Synthesis and Characterization of a Bifunctional Ion Exchange Resin with Polystyrene-Immobilized Diphosphonic Acid Ligands

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SYNOPSIS

A new ion exchange resin for the selective complexation of metal ions has been synthesized by functionalizing vinylbenzyl chloride–styrene–divinylbenzene copolymer beads with the sodium salt of tetra(isopropyl) methylene diphosphonate. The effects of bifunctionality, matrix rigidity, degree of functionalization, and macroporosity on final resin properties have been quantified. A sulfonic acid–diphosphonic acid bifunctional resin is highly selective with rapid complexation kinetics. A macroporous polymer matrix crosslinked with 10% divinylbenzene provides optimum results; for example, 99.7% Eu(III) is complexed from a $1M$ nitric acid solution with a 30-min contact time. The importance of physical crosslinking as well as chemical crosslinking in limiting access of substrates into polymer-supported reagents is discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymer-supported reagents are being developed as selective complexing agents for applications in the recovery of metal ions from the environment and as catalysts in organic reactions.[1] Representative examples of such polymers include[2] oligoethyleneimines bound to crosslinked poly-(2,3-epithiopropyl methacrylate)[3] for the complexation of Hg(II), Ag(I), and Cu(II) from solutions with pH < 3; polystyrenic picolylamine for the selective complexation of Cu(II)[4]; supported quinaldic acid for Cd(II) complexation[5]; and an aminophenol resin modified with mercaptoacetyl chloride for the tight binding of Ag(I) and Cu(II) ions.[6]

Polymers with immobilized phosphorus acid ligands are important ion-complexing agents due to their selectivity toward heavy metal ions.[7-10] Studies have also focused on their use as supports for metals in heterogeneous catalysis.[11] Immobilized diphosphonic acid ligands, synthesized by incorporating the tetraethyl ester of vinylidene diphosphonic acid (I) into a styrene-based network (II), display a level of ionic selectivity far greater than expected from results with the comparable monophosphonate polymer.[12] This is due to the geminal arrangement of the diphosphonate groups, as has been reported with the corresponding small molecule analogue, methylene diphosphonic acid.[13]

To explore further the ionic selectivity of polymers with immobilized gem-diphosphonic acid ligands, ion exchange resins were prepared by the covalent bonding of tetraisopropyl methylene diphosphonate (III) to vinylbenzyl chloride–styrene–divinylbenzene copolymers (Fig. 1). The ion-complexing properties of the resins are quantified with Eu(III) from acidic solutions.[†]

[†] While this report was being written, an article appeared [M. J. Sundell, K. B. Ekman, B. L. Svarfar, and J. H. Nasman, *React. Polym.*, **25**, 1 (1995)] that detailed the immobilization of tetraisopropyl methylene diphosphonate to vinylbenzyl chloride grafted to polyethylene films. Results from the Nasman group are complementary to the present report.

Scheme 1
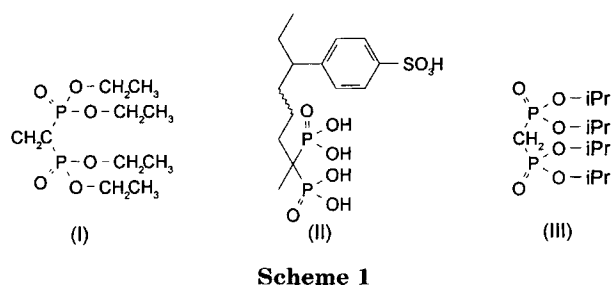
EXPERIMENTAL

Synthesis

Vinylbenzyl chloride (VBC)–styrene (St)–divinylbenzene (DVB) copolymer beads are synthesized by suspension polymerization with 0.5% benzoyl peroxide as initiator. Polymerization is carried out by heating 1 h each at 60°, 70°, and 80°C, and then 7 h at 90°C. An aqueous phase of 2% NaCl and 1% poly(vinyl alcohol) stabilizer is contacted with the organic phase in an 8 : 3 volume ratio. Macroporous polymers are formed by adding 50% (by volume) of a 1 : 1 (w/w) solution of dodecane and toluene as diluents to the organic phase.

The copolymers are functionalized with the sodium salt of tetraisopropyl methylene diphosphonate (R_4MDA). In a typical example, 3 g copolymer is contacted with a solution of 0.92 g sodium, 13.86 g R_4MDA, and 50 mL toluene and then refluxed for 24 h. The resins are collected and washed with toluene, toluene/acetone, and acetone. The Fourier transform infrared (FTIR) spectrum is consistent with the proposed structure; the P $=$ O peak is seen at 1252 cm^{-1} and the P $—$ O (ester) peak appears at 989 cm^{-1}. The diphosphonate ester ligands are hydrolyzed to form the diphosphonic acid resins by refluxing with concentrated HCl for 6 h.

