Functionalized Polymer Foams as Metal Ion Chelating Agents with Rapid Complexation Kinetics

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ABSTRACT: Foams prepared from vinylbenzyl chloride and crosslinked with divinylbenzene were functionalized with trialkylphosphite and tetralkylvinylidene diphosphonate. It was determined that the foams could be uniformly functionalized. Batch studies with the functionalized foams show that high levels of metal ion complexation can be achieved. Foams may therefore offer an important alternative to beads for rapid complexation reactions due to their highly porous structure. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1911–1916, 1998

Key words: crosslinked foams; ion exchange; metal ion separations; phosphonic acids

INTRODUCTION

The selective complexation of a targeted metal ion from multi-ion solutions is an important objective for many applications, including the treatment of water for removal of radioactive and nonradioactive heavy metal ions. As a result, studies have focused on the immobilization of ligands with different ion-complexing properties to polymer supports.[1] Examples include pyridinone,[2] iminodiacetic acid,[3] aminoglucitol,[4] thiopyrazole,[5] oximes,[6] and dithiocarbamates.[7] The most common polymer supports to which the ligands are immobilized are microporous (that is, gel) polystyrene or polyacrylate beads. While convenient to prepare and utilize, gel beads can limit diffusion of substrates to the ligands, especially at the higher crosslink levels required to resist pressure drops in continuous operations. An increase in the rates of diffusion is possible with macroporous beads,[8] which are agglomerated microspheres separated by macrochannels.[9] Macroporous styrenic and acrylic rods have been prepared by the polymerization of monomers inside a column in the presence of a porogen.[10,11] These rods, with porosities of up to 50%, have been used in chromatographic separations due to the increased rate of substrate diffusion through the polymer matrix relative to beads.

Porous polyurethane foams have been utilized in ion exchange chromatography because of their enhanced kinetics and reduced need for forced flow through columns.[12,13] They have also been used in the batch extraction of metal ions.[14,15] Solvent extractants[16] and liquid ion exchangers[17] are physically sorbed into the foams and act as the metal ion chelants.

This research examines the ion-complexing ability of crosslinked poly(vinylbenzyl chloride) based high-porosity foams that have been modified with covalently bound ligands. The foams were synthesized by water-in-oil emulsion polymerizations.[18] This article emphasizes the modification of the foams with phosphorus acids because of their ability to complex metal ions by

ion exchange and coordination at the phosphoryl oxygen, depending on the solution pH.[19] Phosphonate ester ligands were also studied in order to ascertain whether the foams allow ionic complexation to occur with hydrophobic ligands. The results were compared with those for gel and macroporous beads.

EXPERIMENTAL

The suspension polymerization of vinylbenzyl chloride (VBC) has been described.[20] Both gel and macroporous (MR) beads were used in the present studies. The particle size diameters were 0.075–0.15 mm for the former and 0.25–0.42 mm for the latter. The gel beads were crosslinked with 2 and 20% divinylbenzene (DVB). The MR beads had a void volume of 50% and were crosslinked with 5 and 20% DVB.

Poly(VBC) foams were prepared at Los Alamos National Laboratory by emulsion polymerization.[18] The cylindrically shaped foam particles (approximately 1 cm in diameter and 10 cm in length), with densities less than 0.1 g/cc and porosities greater than 95%, were crosslinked with 2.5 and 20% DVB. Prior to functionalization, the foams were extracted with methanol for 17 h in a Soxhlet apparatus to remove the sorbitan monooleate surfactant used during polymerization. The foams were dried in an oven at 60°C for 17 h.

The phosphonic acid resins were synthesized by the reaction of triisopropyl phosphite on the —CH$_2$Cl groups in an Arbusov reaction.[21] The phosphonate diester beads which form after a 17-h reflux were washed with acetone and 1N HCl. The diester ligands were hydrolyzed to the acid by refluxing the beads in concentrated HCl for 24 h. The beads were conditioned by eluting with 1 L of H$_2$O, 4 wt % of NaOH, H$_2$O, 4 wt % of HCl, and H$_2$O (each over a 1 h period). Since the functionalization reaction was not expected to depend on the physical form of the polymer, the phosphonic acid foam was prepared in the same manner as the beads. The foam, however, did require a 12-fold increase in the amount of phosphite used relative to what was required with the beads due to a loss of fluidity brought about by their much greater ability to sorb the phosphite. Excessive swelling caused the 2.5% DVB foam to break apart into smaller pieces during the reaction. The 20% DVB foam, however, remained whole throughout the reaction.

