To the Graduate Council:

I am submitting herewith a dissertation written by Darrell W. Crick entitled "Bifunctional Ion Exchange Resins: Synthesis and Characterization of Ion-Selective Polymers." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Spiro D. Alexandratos, Major Professor

We have read this dissertation
and recommend its acceptance:

Charles A. Lane

Paul Phillips

Accepted for the Council:

Associate Vice Chancellor
and Dean of the Graduate School

# BIFUNCTIONAL ION EXCHANGE RESINS:

# SYNTHESIS AND CHARACTERIZATION

# OF

# ION-SELECTIVE POLYMERS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Darrell W. Crick

May 1994

To my wife Donna and to my family

# ACKNOWLEDGEMENTS

I would like to thank Professor Spiro D. Alexandratos for his outstanding guidance and friendship during the course of this work. I would also like to thank Professors Jeffrey Kovac, Charles Lane, and Paul Phillips for their work as members of my committee. Assistance in performing radiotracer studies at Oak Ridge National Lab was provided by Faith and Gerry Case and Dr. Bruce Moyer. This research would not have been possible without the help and support of my co-workers. Special thanks are due to Frank, Cori, Cheryl, Robert, John, Roy, Donna, Andrzej, Jozsef, Paul, and Susan. Extensive assistance and support has also been provided by my wife, Donna, who has often been neglected for the sake of this research. I am grateful for the many members of my extended family who have given much inspiration, support and encouragement during the difficult times. Finally, I would like to thank the University of Tennessee, Department of Chemistry and the Department of Energy, Offices of Basic Energy Sciences and Advanced Energy Projects for financial support.

## ABSTRACT

The synthesis and characterization of numerous *dual mechanism bifunctional polymers* (DMBPs) were accomplished. Class II (ion exchange/coordination) DMBPs based on phosphonic acid esters were synthesized and their metal ion complexation abilities evaluated in low pH environments. A bifunctional phosphonate mono/diethyl ester complexed far more silver than either monofunctional resin or a mixed bed of the monofunctional resins. A *supported ligand synergistic interaction* was thus displayed. Studies with a series of dialkyl phosphonate esters revealed that steric interactions between the ester alkyl groups and bulky metal salts can enhance the selectivity of the diester resins. Class II DMBPs containing either carboxylic or phosphonic acid groups in conjunction with penta(ethylene glycol) ligands were synthesized and characterized in detail. Preliminary investigations of the metal ion affinity of these networks revealed that the presence of the acidic groups modified the binding constant between the resin and sodium picrate. Direction for future research was provided.

A limited amount of research aimed at the synthesis of uniform Class III (ion exchange/precipitation) DMBPs was completed. A possible side reaction which limits the utility of the partially functionalized phosphonic acid resin was identified and means of reducing its occurrence were briefly evaluated.

The feasibility of producing DMBPs through the synthesis of interpenetrating polymer networks (IPNs) was investigated and found to be

viable. A series of well-characterized polystyrene-based IPNs containing both pyridine and acrylic acid groups were synthesized and methods for determining their binding constants with metal ions were examined. The IPNs were selective for copper over cobalt.

Scouting studies designed to produce a novel ion exchange resin containing geminal diphosphonic acid groups were completed. It was shown that the polymer could be prepared in bead form by conventional suspension polymerization techniques and that the resin displayed excellent metal ion uptake abilities.

Finally, solid-state NMR spectroscopy was used to characterize the resins. The extent of reaction and possibility of network degradation during hydrolysis of the bifunctional IPNs was examined. It was found that the hydrolysis proceeded to completion without any unwanted side reactions. Phosphonic acid and phosphonate ester resins were characterized by solid-state $^{31}P$ spectra. The interaction of ligands on the amine-containing class II and III resins was demonstrated and shown to be dependent upon the synthetic conditions.

TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

FIGURE PAGE

# INTRODUCTION

The development of efficient separation technologies is important to the environmental and economic health of society. As a result of nuclear weapons programs and years of environmental neglect by both government and industry, the United States is faced with widespread contamination of soil and groundwater which poses a threat to the health of its citizens. It has been estimated that over 25,000 hazardous waste sites exist in this country and that the cost of remediation will exceed 1 trillion dollars.[1] A stark example of this problem is the Hanford nuclear site located near Richland, Washington. Built to produce plutonium, Hanford is now estimated to contain 1.4 billion cubic meters of hazardous material, much of it high-level radioactive waste, spread over 560 square miles of land.[2] Compounding the problem is that much of the waste exists in complex mixtures which must be separated prior to transfer to a safe storage area. Not uncommonly, radioactive ions are present in low pH solutions which contain high levels of dissolved solids and/or organic compounds. The complexity of such mixtures poses a formidable challenge to existing separations methods.

While the Hanford site is possibly the most conspicuous example, it is certainly not unique among hazardous waste sites. A need exists for the development of improved technologies in order to make remediation of these sites both chemically and economically viable.

Two techniques which have found widespread use in both remediation and pollution prevention are solvent extraction and ion exchange. In solvent extraction a compound capable of interacting (such as through complex formation) with the ion to be extracted is contacted with an aqueous solution containing the target metal ion. The extractant, commonly dissolved in an organic solvent, brings the metal ion into the organic phase as the interaction occurs. After the organic phase has been loaded with metal ions, the phases are allowed to separate and the metal is recovered by treatment with an appropriate stripping solution. The recovered metals can then be recycled or disposed of in a safe manner.[3]

A wide variety of compounds have been synthesized and utilized for selective metal ion extractions. Two of the more common extraction agents are di-2-ethylhexyl phosphoric acid which has been used for uranium[4] and rare earth recovery[5] and tri-n-butyl phosphate which, in addition to other applications, is used in nuclear plants to separate uranium and plutonium from spent fuel.[6]

Solvent extraction is a popular technique due to its rapid kinetics of extraction and the high degree of selectivity which may be obtained. However, this method does possess some disadvantages. Solvent extraction is not economical with dilute metal ion solutions due to the large volumes of liquid which must be handled.[7] A more serious problem is that most extractants have a finite solubility in water. Loss of extractant increases the operating cost of the

system in addition to the difficulties caused by the introduction of a potentially toxic compound into the aqueous phase. The advantage gained by recovery of a toxic metal can be completely offset by the introduction of a significant amount of a toxic organic chemical into the treated stream.

In ion exchange the loss of extractant to the aqueous phase is avoided since the extracting groups are covalently attached to an insoluble support, usually an organic polymer. The aqueous phase is passed through a column containing the ion exchange resin which removes the metal by replacing it with an innocuous ion such as $H^+$ (Figure 1).[8] Alternatively, a large number of chelating resins have been synthesized which function via complex formation with the target ion.[9] After the exchanger has been loaded, the metal is stripped from the resin by passage of an appropriate solution through the bed resulting in a regenerated column of exchanger and a solution containing the extracted metal. Unlike solvent extraction systems, ion exchange works well with dilute solutions since the volume of exchanger does not have to be increased. In general, ion exchange resins can be loaded and regenerated many times without a significant loss of capacity.[10] Although the initial cost of an ion exchange system can be quite high, the long lifetime of the resins will, in most cases, make the process quite economical in the long term. A disadvantage is that the kinetic performance of ion exchange systems is usually poorer than that of solvent extraction, but it can be enhanced by manipulation of physical properties of the polymer such as the degree of cross-linking and porosity.

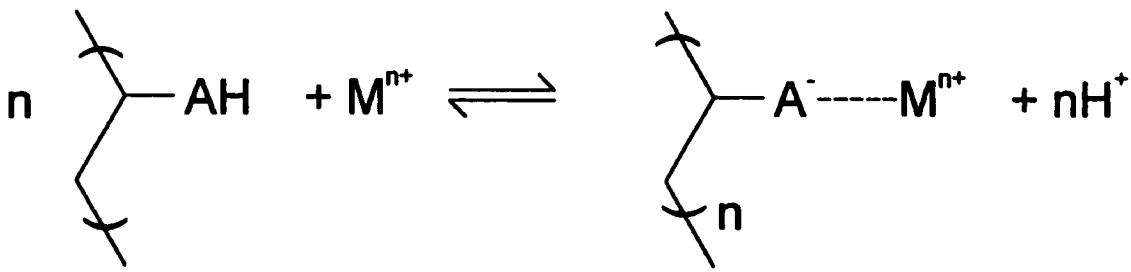



Figure 1. General equation for ion exchange with a protonated support.

The history of ion exchange has been traced by some to the purification of the water at Marah described in the book of Exodus.[8,11,12] Although poorly understood at the time, naturally occurring ion exchange materials were increasingly described and used during the 19th and early 20th centuries.[12-15] Various minerals (chiefly aluminosilicates) have been used as ion exchange materials and, at one time, sulfonated coal was commercially available.[8] In 1935, Adams and Holmes discovered the ion exchange properties of phenol-formaldehyde polymers[16] which were made more efficient by sulfonation.

A major advance in the production of synthetic ion exchange resins was the production of cross-linked supports via free-radical copolymerization of vinyl monomers with divinyl cross-linking agents.[17-20] Spherical ion-exchange particles can be prepared by suspension copolymerization of such monomers.[8] In suspension polymerization, a mixture of an organic phase (containing vinyl monomer, divinyl cross-linking agent, and free radical initiator) and an aqueous phase containing suspension stabilizers is stirred to produce a suspension of organic droplets in the aqueous layer. The stabilizers serve to prevent agglomeration of the droplets. The temperature is then raised to the point where the initiator will cause polymerization, forming spherical particles from the monomer droplets.[8] Ion exchange membranes were prepared soon after the introduction of beads and their use has become quite widespread[21] although no further discussion will be included here.

Beads of polystyrene cross-linked with divinylbenzene prepared by suspension polymerization are still the material of choice for ion exchange supports due to their chemical versatility and the ease with which their physical properties can be manipulated. The aromatic ring of the styrene unit is easily transformed into a wide variety of chemical structures and the physical properties of the network can be controlled by the amount of cross-linking agent present and the degree of porosity introduced into the network.

