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I am submitting herewith a dissertation written by Subramanian Natesan entitled "Synthesis and Characterization of Polymer-Supported Calix[4]arenes and Bifunctional Ion-Exchange Resins for Selective Metal Ion Complexation." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Spiro Alexandratos, Major Professor

We have read this dissertation
and recommend its acceptance:

Michael Sepaniak

Mark Dadmun

John Fellers

Accepted for the Council:

Associate Vice Chancellor and
Dean of The Graduate School

SYNTHESIS AND CHARACTERIZATION OF POLYMER-SUPPORTED CALIX[4]ARENES AND BIFUNCTIONAL ION-EXCHANGE RESINS FOR SELECTIVE METAL ION COMPLEXATION

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Subramanian Natesan

August 1999

DEDICATION

This dissertation is dedicated to my parents

Natesan, S. and Bhagyalakshmi, N.

who first instilled in me the value of education

and for their unconditional love, support and inexhaustible

source of encouragement

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I am truly grateful to my parents for their love, unwavering support and encouragement to help realize my dreams. The sacrifices they made and the hardships they were put through financially and emotionally to provide me with better opportunities cannot be expressed in words and this dissertation is as much theirs as it is mine. I also

want to thank my grandmother and sisters for their love, affection and belief.

At the end I want to thank my best friends Karthik, Bhaskar, Vasanth and Bob. They are living examples of the saying "A friend in need is a friend indeed". I cannot say enough as to how much they mean to me and needless to say it would have been impossible to complete this arduous journey without them.

ABSTRACT

Bifunctional ion-exchange resins and polymer-supported calix[4]arenes have been synthesized and characterized. The ion-selectivity of these polymers was evaluated.

Phosphonic acid polymers were synthesized from polystyrene beads at varying levels of crosslinking and studied for their ability to complex Eu(III) and Fe(III) from varying acid concentrations. The percent complexed decreased with increasing crosslinking and acid concentrations regardless of the type of support used. However, by introducing a hydrophilic sulfonic acid ligand into the polymer matrix, rapid kinetics was obtained even with a highly crosslinked gel from high ionic strength solutions due to increased accessibility. The principle of bifunctionality is thus proposed as an alternative to macroporosity for enhanced complexation kinetics.

Complexation of metal ions through a mechanism of inter- and intra-ligand cooperation for enhanced ionic selectivities was evaluated. The diphosphonic acid resin, due to the possibility of intra-ligand cooperation of the phosphoryl groups, had high affinities for all metal ions studied especially in less acidic solutions. The dicarboxylic acid resin was ineffective at the pH studied due to protonation of the carbonyl oxygen. The complexation behavior of the phosphonoacetic acid resin was comparable to the monophosphonic acid resin, leading to the belief initially that cooperation of the phosphoryl-carbonyl groups was not possible by intra-ligand cooperation. However, the ability of a β-ketophosphonate resin to complex high amounts of Cd(II) from a 0.10 N

HNO_3 solution showed that they can in fact cooperate by an intra-ligand mechanism for enhanced affinities. Hydrogen bonding of the carboxylic acid proton to the phosphoryl oxygens was proposed as the reason for poor affinities displayed by the phosphonoacetic acid resin.

Calix[4]arene and phosphorylated calix[4]arene were successfully immobilized onto crosslinked polystyrene supports. The former was able to complex Cs(I) from a 1 N NaOH solution in amounts greater than 96% while the latter was effective in complexing transition metal ions from acidic solutions. The effective cooperation of the ligating groups arranged around the cavity was responsible for the high selectivities displayed by these resins.

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INTRODUCTION

Contamination of water in the environment by toxic metal ions is a significant problem. The ill effects of metal ions such as lead, mercury, chromium and radionuclides on human health are well documented.[1] While development of nuclear weapons and power generation has led to the accumulation of nuclear waste, the sources of heavy metal ions have been primarily from industrial waste generated by electroplating, hydrometallurgy, metal fabrication, textiles and leather processing.[1]

A common denominator in all of these wastes is that the toxic metal ion is present in a complex mixture along with other environmentally benign ions such as Na^+, K^+, $Ca^{2+}$and Mg^{2+}. Separation technologies are thus needed that are highly selective in the removal of the targeted metal ion.

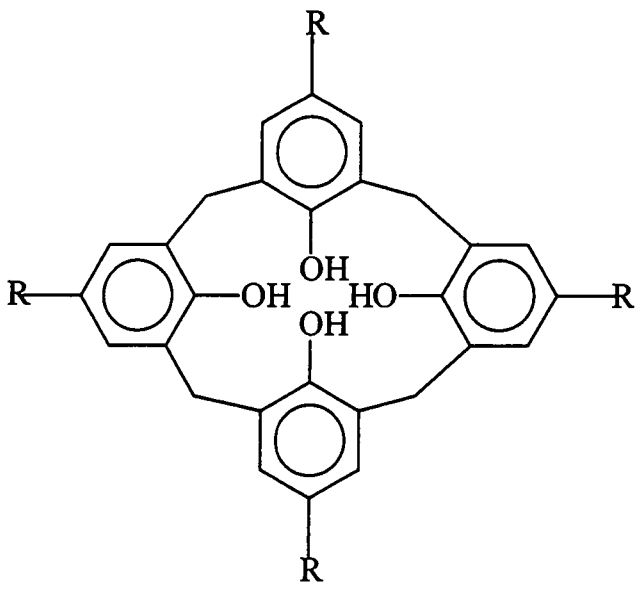
Solvent extraction has been, in many cases to date, the best available technology for the removal and recovery of metal ions from aqueous solutions.[2,3] Loss of the extractant from the organic phase into the aqueous phase due to its finite solubility as well as to incomplete phase separation, can raise serious environmental concerns.

Polymer-supported reagents can provide an important alternative to solvent extraction in the treatment of aqueous solutions. The immobilization of ion-selective ligands on to crosslinked polymers provides a wide array of resins that can be used for a variety of applications in an environmentally compatible manner.

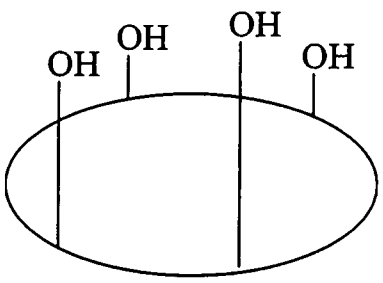
Recent review articles[4-6] have discussed, the different polymer supports that are available and the various ligands that have been immobilized for the selective

complexation of targeted metal ions. One category of polymers that have drawn considerable attention is the dual mechanism bifunctional polymers (DMBP) which have shown that both selectivity and kinetics of complexation can be improved by a combination of ligands immobilized on the same polymer.[7-12] The commercially available Diphonix® resin[13-20] is a classic example of a DMBP. It is a bifunctional chelating ion exchange resin that contains geminally substituted diphosphonic acid groups and sulfonic acid groups chemically bonded to a styrene-divinylbenzene polymer network. The hydrophilic sulfonic acid group allows for the rapid access of all metal ions into the polymer matrix and the diphosphonic acid group then selectively complexes certain metal ions through intra-ligand cooperation of the phosphoryl moieties.

In the search for ion-selective ligands, a lot of attention has been focused on a novel class of macrocyclic ligands called calixarenes. This family of macrocycles is prepared by the base-induced condensation reaction between para-substituted phenols and formaldehyde[21,22]. Procedures have been devised to obtain varying numbers of phenolic residues within the macrocycle; rings with 4, 6 or 8 phenolic residues are most commonly studied. The number of phenolic units in the macrocycle are designated by the value "n" in the general term calix[n]arene. The substituted alkyl group in the para position is usually a t-butyl group. The structure of calix[4]arene is shown in Figure 1.1(**1a**) in a flat two-dimensional representation. Its actual structure is in the shape of a basket and, conventionally the upper rim is considered to be that bearing the alkyl substituents while the lower rim has the phenolic groups. Figure 1.1 (**1b**) depicts the short-hand notation we will be using for calix[4]arene. The methylene bridges make the molecules flexible and



1a



1b

Figure 1.1. Structure of Calix[4]arene

1a Two dimensional structural representation

1b Short-hand notation

allows them to adopt different conformations (Figure 1.2).[23]

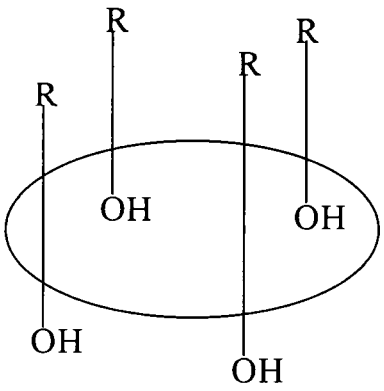
Calixarenes are important because: a) they are readily synthesized from relatively inexpensive starting materials; b) large quantities can be made at a given time without the necessity of high dilution techniques; and c) their structure allows for modification at either the upper or lower rim thus preorganizing different ligating groups. Preorganizing the ligands leads to their orientation in a given direction and variations in cavity size. The metal ion sequestering properties (either due to encapsulation within the cavity or by ligating groups preorganized around the rim) has been used in the complexation of radionuclides such as cesium and uranium.[24-31] Other applications include ion-selective electrodes,[32-34] phase transfer agents,[35,36] catalysis,[37,38] molecular recognition via host-guest chemistry,[39,40] Langmuir-Blodgett films and membranes.[41,42]

Phosphorus-based ligands are known for their selectivity towards transition metal ions, lanthanides and actinides.[43] Given the ability of calixarenes to preorganize the ligands by appropriate modification, it can be expected that phosphorylated calixarenes will have important ion-complexing properties. While research on ligand-modified calixarenes has been reviewed,[23,43-48] the present contribution focuses on soluble calixarenes modified with phosphorus-based ligands in order to emphasize the unique potential of such molecules for metal ion separations and on methods for immobilizing calixarenes. This survey is thus divided into three parts:

I. Transition metal complexes of phosphorylated calixarenes

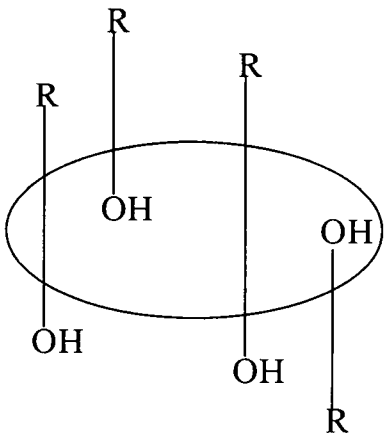
II. Application of phosphorylated calixarenes as extractants

III. Immobilization of calixarenes onto inorganic and organic supports



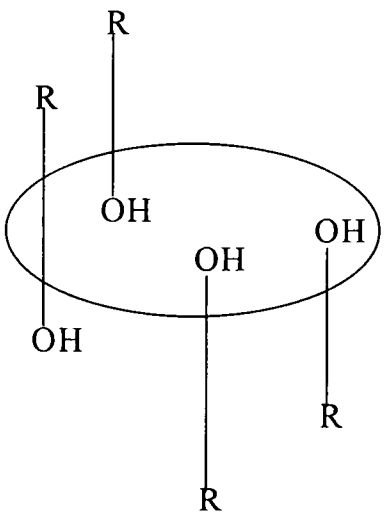
Cone

2a



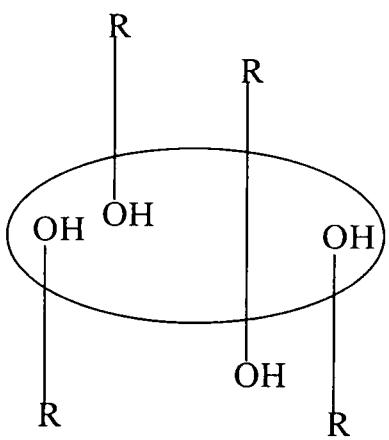
Partial Cone

2b



1, 2-Alternate

2c



1, 3-Alternate

2d

Figure 1.2. Conformations of Calix[4]arenes

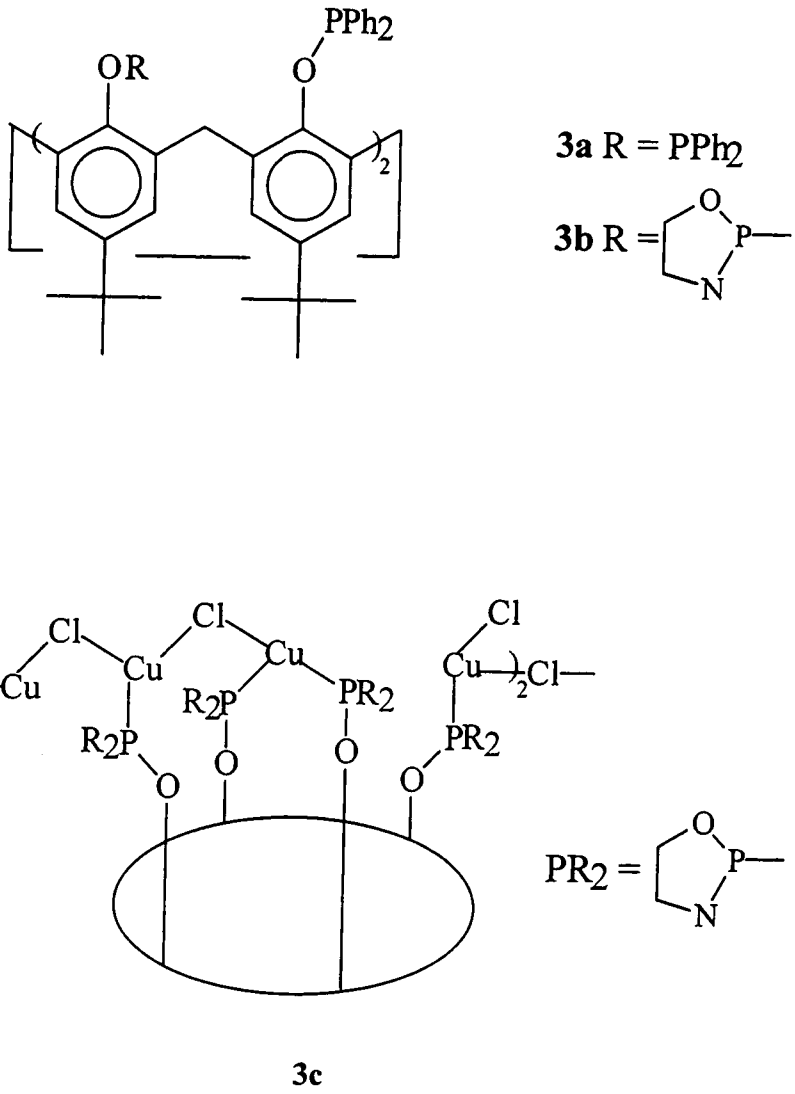
Transition metal complexes of phosphorylated calixarenes

Phosphino, phosphinite and phosphine-functionalized calixarenes

Tetraphosphino and tetra-(1,3,2-oxazaphospholidone)-substituted calix[4]arenes (Figure 1.3, **3a** and **3b**) were synthesized in the cone conformation and the ability of the latter to complex Cu(I) was studied.[49] By reacting **3b** with Cu(CO)Cl in a 1:8 ratio, a polymetal species (**3c**) was formed. Complex **3c** was a centrosymmetric molecule in which eight phosphorus donor atoms derived from two p-tert-butylcalix[4]arene molecules were bound to six copper atoms. Dimerization was a result of a compromise between ligand flexibility and the coordination requirements of Cu(I). The chlorine served to act as both a bridging ligand and a coordinator to Cu(I).

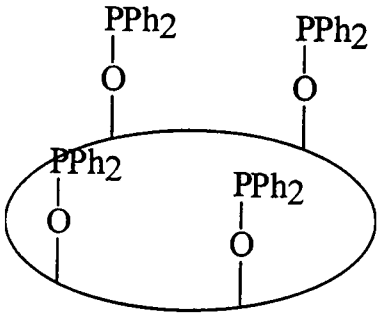
Floriani et al.[50] have prepared the tetra-functionalized phosphinocalix[4]arene **4a** (Figure 1.4) whose cone conformation was confirmed by ^{1}H and ^{31}P NMR. When reacted with the iron(0)carbonyl complex $[Fe(CO)_3(\eta\text{-}C_8H_{14})_2]$ in the presence of an excess of cyclooctene at low temperature, structure **4b** was obtained. The phosphinocalix[4]arene acted as a bidentate ligand and each pair complexed a $Fe(CO)_3$ fragment in a cis geometry. It was also determined that each Fe atom was complexed in a pseudo-trigonal bipyramidal coordination geometry.

A variety of mono- and diphosphino calix[4]arenes in the cone conformation have been synthesized and studied for their complexing ability.[51] The monophosphino calix[4]arene was found to form trans-$[MCl_2L_2]$ (L = ligand) complexes (M= Pd(II) or Pt(II))exclusively (Figure 1.5, **5a**). Depending on the amount of ligand reacted, the diphosphino calix[4]arene acted as bridging ligands and formed a di- or tetrametallic

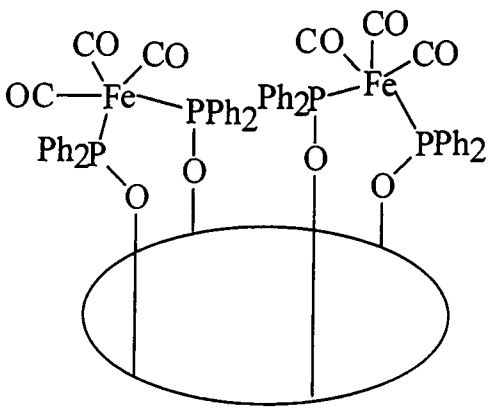


3c

Figure 1.3. Phosphino-substituted calix[4]arenes
3a, 3b Structures of the two phosphino-substituted calix[4]arenes
3c Cu(I) complex of **3b**

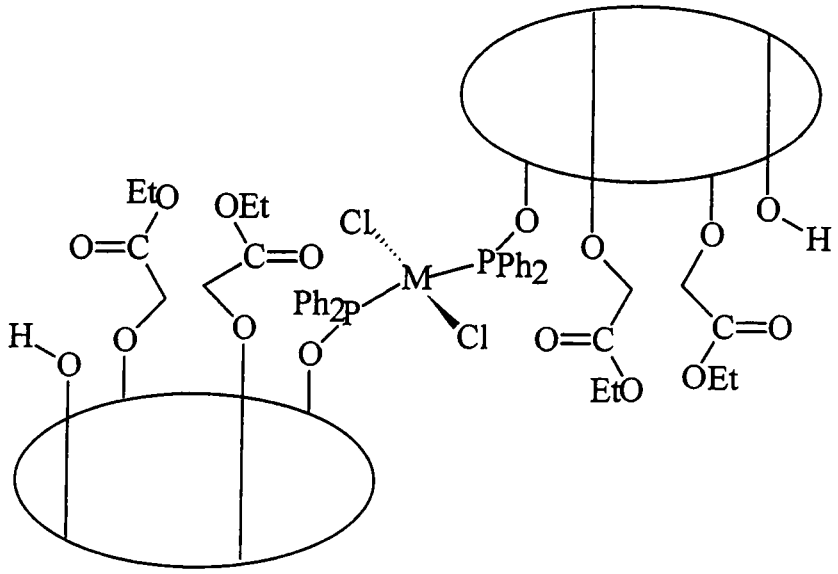


4a

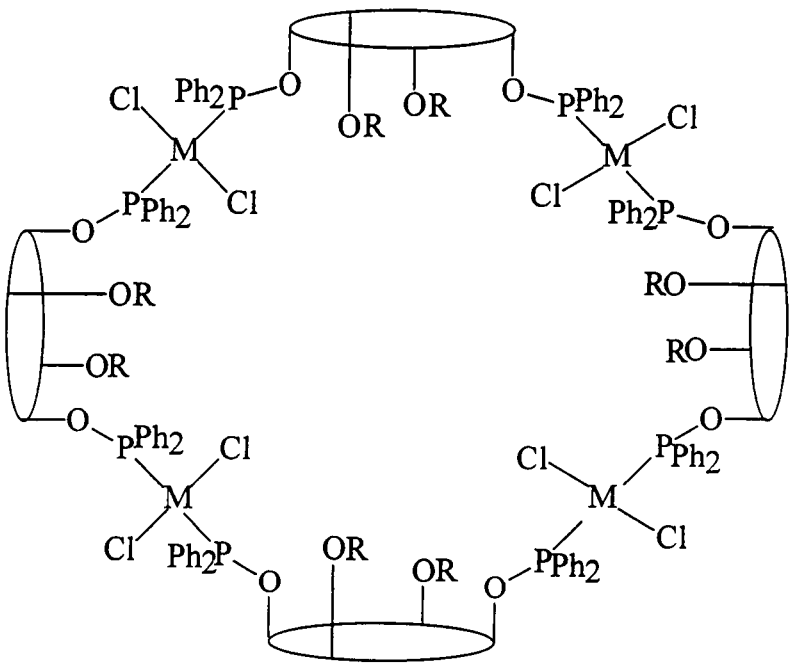


4b

Figure 1.4. Tetraphosphino-substituted calix[4]arene
4a Representation of the tetraphosphino-substituted calix[4]arene
4b Structure of the Fe(0) complex of **4a**



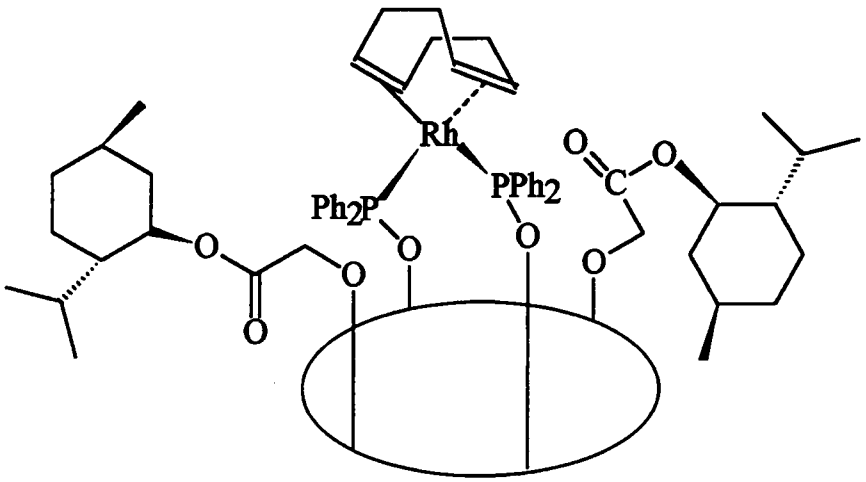
5a



R= CH_2CO_2Et

5b

Figure 1.5. Mono and diphosphino-substituted Calix[4]arenes
5a Pt(II) and Pd(II) complexes of monophosphino-substituted calix[4]arene
5b Tetrametallic complex of diphosphino-substituted calix[4]arene



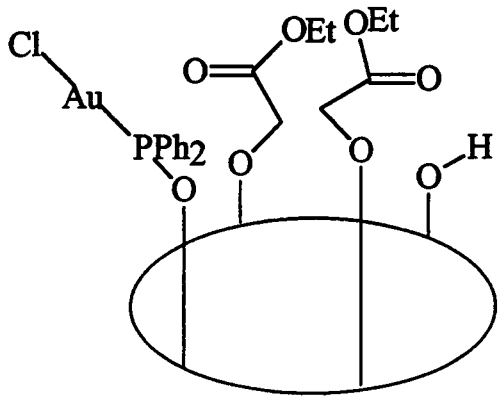
5c

Figure 1.5 (contd.). Structure of Rh(I) complex of diphosphino-diester

species (**5b**) with a trans stereochemistry. The nature of the other substituents determined the extent of oligomerization. Unsymmetrical compounds yielded dimers while symmetrical ones formed the tetramers. Reaction of the diphosphino calix[4]arene with $[Rh(cod)(THF)_2]^+$ (cod = cyclooctadiene) gave the cis-chelate complex (**5c**). The chelating behavior was attributed to overlap of the phosphorus lone pair electrons with the d-orbitals of the metal. The repulsive interaction of the bulky ester groups with the $[Rh(cod)]^+$ caused a parallel orientation of the aryl ester groups hence bringing the two phosphorus atoms close together and favoring chelation.

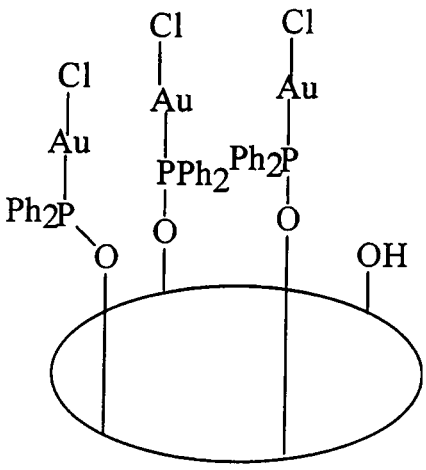
The steric effect in the coordination of metal ions has been studied by dealkylating the upper rim of a calix[4]arene substituted with phosphine and ester groups.[52] The monophosphinocalix[4]arene readily formed a monomeric complex with Au(I) when reacted with [AuCl(tht)] (tht = tetrahydrothiophene)(Figure 1.6, **6**). Reaction of the monophosphinite with either $[PdCl_2(PhCN)_2]$ or the corresponding Pt analogue yielded a trans complex (**5a**) where the metallo center bridged two calixarene molecules. The bulkiness of the trans-phosphinites resulted in subtle modifications to the calixarene molecule where one phenoxy ring was pushed into the cavity. It was hoped that such structures would provide valuable complexation and/or catalytic properties.

Tri- and tetraphosphino-p-tert-butylcalix[4]arenes were studied for their ability to complex Au(I), Pt(II) and Pd(II).[53] While both tri- and tetraphosphinocalix[4]arenes acted as monodentate ligands for Au(I) complexation (Figure 1.7, **7a** and **7b**), Pt(II) and Pd(II) were chelated to form a bimetallic complex by the tetraphosphinate in a cis geometry (**7c**).

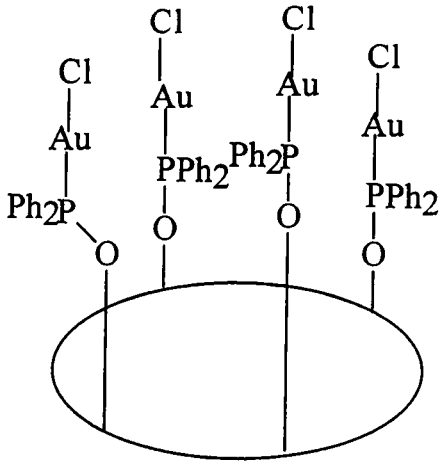


6

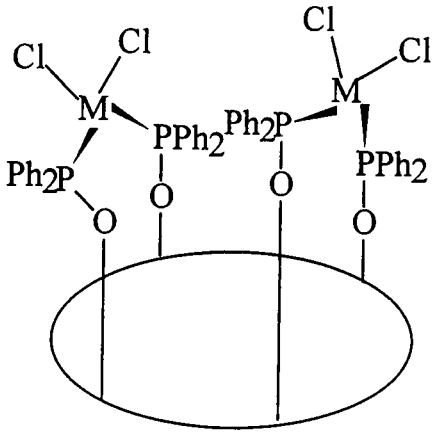
Figure 1.6 Au(I) complex of monophosphinocalix[4]arene



7a



7b



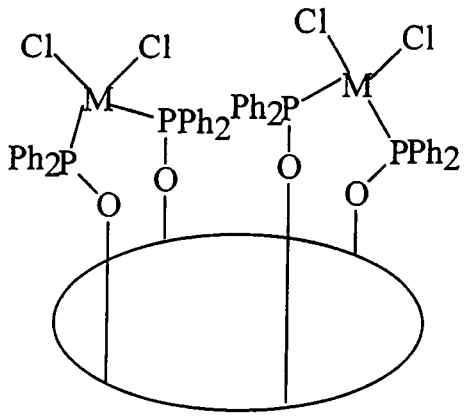
M = Pt, Pd

7c

Figure 1.7. Tri and tetraphosphinocalix[4]arenes
7a Au(I) complex of triphosphinocalix[4]arene
7b Au(I) complex of tetraphosphinocalix[4]arene
7c Bimetallic complex of tetraphosphinocalix[4]arene

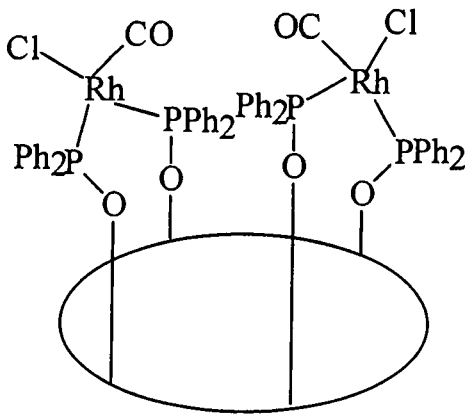
The tetraphosphino-calix[4]arenes have been investigated for their ability to form monometallic, homodimetallic and heterodimetallic complexes.[54] When p-tert-butyl-tetraphosphinocalix[4]arene in its cone conformation was reacted with 2 equivalents of $[(cod)MCl_2]$ (M = Pt or Pd) a homodimetallic complex (**8a,** Figure 1.8) was observed where each of the pairs of adjacent phosphorus atoms were chelating the metal in a cis-geometry. A cis-analogue was also obtained when the calixarene was reacted with $[Rh(CO)_2Cl]_2$ (**8b**). Monometallation was obtained with $NiCl_2$ (**8c**) regardless of the amount used. $PdCl_2$ yielded the monometallated form by using a 1:1 ratio of ligand to metal, but the complex lacked stability as it underwent disproportionation over a two week period. $PtCl_2$ formed the bimetallic complex regardless of the stoichiometry used. Synthesis of a heterodimetallic complex was attempted by reacting **8c** with $[(cod)MCl_2]$ (M = Pd, Pt) or $[(nbd)Mo(CO)_4]$ (nbd = norbornadiene). The former resulted in complete trans metallation forming the homodimetallic complex while the latter exclusively formed the heterodimetallic complex (**8d**). The complexation reactions were also compared with p-tertbutylcalix[4]arene tetrakis(dimethylphosphinite). The latter has less steric hindrance on the P_4 set of donor atoms and increased basicity from the electron donating methyl groups. This molecule formed a homodimetallic complex with the three metals (Pd, Pt and Ni) in a cis geometry (**8e**). The geometry of the complex was deduced by ^{31}P NMR, ^{1}H NMR and X-ray structural analysis.

The binding properties of tetra-t-butyl-tetrakis(bis-diphenylphosphinomethoxy)calix[4]arene (**9a,** Figure 1.9) and tetra-t-butyl-tetrakis(1,3,5-trimethyl-4,6-dioxo-1,3,5-triaza-2-phosphorinan-2-yl)calix[4]arene(**9b**) to gold have

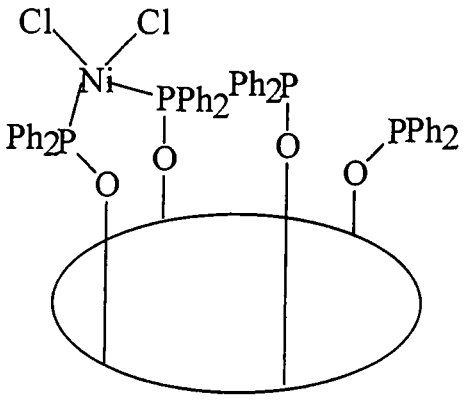


M = Pt or Pd

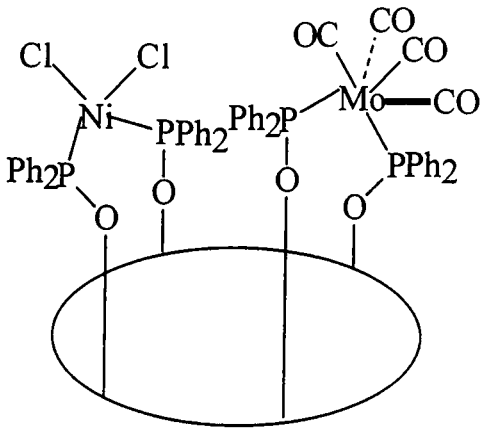
8a



8b

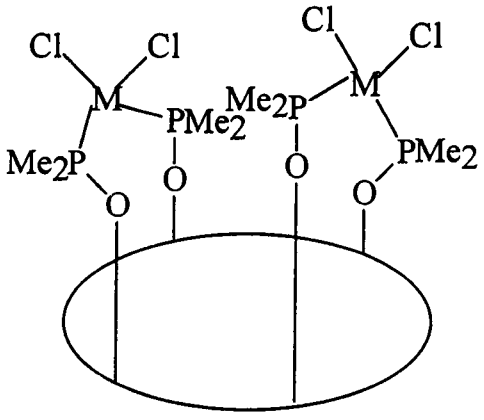


8c



8d

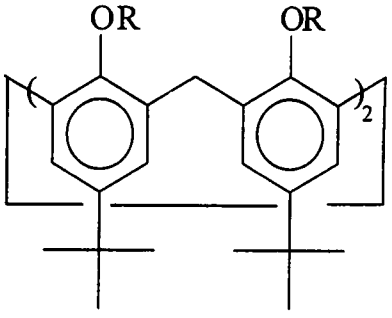
Figure 1.8. Tetraphosphino-substituted calix[4]arenes
8a Pt(II) or Pd(II) complex of tetraphosphinocalix[4]arene
8b Rh(I) complex of tetraphosphinocalix[4]arene
8c Mononickel complex of tetraphosphinocalix[4]arene
8d Heterodimetallic complex of tetraphosphinocalix[4]arene



M = Ni, Pt or Pd

8e

Figure 1.8 (contd.). Homodimetallic complex of tetra(dimethylphosphino)calix[4]arene



9a R = CH_2PPh_2

9b R =

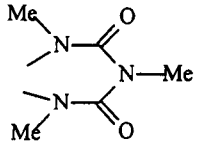
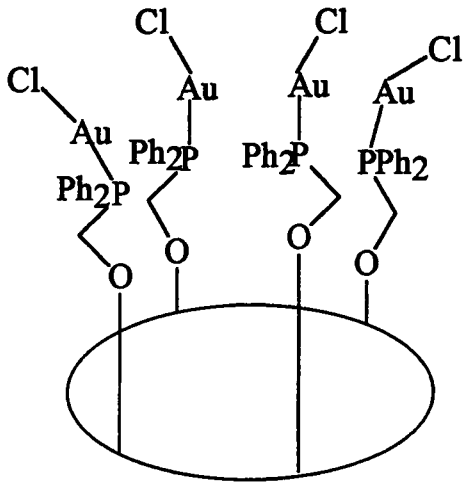
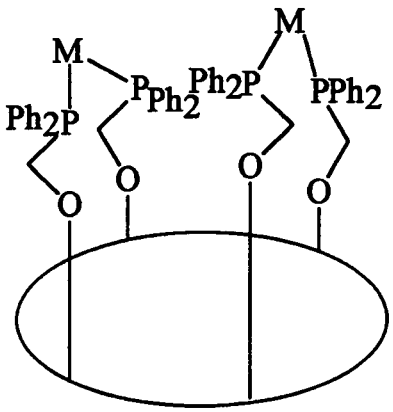


Figure 1.9. Tetraphosphinite-substituted calix[4]arene
9a Structure of tetraphosphinite-substituted calix[4]arene
9b Tetra(triazaphosphorinan-2-yl)-substituted calix[4]arene



9c

Figure 1.9 (contd.). Au(I) complex with **9a**

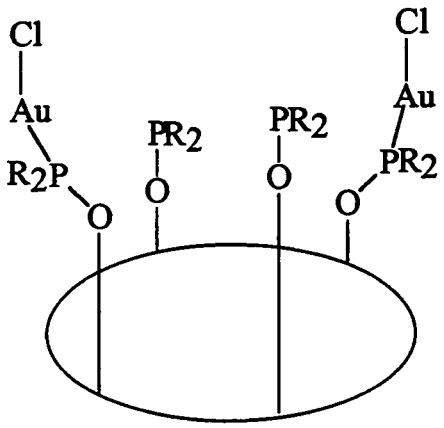


M = Au or Ag *

* Counterion = 2 BF_4^- for A

Counterion = 2 PF_6^- for A

9d



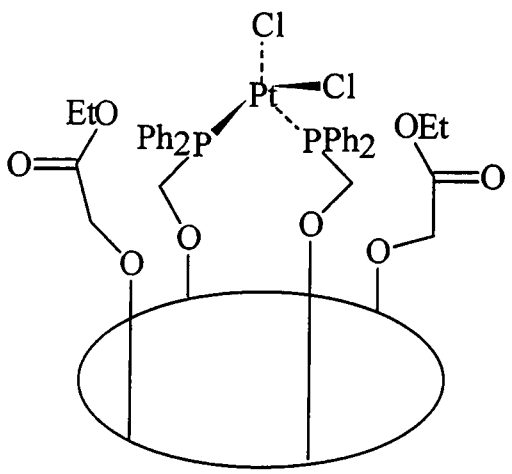
9e

Figure 1.9 (contd.). **9d** Digold and disilver complex with **9a**
9e Digold complex with **9b**

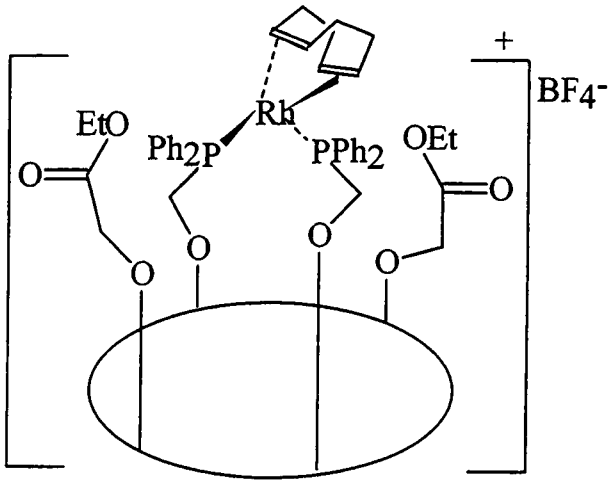
been investigated.[55] Reaction of **9a** with [AuCl(tht)] in a 1:4 ratio formed a tetranuclear complex (**9c**) where the P(III) is bound to Au(I). The analogous tetragold complex of **9b** could also be prepared in the same manner.

Intra-molecular migration of the gold fragments between the various binding sites was studied by partially aurating the phosphino-calix[4]arenes. Reacting **9a** with [AuCl(tht)] in a 1:1, 1:2 or 1:3 ratio yielded a mixture with varying levels of auration. A disilver complex could, however, be obtained by reacting the tetragold complex **9c** with $AgBF_4$ in a 1:4 ratio followed by addition of **9a**. Molecular modelling studies on a hypothetical digold complex of **9a** and the corresponding disilver complex showed that the tetraphosphino-calix[4]arene acted as a double chelator (**9d**). The ^{31}P NMR spectrum of completely aurated complex **9c** exhibited sharp signals (owing to its symmetry) when compared to the partially aurated species which displayed broad signals. Intra-molecular migration of the metal ions from one site to another was given as the reason for this effect. This was confirmed by the successful synthesis of the digold complex of **9c**, obtained by reacting it with either [AuCl(tht)] in a 1:2 ratio or an excess of $[Au(tht)(MeCN)]^+$ (**9e**).

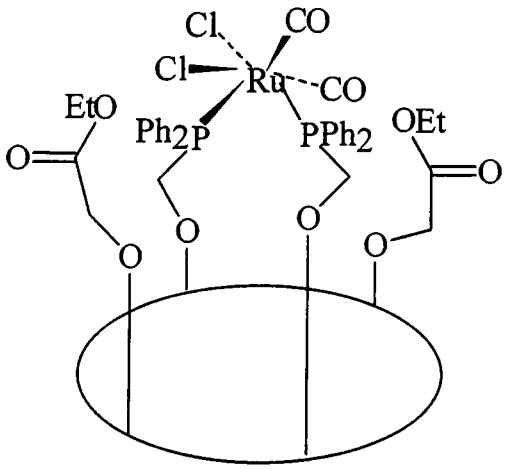
Calix[4]arene substituted with two diethylacetoxy and two diphenylphosphinomethoxy groups has been investigated in its cone conformation for its ability to complex platinum, rhodium and ruthenium.[56] When reacted with $PtCl_2(PhCN)_2$ in THF, Pt(II) was chelated by the two P(III) donor atoms in a cis geometry (**10a**, Figure 1.10). Cis chelation was also observed with rhodium (**10b**). However, when $RuCl_3$ was reacted with CO followed by addition to the ligand, chelation of Ru(III) was achieved through a trans geometry (**10c**). The stereochemistries of all the complexes were



10a



10b



10c

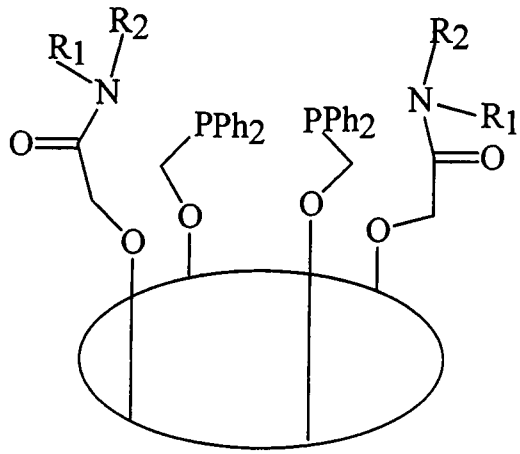
Figure 1.10. Diphosphinite-diester-substituted calix[4]arenes
10a Pt(II) complex of diphosphinite-diester
10b Rh(I) complex of complex of diphosphinite-diester
10c Ru(III) complex of diphosphinite-diester

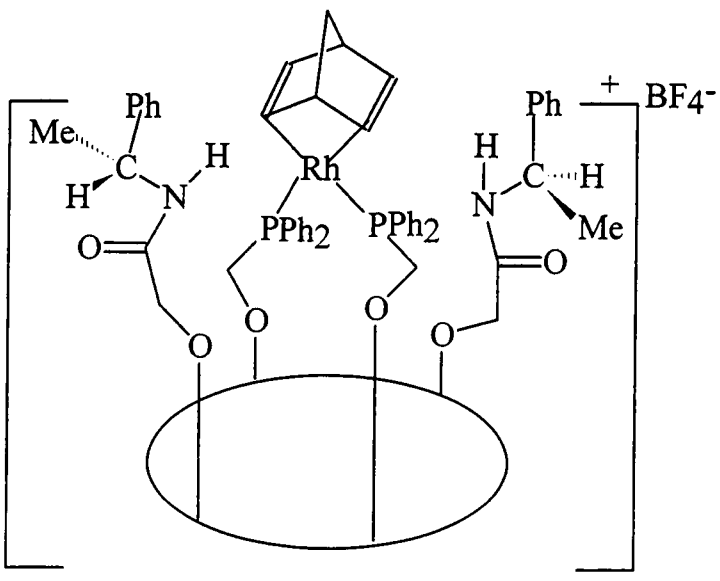
established by ^{1}H NMR.

Loeber et al.[57] have synthesized diamide-diphosphino-hybrids of calix[4]arene (**11a, 11b**, Figure 1.11) in a cone conformation. Reaction of $Rh[Cl(nbd)]_2$ with $AgBF_4$ in a 1:2 ratio followed by the addition of **11b**, yielded a monomeric complex (**11c**) where the Rh(I) was chelated by two phosphorus in a cis geometry. Formation of a cis complex (**11d**) was also observed when **11a** was reacted with $[PtCl_2(cycloocta\text{-}1,5\text{-}diene)_2]$. The structure of the complex was established by both ^{1}H NMR and X-ray diffraction studies. The metal ion in these complexes was found to be located above a hemispherical cavity formed by four functional groups in order to minimize steric interactions between the phosphine and amide groups. Hydroformylation of styrene with the Rh complex **11c** as the catalyst produced 2-phenylpropanal and 3-phenylpropanal in a 95:5 ratio. Though a high regioselectivity could be achieved, the observed rates were slow. The authors attributed this to steric hindrance caused by partial encapsulation of the metal center, hence preventing approach of the substrate.

A Pt-H moiety has been entrapped in a macrocycle cavity by reaction of trans-$[PtH(Cl)(PPh_3)_2]$ with tetra-t-butyl-bis(diethylcarbamoylmethoxy)-bis(diphenylphosphinomethoxy)calix[4]arene (**12a**, Figure 1.12).[58] This has been confirmed by X-ray analysis and NMR studies. The Pt metal was found to be chelated by the two P(III) atoms in a trans geometry. The encapsulated platinum hydrides were well suited for selective homogeneous transformations. This was demonstrated by reaction of the complex (**12a**) with tetracyanoethylene resulting in the quantitative transformation to the platinum(0) complex (**12b**).

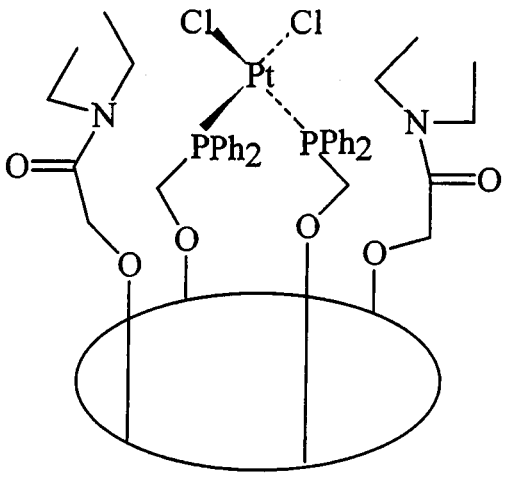
11a $R_1=R_2=Et$
11b R_1= -CHMePh
R_2=H





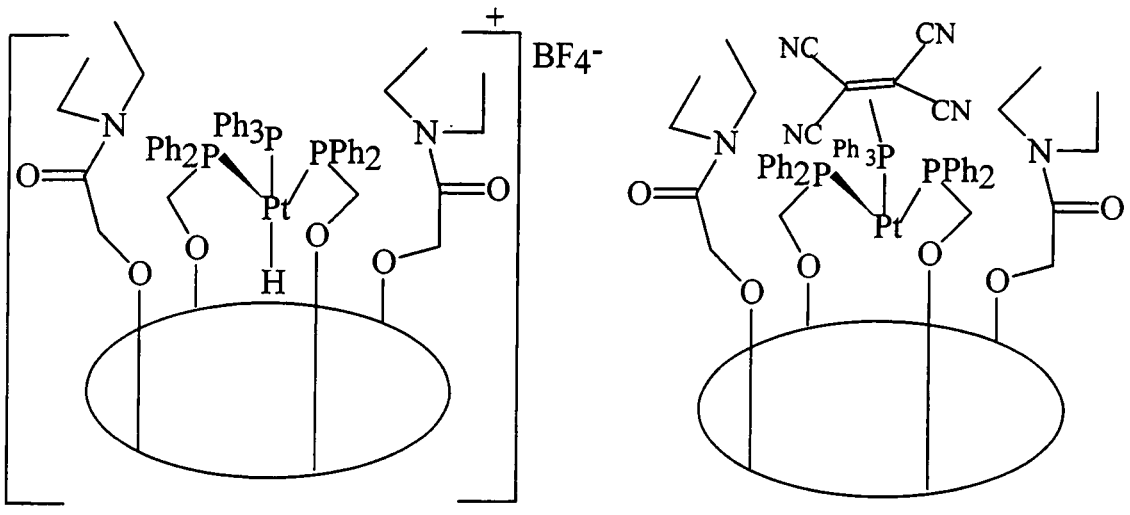
11c

Figure 1.11. Diphosphinite-diamide substituted calix[4]arenes
11a, b Structural representations
11c Rh(I) complex of **11b**



11d

Figure 1.11 (contd.). Pt(II) complex of **11a**



12a **12b**

Figure 1.12. Pt complexes of diphosphinite-diamide-substituted calix[4]arenes
12a Pt-H entrapped within a calix[4]arene cavity
12b Formation of Pt(0) complex from **12a**

Weiser et al. have synthesized the trans platinum hydride complex of diphenylphosphinite by varying the functionality at the other two phenolic oxygens in the calix[4]arene (**13a-c**, Figure 1.13).[59] This modified of the chemical properties and the environment of the encapsulated hydride. The auxiliary binding functions were helpful in promoting substitution reactions at the metal center. The synthesized complex allowed the study of substitution reactions both within and outside the cavities.

