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Article

Polyols as Scaffolds in the Development of Ion-Selective Polymer-Supported Reagents: The Effect of Auxiliary Groups on the Mechanism of Metal Ion Complexation

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In developing ion-selective polymer-supported reagents, the inherent affinity of a given ligand for a targeted metal ion is found to be affected by auxiliary groups on a scaffold. A series of polyols (ethylene glycol, glycerol, tris(hydroxymethyl)ethane, pentaerythritol, and pentaerythritol triethoxylate) are immobilized onto cross-linked poly(vinylbenzyl chloride), then monophosphorylated. The pentaerythritol, glycerol, and pentaerythritol triethoxylate polymers have the highest affinities for both trivalent and divalent ions. The distribution coefficients of divalent ions (Pb(II), Cd(II), Cu(II), Ni(II), and Zn(II)) correlate with the Misono softness parameter, reflecting a single-site interaction between the metal ion and the phosphoryl oxygen. The distribution coefficients for trivalent ions are in the order Fe(III) < Al(III) < Y(III) $\lesssim$ La(III) $\sim$ Eu(III) $\sim$ Lu(III). For example, the phosphorylated pentaerythritol polymer has distribution coefficients (also reported as percent complexed) for Fe of 68.4 (75.3%); for Al of 182 (88.5%); and for the rare earth ions Y, Lu, Eu, and La of 374 (94.4%), 1390 (98.4%), 1690 (98.4%), and 708 (96.9%), respectively, from solutions at pH 2.0. The opposite trend (i.e., Fe(III) > Al(III) > (rare earths)) correlates with their hardness, acidity, electron affinity, electronegativity, and formation constants with soluble complexants, including tributyl phosphate. A binding mechanism is proposed wherein the polymer initially has the auxiliary −OH groups hydrogen-bonded to the phosphate ligand; then, binding to the polarizable phosphoryl oxygen with the divalent ions dominates, while the trivalent ions are drawn closer to the phosphoryl oxygen because of their greater charge and, once closer, bind in a multisite interaction with both the phosphate and −OH groups.

Introduction

The design of ion-selective polymers depends upon an understanding of the mechanisms by which a ligand bound to a polymer support interacts with metal ions. Such polymers are of interest to applications that include catalysis,[1] sensors,[2] toxicology,[3] analysis,[4] water treatment,[5] and environmental remediation.[6] Most commonly, a molecule known to have a high affinity for a given ion is immobilized to produce an ion-selective polymer-supported reagent: for example, bipyridine forms a complex with Cu(II),[7] as does the analogous polymer;[8] soluble[9] and immobilized[10] guanidine have a high affinity for Au(III), and the selectivity of soluble siderophores for Fe(III)[11] is retained once immobilized.[12]

A more general first-principles approach is to keep the ion-binding ligand constant and tune its selectivity by changing its microenvironment. Scaffolds provide a means of accomplishing this in a controlled manner. Scaffolds are

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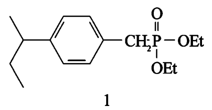
Chart 1



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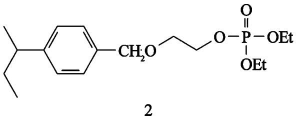

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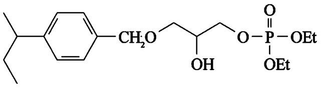

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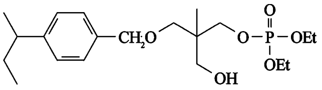

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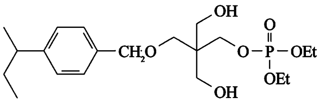

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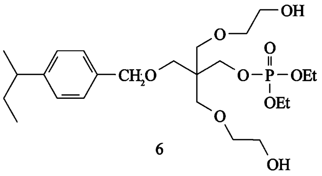

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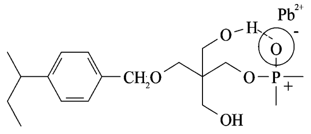
Chart 2



(I)

molecules with multiple functional groups in a known stereochemical arrangement that can act as templates for further modification reactions. Examples include cyclodextrin modified with phosphine units to form a Rh-containing catalyst,[13] calixarene modified with quaternary ammonium groups for use as a phase-transfer catalyst,[14] and oligopeptides modified with pyridine to form multimetallic compounds.[15] This approach suggests that ion-selective polymer-supported complexants can be designed by modifying a polymer with a scaffold and then modifying the scaffold with a ligand. The remaining (auxiliary) groups on the scaffold can, depending on their chemical structure, affect the ion-binding properties of the ligand by (1) interacting with the ligand or (2) interacting with the metal ion or (3) interacting with both the ligand and the metal ion. Introducing a scaffold has the advantage of placing the auxiliary groups in well-defined positions around the ligand, and their effect can be monitored by FTIR.

