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Christy L. Stine  
*University of Tennessee - Knoxville*

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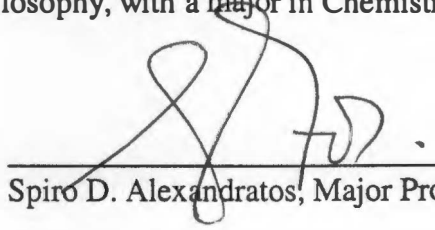
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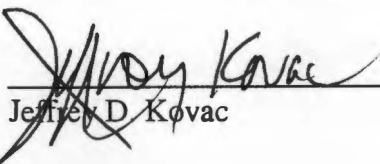
I am submitting herewith a thesis written by Christy L. Stine entitled "Polymer-Supported 14-Crown-4 and Bifunctional Resins for Selective Metal Ion Complexation: Synthesis and Characterization." I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.



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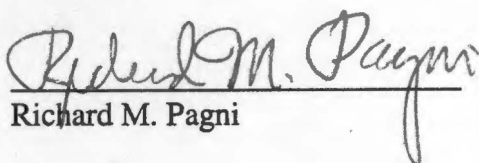
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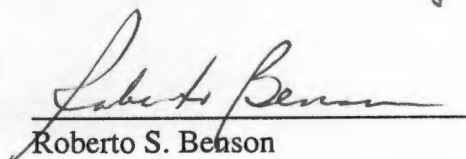
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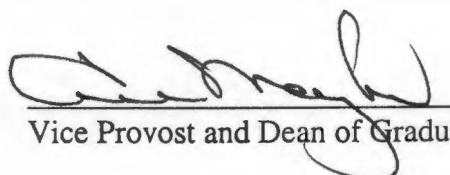
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Roberto S. Benson

Acceptance for the Council:



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Vice Provost and Dean of Graduate Studies



**POLYMER-SUPPORTED 14-CROWN-4 AND BIFUNCTIONAL RESINS  
FOR SELECTIVE METAL ION COMPLEXATION:  
SYNTHESIS AND CHARACTERIZATION**

**A Dissertation**

**Presented for the**

**Doctor of Philosophy**

**Degree**

**The University of Tennessee, Knoxville**

**Christy L. Stine**

**August 2002**

Thesis  
20026  
.S755

## **DEDICATION**

**This dissertation is dedicated to my husband Dan for his patience,  
strength, understanding and unconditional love.**

**And for without whom none of this would be possible.**





## ACKNOWLEDGEMENTS

First and foremost, I would like to thank Professor Spiro D. Alexandratos. His encouragement, guidance and kindness, as well as insight, have shaped me into the chemist that I am today. His graciousness cannot be measured. I would also like to express appreciation to Professors Jeffrey Kovac, Richard Pagni and Roberto Benson for serving on my committee and for their helpful support.

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## ABSTRACT

Polymer-supported 14-crown-4 and bifunctional resins containing amine and phosphonate ester ligands were synthesized and characterized. Complexation studies were performed to evaluate the metal ion selectivity of the resins.

The immobilization of 14-crown-4 onto crosslinked polymer supports for the complexation of Li(I) from aqueous solutions was studied. Many methods were attempted, but etherification of the hydroxymethyl form of 14-crown-4 was found to be the most successful. The polymers examined were poly(vinylbenzyl chloride), poly(vinylbenzyl chloride)-co-acrylamide and poly(glycidyl methacrylate). The amount of Li(I) complexed by the crown ether supported polymers was affected by the polarity (i.e., hydrophilicity) of the polymer matrix. The greater the hydrophilicity of the polymer matrix, the greater the amount of Li(I) complexed. The degree of functionalization of the crown ether was found to be affected by the resin porosity and the reaction conditions. Of the resins studied, the poly(glycidyl methacrylate) demonstrated the best performance.

Bifunctional resins containing dialkyl phosphonate esters and dialkylamines with groups corresponding to the phosphonate esters were prepared. Preliminary complexation experiments were performed using a bifunctional resin consisting of the methyl forms of the phosphonate and amine. For comparison, monofunctional analogues of the bifunctional resin and a dimethylamine-contacted fully functionalized dimethyl phosphonate ester were also prepared. Complexation results indicated that hydrolysis occurred with the dimethylamine-contacted phosphonate ester resin based on increased metal ion sorption capacities. Analysis for acid capacity and by FTIR demonstrated that

a low level of hydrolysis occurred. Hydrolysis was also demonstrated with several other amines used for example, ethylenediamine and piperidine. Upon characterization of the butyl and ethyl analogues of the amine-contacted fully functionalized phosphonate ester resin, it was seen that hydrolysis did not occur. In complexation studies at the butyl/butyl form of the bifunctional resin demonstrated increased metal ion sorption capacity, in comparison to the other butyl resins synthesized however, the ethyl/ethyl form of the bifunctional resin did not.

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# CHAPTER 1

## INTRODUCTION

Macrocyclic compounds containing oxygen, nitrogen and sulfur as donor atoms have gained attention for their ability to form stable complexes with ions within their central cavity. The strong complexation properties exhibited by crown ethers towards metal ions have led to their incorporation into polymeric matrices.<sup>1, 2, 3, 4, 5, 6, 7</sup> Polymer-supported reagents offer many advantages, including ease of handling and recoverability when used in the removal of toxic metal ions from the environment.<sup>8, 9, 10</sup> Due to increased concern with the remediation of wastewater, polymer-supported reagents, including immobilized crown ethers, have been studied for the selective removal of targeted metal ions.<sup>11, 12</sup>

The stability of the crown ether-metal ion complex is dependent on the number and geometrical placement of the ether donor atoms. Of particular importance is the size and shape of the cavity relative to the cation size.<sup>13</sup> Though crown ethers are most stable when they form complexes with ions having ionic diameters equivalent to that of their cavity, they can also form complexes with ions of larger sizes.<sup>14</sup> When the ion is able to fit within the cavity, the crown ether-metal ion complex forms in a 1:1 ratio. If the ion is larger than that of the crown cavity, there is a tendency for the crown ether moieties to “sandwich” the metal ions between adjacent crown units.<sup>15</sup>

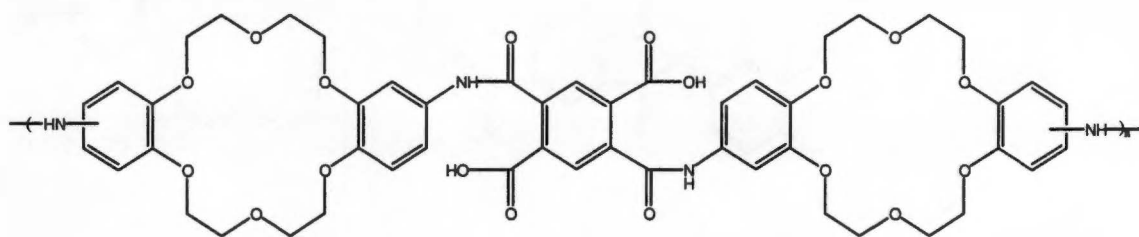
There are two principal methods by which crown ethers can be incorporated into polymer matrices. The first mode is through direct polymerization of the crown ether by a condensation reaction where the crown ether is incorporated within the backbone of the

polymer. This type of reaction has the advantage of yielding a copolymer with a well-defined structure though there may be limited accessibility of the metal ion into the matrix. The second mode is reaction of the crown ether with functional groups that are covalently bound to the polymer backbone. This reaction requires the crown ether to have a reactive functional group that can bond to the polymer and a proper choice of support can produce a grafted crown ether with enhanced ionic accessibility.<sup>8, 16</sup>

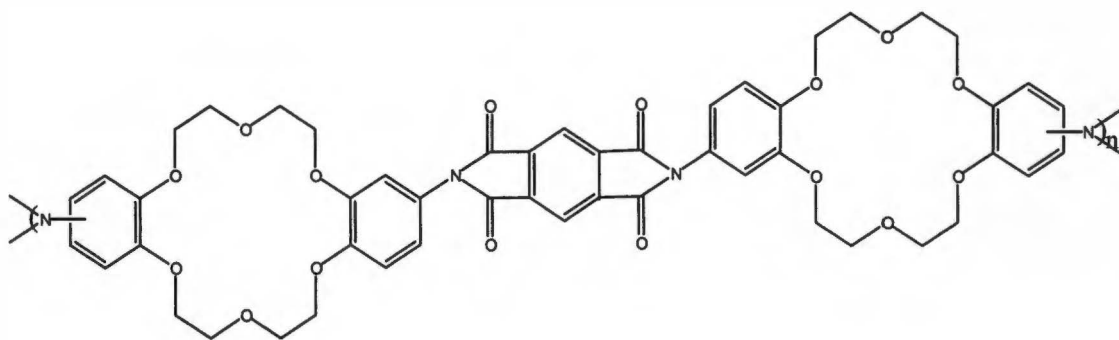
The first crown ethers contained only oxygen donor atoms; nitrogen and sulfur-containing crown ethers have subsequently been produced and have gained increased applicability to separations. Due to differences in polarizability, nitrogen-containing crown ethers (azacrowns) and sulfur-containing crown ethers (thiacrowns) display different ionic selectivities than oxygen-containing crown ethers. These differences in behavior as a function of donor atoms can be explained by hard-soft acid-base theory.<sup>17,18</sup> Soft ligands, such as those that contain sulfur, provide polarizable sites that have increased affinities for softer metal ions, which include precious metals. In contrast, hard ligands that have sites of low polarizability have increased affinities for harder metal ions such as the alkali and alkaline earth metals.<sup>19, 20</sup>

## **CROWN ETHERS**

Crown ether resins prepared with the crown moiety in the backbone by reaction with dianhydrides yield polymer with different degrees of flexibility.<sup>21</sup> The polymer consisting of the polyamic acid (Figure 1.1) and the 18-crown-6 moiety had a greater binding ability with alkali and alkaline earth metals in aqueous solutions than that of its polyimide analogue (Figure 1.2). The carboxylic acid residues on the polyamic acid contributed to this increased



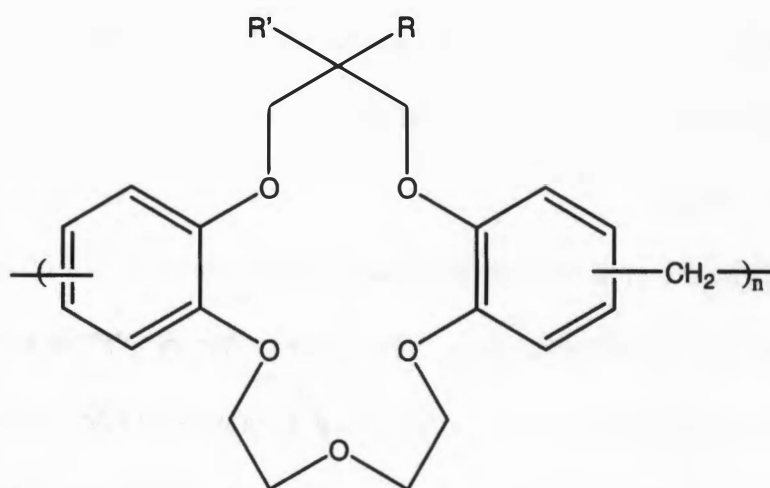
**Figure 1.1.** Crown ether polyamic acid system



**Figure 1.2.** Crown ether polyimide system

uptake capacity. The selectivities followed the trend  $K > Rb, Na > Cs > Li$  and  $Ca > Sr > Ba > Mg$ . The 15-crown-5 / polyamic acid resin displayed selectivities of  $Na > K > Li, Rb > Cs$  and  $Ca > Mg > Sr > Ba$ . When metal binding studies were done using the same resins in methanol solution, the metal ion capacities increased; this was attributed to an increase in solubility of the polymers. The uptake trends in methanol were generally consistent with those in aqueous solution.

A polymeric crown ether was prepared by the condensation of formaldehyde with dibenzo-containing crown ether moieties.<sup>22</sup> The crown ether was also functionalized with a pendant acid group (carboxylic acid, phosphonic acid monoethyl ester, phosphonic acid or sulfonic acid) to study the effects that the functionality had on the binding ability of the resin for Pb(II) with Zn(II) under competitive conditions (Figure 1.3). Along with the acid substituent, the crown ether moieties also contained a geminal substituent that varied from hydrogen to methyl to propyl. In studying the carboxylate-functionalized crown resins (a, b and c), it was found that resins a and b were able to selectively bind Pb(II) at pH 3 while resin c did not complex either. This was attributed to the length of the alkyl substituent bound to the crown ether which prevented the metal cation from coordinating within the crown cavity. The experiment was repeated with the phosphonate monoester crown resins d and e, where it was found that resin d was selective for Pb(II) at pH 1.8 in the presence of Zn(II), while resin e showed no affinity for either cation. Resin f was similar to resin d, differing only by having a longer spacer chain attached to the acid moiety. It was found that although there was still selectivity for Pb(II), the increased chain length reduced the metal binding ability. Phosphonic acid-substituted crown ether resins g and h were selective for



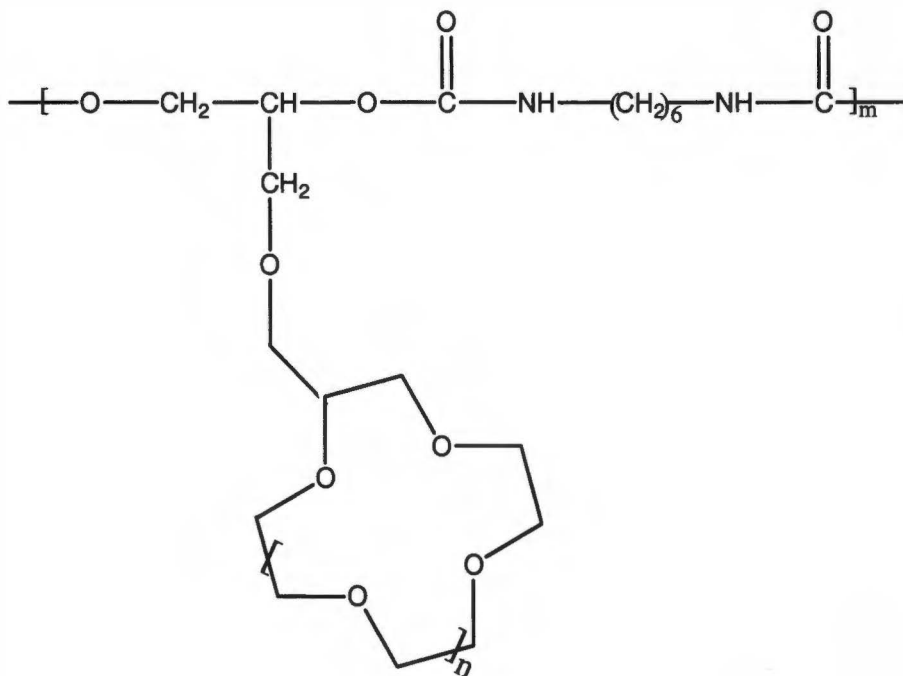
	<u>R'</u>	<u>R</u>
a	H	OCH <sub>2</sub> CO <sub>2</sub> H
b	CH <sub>3</sub>	OCH <sub>2</sub> CO <sub>2</sub> H
c	C <sub>3</sub> H <sub>7</sub>	OCH <sub>2</sub> CO <sub>2</sub> H
d	H	OCH <sub>2</sub> P(O)(OEt)OH
e	C <sub>3</sub> H <sub>7</sub>	OCH <sub>2</sub> P(O)(OEt)OH
f	H	O(CH <sub>2</sub> ) <sub>3</sub> P(O)(OEt)OH
g	CH <sub>3</sub>	OCH <sub>2</sub> PO <sub>3</sub> H <sub>2</sub>
h	C <sub>3</sub> H <sub>7</sub>	OCH <sub>2</sub> PO <sub>3</sub> H <sub>2</sub>
i	H	O(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H
j	C <sub>3</sub> H <sub>7</sub>	O(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H

**Figure 1.3.** Acid-functionalized polymeric crown ether

Pb(II) at pH 2, though the binding capacity for Zn(II) increased as the pH increased. The sulfonic acid-substituted crown ether polymers were also studied for Pb(II) selectivity and it was found that resins **i** and **j** quantitatively complexed both Pb(II) and Zn(II) at pH values of 2 and higher.

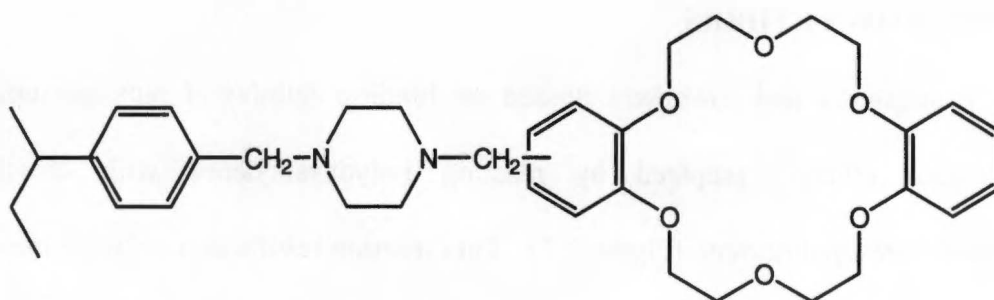
Resins formed by the copolymerization of a crown ether monomer with diisocyanate groups were studied by competitive extraction with alkali metals (Figure 1.4).<sup>23</sup> The repeat unit was 2(2,3-dihydroxypropoxy)methyl-crown ether, with the crown moiety varying from 12-crown-4 to 24-crown-8. The alkali metals were each at 0.25 M in 1.4 N HNO<sub>3</sub>. Polymeric 12-crown-4 selectively complexed sodium, not lithium ions as expected. This was explained by the greater degree of hydration exhibited by lithium in comparison to the other alkali metals.<sup>24</sup> The Na(I) complexed by the resin was in a 2:1 sandwich complex of the ion between two adjacent crown ether units. The polymer containing the 15-crown-5 moiety was selective for K(I) rather than the expected Na(I). The remaining polymeric crown ethers followed the trend predicted by the size of the crown cavity: 18-crown-6 was selective for K(I), 21-crown-7 was selective for Rb(I) and 24-crown-8 was selective for Cs(I).

A resin consisting of dibenzo-18-crown-6 bound to crosslinked polystyrene was studied for its affinity for Pd(II) and Pt(II) (Figure 1.5).<sup>25</sup> Both are soft ions and do not typically form complexes with hard (oxygen-containing) crown ethers. However, the anionic chlorides [PdCl<sub>4</sub>]<sup>2-</sup> and [PtCl<sub>4</sub>]<sup>2-</sup> were found to form ion pairs with the crown ether-alkali cation complex when the resin was contacted with K<sub>2</sub>PdCl<sub>4</sub> and K<sub>2</sub>PtCl<sub>4</sub> in solutions of varying KCl concentrations. The resin was found to have a greater sorption capacity for K<sub>2</sub>PdCl<sub>4</sub> than K<sub>2</sub>PtCl<sub>4</sub>. It was estimated that the dibenzo-18-crown-6 resin was able to bind



**Figure 1.4.** Polyurethane-containing crown ether





**Figure 1.5.** Polymer-supported dibenzo-18-crown-6

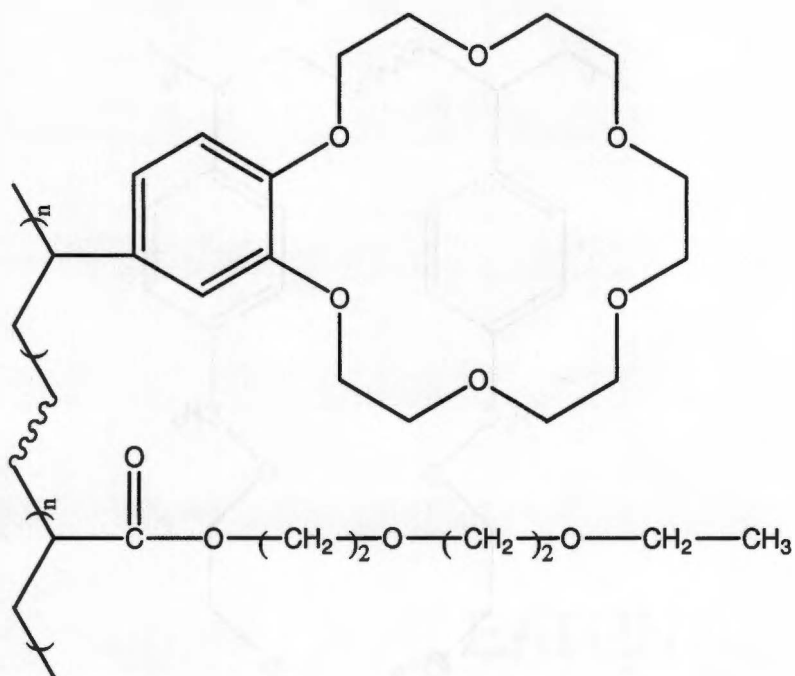
one  $[\text{PtCl}_4]^{2-}$  and up to two  $[\text{PdCl}_4]^{2-}$  per crown ether unit. The resin complexed both Pd(II) and Pt(II) in competitive studies from a solution of 0.50 M KCl, though Pt(II) was complexed to a greater extent.

A study of membrane-supported benzo-18-crown-6 was done to examine the transport affinities for alkali metals (Figure 1.6).<sup>26</sup> Polystyrene was copolymerized with di(ethylene glycol) ethyl ether acrylate in varying amounts. The polymer was studied for the extraction of K(I) from a solution of only K(I) and those containing other alkali metal salts.

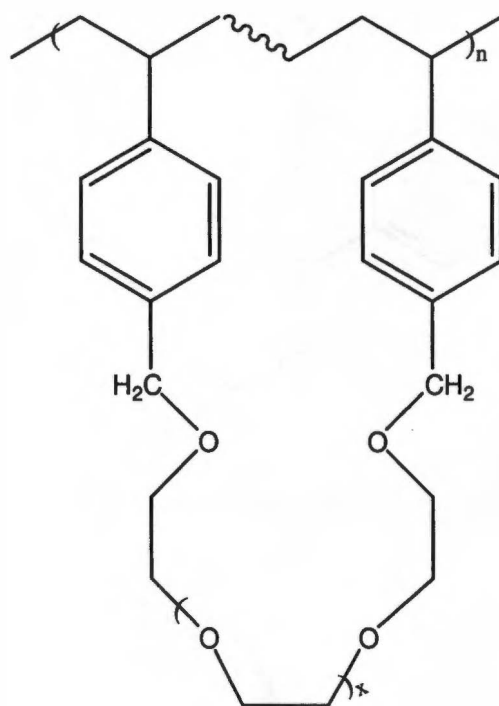
### **PSEUDOCROWN ETHERS**

Warshawsky and coworkers studied the binding abilities of polymer-supported pseudocrown ethers<sup>27</sup> prepared by reacting polyoxyalkylenes with crosslinked chloromethylated polystyrene (Figure 1.7). This reaction results in a polymer that has a number of possible conformations of the macrocycle moiety. The structure differs from the more ordered structure of a polymer-supported crown ether. The polymeric pseudocrown ethers were studied for their ability to complex Au(III), Fe(III) and Zn(II) as chlorides, bromides and iodides. The number of oxygen atoms contained in the polymeric macrocycle varied from three to fourteen. The polymeric pseudocrown ether with fourteen oxygen atoms was found to perform best with  $\text{AuCl}_4^-$ ,  $\text{FeCl}_4^-$ , and  $\text{ZnCl}_4^{2-}$  due to its large cavity size. The polymers with nine and ten oxygen atoms also performed well with the anions. No complexation was found with macrocycles having less than four oxygen atoms. Comparing the anionic halides of Au(III) and Fe(III), the affinity trend was  $\text{MBr}_4^- > \text{MCl}_4^- > \text{ML}_4^-$ .

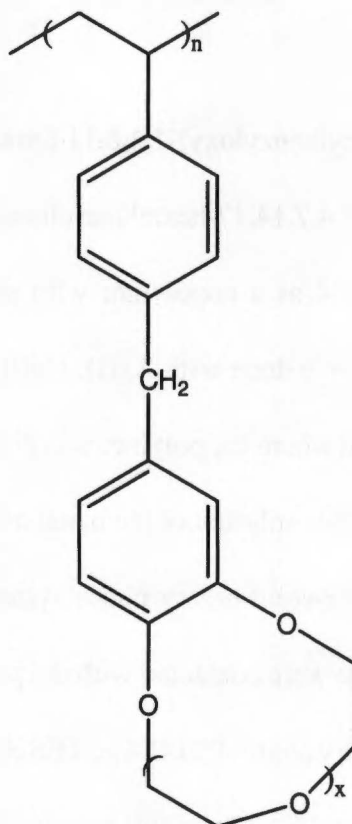
Polymer-supported benzocrown ethers were studied for their alkali ion affinities.<sup>28</sup> The crown ether cavity size contained four, five, six and eight oxygen atoms (Figure 1.8).



**Figure 1.6.** Membrane-supported benzo-18-crown-6



**Figure 1.7.** Polymer-supported pseudocrown ether



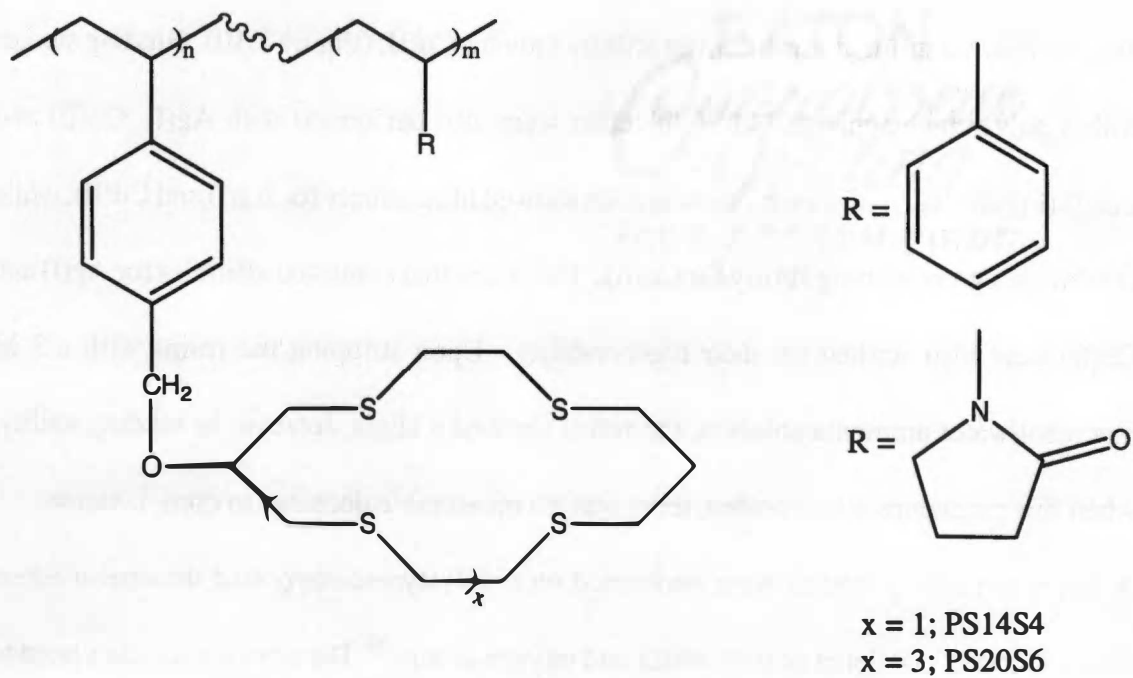
**Figure 1.8.** Polymer-supported benzocrown ether

All of the polymer-supported crown ethers displayed a similar trend of  $K > Cs > Na > Li$  except for a minimal difference in coordination of Cs and Na with the crown-4 and crown-5 resins. The metal salts studied were in the perchlorate, thiocyanate and bromide salts in methanol and the temperatures were varied from 20 – 60 °C.

## **THIACROWN ETHERS**

Homopolymers of poly(6-(4'-vinylbenzyloxy)-1,4,8,11-tetrathiacyclotetradecane) (PS14S4) and poly(9-(4'-vinylbenzyloxy)-1,4,7,14,17-hexathiacycloeicosane) (PS20S6) were prepared (Figure 1.9)<sup>29</sup> along with PS14S4 as a copolymer with styrene and N-vinylpyrrolidone (NVP). Complexation studies were done with Ag(I), Hg(II), Cu(II), Ni(II) and Cd(II) in a liquid-liquid binary phase system where the polymer was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and contacted with an equal volume of an aqueous solution of the metal nitrate form. An additional set of experiments was done in a water-solid binary phase system where aqueous solutions of silver, mercury and copper nitrate were contacted with the polymer in the absence of organic solvent. In the liquid-liquid binary phase, PS14S4 and PS20S6 were selective for Ag(I) and Hg(II), probably because Ag(I) and Hg(II) are soft acids and have a greater affinity towards soft bases such as thiacrowns. In the water-solid binary phase, only PS14S4-NVP showed an affinity for Ag(I). The reason ascribed for the decreased complexing ability of the other resins was their hydrophobicity. The PS14S4-NVP copolymer had increased hydrophilicity due having 74 mol% NVP. The soft acid binding capacity of the PS14S4 homopolymer and the styrene copolymer with 10 mol% PS14S4 was studied in Ag(I) and Hg(II) solutions at pH values from 1.6 to 5.8; in all cases, the resins complexed both ions.

Polystyrene-supported thiacrown ethers were studied to determine their binding

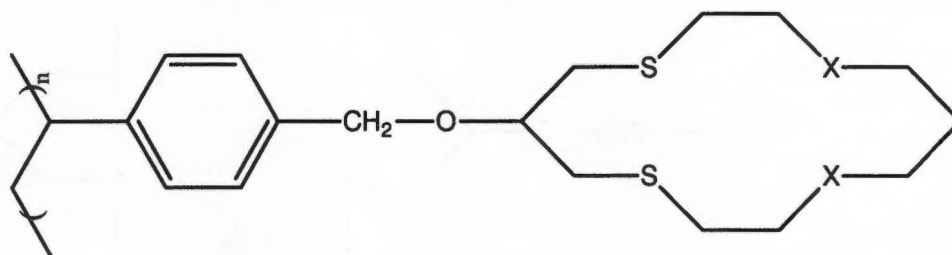


**Figure 1.9.** Copolymer containing polymer-supported thiacrown ether

affinities for Ag(I), Cu(II) and Cd(II) in methanol/water (4:1 v/v).<sup>30</sup> The studies were performed with microporous, porous and macroporous resins. With Ag(I), the microporous and porous resins had high affinities while the macroporous resin had a very low affinity (Figure 1.10). With Cu(II) and Cd(II), the amount of Cu(II) complexed by the resins decreased as the porosity of the resins decreased, while the degree of Cd(II) complexation was consistently low. Complexation studies with the macroporous analogue containing two oxygen and two sulfur atoms found an affinity only for Cu(II) (Figure 1.10). Binding studies with a polystyrene-supported 20S6 thioether were also performed with Ag(I), Cu(II) and Cd(II) (Figure 1.11). The macroporous resin showed little affinity for Ag(I) and Cd(II), while exhibiting a great binding ability for Cu(II). The resins that exhibited affinities for Ag(I) and Cu(II) were also studied for their regenerability. Upon stripping the resins with a 3 M methanol/water ammonia solution, the resins showed a slight decrease in binding ability; when this procedure was repeated, there was no measurable decrease in complexation.

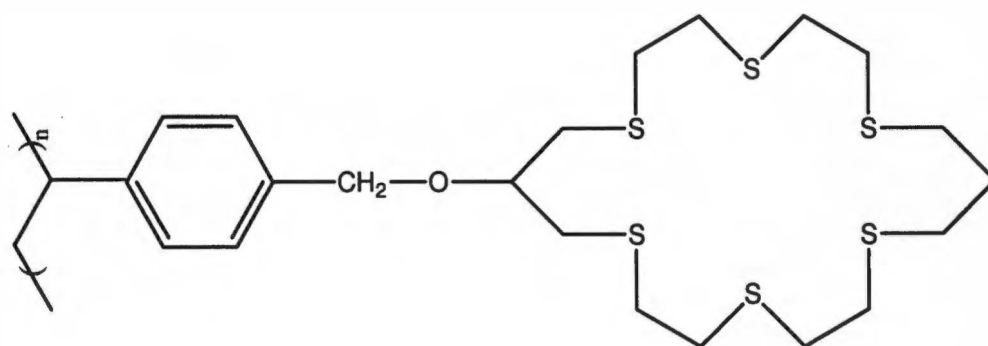
A series of binding studies were performed on a polystyrene-supported thiocrown ethers where the rings consisted of both sulfur and oxygen atoms.<sup>20</sup> The crown size was varied to study the complexation with different metal cations from aqueous solutions (Figure 1.12). The resins exhibited selectivities of Ag(I), Au(III) > Pd(II), Pt(IV), Hg(II), Cu(II) > Zn(II), Mg(II), K(I). The greater the number of sulfur atoms in the crown, the greater the affinity for Ag(I). In competition studies with solutions of Ag(I), Cu(II) and Zn(II) contacting resins PC3 and PC5, both resins demonstrated a greater binding affinity for Ag(I). In solutions of Au(III), Pd(II) and Pt(IV) in different combinations, both resins quantitatively complexed Au(III) and showed a selectivity order of Au(III) > Pd(II) > Pt(IV).



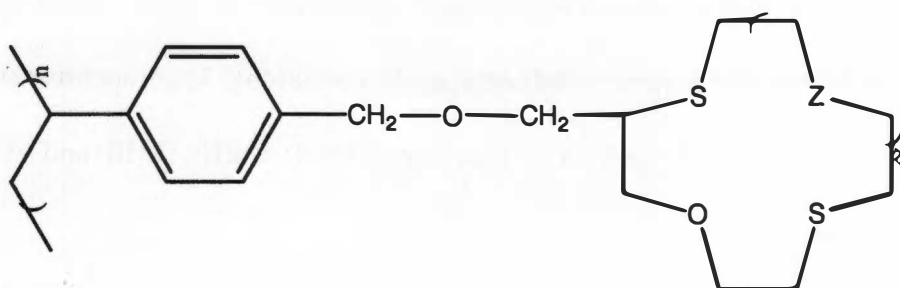


- a. X = S
- b. X = O

**Figure 1.10.** Polystyrene-supported thiacrown ether containing sulfur and oxygen atoms



**Figure 1.11.** Polystyrene-supported 20S6 thioether



PC1: Z = S, m = 0;    PC2: Z = S, m = 1;    PC3: Z = S, m = 2  
 PC4: Z = O, m = 1;    PC5: Z = O, m = 2;    PC6: Z = O, m = 3

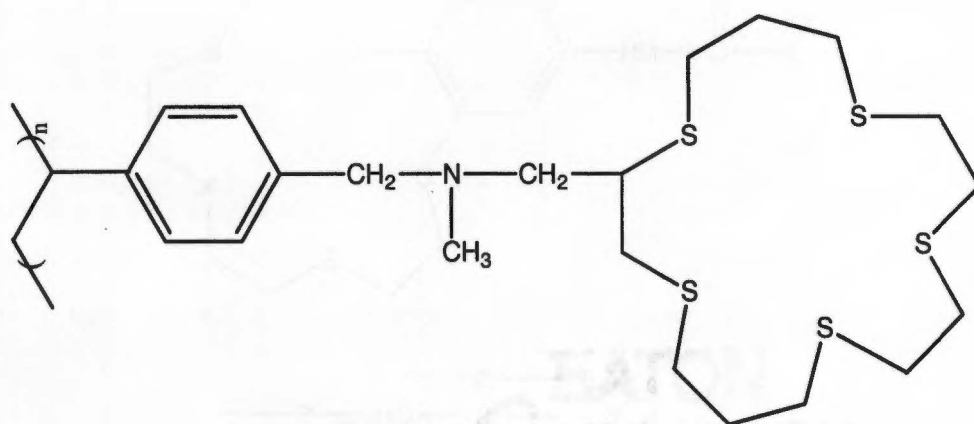
**Figure 1.12.** Polystyrene-supported thiacrown ether containing sulfur and oxygen atoms

The complexation of Hg(II) was studied with a 2-aminomethylthiacrown ether that had been immobilized onto a polystyrene support (Figure 1.13).<sup>10</sup> The resin was contacted with buffered Hg(II) aqueous solutions to evaluate its performance at various concentrations, pH values and contact times. It was found that the resin had a very high affinity for Hg(II) under all conditions. With pH values ranging from 1.46 to 6.12 and contact times as low as 30 minutes, the resin was able to complex >95% Hg(II) from all solutions. The rapid rate of complexation was attributed to the increased hydrophilicity of the resin due to the trialkylamine moiety that is protonated under acidic conditions. In competitive studies, the resin selectively complexed Hg(II) in the presence of Pb(II), Cd(II), Fe(III) and Al(III) under acidic conditions.

