Synthesis and Ion-Complexing Properties of a Novel Polymer-Supported Reagent with Diphosphonate Ligands

Spiro D. Alexandratos,*,† Andrzej W. Trochimczuk,† Darrell W. Crick,† E. Philip Horwitz,‡ Ralph C. Gatrone,‡ and Renato Chiarizia‡

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600, and Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439-4831

Received July 5, 1995; Revised Manuscript Received November 8, 1995[⊗]

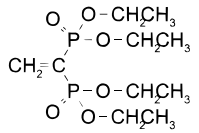
ABSTRACT: A new chelating resin with diphosphonate groups has been synthesized from the tetraethyl ester of 1,1-vinylidenediphosphonic acid. Comonomers such as acrylonitrile allow the sterically hindered monomer to be incorporated into the polymer network. A copolymer was prepared by suspension polymerization in high yield with diphosphonate, acrylonitrile, and styrene in the monomer solution at a 4.5:1:3.1 weight ratio and 5 wt % divinylbenzene as the cross-link agent. Bifunctionality enhances metal ion complexation kinetics. The diphosphonate ligands are selective chelators, while sulfonic acid ligands covalently bound to the phenyl groups enhance the accessibility of metal ions in the polymer matrix. The complexing ability of the polymer is studied with Eu(III) as the target ion in 0.04−4.0 N HNO_3 solutions in both the presence and absence of 0.40 N $NaNO_3$. A sulfonic acid ion exchange resin complexes 14.3% Eu(III) while the diphosphonate-based polymer complexes 96.5% from a 1 N HNO_3/0.4 N $NaNO_3$ solution.

Introduction

Polymer-supported reagents are important in catalysis, organic synthesis, trace analysis, and environmental separations.[1] Ion-selective polymers are especially important because of their ability to retain immobilized metals when used as catalysts and their ability to complex targeted metal ions (usually toxic or precious) from the environment or other aqueous media. Representative examples include amination of chloromethylated polystyrene with 1,3-diaminopropane to yield a resin able to complex gold from cyanide solutions,[2] polymers with dihydroxamic acid groups for uranyl ion selectivity,[3] polymeric 8-hydroxyquinoline for high copper affinity,[4] a supported quinaldic acid resin for the complexation of cadmium,[5] a poly(vinylbenzaldoxime) for the selective complexation of ferric ions,[6] oligo(ethylene sulfides) for high selectivity of mercuric chloride and silver salts,[7] and immobilized crown ethers for the selective complexation of palladium, gold, silver, and mercury salts.[8]

Immobilized phosphorus acid ligands are much more selective than sulfonic acid ligands, especially in highly acidic solutions, due to the strongly coordinating phosphoryl oxygen.[9] Phosphorus-based ion exchange resins are most often prepared by chemical modification of styrene/divinylbenzene copolymers with monophosphonate ligands.[10] The polymerization of vinyl monomers with phosphorus functional groups has received limited attention.[11] It is known, however, that compounds with diphosphonate ligands have very high stability constants with metal ions. For example, methylenediphosphonic acid forms a complex with Eu(III) which is 1000 times stronger than the europium complex with the comparable dicarboxylate.[12] Given that the readily available diphosphonic acids are soluble in water, which obviates their application to the retention or recovery of metal ions from aqueous solutions, it was decided to immobilize the diphosphonate ligand within a polymer matrix in order to prepare a new series of ion exchange resins with high metal ion affinities.

The current research focuses on the polymerization of the tetraethyl ester of 1,1-vinylidenediphosphonic acid (I). Disubstituted monomers with bulky groups are, in



(I)

general, sterically hindered in the chain propagation step, and this could limit polymer formation. The inability of methyl α-ethylacrylate to homopolymerize has been noted.[13] It has been found, however, that sterically hindered monomers can form polymers because the same factors which depress the rate of propagation also lead to low values for the rate of termination, thus allowing the polymerization of monomers such as the dialkyl fumarates.[14] The present report details the methods by which polymerization of the vinylidenediphosphonate is completed and the rate of ionic complexation of the final copolymer is maximized.

Experimental Section

The tetraethyl ester of vinylidenediphosphonic acid (Et_4-VDPA) was synthesized by reacting vinylidenediphosphonic acid with triethyl orthoformate.[15] Diethyl vinylphosphonate was synthesized by dehydrobromination of bromoethyl diethyl phosphonate.[16] Other monomers were obtained from Aldrich and used as received. The poly(vinyl alcohol) used as suspension stabilizer was obtained from Fluka (Fluka 15000; degree of polymerization 300, 86−89 mol % hydrolyzed). Technical grade divinylbenzene (DVB) contained 55.4% *m*- and *p*-isomers, the remainder being primarily ethylstyrene monomers. It was washed with 2 N NaOH to remove the inhibitor. As is standard, the % DVB values in the text and tables refer to the amount of DVB isomers in the monomer solutions.

Bulk polymerization was carried out in sealed 4 mL vials containing 1 g of monomer solution which had been purged

† University of Tennessee.
‡ Argonne National Laboratory.
[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

with nitrogen for 5 min prior to polymerization. Time and temperatures are as indicated in the text. After reaction, the polymer was extracted with toluene.

