Synthesis and Characterization of Highly Porous Poly(methacrylic-co-triethylene glycol dimethacrylate) by Suspension Polymerization

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ABSTRACT: Porous poly(methacrylic-co-triethyleneglycol dimethacrylate) (MAA-3G) was prepared by suspension polymerization using benzoyl peroxide as an initiator, poly(vinyl alcohol) as a protective colloid, and n-hexane as a porogenic agent. The prepared polymer was base hydrolysed using hydroxyl amine and sodium methoxide into the corresponding polyhydroxamic acid (HYOX). The metal binding behavior of polyhydroxamic acid with various metal ions, the effect of pH on the metal ion capturing, and the selectivity of the resin towards the different metal ions were also examined by means of atomic absorption spectrophotometer. The thermal stability of the prepared base-hydrolysed polymer and the metal polymer complex was examined by thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC). The prepared porous polymer methacrylic-co-triethyleneglycol dimethacrylate and its different modulated forms were characterized by means of FTIR specroscopy and scanning electron microscope. The hydroxamic acid content was also examined by elemental analysis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 149–159, 1999

Key words: suspension polymerization; porous polyhydroxamic acid; chelating polymer; methacrylic acid; triethylene glycol dimethacrylate

INTRODUCTION

Porous polymeric materials are used as sorbents, stationary phase for gas chromatography, ion-exchange resins, membrane materials and carriers for catalysts, as well as biologically active substances.[1–2] Among the various functional polymers, chelating resins attained considerable attention in some fields such as removal of harmful trace metal ions because of their high selective-adsorption capacity.[3–6] Kern[7] and Shults synthysized the polyhydroxamic acid (HYOX) resins from poly(methyl acrylates) and investigated the adsorption behavior towards metal ions. The relationship between the structure of HYOX and its chelating ability were investigated by Philips and Fritz.[8–9] Crosslinked polymer particles with a permanent macroporous structure (pore size > 500 Å in diameter) are the most efficient materials for many separation processes, the macropores of the particles allow biomolecules in the general size of 500,000 Da to be separated.[10–11] Such polymer particles are normally produced with suspension polymerization by adding an inert diluent to the polymerizing mixture. After polymerization, the inert diluent is removed, leaving a porous structure within the polymer particles.[12–13] Moderately crosslinked poly-

Figure 1   Synthesis of porous polyhydroxamic acid.

(methacrylic) gels are widely used as carboxilic cation exchangers in water treatment and as specific sorbents, e.g., in separation processes for antibiotics.[14] Gustafson[15] assumed that the copolymer of methacrylic acid and divinyl benzene (5%) was a homogeneous gel, but Gregor et al.[16–17] assumed that crosslinked methacrylic polymers are composed of chains having widely distributed lengths between the network junction points. Porous structures in polymer networks are known to be formed as a result of phase separation during their formation process.[18,19] The total volume of voids (pores) in the network increases as the concentration of bifunctional monomer (crosslinker), or that of diluent increases, or as the solvating power of the diluent decreases. Relationship between the synthesis conditions and the porous structure of hydrophilic copolymers such as styrene-divinyl benzene copolymers have been studied for many years.[20,21] The aim of the present work is to synthesize a porous resin of high metal-ion-absorption capacity.

EXPERIMENTAL

Methacrylic acid (MAA) and triethylene glycol dimethacrylate (3G) supplied from Redel de Haën AG. (Germany) were purified by being passed through acive alumina. Poly(vinyl alcohol) (molecular weight 70,000–100,000 hot-water soluble), and benzoyl peroxide reprecipitated from chloroform solution by methanol were supplied from Sigma Chemical Company. n-Hexane and all the metal salts supplied from El Nasr Pharmacetical Company (Cairo, Egypt) were of analytical grade.

Suspension Copolymerization of MAA and 3G

Copolymerization was carried out in a 500 mL round bottom three neck flask fitted with a mechanical stirrer, nitrogen inlet and condenser. The reaction was carried at 80 + 1°C 0.200 mL distilled water 1% poly(vinyl alcohol) solution was

a

b

Figure 2 Scanning electron microscope of poly methacrylic acid-co-tri ethylene glycol dimethacrylate beads. (a) Magnification $\times 150$, (b) $\times 1000$.

first introduced in to the reactor, heated to the reaction temperature, stirred at 500 rpm and flushed with nitrogen for 15 min.