Complexes bearing unsaturated metal atoms located at the bottom of the calixarene's hydrophobic cavity can act as bifunctional molecular recognition agents. The luminescence properties and ionic interactions of such a derivative based on an iridium(I) complex of diphosphinite and diphosphino calix[4]arene in the cone conformation has been evaluated.[60] Treatment of $[IrCl(cod)]_2$ with $AgSbF_6$ in a 1:2 ratio and subsequent reaction with 2 equiv of phosphinite provided a structure where Ir was chelated by the two P(III) ligands (**14a**, Figure 1.14). The monomeric nature of the complex was confirmed by osmometry measurements. Attempts to increase the proximity of the iridium to the cavity was done by reacting the iridium(I) salt with phosphino-calixarene (where the phosphorus is attached directly to the phenolic oxygen). This reaction resulted in the formation of a bridged metallic complex (**14b**). The emission and absorption spectra for the iridium complexes (**14a** and **b**) were determined. The perturbation on the emission lifetimes was also evaluated by adding either Li^+, Na^+ or UO_2^{2+} salts to the complexes dissolved in ethanol. The emission lifetimes of the complexes after addition of the metal ions was found to be $UO_2^{2+} < Li^+ < Na^+$ for both. Shorter emission lifetimes obtained with uranyl ions suggested better binding affinity with the ionophoric cavity. Since UO_2^{2+}

13a R=C(O)NEt_2
13b R = C(O)NHCHMePh
13c R = CH_2OMe

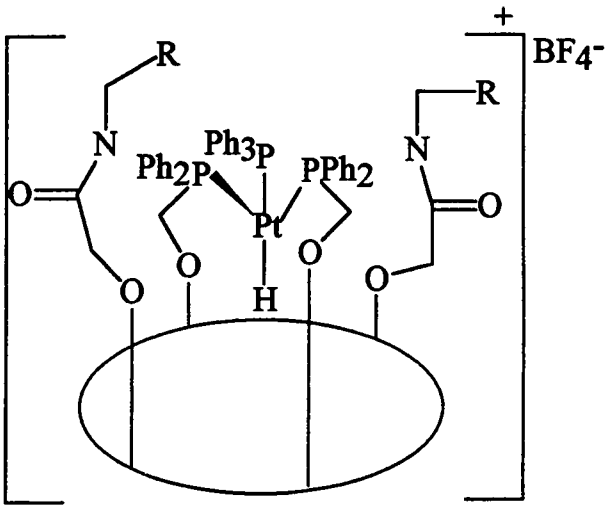
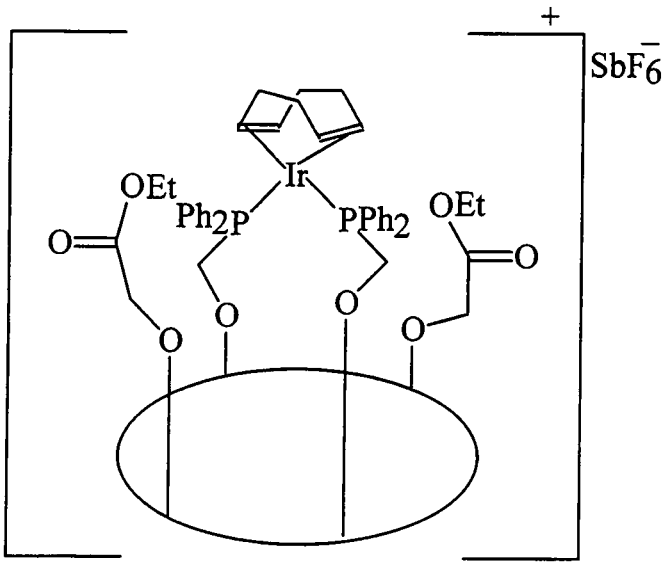
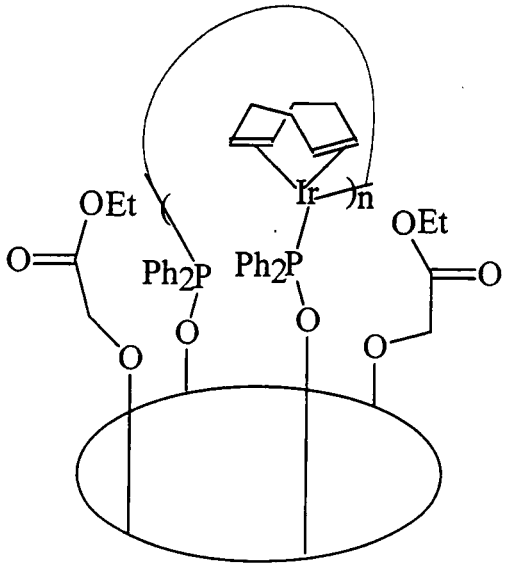


Figure 1.13. Structures of various entrapped Pt-H calix[4]arenes



14a



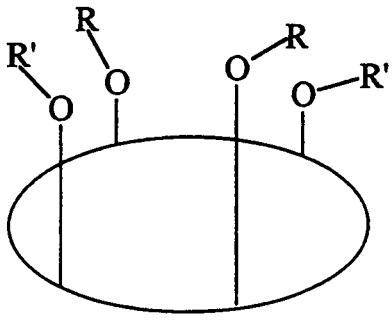
14b

Figure 1.14. Ir(I) complexes of phosphorylated calix[4]arenes
14a Ir(I) chelate complex with diphosphinitecalix[4]arene
14b Ir(I) bridged complex with diphosphinocalix[4]arene

requires a pseudoplanar hexadentate geometry and the complexes studied here do not provide such structural ability, it was speculated that the ester groups were also participating in binding of the UO_2^{2+}.

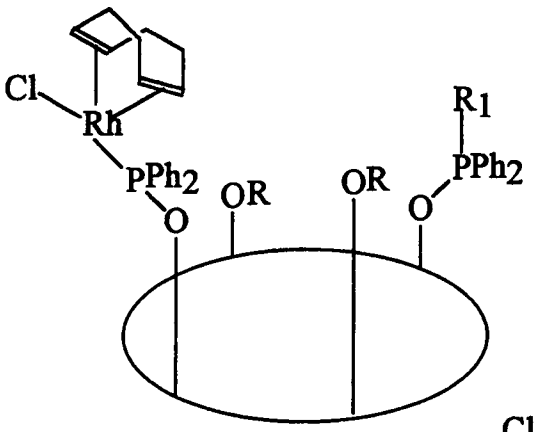
Cameron et al.[61] have compared the ability of 1,3-diphosphino- and 1,3-diphosphinite calix[4]arenes (**15a** and **b**, Figure 1.15) to complex various transition metal ions. When diphosphinocalix[4]arene was reacted with 0.5 or 1 mol of $[Rh(cod)Cl]_2$, a bimetallic or monometallic complex was obtained (**15c** and **d**). The phosphine oxide formed (**15d**) was attributed to oxidation of the sample during handling. In either case there was only monodentate coordination to the P(III). The Cu(I) complex prepared by reaction of **15a** with $[Cu(CH_3CN)_4]PF_6$ formed a monometallic complex bis-coordinated to the P(III) atoms (**15e**). Preferred coordination geometries of the metal ions and steric constraints imposed by the ligand were the reasons for this difference. Molecular models indicated that it was easier to form a tetrahedral bidentate complex with Cu(I) than it was to form the square planar bidentate complex with Rh(I). The diphosphinite ligand (**15b**) also formed bidentate complex with Cu(I) when reacted with $[Cu(CH_3CN)_4]PF_6$ (**15f**). Reaction of both cis and trans-bis(acetonitrile)$PtCl_2$ with **15b** produced a bidentate platinum complex in the cis geometry (**15g**), the structure of which was confirmed by ^{31}P NMR.

Tetraphosphinite and tetraphosphine-p-tert-butylcalix[4]arenes (structure **17** with $X=CH_2CH_2PPh_2$ for the phosphinite and $X = CH_2CH_2OPPh_2$ for phosphine) have been investigated for their coordinating abilities with Pt(II), Pd(II) and Rh(I).[62] Hydroformylation and hydroalkoxycarbonylation reactions were studied with these



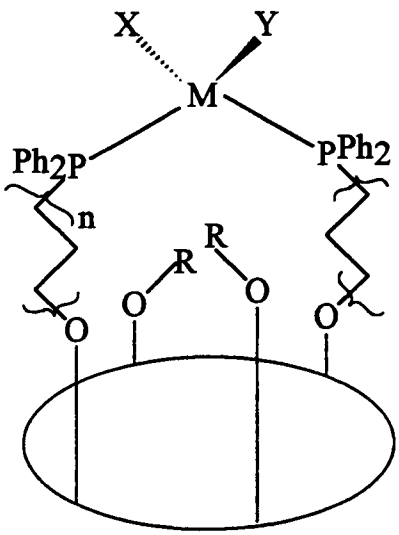
15a R = $CH_2CH_2CH_3$
R' = PPh_2
15b R = $CH_2CH_2CH_3$
R' = CH_2CH_2PPh

Figure 1.15. Structures of phosphorylated-calix[4]arenes



15c R_1 =

15d R_1= =O



15e n=0; M=Cu(I), X=PF_6^-, Y=CH_3CN
15f n=1; M=Cu(I), X=PF_6^-, Y=CH_3CN
15g n=1; M=Pt(II), X=Y=Cl^-

Figures 1.15 (contd.). **15c, 15d** Rh(I) complexes of diphosphinocalix[4]arene
15e-g Cu(I) and Pt(II) complexes of **15a** and **b**

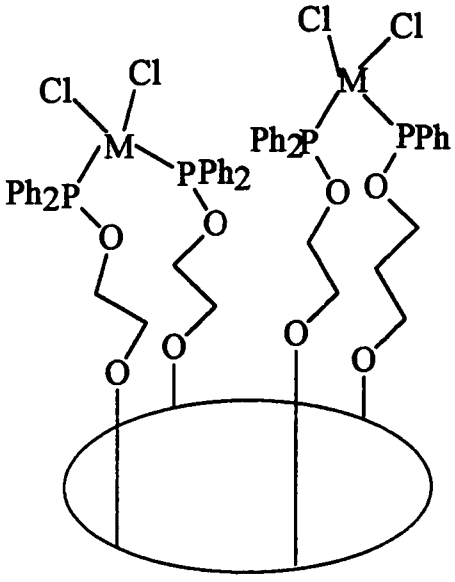
catalysts. Reaction of the phosphinite with $MCl_2(PhCN)_2$ (M= Pt or Pd) in a 1:2 ratio produced the dinuclear complex where pairs of the adjacent P(III) atoms chelated to the metal ion in a cis geometry. Reaction with $[Rh(nbd)Cl]_2$ produced a di- or tetranuclear complex depending on the ratio in which it was reacted (ligand to salt ratios of 2:1 or 1:1).

Complexes with the phosphine ligand were also studied.[62] The phosphine formed a dinuclear complex with both Pt(II) and Pd(II). The former was obtained exclusively in the cis arrangement (**16**, Figure 1.16) and the latter in a mixture of cis and trans geometries. Complexation of Rh(I) with the phosphinite ligand was similar to that obtained with Pd(II).

The Pt(II) and Rh(I) complexes of both the phosphinite and phosphine were studied for the hydroformylation of styrene.[62] The activity and chemoselectivity for the phosphine catalysts were observed to be much higher than the phosphinite. However, the regioselectivity was temperature independent for the latter. Both the Rh-phosphine and Rh-phosphinite catalysts were lower in activity than conventional catalysts. Regioselectivity to the branched aldehydes was superior for the phosphinite even at higher temperatures. Hydroalkoxycarbonylation of styrene with Pd-phosphine and Pd-phosphinite produced low conversions for the former and reasonable yields with the latter. The reaction, however, was not selective.

Calixarenes containing phosphorinanones

Various tetra-phosphorinanones (**17a-c**, Figure 1.17) in the cone conformation have been synthesized.[63] Reaction of **17c** with [AuCl(tht)] resulted in the formation of a



M = Pt, Pd

16

Figure 1.16. Pt(II) and Pd(II) complexes of tetraphosphinite

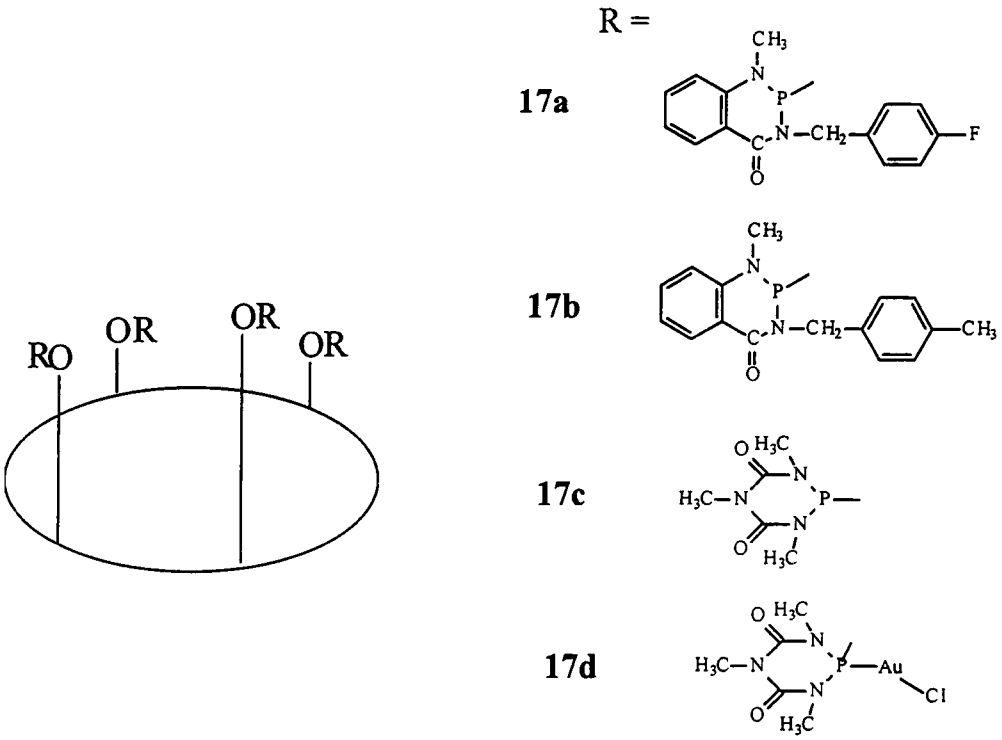
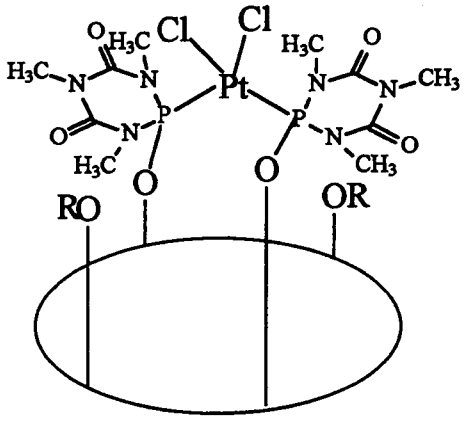


Figure 1.17. Phosphorus and fluorine containing calix[4]arenes
17a-c Structures
17d Au(I) complex of **17c**



17e

Figure 1.17 (contd.). Pt(II) complex of **17c**

tetrakis-Au(I) complex (**17d**). When reacted with [$PtCl_2$(cod)], **17c** yielded the trans-monometallic complex (**17e**) where the Pt(II) was chelated by two opposite P(III) atoms. The identity of the complexes were established by ^1H, ^{13}C, ^{31}P NMR spectroscopy, IR, mass spectroscopy and elemental analysis.

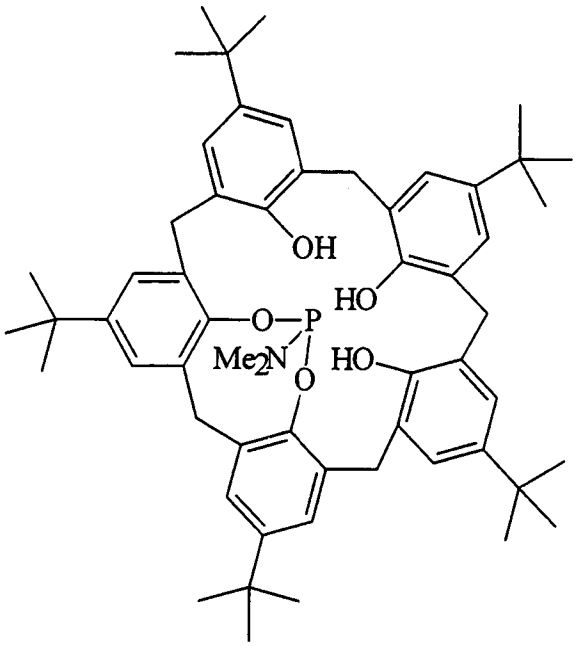
P-bridged calix[5]arene

p-Tert-butylcalix[5]arene has been converted to **18a** (Figure 1.18) by reaction with tris(dimethylamino)phosphine.[64] Coordination of the unsubstituted phenolic oxygens to tungsten was achieved by reacting **18a** with [$W(tBuN)_2$(NHtBu)](**18b**). A weak P-W interaction was detected by ^{31}P NMR. However, when converted to **18c** by ligand exchange of NHtBu with triflate, the phosphorus-tungsten distance decreased, resulting in better coordination.

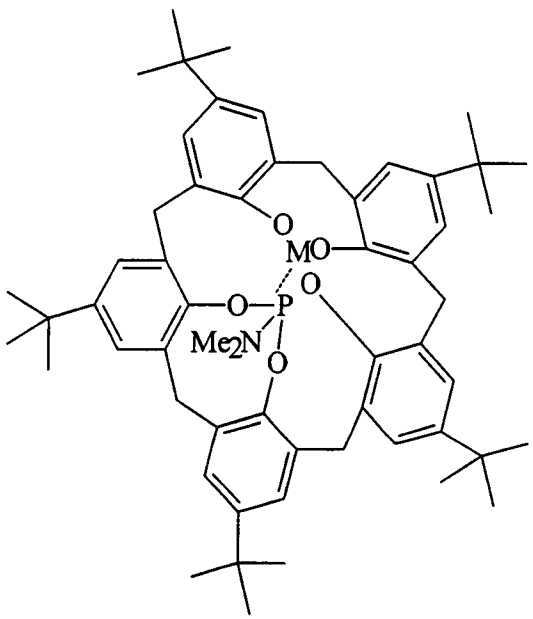
Application of phosphorylated calixarenes as extractants

Phosphine oxide-substituted calixarenes

The di- and tetraphosphine oxide substituted p-tetra-t-butylcalix[4]arenes in the cone conformation (**19a** and **19b**, Figure 1.19) were tested for their complexing affinity for and transporting ability of alkali metal ions.[65] Both **19a** and **19b** were found to form 1:1 complexes with alkali cations. The strong complexing ability of the amide functionality was confirmed by the higher binding affinity of **19a** for Li^+, Na^+, and K^+ relative to **19b**. NMR studies on the complexes of **19a** suggested that the Na^+ and K^+ were encapsulated in the cavity forming a C_2 symmetrical complex. Both compounds had transport efficiencies similar to their respective complexing abilities: $Na^+ \approx Li^+ > K^+ > Rb^+ > Cs^+$ for **19a**; $K^+ > Rb^+ > Li^+ > Cs^+ > Na^+$ for **19b**.



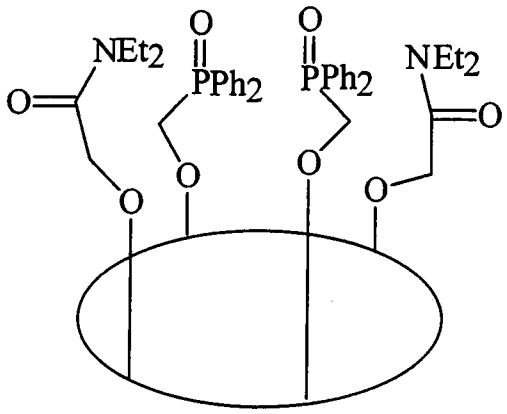
18a



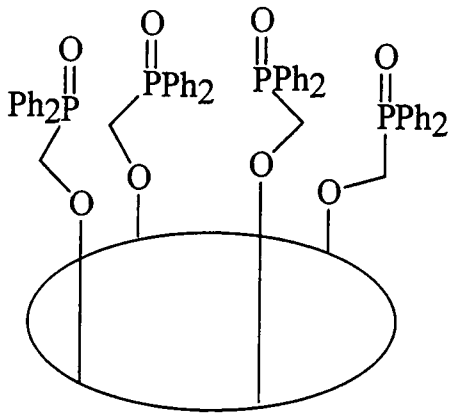
18b M = W(t-BuN)(t-Bu)(NH)

18c M = W(t-BuN)(OTf)

Figure 1.18. P-bridged calix[5]arene
18a Structure
18b Tungsten complex of **18a**; **18c** Tungsten complex of **18a**



19a



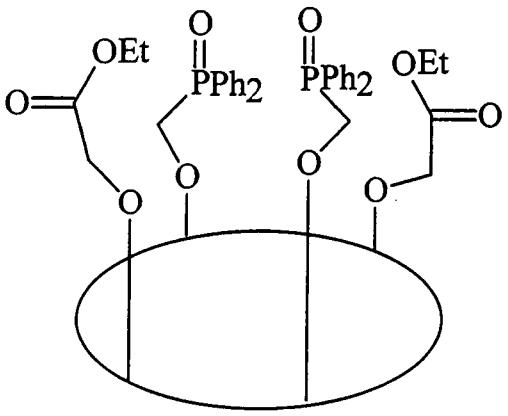
19b

Figure 1.19. Phosphine oxide-substituted calix[4]arenes
19a Diphosphine oxide
19b Tetraphosphine oxide

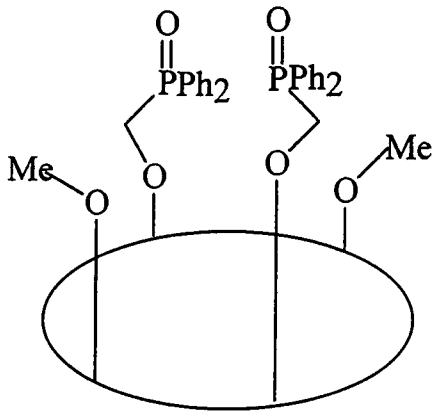
The tetraphosphine oxide of calix[4]arene (**19b**) has been studied for its extractive properties of rare earth metals by Yaftian et al.[66] An ion pair stoichiometry of one metal (La, Eu, Er or Y) per ligand was observed for the extracted species. An increase in polarity of the solvent increased the distribution coefficient ($CHCl_3 < CH_2Cl_2 < (CH_2)_2Cl_2 < PhNO_2$). When subjected to a competitive extraction of different rare earth metal ions (La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb and Y), cooperation of the phosphine oxide groups allowed for higher efficiency and separation factors than traditional extraction agents like tri-n-octylphosphine oxide. The extraction efficiency of the tetraphosphine oxide-calix[4]arene has also been established by doing transport studies through a supported liquid membrane mediated by the ligand in o-nitrophenyl hexyl ether.[67]

A series of phosphine oxide ligands (**19a**, **19b**, **20a** and **20b**) have been tested for their ability to extract Ag(I)[68] and compared to dicyclohexano-18-crown-6 (DC18C6, **20c**, Figure 1.20). The affinity for Ag(I) was found to be in the order of **19a** > **20b** > **20c** ≈ **19b** > **20a**. The good performance of **19a** was attributed to the high basicity of the amide groups, large number of oxygen atoms for complexation, and a better matching of the cavity size for the Ag(I) generated by the four pendant arms. NMR and IR data substantiated an encapsulated Ag(I) ion in the ionophoric cavity of **19a**. It was also was able to extract trace amounts of Ag(I) from a large excess of Cu(II). The transport efficiency of **19a** yielded results comparable to complexation.

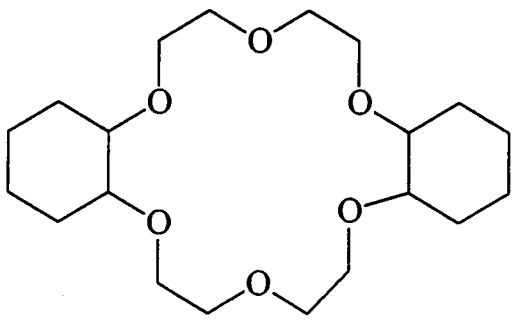
The effect of varying the number of phosphine oxide groups and the conformation of the functionalized calix[4]arene on the separation of the rare earth metals has also been



20a

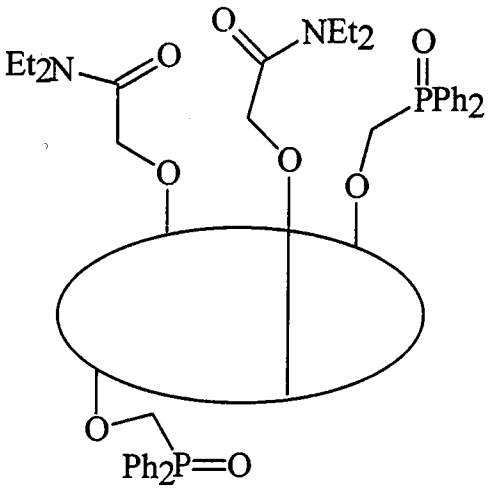


20b

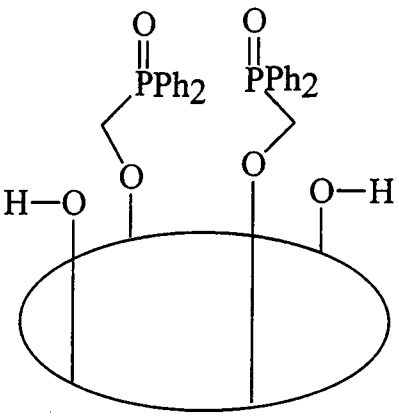


20c

Figure 1.20. Diphosphine oxides of calix[4]arene
20a Diphosphine oxide-diester
20b Diphosphine oxide-diether
20c Dicyclohexano-18-crown-6 (DC18C6)



20d



20e

Figure 1.20 (contd.). **20d** Diphosphine oxide in the partial cone conformation
20e Dihydroxy-diphosphine oxide

investigated.[69] The efficiency and selectivity of extraction increased with increasing number of phosphine oxide groups with best results obtained for the tetraphosphorylated compound (**19b**). The inferior performance of the mixed diamide-diphosphine oxide-calix[4]arene in the partial cone conformation (**20d**) emphasized the importance of cooperation of all the phosphine oxide groups for optimum extraction and selectivity.

Fully substituted phosphine oxide-calix[n]arenes where the phosphoryl groups were two carbons away from the phenolic oxygens (**21a-f**, Figure 1.21) have been studied for their ability to separate lanthanides and actinides.[70] The size of the cavity (n = 4, 6 or 8) and the effects of upper rim dealkylation were the variables studied to improve the separation. The extraction of Th(IV) as thorium nitrate was found to be in a 1:2 ratio of ligand:metal species in the case of the dealkylated calix[n]arene phosphine oxides, while the ratio was greater than 2 for the alkylated calix[n]arenes suggesting coextraction of complexes with other stoichiometries and/or nitric acid. The absence of t-butyl groups on the upper rim increased the efficiency of Th(IV) extraction with the order being **21e** >**21f** >**21d**. The ability of the phosphine oxides to extract Np-237, Pu-239 and Am-241 by a supported liquid membrane was then evaluated.[70] While the hexamer **21b** was the best p-alkylated extractant for Np and Pu, the dealkylated octamer phosphine oxide (**21f**) was the best ligand overall for extraction of the three nuclides. The stripping efficiency of (**21f**) was found to be comparable to the conventional extractant (N, N-dioctylcarbamoylmethyl)diphenylphosphine oxide (CMPO).

The ability to complex alkali, alkaline earth and f-element cations was

21a R = tBu, n=4
21b R=tBu, n=6
21c R=tBu, n=8
21d R=H, n=4
21e R=H, n=6
21f R=H, n=8

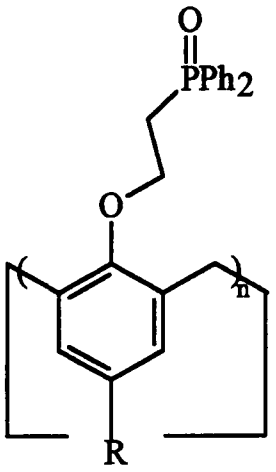


Figure 1.21. Phosphine oxides with two methylene units

21g n=4
21h n=5

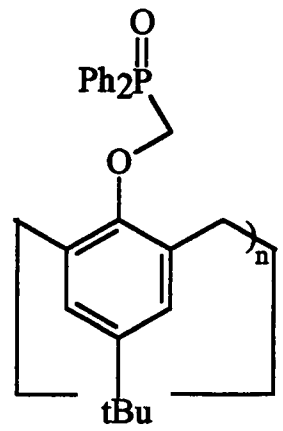


Figure 1.21 (contd.). Phosphine oxides with one methylene unit

21i R=NEt_2
21j R=OtBu

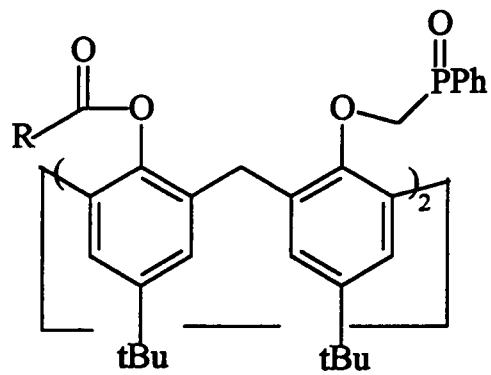


Figure 1.21(contd.). Mixed phosphine oxides

investigated[71] with the following substituted calix[n]arenes: a) phosphine oxide with two methylene units from the phenolic oxygen and n= 4, 6 or 8 on the alkylated or dealkylated calixarene (**21a-f**), b) phosphine oxide with one methylene unit, **21g** (n = 4) and **21h** (n = 5) and c) mixed phosphine oxide with ester (**21i**) or amide (**21j**) groups.

The long chain tetraphosphine oxide-substituted calix[4]arenes (**21a** and **d**) performed poorly in extracting all the alkali cations while the short chain tetramer (**21g**) showed an affinity for K^+. The pentamer (**21h**), however, displayed higher affinity for these ions with selectivities in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. The ability of the tetramer to complex Group IA ions was increased by using mixed ester/amide phosphine oxides (**21i** and **j**). Amide **21i** had the highest affinity for Na^+ over any ligand studied. Group IIA cations were better complexed by **21g** and **h** with affinities in the order of $Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+}$. Complexation by the pentamer **21h** was, however, far superior with about 63% Ca^{2+} complexation. Substitution of diesters (**21j**) with (**21i**) improved the complexing ability but they were still inferior to the pentamer **21h**.

Extraction of Eu(III) and Th(IV) by the calixarene-phosphine oxides (**21a-j**) was far superior when compared to conventional extractants like TOPO and CMPO. The calixarene derivatives extracted more Th(IV) than Eu(III). Dealkylated calixarenes (**21d-f**) were more efficient than the alkylated analogues with the order of extracting ability being hexamer > octamer > tetramer for the former and hexamer > tetramer > octamer respectively for the latter. The short chain tetramer **21g** was better than **21a**. The pentamer **21h** was found to extract these ions poorly. The ligand to metal ratio for both

Eu(III) and Th(IV) was found to 1:2 suggesting a bis-ligand species.

The selectivity towards Eu(III) by the tetraphosphine oxide-substituted calix[4]arene (**21a**) has been taken advantage of by encapsulating them in a PVC membrane and used as an ion selective electrode (ISE) for detecting Eu(III)[72] and Ca^{2+}.[73] Calcium-selective optical membranes have also been developed.[74]

Calixarene Phosphates

Bis (phosphate ester)-substituted calix[4]arenes (**22a** and **b**, Figure 1.22) synthesized in the cone conformation by reaction of calix[4]arene with chlorodiethylphosphate in the presence of triethylamine has been found to be selective for Li^+.[75] The stability constants in THF solutions for **22b** were 5.43 for Li^+, 4.40 for Na^+ and 3.89 for K^+.

Phosphate diesters of t-butylcalix[4]arenes were investigated for their ability to complex Li^+, Na^+ and K^+ using solvent extraction and liquid membrane transport experiments (**23a-c**, Figure 1.23).[76] While the phosphorylated-calixarene was superior than its unphosphorylated precursor, remarkable selectivities have not been displayed. However, transport studies on the different phosphate esters have shown the affinities to be in the order of $Li^+ > Na^+ > K^+$. Compound **23b** showed a better Li^+/K^+ and Na^+/K^+ selectivity than the other esters studied.

A wide array of phosphate esters of p-tetra-alkylcalix[n]arenes have been synthesized.[77] They did not display marked selectivity in the separation of lanthanides and actinides when compared to analogous phosphine oxide-substituted calix[4]arene. In another example, bridged calix[4]arene diphosphate (**24**, Figure 1.24) was tested as a

22a R=tBu
22b R=H

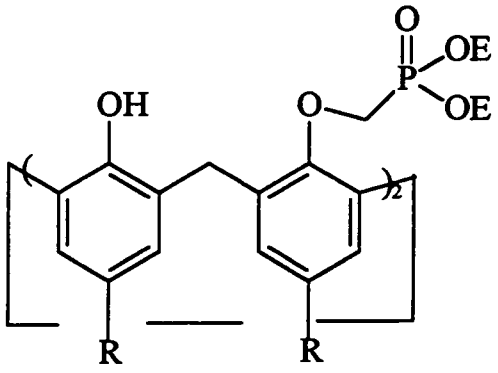


Figure 1.22. Bis(phosphate ester) of calix[4]arenes

23a R=Me
23b R=Et
23c R=nPr

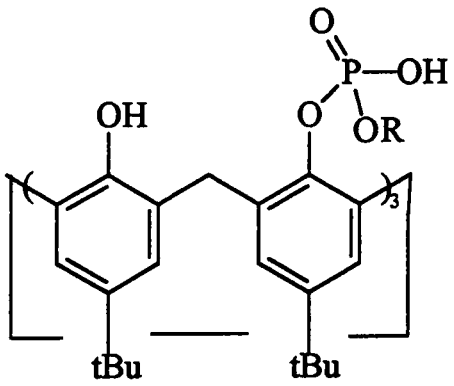
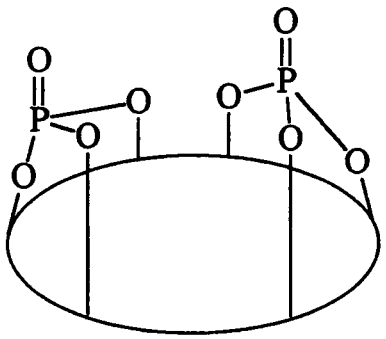


Figure 1.23. Phosphate esters of p-tetrabutylcalix[4]arenes



24

Figure 1.24. Bridged calix[6]arene diphosphates

selective lanthanide receptor.[78] Experimental data for this study was not reported.

Upper rim functionalized calixarenes

Actinide separations by the TRUEX process have been carried out with CMPO.[79] An analogous functionality, $-NHC(O)CH_2P(O)Ph_2$, has been tethered to each of the phenyl rings in the upper rim of various calix[4]arene tetraalkyl ethers and a calix[5]arene pentaalkyl ether (**25a-h**, Figure 1.25).[80] Their ability to extract Eu, Th, Np, Pu and Am from a 1N HNO_3 solution into methylene chloride or o-nitrophenylhexyl ether was studied. The calixarene based ligands were far superior in their extracting ability than conventional CMPO owing to the cooperation induced by several ligating groups within one molecule. Their efficiency of transport was also much higher when used in a supported liquid membrane. Methylenephosphonic acid groups have been substituted in the upper rim of calix[6]arene (**26**, Figure 1.26).[81] This ligand has shown excellent affinity for uranyl ions (UO_2^{2+}) forming a 1:1 complex with a stability constant of $10^{17.5}$.

Immobilization of calixarenes onto organic and inorganic supports

Calixarenes have been immobilized onto polymers by a) functionalizing an existing support, b) step-growth polymerization of appropriate monomers or c) chain-growth polymerization of vinyl-substituted monomers.

Functionalization of an existing support

Silica-bonded calixarenes. Calix[4]arene tetraethyl ester (**27a**, Figure 1.27) and calix[6]arene hexaethyl ester (**27b**) were chemically incorporated into silica particles through a hydrosilanization reaction at the upper rim.[82,83] When packed into a column and using a 50/50 methanol/water solution as the mobile phase, the former was selective

25a n=4, R=C_5H_{11}
25b n=4, R=CH_2CH(n-Bu)(Et)
25c n=4, R=$C_{10}H_{21}$
25d n=4, R=$C_{12}H_{25}$
25e n=4, R=$C_{14}H_{29}$
25f n=4, R=$C_{16}H_{33}$
25g n=4, R=$C_{18}H_{37}$
25h n=5, R=$C_{14}H_{29}$

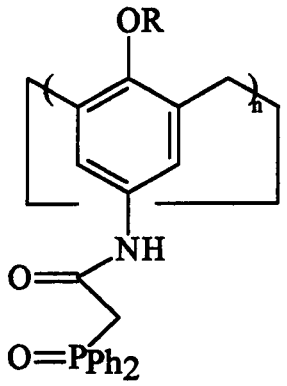


Figure 1.25. Calixarene analogues of CMPO

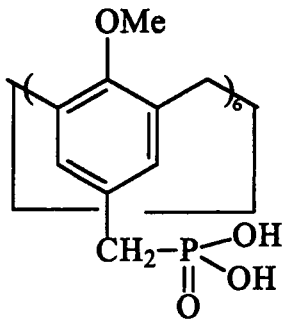


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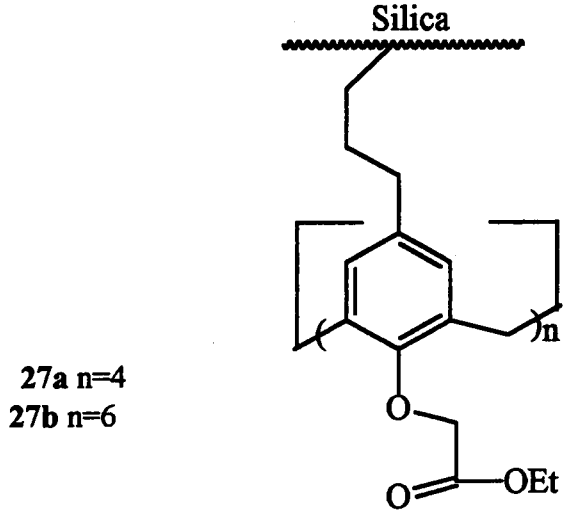
Figure 1.26. Upper rim functionalized calix[6]arene phosphonic acid



27a n=4
27b n=6

Figure 1.27. Silica-bonded calix[n]arene ethyl esters

towards Na^+ while the latter towards Cs^+, Rb^+ and K^+.

Chelating calix[4]arene hydroxamates supported onto silica particles (**28**, Figure 1.28) have been studied [84] for their uptake of different transition metal ions at varying solution pH. While Pb(II) was quantitatively complexed at a pH of 3.5 and Cu(II) at pH 7, the other metal ions (Ni(II), Zn(II), Mn(II) and Co(II)) were not removed in excess of 90% even at an increased pH.

Silica-bonded tetrameric calixarene tetradiethylamide (**29**, Figure 1.29) was evaluated[85] for its chromatographic selectivity. Retention of Na^+ over other alkali cations and of Ca^{2+} over Mg^{2+} was observed. Selective chromatographic separation of Cs^+ and K^+ has been achieved with 1,3-alternate calix[4]arenecrown-6 and calix[4]arenecrown-5 (**30a** and **30b**, Figure 1.30) covalently bound to silica gel.[86]

Organic polymer-supported calixarenes. Calix[6]arene has been attached via the upper rim through a sulfonamide linkage by reaction of a hexasulfonyl chloride of calix[6]arene with a 30% aqueous solution of polyethyleneimine (**31**, Figure 1.31).[87] The resin was found to have high affinity for UO_2^{2+} ions. Attempts to incorporate the calixarene onto crosslinked aminopolystyrene proved unsuccessful.

Friedel-Crafts reaction of linear polyacryloyl chloride with calix[4]arene tetraester resulted in the calixarene attached via the upper rim to the polymer support (**32**, Figure 1.32).[88] Selective complexation of Na^+ was observed with this polymeric calixarene.

Calix[4]arene has also been attached through the lower rim to an oligomer of epichlorohydrin (MW = 1074) (**33a-c**, Figure 1.33).[89] Extraction of Fe(III), Ni(II), Co(II)and Cu(II) as a function of pH was studied. Polymer **33c** had a high affinity (82%)

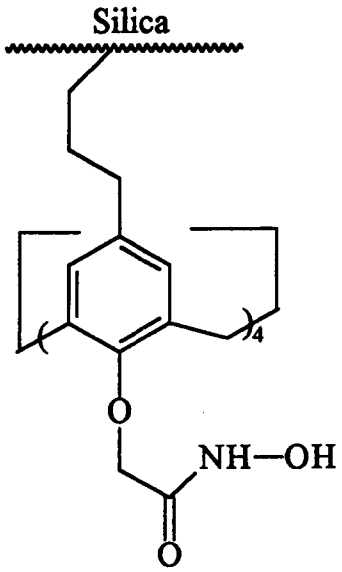


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Figure 1.28. Calix[4]arene tetrahydroxamates bonded to silica

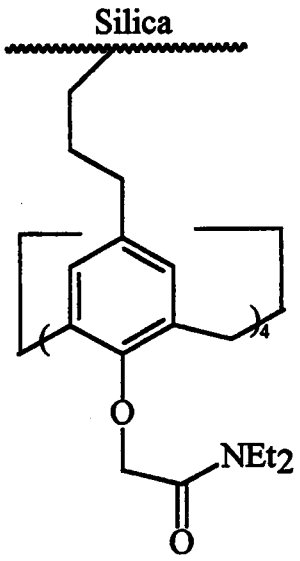

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Figure 1.29. Silica-bonded calix[4]arene tetradiethylamide

30a n=1
30b n=2

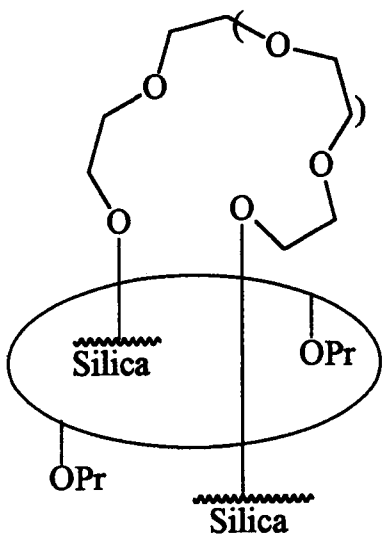

Figure 1.30. Silica-bonded calix[4]arene crown

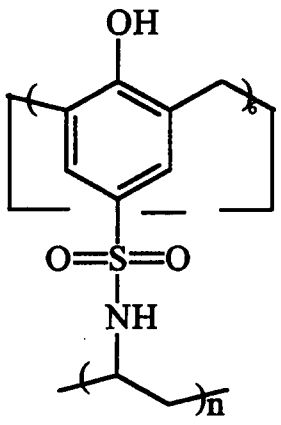

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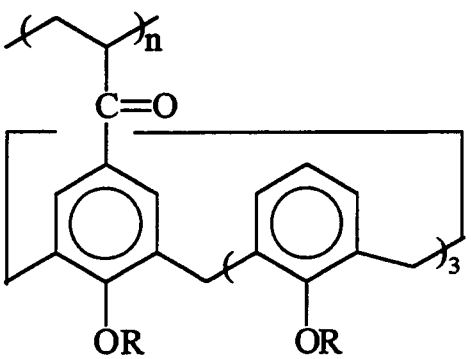
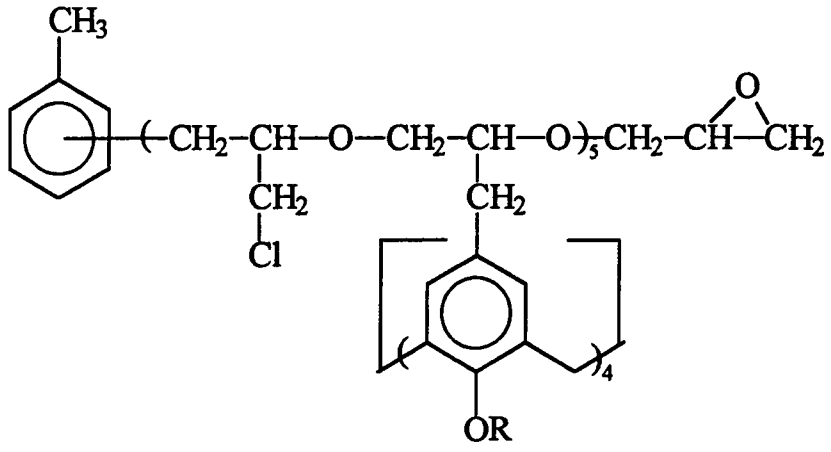
Figure 1.31. Calix[6]arene immobilized onto polyethyleneimine support



$R = CH_2COOC_2H_5$

32

Figure 1.32. Calix[4]arene tetraester supported onto polyacryloyl chloride



33a R=$CH_2CO_2CH_2CH_3$
33b R=C(O)Ph
33c R=H

Figure 1.33. Calix[4]arene supported onto oligomeric epichlorohydrin

for Fe(III) even at a pH of 2.2 compared to its monomeric analogue (8.4%). The affinity for other ions was low.

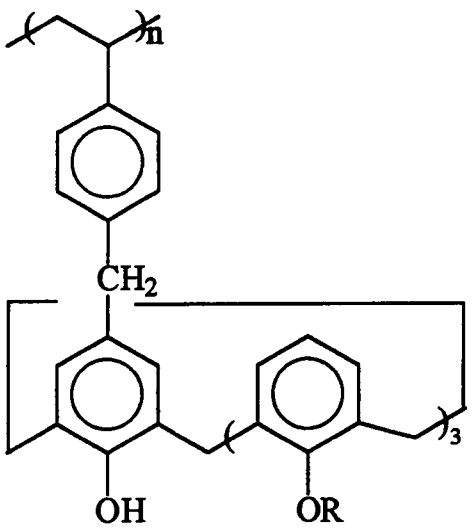
Calix[4]arene-supported linear polymers have been studied for their extracting ability of Fe(III):[90] calix[4]arene attached to chloromethylated poly(styrene) via the upper rim (**34a** and **34b**, Figure 1.34), hydroxycalix[4]arene attached to the lower rim (**35a** and **35b**, Figure 1.35), and the tetraester of calix[4]arene in a 1,3-alternate conformation attached by the upper rim to polyacryloyl chloride (**36a** and **36b**, Figure 1.36). High selectivity for Fe(III) was observed with **35b** at a pH of 3.8.