A cylindrical 150 mL reactor equipped with stirrer and reflux condenser was used for suspension polymerizations. A typical run consisted of 30 g of monomer solution (for example, 13.5 g of Et_4VDPA, 3.00 g of acrylonitrile, 9.30 g of styrene, 2.70 g of technical grade DVB, and 1.5 g of azobis(isobutyronitrile)) and 80 mL of aqueous phase containing 10 g of $CaCl_2$ and 0.45 g of poly(vinyl alcohol). The suspension was stirred at 223 rpm for 18 h at 75 °C. The polymer beads were washed with water and acetone, extracted with toluene, and dried. All polymers were hydrolyzed by refluxing with concentrated HCl for 18 h.

The following data are specific for each copolymer listed in Tables 1−4.

Table 1 (All DVB weights are to total grams of technical grade DVB added.)

Et_4VDPA/DVB Copolymer: 0.77 g of Et_4VDPA, 0.18 g of DVB, 0.05 g of BPO; 10 wt % cross-linking. Obtained 0.42 g of polymer; 42% yield. Phosphorus content: theoretical 5.13 mmol/g; found 3.90 mmol/g; 77% incorporation.

Et_4VDPA/VPr/DVB Copolymer: 0.45 g of Et_4VDPA, 0.24 g of VPr, 0.27 g of DVB, 0.04 g of AIBN; 15 wt % cross-linking. Obtained 0.66 g of polymer; 66% yield. Phosphorus content: theoretical 3.00 mmol/g; found 3.57 mmol/g; 119% incorporation.

Et_4VDPA/BA/DVB Copolymer: 0.45 g of Et_4VDPA, 0.32 g of BA, 0.18 g of DVB, 0.05 g of BPO; 10 wt % cross-linking. Obtained 0.72 g of polymer; 72% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.40 mmol/g; 80% incorporation.

Et_4VDPA/AN/DVB Copolymer: 0.45 g of Et_4VDPA, 0.33 g of AN, 0.18 g of DVB, 0.04 g of BPO; 10 wt % cross-linking. Obtained 0.75 g of polymer; 75% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.39 mmol/g; 80% incorporation.

Et_4VDPA/EA/DVB Copolymer: 0.45 g of Et_4VDPA, 0.32 g of EA, 0.18 g of DVB, 0.05 g of BPO; 10 wt % cross-linking. Obtained 0.78 g of polymer; 78% yield. Phosphorus content: theoretical 3.00 mmol/g; found 3.00 mmol/g; 100% incorporation.

Et_4VDPA/St/AN/DVB Copolymer: 0.45 g of Et_4VDPA, 0.31 g of St, 0.10 g of AN, 0.09 g of DVB, 0.05 g of BPO; 5 wt % cross-linking. Obtained 0.68 g of polymer; 68% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.58 mmol/g; 86% incorporation.

Et_4VDPA/BA/VAc/DVB Copolymer: 0.45 g of Et_4VDPA, 0.22 g of BA, 0.11 g of VAc, 0.18 g of DVB, 0.04 g of AIBN; 10 wt % cross-linking. Obtained 0.69 g of polymer; 69% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.77 mmol/g; 92% incorporation.

Table 2. Et_4VDPA/BA/DVB Copolymer: 0.45 g of Et_4VDPA, 0.375 g of BA, 0.135 g of DVB, 0.04 g of BPO; 7.5 wt % cross-linking. Obtained 0.698 g of polymer; 69.8% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.30 mmol/g; 76.6% incorporation.

Et_4VDPA/BA/DVB Copolymer: 0.45 g of Et_4VDPA, 0.32 g of BA, 0.18 g of DVB, 0.04 g of BPO; 10 wt % cross-linking. Obtained 0.72 g of polymer; 72% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.63 mmol/g; 80% incorporation.

Et_4VDPA/BA/DVB Copolymer: 0.45 g of Et_4VDPA, 0.285 g of BA, 0.225 g of DVB, 0.04 g of BPO; 12.5 wt % cross-linking. Obtained 0.707 g of polymer; 70.7% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.57 mmol/g; 85.8% incorporation.

Et_4VDPA/BA/DVB Copolymer: 0.45 g of Et_4VDPA, 0.24 g of BA, 0.27 g of DVB, 0.04 g of BPO; 15.0 wt % cross-linking. Obtained 0.705 g of polymer; 70.5% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.55 mmol/g; 85.1% incorporation.

Et_4VDPA/BA/DVB Copolymer: 0.45 g of Et_4VDPA, 0.195 g of BA, 0.315 g of DVB, 0.04 g of BPO; 17.5 wt % cross-linking. Obtained 0.717 g of polymer; 71.7% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.59 mmol/g; 86.3% incorporation.

Table 3. All copolymers are 0.45 g of Et_4VDPA, 0.285 g of BA, 0.225 g of DVB, 0.04 g of BPO; 12.5 wt % cross-linking. Obtained 0.644, 0.736, 0.707, and 0.698 g of polymer, respectively; 64.4, 73.6, 70.7, and 69.8% yields, respectively. Phosphorus content: theoretical for all 3.00 mmol/g; found 2.57, 2.64, 2.57, and 2.48 mmol/g, respectively; 85.6, 88.1, 85.8, and 82.6% incorporation, respectively.