Various means of introducing porosity exist.[22,23] The addition of a good solvent for both monomer and polymer to the organic phase results in the formation of small pores (less than 250 Å). Larger pores can be obtained by adding a linear polymer to the monomer mixture and then extracting it once the polymerization has been completed or, more commonly, by addition of a compound which is a good solvent for the monomers but not the polymer. Thus, the polymer precipitates during the course of the polymerization leading to the formation of a bead with pores several hundred angstroms in diameter. Such polymers are called macroporous or macroreticular (MR).

The most widely used cation exchange resin is still the polystyrene-supported sulfonic acid resin (Figure 2). The sodium salt of this resin is used in household and industrial water softening systems for the removal of iron, manganese, calcium and magnesium while the hydrogen form is used in conjunction with an anion exchanger in the hydroxide form (Figure 3) to deionize water (Figure 4).

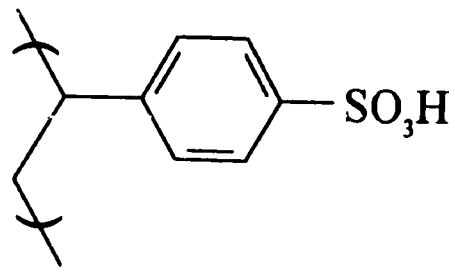



Figure 2. Sulfonic acid resin.

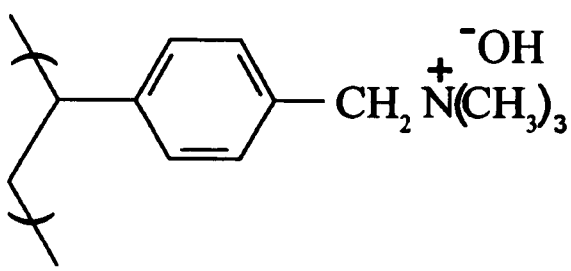



Figure 3. Hydroxide form of a strong base anion exchange resin.

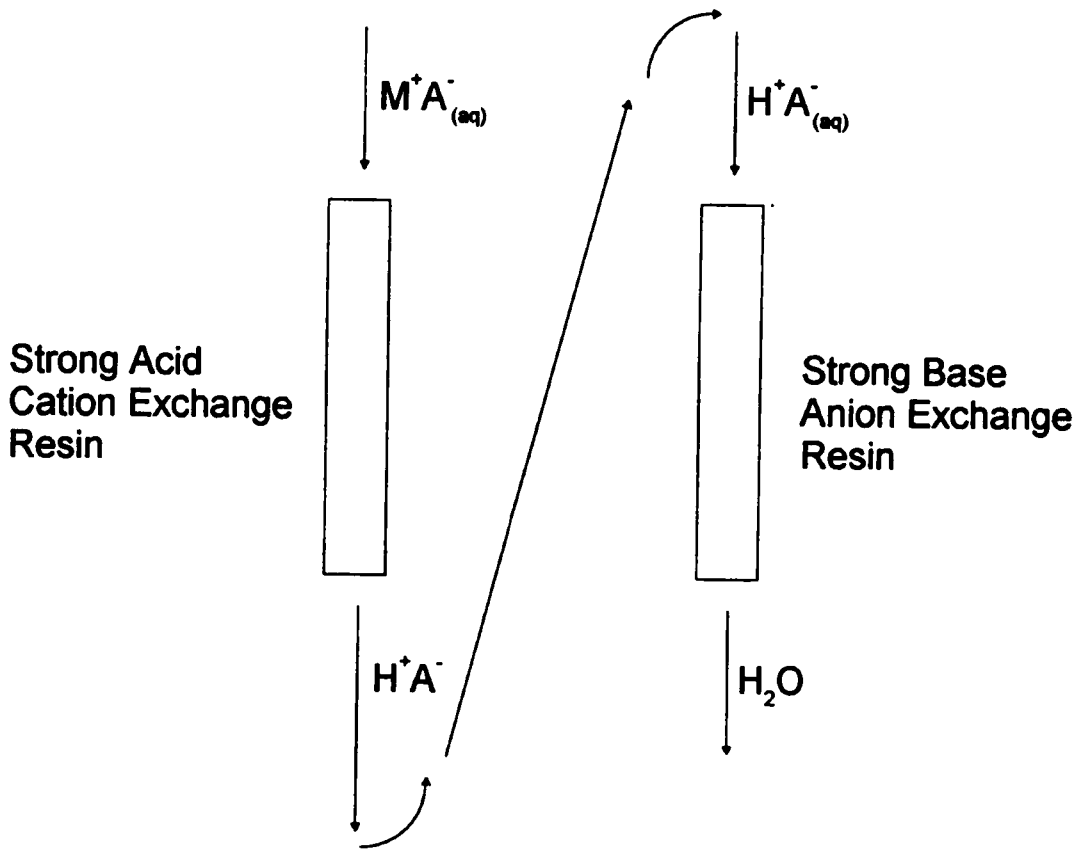



Figure 4. Deionization of water with ion exchange resins.

While efficient in removing cations, the sulfonic acid resin is quite non-selective due to a narrow range of reaction free-energies for the exchange of various metal ions.[24,25] As a consequence, the sulfonic acid resin cannot be used to separate trace amounts of a given metal ion from high concentrations of others.

The carboxylic acid resin (Figure 5) can be prepared by suspension polymerization of acrylic or methacrylic acid esters followed by hydrolysis to the carboxylic acid.[8] While much more selective than the sulfonic acid resin, the carboxylic acid ligand has a lower acidity which limits its usefulness in low pH environments. Of intermediate strength are the phosphorus-based acids which will be discussed in greater detail later.

The production of selective resins which can operate over a wide range of experimental conditions has, in general, relied upon the attachment of either chelating groups or highly selective ligands to the polymer matrix. In most cases, the behavior of small molecule ligands is retained upon attachment to a polymer backbone (although modifications do occur). Numerous reviews have appeared on the subject of selective resins[9,26-29] and a number have become commercially important.

The most common is the iminodiacetic acid resin (Figure 6), commercially available as Ionac SR-5, Dowex A-1, and Chelex 100. This resin is selective for transition metals and has been used for their removal from seawater at near neutral pH.[30] Polymer-supported picolylamine[31] (Figure 7)

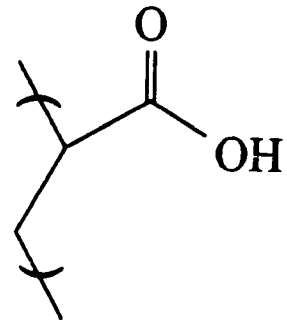



Figure 5. Carboxylic acid resin.

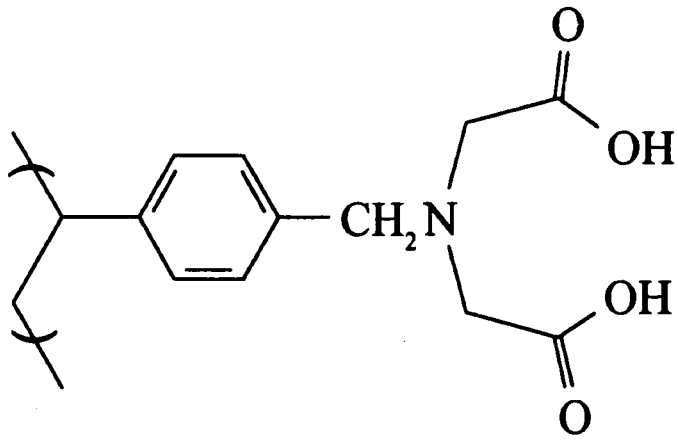



Figure 6. Iminodiacetic acid resin.

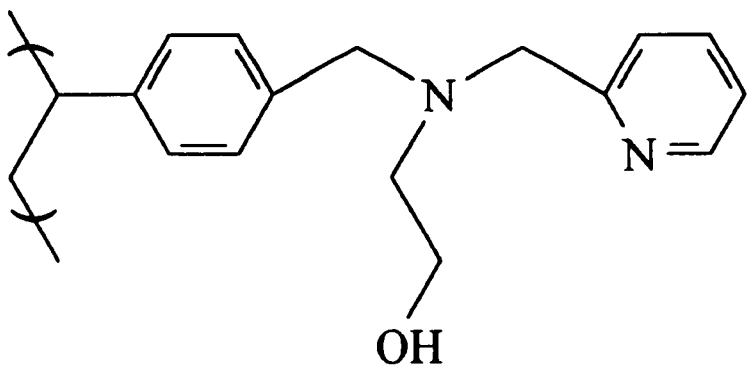



Figure 7. Polymer-supported picolylamine.

exhibits selectivity for copper as does supported 8-hydroxyquinoline (Figure 8).[27] Sulfur containing groups can also be quite selective. The isothiouronium resin (Figure 9), available as Ionac SR-3, is selective for $Au^{3+}$ and platinum group metals while the thiol resin (Figure 10, available as Ionac SR-4) is highly selective for mercury.[9]

Despite their selectivity, many of these resins have a limited range of utility due to the chemical properties of the functional group. As mentioned earlier, the weakly acidic resins must be used in neutral or alkaline environments due to excessive competition from the hydrogen ion at low pH. The isothiouronium resin must be used in acidic environments due to degradation of the functional group at high pH.[32] The "purity" of the functional groups is also of concern when multistep syntheses are necessary. Due to the cross-linked nature of the resins, it is not possible to separate unreacted sites at various stages of the synthesis. Reactions must therefore be nearly quantitative in order to yield a resin with a high percentage of the desired functionality. Due to these reasons and the increasingly complex separations which must be performed, the design and synthesis of selective resins is still a very active field of research. Numerous novel resins with enhanced extraction properties have been synthesized in recent years.

A chelating resin containing benzoylacetanilide groups (Figure 11) was capable of separating $Ti^{4+}$ from $Fe^{3+}$, $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Na^{+}$, $K^{+}$, $Ca^{2+}$, $Mg^{2+}$,

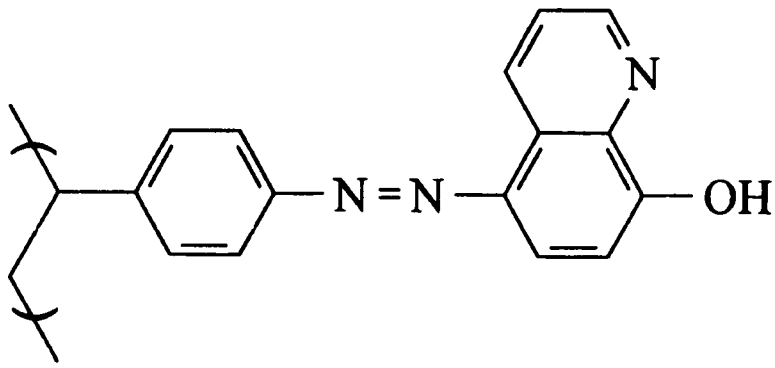



Figure 8. Polymer-supported 8-hydroxyquinoline.