Step-growth polymerization of appropriate monomers

A mixture of 1,3-dimethoxycalix[4]arene and bisphenol-A in different ratios have been reacted with NaH (as the deprotonating agent) followed by reaction with either dibromomethane to form the polyether (**37a** and **37b**) or terephthaloyl chloride to form the polyester (**37c**, Figure 1.37).[91] The Ag(I) extraction by the polyether containing calix[4]arene **37a**, **37b** was approximately 100-fold greater than the small molecule analogue (i.e., tetrapropylether substituted calix[4]arene).

Chain-growth polymerization of a vinyl-substituted calixarene

A polymerizable vinyl group was introduced by selective hydrolysis of a single ester group in a calix[4]arene-tetra ester followed by reaction with 2-hydroxyethyl methacrylate. The polymer (**38**, Figure 1.38) synthesized from this monomer was found to selectively complex Na^+.[92]



34a R = COPh
34b R = H

Figure 1.34. Calixarene supported via the upper rim to chloromethylated polystyrene

35a R = COPh
35b R = H

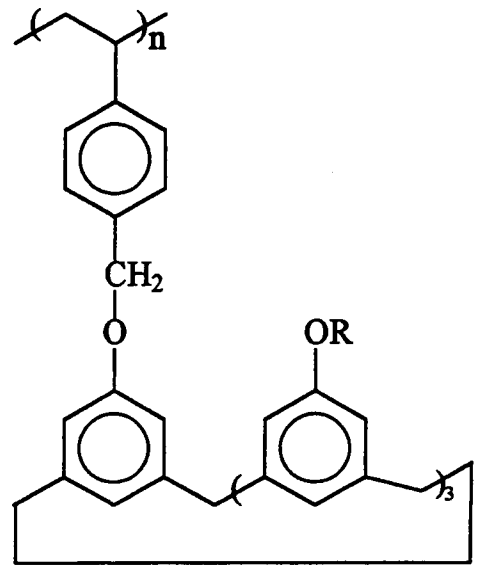


Figure 1.35. Calix[4]arene supported on chloromethylated polystyrene via lower rim

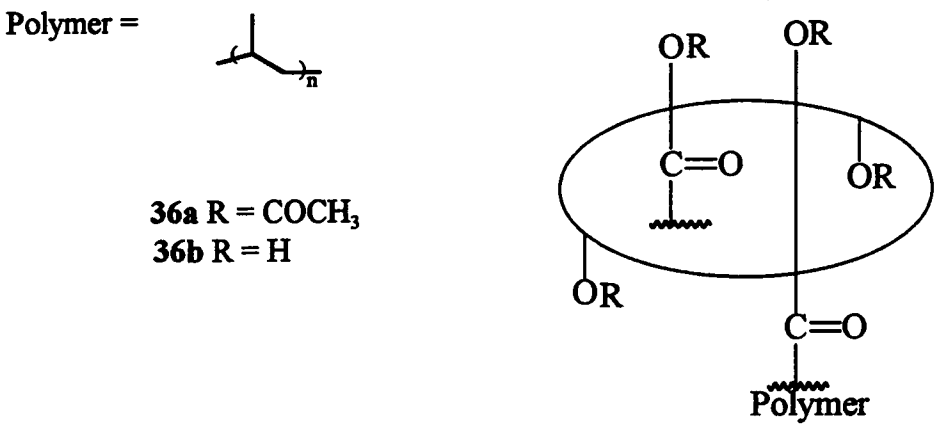
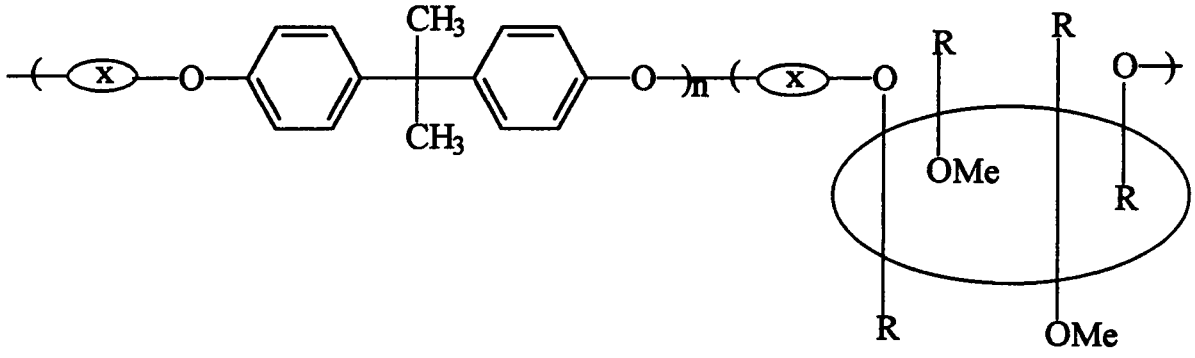
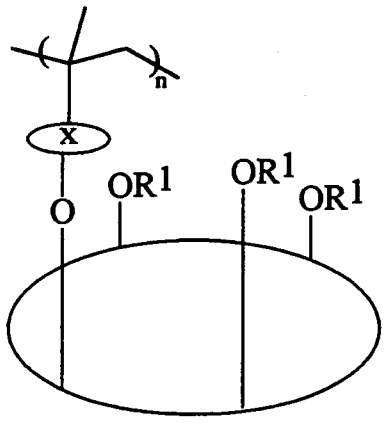


Figure 1.36. Calix[4]arene immobilzed via the upper rim to polyacryloyl chloride



37a R=H, X=CH_2
37b R=tBu, X=CH_2
37c R=H, X=p-$C(O)C_6H_4C(O)$

Figure 1.37. Calix[4]arene-bisphenol-A copolymers



R^1=CH_2CO_2Et
X=$(O)COCH_2CH_2CO_2CH_2$
38

Figure 1.38. Calix[4]arene methacrylate polymer

This introductory review has shown that phosphorylated-calixarenes offer numerous possibilities for the selective complexation of metal ions. The ordered structures obtained from complexes with transition metal ions can be used in stereo-selective synthesis while their selectivity towards actinides and lanthanides can be utilized in the removal of radionuclides from water. Only very few studies into the immobilization of calixarenes onto polymer supports have been reported. Successful immobilization onto crosslinked polymer supports could open up a new area of selective polymer-supported reagents for catalysis and metal ion separations.

This dissertation first describes the importance of bifunctionality in improving the kinetics of complexation (Chapter 2). We report that a low level of complexation need not necessarily be due to poor affinity but could also be due to decreased accessibility of ions into the polymer matrix. A bifunctional phosphonic/sulfonic acid polymer supported on a highly crosslinked polymer gel is still able to have rapid complexation kinetics from high ionic strength solutions. The ability of the sulfonic acid ligand to prevent the collapse of the polymer matrix allows the ions to access the matrix and the phosphonic acid then selectively complexes the targeted metal ion. Chapter 3 develops the idea of increasing metal ion affinities of polymers by an inter- or intra-ligand cooperation mechanism. This will help in the fundamental understanding of highly selective polymers. Lastly (Chapter 4), the synthesis of calix[4]arene and phosphorylated calix[4]arene supported polymers are discussed. This is the first known example of supporting calixarenes onto crosslinked polymer supports and the first time ever that a phosphorylated calixarene has been

immobilized onto any kind of support. The cooperation of the ligating groups has induced high selectivity in the metal ion complexation by these polymers. The calix[4]arene polymer was highly selective for the removal of Cs(I) while the phosphorylated version was specific for the complexation of Fe(III) and Pb(II).

CHAPTER 2

ION-SELECTIVE POLYMER-SUPPORTED REAGENTS: THE PRINCIPLE OF BIFUNCTIONALITY

Introduction

The design and development of ion-selective polymer supported reagents is important to applications in environmental remediation, removal of toxic metal ions from industrial process streams, and the recovery of precious metals from low grade ores. The use of polymer supported reagents in these applications require that they not only be very selective, but also should display fast kinetics of complexation.

The commercially available sulfonic acid resin is insufficiently selective to permit the complexation of a targeted ion present in trace quantities in a solution with ions such as sodium, magnesium and calcium in much higher concentration.[93] Ion exchange resins with carboxylic acid ligands can be more selective but are limited by a relatively high pK_a value. Chelating resins have been prepared with targeted selectivities: dioxocyclam has been immobilized on crosslinked methacrylates and used to complex Cu(II);[94] immobilized pyridinone is selective for Fe(III)[95] and polymeric dioximes have a high affinity for Ni(II).[96] Their application can be problematic, however, because high levels of complexation can be dependent on long contact times,[97] use of very small particle size,[98] or the presence of non-aqueous solvents.[99]

Dual mechanism bifunctional polymers[7-12] have introduced the concept of using multiple ligands on the same polymer each for a different purpose, viz., a ligand that

would increase the accessibility of ions into the polymer matrix and a ligand that would selectively complex targeted metal ions.

The goal of the present research is to synthesize highly selective polymer supported reagents at different crosslinking levels. The effect of the type of support (microporous or macroporous) on the complexation kinetics of phosphonic acid resins will be studied. Also, the feasibility of increased kinetics in gel resins by sulfonation of the phosphonic acid resin to form a bifunctional polymer will be evaluated. Lastly, the levels of sulfonation on the resin will be varied to determine their effect on the kinetics of complexation.

Experimental

Suspension copolymerization of vinylbenzyl chloride and divinylbenzene

The copolymer beads were prepared from vinylbenzyl chloride (VBC) and divinylbenzene (DVB) by suspension polymerization. Beads were prepared with 5, 12 and 20% DVB. Both microporous (gel) and macroporous (MR) beads were prepared, the latter with 50 wt% 4-methyl-2-pentanol in the monomer solution. Beads that were used in the functionalization reactions had particle size in the range of 0.42-0.60 mm.

Suspension copolymerization of vinylbenzyl chloride, styrene and divinylbenzene

The suspension copolymerization was carried out with VBC and styrene in a mole ratio of 1:1.44 with crosslinking levels at both 5 and 12% DVB. The gel beads were sieved to a particle size of 0.42 -0.60 mm.

Synthesis of monofunctional phosphonic acid resin (MPA)

The VBC copolymer beads were reacted with triisopropyl phosphite at reflux temperature for 17 h. The beads were washed with ethanol and water after the excess solution was siphoned off. The ester formed was hydrolyzed by refluxing the resin with conc HCl for 17h (Figure 2.1). The beads were then washed with water and conditioned with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. The resin was characterized by % solids(g_{dry}/g_{wet} x 100), phosphorus elemental analysis and acid capacity.

Synthesis of bifunctional phosphonic/sulfonic acid resin (BPSA)

After the synthesis of the phosphate ester as described earlier, the resin was azeotropically distilled with heptane to remove excess water trapped in the polymer matrix, Büchner dried, and preswollen in ethylene dichloride (EDC) for 2 h. A mixture of EDC/chlorosulfonic acid was then slowly added dropwise at 0°C. After the addition, the reaction was allowed to proceed at room temperature for 48 h (Figure 2.2). The excess solution was siphoned off and the beads were washed in the following sequence: 100/0, 75/25, 50/50, 25/75 and 0/100 v/v dioxane/water. The resin was then conditioned by eluting 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. The resin was characterized by the percent solids, phosphorus elemental analysis and acid capacity.

Metal ion studies

The metal ion studies were performed by contacting enough of the 5 and 12% DVB resins to give 1 mequiv of phosphorus ligands (based on the phosphorus capacity) with 10 mL of 10^{-4} N $Eu(NO_3)_3$ and $Fe(NO_3)_3$ solutions in 0.10 and 1.00 N HNO_3 at 0.5

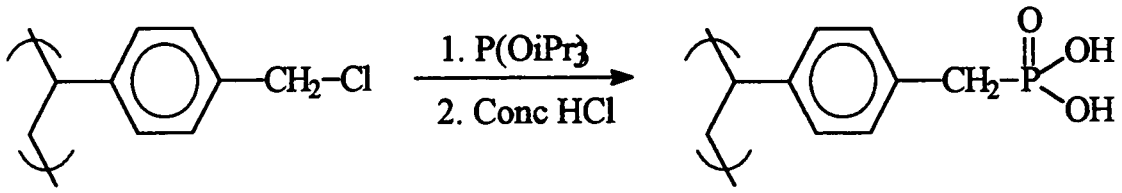


Figure 2.1. Synthesis of monofunctional phosphonic acid resin (MPA)

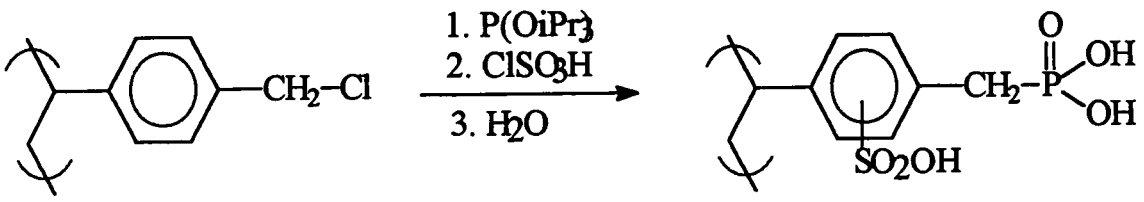


Figure 2.2. Synthesis of bifunctional phosphonic/sulfonic acid resin (BPSA)

and 24 h contact times. In the case of 20% DVB resins, only 0.5 g (wet weight) was used in the contact studies. Each resin was pre-equilibrated with either 0.10 N or 1.00 N HNO_3 prior to contact with the metal-containing solution. The amount of metal complexed was determined by an atomic absorption spectrometer. Eu(III) was detected in the emission mode at a wavelength of 459.4 nm while Fe(III) was detected at 248.3 nm in the absorption mode. The results are reported as both the percent metal complexed and the distribution coefficient D, which is defined as:

$$\frac{\text{mequiv } M^{n+} \text{ on the resin / } g_{dry} \text{ resin}}{\text{mequiv } M^{n+} \text{ in solution / mL solution}}$$

Results and Discussion

VBC and DVB were copolymerized by suspension polymerization. The effect of matrix rigidity was studied at three different crosslink levels: 5, 12 and 20 wt% DVB. Both microporous (gel) and macroporous (MR) beads were prepared. The MR polymers had 50% pore volume. The functionalization reactions were carried out on beads sieved to 0.42-0.60 mm because rate studies at this particle size are sensitive to differences in polymer architecture and because it is a size that is useful in process applications.

The monofunctional phosphonic acid resins (MPA) were synthesized by first reacting the VBC copolymer beads with triisopropyl phosphite (Arbuzov reaction) followed by hydrolysis with conc. HCl for 17 h (Figure 2.1). The resins were washed with water and conditioned. The bifunctional phosphonic/sulfonic acid resins (BPSA) were synthesized by chlorosulfonation of the phosphonate ester followed reaction of the resins with water, washing and conditioning.

The resins that were synthesized fall into three categories: MPA-gel, MPA-MR and BPSA gel. Each was prepared at crosslink levels of 5, 12 and 20 wt% DVB. Gel resins have a high volume capacity, which is advantageous in large scale applications, but high crosslink levels may be needed to increase attrition resistance and decrease swelling (in order to minimize the pressure drop in column applications). Higher crosslink levels can limit substrate accessibility into the polymer matrix and, to counter this, macroporous supports are commonly used. Macroporous resins, however, can be less resistant to attrition and often require greater levels of crosslinking; they also have lower volume capacities. Since the principal goal of this research was to determine if complexation kinetics can be maximized in highly crosslinked gel resins, the effect of macroporosity was compared to bifunctionality. In the latter case, the possibility was considered that by introducing a hydrophilic ligand such as the sulfonic acid group into the polymer, accessibility of the metal ions into the matrix could be increased and the phosphonic acid ligand could then selectively complex the targeted metal ion.

The properties of the resins are reported in Table 2.1. The phosphonic acid gel resins (MPA) showed an increased percent solids with increasing crosslink level. The 5% and 12% DVB MPA gel resins were almost completely functionalized, as determined by comparing their actual phosphorus capacities (4.33 and 3.68 mequiv/g, respectively) with values assuming complete phosphorylation of the -CH_2Cl groups (4.65 and 4.12 mequiv P/g, respectively). The 20% DVB MPA gel resin was functionalized to only 26% of its maximum value (experimental and theoretical phosphorus capacities of 0.91 and 3.47 mequiv/g, respectively): it was more difficult to functionalize due to limited reagent

Table 2.1

Characterization of MPA and BPSA resins

Resin code	Resin name	Type	% DVB	% Solids	Phosphorus capacity (mequiv/g)	Acid capacity (mequiv/g)
SN-02-223B	MPA	gel	5	63.9	4.33	8.68
SN-02-223A	MPA	gel	12	72.8	3.68	7.25
SN-02-147	MPA	gel	20	87.5	0.91	1.70
SN-02-217	MPA	MR	5	33.6	4.08	8.57
SN-03-100	MPA	MR	12	29.5	3.37	6.33
SN-03-244	MPA	MR	20	34.7	2.45	5.00
SN-01-046	BPSA[a]	gel	5	42.0	3.30	9.70
SN-03-222	BPSA[a]	gel	5	43.1	3.16	10.30
SN-01-092	BPSA[b]	gel	12	60.0	2.80	8.47
SN-03-223	BPSA[b]	gel	12	61.2	2.73	8.91
SN-02-158B	BPSA	gel	20	75.2	0.85	2.13

a same resin, different batches
b same resin different batches

accessibility into the highly crosslinked matrix. All the MPA gel resins were completely hydrolyzed since the acid capacity was almost twice the phosphorus capacity at each crosslink level. Complete hydrolysis of the 20% DVB MPA gel resin is also an indication that the ligands are accessible to ions in solution.

The solids level drops significantly with the MPA MR resins, regardless of the crosslink level. This was attributed to water being held in the large macrochannels under hydrated conditions. While functionalization of the MPA MR resins at 5% and 12% DVB was comparable to their gel analogues, the 20% DVB MPA MR was 71% functionalized, indicating a greater substrate accessibility due to the macroporosity. In each case, the acid capacity was, within experimental error, twice the phosphorus capacity indicating complete hydrolysis.

Bifunctional phosphonic/sulfonic acid (BPSA) gel resins showed an increasing hydrophobicity, as indicated by the increasing solids with increasing crosslinking of the polymer matrix. Their solids level are lower than their MPA gel analogues because of the presence of the hydrophilic sulfonic acid ligand in the polymer backbone. The theoretical phosphorus to acid site ratio in the BPCA resin is 1:3. This was found to be the case, within experimental error, in the 5% and 12% BPSA gel resins, whereas the ratio was 1:2.6 in the 20% BPSA gel resin.

The ability of MPA gel resins to complex Eu(III) from 0.10 and 1.00 N HNO_3 is summarized in Table 2.2. Kinetics of complexation was evaluated from 0.5 h contact studies. Equilibrium studies were also done at a 24 h contact time. At 0.5 h and 24 h contact times, the 5 and 12% DVB resins complex >94% Eu(III) from 0.1 N HNO_3.

Table 2.2

Complexation of Eu(III) from 10^{-4} N $Eu(NO_3)_3$ in 0.10 and 1.00 N HNO_3 at 0.5 h and 24 h contact times by MPA gel resins

% DVB	0.10 HNO_3		1.00 HNO_3	
	0.5 h	24 h	0.5 h	24 h
5	97.7† ($1.77x10^3$)‡	99.4 ($6.88x10^3$)	31.7 (21.3)	35.0 (24.7)
12	94.4 (705)	99.0 ($4.02x10^3$)	3.20 (1.24)	8.34 (3.41)
20	3.60 (0.95)	25.5 (16.1)	0.61 (0.15)	4.37 (1.11)

† percent metal complexed
‡ Distribution coefficient (D)

Complexation by the 20% DVB MPA gel resin was at a much lower level due to limited accessibility into the highly crosslinked resin, even from dilute acid solution. Complexation from 1.00 N HNO_3 was very low for all three resins, though the effect of crosslinking on the amount of Eu(III) complexed continues to be 5%>12%>20% DVB. Results with Fe(III) under identical conditions are given in Table 2.3 with the same general trends being observed.

The low levels of Eu(III) or Fe(III) complexation from 1.00 N HNO_3 with the MPA gel resins can be due to thermodynamics (i.e., effective competition for the ligands by H^+ in the highly acidic solution) or kinetics (i.e., accessibility of the metal ions into the polymer matrix). Results with the MPA MR resins show that kinetics is an important variable that must be evaluated before conclusions regarding ligand-ion affinities can be made. Eu(III) complexation from 0.10 N HNO_3 (Table 2.4) was almost quantitative for both the 5% and 12% DVB resins at both the contact times. The 20% DVB MPA resin which complexed very low levels as a gel, complexed >90% as an MR at 24 h but approximately 30% at 0.5 h, which indicated that equilibrium was reached slowly. Eu(III) complexation, however from 1.00 N HNO_3 still continued to be low. Results with Fe(III) complexation were similar to those for Eu(III) from 0.10 N HNO_3 solution (Table 2.5); complexation remained high for both 5% and 12% DVB resins while the 20% resin complexed 90.6% Fe(III) at 24 h but only 13.7% at 0.5 h.

A comparison of the results in Tables 2.2-2.5 led to the conclusion that macroporosity enhanced the rate of complexation, at least when the degree of crosslinking did not exceed 12% DVB. However macroporosity did not help in the complexation of

Table 2.3

Complexation of Fe(III) from 10^{-4} N $Fe(NO_3)_3$ in 0.10 and 1.00 N HNO_3 at 0.5 h and 24 h contact times by MPA gel resins

% DVB	0.10 HNO_3		1.00 HNO_3	
	0.5 h	24 h	0.5 h	24 h
5	98.0† ($2.47x10^3$)‡	100 (∞)	74.3 (131)	96.7 ($1.34x10^3$)
12	43.9 (28.6)	98.0 ($1.82x10^3$)	13.9 (5.98)	74.3 (129)
20	0 (0)	3.26 (0.34)	3.95 (1.04)	3.95 (1.05)

† percent metal complexed
‡ Distribution coefficient (D)

Table 2.4

Complexation of Eu(III) from 10^{-4} N $Eu(NO_3)_3$ in 0.10 and 1.00 N HNO_3 at 0.5 h and 24 h contact times by MPA MR resins

% DVB	0.10 HNO_3		1.00 HNO_3	
	0.5 h	24 h	0.5 h	24 h
5	98.3† (2.39×10^3)‡	99.5 (7.75×10^3)	28.8 (16.8)	30.8 (18.4)
12	99.1 (3.51×10^3)	100 (∞)	22.2 (8.94)	25.9 (10.9)
20	31.2 (26.1)	90.4 (553)	1.26 (0.74)	8.32 (5.23)

† percent metal complexed
‡ Distribution coefficient (D)

Table 2.5

Complexation of Fe(III) from 10^{-4} N $Fe(NO_3)_3$ in 0.10 and 1.00 N HNO_3 at 0.5 h and 24 h contact times by MPA MR resins

% DVB	0.10 HNO_3		1.00 HNO_3	
	0.5 h	24 h	0.5 h	24 h
5	100† (∞)‡	100 (∞)	94.5 (729)	96.7 ($1.25x10^3$)
12	98.2 ($1.67x10^3$)	98.2 ($1.67x10^3$)	99.5 ($6.23x10^3$)	100 (∞)
20	32.3 (27.3)	100 (∞)	13.7 (9.09)	90.6 (551)

† percent metal complexed
‡ Distribution coefficient (D)

Eu(III) from highly acidic solution. From these results, it can be deduced that an inherently high affinity for the metal ion is required for increased kinetics in the MPA MR resins since the phosphonic acid ligand has a higher affinity for Fe(III) than for Eu(III) in highly acidic solutions.

Results from the BPSA gel resins for complexation of Eu(III) and Fe(III) are summarized in Tables 2.6 and 2.7. The kinetic results at 0.5 h contact time and in highly acidic solution for Eu(III) was significantly different when compared to the results from both the MPA gel and MR resins. These results from the BPSA gel resins emphasize the importance of ensuring that the ligand-ion pair are at equilibrium before conclusions about inherent affinities are made: introduction of an access ligand into the polymer matrix lead to the quantitative recovery of both Eu(III) and Fe(III) regardless of the degree of crosslinking from both low and high acid solutions even at a 0.5 h contact time. Complexation of Eu(III) by BPSA gel resins in the presence of a 4 N $NaNO_3$ solution where the Eu(III):Na(I) ratio was 1:12000 has shown that the sulfonic acid ligand was not responsible for the significant amount of complexation from highly acidic solutions.[100] The low complexation by 20% DVB resin noted in Tables 2.2-2.5 was thus found to be a function of ligand accessibility. Bifunctionality allowed for the highly crosslinked gel resins to complex far more efficiently than making macroporous resins.

Once the importance of bifunctionality was established, the next goal was to optimize the kinetics by varying the levels of sulfonation in the polymer matrix. Arbuzov reaction on the VBC/styrene gel copolymer beads gave the phosphonate ester resin. It was hoped that, when reacted with $ClSO_3H$, only the phenyl groups in the styrene moiety

Table 2.6

Complexation of Eu(III) from 10^{-4} N $Eu(NO_3)_3$ in 0.10 and 1.00 N HNO_3 at 0.5 h and 24 h contact times by BPSA gel resins

% DVB	0.10 HNO_3		1.00 HNO_3	
	0.5 h	24 h	0.5 h	24 h
5	99.6† ($8.47x10^3$)‡	100 (∞)	94.2 ($6.02x10^3$)	100 (∞)
12	100 (∞)	100 (∞)	95.5 (624)	100 (∞)
20	100 (∞)	100 (∞)	93.8 (395)	97.5 ($1.04x10^3$)

† percent metal complexed
‡ Distribution coefficient (D)

Table 2.7

Complexation of Fe(III) from 10^{-4} N $Fe(NO_3)_3$ in 0.10 and 1.00 N HNO_3 at 0.5 h and 24 h contact times by BPSA gel resins

% DVB	0.10 HNO_3		1.00 HNO_3	
	0.5 h	24 h	0.5 h	24 h
5	100† (∞)‡	100 (∞)	100 (∞)	100 (∞)
12	100 (∞)	100 (∞)	100 (∞)	100 (∞)
20	100 (∞)	100 (∞)	97.3 (939)	100 (∞)

† percent metal complexed
‡ Distribution coefficient (D)

would be sulfonated. If this could be achieved, then, the levels of sulfonation could be varied by changing the amounts of styrene during copolymerization with VBC. Two phosphonate ester resins of the VBC/styrene gel copolymer were synthesized at 5% and 12% DVB crosslink levels. These resins were either hydrolyzed by conc HCl to give VBC/styrene monofunctional phosphonic acid (VSMPA) resins or reacted with chlorosulfonic acid followed by quenching with water to obtain VBC/styrene bifunctional phosphonic/sulfonic acid (VSBPSA) resin. The characterization data is reported in Table 2.8. The VSMPA gel resins at 5% and 12% crosslink level were quantitatively phosphorylated. Their phosphorus capacities of 2.53 and 2.21 respectively, were in good agreement with their theoretical capacities of 2.60 and 2.29 mequiv/g. Acid capacities of the resins (5.00 and 4.37 mequiv/g respectively for the 5% and 12% crosslinked resins) being twice their respective phosphorus capacities suggested they were completely hydrolyzed. The 5% crosslinked bifunctional resin (VSBPSA), SN-01-053, had an acid capacity more than thrice the phosphorus capacity. This suggested that the phenyl groups in both the styrene and the VBC moieties were getting sulfonated. In the case of the 12% VSBPSA resin (SN-01-099), the acid capacity, however, was thrice the phosphorus capacity. This discrepancy could be due to the incomplete hydrolysis of the phosphonate ester by the HCl generated during quenching. This resin is more hydrophobic than the former. The solids level of the resins drop after sulfonation due to the increased hydrophilicity of the matrix.

The complexation of Eu(III) from 10^{-4} N $Eu(NO_3)_3$ in 0.10 N HNO_3 at 0.5 h and 24 h contact time is given in Table 2.9. When the crosslinking level was increased in the

Table 2.8

Characterization of VBC/styrene functionalized gel resins

Resin code	Resin name	% DVB	% Solids	Phosphorus capacity (mequiv/g)	Acid capacity (mequiv/g)
SN-01-052	VSMPA	5	71.8	2.53	5.00
SN-01-087	VSMPA	12	82.3	2.21	4.37
SN-01-053	VSBPSA	5	40.6	1.65	7.52
SN-01-099	VSBPSA	12	61.5	1.69	5.07

Table 2.9

Complexation of Eu(III) from 10^{-4} N $Eu(NO_3)_3$ in 0.10 N HNO_3 at 0.5 h and 24 h contact times by the VBC/styrene functionalized gel resins

Resin name	% DVB	0.5 h	24 h
VSMPA[a]	5	69.9† (57.5)‡	97.9 (3.31×10^3)
VSMPA[a]	12	34.6 (11.5)	76.4 (70.6)
VSBPSA[b]	12	100 (∞)	100 (∞)

† percent metal complexed
‡ Distribution coefficient (D)
a VBC/styrene monofunctional phosphonic acid resin
b VBC/styrene bifunctional phosphonic/sulfonic acid resin

VSMPA resins from 5% to 12% DVB, the amount complexed decreased due to decreased accessibility into a more hydrophobic polymer matrix. The importance of having a hydrophilic bifunctional ligand in maximizing the complexation kinetics is once again emphasized by comparing the 12% crosslinked VSMPA (SN-01-087) and VSBPSA (SN-01-099). Eu(III) is completely removed even at a 0.5 h contact time.

A limited study was also done on complexation of Eu(III) in 1.00 N HNO_3 and Fe(III) in 0.10 and 1.00 N HNO_3 at a 24 h contact time. A competition study for the complexation of Fe(III) in the presence of 0.4 N Na(I) from a 0.10 N HNO_3 was also done (Table 2.10). The 5% DVB VSMPA gel resin followed a similar trend as its MPA analogue for the complexation of Eu(III) and Fe(III). The selectivity of the resin was displayed by its ability to complex 88.1% Fe(III) even in the presence of excess sodium ions. The monofunctional 12% DVB gel resin complexes very low amounts of all the metal ions. The hydrophobic nature of the polymer matrix is responsible for this behavior. The bifunctional resin almost quantitatively complexes all the metal ions, as expected. The results from the sodium studies of the bifunctional resin shows that the sulfonic acid ligand is not responsible for the increased complexation.

Though the series of experiments discussed above reemphasized the importance of bifunctionality, kinetics could still not be optimized by varying the levels of sulfonation. The next approach taken was to vary the mole ratios of $ClSO_3H$ in the sulfonation of a phosphonate ester resin. A 5% DVB gel phosphonate ester resin (SN-01-230) was reacted with either a 1:0.25 or 1:0.5 mole ratio of phosphorus to $ClSO_3H$ in two separate experiments to effect 25% or 50% sulfonation. It could not be concluded, however,

Table 2.10

Complexation studies of VBC/styrene functionalized gel resins at 24 h contact time

Resin name	% DVB	Eu(III) in 1.00 N HNO_3	Fe(III)		
			0.10 N HNO_3	1.00 N HNO_3	0.10 N HNO_3/0.4 N $NaNO_3$
VSMPA[a]	5	34.2† (12.7)‡	93.2 (332)	89.2 (201)	88.1 (181)
VSMPA	12	10.8 (2.61)	2.42 (0.54)	9.62 (2.31)	20.8 (5.67)
VSBPSA[b]	12	100 (∞)	100 (∞)	95.2 (351)	100 (∞)

† percent metal complexed
‡ Distribution coefficient (D)
a VBC/styrene monofunctional phosphonic acid resin
b VBC/styrene bifunctional phosphonic/sulfonic acid resin

whether the resins were sulfonated as the phosphorus capacities of the resins were 4.35 and 4.37 mequiv/g respectively, which was almost the same as the phosphonic acid itself (4.59 mequiv/g). Since it was not clear whether sulfonation did take place, a 12% DVB gel phosphonate ester resin (SN-01-233) was reacted with $ClSO_3H$ in either a 1:25 or 1:50 mole ratio. After washing and conditioning, the resins were analyzed. A phosphorus capacity of 2.77 mequiv/g and an acid capacity of 8.98 mequiv/g for the latter indicated that the resin was completely sulfonated. In the case of the former, however, the resin was partially sulfonated (phosphorus capacity of 3.31 mequiv/g and acid capacity of 8.06 mequiv/g). Since the difference from the theoretical values (phosphorus capacity of 3.61 mequi/g, acid capacity of 7.21 mequiv/g) were only marginal, the amount of sulfonation could not be quantified. Hence, characterization of the resins by sulfur elemental analysis was attempted. Determination of the amount of sulfur in benzenesulfonic acid and benzenesulfonamide was done using an analytical procedure devised by Siegfriedt.[130] Due to the difficulty in detecting the end point on a consistent basis, the amount of sulfur could not be determined accurately. The sulfonated resins were, thus, not analyzed.

Conclusions

A low level of complexation by an inherently selective resin in high acid solutions was most often attributed to competition by protons for the binding sites. At least in the case of the phosphonic acid resin, this has now been disproven. Results from this research suggest that collapse of the microporous structure in high ionic strength solutions is an alternate cause of low levels of metal ion complexation. This collapse may be brought about by insufficient hydration of the ligands when the polymers are in such solutions.

Introduction of the polar sulfonic acid ligand into the polymer matrix increased the hydrophilicity of the resin which led to an increase in ionic accessibility. Matrix hydrophilicity could not be measured by percent solids when comparing macroporous to the bifunctional gel resin: the former had lower percent solids than the latter, yet were outperformed by them. The low percent solids in the MR MPA resin was due to the water in the macropores while metal ion complexation is dependent on water in the micropores- a condition best achieved by bifunctionality.

Varying the levels of bifunctionality to determine any effect on the complexation kinetics could not be achieved. While the VBC/styrene copolymer gave non-selective sulfonation, varying the mole ratio of $ClSO_3H$ resulted in only marginal changes in the phosphorus and acid capacities of the resin compared to its precursor. The sulfur content in the resin could not be analyzed with the existing analytical procedure due to the difficulty in detecting the end point. While changing the mole ratio of $ClSO_3H$ does offer a route to partial sulfonation, a better analytical technique is required to characterize the resin for its sulfur content.

This research proposes the principle of bifunctionality: polymer-supported reagents with enhanced metal ion complexation rates require the presence of an access ligand along with a recognition ligand for the targeted selectivity. Bifunctionality is found to be an important alternative to macroporosity for rapid complexation kinetics.

CHAPTER 3

SYNTHESIS OF POLYMER-SUPPORTED REAGENTS WITH ENHANCED METAL ION AFFINITIES: MECHANISTIC STUDIES

Introduction

The need for the development of selective polymer supported reagents has been discussed in the previous chapters. Selectivity in a polymer-supported reagents towards metal ions can be introduced by a number of methods. Polymer-supported crown ethers complex Group IA metal ions based on the ability of the particular cation to fit into the crown cavity.[101] Resins with coordinating ligands display selectivity based on the principles of hard-soft acid-base theory.[102] It states that hard acids prefer to associate with hard bases and soft acids prefer to associate with soft bases. A hard base is one where the donor atom has low polarizability and high electronegativity while a hard acid is one that has small size, high positive oxidation state which lead to low polaraizability. Polymeric 8-hydroxyquinoline has a high affinity for Cu(II),[103] immobilized aldoximes are selective for Fe(III)[104] while polymers functionalized with oligoethylene sulfides have high selectivity for silver and mercury salts.[105]

Dual mechanism bifunctional polymers selectively complex metal ions by a two step process: an access mechanism (by ion-exchange) into the polymer matrix followed by a highly selective recognition mechanism (by redox, coordination or precipitation reactions).[7-12]

The goal of the present research is to synthesize highly selective polymer-supported reagents. Bifunctional ligands will be immobilized in such a way as to allow for the study of both inter- and intra-ligand cooperation to maximize metal ion affinities. Understanding the mechanism of complexation through ligand cooperation would provide a fundamental understanding to effectively design highly selective polymers to complex targeted metal ions.

Experimental

Synthesis of VBC-DVB copolymers

The copolymers were synthesized by suspension polymerization. All the ligands were supported on 2% DVB crosslinked gel resins. The particle size of the copolymer beads used in these reactions were in the range of 0.075 mm- 0.15 mm, unless otherwise noted. Macroporous (MR) polymer supports crosslinked with 20%, 25%, 30% and 40% DVB were also synthesized by including 4-methyl-2-pentanol as the diluent. The MR copolymers had a pore volume of 50% and a particle size in the range of 0.25-0.43 mm.

Synthesis of 2% DVB gel monophosphonic acid resin (MPA)

Triisopropylphosphite was added to the copolymer beads and the mixture was refluxed for 24 h. The resin was washed with ethanol and water and hydrolyzed to the phosphonic acid by heating with conc. HCl at reflux temperature for 24 h (Figure 3.1). The beads were recovered and washed with water. The resin was then conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. The resin was characterized by percent solids, phosphorus elemental analysis and acid capacity.

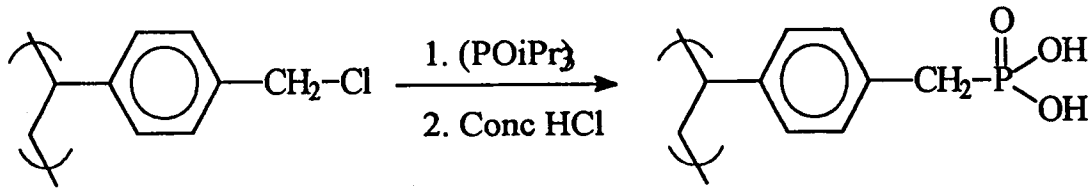


Figure 3.1. Synthesis of monophosphonic acid resin (MPA)

Synthesis of 2% DVB gel monocarboxylic acid resin (MCA)

The copolymer beads were swelled in acetonitrile, a 28 wt% aqueous solution of KCN added and the reaction heated at reflux temperature for 72 h. Excess solution was siphoned off and the beads were washed with water. The cyano groups were hydrolyzed to the carboxylic acid by refluxing with excess conc. HCl for 24 h (Figure 3.2). The resin was washed with water and conditioned with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. It was characterized by FTIR (Figure 3.3), percent solids, phosphorus elemental analysis and acid capacity.

Synthesis of 2% DVB gel bifunctional phosphonic/carboxylic acid resin (BPCA)

The copolymer was swelled in acetonitrile, a 18 wt% aqueous solution of KCN added, and the mixture heated at reflux temperature for 24 h. The resin was washed with water, ethanol and acetone. After vacuum drying the resin at 80°C overnight, excess triisopropylphosphite was added and the mixture refluxed for 17 h. The resin was washed with water after siphoning off the excess solution. Hydrolysis was effected by refluxing the resin with an excess of conc HCl for 24 h (Figure 3.4). The resin was washed with water and conditioned by elution with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. It was characterized by FTIR (Figure 3.5), percent solids, phosphorus elemental analysis and acid capacity.

Synthesis of 2% DVB gel phosphonoacetic acid resin (PAA)

Triethylphosphonoacetate was added dropwise to a dispersion of NaH in xylene under an atmosphere of nitrogen. After the bubbling subsided (indicating complete deprotonation), VBC copolymer beads were added to the reaction mixture and heated at

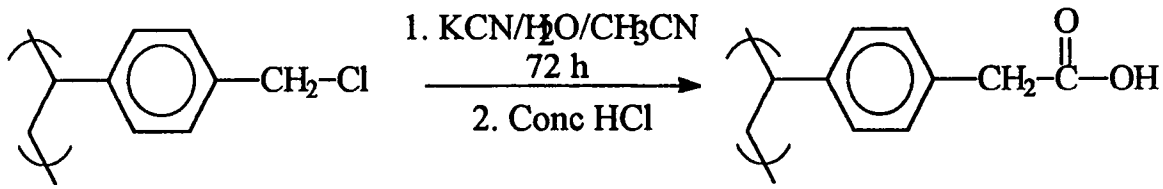


Figure 3.2. Synthesis of monocarboxylic acid resin (MCA)

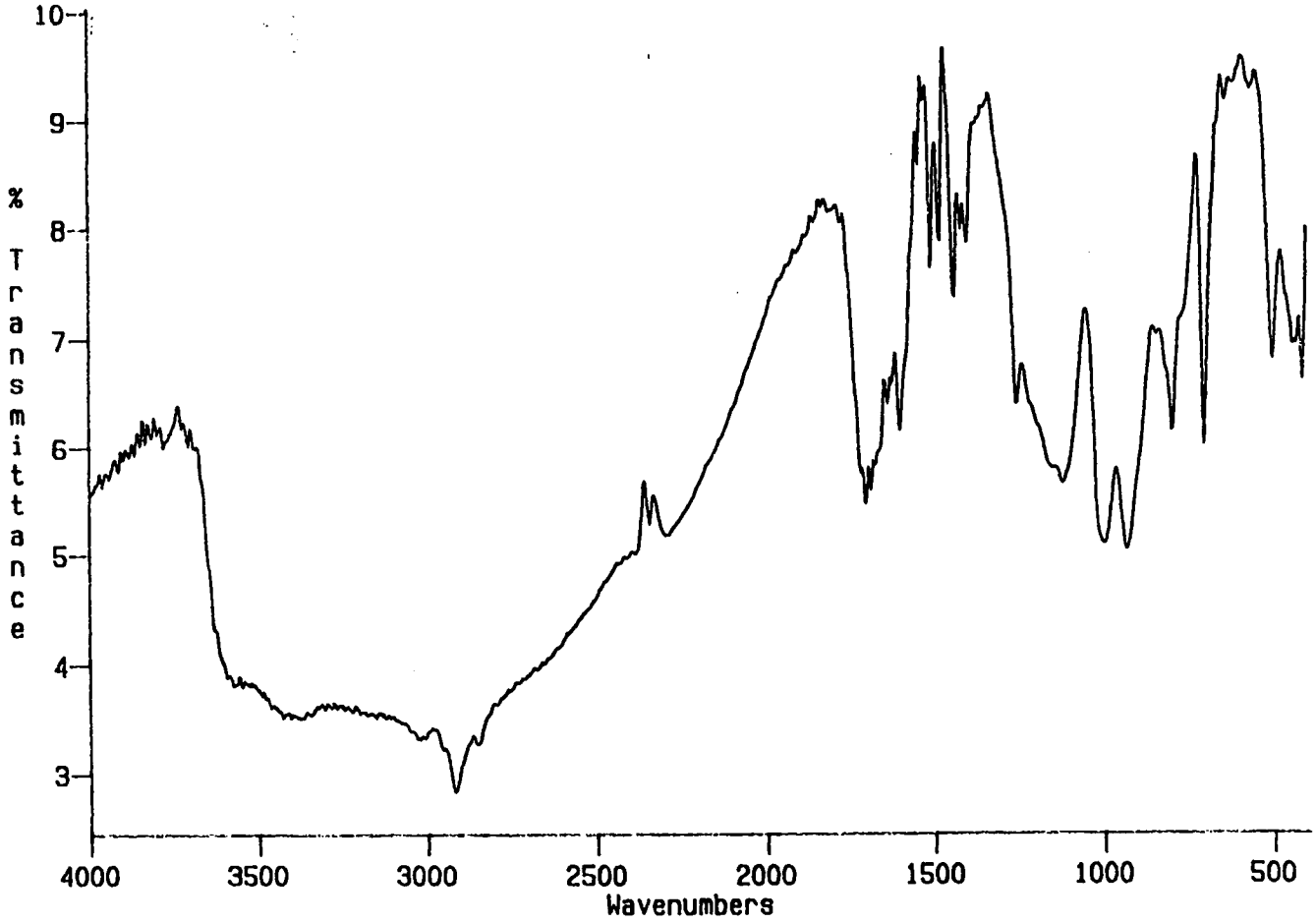


Figure 3.3. FTIR spectrum of MCA resin

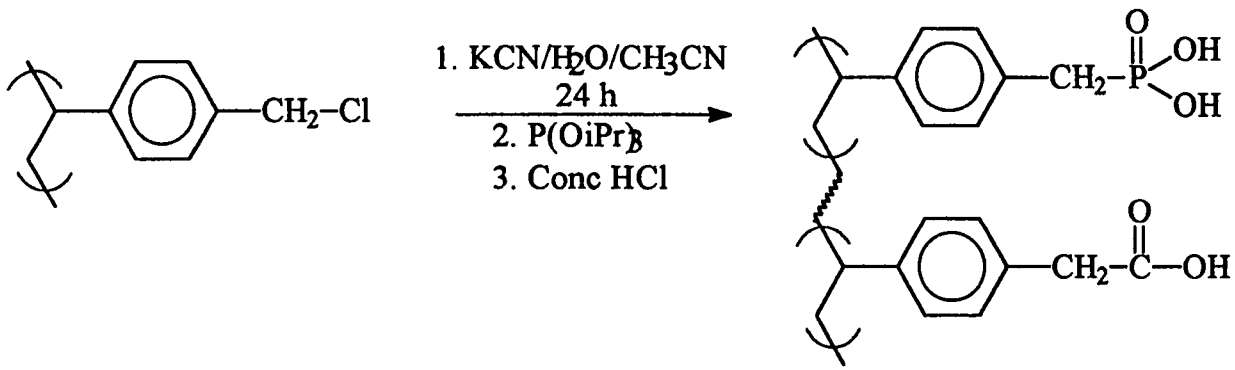


Figure 3.4. Synthesis of bifunctional phosphonic/carboxylic acid resin (BPCA)

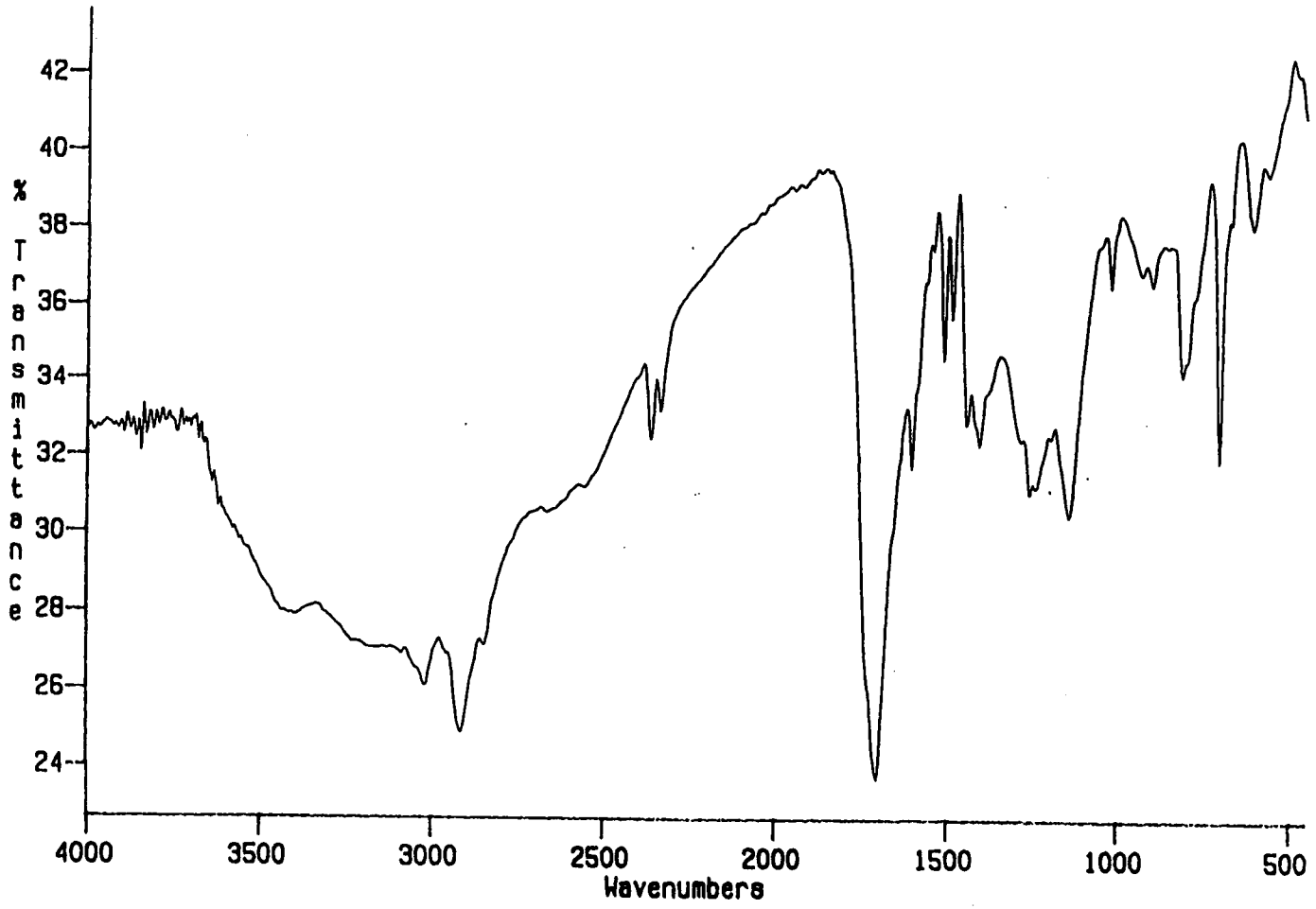


Figure 3.5. FTIR spectrum of BPCA resin

reflux temperature for 24 h. The resin was washed with ethanol and the polymer matrix was solvent exchanged with $CHCl_3$. Bromotrimethylsilane was then added to the beads pre-swollen in $CHCl_3$ and the mixture was refluxed for 24 h. Excess solution was siphoned off, the resin washed throughly with acetone and hydrolyzed with a 3 N NaOH solution at reflux temperature for 24 h. The resin was washed with water and conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. The resin was characterized by percent solids, phosphorus elemental analysis and acid capacity.