The phosphonate ester polymers were synthe-

Table I Characterization of Phosphonic Acid Polymers

Polymer Type	% DVB	% Solids	P Capacity[a]	Acid Capacity[b]
Gel	2	57.91	4.83	9.34
MR	5	37.26	4.37	8.91
Foam	2.5	4.30	4.64	10.51
Gel	20	76.16	2.83	5.87
MR	20	33.90	2.65	5.57
Foam	20	9.53	3.82	8.60

[a] Phosphorus capacity, mmol/g.
[b] Total acid capacity, mmol/g.

sized in the same manner except that they did not undergo a hydrolysis with HCl. Diethyl and diisopropyl phosphonate esters were obtained with triethyl and triisopropyl phosphite, respectively. The esters were washed with 95% ethanol and conditioned with 1 L of water, 1 L 4 wt % of HCl and 2 L of water.

The diphosphonate polymers were synthesized by adding an excess of the sodium salt of tetraisopropyl methylenediphosphonate in toluene to the polymers and refluxing for 24 h. The polymers used to form the diphosphonic acid ligands were refluxed in concentrated HCl for 24 h after being washed with toluene, acetone, 50/50 acetone–water, and water. The diphosphonate esters were washed and conditioned as described for the phosphonate esters. The diphosphonic acid polymers were washed with water and conditioned in the same manner as the phosphonic acid polymers.

The metal ion studies were performed with enough polymer to give 1 milliequivalent of ligands in contact with 10 mL 10^{-4}N metal nitrate solutions in 0.04 or 1N HNO$_3$ for 30 min or 24 h, as indicated. Results were tabulated in terms of the percentage of metal ion complexed from solution and the distribution coefficient D, defined as the ratio of the milliequivalents of metal ion in 1 g (dry weight) of polymer to the milliequivalents of metal ion remaining in 1 mL of solution.

RESULTS AND DISCUSSION

Characterization

The polymers were characterized by the percent solids [$(g_{dry}/g_{wet}) \times 100$], phosphorus elemental analyses, and total acid capacities. As seen in Table I, complete functionalization is achieved with

Table II   Characterization of Diphosphonic Acid Polymers

Polymer Type	% DVB	% Solids	P Capacity[a]	Acid Capacity[c]
Gel	2	60.48	4.44 (6.73)[b]	8.16
MR	5	35.33	2.47 (6.51)	4.47
Foam	2.5	4.50	4.02 (6.70)	8.90
Foam	20	9.53	3.08 (5.30)	5.76

[a] Phosphorus capacity, mmol/g.
[b] Theoretical values assuming complete functionalization of the —CH_2Cl groups.
[c] Total acid capacity, mmol/g.

the lightly crosslinked phosphonic acid polymers: The theoretical phosphorus capacities for the polymers crosslinked with 2, 2.5, and 5% DVB are 4.91, 4.87, and 4.69 mmol/g, respectively, in close agreement with the experimental values (4.83, 4.64, and 4.37 mmol/g, respectively). The —CH_2Cl ligands in the 20% DVB foam are more accessible during functionalization than beads crosslinked to the same level, given its higher phosphorus capacity (2.83 and 2.65 mmol P/g gel and MR beads, respectively, versus 3.82 mmol P/g for the foam; the theoretical capacity is 3.52 mmol P/g). It is important to note that the 20% DVB foam did not break up during the functionalization reaction; the high phosphorus capacity is thus evidence that the reagents can access the —CH_2Cl sites within the foam. The acid capacities for the beads are all approximately twice the phosphorus capacities, indicating complete hydrolysis of the diester ligands. The acid capacities of the foams are sometimes greater than twice the phosphorus capacities, indicating either the difficulty in getting an accurate weight from the low solids material or the presence of residual HCl within their extensive pore structure. The percentage of solids decrease when comparing the gel with the MR beads. The foams have the lowest solids levels due to their increased porosity.

The capacities of the diphosphonic acid resins are given in Table II. As seen by comparing the theoretical to the experimental phosphorus capacities, the 20% DVB foam was functionalized to a greater extent than the 5% DVB MR beads. This is attributed to a greater accessibility within the foam. The foams again display a very low solids content.

The diethyl, diisopropyl, and tetraisopropyl phosphorus esters are characterized in Table III.

The macroporous beads have a much higher solids level than any of the foams.

Metal Ion Studies: Phosphonic Acid Polymers

The phosphonic acid polymers were contacted with Eu(III), Fe(III), Cu(II), and Pb(II) nitrate solutions in 0.04N HNO_3. As seen in Table IV, the gel beads, MR beads, and foam performed equally well at 30 min in the complexation of Eu(III) and Fe(III), though the foam complexed less Cu(II) and Pb(II) than the beads. At a 24-h contact time, the foam gave similar results to the beads for both copper and lead ions. The apparently slower rates of complexation for the foam with copper and lead may be due to a collapse of the microporous structure during functionalization or conditioning, and this is more readily overcome by the trivalent ions for which the phosphonic acid ligand has a greater affinity.