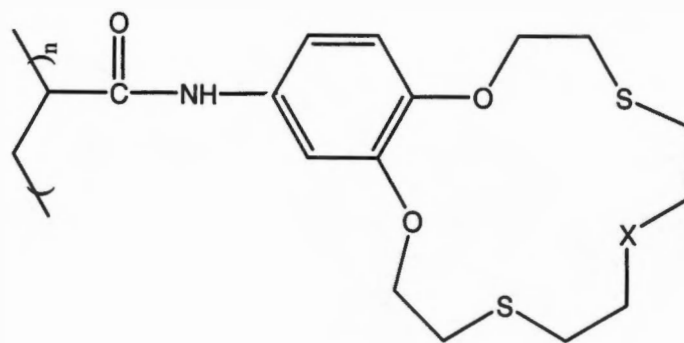
Metal binding studies were performed on thiacycrown ethers that had been bound by an amide linkage to the polymer backbone (Figure 1.14).<sup>31</sup> The thiacycrown ethers had both oxygen and sulfur atoms in the crown ring. The polymer, dissolved in chloroform, complexed both Ag(I) and Hg(II) from aqueous solutions. Though crown ethers consisting solely of oxygen as the donor atoms have a high affinity for alkali and alkaline earth metals, the mixed donor crowns have a low affinity for Na(I), K(I) and Ca(II). The polymers were also inefficient in complexing Cd(II), Co(II), Pd(II) and Fe(III). There was no significant difference in complexing ability when comparing a thiacycrown with five donor atoms vs. that of six donor atoms.

### **AZACROWN ETHERS**

Azathiacycrown ethers immobilized onto oxirane and thirane analogues of poly(glycidylmethacrylate) (GMA-O and GMA-S) have been prepared (Figure 1.15).<sup>32</sup> The

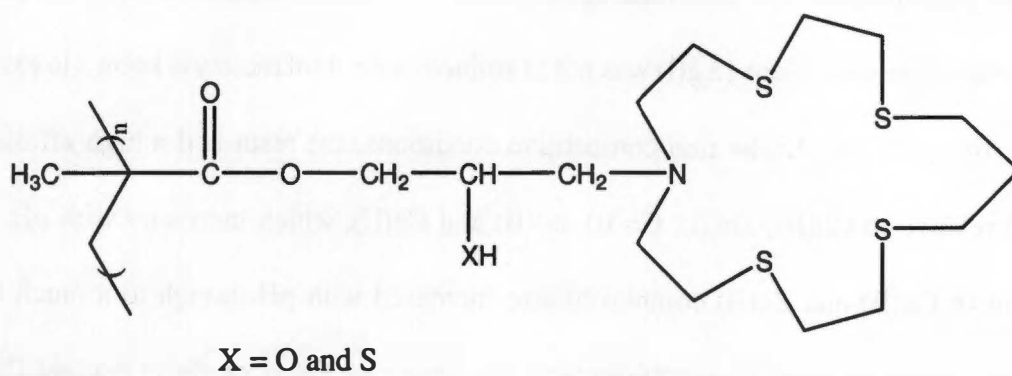


**Figure 1.13.** Polystyrene-supported 2-aminomethylthiacrown ether



- a. X = —S—  
 b. X = —S—(CH<sub>2</sub>)<sub>3</sub>—S—

**Figure 1.14.** Polymer-supported thiacrown ether with amide linkage

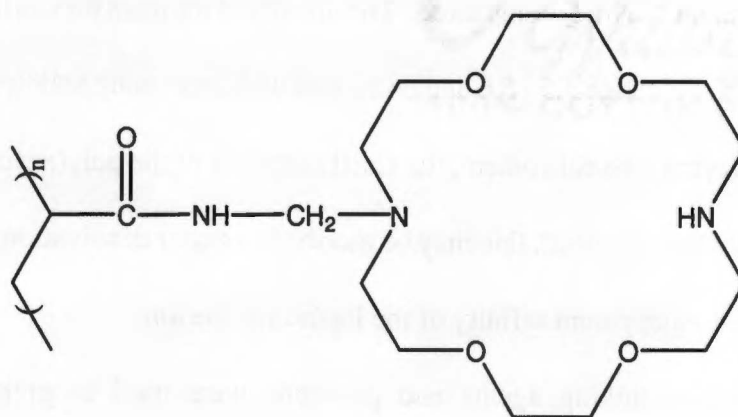


**Figure 1.15.** Polymer-supported azathiacrown ether

azathiacrown moiety contained one nitrogen and four sulfur atoms. Non-competitive and competitive metal ion studies were performed using metal salts in buffer solutions at pH values of 0.9 to 2.3 (in chloride or nitrate) and 2.5 to 6.0 (in acetate). In competitive binding studies using the chloride forms of Cu(II), Cd(II), Zn(II), Co(II) and Ni(II), the GMA-O resin showed an affinity for Cu(II) which increased with pH and a concomitant decrease in the amount of Cd(II) complexed. A competitive study with the nitrate form of Ag(I), Cu(II), Cd(II) and Zn(II) showed that the resin selectively complexed significant amounts of Ag(I) from all pH solutions. The sulfur analogue, GMA-S, was also studied under non-competitive and competitive conditions (Ag(I) was not examined as the thiol moiety is known to exhibit a high affinity for it). Under non-competitive conditions, the resin had a high affinity for Cu(II) relative to Cd(II), Zn(II), Co(II), Ni(II) and Ca(II), which increased with pH. The amount of Cd(II) and Zn(II) complexed also increased with pH though to a much lesser degree. Under competitive conditions with the same metal ions as above (except Ca(II)), GMA-S selectively complexed Cu(II) and the capacity increased with increasing pH.

Metal ion affinities were studied with an azacrown ether that had been immobilized onto a polyacrylamide gel.<sup>33</sup> The azacrown ether consisted of two nitrogen and four oxygen donor atoms (Figure 1.16). Complexation studies were performed in both water and methanol with alkali, alkaline earth and transition metals. In all studies, the distribution coefficients were higher in methanol than in water, probably due to differences in solvation of the ions. In both solvents, the polymer exhibited a high affinity for both Ag(I) and Hg(II) and was selective for alkaline earth over alkali metal ions. Complexation increased with increasing ionic diameter. With transition metals other than Ag(I) and Hg(II), the polymer



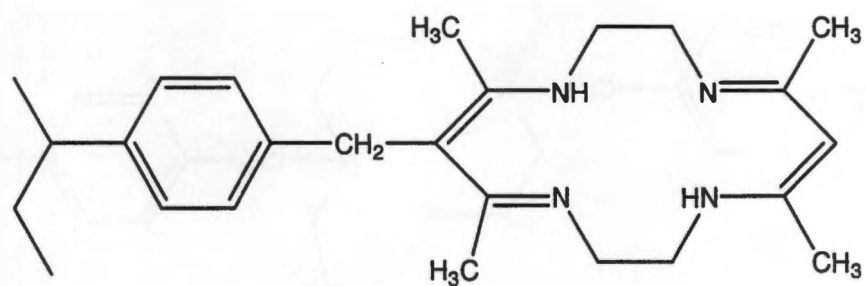


**Figure 1.16.** Polyacrylamide-supported azacrown ether containing nitrogen and oxygen atoms

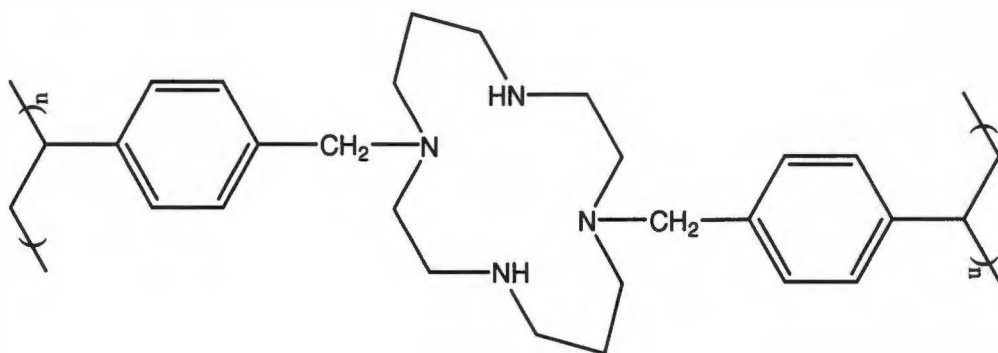
had a significantly higher affinity for Cd(II) and Zn(II) than Ni(II) and Co(II) in both water and methanol. Results were determined by potentiometric titration in water and conductimetry in methanol.

An azacrown ether was immobilized onto an iodomethylstyrene polymer (Figure 1.17)<sup>34</sup> and examined for metal ion binding properties using aqueous solutions of Cu(II) and Ni(II) acetate. The resin was selective for Cu(II) in a buffered solution at pH 5.6; there was no significant amount of Ni(II) complexed. The affinity of the resin for Cu(II) increased with increasing pH over the range 3.5 - 5.6 and decreased with increasing solution ionic strength. In solutions of varying ethanol content, the Cu(II) capacity of the poly(azacrown) increased as the ethanol content increased; this may be ascribed to easier desolvation of the metal ion and thus an increased apparent affinity of the ligand for the ion.

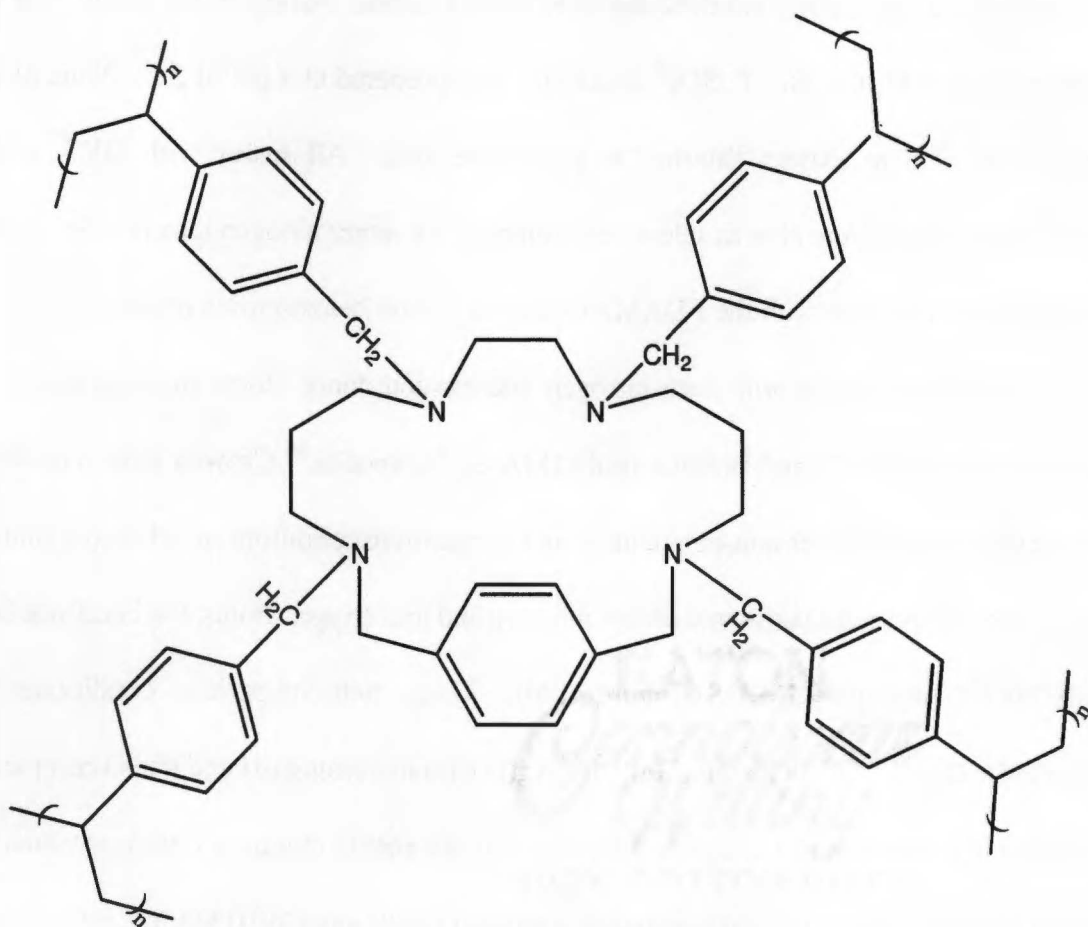
Different crosslinking agents and porogens were used to prepare a series of chloromethylated polystyrene supports which were then functionalized with an azacrown ether and the ion binding affinities determined (Figure 1.18).<sup>35</sup> One resin contained a benzocrown moiety (Figure 1.19). The crosslinking agents were divinylbenzene (DVB), ethylene glycol dimethacrylate (EGDMA) and ethylenediamine dimethacrylate (EDADMA); the porogens were dimethyl sulfoxide (DMSO), dodecanol and toluene. The metal ion studies, consisting of equimolar amount of the perchlorate salts of Na(I), Zn(II), Cu(II) and Ni(II) at pH 6, demonstrated that all resins were selective for Cu(II). The resin prepared with EDADMA and DMSO was also able to complex Ni(II). The benzocrown resin complexed significant amounts of Na(I) as well as Cu(II). It and its non-benzo analogue prepared with DVB and DMSO were examined for their ion binding affinities in a solution of equimolar



**Figure 1.17.** Iodomethylstyrene-supported azacrown ether



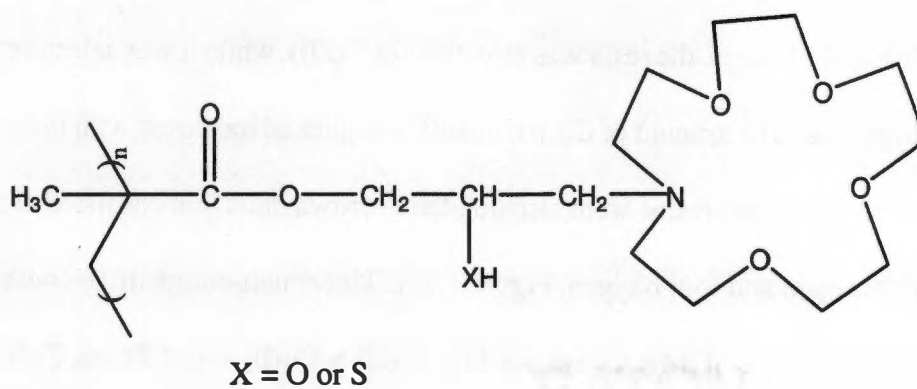
**Figure 1.18.** Azacrown ether crosslinked chloromethylated polystyrene



**Figure 1.19.** Benzo-containing azacrown ether crosslinked chloromethylated polystyrene

amounts of Na(I), K(I), Cs(I), Ni(II), Fe(II) and Hg(II). The benzo-containing azacrown moiety was able to extract all metals except Hg(II) and showed significant selectivity for Fe(II). The non-benzo-crown extracted only trace amounts of Ni(II) and Hg(II). The polymers were also studied for their ability to extract anions. An equimolar solution of the sodium salts of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> was prepared at a pH of 2.5. None of the resins was able to extract fluorine or phosphate ions. All resins with DVB as the crosslinking agent were able to selectively complex the larger halogen ions (I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup>); the trend was reversed with the EDAMA-crosslinked non-benzo-crown resins.

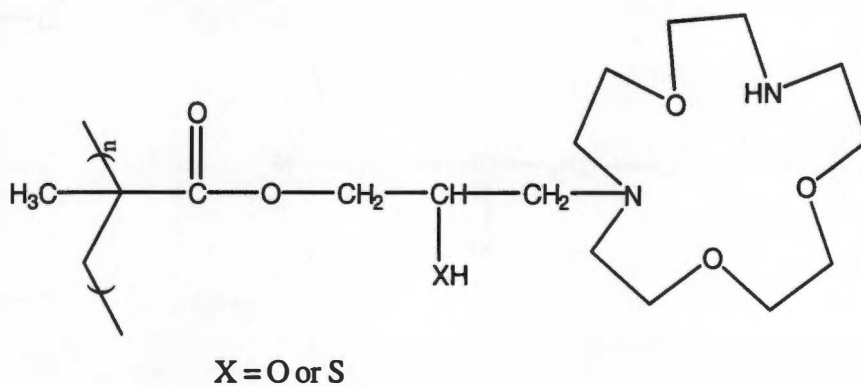
Azacrown ethers with both nitrogen and oxygen donor atoms were supported on oxirane (polyGMA-O) and thiirane (polyGMA-S) backbones.<sup>36</sup> Crowns with five donor atoms were studied under non-competitive and competitive conditions in buffered solutions. A polymer-supported azacrown with one nitrogen and four oxygen atoms was bonded to both polyGMA-O and polyGMA-S (Figure 1.20). Under non-competitive conditions, the polyGMA-O resin had a greater affinity for Ag(I) with increasing pH and it also complexed Cd(II) at pH values from 1.2 to 5.5. The resin was not able to complex significant amounts of Cu(II) and Zn(II). The thio analogue complexed Cu(II) and Cd(II) but had little affinity for Zn(II) and Ca(II); it was not studied with Ag(I) as the pendant thiol group is known to bind significant amounts of Ag(I).<sup>32</sup> Under competitive conditions, the polyGMA-O resin complexed Ag(I) predominately, though some Cu(II) was also extracted from a solution containing the nitrate forms of Ag(I), Cu(II), Cd(II) and Zn(II). The polyGMA-S resin was moderately selective for Cu(II) from a solution of Cu(II), Cd(II), Zn(II) and Ca(II). The studies were repeated with polyGMA-O and polyGMA-S containing crown units with two



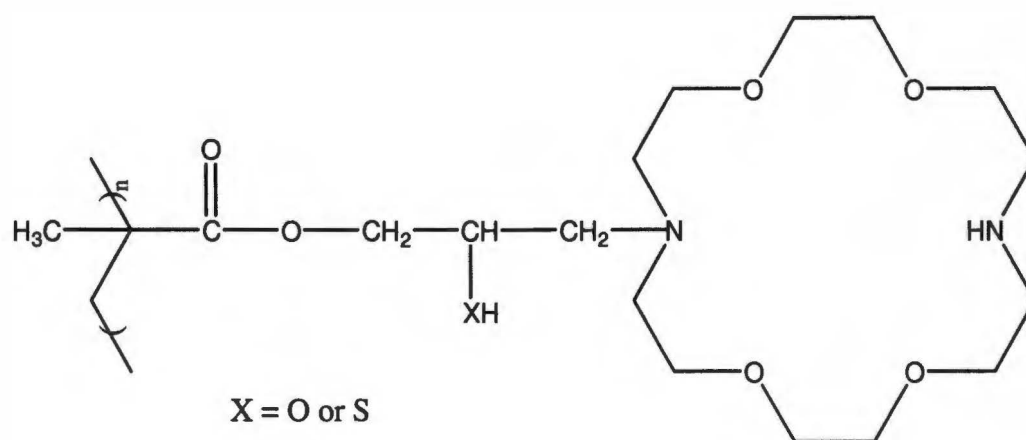
**Figure 1.20.** Polymer-supported azacrown ether containing nitrogen (one) and oxygen (four) atoms

nitrogen and three oxygen as the donor atoms (Figure 1.21). The former exhibited the highest affinity for Ag(I) under non-competitive conditions though it was also able to extract Pb(II) and Cu(II). The level of complexation increased with increasing pH. The resin had little affinity for Cu(II), Zn(II), Co(II) and Ni(II). PolyGMA-S had a greater affinity for Cu(II) over Cd(II) with increasing pH and no significant affinity for Zn(II), Co(II), or Ni(II). PolyGMA-O resin was contacted with a solution of the chloride salts of Cu(II), Cd(II), Zn(II), Co(II) and Ni(II) and a solution of the nitrate salts of Ag(I), Pb(II), Cu(II), Cd(II) and Zn(II). With the chlorides, the resin was selective for Cd(II), while it was selective for Ag(I) among the nitrates. The amount of Cd(II) or Ag(I) complexed increased with increasing pH. The oxirane and thiirane resins were also bonded to crown units that consisted of six donor atoms (two nitrogen and four oxygen, Figure 1.22). Under non-competitive conditions, the selectivity series for polyGMA-O was Ag(I) > Pb(II) > Cd(II) > Cu(II) and Zn(II) and for polyGMA-S was Pb(II) > Cu(II) > Cd(II) > Zn(II) > Co(II) and Ni(II). Under competitive conditions, polyGMA-O had little selectivity for any of the metals studied in the chloride form (Cu(II), Cd(II), Zn(II), Co(II) and Ni(II)) while, as nitrates, the resin selectively extracted Ag(I) and Pb(II) from a solution containing Ag(I), Pb(II), Cd(II), Cu(II) and Zn(II). PolyGMA-S was able to extract Cu(II) and Cd(II) from a solution of Cu(II), Cd(II), Zn(II), Co(II) and Ni(II).





**Figure 1.21.** Polymer-supported azacrown ether containing nitrogen (two) and oxygen (three) atoms



**Figure 1.22.** Polymer-supported azacrown ether containing nitrogen (two) and oxygen (four) atoms

## CHAPTER 2

### POLYMER-SUPPORTED 14-CROWN-4 AND ITS LITHIUM SORPTION CAPACITIES

#### INTRODUCTION

Polymer-supported reagents that are capable of complexing targeted metal ions from aqueous solutions are an important area of research.<sup>12,37</sup> Polymer-supported crown ethers are known to be metal-selective reagents and, therefore, have great significance in this field.<sup>38,39</sup> There are many advantages to covalently bonding the crown ether to the polymeric backbone including the ease of reaction work up and recovery of the support.<sup>40</sup>

Incorporation of crown ethers into a polymer network can be done either by copolymerization or by grafting. In order to copolymerize a crown ether, it must contain a polymerizable group.<sup>41</sup> Though copolymerization can be difficult due to the need for comparable reactivity ratios, it is possible to produce a well-defined structure; however, the crown ether may be somewhat inaccessible.<sup>41,42</sup> Grafting is feasible if the crown ether has a functional group that can be further reacted with a moiety on the polymer backbone. Immobilization of a crown ether by this mechanism can leave the crown ether more accessible. Due to the ease of reaction in many cases, the latter is preferred.

Given the selectivity of crown ethers towards alkali and alkaline earth metal cations<sup>40</sup>, the purpose of this chapter is to present a polymer-supported crown ether that demonstrates a selectivity towards the lithium ion. The importance of this project was due to the need for remediation of lithium found in ground water near the Oak Ridge Y-12 plant, which was at a concentration that was high enough to be harmful to marine

life.<sup>43</sup> The presence of lithium in the ground water is a result of land-disposal of lithium waste produced in the manufacturing of nuclear weapons, shielding and reactor control rods. Because there was a need for selective removal of lithium from the ground water, a 14-crown-4 molecule was chosen to be polymer-supported as it has been demonstrated that crown ethers with 13 and 14 member rings containing four oxygen atoms display great affinities for the lithium cation.<sup>3,44</sup> The selectivity of the polymer-supported 14-crown-4 will be discussed.

## **EXPERIMENTAL**

### **Synthesis of 6-Methylene-2,2,3,3,9,9,10,10-Octamethyl-14-Crown-4 (14C4)**

The vinyl substituted crown ether was synthesized in a multistep reaction that was completed by the synthetic route described by Sachleben and coworkers.<sup>44</sup>

### **Synthesis of 6-Keto-2,2,3,3,9,9,10,10-Octamethyl-14-Crown-4 (14C4=O)**

The keto- substituted 14-crown-4 was produced by ozonolysis of 14C4 in the presence of ethyl acetate and then dimethyl sulfide (DMS). The reaction product was purified for further use.

### **Synthesis of 6-Hydroxymethyl-2,2,3,3,9,9,10,10-Octamethyl-14-Crown-4 (14C4OH)**

The alcohol substituted crown ether was prepared by the reaction of 14C4 with borane dimethyl sulfide complex in a solution of tetrahydrofuran (THF). Upon reaction, a solution of 30% hydrogen peroxide was added. The product was then purified for use.

### **Synthesis of Copolymers**

Vinylbenzylchloride (VBC) and glycidyl methacrylate (GMA) copolymers were synthesized by suspension polymerization with the exception of the VBC/acrylamide

(VBC/AA) resin that was copolymerized by bulk polymerization. The macroporous resins (MR) were prepared with 5% divinylbenzene (DVB) crosslinking. Gel resins consisted of 2% DVB crosslinking. The size of the beads studied was 150-250  $\mu\text{m}$ .

### **Synthesis of Poly(Aminomethylstyrene) (AMS)<sup>45</sup>**

The Gabriel synthesis was performed on VBC beads by successive reactions with potassium phthalimide and hydrazine to prepare AMS. The resin was prepared on both gel and MR beads. Nitrogen elemental analysis was performed to analyze the resin after it had been washed.

### **Synthesis of AMS-Supported Vinyl Resin in THF**

Acrylonitrile (AN), VBC and methyl methacrylate (MMA) were each reacted with AMS in the presence of THF. The reactions were performed on gel resins. Upon reaction completion, the resins were washed and analysis of nitrogen capacity was performed.

### **Synthesis of AMS-Supported Vinyl Resin in Diethylamine (Et<sub>2</sub>NH) and Dimethyl Sulfoxide (DMSO)**

AN and vinylidene-1,1-diphosphonic acid tetraethyl ester (VDPE) were reacted with AMS in the presence of Et<sub>2</sub>NH and DMSO. The reactions with AN were performed on both gel and MR beads, and upon completion, washed and analyzed by nitrogen elemental analysis. The reactions with VDPE were performed only on gel beads and the resulting resins were washed and analyzed for both nitrogen and phosphorus capacities.

### **Synthesis of AMS-Supported 14C4**

The reactions involving 14C4 with AMS were performed in a similar manner as the reactions with AN and VDPE, using Et<sub>2</sub>NH and DMSO. The molar ratios were

varied and the resulting resins were washed before performing nitrogen elemental analysis.

### **Schiff Base Reaction of AMS and Benzophenone**

The reaction of benzophenone with AMS was performed two different ways. The first involved the use of potassium hydroxide and THF, while the other involved the use of titanium (IV) chloride and Et<sub>2</sub>NH. Nitrogen elemental analysis was performed on the resins upon washing.

### **Schiff Base Reaction of AMS and 4-Methyl-2-Pentanone (MIBK) and Cyclohexanone**

Absolute ethanol was used in the Schiff base reactions of MIBK and cyclohexanone with AMS. A comparative experiment was performed with MIBK utilizing dioxane as the solvent. The reactions with cyclohexanone were performed on both gel and MR resins; the reaction time and temperature were varied. Nitrogen capacity was determined upon washing of the resulting resins.

### **Schiff Base Reaction of AMS and 14C4=O**

The reaction of AMS and 14C4=O was performed in the presence of 100% ethanol in a manner similar to that of the reactions with MIBK and cyclohexanone. Molar ratios were varied, as well as reaction time. The resin was characterized by nitrogen elemental analysis.

### **Hydride Abstraction of $\beta$ -Ketophosphonate Ethyl Ester Resin**

The  $\beta$ -ketophosphonate ethyl ester resin was reacted with sodium hydride (NaH) and then a vinyl-containing compound (AN or VDPE) in the presence of dioxane. Gel, xerogel and MR resins were investigated. Upon reaction, the resin containing AN was

analyzed for nitrogen and phosphorus content and the VDPE, for phosphorus content.

### **Hydride Abstraction of $\beta$ -Ketophosphonate Ethyl Ester Resin and Reaction with 14C4**

The reaction of 14C4 and  $\beta$ -ketophosphonate ethyl ester resin that had been deprotonated was performed in the presence of dioxane. The reaction was studied using gel, xerogel and MR beads. The resulting resin was analyzed for phosphorus content.

### **Etherification Reactions with Various Alcohols**

Etherification was performed by the deprotonation of a number of alcohols before coming in contact with the appropriate polymer. The alcohols studied were benzyl alcohol (BA), cyclohexanol, 1-pentanol and diethylene glycol monomethyl ether. Reactions utilizing VBC were analyzed by chlorine elemental analysis upon reaction completion. Reactions using VBC/AA copolymers were analyzed by nitrogen and chlorine capacity.

### **Etherification Reactions with 14C4OH**

Etherification reactions using 14C4OH were performed on VBC, VBC/AA and GMA copolymers in the presence of NaH and dioxane. The time and temperature of reaction were varied, as well as matrix porosity. Resins produced by the use of VBC were characterized by chlorine elemental analysis, while the VBC/AA copolymers were characterized by both chlorine and nitrogen elemental analysis. Reactions with GMA did not have an appropriate target atom that could characterize the resins so the degree of functionalization was estimated by contact with concentrated metal ion solutions.

## RESULTS AND DISCUSSION

Noted above, crown ethers are introduced into polymers in two different ways: direct polymerization and grafting reactions. The difficulty in preparing 14C4 and the limited batch sizes from which it was recovered were serious considerations when deciding which methods to use to immobilize the crown ether. The 14C4 contained a vinyl group that could be modified to produce different functional groups, and this allowed for both modes of immobilization. The final 14C4 compounds decided upon were done so because of the ease of modification and the prospect that the product would be found in high yields. Therefore, the three 14C4 products used were the one containing the vinyl substituent (14C4), a ketone form of 14C4 (14C4=O) and hydroxymethyl 14C4 (14C4OH).

### Copolymerization of 14C4

The first attempts at immobilization used bulk and solution polymerizations. Free radical polymerization of the vinyl 14C4 was attempted but reaction did not occur due to steric hindrance of the crown ether. Further experiments were performed to copolymerize 14C4 with a number of different monomers, including VBC. Many experiments were carried out, each time with varying conditions, to determine the most effective method. The variables studied were the molar ratios, degree of crosslinking, amount of initiator and the presence of solvent. Elemental analysis and FTIR spectroscopy were performed to verify that 14C4 was incorporated into the polymer. With FTIR spectroscopy, it was difficult to quantitatively determine the degree of copolymerization of 14C4 with the other monomers. Chlorine and nitrogen elemental analyses performed on the resulting polymers were also difficult to use for estimation of



the degree of reaction because of the large increase in molecular weight of the resulting polymer; even a small amount of 14C4 would significantly change the chlorine or nitrogen capacity.

Another problem arose from the method used to prepare the copolymers. The resins produced by bulk polymerization in borosilicate scintillation vials solidified within them. The resins were isolated by shattering the vials with a hammer, the glass pieces were removed and the polymers were broken into smaller pieces by repeated hammering. This resulted in polymer pieces that were not consistent in size and shape. There were similar difficulties with the solution polymerizations. Upon completion of copolymerization, although the resin was pliable, it had to be broken and scraped out of the vial and, again, the remaining pieces did not have the same size or shape.

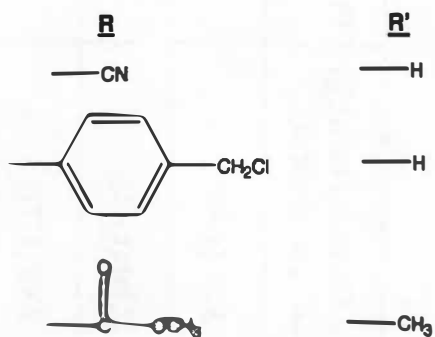
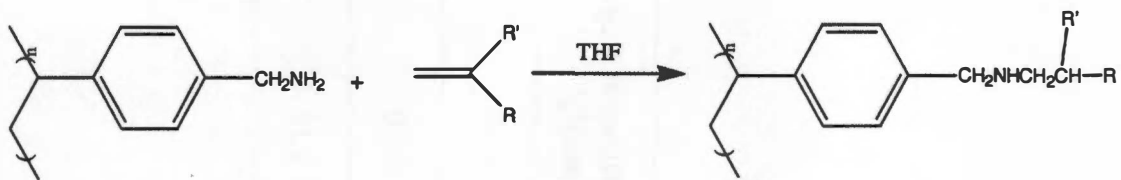
### **Vinyl Addition to AMS**

It became apparent that the attempts to incorporate 14C4 into the polymer by direct copolymerization were not feasible due to steric hindrance around the vinyl group. For example, upon copolymerization with VBC (7.3% crosslinked), a chlorine capacity of 6.28 meq/g was found, indicative of no reaction as the theoretical calculated value of polymerization without the incorporation of 14C4 was 5.69 meq/g. Had the copolymerization proceeded as expected, the chlorine capacity of the resulting polymer would decrease with the addition of 14C4 because of the increase in molecular weight. This finding was consistent with a copolymerization at higher degrees of crosslinking (17.0%), with a theoretical chlorine capacity of 4.54 meq/g upon no reaction with 14C4, the true chlorine capacity was 4.81 indicating no reaction. The difficulty of direct copolymerization of crown ethers is consistent with reports in the literature.<sup>6</sup> Grafting

reactions were next attempted and chosen based on the functional groups that could be prepared on the vinyl substituent of 14C4. Because of this, the first in the series of experiments consisted of reactions that allowed the vinyl form of the crown ether to be used.

The first type of reaction performed utilized aminomethylated polystyrene (AMS) and 14C4. Control reactions were attempted before 14C4 was used due to the limited supply of the compound in order to explore reaction conditions. Reactions were performed with AN, VBC and MMA in THF<sup>46</sup> on 2% crosslinked gel beads for 22 h (Figure 2.1). Nitrogen capacity was determined to estimate the percent reaction (Table 2.1). The percent functionalization values were calculated by using the nitrogen capacity of the precursor AMS resin, 3.10 meq/g, and comparing that to the actual and theoretical nitrogen capacities for each resin formed. AMS-supported VBC was found to have a final nitrogen capacity of 2.80 meq/g, indicating 18.1% functionalization. Both AMS-supported AN and MMA were found to be 9.8% functionalized, with nitrogen capacities of 3.23 and 2.97 meq/g, respectively, though it is unclear of how accurate the calculation for the AN-containing resin is as there is the addition of nitrogen to the resin. Nonetheless, it was found that with all of the compounds used, the degree of functionalization was limited.