Metal ion studies

The metal ion studies were performed by weighing an amount of resin that would yield one milliequivalent of phosphorus in the case of the phosphorus acid resins and one milliequivalent of acid sites in the case of MCA and DCA resins. For the mixed-bed resin, amounts of MPA and MCA resins were weighed in a mole ratio identical with that found in BPCA resin. The metal ion solutions consisted of 10^{-4} N $Fe(NO_3)_3$, $Cd(NO_3)_2$, $Ni(NO_3)_2$ and $Zn(NO_3)_2$, each in 0.010, 0.10 and 1.0 N HNO_3 solutions. Each resin was contacted with 10 mL of the contact solution for 24 h. The amount of metal ions complexed was determined by an atomic absorption spectrometer at wavelengths of 248.3 nm, 228.8 nm, 232.0 nm and 213.9 nm for detecting Fe(III), Cd(II), Ni(II) and Zn(II), respectively. The results are reported both as percent metal complexed and as the distribution coefficient. The distribution coefficient, D, is defined as:

$$\frac{\text{mequiv } M^{n+} \text{ on the resin / } g_{dry} \text{ resin}}{\text{mequiv } M^{n+} \text{ in solution / mL solution}}$$

Results and Discussion

A series of ion-selective polymers were synthesized and their metal ion affinities determined to understand the different mechanisms of complexation. The bifunctional ligands that were immobilized were designed so as to allow for the possibility of cooperation between the two binding sites in either an intra-ligand [diphosphonic acid (DPA), dicarboxylic acid (DCA) and phosphonoacetic acid (PAA)] or inter-ligand [bifunctional phosphonic/carboxylic acid (BPCA), monophosphonic acid (MPA) and monocarboxylic acid (MCA)] manner when the metal ions were complexed. All functionalization reactions were performed on poly(VBC) beads crosslinked with 2% DVB. The particle size of the beads were in the range of 0.075-0.15 mm. The lightly crosslinked polymer support provides a highly flexible polymer matrix which in turn allows for the ligands to cooperate by an inter-ligand mechanism in metal ion complexation. The small particle size of the beads helps in increasing the extent of functionalization due to increased surface area of the polymer.

Synthesis of the MPA resin (SN-02-118) was accomplished by an Arbuzov reaction followed by hydrolysis with conc HCl. The resin was washed with water and conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. The resin properties are summarized in Table 3.1. A percent functionalization of >96% was achieved. An acid capacity of twice the phosphorus capacity indicates complete hydrolysis of the ester sites.

Synthesis of the MCA resin (SN-02-104) was done by swelling the poly(VBC) beads in acetonitrile, an aqueous solution of KCN added, and the mixture refluxed for

Table 3.1

Characterization of 2% DVB gel resins

Resin code	Resin name	% Solids	Phosphorus capacity (mequiv/g)	Acid capacity (mequiv/g)	% Functional-ized
SN-02-104	MCA	58.3	N/A	5.42	91.2
SN-02-118	MPA	47.1	4.68	9.73	96.1
SN-03-090	BPCA	59.6	2.57	7.35	-
SN-03-175	PAA	48.0	1.31	3.20	33.9
LH-05-110	PAA†	56.2	2.32	5.92	61.7
LH-04-205	DPA†	57.3	4.44	7.52	67.3
LH-04-242	DCA†	46.8	N/A	5.89	67.2

† resins supplied by Dr. Latiff Hussain

72 h. The excess solution was siphoned off and the beads were throughly washed with water prior to hydrolysis with conc HCl. The resin was washed with water after hydrolysis and conditioned with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. The resin had an acid capacity of 5.42 mequiv/g indicating about 91% functionalization (Table 3.1). The lack of the cyano stretching peak at 2250 cm^{-1} coupled with the formation of C=O (1705 cm^{-1}) and -OH (3400 cm^{-1}) peaks in the FTIR spectrum (Figure 3.3) suggests complete hydrolysis.

The BPCA resin (SN-03-090) was synthesized according to the scheme in Figure 3.4. Partial cyanation of poly(VBC) beads, followed by an Arbuzov reaction on the unsubstituted chloro groups and hydrolysis yielded the bifunctional resin. Partial cyanation was accomplished by controlling the reaction time. VBC copolymer beads were refluxed with KCN/water/acetonitrile mixture for 24 h. Chlorine capacity of 3.69 mequiv/g indicated that the resin (SN-02-096) was 43% cyanated. Following Arbuzov reaction and hydrolysis, the resin (SN-02-102), was washed with water and conditioned with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. The FTIR spectrum of the resin (Figure 3.5) showed a broad -OH stretching peak at 3400-3600 cm^{-1}, a C=O stretching peak at 1720 cm^{-1} and a P=O stretching peak at 1259 cm^{-1}, indicating the formation of the bifunctional resin. It had a phosphorus capacity of 3.20 mequiv/g and an acid capacity of 8.54 mequiv/g. A mass balance of 0.98 g/g obtained for this resin was very close to the expected value of 0.96 g/g indicating the absence of other side reactions. Another cyanation reaction similar to the one earlier was attempted where the time of reflux with KCN solution was increased to 28 h. The BPCA resin (SN-03-174) obtained

after the Arbuzov /hydrolysis reaction had no phosphorus capacity and had an acid capacity of 5.13 mequiv/g. Cyanation is thus, a time sensitive reaction. The resin that was used in all metal ion studies, SN-03-090, was synthesized under the same conditions as SN-02-102. After 24 h cyanation, the resin had a chlorine capacity of 3.26 mequiv/g and a nitrogen capacity of 3.79 mequiv/g calculating to about 53% cyanation. After phosphorylation-hydrolysis, the phosphorus and acid capacities of the resin were 2.57 and 7.35 mequiv/g, respectively (Table 3.1). A mass balance of 0.87 g/g (expected 0.96 g/g) indicates that all the chloro groups were not quantitatively replaced during the Arbuzov reaction.

Resins which allow for the study of intra-ligand cooperation (DPA, DCA and PAA) were provided by Dr. Latiff Hussain. The characterization data has been published[106] and is provided in Table 3.1 for comparative purposes. The structures of these resins are shown in Figures 3.6-3.8. More of the PAA resin was synthesized for the present study. VBC copolymer beads were reacted with the sodium salt of diethylphosphonoacetate at reflux temperature for 24h. The beads were recovered and reacted with bromotrimethylsilane followed by 2 N NaOH to obtain the PAA resin (SN-03-175). The phosphorus capacity of 1.31 mequiv/g for the resin was low compared to that of 2.32 mequiv/g obtained by Dr. Latiff Hussain (Table 3.1). However, as will be seen later, the low functionalization in the former had no bearing on its ability to complex metal ions.

All complexation studies were done by contacting an amount of resin that gives one mequiv ligand sites with a 10^{-4} N metal nitrate solution at various pH for 24 h. Both

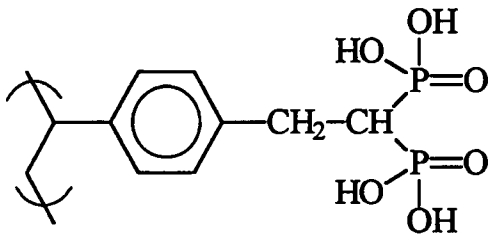


Figure 3.6. Diphosphonic acid resin (DPA)

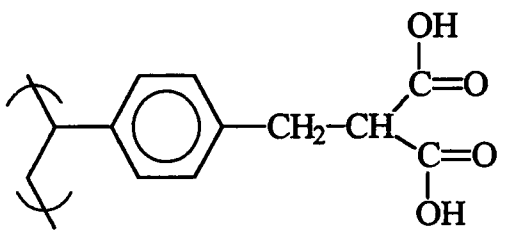


Figure 3.7. Dicarboxylic acid resin (DCA)

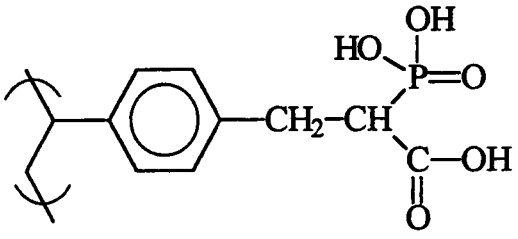


Figure 3.8. Phosphonoacetic acid resin (PAA)

the percent metal complexed and the distribution coefficient (D) were determined. Complexation of the metal ions from 0.01 N HNO_3 solutions are reported in Table 3.2. The percent complexation of Fe(III), Cd(II) and Zn(II) by MPA, DPA and PAA are >99%. The phosphonic acid ligand has an intermediate acid strength[106] and can ion-exchange with all the metal ions at this pH, resulting in a lack of selectivity. Complexation by the BPCA resin was slightly lower than the resins noted above for these metal ions. In order to isolate the effect of having the phosphonic and carboxylic acid ligands on the same polymer support in the BPCA resin, sorption studies were also carried out with a mixed bed of MPA and MCA in a mole ratio identical to that found with BPCA. Except for the complexation of Zn(II), the results from the mixed bed were similar to the MPA resin suggesting that the presence of the carboxylic acid ligand in BPCA is somehow impeding its ability to complex metal ions. The affinity towards Ni(II) by all the phosphorus based ligands studied offered the interesting trend DPA>MPA≈mixed bed>PAA>BPCA. The results suggest that ion-exchange by the acid sites in DPA followed by intra-ligand cooperation of the phosphoryl oxygens was responsible for the quantitative complexation of Ni(II) by the DPA resin while the lack of intra-ligand cooperation in the MPA resin was responsible for its lower complexation. It was initially thought that there was no intra-ligand cooperation between the P=O and C=O ligands in PAA following ion-exchange since it complexed only 94.9 % Ni(II) (D = 430). However, the BPCA resin had a yet lower affinity of 84.1% Ni(II) (D = 131). This result was interesting because the mixed bed performed comparably to the MPA resin. The results thus suggest that the presence of a carboxylic acid ligand in the BPCA resin hinders

Table 3.2

Metal ion complexation by the 2% DVB gel resins from 0.01 N HNO_3

Resin code	Resin name	Fe(III)	Cd(II)	Ni(II)	Zn(II)
SN-02-118	MPA[a]	100[†] (∞)[‡]	99.6 ($1.35x10^4$)	95.4 (831)	100 (∞)
SN-02-104	MCA[b]	10.8 (6.05)	10.2 (5.66)	0 (0)	26.4 (19.4)
SN-03-090	BPCA[c]	99.1 ($2.68x10^3$)	98.9 ($2.28x10^3$)	84.1 (131)	95.5 (529)
LH-04-205	DPA[d]	100 (∞)	100 (∞)	100 (∞)	100 (∞)
LH-04-242	DCA[e]	100 (∞)	32.6 (15.5)	18.3 (7.20)	29.2 (13.3)
LH-05-110	PAA[f]	96.2 (582)	99.9 ($1.66x10^4$)	94.9 (430)	99.6 ($5.91x10^3$)
SN-03-175	PAA[g]	97.5 (498)	-	-	100 (∞)
SN-02-118 + SN-03-104	Mixed[h] bed	100 (∞)	100 (∞)	97.2 (774)	84.2 (122)

† Percent metal complexed
‡ Distribution coefficient
a 2% DVB gel monophosphonic acid resin
b 2% DVB gel monocarboxylic acid resin
c 2% DVB gel bifunctional phosphonic/carboxylic acid resin
d 2% DVB gel diphosphonic acid resin
e 2% DVB gel dicarboxylic acid resin
f 2% DVB gel phosphonoacetic acid resin
g 2% DVB gels monophosphonic + monocarboxylic acid resin

its ability to complex metal ions. It was hypothesized that an inter-ligand hydrogen bond between the proton of the carboxylic acid with the phosphoryl oxygen is responsible for the decreased ability of the phosphoryl groups to coordinate metal ions. The higher amounts of Ni(II) complexed by the PAA resin (94.9%) compared to the BPCA resin (84.1%) suggests that the P=O and C=O ligands in PAA can in fact cooperate by an intra-ligand mechanism. However, intra-ligand hydrogen bonding between the proton of carboxylic acid with the phosphoryl oxygen in the PAA resin (Figure 3.9) probably decreased its ability to coordinate as effectively as just the phosphoryl oxygens in DPA. In the MCA resin, the poor affinities to all the metal ions studied was attributed to the competition of the protons for the coordinating sites. Since the carboxylic acid is weakly acidic, the protons are not ionized at the pH studied and the coordination of the metal ions to the carbonyl oxygen is the only possibility. Complexation by the DCA resin followed the order Fe(III)>>Cd(II)≈Zn(II)>Ni(II). Intra-ligand cooperation of the carbonyl oxygens was able to overcome the proton competition in the case of DCA.

Metal ion complexation studies in 0.10 N HNO_3 solutions are reported in Table 3.3. All the phosphorus based resins displayed a high affinity for Fe(III). This is beleived to be caused by an increase in entropy that occurs with the loss of water from the ion upon coordination by the phosphoryl oxygen.[107] The complexation of the other metal ions was greatly reduced in the MPA resin due to competition by the proton for the phosphoryl oxygen. Metal ion affinities for the DPA resin was in the order of Fe(III)>Cd(II)>Zn(II)>Ni(II). The amounts complexed by DPA are significantly higher than the MPA resin due to intra-ligand cooperation of the phosphoryl oxygens. While,

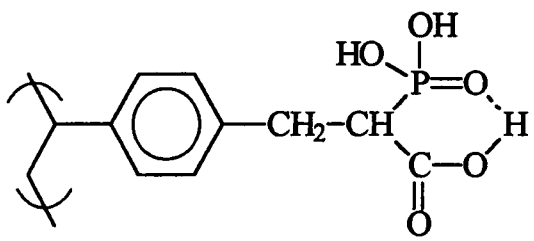


Figure 3.9. Proposed mechanism to explain the inability of PAA to coordinate effectively

Table 3.3

Metal ion complexation by the 2% DVB gel resins from 0.10 N HNO_3

Resin code	Resin name	Fe(III)	Cd(II)	Ni(II)	Zn(II)
SN-02-118	MPA	99.6[a] ($1.25x10^4$)[b]	37.7 (29.7)	23.4 (14.9)	24.4 (16.8)
SN-02-104	MCA	5.95 (3.16)	5.35 (2.80)	5.00 (2.62)	12.8 (7.22)
SN-03-090	BPCA	98.8 ($1.94x10^3$)	28.8 (10.0)	13.2 (3.73)	16.0 (4.68)
LH-04-205	DPA	100‡ (∞)	98.4‡ ($1.50x10^3$)	62.7 (49.3)	78.0 (103)
LH-04-242	DCA	38.4‡ (11.3)	3.38‡ (1.03)	0 (0)	0 (0)
LH-05-110	PAA	96.0‡ (551)	41.4‡ (16.4)	17.7 (4.83)	34.8 (6.45)
SN-02-118 + SN-03-104	MPA + MCA	100 (∞)	40.9 (15.7)	20.8 (5.89)	32.4 (28.5)

a Percent metal complexed

b Distribution coefficient

‡ Results provided by Dr. Latiff Hussain

Fe(III) was complexed quantitatively, the complexation of other metal ions was less than from a 0.01 N HNO_3 solution due to protonation of the phosphoryl oxygens.

Since the predominant complexation mechanism at this pH is through coordination by the phosphoryl oxygens, the trends displayed by the DPA resin can be rationalized on the basis of hard-soft acid-base theory. Since phosphoryl oxygen is a soft base, it coordinates a soft acid like Cd(II) more effectively than Zn(II) and Ni(II) (border line acids). It must however be noted that even though Fe(III) is a hard acid, the high affinity is due to the entropy effect discussed earlier.

Complexation behavior for BPCA and PAA resins in 0.10 N HNO_3 solution were similar to the trends displayed in 0.01 N HNO_3 solution. While, intermolecular hydrogen bonding in BPCA resin was the reason offered for its decreased complexation compared to MPA resin, intramolecular hydrogen bonding was responsible for the significant decrease in the complexation by PAA resin compared to DPA resin. The mixed bed resin, again, performed similarly to the MPA resin reaffirming the detrimental effect the carboxylic acid ligand has on the ability of the phosphoryl oxygen in BPCA resin to complex metal ions effectively. Both MCA and DCA resins performed poorly under these increased acidic conditions, as expected.

Metal ion complexation from 1.0 N HNO_3 solutions are presented in Table 3.4. As expected, all the phosphorus based resins complexed Fe(III) in higher amounts than other metal ions. In comparing the D values for Fe(III) by the phosphorus acid resins, the affinity for this metal ion was in the order of DPA>mixed bed≈MPA>PAA>BPCA. This trend reemphasizes the importance of intra-ligand cooperation to enhance metal ion

Table 3.4
Metal ion complexation by the 2% DVB gel resins from 1.0 N HNO_3

Resin code	Resin name	Fe(III)	Cd(II)	Ni(II)	Zn(II)
SN-02-118	MPA	96.8[a] ($1.49x10^3$)[b]	8.30 (14.9)	0 (0)	7.41 (3.90)
SN-02-104	MCA	9.67 (5.32)	11.8 (6.45)	0 (0)	10.9 (6.08)
SN-03-090	BPCA	92.7 (311)	9.08 (2.43)	1.91 (0.47)	8.10 (2.18)
LH-04-205	DPA	100‡ (∞)	20.3‡ (4.93)	0 (0)	9.08 (2.92)
LH-04-242	DCA	0‡ (0)	3.46‡ (1.02)	0 (0)	3.47 (1.15)
LH-05-110	PAA	96.7‡ (688)	5.45‡ (1.27)	0 (0)	-
SN-03-175	PAA	97.5 (498)	13.3 (1.85)	-	6.93 (0.90)
SN-02-118 + SN-03-104	MPA + MCA	99.9 ($3.81x10^4$)	8.63 (2.14)	0 (0)	5.39 (1.31)

a Percent metal complexed
b Distribution coefficient
‡ Results provided by Dr. Latiff Hussain

affinities (in the case of DPA resin), reduced complexation due to decreased intra-ligand cooperation (in PAA resin) caused by intramolecular hydrogen bonding and decreased complexation (in BPCA) due to intermolecular hydrogen bonding (when compared to MPA resin and the mixed bed system). The carboxylic acid resins (DCA and MCA) were ineffective.

Equilibrium in an extraction process is represented by the equation below:

$$M^{+n} + nA^- + R\text{-}H \rightleftharpoons R_n\text{-}M + nH^+ + nA^-$$

M^{+n} = metal ion in aqueous solution

A^- = associated anion in aqueous solution

R-H = resin phase in the acid form

R_n-M = resin phase in the metal-exchanged form

The standard equilibrium constant is then given by the equation

$$K = ([R_n\text{-}M]\ [H^+]^n) / ([M^{+n}]\ [RH])$$

This equation can then be rewritten in terms of distribution coefficient as

$$D = [H^+]^{-n}\ K\ [RH]^n$$

The logarithmic of this equation

$$\log D = n\ pH + (n \log [RH] + \log K)$$

is very useful as it emphasizes the dependence of the extraction on solution pH. Measuring log D as a function of pH of the aqueous solution may be expected to yield a straight line with slope n, the number of protons exchanged for each metal ion transferred to the resin phase. For a pure ion-exchange resin, the slope is also the valence of the metal ion while, for a purely coordinative mechanism, a slope of zero is expected since no

protons are exchanged into the solution and the extraction is pH dependent.

Slope analysis of logD vs pH plot was done for the MPA, BPCA and PAA resins but calculations are only approximate since only three (and in some cases two) data points were used in the analysis. Slopes of 0.93, 1.48, 1.75 and 0.64 were obtained for Fe(III), Cd(II), Ni(II) and Zn(II), respectively for MPA. These slopes suggest that the coordinative component may be an important part of the complexation mechanism atleast for Fe(III) and Zn(II). The slopes for Fe(III), Cd(II), Ni(II) and Zn(II) for BPCA were 0.47, 1.49, 1.22 and 1.19, respectively. This trend was similar to the MPA resin. The PAA resin showed a very interesting trend: while Fe(III) had a slope of -0.07, slopes for the other ions were approximately 2 (Cd(II) = 2.06, Ni(II) = 1.95 and Zn(II) = 1.91). These slopes suggest that, except for Fe(III), all other ions are complexed exclusively by ion-exchange. This is again consistent with intramolecular hydrogen bonding by the carboxylic acid proton to the phosphoryl oxygen hindering its ability to coordinate metal ions (except Fe(III)). Only the entropy effect with Fe(III) is able to overcome this strong hydrogen bonding.

The hypothesis of intramolecular hydrogen bonding decreasing the ability of a resin to complex metal ions was tested by comparing PAA with a β-ketophosphonic acid resin in complexing ability for Cd(II) from 0.10 N HNO_3 solution. β-ketophosphonic acid resin (Figure 3.10) synthesized by Dr. Latiff Hussain, had a phosphorus capacity of 2.76 mequiv/g and an acid capacity of 6.83 mequiv/g.[106] The resin complexed 78.4% Cd(II) (D of 100.1) compared to 13.3% (D of 1.85) for the PAA resin. The absence of the carboxylic acid proton in the former thus allows for intra-ligand cooperation between the

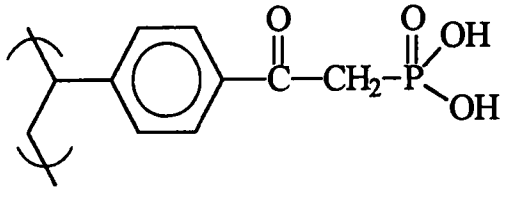


Figure 3.10. β-ketophosphonic acid resin

C=O and P=O groups in the β-ketophosphonate resin.

It was hoped that the effect of intermolecular hydrogen bonding could be studied by synthesizing a highly crosslinked BPCA polymer because the immobility of the polymer matrix would prevent hydrogen bonding by the carboxylic acid proton with the phosphoryl oxygen of the phosphonic acid ligand. Cyanation was first attempted on 40% DVB crosslinked MR beads (both 0.25-0.43 mm, 0.075-0.15 mm) with 29 wt% aqueous KCN at 72 h and 7 days reflux. There was no functionalization in any of them, indicating that reaction time and particle size had no effect on functionalization because the cyanide ion was too hydrophilic ionic to get into the hydrophobic polymer matrix. Cyanation with 29 wt% aqueous KCN in acetonitrile was also attempted with 30%, 25% and 20 % crosslinked polymers with no success. To allow for increased accessibility of the cyanide into the polymer matrix, cyanation was attempted with a phase transfer catalyst. The beads were swelled in ethylene dichloride (EDC) and an aqueous solution of NaCN was added to the beads along with ADOGEN 464 (a phase transfer catalyst). Results, again, were negative. Cyanation of VBC copolymer beads crosslinked with 20% and 25% DVB was also attempted with DMF as the solvent at 80°C for 96 h. After hydrolysis with conc HCl, the resins had an acid capacity of 1.43 mequiv/g (theoretical, 3.97 mequiv/g) and 1.26 mequiv/g (theoretical, 3.59 mequiv/g). Low percent functionalization even after a four day reaction, suggested that all the replaceable chloro groups have reacted. Attempts to initially phosphorylate the VBC copolymer partially by controlling both the mole ratio and time of reaction were also not successful. Steric factors and reagent hydrophilicity contributed to the inability to synthesize a highly crosslinked BPCA resin.

Conclusions

Coordination through the carbonyl oxygen was the only mode of complexation possible for the carboxylic acid resins (MCA and DCA) at the pH studied. Protonation of the carbonyl oxygen was responsible for the poor affinities of these resins although DCA was able to complex the metal ions more effectively at pH 2 due to the possibility of intra-ligand cooperation of the carbonyl groups.

The inherent affinity for Fe(III) was responsible for the high percent complexation by the phosphorus acid resins. Intra-ligand cooperation of the phosphoryl groups in DPA resin was attributed to the high affinity for all the metal ions studied at pH 1 and 2. Protonation however, decreases the amounts complexed by the former resin.

Metal ion complexation by BPCA was lower than MPA and the mixed bed resin. The results seem to indicate hindrance to coordination by intermolecular hydrogen bonding between the carboxylic acid proton to the phosphoryl oxygen. Intermolecular hydrogen bonding was, however, not strong enough to disrupt the coordinating ability of the phosphoryl oxygen as indicated by slope analysis of the log D vs pH plot.

Results of complexation from 0.10 N HNO_3 solution seemed to indicate initially that the phosphoryl and carbonyl oxygens cannot cooperate by an intra-ligand mechanism to complex metal ions. However, a complexation of 78.4% Cd(II) by the β-ketophosphonic acid resin indicated that they can indeed cooperate effectively by intra-ligand cooperation. The results suggest that decreased complexation does not necessarily imply lack of cooperation but could also be due to the intramolecular hydrogen bonding between the carboxylic acid proton and the phosphoryl oxygen. The slope analysis of the

log D vs pH plot was also consistent with this conclusion. Highly crosslinked BPCA resin could not be functionalized due to reagent hydrophilicity and steric hindrance to reaction.

CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF CALIX[4]ARENE AND PHOSPHORYLATED CALIX[4]ARENE POLYMERS FOR SELECTIVE METAL ION SEPARATIONS

Introduction

Selective extracting agents based on calixarenes have been studied extensively and discussed in detail in Chapter 1. The modifications via the upper or lower rim with appropriate ligating groups offer a plethora of possibilities to complex a wide range of metal ions. The importance of selective polymer supported reagents for efficient removal of toxic metal ions has been the subject of several review articles.[4-6] The high selectivity of the functionalized calixarenes can be taken advantage of in the selective complexation of metal ions by immobilizing them onto crosslinked polymer supports.

Published reports on the synthesis of polymeric calix[4]arenes, as has been discussed earlier, are very limited and synthesis of ion selective resins based on supporting calixarene onto crosslinked polymer beads has not been accomplished thus far. The goal of the present research is to support calix[4]arene and phosphorylated calix[4]arene onto crosslinked polymer beads and study their ability to selectively complex metal ions.

Experimental

Synthesis VBC-DVB copolymers

The copolymers were synthesized by suspension polymerization. The resins used for the complexation studies were synthesized from a 5% DVB crosslinked macroporous

(MR) polymer support with a particle size of 0.15-0.25 mm. Gel beads crosslinked with 2% DVB (particle sizes of 0.075-0.15 mm and 0.15-0.25 mm) and 1% DVB xerogel beads (particle size of 0.25-0.43 mm) were used in control reactions to establish the ideal support for immmobilization of calix[4]arene.

Synthesis of poly(4-chlorophenylbenzoate)

A solution of 4-chlorophenol in pyridine was added to the acid chloride resin and the mixture refluxed for 24 h (Figure 4.1). The resin was washed, dried and characterized by chlorine elemental analysis.

Synthesis of tetra(t-butyl)calix[4]arene (TBC)

Reaction of p(t-butyl)phenol with formalin in an alkaline medium (Figure 4.2) resulted in a crude product that was recrystallized from toluene. It had a melting point of 336-340°C (reported mp 342-344°C).[109] The product was analyzed by FTIR (phenolic -OH stretching peak at 3200 cm^{-1}, Figure 4.3).

Synthesis of tetrahydroxycalix[4]arene (THC)

THC was dealkylated by a reverse Friedel-Crafts reaction (Figure 4.4) with phenol and toluene in the presence of aluminum chloride. It was recrystallized from a chloroform-methanol mixture and had a melting point of 309-310°C (reported mp 313-315°C).[109] The compound was also characterized by mass spectrometry. In the spectrum (Figure 4.5), m/z peaks at 424, 447 and 464, correspond to the parent compound, its sodium and potassium adducts, respectively. These results were consistent with its expected molecular weight of 424 g / mol.

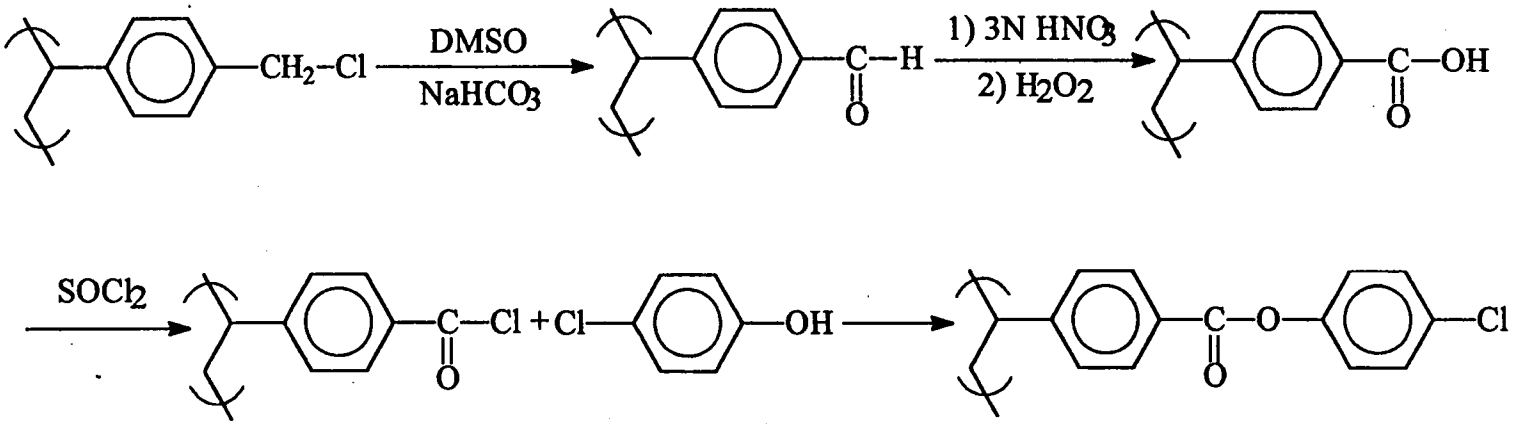


Figure 4.1. Immobilization of 4-chlorophenol onto a polymer support as an ester

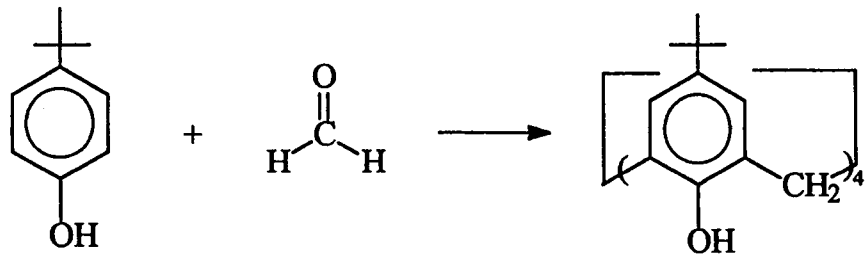


Figure 4.2. Synthesis of tetra(t-butyl)calix[4]arene

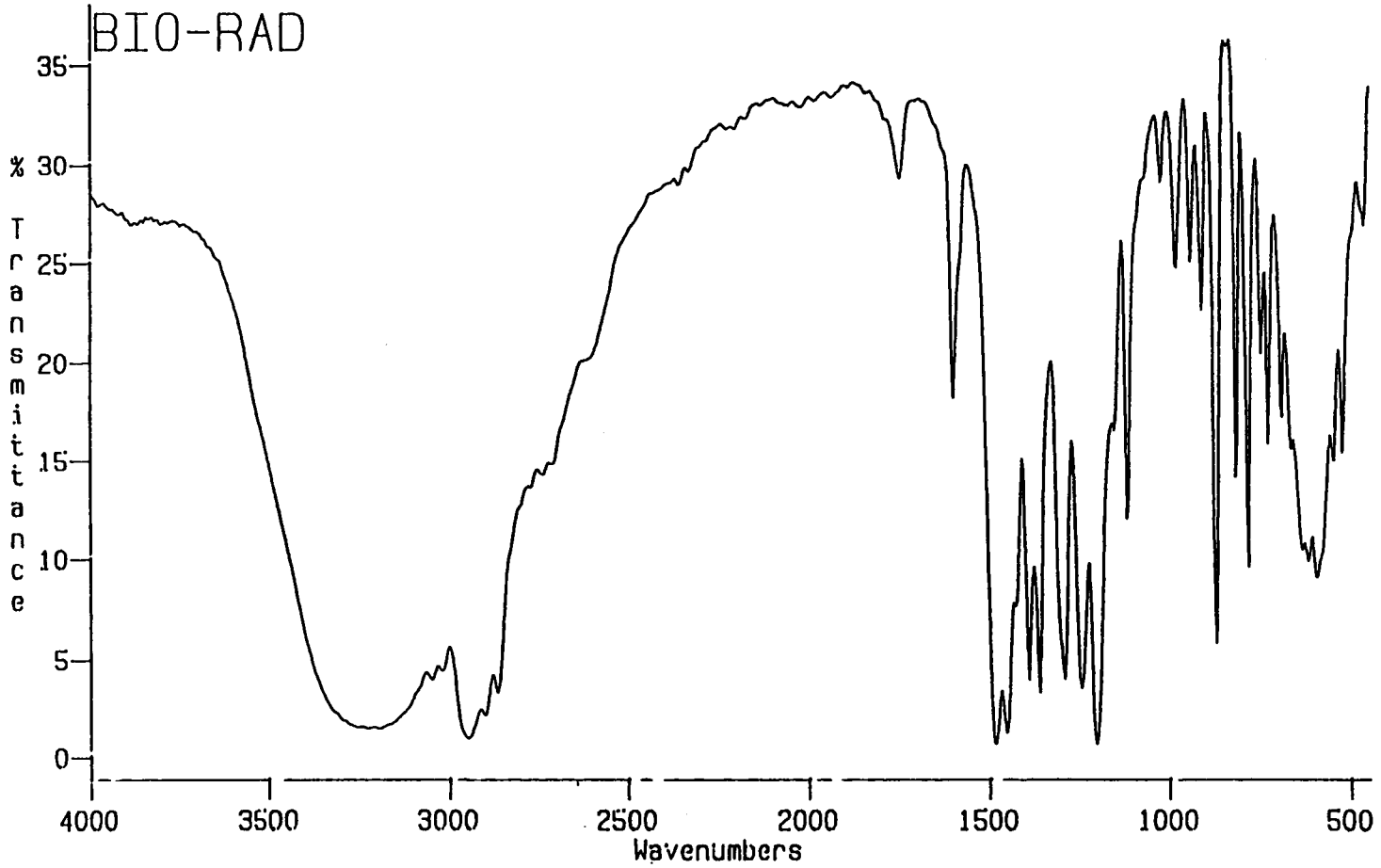


Figure 4.3. FTIR spectrum of tetra(t-butylcalix[4]arene

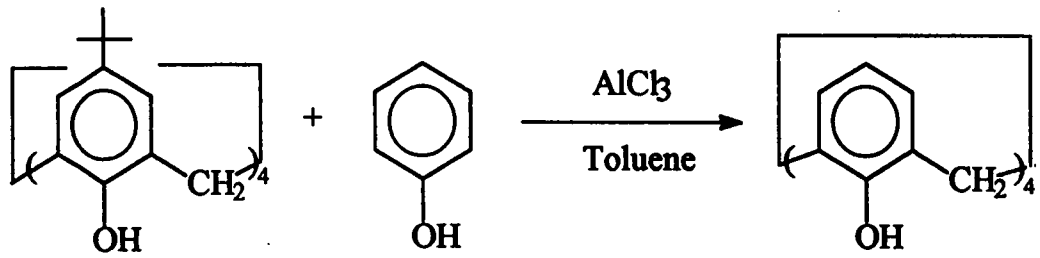


Figure 4.4. Synthesis of tetrahydroxycalix[4]arene

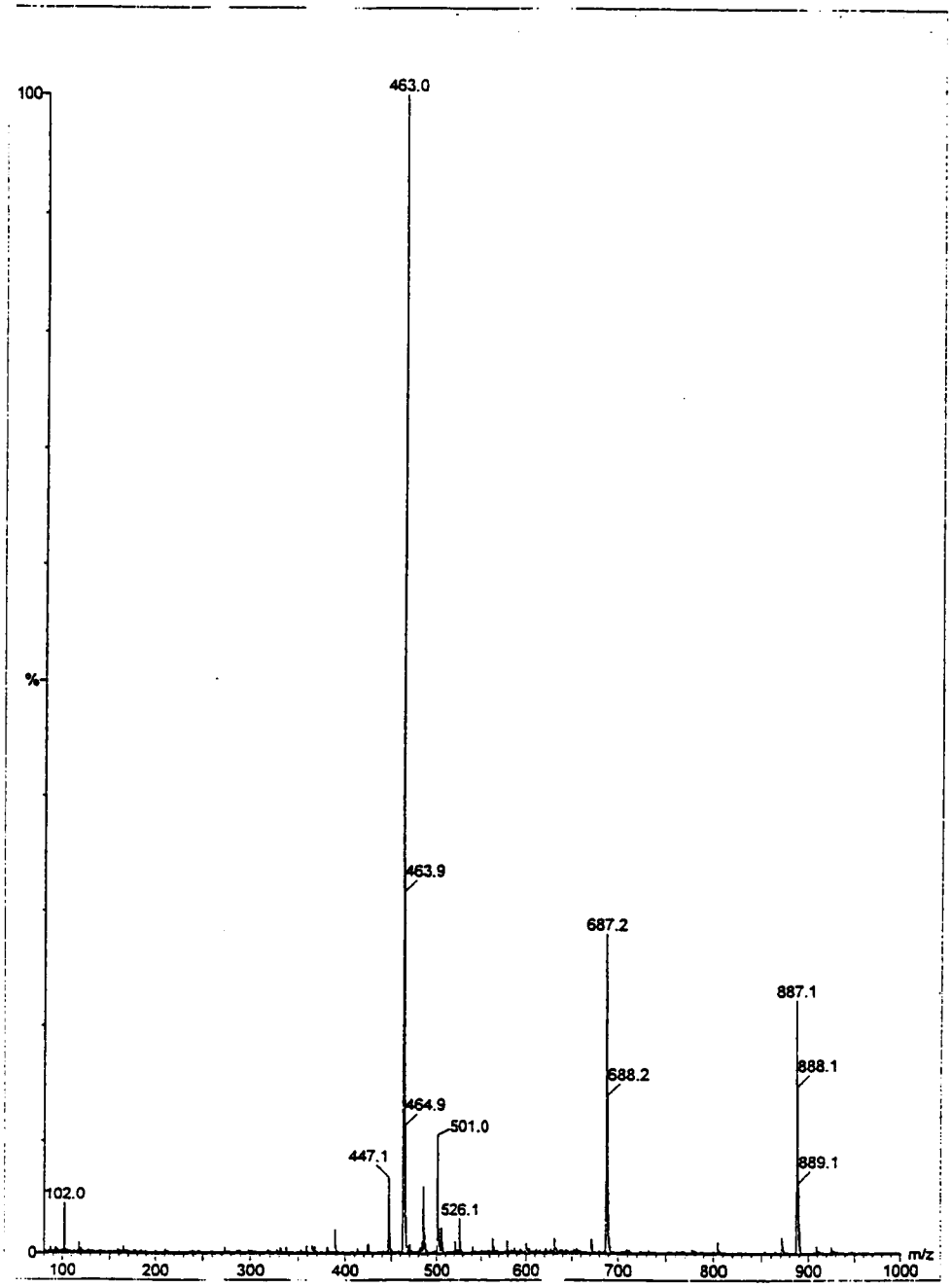


Figure 4.5. Mass spectrum of tetrahydroxycalix[4]arene

Synthesis of hydroxycalixarene ester resin (HCER)

A procedure similar to the immobilization of 4-chlorophenol was followed (Figure 4.1). The amounts of THC (2.5 or 5.0 moles) and the type of support (2% DVB gel, 5% DVB MR or 1% DVB xerogel beads) were varied to optimize the reaction conditions for maximized functionalization.

Synthesis of polymer-supported phenol

A solution of phenol in dioxane was deprotonated with NaH and refluxed with VBC copolymer beads (Figure 4.6) . The type of support (2% DVB gel or 5% DVB MR) and the time of reaction (17 or 72 h) were varied.

Synthesis of tribenzoyloxycalix[4]arene (BzC)

THC was reacted with benzoyl chloride at room temperature with pyridine as the solvent (Figure 4.7). The product was recrystallized from a chloroform-methanol mixture and had a melting point of 274-276 °C (reported mp 276-277 °C).[109] The FTIR spectrum (Figure 4.8) had the C=O and -OH stretching peaks at 1728 cm^{-1} and 3529 cm^{-1}, respectively.

Synthesis of bis(diethoxyphosphoryloxy)dihydroxycalix[4]arene (BPC)

BPC was synthesized according to the scheme in Figure 4.9 by reacting THC with diethylchlorophosphate (DECP). It was recrystallized from isopropanol and had a melting point of 220-222°C (reported mp 215-220°C).[110] The compound was further characterized by FTIR (P=O stretching at 1273 cm^{-1} and -OH stretching at 3534 cm^{-1}, Figure 4.10) and phosphorus elemental analysis.

