

Synthesis of porous poly(hydroxamic acid) from poly(ethyl acrylate-co-divinylbenzene)

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Summary

Porous poly(hydroxamic acid) resins were prepared by suspension polymerization of poly(ethyl acrylate-co-divinylbenzene) followed by the reaction with hydroxylamine via nucleophilic substitution. Various degree of dilution and crosslinking ratio were applied to obtain suitable material for use as a chelating polymer. The effects of degree of dilution and crosslinking ratio on the surface morphology, hydroxamic acid group content, and apparent density were investigated in detail.

Introduction

Hydroxamic acids have been known for their chelation ability with heavy metals. It has been found to be an effective chelating ligand with the ions such as V^{5+} , Fe^{3+} , Mo^{6+} , Ti^{4+} , Hg^{2+} , Cu^{2+} , and UO_2^{2+} . A number of hydroxamic acid polymers have been synthesized by various methods to use as a chelating polymer. The chelating resins containing hydroxamic acid group are currently not commercially available but many studies have been accomplished to synthesize this type of chelating resin.

Kern and Schulz (1) synthesized polymeric hydroxamic acid by the reaction with poly(methyl acrylate) and hydroxylamine in benzene. Several other resins containing hydroxamic acid groups have been prepared from Amberlite IRC-50 by conversion of the carboxylic acid to the acid chloride (2) or to an ester (3) followed by treatment with hydroxylamine. Another approach consists in the treatment of polyacrylonitrile with hydroxylamine followed by hydrolysis of the intermediate amidoxime to synthesize chelating ion exchange resins containing pendant hydroxamic acid groups (4). Poly(acrylic acid) (5) and polyacrylamide (6) are other starting materials. Vernon and Eccles (7 - 9) synthesized resins from acrylonitrile - divinylbenzene copolymers and studied their chelating abilities for various metal ions.

In this present study, a new synthetic method to prepare a porous resin matrix from poly(ethyl acrylate-co-divinylbenzene) with a diluent has been developed and the resin bead was treated with hydroxylamine in the presence of sodium methoxide to obtain poly(hydroxamic acid), which would be used as a chelating polymer.

Experimental

Materials and reagent

Ethyl acrylate (EA) was washed twice with aqueous 5 % sodium hydroxide solution to remove inhibitors, then with distilled water several times. After washing, it was dried on calcium chloride for 24 hours. Divinylbenzene (DVB) as a crosslinking agent was 55 % mixture with ethylvinylbenzene and used as received.

The following chemicals : sodium sulfate, calcium carbonate, gelatine, 2,2,4-trimethyl pentane

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(TMP), hydroxylamine hydrochloride, sodium methoxide, solvents, and other reagents of GR grade were used without further purification.

Preparation of Crosslinked Resin Bead

Suspension polymerization of poly(ethyl acrylate-co-divinylbenzene)

Monomer EA was copolymerized with DVB by suspension polymerization technique. 600 ml distilled water, 9 g sodium sulfate, 6 g calcium carbonate, 30 ml of a 2 % aqueous gelatine solution were placed in a 1 l three-necked flask equipped with reflux condenser, mechanical stirrer, and thermometer. With stirring 0.2 g benzoyl peroxide, about 40 g of EA and DVB monomer mixture, and appropriate amount of TMP used as a diluent were added into the flask. The temperature of the stirred solution was raised to 95°C, maintained for an hour, lowered to 85°C, and then maintained for 4 hours. The resulting copolymer was filtered and washed with 1 N hydrochloric acid solution, distilled water, and methanol. Finally it was extracted with acetone in a Soxhlet apparatus for 24 hours and dried in air and in a vacuum oven at 40 °C for 24 hours.

Preparation of hydroxamic acid resin

To convert this resin into poly(hydroxamic acid) resin, 20.85 g of 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. 17.29 g of sodium methoxide was put into the solution followed by an addition of 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. And then it was extracted in a Soxhlet apparatus with acetone for 24 hours, air-dried, and dried *in vacuo* at 40 °C for 24 hours.

Characterization and Analysis

Infrared spectroscopy

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

Hydroxamic acid group content

Hydroxamic acid group content was derived from nitrogen content determined by Kjeldahl's microanalysis method (10).

Morphological observation

The resin surface was coated with gold and observed with scanning electron microscope (SEM, Philips XL-20 or Hitachi S-2500C).