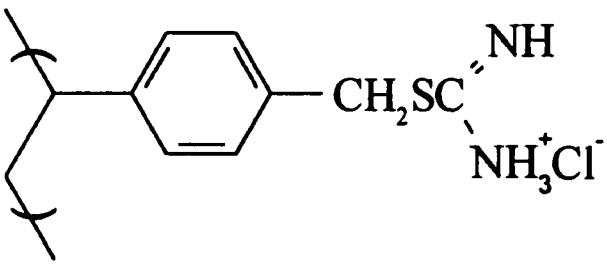



Figure 9. Isothiouronium resin.

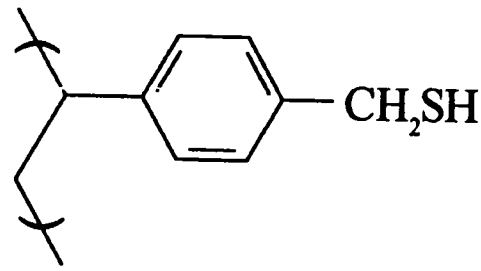



Figure 10. Thiol resin.

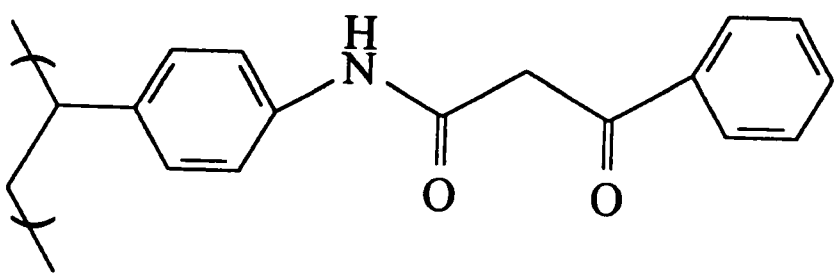



Figure 11. Polymer-supported benzoylacetanilide.

and $Al^{3+}$ in the pH range 1.3-2.0 and could separate $U^{6+}$ at pH 3.2 and $Be^{2+}$ at pH 4.0 from the same mixture of ions.[33,34]

Certain resins containing hydroxyl groups have been found to display selectivity. Polymers from N-(4-carboxy-3-hydroxyphenyl)maleimide (Figure 12) show selectivity for $Ni^{2+}$, $Fe^{3+}$, and $Pb^{2+}$ over $Ca^{2+}$, $Cr^{3+}$, $Cu^{2+}$, $Zn^{2+}$, and $Cd^{2+}$ while a modified phenol-formaldehyde polymer (Figure 13) was selective for $Cu^{2+}$ over $Co^{2+}$ in the pH range 4-8.[35,36] A resin containing methylaminoglucitol groups (Figure 14) was used for the recovery of boric acid from brines and the separation of the oxyanions of aluminum, gallium, germanium, lead, vanadium and molybdenum in similar media.[37,38]

Crown ethers have also been incorporated into numerous polymers. A recent paper reports the synthesis of crown ether containing resins prepared form bismaleimides (Figure 15).[39] The resulting polymers show selectivity in the order $K^+ > Rb^+ > Na^+ > Cs^+ > Li^+$. Silica gel has also been used as a support. 1,5-dithia-19-crown-6 and 1,4,7,10-tetrathia-18-crown-6 (Figures 16 and 17) were chemically bonded to silica gel and show binding constants to $Pd^{2+}$, $Au^{3+}$, $Ag^+$, and $Hg^{2+}$ at least ten orders of magnitude greater than those to Group I, Group II, and other transition metal ions.[40]

Oximes, hydroxylamine, and Schiff bases have found widespread use as selective polymers. Poly(vinyl benzaldoxime) (Figure 18) has been prepared and is selective for $Fe^{3+}$ over $Mn^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Ni^{2+}$, $Co^{2+}$, and $Zn^{2+}$.[41] Salicylaldoxime-formaldehyde resin (Figure 19) shows the affinity series

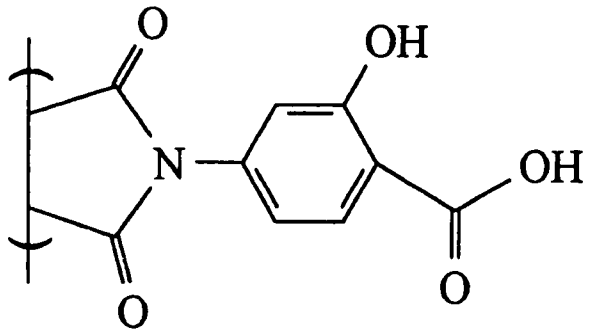



Figure 12. Poly(N-(4-carboxy-3-hydroxyphenyl)maleimide).

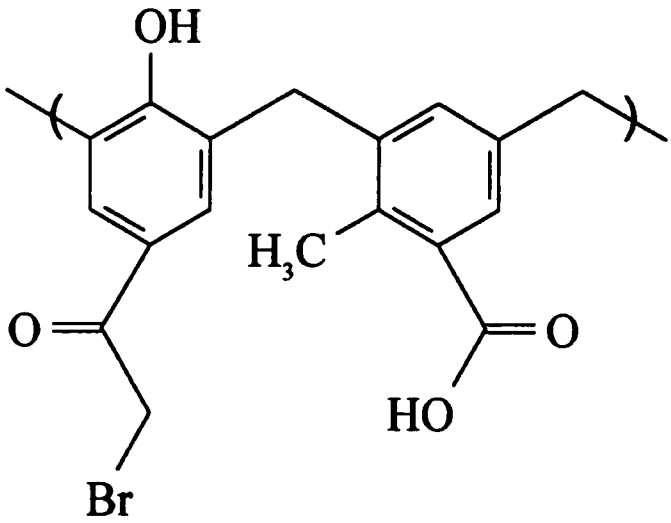



Figure 13. Phenol-formaldehyde based resin.

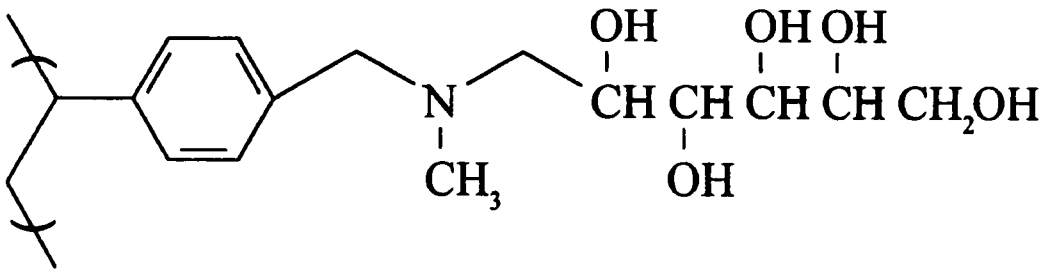



Figure 14. Polymer-supported methylaminoglucitol.

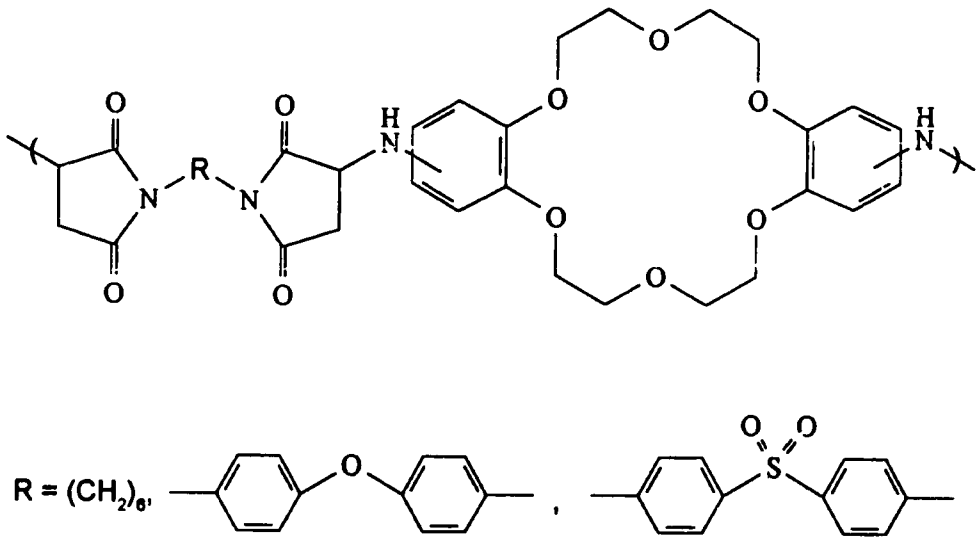



Figure 15. Crown ether containing resin.

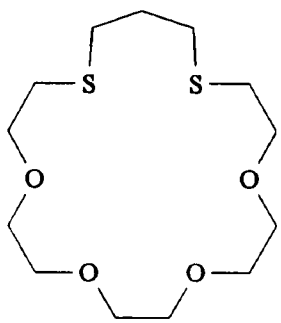


Figure 16. 1,5-dithia-19-crown-6.

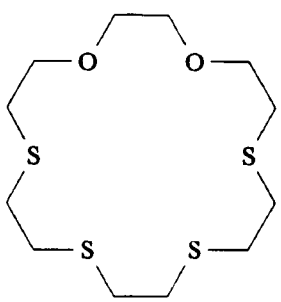


Figure 17. 1,4,7,10-tetrathia-18-crown-6.