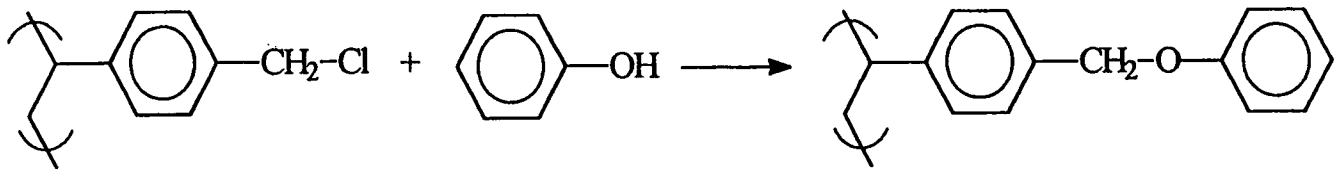


Figure 4.6. Synthesis of polymer-supported phenol

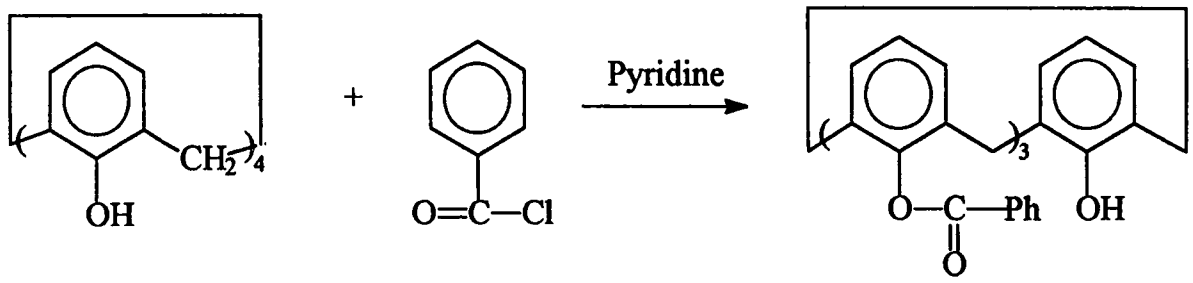


Figure 4.7. Synthesis of tribenzoyloxycalix[4]arene

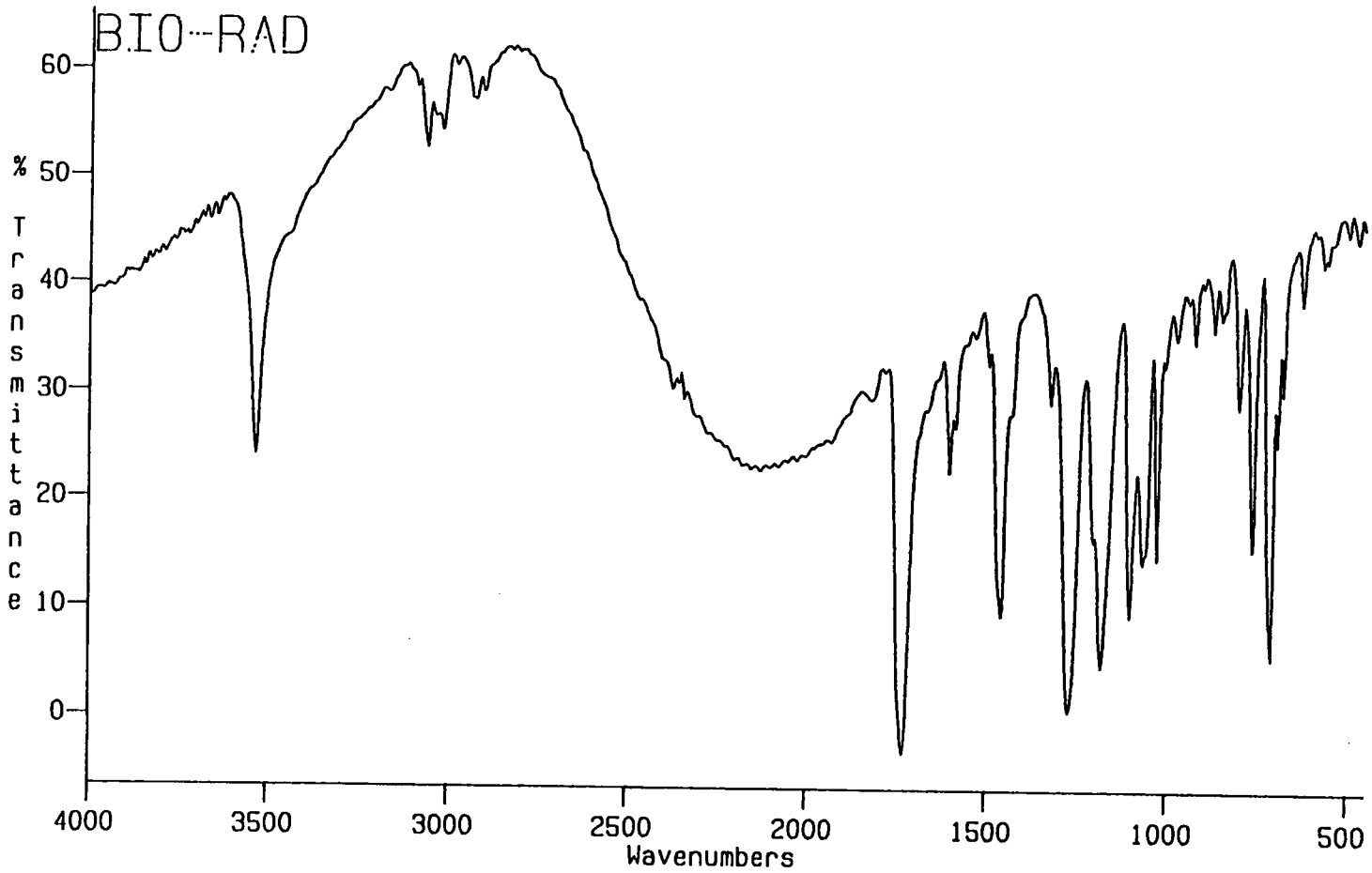


Figure 4.8. FTIR spectrum of tribenzoyloxycalix[4]arene

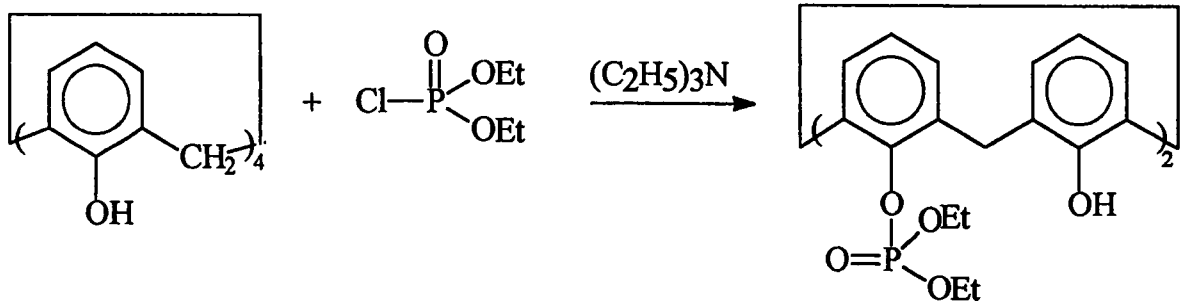


Figure 4.9. Synthesis of bis(diethoxyphosphoryloxy)calix[4]arene

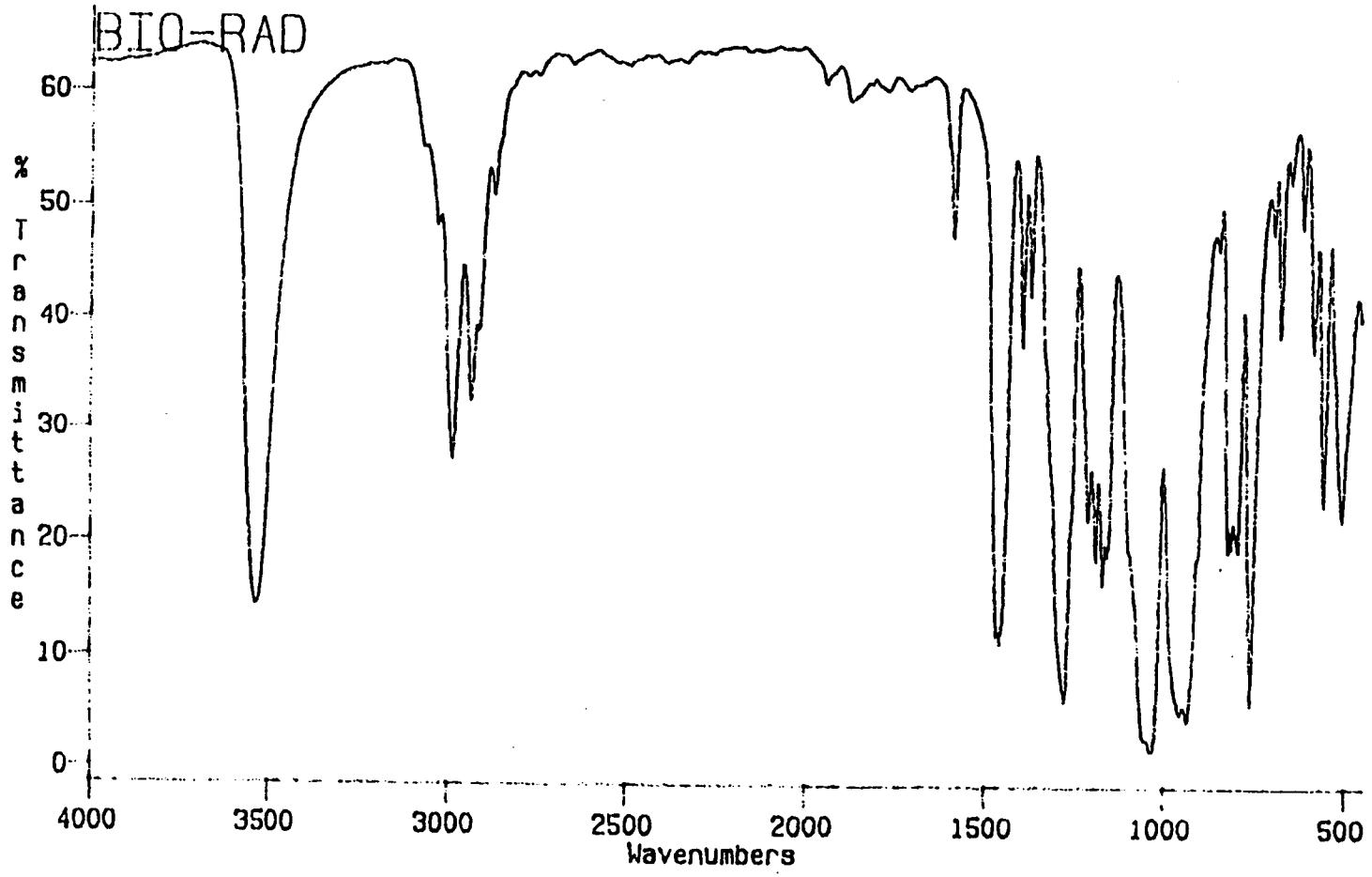


Figure 4.10. FTIR spectrum of bis(diethoxyphosporyloxy)calix[4]arene

Synthesis of polymer-supported tribenzoyloxycalix[4]arene resin (BzCR)

A solution of BzC in DMF was deprotonated with NaH and refluxed with VBC copolymer beads for 72 h (Figure 4.11). The resin was washed, vacuum dried overnight at 70°C, and characterized by FTIR (Figure 4.12) and chlorine elemental analysis.

Synthesis of hydroxycalix[4]arene resin (HCR)

Complete hydrolysis of the benzoyl groups was effected by refluxing the resin with an ethanolic solution of NaOH in THF (Figure 4.13). The resin was washed, conditioned by eluting 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water, and characterized by phenolic acid capacity and FTIR (for the disappearance of C=O stretching peak and formation of -OH stretching peak, Figure 4.14).

Synthesis of bis(diethoxyphosphoryloxy)calix[4]arene resin (BPCER)

A solution of BPC in DMF was deprotonated with NaH and refluxed with VBC copolymer beads for 72 h (Figure 4.15). The resin was washed with DMF, water, dioxane, THF and acetone, vacuum dried overnight at 70°C and characterized by FTIR (Figure 4.16) and phosphorus elemental analysis.

Attempted synthesis of bis(dihydroxyphosphoryloxy)calix[4]arene resin (BPCAR)

BPCER was swelled in chloroform and reacted with bromotrimethylsilane (BTMS) for 24 h (Figure 4.17). The resin was washed, conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water, characterized by phosphorus elemental analysis, acid capacity and FTIR (Figure 4.18).

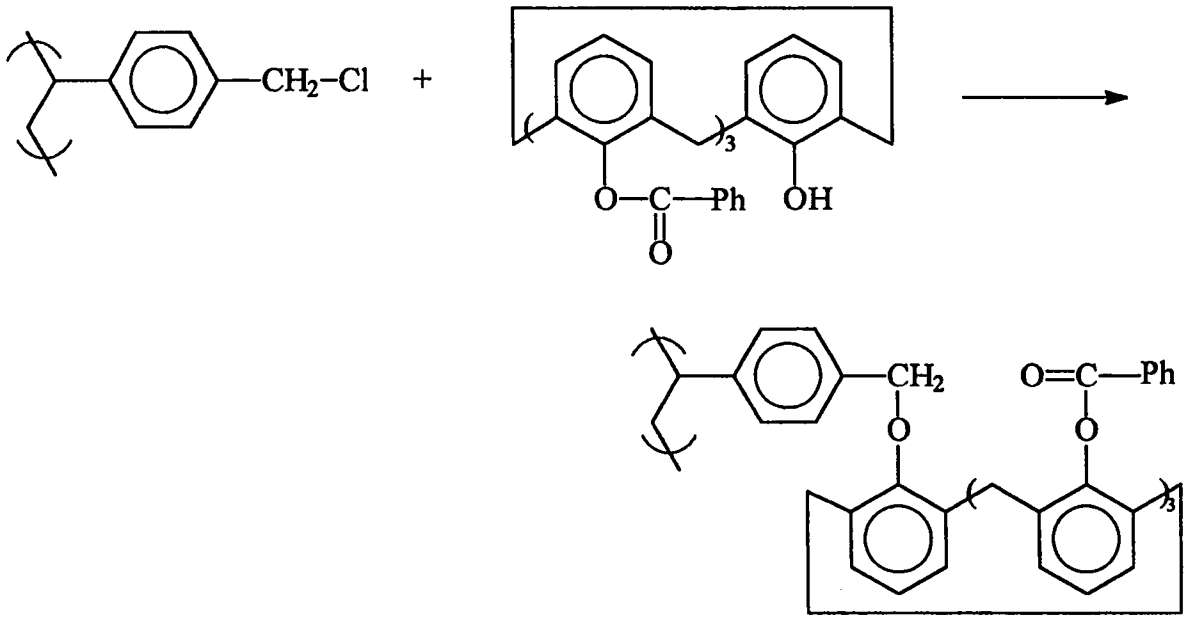


Figure 4.11. Synthesis of polymer-supported tribenzoyloxycalix[4]arene

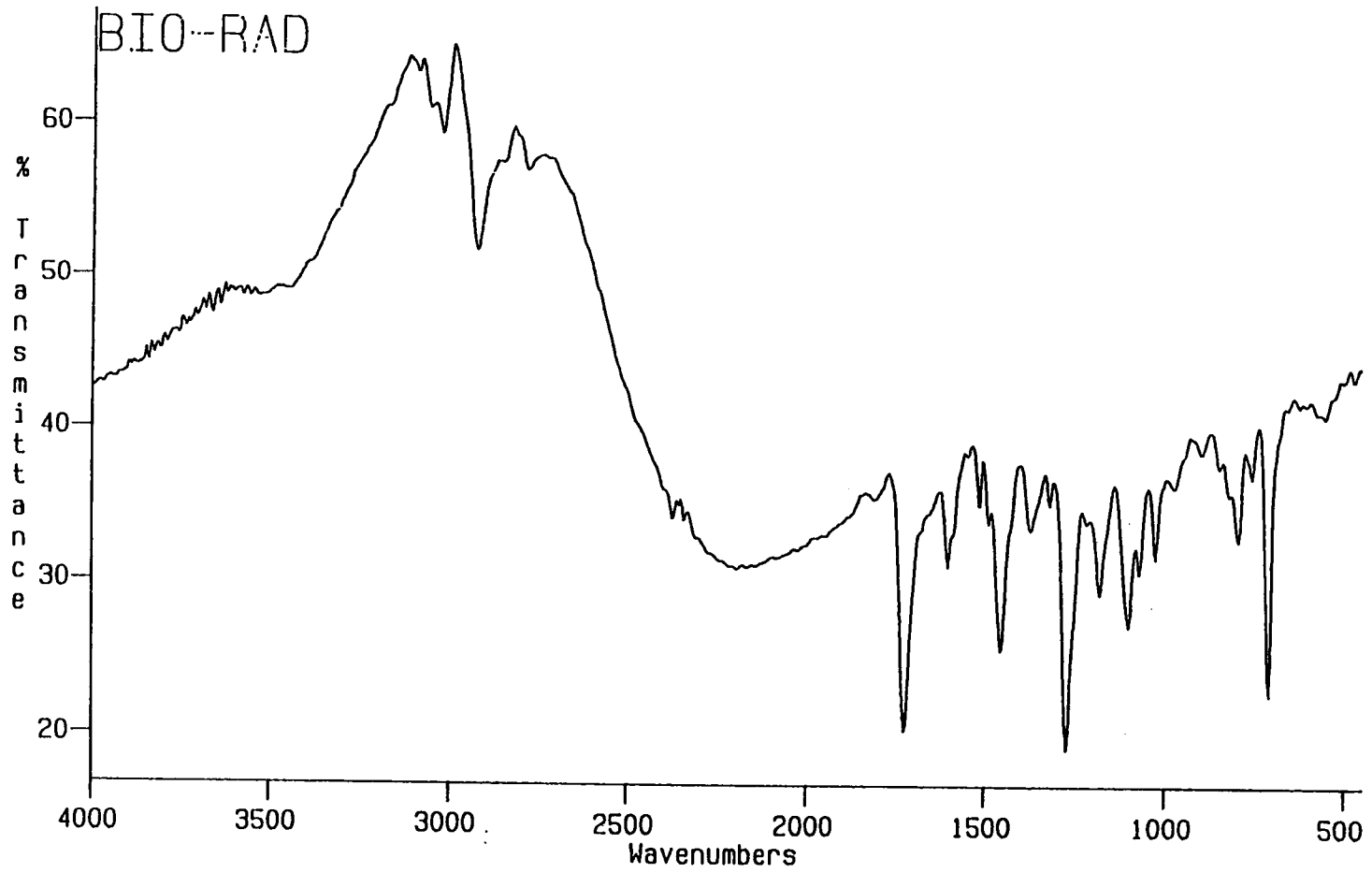


Figure 4.12. FTIR spectrum of polymer supported tribezoyloxycalix[4]arene

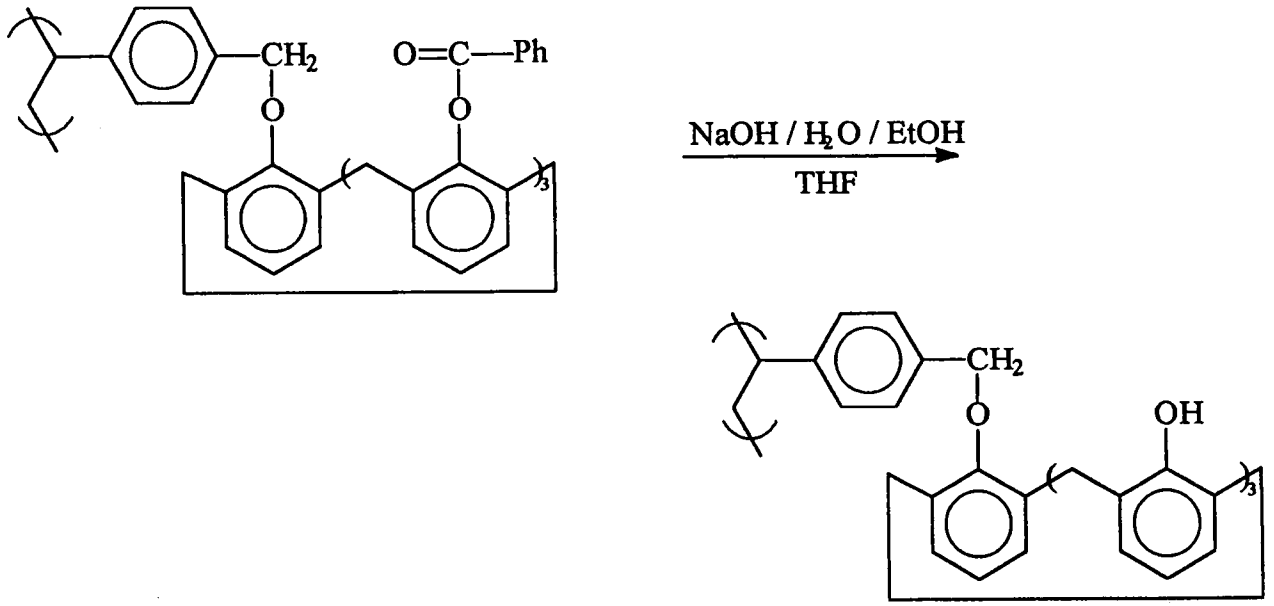


Figure 4.13. Synthesis of polymer-supported tetrahydroxycalix[4]arene

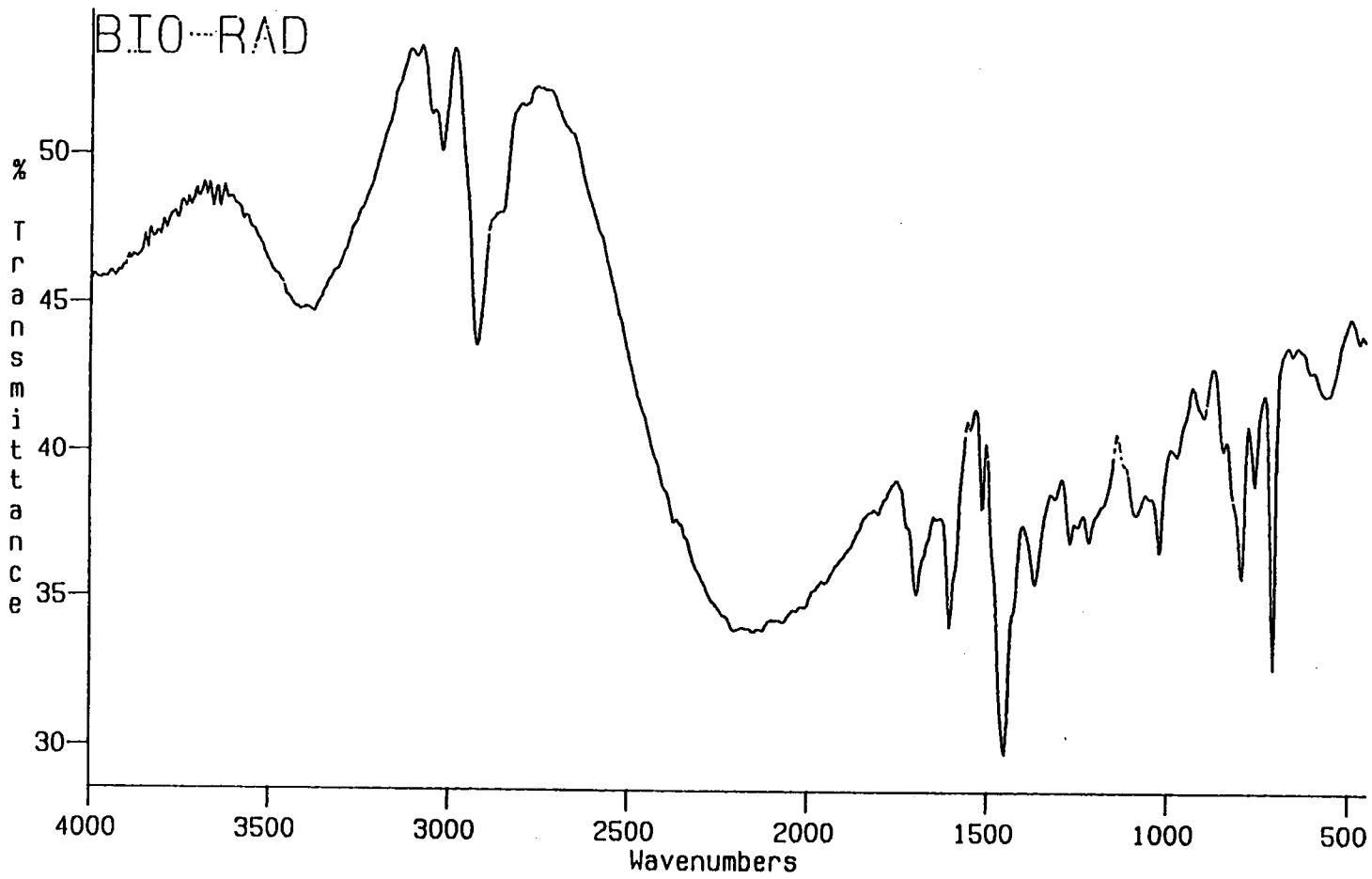


Figure 4.14. FTIR spectrum of polymer supported hydoxycalix[4]arene

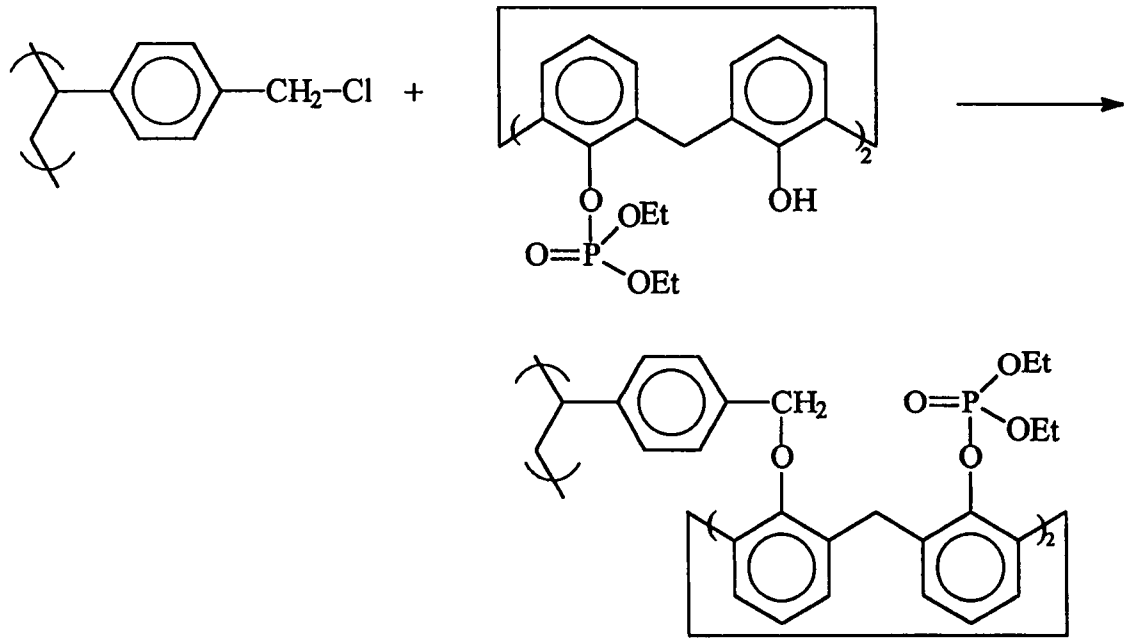


Figure 4.15. Synthesis of polymer-supported bis(diethoxyphosphoryloxy)calix[4]arene

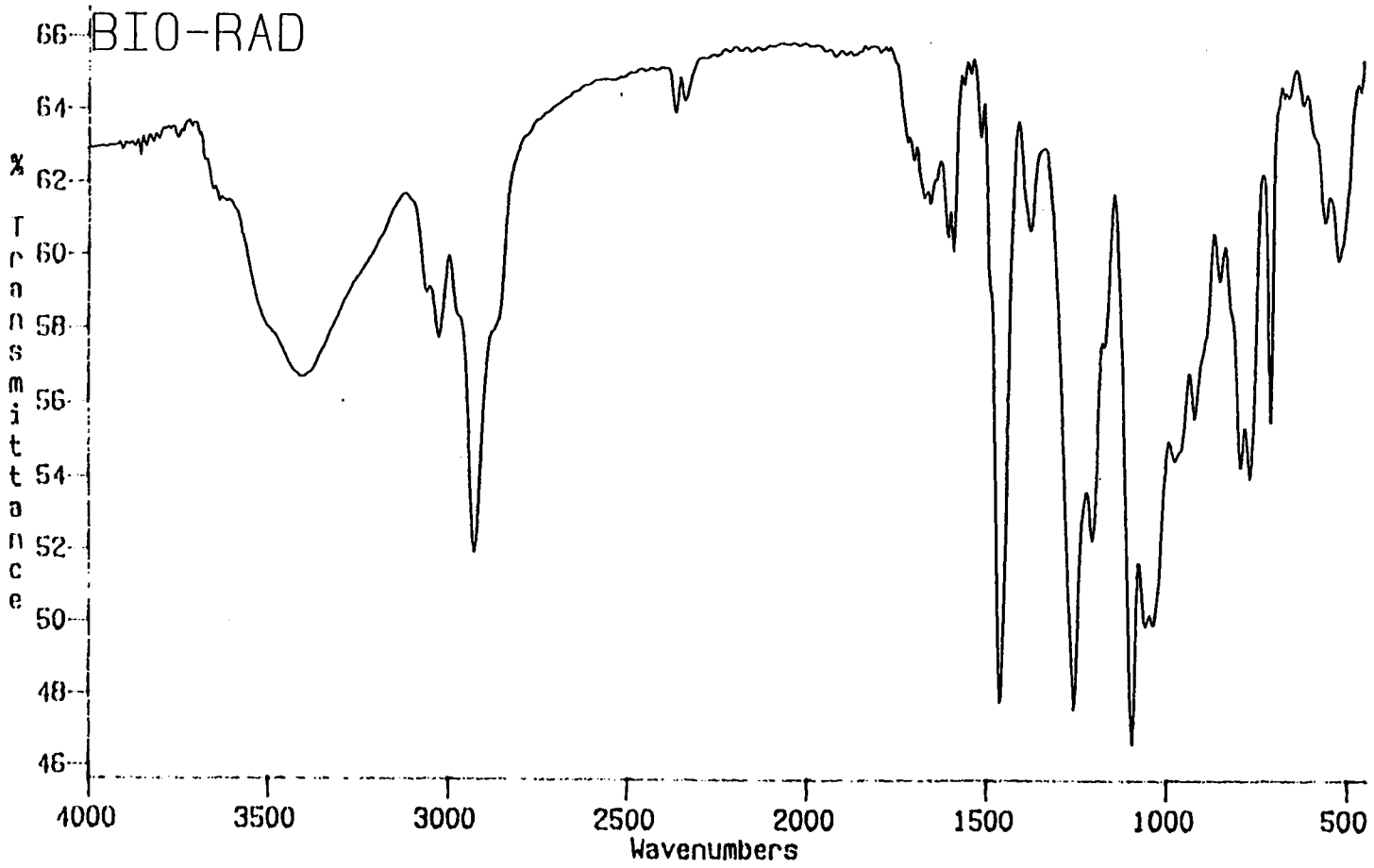


Figure 4.16. FTIR spectrum of bis(diethoxyphosphoryloxy)calix[4]arene supported polymer

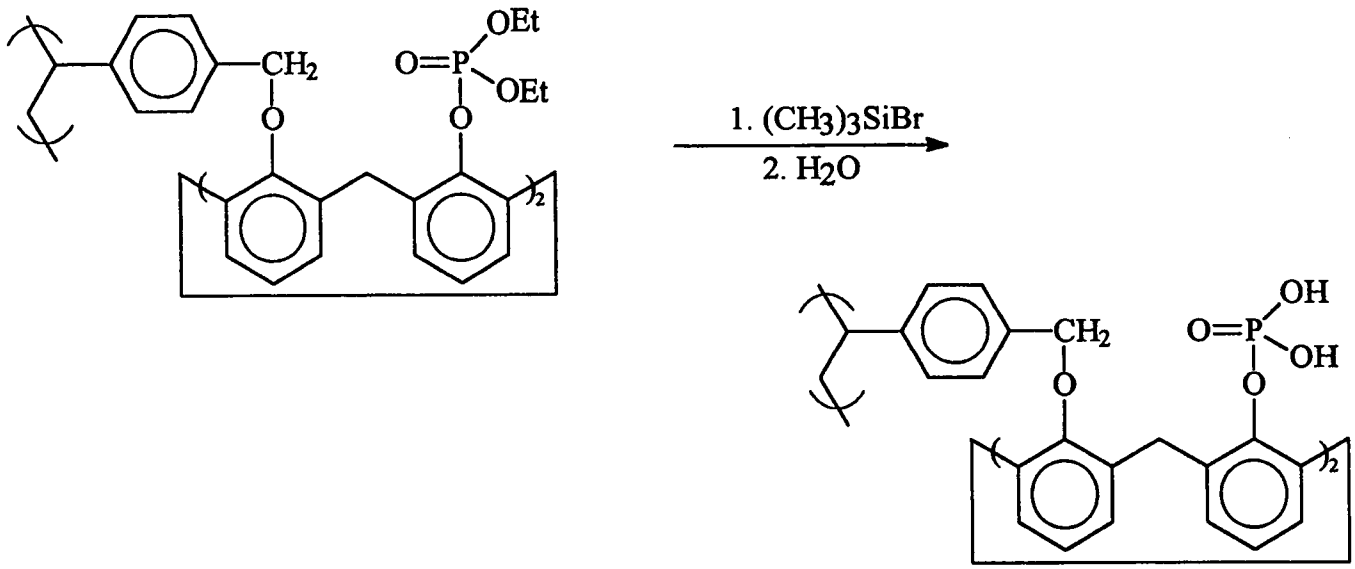


Figure 4.17. Attempted hydrolysis of polymer-supported bis(diethoxyphosphoryloxy)calix[4]arene

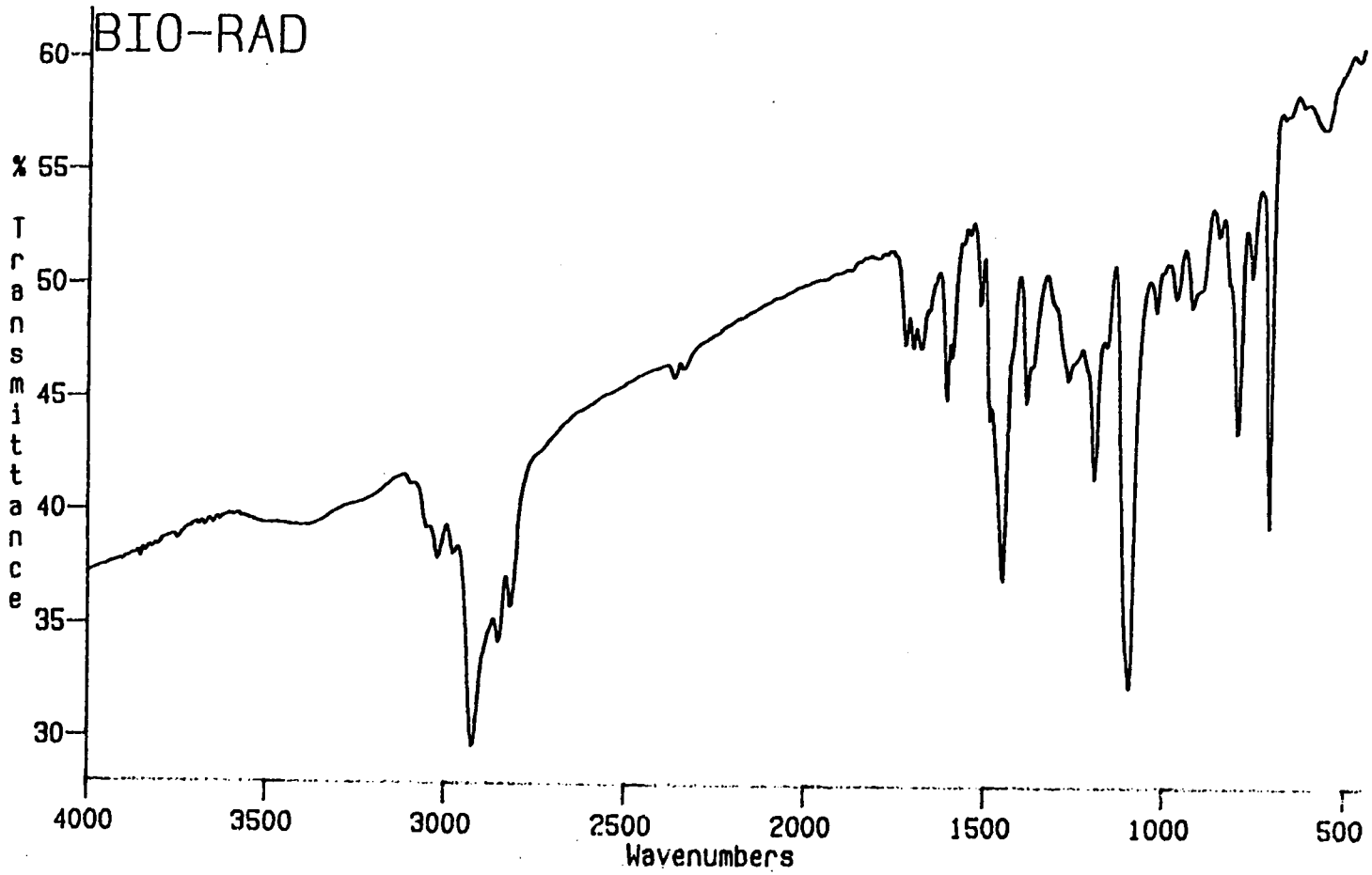


Figure 4.18. FTIR spectrum after hydrolysis of the phosphorylated calix[4]arene resin

Polymerization of p-acetoxystyrene

A mixture of p-acetoxystyrene, DVB (5 wt%) and benzoyl peroxide (5 wt%) were suspended in an aqueous solution containing polyvinyl alcohol and $CaCl_2.2H_2O$. The suspension was heated to 85°C and maintained at that temperature for 17 h. The beads were recovered, washed with water, soxhlet extracted with toluene, oven dried at 60°C and sieved to a particle size of 0.075-0.15 mm.

Synthesis of hydroxystyrene resin (HSR)

The poly(p-acetoxystyrene) copolymer was suspended in a 29.6% ammonium hydroxide solution and heated at 85°C for 7 h. (Figure 4.19). This procedure was repeated with fresh ammonium hydroxide solution each time for 17 h, 7 h and 17 h. The beads were siphoned off and washed with water. The resin was conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water, characterized by FTIR and phenolic acid capacity (Figure 4.20).

Synthesis of diethoxyphosphoryloxypolystyrene (PER)

HSR was reacted with DECP in the presence of triethylamine with THF as solvent at room temperature for 24 h (Figure 4.21). The resin was washed with dioxane, water and ethanol, characterized by phosphorus elemental analysis and FTIR (Figure 4.22).

Synthesis of dihydroxyphosphoryloxypolystyrene (PAR)

PER was swelled in chloroform and reacted with BTMS at room temperature under an atmosphere of nitrogen for 24 h (Figure 4.23). The resin was washed with dioxane and water, conditioned by eluting 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. It was characterized by phosphorus elemental analysis and acid capacity.

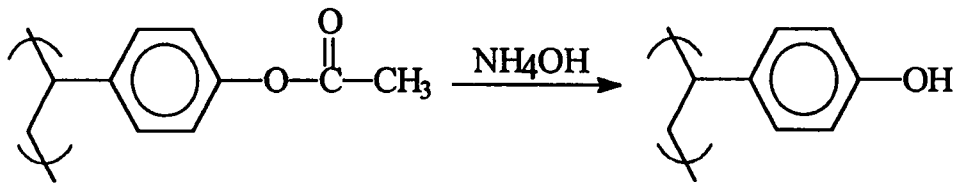


Figure 4.19. Synthesis of polyhydroxystyrene

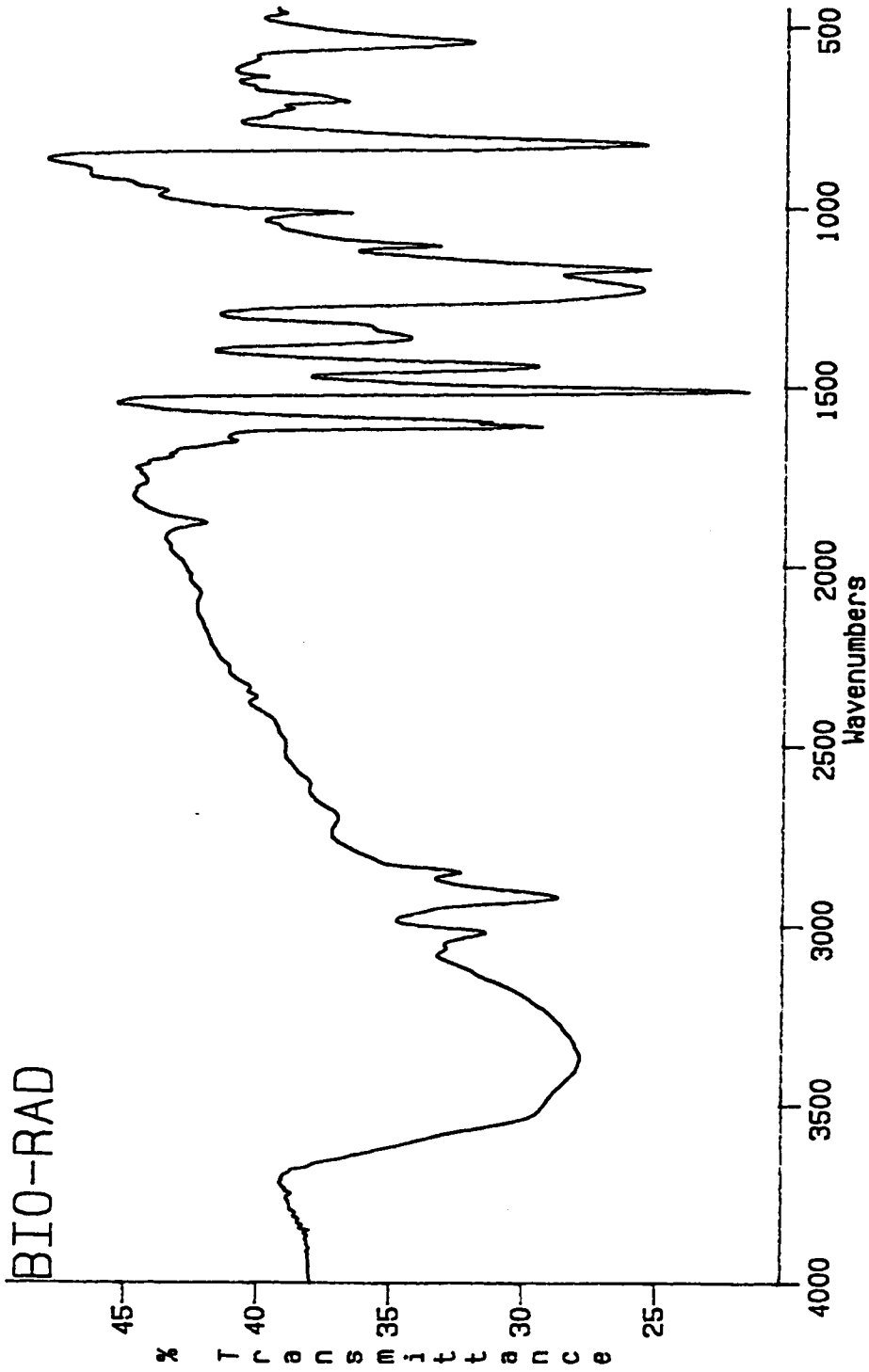


Figure 4.20. FTIR spectrum of polyhydroxystyrene resin

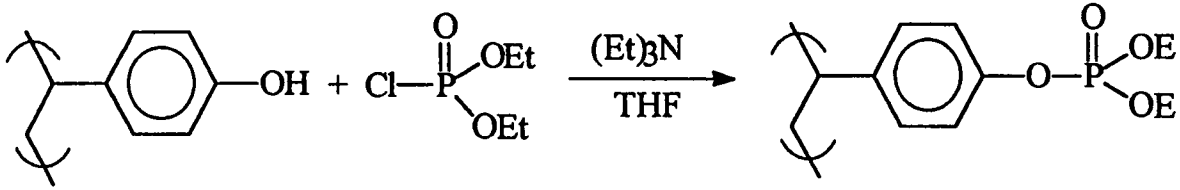


Figure 4.21. Synthesis of diethoxyphosphoryloxypolystyrene

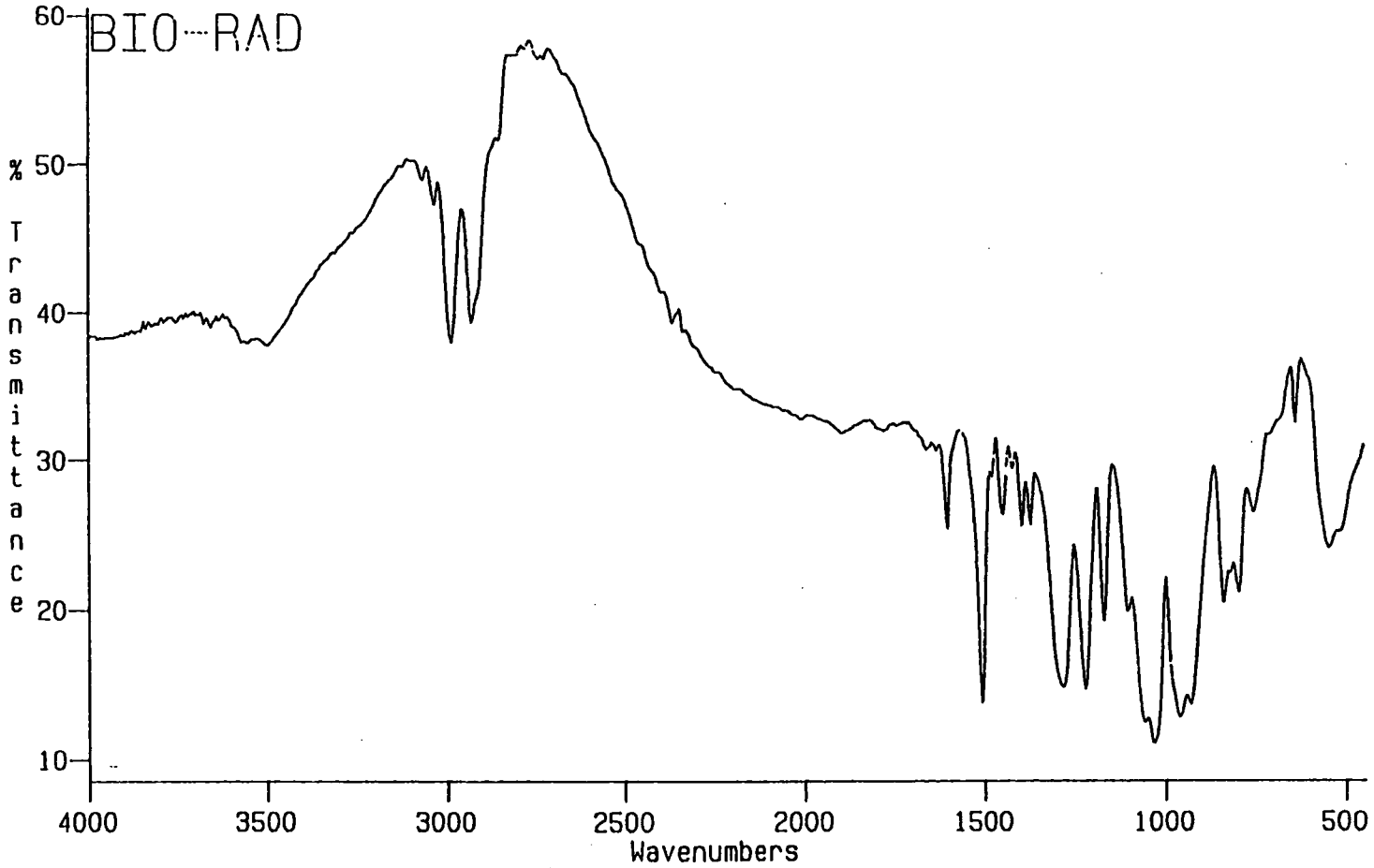


Figure 4.22. FTIR spectrum of phosphorylated polyhydroxystyrene resin

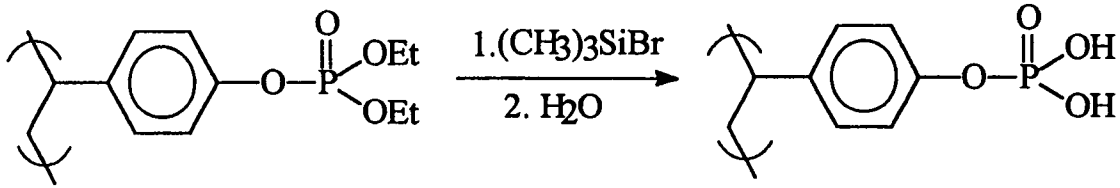


Figure 4.23. Synthesis of dihydroxyphosphoryloxypolystyrene

Metal ion studies

Complexation studies were done by contacting 0.5 g wet weight of resins with appropriate solutions containing 1x 10^{-4} N M^{n+}. Cs(I) studies were performed in 1N NaOH solution while Fe(III), Pb(II), Ni(II) and Cu(II) were studied in both 0.01 N and 0.10 N HNO_3 solutions. Each resin was pre-equilibrated with the appropriate solvent matrix prior to contact with 10 mL of metal ion solution for 24 h. The concentration of the solution after contact was determined by atomic emission spectroscopy for Cs(I) ion and by atomic absorption spectroscopy for the other metal ions. Wavelengths of 852.1, 232.1, 324.8, 248.3 and 283.3 nm were used to study Cs(I), Ni(II), Cu(II), Fe(III) and Pb(II), respectively. The results are reported both as percent metal complexed and distribution coefficient. The distribution coefficient (D) is defined as:

$$\frac{(\text{Mequiv of } M^{n+} \text{ in the resin}/g_{dry} \text{ resin})}{(\text{Mequiv } M^{n+} \text{ in solution / mL solution})}$$

Results and Discussion

Immobilization of calix[4]arenes onto polymer supports via the lower rim was investigated in the present research. The type of support, amounts of reagent, time of reaction and method of immobilization (ester or ether) were the variables studied to maximize functionalization. The characterization of the calix[4]arene supported resins and their metal ion affinities are also discussed.