Bifunctional sulfonic/diphosphonic acid resins are prepared by contacting the unhydrolyzed copolymers with a 10% (v/v) solution of chlorosulfonic acid in ethylene dichloride (15 mL/g polymer) at room temperature for 6 h followed by washing with ethylene dichloride, dioxane, and water.

All resins are conditioned by eluting with 1 L each of water, $1M$ NaOH, water, $1M$ HCl, and water.

Characterization

The phosphorus capacity is determined by digesting 20 mg copolymer in a 1 : 2 (v/v) solution of HNO$_3$/HClO$_4$ and subsequent reaction with amidol and ammonium molybdate.[14] Values are reproducible to ±0.05 mmol/g.
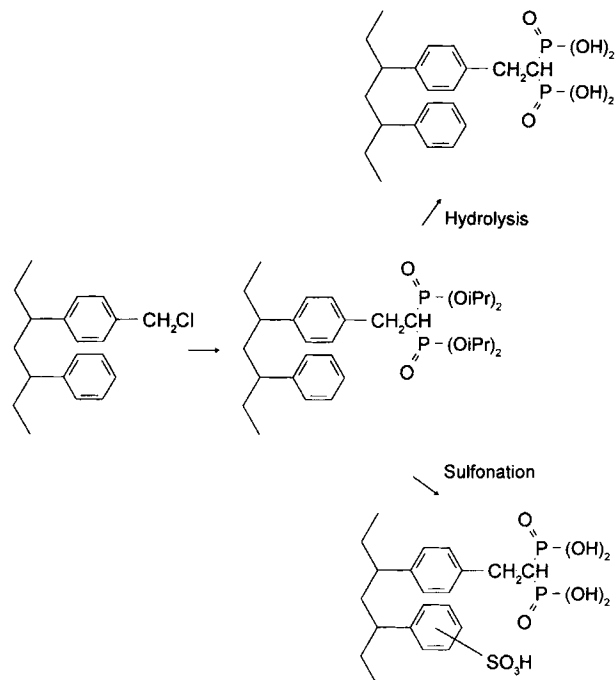
Figure 1 Synthesis of monofunctional and bifunctional ion exchange resins.

The percent solids ($g_{dry}/g_{wet} \times 100$) is determined by centrifuging excess water from the beads, drying them in an oven held at 110°C for 24 h, and taking the ratio of dry to wet weights. The acid capacity is determined by contacting 1 g resin with 200 mL $0.1M$ NaOH/5% NaCl for 24 h, and then back-titrating a 50-mL aliquot with $0.05M$ H$_2$SO$_4$.

Metal Ion Contact Study

The resins are contacted with $10^{-4}M$ Eu(NO$_3$)$_3$ in $1M$ and $5M$ HNO$_3$ as well as with $1M$ HNO$_3$/0.4 M NaNO$_3$. Enough resin to give 0.05 mmol phosphorus is shaken with 5 mL solution for 0.5 and 24 h. The europium concentration remaining in solution is measured with a Perkin-Elmer Model 3100 using atomic emission at a wavelength of 459.4 nm.

RESULTS AND DISCUSSION

The sodium salt of R_4MDA[15] was reacted with different VBC–St–DVB copolymers in order to quantify the effect of the VBC–St ratio, matrix rigidity, and macroporosity on the degree of functionalization (Fig. 1). Steric hindrance to complete functionalization by the bulky tetraisopropyl ligands is indicated by the fact that the 2% crosslinked VBC copolymer reacts to give a phosphorus capacity of 3.34

Table I Functionalization of Crosslinked Vinylbenzyl Chloride–Styrene Copolymers with Tetraisopropyl Methylene Diphosphonate

Percent DVB	Mole Ratio (VBC/St)	Phosphorus Capacity (mmol/g)	Percent Functionalization
2.0	1 : 0	3.34	55.0
2.0	2 : 1	3.30	71.8
2.0	1 : 2	2.31	71.8
5.0	2 : 1	1.63	24.6
5.0[a]	2 : 1	2.47	45.1
7.5[a]	2 : 1	2.33	43.4
10.0[a]	2 : 1	2.25	43.1
12.5[a]	2 : 1	1.96	36.5

[a] Macroporous polymer.