Polyols can be effective scaffolds: they are readily immobilized onto polymers, they can be modified with ion-binding ligands, and they place auxiliary −OH groups in different positions around the ligand depending on the polyol used. The groups can then interact directly with the ligand by hydrogen-bonding, directly with the metal ion through its lone pair electrons, or with both the ligand and the metal ion. To examine this, a series of polyols were bonded to cross-linked poly(vinylbenzyl chloride) and then phosphorylated. Starting with the phosphonate (**1**) and phosphorylated glycol (**2**) as controls, phosphorylated glycerol (**3**), tris(hydroxymethyl)ethane (**4**), pentaerythritol (**5**), and pentaerythritol triethoxylate (**6**) were prepared (see Chart 1). Contacting these polymers with a representative set of divalent transition metal ions (Pb(II), Cd(II), Cu(II), Ni(II), and Zn(II)) showed that the −OH groups affect the polarizability of the phosphoryl oxygen through hydrogen bonding, which increased the electron density at the phosphoryl oxygen (I) and increased the ligand's affinity for soft ions (see Chart 2).[16] The hydrogen-bonding interaction was evident through FTIR spectra of the polymers and has been reported with soluble molecules such as α-aminophosphonochloridates.[17] The polymers had increasing affinities for Pb(II) in the order **5** > **3** > **6** > **4** > **2**. Polarizability was identified as the dominant factor by the linear correlation between the metal ion distribution coefficients and the Misono softness parameter,[18] a measure of the ion's ability to form a dative π bond from it to the ligand. The single-site interaction thus allows for the correlation with one parameter representing a given metal ion.

A number of parameters have been used to quantify the bonding characteristics of metal ions, including softness, acidity, electronegativity, covalent index, first hydrolysis constant, hydration enthalpy, and ionic index.[19] Of these, the hydration enthalpy and the ionic index (Z^2/r, the ratio of the square of the valence, Z, to the ionic radius)[20] clearly distinguish trivalent from divalent ions (Table 1).[21] The ionic index has been used to correlate metal ion affinities of biological macromolecules.[22] Trivalent ions have a stronger Coulombic interaction than divalent ions with a given ligand. The affinity of a ligand for trivalent ions can parallel their acidity and is evidence of an electrostatic interaction; for example, with phosphinic[23] and phosphonic[24] acid ion exchange resins, and with tributyl phosphate,[25] the affinities are Fe(III) > Al(III) > La(III).

The first phase in designing an ion-selective polymer is understanding whether the ionic affinity of a ligand can be varied by the microenvironment surrounding the ligand. Research has established the mechanism by which auxiliary groups influence the affinity of the phosphate ligand for divalent ions.[16] The objective of this research was to determine whether auxiliary groups can alter the inherent

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Table 1. Hydration Enthalpies (kJ/mol) and Ionic Indices of Divalent and Trivalent Ions

	Pb^{2+}	Cd^{2+}	Mn^{2+}	Cr^{2+}	Fe^{2+}	Zn^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}
ΔH_{hydr}	−1480	−1806	−1845	−1850	−1920	−2044	−2054	−2100	−2106
Z^2/r	3.36	4.21	4.82	5.00	5.13	5.41	5.37	5.48	5.80

	La^{3+}	Y^{3+}	Eu^{3+}	Lu^{3+}	In^{3+}	Tl^{3+}	Fe^{3+}	Cr^{3+}	Al^{3+}
ΔH_{hydr}	−3283	−3620		−3758	−4109	−4184	−4376	−4402	−4660
Z^2/r	8.72	10.0	9.50	10.4	11.2	13.4	14.0	14.6	16.8

affinity of the phosphate ligand for trivalent ions, Fe(III) > Al(III) > La(III); Y(III), Eu(III), and Lu(III) were included in the study to give a representative set of trivalent ions based on the ionic index. The polyols are especially appropriate scaffolds because of the opposing ways in which the −OH groups can influence the affinity of trivalent ions. Through their ability to increase the polarizability of the phosphoryl oxygen, they continue to favor complexation of Fe(III) over La(III) since transition metals interact with a greater covalency than lanthanides[26] (the latter display a low degree of covalency[27] because the 4f electrons are shielded[28]); binding that occurs through the P═O should thus show the standard order of Fe(III) > Al(III) > La(III). However, since the −OH groups in carbohydrates are known to form complexes with lanthanides,[29] a change in the order would indicate −OH group participation in the binding mechanism.