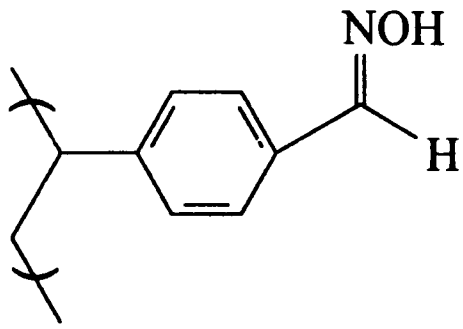



Figure 18. Poly(vinyl benzaldoxime).

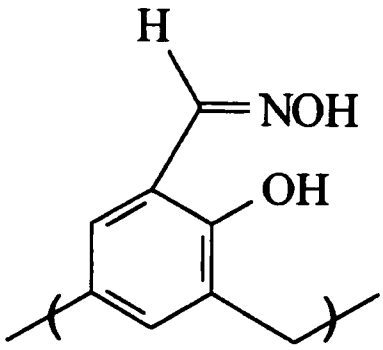



Figure 19. Salicylaldoxime-formaldehyde resin.

$Pb^{2+} \approx Zn^{2+} \approx Ni^{2+} > Cu^{2+} > Cd^{2+} > Pd^{2+} > Mn^{2+} > Fe^{2+} > Co^{2+}$ at pH 8.[42] Glycinohydroxamate resin (Figure 20) was prepared from acrylonitrile-divinylbenzene copolymer and displayed a range of stability constants in the order $Fe^{3+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Co^{2+} > Mn^{2+} > Cd^{2+} > Ni^{2+}$.[43] Polymers containing dihydroxyamic acid groups were prepared by reaction of chloromethylated polystyrene with diethyl malonate and hydroxylamine. These materials showed good absorption of $UO_2^{2+}$ but not of Ni, Co, Cr, or Cd.[44] Phenol-formaldehyde based resins containing 2,4-dinitrophenylhydrazone groups have been prepared and show a slight degree of selectivity. For example, the polymer based on 4-hydroxyacetophenone-formaldehyde resin (Figure 21) shows a moderate trend of the order $Mg^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+} > Cu^{2+} > Co^{2+}$ at pH 6.[45,46] Selective separation of uranyl ions from simulated seawater has been achieved through the use of cellulose-based materials having three coplanar carboxy, amidoxime-hydroxamic acid, or amidrazone-hydrazide groups.[47]

A large body of literature exists describing the use of amine-containing polymers for selective separations. A polymer with amino groups bound directly to the backbone was obtained by copolymerization of the vinylamine synthon N-vinyl-*tert*-butylcarbamate with either styrene, methyl methacrylate, or methacrylic acid and a cross-linking agent. Those resins which did not possess carboxyl groups were selective for Cu over Pb and Cd.[48] The reaction of polyethyleneimine with poly(vinyl benzaldehyde) produces the resin shown in

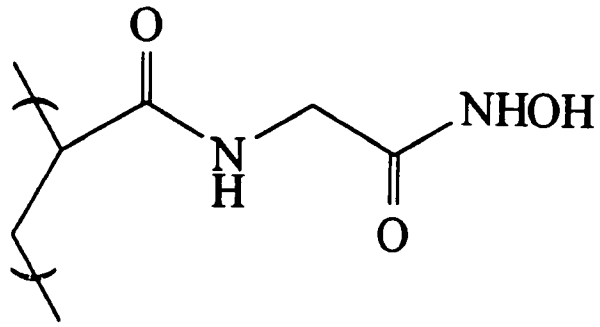



Figure 20. Glycinohydroxamate resin.

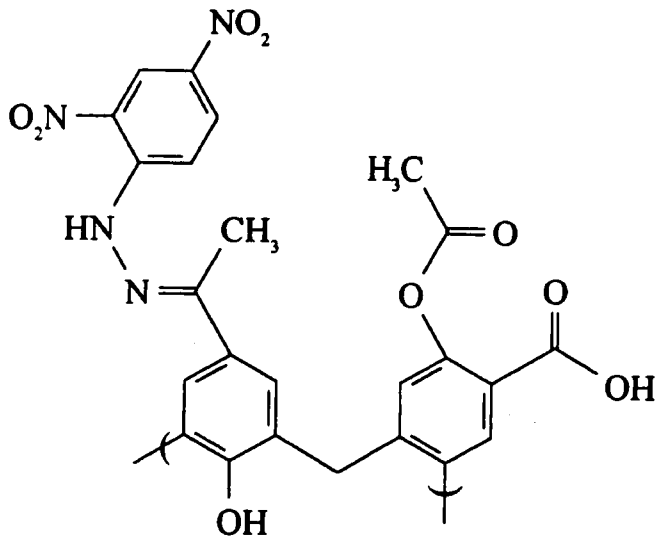
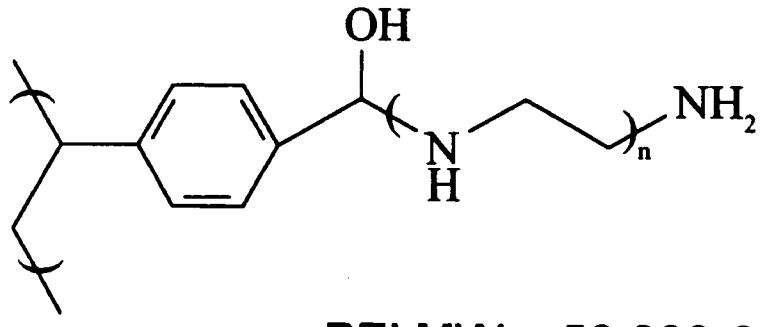



Figure 21. Supported 2,4-dinitrophenylhydrazone.




PEI MW = 50,000-60,000

Figure 22. Supported polyethyleneimine.

Figure 22 which has a high selectivity for $Fe^{3+}$ over $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Fe^{2+}$, $Zn^{2+}$, and $Mn^{2+}$.[49] A similar material prepared from the reaction of acrylonitrile-divinylbenzene copolymer with diethylenetriamine was selective for ruthenium.[50] Short polyethyleneimines (from ethylenediamine to tetraethylenepentaamine) were reacted with cross-linked poly(2,3-epithiopropyl methacrylate) to yield polymers (Figure 23) capable of sorbing $Hg^{2+}$, $Ag^{+}$, and $Cu^{2+}$ at pH<3, $Co^{2+}$, $Ni^{2+}$, and $Cd^{2+}$ at pH>3, $Mn^{2+}$ at pH>7 and $Ca^{2+}$ at pH>8.[51] Amination of chloromethylated polystyrene with either 1,3-diaminopropane (DAP) or 2,4-diamino-2-methylpentane (DAMP) produced resins capable of extracting gold from cyanide solutions. The order of selectivity was Au>Zn>Ni>Ag>Co>Cu for the DAMP resin and Zn>Au≈Co> Ni≈Ag>Cu for DAP.[52]

Heterocyclic amines have also been widely studied. Poly(4-vinylpyridine) has a high binding constant for copper which can be increased even further by preorganization of the ligand. Thus, poly(4-vinylpyridine) adsorbed onto silica gel impregnated with $CuSO_4$ and then cross-linked with 1,4-dibromobutane had a 220-fold larger binding constant than non-silica-supported poly(4-vinylpyridine).[53] Increased loading and stripping kinetics were also noted for uranium.[54] Copolymers of 4-acetoxystyrene and 4-vinylpyridine were prepared.[55] After hydrolysis the resin contains weakly acidic phenolic groups as shown in Figure 24 and the resin is selective for Hg, Cd, Cu, and Ni. Polymer bound 2-pyridyl-2-imidazole and 2-aminomethylpyridine are capable of separating $Cu^{2+}$ from $Zn^{2+}$ even in a 250-fold excess of $Zn^{2+}$.[56] An acrylic resin

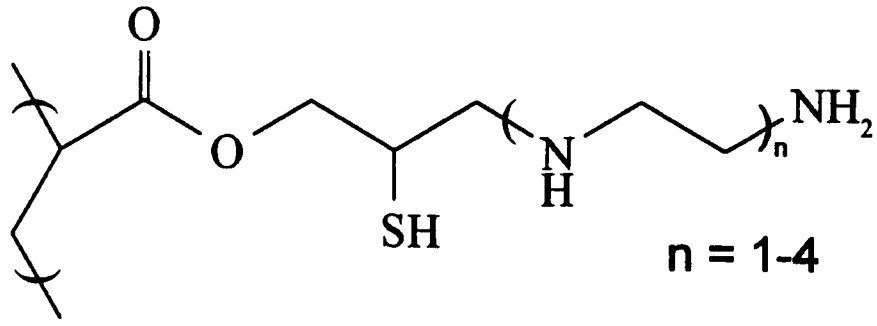



Figure 23. Mercapto-polyethyleneimine resin.

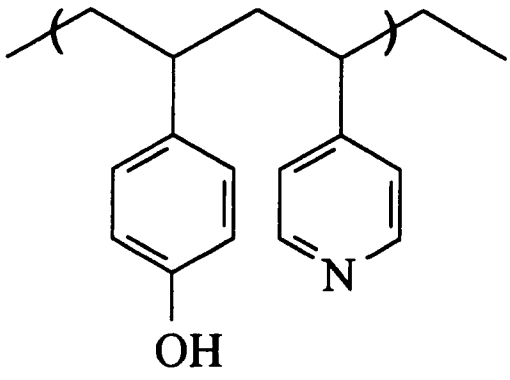



Figure 24. Phenol-pyridine resin.

containing both sulfur and an imidazole group (Figure 25) was selective for $Cu^{2+}$ over $Ni^{2+}$, $Zn^{2+}$, and $Cd^{2+}$.[57] A chelating resin containing pyridine units (Figure 26) was found to be selective for $Fe^{3+}$.[58] In tetrahydrofuran solutions, the metal ion affinity followed the order $Fe^{3+} > Cr^{3+} > > Co^{2+} > Cu^{2+} > Ni^{2+}$ although the utility of this resin is severely limited by its lack of swelling in water.