The monomer mixture MAA (20 mL) and 3G (15 mL) was purified from inhibitor by passing through acive alumina for 1 h. n-Hexane (5 mL) was added to the purified monomer mixture as the porogenic agent. Finally, benzoyl peroxide (0.5 g) was dissolved in the monomer phase. The monomer phase was introduced to the reactor in a stepwise manner in 30 min, in order to ensure good monomer phase dispersion. The copolymerization reaction was shown to be completed after $\sim$ 150 min where spherical beads were formed.

Purification

The copolymer beads were first washed with water and then subjected to a soxhlet extraction with acetone for 8 h to dissolve any homopolymer and finally dried at 40°C.

Solvent Treatment

The copolymer beads were subjected to a large series of low polarity and high polarity solvents and it was found that the copolymer beads are completely insoluble in cyclohexanol, cyclohxanone, xylene, DMF, DMSO, methylene chloride, chloroform, dioxane, and ethylmethyl ketone.

Average Particle Size

A large number of sample particles of poly(MAA-3G) were imaged using SEM, and the average particle diameter was found to be 324 μm.

Scanning Electron Microscope Treatment

The porous polymer particles were first gold plated and then were imaged using SEM (Js 20 Tokyo, Japan). Figure 2(a) shows the completely spherical porous poly(MAA-3G) beads. Figure 2(b) shows a higher magnification of Figure 2(a) indicating high specific surface area.

Thermal Gravimetric Analysis TGA

Figures 5–7 show three thermal gravimetric analysis spectra of poly(MAA-3G), HYOX, and nickel complex of poly(HYOX) respectively. The differential curves show that the three samples loss is 4.775 to 10.44 weight % at $\sim$ 100°C which may be attributed to the presence of absorbed water molecules within the polymeric chains. As seen in Figures 5–7 the three samples are thermally stable up to 180°C. The peaks which appear after 200°C are attributed to the chemical decomposition of the resin samples, i.e., loss of CO_2, NH_3. This thermal stability enables the use of such poly(HYOX) resin in the field of chromatographic separation techniques.

Figure 3   FT-IR spectrum: Polymethacrylic acid-co-Triethylene glycol di methacrylate (MAA-3G).

Differential Scanning Calorimeter (DSC)

The same three samples poly(MMA-3G), HYOX and Ni^{2-}-HYOX complex) were subjected to DSC measurements and represented in Figures 8–10, the first three endothermic peaks at $\sim 100°C$ in the three figures are attributed to the loss of moisture. The second three endothermic peaks at 237.76°C for (HYOX), 235.13°C for (MAA-3G) and 261.29°C for (Ni-HYOX) are attributed to significant thermal decomposition. The third three peaks in the charts are endothermic for MAA-3G and HYOX and exothermic for (Ni^{2+}-HYOX) complex, which is attributed to the nickel ion coordination with poly(HYOX). The nickel complex decomposition peak at 344°C is shown to be sharp compared with that of MAA-3G and HYOX which may be attributed to the attachment of the polymeric chains by the nickel ion.

First- and Second-Run DSC

One sample of polyhydroxamic acid ~ 3.0 mg was subjected to first and second runs to ensure

Figure 4   FT-IR spectrum: Poly hydroxamic acid with its metal complexes, (a) poly hydroxamic acid pure, (b) Ni-HYOX, (c) Fe-HYOX, (d) Pd-HYOX, (e) Co-HYOX, (f) Cu-HYOX.

Figure 5 TGA spectrum: Poly methacrylic acid-co-triethylene glycol di methacrylate (MAA-3G).

Figure 6 TGA spectrum: Poly hydroxamic acid (HYOX).