Experimental Section

The polymer supports are prepared through the suspension polymerization of vinylbenzyl chloride and 2 wt % divinylbenzene. The beads have a particle size of 250–425 μm and are extracted with toluene prior to drying and functionalization. All chemicals are purchased from the Acros or Sigma-Aldrich chemical companies.

The syntheses of polymers **1**−**6** have been detailed.[16] Polymer **1** is prepared through the reaction of cross-linked poly(vinylbenzyl chloride) beads with triethyl phosphite. Polymers **2**−**6** are prepared by forming the sodium salts of ethylene glycol, glycerol, tris(hydroxymethyl)ethane, pentaerythritol, and pentaerythritol triethoxylate with NaH in *N*-methylpyrrolidone (or dioxane for the glycol), contacting the solutions with the beads, then phosphorylating with diethyl chlorophosphate in pyridine. The polyols were monophosphorylated to give phosphorus capacities of 3.78 (**1**), 2.62 (**2**), 2.90 (**3**), 2.57 (**4**), 2.98 (**5**), and 2.36 (**6**) mmol/g.

Metal ion studies were performed under conditions already reported.[16] Metal nitrate (Al(III), Fe(III), Y(III), Lu(III), Eu(III), and La(III)) solutions (10^{-4} N) were prepared in a background of aqueous HNO_3 at acidities noted in the following section. A mass of Buchner-dried resin to give 1.0 mmol of phosphorus ligands was pre-equilibrated with the background solution (three times for 15 min each) and then shaken with 10 mL of the metal ion solution for 17 h. Final concentrations were determined by inductively coupled plasma-atomic emission spectrometry (Spectroflame M120E). The quantity of metal complexed by the polymer was calculated by difference from the levels in the initial and final solutions. Results are reported as percent complexation (mmol $M^{n+}_{polymer}$/mmol $M^{n+}_{(initial)soln}$) and as distribution coefficients ((mmol $M^{n+}_{polymer}$ per $g_{polymer}$)/(mmol $M^{n+}_{(final)soln}$ per $mL_{(final)soln}$)). All experiments were done in triplicate; the percent complexations are reproducible to ± 3% (which results in the distribution coefficients being reproducible to better than ± 10%).

FTIR spectra were recorded on a Bomem spectrophotometer with KBr pellets of the polymers.

Results

The affinities of polymers **1**−**6** for Al(III), Fe(III), Y(III), Lu(III), Eu(III), and La(III) as a function of pH are reported in terms of percent complexation and distribution coefficients (Table 2). No polymer has an affinity for trivalent ions from 1 M HNO_3 (i.e., pH 0). The phosphonate **1** has only a moderate affinity for trivalent ions as the pH approaches 3. The affinity of polymer **2** for all ions is low, even at pH 2.9. There is no steric hindrance to complexation by the polymer support given that the phosphoryl oxygen is four atoms closer to the support in **1** relative to **2**, yet its distribution coefficients are greater.

The introduction of an −OH group to give polymer **3** results in a greater extent of complexation for the trivalent ions. The affinities for the rare earth (RE) ions Y, Lu, Eu, and La are ≥80% at pH 2.0 and ≥94% at pH 2.6. The affinity for Fe remains moderate, even at pH 2.9, while that for Al is significantly greater. The stereochemical placement of the −OH group is important to the ionic affinities: polymer **4** also has one −OH group, but its affinities are much lower than **3** (being comparable to **2**, which has no −OH groups). Polymer **5**, with two −OH groups, has a significantly higher affinity for the ions than polymer **3** (the difference is evident from solutions at pH 1.0 where **5** has affinities of 51.0, 59.6, and 54.0% for La, Eu, and Lu, respectively, while **3** has affinities of 32.3, 35.9, and 34.4% for the ions in the same sequence). The Fe affinity at pH 2.6 is greater for **5** than for **3**. However, the placement of the −OH groups is as important as the number of −OH groups: polymer **6**, also with two −OH groups, has lower affinities than **5** and is comparable to (or somewhat lower than) **3**. While **6** achieves high levels of trivalent ion complexation, it requires a pH in excess of 2.6 to accomplish this, in contrast to **5**, which achieves it at pH 2.0. Generally, then, the polymers have affinities for the trivalent ions in the order **5** > **3** > **6** > **4** ∼ **2**. For polymers with significant complexation at pH ≥ 2.0 (i.e., **3**, **5**, and **6**), the REs have comparable affinities, and the overall order is REs > Al(III) ≥ Fe(III).