Table 4 (Percent yield and percent incorporation data apply to unhydrolyzed polymers.)

Copolymer Obtained in the Absence of EHA: 4.50 g of Et_4VDPA, 3.20 g of EA, 1.80 g of DVB, 0.50 g of BPO; 10 wt % cross-linking. Obtained 6.28 g of polymer; 62.8% yield. Phosphorus content: theoretical 3.00 mmol/g; found 1.96 mmol/g; 65.4% incorporation.

Copolymer Obtained in the Presence of 10 wt % EHA: 4.50 g of Et_4VDPA, 3.20 g of EA, 1.80 g of DVB, 0.50 g of BPO, 1.00 g of EHA; 1:10 wt ratio of EHA to monomers; 10 wt % cross-linking. Obtained 6.65 g of polymer; 66.5% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.25 mmol/g; 75% incorporation.

Copolymer Obtained in the Presence of 25 wt % EHA: 4.50 g of Et_4VDPA, 3.20 g of EA, 1.80 g of DVB, 0.50 g of BPO, 2.50 g of EHA; 2.5:10 wt ratio of EHA to monomers; 10 wt % cross-linking. Obtained 7.22 g of polymer; 72.2% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.28 mmol/g; 75.9% incorporation.

Copolymer Obtained in the Presence of 50 wt % EHA: 4.50 g of Et_4VDPA, 3.20 g of EA, 1.80 g of DVB, 0.50 g of BPO, 5.00 g of EHA; 5:10 wt ratio of EHA to monomers; 10 wt % cross-linking. Obtained 7.06 g of polymer; 70.6% yield. Phosphorus content: theoretical 3.00 mmol/g; found 2.42 mmol/g; 80.7% incorporation.

Sulfonation of the cross-linked vinylidenediphosphonate/acrylonitrile/styrene polymer was accomplished by stirring 10 g of beads with 100 mL of 10% (v/v) chlorosulfonic acid in ethylene dichloride for 1 h at 25 °C. The beads were then washed with ethylene dichloride, dioxane, and water, followed by conditioning with 1 L of H_2O, 1 N NaOH, H_2O, 1 N HCl, and H_2O. Sulfonation of 5% DVB polystyrene beads was carried out according to established procedures.[17] The acid capacity was 5.36 mequiv/g.

The water content of the polymers, reported as percent solids ($(grams_{dry}/grams_{wet}) \times 100$), was measured by centrifuging off excess water from the beads using a centrifuge tube fitted with a glass frit filter and weighing them before and after drying at 110 °C for 17 h.

The acid capacity was measured by contacting 0.8 g of dry resin in the acid form with 100 mL of 0.100 N NaOH containing 5% NaCl for 17 h and back-titrating the excess base with 0.1200 N H_2SO_4.

Phosphorus elemental analysis was carried out by digesting 20 mg of resin with 15 mL of perchloric/nitric acid (2:1 v/v) solution followed by reaction with amidol and ammonium molybdate.[18]

Results are reported in terms of *percent yield* ($(weight_{isolated\ polymer}/weight_{monomers}) \times 100$) and *percent incorporation* ((experimental mmoles of phosphorus in the isolated polymer/theoretical mmoles of phosphorus if all monomer added incorporates into the polymer) × 100).

FTIR spectra were recorded on a Bio-Rad FTS-7 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC 250. Solid-state ^{31}P NMR spectra were recorded on a Nicolet NT-200 spectrometer operating at 80.988 MHz using a Doty probe.

Metal ion analyses were carried out by contacting enough resin to give 0.05 mmol of P with 5 mL of 10^{-4} N $Eu(NO_3)_3$ in 0.04, 1.0, 4.0, or 5.0 N HNO_3 for 0.25−24 h. In some cases, noted in the text, the solutions also contained 0.40 N $NaNO_3$. The Eu(III) left in solution was measured by atomic emission with a Varian 1475 spectrophotometer.

Results and Discussion

Initial experiments with vinylidenediphosphonic acid (VDPA) showed a lack of homopolymerizability. For example, 250 mg of VDPA was dissolved in 5 mL of water and heated at 60 °C/6 h in the presence of 25 mg of potassium persulfate. A ^{1}H NMR spectrum of the compound recovered after drying was identical to that

of the starting material, indicating no loss of unsaturation and therefore no polymerization. Copolymerization with highly polymerizable monomers was found to be feasible: a solution of 250 mg of VDPA, 250 mg of methylenebis(acrylamide), and 25 mg of potassium persulfate in 10 mL of water at 60 °C resulted in gelation after 20 min. The recovered polymer, after being washed and dried under vacuum, had a phosphorus capacity of 1.90 mmol/g, indicating 37.5% incorporation of the VDPA monomer. The solid-state ^{31}P NMR spectrum shows a peak at 27.5 ppm; for comparison, the corresponding spectrum for polystyrene-bound $-CH_2P(O)(OH)_2$ has a peak at 31.6 ppm.

Once it was shown that it was possible to incorporate VDPA within a polymer network, the formation of polymers in the form of beads became the focal point because application of the diphosphonic acid ion exchange resin to separations was an important goal. Defining an appropriate aqueous phase in the suspension polymerization which would allow for the isolation of beads in high yield was not, however, possible due to the hydrophilicity of the VDPA. In a typical example, suspension polymerization of VDPA in the presence of 20% bis(acrylamide) and 5% potassium persulfate yielded beads with 66.7% VDPA incorporation but in only 39.8% yield.

