Bifunctional Coordinating Polymers: Auxiliary Groups as a Means of Tuning the Ionic Affinity of Immobilized Phosphate Ligands

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ABSTRACT: A series of coordinating polymers are synthesized by immobilizing polyols (ethylene glycol, glycerol, 1,1,1-tris(hydroxymethyl)ethane, pentaerythritol, and pentaerythritol triethoxylate) onto cross-linked poly(vinylbenzyl chloride) and then monosubstituting with diethyl phosphate ligands. Ionic affinities are determined with a series of divalent transition metal ions: Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}. For each polymer, the variable controlling the affinity, as measured by the distribution coefficient, D, is the polarizability of the transition metal ion, as measured by the Misono softness parameter, σ. For $D \geq 0$, the correlation is $D = S\sigma + \sigma_{\min}$, where S is the selectivity and $\sigma_{\min}$ is the minimum softness of a divalent transition metal ion which must be exceeded for coordination to occur. The values of S are 3810 (pentaerythritol), 1480 (pentaerythritol triethoxylate), 1340 (glycerol), 474 (tris(hydroxymethyl)ethane), and 21 (glycol); increasing S indicates greater selectivity. It is proposed that, though coordination occurs through the phosphate ligand, selectivity varies as a function of the polyol: the −OH groups act as auxiliary groups in modifying the polarizability of the phosphate ligands (the primary ligand) through hydrogen bonding and, as a result, affecting the selectivity of the primary ligand. Interaction between the −OH and phosphate moieties is evident in FTIR spectra of the polymers with the absorbance of a band within the range 874−895 cm^{-1}.

Introduction

The selective complexation of metal ions from aqueous solutions has important implications for environmental science, ion chromatography, and sensor technology.[1] Ion-exchange resins display high ionic affinities when the solution pH exceeds the ligand pK_a, but this may not be coupled with high selectivity.[2,3] Cross-linked polymers with structurally intricate coordinating ligands have thus been studied and enhanced selectivity found when the coordinating moiety complements the properties of the targeted metal ion.[4] Variables that characterize a metal ion include its coordination geometry, polarizability, valence electron configuration, ionization potential, and ionic radius.[5] Modeling a ligand on the complex geometry of a targeted metal ion is problematic since a metal can form a variety of geometrical structures: for example, Cu^{2+} complexes with tris(2-aminoethyl)amine vary between trigonal bipyramidal and square pyramidal,[6] Zn^{2+} phosphonate complexes have octahedral and tetrahedral structures,[7] and Cd^{2+} phenoxide complexes have square planar, distorted tetrahedral, and bipyramidal geometries.[8] On the other hand, the hard−soft−acid−base (HSAB) principle[9] has proven useful in utilizing differences in polarizability to predict metal−ligand binding.[10] Thus, the affinity of nitrogen-containing polycarboxylates for In(III),[11] tetrakis(2-pyridylmethyl)ethylenediamine for Cd(II),[12] hydrotris(methimazolyl)borate for Hg(II),[13] and sulfur-containing macrocycles for Ag(I)[14] all utilize the HSAB theory to explain the results.

The objective of this research is the design of polymer-supported reagents that selectively complex metal ions by tuning the polarizability of the immobilized ligand. Polarizability was chosen as the target variable because it could be controlled with relatively simple ligands. The underlying concept is to place a coordinating ligand (the primary ligand) near a functional group (the auxiliary group) that would be expected to interact with the primary ligand, altering its electron density and thus its polarizability and ionic affinities. In identifying the moieties to be used, it was noted that α-aminophosphonochloridates alter the electron density at the phosphoryl moiety by intramolecular hydrogen bond formation:[15] reaction by triethylamine at the phosphorus occurred only if the Fmoc-protected amine was secondary while conversion to a tertiary amine by, for example, methylation obviated reaction by the NEt_3. This, as well as NMR evidence, led to the conclusion that hydrogen bonding between the NH and P═O moieties increased polarization of the phosphorus−oxygen bond which, in turn, made the phosphorus more electron-deficient and thus more reactive toward nucleophilic attack. Since electron density changes at the phosphoryl oxygen will affect its polarizability, diethyl phosphate was chosen to be the primary ligand given that the phosphoryl oxygen coordinates metal ions in soluble complexants such as tributyl phosphate.[16] The hydroxyl group was chosen as the auxiliary group given its propensity for hydrogen bonding and the availability of a wide array of alcohols. The microenvironment around the phosphate is thus varied by bonding it to polyols (ethylene glycol, glycerol, 1,1,1-tris(hydroxymethyl)ethane, pentaerythritol, and pentaerythritol triethoxylate) that are immobilized on poly(vinylbenzyl chloride) beads cross-linked with 2% divinylbenzene, giving polymers **2**−**6**; polymer **1** is the phosphonate diester resin and is included for comparative purposes (see Chart 1). A low level of cross-linking was chosen so that access of metal ions into the matrix would not be hindered.

