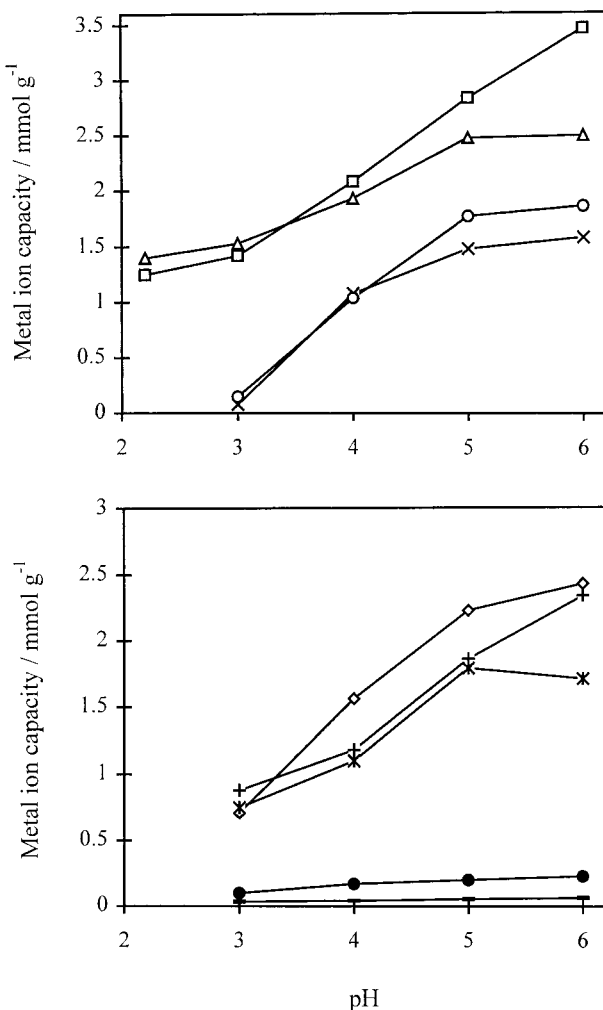
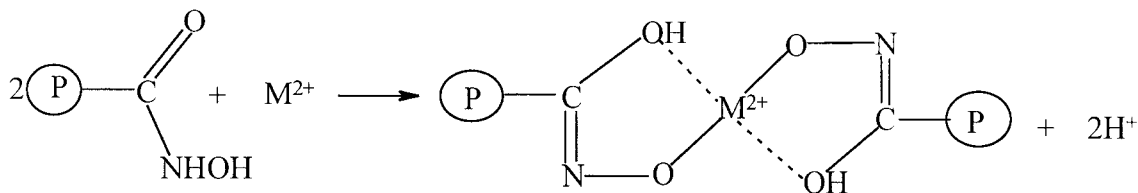


Figure 3 Metal ion capacities of poly(hydroxamic acid) resin as a function of pH. Batch technique; amount of resin, 0.2000 g; resin particle size, 100–200 μm ; shaking time, 24 h. —□—, Copper; —△—, Iron; ×, Cadmium; —○—, Cobalt; +, Nickel; ◇, Chromium; *, Zinc; —●—, Arsenic; —●—, Lead.

resin are similar to those of other research workers, the rate of sorption is much better ($t_{1/2} < 5$ min) than for other reported poly(hydroxamic acid) resins.



Scheme 2 Complex formation of poly(hydroxamic acid) and a bivalent metal ion.