Inverse suspension polymerization under a wide variety of conditions also did not lead to the formation of beads in good yield. Cellulose acetate butyrate was used as the suspension stabilizer in continuous phases which included 1,2-dichloroethane,[19] toluene, and heptane. The aqueous phase consisted of either water or water/dimethylformamide mixtures. In all cases, beads were formed to only a small extent, with most polymer present as irregularly shaped particles. Rather than continue with a complete study of inverse suspension polymerization which, even if successful, would encounter serious environmental problems in large-scale preparations, it was decided to adapt the monomers to a standard (oil-in-water) suspension polymerization.

The organophilicity of VDPA is much enhanced by esterification, and optimum copolymerization conditions were defined with the tetraethyl ester (Et_4VDPA). Variables included the type and level of comonomers and cross-linking agent. Since one important application for the final resin was to be complexation of actinides from highly acidic solutions, the requirement for resin stability under such conditions limited the choice of comonomers and cross-linking agents. Et_4-VDPA was found to copolymerize with cross-linking agents such as diethylene glycol diacrylate, but the resulting resins are unstable in highly acidic media due to hydrolysis of the diacrylate. Divinylbenzene (DVB) is thus the preferred cross-linking agent.

Steric factors inherent to 1,1-disubstituted monomers can preclude the formation of high molecular weight polymers of Et_4VDPA. Copolymerization with 10% DVB is possible, though the polymer forms in only 42% yield. Additionally, the network allows only limited access of metal ions: 44.1% of the Eu(III) is complexed from a 0.04 N HNO_3 solution after a 30 min contact time (Table 1). A proper choice of comonomers was found to significantly increase polymer yield and diphosphonate incorporation. As shown in Figure 1, yield and incorporation decrease as the amount of Et_4VDPA increases with butyl acrylate (BA) added as the comonomer. The highest polymer yield (76.9%) and incorporation (87.7%) result from an initial solution concentration of 45% Et_4-VDPA. Lower initial Et_4VDPA concentrations were not studied because the final phosphorus capacity would be too low to be useful in ion complexation studies. Polymerization of styrene/BA/DVB under the same conditions gives a 96% yield.

Table 1. Effect of Comonomers on Tetraethyl Vinylidenediphosphonate Polymerization[a]

comonomer(s)	% yield	% Et_4VDPA incorporation	gel point (min)	% Eu(III)[b]
[none]	42	77	135−165	44.1
vinyl propionate[c]	66	119	42−62	5.1
butyl acrylate	72	80	53	92.2
acrylonitrile	75	80	18	10.0
ethyl acrylate	78	100	47	97.5
styrene/acrylonitrile[d]	68	86	107	10.0
butyl acrylate/vinyl acetate[e]	69	92	132	13.6

[a] Bulk polymerization with 45% Et_4VDPA, 10% DVB, 5% BPO, and 32% comonomer. [b] Complexation of Eu(III) from 0.04 N HNO_3 at a 0.5 h contact time. [c] 15% DVB, 27% comonomer. [d] 21% styrene, 10% acrylonitrile. [e] 21% butyl acrylate, 10% vinyl acetate.

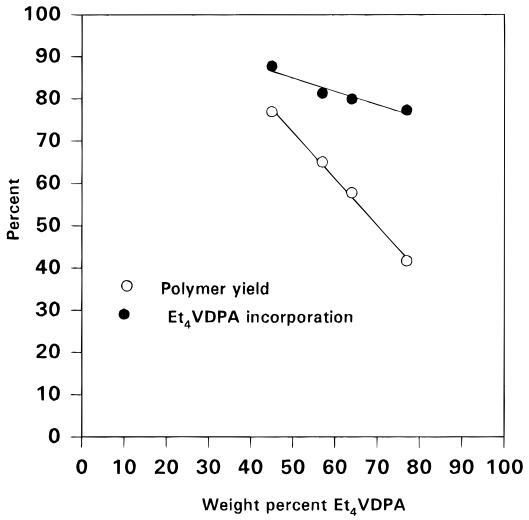


Figure 1. Effect of Et_4VDPA concentration in the initial monomer solution on polymer yield and diphosphonate incorporation.

The decrease in polymer yield with increasing Et_4-VDPA concentration may be rationalized by steric hindrance to polymerization as well as a chain transfer mechanism. The free radical polymerization of diethyl vinylphosphonate (Et_2VPA) also results in polymer chains with very low degrees of polymerization.[20] When Et_2VPA replaces the 45% Et_4VDPA on a weight basis, a decrease in both yield (59.3%) and incorporation (65.6%) is observed. When the Et_4VDPA is replaced on an equimolar basis (thus decreasing the weight ratio of phosphorus monomer to BA), the level of incorporation remains low (58.7%) while the polymer yield increases to 72.5%. Low yield and incorporation are expected when chain transfer limits the polymer's molecular weight, thus decreasing the probability that each chain will be part of a larger cross-linked macromolecular network and allowing for more of the oligomers to be lost during Soxhlet extraction. In the present case, the situation is compounded by the presence of bulky phosphonate ligands.