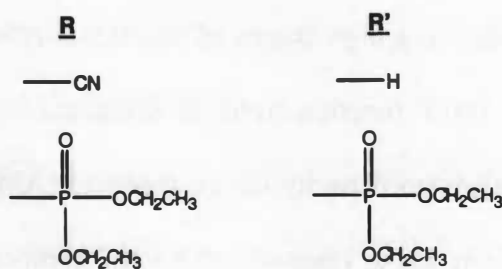
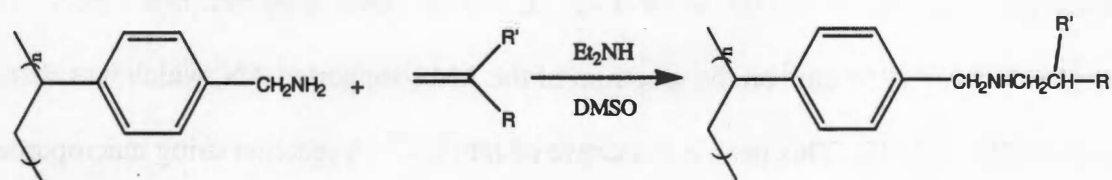
The lack of progress using the previous reaction led to another method to functionalize the vinyl compounds onto AMS using Et<sub>2</sub>NH and DMSO (Figure 2.2).<sup>47</sup> AN was used in the exploratory experiments. When comparing reactions on 2% crosslinked gel resins, it was found the reaction produced a highly functionalized resin. Experiments at 80 °C and 150 °C for 17 hours indicated that there was little influence of



**Figure 2.1.** Reaction of AMS-supported vinyl compounds in THF

**Table 2.1****Vinyl addition reactions in the presence of THF**

<b>Vinyl Compound</b>	<b>Reaction Conditions</b>	<b>Nitrogen Capacity (meq/g) Actual (Theoretical)</b>	<b>Precursor Nitrogen Capacity (meq/g)</b>	<b>% Functionalization</b>
AN	22 h, 25 °C	3.23 (4.43)	3.10	9.8
VBC	22 h, 40 °C	2.80 (1.44)	3.10	18.1
MMA	22 h, 40 °C	2.97 (1.77)	3.10	9.8



**Figure 2.2.** Reaction of AMS-supported vinyl compounds  
using Et<sub>2</sub>NH and DMSO

temperature (Table 2.2). The nitrogen capacities of the resins were 9.06 and 8.82 meq/g for the reactions done at 80 °C and 150 °C, respectively. Based on the theoretical values calculated from the nitrogen capacity of the precursor resin (6.11 meq/g), it was estimated that there was 100% functionalization. Again, it is unclear of how accurate this calculation is due to the addition of nitrogen atoms to the resin from the AN. An FTIR spectrum was taken of the product formed at 150 °C though it was difficult to discern differences with that of the precursor resin. It can be noted, however, that a peak was found at roughly 2250  $\text{cm}^{-1}$  on the spectrum of the AMS-supported AN, which was absent on the FTIR of AMS. This peak is indicative of nitriles.<sup>48</sup> A reaction using macroporous AMS beads at 150 °C for 17 hours demonstrated that enhanced accessibility of AN into the polymer also resulted in a high degree of functionalization. The macroporous resin was also found to be 100% functionalized, as estimated by the nitrogen content, 7.83 meq/g, based on the nitrogen capacity of the precursor AMS resin (5.12 meq/g). The success of these reactions led to reactions of a vinyl compound that was very sterically hindered, VDPE. Reactions were performed with AMS and VDPE in the presence of  $\text{Et}_2\text{NH}$  and DMSO at reflux. All of the reaction conditions were held constant with the exception of reaction time (Table 2.3). At a reaction time of 17 hours, the AMS-supported VDPE was found to be 68.6% functionalized, with a phosphorus capacity of 1.42 meq/g. As the reaction time was increased to 59 hours, the phosphorus content was determined to be 1.57 meq/g, or 75.9% functionalized. The final time dependent experiment (96 hour reflux) resulted in a resin that was 95.7% functionalized, with a phosphorus capacity of 1.98 meq/g. It was observed that increased reaction time resulted in resins that had a higher amount of functionalization. An FTIR spectrum was obtained

**Table 2.2****Reactions of AMS with AN in the presence of Et<sub>2</sub>NH and DMSO**

<b>Resin Type</b>	<b>Reaction Temperature</b>	<b>Nitrogen Capacity (meq/g) Actual (Theoretical)</b>	<b>Precursor Nitrogen Capacity (meq/g)</b>	<b>% Functionalization</b>
Gel	80 °C	9.06 (8.74)	6.11	100
Gel	150 °C	8.82 (8.74)	6.11	100
MR	150 °C	7.83 (7.32)	5.12	100

**Table 2.3****Reactions of AMS with VDPE with varying reaction times**

<b>Reaction Time</b>	<b>Phosphorus Capacity (meq/g) Actual (Theoretical)</b>	<b>Precursor Nitrogen Capacity (meq/g)</b>	<b>% Functionalization</b>
17 h	1.42 (2.07)	6.24	68.6
59 h	1.57 (2.07)	6.24	75.9
96 h	1.98 (2.07)	6.24	95.7

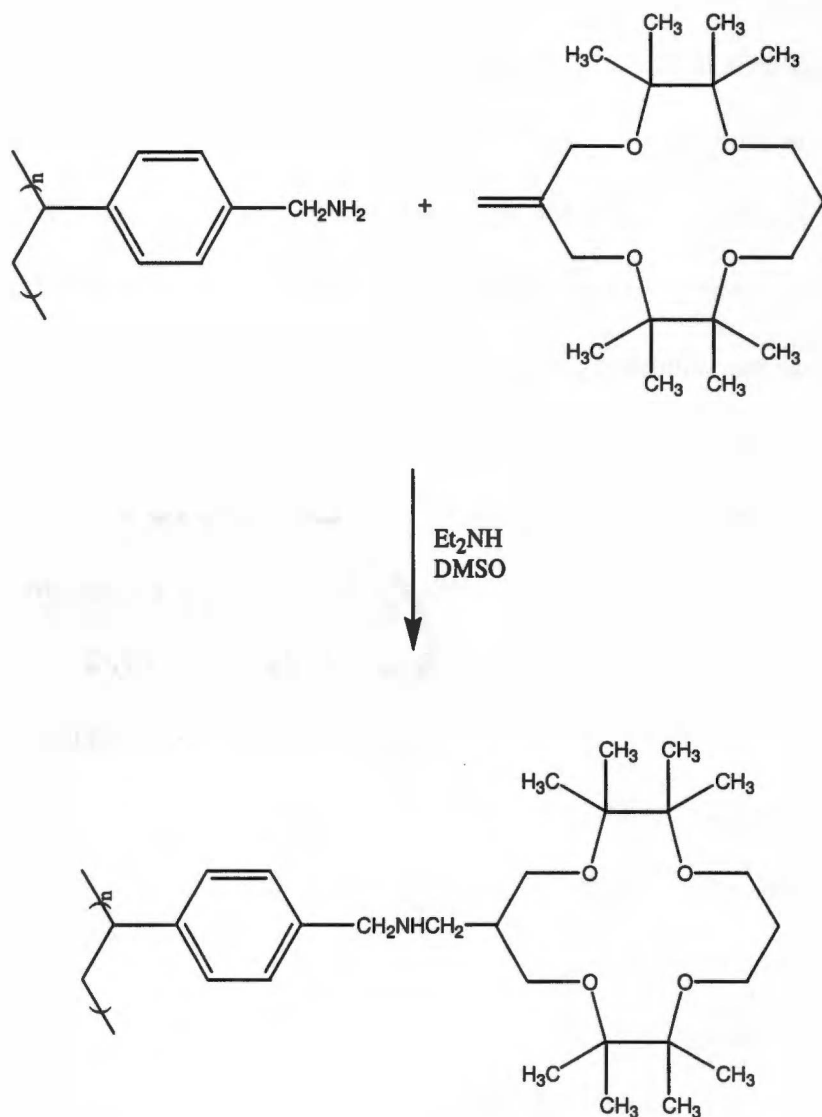


for the resin formed in the 59 hour experiment; however, the resolution was poor and it was not possible to see any peaks distinctive of phosphoryl groups. Reactions with AMS and 14C4 were performed in Et<sub>2</sub>NH and DMSO under similar conditions (Figure 2.3). In the first attempt, the molar ratios used were the same as those with AN and VDPE (1:1.7:1.7, AMS:vinyl compound:Et<sub>2</sub>NH). Two additional reactions were attempted where the molar ratios of 14C4 and Et<sub>2</sub>NH were doubled when compared to the previous experiment and one utilized wet AMS beads and the other dry AMS beads. Nitrogen elemental analysis indicated that there was little difference in the amount of reaction that took place when the conditions were altered (Table 2.4). The initial experiment, which had a molar ratio of 1:1.7:1.7 for AMS:14C4:Et<sub>2</sub>NH, had a percent reaction of 36.8%, with a nitrogen capacity of 4.51 meq/g (nitrogen capacity of AMS precursor resin: 6.11 meq/g). There was little difference when the molar ratios of 14C4 and Et<sub>2</sub>NH were doubled, both with wet and dry beads. The wet resin was found to have a percent functionalization of 34.3% (4.62 meq N/g), while the dry resin had a percent functionalization of 40.2% (4.36 meq N/g). Though there was some functionalization, it was decided that other methods may be more effective in yielding a resin with a significant amount of 14C4.

### **Schiff Base Reactions**

The addition of amines to aldehydes and ketones allows the formation of imines. The ease of the Schiff base reaction along with evidence that this reaction yields product in good quantities led to the next set of experiments.<sup>49</sup>

A ketone form of 14C4 (14C4=O) was produced by ozonolysis of the vinyl form of the crown ether (Figure 2.4). Reaction of this functional group with the AMS resin

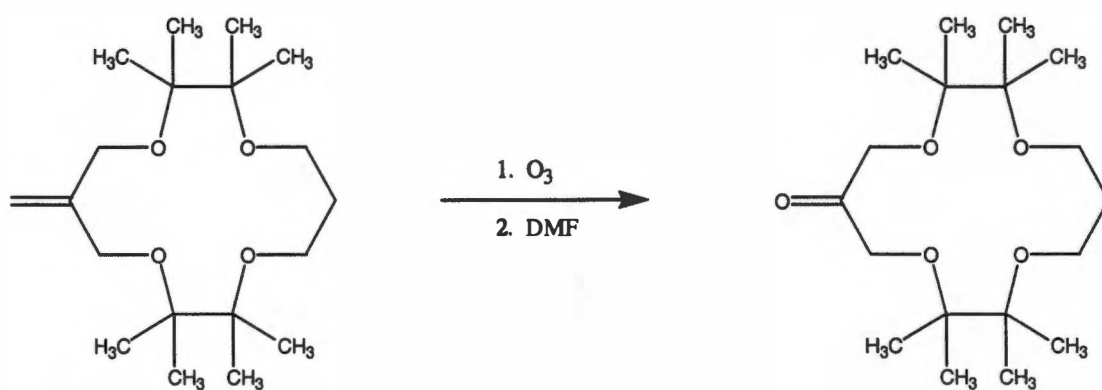


**Figure 2.3.** Reaction of AMS-supported 14C4

**Table 2.4**

**Reactions with AMS and 14C4**

<b>Molar Ratio AMS:14C4:Et2NH</b>	<b>Nitrogen Capacity (meq/g) Actual (Theoretical)</b>	<b>Precursor Nitrogen Capacity (meq/g)</b>	<b>% Functionalization</b>
1:1.7:1.7	4.51 (1.76)	6.11	36.8
1:3.4:3.4	4.62 (1.76)	6.11	34.3
1:3.4:3.4	4.36 (1.76)	6.11	40.2



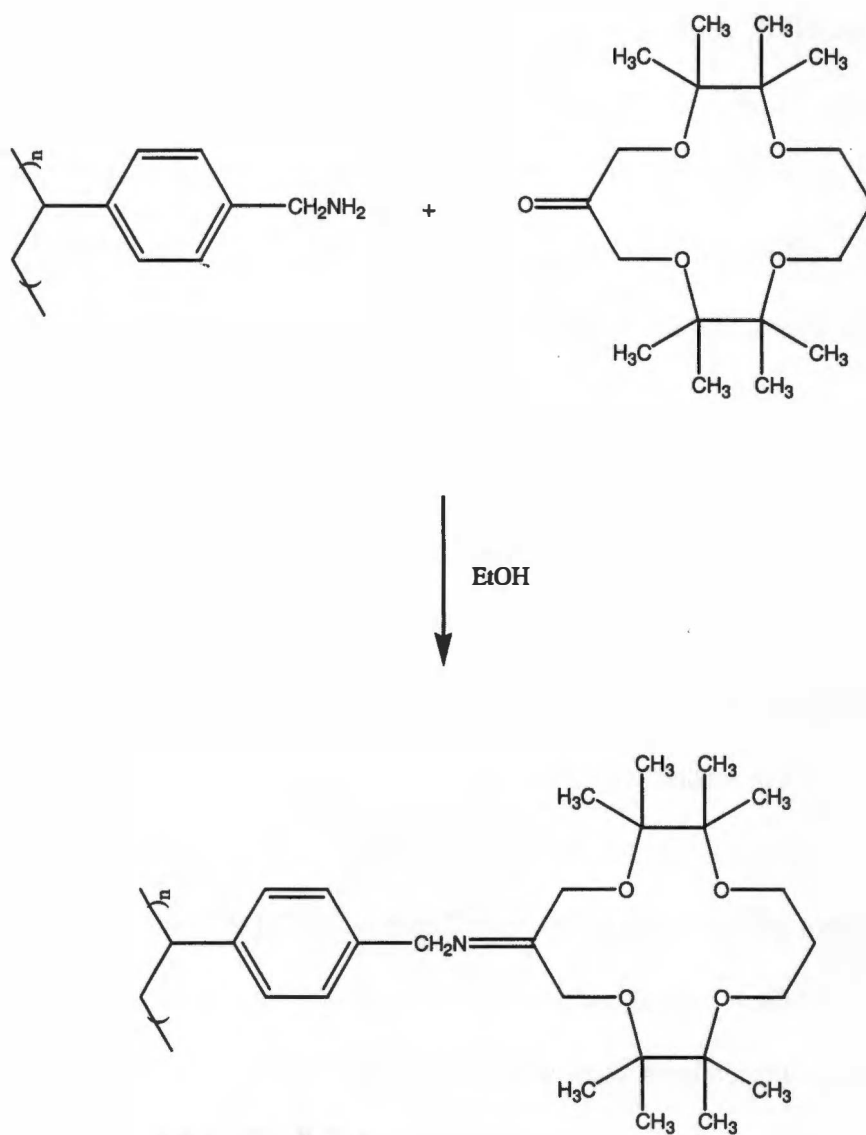
**Figure 2.4.** Ozonolysis of 14C4

would generate a polymer with the crown ether grafted by an imine linkage (Figure 2.5). Due to the limited quantity of 14C4=O, several control reactions were performed with AMS and a number of aldehydes and ketones to investigate the types of conditions that were the most effective for immobilization. Reactions were carried out on both gel and MR forms of the AMS resin, 150-250  $\mu\text{m}$  in size.

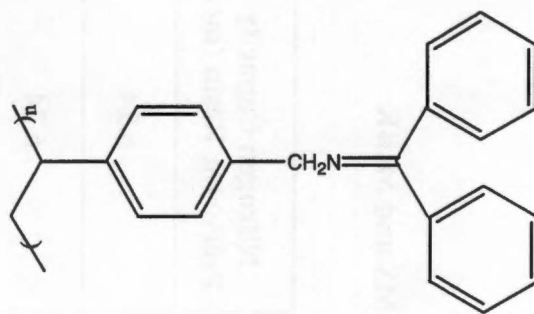
The first set of reactions involved the immobilization of benzophenone onto gel beads (Figure 2.6). A thirteen-fold excess of benzophenone was added to AMS in the presence of potassium hydroxide and THF.<sup>50</sup> This reaction was refluxed for 17 hours and the resulting polymer was evaluated for nitrogen content. A final nitrogen capacity of 5.01 meq/g indicated 29.4% functionalization. Another synthesis was set up with AMS and benzophenone in the presence of titanium (IV) chloride and THF with a seven day reaction time.<sup>51</sup> No reaction occurred by this method (6.05 meq N/g). The results of these experiments can be explained by the bulkiness of the benzophenone.

Two reactions were performed on gel beads with the less sterically hindered ketone 4-methyl-2-pentanone (or methyl isobutyl ketone, MIBK), one in absolute ethanol and the other in dioxane. Upon reflux for 96 hour with a fivefold excess of MIBK to AMS, it was found that both solvents gave the same results (Table 2.5). Nitrogen elemental analysis showed that the resin (Figure 2.7) formed in ethanol had a nitrogen capacity of 4.70 meq/g (64.7% functionalized), while the resin formed in dioxane was found to be to have a nitrogen capacity of 4.75 meq/g (62.6% functionalized). Further reactions using this procedure used absolute ethanol as it is less expensive and less toxic than dioxane.

A set of control reactions was performed with cyclohexanone (Figure 2.8), as a



**Figure 2.5.** Synthetic scheme of Schiff base reaction of AMS and 14C4=O



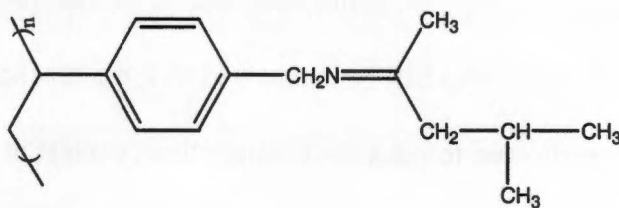
**Figure 2.6.** Product of Schiff base reaction of AMS with benzophenone

**Table 2.5**

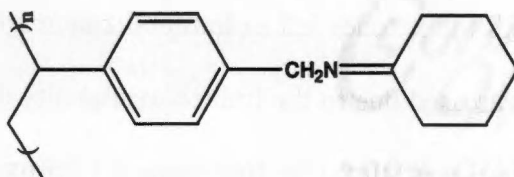
**Schiff base reactions of AMS and MIBK**

<b>Solvent</b>	<b>Nitrogen Capacity (meq/g) Actual (Theoretical)</b>	<b>Nitrogen Capacity of Precursor Resin (meq/g)</b>	<b>% Functionalization</b>
Ethanol	4.70 (3.86)	6.24	64.7
Dioxane	4.75 (3.86)	6.24	62.6





**Figure 2.7.** Product of Schiff base reaction of AMS with 4-methyl-2-pentanone



**Figure 2.8.** Product of Schiff base reaction of AMS with cyclohexanone

model of a cyclic ketone. Three reactions were completed, one at 25 °C for 40 hours and two at reflux for 24 hours. The reaction at 25 °C and one at reflux were done on MR beads, and the second reflux reaction was on a gel resin. Nitrogen content was analyzed to estimate functionalization by comparing the results of the product to that of the precursor resin. Reactions on the MR resin showed that the reaction proceeded further when the contents were allowed to react for a longer time, even if at a lower temperature (Table 2.6). The reaction of cyclohexanone with AMS MR beads at 25 °C for 40 hours produced a resin that was 77.0% functionalized (3.50 meq N/g). The same type of resin, when reacted at reflux for 24 hours had a nitrogen capacity of 3.82 meq/g, which indicated that it was 70.9% reacted. When comparing the two reactions done with identical conditions on different types of resins, it was found that the gel resin was functionalized to a higher yield than that of the MR. The gel resin was found to have a nitrogen content of 3.86 meq/g, which demonstrated 100% reaction. This result was somewhat surprising as the MR resin has a greater porosity than the gel resin, which allows for increased accessibility.<sup>52</sup>

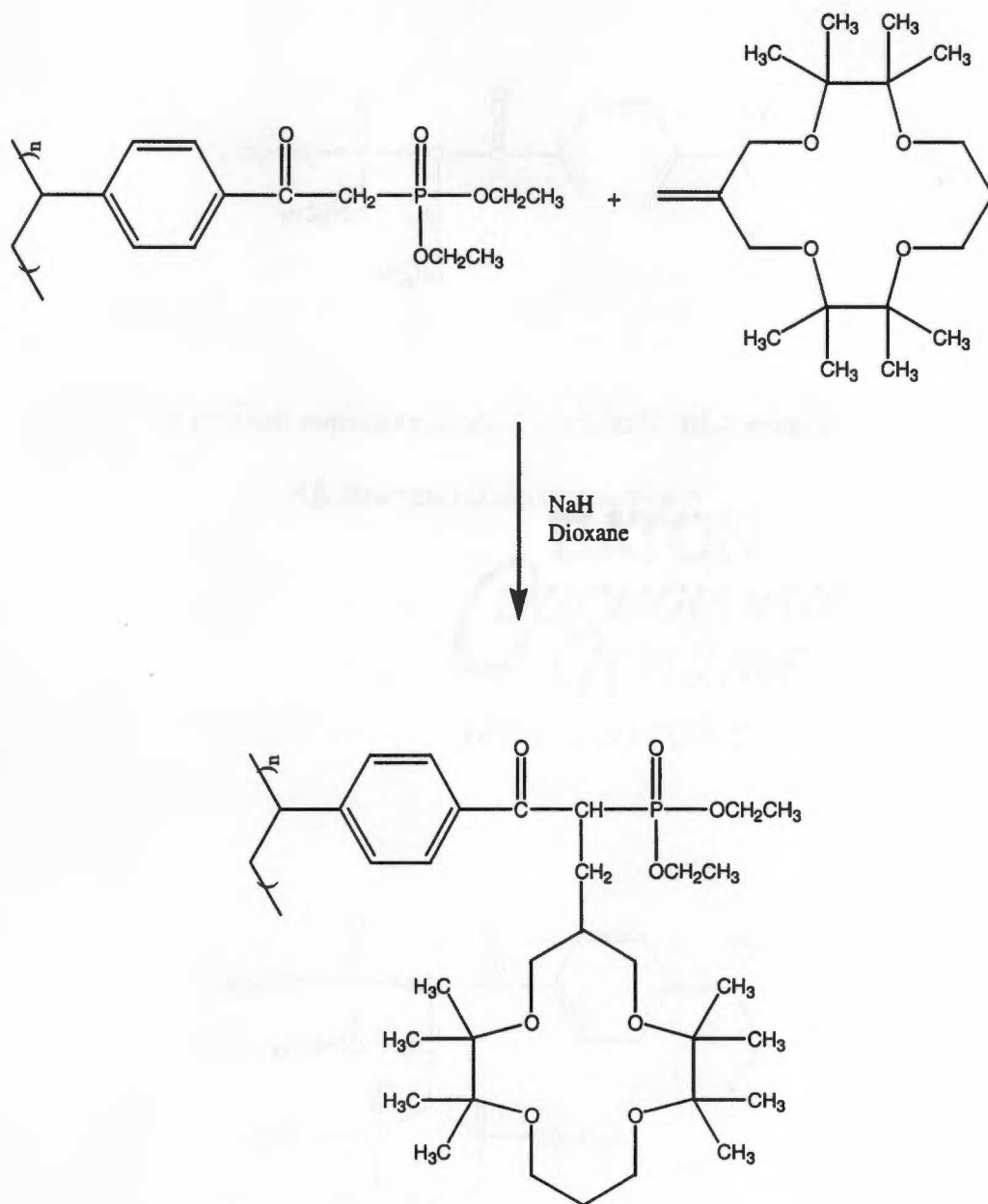
The reactions with the ketones led to immobilization attempts with  $^{14}\text{C}_4=\text{O}$ . A one-to-one molar ratio was used due to the limited availability of  $^{14}\text{C}_4=\text{O}$ . The reaction with AMS beads in ethanol was stirred for four days at a reflux. The resulting resin was expected to have a nitrogen capacity of 1.53 meq/g, based on the theoretical molecular weight of the resin produced. The actual nitrogen capacity of the resin was 3.33 meq/g. Compared to the capacity of the precursor AMS resin, 5.12 meq/g, functionalization with  $^{14}\text{C}_4=\text{O}$  did occur to some extent.

**Table 2.6****Schiff base reactions with cyclohexanone**

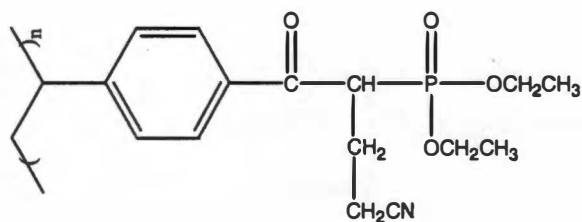
<b>Molar Ratio AMS:Cyclohexanone</b>	<b>Reaction Conditions</b>	<b>Resin</b>	<b>Nitrogen Capacity (meq/g) Actual (Theoretical)</b>	<b>Nitrogen Capacity of Precursor Resin (meq/g)</b>	<b>% Functionalization</b>
1:5	40 h, 25 °C	MR	3.50 (3.08)	4.94	77
1:5	24 h, reflux	MR	3.82 (3.25)	5.21	70.9
1:5	24 h, reflux	Gel	3.85 (3.86)	6.19	100

## Hydride Abstraction of B-ketophosphonate ester resin

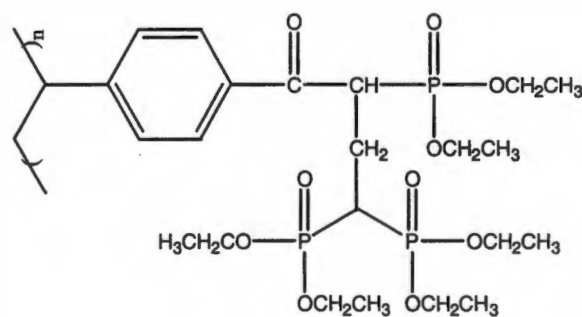
Nucleophiles, such as carbanions, can add to vinyl groups.<sup>53</sup> This led to the investigation of the possible immobilization of the vinyl 14C4 onto a  $\beta$ -ketophosphonate ethyl ester resin. The methylene moiety in the  $\beta$ -ketophosphonate was deprotonated and then contacted with the vinyl compound (Figure 2.9). Many control experiments were completed with AN and VDPE (Figures 2.10 and 2.11). AN is sterically hindered around the electron-deficient double bond while VDPE is more sterically hindered, as in the 14C4. All experiments used three moles of the vinyl-containing compound and five moles of NaH for every mole of phosphonate on the resin. The reaction time was held at 24 hours. Studies involving AN were done using gel and xerogel beads. (Xerogel beads are mesoporous and thus have greater porosity compared to microporous gel beads.) Upon binding of the vinyl compound onto the resins, the phosphorus content of both matrix types decreased when compared to the precursor resin (Table 2.7). This is expected based on the increased molecular weight of the repeat unit. The calculations of the theoretical elemental capacities of 1.72 and 2.68 meq/g for the gel and xerogel resins, respectively, were based on the phosphorus content of the precursor resins (gel resin: 2.05 meq/g; xerogel resin: 3.18 meq/g). The actual phosphorus capacities of each resin were found to be lower than that of the predicted theoretical values, 1.47 meq/g (gel) and 1.90 meq/g (xerogel). This finding was quite puzzling. Therefore, the nitrogen capacities were used to determine the percent functionalization of the resins as the precursor resin did not contain nitrogen atoms. The gel-supported AN resin had a nitrogen capacity of 1.23 meq/g indicating 71.5% functionalization, while the xerogel-supported AN resin had a nitrogen capacity of 2.02 meq/g, indicating 75.4%



**Figure 2.9.** Synthetic scheme of hydride extraction of  $\beta$ -ketophosphonate ester resin and reaction with 14C4



**Figure 2.10.** Product of hydride extraction reaction of  $\beta$ -ketophosphonate ester with AN



**Figure 2.11.** Product of hydride extraction reaction of  $\beta$ -ketophosphonate ester with VDPE

**Table 2.7**

**Comparison of resin matrix of  $\beta$ -ketophosphonate ester resin upon reaction with AN**

<b>Resin</b>	<b>Nitrogen Capacity (meq/g) Actual (Theoretical)</b>	<b>Phosphorus Capacity (meq/g) Actual (Theoretical)</b>	<b>Phosphorus Capacity of Precursor Resin (meq/g)</b>	<b>% Functionalization</b>
gel	1.23 (1.72)	1.47 (1.72)	2.05	71.5 (based on nitrogen capacity)
xerogel	2.02 (2.68)	1.90 (2.68)	3.18	75.4 (based on nitrogen capacity)

functionalization. The nitrogen capacities measured for both types of resins did reveal a significant amount of nitrogen present, though there was little difference between the gel and xerogel resins. This was somewhat unexpected since the xerogel resin has a greater interchain distance that allowed for increased accessibility, which was not demonstrated here.

Control reactions performed with VDPE were inconclusive. The reactions resulted in a phosphorus capacity that was similar to the phosphorus content of the precursor  $\beta$ -ketophosphonate resin, indicating little or no functionalization of the resin (Table 2.8). For example, a gel resin that had phosphorus capacity of 2.98 meq/g for the precursor resin had a phosphorus capacity of 2.85 meq/g upon reaction with VDPE (theoretical capacity: 4.33 meq P/g). The difference in phosphorus contents when comparing the reacted resin to the precursor is negligible and it can be assumed that no reaction had taken place.

When attempting the immobilization of VDPE, many factors were considered. Accessibility of the resin was studied with gel and xerogel beads with 2% crosslinking; MR beads were also utilized at 5 and 10% crosslinking. Under similar reaction conditions, with the exception of resin matrix, there was no difference in the degree of functionalization of the gel, xerogel, 5% XL MR and 10% XL MR beads: no reaction took place. The gel resin (CS<sub>2</sub>-02-077) and the xerogel resin (CS<sub>2</sub>-02-144) had phosphorus capacities of 2.85 and 2.94 meq/g, respectively, while the theoretical capacities were 4.33 and 4.62 meq/g. As the precursor resins started out with phosphorus contents of 2.98 meq/g (CS<sub>2</sub>-02-077) and 3.18 meq/g (CS<sub>2</sub>-02-144), it is seen that the reactions did not take place. When comparing the MR resins, CS<sub>2</sub>-02-161 (5% XL) and



**Table 2.8****Comparison of resin matrix of  $\beta$ -ketophosphonate ester resin and reaction conditions with VDPE\***

<b>Resin Code and Type</b>	<b>Addition of Reactants</b>	<b>Deprotonation Reagent</b>	<b>Phosphorus Capacity (meq/g) Actual (Theoretical)</b>	<b>Phosphorus Capacity of Precursor Resin (meq/g)</b>
CS <sub>2</sub> -02-077 gel	Same time	NaH	2.85 (4.33)	2.98
CS <sub>2</sub> -02-105 gel	17h (25°C) deprotonation before VDPE added	NaH	2.24 (4.33)	2.98
CS <sub>2</sub> -02-144 xerogel	Same time	NaH	2.94 (4.62)	3.18
CS <sub>2</sub> -02-115 xerogel	24h (25°C) deprotonation before VDPE added	NaH	3.18 (4.62)	3.18
CS <sub>2</sub> -02-161 MR(5%XL)	Same time	BuLi	2.62 (4.32)	2.97
CS <sub>2</sub> -02-197 MR(5%XL)	24h (reflux) deprotonation before VDPE added	NaH	2.74 (4.32)	2.97
CS <sub>2</sub> -02-052 MR(10%XL)	Same time	NaH	2.95 (4.13)	2.84
CS <sub>2</sub> -02-116 MR(10%XL)	24h (25°C) deprotonation before VDPE added	NaH	2.84 (4.13)	2.84

\* All reactions took place under an inert atmosphere (N<sub>2</sub> or Ar) unless otherwise noted.

CS<sub>2</sub>-02-052 (10% XL), the phosphorus capacities were found to be 2.62 and 2.95 meq/g, respectively, while the theoretical capacities were 4.32 and 4.13 meq/g, respectively. Again, it was observed that the reactions did not take place as the precursor resins had phosphorus capacities of 2.97 meq/g (CS<sub>2</sub>-02-161) and 2.84 meq/g (CS<sub>2</sub>-02-052). Based on these results, it can be noted that the differences in polymer matrices appeared to have little influence in the degree of functionalization.

Experiments were performed with NaH and butyllithium to see if one was a more effective reagent to use in the immobilization of VDPE. The results shown in Table 2.8 indicate that the deprotonation reagent did not affect the degree of functionalization. For most reactions, NaH was used but when the reagent was changed to butyllithium, reaction still did not occur. For example when comparing the MR resins mentioned above, CS<sub>2</sub>-02-161 and CS<sub>2</sub>-02-052, CS<sub>2</sub>-02-161 used butyllithium, while CS<sub>2</sub>-02-052 used NaH.

Deprotonation conditions were also varied to observe the extent of reaction. Initial reactions were performed with all of the reagents in solution at the same time. This method involved the presence of VDPE while the protons of the resin were abstracted. When analysis revealed that this method was not successful, deprotonation of the resin was attempted before addition of VDPE. This method was tried with varying times of deprotonation, and even temperature. To compare gel resins, a reaction was performed with all of the reagents added to the beads simultaneously (CS<sub>2</sub>-02-077), while one proceeded by the deprotonation of the beads with NaH for 17 hours at 25 °C (CS<sub>2</sub>-02-105). The precursor  $\beta$ -ketophosphonate resin was identical for both reactions (2.98 meq P/g), which allowed for the same calculated theoretical value (4.33 meq P/g). Under

both conditions, no reaction proceeded, indicated by the phosphorus capacities of 2.85 meq/g (CS<sub>2</sub>-02-077) and 2.24 meq/g (CS<sub>2</sub>-02-105). The same comparison was done with xerogel beads, with the exception of a 24 hour deprotonation time instead of 17 hours. CS<sub>2</sub>-02-144 was formed upon the simultaneous addition of the reagents, while CS<sub>2</sub>-02-115 had an extended deprotonation time. Like with the gel resins, the same precursor resin was used so the starting and theoretical phosphorus capacities were the same, 3.18 and 4.62 meq/g, respectively. The resulting polymers had phosphorus capacities of 2.94 meq/g (CS<sub>2</sub>-02-144) and 3.18 meq/g (CS<sub>2</sub>-02-115), which concluded that reactions did not occur. It was demonstrated above that reactions did not take place when NaH and VDPE were added to MR beads at the same time (CS<sub>2</sub>-02-161 and CS<sub>2</sub>-02-052) so experiments were performed with differing deprotonation conditions. CS<sub>2</sub>-02-197, a 5% XL MR resin, had a deprotonation time of 24 hours at reflux before the addition of VDPE, while CS<sub>2</sub>-02-116, a 10% XL MR resin, had a deprotonation time of 24 hours at 25 °C. CS<sub>2</sub>-02-197 had a theoretical phosphorus capacity of 4.32 meq/g, while the capacity of the precursor resin was 2.97 meq P/g. The theoretical phosphorus capacity of CS<sub>2</sub>-02-116 was 4.13 meq/g, while the capacity of the precursor resin was 2.84 meq P/g. Again, no reaction proceeded, indicated by the phosphorus capacities of 2.74 meq/g (CS<sub>2</sub>-02-197) and 2.84 meq/g (CS<sub>2</sub>-02-116). It can be noted by the results of the above-mentioned variances in conditions that there was little effect in the level of functionalization.