The metal ions selected to probe the phosphate ligand in its different microenvironments encompass a range of polarizability, as quantified by the Misono softness

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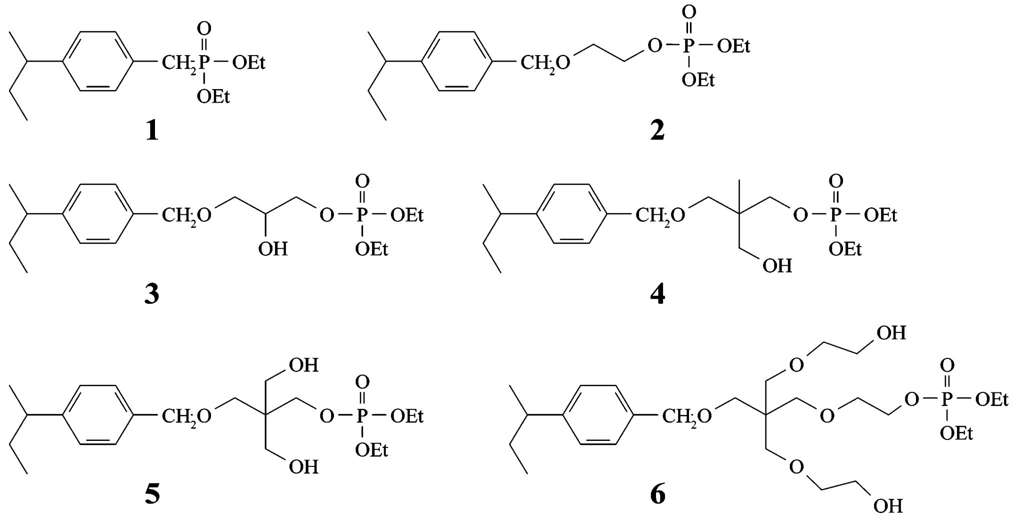
Chart 1



parameter, σ, which is also a measure of the ion's ability to form a π-bond (softer ions have larger σ values):[17] Pb^{2+} (0.40), Cd^{2+} (0.30), Cu^{2+} (0.28), Ni^{2+} (0.25), and Zn^{2+} (0.24). Metal ion contact studies are done in a background of 0.01 M HNO_3, a solution which is of high enough acidity to prevent metal ion hydrolysis but not high enough to have the acid compete with the metal ions for binding to the phosphoryl oxygen.

Experimental Section

Copolymer beads of vinylbenzyl chloride (VBC) and 2 wt % divinylbenzene (DVB) were prepared by suspension polymerization with 0.5% of benzoyl peroxide as initiator. The VBC was a mixture of meta- and para-isomers in a 60:40 ratio. After polymerization, the beads were washed with water and extracted with toluene. VBC, DVB, and reagent-grade ethylene glycol, glycerol, 1,1,1-tris(hydroxymethyl)ethane, pentaerythritol, pentaerythritol triethoxylate, diethyl chlorophosphate, triethyl phosphite, lead nitrate, copper nitrate, cadmium nitrate, nickel nitrate, and zinc nitrate, as well as lead, cadmium, copper, nickel, and zinc ICP standard solutions, were purchased from Sigma-Aldrich or Acros Chemical. The molar ratio of polyol to NaH was always significantly greater than unity in order to ensure predominant monoalkoxide formation: the values for glycol, glycerol, tris, pentaerythritol, and pentaerythritol triethoxylate were 6.4, 5.4, 3.0, 3.0, and 3.0, respectively. The higher values were needed for glycol and glycerol because the excess polyol in each case solubilized the alkoxide and prevented precipitation.