Curve 1: TGA
File info: 456   Tue Dec 2 11:42:53 1997
Sample Weight: 7.780   mg
C (N1 Comp) Prof Bakr/Faizalla   C (N1 Comp) Prof Bakr/Faizalla

ΔY -8.585 Wt. %
ΔY -6.386 Wt. %
ΔY -33.54 Wt. %

Peak 262.1 °C
Area -6.403 Wt. %

ΔY -27.71 Wt. %

ΔY -5.507 Wt. %

Peak 340.96 °C
Area -21.58 Wt. %

Peak 350.94 °C
Area -24.53 Wt. %

Powder   Engr E. Mokhtar
TEMP1: 50.0 C   TIME1:   0.0 min RATE1:   10.0 C/min   PERKIN-ELMER
TEMP2: 800.0 C   7 Series Thermal Analysis System
                                          Tue Dec 2 11:58:02 1997

Figure 7 TGA spectrum: Nickel complex of poly hydroxamic acid (HYOX).

KR - B-

File Name:	BAKRB.D60
Detector Type:	Shimadzu DSC-50
Acquisition Date:	97/12/06
Acquisition Time:	10:18:57
Sample Name:	NO. B
Weight:	2.410[mg]
Cell:	Aluminum
Atmosphere:	Nitrogen
Rate Flow:	30.00[ml/min]
Operator:	WARD

Temp Program

Rate	Hold Temp	Hold Time
[C/min]	[C]	[min]
10.0	500.0	0.0

DSC
mW

-0.39J
-0.16kJ/g

425.57C

-0.72J
-0.30kJ/g

235.13C

0.23J
97.32J/g

102.27C

Temp[C]

Figure 8 DSC spectrum: Poly methacrylic acid-co-triethylene glycol di methacrylate (MAA-3G).

Figure 9 DSC spectrum: Poly hydroxamic acid (HYOX).

the presence of moisture and the thermal stability of the resin HYOX. DSC in nitrogen atmosphere. From Figures 11 and 12 the peak at 100°C attributed to the presence of moisture was diminished. The second run shows that the polymer can be used several times without physical or chemical change.

RESULTS AND DISCUSSION

Absorption of Metal Ions by the Resin Poly(HYOX)

The chelating capacity of the resin for different s, p and d blocks metal ions was determined by the batch method. Accurately weighed resin samples

Figure 10 DSC spectrum: Nickel complex of poly hydroxamic acid (HYOX).

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Temp Program
Rate        Hold Temp Hold Time
[C/min]     [C]       [min]
10.0        200.0     0.0
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File Name:          AHMED.D20
Detector Type:      Shimadzu DSC-50
Acquisition Date:   97/12/30
Acquisition Time:   10:10:21
Sample Name:        POLYESTER
Weight:             3.170[mg]
Cell:               Aluminum Seal
Atmosphere:         Nitrogen
Rate Flow:          30.00[ml/min]
Operator:           WARD
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Figure 11 DSC spectrum: First run. Poly hydroxamic acid (HYOX).

(0.1 g) were equilibrated with 50 mL of 2000 ppm metal ion solutions in measuring flasks 50 mL for 24 h. After reaching equilibrium, the amount of metal ions remaining in the solution was determined by means of atomic absorption spectrophotometer. The data are given in Table I, from Table

Figure 12 DSC spectrum: First run. Poly hydroxamic acid (HYOX).

I, it is shown that the porous resin particles have very high metal-ion-absorption capacity. It reaches about ten times compared[1] with that prepared from ethylacrylate-co-divinyl benzene-co-ethylene glycol dimethacrylate. This is attributed to the higher hydrophilic character. The order of increasing absorption capacity is shown in Table II. Since the chelation is thought to be through the lone pair of the nitrogen in the hydroxamic acid group (—NHOH). The higher the electronegativity of the metal ion, the higher the absorption capacity of the resin. The data given in Table II agrees with the above statement, with the exception of copper and paladium ions as they have the highest electronegativity values but they don not have the highest metal-ion-absorbtion capacity. As the ionic radius decreases the diffusion of the metal ion through the polymer network increases with the result of higher absorption capacity. The data given in Table II are in agreement with the above concept but lead ion Pb^{2+} which have the largest ionic radius 1.2 Å is shown