Based on the results in Figure 1, the concentration of Et_4VDPA was set at 45% in subsequent studies. The effect of comonomers on yield and incorporation is given in Table 1. The acrylates and acrylonitrile

Table 2. Effect of DVB Cross-Linking on Et_4VDPA/BA Polymer Yield and Diphosphonate Incorporation[a]

DVB (wt %)	phosphorus capacity (mmol/g)	% yield	% incorporation
7.5	2.30	69.8	76.6
10.0	2.63	72.0	80.0
12.5	2.57	70.7	85.8
15.0	2.55	70.5	85.1
17.5	2.59	71.7	86.3

[a] Bulk polymerization at 80 °C with 45% Et_4VDPA and 5% BPO; the ratio changes from 10% DVB/32% BA as the amount of DVB is varied.

Table 3. Effect of Temperature on Et_4VDPA/BA Polymer Yield and Diphosphonate Incorporation[a]

temp (°C)	phosphorus capacity (mmol/g)	gel point (min)	% yield	% incorporation
60	2.57	>310	64.4	85.6
70	2.64	160−180	73.6	88.1
80	2.57	64	70.7	85.8
90	2.48	37	69.8	82.6

[a] Bulk polymerization at 80 °C with 45% Et_4VDPA, 12.5% DVB, and 4% BPO.

significantly increase polymer yields relative to the yield in their absence. Styrene can be incorporated as a mixture with acrylonitrile. Vinyl propionate gives Et_4-VDPA incorporation greater than 100% because the amount of comonomer present in the polymer is much less than expected from the initial solution concentration.

Metal ion complexation after hydrolysis of the ester sites is an important property. The applicability of an ion exchange resin is measured not only by its selectivity but also by its ability to rapidly complex a high level of the targeted metal ion. As shown in Table 1, only the acrylate comonomers yield a polymer with acceptable accessibility to Eu(III) ions in an acidic solution after a 0.5 h contact time. The concept of ionic accessibility is discussed further below.

A study of the effect of cross-link level, polymerization temperature and time, and initiator level and type was undertaken with Et_4VDPA/BA/DVB. Table 2 shows that the yield and incorporation are invariant to levels of DVB greater than 7.5%. The DVB levels indicated are thus sufficient to maximize the formation of a network structure with the Et_4VDPA and BA comonomers. The temperature of polymerization within the range 60−90 °C has no effect on the yield or incorporation of copolymer made with 12.5% DVB though it strongly influences the time to gelation (Table 3). Increasing the polymerization time with the same initial monomer solution within the range 2−68 h at 80 °C shows that increasing the time from 2 to 6 h increases the yield but has much less effect on Et_4VDPA incorporation into the polymer (Figure 2). The data indicate the polymer which forms is uniform in its composition throughout the reaction time given the relatively constant level of diphosphonate incorporation.

The initiator level can influence the yield in free radical polymerization reactions.[20] In the present study, 3% benzoyl peroxide (BPO) is the minimum level appropriate for polymerization of a 10% DVB/45% Et_4-VDPA/BA solution at 80 °C (Figure 3). The polymer yield is dependent on the BPO level, as would be expected if degradative chain transfer were an important component of the overall reaction. A comparative study of initiators (lauroyl peroxide (LPO), BPO, and

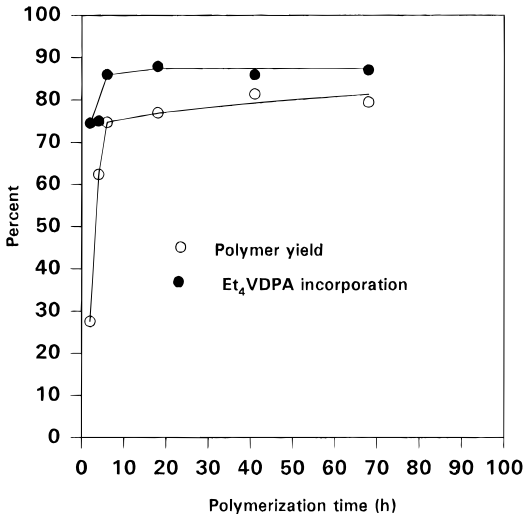


Figure 2. Effect of polymerization time on polymer yield and diphosphonate incorporation.

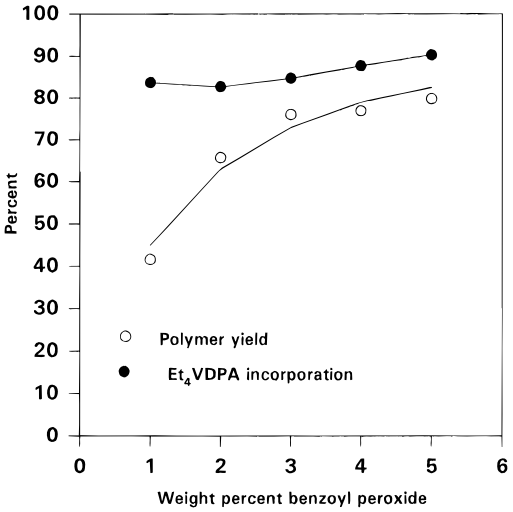


Figure 3. Effect of initiator concentration on polymer yield and diphosphonate incorporation.

azobis(isobutyronitrile) (AIBN)) at 5% of the monomer solution shows LPO to be ineffective and AIBN to be somewhat preferred over BPO: for LPO, BPO, and AIBN, 103, 86, and 100% of the Et_4VDPA is incorporated into the polymer with 36, 68, and 70% isolated yields for the three initiators, respectively.