Synthesis of Phosphonate Diester Polymer (1). Ten grams of copolymer beads was swollen in 100 mL of triethyl phosphite for 2 h and refluxed for 17 h. The beads were washed with acetone, acetone/water, and water and then conditioned by eluting with 1 L each of 1 M NaOH, H_2O, 1 M HCl, and H_2O. The resulting resin had a phosphorus capacity of 3.78 mmol/g (theoretical P capacity for 100% reaction is 3.78 mmol/g).

Synthesis of Phosphorylated Glycol Polymer (2). Ten grams of NaH (60% dispersion) was slowly added to 100.0 g of ethylene glycol and 100 mL of dioxane in a 250 mL round-bottom flask fitted with a condenser, overhead stirrer, and gas inlet tube. The mixture was stirred at room temperature under N_2 flow for 2 h. To the resulting glycolate, 6.0 g of copolymer beads swollen in 40 mL of dioxane for 2 h was added. The reaction was refluxed for 17 h. The solution was removed, and the beads were washed with dioxane, dioxane/water (1:1) and water and then vacuum-dried at 70 °C for 12 h.

The glycolate polymer was phosphorylated with diethyl chlorophosphate (DECP) in pyridine. The beads (2.0 g) were swollen in 50 mL of pyridine for 2 h in a 250 mL round-bottom flask. DECP (10 mL) was added, and the reaction was stirred for 17 h at room temperature. The beads were washed with 100 mL of methanol, methanol/water (1:1), and water and then conditioned as above. The polymer had a phosphorus capacity of 2.62 mmol/g (theoretical P capacity for 100% reaction is 3.06 mmol/g).

Synthesis of Phosphorylated Glycerol Polymer (3). Eight grams NaH (60% dispersion) was slowly added to 100.0 g of glycerol and 200 mL of *N*-methylpyrrolidinone (NMP) in a 500 mL round-bottom flask fitted with a condenser, overhead stirrer, gas inlet tube, and thermometer. The mixture was stirred at room temperature under N_2 flow for 2 h. Copolymer beads (10.0 g) swollen in 50 mL of NMP for 2 h were then added to the solution. The reaction was kept at 80 °C for 24 h. The solution was removed, and the beads were washed with 100 mL each of NMP, NMP/water (1:1), and water and then vacuum-dried at 70 °C for 12 h. Phosphorylation followed the procedure given above. The resulting polymer had a phosphorus capacity of 2.90 mmol/g (theoretical P capacity for 100% reaction is 2.79 mmol/g).

Synthesis of Phosphorylated Tris(hydroxymethyl)ethane Polymer (4). The procedure is the same as that for polymer **3**, except for the following: use 50.0 g of tris(hydroxymethyl)ethane and 6.0 g of NaH (in 200 mL of NMP); stir that solution at 80 °C for 2 h; add 5.0 g of copolymer beads (in 50 mL of NMP) and continue as above. The resulting polymer had a phosphorus capacity of 2.57 mmol/g (theoretical P capacity for 100% reaction is 2.58 mmol/g).

Synthesis of Phosphorylated Pentaerythritol Polymer (5). The procedure is the same as that for polymer **3**, except for the following: use 60.0 g of pentaerythritol and 6.0 g of NaH (in 300 mL of NMP); stir that solution at 80 °C for 2 h; add 6.0 g of copolymer beads (in 30 mL of NMP) and continue as above. The resulting polymer had a phosphorus capacity of 2.98 mmol/g (theoretical P capacity for 100% reaction is 2.47 mmol/g).