Apparent density, and specific surface area

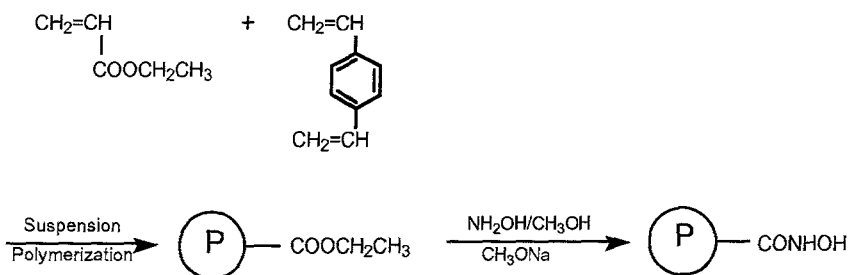
Apparent density was determined by the graduated cylinder method (11). The specific surface area was determined by the BET method (12) with N₂ adsorption on a Quantasorb surface area apparatus.

Results and discussion

The presence of the hydroxamic acid group in the resin has been confirmed by several methods (3). The first is a visual color test. Among many metal ions, vanadium ion gives a intense purple complex on binding with hydroxamic acid groups in acidic solution. The

formation of an intense purple complex between the hydroxamic acid resin and vanadium ion has been reported by Petrie (3). Infrared spectroscopy has been applied to show the presence of the hydroxamic acid group and nitrogen analysis of the final product can be also used. Acrylic polymer beads crosslinked with DVB are prepared from various combination of monomers with diluent (13 - 15), but few containing EA (16).

The synthetic routes for poly(hydroxamic acid) resins are shown in Scheme.



Scheme. Synthesis of poly(hydroxamic acid) resin.

The infrared spectrum of the EA-DVB copolymer (Fig.1 (a)) exhibits the C=O absorption at 1733 cm^{-1} along with absorption in the $700\text{-}1000 \text{ cm}^{-1}$ region caused by the aromatic rings in the DVB portion of the polymer. The infrared spectrum of the poly(hydroxamic acid) resin shown in Fig.1 (b) displays the characteristic absorptions of hydroxamic acids (17), the amine stretching absorption at 3400 cm^{-1} and new absorption at 1680 cm^{-1} (near C=O at 1730 cm^{-1}).

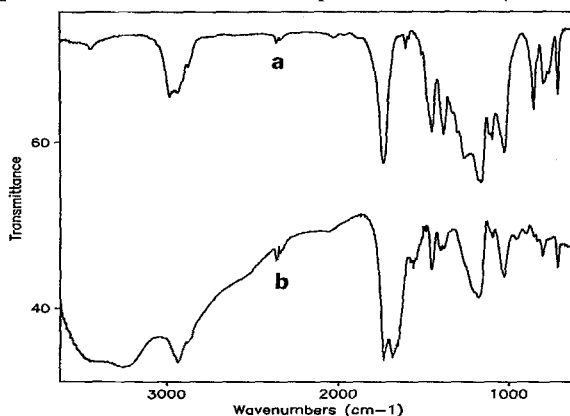


Fig.1 : Infrared spectra of (a) poly(EA-co-DVB) and (b) poly(hydroxamic acid).

The hydroxamic acid group content as calculated by the Kjeldahl's microanalysis method was shown in Fig.2. The values tend to decrease with increase in crosslinking ratio resulting from low ethyl acrylate content in the resin, rigid structure resulting that the small reagents cannot penetrate resin matrix deeply, and low compatibility with methanol used as a hydroxamation reaction medium. At lower crosslinking ratios as 5 and 8 mol%, resins prepared with dilution

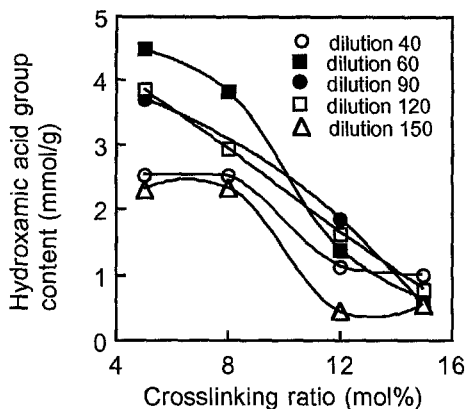


Fig. 2. : Hydroxamic acid group content of poly(hydroxamic acid) resins.

ratios as 5 and 8 mol%, resins prepared with dilution 60 and 120 vol% have more hydroxamic acid ligands than other resins expecting good adsorption capacity for metal ions.