Table I   Effect of pH on the Metal Binding Behavior of Poly(Hydroxamic) Acid

pH	Cd^{2+}	$Cr3^+$	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Pd^{2+}	Na^+	Pb^{2+}
0–1	39.02	48.02	49.50	56.02	60.50	53.04	58.03	50.92	64.85
1.1–2	43.02	65.01	84.50	87.03	87.30	70.02	83.21	57.65	70.15
2.1–3	56.04	78.03	84.40	92.02	89.00	79.59	87.00	68.35	76.76
3.1–4	64.53	83.02	86.60	93.01	90.45	83.26	89.25	75.65	86.69
4.1–5	79.51	85.02	89.60	98.95	91.00	85.54	90.36	80.02	90.88
5.1–6	82.02	89.04	91.25	99.02	93.35	87.01	90.36	80.23	92.00

Metal ion extracted % from 2000 ppm 100 mL salt solution of the poly hydroxamic acid resin (0.1 g).

to have high absorption capacity over the rest of the metal ions. The counterplay of the electronegativity and the ionic radius in addition to the thermodynamics of the chelation process determine the absorbtion capacity of each metal ion.

Effect of pH Poly(HYOX) the Metal Ion Absorption Capacity of the Resin

The chelating capacity of the resin poly(HYOX) for different metal ions was determined by the batch method described above at the acidic pH range 0–6. The data are given in Table I. From Table I, it is shown that the increase of hydrogen ion concentration [H^+] decreases the metal-ion-absorption capacity, which is explained by the protonation of the nitrogen atom of the poly-(HYOX) over which metal ion chelation occurs.

Metal Resin Kinetics

Resin samples (0.10 g) were placed in a 50 mL measuring flask containing 2000 ppm metal ion solutions. Shaking was begun immediately upon addition of the resin samples. At a regular time intervals (1 min), 10 mL of the residual solution was titrated against EDTA (0.01M) via compleximetric titration, and the concentration of the metal ion remaining in solution was determined. Table III shows the time required to reach the equilibrium state with different metal ions.

From Table III, it is shown that cobalt ion reaches the equilibrium after 3 min. However,

chromium ion reaches the equilibrium after 7 min. The metal ions Pb, Co, Fe, Ni, Cu are faster in reaching the equilibrium than Na and Cr. These results are shown to be compatible with the Pauling's electronegativity values.[22] In other words, the higher the metal ion electronegativity, the faster the rate of chelation.

Selectivity of the Prepared Poly(HYOX) towards the Different Metal Ions

Resin samples (0.10 g) were placed in a 100 mL measuring flask, containing two metal ions, each of which have a concentration of 2000 ppm. The samples were left for 24 h to ensure reaching the equilibrium state. The concentration of each metal ion was determined by means of atomic absorption spectrophotometry. The data are given in Table IV. From Table IV, it is clear that the selective absorption behavior does not change from the separate to the mixed state. The maximum relative difference was observed for the ion pair Cd/Na ($-0.54/-97.4$), which have an electronegativity difference of 0.77, and the minimum relative difference was observed for the ion pair Pd/Cu ($-44/-42$), which have electronegativity difference of 0.3.

IR Spectroscopy[23]

Comparison of the IR spectra of poly(MAA-3G) and its derivatives are shown in Figures 3, and 4 and Table V. All the IR figures show the charac-

Table II   The Electronegativity and the Ionic Radius of the Metal Ions

Property	Na^{2+}	Cd^{2+}	Cu^{2+}	Cr^{2+}	Pd^{2+}	Fe^{2+}	Pb^{2+}	Ni^{2+}	Co^{2+}
Electroegativity	0.93	1.7	1.9	1.6	2.2	1.8	1.8	1.8	1.8
Ionic radius Å	0.98	0.97	0.96	0.84	0.86	0.76	1.2	0.72	0.74

Table III   The Time Required to Reach the Equilibrium for Some Metal Ions

Metal Ion	Na^+	Pb^{2+}	Cr^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}
Time of equilibrium (min)	8.0	5.0	7.0	3.0	5.5	4.5

teristic peaks of (—C=O, N—H, O—H, C—N). The IR figures and Table V show the effect of metal ion interaction with the porous polymeric material.