Immobilization of calix[4]arene as an ester

Synthesis. To determine the optimum conditions for immobilizing calix[4]arene by an ester linkage, control reactions were done by reacting 4-chlorophenol with an acid chloride resin. The purpose of this reaction was to ascertain the ideal amounts of THC and type of support that will yield maximum functionalization. Synthesis of calix[4]arene though simple, involves tedious crystallization procedures. Also, because of its high molecular weight (424 g/mole), larger amounts of calixarene have to be used in a given reaction. For example, functionalization of a 5 g batch of acid chloride resin would involve using 31.8 g of THC at a 1:2.5 mole ratio of -C(O)Cl to THC. The acid chloride resin synthesized according to the scheme in Figure 4.1, was swelled in pyridine, a solution of 4-chlorophenol in pyridine was added and the mixture was heated at reflux for 24 h. The resin was washed with water and ethanol, and vacuum dried at 70°C overnight. It can be seen from Table 4.1 that comparable functionalization can be obtained even by reducing the amount of 4-chlorophenol to half the initial amount (5 moles to 2.5 moles). The gel resin out performed the MR resin in the esterification reaction with 4-chlorphenol (Table 4.2). One would have expected higher levels of functionalization with the latter given the fact that MR polymers offer higher accessibility to the reactive sites. This result, however, was consistent with the decreased accessibility of the reagent into the gel phase of the MR resin due to increased crosslinking. The effect of the polymer support on the percent esterification was also studied (Table 4.3). A 2.5 mole excess of THC dissolved in pyridine was added to the acid chloride resin and refluxed for 24 h. The resin was washed with water, acetone, toluene, and acetone and

Table 4.1

Esterification of acid chloride resin: effect of 4-chlorophenol mole ratio on percent ester formation in MR copolymers[a]

Resin code	Acid chloride: 4-chlorophenol	Chlorine capacity (mequiv/g)	Mole% functionalization[b]
SN-04-061	1:5	2.57	60.8
SN-04-066	1:2.5	2.72	66.0

a Particle size 0.15-0.25 mm

b Calculated by (moles ligand/total moles)*100

Table 4.2

Esterification of acid chloride resin:
effect of polymer support on the immobilization of 4-chlorophenol

Resin code	Type of support	Chlorine capacity (mequiv/g)	% Functionalization
SN-04-066	MR[a]	2.77	60.8
SN-04-072	Gel[b]	3.15	72.4

a Particle size 0.15-0.25 mm
b Particle size 0.075-0.15 mm

Table 4.3

Effect of polymer support on the immobilization of calix[4]arene by esterification

Resin code	Polymer support	Particle size (mm)	% Solids	Acid capacity after esterification (mequiv/g)
SN-04-076	5% DVB MR	0.15-0.25	48.9	2.69
SN-04-088	1% DVB xerogel	0.25-0.43	50.0	4.23
SN-04-106	2% DVB gel	0.075-0.15	64.1	5.19

conditioned by eluting with 1 L each of water, 4 wt % NaOH, water, 4 wt% HCL and water. Quenching with water converted the unreacted acid chloride sites to carboxylic acid. If THC was not incorporated, a carboxylic acid resin would form with an acid capacity of 6.06 mequiv/g. One would expect a decreased acid capacity on esterification with calix[4]arene and hence this could be used to quantify the percent functionalization. However, the phenolic protons in the calix[4]arene moiety can also be ionized with the NaOH solution used for measuring the total acid capacity (HCR resin, SN-04-220, had a value of 1.13 mequiv/g). Thus, the acid capacity of HCER resin obtained would be a measure of both carboxylic and phenolic protons, but the mequiv/g of the acid sites in HCER would be significantly lower than just the carboxylic acid resin because of the large calix[4]arene moiety incorporated into the polymer. Hence, an estimate of percent esterification can be made. Esterification was studied with three different supports; 5% DVB MR, 1% DVB xerogel and 2% DVB gel beads (Table 4.3). Maximum functionalization was obtained with the MR support. The large macro-channels are probably providing increased accessibility to the reactive sites.

Phosphorylation of immobilized calix[4]arene ester resin. Phosphorylation of the unsubstituted phenolic -OH groups of the calixarene moiety in HCER (SN-04-076) was attempted by reaction with DECP/triethylamine in THF as the solvent. After a room temperature reaction for 24h, the resin was washed with dioxane, water and ethanol, and vacuum dried. The resin (SN-04-101), had a phosphorus capacity of 0.77 mequiv/g. The extent of phosphorylation was not known since the percent esterification of its precursor could not be quantified.

Cs(I) complexation studies. Since calix[4]arene has a high affinity for Cs(I),[111] a comparative study was done with the carboxylic acid resin (CAR) and the calix[4]arene ester resin (HCER) to confirm its immobilization (Table 4.4). At a 24 h contact time, HCER complexed 65.9 % Cs(I) (D value of 39.0), while CAR complexed only 21.7% (D value of 7.78) . The affinity for Cs(I) shown by HCER was an indication of THC being successfully immobilized on the polymer. However, the amount of complexation by HCER was significantly lower than expected given the ligands high affinity for Cs(I). This could be due to hydrogen bonding of the phenolic protons to the carboxylate ligand, since the calix[4]arene ligand is not completely deprotonated at the pH in which the contact study was done (13.00).[112]

Since the acid capacity of HCER could not be used to accurately quantify THC incorporation and also because it was felt that the level of Cs(I) complexation could be much improved, an alternate mode of functionalization was sought to better understand the structure of the supported calixarene and the mechanism of metal ion complexation. Nucleophilic attack on the chloro groups in the VBC copolymer with a phenolate ion by a Williamson ether synthesis could provide a well defined calixarene-supported resin. Immobilization of THC by an etherification reaction was thus pursued.

Immobilization by Etherification

Synthesis. Conditons for immobilization were determined using control reactions of VBC copolymers with phenol. Phenol was dissolved in an appropriate solvent, reacted with an equimolar amount of NaH and refluxed with VBC copolymer beads for either 17 or 72 h. The beads were washed with dioxane, water and acetone, then vacuum dried. The effect

Table 4.4

Percent Cs(I) complexed from 1 N NaOH[a]

Resin code	Resin name	% Cs(I) complexed	D
SN-04-033	CAR	21.7	7.78
SN-04-076	CER	65.9	39.0

a Contact time 24 h

of particle size on percent functionalization for gel copolymers are reported in Table 4.5. Decreased particle size gave increased functionalization (SN-04-112). Though this trend was consistent with increased surface area of the polymer in the smaller sized beads, there was another variable introduced due to an inadvertent change of solvent. In the first reaction (SN-04-078), THF (bp 65-67°C) was used as the solvent while dioxane (bp 100-102 °C) was used for the second resin (SN-04-112) inadvertently. The change in reaction temperature on percent etherification was not known. Dioxane, however, was used for all subsequent control reactions. The effect of the polymer support on percent functionalization is presented in Table 4.6. Gel and MR copolymers were compared for their ability to be etherified with phenolate ion at 17 h reflux. Smaller sized gel beads had a higher percent etherification (45.9%) than the MR (31.5%) support. However, for the 72 h reaction (Table 4.7), the percent functionalization was higher with the MR support (80.3%) than the gel copolymer (56.5%). Thus, a 5%DVB VBC MR copolymer with a particle size of 0.15-0.25 mm was used as the support for the etherification reactions with calix[4]arene.

Preparation of the anion form of calix[4]arene for subsequent etherfication was attempted by reacting a solution of THC in dioxane with four equivalents of NaH but the product precipitated out of solution being perhaps too ionic to be solvated. Attempts to retain a homogeneous solution was done by changing solvents (including use of mixed solvents) and/or the mole ratio of NaH. When a solution of THC in either toluene or 9:1 v/v ratio of THF: toluene was reacted with four equivalents of NaH, a precipitate was still observed. Using only 2.5 equivalents of NaH (in either a 10:1 v/v dioxane:DMF or

Table 4.5

Etherification of VBC gel copolymers with phenol: effect of particle size on percent etherification

Resin code	Particle size (mm)	Chlorine capacity (mequiv/g)	Mole% etherification
SN-04-078	0.18-0.25	3.68	34.1
SN-04-112	0.15-0.25	2.90	45.9

Table 4.6

Etherification of VBC copolymers with phenol: effect of polymer support on percent functionalization

Resin code	Support	Particle size (mm)	Time of reaction (h)	Chlorine capacity (mequiv/g)	% Etherification
SN-04-112	2% DVB gel	0.075-0.15	17	2.90	45.9
SN-04-113	5% DVB MR	0.15-0.25	17	3.65	31.5

Table 4.7

Etherification of VBC copolymer with phenol: effect of polymer support on percent functionalization

Resin code	Support	Particle size (mm)	Time of reaction (h)	Chlorine capacity (mequiv/g)	% Etherification
SN-04-114	2% DVB gel	0.075-0.15	72	2.26	56.5
SN-04-115	5% DVB MR	0.15-0.25	72	0.90	80.3

DMF:toluene) still produced a precipitate. Reaction with only a 1.11 mole excess of NaH with a solution of THC in 10:1 v/v DMF:toluene also gave the same end result even though it was thought that the monoanion would remain in solution.

Alternate methods of etherification were explored due to the inability of obtaining a homogenous mixture on deprotonation of THC. If the chloro groups in the VBC copolymer were to be replaced with a better leaving group (e.g., p-toluenesulfonate), the lone pair of electrons on the phenolic oxygens of calix[4]arene could be nucleophilic enough to effect the substitution reaction. VBC copolymer was thus reacted with sodium p-toluenesulfonate (10-fold excess) in acetonitrile at 72 h reflux. Both 5% DVB MR (particle size of 0.15-0.25 mm) and a 2% DVB gel copolymer (0.075-0.15 mm) were studied as possible supports. Functionalization of the gel copolymer beads could not be accomplished and the MR copolymer was only about 33% substituted (Cl capacity of 3.90 mequiv/g after substitution). The inability of the hydrophilic reagent to access the hydrophobic polymer matrix was the reason for the low level of functionalization. Hence this route was not pursued further.

Benzoylation of THC results in a compound where three of the four phenolic OH groups have been substituted.[109] It was thought that deprotonation of this compound will not produce a precipitate since the monoanion would still allow for solvation by an appropriate solvent. This was found to be the case. A solution of tribenzoyloxycalix[4]arene (BzC) in DMF was deprotonated with an excess amount of NaH (mole ratio of 1:1.8 of BzC to NaH), the mixture added to the beads swelled in DMF and refluxed for 72h. For the BzCR with resin codes SN-04-129, SN-04-186 and SN-04-

195, BzC to NaH was in the mole ratio of 1:1.8. The immobilization of BzC was confirmed by FTIR (carbonyl stretching peak at 1720 cm^{-1}, Figure 4.12). These resins had almost no chlorine present (Table 4.8), except for resin SN-04-214, the reason for which is discussed in page 166. This was initially interpreted as quantitative functionalization. However, an inconsistency soon became evident. Immobilizing a large ligand onto a polymer support would result in significant weight change of the resin. For example, if 5g of a 5% DVB MR copolymer was completely etherified with THC, the final weight of the resin would be 16.4 g. Since all of the above resins had a final weight on the order of 7 g (from a starting point of 5 g), it was construed that the functionalization might not be quite as high. The reasons for the chlorine loss are discussed in page 162.

Deprotection of the benzoyl groups in the BzCR with resin code SN-04-129 was first attempted by adding an aqueous solution of 0.71N KOH in dioxane to the resin and refluxing the mixture for 17h. The resin (SN-04-131) was washed with water and conditioned as described earlier. The carbonyl stretching peak still present in the FTIR spectrum of the dried resin (Figure 4.24) indicated incomplete hydrolysis. Rehydrolysis by doubling the concentration of KOH still did not allow for complete hydrolysis. The lack of hydrolyis was tested by phosphorylating the resin (SN-04-135) with DECP in triethylamine/THF mixture at room temperature for 24 h. A low functionalization (phosphorus capacity of SN-04-137 was 0.415 mequiv/g) further implied incomplete hydrolysis.

Hydrolysis was then attempted (on a BzCR, SN-04-142) with a 1.5 N aqueous solution of NaOH in dioxane. The resin (SN-04-147) was washed with water and

Table 4.8

Characterization of BzCR

Resin code	Chlorine capacity (mequiv/g)
SN-04-129	0[a]
SN-04-142	-[b]
SN-04-186	0.49[a]
SN-04-195	0[a]
SN-04-214	1.49[c]

a BzC to NaH mole ratio of 1:1.8
b Chlorine capacity not evaluated
c BzC to NaH mole ratio of 1:1

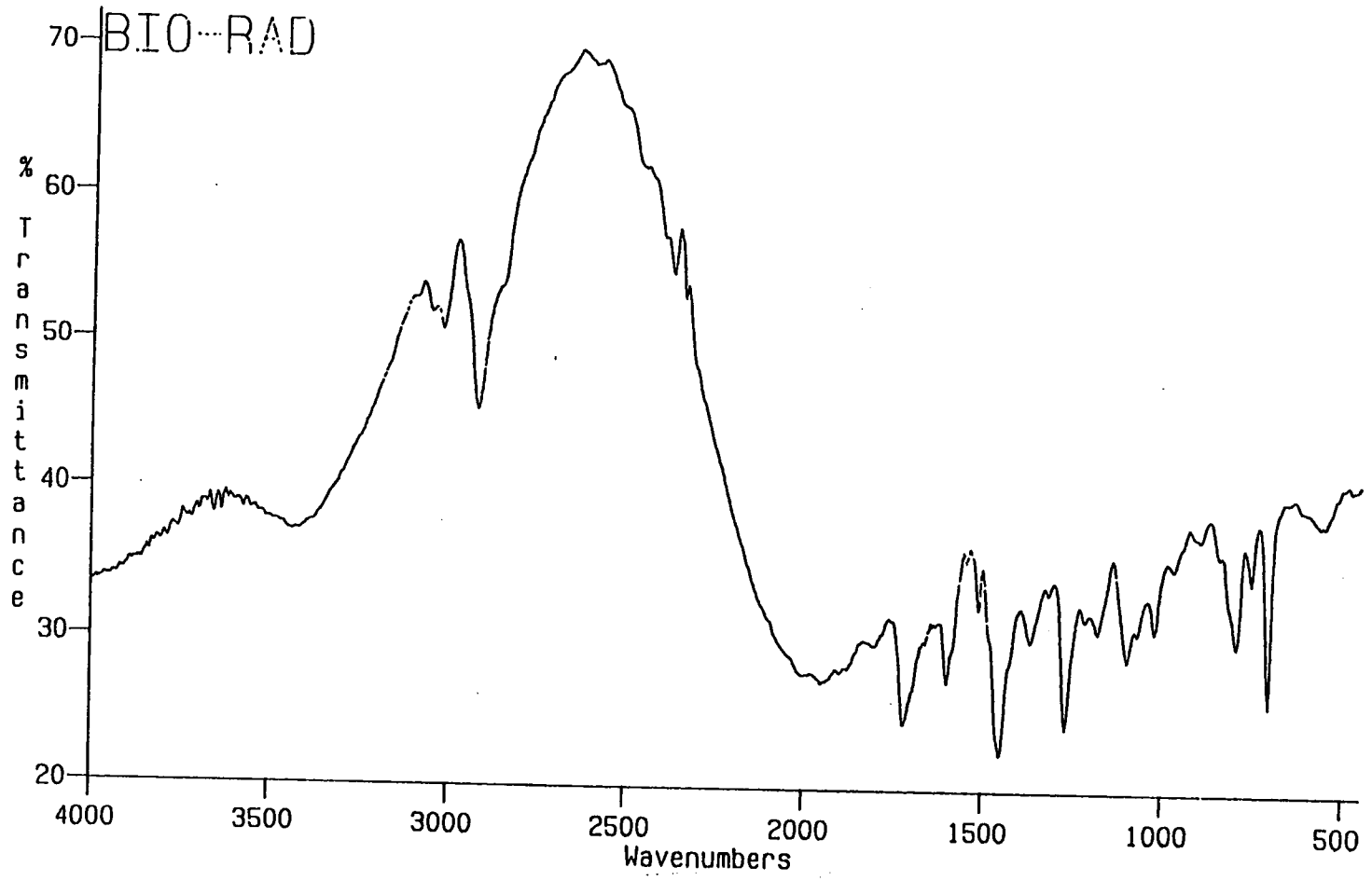


Figure 4.24. FTIR spectrum after hydrolysis of tribenzoyloxycalix[4]arene supported resin with 0.71 N KOH / dioxane

conditioned. The resin had a percent solids of 49.4, a phenolic -OH capacity of 0.78 and a chlorine capacity of 1.48 mequiv/g. As will be seen in page 175, the phenolic -OH capacity is not an accurate measure of all the ionizable protons and can only be used as a qualitative measure of the extent of hydrolysis. FTIR provides more conclusive evidence of hydrolysis. For the resin, SN-04-147, the FTIR spectrum still indicated incomplete hydrolysis. However, the more surprising result was the presence of chlorine in this resin while the one made earlier (SN-04-135) had none. It was later found out that the former resin used NaH only in a 1.11 excess while the latter was at 1:1.8; the importance of using an appropriate amount of NaH is discussed in page 162.

Yilmaz and co-workers have devised a hydrolysis procedure which results in complete removal of the benzoyl groups.[89] A modified procedure was used to rehydrolyze SN-04-147. A 5N aqueous solution of NaOH in ethanol was added to the resin swelled in THF and refluxed for 24h. The increase in phenolic -OH capacity to 1.43 mequiv/g coupled with the loss of the C=O peak in the FTIR spectrum (Figure 4.15) confirmed the complete hydrolysis of BzCR. The resins SN-04-186 and SN-04-195 were also hydrolyzed in a similar manner to obtain HCR with resin codes SN-04-188 and SN-04-198 (Table 4.9). It must be noted that, earlier, it was assumed there was complete functionalization with SN-04-186 and SN-04-195. On hydrolysis it should have had a phenolic -OH capacity of 5.39 mequiv/g (assuming ionization of three protons). Phenolic -OH capacities of 1.72 and 1.10 mequiv/g were not due to incomplete hydrolysis since the FTIR spectrum had no carbonyl stretching peak. Thus, the loss of chlorine had to be due to replacement by some other group. A nitrogen elemental analysis of BzCR (SN-04-195)

Table 4.9

Summary of hydrolysis procedures for BzCR

Resin code	Reagent/solvent used in hydrolysis	% Solids	Phenolic -OH capacity (mequiv/g)	Cl capacity (mequiv/g)
SN-04-147	$NaOH/H_2O$/dioxane (72h reflux)	49.4	0.78	1.48
SN-04-154	THF/$NaOH/H_2O$/ ethanol (24h reflux)	36.0	1.43	-[a]
SN-04-188	THF/$NaOH/H_2O$/ ethanol (48h reflux)	27.8	1.72	N/A[b]
SN-04-198	THF/$NaOH/H_2O$/ ethanol (48h reflux)	34.1	1.10	N/A
SN-04-220	THF/$NaOH/H_2O$/ ethanol (48h reflux)	40.6	1.57	1.49

a Chlorine capacity not evaluated
b Precursor had no chlorine

was done to determine whether the solvent DMF was participating in the reaction. A low nitrogen capacity of 0.41 mequiv/g suggested lack of participation by the solvent in the reaction. Since NaH was used in almost two-fold excess (in the case of SN-04-186 and SN-04-195), loss of Cl by attack of hydride was the next possibility considered. A control reaction was done by reacting VBC beads with a mixture of DMF and NaH at reflux temperature for 72 h. The resin (SN-04-203) was washed with DMF, water and acetone followed by vacuum drying overnight at 70°C. Complete loss of chlorine suggested that hydride attack was taking place on the $-CH_2Cl$ groups during the synthesis of BzCR. The reaction conditions were thus modified to circumvent this problem. SN-04-214 was prepared by reaction of deprotonated BzC (obtained using an equimolar amount of NaH) with VBC copolymer at reflux for 72 h. It had a chlorine capacity of 1.49 mequiv/g (Table 4.9). On hydrolysis with ethanolic NaOH in THF, the resin (SN-04-220) had a phenolic acid capacity of 1.57 and a chlorine capacity of 1.34 mequiv/g. Based on the extent of immobilization and presence of three phenolic protons in the calix[4]arene moiety, one would have expected a higher phenolic -OH capacity. pK_a studies have been done on tetra(p-nitro)calix[4]arene and the following values were assigned: $pK_1 < 0$, $pK_2 = 10.3 \pm 0.3$ and $pK_3 = 13 \pm 1$.[113] Inference can be drawn from these studies that the phenolic protons are not completely ionized during the acid capacity measurements and hence, a low phenolic capacity obtained. Further, mass balance calculation on HCR (SN-04-220) assuming one proton being ionized gave a value of 1.05 g/g in good agreement with the expected value of 0.91 g/g.

Since the hydrolysis of the benzoylated resins was done with an ethanolic NaOH

solution, reaction at unsubstituted -CH_2Cl groups with ethoxide must also be considered. MR copolymers crosslinked with 5% DVB were reacted with an ethanolic solution of NaOH in THF at reflux temperature for 48 h. There was a 20.4 mole percent loss of chlorine relative to the copolymer(from 5.90 to 4.01 mequiv/g). However, given the presence of chlorine in the resin (SN-04-220) and results from the Arbuzov reaction (discussed in page 174), suggest that this reaction is unlikely to occur due to unfavorable steric interactions.

Phosphorylation of HCR. The resin was reacted with DECP in a triethylamine/THF mixture at room temperature for 24h. It was washed with dioxane, water, 2 wt% NaOH and ethanol followed by drying under vacuum. HCR's SN-04-154 and SN-04-188 were phosphorylated under the same conditions (Table 4.10). The resins SN-04-158 and SN-04-192 had phosphorus capacities of 0.96 mequiv/g and 1.74 mequiv/g, respectively. The reason for this discrepancy is not clear at the present time even though their precursors had comparable phenolic capacities. In either case, the resins were only partially phosphorylated because complete substitution at all -OH groups would have produced a resin with a phosphorus capacity of 3.11 mequiv/g. A definite conclusion could not be made as to whether there was uniform substitution or if the phosphorus capacity was a statistical average of different levels of substitutions.

Hydrolysis of the phosphate ester within the calixarene moiety was attempted using bromotrimethylsilane (BTMS). It is a mild hydrolyzing agent and has been used in the selective hydrolysis of phosphonate esters.[114] The resins were swelled in chloroform and refluxed for 17h after addition of BTMS. They were then washed with dioxane and

Table 4.10

Attempted phosphorylation of HCR

Resin code	P capacity (mequiv/g)
SN-04-137	0.41
SN-04-158	0.96
SN-04-192	1.74

water and conditioned. Lack of phosphorus in both the resins (Table 4.11) suggested that the phosphate group was being cleaved off the macrocycle on hydrolysis. Further experiments to determine the reasons for the cleavage are discussed on page 168. Additionally, since phosphorylation after immoblization of the calixarene ligand onto the polymer support led to uncertainty as to the level of phosphorylation in each ring, synthesis of the resin using a different route where the extent of phosphorylation in each calix[4]arene moiety is accurately known was pursued.

Synthesis and immoblization of bis(diethoxyphosphoryloxycalix[4]arene).

Bis(diethoxyphosphoryloxy)calix[4]arene (BPC) was synthesized in the cone conformation, where two of the four -OH groups are substituted with phosphate esters,[110] dissolved in DMF, contacted with 2 equivalents of NaH (with the aim of deprotonating both -OH groups on the calixarene) and reacted with the VBC copolymer beads at reflux temperature for 72 h. The resin was washed with DMF, water and acetone, then vacuum dried. All the resins presented in Table 4.12 were synthesized by the conditions described above. The FTIR spectrum (Figure 4.16) has the phosphoryl stretching peak at 1247 cm^{-1} indicating incorporation of BPC onto the polymer support. The phosphorus capacities of the resins were between 1.40 and 1.78 mequiv/g compared to the theoretical value of 2.41 mequiv/g for a completely functionalized resin. The resins, however, had no remaining chlorine. The results are consistent with reaction at the $-CH_2Cl$ groups by NaH that had not been consumed by the deprotonation reaction. In order to determine whether two equivalents of NaH is an excess in the reaction (as it would be if both phenol groups on the calixarene could not be deprotonated due to electronic factors), the calixarene was

Table 4.11

Characterization of BPCAR

Resin code	% Solids	Phosphorus capacity (mequiv/g)	Phenolic -OH Capacity (mequiv/g)
SN-04-191	41.4	0.24	1.80
SN-04-194	43.1	0.20	1.84

Table 4.12

Characterization of BPCER

Resin code	Phosphorus capacity (mequiv/g)	% Functionalization
SN-04-213	1.78	42.0
SN-04-230	1.45	25.6
SN-04-252	1.40	23.8

contacted with one equivalent of NaH. Since there was only enough hydride to deprotonate one phenol, it was expected that all of the reagent would be consumed. Surprisingly, it was found that the resin (SN-04-302) prepared under these conditions still lacked chlorine. It was then concluded that complete deprotonation probably occurred over a much longer time than expected: the time allowed for deprotonation of BPC (2 h) was not long enough to consume all NaH, which then reacted with the $-CH_2Cl$ groups in the VBC copolymer. Further experiments are needed to confirm this.

Hydrolysis of BPCER. Since previous attempts at hydrolysis at elevated temperatures resulted in cleavage of the phosphate ester groups from the macrocycle, hydrolysis was carried out with BTMS at room temperature. It can be seen from Table 4.13 that even the room temperature reaction resulted in cleavage of the phosphate ester groups from the macrocycle. The mechanism of cleavage was thought to be as follows: the unsubstituted -OH group in the calixarene was reacting with excess BTMS to produce HBr which protonated the phenolic oxygen attached to phosphorus, nucleophilic attack by the bromide ion on the phosphoryl group followed causing cleavage of the phosphate from the ring. Experiments to study this hypothesis are described below. A lightly crosslinked p-acetoxystyrene copolymer supplied by Hoechst-Celanese corporation (HCC) was hydrolyzed to obtain the hydroxystyrene resin HSR (SN-04-163D). The resin had a phenolic -OH capacity of 6.56 mequiv/g (Table 4.14). Since the composition of the parent copolymer was not revealed, the theoretical capacity could not be calculated. The crosslinking level in the resin seemed to be about 1% based on its swelling behavior: the resin swelled more than thrice its volume when eluted with 4 wt% NaOH. The resin was

Table 4.13

Characterization of BPCAR

Resin code	% Solids	Phosphorus capacity (meq/g)	Acid Capacity (meq/g)
SN-04-219	41.0	0.12	1.23
SN-04-232	26.5	0.33	1.27
SN-04-254	32.9	0.27	1.24

Table 4.14

Characterization of HSR

Resin code	% DVB	Polymer support	% Solids	Phenolic -OH capacity (mequiv/g)
SN-03-135C	1*	gel	19.3	6.56
SN-04-163D	1*	gel	23.8	6.85
SN-04-273D	5	MR	45.8	3.71
SN-04-281D	5	gel	55.9	3.46

* Composition unknown; however, swelling behavior and phosphorylation experiments suggest 1% DVB crosslinking

phosphorylated with DECP in triethylamine/THF mixture at room temperature for 24 h. To attain partial functionalization, a OH:DECP ratio of 1:0.8 was used. By doing so, the resin would have both phosphate ester and unsubstituted -OH groups. The product had a phosphorus capacity of 3.33 mequiv/g (Table 4.15). Hydrolysis of the resin was done separately with either BTMS or chlorotrimethylsilane (CTMS). In the case of the latter, it was hoped that the HCl formed would not be quite as effective as HBr in causing cleavage of the phosphoric acid group from the ring. On characterization, it was found that BTMS provided complete hydrolysis without loss of phosphorus (Table 4.16). The resin SN-04-239A had a percent solids of 10.4, a phosphorus capacity of 3.77 mequiv/g and an acid capacity (11.72 mequiv/g). The acid capacity was more than twice the phosphorus capacity owing to the error introduced in its calculation by using the low solids number. CTMS was found to be ineffective for the hydrolysis of phosphate ester giving the resin a high solids level and low acid capacity. The reason for the decrease in phosphorus capacity from 3.33 to 2.74 mequiv/g was unclear. The mechanism of cleavage was thus not understood from these studies and more research needs to be done to deduce the exact mechanism.

Resins HCR (SN-04-220) and BPCER (SN-04-252) were studied for their metal ion affinities. Additional studies with calix[4]arene/phosphonic acid resin, hydroxystryrene resin (HSR), diethoxyphosphoryloxypolystyrene (PER) and dihydroxyphosphoryloxypolystyrene (PAR) described below, help in understanding the mechanism of complexation.

Table 4.15

Characterization of PER

Resin code	Phosphorus capacity (mequiv/g)
SN-04-144	3.91
SN-04-236	3.33
SN-04-267	3.90
SN-04-286	3.76

Table 4.16

Characterization of PAR

Resin code	Reagent used in hydrolysis	% Solids	Phosphorus capacity (mequiv/g)	Acid Capacity (mequiv/g)
SN-04-178[a]	$(CH_3)_3SiBr$	16.0	4.46	10.77
SN-04-239A[b]	$(CH_3)_3SiBr$	10.4	3.77	11.72
SN-04-239B[b]	$(CH_3)_3SiCl$	40.6	2.74	3.13

a Used for metal ion studies

b Used as control for determining the mechanism of hydrolysis of BPCER

Attempted synthesis of bifunctional calix[4]arene/phosphonic acid resin. The reaction of unsubstituted chloro groups in BzCR (SN-04-214) followed by hydrolysis would produce a resin having hydrolyzed calixarene and phosphonic acid groups immobilized in the polymer backbone. Such a resin would allow for the phosphonic acid groups to cooperate with the calix[4]arene moiety by an inter-ligand mechanism and this may yield a resin with different ion selectivity series. BzCR (SN-04-214) was refluxed with an excess of triethyl phosphite for 24 h, followed by hydrolysis with concentrated HCl for 24 h. The resin was washed with water and conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. The resin had 46.1% solids, an acid capacity of 2.02 mequiv/g, a phosphorus capacity of 0.15 mequiv/g and a chlorine capacity of 1.86 mequiv/g. The results indicate that unreacted chloro groups could not be substituted by phosphonate ester groups possibly due to unfavorable steric interactions of the large macrocycle. This result was also consistent with ruling out the possibility of ethanolic NaOH replacing unreacted chloro groups in the resin

Synthesis of hydroxystyrene resin and its phosphorylated analogue. HSR was obtained by the hydrolysis of p-acetoxystyrene copolymer supplied by HCC. Characterization of the resins (SN-04-163D) is reported in Table 4.14. As the crosslinking level of the HCC resin was not revealed, synthesis of a 5% DVB MR copolymer was attempted from p-acetoxystyrene monomer to obtain a well defined structure. The copolymer (SN-04-271) was synthesized with 4-methyl-2-pentanol as diluent during the polymerization but the beads were not opaque, as one would expect with MR copolymers. Changing the diluent to cyclohexanol (SN-04-274) had no effect on the beads' opacity. Hence, a 5%

DVB p-acetoxystyrene gel copolymer was synthesized (SN-04-280). In order to make a reasonable comparison with the other MR resins, smaller particle size beads (0.075-0.15 mm) were synthesized. On hydrolysis, the resin had 55.9% solids and a phenolic -OH capacity of 3.46 mequiv/g. In both hydrolyzed resins (SN-04-273D and SN-04-281D), the phenolic -OH capacities were much lower than the expected (theoretical value of 6.83 mequiv/g). The FTIR spectrum (Figure 4.22), however, indicated complete hydrolysis based on disappearance of the C=O peak coupled with the appearance of the -OH stretching peak at 3250 cm^{-1}.

Phosphorylation of HSR was done by reaction with DECP in a THF/triethylamine solution at room temperature for 24h. Capacities of the phosphorylated resins (PER) are presented in Table 4.15. Resins SN-04-144 and SN-04-267, were obtained by phosphorylation of the HCC resin and would have a theoretical phosphorus capacity of 3.86 mequiv/g assuming a 1% DVB crosslinking level. Their capacities of 3.9 mequiv/g are consistent with this assumption. The 5% DVB gel HSR (SN-04-281D) was also phosphorylated by the same procedure. The resin had a phosphorus capacity of 3.76 mequiv/g which is within experimental error of the theoretical capacity of 3.63 mequiv/g. The phosphorus capacities confirmed that full hydrolysis occurred in the previous step.

Dihydroxyphosphoryloxypolystyrene (PAR) was synthesized by hydrolysis of PER with BTMS in chloroform at reflux temperature for 24 h. Quantitative hydrolysis was achieved with the resin (SN-04-178) having a phosphorus capacity of 4.46 mequiv/g and an acid capacity of 10.77 mequiv/g (Table 4.16). The somewhat high acid capacity was again attributed to the low solids level (16.0%).

Stability studies. The stability of the phosphoric acid ligand in acidic solutions at room temperature was studied by contacting PAR with 0.01 N, 0.10 N and 1.0 N nitric acid solutions for 24 h. Any loss of phosphorus capacity after contact would suggest cleavage of the phosphoric acid moiety from the polymer backbone due to hydrolysis. From Table 4.17, it can be seen that the resins were stable under these conditions.

Cs(I) complexation studies. Results from complexation studies with Cs(I) in 1N NaOH at a 24 h contact time are reported in Table 4.18. The calix[4]arene-supported resin (HCR, SN-04-220) had a very high affinity for Cs(I)(96.7%) compared to hydroxystyrene resin (HSR) (33.5%). Crystal structure determination of a monocesium derivative of calix[4]arene has shown that Cs(I) may be involved in polyhalypto interactions with carbon atoms of the phenyl rings as well as coordination to the phenolic oxygens.[112] Thus, both cavity size and cooperation of the phenolic oxygens in coordinating the Cs(I) were thought to be responsible for the high affinity shown towards Cs(I) by the HCR. In the case of HSR (SN-04-163D) where phenolic oxygen is the only binding site, the percent Cs(I) complexed decreased. The higher percent complexation of Cs(I) by the HCR compared to HCER also was consistent with the assumption of hydrogen bonding of the unionized phenolic protons to the carboxylate groups hindering the ability of the latter to complex Cs(I) effectively.

HSRs prepared from both HCC (SN-04-163D) and 5% DVB gel (SN-04-281D) copolymers performed comparably. Thus, it was concluded that any difference in their level of crosslinking had no effect on their ability to complex Cs(I).

Substitution at the phenolic oxygen by the phosphate ester group in PER

Table 4.17

Acid stability studies of PAR[a]

Contact acid solution	Phosphorus capacity (before) (mequiv/g)	Phosphorus capacity (after) (mequiv/g)
0.01 N HNO_3	4.46	4.55
0.10 N HNO_3	4.46	4.64
1.0 N HNO_3	4.46	4.56

a Contact time 24 h

Table 4.18

Contact studies with $1x10^{-4}$ N $CsNO_3$/1N NaOH at 24 h contact time

Resin code	Resin name	% Cs(I) complexed	D
SN-04-163D	HSR[a]	33.5	34.5
SN-04-267	PER[b]	8.10	2.28
SN-04-281D	HSR[c]	35.6	27.7
SN-04-220	HCR[d]	96.7	1206
SN-04-252	BPCER[e]	43.9	67.7

a Hydroxystyrene resin prepared from HCC copolymer
b Diethoxyphosphoryloxypolystyrene
c Hydroxycalix[4]arene resin
d Hydroxystyrene resin made from 5% DVB gel copolymer
e Bis(diethoxyphosphoryloxy)calix[4]arene resin

decreased the percent Cs(I) complexed to 8.10 % (D = 2.28). The phosphoryl oxygens are probably of not high enough basicity to complex Cs(I). The BPER resin, having two phenolic oxygens bearing phosphate ester groups and one unsubstituted -OH group complexed 43.9% Cs(I) (D value of 67.7). This value is significantly lower than HCR, but was comparable to HSR. The lower percent Cs(I) complexed could be due to steric hindrance from the large phosphate ester groups disallowing the Cs(I) into the cavity and the absence of more than one phenoxide ligand.

Complexation studies with transition metal ions. The metal ion complexation study from 0.01 N HNO_3 is presented in Table 4.19. HSR and HCR performed poorly at this pH. BPCER, however followed an interesting trend. Fe(III) and Pb(II) were quantitatively complexed from solution while Cu(II) and Ni(II) were 66.6% (D value of 166) and 37.5% (D value of 51.7) complexed, respectively. The selectivity displayed by the resin could be due to three possible reasons:

(1) *Phosphoryl oxygens act as independent binding sites.* The only difference between the phosphorylated calix[4]arene resin (BPCER) and hydroxycalix[4]arene resin (HCR) is the presence of two phosphate ester groups attached to the phenolic oxygens in the calixarene moiety. To determine if the selectivity was attained only through coordination by phosphoryl oxygens, complexation studies were performed with phosphorylated hydroxystyrene resin (PER, SN-04-267). If this resin displays selectivities as BPER, then one can conclude that coordination by phosphoryl oxygen was responsible for the selectivity. However, the resin

Table 4.19

Metal ion complexation from 0.01 N HNO_3*

Resin code	Resin name	Fe(III)	Pb(II)	Cu(II)	Ni(II)
SN-04-178	PAR	100†(∞)‡	100 (∞)	99.3(1.7x10^4)	100(∞)
SN-04-163D	HSR	2.82(1.85)	3.02(1.96)	5.77(3.95)	2.50(1.60)
SN-04-220	HCR	6.00(2.91)	7.36(3.67)	13.6(7.25)	7.50(3.77)
SN-04-252	BPCER	100(∞)	100(∞)	66.6(166)	37.5(51.7)
SN-04-267	PER[a]	10.5(3.33)	12.0(3.68)	5.19(1.40)	4.73(1.36)
SN-04-281D	HSR	10.0(5.61)	12.1(6.80)	4.78(2.48)	8.39(4.56)
SN-04-286	PER[b]	10.0(5.65)	3.76(1.99)	4.78(2.56)	8.39(4.43)

* The concentrations of the contact solutions were 1x10^{-4} N M^{n+}
† Percent metal complexed
‡ Distribution coefficient
a Prepared from SN-04-163D
b Prepared from SN-04-281D

(PER) had poor affinities for all the metal ions studied. Before making conclusions about the inability of PER to complex metal ions, accessibility also needs to be considered. Since the resin is hydrophobic, inability of the metal ions to access the binding sites could be a reason for poor affinities. Hence an analogous PER prepared at a smaller particle size (SN-04-286) was studied. The increased surface area could allow for increased accessibility, but it performed similarly to SN-04-267 suggesting that low complexation was not due to decreased accessibility but the inability of the phosphoryl oxygen to coordinate the metal ions.

(2) *Ion exchange by the possible presence of phosphorus acid sites in the calix[4]arene moiety*: Increased complexation of metal ions could be due to ion-exchange of the metal ions. Resin having phosphorus acid ligands, PAR (SN-04-278) was found to quantitatively complex the metal ions studied (except for Cu(II), 99.3% complexed). The lack of selectivity shown by this resin confirms the absence of phosphorus acid sites in BPER.

(3) *Cooperation of the phosphoryl oxygens due to preorganization around the cavity*: Complexation studies with HCR, HSR, PER and PAR have shown that the cavity, binding to phenolic or phosphoryl oxygens and ion-exchange were not responsible for the unique selectivities displayed by the phosphorylated calix[4]arene resin (BPER). Phosphoryl oxygens by themselves might not be effective in complexing metal ions, but preorganization of the ligand around the cavity may induce cooperation

resulting in selective complexation of metal ions.

Complexation of the metal ions from a 0.10 N HNO_3 solution was also (Table 4.20). Complexation by HSR, HCR and PER was low and comparable to studies from 0.01 N HNO_3. For PAR, the affinity was in the order of Fe(III)>Pb(II)>Cu(II)≈Ni(II). At a lower pH, the mechanism of complexation changes to coordination and hence the displayed selectivity. In the case of BPCER, even though the resin was selective (with affinities in the order of Fe(III)>Pb(II)>Cu(II)>Ni(II)), the percent metal complexed was significantly lower than in 0.01 N HNO_3 solution.

A limited study with Fe(III) in a pH 5 acetate buffer (0.60 N) showed for HSR (SN-04-163D), HCR (SN-04-220) and PER (SN-04-144), percent complexation of 50.9% (D value of 72.8), 45.6% (D value of 35.0) and 17.5% (D value of 8.41), respectively. Decreased proton competition for the oxygen allowed for increased complexation by these resins. Studies were also performed for Eu(III) complexation from a 0.10 N HNO_3 solution with HSR (SN-04-163D), HCR (SN-04-220) and PAR(SN-04-178). Complexation of Eu(III) was quantitative in PAR and 0% for the other two. While inability of phenolic oxygens to bind the metal ion was reason for the lack of Eu(III) complexation by HSR and HCR, the ability of the phosphoric acid resin (PAR) to ion-exchange was the reason for the quantitative complexation by this resin.

Conclusions

There is no literature precedent for immobilizing calix[4]arene onto crosslinked polymer supports. Both the calix[4]arene and its phosphorylated analogues have been successfully immobilized on to the polymer support in this research. HCR had a high

Table 4.20

Metal ion complexation from 0.10 N HNO_3*

Resin code	Resin name	Fe(III)	Pb(II)	Cu(II)	Ni(II)
SN-04-267	PER	4.16†(1.17)‡	5.03(1.38)	7.46(2.24)	6.15(1.83)
SN-04-178	PAR	98.2(5863)	68.2(296)	49.5(131)	43.5(104)
SN-04-163D	HSR	4.86(3.20)	5.86(3.91)	5.36(7.41)	5.49(3.63)
SN-04-220	HCR	2.47(1.09)	8.83(4.19)	5.36(2.45)	5.49(2.49)
SN-04-252	BPER	79.7(330)	68.1(161)	11.2(8.91)	5.00(4.36)

* The concentrations of the contact solutions were $1x10^{-4}$ N M^{n+}

† Percent metal complexed

‡ Distribution coefficient

affinity for Cs(I) in basic solutions. The receptor property of the calix[4]arene combined with coordination by phenolic oxygens was the reason for its high affinity.

Preorganization of the phosphoryl ligands around the calix[4]arene cavity allowed the ligands to cooperate in the selective complexation of metal ions from dilute acid solutions (0.01 N HNO_3). When the acidity of the solution was increased to 0.10 N HNO_3, there was decreased complexation due to proton competition for the binding sites. The selectivity, however, was retained.

Immobilization of calixarene on to crosslinked polymer supports has opened up new avenues for synthesizing highly selective polymer supported reagents. To exploit this enormous potential, one needs to first understand the mechanism of complexation. Future research efforts should be directed towards this.

CHAPTER 5

EXPERIMENTAL PROCEDURES

All chemicals were used without further purification and were obtained from common chemical companies. Metal ion solutions for contact studies were prepared using Class A glass pipettes and volumetric flasks.

Synthesis

Vinylbenzyl chloride copolymer synthesis[115]

Copolymer beads were prepared either as gels or MRs by suspension copolymerization. The percent crosslinking with divinylbenzene was varied according to needs. A representative procedure for the synthesis of 150 g polyvinylbenzyl chloride beads crosslinked with 2% divinylbenzene by suspension copolymerization is discussed.

The monomers and the initiator forming the organic phase was dispersed in water containing suspending agent and stabilizer. The organic phase comprising of 143.1 g vinylbenzyl chloride (VBC), 5.4 g divinylbenzene (at 55.4% purity) and 1.5 g benzoyl peroxide was mixed throughly in a 250 mL Erlenmeyer flask. The aqueous phase consisted of 1.44 g pharmagel dissolved by heating to 50°C in 158.3 mL water. This was then added to a solution prepared by dissolving 17.9 g polydiallyldimethylammonium chloride (PADMAC) and 9.5 g boric acid in 316.5 mL water. The pH of the aqueous phase was adjusted to 10.3 by adding 50% NaOH solution. Both the aqueous and organic phase were sparged with nitrogen for 10 minutes. The aqueous phase was poured into a 3 necked round bottom flask fitted with condenser, nitrogen inlets, thermometer and

overhead stir apparatus (stir motor, shaft with a single paddle blade and stir bearing). The height of the stir shaft was adjusted till the paddle was just immersed in the aqueous phase. The organic phase was added, and the stir motor turned on for 2 minutes, at the end of which no separation of phases occurred. The stir speed was set for the desired beads size (for e.g., a stir speed of 730 RPM yielded predominantly beads with a size of 0.075-0.15 mm). The reaction mixture was heated to 80°C over a 2 h period (7°C every 15 minutes) with a heat lamp and maintained at this temperature for 10 h. The temperature was controlled with a thermowatch sensor attached to the thermometer. At the end of this period, 100 mL of water was added and the mixture refluxed for 2 h. The excess solution was siphoned off and the beads were washed three times each with 10^{-4} N HCl, soxhlet extracted with toluene for 17 h, and oven dried at 60°C. The beads were sieved to the desired size using U.S. standard screens. Macroporous copolymer beads (MR) were prepared using a similar procedure, except that 50% of the organic phase was replaced by 4-methyl-2-pentanol as the diluent.

Synthesis of monophosphonic acid resin[116]

VBC copolymer beads crosslinked with 2% DVB gel (15 g) was placed in a 500 mL three necked round bottom flask fitted with a stir apparatus and condenser. Triisopropyl phosphite (150 mL) was added and the mixture refluxed for 17 h. The solution was siphoned off, beads washed with ethanol and water (3 times each) and hydrolyzed further by refluxing with 200 mL of conc HCl for 17 h. The resin was washed three times with water, placed in a fritted glass column, and conditioned by successive elutions with 1 L of water, 4 wt% NaOH, water, 4 wt% HCl and water. It was further

soxhlet extracted with water for 17 h, reconditioned and characterized by percent solids, phosphorus elemental analysis and acid capacity.

Synthesis of bifunctional phosphonic/sulfonic acid resin[116]

The phosphonate ester was prepared using similar procedures described in the earlier section. The Büchner dried phosphonate ester resin, 15 g, was then extracted with 150 mL of heptane to remove water trapped in the micropores, transferred to a 250 mL three neck round bottom flask fitted with a stir apparatus and addition funnel, and swelled in 150 mL of ethylene dichloride (EDC) for 1 h. A mixture of 15 mL of chlorosulfonic acid/60 mL EDC was added dropwise via addition funnel while the flask was cooled with an ice-bath. The reaction was allowed to proceed at room temperature for 48 h. The excess solution was siphoned off and the resin quenched with aqueous dioxane (in the sequence 90%, 75%, 50%, 25% and 10%). It was then transferred to a glass frit column, conditioned by eluting with 1L each of water, 4 wt% NaOH, water, 4 wt% HCl and water, and characterized by percent solids, phosphorus elemental analysis and acid capacity.

Synthesis of monocarboxylic acid resin

VBC copolymer beads crosslinked with 2% DVB (18 g) were swelled with 200 mL of acetonitrile in a 500 mL three necked round bottom flask fitted with a condenser and stir apparatus. An aqueous solution of potassium cyanide, prepared by mixing 76.8 g KCN in 200 mL of water was added to the round bottom flask and heated at reflux for 72 h. The beads were recovered, washed three times with water and hydrolyzed by refluxing with 200 mL conc HCl for 24 h. The resin was washed with water and

conditioned in a glass frit column with 1 L elutions of water, 4 wt% NaOH, water, 4 wt% HCl and water, and characterized by percent solids, acid capacity and FTIR.

Synthesis of bifunctional phosphonic/carboxylic acid resin

Cyanation of VBC copolymer beads (15 g) was carried out by the procedure described in the previous section but, the time of the reaction was decreased to 24 h to allow for partial cyanation. The excess solution was removed and the resin washed with water and ethanol (three times each) followed by refluxing with 200 mL triisopropyl phosphite for 24 h. After reaction, the solution was siphoned off and the beads washed with water and hydrolyzed by refluxing with 200 mL of conc HCl for 24 h. The bifunctional resin was washed with water and conditioned in a glass frit with 1 L elutions of water, 4 wt% NaOH, water, 4 wt% HCl and water. Resin characterization was done by percent solids, phosphorus capacity, acid capacity and FTIR.

