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Preparation of polystyrene resin with pendant vicinal dioxime groups

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SUMMARY:

Preparation of macroporous polystyrene beads having pendant vicinal dioxime groups and their metal chelating ability is described. Acetylated polystyrene resin crosslinked with 2 mol-% divinyl benzene was oxidized with SeO_2 to give the polymer bearing glyoxyloyl side groups. Then, treating with hydroxylamine, the polymer possessing dioxime groups was obtained. Metal absorbtivity and decomplexation of the resulting polymeric resin were investigated in a wide pH range.

ZUSAMMENFASSUNG:

Die Herstellung makroporöser Polystyrolkügelchen mit Dioximgruppen und deren Fähigkeit zur Metallkomplexierung wird beschrieben. Ein mit 2 mol-% Divinylbenzol vernetztes acetyliertes Polystyrol wurde mit SeO_2 zu einem Polymeren mit Glyoxyloylgruppen oxidiert, die anschließend mit Hydroxylamin zu Dioximgruppen umgesetzt wurden. Die Metallkomplexierung dieses Harzes wurde in einem weiten pH-Bereich untersucht.

Introduction

Metal-chelating polymeric resins have been used in hydrometallurgical applications such as recovery of rare metal ions from sea water[1] and removal of radioactive trace metal ions from wastes[2].

Vicinal dioximes are known to form stable chelates with transition metal ions in neutral or weakly alkaline solutions. There have been numerous examples of polymers having oxime groups in the main[3] and side chains[4].

In the present study we describe the preparation of macroporous polystyrene resin (crosslinked with 2 mol-% DVB) possessing vicinal dioxime

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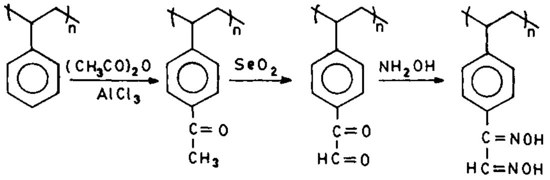
groups in pendant form. The procedure involves three steps: (1) acetylation, (2) SeO_2 oxidation, (3) oximation by hydroxylamine:



The resulting chelating polymer has been found to be susceptible to complex formation with Ni(II), Co(II), Cu(II) and Zn(II) ions. Metal binding ability and decomplexation reactions have been investigated.

Experimental

All the chemicals used were analytical-grade, commercial products and used without any further purification.

Conversion and degree of functionalization (DF) were followed by IR spectroscopy (Shimadzu Model 400), elemental analysis and weight increments.

Preparation of polystyrene resin: Macroporous polystyrene beads (200–400 mesh) crosslinked with 2 mol-% DVB were prepared as described before[5]. For comparison of functionalization and metal binding capability, linear polystyrene was also prepared by emulsion polymerization (η_{inh} = 120 ml/g at 30 ± 0.1 °C in toluene, Cannon-Fenske viscometer) according to the literature[6].

Acetylation: Friedel-Crafts acetylations of linear polystyrene and polystyrene beads were carried out by the procedures given in the literature[7].

SeO_2 oxidation: 10 g acetylated resin were placed in 120 ml dioxane and left overnight. 13.9 g (95 mmol) selenium dioxide were added and refluxed for 18 h. After cooling, the reddish-brown resin was filtered and washed with excess of water and alcohol, dried in vacuo at 40 °C for 24 h. Yield 10.64 g.

A similar procedure was followed for oxidation of acetylated linear polystyrene. The yield was 10.8 g.

Preparation of the resin with dioxime groups: 14 g (0.2 mol) hydroxylamine hydrochloride in 75 ml dioxane were neutralized with 8 g (0.2 mol) NaOH in 15 ml water. Precipitated NaCl was filtered and the filtrate was added to a flask containing 9.5 g oxidized beads in 50 ml dioxane. The mixture was refluxed for 18 h and filtered, washed with water and ethanol and dried in vacuo at room temperature; yield 9.7 g.

The same procedure affords 9.6 g oximated product for the case of 8.2 g linear polystyrene having glyoxyloyl units.