mmol/g while the VBC–St copolymer prepared with a 2 : 1 molar ratio reacts to give the same capacity (Table I). The percent functionalization is 55.0% for the former and 71.8% for the latter. Increasing the crosslink level of the VBC–St copolymer from 2 to 5% DVB sharply decreases the degree of functionalization from 71.8 to 24.6%, further emphasizing the sensitivity of this reaction to steric factors within the polymer gel phase. Increasing the surface area of the polymer through its macroporosity only partially compensates for the increased crosslink level, as indicated by the increase in the degree of functionalization from 24.6 to 45.1%. This level of macroporosity makes the polymer insensitive to increases in matrix crosslinking up to 10% DVB (43.1% degree of functionalization). Steric effects begin to dominate again at 12.5% DVB as the degree of functionalization decreases to 36.5%.

The low degree of functionalization with polymer crosslinked at >2% DVB is most likely due to the steric bulk of the ester ligands in the R_4MDA. Re-

ducing the steric bulk of the methylene diphosphonate by utilizing the tetraethyl ester increases the phosphorus capacity for the 7.5% DVB macroporous resin from 2.33 to 3.38 mmol/g. There is no effect on the degree of functionalization with the tetraisopropyl ester if the reaction solvent is changed from toluene to the more polar dioxane: The 5% DVB gel remains at 1.63 mmol/g and the 5% DVB macroporous resin changes from 2.47 to 2.53 mmol/g. Addition of 15-crown-5 to a toluene solution of the sodium salt of R_4MDA also leads to no increase in the phosphorus capacity. Arbusov reactions on the same polymer supports with the less bulky triisopropyl phosphite lead to quantitative reaction at the $-CH_2Cl$ moieties.[16]

Given that the sites most accessible to functionalization are those that are going to be most accessible to metal ion complexation, the resins noted in Table I were further modified by hydrolysis of the ester sites to form ion exchange resins with diphosphonic acid ligands. Properties of the resins are presented in Table II. The acid capacities of resins crosslinked with 2 and 5% DVB are almost twice as high as the phosphorus capacities, indicating almost complete hydrolysis. For the more rigid matrices, however, approximately 20% of the ester sites remain unhydrolyzed. Resins prepared with 2% DVB (1 : 2 VBC–St) and 5% DVB (gel) are more hydrophobic, as indicated by their percent solids (71.13 and 81.77%, respectively). Macroporous resins have lower solids than the gel resins, despite a higher crosslink level, due to water held within the macropores.

Bifunctional resins with sulfonic and phosphonic acid ligands have much greater rates of complexation than monofunctional phosphonic acid resins while retaining similar levels of selectivity.[16] Given that polymeric diphosphonic acids are more selective than comparable monophosphonic acids,[12] the di-

Table II Monofunctional Ion Exchange Resins with Diphosphonic Acid Ligands

Percent DVB	Mole Ratio (VBC/St)	Phosphorus Capacity (mmol/g)	Acid Capacity (mmol/g)	Percent Solids
2.0	1 : 0	4.86	9.30	56.55
2.0	2 : 1	4.32	8.75	56.74
2.0	1 : 2	2.86	5.47	71.13
5.0	2 : 1	1.95	3.12	81.77
5.0[a]	2 : 1	3.05	5.79	40.33
7.5[a]	2 : 1	2.72	4.08	40.91
10.0[a]	2 : 1	2.54	4.07	39.94
12.5[a]	2 : 1	2.22	3.74	38.79

[a] Macroporous polymer.

phosphonate ester resins given in Table I were sulfonated (and simultaneously hydrolyzed) in order to determine whether bifunctionality would yield a series of highly selective resins (Fig. 1). As shown in Table III, sulfonation leads to a sharp decrease in the percent solids and a concomitant increase in the acid capacities for all resins. The greatest decrease in percent solids occurs with the resin made from copolymer with the highest styrene content (1 : 2 VBC–St), which goes from 81.77% before sulfonation to 24.65% after sulfonation. The unsubstituted phenyl moiety is more readily sulfonated than the diphosphorylated aromatic ring, as indicated by the fact that the resin produced from VBC copolymer increases only slightly in acidity after sulfonation (from 9.30 to 9.73 mmol/g). This is due to steric hindrance by the diphosphonate ligand as well as its electron-withdrawing character, which deactivates the ring toward electrophilic aromatic substitution. The increase in acidity with the VBC copolymer may be due to sulfonation of the ethylphenylene moieties also present in the copolymer from the technical grade DVB.