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Table 2. Trivalent Ion Affinities as Percent Complexation (and Distribution Coefficients) for Phosphonate and Phosphorylated Polymers

	polymer **1** (phosphonate)				polymer **2** (glycol)			
	pH 0.0	pH 2.0	pH 2.6	pH 2.9	pH 0.0	pH 2.0	pH 2.6	pH 2.9
Al		19.3% (6.15)	44.6% (20.4)	38.9% (16.6)	1.01% (0.162)	9.68% (1.68)		13.2% (3.12)
Fe		37.1% (15.0)	47.7% (22.6)	47.4% (23.5)	10.7% (1.86)	14.4% (2.69)		21.1% (5.61)
Y		24.8% (8.41)	46.9% (22.3)	43.9% (20.5)	10.9% (2.46)	14.9% (3.61)	13.4% (3.16)	16.9% (4.07)
Lu		20.8% (7.51)	32.8% (13.7)	44.5% (21.2)	5.94% (1.32)	15.6% (3.85)	19.7% (5.03)	22.0% (5.66)
Eu		20.3% (6.88)	34.1% (14.9)	51.5% (30.2)	7.79% (1.79)	15.7% (3.85)	19.1% (5.01)	22.0% (5.87)
La		16.0% (5.48)	28.8% (11.3)	46.6% (25.8)	5.41% (0.939)	16.9% (3.22)		19.5% (5.12)

	polymer **3** (glycerol)				polymer **4** (tris(hydroxymethyl)ethane)			
	pH 0.0	pH 2.0	pH 2.6	pH 2.9	pH 0.0	pH 2.0	pH 2.6	pH 2.9
Al	2.06% (0.461)	72.8% (62.2)	93.7% (345)	91.2% (246)	3.03% (0.530)	10.8% (2.03)	7.77% (1.76)	17.6% (4.42)
Fe	10.4% (2.51)	48.7% (22.7)	56.8% (31.1)	70.1% (55.3)	14.4% (2.83)	17.6% (3.59)	14.9% (3.66)	26.3% (7.46)
Y	8.60% (2.05)	88.6% (244)	96.7% (712)		12.6% (2.71)	18.3% (4.17)	15.3% (3.77)	21.5% (5.66)
Lu	8.95% (2.18)	84.4% (117)	95.9% (512)	99.8% (11870)	7.36% (1.66)	14.7% (3.62)	18.3% (4.67)	21.0% (5.68)
Eu	12.7% (3.13)	84.1% (124)	96.0% (533)	99.8% (11990)	8.32% (1.95)	12.9% (3.16)	19.7% (5.23)	23.9% (6.75)
La	17.7% (4.53)	80.6% (91.8)	94.2% (361)	99.2% (3060)	10.5% (1.97)	15.1% (2.98)	15.0% (3.62)	25.9% (7.08)

	polymer **5** (pentaerythritol)				polymer **6** (pentaerythritol triethoxylate)			
	pH 0.0	pH 2.0	pH 2.6	pH 2.9	pH 0.0	pH 2.0	pH 2.6	pH 2.9
Al	4.12% (0.977)	88.5% (182)	96.8% (705)	98.9% (2070)	18.5% (3.93)	45.2% (14.3)	66.0% (37.9)	83.5% (97.3)
Fe	28.0% (8.63)	75.3% (68.4)	90.8% (233)	96.7% (684)	24.2% (5.52)	48.9% (16.5)	69.7% (43.8)	88.6% (149)
Y	15.8% (4.09)	94.4% (374)	99.1% (2380)		14.3% (3.08)	56.4% (24.1)	97.2% (651)	99.4% (3080)
Lu	13.5% (3.55)	98.4% (1390)			13.3% (2.92)	55.2% (23.8)	96.9% (617)	99.8% (8170)
Eu	18.7% (5.13)	98.7% (1690)			10.1% (2.13)	58.0% (26.3)	98.5% (1270)	99.6% (5270)
La	24.8% (7.40)	96.9% (708)			12.6% (2.47)	59.1% (24.9)	98.4% (1200)	99.8% (9280)