Synthesis of Phosphorylated Pentaerythritol Triethoxylate Polymer (6). The procedure is the same as that for polymer **3**, except for the following: use pentaerythritol triethoxylate with 5.0 g of NaH; stir that solution at 80 °C for 2 h; add 4.0 g of copolymer beads (in 50 mL of NMP) and continue as above. The resulting polymer had a phosphorus capacity of 2.36 mmol/g (theoretical P capacity for 100% reaction is 1.85 mmol/g).

Characterization. The experimental details for the phosphorus and chlorine elemental analyses have been reported.[18]

Metal Ion Studies. The metal ion affinities were quantified by batch equilibration experiments with 10^{-4} N metal nitrate (Pb(II), Cd(II), Cu(II), Ni(II), and Zn(II)) solutions in 0.010 M HNO_3. Enough Buchner-dried resin to give 1.0 mmol of phosphorus ligands was preequilibrated with the background solution (three times for 15 min each) and then shaken with

Scheme 1

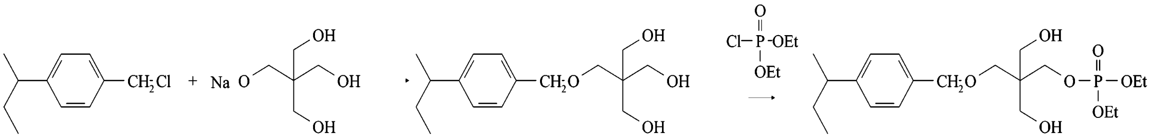


Table 1. Metal Ion Affinities of the Phosphonate (1) and Phosphate (2−6) Polymeric Reagents as Percent Complexed (and Distribution Coefficients)

	polymer **1**[a]	polymer **2**[b]	polymer **3**[c]	polymer **4**[d]	polymer **5**[e]	polymer **6**[f,g]
Pb^{2+}	6.10% (0.946)	12.9% (3.51)	89.9% (237)	76.1% (79.0)	96.1% (651)	90.7% (245)
Cd^{2+}	5.09% (0.771)	0.71% (0.169)	78.9% (92.7)	46.4% (21.6)	88.2% (202)	64.7% (44.2)
Cu^{2+}	4.12% (0.629)	2.54% (0.625)	79.2% (102)	44.7% (20.1)	89.6% (225)	73.0% (63.1)
Ni^{2+}	0.67% (0.299)	1.64% (0.316)	55.9% (24.9)	6.21% (1.61)	77.4% (92.1)	20.3% (3.92)
Zn^{2+}	0.44% (0.0831)	0.16% (0.0423)	46.5% (23.2)	23.5% (7.68)	41.9% (14.9)	43.5% (18.3)

[a] Diethyl phosphonate. [b] Glycol/phosphate. [c] Glycerol/phosphate. [d] Tris(hydroxymethyl)ethane/phosphate. [e] Pentaerythritol/phosphate. [f] Pentaerythritol triethoxylate/phosphate. [g] All values are given to three significant figures; however, the reproducibility in the percent complexed values is ±3%.

10 mL of the given metal ion solution for 17 h. Final concentrations were determined by ICP-AES (Spectroflame M120E).

Results

The functionalization reaction is indicated by Scheme 1 with pentaerythritol as a representative example. Two assumptions were made: (i) the sodium alkoxide prepared by reaction of NaH with an excess of the corresponding alcohol would react in a 1:1 ratio with the CH_2Cl groups on the polymer, and (ii) diethyl chlorophosphate (DECP) would react at only one −OH group. In all cases, there was no chlorine in the beads after contact with the alkoxide, indicating that reaction went to completion. The degree to which secondary cross-linking occurred by reaction of a single alkoxide with neighboring $-CH_2Cl$ groups was estimated by comparing the experimental phosphorus capacity with the one expected if there was monosubstitution and subsequent monophosphorylation. The results with ethylene glycol indicate that approximately 10% secondary cross-linking may be possible (the phosphorus capacities are reproducible to ±0.2 mmol/g). However, the phosphorus capacities for both the glycerol and tris resins are very close to theoretical assuming monosubstitution. (It is possible that some secondary cross-linking occurs, and the phosphorus capacity is increased by substitution at more than one −OH group per alcohol moiety; however, it has been found that disubstitution of the polyols is difficult, even at high DECP levels.) When also considering the results with the pentaerythritol and triethoxylate resins, it is possible to conclude that there may be, at most, 10% disubstitution by the alkoxide and little subsequent polysubstitution. (Numerous batches of each resin have been made, and the metal ion results reported here are consistently reproducible.)