Tab. 1. Elemental analyses and degrees of functionalization (DF) for the resins in each step.

	C (%)	H (%)	N (%)	Conversion[a] (%)	DF (mmol/g resin)
Acetylated PS resin	85.55	7.12	—	61.2	4.56
SeO_2 oxidation product	80.52	5.92	—	99.6	4.27
Resin with dioxime groups	73.04	4.08	8.41	78.0	3.10

[a] Calculated from the elemental analysis.

Elemental analyses of the products obtained in each reaction step are listed in Tab. 1.

Determination of the metal absorptivity: The metal absorptivity of the resin with pendant dioxime groups was examined for Cu(II), Ni(II), Co(II) and Zn(II) ions at different pH values. 50 ml of 0.08 M solutions of $CuCl_2 \cdot 2H_2O$, $ZnCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ were prepared. The following general procedure was applied for each solution:

50 ml of the metal ion solution and 1 g resin were placed in a two-necked flask equipped with a dropping funnel containing 1 M NaOH solution. While stirring with a magnetic stirrer, one or two drops of concentrated HCl solution were added so that pH was around 1–2. Then the pH was changed by adding NaOH solution; after stirring for 15 min, the pH was measured by a pH meter. A few beads were taken out of the flask, washed with water and transferred into 5 ml of 1 M HCl solution. After standing for 24 h, the amount of metal ion released from the test sample into HCl solution was determined by atomic absorption spectrophotometry. The procedure was repeated in each pH change by further adding NaOH solution.

Results and discussion

Conversion determination and characterization of the products obtained in each reaction step were carried out by IR spectroscopy and elemental analysis. The characteristic carbonyl group vibration of acetylated resin appears at 1 690 cm^{-1} in its IR spectrum (Fig. 1). Additionally, the methyl vibration of acetyl group is observed at 1 350 cm^{-1}. After the SeO_2 oxidation step, this methyl group vibration disappears completely and double bands are observed at 1 680 and 1 720 cm^{-1}, which are expected for 1,2-dicarbonyl compounds (Fig. 1). Elemental analysis of the product also indicates an almost quantitative transformation by SeO_2 oxidation. In the IR spectrum of the oximated resin, the sharp carbonyl vibrations are not observed, instead a broadened

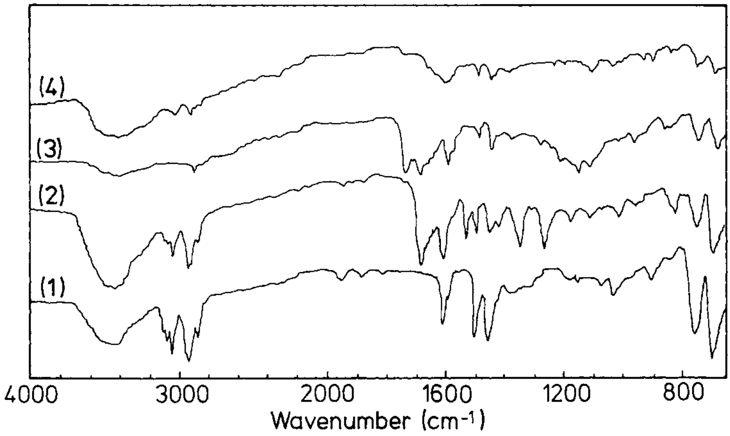
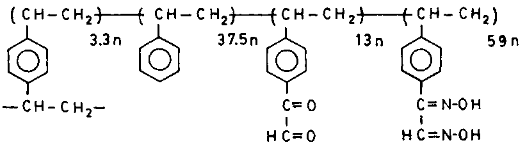


Fig. 1. IR spectra of functionalized polystyrene resins (crosslinked with 2 mol-% DVB): (1) polystyrene, (2) acetylated polystyrene, (3) SeO_2 oxidized polystyrene, (4) resin containing vicinal dioxime groups.

azomethine (C=N) stretching vibration is observed in the 1620–1630 cm^{-1} range. These evidences establish the expected transformations in each reaction step. Similar bands are also observed in the spectra of the products starting from linear polystyrene.