Discussion

Phosphorylated polymers **2**−**6** do not complex divalent and trivalent ions in solutions of 1 M HNO_3 due to competition between H^+ and the metal salt for binding sites. As has been reported, polarizable divalent ions have a high affinity for phosphoryl oxygens that become more polarizable by hydrogen bonding to the auxiliary −OH groups.[16] The affinities follow the Misono softness parameter and reflect the ability of the ion to enter into a covalent π-bond interaction. The complexing strength of the polymers for divalent ions is **5** > **3** > **6** > **4** > **2**. The order is the same for trivalent ions except that **4** has the same low affinity as **2**. As is most apparent from the range of distribution coefficients with the glycerol (**3**) and pentaerythritol (**5**) polymers from solutions at and above pH 2 (Table 2), the affinities are in the order REs > Al(III) > Fe(III). Polymers **1**, **2**, and **4** have similarly low distribution coefficients, while polymer **6** shows REs > Al(III) ∼ Fe(III).

Metal Ion Parameters. Inferring the mechanism by which metal ions bind with a ligand is facilitated by correlating distribution coefficients with a parameter representative of the given ions. The formation constant of the metal ion in its reaction with the hydroxide ion is a measure of its acidity;[30] the logarithmic values for the ions being studied are Y (6.3), La (5.5), Eu (−), Lu (6.4) < Al (9.03) < Fe (11.81).[31] A hardness scale was developed by combining these constants with those for the reaction with ammonia[29] to give Y (5.9), La (5.3), Eu (−), Lu (5.7) < Al (6.7) < Fe (8.0). Electron affinities may correlate reactions involving hard ligands better than the hardness scale,[32] but the trend remains the same: Y (20.52), La (19.18), Eu (−), Lu (20.96) < Al (28.45) < Fe (30.65). Electronegativities also follow the same trend:[33] Y (1.291), La (1.327), Eu (−), Lu (−) < Al (1.691) < Fe (1.726). The parameters all follow a trend opposite that of the distribution coefficients when the metal ions interact with the phosphorylated polymers: REs > Al > Fe.

Formation Constants. Organic reaction mechanisms can be identified through linear free-energy relationships wherein one set of equilibrium constants is correlated with another.[34] This may be extended to metal ion complexation reactions by attempting to correlate distribution coefficients with metal ion formation constants involving soluble complexants. In the reaction of acetylacetone with rare earth, aluminum, and ferric ions,[35] the formation constants (as logarithms) are Y (6.4), La (5.1), Eu (6.0) < Al (8.6) < Fe (9.8). The reaction of these ions with the catecholate ligand follows the same trend and correlates with the hydroxide formation constants.[36] A comprehensive study of formation constants with 5,7-dibromo, dichloro, and dinitro derivatives of 8-hydroxyquinoline N-oxide determined that, in each case, the affinities are REs < Al < Fe:[37] for dibromo, the logarithmic values are Y (8.74), La (7.81), Lu (9.39) < Al (10.20) < Fe (11.06); for dichloro, they are Y (8.31), La (7.81), Lu (8.88) < Al

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(9.23) < Fe (10.42), and for dinitro, they are Y (4.12), La (3.57), Lu (4.56) < Al (4.80) < Fe (5.29). For each compound, affinity increases with increasing metal ion acidity. The pK_a values for the three compounds are 11.60 (dibromo), 11.50 (dichloro), and 6.87 (dinitro); comparison to the formation constants shows that ionic affinity increases as the ligand pK_a increases. It is thus concluded that the affinity series REs < Al < Fe for each complexant is due to a dominant electrostatic attraction since a given metal ion has increasing affinity for ligands with increasing basicity. The formation constants parallel the order of the metal ion parameters, and again, the trend is opposite that with the phosphorylated polyols. The trend is also not consistent with the enthalpies of hydration and ionic indicies (Table 1).