Supported quinaldic acid (Figure 27) was shown to have a high selectivity for cadmium.[59] $Cd^{2+}$ was selectively extracted from 30% $H_3PO_4$ solutions containing Fe, Ca, Cd, Mg, and U. Supported dipicolinic acid resin (Figure 28) was used to separate the chloro complexes of palladium, platinum and gold.[60] At pH≤0 only gold was extracted. Polystyrene-supported 2,6-diformylpyridine bis(2'-pyridylhydrazone) (Figure 29) was selective for $Cu^{2+}$ over $Co^{2+}$, $Ni^{2+}$, and $Zn^{2+}$.[61] Dehydrodithizone modified polymers (Figure 30) were selective for Au, Pd, Pt, Os, Ir, and Ru over Rh, Cu, Ni, and Fe in 1.0 M HCl.[62] Resins containing benzimidazole ligands (Figures 31 and 32) were found to be selective for $Cu^{2+}$ over $Co^{2+}$, $Ni^{2+}$, and $Cd^{2+}$.[63,64] Polybenzimidazole itself (Figure 33) has been shown to have ion selective properties[65] and, when modified with epichlorohydrin, can function as a support for the attachment of other ligands. When dimethylglyoxime is attached to polybenzimidazole (Figure 34), the polymer shows binding constants in the order $Co^{2+} > Fe^{3+} > Cu^{2+}$, $Ni^{2+} > Mn^{2+} > UO_2^{2+}$ although the loading capacities are quite low.[66] Other ligands have been attached to polybenzimidazole to yield selective resins.[67-70]

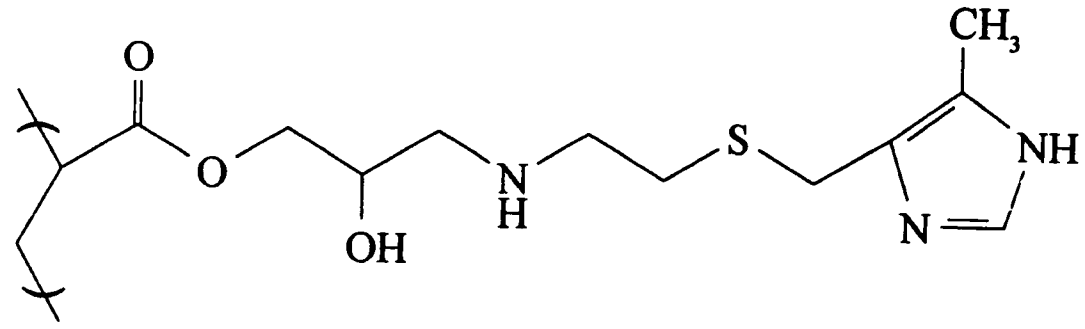



Figure 25. Supported 4-[(2-aminoethyl)mercaptomethyl]-5-methylimidazole.

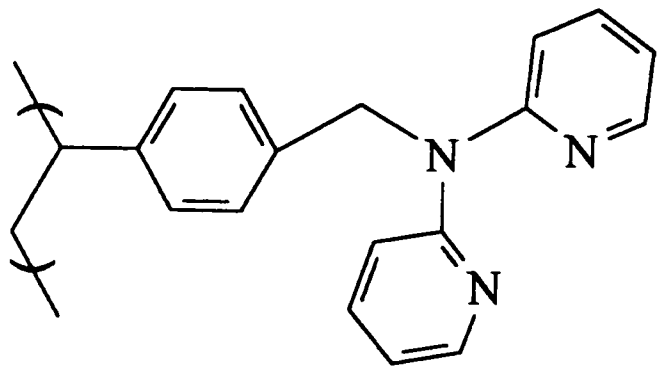



Figure 26. Chelating pyridine resin.

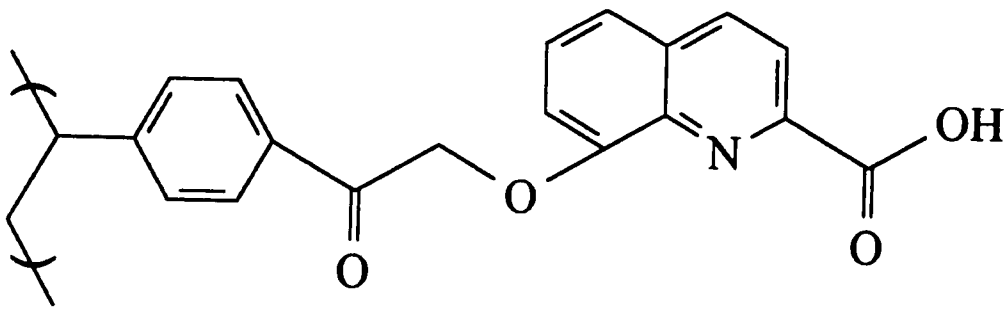



Figure 27. Supported quinaldic acid.

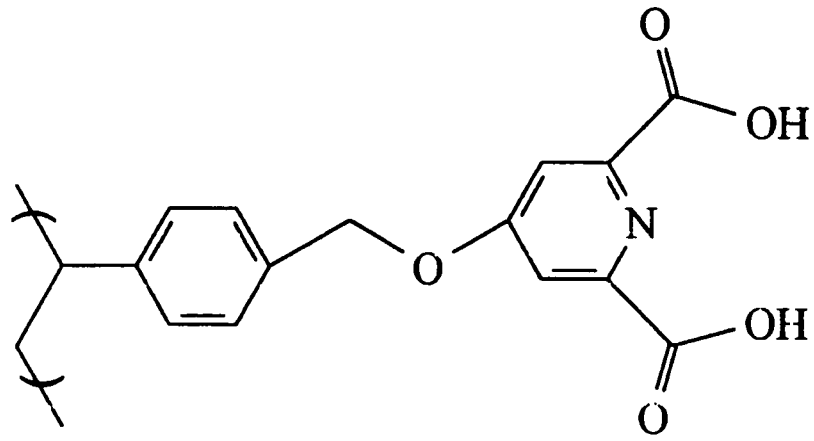



Figure 28. Supported dipicolinic acid.

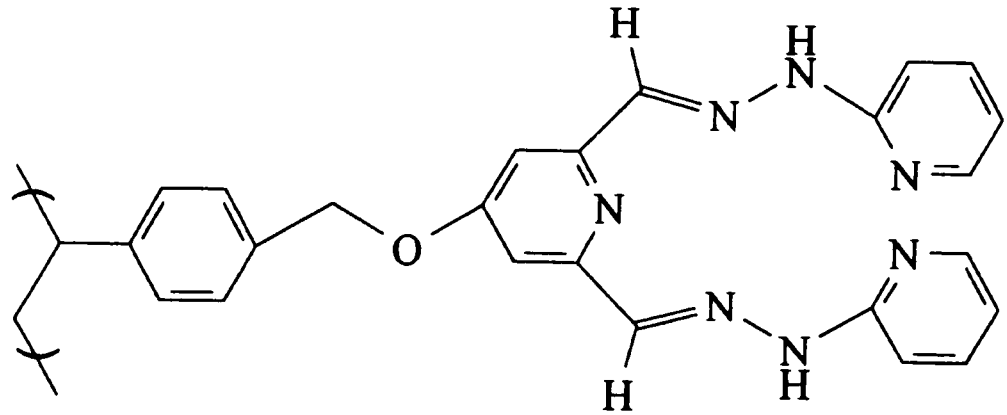



Figure 29. 2,6-diformylpyridine bis(2'-pyridylhydrazone) resin.

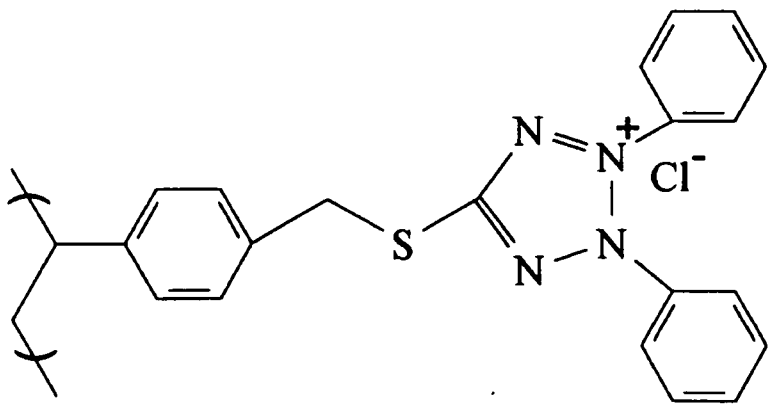



Figure 30. Dehydrodithizone resin.

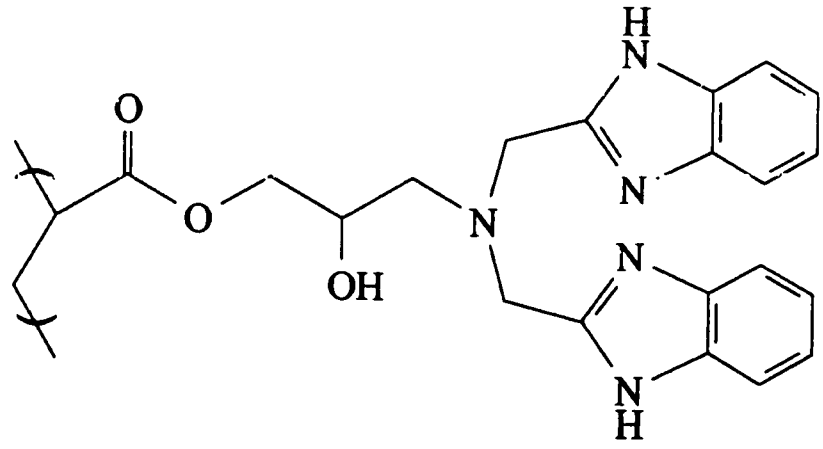



Figure 31. Supported N,N'-bis(2-benzimidazolylmethyl)amine.

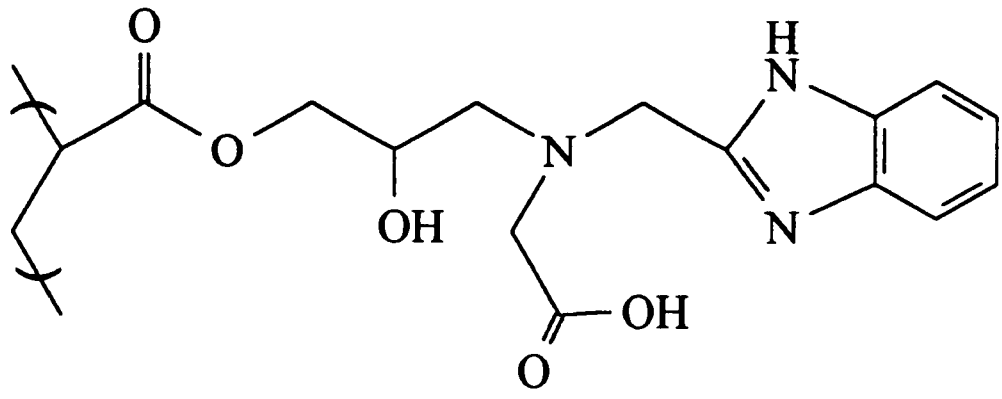



Figure 32. Supported 4-(2'-benzimidazole)-3-azabutanoic acid.