As noted earlier (Table 1), the hydrolyzed Et_4VDPA/BA/DVB copolymer is able to complex a high level of Eu(III) from dilute acid solution. Since it is known, however, that a macroporous structure is important to complexing ions rapidly from more acidic solutions,[21] a study was undertaken of macroporous diphosphonate copolymers. A comonomer solution which included 10% DVB and 45% Et_4VDPA was used for both microporous (gel) and macroporous polymers except, for the latter, varying levels of diluent were added, viz., 10, 25, and 50% 2-ethylhexanol (EHA). Though porosity measurements were not made, it is known that increasing levels of diluent increase the extent of macroporosity.[22] The kinetics were also compared to a sulfonic acid ion exchange resin of similar hydrophilicity (as measured by the ratio of dry to wet weight). Because ethyl acrylate was found to give a higher polymer yield than butyl acrylate in bulk polymerization studies in the presence of 50% EHA (73% vs 64%, respectively) with comparable levels of incorporation (76% vs 74%, respec-

Table 4. Suspension Polymerization of Macroporous Et_4VDPA/EA/DVB Resins with 2-Ethylhexanol as Diluent

% EHA	phosph capacity (mmol/g)	% yield	% incorpn	% solids	acid capacity (mmol/g)	% Eu from[a] 0.04 N HNO_3	% Eu from 1 N HNO_3	% Eu from 5 N HNO_3
0	2.38	62.8	65.4	62.4	8.25	97.5	27.0	13.3
10	2.64	66.5	75.0	53.9	8.24	100	43.7	25.6
25	2.75	72.2	75.9	50.2	8.12	100	43.9	26.6
50	2.73	70.6	80.7	47.6	8.12	100	78.7	32.3
$-SO_3H$[b]				50.0	5.74		44.9	

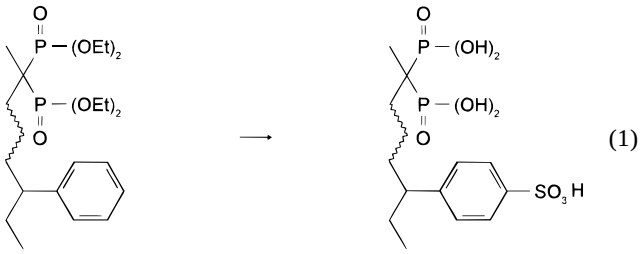
[a] Percent Eu(III) complexed from a solution of the indicated acidity; 0.5 h contact time. [b] Sulfonic acid cation exchange resin.

tively), it was utilized in subsequent studies. As shown in Table 4, under suspension polymerization conditions the polymer yield decreases to very low levels even when the aqueous phase consists of a saturated calcium chloride solution with poly(vinyl alcohol) as stabilizer. This discrepancy in yield between bulk and suspension polymerization is due to the fact that the latter are isolated yields of polymer beads and do not include the polymer which formed as powder. Gel and macroporous polymers have comparable phosphorus capacities and monotonically decreasing percent solids ($grams_{dry}$/$grams_{wet}$ polymer) which reflect the increased amount of water sorbed by the increasing level of macropores. Note that the acid capacities are greater than twice the phosphorus capacities due to the presence of the carboxylic acid ligands formed from hydrolysis of the acrylate.

The influence of macroporosity on metal ion complexation is most clearly seen by contacting the polymers with a Eu(III) solution in 1 N HNO_3. The resin with greatest macroporosity complexes 78.7% Eu(III), which significantly outperforms the sulfonic acid resin. Resins with lower porosities outperform the gel resin and equal the performance of the sulfonic acid resin. The low level of complexation with the gel resin at 0.5 h is an artifact of the limited swelling of the polymer when fully protonated and, hence, of the limited access of ions into the network; at equilibrium (24 h contact), the gel complexes as much as the macroporous resins (77.8% Eu(III)). The extent of complexation is quantitative in less acidic solutions (97.5% complexation from 0.04 N HNO_3) where greater swelling of the polymer is possible and decreases to 13.3% in 4 N HNO_3 where swelling of the polymer is minimal. The performance of the polymers at a short contact time is important in the present study given the goal of defining conditions which maximize ligand accessibility to metal ions in solution. While macroporosity is one mechanism of enhancing complexation rates, identifying an appropriate diluent for different copolymers can be difficult since it must be capable of dissolving the monomers while allowing for the polymer to precipitate after a certain degree of polymerization has been reached. Additionally, the diluent must not interfere with high isolated yields of polymer as beads. Gel copolymers with enhanced complexation rates are thus important since no diluent is required and such resins have greater volume capacities and attrition resistance than the macroporous analogues. The synthesis of such copolymers was the next phase of the research.