The metal ion affinities for each polymer-supported reagent are given in Table 1. The phosphonate polymer (**1**) has no affinity for any of the five transition metal ions. This is not due to the proximity of the polymer backbone to the ligand since its performance is similar to that of polymer **2**, in which the phosphoryl oxygen is four atoms further removed from the backbone. Additionally, both polymers have a very high affinity for Au(III): the amounts complexed by **1** from solutions of 10^{-4} N $AuCl_3$ in 0.01, 1.0, and 5 M HNO_3 are 99.8%, 99.6%, and 97.1%, respectively. The amounts complexed from the same concentrations of HCl are 99.8%, 99.6%, and 99.9%, respectively. Identical results are obtained with the phosphorylated glycol polymer. Polymers **3**−**6** are distinguished by having one or two −OH groups proximate to the phosphoryl group and, in each case, have much greater ionic affinities than polymers **1** and **2**. Each of the unphosphorylated polyols complex <5% of the divalent metal ions from solutions of 0.01 M HNO_3.

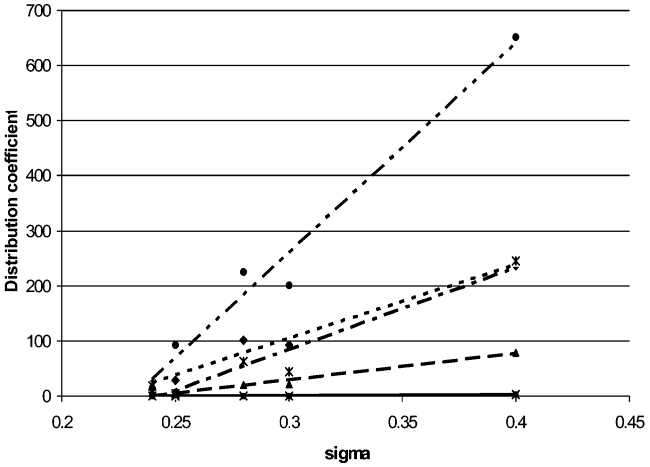


Figure 1. Correlation of metal ion distribution coefficients vs sigma values for the phosphorylated polymers substituted with pentaerythritol (●), glycerol (◆), pentaerythritol triethoxylate (*), tris(hydroxymethyl)ethane (▲), and glycol (×).

In comparing the ionic affinities within each polymer, the general trend is Pb > Cd ≥ Cu > Ni ≥ Zn. This trend mirrors that of the ionic polarizabilities, as quantified by the Misono softness parameter (σ): Pb^{2+} (0.40), Cd^{2+} (0.30), Cu^{2+} (0.28), Ni^{2+} (0.25), and Zn^{2+} (0.24). Figure 1 illustrates the trends by plotting the distribution coefficients vs the σ values. The graph shows the lines with $D \geq 0$ since the distribution coefficient can only have values greater than zero. The slopes, intercepts along the x-axis, and correlation coefficients are given in Table 2.

The results in Figure 1 and Table 2 correspond to eq 1:

$$D = S\sigma + \sigma_{\min} \qquad (1)$$

where S is the selectivity of the polymer (an increasing slope is consistent with increasing selectivity) and $\sigma_{\min}$ is the value of σ at $D = 0$, the minimum value it must have for any complexation to occur.

Table 2. Linear Correlations for Polymers 1−6[a]

polymer	slope	x-axis intercept	correlation coeff
1	5	0.18	0.875
2	21	0.25	0.935
3	1340	0.22	0.986
4	474	0.24	0.983
5	3810	0.23	0.988
6	1480	0.24	0.968

[a] The values for **1** and **2** are given for comparative purposes; complexation by those resins is very low, which leads to slopes (and correlations) that are much lower than those for the other resins.