The resin produced from the 1 : 2 VBC–St copolymer has a theoretical phosphorus capacity of 2.12 mmol/g, in agreement with the experimental value (1.96 mmol/g). Its theoretical sulfonic acid capacity (3.15 mmol/g, assuming complete hydrolysis of the diphosphonate ester ligands after sulfonation), is somewhat less than determined experimentally (4.08 mmol/g), probably due to partial sulfonation of rings other than the unsubstituted phenyl groups. The more highly crosslinked resins also increase in acid capacity after sulfonation but with a less steep decline in percent solids due to water held within the macropores of the precursor resins.

The ability of both (hydrolyzed) monofunctional and (sulfonated) bifunctional resins to complex

Eu(III) metal ions in solution is quantified in Table IV. In $1M$ HNO_3 at equilibrium (24 h contact time), the monofunctional resins complex very high levels of Eu(III); only the 5% DVB gel resin, which has the highest percent solids, complexes much less than 90%. Increasing the acid strength to $5M$ results in a significant decrease in the level of Eu(III) complexed, with macroporous resins outperforming gel resins. At a short contact time (0.5 h), where diffusion into the matrix is the controlling variable, macroporous resins outperform gel resins from $1M$ HNO_3 solutions. Among the macroporous resins, matrix rigidity is an additional factor controlling the amount complexed, with a trend of 10% DVB > 12.5% DVB > 7.5% DVB > 5% DVB. The trend is the same when the Eu(III) is complexed from $5M$ HNO_3 solutions.

The gel and macroporous supports act similarly at equilibrium in both $1M$ and $5M$ HNO_3 when sulfonic acid ligands are introduced into the diphosphonic acid resins (Table IV). When decreasing the contact time to 0.5 h in $1M$ HNO_3 solutions, Eu(III) complexation remains high for both gel and macroporous resins. From $5M$ HNO_3, the bifunctional gel resins complex much more Eu(III) than the comparable monofunctional resins while the macroporous resins still outperform all gel resins. The bifunctional macroporous resins show increasing complexation at the short contact time with the same trend as found with the monofunctional resins (10% DVB > 12.5% DVB > 7.5% DVB > 5% DVB).

To determine whether the high levels of complexation with the bifunctional resins are due to ion exchange by the sulfonic acid ligands, Eu(III) complexation was quantified from $1M$ $HNO_3/0.4M$ $NaNO_3$ solutions. If the nonselective sulfonic acid ligands are responsible for the high levels of europium complexation by ion exchange, they should complex the sodium ions present in great excess over

Table III   Bifunctional Resins with Sulfonic Acid/Diphosphonic Acid Ligands

Percent DVB	Mole Ratio (VBC/St)	Phosphorus Capacity (mmol/g)	Acid Capacity (mmol/g)	Percent Solids
2.0	1 : 0	3.87	9.73	25.67
2.0	2 : 1	3.18	9.46	30.07
2.0	1 : 2	1.96	8.00	24.65
5.0	2 : 1	1.42	6.37	46.93
5.0[a]	2 : 1	2.26	7.98	25.71
7.5[a]	2 : 1	2.03	6.14	28.17
10.0[a]	2 : 1	2.04	6.94	26.92
12.5[a]	2 : 1	1.72	4.79	28.91

[a] Macroporous polymer.

Table IV   Percent Europium Complexed by Monofunctional and Bifunctional Resins

DVB/VBC : St	Porosity	M/B[a]	Percent Eu(III) Complexed from Nitric Acid/Sodium Nitrate (M/M)					
			Contact Time at 0.5 h			Contact Time at 24 h		
			$1M/-$	$1M/0.4M$	$5M$	$1M/-$	$1M/0.4M$	$5M$
2.0//1 : 0	Gel	M	46.0	43.0	17.6	93.8	93.0	53.1
2.0//2 : 1	Gel	M	33.1	24.8	12.6	93.1	91.6	51.1
2.0//1 : 2	Gel	M	25.1	27.8	8.1	86.0	86.7	41.3
5.0//2 : 1	Gel	M	11.4	13.6	15.2	70.7	64.8	25.5
5.0//2 : 1	MR[b]	M	69.2	91.7	43.4	96.7	95.7	74.0
7.5//2 : 1	MR	M	78.4	76.5	45.9	99.5	100	74.4
10.0//2 : 1	MR	M	89.6	84.0	52.1	99.6	99.4	69.5
12.5//2 : 1	MR	M	83.5	72.7	47.2	98.5	98.5	64.3
2.0//1 : 0	Gel	B	95.0	90.8	43.7	96.1	99.3	71.5
2.0//2 : 1	Gel	B	88.5	89.8	35.9	100	100	79.1
2.0//1 : 2	Gel	B	93.0	95.1	45.9	92.3	98.1	60.7
5.0//2 : 1	Gel	B	100	94.1	52.7	100	99.4	65.6
5.0//2 : 1	MR	B	98.4	65.7	60.1	100	99.5	70.0
7.5//2 : 1	MR	B	98.1	94.5	63.0	100	100	76.1
10.0//2 : 1	MR	B	99.7	97.4	73.0	100	100	79.1
12.5//2 : 1	MR	B	98.6	95.8	65.8	100	100	78.0