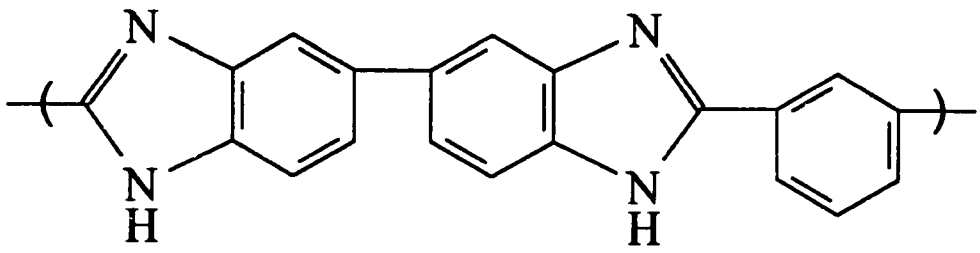



Figure 33. Polybenzimidazole.

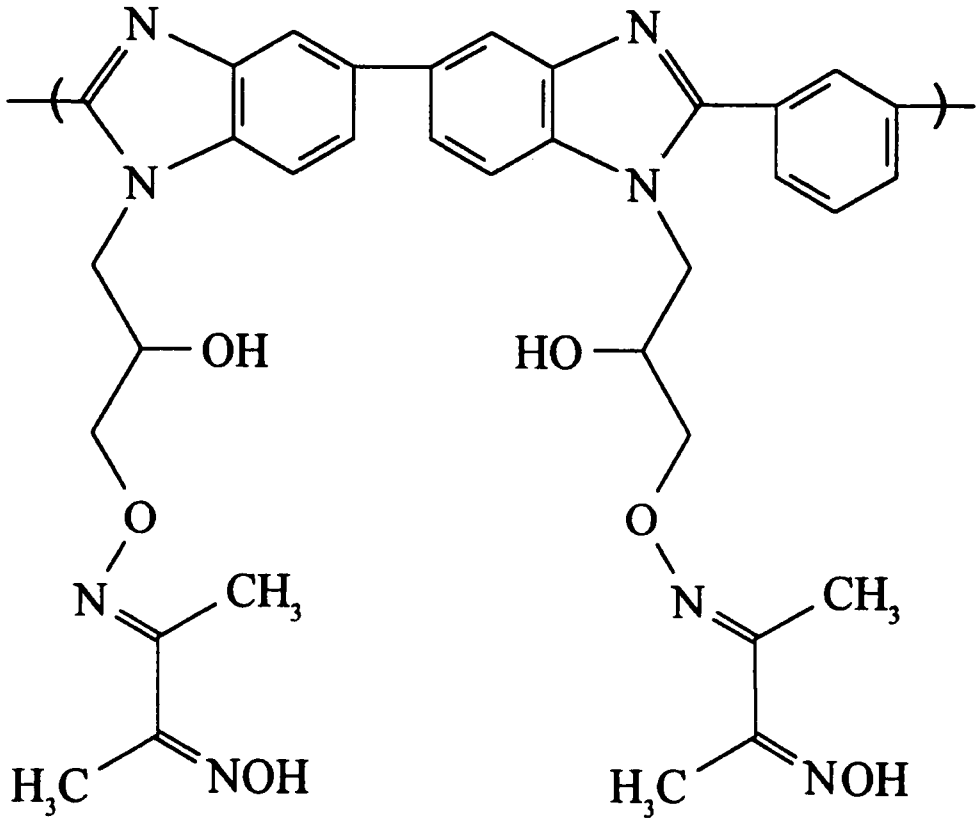



Figure 34. Polybenzimidazole-supported dimethylglyoxime.

Sulfur containing polymers are, in general, selective for heavy metal ions. Polymers functionalized with oligoethylene sulfides (Figure 35) had high selectivity for $HgCl_2$ and $Ag^+$ salts over $Pb^{2+}$, $UO_2^{2+}$, $Cu^{2+}$, $Fe^{3+}$, and $Cd^{2+}$.[71] An aminophenol resin modified with mercaptoacetyl chloride (Figure 36) possessed a high affinity for $Ag^+$ and $Cu^{2+}$,[72] while one containing dithiol units (Figure 37) had a high selectivity for Ag, Hg, Pt, and Pd.[73,74] Thiolex (Figure 38), a biomimetic polymer based on Cd-binding proteins, had a 25-fold greater affinity for $Cd^{2+}$ than for $Zn^{2+}$.[75] Supported thiosemicarbazide (Figure 39) can be used to separate $Pd^{2+}$, $Pt^{4+}$, $Rh^{3+}$, $Ru^{3+}$, and $Ir^{3+}$.[76] $Ir^{3+}$ is not sorbed by the resin and the other metals are separated by controlling the stripping conditions.

Polymers containing phosphorus-based ligands are also useful as selective resins. A unique supported phosphinimine resin (Figure 40) was quite selective for iron, having a selectivity series of $Fe^{3+} > Fe^{2+} > Cu^{2+} > Ni^{2+} \approx Co^{2+} > Zn^{2+} > Mn^{2+}$.[77] More commonly, phosphorus-based acids have been used as selective metal ion extractants. Phosphorus-based acids have an intermediate acid strength when compared with the conventional sulfonic and carboxylic acid resins. Thus, they are generally more selective than the strong acid polymers and can be used over a wider pH range than the carboxylic acid resin.

Phosphorus acid resins have been prepared both by polymerization of phosphorus-containing polymers[78-81] and by functionalization of existing networks.[82-84] Polystyrene-based phosphinic acid and phosphonic acid resins

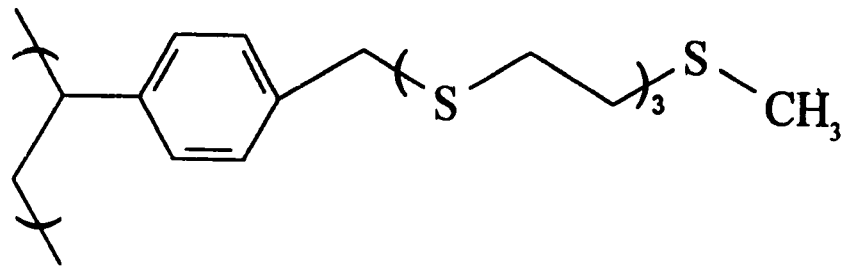



Figure 35. Supported oligoethylene sulfide.

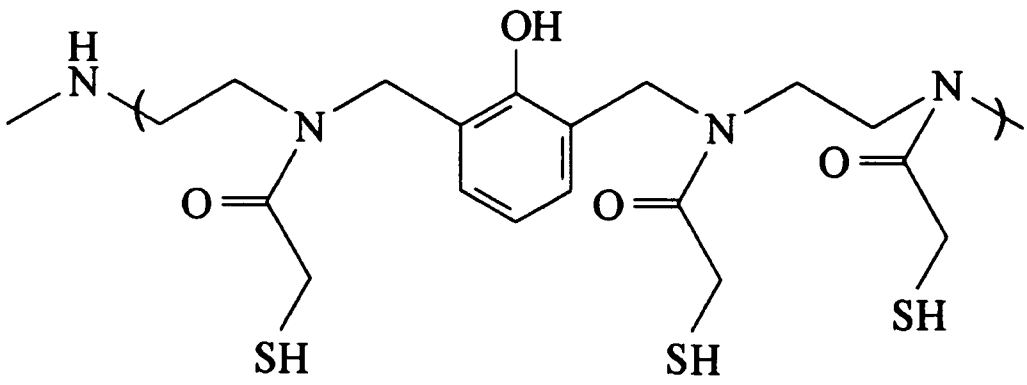



Figure 36. Aminophenol resin containing mercaptoacetamide groups.

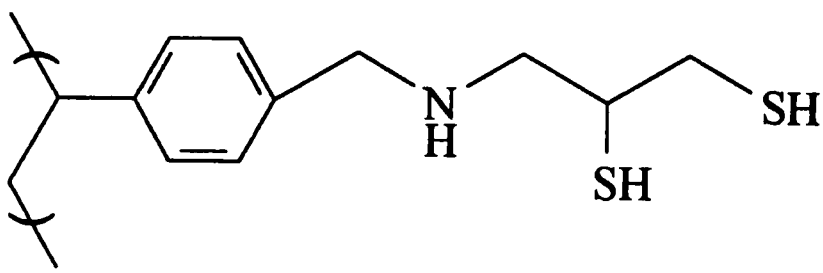



Figure 37. Dithiol resin.

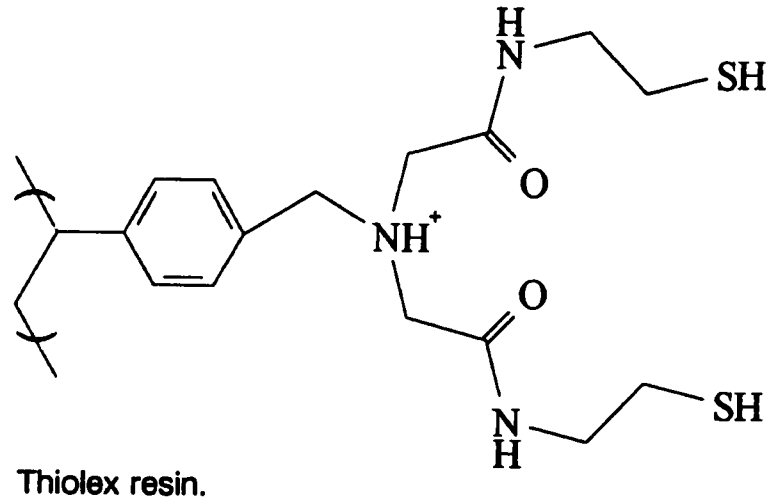



Figure 38. Thiolex resin.