An additional trend becomes evident when comparing the affinities of each ion for the phosphate-substituted polymers: generally, a given ion has an affinity for the polymers in the order **5** > **3** > **6** > **4** > **2** (with Pb, the difference between **3** and **6** is negligible; with Zn, the ion with the lowest affinities for the different polymers, **5**, **3**, and **6** behave comparably). There is thus a clear difference in performance of the different polymers, with the phosphate ligand bonded to pentaerythritol (**5**) having the highest affinity for the divalent transition metal ions while that with no −OH groups proximate to the P═O (**2**) having the lowest metal ion affinities.

Discussion

Results with the phosphonate diester polymer indicate that the phosphoryl oxygen does not have an inherent affinity for divalent transition metal ions from 0.01 M HNO_3 solutions; additionally, no complexation is evident as the acid strength is increased up to 5 M. Identical results are obtained with the phosphorylated glycol polymer, indicating that the difference is not due to any electronic difference that may exist between phosphate and phosphonate ligands or to the proximity of the phosphoryl oxygen to the polystyrene backbone. Accessibility of the metal ions to the ligand is not a variable, as indicated by the high levels of complexation of Au(III) from acidic solutions. Furthermore, while the phosphonate polymer has no affinity for Fe(III) from 5 M HNO_3, it complexes 95.4% Fe(III) from a 10^{-4} N solution of $FeCl_3$ in 5 M HCl. Protonation of the phosphoryl oxygen allows for complexation of $FeCl_4^-$, following the same mechanism as that for complexation of the Au(III) anion. The complexation of $H^+AuCl_4^-$ by neutral phosphates has been observed with tris(2-ethylhexyl)phosphate and is due to the ability of the phosphoryl oxygen to hydrogen bond with the H^+.[19]

Linearity in the D vs σ correlation indicates that the polarizability of the divalent transition metal ion is a dominant variable in determining affinity. An increasing slope indicates increasing selectivity. Intersection at a common point on the x-axis (average of +0.24) by the five phosphate polymers indicates that a minimum softness is required for complexation to occur; it is likely that this value will be a function of the primary ligand though this remains to be determined.

It is important to develop an understanding of the origin of the different selectivities displayed by the polymers in order to predict the performance of other polymers that can be designed. If the linearity in the D vs σ correlation indicates that the polarizability of the transition metal ion is the dominant variable, then it is the polarizability of the phosphate ligand that is the principal determinant in the observed affinity and selectivity. Though it is possible that the selectivity changes because the −OH groups in the phosphate polymers bind to the transition metal ions, the different geometrical preferences of the ions would not lead us to expect that linearity with σ would be maintained. Additionally, the unphosphorylated polyols have no affinity for the five divalent transition metal ions from 0.01 M HNO_3. The hypothesis now proposed to account for the experimental observations is that *the −OH groups in a given polymer act as auxiliary groups to activate the phosphoryl oxygen by increasing its softness, and it is the resulting differences in polarizability that affect binding to the metal ions to different degrees*. This activation is necessary given that the phosphonate and phosphorylated glycol polymers have no divalent ion affinity.

Intramolecular hydrogen bonding between −OH and P═O moieties has long been known.[20] A conformational analysis of (2-hydroxyalkyl)phosphonates by ^{31}P NMR ascribed deshielding at the phosphorus to decreased π donation from intramolecular hydrogen bonding between the phosphoryl oxygen and the −OH group.[21] (Metal salts added to acetone-d_6 solutions of the phosphonates were bound to the phosphoryl oxygen, as evidenced by downfield shifts of the ^{31}P signals.) The IR band of the P═O moiety showed almost no shift despite its involvement in hydrogen bonding.[22] In an FTIR study of hydrogen bonding in poly(alkylene phosphate)s, the P═O stretch was at 1218 cm^{-1}, the (P)O−C stretch was at 1058 cm^{-1}, and bands at 890 and 816 cm^{-1} were assigned to the asymmetrical and symmetrical P−O(C) stretching vibrations, respectively, both of which are relatively weak.[23] As the temperature was increased, the extent of hydrogen bonding decreased, but the effect on the position of the IR bands was negligible until the temperature was close to the melting point. There was, however, an appreciable change in the intensity of the bands, and this was especially apparent with the P−O(C) stretch at 891 cm^{-1}: upon heating from 26 to 56 °C, there was a significant decrease in peak intensity.