Though there was little success with the VDPE, functionalizations were attempted with 14C4. The same molar ratios used in the control reactions were utilized here and, because there was little difference found when varying the conditions, the reaction was

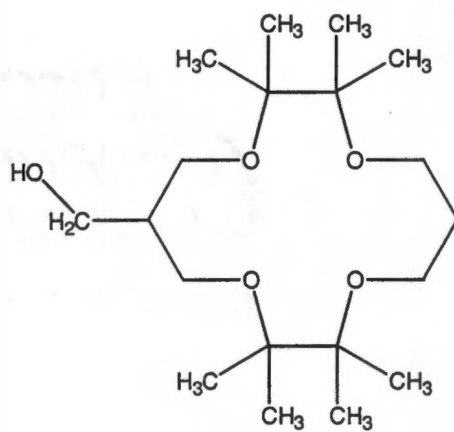
performed upon addition of all reagents to the flask at the same time. After reflux for 24 hours, the resins were analyzed for phosphorus capacity. Like the VDPE reactions, the reactions with 14C4 were performed on gel, xerogel and MR beads. However, unlike the VDPE reactions, there appeared to be some functionalization of 14C4 onto the resin (Table 2.9). The gel resin (CS<sub>2</sub>-02-004) functionalized with 14C4 had a phosphorus capacity of 1.56 meq/g, indicating 55.8% functionalization. When the reaction was repeated with xerogel beads (CS<sub>2</sub>-02-093), 40.4% reaction occurred as demonstrated by the phosphorus content of 2.49 meq/g. This finding was somewhat unpredictable since the increased accessibility of the xerogel did not result in enhanced functionalization, when compared to the gel resin. Reactions were also done to support the 14C4 onto MR beads (10% XL). Three identical reactions were performed on the same precursor resin at different times, CS<sub>2</sub>-02-034, CS<sub>2</sub>-02-039 and CS<sub>2</sub>-02-070. CS<sub>2</sub>-02-034 was found to be 69.3% functionalized, as indicated by the phosphorus capacity of 1.78 meq/g, while CS<sub>2</sub>-02-039 had a phosphorus capacity of 1.81 meq/g demonstrating 67.3% functionalization. The reaction of CS<sub>2</sub>-02-070 had a capacity of 1.99 meq P/g, indicating 55.6% functionalization. The differences in the percent functionalization of the MR resins is a bit surprising, though when a comparison is made of the phosphorus capacities, it is observed that a small difference in capacities can result in a significant difference in percentages. For this reason, the certainty of the degree of functionalization is unclear.

### **Etherification Reactions**

The final set of control reactions involved etherification of the alcohol-modified 14C4 (14C4OH) (Figure 2.12). Initial experiments performed on VBC gel beads with a variety of alcohols in a manner like that of the  $\beta$ -ketophosphonate resin (hydride

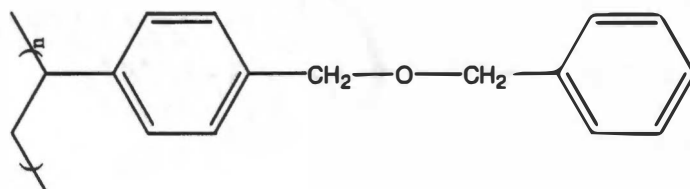
**Table 2.9****Characterization results for reactions of  $\beta$ -ketophosphonate ester resin with  $^{14}\text{C}$** 

<b>Resin Code</b>	<b>Resin Type</b>	<b>% Crosslinking</b>	<b>Phosphorus Capacity (meq/g) Actual (Theoretical)</b>	<b>Phosphorus Capacity of Precursor Resin (meq/g)</b>	<b>% Functionalization</b>
CS <sub>2</sub> -02-004	gel	2%	1.56 (1.03)	2.23	55.8
CS <sub>2</sub> -02-093	xerogel	2%	2.49 (1.47)	3.18	40.4
CS <sub>2</sub> -02-034	MR	10%	1.78 (1.31)	2.84	69.3
CS <sub>2</sub> -02-039	MR	10%	1.81 (1.31)	2.84	67.3
CS <sub>2</sub> -02-070	MR	10%	1.99 (1.31)	2.84	55.6



**Figure 2.12.** Structure of 14C4OH

abstraction; all reactants combined simultaneously). It was thought that it would be better to deprotonate the alcohol in a solution of dry dioxane for a period of time before adding the copolymer beads so as to ensure complete deprotonation. However, based on the results with VDPE and the hydride abstraction of the  $\beta$ -ketophosphonate resins, mentioned previously, there was no conclusive evidence that one method was better than the other though the reaction that involved the deprotonation in a separate flask was adopted. Upon reaction, a chlorine elemental analysis was performed on the resins to evaluate how far the reaction had proceeded. To determine whether MR beads would allow for a greater degree of functionalization, benzyl alcohol (BA) was reacted with VBC beads of different porosity under identical conditions (Figure 2.13). Upon chlorine analysis, it was seen that there was some difference in results, though not greatly significant (Table 2.10). Upon etherification of VBC gels and BA, the chlorine capacity decreased from 6.68 to 2.36 meq/g (theoretically the chlorine capacity should be 0 meq/g), demonstrating 64.7% functionalization. When the identical reaction was completed with VBC MR beads, the chlorine capacity decreased from 5.96 to 2.82 meq/g, indicating 52.7% functionalization. The results comparing the two reactions were somewhat surprising as MR beads have enhanced accessibility due to greater interchain distances. A third reaction was performed using MR beads under the same reaction conditions with the exception of reaction time, which was increased from 72 hours to seven days. The reaction product had a chlorine capacity of 1.56 meq/g, down from the initial value of 5.96 meq/g, which indicated 73.8%. When comparing the gel reaction and the MR reactions, there was no significant difference in the percent functionalizations. Further control experiments were done with cyclohexanol (Figure



**Figure 2.13.** Etherification reaction product of VBC with benzyl alcohol



**Table 2.10**

**The effect of porosity and reaction conditions on the degree of functionalization of etherification reactions involving VBC and BA**

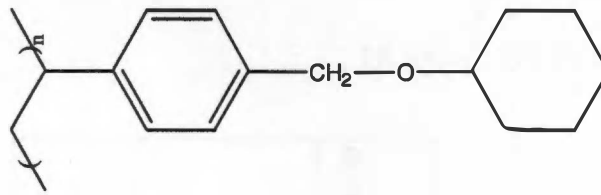
<b>Resin Type</b>	<b>Molar Ratio VBC:NaH:BA</b>	<b>Reaction Conditions</b>	<b>Chlorine Capacity (meq/g) Actual (Theoretical)</b>	<b>% Functionalization</b>
Gel	1:2.5:2.5	72 h, reflux	2.36 (0.00)	64.7
MR	1:2.5:2.5	72 h, reflux	2.82 (0.00)	52.7
MR	1:2.5:2.5	7 day, reflux	1.56 (0.00)	73.8

\* Initial chlorine capacity of gel resin = 6.68 meq/g

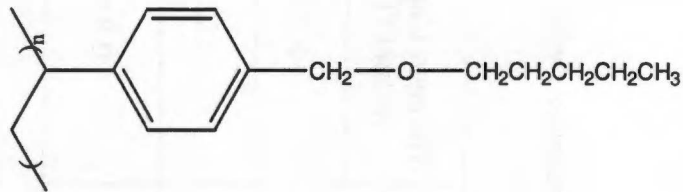
\*\* Initial chlorine capacity of MR resin = 5.96 meq/g

2.14), 1-pentanol (Figure 2.15) and diethyleneglycol monomethyl ether (Figure 2.16) with MR beads to investigate extent of reaction (Table 2.11). Upon reaction of VBC with cyclohexanol, it was found that the reaction proceeded to 16.1% based on the decrease in chlorine capacity of the resins from 5.96 to 5.00 meq/g. When the reaction was repeated using 1-pentanol, the resin was found to be 34.2% functionalized, indicated by the decrease in chlorine content from 5.96 to 3.92 meq/g. The reaction of VBC with diethylene glycol monomethyl ether produced a resin with a high percent functionalization, 86.1%, as determined by the final chlorine content of 0.83 meq/g, as compared to that of the precursor resin, 5.96 meq/g.

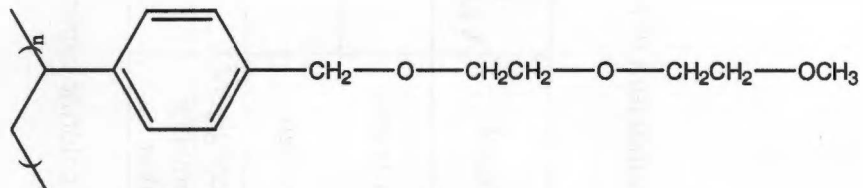
Upon reaction of 14C4OH with VBC MR beads (Figure 2.17), chlorine elemental analysis indicated that reaction did take place though not to completion (3.51 meq/g remaining on resin; % functionalization of 41.1%). A metal ion study was done by contacting the resin with  $10^{-4}$  N Li(I) solution and analyzed by atomic emission spectroscopy. No Li(I) sorption was found. Since lack of complexation could be due to hydrophobicity of the polymeric support, the next reaction involved modification of the polymer to enhance hydrophilicity. A copolymer of VBC and acrylamide in equal molar amounts resulted in a support that could be analyzed by both chlorine and nitrogen elemental analysis. The copolymer was produced by bulk polymerization and ground into pieces that were 150-250  $\mu\text{m}$ . Upon reaction with 14C4OH (Figure 2.18), under the same conditions, chlorine and nitrogen elemental analyses (2.32 and 3.82 meq/g, respectively), indicated that reaction did take place. A metal ion study was performed in  $10^{-4}$  N Li(I) and it was found that the polymer-supported crown ether contained 40% Li(I).



**Figure 2.14.** Etherification reaction product of VBC with cyclohexanol



**Figure 2.15.** Etherification reaction product of VBC with 1-pentanol

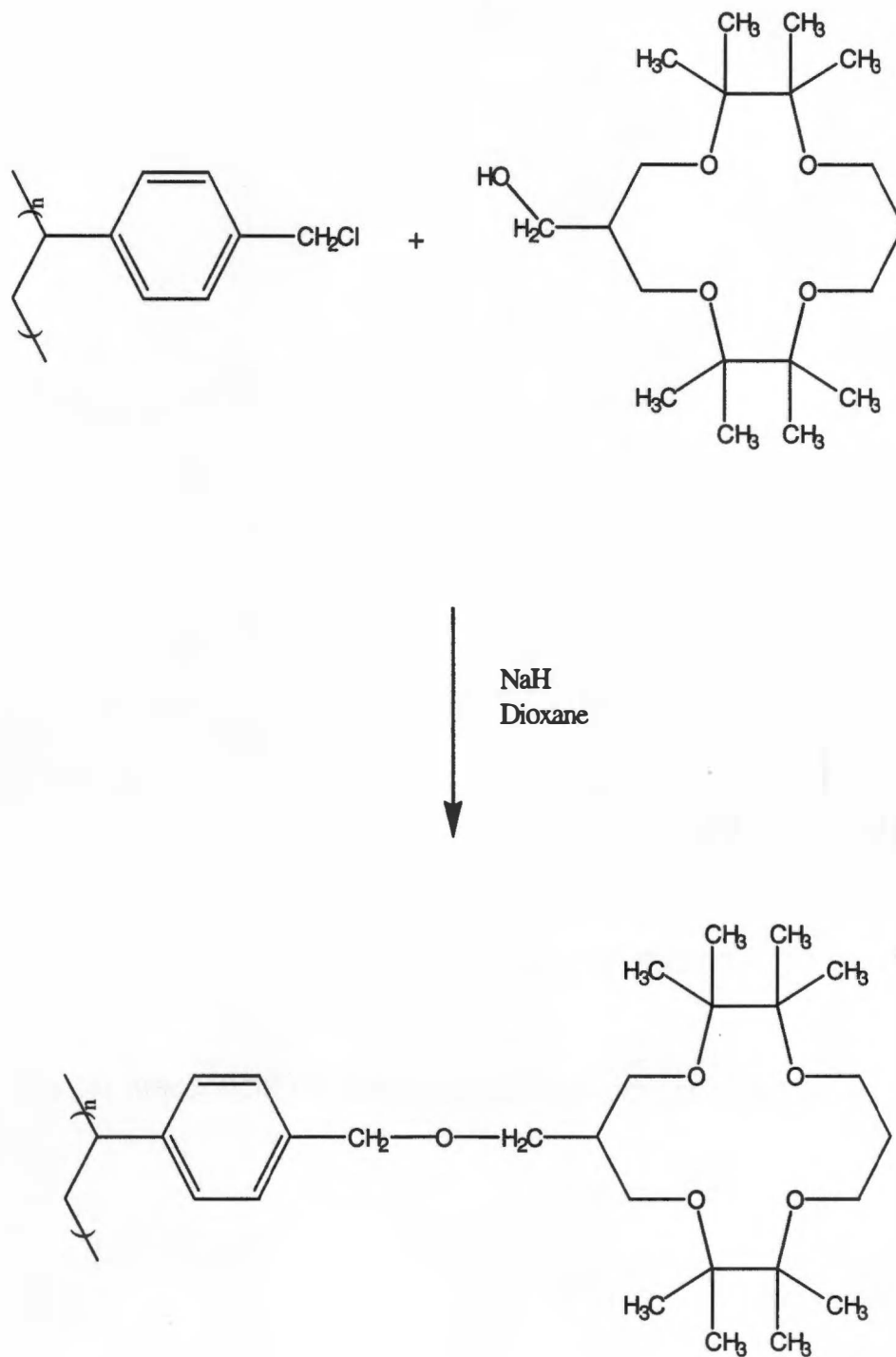


**Figure 2.16.** Etherification reaction product of VBC with  
diethyleneglycol monomethyl ether

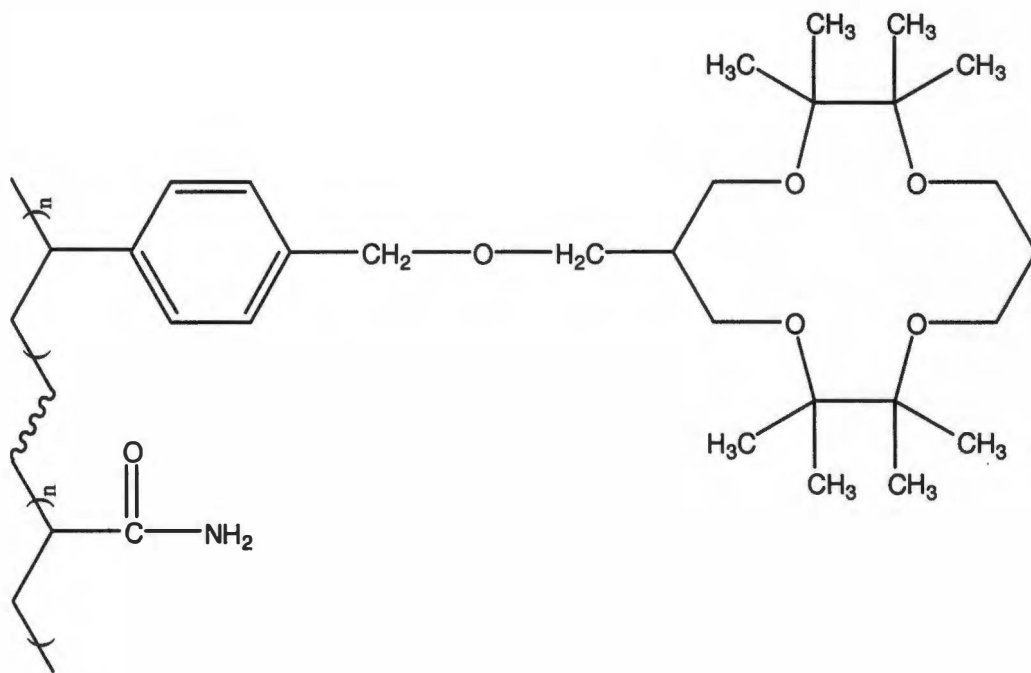
**Table 2.11****Comparison of alcohols used in etherification reactions with VBC MR beads\***

<b>Alcohol</b>	<b>Molar Ratio VBC:NaH:Alcohol</b>	<b>Reaction Conditions</b>	<b>Nitrogen Capacity (meq/g) Actual (Theoretical)</b>	<b>% Functionalization</b>
Cyclohexanol	1:2.5:2.5	72 h, reflux	5.00 (0.00)	16.1
1-Pentanol	1:2.5:2.5	72 h, reflux	3.92 (0.00)	34.2
Diethyleneglycol Monomethyl Ether	1:2.5:2.5	72 h, reflux	0.83 (0.00)	86.1

\* Initial chlorine capacity of VBC MR resin = 5.96 meq/g



**Figure 2.17.** Etherification reaction of VBC with 14C4OH

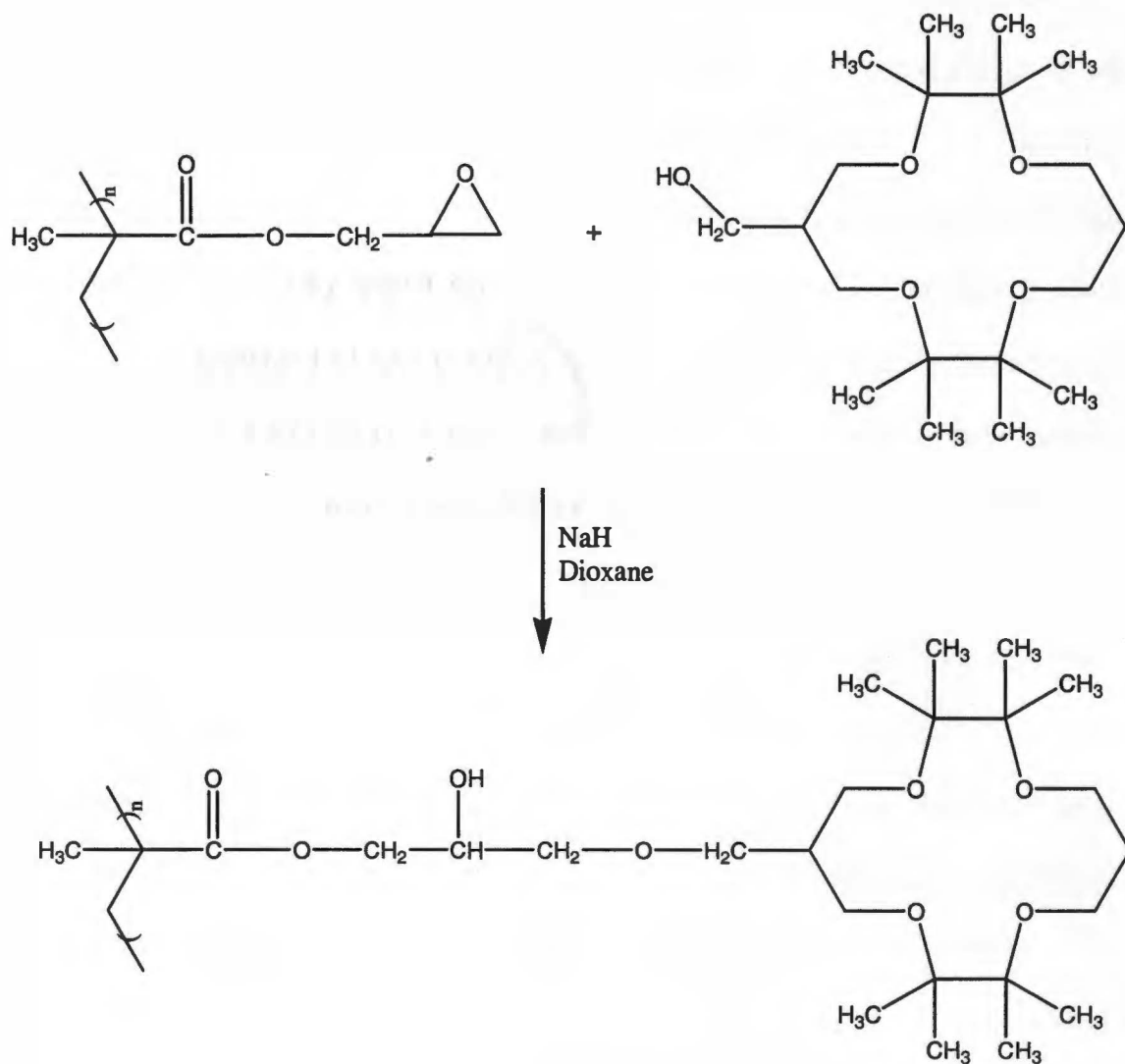


**Figure 2.18.** Etherification reaction product of VBC/AA with 14C4OH

Once again to test the hydrophilicity theory, GMA, a more hydrophilic polymer than VBC and VBC/AA, was used to support the crown ether.<sup>54,55</sup> Again, the same reaction was performed on GMA gels and MRs (Figure 2.19) but because there was no easy way to analyze the resin by elemental analysis, FTIR was used. Typical FTIR peaks for the epoxy ring vibration and the (C-H) stretch of GMA include 850, 910, 1340 and 1480  $\text{cm}^{-1}$ .<sup>56,57,58</sup> All of the GMA/14C4OH resins displayed these key peaks; however, they were weaker than those on the GMA FTIR spectra, indicating that reactions did take place, though not to completion. A metal ion contact study was performed with  $10^{-4}$  N Li(I) and both resins were able to complex 100% of the Li(I) present in the aqueous solution (Table 2.12). From these results, it can be assumed that the hydrophilicity of GMA aids in allowing metal ions access into the polymer matrix.

As mentioned previously, the degree of functionalization of the GMA/14C4OH resins was not characterized by elemental analysis due to the lack of an easily identifiable atom such as nitrogen, phosphorus or chlorine, so it was approximated by the Li(I) saturation capacity. Unlike the initial studies performed with  $10^{-4}$  N Li(I), saturation studies were done with  $10^{-1}$  N Li(I).

Because the contacted solutions were too concentrated to be analyzed using AE, the solutions were diluted down by a factor of 1:1000 in steps of 1:10, 1:2, 1:50 so as to be utilized. In the initial reaction of GMA with 14C4OH, deprotonation of the alcohol was done by contacting it with NaH for one hour at room temperature before refluxing with the beads. The resin (CS<sub>2</sub>-03-179) absorbed 100% of the Li(I) from the  $10^{-4}$  N solution but none from the  $10^{-1}$  N solution. This may be because the amount of Li(I) present in the concentrated solution is large enough so that a small amount complexed



**Figure 2.19.** Etherification reaction of GMA with 14C4OH



**Table 2.12****Complexation of Li(I) from  $10^{-4}$  N  $\text{LiNO}_3/\text{H}_2\text{O}$** 

<b>Resin</b>	<b>% Li(I) Complexed</b>
VBC (gel)	0.00
VBC/AA (gel)	40.0
GMA (gel)	>99.5

may not have been experimentally detected. In an attempt to increase the amount of 14C4OH that was supported onto the polymer, the synthesis of CS<sub>2</sub>-03-217 was performed in the same manner CS<sub>2</sub>-03-179 except that deprotonation of 14C4OH was done at 60°C for one hour. It was thought that the increased temperature would give more complete deprotonation of 14C4OH. The resulting polymer complexed 100% Li(I) from the 10<sup>-4</sup> N solution and 1.74% (0.085 meq/g) Li(I) from the 10<sup>-1</sup> N solution. In the next reaction, deprotonation was done for 17 hours at 60 °C. The functionalized polymer (CS<sub>2</sub>03-242) complexed 100% Li(I) from the 10<sup>-4</sup> N solution and 8.25% (0.41 meq/g) from the 10<sup>-1</sup> N solution. It was apparent that the increased temperature combined with the longer deprotonation time was able to yield a more functionalized polymer-supported crown ether. The results with the GMA gel resins can be seen in Table 2.13.

Similar reactions were performed on GMA MR resins to see if the increased porosity would affect accessibility of Li(I) into the polymer matrix. The reactions were evaluated in the same manner as the GMA gel beads. Deprotonation of CS<sub>2</sub>-03-248 took place at room temperature for one hour before the 72 hour reflux with the beads. Upon contact with 10<sup>-4</sup> N Li(I), it was found that the resin complexed 100% Li(I). Unlike the GMA gel resin studied under the same conditions, the GMA MR beads complexed 8.60% (0.44 meq/g) Li(I) from the 10<sup>-1</sup> N solution. This indicated that accessibility was a variable. This reaction was repeated and instead of changing the deprotonation time of 14C4OH, the reflux time was increased from 72 hours to 7 days. The resulting polymer, CS<sub>2</sub>-03-272, absorbed 100% Li(I) from the 10<sup>-4</sup> N solution and 6.14% (0.61 meq/g) from a solution of 2.0 X 10<sup>-1</sup> N Li(I). Just as dilutions had been done for the 1.0 X 10<sup>-1</sup> N Li(I) solutions, dilutions were also done for 2.0 X 10<sup>-1</sup> N Li(I). The dilution factor was 1:2000

**Table 2.13**

**Results of GMA and 14C4OH in varying deprotonation conditions**

<b>Resin Code</b>	<b>Resin Type</b>	<b>Deprotonation Conditions</b>	<b>Li(I) Concentration</b>	<b>Li(I) Capacity (meq/g)</b>
CS <sub>2</sub> -03-179	Gel	1 h, 25°C	10 <sup>-1</sup> N LiNO <sub>3</sub> /H <sub>2</sub> O	< 3.6 X 10 <sup>-4</sup>
CS <sub>2</sub> -03-217	Gel	1h, 60°C	10 <sup>-1</sup> N LiNO <sub>3</sub> /H <sub>2</sub> O	0.085
CS <sub>2</sub> -03-242	Gel	17 h, 60°C	10 <sup>-1</sup> N LiNO <sub>3</sub> /H <sub>2</sub> O	0.41

(by volume) in increments of 1:10, 1:2, 1:2, and 1:50. The increased reaction time combined with the increased porosity yielded a polymer-supported crown ether that displayed the highest degree of functionalization when compared to all of the resins synthesized.

Because crown ethers have an affinity for alkali metals<sup>23,59,60</sup>, a metal ion contact study was done with a solution that had  $10^{-4}$  N Li(I) and an excess sodium ions. (Table 2.14). The first study contained  $10^{-3}$  N Na(I), a ten-fold excess of Na(I) to Li(I) and the resin, CS<sub>2</sub>-03-179, was able to complex 97.7% Li(I). A second metal ion study was done of Li(I) in the presence of  $10^{-1}$  N Na(I) and the same resin as able to complex 99.6%. The polymer-supported crown ether thus displays good selectivity for Li(I).

## CONCLUSIONS

The removal of Li(I) from aqueous solutions using a 14-crown-4 moiety was the target of this project. Though many attempts were made to immobilize the various forms of 14-crown-4, the method that was utilized was etherification. Experiments demonstrated that the amount of Li(I) that can be complexed by the polymer-supported 14C4OH is affected by the hydrophilicity of the polymer matrix. It can be seen that the greater the hydrophilicity, the greater the amount of complexation by the polymer-supported crown ether. VBC, which did not complex any Li(I), is a non-polar, hydrophobic resin, while the introduction of AA into the VBC/AA copolymer resulted in a resin that is somewhat more hydrophilic due to the addition of a polar component. This is demonstrated by the increased sorption of Li(I) by the resin. GMA is notably hydrophilic<sup>54,55</sup>, and as a result, enhanced sorption of Li(I) was observed. Of the three

**Table 2.14****Selectivity of Li(I) in the presence of excess Na(I) (GMA resins)**

<b>Resin Code</b>	<b>Resin Type</b>	<b>Li(I) Concentration</b>	<b>Na(I) Concentration</b>	<b>% Li(I) Complexed</b>
CS <sub>2</sub> -03-179	Gel	10 <sup>-4</sup> N LiNO <sub>3</sub> /H <sub>2</sub> O	10 <sup>-3</sup> N NaNO <sub>3</sub> /H <sub>2</sub> O	97.7
CS <sub>2</sub> -03-179	Gel	10 <sup>-4</sup> N LiNO <sub>3</sub> /H <sub>2</sub> O	10 <sup>-1</sup> N NaNO <sub>3</sub> /H <sub>2</sub> O	>99.5

copolymers studied, VBC, VBC/AA and GMA, GMA had the highest performance due to its hydrophilicity. Crown ether (14C4OH) functionalized GMA gels are able to selectively complex Li(I) when in the presence of excess Na(I).

# CHAPTER 3

## BIFUNCTIONAL RESINS CONTAINING AMINE AND PHOSPHONATE ESTER LIGANDS

### INTRODUCTION

The development of selective polymer-supported reagents for the removal of metal ions from aqueous solutions is a well-noted area of research. The optimization of the sorption capacity for given metal ions can be achieved by proper design of the polymeric system. Ligands vary in their chelating abilities for different metal ions based on hard-soft acid-base theory.<sup>17,18</sup> With this in mind, it is logical to design a polymer that has differing characteristics, with the ligands working synergetically to give enhanced properties. Bifunctional resins are widely used for this purpose.<sup>61,62,63</sup> When compared to the monofunctional resin, the bifunctional resin should have enhanced sorption capacities for a wider range of metal ions due to the cooperation of the ligands.<sup>64</sup> This is typically accomplished by use of dual mechanism bifunctional resins that utilize an access mechanism, which brings metal ions into the polymer matrix, and a recognition mechanism, which allows for the appropriate ligand to selectively complex the metal ion for which it has an affinity.<sup>12,65,66</sup>

Amine and phosphonate ligands are widely used<sup>67,68,69,70,71,72</sup> as metal ion complexants and their immobilization on the same polymer backbone to study the resulting metal sorption capacities was the focus of this research. The inter-ligand cooperation was studied for selective complexation with a number of metal ions. The metal ion affinities of the bifunctional resins synthesized were compared to that of their

monofunctional analogues to determine whether increased selectivity was observed. The phosphonates studied were dialkyl phosphonate esters, while the amines were, primarily, dialkylamines with groups that corresponded to the phosphonate esters.

## **EXPERIMENTAL**

### **Synthesis of Copolymers**

The 5% crosslinked macroporous vinylbenzylchloride (VBC) copolymer was synthesized by suspension polymerization. The size of the beads studied was 75-150  $\mu\text{m}$ .

### **Synthesis of Monofunctional, Fully Functionalized Phosphonate Ester Resins**

The phosphonate resins were prepared by the Arbusov reaction. The appropriate trialkyl phosphite was refluxed, in excess, with VBC for 48 h. All resins were macroporous. Upon completion, the resins were washed and characterized by phosphorus elemental analysis.

### **Synthesis of Monofunctional, Partially Functionalized Phosphonate Ester Resins**

The partially functionalized phosphonate esters were synthesized by refluxing the VBC beads with the appropriate trialkyl phosphite in the presence of toluene. To obtain the desired degree of functionalization, the molar ratios were varied depending on the trialkyl phosphite used. The reaction contents were stirred at room temperature for 24 h, before being refluxed for an additional 24 hours. The completed resins were washed thoroughly and characterized by phosphorus elemental analysis.

### **Synthesis of Bifunctional Resins**

The partially functionalized phosphonate resins were reacted with the corresponding dialkyl amine in the presence of dioxane. The reaction contents were



refluxed for 48 hours, upon which time the resins were washed and their nitrogen and phosphorus capacities were evaluated by elemental analyses. All structures depicted of bifunctional resins represent random copolymers.

### **Synthesis of Amine-Contacted, Fully Functionalized Phosphonate Ester Resins**

The fully functional phosphonate resins were refluxed in excess of the corresponding dialkyl amine for 48 h. The reactions were performed in the presence of dioxane. Upon completion, the resins were washed and characterized by both nitrogen and phosphorus elemental analysis.

### **Synthesis of Monofunctional Dialkyl-Aminated Resins**

Monofunctional amine-substituted resins were prepared by the reaction of VBC with excess dialkyl amine in the presence of dioxane. The reaction contents were refluxed for between 20 and 48 h. When the reactions were completed, the contents were washed and their nitrogen capacities were evaluated by elemental analysis.

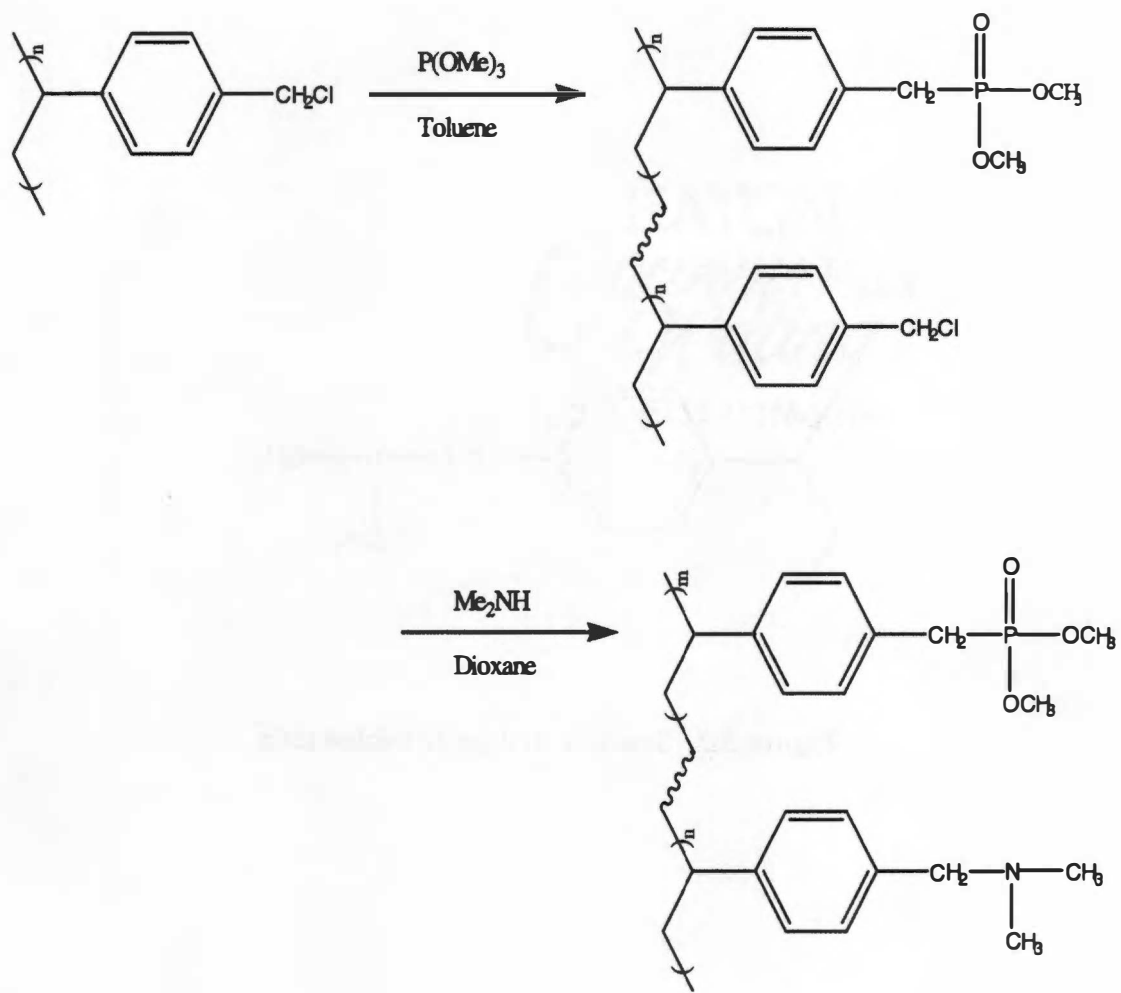
## **RESULTS AND DISCUSSION**

As noted above, there is a great importance in the use of bifunctional polymer-supported reagents for the removal of metal ions from aqueous solutions. Due to the wide usage of phosphonate and amine resins, it was thought to design a new series of resins which had both moieties to determine how well they would cooperate to bind metal ions. The ideal situation would result in a resin that was fifty percent functionalized with one moiety and upon further reaction, the other ligand would fill in the gaps to produce a polymer that was fully functionalized with two separate ligands. The initial experiments to determine the appropriate amount required to prepare a resin that was only 50%

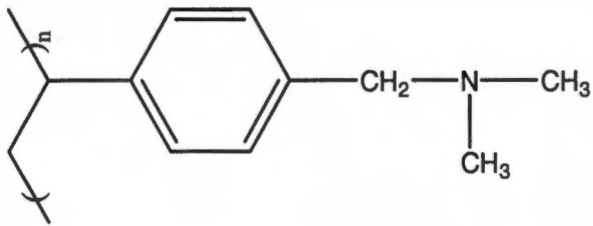
functionalized were carried out by varying the molar ratios, solvents and reaction times. It was easier to control the resin composition by first immobilizing the phosphonate ester and then further reacting with an excess of the dialkyl amine.