Mechanism. The critical structural features of polymers **3**−**6** are the phosphate ligand and the auxiliary −OH groups. The pH is too low to ionize the −OH groups, and they have no significant affinity for di- and trivalent ions prior to phosphorylation: immobilized pentaerythritol complexes < 5% of di- and trivalent ions from solutions at pH 2. Carbohydrates bind dextran and poly(vinyl alcohol) at pH 6–8,[38] and binding to Cu^{2+} is weak until pH > 5.[39]Trivalent ions form stronger complexes than divalent ions with xylitol and sorbitol, with the highest affinities evident for lanthanides.[40] Aluminum forms complexes with ribose at acidic pH as the hydrated ion.[41] The arrangement of −OH groups in the carbohydrates is important to complex formation: different affinities are due to steric factors in the bonding interaction between the −OH groups and the metal ion. The rare earths bind to −OH groups in the same manner.[42]

The following mechanism is consistent with the results and literature precedent:

i.. The absence of a correlation between the distribution coefficients and parameters for the trivalent ions suggests a multisite interaction.

ii.. The affinity of trivalent ions for polymers **3**, **5**, and **6** is due to an electrostatic interaction with the phosphate ligand coupled to binding with the −OH groups, and those groups are responsible for a favorable coordination environment for the ions in the order REs > Al> Fe.

iii.. The rare earths have the highest affinities due to their stronger interaction with the −OH groups, as indicated by the carbohydrate results and their higher coordination numbers with numerous classes of compounds, including saccharides.[43]

iv.. Polymer **5** has the highest affinities for the divalent ions due to single-site coordination at the phosphoryl oxygen and the highest affinities for the trivalent ions due to multisite coordination at the phosphoryl oxygen and −OH groups (Figure 1).

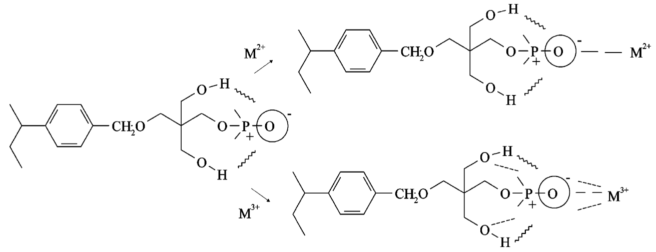

Figure 1. Interaction of phosphorylated pentaerythritol with divalent and trivalent ions.

v.. The Thorpe−Ingold effect precludes the −OH groups in polymer **4** from interacting with the trivalent ions: the stronger-than-expected hydrogen bond is evident in the FTIR spectrum[16] and is too strong to break for coordination with the ions.

vi.. Polymer **2** has very low complexing ability due to an absence of −OH groups for coordination and a low basicity of the phosphoryl oxygen.

vii.. Polymer **1** is comparable to **2** at pH 2 and better than **2** at pH ≥ 2.6 due to the increased basicity of the phosphonate versus the phosphate ligand.

FTIR Spectra. FTIR spectra indicate that the phosphate ligand and the −OH groups are initially hydrogen-bonded, and the correlation with the divalent ion softness parameter suggests that the hydrogen bond is retained after complexation of the ion.[16] The ability of a phosphoryl oxygen to coordinate divalent ions while remaining hydrogen-bonded to a neighboring −OH group has been reported with 2-hydroxy-3-benzoylpropyl phosphonic diester by ^{17}O NMR spectroscopy.[44] A study of metal-complexed **5** by Fourier-transform IR spectroscopy−attenuated total reflection (FTIR-ATR) is in progress in order to gain spectroscopic evidence for binding at the P═O and −OH groups.

Uranyl Affinity. Complexation of oxocations by carbohydrates has been reported.[45] The stereochemistry of the −OH groups is important to the strength of the complex being formed. A study with the uranyl ion is consistent with results in the current report:[46] at pH 1, 2, and 3.2, the percent complexed by polymer **5** is 92.4%, 99.4%, and 100%, respectively; for polymer **2**, it is 38.8%, 24.9%, and 28.8%; and for polymer **1**, it is 49.7%, 51.5%, and 77.4%, again indicating the importance of changes in the basicity of the phosphoryl oxygen. (Participation of the −OH groups is likely, especially given the high coordination number of the uranyl ion,[47] and FTIR-ATR studies are in progress.)

Conclusions

Functionalized scaffolds provide a versatile pathway to the design of ion-selective polymer-supported reagents.

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Polyols have −OH groups that modify the microenvironment around a primary ligand, thus affecting the observed ionic affinities by direct interaction with the ligand and, in some cases, with the metal ion as well. Molecular modeling studies will show whether binding requires a reorganization of the −OH groups toward the trivalent ion or whether hydrogen bonding is retained after electrostatic binding to the trivalent ion occurs (though results with **4** suggest that the hydrogen bond is retained after the trivalent ion is bound; additionally, the effectiveness of polymer **3** is due to its increased basicity, and that basicity would decrease to that of **2** in the absence of the hydrogen bond). Polyamines provide $-NR_2$ groups for additional interactions, and such studies are in progress.

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