As noted earlier, the 2.5% DVB foams broke into smaller pieces during functionalization. Phosphonic acid foams with 20% DVB were prepared due to their greater resistance to attrition during functionalization and contact studies. The increased rigidity of the polymer matrix can, however, lead to lower complexation of the metal ions because of a decreased accessibility of the metal ions to the ligands in the polymer. Gel and MR beads were included for comparison. Contact studies from 0.04N HNO_3 solutions are reported in Table V. The amount of Eu(III) and Pb(II) complexed was approximately the same for each of the 20% DVB phosphonic acid polymers. There was a small decrease in the percentage of Eu(III) and Pb(II) complexed by these polymers relative to the less crosslinked polymers; the somewhat

Table III   Characterization of the Phorphorus Ester Polymers

Polymer Type	Ester	% DVB	% Solids	P Capacity[a]
MR	Diethyl	5	50.86	3.60
MR	Diisopropyl	5	52.80	3.30
MR	Tetraisopropyl	5	40.01	2.15
Foam	Diethyl	2.5	9.90	3.76
Foam	Diisopropyl	2.5	15.84	3.39
Foam	Tetraisopropyl	2.5	8.65	3.31
Foam	Diethyl	20	11.18	2.95
Foam	Diisopropyl	20	10.53	2.77
Foam	Tetraisopropyl	20	9.50	2.41

[a] Phosphorus capacity, mmol/g.

Table IV   Metal Ion Complexation by Phosphonic Acid Polymers from 0.04N HNO₃ Solutions

Polymer	Eu(III)	Fe(III)	Cu(II)	Pb(II)
2% DVB gel[a]	100[c] (∞)[d]	97.73 (2060)	76.93 (161)	90.64 (468)
5% DVB MR[a]	100 (∞)	100 (∞)	73.85 (124)	92.17 (512)
2.5% DVB foam[a]	98.71 (3790)	95.28 (1000)	43.08 (34.5)	73.80 (128)
2.5% DVB foam[b]	98.85 (30060)	100 (∞)	77.61 (161)	91.52 (501)

[a] 30-min contact time.
[b] 24-h contact time.
[c] Percent complexed.
[d] Distribution coefficient.

greater complexation of Pb(II) by the 20% DVB foam is an exception. Significant differences are seen between the 20% DVB polymers with Fe(III) and Cu(II), with distribution coefficients decreasing in the following order: foam > MR beads > gel beads. The 20% DVB foam complexed the same amount of Eu(III) and more Cu(II) than its 2.5% DVB crosslinked analogue. The 20% DVB gel and MR beads complexed much less Fe(III) and Cu(II) than the less crosslinked beads. The results are consistent with a more open structure for the foam relative to the beads and a greater resistance to pore collapse by the 20% DVB foam. The 24-h contact study with the 20% DVB polymers shown in Table V indicates that they approach equilibrium within 30 min when complexing europium, copper, and lead; only the foam reaches equilibrium as rapidly with iron. The foam is less influenced by an increase in matrix rigidity from 2.5 to 20% DVB than the beads because of its high level of porosity. At 24 h, the 2.5 and 20% DVB foams have identical complexing abilities.

Metal ion studies in 1N HNO₃ with 30-min and 24-h contact times (Table VI) show that the foam is able to complex greater levels of each metal

nitrate than the gel or MR beads (except for iron, where the high affinity of the ligand for the ion makes all three supports act comparably at equilibrium). The more rapid complexation by the foam in the highly acidic solution is probably due to greater pore collapse within the beads, arising from poor hydration of the ligands in the high ionic strength solution.

The europium study was repeated from a 1N HNO₃−0.4N NaNO₃ solution with a 30-min contact time. The 2% DVB gel, 5% DVB MR, and 2.5% DVB foam complexed 7.82, 14.80, and 22.66% Eu(III), respectively (distribution coefficients of 4.10, 7.60, and 14.6, respectively). These results are comparable to those from 1N HNO₃ and indicate the inherent selectivity of phosphorus acid ligands for heavy metal ions over sodium ions, even when the latter are present in great excess.