### **Methyl Resins**

The initial bifunctional resin prepared utilized the methyl form of the dialkyl phosphonates and dialkyl amines to obtain the simplest combination. To prepare the 50% functionalized phosphonate ester, VBC was reacted with a 40 molar excess of trimethyl phosphite for 24 hours at room temperature, and then refluxed for another 24 h. The resin (CS<sub>2</sub>-06-084) was washed and evaluated for phosphorus content. This synthetic process produced a resin that had a phosphorus capacity of 2.28 meq/g, where the theoretical value for the degree of desired functionalization was 2.40 meq/g. The resin was further reacted with a ten-fold excess of dimethylamine for 20 h at reflux (Figure 3.1). Upon washing with ethanol and water, the resin was eluted with a sequence of one liter each of distilled H<sub>2</sub>O, 4 wt% NaOH and again with H<sub>2</sub>O. The resulting polymer was determined, by elemental analyses, to have a nitrogen capacity of 1.84 meq/g and a phosphorus capacity of 2.10 meq/g, the theoretical value for both analyses being 2.23 meq/g. Complexation studies were performed in 0.06 N acetic acid/pH 5 acetate buffer with a metal ion concentration of 10<sup>-4</sup> N. The metals studied were Cd(II), Co(II), Cr(III), Ni(II), Pb(II) and Zn(II), in separate experiments. As a control, metal ion studies were performed on the monofunctional dimethylamine resin, CS<sub>2</sub>-06-067 (Figure 3.2) to compare the results to the bifunctional resin. The results can be seen in Table 3.1. It can be observed in this set of data that the bifunctional resin demonstrates a higher affinity for the metal ions studied than that of the monofunctional dimethylamine resin. For



**Figure 3.1.** Synthetic scheme of bifunctional methyl/methyl resin preparation



**Figure 3.2.** Structure of dimethylamine resin

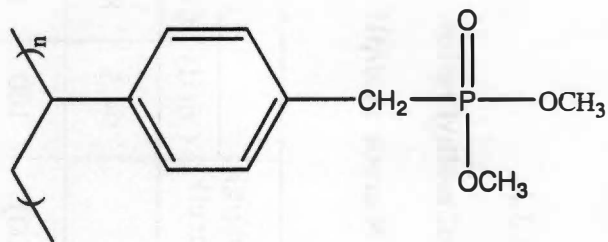
**Table 3.1**

**Elemental analysis and metal ion study results of methyl resins. Metal ion studies were done at a concentration of  $10^{-4}$  N in 0.06 N acetic acid/pH 5 acetate buffer.**

Resin Code	Composition	P Cap (meq/g) Act (Theoret)	N Cap (meq/g) Act (Theoret)	Percent Absorbed					
				Cd(II)	Co(II)	Cr(III)	Ni(II)	Pb(II)	Zn(II)
CS <sub>2</sub> -06-084	Me Bifunctional	2.10 (2.23)	1.84 (2.23)	100	99.1	100	88.7	99.8	100
CS <sub>2</sub> -06-067	Me Amine	---	4.51 (5.61)	11.2	4.6	49.4	0.0	15.0	10.9

example, the bifunctional resin complexed > 99% Cd(II), Co(II), Cr(III), Pb(II) and Zn(II), while the resin complexed 88.7% Ni(II). In contrast, the monofunctional dimethylamine resin sorbed 49.4% Cr(III) and < 20% of the remaining metal ions studied.

This study, though insightful, was incomplete. Further metal ion studies were performed with the monofunctional dimethyl phosphonate ester, CS<sub>2</sub>-06-129 (Figure 3.3) to compare the results to the bifunctional methyl/methyl resin. This study was needed to verify that the bifunctional resin demonstrated greater affinities for a range of metal ions in comparison to each of the monofunctional resins containing the same ligands. A control reaction was performed on the monofunctional fully functionalized dimethyl phosphonate ester by reacting it with 100-fold excess of dimethyl amine (CS<sub>2</sub>-06-134) to investigate its metal ion affinities as well. It was initially thought that no reaction would take place and that the metal ion study results would be the same as that of the monofunctional dimethyl phosphonate ester resin. Like the bifunctional and aminated resins, these resins were washed thoroughly and then eluted with a sequence of distilled H<sub>2</sub>O, 4 wt% NaOH and again with H<sub>2</sub>O. The same metal ion solutions were used as before: 10<sup>-4</sup> N M<sup>n+</sup> in 0.06 N acetic acid/pH 5 acetate buffer. The results were quite surprising. As seen in Table 3.2, in all of the studies, the monofunctional dimethyl phosphonate resin absorbed great quantities of each of the metal ions studied, Cd(II), Co(II), Cr(III), Ni(II), Pb(II) and Zn(II), but the “aminated” form of the same resin performed even better. For example, when comparing the monofunctional dimethyl phosphonate ester with its “aminated” analogue, with Cd(II) (94.5% vs. 100%), Co(II) (83.4% vs. 100%), Cr(III) (72.1% vs. 89.5%), Ni(II) (75.1% vs. 98.8%), Pb(II) (85.5%



**Figure 3.3.** Structure of dimethyl phosphonate ester resin

Table 3.2

Elemental analysis and metal ion study results of methyl resins. Metal ion studies were done at a concentration of  $10^{-4}$  N in 0.06 N acetic acid/pH 5 acetate buffer.

Resin Code	Composition	P Cap (meq/g) Act (Theoret)	N Cap (meq/g) Act (Theoret)	Percent Absorbed					
				Cd(II)	Co(II)	Cr(III)	Ni(II)	Pb(II)	Zn(II)
CS <sub>2</sub> -06-129	Me Phosphonate	3.82 (4.02)	---	94.5	83.4	72.1	75.1	85.5	91.6
CS <sub>2</sub> -06-134	Me Phosphonate + Me <sub>2</sub> NH	3.58 (3.82)	0.39 (0.00)	100	100	89.5	98.8	99.9	100



vs. 99.9%) and Zn(II) (91.6% vs. 100%), each metal ion had greater complexation with the “aminated” resin. This was a puzzling discovery as it was assumed that the “aminated” resin would perform identically to that of its precursor. FTIR spectra of the monofunctional dimethyl phosphonate ester resin, CS<sub>2</sub>-06-129, showed a distinct peak that is characteristic of phosphonate diesters<sup>48</sup> at 1256 cm<sup>-1</sup> (Figure 3.4). Upon contact with dimethylamine, the new resin, CS<sub>2</sub>-06-134, did not have the same distinct peak (Figure 3.5). Instead, the peak had shifted to 1198 cm<sup>-1</sup>, which is typical of phosphonic acids.<sup>48</sup> This change in spectra indicated base catalyzed hydrolysis of the phosphonate diester and could be the reason for the enhanced affinity for the “aminated” phosphonate due to ion-exchange rather than complexation. It was important to determine whether or not the bifunctional methyl/methyl resin was also undergoing hydrolysis upon reaction with the dimethylamine. An FTIR spectrum was taken of the bifunctional resin, CS<sub>2</sub>-06-084 (Figure 3.6), and it was seen that there was a peak at 1189 cm<sup>-1</sup>, which was similar to that of the “aminated” fully functionalized phosphonate ester. As this was a peak in the range distinctive for phosphonic acids, it was assumed that the bifunctional resin was also undergoing hydrolysis to some extent. This result, however, was not quantified since an acid capacity was not performed because there was not enough resin remaining.

The results of the study with methyl resins led to further investigations of reactions that could also allow the phosphonate diester to undergo base catalyzed hydrolysis. In side-by-side reaction flasks, two reactions were set up using the phosphonate dimethyl ester resin. In one flask, an excess of dimethylamine was added (CS<sub>2</sub>-06-161), and to the other, a solution of NaOH at a pH (13.2) similar to that of dimethylamine solutions (CS<sub>2</sub>-06-160). Both reactions were refluxed for 48 h, at which

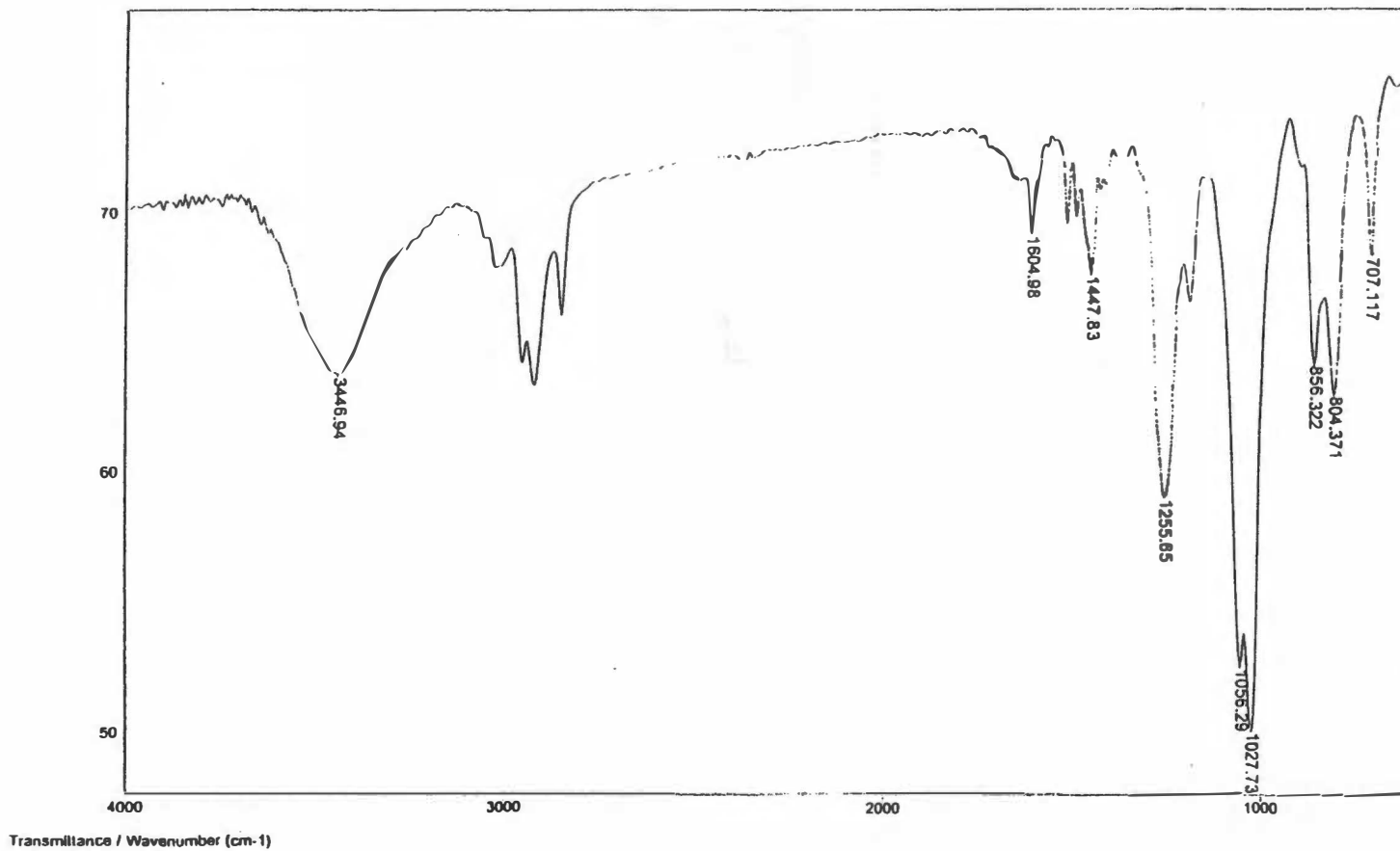


Figure 3.4. FTIR spectrum of dimethyl phosphonate ester resin (CS<sub>2</sub>-06-129)

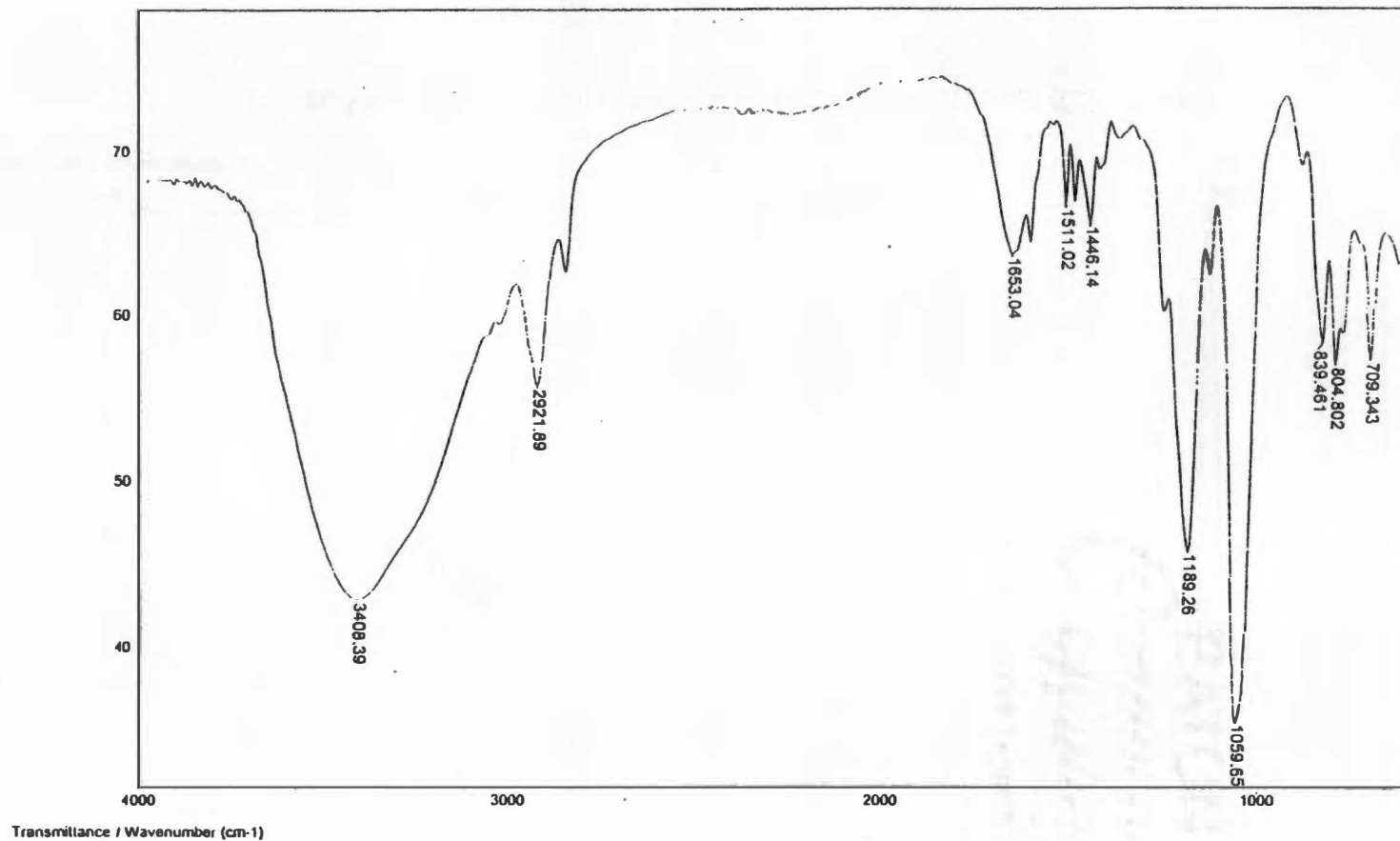


Figure 3.5. FTIR spectrum of dimethylamine-contacted fully functional dimethyl phosphonate ester resin (CS<sub>2</sub>-06-134)

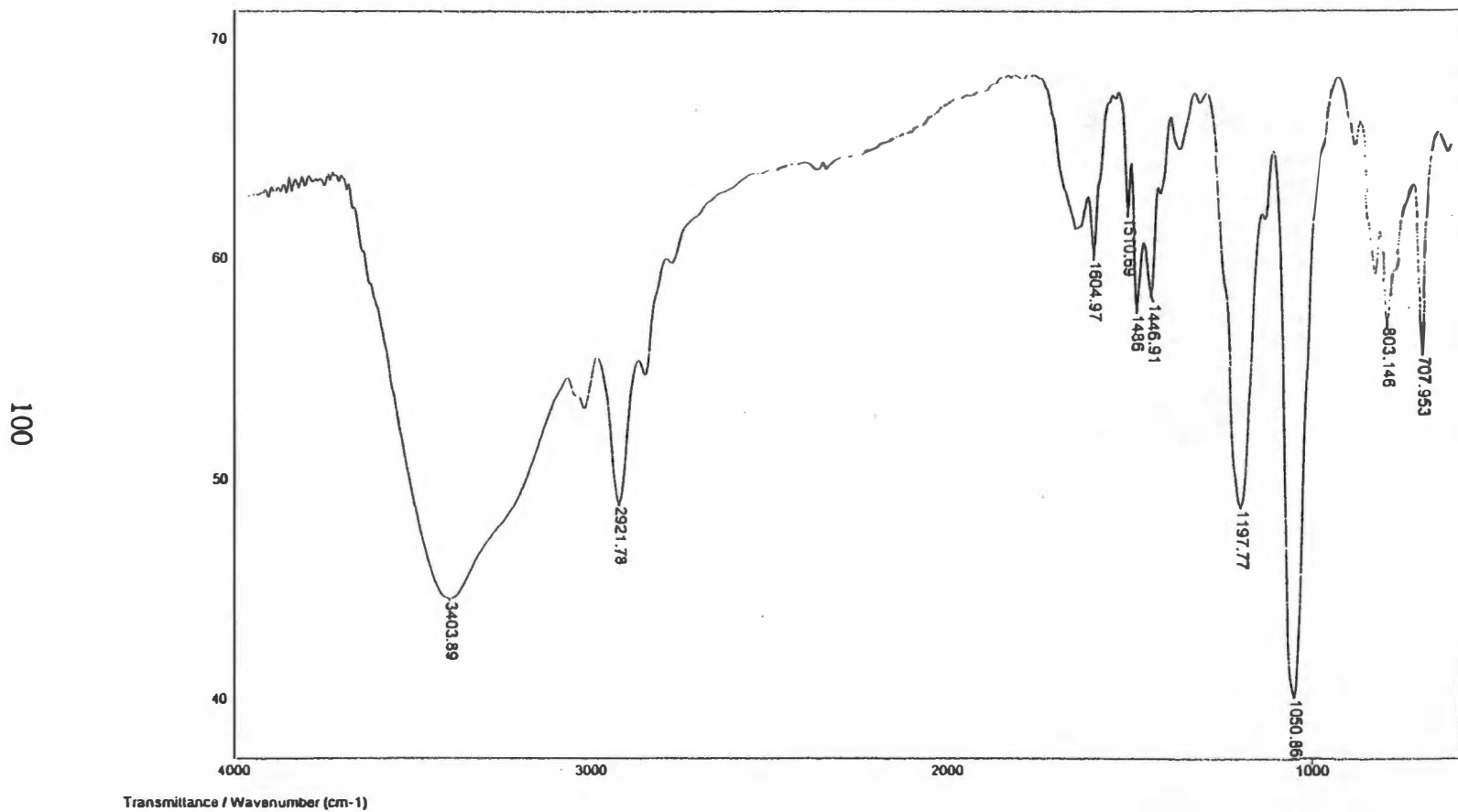


Figure 3.6. FTIR spectrum of bifunctional methyl/methyl resin (CS<sub>2</sub>-06-084)

time they were washed thoroughly and eluted with distilled H<sub>2</sub>O, 4 wt% NaOH and again with H<sub>2</sub>O. Upon completion, the resins, with their precursor (CS<sub>2</sub>-06-156), were analyzed by phosphorus, nitrogen and acid capacities. The results (Table 3.3) show that something had happened to modify the precursor resin. Upon comparison of CS<sub>2</sub>-06-156 to CS<sub>2</sub>-06-161, the phosphorus capacity decreased from 3.54 meq/g (CS<sub>2</sub>-06-156) to 2.73 meq/g upon reaction with dimethylamine. Because a reaction between the fully functionalized dimethyl phosphonate ester and dimethylamine was not expected, it was surprising to see a change in the phosphorus capacity of the resin because, theoretically, the value should have remained the same. A decrease in phosphorus capacity was also seen when comparing CS<sub>2</sub>-06-156 to CS<sub>2</sub>-06-160 (3.54 vs. 2.90 meq/g). The nitrogen capacities of the three resins were not significant, each resin had a capacity less than 0.5 meq/g. The acid capacities, however low, did demonstrate a difference between the monofunctional phosphonate dimethyl ester (0.24 meq/g) and that of the same resin reacted with NaOH (0.77 meq/g) and dimethylamine (0.69 meq/g). The results found by the acid capacities were supported by the FTIR spectra of each of the resins. The monofunctional dimethyl phosphonate ester, (CS<sub>2</sub>-06-156), had a distinct peak at 1252 cm<sup>-1</sup> (Figure 3.7), typical of phosphonate diesters, while the other two resins, CS<sub>2</sub>-06-160 and CS<sub>2</sub>-06-161 (Figures 3.8 and 3.9), displayed peaks typical for phosphonic acids at 1191 cm<sup>-1</sup> and 1186 cm<sup>-1</sup>, respectively.

To determine the metal binding properties of the above resins, studies were done with a number of cations including Cd(II), Co(II), Cr(III), Li(I), Ni(II), Pb(II) and Zn(II). All contact solutions consisted of 10<sup>-4</sup> N M<sup>n+</sup> in 0.06 N acetic acid/pH 5 acetate buffer. The results of this study are documented in Table 3.4. It was observed that in most of the

**Table 3.3**

**Elemental analysis of methyl resins studied for possible base catalyzed hydrolysis**

<b>Resin Code</b>	<b>Composition</b>	<b>P Capacity (meq/g) Actual (Theoretical)</b>	<b>N Capacity (meq/g) Actual (Theoretical)</b>	<b>Acid Capacity (meq/g) Actual (Theoretical)</b>
CS <sub>2</sub> -06-156	Me Phosphonate	3.54 (4.02)	0.16 (0.00)	0.24 (0.00)
CS <sub>2</sub> -06-161	Me Phosphonate + Me <sub>2</sub> NH	2.73 (3.54)	0.41 (0.00)	0.69 (0.00)
CS <sub>2</sub> -06-160	Me Phosphonate + NaOH	2.90 (3.54)	0.25 (0.00)	0.77 (0.00)

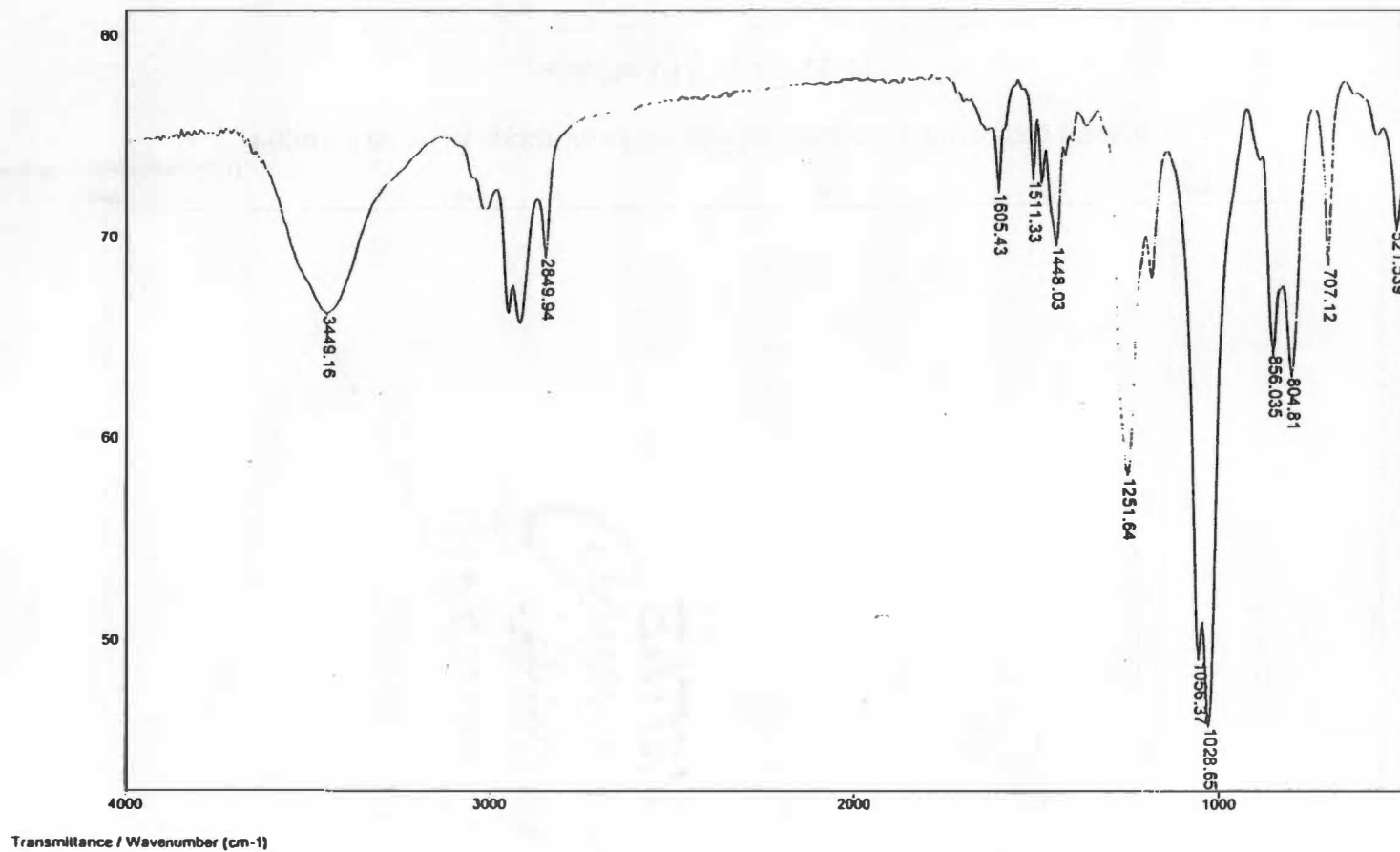


Figure 3.7. FTIR spectrum of dimethyl phosphonate ester resin (CS<sub>2</sub>-06-156)

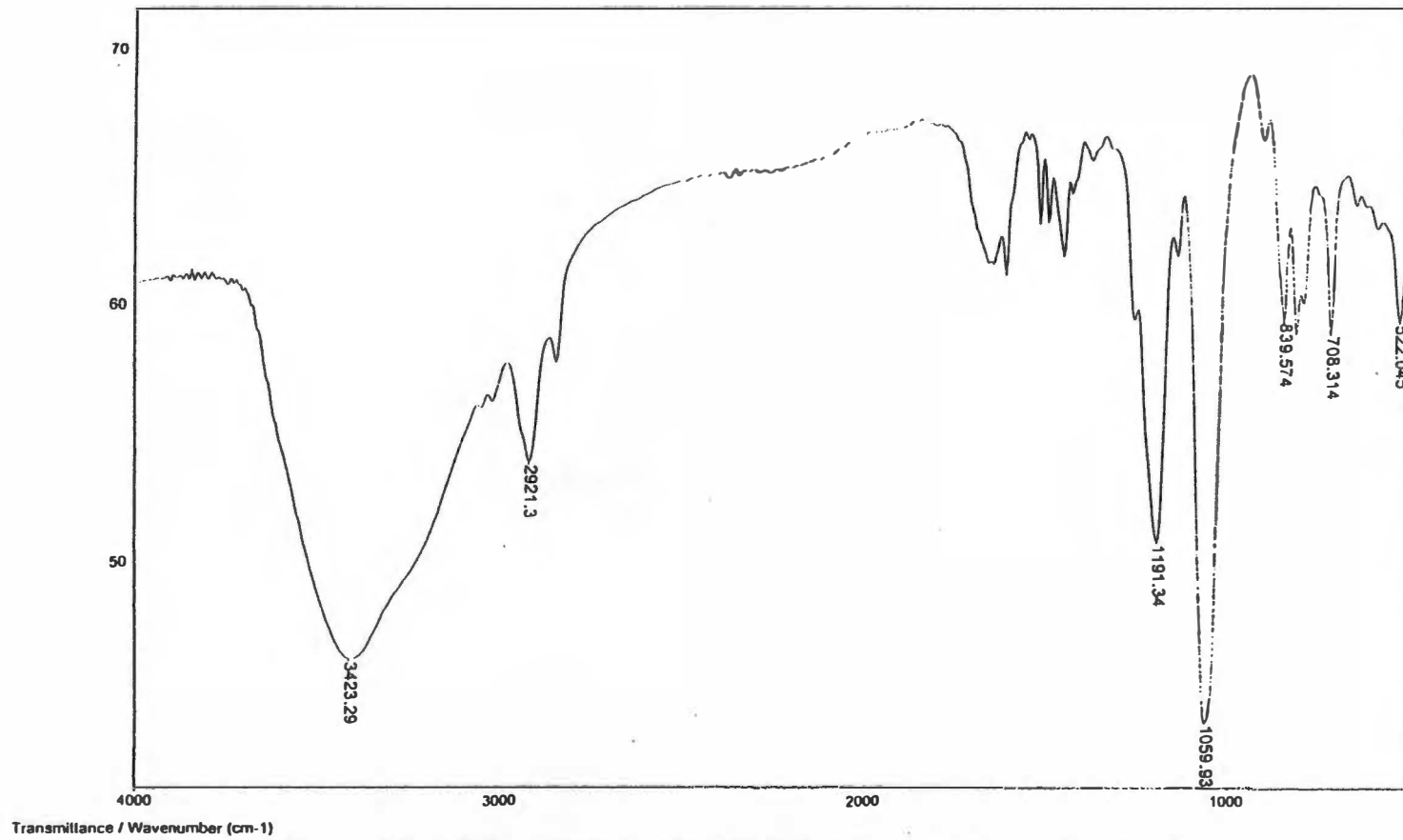


Figure 3.8. FTIR spectrum of dimethyl phosphonate ester resin reacted with NaOH (CS<sub>2</sub>-06-160)



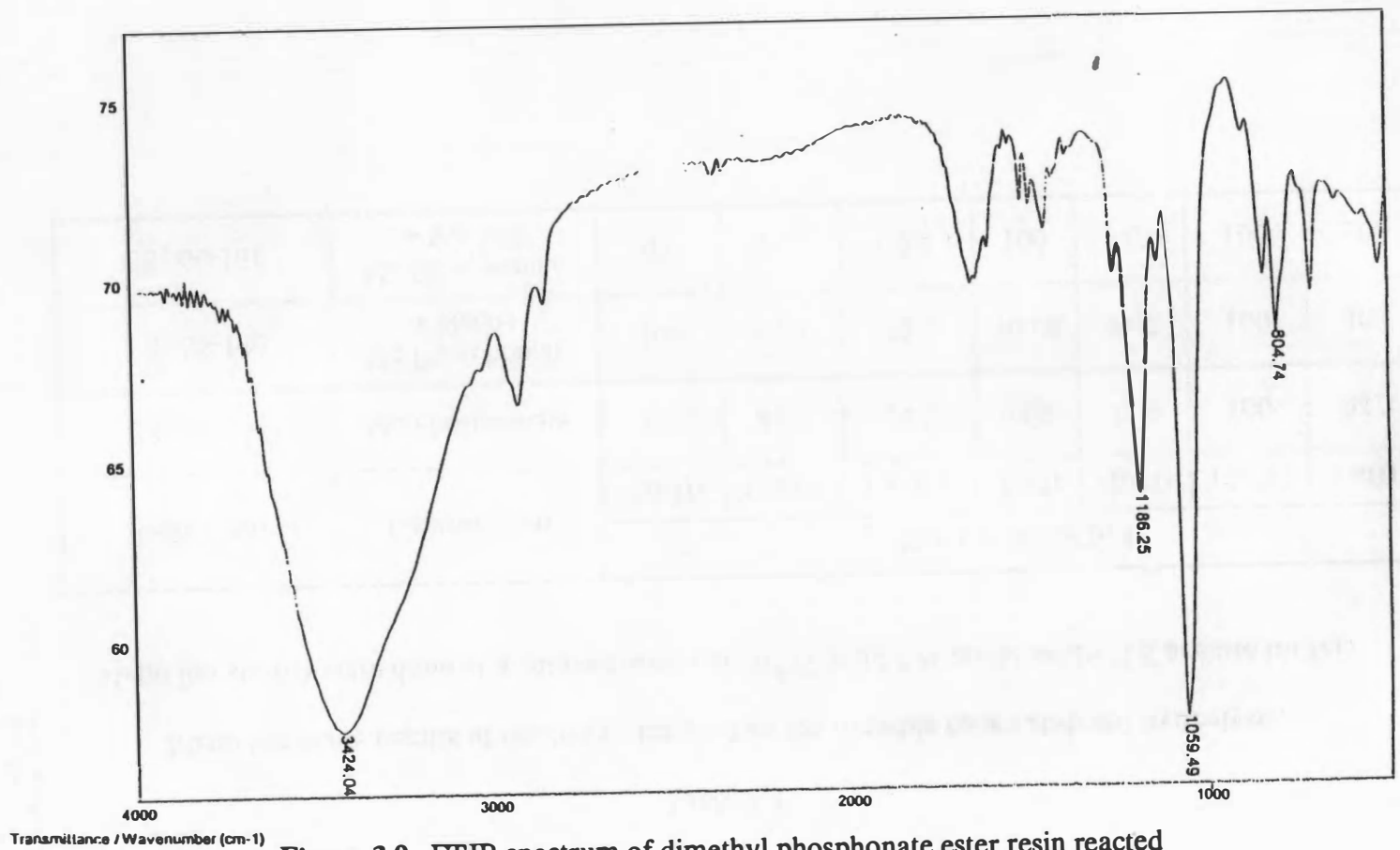


Figure 3.9. FTIR spectrum of dimethyl phosphonate ester resin reacted with dimethylamine (CS<sub>2</sub>-06-161)

**Table 3.4**

**Metal ion study results of methyl resins studied for possible base catalyzed hydrolysis.**

**Metal ion studies were done at a concentration of  $10^{-4}$  N in 0.06 N acetic acid/pH 5 acetate buffer.**

Resin Code	Composition	Percent Absorbed						
		Cd(II)	Co(II)	Cr(III)	Li(I)	Ni(II)	Pb(II)	Zn(II)
CS <sub>2</sub> -06-156	Me Phosphonate	95.7	81.3	29.9	75.9	73.9	100	94.3
CS <sub>2</sub> -06-160	Me Phosphonate + NaOH	100	98.2	79.4	100.0	91.7	100	100
CS <sub>2</sub> -06-161	Me Phosphonate + Me <sub>2</sub> NH	100	96.3	79.4	100	91.7	100	100

metal ion contact studies, CS<sub>2</sub>-06-160 and CS<sub>2</sub>-06-161 performed better than that of their precursor resin, CS<sub>2</sub>-06-156. However, with some of the metal ions, the difference was minor. All three resins complexed 100% of the Pb(II) ions in solution, while for Cd(II) and Zn(II), CS<sub>2</sub>-06-156 complexed more than 94% of the metal ions and CS<sub>2</sub>-06-160 and CS<sub>2</sub>-06-161 complexed 100%. The remaining contact studies showed differences between the monofunctional dimethyl phosphonate ester resin, CS<sub>2</sub>-06-156, and the base-contacted resins, CS<sub>2</sub>-06-160 and CS<sub>2</sub>-06-161, that were more pronounced. CS<sub>2</sub>-06-156 complexed 82.3% Co(II) while CS<sub>2</sub>-06-160 and CS<sub>2</sub>-06-161 complexed > 96% Co(II). With Li(I) and Ni(II), CS<sub>2</sub>-06-160 and CS<sub>2</sub>-06-161 absorbed > 91% of the metal ions in solution while the precursor resin absorbed approximately 75% of the ions. With Cr(III), CS<sub>2</sub>-06-156, absorbed less than half of the metal ions than the base-contacted resins (29.9% vs. 79.4% for each of the latter). Though the base-contacted resins performed better than the precursor resin, the resin's exact structure remains uncertain. However, the following is suggested: the base catalyzed hydrolysis, upon reaction with dimethylamine, is generating acid sites on the phosphonate esters, as demonstrated by acid capacities. The acid sites can allow for enhanced complexation as the resin can now ion-exchange, as well as complex the metal ions in solution.