Dual mechanism bifunctional polymers have been defined as a category of resins which are synthesized with two different types of functional groups: one provides nonselective access into the polymer network, and the other reacts selectively with a targeted substrate, thus isolating one component from a multicomponent solution.[23,24] This concept was extended in the present research by synthesizing a polymer where the diphosphonate ligand provides ionic selectivity and a second type of ligand provides rapid ionic accessibility. The hydrophilicity and low pK_a of the sulfonic acid ligand made it the ligand of choice for the access mechanism. Selective complexation of certain ions by the diphosphonate ligand then occurs when the ions enter the polymer matrix.

To synthesize a polymer with both sulfonic and diphosphonic acid ligands, it became necessary to have a precursor with a group to which the sulfonate ligand could be bound. Sulfonation of a phenyl ring is straightforward and would have the added advantage of simultaneously deesterifying the diphosphonate ligand (eq 1).



(1)

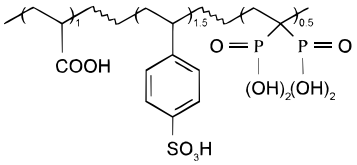
A bulk polymerization of 450 mg of Et_4VDPA, 250 mg of BA, and 250 mg of styrene, with 5% DVB and 5% BPO, yielded polymer in only 44% yield and 300 min to the gel point. It was later found that the addition of acrylonitrile (AN) to the monomer solution minimized the time to gelation: a comparable polymerization substituting AN for BA on a weight basis gave polymer in 71% yield with 21 min to the gel point. Suspension polymerization of 45% Et_4VDPA, 10% acrylonitrile, 31% styrene, 5% DVB, and 5% initiator gave beads in 70% yield and 96.4% incorporation of the diphosphonate monomer into the network. FTIR spectra of this copolymer and that obtained after hydrolysis in concentrated HCl are consistent with the proposed structures. In the unhydrolyzed polymer, the backbone methylene groups appear at 2927 and 2854 cm^{-1}, a broad peak at 1069−1018 cm^{-1} represents the P—O—C of the phosphonate ester group, the P═O stretch appears at 1245 cm^{-1}, and the cyano group stretch occurs at 2235 cm^{-1}. In the hydrolyzed polymer, the methylene group absorbs at 2921 and 2851 cm^{-1}, the broad 1069−1018 cm^{-1} peak is greatly diminished, the P═O stretch is still strong at 1238 cm^{-1}, the peak at 2235 cm^{-1} is almost nonexistent, and a small, broad but identifiable peak at 2340 cm^{-1} appears (which is absent in the unhydrolyzed polymer) due to the P—O—H stretching vibration.[25,26]

After hydrolysis and washing with NaOH, HCl, and water, the polymer was dried and the phenyl rings were sulfonated by reaction with chlorosulfonic acid. Table 5 shows that the phosphorus capacity decreases from 2.32 mmol/g in the precursor to 1.64 mmol/g in the final product. The acid capacity increases from 4.49 to 7.31 mmol/g, which reflects not only the sulfonate and

Table 5. Ion-Complexing Abilities of Diphosphonic Acid, Diphosphonic/Sulfonic Acid, and Sulfonic Acid Polymers

resin	% solids	acid capacity (mmol/g)	phosph capacity (mmol/g)	% Eu from 1 N HNO_3	% Eu from 1 N HNO_3/ 0.4 N $NaNO_3$	% Eu from 4 N HNO_3
diphosph acid	48.77	4.49	2.32	32.8		
diphosph/$-SO_3H$	29.56	7.31	1.64	98.3	96.5	53.2
$-SO_3H$	50.00	5.74		44.9	14.3	5.6

diphosphonate groups but also the carboxylic acid groups produced by hydrolysis of the cyano moieties. The carboxylic acid ligands do not participate in the binding of metal ions due to their high pK_a unless relatively high pH solutions are used. The ratio of sulfonic:phosphonic:carboxylic acid sites is calculated to be 1.5:1:1 corresponding to 66% sulfonation of the phenyl rings present in the precursor. The hydrophilicity of the sulfonic acid ligands results in a decrease of the solids level from 48.77 to 29.56% after sulfonation. Structure II is consistent with the calculated acidities,



(II)

which assume complete incorporation of the styrene and acrylonitrile present in the monomer solution, and the phosphorus elemental analysis. This is verified by sulfur elemental analysis:[27] structure II is calculated to have a sulfur content of 2.39 mmol/g; a similarly made sample has a phosphorus elemental analysis of 1.86 mmol/g (vs 1.64 mmol/g in the present case) and a sulfur elemental analysis of 2.68 mmol/g.

The dual access/recognition mechanisms are evident from the Eu(III) complexation experiments. Whereas the diphosphonic acid polymer complexes 32.8% of the Eu(III) present in 1 N HNO_3, the sulfonate/diphosphonate polymer complexes 98.3%, also outperforming the sulfonic acid resin which complexes 44.9% Eu(III). The diphosphonate ligands are responsible for the observed selectivity, and the sulfonate ligands enhance accessibility. When contacting the polymers with Eu(III) in a 1 N HNO_3 solution containing 0.4 N $NaNO_3$, Eu(III) complexation for the sulfonic acid resin decreases from 44.9 to 14.3% due to its tendency to complex all metal ions, including sodium ions present in much greater excess; on the other hand, Eu(III) complexation for the sulfonate/diphosphonate polymer remains virtually quantitative (98.3% to 96.5%) as the diphosphonate ligands complex Eu(III) over sodium. Ion exchange, even for the sulfonic acid group, is low from highly acidic solutions; the sulfonate/diphosphonate polymer complexes 53.2% Eu(III) from 4 N HNO_3, while the sulfonic acid resin complexes 5.6%. This greater affinity by the diphosphonate ligand is due to the coordinating ability of the phosphoryl moieties. The selectivity inherent to diphosphonate-based polymers over a wide pH range has been detailed.[28] Solid-state ^{31}P NMR spectroscopy and protonation constants have further characterized the resin.[27]

Conclusions

A new ion exchange resin with *gem*-diphosphonic acid ligands has been synthesized for the selective complexation of metal ions. Introducing sulfonic acid ligands into the matrix enhances the kinetics of complexation significantly.