Synthesis of phosphonoacetic acid resin

NaH (4 g) was dispersed in 80 mL of xylene (dry) contained in a three necked 250 mL round bottom flask fitted with a stir apparatus, condenser and addition funnel. 25g of triethylphosphonoacetate was added dropwise to this mixture and the reaction proceeded until bubbling subsided. VBC copolymer gel crosslinked with 2% DVB (7 g) was added and the mixture refluxed for 24 h. The resin was washed with absolute ethanol (three times), solvent exchanged 3 times with dry $CHCl_3$, preswollen in 100 mL dry $CHCl_3$ and 25 g of bromotrimethylsilane added. The mixture was heated at reflux for 24 h. A gelatinous mass that was formed dissolved by adding ethanol, the excess solution removed, the resin washed three times with acetone and hydrolyzed by refluxing with 150

mL 3 N NaOH for 24 h. The beads were recovered, washed with water and conditioned in a glass frit by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. The resin was characterized by percent solids, phosphorus capacity and acid capacity.

Synthesis of poly(4-chlorophenylbenzoate) resin

VBC MR copolymer beads crosslinked with 5% DVB (5 g) was swelled in 125 mL of DMSO for 2 h in a 3 necked round bottom flask fitted with an overhead stirrer and an condenser. $NaHCO_3$ (15 g) was then added and the mixture refluxed for 8 h. The aldehyde resin obtained was washed with hot water, ethanol and water. The oxidation of the aldehyde resin was carried out in two steps to ensure complete conversion to carboxylic acid. First, 100 mL of 30% aqueous dioxane and 200 mL of 3 N HNO_3 was added and the mixture refluxed for 17 h. After the resin was washed 3 times with water, 100 mL of dioxane and 200 mL 30 wt% H_2O_2 was then added and the mixture heated at 80°C for 17 h. The resin was washed 3 times with water after the excess solution was siphoned off.

The Büchner dried resin (2 g) was placed in a 250 mL three necked round bottom flask fitted with a condenser and overhead stirrer, azeotropically distilled with 100 mL of heptane, and 75 mL of thionyl chloride added and refluxed for 24 h. The excess thionyl chloride was siphoned off and the acid chloride resin washed three times with toluene under an atmosphere of nitrogen. The resin was then allowed to swell in 50 mL of dry pyridine and a solution of 11.1 g 4-chlorophenol dissolved in 50 mL of dry pyridine added and heated at reflux for 24 h. The solution was siphoned off and the beads washed with

water, ethanol, and soxhlet extracted with ethanol for 17 h and vacuum dried overnight at 80°C. It was characterized by chlorine elemental analysis.

Synthesis of tetra-t-butylcalix[4]arene[109]

A mixture of 100 g t-butylphenol, 67.4 g formalin (37 wt% formaldehyde) and 2.4g 50 wt% NaOH were weighed into a 1 L (ground glass jointed) Erlenmeyer flask fitted with a dean stark trap and condenser. The flask was placed in oil-bath maintained at a temperature of 120°C for 3 h. An yellow friable solid was obtained. This was then combined with two more batches prepared similarly, powdered and placed in a 5 L three necked round bottom flask fitted with stir apparatus, Claisen's adaptor (fitted with a thermometer) and gas inlets. Diphenyl ether (3 L) was added and the mixture heated to 150°C under a vigorous flow of nitrogen (to remove the water that was formed). After approximately 30 minutes, the temperature was increased to 250°C, the condenser (with its mouth attached to a tube containing the Drierite) fitted and the mixture heated for 15 h. At the end of the reaction, it was treated with 3 L of ethyl acetate for 30 minutes and the slurry filtered through a glass-frit funnel to recover the solid and washed further with 1 L glacial acetic acid for 30 minutes. The crude product recovered was purified by crystallization.

Crystallization procedure. The crude product (5 g) was dissolved by heating with 75 mL of toluene. A light yellow solution was obtained. A glass funnel (ground glass jointed) was fitted to a 250 mL Erlenmeyer flask containing 25 mL toluene, pleated filter paper placed in its mouth and covered with a glass petri-dish. The setup was heated in a hot plate. As the toluene started to boil and condensation started to occur on the petri-dish,

the hot yellow solution containing the crude product was poured quickly into the funnel and the filtrate was allowed to crystallize overnight. The crystals were recovered, vacuum dried at 60°C overnight to obtain shiny-white platelets in 35% yield. The compound was characterized by melting point measurement and FTIR.

Synthesis of tetrahydroxycalix[4]arene[109]

Dealkylation of TBC was done by a reverse Friedel-Crafts reaction. A mixture of $AlCl_3$ (588 g) and toluene (2 L) was placed in a 5 L three necked round bottom flask fitted with a stir apparatus and gas inlet tubes. Under a gentle sweep of nitrogen, 560 g TBC, 379 g phenol and 2 L of toluene were added and the reaction proceeded at room temperature for 4 h. The mixture was poured into a large beaker containing 1 L of 4 wt% HCl and stirred throughly. The organic phase was separated using a separatory funnel and the solvent removed by a rotary evaporator maintained at 60°C. An orange colored solid that was recovered was washed with 1 L methanol for 30 minutes and recovered as a white powder by filtration. The powder was then taken in a large beaker and dissolved by heating in 2 L chloroform, followed by slow addition of methanol (upto 2.5 L). The mixture was allowed to stand overnight and the crystals recovered by filtration. The compound was vacuum dried at 60°C overnight to obtain white plate like crystals in 72% yield. It was characterized by melting point measurements, FTIR and mass spectrometry.

Synthesis of tribenzoyloxycalix[4]arene[109]

THC (80 g) was dissolved in 900 mL of pyridine in a 500 mL three necked round bottom flask fitted with an addition funnel, gas inlet tubes and an overhead stirrer. Benzoyl chloride (195 mL) was added over a 15 minute period via addition funnel while

the mixture was being cooled in an ice-bath. The reaction was proceeded for an hour each at ice-bath and room temperature. It was poured into a beaker containing 1 L of water and filtered to obtain yellowish-white solid. The crude product was dissolved by heating in 800 mL of chloroform followed by methanol addition (≈2 L). The mixture was allowed to stand overnight. The crystals were recovered by filtration, vacuum dried overnight at 60°C and obtained in >90% yield. It was characterized by melting point measurements and FTIR.

Synthesis of bis(diethoxyphosphoryloxy)calix[4]arene[110]

THC (150 g) was dissolved in 2 L chloroform (dry) and placed in a 3 L three necked round bottom flask fitted with a condenser, addition funnel and overhead stirrer. Triethylamine (375 mL), DECP (275 mL) added and the mixture refluxed for 5 h. Following solvent removal using a rotary evaporator at 60°C, the crude produce was crystallized from 2 L isopropanol to obtain white plate-like crystals in 65% yield. The compound was characterized by phosphorus elemental analysis, melting point measurement and FTIR.

Synthesis of hydroxycalix[4]arene ester resin

Poly VBC MR copolymer beads crosslinked with 5%DVB (5g) was placed in a 250 mL three necked round bottom flask equipped with a condenser and over head stirrer. DMSO (125 mL)and $NaHCO_3$ (15 g) were added followed by refluxing the mixture for 8 h. The aldehyde resin obtained was washed with hot water, ethanol and water. The conversion to carboxylic acid resin was achieved in two steps. First, 100 mL of 30% aqueous dioxane and 200 mL of 3 N HNO_3 was added and the mixture refluxed for 17 h.

After water washing the resin three times, the second step was carried out where, 100 mL of dioxane and 200 mL 30 wt% H_2O_2 were added and heated at 80°C for 17 h. The carboxylic acid resin was washed 3 times with water after siphoning off the excess solution.

The resin was Büchner dried and 2.6 g was placed in a 250 mL three necked round bottom flask fitted with a condenser and overhead stirrer, azeotropically distilled with 100 mL of heptane to remove water trapped in the beads. Heptane was removed and 75 mL of thionyl chloride was added and the mixture refluxed for 24 h with the mouth of the condenser fitted with a Drierite tube. The excess thionyl chloride was removed and the acid chloride resin was washed three times with toluene under an atmosphere of nitrogen. Following this, the resin was swelled in 50 mL of dry pyridine and a solution of 20.4 g THC dissolved in 100 mL dry pyridine was added and refluxed for 24 h. The solution was siphoned off and the beads were washed with water, acetone, toluene, and acetone. The resin was conditioned in a glass frit column by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. It was characterized by percent solids and acid capacity.

Synthesis of polymer-supported phenol

A mixture of 1.45 g NaH, 3.1 g phenol and 100 mL dioxane (dry) were mixed in a 250 mL ground glass jointed Erlenmeyer flask fitted with a Claisen's adaptor and gas inlet tubes under a gentle sweep of nitrogen for 1 h. VBC copolymer beads (2 g) were placed in a three necked 250 mL round bottom flask equipped with a condenser (containing a Drierite tube) and an overhead stirrer. The solution was transferred from the Erlenmeyer

flask to the round bottom and the mixture refluxed for 17 h. The excess solution was removed and the beads washed with dioxane, water and acetone (three times each) and vacuum dried overnight at 80°C. The resin was characterized by chlorine elemental analysis.

Synthesis of polymer-supported tribenzoyloxycalix[4]arene resin

VBC MR copolymer beads crosslinked with 5% DVB (5 g) were swelled in 150 mL of DMF for 2 h in a three necked 2 L round bottom flask equipped with an overhead stirrer and condenser (containing a Drierite tube). A solution formed by dissolving 57.0 g tribenzoyloxycalix[4]arene in 750 mL DMF was contained in a 1 L Erlenmeyer flask fitted with a Claisen's adaptor and gas inlet tubes and 6.6 g NaH was added under a gentle sweep of nitrogen. The reaction was proceeded for 2 h at the end of which an orange colored solution was obtained. This was transferred to the round bottom containing the beads and the mixture refluxed for 72 h. The excess solution was siphoned off and the resin washed three times each with DMF, water and acetone. It was vacuum dried at 90°C overnight, and characterized by FTIR and chlorine elemental analysis.

Synthesis of hydroxycalix[4]arene resin

BzCR (5 g) was placed in a 500 mL round bottom flask equipped with a condenser and an overhead stirrer and swelled in 200 mL of THF for 2 h. A solution of 40 g 50 wt% NaOH, 100 mL water, 200 mL ethanol was added and the mixture refluxed for 48 h. The excess solution was siphoned off, the resin washed three times with water and conditioned in a fritted glass column by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. It was characterized by chlorine elemental analysis, percent solids and

phenolic acid capacity.

Synthesis of bis(diethoxyphosphoryloxy)calix[4]arene resin

To a solution formed by dissolving 57.0 g BPC in 750 mL DMF in a 1 L ground glass jointed Erlenmeyer flask (fitted with a Claisen adaptor and gas inlet tubes) was added 6.6 g NaH under a gentle nitrogen sweep. The reaction was proceeded for 2 h at room temperature. VBC MR copolymer beads crosslinked with 5% DVB were swelled in 100 mL DMF for 2h in a 2 L three necked round bottom flask fitted with a condenser (containing a Drierite tube) and an overhead stirrer. The solution from the Erlenmeyer was transferred to the round bottom and the mixture refluxed for 72 h. The excess solution was removed, the resin washed three times with DMF, water, dioxane, THF and acetone and the beads conditioned in fritted glass column by eluting with 1 L each of ethanol and water. It was characterized by FTIR, phosphorus and chlorine elemental analysis.

Attempted hydrolysis of BPCER

BPCER (1 g) was swelled with 25 mL dry chloroform for 2 h in a three necked 250 mL round bottom flask equipped with an overhead stirrer and gas inlet tubes. Bromotrimethylsilane (4 mL) was added and the reaction proceeded at room temperature for 24 h under an atmosphere of nitrogen. The excess solution was removed, the resin washed with chloroform, dioxane, and water and conditioned in a fritted glass column by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. It was characterized by percent solids, phosphorus elemental analysis, acid capacity and FTIR.

Polymerization of p-acetoxystyrene

The organic phase was prepared by mixing 2.3 g (5 wt%) divinylbenzene (at 55.4% purity), 21.5 g p-acetoxystyrene and 1.2 g benzoylperoxide (5 wt%). The aqueous phase made by combining 0.84 g polyvinyl alcohol (MW of 150000), 13.4 g $CaCl_2$ and 54 g water was transferred to a 250 mL three necked round bottom flask fitted with a condenser, stir apparatus and a Claisen's adaptor. The stir paddle was adjusted for it to be just immersed in the aqueous phase. The organic and aqueous phase were sparged separately with nitrogen for 15 minutes to exclude oxygen. The organic phase was then poured into the round bottom and the stir speed was adjusted to obtain the desired beads size. The temperature was controlled with a thermometer connected to a thermowatch sensor. The contents were heated to 85°C over a 2 h period and maintained at this temperature for 17 h. The beads were washed three times with water, soxhlet extracted with toluene for 17 h, oven dried at 60°C and sieved to the desired size using U.S. standard screens.

Synthesis of hydroxystyrene resin

Polyacetoxystyrene beads (4 g) were placed in a 250 mL three necked round bottom flask equipped with a condenser and overhead stirrer. A 29.6 wt% ammonium hydroxide solution (100 mL) was added and the reaction heated at 85°C for 7 h. The excess solution was removed and the resin washed three times with water. The hydrolysis was repeated three more time using fresh ammonium hydroxide (100 mL) each time at reaction times of 17 h, 7 h and 17 h. The excess solution was siphoned , the resin washed three times with water and conditioned in fritted glass column by eluting with 1 L each of

water, 4 wt% NaOH, water, 4 wt% HCl and water. The resin was characterized by percent solids, phenolic acid capacity and FTIR.

Synthesis of diethoxyphosphoryloxypolystyrene[117]

HSR (4.5 g) was swelled in a mixture of 60 mL anhydrous THF/16 mL triethylamine in a 250 mL three necked round bottom flask equipped with gas inlet tubes and addition funnel. A solution of 19.8 g diethylchlorophosphate in 30 mL anhydrous THF was then added dropwise under an atmosphere of nitrogen while the contents were being cooled in an ice-bath. The reaction was proceeded at ice-bath temperature for 2 h and at room temperature for 48 h. The excess solution was removed and the resin washed with dioxane, 100 mL 2 wt% NaOH solution, water, ethanol and acetone. After vacuum drying the resin at 80°C overnight, it was characterized by FTIR and phosphorus elemental analysis.

Synthesis of dihydroxyphosphoryloxypolystyrene

PER (5 g) was preswelled in 100 mL $CHCl_3$ for 1 h in a 250 mL three necked round bottom flask fitted with a condenser (containing a Drierite tube) and an overhead stirrer. Bromotrimethylsilane (25 mL) was added and the mixture refluxed for 17 h. The excess solution was removed, the resin washed with dioxane and water, and conditioned in a fritted-glass column by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. It was characterized by FTIR, percent solids, phosphorus elemental analysis and acid capacity.

Attempted synthesis of phosphine oxide resin

NaH (4.40 g) was suspended with 150 mL of toluene in a ground glass jointed

250 mL Erlenmeyer flask equipped with a Claisen adaptor and glass inlet tubes. Methylenebis(diisopropylphosphonate ester) (MDA, 34.4 g) was added to this mixture and stirred overnight under an atmosphere of nitrogen. It was then transferred to a 250 mL round bottom flask containing 1.53 g poly VBC. An overhead stirrer and a condenser were fitted and the mixture refluxed for 24 h. The resin was washed with ethanol and water after the excess solution was siphoned off. Hydrolysis of the ester was effected by refluxing with 150 mL conc HCl for 17 h. The resin was washed with water and conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water in fritted glass column. It was characterized by percent solids, acid capacity and phosphorus elemental analysis. Conversion to acid chloride was accomplished by placing the Büchner dried acid resin in a 250 mL three necked round bottom flask, extracting with150 mL heptane followed by refluxing with 100 mL thionyl chloride for 17 h. The resin was washed with toluene, solvent exchanged twice 100 mL of 70/30 v/v cyclohexane/THF mixture for 15 minutes and 7 mL phenyl lithium (1.8 M solution in 70/30 v/v cyclohexane/ether) added dropwise. The reaction was proceeded at room temperature for 42 h. The resin was washed with a dioxane/water mixture (with the amount of water being progressively increased) and conditioned by eluting 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. It was characterized by percent solids, phosphorus elemental analysis and acid capacity.

Synthesis of methylenebis(diphenylphosphine oxide)[118]

A solution of triphenylphosphine (26.2 g) in 200 mL anhydrous THF was placed in a 250 mL three necked round bottom flask, equipped with a magnetic stirrer and gas inlet

tubes. Lithium (1.58 g) cut into small pieces was added to the solution and the mixture stirred overnight under an atmosphere of nitrogen. It was then transferred into a 3 necked 250 mL round bottom flask equipped with a condenser and a magnetic stirrer through a double tipped needle. A solution of 9.35 g t-butyl chloride in 50 mL THF was added, and the mixture refluxed for 45 minutes. On cooling a solution of 4.25 g methylene chloride in 50 mL THF was added dropwise and the mixture refluxed for 5 h. It was cooled, centrifuged to remove solid LiCl and the solvent removed by a rotary evaporator (maintained at a temperature of 60°C) to obtain a greenish yellow oil. It was crystallized from ethanol (100 mL) to obtain glistening needle like crystals in 32% yield. The product was characterized by FTIR and phosphorus elemental analysis. The oxidation of the phosphine to phosphine oxide was effected by reacting 6 g of the diphosphine with 100 mL 30 wt% hydrogen peroxide overnight in a 250 mL Erlenmeyer flask. The suspension was filtered, crude product recovered, and crystallized from 50 mL toluene. It was characterized by FTIR and phosphorus elemental analysis.

Synthesis of Diphonix-A gel copolymer beads[12]

An organic phase comprising of 92.8 g vinylidenedtetraisopropyldiphsophonate ester (VDPE), 53.7 g VBC, 31.0 g acrylonitrile (AN), 18.6 g DVB and 10.3 g azobisisobutyronitrile (AIBN) were mixed in a 500 mL Erlenmeyer flask. This mixture was then sparged with nitrogen for 15 minutes. The aqueous phase containing 285.5 g $CaCl_2.2H_2O$, 3.10 g Gohsenol (polyvinyl alcohol) and 550 g water was added to a 1 L three necked round bottom flask, fitted with a stir apparatus, Claisen adaptor, condenser and gas inlet tubes. The height of the stir paddle was adjusted so as to be just immersed in

the aqueous phase. After sparging the aqueous phase with nitrogen, the organic phase was poured into the flask and the stir speed adjusted for the desired beads size. The temperature was increased gradually to 60°C and held at this temperature for 1 h. The following heating sequence was followed: 1 h at 70°C, 2 h at 75°C and 17 h at 80°C. After polymerization, the beads were washed three times with water, soxhlet extracted with toluene for 17 h, oven dried at 60°C and sieved to the desired beads size using U.S. standard screens.

Synthesis of Diphonix-Cs gel resins[119]

Diphonix-A copolymer (5 g) was placed in a 250 mL three necked round bottom flask fitted with an overhead stirrer and condenser. Conversion of the chloro groups to aldehyde was effected by refluxing with a mixture of 15 g $NaHCO_3$, and 125 mL dimethyl-sulfoxide (DMSO) for 8 h. The excess solution was removed and the beads washed with hot water, ethanol and water. A mixture of 31.0 g phenol, 21.4 g formalin (37 wt% aqueous formaldehyde) and 0.36 g oxalic acid were added and refluxed for 17 h. The excess solution was siphoned off, the resin washed three times with acetone and the procedure repeated again. After water washing, the resin was conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. It was characterized by percent solids and acid capacity.

Synthesis of spacer chain α-ketophosphonic acid resin

Polystyrene copolymer crosslinked with 2% DVB(15 g) was swelled in 100 mL ethylene dichloride (EDC) in a 500 mL three necked round bottom flask fitted with an overhead stirrer and condenser. $AlCl_3$ (48 g), a solution of 36 g succinic anhydride in 200

mL nitromethane were then added while the round bottom flask was cooled under an ice-bath. The reaction was allowed to proceed at room temperature for 48 h. It was poured into ice, mixed throughly, the slurry wet sieved to recover the beads. They were washed with water, 4 wt% HCl, water, dioxane and water. It was conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water and characterized by percent solids and acid capacity. After Büchner drying the acid resin, it was extracted with 200 mL heptane, and refluxed with 250 mL $SOCl_2$ for 48 h. The excess toluene was siphoned off and the resin washed 5 times with toluene. Triethyl phosphite (200 mL) was added and the mixture refluxed for 17 h. The resin was washed ethanol and water and hydrolyzed subsequently by refluxing with 200 mL conc HCl for 24 h. It was washed with water and conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. The resin was characterized by percent solids, acid capacity and phosphorus elemental analysis.

Attempted Strecker reaction on aldehyde resin

VBC copolymer beads at 2% crosslink level (5 g) was refluxed with a mixture of 15 g $NaHCO_3$, 125 mL dimethyl sulfoxide (DMSO) in a 250 mL three necked round bottom flask fitted with a stir apparatus and condenser for 8 h. The resin was washed 3 times each with hot water, ethanol and water and recovered. The aldehyde resin (3 g) was swelled in 50 mL of dimethylformamaide (DMF) and 50 g diethyl phosphite and 26.2 g ammonium acetate was added. The contents (placed in a 250 mL 3 necked round bottom flask fitted with a condenser and stir apparatus) were refluxed for 72 h. The resin was washed three times with water and methanol, soxhlet extracted with methanol for 17 h and

vacuum dried at 60°C over night. It was characterized by nitrogen and phosphorus elemental analysis. It was hydrolyzed by refluxing with 150 mL conc HCl for 24 h. The resin was washed with water, conditioned using procedures described earlier and characterized by percent solids, phosphorus and nitrogen elemental analysis and acid capacity.

Attempted aminophosphonate ester resin synthesis by reaction with benzylcarabamate

Aldehyde resin (2 g) was swelled overnight in 150 mL of glacial acetic acid in a 3 necked round bottom flask fitted with a stir apparatus and condenser. A mixture of 41 g benzyl carbamate, 84.2 g triphenyphosphite added, and refluxed for 17 h. The resin was washed 3 times with ethanol followed by soxhlet extraction with ethanol for 17 h. The resin was vacuum dried at 70°C overnight and characterized by nitrogen and phosphorus elemental analysis.

Attempted synthesis of the α-aminophosphonic acid resin via reduction of an oxime of the α-ketophosphonate ester

This resin was obtained by a multistep procedure.

Synthesis of carboxylic acid resin. Aldehyde resin(15 g) was placed in a 500 mL three necked round bottom flask fitted with stir apparatus and condenser and preswollen in 100 mL of a 30% aqueous dioxane solution. A 3 N HNO_3 solution (200 mL) was added and the refluxed for 17 h. The excess solution was removed and the resin washed three times with water, heated further with 100 mL dioxane and 200 mL of 30 wt% H_2O_2 at 80°C for 20 h. The resin was washed 3 times with water.

Synthesis of acid chloride resin. The carboxylic acid resin was Büchner dried, placed in a 3 necked 500 mL round bottom fitted with a condenser and overhead stirrer, and extracted with heptane for 4 h. The excess solution was removed, 250 mL thionyl chloride added and refluxed for 24 h. The resin washed three times with toluene.

Synthesis of α-ketophosphonate ester resin. Triisopropyl phosphite (200 mL) was added to the acid chloride resin and refluxed for 24 h. The resin was washed with ethanol, water and acetone and vacuum dried overnight at 70°C overnight. It was characterized by phosphorus elemental analysis.

Synthesis of oxime resin. The ketophosphonate ester resin was heated with a solution of 94 g hydroxylamine hydrochloride in 200 mL (1:1 v/v) pyridine/methanol (dry) at 80°C for 24 h. The excess solution was removed and the resin washed with methanol, water, acetone and ethanol and vacuum dried overnight at 70°C. It was characterized by nitrogen and phosphorus elemental analysis.

Reduction of the oxime resin. The oxime resin (15 g) was swelled in 40 mL of anhydrous tetrahydrofuran (THF) for 1 h. Chlorotrimethylsilane (123 mL) was mixed with 237 mL 2 M $LiBH_4$-THF solution in a 500 mL round bottom flask under an atmosphere of nitrogen to obtain a white suspension. This was transferred to the round bottom flask containing the resin through a double tipped needle. Brisk effervescence was observed following the transfer. The reaction was allowed to proceed at room temperature for 48 h. The resin was washed with dioxane, water and acetone and vacuum dried at 70°C overnight. It was characterized by nitrogen and phosphorus elemental analysis.

Hydrolysis of the aminophosphonate ester resin. After reduction, the resin was refluxed

with 200 mL of conc HCl for 17 h, washed three times with water and conditioned by the methods described earlier. It was characterized by percent solids, nitrogen and phosphorus elemental analysis and acid capacity.

Attempted synthesis of the β-aminiphosphonic acid resin

The resin was prepared by a mutistep synthesis.

Friedel-Crafts reaction of polystyrene beads. Polystyrene copolymer beads, 2% DVB crosslinked (10 g) were swelled in 40 mL of carbon disulfide for 48 h in a 500 mL 3 necked round bottom flask fitted with a condenser, overhead stirrer and gas inlet tubes. A mixture of 40 g $AlCl_3$ and 50 mL carbon disulfide was then added and purged with nitrogen. A solution of 39 g bromoacetyl bromide in 10 mL of carbon disulfide was added dropwise while the flask was being cooled in an ice-bath. The reaction was proceeded for 48 h at room temperature. The excess solution was removed and the resin quenched with aqueous dioxane (10%, 25%, 50%, 75% and 90%), followed by washing with water, ethanol and acetone and vacuum drying at 70°C overnight.

Synthesis of the β-ketophosphonate ester resin. The above resin was refluxed with 150 mL of triisopropyl phosphite and refluxed for 17 h. It was washed with water and ethanol after the excess solution was removed. Part of the resin was oven dried at 110°C and characterized by phosphorus elemental analysis.

Synthesis of the oxime resin. The resin was placed in a 1 L three necked round bottom flask equipped with overhead stirrer and condenser. It was solvent exchanged with methanol (three times), a solution of 69 g hydroxylamine hydrochloride in 500 mL of 1:1 v/v pyridine/methanol added and the reaction mixture heated at 90°C for 17 h. The resin

was washed three times each with water, dioxane and acetone and oven dried at 60°C for 4 h. It was characterized by nitrogen and phosphorus elemental analysis.

Reduction of the oxime resin. The oxime resin (10 g), 50 mL anhydrous THF were taken in a 250 mL three necked round bottom flask fitted with an overhead stirrer addition funnel and glass inlet tubes. The mixture was purged with nitrogen for 10 minutes. A 2 M solution of $LiBH_4$ (67.5 mL) was mixed with 34.3 mL of chlorotrimethylsilane in a 250 mL round bottom flask. The white dispersion obtained was transferred to the round bottom containing the resin using a double tipped needle and the reaction proceeded at room temperature for 48 h. The excess solution was siphoned off, the beads washed with THF, dioxane, water and acetone (three times each) and vacuum dried overnight at 70°C. The resin was characterized by nitrogen and phosphorus elemental analysis.

Synthesis of the β-aminophosphonic acid resin. Hydrolysis of the aminophosphonate ester resin was effected by placing 3 g of the resin in a 250 mL three necked round bottom flask equipped with overhead stirrer and condenser, and refluxing for 17 h with conc HCl. The beads were recovered, washed with water and conditioned by the methods described earlier. The resin was characterized by percent solids, phosphorus and nitrogen elemental analysis and acid capacity.

Characterization

Percent solids

All conditioned resins were stored under water. For characterization and complexation studies, the excess water in a resin was removed by a process called Büchner drying. Wet resin was placed in a Büchner funnel and covered with a square

latex sheet and held in place with a rubber band. A vacuum (710 mm Hg) was applied for 5 minutes. An amount of the Büchner dried resin was place in a preweighed scintillation vial. The weight of the resin was accurately determined with an analytical balance. The resin was then allowed to dry in a 110°C oven for 17 h. The vial was removed and allowed to cool in a desiccator and its mass after drying determined. The percent solids was calculated as:

$$\frac{\text{(Weight of the Büchner dried resin)x100}}{\text{(Weight of oven dried resin)}}$$

Total acid capacity

An accurate amount (≈1 g) of Büchner dried resin was accurately weighed into a 250 mL Erlenmeyer flask using an analytical balance. A volume of 200 mL standardized 0.10 N NaOH containing 5 wt% NaCl was transferred through a pipette and the flask was sealed with a ground glass stopper and gently stirred for 17 h. The solution was removed and two 50 mL aliquots were titrated to a phenolphthalein end point with a standardized 0.10 N HCl. The total acid capacity was calculated as:

$$\frac{\text{[(Volume NaOH)(N NaOH)]-[4(Volume HCl)(N HCl)]}}{\text{(wt. Büchner dried resin)(\%solids)}}$$

Phenolic -OH capacity[119]

Büchner dried resin was accurately weighed (≈0.5 g) into a 100 mL round bottom flask using an analytical balance. A volume of 25 mL standardized 0.10 N NaOH containing 5 wt% NaCl was transferred into the flask using a glass pipette and the mass of the flask was determined. The water was removed using a rotary evaporator by heating to

70°C until the resin appeared dry. The flask was removed and water added until the original total mass was obtained. The flask was sealed with a ground glass stopper and allowed to stir for 30 minutes. The solution was removed and two 10 mL aliquots were titrated against standardized 0.10 N HCl to phenolphthalein end point. The phenolic acid capacity was determined as:

$$\frac{[(\text{Volume of NaOH})(\text{N NaOH})]-[2.5(\text{Volume HCl})(\text{N HCl})]}{(\text{wt. Büchner dried resin})(\%\text{solids})}$$

Phosphorus elemental analysis

Phosphorus elemental analysis was done initially by the perchloric acid method. Perchlorate salts when allowed to dry are shock sensitive agents and, hence the safer sulfuric acid method was used subsequently. Both methods are described.

Perchloric acid method.[120] Oven dried resin (~20 mg) was accurately weighed into a 125 mL Erlenmeyer flask (samples done in duplicate to obtain concordant values). A mixture containing 5 mL conc HNO_3 and 10 mL of conc $HClO_4$ was added and heated on a hot plate for 2-3 h during which, the beads were completely digested and a clear solution obtained. The heating was monitored at all times to make sure that complete evaporation did not take place owing to the explosive nature of perchlorates. The solution was cooled and transferred quantitatively into a 100 mL volumetric flask and made upto mark. A 5 mL aliquot was transferred into a 50 mL volumetric flask. To this was added 3.5 mL conc $HClO_4$, 4.5 mL amidol solution (prepared by mixing 1 g recrystallized 2,4-diaminophenol dihydrochloride, 10 g Na_2SO_3, 2.7 g conc H_2SO_4 and 90 g water) and 3.5 mL molybdate solution (prepared by dissolving 4.4 g ammonium molybdate in 50 g water). A blank

solution was also prepared in another volumetric flask containing all the reagents except the phosphorus solution. The solutions were made upto mark and allowed to develop for 30 minutes. The phosphorus content was measured using a Bausch & Lomb spectrophotometer 21 set at a wavelength of 700 nm. The instrument was zeroed with blank and the absorbance value of the samples was then read. Calibration curve was obtained for the instrument using dihydrogen phosphate standards and the slope and the intercept values were determined. The phosphorus capacity was calculated (in mequiv/g) by the formula:

$$\frac{\text{(Absorbance)(1000 mL)}}{(g_{resin})(30.974\ \text{mg/mequiv})(\text{slope mL/mg})}$$

Sulfuric acid method. This method was developed at the Eichrom Industries by Dr. Frank Chang. Oven dried resin (~20 mg) was weighed accurately into a 125 mL Erlenmeyer flask (experiment done in duplicate), 400 μL of 0.5 M $CuSO_4$ solution and 10 mL conc H_2SO_4 solution added, and the mixture heated on a hot plate for 2-3 h until the beads were completely digested and a clear solution seen. The solution was allowed to cool and 75 mL water, and 2 g potassium persulfate added and the solution further heated for 2 h until the volume of the solution reduced to approximately 50 mL. On cooling, 50 wt% NaOH was added dropwise until the solution just turned brown. The solution was then brought to neutral pH by dropwise addition of 2 wt% H_2SO_4. This was transferred quantitatively to a 100 mL volumetric flask and made upto the mark. A 25 mL aliquot was transferred to a 50 mL volumetric flask and 10 mL of vanadate-molybdate solution (prepared by 2.5 g ammonium molybdate tetrahydrate, 0.13 g ammonium metavanadate, 33 mL conc HCl

and 67 g water) added and the solution made upto mark. A blank was also prepared without the analyte. The absorbance values were read as before and the phosphorus capacity (in mequiv/g) was determined using the formula:

$$\frac{4[(\text{Absorbance-intercept})/\text{slope}]}{[(30.974\ \text{mg/mequiv})(g_{\text{dry resin}})]}$$

Nitrogen Elemental Analysis[121]

Oven dried resin (~0.2 g) was weighed accurately into a 500 mL 3 necked round bottom flask and 0.25 g $CuSO_4$, 10 g K_2SO_4, 25 mL conc. H_2SO_4, a few boiling chips added successively. Two of its necks were stoppered while a long open end condenser was attached to the third one. The mixture was first heated gently for 2 h and then vigorously for 8 h. A light blue solution was obtained. The condenser was removed and any droplets of solution sticking on the walls of the condenser were washed down to the flask with minimum amount of distilled water. The stoppers were also removed and washed down to the flask with water. While one neck of the round bottom flask was fitted with an addition funnel containing 150 mL of 6 N NaOH, the other was fitted with a distillation set up. The end of the distillation set up contained a plastic funnel, the mouth of which was just immersed in a 600 mL beaker containing 50 mL of standardized 0.10 N HCl. The sodium hydroxide was slowly added with rigorous stirring. On complete addition, the solution (which turned brown) was heated to distill water into the beaker containing the acid. The solution being collected contains ammonia obtained by conversion from nitrogen in the resin. The collection was done until the distillate was no longer basic. At this point, the distillation set up was dismantled and the solution collected

in the beaker transferred quantitatively into a 250 mL volumetric flask and made upto mark. Two 50 mL aliquots were titrated against standardized 0.10 N NaOH solution containing 5 wt% NaCl to bromocresol green end point. The nitrogen capacity was calculated using the formula:

$$\frac{[(\text{Volume HCl})(\text{N HCl})-[5(\text{Volume NaOH})(\text{N NaOH})]}{g_{resin}}$$

Chlorine elemental analysis

The digestion of the resin was done in a Parr bomb calorimeter. Oven (~0.20 g) dried resin and 0.60 g of mineral oil were weighed accurately into a metal capsule. The top part of the bomb had a holder onto which the capsule was fitted. A 10 cm nickel alloy fuse wire was connected to the stem in the form of a loop with the loop just immersed in the oil contained in the capsule. A 5 mL solution of 5 wt% $NaHCO_3$ was added to the bomb and the wall rinsed with the solution. The top part was then fitted tightly and held in place with a screw cap. The bomb was filled with oxygen at 30 atm. The bleeder was opened to release all the oxygen. This procedure was repeated twice. Finally, the bomb was once again filled with oxygen at 30 atm and placed in a bucket of water with the bomb being completely submerged in it. The wire leads were attached and the fuse wire ignited. The bomb was allowed to cool, the bleeder opened to release the pressure and the screw cap opened. The contents of the bomb were transferred to a 400 mL beaker. The inner surface and the capsule were throughly washed with water into the beaker. The solution in the beaker was filtered into a 250 mL volumetric flask and made upto mark. Two 25 mL aliquots were transferred into a 125 mL Erlenmeyer flask, 2 mL 2 N HNO_3

and 10 mL 0.0500 N $AgNO_3$ added, and the solution heated in a hot plate until coagulation of AgCl was seen. The solution was filtered through a pleated filter paper into a 125 mL Erlenmeyer flask and 3 mL of $FeNH_4(SO_4)_2$ in 2 N HNO_3 was added. It was titrated against 0.05 N NH_4SCN to the first appearance of light brown color. The chlorine capacity was determined using the formula:

$$\frac{10[(\text{N } AgNO_3)(\text{Volume } AgNO_3)-(\text{N } NH_4SCN)(\text{Volume } NH_4SCN)]}{g_{\text{dry resin}}}$$

Attempted sulfur elemental analysis[122]

Oven dried resin (0.10 g) and 0.7 g mineral oil were accurately weighed into the capsule for a Parr bomb calorimeter. Nano-pure water (5 mL) was added to the bomb and the walls were rinsed throughly. The capsule was placed in the holder and 10 cm nickel alloy fuse wire was connected to the stem in the form of a loop with the loop just immersed in the oil of the capsule. The top part was fitted to the bomb and held tightly in place with a screw cap. Oxygen gas was filled at 30 atm pressure and the bleeder opened to release the gas. This was repeated twice and finally the bomb was once again filled with oxygen at 30 atm. It was completely submerged in a bucket of water and checked for any leaks. The leads were inserted and the fuse wire ignited. The bomb was allowed to cool, the pressure released and the contents washed into a 400 mL beaker with 90 mL of nano-pure water. Br_2 (3 mL) was added and heated until its color was completely discharged. A few drops of phenolphthalein was added and a 0.10 N NaOH solution added until it just turned pink. The contents were filtered through a pleated filter paper into a 250 mL Erlenmeyer flask. The solution was evaporated until the volume was

reduced to ≈20 mL. It was cooled and 0.05 N HCl was added dropwise until the solution just turned clear. Tetrahydroxyquinone (10.5 mg) and 20 mL ethanol were added and titrated with 0.02 N $BaCl_2$. Observation of the end point through an orange filter was attempted. However, due to cloudiness of the mixture, the end point could not be detected on a consistent basis. The sulfur capacity was calculated using the formula:

$$\frac{[(\text{N } BaCl_2)(\text{Volume } BaCl_2)]10}{g_{\text{dry resin}}}$$

Infrared spectroscopy

The infrared spectra of samples were recorded as KBr pellets on a Bio-Rad FTS-7 FTIR spectrometer. A total of 32 scans were accumulated at a resolution of 8 wavenumbers. The KBr pellet of a sample was prepared by first grinding it in an agate mortar and pestle. Approximately 120 mg of a 1 wt% mixture of sample in KBr was taken in a die and pressure was applied using a hydraulic pump to make the pellet.

Complexation Studies

Contact solutions

The contact solutions were prepared with nano-pure water along with reagent grade metal salts and acids.. Stock solutions were prepared in concentrations of 10^{-3} N in a 1 L volumetric flask using an appropriate matrix. Lower concentrations were prepared by subsequent dilutions. All contact solutions contained the appropriate metal nitrate and had a concentration of 10^{-4} N. They were prepared by pipetting 10 mL of the stock solution into a 100 mL volumetric flask and making upto mark with the appropriate matrix.

Metal ion studies

Contact studies were done by weighing an amount of Büchner dried resin that would give one milliequivalent ligand sites into a 20 mL scintillation vial (unless otherwise noted). The resin was preequilibrated with 10 mL of the appropriate matrix for 15 minutes in a Burrell wrist-action shaker. The solution was removed using a Pasteur pipet attached to an side-arm flask (fitted to an aspirator) through a rubber tubing. The preequilibration was repeated three more times. Contact solution (10 mL) was pipetted into the vial and then shaked for the appropriate time. The contacted solution was removed with a Pasteur pipette and transferred to a clean scintillation vial. The amount of metal ion complexed was determined using a Perkin-Elmer atomic absorption/emission spectrometer. Depending on the metal ion studied, the spectrometer was set either to an emission or absorption mode.

Atomic absorption/emission spectroscopy

The metal ion solutions were analyzed with a Perkin-Elmer 3100 atomic absorption/emission spectrometer. The appropriate parameters used for each metal ion studied are reported in Table 5.1. Europium and cesium solutions were spiked with 4000 ppm KCl to prevent ionization. A red filter was also used for the cesium analysis.

Table 5.1

Atomic absorption/emission parameters

Metal ion	AA/AE	Wavelength (nm)	Flame
Eu(III)	AE	459.4	nitrous oxide/acetylene
Cs(I)	AE	852.1	nitrous oxide/acetylene
Fe(III)	AA	248.3	air/acetylene
Ni(II)	AA	232.0	air/acetylene
Cu(II)	AA	324.8	air/acetylene
Zn(II)	AA	213.9	air/acetylene
Pb(II)	AA	283.3	air/acetylene
Cd(II)	AA	228.8	air/acetylene

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APPENDIX

A. Attempted synthesis of diphosphine oxide resin

Diphosphine oxide based compounds are neutral chelating agents and are known for their ability to selectively extract lanthanides and actinides.[43] Their immobilization onto a 2% DVB crosslinked VBC gel copolymer was attempted. Methylenebis(tetraisoporpyldiphosphonate ester) was dissolved in toluene and deprotonated with NaH (1 equivalent) overnight under an atmosphere of nitrogen. This mixture was then added to the copolymer beads and refluxed for 17 h. The beads were recovered, washed with toluene, ethanol and water. Hydrolysis of the ester was carried out by refluxing with conc HCl for 17 h. The resin was washed with water and conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. It had a 71.3% solids, a phosphorus capacity of 1.66 mequiv/g and an acid capacity of 2.90 mequiv/g. Within experimental error, the acid capacity was twice the phosphorus capacity indicating complete hydrolysis. The conversion to acid chloride was done by first extracting the Büchner dried resin with heptane and then refluxing with excess thionyl chloride for 17 h. The resin was washed with toluene and solvent exchanged three times with 70/30 v/v cyclohexane/THF mixture. To obtain the bis(diphenylphosphine oxide) resin, it was swelled in 100 mL of the mixed solvent followed by reaction with a solution of phenyl lithium(in cyclohexane-ether mixture). After a 48 h reaction at room temperature, the excess solution was siphoned off and the resin washed with toluene, aqueous dioxane (with the volume of dioxane being gradually decreased). It was conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water. It had a 67.5% solids, a phosphorus capacity of 0.84 mequiv/g and

an acid capacity of 2.53 mequiv/g. Compared to the diphosphonic acid resin, the phosphorus capacity of the phosphine resin was reduced by half while the acid capacity was similar. The results were inconclusive since the decreased phosphorus capacity suggested conversion to phosphine oxide, but, the high acid capacity could also be interpreted as lack of a reaction. It was thought that perhaps the incomplete chlorination of the diphosphonic acid with $SOCl_2$ resulted in the unreacted acid sites reacting with phenyl lithium and thus, hindering its reaction with the acid chloride sites. To test this hypothesis, synthesis of acid chloride resin from a phosphonate ester was attempted. A diisopropyl phosphonate ester resin was prepared by refluxing a mixture of 5% DVB-VBC gel copolymer and triisopropyl phosphite for 17 h. The beads were washed with ethanol and water and azeotropically distilled with heptane to remove any trapped water in the polymer matrix. They were then refluxed with thionyl chloride for 17 h. The chlorine capacity of the resin was found to be 1.56 mequiv/g (7.94 mequiv/g, theoretical). To test if the lack of chlorination was due to steric hindrance (caused by bulky isopropyl groups) or due to lack of reactivity of the ester, chlorination was attempted on a dimethylphosphonate ester resin (prepared by reaction of VBC copolymer with trimethyl phosphite). The chlorine capacity of the resin was 2.23 mequiv/g against an expected value of 7.94 mequiv/g for a completely chlorinated resin. The slightly higher phosphorus capacity was probably due to the less bulky methyl esters moieties in the resin and not due to higher functionalization. Thus, chlorination of phosphonate esters could not be accomplished due to poor reactivity of the ester groups.

Change in chlorinating agent (PCl_5) to effectively chlorinate phosphonic acid resin

was then attempted. Chlorination with a 12% DVB gel phosphonic acid in THF and methylene dichloride gave resins with chlorine values of respectively 0.066 mequiv/g and 1.58 mequiv/g. When the crosslink level of the phosphonic acid resin was decreased to 2% DVB, the resin had an increased chlorine capacity of 3.95 mequiv/g. At the most only 50% functionalization was obtained even with the lightly crosslinked resin. Due to lack of efficient chlorination the resin was unsuitable for further reaction with phenyl lithium. Hence, an alternate method of phosphine oxide immobilization was attempted.

Bis(diphenylphosphino)methane[118] converted to methylenebis(diphenylphosphine oxide) by reaction with 30 wt% H_2O_2 at room temperature overnight. It was characterized by phosphorus elemental analysis (4.54 mequiv/g). Subsequent deprotonation of this compound with NaH, followed by reaction with VBC copolymer beads could result in the synthesis of the diphosphine oxide-supported polymer. Future research can be focused on the immobilization of this ligand onto polymer supports and evaluating their ion complexing properties.

B. Synthesis of Diphonix-Cs gels

Diphonix-A 5% DVB copolymer gel was synthesized by copolymerizing VDPE, VBC, AN and DVB (5 wt%) with AIBN as the initiator. The -CH_2Cl groups were then oxidized by heating with DMSO and $NaHCO_3$ for 8 h to benzaldehyde groups. The phenol-formaldehyde polymer was then grafted to the copolymer beads through these sites. The grafting was achieved by refluxing the copolymer with phenol, formalin (37 wt% aqueous formaldehyde) and oxalic acid (catalyst). The time of reaction and concentration of the reagents were varied. Sulfonation of the resin was also done. The

different conditions under which these resin were made are summarized in Table B.1. Their ability to complex Cs(I) from a 1 N solution of NaOH at a 60 minute contact time is described in Table B.2.

For 5 g of the Diphonix resin, the amounts of phenol/formaldehyde/oxalic used were 31 g/21.4 g/0.36 g. In comparing A and B, the amount of reagents were doubled in the case of the latter and the reaction time in both the cases was 17 h. The percent Cs(I) complexed decreased from 98.3% (D of 859) to 91.2% (D of 184) when the amount of reagents were doubled. Since the total (OH) capacity was not obtained in the latter case, an exact correlation could not be made. It was speculated that the ratios in the case of former were more ideal for grafting the phenol-formaldehyde polymer. In comparing A and C, the reaction was repeated twice in the case of the latter. The total (OH) capacity increased from 1.55 mequiv/g (for A) to 2.54 mequiv/g (for C). Their complexing ability of Cs(I) also increased accordingly (98.3%, D of 859 to 99.1%, D of 1.90×10^3). Sulfonation of C was done by reacting with fuming sulfuric acid either for 4 h (resin D) or 30 minutes (resin E). Their acid capacities were respectively 5.94 mequiv/g and 3.23 mequiv/g respectively. Results from the acid capacity leads to the conclusion that both the resins were sulfonated and degree of sulfonation could be varied with time. In comparing the Cs(I) complexing abilities of resins C, D and E, it was seen that the non-sulfonated resin (C) performed the best (99.1%, D of 1.90×10^3) while the sulfonated resins did not complex quite as well. Partially sulfonated resin E, however, performed better than the fully sulfonated resin D (95.4%, D of 361 vs 77.2%, D of 79.6). The decrease in complexation by the resin D could be either due to a negative effect of sulfonic acid

Table B.1

Characterization of Diphonix-Cs gels

Resin code	Reaction conditions	% Solids	Acid capacity (mequiv/g)
SN-02-239A	A	64.5	-
SN-02-239B	B	67.0	1.55
SN-03-124A	C	65.5	2.54
SN-03-126	D	45.3	5.94
SN-03-138	E	51.4	3.23

A = (1:10:8 aldehyde sites:phenol:formalin, catalyst; 0.72 g oxalic acid), 1x17 h reflux.