It was also attempted to oxidize the acetylated resin by using nitrous acid or n-propyl nitrite in dioxane. However, only 1.5–2% conversion was obtained. According to the calculations depending on elemental analysis (Tab. 1) of the products in each step, the chemical structure of the resulting resin can be depicted as shown below.



This structure shows that SeO_2 oxidation has been completed quantitatively, whereas the next oximation step has not been carried out in high conversion yields. This result can be ascribed to the hydrophobic property of the resin, because the reaction with hydroxylamine has been performed in presence of water. Thus, hydrophilic hydroxylamine could not penetrate to the glyoxyloyl groups in the micropores.

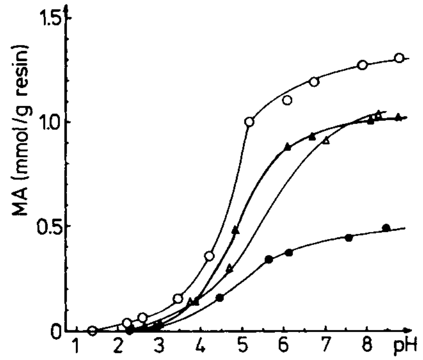


Fig. 2. Variation of metal absorption (MA) of the resin possessing pendant dioxime groups with pH: ○) Ni(II), (▲) Cu(II), (△) Co(II), (●) Zn(II).

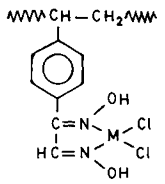
On the other hand, in the alkaline medium some of the glyoxyloyl groups may be expected to change into carboxy groups. However, we were not interested in differentiation of probable carboxy groups.

Metal absorptions of the resin

The metal ion binding ability of the resulting polymeric resin having dioxime groups is given in Fig. 2 for Cu(II), Co(II), Ni(II) and Zn(II) ions in various pH ranges. These metal absorption curves indicate that the selectivity order for metal ions is as follows:

Ni(II) > Cu(II) > Co(II) > Zn(II)

Zn(II) absorption is extremely lower compared to the other metal ions. The most predominant absorbed ion is Ni(II). There is no distinct selectivity between Co(II) and Cu(II) ions in neutral conditions. Moreover, the resin becomes brittle after metal absorption.



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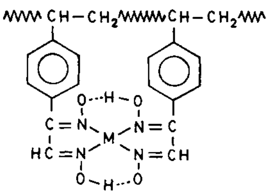

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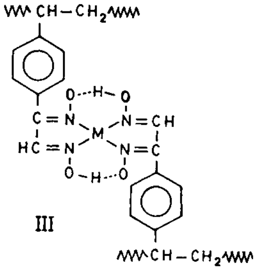

III

This behaviour can be ascribed to an increase in crosslink density by metal chelation. Three types of chelation can be considered through pendant dioxime groups, as shown above:

1:1 (I) and 1:2 (II) metal/ligand complexes can be expected to form predominantly owing to the restriction of the flexibility of chelating dioxime groups in the crosslinked polymer. In aqueous conditions the resin does not swell and inner micropores are inaccessible for metal ions. So, many of embedded dioxime groups remain inactive to form metal chelates. This fact has been described as "matrix effect" by Koster and Schmuckler[8] who studied related polymers. Moreover, the formation of neutral dioxime complexes may increase hydrophobicity of the resin. Of course, this also causes an additional difficulty for metal ions to penetrate into the resin.

A comparison of Tab. 1 and Fig. 2 implies that the amounts of metal ions absorbed per gram resin are less than expected from the DF values. This result is consistent with the above consideration, whereas in linear polymers the chain flexibility permits intermolecular chelation (III). Indeed, in this study we obtained darkened and insoluble nickel and cobalt complexes of linear polystyrene with dioxime side groups. In conclusion, in aqueous medium the microporous resin behaves like a macroreticular resin in which the functions at the surface are available for chemical interactions; metal uptake is less than that of low molecular weight dioximes.

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