A comparison of the FTIR spectra of polymers **2**−**6** shows them to be similar, including the P═O band position, except for a band that varies within the range 895−874 cm^{-1} depending on the polymer. As shown in Figure 2, the phosphorylated glycol **2** has a weak band at 894.9 cm^{-1} while bands for the glycerol **3**, pentaerythritol triethoxylate **6**, tris(hydroxymethyl)ethane **4**, and pentaerythritol **5** polymers appear with increasing intensity at 889.1, 877.6, 875.6, and 873.7 cm^{-1}, respectively. There is also a band at 818 ± 1 cm^{-1} that does not shift. The absence of a band at 895−874 cm^{-1} in the phosphonate diester indicates that it is not due to the $P-O(CH_2CH_3)$ moieties. As a result, it is assigned to the asymmetrical stretch of the other $P-O(CH_2C)$ bond. Hydrogen bonding is thus most likely to occur with all oxygens bonded to the phosphorus (though not necessarily in every ligand given that there are other oxygens in the ligand); the IR, however, changes only when hydrogen bonding occurs at the $P-O(CH_2C)$, probably because there is no other band in that region originally present to obscure the new formation. The increasing intensity may be evidence of increased hydrogen bonding along the series **5** > **4** > **6** > **3** > **2**. (Polymer **2** has no −OH groups for hydrogen bonding, and so the peak at 894.9 is the "inherent" $P-O(CH_2C)$ stretch within this group of polymers.)

When the phosphoryl oxygen is being hydrogen bonded by the neighboring −OH group, it can gain

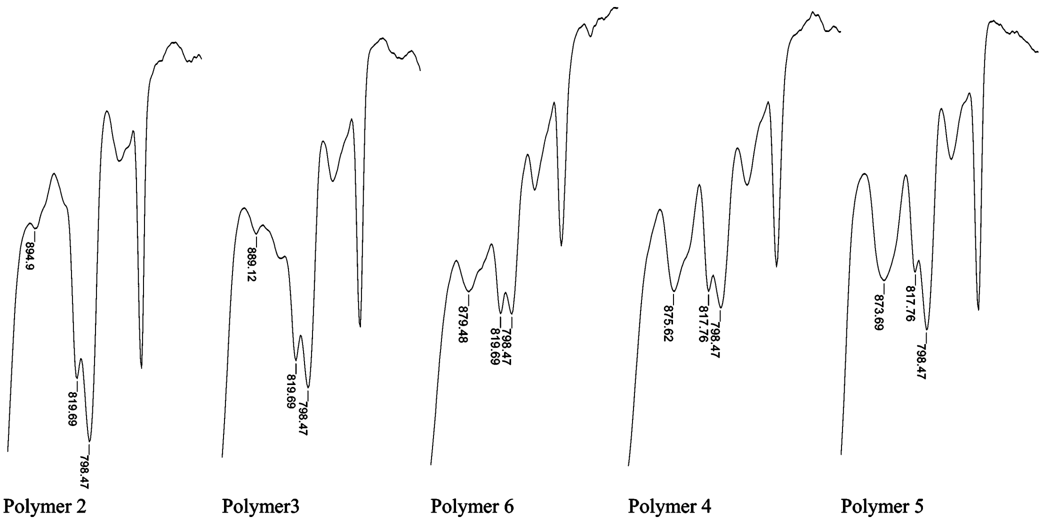


Figure 2. FTIR spectra of phosphorylated polymer **2** (glycol), **3** (glycerol), **6** (pentaerythritol triethoxylate), **4** (tris(hydroxymethyl)ethane), and **5** (pentaerythritol) in the region below 895 cm^{-1}.