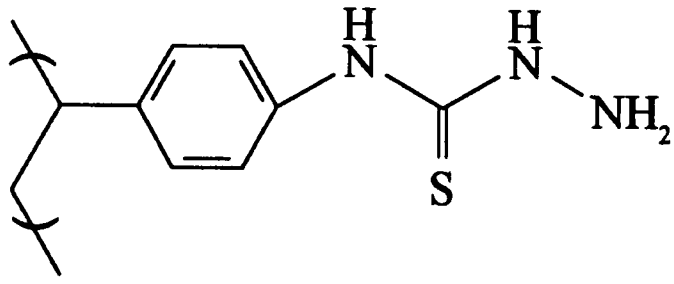



Figure 39. Supported thiosemicarbazide.

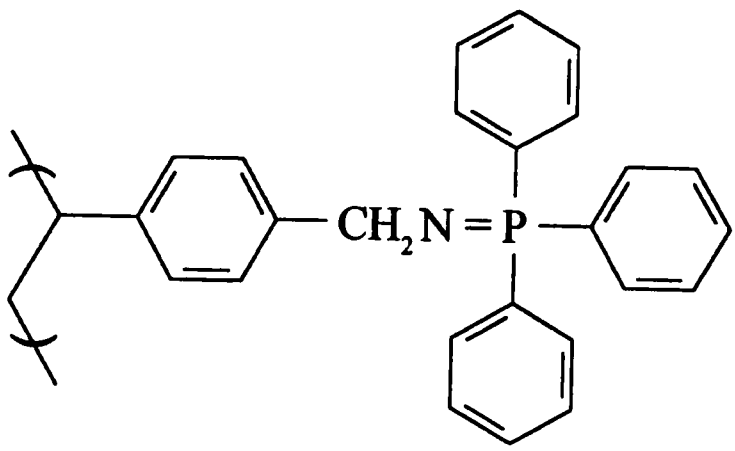



Figure 40. Supported phosphinimine.

were once commercially available as Duolite C-62 and C-63 (Figures 41 and 42).[85]

A full understanding of the mechanism by which phosphorus-based acids function as selective extractants requires knowledge of the concept of reactive ion exchange (RIEX), developed by Helfferich and Janauer.[8,86] In RIEX, the initial ion exchange process is followed by reaction of the appropriate exchanged species, imparting a degree of selectivity to the extraction. Given the widely differing chemical properties of various classes of metal ions, it then becomes possible to design a reactive ion exchange resin capable of increased selectivity for a specific ion or closely related group of ions. Phosphorus-based acids are well suited for reactive ion exchange.

Alexandratos and co-workers have developed a new class of polymers, Dual Mechanism Bifunctional Polymers (DMBPs), which couple an access mechanism (ion exchange) to a selective recognition mechanism.[87] To date, three classes have been developed which are differentiated by means of the recognition mechanism. The Class I DMBP, an ion exchange/redox polymer, is exemplified by the polystyrene-based phosphinic acid resin (Figure 43) which possesses both primary and secondary phosphinic acid sites. Ions are brought into the network via ion exchange with the acidic hydrogen followed by a recognition step which involves reduction (by the P-H bond) of only those ions with an appropriate reduction potential. The reduction of both $Ag^{+}$ and $Hg^{2+}$ to the respective metal has been demonstrated.[88] In addition, the phosphoryl

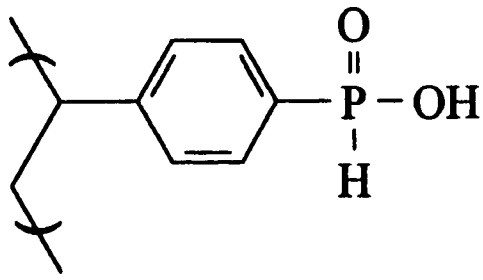



Figure 41. Duolite C-62, phosphinic acid resin.

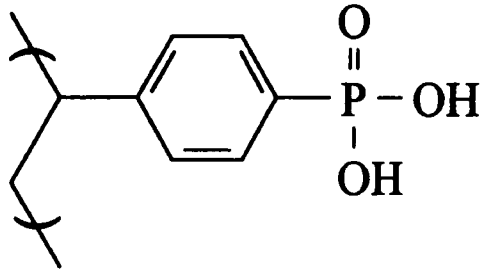



Figure 42. Duolite C-63, phosphonic acid resin.

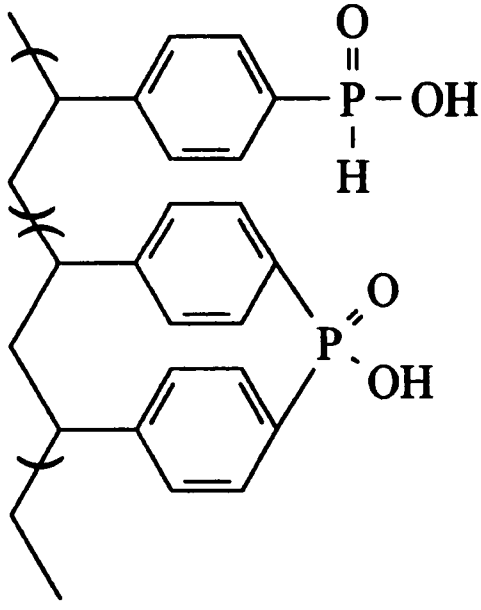



Figure 43. Class I DMBP.

oxygen can function as a ligand for some metal ions. As a result, the phosphinic acid resin is capable of metal extraction in strongly acidic solutions where ion exchange is not expected to be a predominant process.[89]

The Class II DMBPs couple a coordinative recognition mechanism to ion exchange. After gaining access to the network through the ion exchange group, ions are selectively coordinated to a second type of site within the polymer. The initial Class II resins utilized a phosphoryl oxygen or an amine group to coordinate metal ions (Figure 44).[90] The affinity of the resin can be controlled by varying the basicity of the coordinating group by changing the substituents affecting the coordinating atom. The principles of hard-soft acid-base theory[91,92] have been used to design the Class II DMBPs. Hard-soft acid-base theory states that hard acids (in general, small, highly charged, non-polarizable ions) prefer to bind with hard bases and soft acids (large, lower charged, polarizable ions) prefer to coordinate to soft bases. The basicity of the phosphoryl oxygen can be manipulated by choice of the substituents on the phosphorus atom.

The third class of DMBPs utilizes a precipitation reaction as the recognition mechanism. Quaternary amine sites are used in conjunction with phosphonic acid groups (Figure 45) to selectively remove those ions which form precipitates with the counterion on the amine site.[93] For example, a class III resin with chloride counterions on the amine sites can be used to separate metals which form insoluble chlorides (such as $Ag^+$).

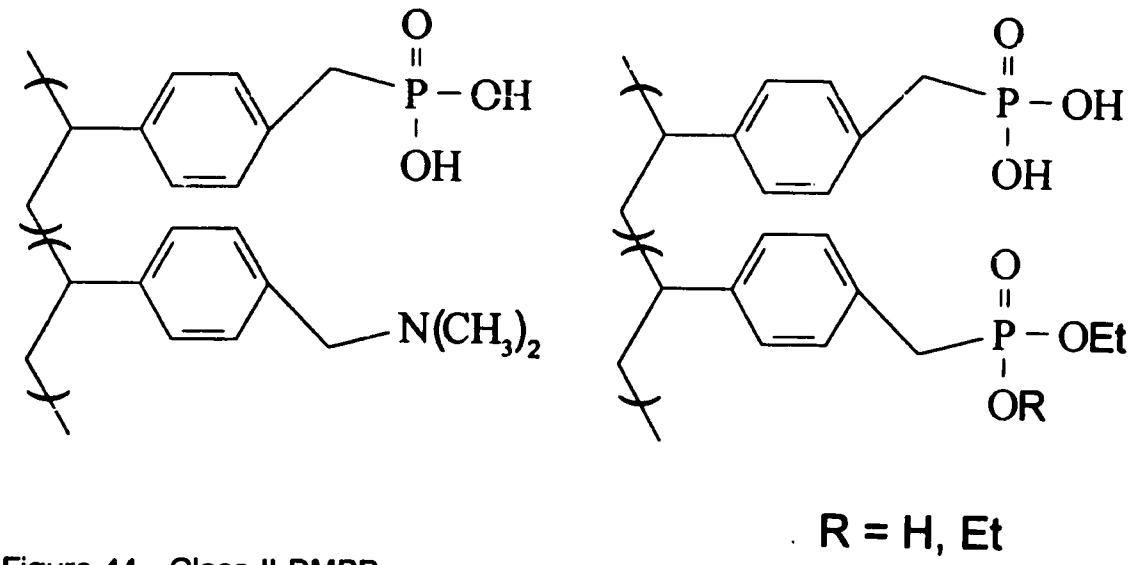



Figure 44. Class II DMBPs.

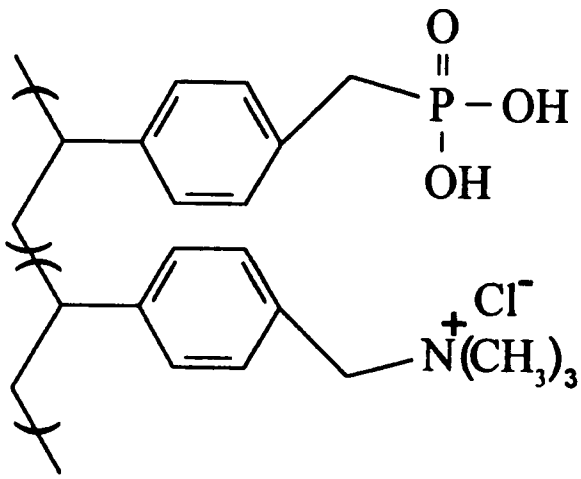



Figure 45. Class III DMBP.