It is well known that macroporous styrene-divinylbenzene copolymers are obtained when the ratio of DVB and inert medium volume overcomes a certain critical value in order to get a permanent structure (18). Also the formation of the macroporosity depends on the kinds and amounts of diluent and crosslinking agent. In EA-DVB system, monomer EA dissolves the resulting poly(ethyl acrylate) during polymerization process. TMP acting as a precipitating diluent plays a less important role when used by small quantity (dilution 40 and 60 vol%). Therefore gel-type resins were obtained at low degree of dilution and crosslinking ratio and these results are illustrated in Table 1. Despite the use of diluent, bead formation is fairly good except the case of high dilution. Bead destruction was accompanied during polymerization when high dilution (150 vol %) was applied, which resulted in powdery resin beads. Surface morphology of resin beads is shown in Fig.3 exhibiting gel-type resins (a), (b) and

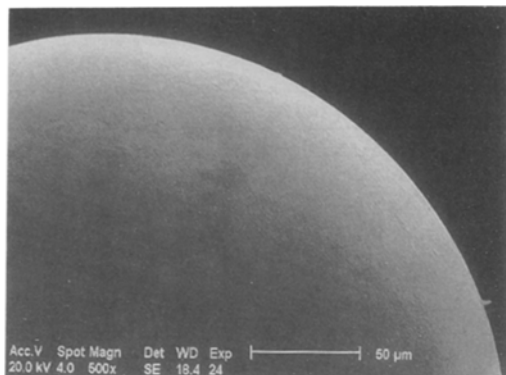
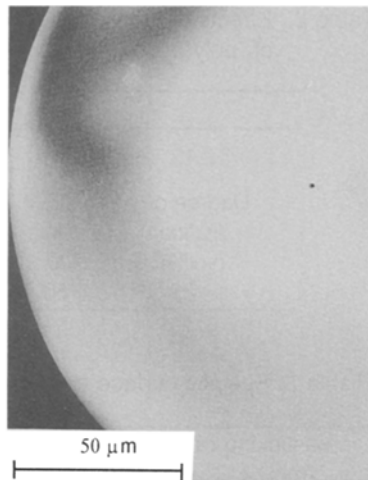
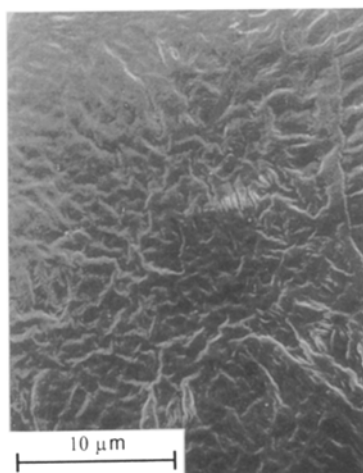
Table 1. Morphological appearance of various EA/DVB copolymers

Dilution (vol%)	DVB (mol%)			
	5	8	12	15
40	G	G	G	G
60	G	G	MP	MP
90	G	G	MP	MP
120	G	MP	MP	G
150	P	P	P	P

G : gel-type resin

P : powdery resin

MP : macroporous resin

**a****b****c****d****Fig.3 :**

SEM photographs of (a) crosslinking ratio 8 mol%, dilution 60 vol%, (b) crosslinking ratio 12 mol%, dilution 40 vol%, (c) crosslinking ratio 12 mol%, dilution 120 vol%, and (d) crosslinking ratio 15 mol%, dilution 90 vol%.

Table 2. Effects of crosslinking ratio and degree of dilution on the apparent density of poly(hydroxamic acid) resins

		DVB (mol%)			
		5	8	12	15
Degree of dilution (vol%)	40	0.671	0.645	0.638	0.594
	60	0.684	0.60	0.483	0.450
	90	0.556	0.571	0.383	0.422
	120	0.310	0.30	0.336	0.288
	150	0.150	0.163	0.285	0.161

Table 3. Specific surface area of various resins

crosslinking ratio (mol%)	degree of dilution (vol%)	morphology	specific surface area* (m ² /g)
8	40	gel	6.87
8	120	macroporous	14.1
8	150	powdery	4.35

* determined by BET method (12)

macroporous resins (c), (d) which show smooth and corrugated surfaces respectively.

Table 2 shows the influence of the crosslinking ratio and degree of dilution on the apparent density of the copolymers. It was verified that a more diluted system leads to copolymers with higher porosity, but the effect of DVB content on the apparent density was not great. The effects of dilution on the specific surface area of resins crosslinked with 8 mol% DVB are depicted in Table 3. Macroporous resin has higher specific surface area than other types of resins such as gel-type and powdery resins.

Further details on the metal binding properties will be published soon.

Conclusion

Chelating resins with hydroxamic acid group were synthesized from porous poly(EA-co-DVB) by suspension polymerization followed by the nucleophilic substitution reaction. Hydroxamic acid group content, apparent density, and morphology were greatly influenced by polymerization conditions, i.e., dilution and degree of crosslinking.

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