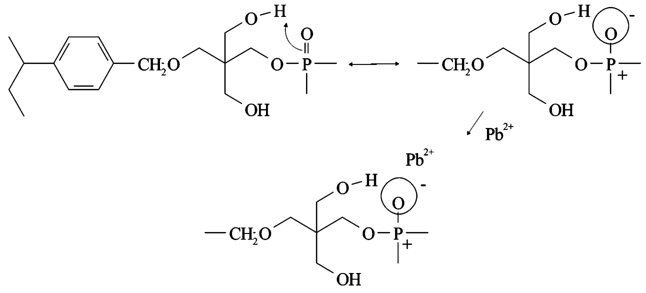


Figure 3. Increased electron density at the phosphoryl oxygen due to hydrogen bonding in immobilized pentaerythritol and subsequent complexation of lead ions.

electron density and thus become softer if the hydrogen bond draws electron density from the oxygen and reduces back-donation into the phosphorus (Figure 3). In this case, intramolecular hydrogen bonding entails the formation of a seven-membered ring in polymer **3**, an eight-membered ring in polymers **4** and **5**, and a 14-membered ring in polymer **6**. While intermolecular interactions may not be precluded, especially in **6**, macrocycles are formed more readily on polymers due to isolation of the sites,[24] and a study of γ-hydroxyphosphoryl compounds found seven-membered rings to be preferred over five-membered rings.[25]

The greater the hydrogen bonding, the greater the band intensity, and aside for the position of the tris(hydroxymethyl)ethane polymer (which appears with greater intensity than expected if the series were to follow the distribution coefficients), the greater the affinity of the phosphoryl oxygen for metal ions. Hydrogen bonding by the −OH group to the phosphoryl oxygen is unchanged after the metal ion binds to the P=O, thus maintaining the softness of the ligand: an ^{17}O NMR study of 2-hydroxy-3-benzoylpropylphosphonate diester found that the P=O and C=O moieties chelate metal ions to form an eight-membered ring with the −OH group retaining its role in intramolecular hydrogen bonding and not interacting with the metal ion, as indicated by the absence of a shift in the −OH peak before and after addition of the metal salt.[26]

Hydrogen bonding through cyclization is supported by the seemingly anomalous position of the tris(hydroxymethyl)ethane band. Comparing the metal affinity sequence **5** > **3** > **6** > **4** > **2** with the band intensities **5** > **4** > **6** > **3** > **2** shows that polymers **3** and **4** have exchanged position, with **4** having a greater intensity than **3**. If this is indicative of the extent of cyclization, interaction of the hydroxyl group with the phosphoryl oxygen to form a ring would be favored by **4** over **3** due to the Thorpe−Ingold effect.[27] The interaction is thus a necessary condition for enhanced metal ion complexation, but it is not the only variable since **3** has a greater ionic affinity than **4**. The methyl group may decrease the overall hydrophilicity of the ligand, and this, in turn, can decrease the extent of complexation. This points to one additional consideration for design criteria: not only will the variables controlling the M^{n+}−L interaction need to be defined and quantified, but a variable that defines the hydrophilicity of the polymeric microenvironment will also have to be considered.

Conclusions

The results of the experiments reported here and literature precedent are consistent with a mechanism wherein the phosphate ligands hydrogen bond with surrounding −OH groups, that bonding interaction influences the electron density (i.e., the softness) of the phosphoryl oxygen, and the resulting variation in polarizability influences the ability of the phosphate ligand to complex divalent transition metal ions and the observed selectivity of the polymer-supported reagent. Selectivity is thus a function of the primary (phosphate) ligand and auxiliary groups can be used to modify the selectivity of the primary ligand. Correlating the distribution coefficients with the Misono softness parameter allows a determination of the minimum softness required by a metal ion for complexation to occur. Research is in progress with trivalent ions and polymers wherein the auxiliary groups are varied in order to determine the effect on selectivity and $\sigma_{\min}$. Additionally, the phosphorylated polymers are the subject of a ^{31}P NMR study. While the results will be presented in due course, it is already clear that the NMR spectra confirm hydrogen bonding due to broadening of the phosphorus peaks in polymers **3**−**6** relative to polymer **2**. Data analysis continues in order to determine the relative importance of other variables (such as electrostatic attraction) to the bonding interaction.

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