Multiple metal ion contact studies were performed with the three resins (CS<sub>2</sub>-06-156, CS<sub>2</sub>-06-160 and CS<sub>2</sub>-06-161) to quantify their saturation capacities. The studies were done with Co(II) in 0.06 N acetic acid/pH 5 acetate buffer, ranging in concentration from 10<sup>-4</sup> N to 1.0 N.

The bifunctional methyl/methyl resin (CS<sub>2</sub>-06-084) was also added for comparison. The results are summarized in Table 3.5. It can be noted that in the metal

**Table 3.5**

**Metal ion study results of methyl resins at varying concentrations of Co(II)  
in 0.06 N acetic acid/pH 5 acetate buffer**

Resin Code	Composition	Co(II) Absorbed (meq/g)				
		$10^{-4}$ N	$10^{-3}$ N	$10^{-2}$ N	$10^{-1}$ N	1.0 N
CS <sub>2</sub> -06-156	Me Phosphonate	$4.56 \times 10^{-3}$	$3.31 \times 10^{-2}$	$9.13 \times 10^{-2}$	$7.64 \times 10^{-2}$	1.81
CS <sub>2</sub> -06-160	Me Phosphonate + NaOH	$5.09 \times 10^{-3}$	$5.16 \times 10^{-2}$	$5.10 \times 10^{-1}$	2.64	5.27
CS <sub>2</sub> -06-161	Me Phosphonate + Me <sub>2</sub> NH	$5.08 \times 10^{-3}$	$5.08 \times 10^{-2}$	$5.09 \times 10^{-1}$	2.75	6.36
CS <sub>2</sub> -06-084	Me Bifunctional	$4.37 \times 10^{-3}$	$4.37 \times 10^{-2}$	$3.79 \times 10^{-1}$	$7.38 \times 10^{-1}$	2.61

ion solutions of  $10^{-4}$  N,  $10^{-3}$  N and  $10^{-2}$  N, there was little difference in the degree of sorption among the resins. Differences were apparent at a concentration of  $10^{-1}$  N. The base-contacted resins sorbed much greater quantities of Co(II) than the other resins. This trend was also observed in the 1.0 N Co(II) solutions. This indicated that acid sites, though not in great amounts, did affect the amount of metal ions absorbed by the resins.

The results obtained with the monofunctional dimethyl phosphonate ester resin, with and without further contact with base, at a higher concentration of metal ions, indicated that this method was effective in studying the resins ability to chelate. Metal ion studies were performed on the methyl resins that had been initially investigated in dilute metal ion solutions. The remaining resins, CS<sub>2</sub>-06-203, a monofunctional dimethyl phosphonate ester resin, CS<sub>2</sub>-06-220, a dimethylamine-contacted fully functionalized dimethyl phosphonate ester resin and CS<sub>2</sub>-05-267, a monofunctional dimethyl amine resin, were synthesized to be used in this study for comparison. Elemental analyses for the new resins are given in Table 3.6. CS<sub>2</sub>-06-203 was found to have a phosphorus capacity of 3.51 meq/g, while its dimethylamine-reacted analogue, CS<sub>2</sub>-06-220, had a phosphorus capacity of 3.29 meq/g. Acid capacities were found to be 0.27 meq/g for CS<sub>2</sub>-06-203 and 0.53 meq/g for CS<sub>2</sub>-06-220. The differences in the resins were not significant by elemental analyses so FTIR spectra were taken to determine the presence of either the diester phosphonate or phosphonic acid peak. The monofunctional dimethyl phosphonate resin, CS<sub>2</sub>-06-203, had a peak at  $1248\text{ cm}^{-1}$  (Figure 3.10), indicative of phosphonate diester, while the bifunctional methyl/methyl resin, CS<sub>2</sub>-06-084 (Figure 3.6), and the dimethylamine-contacted fully functional dimethyl phosphonate resin, CS<sub>2</sub>-06-220 (Figure 3.11), displayed peaks at  $1198\text{ cm}^{-1}$  and  $1191\text{ cm}^{-1}$ , respectively,

**Table 3.6**  
**Elemental analysis results of set of methyl resins**

<b>Resin Code</b>	<b>Composition</b>	<b>P Capacity (meq/g) Actual (Theoretical)</b>	<b>N Capacity (meq/g) Actual (Theoretical)</b>	<b>Acid Capacity (meq/g) Actual (Theoretical)</b>
CS <sub>2</sub> -06-203	Me Phosphonate	3.51 (4.02)	---	0.27 (0.00)
CS <sub>2</sub> -06-084	Me Bifunctional	2.10 (2.23)	1.84 (2.23)	---
CS <sub>2</sub> -06-220	Me Phosphonate + Me <sub>2</sub> NH	3.29 (3.51)	0.53 (0.00)	0.53 (0.00)
CS <sub>2</sub> -05-267	Me Amine	---	4.41 (5.64)	---

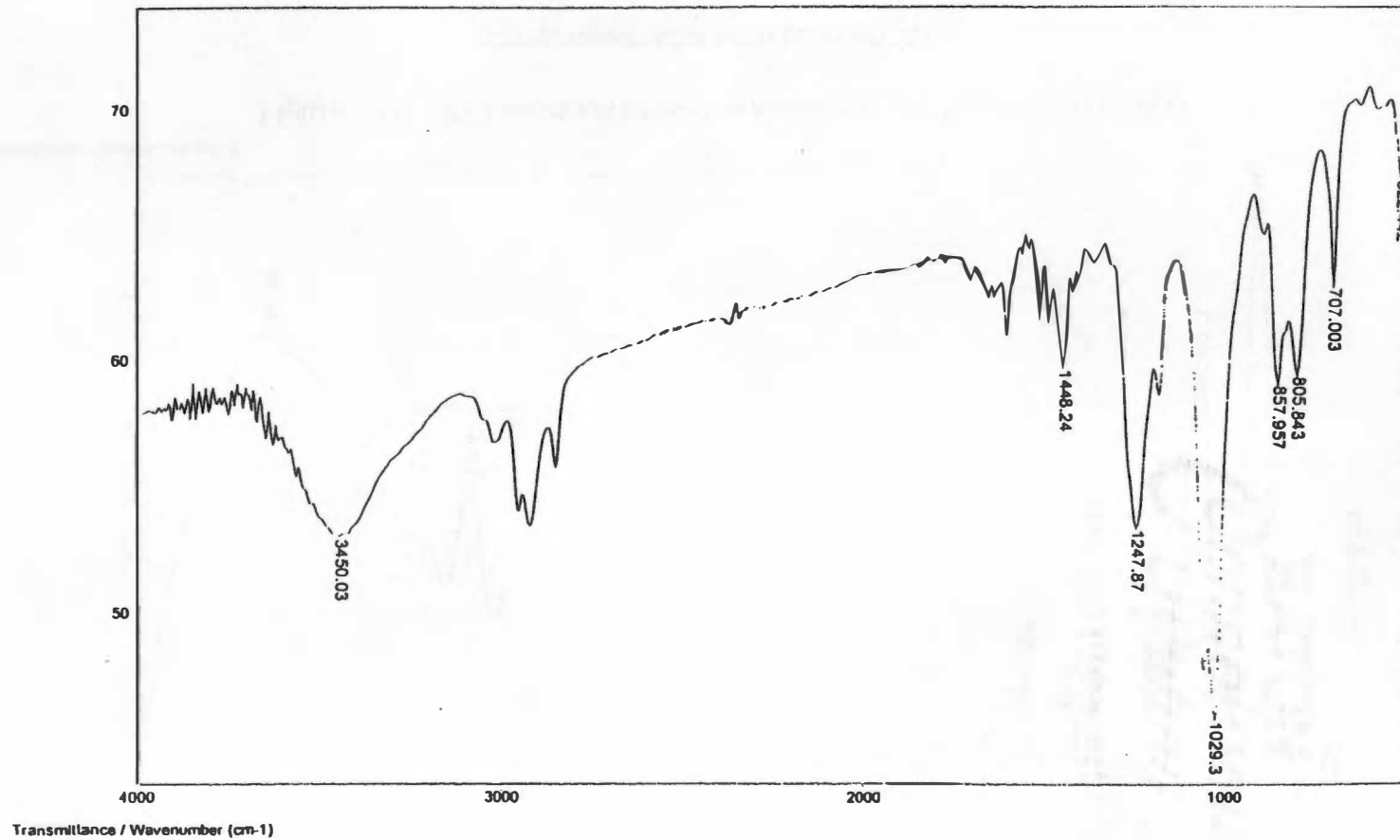


Figure 3.10. FTIR spectrum of dimethyl phosphonate ester resin (CS<sub>2</sub>-06-203)

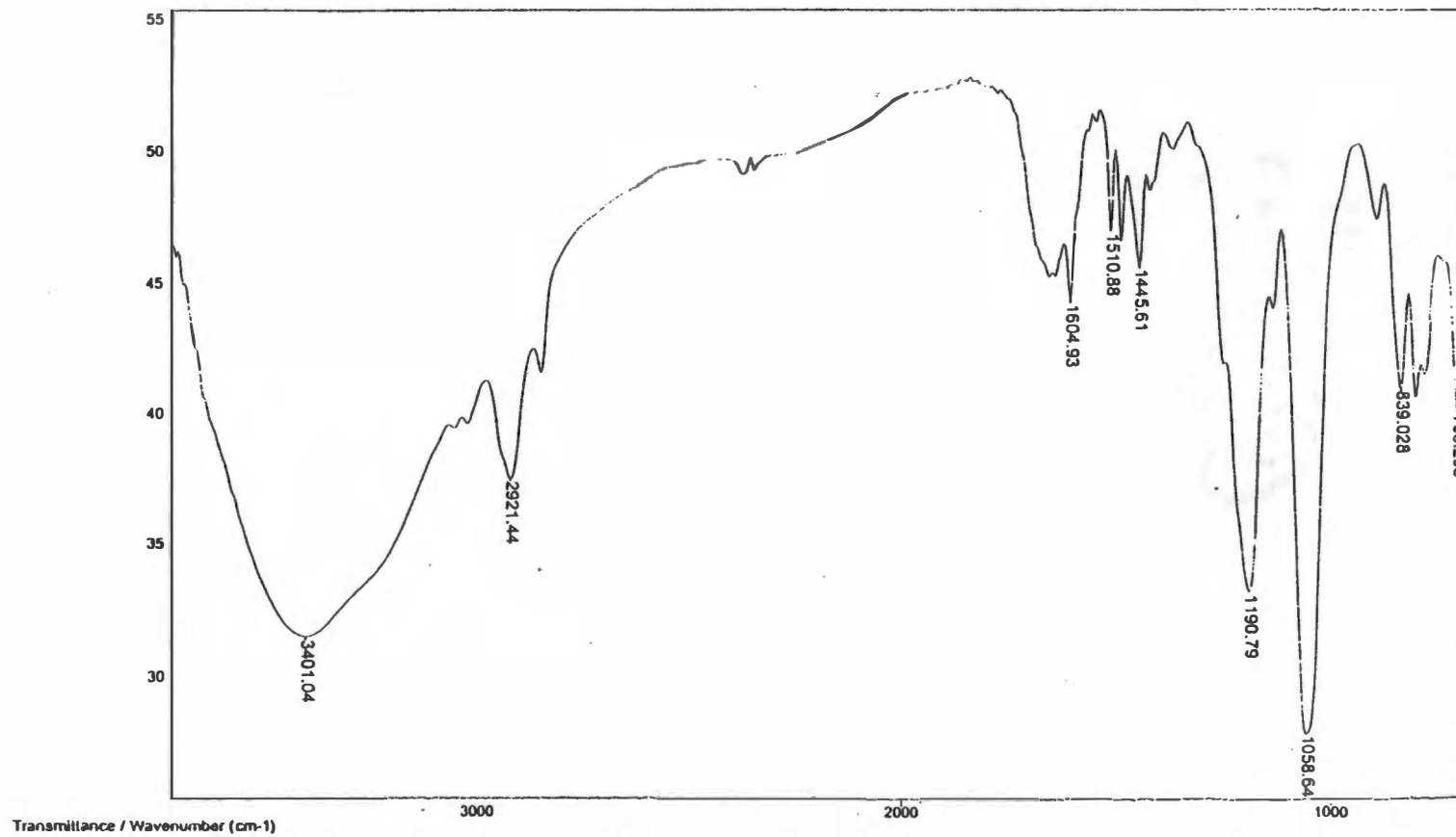


Figure 3.11. FTIR spectrum of methyl aminated fully functional dimethyl phosphonate ester resin (CS<sub>2</sub>-06-220)



indicating the presence of phosphonic acid sites. Titration of acid sites of CS<sub>2</sub>-06-203 and CS<sub>2</sub>-06-220 gave 0.27 and 0.53 meq/g, respectively. The limited amount of CS<sub>2</sub>-06-084 prevented analysis of acid content so the amount present was not quantified.

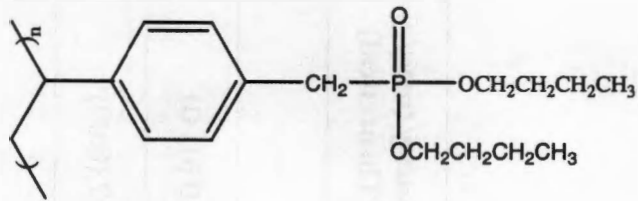
Metal ion (Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II)) contact studies were done with the four methyl resins at a concentration of 10<sup>-1</sup> N in 0.06 N acetic acid/pH 5 acetate buffer. With every metal ion study, the dimethylamine-contacted fully functional dimethyl phosphonate ester resin, CS<sub>2</sub>-06-220, outperformed all of the other resins (Table 3.7). The bifunctional methyl/methyl resin, CS<sub>2</sub>-06-084, absorbed greater quantities of metal ions than either of the monofunctional resins, CS<sub>2</sub>-06-203 and CS<sub>2</sub>-05-267, though not to the extent of CS<sub>2</sub>-06-220. The results with CS<sub>2</sub>-06-220 were somewhat surprising as the acid capacity was found to be only 0.53 meq/g.

### **Butyl Resins**

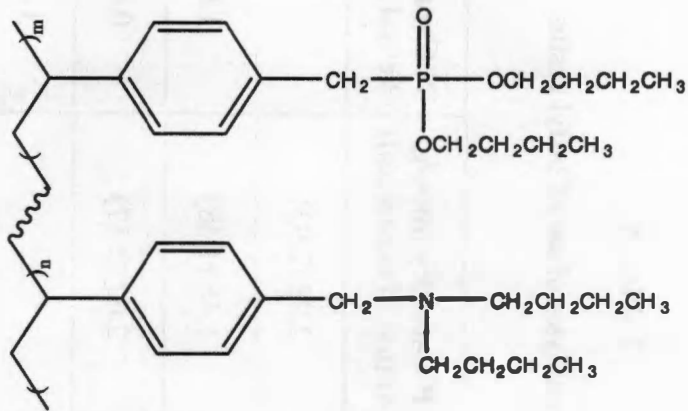
The monofunctional dibutyl phosphonate ester was studied because it was thought to be more difficult to hydrolyze with dibutylamine due to the steric hindrance of the alkyl groups. The resins studied included a monofunctional dibutyl phosphonate ester (Figure 3.12), CS<sub>2</sub>-06-132, a bifunctional butyl/butyl resin (Figure 3.13), CS<sub>2</sub>-06-266, a dibutylamine-contacted fully functional dibutyl phosphonate ester, CS<sub>2</sub>-07-015 and a monofunctional dibutylamine resin (Figure 3.14), CS<sub>2</sub>-06-069. The resins were synthesized in the same manner as that of the methyl resins and then characterized by elemental analyses (Table 3.8), as well as by FTIR. The FTIR spectra of CS<sub>2</sub>-06-132 (Figure 3.15) displayed a distinct peak at 1249 cm<sup>-1</sup>, which is representative of phosphonate diesters. When comparing both, CS<sub>2</sub>-06-266 and CS<sub>2</sub>-07-015, it was seen that they had distinct peaks at 1249 cm<sup>-1</sup> and 1251 cm<sup>-1</sup>, respectively (Figures 3.16 and

**Table 3.7****Metal ion study results of methyl resins using a metal ion concentration of  $10^{-1}$  N****in 0.06 N acetic acid/pH 5 acetate buffer**

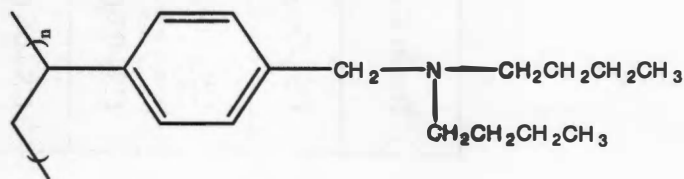
Resin Code	Composition	Quantity Absorbed (meq/g)					
		Cd(II)	Co(II)	Cu(II)	Ni(II)	Pb(II)	Zn(II)
CS <sub>2</sub> -06-203	Me Phosphonate	$4.85 \times 10^{-1}$	$2.58 \times 10^{-1}$	$5.86 \times 10^{-1}$	$2.31 \times 10^{-1}$	$6.28 \times 10^{-1}$	$5.86 \times 10^{-1}$
CS <sub>2</sub> -06-084	Me Bifunctional	$8.99 \times 10^{-1}$	$8.45 \times 10^{-1}$	1.09	$6.73 \times 10^{-1}$	1.74	1.09
CS <sub>2</sub> -06-220	Me Phosphonate + Me <sub>2</sub> NH	2.69	2.57	2.94	2.14	3.33	2.94
CS <sub>2</sub> -05-267	Me Amine	$4.57 \times 10^{-1}$	$4.38 \times 10^{-1}$	$4.53 \times 10^{-1}$	$6.00 \times 10^{-2}$	$3.74 \times 10^{-1}$	$4.53 \times 10^{-1}$



**Figure 3.12** Structure of dibutyl phosphonate ester resin



**Figure 3.13** Structure of bifunctional butyl/butyl resin



**Figure 3.14** Structure of dibutylamine resin

**Table 3.8**  
**Elemental analysis of set of butyl resins**

<b>Resin Code</b>	<b>Composition</b>	<b>P Capacity (meq/g) Actual (Theoretical)</b>	<b>N Capacity (meq/g) Actual (Theoretical)</b>	<b>Acid Capacity (meq/g) Actual (Theoretical)</b>
CS <sub>2</sub> -06-132	Bu Phosphonate	2.98 (2.93)	---	---
CS <sub>2</sub> -06-266	Bu Bifunctional	1.48 (1.38)	1.81 (1.38)	0.10 (0.00)
CS <sub>2</sub> -07-015	Bu Phosphonate + Bu <sub>2</sub> NH	2.62 (2.57)	0.47 (0.00)	0.17 (0.00)
CS <sub>2</sub> -06-069	Bu Amine	---	3.49 (3.71)	---

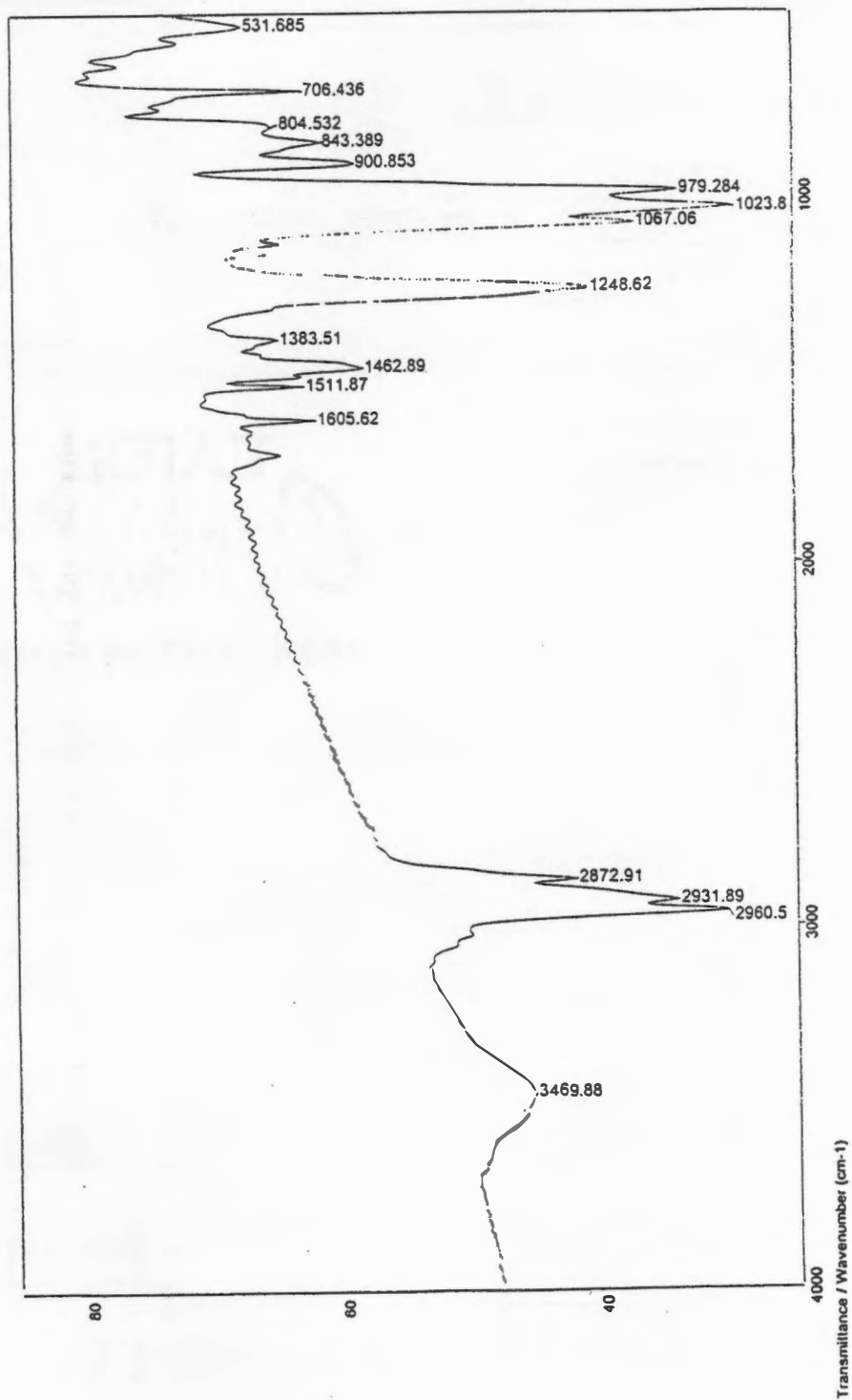


Figure 3.15. FTIR spectrum of dibutyl phosphonate ester resin (CS<sub>2</sub>-06-132)

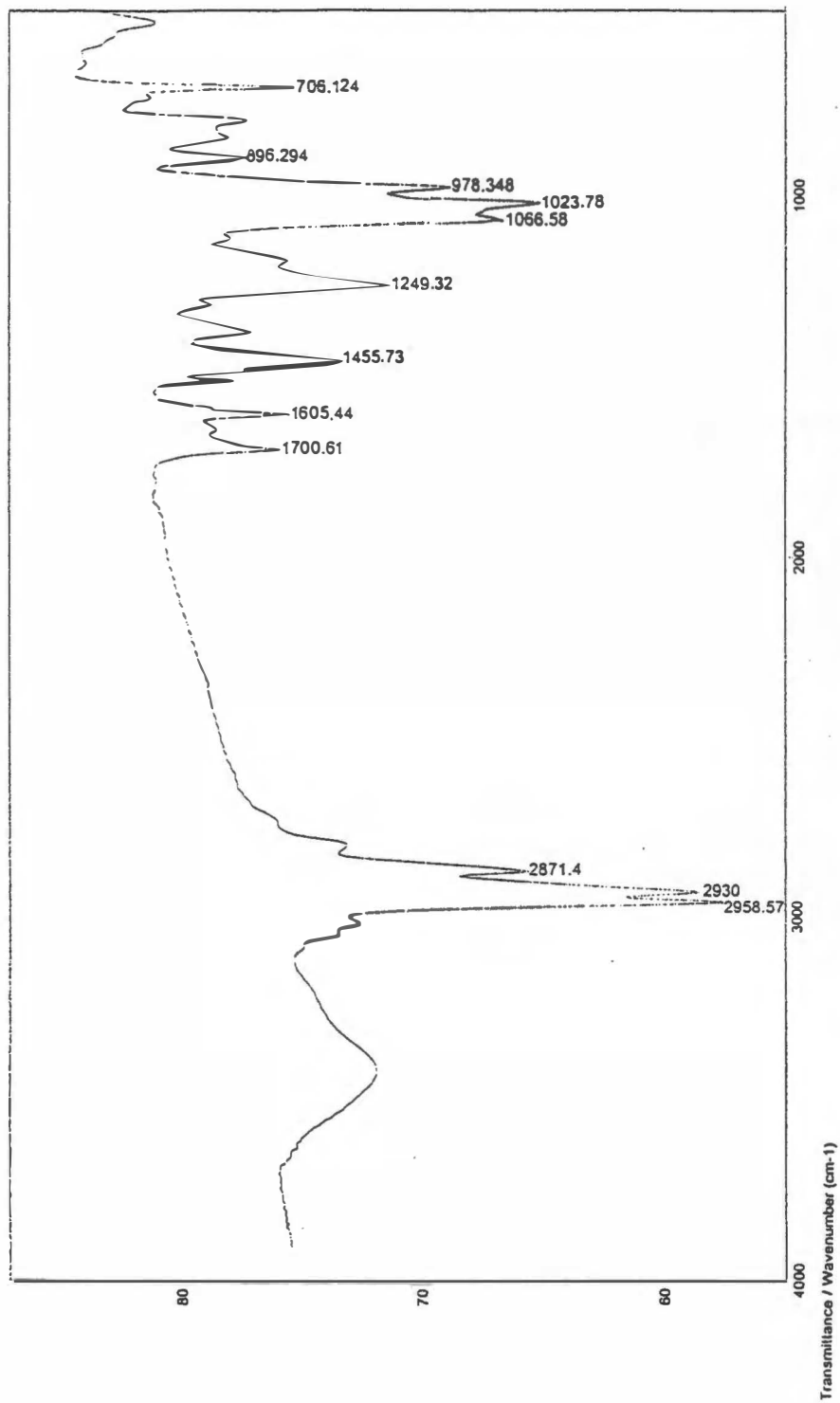
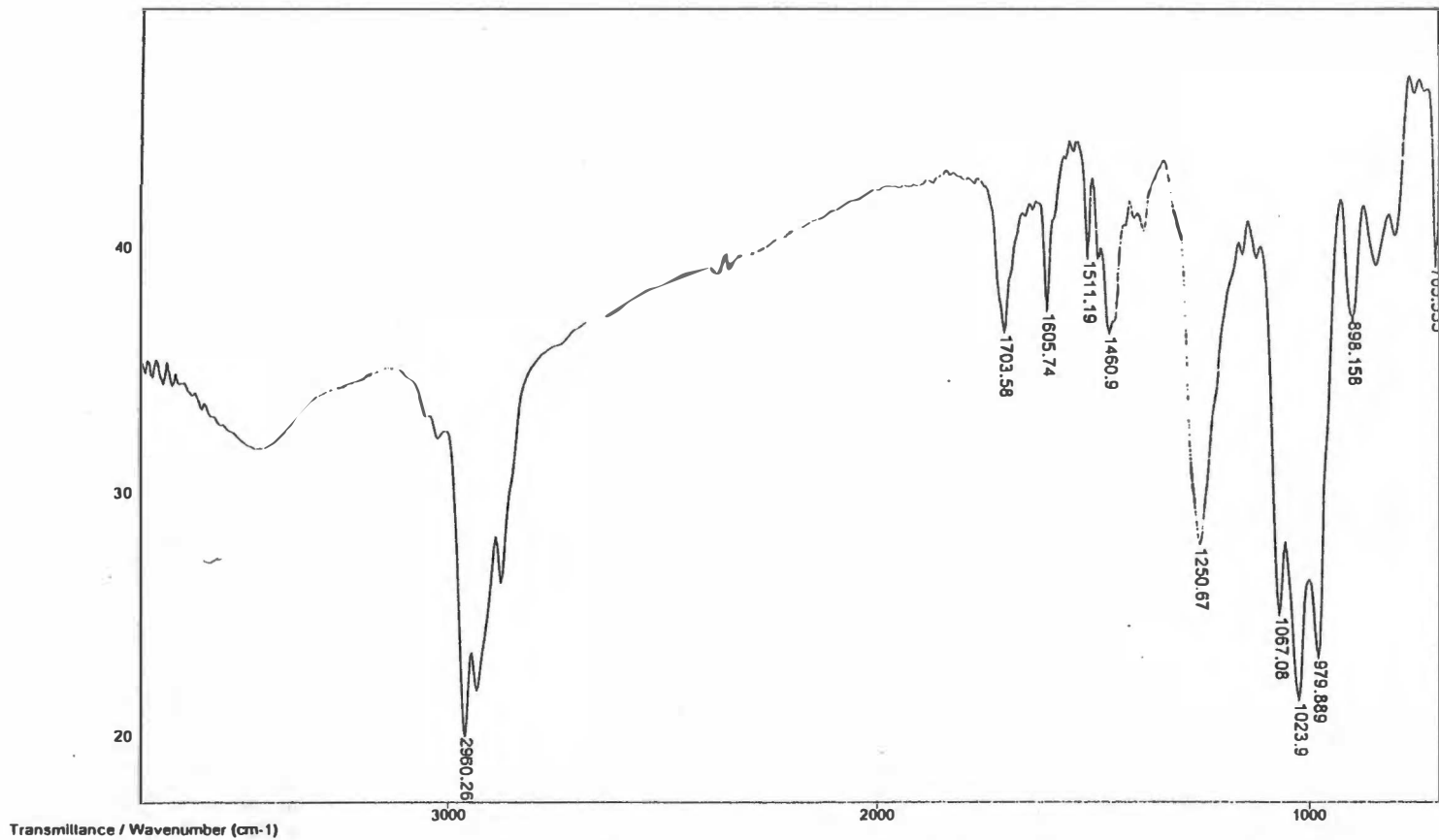


Figure 3.16. FTIR spectrum of bifunctional butyl/butyl resin (CS<sub>2</sub>-06-266)

3.17). There appeared to be a small shoulder peak at  $1182\text{ cm}^{-1}$  on the bifunctional butyl/butyl resin spectra that may imply there are acid sites present, though not to the extent of the methyl resins. This allowed for the conclusion that hydrolysis did not occur upon reaction with dibutylamine in the formation of the bifunctional butyl/butyl resin and the dibutylamine-contacted fully functional dibutyl phosphonate ester resin. The acid capacity values supported the idea that base catalyzed hydrolysis did not occur with CS<sub>2</sub>-06-266 and CS<sub>2</sub>-07-015. With both aminated resins, the acid capacity was found to be less than 0.20 meq/g. The results of the phosphorus and nitrogen contents demonstrated that the resins had structures that were expected, based on the comparison to the calculated theoretical values.

The resins were then contacted with  $10^{-1}\text{ N}$  Cd(II), Co(II), Cu(II), Ni(II), Pb(II), and Zn(II) in a solution of 0.06 N acetic acid/pH 5 acetate buffer. The results are given in Table 3.9. The bifunctional butyl/butyl resin complexed greater quantities of metal ions than the dibutylamine-contacted resin except in the case of Cu(II). CS<sub>2</sub>-06-266 and CS<sub>2</sub>-07-015 sorbed Co(II) to the greatest extent, having a capacity greater than 1 meq/g. In most studies, the differences in sorption were minor, though significant. There were some inconsistencies in trends with the four butyl resins though the monofunctional dibutyl ester resin had a higher capacity for metal ions than either of the aminated phosphonate resins.