B = (1:20:16 aldehyde sites:phenol:formalin, catalyst; 1.44 g oxalic acid), 1x17 h reflux.

C = (1:10:8 aldehyde sites:phenol:formalin, catalyst; 0.36 g oxalic acid), 2x17 h reflux.

D = (1:10:8 aldehyde sites:phenol:formalin, catalyst; 0.36 g oxalic acid), 2x17 h reflux, followed by 4 h sulfonation at room temperature with fuming sulfuric acid.

E = (1:10:8 aldehyde sites:phenol:formalin, catalyst = 0.36 g oxalic acid), 2x17 h reflux, followed by 0.5 h sulfonation at room temperature with fuming sulfuric acid.

Table B.2

Complexation of Cs(I) from 1 N NaOH at a 1 h contact time

Resin Code	Reaction Conditions	% Cs(I) complexed
SN-02-239A	A	98.3 (859†)
SN-03-239B	B	91.2 (184)
SN-03-124A	C	99.1 (1.90×10^3)
SN-03-126	D	77.2 (79.6)
SN-03-137	E	95.4 (361)

† distribution coefficient

groups on Cs(I) complexation or a lesser mequiv phenolic sites available for complexation. Sulfonated resin weighed more (due to its higher molecular weight) and in calculating distribution coefficient, one determines the mequiv absorbed per gram of dry resin. To correlate the distribution coefficients better, the mequiv metal absorbed per mequiv phenolic sites was divided by the mequiv metal in solution per mL of solution. This is defined as D'. The resins C and E had values of 1.07×10^6 and 7.07×10^4 respectively. Difference in complexing ability as can be seen was not quite that different when compared in terms of D'. However, the sulfonated version was still inferior. It was postulated that the complexation of Cs(I) was best attained in a hydrophobic environment which allows for a better π-π interaction. By sulfonating the resin, the hydrophilicity of the polymer matrix was probably hindering the optimum π-π interaction resulting in the decreased complexation.

A limited study was also done to determine the complexing ability of resin A in 0.01 N HNO_3 with various metal nitrates. These results are summarized in Table B.3. The metal ions studied were Fe(III), Ni(II), Cu(II) and Pb(II). The amounts complexed were respectively 54.3%, 0%, 6.65% and 21.1%. In the case of a Diphonix-Cs gel, there is a linear phenol-formaldehyde oligomer adjacent to the diphosphonate ester. It was hoped that an inter-ligand cooperation between the diphosphonate ester and the phenol-formaldehyde polymer would enhance metal ion affinities. A low complexation of the metal ions indicated lack of such cooperation. However, it must be noted that low complexation could also be due to the steric factors caused by the bulky isopropyl groups hindering the ability of the phosphoryl oxygens to coordinate with the metal ions. Further

Table B.3

Metal ion complexation studies of Diphonix-Cs gel (SN-02-239B) from 0.01 N HNO_3 at a 24 h contact time

Metal Ion	% Metal Complexed
Fe(III)	54.3 (27.9†)
Pb(II)	21.1 (6.33)
Ni(II)	0
Cu(II)	6.65 (1.82)

† distribution coefficient

studies with Diphonix-Cs gels prepared from ethyl esters could help in determining the possibility of inter-ligand cooperation in such resins.

C. Attempted synthesis of poly(VBC)- supported Novolac resins

Grafting of Novolac resins onto VBC copolymer was attempted. The VBC copolymer was first converted to the aldehyde resin by heating with a mixture of DMSO and $NaHCO_3$ for 8 h at reflux temperature. The Novolac polymer was then grafted onto the polymer support using the aldehyde sites as the handle. The type of support, percent DVB crosslinking, amounts of reagents (phenol, formalin & oxalic acid) were varied to maximize the percent functionalization. These results are summarized in Table C.1. It can be seen that the acid capacities were much lower than that for the Diphonix-Cs gels discussed earlier. As a consequence, the maximum amount of Cs(I) complexed by one of these resins was 89.4% (D of 286). Different variables discussed earlier were studied and still the results from Diphonix-Cs gels could not be matched. The inability to maximize the functionalization of VBC copolymer with Novolac is not clearly understood at the present time.

D. Study of spacer chain effect on complexation kinetics

α-Ketophosphonate resins have carbonyl and phosphoryl groups that can cooperate by an intra-ligand mechanism to selectively complex metal ions. In a typical α-ketophosphonate resin (Figure D.1), the carbonyl group is very close to the polymer backbone. It was hypothesized that by removing the ketophosphonate group farther from

Table C.1

Characterization of Novolac resins

Resin Code	Reaction Conditions	Type of Support	Particle Size (mm)	% Solids	Total (OH) capacity (mequiv/g)	% Cs(I) Complexed
SN-04-146	I	5% DVB MR	0.15-0.25	34.8	1.11	-
SN-04-156	I	5% DVB MR	0.15-0.25	36.4	0.93	-
SN-04-166	I	5% DVB MR	0.075-0.15	57.3	0.55	-
SN-04-167	I	2% DVB gel	0.075-0.15	69.9	0.83	72.7 (85.9†)
SN-04-234D	II	2% DVB gel	0.15-0.25	57.0	0.69	-
SN-04-240D	II	2% DVB gel	0.15-0.25	78.9	0.51	-
SN-04-246D	III	2% DVB gel	0.075-0.15	58.2	1.07	88.6 (235)
SN-04-255D	IV	2% DVB gel	0.075-0.15	58.8	1.30	89.4 (286)
SN-04-283C	III	5% DVB MR	0.15-0.25	21.6	1.42	51.4 (91.2)
SN-04-290D	II	1% DVB gel	0.075-0.15	54.8	1.17	83.7 (163)
SN-04-296D	V	2% DVB gel	0.075-0.15	62.1	-	72.8 (74.1)

† distribution coefficient
I = (1:10:8 aldehyde sites:phenol:formalin, catalyst = 0.36 g oxalic acid), 2x17 h reflux.
II = (1:10:8 aldehyde sites:phenol:formalin, catalyst = 0..36 g oxalic acid), 3x17 h reflux.
III = (1:10:8 aldehyde sites:phenol:formalin, catalyst = 0.72 g oxalic acid), 3x17 h reflux.
IV = (1:10:8 aldehyde sites:phenol:formalin, catalyst = 1.44 g oxalic acid), 3x17 h reflux.
V = (1:20:16 aldehyde sites:phenol:formalin, catalyst = 0.72 g oxalic acid), 3x17 h reflux

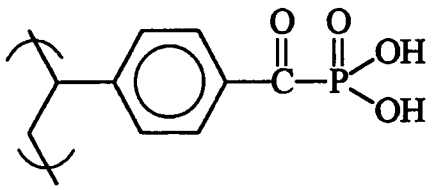

Figure D.1. Structure of α-ketophosphonic acid resin

the polymer backbone, the kinetics of complexation can be improved due to decreased steric hindrance. The synthesis and complexation of such a resin is discussed. The schematic representation of the synthesis is shown in Figure D.2. Friedel-Crafts acylation with succinic anhydride on a polystyrene copolymer gel crosslinked with 2% DVB (particle size of 0.075-0.15 mm) with $AlCl_3$ as catalyst yielded the carboxylic acid resin. The resin had a percent solids of 61.1% and an acid capacity of 3.02 mequiv/g (theoretical; 4.76 mequiv/g). Conversion to the acid chloride was accomplished by refluxing with thionyl chloride and subsequent reaction with triisopropyl phosphite provided the α-ketophosphonate group attached to the polymer backbone through a spacer chain. Hydrolysis of the resin by refluxing with conc HCl gave the spacer chain α-ketophosphonic acid resin (II). The resin had a percent solids of 62.3%, acid capacity of 4.16 mequiv/g and a phosphorus capacity of 1.25 mequiv/g. Based on the phosphorus and acid capacities, it was calculated that the resin contained 36% ketophosphonate sites, 24% carboxylic acid sites and the rest being unreacted styrene moieties from the first step. The kinetics of complexation of Eu(III) from 0.10 and 1.0 N HNO_3 solutions at 0.5 h and 24 h was compared with I (Table D.1). Their complexing abilities were similar for complexation from 0.10 N HNO_3 solution with equilibrium being reached even at 0.5 h contact time. However, the results of complexation from a 1.0 N HNO_3 solutions are quite surprising because, the resin without the spacer chain had faster kinetics. This was attributed to the decreased accessibility of the ions in to the polymer matrix. At this pH the only mechanism of complexation is through intra-ligand chelation. The slow kinetics was probably due to the decreased accessibility of the metal ions into the polymer matrix

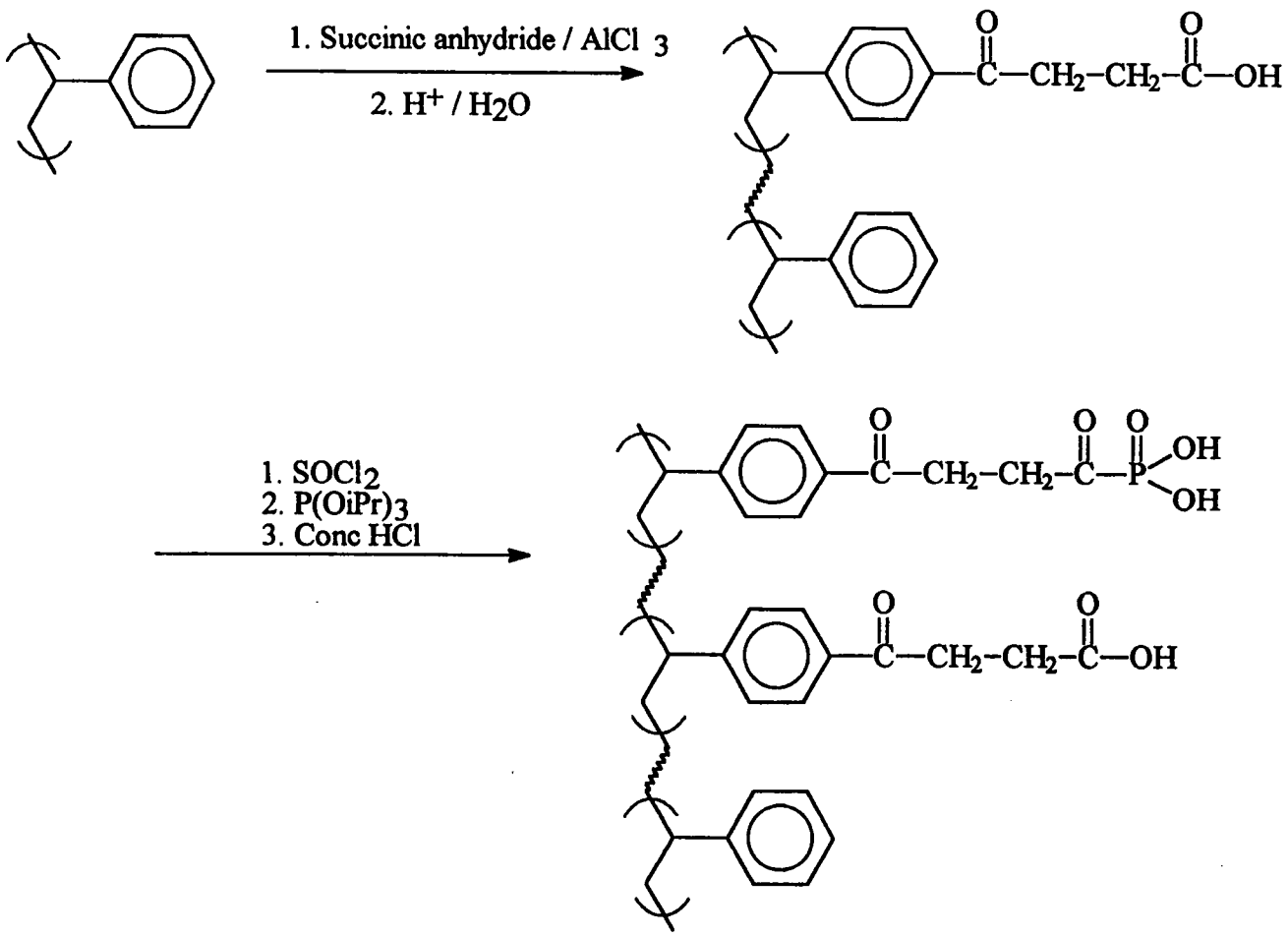

Figure D.2. Synthesis of spacer-chain α-ketophosphonic acid resin

Table D.1

Complexation of Eu(III) by ketophosphonic acid resins

	0.10 N HNO_3		1.0 N HNO_3	
Resin	0.5 h	24 h	0.5 h	24 h
α-ketophosphonate	99.3 ($4.59x10^3$)†	99.2 ($4.19x10^3$)	91.1 (348)	99.1 ($3.64x10^3$)
Spacer-chain ketophosphonate	98.7 ($1.17x10^3$)	99.1 ($1.53x10^3$)	60.8 (22.8)	91.9 (167)

† distribution coefficient

(caused by the presence of unfunctionalized styrene moieties in the polymer backbone). To test this hypothesis, the spacer chain resin was sulfonated to make the polymer backbone more hydrophilic and hence, allow for better accessibility of the metal ions. The kinetic studies for complexation of Eu(III) from a 1.0 N HNO_3 solution were done. The percent Eu(III) complexed was 94.9% (D; 887) and 95.1% (D; 915), respectively. The dramatic increase in the kinetics was consistent with the hypothesis of decreased accessibility.

Thus the spacer chain had no effect on increasing the complexation kinetics from dilute acid solutions. However, from a highly acidic solution (1.0 N HNO_3), its kinetics was in fact slower due to the decreased accessibility of the metal ions caused by the hydrophobic nature of the polymer. This was proved by the ability to increase the kinetics by the introduction of hydrophilic sulfonic acid ligand into the polymer back bone.

E. Attempted synthesis of aminophosphonic acid resin

Introduction

The importance of intra-ligand cooperation for increasing metal ion affinities in polymer-supported reagents has been emphasized by the research work discussed in Chapter 3. In the present research, the synthesis of polymer-supported reagents analogous to class II DMBPs was attempted. While the access mechanism would still be ion-exchange, coordination would be the recognition mechanism whereby the resin has two cooperating ligands for high ionic selectivities.

Aminomethylphosphonic acid is a ligand where the amino group and the phosphoryl oxygen can cooperate to complex metal ions because of their ability to form a

stable ring structure. There were a few examples in the literature where this ligand has been immobilized onto polymer supports. These resins are typically obtained by amination of chloromethylated polystyrene followed by reaction with formaldehyde and phosphorus acid to give the α-aminomethylphosphonic acid resin. Complexation studies on this resin for a wide range of metal ions have been published.[123-126] The aminomethylphosphonic acid resins synthesized thus far had the phosphonate bonded through the amino group and inductive effects could influence the ligand's binding ability.

The goal of the present research was to synthesize an aminophosphonic acid resin where the amino group would not be affected by inductive and steric effects from the phosphonate. These resins would help in the fundamental understanding of the mechanism of complexation. The aminophosphonic acid resin would thus have a free amino group alpha to the phosphonic acid group. Different synthetic routes to making this resin were investigated.

Experimental

Synthesis VBC-DVB copolymers

VBC-DVB copolymers were synthesized by suspension polymerization. Gels, MRs and xerogels were used in the functionalization reactions. The xerogel beads, which are very flexible and have a large swelling capacity are prepared by polymerization in the presence of a good solvent for the polymer.[127] For the present study, a xerogel copolymer crosslinked with 1 % DVB, was supplied by Dr. Kelly Ripperger (resin code KR-07-206). The percent DVB used in crosslinking for the gels and MRs were 2% and 5%, respectively. The particle size used for gels, MRs and xerogels were 0.075-0.15 mm,

0.15-0.25 mm and 0.15-0.25 mm, respectively, unless or otherwise noted. A smaller particle size was used with the gel beads to optimize the degree of functionalization. The pore volume in the MR beads was 50%.

Synthesis of Styrene-DVB copolymer

This copolymer was supplied by Dr. Robert Beauvais (resin code RB-03-138), and was a 2% DVB crosslinked gel. The particle size used for the functionalization was in the range of 0.075-0.15 mm.

Synthesis of aldehyde resin from VBC copolymer beads

The aldehyde resin was synthesized by refluxing a mixture of poly(VBC) beads with $NaHCO_3$/DMSO solution for 17 h. The resin was washed with water and ethanol and vacuum dried.

Synthesis of α-aminomethylphosphonate ester resin by the Strecker reaction

The aldehyde resin was reacted with a mixture of ammonium acetate and diethylphosphite at reflux temperature for 72 h (Figure E.1). The resin was washed with water and methanol followed by soxhlet extraction with methanol. The ester was hydrolyzed to the acid by reaction with conc HCl (reflux temperature) for 17 h. The resin was washed with water and conditioned by elution with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water.

Synthesis of α-aminomethylphosphonate ester resin by reaction with benzylcarbamate

The aldehyde resin was swelled in glacial acetic acid overnight. A mixture of benzyl carbamate and tri(ethyl or phenyl) phosphite was added to the resin and the mixture

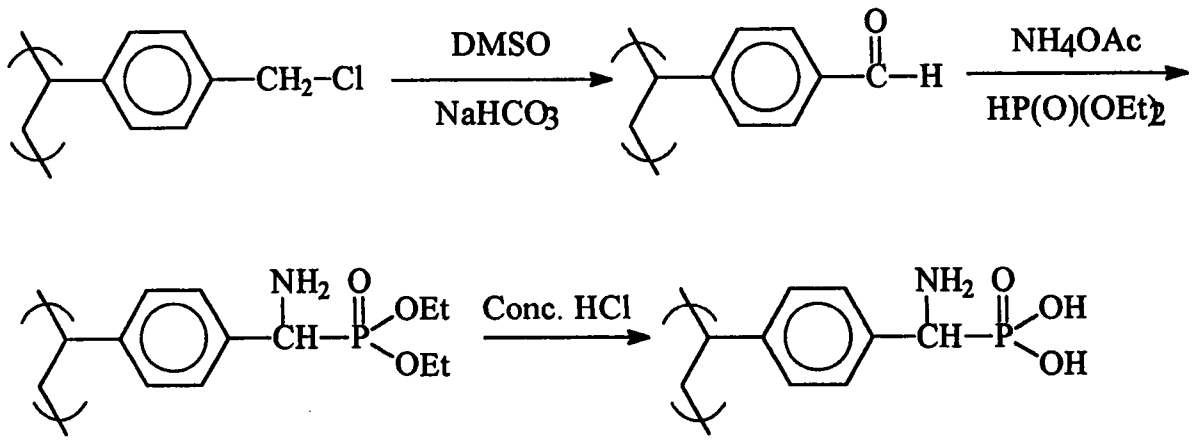

Figure E.1. Aminophosphonic acid resin synthesis by Strecker reaction

was refluxed for 72h (Figure E.2). The resin was washed with ethanol and dried under vacuum. Hydrolysis with conc HCl gave the aminophosphonic acid resin. Conditioning of the resin was done as described earlier.

Synthesis of α-aminomethylphosphonate ester resin by reaction with t-butyl amine

The aldehyde resin was refluxed with a mixture of DMF and t-butyl amine for 72 h (Figure E.3). The resin was washed with ethanol, THF and acetone, then vacuum dried.

Synthesis of α-aminomethylphosphonate ester resin from the oxime of the α-ketophosphonate ester

The resin was prepared by multistep reactions on an aldehyde resin (Figure E.4). Each of these steps is described below.

Synthesis of carboxylic acid resin. The aldehyde resin was oxidized to the carboxylic acid resin by a two step process. In the first step, the resin was swelled in a dioxane/water mixture followed by heating with a 3 N HNO_3 solution at reflux temperature for 20 h. After washing the resin with water, it was reacted with a dioxane/30 wt% H_2O_2 mixture at 80°C for 20 h. The resin was washed with water, Büchner dried and extracted with heptane azeotropically to remove water from the polymer matrix.

Synthesis of acid chloride resin. Heating the carboxylic acid resin at reflux temperature with thionyl chloride for 48 h under a nitrogen atmosphere resulted in its conversion to the acid chloride. The beads were siphoned off and washed thoroughly with toluene.

Synthesis of α-ketophosphonate ester resin. Arbuzov reaction of the acid chloride resin was done by refluxing it with triisopropyl phosphite for 24 h in an inert atmosphere. The resin was washed with water, ethanol and acetone, and then vacuum dried.

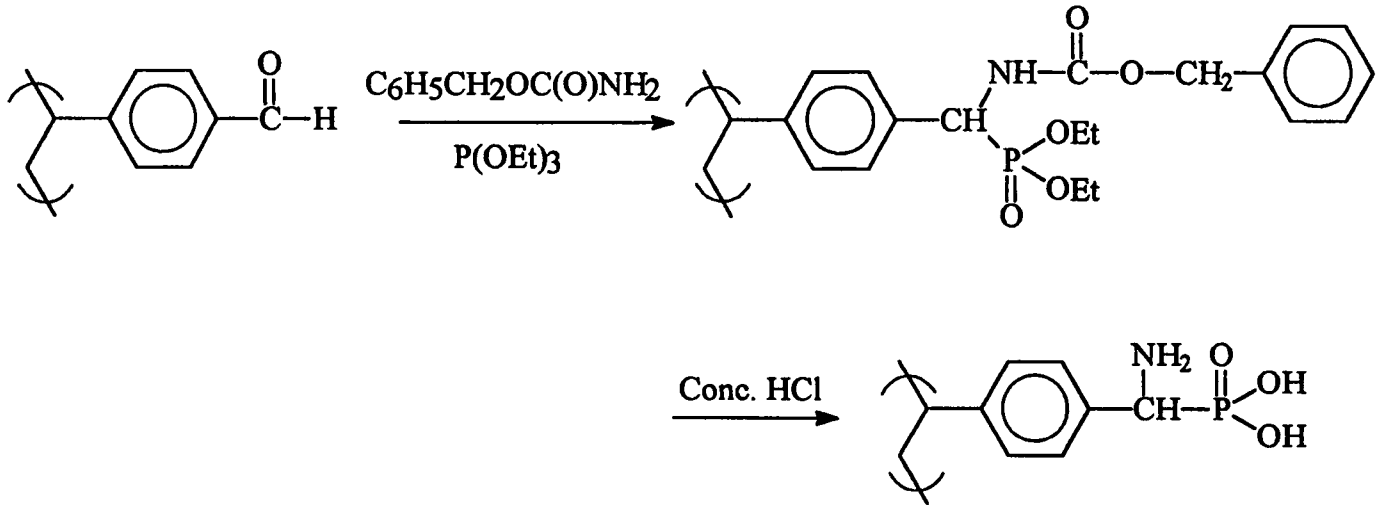

Figure E.2. Aminophosphonic acid resin via benzylcarbamate reaction

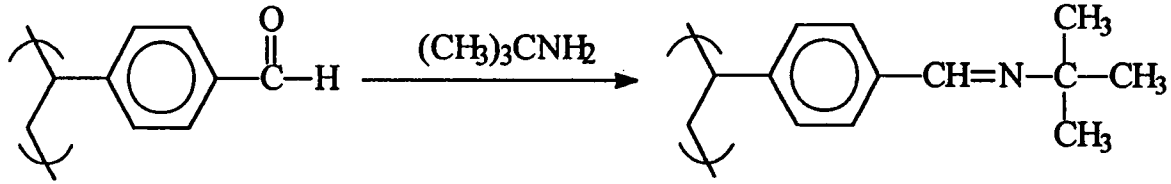

Figure E.3. Synthesis of aminphosphonate ester from Schiff base intermediate

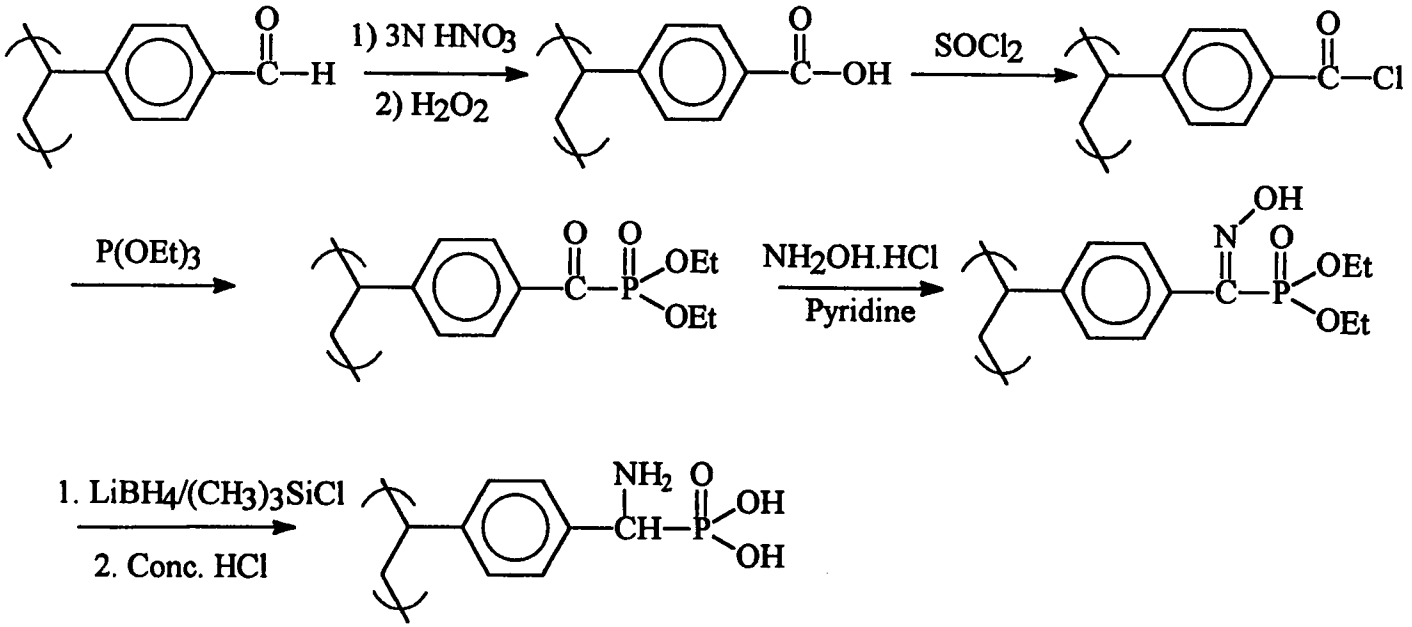

Figure E.4. Synthesis of aminophosphonic acid resin from oxime of an α-ketophosphonate ester

Synthesis of oxime of ketophosphonate ester. The ketophosphonate ester resin was reacted with hydroxylamine hydrochloride at 80°C for 24 h in pyridine/methanol to produce the oxime resin. The resin was washed with methanol, water and acetone and vacuum dried.

Synthesis of aminophosphonate ester resin by oxime reduction. The oxime resin was swelled in THF and a 1:2 mixture of $(CH_3)_3SiCl$ and 2 M $LiBH_4$ was added. Reaction was allowed to proceed at room temperature for 48 h. The resin was washed with dioxane and water.

Synthesis of aminophosphonic acid resin. After reduction, the resin was refluxed with conc HCl for 24 h. It was washed with water and conditioned by eluting with 1 L each of water, 4 wt% NaOH, water, 4 wt% HCl and water.

Synthesis of β-aminoethylphosphonate ester resin from the oxime of the β-ketophosphonate ester

A Friedel-Crafts reaction was first done on polystyrene beads with bromoacetyl bromide in CS_2 as the solvent. An Arbuzov reaction of this resin with triisopropyl phosphite at reflux temperature for 24 h gave the β-ketophosphonate ester resin. The oxime reaction, reduction and subsequent hydrolysis were done according to the procedures described above to obtain the β-aminoethylphosphonic acid resin (Figure E.5).

Results and Discussion

Synthesis of the α-aminophosphonic acid resin was attempted by different methods. An aldehyde resin prepared by the oxidation of crosslinked VBC beads was used as the starting material for the reactions studied.

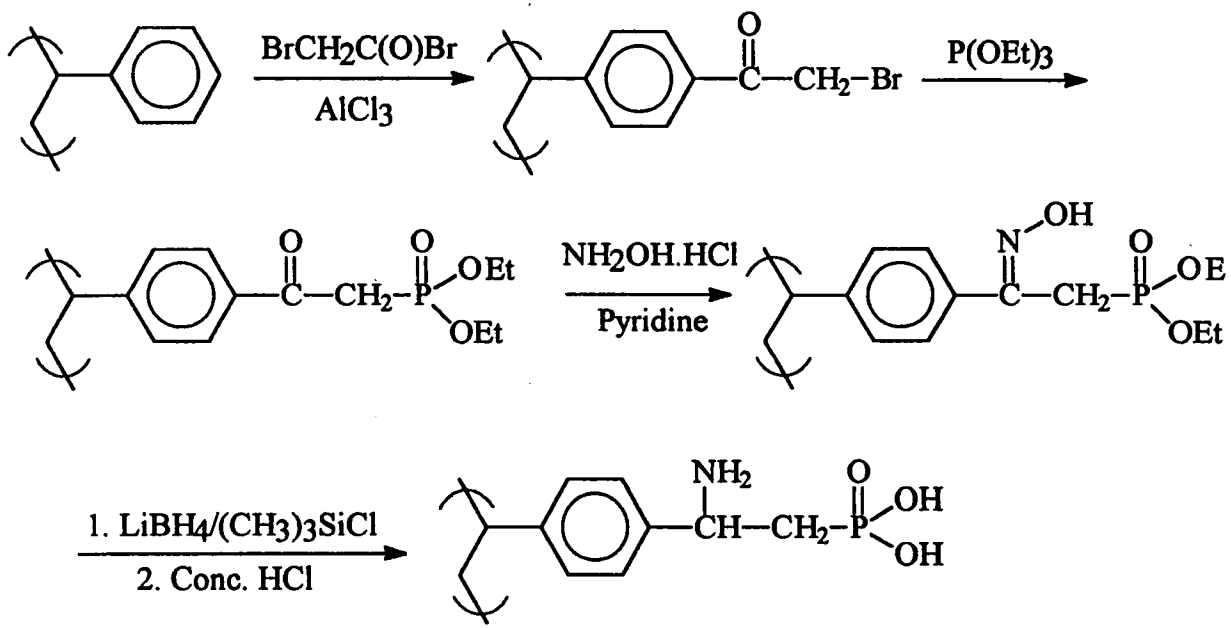

Figure E.5. Synthesis of aminophosphonic acid resin from oxime of β-ketophosphonate ester

Synthesis of the α-aminomethylphosphonic acid resin by the Strecker synthesis

Diethyl α-aminobenzylphosphonate has been synthesized by a Strecker-type reaction in good yield.[128] This reaction was extended to a polymer-supported aldehyde resin. Oxidation of the chloromethyl groups in the VBC copolymer to the aldehyde was effected by reaction with dimethylsulfoxide (DMSO) in the presence of a base ($NaHCO_3$). A solution of ammonium acetate in ethanol and diethyl phosphite were then added to the aldehyde resin and the mixture heated at 60°C for 72 h. The FTIR spectrum of the resin (SN-03-158) did not have the characteristic P=O stretching peak at 1240 cm^{-1} indicating lack of reaction. To ascertain if the literature procedure for the synthesis of the small molecule analogue was reproducible, a mixture of ammonium acetate in ethanol, benzaldehyde and diethyl phosphite in the presence of molecular sieves was heated at 60°C for 4 h. The expected product could be obtained. Thus, there were two possible reasons for the reaction not taking place in the polymeric analogue:

1. Incompatibility of the solvent: ethanol, being too polar, does not swell the hydrophobic polymer matrix preventing access of the reagents into the beads.
2. Temperature of the reaction: since this is an equilibrium reaction, a higher reaction temperature might be needed to drive the equilibrium towards the products.

Use of DMF can address both problems, since it is not only compatible with the polymer matrix, but also has a high boiling point (153°C) allowing the reaction to be carried at a higher temperature. With DMF as the solvent, the reaction was carried out at reflux temperature for 72 h. The resin had a nitrogen capacity of 0.86 mequiv/g and a phosphorus capacity of 0.93 mequiv/g. Though the nitrogen and phosphorus capacities of

the resin (SN-03-165) were in a 1:1 ratio, the resin was only 22.6% functionalized. The first step in the mechanism is the formation of an imine. The inability of the ionic reagent (ammonium acetate) to access the reactive sites in the hydrophobic polymer matrix could be the reason for the low functionalization. Upon hydrolysis with conc HCl, the resulting resin (SN-03-172) had 59.8% solids, a phosphorus capacity of 0.59 mequiv/g and an acid capacity of 1.34 mequiv/g. The mechanism for the loss of phosphorus after hydrolysis was not understood. The effect of reaction time on percent functionalization was also studied (Table E.1). An increase in reaction time was not important since the resin was functionalized to almost the same extent at a longer time. To elucidate if the imine resin can be phosphorylated, it was further reacted with diethyl phosphite at reflux temperature for 17 h. Hydrolysis of the resin was then attempted with Conc HCl to generate the aminophosphonic acid resin (SN-03-188). The phosphorus, nitrogen and acid capacities of the hydrolyzed resin were 0.77, 0.63 and 1.37 mequiv/g respectively. The actual nitrogen and phosphorus capacities were in agreement with the theoretical capacity of 0.65 mequiv/g calculated based on the percent functionalization of its precursor. However, the capacities of the resin were too low to be useful in complexation studies. The effect of the polymer support in increasing the amount of imine was also studied (Table E.2). A more open matrix had no effect on the amount of imine that formed. Since the functionalization could not be maximized after changing all possible variables, an alternate route was attempted.

Synthesis of α-aminomethlyphosphonic acid resin via the benzylcarbamate reaction

Dialkyl or diphenyl α-(benzyloxycarbonylamino)benzylphosphonates have been

Table E.1

Imine synthesis by reaction of 2% DVB gel resin[a] with ammonium acetate: effect of reaction time on percent functionalization

Resin code	Time of reflux (h)	Nitrogen capacity (mequiv/g)	% Functionalization
SN-03-182	17	1.05	14.5
SN-03-190	72	0.76	10.5

a Particle size 0.075-0.150 mm

Table E.2

Imine synthesis by reaction with ammonium acetate: effect of type of support on percent functionalization

Resin	Type of support	Particle size (mm)	Nitrogen capacity (mequiv/g)	% Functionalization
SN-03-200	1% DVB xerogel	0.075-0.150	0.72	9.97
SN-03-201	2% DVB gel	0.046-0.075	0.99	13.7
SN-03-202	5% DVB MR	0.075-0.150	0.96	13.3

prepared by reaction of benzaldehyde with benzylcarbamate and trialkyl (or triphenyl) phosphite.[129,130] Acid hydrolysis of the product has afforded fair yields of aminophosphonic acids. The phosphite, reaction conditions and the polymer support were studied in extending the reactions to polymers.

A mixture of glacial acetic acid/thionyl chloride, benzylcarbamate and diethylphosphite was added to the aldehyde resin (SN-03-151, 2% DVB, 0.075-0.15 mm) and the reaction was carried out at reflux temperature for 72 h. The beads were washed with water and ethanol. The FTIR spectrum of the resin had no P=O stretching peak expected at 1240 cm^{-1}. The C=O stretching peak seen in the spectrum was probably due to trapped benzylcarbamate in the beads. Glacial acetic acid is probably too polar for swelling the polymer matrix. To allow for better solvation, a slightly modified procedure was used. The aldehyde resin, triethyl phosphite, benzylcarbamate and DMF were heated at reflux for 72 h. After reaction, the resin (SN-04-166) was washed with water and methanol and then vacuum dried. The nitrogen and phosphorus capacities of the resin were 1.08 and 1.12 mequiv/g, respectively indicating a 43.7 % functionalization. This was much higher than functionalization by the Strecker reaction. However, on hydrolysis of the resin with conc HCl, the nitrogen and phosphorus capacities of the resin decreased to 0.37 mequiv/g and 0.91 mequiv/g, respectively. The acid capacity of the resin was 2.01 mequiv/g. While the acid capacity was twice the phosphorus capacity, the nitrogen capacity was only a third of the expected value. The loss of nitrogen might be due to a side reaction taking place during hydrolysis. The mechanism for the formation of side product is unknown at the present time.

In a separate series of reactions, attempts were made to maximize the functionalization of benzylcarbamate on the aldehyde resin by varying the time of reaction and type of support. By increasing the reaction time for a 2% DVB gel aldehyde resin (0.075-0.15mm) from 17 h to 72 h, the nitrogen capacities increased from 1.47 to 1.82 mequiv/g, respectively (Table E.3). As the increase was only marginal, the effect of the polymer support was then studied. This data is presented in Table E.4. Higher percent functionalization was obtained with a 5% DVB MR resin than a 1 % DVB xerogel (39.5 against 24.0%). The macrochannels in the former allow for increased accessibility to the reagents. A 2% DVB gel resin with a smaller particle size than used earlier (0.046-0.075 mm) gave 92.9% functionalization; this was too high relative to the capacities obtained with other resins and in retrospect, should have been checked by repeating the reaction. At the time, it was felt that the high nitrogen capacity was due to trapped benzylcarbamate in the beads. Though, higher percent functionalization was obtained via benzylcarbamate route, the reason for the loss of nitrogen on hydrolysis of this resin was also not clear.

To better understand the mechanism of this reaction and determine the optimum conditions for functionalization, a series of reactions with the small molecule analogue was carried out. The reactions were done by heating the reactant mixture at 80°C for 2 h. Formation of products was followed qualitatively by gas chromatography. The following variables were studied:

Effect of phosphite. Benzaldehyde (1.5 mmol) was reacted with benzylcarbamate (1.0 mmol) and triethyl, triisopropyl or tripehnyl phosphite (1 mmol) in glacial acetic acid (12 mL) as the solvent. Product formation was observed only in the case of triphenyl

Table E.3

Reaction of 2% DVB gel resin[a] with benzylcarbamate: effect of reaction time on percent functionalization

Resin code	Time of reflux (h)	Nitrogen capacity (mequiv/g)	% Functionalization
SN-03-183	17	1.47	40.1
SN-03-191	72	1.82	50.0

a Particle size 0.075-0.150 mm

Table E.4

Reaction of polybenzaldehyde with benzylcarbamate: effect of polymer support on percent functionalization

Resin code	Type of support	Particle size (mm)	Nitrogen capacity (mequiv/g)	% Functionalization
SN-03-204	1% DVB xerogel	0.075-0.150	0.88	24.0
SN-03-205	2% DVB gel	0.046-0.075	3.41	92.9
SN-03-206	5% DVB MR	0.075-0.150	1.45	39.5

phosphite.

Effect of solvent. Benzaldehyde (1.5 mmol), benzylcarbamate (1.0 mmol), and triphenyl phosphite (1 mmol) were reacted in different solvents (ethanol, glacial acetic acid and DMF). Strong product peak was observed with glacial acetic acid, side reaction (extra unassignable peak) with ethanol and no reaction with DMF.

Effect of added acid: In the above control reaction, it was not clear if the presence of an acid is important for the reaction to occur. Maintaining the same amount of reagents, the reaction was done in either THF or ethanol with catalytic amounts (0.017 g) of conc HCl. Product formation was not observed and the phosphite was hydrolyzed.

Since triphenyl phosphite/glacial acetic acid was the only combination where a product was observed, this was also used in the reaction with polymer beads. The aldehyde resin was swelled in glacial acetic acid overnight. Benzylcarbamate and triphenyl phosphite were added in a 20 mole excess (with respect to the aldehyde sites in the resin) were then added and the mixture refluxed for 17h. The resin was washed with ethanol and dried. The effect of the polymer support and particle size on functionalization is reported in Table E.5. For the syntheses attempted, not only was the percent functionalization low but the nitrogen and phosphorus capacities were not in a 1:1 mole ratio. Inconclusive results were obtained from this method.

Synthesis of the α-aminomethylphosphonate resin by a Schiff base reaction with t-butyl amine

Another synthetic route to making aminophosphonic acid has been done by the reaction of a small molecule aldehyde with t-butyl amine to form the Schiff base intermediate.

Table E.5

Synthesis of aminophophonate ester resin by reaction with benzylcarbamate/triphenylphosphite: effect of polymer support and particle size on percent functionalization

Resin code	Type of support	Particle size (mm)	Nitrogen capacity (mequiv/g)	Phosphorus Capacity (mequiv/g)	% Functional-ization†
SN-03-218	5% DVB MR	0.075-0.150	0.64	0.48	33.0
SN-03-255	1% DVB xerogel	0.150-0.250	0.85	0.48	43.8
SN-03-256	5% DVB MR	0.150-0.250	0.35	0.55	18.0

† based on nitrogen capacity

Reaction of this with diethylphosphite and sodium ethoxide gave the desired product.[131] This reaction was attempted on a polymer-supported aldehyde resin (Figure E.3). Conversion of the aldehyde resin (SN-04-187, 2% DVB gel, particle size of 0.075-0.15 mm) to an imine (Schiff base) was attempted by reacting it with a mixture of t-butyl amine and DMF at reflux temperature for 72 h. It product had a nitrogen capacity of 0.49 mequiv/g. The low functionalization was attributed to unfavorable steric interactions between the bulky amine and the aldehyde functionality on the polymer backbone. Since the extent of reaction was low, the Schiff base resin was not reacted further with the phosphite.

Synthesis of the α-aminomethylphosphonate resin from an oxime resin

Aminophosphonates have been synthesized by reducing the oxime of an α-ketophosphonate with a $LiBH_4/ClSi(CH_3)_3$ mixture.[132, 133] The reaction scheme for the polymeric analogue is shown in Figure E.4. An acid chloride resin was first synthesized by oxidation of the aldehyde functionality to a carboxylic acid followed by reaction with thionyl chloride at reflux temperature for 24 h. Reaction of this resin with triethyl phosphite gave the ketophosphonate resin. A 1% DVB xerogel support was used as the starting material. The resin (SN-03-267) was 22.1% functionalized with the α-ketophosphonate group (actual P capacity of 1.24 mequiv/g) while the rest was comprised of the carboxylic acid sites. The conversion of the keto group to an oxime was attempted at two different conditions. In the first reaction, the resin was reacted with a 10 molar excess of hydroxylamine hydrochloride/pyridine (1:1) in methanol, while in the second reaction, it was reacted with hydroxylamine hydrochloride in an excess of pyridine (with

methanol still being the solvent). Both reactions were carried out at room temperature for 24 h. The resins were washed with water, methanol and acetone then vacuum dried. The nitrogen capacities of the resins (SN-03-268A and SN-04-268C) were 1.55 and 1.59 mequiv/g, respectively. The use of excess pyridine in the second case resulted in the same extent of reaction. These values were slightly higher than the expected value of 1.18 mequiv/g (based on the moles of ketophosphonate groups initially present) due to trapped hydroxylamine within the beads. It is likely, however that these conditions gave quantitative conversion to the oxime resin.

Reduction of the oxime resin was attempted as follows: an oxime resin was first synthesized by reaction with a mixture of hydroxylamine hydrochloride in excess pyridine (with methanol as the solvent) at 90°C for 24 h. The resin (SN-03-272) had a nitrogen capacity of 1.38 mequiv/g (calculated value, 1.18 mequiv/g). To the resin was added a mixture $LiBH_4/(CH_3)_3SiCl$ (1:2 mole ratio) with THF as the solvent. The reaction was carried out at room temperature for 48 h followed by washing with THF, ethanol and acetone. The resin had a nitrogen capacity of 2.00 mequiv/g (expected value, 1.45 mequiv/g). Though this value (of 2.00 mequiv/g) was higher than the theoretical value (of 1.45 mequiv/g), it was consistent based on the capacity (of 1.38 mequiv/g) obtained for its precursor (SN-03-272).

The same sequence of experiments was repeated on a 2% DVB gel support (particle size in the range of 0.15-0.25 mm)to study the change of support on percent functionalization. The ketophosphonate resin (SN-04-013) had a phosphorus capacity of 1.76 mequiv/g (percent functionalization of 36.4%). The conversion to oxime was

quantitative with the resin (SN-04-014) having a nitrogen capacity of 1.61 mequiv/g (1.68 mequiv/g calculated based on moles of ketophosphonate group initially present). After reduction of the oxime with $LiBH_4/(CH_3)_3SiCl$, hydrolysis of the resin was attempted with conc HCl at a 17 h reflux to give the aminophosphonic acid resin. The resin (SN-04-024) was washed and conditioned. The resin had nitrogen and phosphorus capacities of 1.15 and 0.97 mequiv/g, respectively. Even though the nitrogen and phosphorus capacities were equimolar, their capacities were significantly lower than the expected capacity of 2.32 mequiv/g. Results from this reaction suggest that there was some side reaction taking place resulting in the loss of the aminophosphonate ligand besides the formation of the expected product. The mechanism and the identity of the side product formation was not understood. Since the α-ketophosphonate resin also had carboxylic acid sites, it was not clear whether these acid sites were inducing the formation of side product. To test this hypothesis, the oxime-reduction-hydrolysis reaction sequence was carried out on a β-ketophosphonate resin which lacked the carboxylic acid sites. The resin was synthesized according to the scheme in Figure E.5. The resin was 32.7% functionalized (phosphorus capacity of 1.83 mequiv/g; theoretical). When converted to the oxime, the resin (SN-04-039) had a nitrogen capacity of 1.35 and a phosphorus capacity of 1.61 mequiv/g. The conversion to the oxime was not complete since the nitrogen capacity was lower than the expected value of 1.75 mequiv/g. This resin was then subjected to the borohydride reduction as above. Elemental analysis of the resin indicated quantitative reduction (nitrogen capacity of 1.45 mequiv/g, phosphorus capacity of 1.57 mequiv/g; theoretical capacity of 1.41 mequiv/g). Hydrolysis of the resin was done as before with conc HCl.

The resin had a solids of 50.2%, nitrogen capacity of 0.75 mequiv/g, phosphorus capacity of 1.27 mequiv/g and acid capacity of 2.73 mequiv/g). Based on the capacities of the precursor, it was expected that the nitrogen and phosphorus capacities would be 2.12 mequiv/g and an acid capacity of 4.24 mequiv/g. The decrease in acid capacity suggested loss of the aminophosphonate group and there are both aminophosphonic and β-ketophosphonic acid sites since the nitrogen and phosphorus capacities were not equal but the acid capacity was twice the phosphorus capacity. Thus, the aminophosphonate ester resin could be synthesized by the reduction of an oxime resin. However, hydrolysis of this reaction with an acid leads to the loss of the amino groups. The mechanism for its loss could not ascertained and further studies are required in future.

Conclusions

Synthesis of an aminophosphonic acid resin was attempted using different synthetic schemes. Accessibility of the ionic reagent (ammonium acetate) into the polymer matrix was responsible for the low levels of functionalization in the Strecker reaction. Attempts to synthesize a Schiff base resin with t-butyl amine as a possible intermediate for making aminophosphonic acid resin were not successful. The reaction may not be occurring due to unfavorable steric interactions of the bulky amine and the aldehyde group in the polymer backbone. Both the benzylcarbamate and the oxime reaction could be used successfully in the preparation of their respective aminophosphonate precursors. However, acid hydrolysis leads to loss of the ligand and formation of unexplained side products. A detailed study needs to be done in the future to understand the mechanism of hydrolysis.

VITA

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