Acknowledgment. We gratefully acknowledge support from the Department of Energy, Office of Basic Energy Sciences, Divisions of Chemical Sciences and Advanced Energy Projects, under contract number W-31-109-ENG-38 to the Argonne National Laboratory. S.D.A. also gratefully acknowledges DOE support through grant DE-FG05-86ER13591 from the Office of Basic Energy Sciences.

References and Notes

(1) Sherrington, D. C., Hodge, P., Eds. *Syntheses and Separations Using Functional Polymers*; Wiley: New York, 1988.
(2) Harris, W. I.; Stahlbush, J. R.; Pike, W. C.; Stevens, R. R. *React. Polym.* **1992**, *17*, 21.
(3) You, H. J.; Jeon, H. J.; Jeon, D. W. *Han'guk Somyu Konghakhoechi* **1992**, *29*, 328; *Chem. Abstr.* **1993**, *119*, 118001e.
(4) Warshawsky, A. *Angew. Makromol. Chem.* **1982**, *109/110*, 171.
(5) Moberg, C.; Weber, M.; Hogberg, K.; Muhammed, M.; Nilsson, A. C. *React. Polym.* **1990**, *12*, 31.
(6) Chanda, M.; Rempel, G. L. *React. Polym.* **1993**, *19*, 201.
(7) Lauth, M.; Frere, Y.; Prevost, M.; Gramain, Ph. *React. Polym.* **1990**, *13*, 73.
(8) Bruening, R. L.; Tarbet, B. J.; Krakowiak, K. E.; Bruening, M. L.; Izatt, R. M.; Bradshaw, J. S. *Anal. Chem.* **1991**, *63*, 1014.
(9) Alexandratos, S. D.; Crick, D. W.; Quillen, D. R. *Ind. Eng. Chem. Res.* **1991**, *29*, 772.
(10) Alexandratos, S. D. *Sep. Purif. Methods* **1992**, *21*, 1.
(11) Efendiev, A. A.; Orujev, D. D.; Sidorczuk, I. I. *React. Polym.* **1983**, *4*, 295. Upton, R. W. *J. Am. Chem. Soc.* **1953**, *75*, 1763.
(12) Nash, K. L.; Horwitz, E. P. *Inorg. Chim. Acta* **1990**, *169*, 245.
(13) Cheng, J. S.; Yamada, B.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1837.
(14) Yamada, B.; Matsumoto, A.; Otsu, T. *Makromol. Chem.* **1991**, *192*, 1921.
(15) Dagenhardt, C. R.; Burdsall, D. C. *J. Org. Chem.* **1986**, *51*, 3488.
(16) Gefter, E. L. *Zh. Obshch. Khim.* **1958**, *28*, 2500.
(17) Bortnick, N. M. U.S. *Patent* 3,037,052, 1962.
(18) Ma, T. S.; McKinley, J. D. *Microchim. Acta* **1953**, 4.
(19) Arshady, R.; Ledwith, A. *React. Polym.* **1983**, *1*, 159.
(20) Pike, R. M.; Cohen, R. A. *J. Polym. Sci.* **1960**, *44*, 531.
(21) Trochimczuk, A. W.; Alexandratos, S. D. *J. Appl. Polym. Sci.* **1994**, *52*, 1273.
(22) Howard, G. J.; Midgley, C. A. *J. Appl. Polym. Sci.* **1981**, *26*, 3845.
(23) Alexandratos, S. D.; Wilson, D. L. *Macromolecules* **1986**, *19*, 280.
(24) Alexandratos, S. D.; Quillen, D. R.; Bates, M. E. *Macromolecules* **1987**, *20*, 1191.
(25) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981.
(26) Corbridge, D. E. C. *Topics in Phosphorus Chemistry*, Grayson, M., Griffith, E. J., Eds.; Wiley: New York, 1969; Vol. 6, pp 235−365.
(27) Nash, K. L.; Rickert, P. G.; Muntean, J. V.; Alexandratos, S. D. *Solv. Extr. Ion Exch.* **1994**, *12*, 193.
(28) Horwitz, E. P.; Chiarizia, R.; Diamond, H.; Gatrone, R. C.; Alexandratos, S. D.; Trochimczuk, A. W.; Crick, D. W. *Solv. Extr. Ion Exch.* **1993**, *11*, 943. Chiarizia, R.; Horwitz, E. P.; Gatrone, R. C.; Alexandratos, S. D.; Trochimczuk, A. W.; Crick, D. W. *Solv. Extr. Ion Exch.* **1993**, *11*, 967.

MA950943U