The primary discovery in this series of experiments, when comparing the results to those of the methyl resins, is that the lack of hydrolysis of the fully functionalized dibutyl phosphonate ester resin may have affected its ability to chelate metal ions. The differences in FTIR spectra indicate a difference in composition, which affects the



**Figure 3.17.** FTIR spectrum of dibutylamine-contacted fully functional dibutyl phosphonate ester resin (CS<sub>2</sub>-07-015)



**Table 3.9**

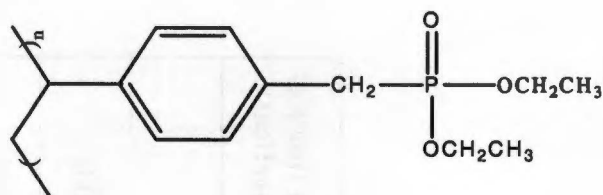
**Metal ion study results of butyl resins at a concentration of  $10^{-1}$  N  
in 0.06 N acetic acid/pH 5 acetate buffer**

Resin Code	Composition	Quantity Absorbed (meq/g)					
		Cd(II)	Co(II)	Cu(II)	Ni(II)	Pb(II)	Zn(II)
CS <sub>2</sub> -06-132	Bu Phosphonate	$3.42 \times 10^{-1}$	$1.38 \times 10^{-1}$	0.00	$9.20 \times 10^{-2}$	$4.62 \times 10^{-1}$	$3.69 \times 10^{-1}$
CS <sub>2</sub> -06-266	Bu Bifunctional	$4.52 \times 10^{-1}$	1.41	$8.70 \times 10^{-2}$	0.00	$7.70 \times 10^{-1}$	$6.12 \times 10^{-1}$
CS <sub>2</sub> -07-015	Bu Phosphonate + Bu <sub>2</sub> NH	$3.31 \times 10^{-1}$	1.06	$2.39 \times 10^{-1}$	0.00	$7.22 \times 10^{-1}$	$5.28 \times 10^{-1}$
CS <sub>2</sub> -06-069	Bu Amine	$4.10 \times 10^{-1}$	$1.15 \times 10^{-1}$	1.59	$1.44 \times 10^{-1}$	$5.33 \times 10^{-1}$	$3.59 \times 10^{-1}$

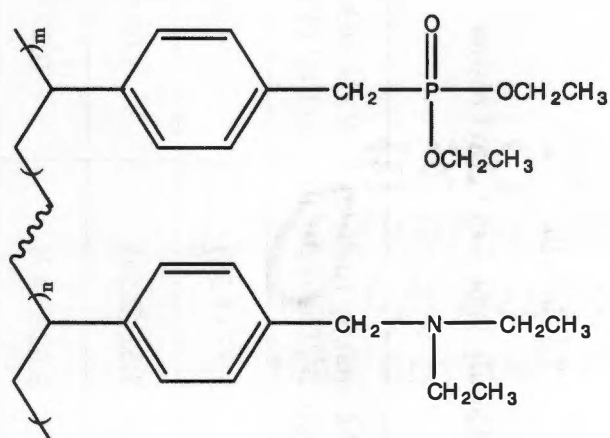
amount of metal complexes by the resins. The dimethylamine-contacted fully functionalized dimethyl phosphonate ester resins appears to have a much greater capacity than that of the butyl analogue of the same resin, which did not appear to have undergone hydrolysis. This could be rationalized that, once hydrolyzed, the internal polymer network becomes somewhat more hydrophilic, resulting in increased accessibility to ions, which can then coordinate through the phosphoryl moiety. The butyl analogue does not demonstrate this phenomenon, which may be attributed to the lack of hydrolysis or the possibility of a decreased ability to complex metal ions.

### **Ethyl Resins**

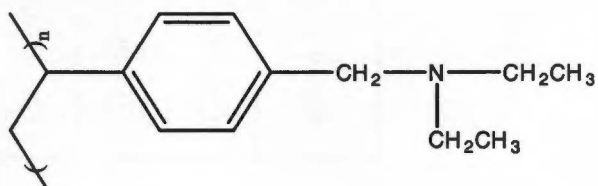
The differences in results discovered between the series of methyl and butyl resins led to further experiments with analogue resins having ethyl side chains. The four signature resins were synthesized: a monofunctional diethyl phosphonate ester (CS<sub>2</sub>-06-097) (Figure 3.18), a bifunctional ethyl/ethyl resin (CS<sub>2</sub>-06-282) (Figure 3.19), a diethylamine-contacted fully functional diethyl phosphonate resin (CS<sub>2</sub>-07-016) and a diethylamine monofunctional resin (CS<sub>2</sub>-06-038B) (Figure 3.20). The resins were synthesized in the same manner as those of the methyl resins. The resins were characterized by elemental analyses (Table 3.10) and FTIR. The FTIR spectra of CS<sub>2</sub>-06-097, CS<sub>2</sub>-06-282 and CS<sub>2</sub>-07-016 each displayed a distinct peak at 1248 cm<sup>-1</sup> (Figures 3.21, 3.22 and 3.23, respectively), indicating the presence of the diester phosphonate. It was seen by IR that hydrolysis did not occur upon further amination of either the bifunctional ethyl/ethyl resin or the diethylamine-contacted fully functional diethyl phosphonate ester. This was quantified by an acid titration on CS<sub>2</sub>-06-282 and CS<sub>2</sub>-07-016, where the results were found to be 0.28 meq/g and 0.26 meq/g, respectively.



**Figure 3.18** Structure of diethyl phosphonate ester resin



**Figure 3.19** Structure of bifunctional ethyl/ethyl resin



**Figure 3.20** Structure of diethylamine resin

**Table 3.10**  
**Elemental analysis of set of ethyl resins**

<b>Resin Code</b>	<b>Composition</b>	<b>P Capacity (meq/g) Actual (Theoretical)</b>	<b>N Capacity (meq/g) Actual (Theoretical)</b>	<b>Acid Capacity (meq/g) Actual (Theoretical)</b>
CS <sub>2</sub> -06-097	Et Phosphonate	3.47 (3.58)	---	---
CS <sub>2</sub> -06-282	Et Bifunctional	2.51 (2.54)	1.04 (2.54)	0.28 (0.00)
CS <sub>2</sub> -07-016	Et Phosphonate + Et <sub>2</sub> NH	2.62 (3.47)	0.27 (0.00)	0.26 (0.00)
CS <sub>2</sub> -06-038B	Et Amine	---	4.50 (4.81)	---

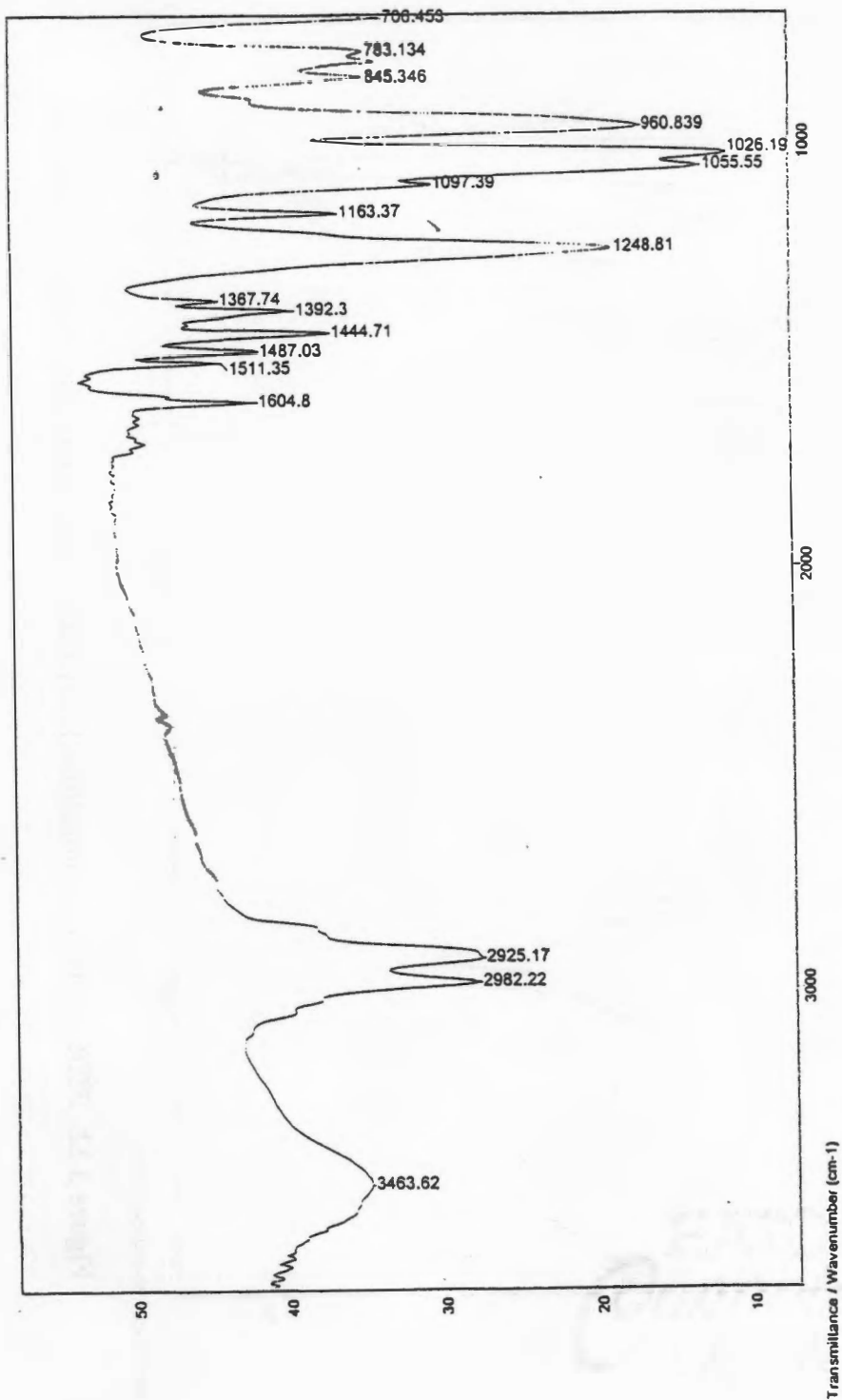


Figure 3.21. FTIR spectrum of diethyl phosphonate ester resin (CS<sub>2</sub>-06-097)

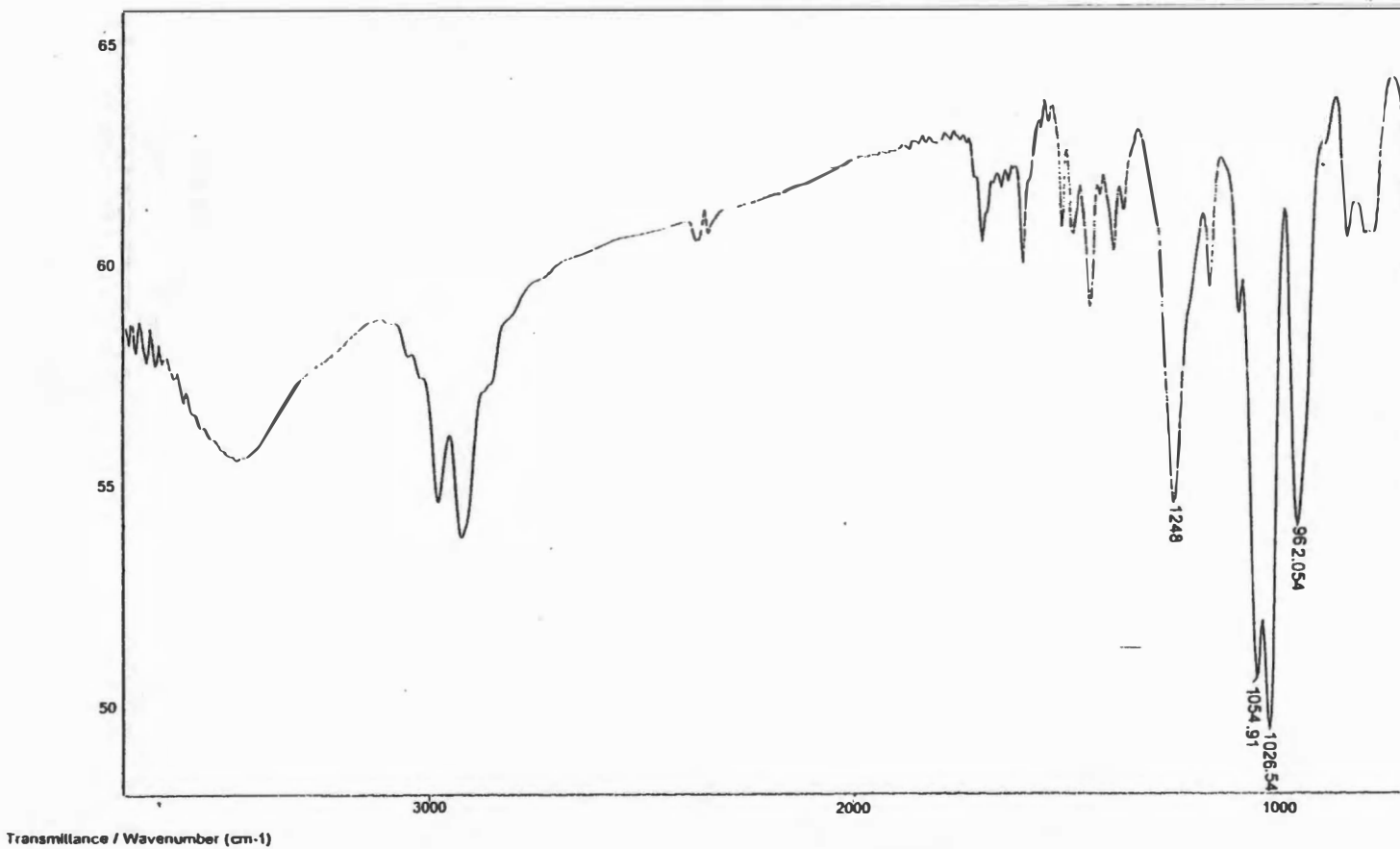
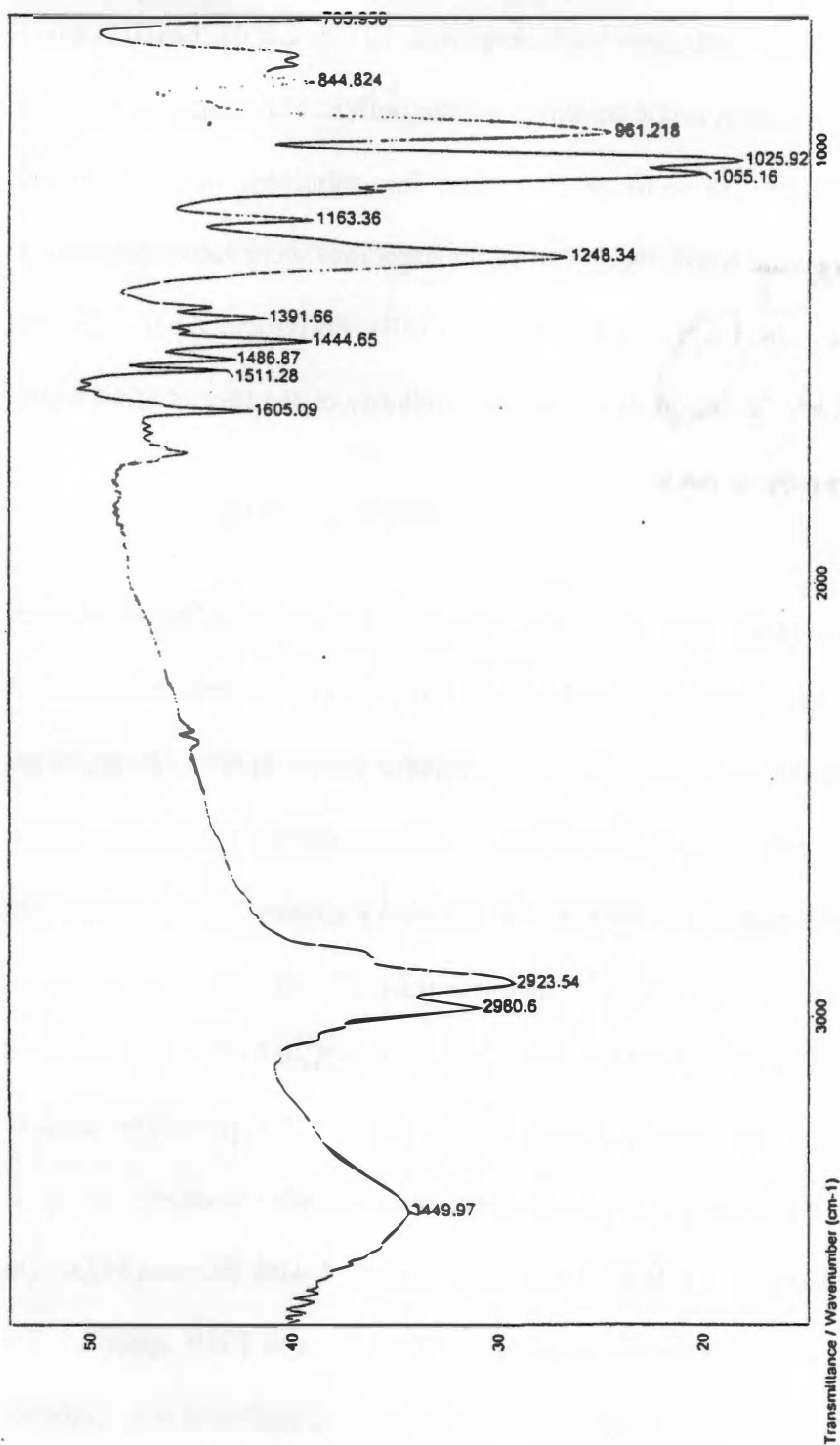


Figure 3.22. FTIR spectrum of bifunctional ethyl/ethyl phosphonate ester resin (CS<sub>2</sub>-06-282)



**Figure 3.23. FTIR spectrum of diethylamine-contacted fully functional diethyl**

**phosphonate ester resin (CS<sub>2</sub>-07-016)**

The phosphorus and nitrogen capacity values were similar to that of their calculated theoretical values, with the exception of the bifunctional ethyl/ethyl resin, which gave a low nitrogen capacity. Metal ion studies were done with  $10^{-1}$  N Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) in 0.06 N acetic acid/pH5 acetate buffer. The results can be seen in Table 3.11. Surprisingly, in most of the metal ion solutions, the bifunctional ethyl/ethyl resin performed the worst, though all of the capacities were somewhat similar in a given metal solution. In the presence of Cd(II), Cu(II), Pb(II) and Zn(II), CS<sub>2</sub>-06-282 had the lowest degree of sorption; however, the similarity of the results of all resins prevents conclusions from being made.

### **Ethylenediamine Resins**

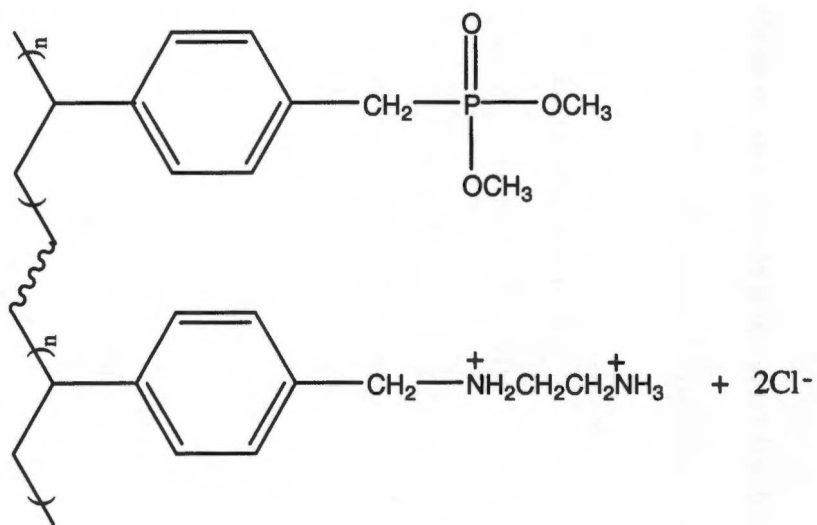
Preparing a bifunctional resin containing phosphonate diester and amine ligands that cooperated in the complexation of metal cations was found to be more difficult than expected. Resins were then synthesized using a primary amine instead of secondary amines, which had been previously studied. It was not clear whether the primary amine would hydrolyze the phosphonate diesters as the secondary amines had, or simply not react at all. For comparison purposes, a bifunctional resin (CS<sub>2</sub>-07-077) and an amine-contacted fully functional dimethyl phosphonate ester resin (CS<sub>2</sub>-07-054) were prepared using ethylenediamine as the primary amine (Figure 3.24). The procedure used to prepare the resins was the same as previously done; however, after washing, the resins were eluted with a sequence of 1 L H<sub>2</sub>O, 4 wt% NaOH, H<sub>2</sub>O, 4 wt% HCl and H<sub>2</sub>O. The resins were characterized by elemental analysis (Table 3.12) and FTIR spectra. The phosphorus contents indicate that the appropriate amount of phosphorus was contained by each resin. The nitrogen capacity of CS<sub>2</sub>-07-077 was slightly lower than expected,



**Table 3.11**

**Metal ion study results of ethyl resins at a concentration of  $10^{-1}$  N  
in 0.06 N acetic acid/pH 5 acetate buffer**

Resin Code	Composition	Quantity Absorbed (meq/g)					
		Cd(II)	Co(II)	Cu(II)	Ni(II)	Pb(II)	Zn(II)
CS <sub>2</sub> -06-097	Et Phosphonate	$5.13 \times 10^{-1}$	$7.52 \times 10^{-1}$	$2.81 \times 10^{-1}$	0.00	$5.61 \times 10^{-1}$	$5.87 \times 10^{-1}$
CS <sub>2</sub> -06-282	Et Bifunctional	$2.88 \times 10^{-1}$	$6.10 \times 10^{-1}$	$1.96 \times 10^{-1}$	0.00	$3.90 \times 10^{-1}$	$3.98 \times 10^{-1}$
CS <sub>2</sub> -07-016	Et Phosphonate + Et <sub>2</sub> NH	$4.62 \times 10^{-1}$	$5.27 \times 10^{-1}$	$3.55 \times 10^{-1}$	0.00	$5.91 \times 10^{-1}$	$4.50 \times 10^{-1}$
CS <sub>2</sub> -06-038B	Et Amine	$4.54 \times 10^{-1}$	$5.67 \times 10^{-1}$	1.84	0.00	$6.35 \times 10^{-1}$	$8.69 \times 10^{-1}$



**Figure 3.24** Structure of bifunctional methyl/EDA resin (CS<sub>2</sub>-07-077)

**Table 3.12****Elemental analysis results of methyl/EDA resins**

<b>Resin Code</b>	<b>Composition</b>	<b>P Cap (meq/g) Act (Theoret)</b>	<b>N Cap (meq/g) Act (Theoret)</b>	<b>Acid Cap (meq/g) Act (Theoret)</b>
CS <sub>2</sub> -07-054	Me/EDA Bifunctional	1.96 (1.77)	2.81 (3.42)	2.66 (0.00)
CS <sub>2</sub> -07-077	Me Phosphonate+ EDA	3.37 (3.51)	0.77 (0.00)	4.55 (0.00)

though in high enough capacity. The nitrogen content of CS<sub>2</sub>-07-054 was found to be approaching 1 meq/g when the value, theoretically, should have been zero. The most surprising results found were the acid capacities of both resins, 2.66 meq/g for the bifunctional resin and 4.55 meq/g for the EDA-contacted fully functional phosphonate diester. Complete hydrolysis of the resins would result in acid capacities that were twice the value of the phosphorus capacities; with each resin, the acid capacity was greater than the phosphorus capacity, though not quite twice. This indicates that the resins consist of mainly phosphonate monoester/monoacid ligands, though it could be that some sites are diacidic. The FTIR spectra of CS<sub>2</sub>-07-077 (Figure 3.25) and CS<sub>2</sub>-07-054 (Figure 3.26) fully support the presence of acid sites by distinct peaks at 1180 cm<sup>-1</sup> and 1183 cm<sup>-1</sup>, respectively. To understand fully the ability of the resins to complex metal ions, studies were done with Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) at a concentration of 10<sup>-1</sup> N in 0.06 N acetic acid/pH 5 acetate buffer (Table 3.13). With each set of metal ions, CS<sub>2</sub>-07-054, the EDA-contacted fully functional dimethyl phosphonate ester performed much better than the bifunctional resin, CS<sub>2</sub>-07-077. In the presence of Cu(II), CS<sub>2</sub>-07-077 performed far better than with any of the other metal ions investigated.

EDA-contacted fully functional diethyl (CS<sub>2</sub>-07-095) and dibutyl (CS<sub>2</sub>-07-096) phosphonate esters were also prepared as a test to see if they were as easily hydrolyzable as the dimethyl phosphonate ester. The resins were prepared in the same manner as the methyl analogue. Upon washing and eluting the resins, elemental analysis (Table 3.14) showed that both CS<sub>2</sub>-07-095 and CS<sub>2</sub>-07-096 consist mainly of monoester/monoacid sites.

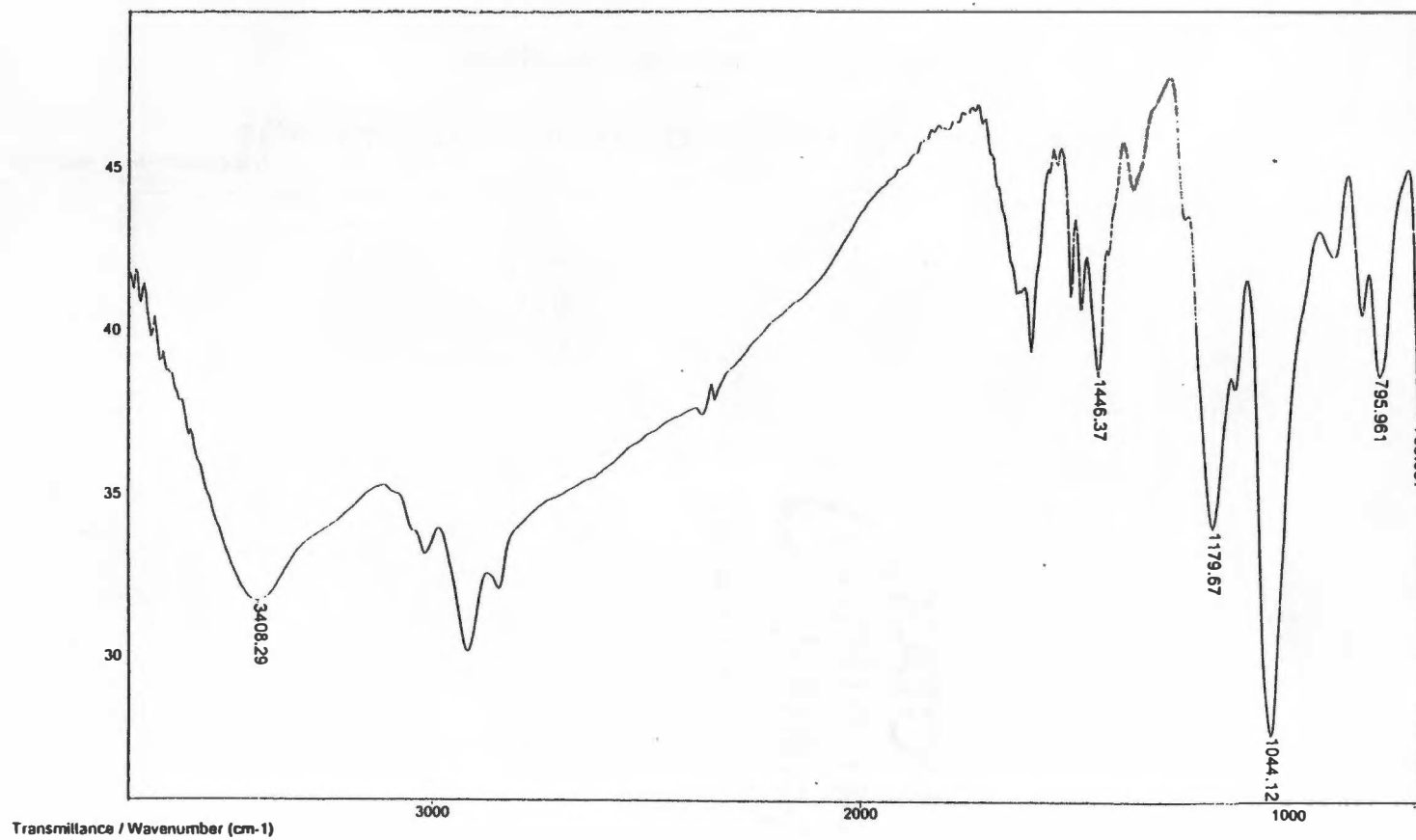
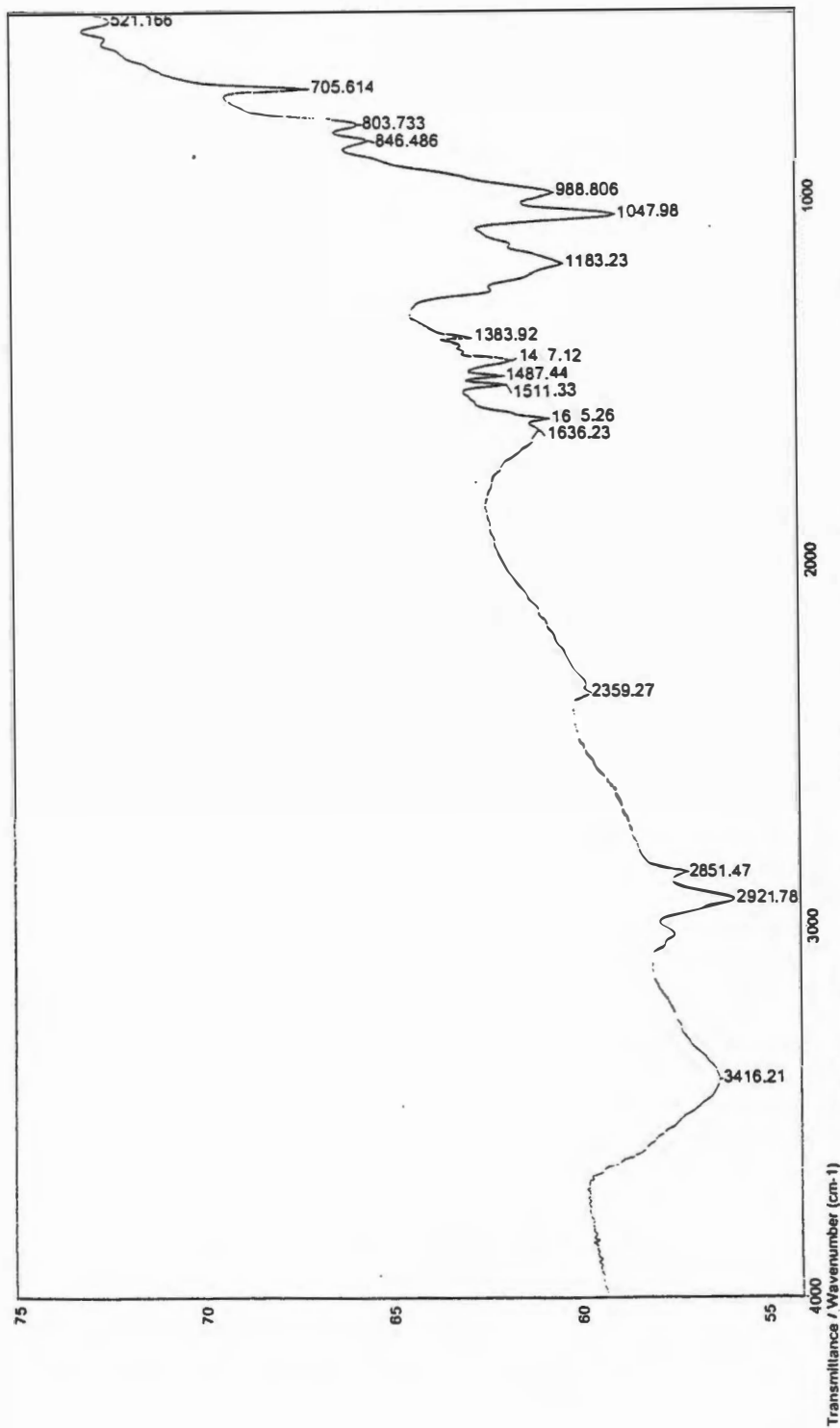


Figure 3.25. FTIR spectrum of bifunctional methyl/EDA resin (CS<sub>2</sub>-07-077)



**Figure 3.26. FTIR spectrum of EDA-aminated fully functional dimethyl**

**phosphonate ester resin (CS<sub>2</sub>-07-054)**

**Table 3.13**

**Metal ion study results of methyl/EDA resins at a concentration of  $10^{-1}$  N  
in 0.06 N acetic acid/pH5 acetate buffer**

Resin Code	Composition	Quantity Absorbed (meq/g)					
		Cd(II)	Co(II)	Cu(II)	Ni(II)	Pb(II)	Zn(II)
CS <sub>2</sub> -07-077	Me/EDA Bifunctional	$4.84 \times 10^{-1}$	$4.75 \times 10^{-1}$	1.54	$6.92 \times 10^{-1}$	$7.52 \times 10^{-1}$	$6.20 \times 10^{-1}$
CS <sub>2</sub> -07-054	Me Phosphonate+ EDA	2.51	2.78	3.04	2.66	3.42	2.73

**Table 3.14****Elemental analysis of ethyl/EDA and butyl/EDA resins**

<b>Resin Code</b>	<b>Composition</b>	<b>P Capacity (meq/g) Actual (Theoretical)</b>	<b>N Capacity (meq/g) Actual (Theoretical)</b>	<b>Acid Capacity (meq/g) Actual (Theoretical)</b>
CS <sub>2</sub> -07-095	Et Phosphonate+ EDA	3.18 (2.98)	NA	3.39 (0.00)
CS <sub>2</sub> -07-096	Bu Phosphonate+ EDA	2.81 (2.57)	NA	3.14 (0.00)



## **Hindered Amines**

It was observed that both primary and secondary resins, given small enough alkyl groups, were able to hydrolyze dialkyl phosphonate esters, so a few experiments were performed by the introduction of more hindered amines to a fully functional dimethyl phosphonate ester to look for hydrolysis. The resins were prepared in the same manner as that of the EDA resins, including the elution sequence. The amines examined were diisopropylamine, piperidine, piperazine and dibutylamine. The elemental analysis results can be seen in Table 3.15. Again, the acid capacities were very high, which was somewhat surprising considering the hindrance of the amines used. It can be observed by comparing the phosphorus and acid contents of the resins that the structure of the phosphonate sites have changed from diester to monoester/monoacid. This allows for the conclusion that the small size of the methyl groups of the phosphonate ester are easily attacked by even hindered amines.

## **Metal Studies in the Presence of Acid and Excess Salt**

The bifunctional butyl/butyl and ethyl/ethyl resins, CS<sub>2</sub>-06-266 and CS<sub>2</sub>-06-282, respectively, were eluted with H<sub>2</sub>O, 4 wt% NaOH, H<sub>2</sub>O, 4 wt% HCl and H<sub>2</sub>O to obtain the protonated form of the resin. Metal ion studies were then performed in the presence of acid and salt to determine the extent of complexation. The metals investigated were Fe(III), Ni(II) and Zn(II) at a concentration of 10<sup>-4</sup> N in a solution of 0.1 N or 1 N HCl, HNO<sub>3</sub>, HOAc and H<sub>2</sub>SO<sub>4</sub> with 0.1 N of the corresponding sodium salt. When contacting Fe(III) in 1 N HCl/0.1 N NaCl, the bifunctional butyl/butyl resin performed much better than the ethyl analogue (56.7 % vs. 15.1%, respectively), whereas the bifunctional ethyl/ethyl resin outperformed the butyl analogue in 0.1 N HCl/0.1 N NaCl (34.8 % vs.