The 20% crosslinked phosphonic acid foam was also examined in 1N HNO₃ at a 30-min contact time. The amounts complexed are 24.88% Eu-(III), 92.84% Fe(III), 16.51% Cu(II), and 15.44% Pb(II) (distribution coefficients of 14.7, 569, 8.72, and 8.06, respectively). The amount complexed thus decreases relative to the performance of the

Table V   Metal Ion Complexation by 20% DVB Phosphonic Acid Polymers from 0.04N HNO₃ Solutions

Polymer	Eu(III)	Fe(III)	Cu(II)	Pb(II)
Gel[a]	95.46[c] (623)[d]	9.98 (3.27)	39.07 (18.9)	86.71 (192)
MR[a]	95.56 (599)	62.41 (46.4)	48.64 (26.4)	88.00 (204)
Foam[a]	98.51 (2900)	98.05 (2180)	62.59 (69.3)	86.09 (268)
Gel[b]	99.63 (7860)	43.34 (22.4)	52.82 (32.9)	90.58 (282)
MR[b]	100 (∞)	98.96 (2440)	52.22 (30.5)	88.00 (204)
Foam[b]	99.85 (24900)	100 (∞)	71.41 (95.4)	92.89 (500)

[a] 30-min contact time.
[b] 24-h contact time.
[c] Percent complexed.
[d] Distribution coefficient.

Table VI   Metal Ion Complexation by Phosphonic Acid Polymers from 1N HNO$_3$

Polymer	Eu(III)	Fe(III)	Cu(II)	Pb(II)
2% DVB gel[a]	13.12[c] (7.20)[d]	87.35 (329)	0	2.99 (1.47)
5% DVB MR[a]	19.70 (10.7)	80.77 (183)	2.63 (1.18)	6.03 (2.80)
2.5% DVB foam[a]	36.14 (29.8)	97.21 (1650)	33.74 (24.1)	31.83 (22.1)
2% DVB gel[b]	24.74 (15.9)	93.07 (647)	0.57 (0.28)	3.93 (1.98)
5% DVB MR[b]	27.65 (16.7)	94.74 (787)	4.53 (2.08)	7.29 (3.44)
2.5% DVB foam[b]	33.04 (22.5)	91.40 (484)	27.61 (17.3)	27.42 (17.1)

[a] 30-min contact time.
[b] 24-h contact time.
[c] Percent complexed.
[d] Distribution coefficient.

2.5% DVB foam as a result of the increased rigidity of the polymer matrix and, therefore, the lower degree of ionic accessibility. Complexation, however, is still greater than for either set of beads, again pointing to the importance of the greater degree of porosity at the higher crosslink level.

Metal Ion Studies: Diphosphonic Acid Polymers

Resins with geminal diphosphonic acid groups have a much greater ability to complex metal ions from solution than comparable monophosphonic acid resins.[22] This observation has now been extended to the case in which the ligands are immobilized on foams; while the 2.5% DVB phosphonic acid foam complexes 33.04% Eu(III) and 91.40% Fe(III) from 1N HNO$_3$ solutions at a 24-h contact time, the diphosphonic acid functionalized foam complexes both cations quantitatively. Diphosphonic acid beads and foams complex far greater levels of Eu(III) than their monophosphonic acid analogues (compare Table VI with Table VII). At 30 min, the 2.5% DVB foam complexes the highest amount of Eu(III), followed by the gel beads, the 20% DVB foam, and the MR beads. The lower metal ion complexation by the 20% DVB foam is due its increased matrix rigidity, while that by the MR beads may be attributed to pore collapse. All of the diphosphonic acid polymers perform comparably at equilibrium.

Metal Ion Studies: Phosphonate Esters

Phosphonate esters have different ionic selectivities than phosphonic acids.[23] Additionally, the metal ion affinities of immobilized alkyl ester ligands can depend on the alkyl group itself.[19] Phosphonate ester polymers, however, have low rates of ionic complexation due to their hydrophobicity, which restricts access into the beads. Initial studies were thus carried out with foams in order to explore whether they can be used as supports for coordinating ligands.

Table VIII reports results from experiments in which phosphonate esters are supported on 5% DVB MR beads, as well as 2.5 and 20% DVB foams and contacted with europium and iron solutions in 1N HNO$_3$ and at a 24-h contact time. Studies done to date with both 20% DVB diester foams yield comparable results at a 30-min contact time. The foams out perform the beads due to their high porosity and low solids content, thus indicating that foams may be useful as supports for coordinating ligands.

CONCLUSIONS

Polystyrene-based foam can be used as a support for ion-complexing ligands. Enhanced complexation kinetics are attributed to the foams' greater

Table VII   Europium Complexation with Diphosphonic Acid Polymers from 1N HNO$_3$

Contact Time	2% DVB Gel	5% DVB MR	2.5% DVB Foam	20% DVB Foam
30 min	96.75[a] (1130)[b]	46.36 (19.4)	99.34 (6040)	77.45 (98.8)
24 h	99.81 (23300)	98.51 (2170)	100	99.28 (3210)

[a] Percent complexed.
[b] Distribution coefficient.