[a] Monofunctional (diphosphonic acid)/bifunctional (sulfonic/diphosphonic acid).
[b] Macroporous.

europium, and a large decrease in europium complexation should result relative to what is found from $1M$ HNO_3 solutions. Table IV shows that the monofunctional resins are unaffected by the presence of sodium ions due to the selectivity of the diphosphonate ligand. For example, at equilibrium, the 2% DVB gel resin complexes 93.8% Eu(III) from $1M$ HNO_3 and 93.0% from $1M$ $HNO_3/0.4M$ $NaNO_3$; the 12.5% DVB macroporous resin complexes 98.5% Eu(III) from both solutions. The bifunctional resins are equally unaffected by the presence of sodium ions: At equilibrium, the 2% DVB resin complexes 96.1% Eu(III) from $1M$ HNO_3 and 99.3% from $1M$ $HNO_3/0.4M$ $NaNO_3$; the 12.5% DVB macroporous resin complexes Eu(III) quantitatively from both solutions. A sulfonic acid ion exchange resin is known to complex 14.3% Eu(III) from the $1M$ $HNO_3/0.4M$ $NaNO_3$ solution.[17]

The results may be rationalized by noting that the bifunctional sulfonic/diphosphonic acid resins were designed to display selective complexation rapidly through a dual access/recognition mechanism. The sulfonic acid ligand would account for the rapid access of all metal ions into the polymer matrix, while the diphosphonic acid ligand would account for the observed selectivity. The results are consistent with this mechanism. It is likely that the access mechanism is a function of the sulfonate li-

gand's hydrophilicity, which makes the polymer compatible with the hydrophilic metal ions. In highly acidic solutions, the recognition mechanism involves coordination of the metal ions by the geminally placed phosphoryl oxygens.

The ion-complexing behavior of the sulfonic/diphosphonic acid resin is consistent with results from the bifunctional sulfonic/phosphonic acid resin reported earlier.[16] The diphosphonic acid ligand displays much higher levels of complexation due to its inherently greater stability constants with metal ions.[13] The sulfonic/phosphonic acid resin complexes more metal from $1M$ HNO_3 than $1M$ $HNO_3/$ $0.4M$ $NaNO_3$ and significantly more than the monofunctional phosphonic acid resin. The sulfonic/diphosphonic acid resin is almost completely unaffected by the presence of sodium ions due to the greater metal ion affinity of the diphosphonic relative to the monophosphonic acid ligand.

The results in Table IV suggest that the macroporous resin crosslinked with 10% DVB gives greater levels of complexation than resin crosslinked with 5, 7.5, or 12.5% DVB. This agrees with conclusions presented earlier[16]: A polymer matrix should be synthesized with sufficient structural rigidity to prevent collapse in concentrated ionic solutions; metal ion complexation rates are maximized when bifunctionality is coupled with a matrix which re-

tains its macroporosity and gel phase microporosity in ionic solutions that do not allow complete solvation of the ligands. The polymer must be balanced between being rigid enough to withstand collapse due to insufficient solvation of the ligands and too rigid to allow metal ions access to the ligands. Diffusional barriers into the polymer gel phase arise from insufficient solvation of the ligands as well as from high levels of a crosslinking agent. The former is an example of what might be termed *physical crosslinking* in the sense that matrix rigidity is reversible in a solvent which is compatible with the ligands and the latter is a *chemical crosslinking* which is irreversible (without the breaking of covalent bonds). The current report suggests that 10% DVB provides an optimum balance. This will be explored further in the synthesis of additional dual mechanism bifunctional polymers. It is interesting to note that the current results are consistent with those reported[12] for the polymer in which the diphosphonate ligand is introduced with the monomeric tetra-isopropyl vinylidene diphosphonate. Further studies with this resin will focus on its selectivity from multicomponent solutions at different pH values.

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