**Table 3.15****Elemental analysis results of methyl/hindered amine resins**

<b>Resin Code</b>	<b>Composition</b>	<b>P Cap (meq/g) Act (Theoret)</b>	<b>N Cap (meq/g) Act (Theoret)</b>	<b>Acid Cap (meq/g) Act (Theoret)</b>
CS <sub>2</sub> -07-161	Me Phosphonate + iPr <sub>2</sub> NH	3.53 (3.33)	0.26 (0.00)	2.96 (0.00)
CS <sub>2</sub> -07-162	Me Phosphonate + Piperidine	3.37 (3.33)	0.65 (0.00)	3.97 (0.00)
CS <sub>2</sub> -07-163	Me Phosphonate + Piperazine	3.27 (3.33)	2.28 (0.00)	4.97 (0.00)
CS <sub>2</sub> -07-207	Me Phosphonate + Bu <sub>2</sub> NH	3.38 (3.33)	0.13 (0.00)	3.64 (0.00)

22.5%, respectively). In the remaining solutions, the only significant amounts (> 20%) of Fe(III) sorbed by the resins were found in the HOAc solutions and in 0.1 N H<sub>2</sub>SO<sub>4</sub>/0.1 N Na<sub>2</sub>SO<sub>4</sub>. In each set of experiments, the ethyl/ethyl resin performed better than the butyl/butyl resin. In 1 N HOAc/0.1 N NaOAc, CS<sub>2</sub>-06-282 and CS<sub>2</sub>-06-266 sorbed 28.0 % and 25.3 % Fe(III), respectively, while in 0.1 N HOAc/0.1 N NaOAc, they absorbed 56.7 % and 37.5 %. In 0.1 N H<sub>2</sub>SO<sub>4</sub>/0.1 N Na<sub>2</sub>SO<sub>4</sub>, the amounts of Fe(III) sorbed were 29.8 % for CS<sub>2</sub>-06-282 and 23.2 % for CS<sub>2</sub>-06-266. With Ni(II) in each of the solutions noted above, the percent absorbed was less than 20% by both bifunctional resins. The one exception to this was the ethyl/ethyl resin which complexed 41% Ni(II) from 0.1 N HOAc/0.1 N NaOAc. There were significant amounts of Zn(II) complexed from the solutions containing HCl and 0.1 N NaCl. The bifunctional butyl/butyl resin complexed more Zn(II) than the ethyl analogue from both solutions. CS<sub>2</sub>-06-282 complexed 70.6 % Zn(II) from 1 N HCl/0.1 N NaCl, while CS<sub>2</sub>-06-266 complexed 98.2 %. CS<sub>2</sub>-06-282 complexed 14.8 % from 0.1 N HCl/0.1 N NaCl, while CS<sub>2</sub>-06-266 absorbed 80.4 %. In the rest of the solutions studied, the only significant amounts of Zn(II) absorbed were found by the bifunctional ethyl/ethyl resin in HOAc/0.1 N NaOAc at both pH values; from 1 N HOAc, CS<sub>2</sub>-06-282 complexed 47.4 % Zn(II), while from 0.1 N, HOAc it complexed 91.9 %. In the rest of the studies, the values obtained were less than 20%. It can be concluded that the anion effect was limited. The bifunctional resins performed better with Fe(III) and Zn(II) in HOAc/NaOAc, a buffer system, and in HCl/NaCl, which has the possibility of forming chloride complexes in solutions of high chloride content. It is apparent with the nitrate and sulfate systems that there was little complexation indicating the lack of tendencies to form anions.

## CONCLUSIONS

The preparation of bifunctional phosphonate diester/dialkylamine resins led to interesting discoveries. The preparation of a series of methyl resins resulted in finding hydrolysis upon reaction of dimethylamine with the phosphonate ester resin. The dimethylamine-contacted fully functional dimethyl phosphonate ester showed by acid capacity and IR that a low level of hydrolysis had occurred within the resin resulting in increased chelation of metal ions relative to that of the bifunctional resin. Control reactions with the fully functional dimethyl phosphonate ester and NaOH confirm base-catalyzed hydrolysis. Upon hydrolysis, the internal polymer network becomes more hydrophilic and this increases accessibility of the metal ions into the matrix allowing for further coordination with the phosphoryl oxygen. Control experiments were performed to determine if the dimethyl phosphonate ester could also be hydrolyzed by different amines. Ethylenediamine resulted in a high degree of hydrolysis, while even hindered amines such as piperidine and dibutylamine also hydrolyzed the resin. No hydrolysis was detected with butyl resins. It was also found that the bifunctional butyl/butyl resin had increased metal ion sorption capacity compared to other butyl resins. The preparation of a series of ethyl resins revealed that hydrolysis did not occur upon amination. The metal ion studies ( $10^{-1}$  N in acetate buffer) demonstrated that the bifunctional ethyl/ethyl resin did not have a high affinity for ions. Upon protonation of the amine of both the bifunctional ethyl/ethyl and butyl/butyl resins, metal ion studies in a variety of acids with their appropriate sodium salt indicated that their metal ion affinities were not as great as the unprotonated forms of the resins in acetate buffer.

## CHAPTER 4

### EXPERIMENTAL PROCEDURES

All chemicals were used without further purification and were obtained from common chemical companies. Reactions requiring the use of precise temperatures were regulated with Therm-O-Watch temperature control devices (Instruments for Research and Industry).

#### SYNTHESIS

##### Copolymer Synthesis<sup>73</sup>

Poly(vinylbenzyl chloride) (VBC) beads which were crosslinked with 5 wt% divinylbenzene (DVB; 55.4% purity) were synthesized by suspension polymerization. The suspension polymerization to synthesize macroreticular (MR) beads consists of two phases, aqueous and organic. The aqueous phase is made up of water, stabilizer and suspending agent while the organic phase is comprised of initiator, monomer, crosslinking agent and diluent. The aqueous phase was prepared by making a solution of 17.9 g poly(diallyldimethylammonium chloride) (PADMAC; Calgon Corp.) and 9.5 g boric acid in 316.5 g distilled water. A second solution was prepared by dissolving 1.4 g Pharmagel in 158.3 g water by heating to 50°C. The two aqueous solutions were then combined and mixed thoroughly before adjusting the pH to 10.3 with 50% sodium hydroxide (NaOH). The aqueous phase was then added to a 1L three-neck round-bottomed flask fitted with a condenser, nitrogen inlet, thermometer adapter and overhead stir apparatus where it was sparged with nitrogen for ten minutes. The organic phase was

prepared by adding together, 1.5 g of benzoyl peroxide (BPO), 135.0 g of VBC, 13.6 g of DVB and 150 g of 4-methyl-2-pentanol (4M2P). The contents of the organic phase were added to a 500 mL Erlenmeyer flask and stirred thoroughly before being sparged for 5 minutes with nitrogen. The organic phase was then added to the aqueous phase and the suspension was swept with nitrogen. The stirrer paddle was adjusted so that it was just immersed in the aqueous phase. To ensure suspension formation, the two phases were stirred at 250 rpm for two minutes, at which the end of no separation of the phases should occur. This was repeated two times during which the bead size was adjusted to the appropriate size by changing the speed of the stirrer. The reaction was heated to 80°C with a heat lamp over the period of two hours by slowly increasing the temperature (7°C every 15 minutes) and then held at that temperature for ten hours. Once the reaction was complete, the round-bottomed flask was fitted with a Dean Stark trap and 100 mL distilled water was added. The contents were refluxed for approximately six hours to remove all of the diluent. Once all of the diluent was removed, the beads were washed once with pH 4 hydrochloric acid (HCl) and then three times with distilled water. The beads were washed for 17 h with toluene in a Soxhlet extractor to remove any remaining oligomers. Upon completion of extraction, the beads were dried at 60°C. The beads were separated by size by using U. S. Standard screens to sieve.

The preparation of microporous (gel) beads was done by similar means however; the amounts of the contents of the organic phase were doubled and the diluent was excluded. The finish off period consisted of a two hour reflux with water before washing instead of the six hour distillation.

The preparation of poly(glycidyl methacrylate) (GMA) and polystyrene (PS) was

done using the same method as that of the macroreticular VBC resins except that VBC was replaced with an equal weight of GMA. In addition, the amount of boric acid was decreased to one-tenth of the original amount used with VBC and the pH was adjusted to 10.0.

### **Synthesis of 6-methylene-2,2,3,3,9,9,10,10-octamethyl-14-crown-4 (14C4)<sup>44</sup>**

#### **Part 1. Preparation of 1,3-bis(4',4',5',5'-tetramethyl-1,3-dioxolano propane (A)**

In a 5 L, three-neck round-bottomed flask, 500 g of pinacol, 340 mL of 1,1,3,3-tetramethoxypropane, 5 g of *p*-toluenesulfonic acid and 1500 mL cyclohexane were added. The reaction was set up as a continuous extractor, using a mixture of water and cyclohexane, to remove all methanol formed. The reaction contents were refluxed for 2 hours upon which time the extractor set-up was disassembled and a distillation condenser was added. Cyclohexane was distilled out to reduce the volume of the solution containing product (~500 mL). To isolate the product, a rotary evaporator was used to remove the remaining cyclohexane.

#### **Part 2. Preparation of 1,1,2,2,8,8,9,9-octamethyl-3,7-dioxanonan-1,9-diol (B)**

In a 12 L, three-neck round-bottomed flask, 1000 g of aluminum chloride was added in portions to 6 L of ice-cold anhydrous ether. Lithium aluminum hydride was then added (83.5 g) in portions of approximately 10 g each. An addition funnel was used to slowly transfer A to the reaction contents. The reaction was stirred for 24 hours upon which time 250 g of ice was added to destroy any remaining hydride. Two liters of 4 N HCl was added slowly by addition funnel. Concentrated HCl was then added to increase the concentration to 6 N at which time the reaction contents separated into two phases. The organic phase was purified by washing with a 50:50 mixture of saturated sodium

chloride (NaCl) and 1 N HCl, water (several times) and a saturated solution of sodium bicarbonate (NaHCO<sub>3</sub>). It was then dried by magnesium sulfate (MgSO<sub>4</sub>) and concentrated by rotary evaporator.

### Part 3. Preparation of 6-methylene-2,2,3,3,9,9,10,10-octamethyl-14-crown-4 (14C4) (C)

To a mixture of 1 L of anhydrous dioxane and 26 g of sodium hydroxide (NaH) (anhydrous), 100 g of **B** was added. The reaction contents were stirred (by magnetic stirrer) and heated (by use of a thermocouple) in an 8 L Parr high pressure reactor under an argon sweep. When the temperature reached 100 °C, 65 mL of 3-chloro-2-chloromethyl-1-propene was added to the reactor with a syringe and needle. The reaction vessel was then sealed and heated to 200 °C and held there for 1.5 hours. Once completed, the reaction was allowed to cool before the pressure was vented. To the reaction contents, 1 L of water was added and then the mixture was concentrated, *in vacuo*, to approximately 200 mL. The concentrated mixture was then dissolved in hexanes, extracted with water, dried (over anhydrous sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>) and concentrated by rotary evaporator. Purification by chromatography on silica gel was done with ethyl acetate/hexanes (0 – 20% gradient).

### Synthesis of 6-Keto-2,2,3,3,9,9,10,10-Octamethyl-14-Crown-4 (14C4=O)

In a flask, which was submerged in a mixture of dry ice in EtOH, ozone (O<sub>3</sub>) was bubbled through a solution of fifteen grams of 14C4 dissolved in 250 mL ethyl acetate. The formation of a blue solution indicated O<sub>3</sub> saturation (~75 minutes), after which time the reaction was stopped and purged with argon, until the solution lost blue hue, before the addition of 6.5 mL of DMS. The reaction was allowed to warm to room temperature.



Product was extracted with 50:50 solution of water and saturated NaCl before being dried with MgSO<sub>4</sub> and concentrated *in vacuo*. Product was in the form of an oil.

#### **Synthesis of 6-Hydroxymethyl-2,2,3,3,9,9,10,10-Octamethyl-14-Crown-4 (14C4OH)**

In a 500 mL one-neck round-bottomed flask submerged in an ice bath, 3 mL of borane-methyl sulfide complex was added to 10 g of 14C4 dissolved in 100 mL of anhydrous THF. Reaction contents were allowed to stir for 1 hour upon which time a mixture of 25 mL 30% hydrogen peroxide and 25 mL of 3 N NaOH was added by an addition funnel. The ice bath was removed and the contents were stirred for 1 hour. When the reaction was completed, hexanes were added to the two-phase system and the aqueous phase was extracted several times with hexanes before being dried over MgSO<sub>4</sub> and concentrated *in vacuo*.

#### **Synthesis of Poly(Aminomethylstyrene) (AMS)<sup>45</sup>**

In a 2 L three-neck round-bottomed flask, 20 g VBC beads were swelled in 200 mL of *N,N*-dimethylformamide (DMF) for several hours. To the mixture, 100 g of potassium phthalimide and 800 mL of DMF were added and the reaction contents were stirred and heated at 80 °C for 17 hours. When the reaction was complete, the contents were washed several times to dissolve any excess potassium phthalimide. The remaining beads were then washed several times with methanol (MeOH). When the beads had been washed sufficiently, 250 mL of MeOH and a mixture of 50 mL hydrazine monohydrate and 10 mL of water was added to the flask. The reaction was stirred and heated to 65 °C for 17 hours upon which time the contents were washed several times with water before being neutralized by the subsequent washings of concentrated HCl, water, 2N NaOH and

water. This resin was prepared from 2% crosslinked gel beads and 5% crosslinked MR beads.

### **Synthesis of AMS-Supported Vinyl Resin in THF<sup>46</sup>**

In a 250 mL three-neck round-bottomed flask, 1.6 g AMS of gel beads were swelled in 50 mL THF. A Claisen adapter was attached to one neck for the use of a gas inlet connection and addition funnel. The other two necks of the flask contained an overhead stirrer shaft and condenser with gas outlet connection, respectively. The reaction contents were swept with nitrogen as 2.7 g of acrylonitrile (AN) was added through the addition funnel. The reaction contents stirred at room temperature for 22 hours, at which time the temperature was increased to reflux (by use of a heat lamp) for 17 hours. When the reaction was complete, the contents were washed several times with THF and methanol (MeOH).

The reactions involving AMS with VBC and methylmethacrylate (MMA) were done in 20 mL borosilicate scintillation vials using one-third of the amounts used with the AN reaction. AMS and THF was added to each vial and sparged with nitrogen before the addition of VBC and MMA. Upon addition of the vinyl compounds, the vials were sealed and heated at 40 °C for 22 hours. The wash sequence of the resulting resins was the same as that of the AN reaction. Each reaction used 2% crosslinked AMS gel beads.

### **Synthesis of AMS-Supported Vinyl Resin in Diethylamine (Et<sub>2</sub>NH) and Dimethyl Sulfoxide (DMSO)<sup>47</sup>**

A molar ratio of 1:17:17 for AMS, vinyl compound, and Et<sub>2</sub>NH was held constant for every reaction performed with AN and VDPE. The reactions with AN used both 2% crosslinked gel beads and 5% crosslinked MR beads, while the reactions with VDPE used

only gel beads (2% crosslinked). To a 250 mL three-neck round-bottomed flask, 1 g of AMS beads, 6.6 g of AN (36.9 g VDPE), 9.1 g of Et<sub>2</sub>NH and 150 mL of DMSO were added. The AN reactions were done for 17 hours at both 80 °C and 150 °C, upon which time they were washed several times with dioxane before being dried at 50 °C, *in vacuo*. The VDPE reactions did not use a set temperature, they were heated to reflux by use of a heat lamp and when the reaction was complete, the resins were washed several times with dioxane, water, ethanol (EtOH) and acetone before being dried in an oven set at 60 °C.

Reactions of AMS with 14C4 were done at molar ratios of 1:1.7:1.7 and 1:3.4:3.4 for AMS (1 g), 14C4 (4.1 g and 7.9 g, respectively) and Et<sub>2</sub>NH (0.9 g and 1.8 g, respectively). The contents were added to a 100 mL three-neck round-bottomed flask with 30 mL of DMSO and heated at 150 °C for 17 hours. Upon reaction completion, the beads were washed with dioxane several times and then dried at 110 °C *in vacuo*.

#### **Schiff Base Reaction in Potassium Hydroxide (KOH) and THF<sup>50</sup>**

In a 250 mL three-neck round-bottomed flask, 1 g of AMS gel beads were allowed to swell in 100 mL of THF before the addition of 18.2 g of benzophenone and 0.6 g of KOH. The reaction contents were refluxed for 17 hours, upon which time they were washed several times with dioxane and then dried at 90 °C in a vacuum oven.

#### **Schiff Base Reaction using Titanium (IV) Chloride<sup>51</sup>**

One gram of AMS gel beads were swelled in 100 mL of toluene in a 250 mL three-neck round-bottomed flask. To the flask, 9.1 g of benzophenone and 30 g of triethylamine were added. The flask was then set up so that an addition funnel was attached to one neck, while the other necks contained an overhead stirrer shaft and a condenser, respectively. Nitrogen was swept through the vessel before the addition of 30

mL of a 1.0 M solution of titanium (IV) chloride in toluene via the addition funnel. Reaction stirred for seven days at 25 °C, upon which time it was washed several times with dioxane and dried at 90 °C in a vacuum oven.

### **Schiff Base Reaction in EtOH**

To a 250 mL round bottomed flask, AMS beads and the appropriate ketone were added so a 1:5 molar ratio was maintained. An example of this was the addition of 5 g of AMS beads and 18.4 g of cyclohexanone to a 500 mL three-neck round-bottomed flask. To this, 350 mL of absolute EtOH was added. The reaction contents were refluxed for 24 hours before being washed several times each with dioxane, water, EtOH and acetone. The resins were then dried in an oven set at 60 °C. For the reaction of AMS with 14C4=O, a molar ratio of 1:3 (AMS:14C4=O) was used and the reaction time was increased to four days.

### **Synthesis of $\beta$ -Ketophosphonate Ethyl Ester Resin**

Twenty grams of beads were added to a 1 L three-neck round-bottomed flask and swelled in 100 mL of carbon disulfide for 2 hours. The flask was lowered into an ice bath before the addition of a slurry of 80.0 g of AlCl<sub>3</sub> and 100 mL of carbon disulfide was added. The vessel was swept with nitrogen and 82.2 g of bromoacetyl bromide was added through an addition funnel. The ice bath was removed after an hour and the reaction contents were stirred for 48 hours. The resin was then quenched by washing with a sequence of a dioxane:water mixture (90:10, 75:25, 50:50, 25:75, 10:90, by volume) and then several times with water, and finally with EtOH. The resin was then

dried in a vacuum oven at 60 °C overnight. Gel, xerogel and MR beads were used in this synthesis.

### **Hydride Abstraction of $\beta$ -Ketophosphonate Ethyl Ester Resin**

To a 100 mL three-neck round-bottomed flask, 2 g of  $\beta$ -ketophosphonate beads were swelled in 25 mL of dioxane. To the flask, 1.3 g of AN and 1.5 g of NaH (60% dispersion in mineral oil), as well as an additional 15 mL of dioxane, were added. The reaction contents were then refluxed for 24 hours under a nitrogen sweep. When the reaction was completed, the resin was washed several times with dioxane and then dried at 80 °C *in vacuo*. When this reaction was repeated with different vinyl compounds, VDPE and 14C4, the molar ratio of 1:3:5.5 (beads:vinyl compound:NaH) was maintained. The reactions involving VDPE were also varied by allowing the beads to react with NaH, both at 25 °C and reflux, before the addition of the VDPE.

### **Etherification Reactions**

In a 100 mL three-neck round-bottomed flask, 1 g of dry VBC beads was swelled in 20 mL of anhydrous dioxane. In separate Erlenmeyer flask (125 mL) with a ground glass joint, 30 mL of dioxane, 0.6 g of NaH (60% dispersion in mineral oil) and 1.6 g of BA were added. A Claisen adapter was attached to the top of the Erlenmeyer flask and a gas inlet was connected to one side of the adapter to allow for the sweep of nitrogen, while a gas outlet was connected to the other side. The flask contents were stirred for one hour, upon which time the flask contents were transferred to the bead-containing round-bottomed flask. The reaction took place over 72 hours under reflux. When completed, the contents were washed several times each with water, EtOH and acetone and then dried in oven set at 60 °C. When this reaction was repeated with a number of alcohols, a

molar ratio of 1:2.5:2.5 (beads:alcohol:NaH) was maintained. For the reactions involving 14C4OH, the deprotonation conditions were varied by increasing the temperature (60 °C) and the time (17 hours).

### **Synthesis of Monofunctional, Fully Functionalized Phosphonate Ester Resins**

Three grams of VBC 5% crosslinked MR beads were refluxed in 150 mL of the appropriate trialkyl phosphite for 48 hours. The functionalized resin was then washed several times with EtOH and water.

### **Synthesis of Monofunctional, Partially Functionalized Phosphonate Ester Resins**

To prepare the partially (~50%) functionalized phosphonate esters, 250 mL of toluene was added to 10 g of VBC MR beads. The appropriate trialkyl phosphite was added and the reaction contents were stirred at 25 °C for 24 hours, followed by a 24 hour reflux. The molar ratios used were 1:40 for VBC:trimethyl phosphite and 1:30 for both VBC:trimethyl phosphite and VBC:tributyl phosphite. The resulting resins were washed several times in water.

### **Synthesis of Bifunctional Resins**

The partially functionalized phosphonate ester was added to a one-neck round-bottomed flask and swelled in dioxane for one hour. The corresponding dialkyl amine (or EDA) was added in the appropriate molar amount, for example; the molar ratio of beads to dimethylamine, diethylamine, dibutylamine and ethylenediamine were 1:10, 1:50, 1:50 and 1:100, respectively. Once the amine was added to the flask, a condenser, attached with a balloon, was connected and the contents were refluxed for 48 hours. The resins were then washed several times with water.

## **Synthesis of Amine-Contacted, Fully Functionalized Phosphonate Resins**

In a one-neck round-bottomed flask, 5 g of the fully functionalized phosphonate resin was swelled in 30 mL of dioxane for 1 hour. A 100-fold molar excess of the appropriate amine was added to the flask before it was sealed with a condenser equipped with a balloon. The contents were refluxed for 48 hours, upon which time the resin was washed several times with water.

## **Synthesis of Monofunctional Dialkyl-aminated Resins**

A 50-fold molar excess of the appropriate amine was added to VBC MR beads which had been swelling in dioxane. The reaction contents were refluxed for 24 hours in a one-necked round-bottomed flask that contained a condenser equipped with a balloon. Upon completion, the beads were washed several times with EtOH and water.

## **CHARACTERIZATION**

### **Percent Solids Determination**

For characterization and metal ion studies, the resins, which were stored in distilled water upon conditioning, were removed from the excess water by vacuum filtration. The wet resin was transferred to a Buchner funnel and covered with a piece of latex rubber, secured with a rubber band. Once in place, the resin was partially dried under a pressure of 710 mm Hg for five minutes. Upon completion, 1 g of sample was accurately weighed, to four decimal places on an analytical balance, into a dry 20 mL borosilicate scintillation vial and allowed to dry at 110°C for 17 h. After allowing the sample to cool to room temperature in a desiccator, it was again, accurately weighed. The percent solids of the resin was calculated by the following equation.

$$\text{Percent Solid} = \frac{\text{Dry Weight of Sample}}{\text{Wet Weight of Sample}} \times 100$$

### Acid Capacity Determination

Acid capacities of the resins were measured at the same time as percent solid determinations. After Buchner drying the resins, a percent solid sample was prepared and separate sample prepared by accurately weighing out 1 g of resin into a 250 mL Erlenmeyer flask. A flat-sided magnetic stir bar was added to the flask, as well as 200.0 mL of a 0.1 N sodium hydroxide solution containing 5 wt% sodium chloride. The resin was allowed to stir in the flask for 17 h on a multipoint stir plate at a speed of 350 rpm. After the designated time, the solution was removed from the resin and two 50.0 mL aliquots were titrated with a standardized 0.1 N hydrochloric acid solution using a phenolphthalein indicator. The acid capacity of the resin was calculated by the following equation.

$$\text{Acid Capacity (meq / g)} = \frac{[(200.0 \text{ mL NaOH})(N \text{ NaOH}) - (4)(\text{mL HCl})(N \text{ HCl})]}{\text{Dry Weight of Sample}}$$

### Nitrogen Elemental Analysis<sup>74</sup>

Into a 500 mL, three-necked round-bottomed flask, 200 - 250 mg of dried resin was accurately weighed. To this, 0.25 g copper (II) sulfate, 10 g potassium sulfate and 25 mL concentrated sulfuric acid were added along with a few boiling chips. A standard 14 inch water jacket condenser was added to the center opening of the round-bottomed



flask and the other two necks were closed with ground glass stoppers. The mixture was heated with a heating mantle connected to a variable regulator, at a lower temperature for one hour, and then at a higher temperature for at least eight hours. The solution appeared to be brown upon heating at the lower temperature but once the temperature was increased for a period of time, the solution became transparent with a faint blue-green color. Once this digestion was completed, there were no signs of any residual resin left in the flask. After allowing the flask to cool, a magnetic stir bar and 100 mL of distilled water were added by washing down the inside of the condenser and one of the stoppers which had been removed. To this apparatus, a 250 mL addition funnel with a pressure equalization arm was added to the joint from which the stopper had been removed. The condenser which had been in the center neck of the flask had been removed and a distillation apparatus was added that contained a funnel which was connected to the apparatus by its neck with a piece of Tygon tubing. This funnel adaptor was submerged in a solution of 50.0 mL of hydrochloric acid in a 600 mL beaker so that none of the funnel was above the solution, and that it was not flat against the bottom of the beaker. Into the addition funnel, 150 mL of 6 N sodium hydroxide was added and when the entire apparatus had been closed, the addition funnel was allowed to drain slowly into the flask. When the last of the sodium hydroxide had been added, the solution became brown in color. The flask again was heated at a higher temperature than that of the digestion process. This distillation was allowed to proceed until the distillate was neutral (one hour) and then the funnel was detached from the condenser before the heat was turned off. The acid solution was quantitatively transferred to a 250 mL volumetric flask with distilled water. Two 50.0 mL aliquots were titrated against standardized 0.1 N sodium

hydroxide containing 5 wt% sodium chloride using a bromocresol green indicator. The nitrogen capacity of the resin in milliequivalents per gram of dry resin was calculated by the equation on the following page.

$$\text{Nitrogen Capacity (meq / g)} = \frac{[(50.0 \text{ mL HCl})(N \text{ HCl}) - (5)(\text{mL NaOH})(N \text{ NaOH})]}{\text{Dry Weight of Sample}}$$

### **Phosphorus Elemental Analysis**

For this procedure, all glassware was cleaned without the use of soap as it could introduce phosphorus contaminants. All samples were analyzed on a Bauche and Lomb Spectrometer 21 that was calibrated regularly with samples containing potassium phosphate monobasic solutions prepared from a stock solution. A linear regression was performed and providing the correlation was at least 0.998, the slope and y-intercept of this line was used in the calculation to determine phosphorus content.

For this analysis, the procedure was performed in duplicate for each resin. Each sample was prepared by accurately weighing out 20 – 25 mg dry resin into Erlenmeyer flasks. To each sample, 400  $\mu\text{L}$  0.5 M copper (II) sulfate and 10 mL concentrated sulfuric acid was added. The mixtures were heated on a hot plate set at a medium-high setting for ~two hours, upon which time, the solutions were clear with a slight yellow tint. Once cooled to room temperature, 2.0 g of potassium persulfate and 75 mL of distilled water were added and the mixtures were heated on a hot plate at a medium-low setting for two hours. The solutions were again allowed to cool to room temperature before being neutralized by the subsequent addition of 50 wt% of NaOH (solution color changed to

brown) and 2 wt% of H<sub>2</sub>SO<sub>4</sub> (solution color changed to clear). The solutions were then transferred to 100 mL volumetric flasks with distilled water and 25.0 mL aliquots were removed and added to 50 mL volumetric flasks. A volume of 10.0 mL of a vanadate-molybdate developing solution<sup>\*\*\*</sup> was added to each sample upon which time they were diluted with distilled water. Another sample was also prepared by adding 10.0 mL of the vanadate-molybdate solution to a 50 mL volumetric flask with water as a background sample. After the samples developed for 15 minutes, and the absorbance readings of each sample was obtained at a wavelength of 470 nm. The phosphorus capacity in milliequivalents of phosphorus per dry gram of resin was obtained from the following equations.

$$\text{mg Phosphorus} = \frac{[\text{Absorbance} - (y - \text{Intercept of Spectrophotometer Calibration})]}{\text{Slope of Spectrophotometer Calibration}}$$

$$\text{Phosphorus Capacity (meq / g)} = \frac{(\text{mg Phosphorus})(4)}{(30.974)(\text{g Dry Sample})}$$

<sup>\*\*\*</sup>Vanadate-molybdate developing solution – In a beaker, 25.00 g of ammonium molybdate tetrahydrate was dissolved in 300 mL of distilled water. In a separate beaker, 1.28 g of ammonium metavanadate was dissolved in 300 mL of distilled water upon being heated to boiling. Upon cooling, 330 mL of concentrated hydrochloric acid was added to the beaker containing the ammonium metavanadate before being transferred it to a 1 L volumetric flask. The solution containing the ammonium molybdate tetrahydrate was also added to the volumetric flask and it was diluted to the mark with distilled water.

## Chlorine Elemental Analysis

Nanopure water was utilized throughout this analysis due to the detectable amounts of chlorine found in distilled water. The Parr bomb calorimeter that was used for this analysis was thoroughly cleaned and rinsed with nanopure water before use. The inner surface of the bomb cylinder was rinsed with 5 mL of a 5 wt% solution of sodium carbonate. The dry resin and mineral oil were weighed into a stainless steel capsule and placed in the bomb holder; amounts are listed in Table 4.1. A 10 cm piece of nickel alloy fuse wire was threaded through the bomb stem holes and secured so that the wire did not touch the metal but did linger just above the surface of the oil. It was important to ensure that the resin was completely covered by oil; however the total weight was not to exceed 1.0 g, so that all of the resin would be digested upon ignition. The bomb was put together and secured. The bleeder was closed and the system was purged with 30 atmospheres of oxygen twice and then filled with 30 atmospheres of oxygen. The bomb was submerged into a water bath and the wire leads were connected to the bomb and the fuse wire was ignited. The bomb was allowed to cool in the water bath for five minutes, upon which time it was removed from the bath and the pressure was slowly bled out. If proper ignition took place, the capsule should be empty of resin and oil and the fuse wire should no longer be in one piece. The inner surface was then scrubbed with a rubber policeman and nanopure water was used to rinse the inner walls and transfer the contents to a 400 mL beaker. The solution was then filtered into a 250 mL volumetric flask. Two 25.0 mL aliquots were removed and each transferred to Erlenmeyer flasks. To each sample, 3 mL of 2 N nitric acid, to remove the carbonate, and 10.0 mL of 0.05 N silver nitrate was added and the samples were then heated to boiling on a hot plate. The same pipette used

**Table 4.1**

**Sample mass information for chlorine elemental analysis**

<b>% Chlorine (by weight)</b>	<b>Sample Mass (g)</b>	<b>Oil Mass (g)</b>
Less than 2	0.8	0
2 – 5	40	0.4
5 – 10	0.2	0.6
10 – 20	0.1	0.7
20 – 50	0.05	0.75

to add the silver nitrate to the bomb samples was also used to prepare two blank samples to be used for the titration standardization. The heated samples were allowed to cool to room temperature in a cool, dark place. The samples were filtered into clean Erlenmeyer flasks to remove the coagulated silver chloride and washed with 0.01 N nitric acid. To both the bomb samples and the blank samples, three mL of a solution of ferric ammonium sulfate in 2 N nitric acid was added as an indicator. The blanks were standardized by titration with a 0.05 N ammonium thiocyanate solution until the first traces of a brick red endpoint was seen. The bomb samples were then titrated in the same manner. The chlorine capacity in milliequivalents per gram of dry resin was calculated by the following equation.

$$\text{Chlorine Capacity} = \frac{[(10)(10.0 \text{ mL AgNO}_3)(N \text{ AgNO}_3) - (\text{mL NH}_4\text{SCN})(N \text{ NH}_4\text{SCN})]}{\text{Dry Weight of Sample}}$$

### **Infrared Spectroscopy**

The infrared spectra of samples were recorded as potassium hydroxide (KBr) pellets on a Bomem FTIR MB100 spectrometer. A total of 32 scans were accumulated at a resolution of 8 cm<sup>-1</sup>. Each sample was prepared as 1 wt% in KBr upon grinding with a mortar and pestle. Approximately 0.1 g of the mixture was then added to a die and put under pressure using a hydraulic pump to form the pellet.

## **COMPLEXATION STUDIES**

### **Contact Studies**

All contact solutions were prepared with nanopure water and reagent grade metal

salts and acids. The glassware utilized consisted of volumetric pipettes and flasks. Metal ion stock solutions were prepared in a concentration of  $10^{-3}$  N in a 500 mL volumetric flask. Solutions with lower concentrations were prepared by performing the appropriate dilutions. All contact solutions containing the proper metal ions consisted of a concentration of  $10^{-4}$  N, prepared by transferring 10.0 mL of the stock solution and diluting it with the appropriate matrix, unless otherwise noted. Unless specifically stated, competitive extraction experiments with a number of metal ions were not performed.

### **Metal Ion Studies**

Metal ion studies were performed by weighing out either 0.1000 g of oven-dried resin or 0.1000 g of Buchner-dried resin (based on the percent solids) into a dry 20 mL borosilicate scintillation vial. The resin was solvent-exchanged, or pre-equilibrated, with approximately 5 mL of the appropriate contact matrix for 15 minutes on a Burrell wrist-action shaker. The solution was removed and discarded by the use of a Pasteur pipette. This process was repeated three additional times. Upon completion of the solvent-exchange process, 5 mL of the contact solution was added, via pipette, to the vial and the sample was shaken for 24 hours unless otherwise noted. The contact solution was removed by a clean, dry Pasteur pipette and transferred to a clean, dry scintillation vial. The sample was then analyzed using a Perkin-Elmer atomic absorption spectrometer with the appropriate flame (air/acetylene) and slit width. The wavelengths used for each of the metal ions studies are listed in Table 4.2.

**Table 4.2**

**Atomic absorption parameters**

<b>Metal Ion</b>	<b>Wavelength (nm)</b>
Cd(II)	228.8
Co(II)	240.7
Cr(III)	357.9
Cu(II)	324.8
Fe(III)	248.3
Ni(II)	232.0
Pb(II)	283.3
Zn(II)	213.9



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## VITA

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