From Table V, the wavelength absorption band of the carbonyl group is shifted to a negligible amount ~ 3 cm^{-1}, except in the case of paladium, the shift was observed to be ~ 16 cm^{-1}. The wavelength absorption band of the (C—N) group is considerably affected by the presence of metal ions. The wavelength is shifted to ~ 17 cm^{-1} to a lower wavelength from poly(HYOX) to metal-HYOX complex. The above results suggest that the carbonyl group of polyhydroxamic acid does not participate in the chelation ineraction except in the case of paladium-polymer complex. Thus, structure (b) is the most probable one for most metal-ion-polymer complex. However, paladium-ion-polymer complex is likely to have structure (a).

(a)   P- C—— NH-OH
          ‖
          O——▶ M^{2+}

HYOX Content

The HYOX content was determined through the estimation of the nitrogen content. The data are given in Table VI. In Table VI it is shown that the higher the time of hydrolysis, the higher the HYOX content. It was observed that if the hydro-

Table IV   Selectivity of the Resin Poly(HYOX) toward the Various Metal Ions

	Metal Ion Pair	Separate ppm	Mixed ppm
1	Na/Pb	1640/1830	649/851
2	Co/Cu	1980/1700	1020/668
3	Cu/Fe	1700/1790	753/902
4	Co/Fe	1980/1790	1121/623
5	Cd/Na	1640/1500	1631/39
6	Cu/Ni	1700/1870	901/879
7	Ni/Co	1870/1980	747/1100
8	Pd/Na	1800/1500	1320/234
9	Pd/Cu	1800/1700	1005/978
10	Ni/Pb	1870/1830	1579/320
11	Cu/Cd	1700/1640	1670/103
12	Cr/Cd	1800/1640	1649/222
13	Pb/Pd	1830/1800	692/1363
14	Ni/Fe	1870/1790	936/1239
15	Cr/Pb	1800/1830	1720/290

Selective binding of metal ions by poly(HYOX) at pH 5.5.

lysis time exceeds 3 h, the resin particles begin to degrade and become more fine.

Poly(HYOX) as a Catalyst-Supporting Material

The following procedures[8] were used to support the prepared polymer with metal and metal oxide catalysts. One g of the porous poly(HYOX) is immersed in different salt solutions (5000 ppm) of (Cr, Fe, Co, Ni, Pd, Cd, and Cu) and stirred at room temperature for 1 h. After the polymer turned to the characteristic color of the salt solution, it was filtered and dried at 60°C. The polymer was resuspended in ethanol. After that, 1.0 g of NaBH$_4$ was added to the suspension to reduce the metal ion M^{2+}, M^{3+} to the metallic state M^0. After 30 min, the polymeric material was turned to the metallic luster. The material was then left in benzene for 3 days after which it was redried and kept in a vial as a metal-porous polymer

(b)   P- C—— NH- OH
          ‖
          O   M^{2+}

Table V   Effect of Metal Ion-Polymer Interaction on the Absorption Wavelength of Some Functional Groups

	Wavelength Absorbtion cm^{-1}						
Functional Group	MMA-3G	HYOX	Co-Complex	Cu-Complex	Cd-Complex	Fe-Complex	Pd-Complex
C=O	1720	1718	1715	1718	1721	1719	1702
C—N	—	1458	1475	1476	1477	1476	1477

Table VI   Effect of Hydrolysis Time on the Hydroxamic Acid Content

Polymer	C%	H%	N%
a	56.0	5.6	0.0
b	46.5	6.2	10.0
c	37.5	5.9	19.0

Elemental analysis of: (a) poly(MAA-3G) dimethacrylate, (b) poly(HYOX) (hydrolysis time, 2 h), (c) poly(HYOX) (hydrolysis time, 3 h).

catalyst. In order to prepare the metal oxide-polymer catalyst. The above procedures were repeated except the reduction process was carried out in water instead of ethanol in which the material was turned black after a few minutes.

CONCLUSION

Porous polyhydroxamic acid resins have been prepared from methacrylic acid and triethylene glycol dimethacrylate by base hydrolysis. The prepared poly(HYOX) showed very high metal-ion-absorption capacity. The chelation process was evidenced to be through the lone pair of the nitrogen atom by means of IR spectroscopy. The prepared polymers was shown to be thermally stable up to 180°C as evidenced by TGA and DSC. Metal-poly hydroxamic acid catalysts were prepared by metal ion reduction using sodium tetrahydroborate $NaBH_4$.

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