Table VIII Metal Ion Studies with Phosphonate Ester Polymers in 1*N* HNO$_3$ Solution

Polymer	Eu(III)	Fe(III)
5% DVB MR–diethyl	4.90[a] (1.86)[b]	8.64 (3.40)
2.5% DVB foam–diethyl	45.26 (31.1)	80.85 (159)
20% DVB foam–diethyl	25.62 (12.0)	34.54 (18.4)
5% DVB MR–diisopropyl	2.83 (0.96)	0.61 (0.20)
2.5% DVB foam–diisopropyl	22.95 (10.1)	20.67 (8.83)
20% DVB foam–diisopropyl	20.48 (7.98)	20.72 (8.23)
5% DVB MR–tetraisopropyl	23.16 (6.47)	47.82 (19.7)
2.5% DVB foam–tetraisopropyl	66.90 (66.9)	82.86 (160)
20% DVB foam–tetraisopropyl	48.35 (22.6)	74.44 (70.3)

[a] Percent complexed.
[b] Distribution coefficient.

porosity and water content relative to beads. The foams show a greater advantage in solutions of high ionic strength, where the collapse of the polymer network is possible due to a decrease in hydration of the ligands. An increased crosslinking of the foams results in a lower metal ion uptake relative to less crosslinked foams, but the foams still maintain a greater accessibility than beads. Column studies are currently underway.

REFERENCES

1. D. C. Sherrington and P. Hodge, Eds., *Synthesis and Separation Using Functional Polymers,* John Wiley, New York, 1988.

2. M. Feng, L. Van der Does, and A. Bantjes, *J. Appl. Polym. Sci.,* **52,** 21 (1994).

3. E. Kalalova, V. Beiglova, J. Kalal, and F. Svec, *Angew. Makromol. Chem.,* **72,** 143 (1978).

4. U. Schilde, H. Kraudelt, and E. Uhlemann, *React. Polym.,* **23,** 131 (1994).

5. M. J. Hudson and B. K. O. Leung, *Eur. Polym. J.,* **28,** 1001 (1992).

6. K. J. Kamble and D. N. Patkar, *J. Appl. Polym. Sci.,* **56,** 1519 (1995).

7. A. Lezzi and S. Cobianco, *J. Appl. Polym. Sci.,* **54,** 889 (1994).

8. A. Guyot, *Pure Appl. Chem.,* **60,** 365 (1988).

9. K. Kun and R. Kunin, *J. Polym. Sci., Part A-1,* **6,** 2689 (1968).

10. F. Svec and J. M. J. Frechet, *Anal. Chem.,* **64,** 820 (1992).

11. C. Viklund, F. Svec, and J. M. J. Frechet, *Chem. Mater.,* **8,** 744 (1996).

12. T. Braun and A. B. Farag, *Anal. Chim. Acta,* **68,** 119 (1974).

13. T. Braun, O. Bekeffy, I. Haklits, K. Kadar, and G. Majoros, *Anal. Chim. Acta,* **64,** 45 (1973).

14. A. S. Khan, W. G. Baldwin, and A. Chow, *Anal. Chim. Acta,* **146,** 201 (1983).

15. M. P. Malony, G. J. Moody, and J. D. R. Thomas, *Analyst,* **105,** 1087 (1980).

16. Cs. Nemeth, J. Somlai, and J. Toth, *J. Radioanal. Nucl. Chem.,* **204,** 285 (1996).

17. F. Vernon, *Sep. Sci. Technol.,* **13,** 587 (1978).

18. J. M. Williams, *Langmuir,* **4,** 44 (1988).

19. S. D. Alexandratos, D. W. Crick, and D. R. Quillen, *Ind. Eng. Chem. Res.,* **30,** 772 (1991).

20. J. H. Barrett, U.S. Pat. 3,843,566 (1974).

21. A. W. Trochimczuk and S. D. Alexandratos, *J. Appl. Polym. Sci.,* **52,** 1273 (1994).

22. E. P. Horwitz, R. Chiarizia, H. Diamond, R. C. Gatrone, S. D. Alexandratos, A. W. Trochimczuk, and D. W. Crick, *Solvent Extr. Ion Exch.,* **11,** 943 (1993).

23. T. Sekine and Y. Hasegawa, *Solvent Extraction Chemistry,* Marcel Dekker, New York, 1977.