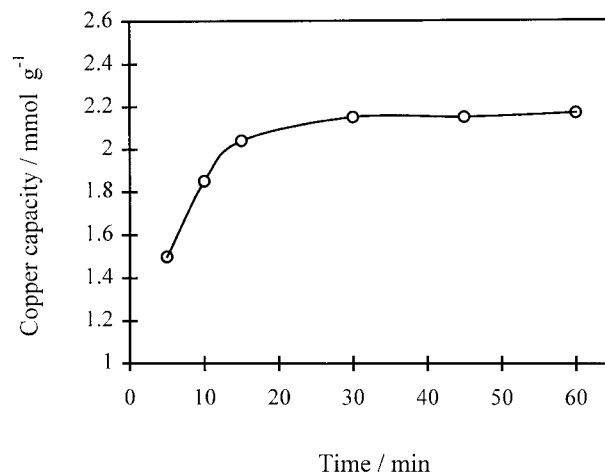


Figure 4 Exchange rate of copper by poly(hydroxamic acid) resin. Batch technique; amount of resin, 0.1500 g; resin particle size, 100–200 μm ; sodium acetate buffer, pH 4.

Effect of HCl on Sorption Capacity

The binding capacities of poly(hydroxamic acid) resin for Cu^{2+} , Fe^{3+} , Co^{2+} , and Cd^{2+} ions were also investigated in the presence of HCl at various concentrations. The Cu^{2+} capacity decreased gradually from 1.31 to 0.05 mmol g^{-1} with increase of the acid concentration from 0.001 to 1.0M HCl (Fig. 5). The capacity for Fe^{3+} follows the same trend as that of copper. Few Co^{2+} or Cd^{2+} ions were sorbed on the resin over the range from 0.1 to 1.0M HCl. The sorption behavior of the resin toward metal ions in the presence of 1.0M HCl reflects the instability of their hydroxamic acid complexes.

Thermogravimetric Analysis

Thermogravimetry (TG) curves for the thermal degradation of PMA-grafted sago starch and poly(hydroxamic acid) resin are presented in Figure 6. The decomposition of PMA-grafted sago starch started at 340°C with a 7% weight loss, whereas the weight loss of poly(hydroxamic acid) resin at

Table I Physical and Chemical Properties of Poly(hydroxamic acid) Chelating Resin

Physical or Chemical Properties	Parameters
Percent of grafting	130
PMA concentration (%)	57
Sago starch concentration (%)	43
Particle size (μm)	100–200
Water regain (g water g^{-1})	90
Cation-exchange capacity (mmol g^{-1})	6.03
Exchange rate ($t_{1/2}$ min)	<5

the same temperature (340°C) is 17%. The main weight loss of PMA-grafted sago starch occurs from 325 to 500°C, whereas for the poly(hydroxamic acid) resin, weight loss occurs from 205 to 560°C. The thermal stability of the poly(hydroxamic acid) resin was slightly higher than was that of PMA-grafted sago starch beyond the temperature of 460°C. It was found that the poly(hydroxamic acid) resin is more thermally stable than is the grafted copolymer sample at higher temperature.

Differential Scanning Calorimetry (DSC) Analysis

The DSC curves of the poly(hydroxamic acid) resin and PMA-grafted copolymer are presented in Figure 7. The PMA-grafted copolymers showed

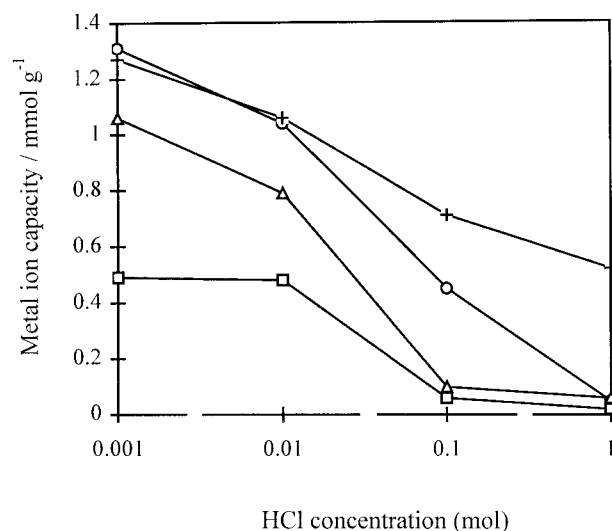


Figure 5 Effect of HCl concentration on the metal ion capacities of poly(hydroxamic acid) resin. Batch technique; amount of resin, 0.1500 g; resin particle size, 100–200 μm ; shaking time, 24 h. —○—, Copper; —△—, Iron; —□—, Cobalt; —◇—, Cadmium.

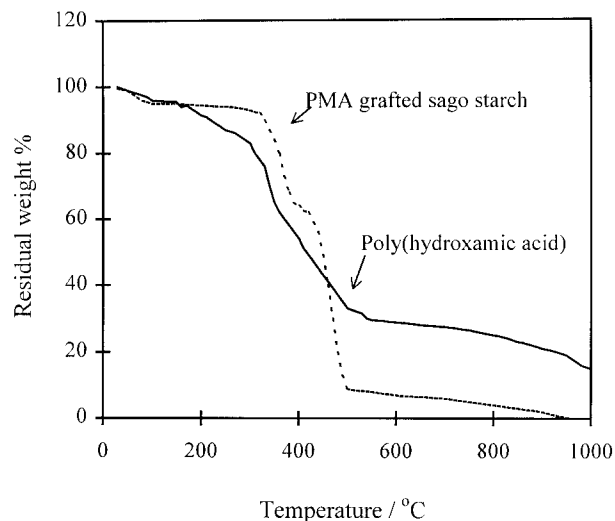


Figure 6 Thermograms of PMA-grafted sago starch and poly(hydroxamic acid) resin.

an endothermic transition at 314 and 417°C with a little initial moisture dehydration, whereas the poly(hydroxamic acid) resin exhibited an exothermic transition at 190°C. There was a new exothermic transition in the poly(hydroxamic acid) resin probably due to the enhancement of the interaction between the carbonyl groups of hydroxamic acid and the hydroxyl groups in the sago starch. The exothermic transition suggested that the hydroxamic acid functional groups were present in the grafted copolymers.

CONCLUSIONS

A chelating resin containing hydroxamic acid as a functional group was synthesized from the PMA-

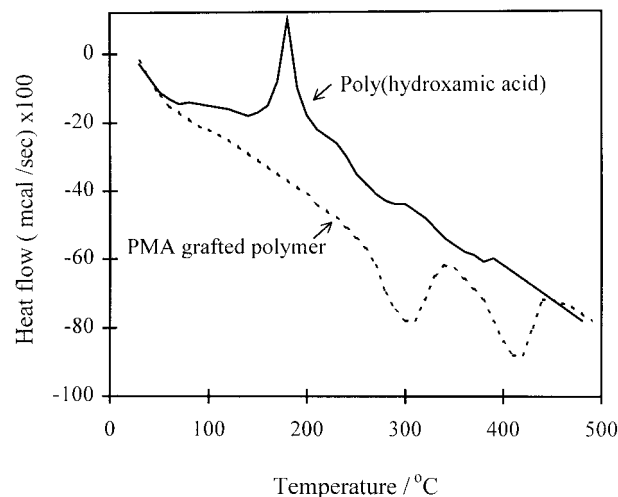


Figure 7 DSC thermograms of PMA-grafted copolymer and poly(hydroxamic acid) resin.

grafted copolymer. The PMA-grafted copolymer was prepared by using an methyl acrylate monomer and sago starch. The chelation behavior of the resin toward some metal ions was examined. The binding ability of the resin for some metal ions was excellent. Also, the rate of exchange was rapid, $t_{1/2} < 5$ min. The sorption capacities of the resin for Cu, Fe, Cr, Ni, Co, Zn, Cd, As, and Pb ions were found to be pH-dependent. The resin has the advantage of a faster rate of equilibrium compared to earlier hydroxamic acid resins, probably due to the presence of the new backbone polymer. In the future, our work will be extended to the extraction of toxic metals from the environment.

This research was supported by an IRPA grant (No. 09-04-02-0057), Ministry of Science and Education, Malaysia, 1997.

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