This dissertation describes a wide range of research aimed at extending the utility of dual mechanism bifunctional polymers. The mechanism of extraction by the phosphonic acid ester Class II resins has been examined as has the synthesis of Class II resins which utilize a pseudo-crown ether group as the coordinating ligand. A limited amount of research was also completed in an attempt to produce a series of uniform Class III resins. Initial studies designed to study the feasibility of producing DMBPs from interpenetrating polymer networks (IPNs) were completed and solid-state nuclear magnetic resonance spectroscopy was used to study these and other resins. Finally, the initial experimental work necessary for the commercial production of a dual mechanism bifunctional polymer has been completed.

# CHAPTER 1

## CLASS II DUAL MECHANISM BIFUNCTIONAL POLYMERS BASED ON PHOSPHONIC ACID ESTERS

### Introduction

Phosphonic acid ester-based Class II resins were previously synthesized and their extraction abilities characterized.[90, 94,95] The mechanism of ion complexation by phosphorus-containing dual mechanism bifunctional polymers was investigated[95-98] with an emphasis on the phosphinic acid resin and the effects of solution pH, metal concentration, and ionic strength. These studies have been extended with a comparison of the Fe, Hg, and Mn extraction abilities of the phosphonate monoethyl and diethyl esters with the well characterized phosphinic and phosphonic acid resins over a wide pH range. The behavior of these and other phosphonate esters has also been examined over a narrower pH range with a wider selection of metals. The influence of the size of the alkyl group present on the phosphonate diesters on their complexation ability has been examined as have the unique properties of a bifunctional phosphonate diester/monoester resin. Radiotracer studies were performed at Oak Ridge National Lab to determine the metal ion affinities of the resins.

Synthesis

In general, the resins required for these studies were synthesized using standard techniques previously developed in this laboratory.[88,90,95,99] A modification was made allowing for the production of well-characterized bifunctional phosphonate monoester/diester and the use of a milder catalyst in the production of phosphonate diester resins (described earlier[95]) has been adopted. Brief descriptions of the syntheses follow.

Phosphonic acid resin was prepared without modification of the standard procedure.[90] Poly(vinylbenzyl chloride) cross-linked with 2% divinylbenzene was swollen in $PCl_3$ (which serves as both reactant and swelling solvent) and functionalization was brought about with a Friedel-Crafts catalyst ($AlCl_3$ for a fully functionalized resin). The highly reactive intermediate formed by this process is then converted to the phosphonic acid resin upon quenching of the reaction with $H_2O$ (Figure 46). All fully functionalized phosphonic acid resins used for these studies were synthesized using a 1.2/1.0 $AlCl_3$/-$CH_2Cl$ ratio and their properties are summarized in Table 1.

The phosphinic acid resin was prepared in a similar manner from polystyrene. Polystyrene (2% divinylbenzene cross-linked) was functionalized with $PCl_3$ using $AlCl_3$ as a catalyst at a level of 0.77 moles $AlCl_3$ per mole of styrene units (Figure 47). The synthesis and characterization of this resin have been extensively studied[99] and no modifications were made for this research.

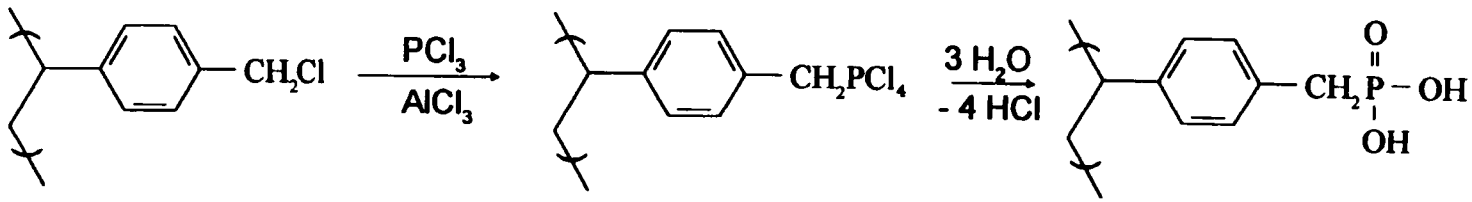



Figure 46. Synthesis of phosphonic acid resin.

Table 1

Characterization of Phosphonic Acid Resins

| Resin | % Solids | Capacities (mequiv/g) | |
|---|---|---|---|
| | | P Capacity | Acid Capacity |
| DC-01-007[a] | 55.7 | 3.80 | 7.75 |
| DC-01-068 | 46.6 | 4.54 | 8.69 |
| DC-01-128 | 48.6 | 4.40 | 8.64 |
| DC-01-194 | 49.1 | 4.11 | 8.47 |
| DC-01-273 | 51.6 | 4.30 | 8.65 |
| DC-02-014 | 54.4 | 4.23 | 8.42 |
| DC-02-119 | 51.6 | 4.66 | 8.82 |
| DC-04-082 | 50.6 | 4.64 | 8.66 |
| DC-06-016 | 52.4 | 4.49 | 8.75 |
| DC-06-146 | 51.4 | 4.73 | 8.59 |

[a] 5% cross-linked resin

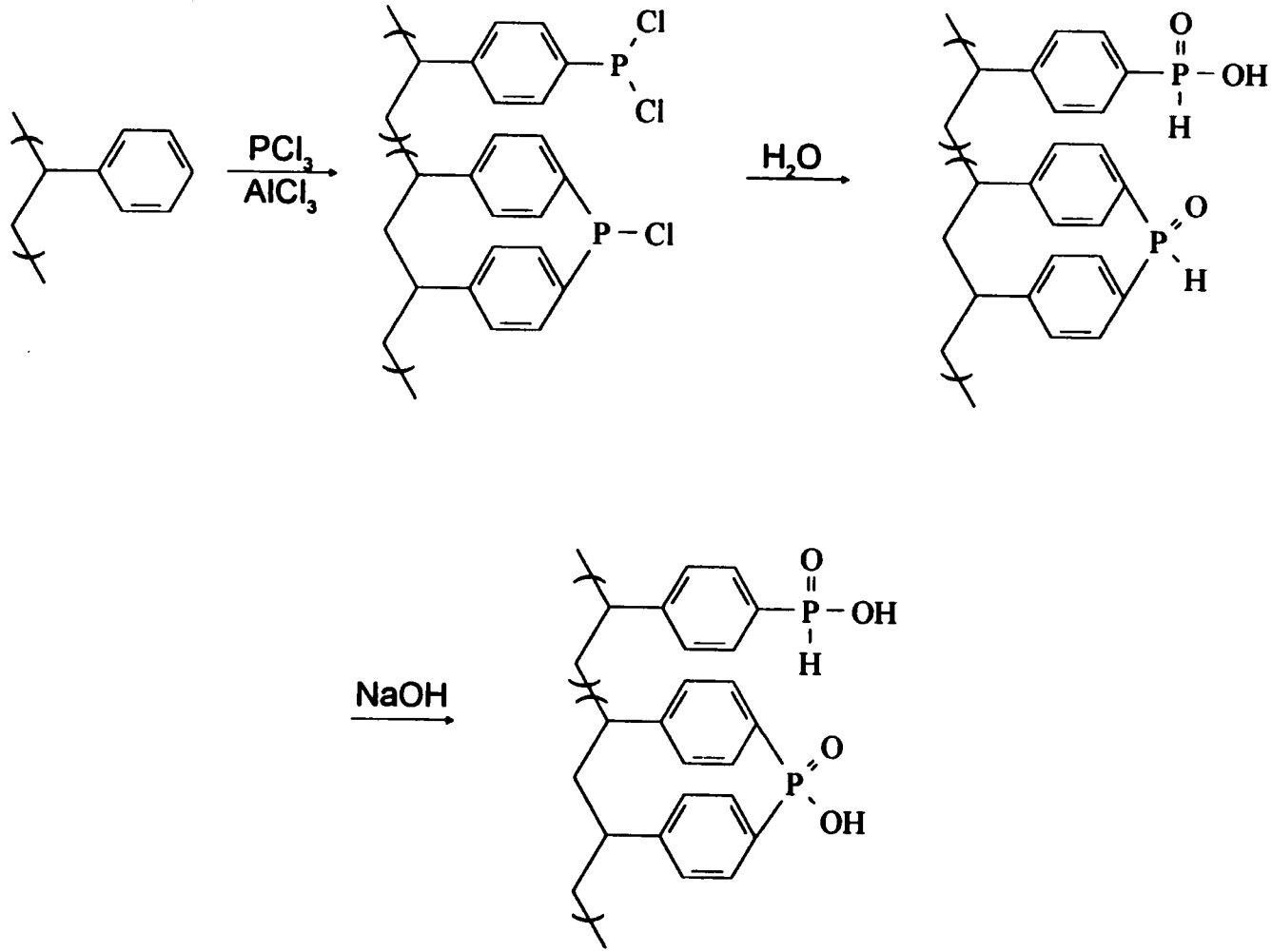



Figure 47. Synthesis of phosphinic acid resin.

Due to the amount of information available concerning its behavior in metal ion extraction, the phosphinic acid resin served as a control for the metal ion studies. The properties of the resins synthesized for these studies are summarized in Table 2.

During the course of the analyses it was found that the primary acid capacity as determined by iodine oxidation was lower than expected. Oxidation with $Ag^+$ yielded numbers which were in closer agreement to those obtained during earlier research.[99] It should be noted that earlier work indicated that the iodine oxidation method was very sensitive to the temperature at which the analysis was conducted and, in general, oxidation with iodine gave slightly different primary acid capacities than did oxidation with $Ag^+$.[95] An investigation of the oxidized resins by FTIR spectroscopy revealed that the P-H bond was not completely oxidized by iodine (Figure 48). Based on these results, it is recommended that the primary acid capacity of the phosphinic acid resin be determined via oxidation with $Ag^+$.

Synthesis of the phosphonate monoethyl ester resin proceeded as described earlier. Poly(vinylbenzyl chloride) was first functionalized with $PCl_3$ and $AlCl_3$ as described for the phosphonic acid resin. The $PCl_3$ was then removed from the functionalized resin by repeated washing with toluene. Quenching of the reactive intermediate was accomplished by cooling the mixture in an ice bath and addition of an equimolar mixture of ethanol and pyridine at a rate slow enough to keep the temperature less than 10 °C. After

Table 2

Characterization of Phosphinic Acid Resins

| | | Capacities (mequiv/g) | | | |
|---|---|---|---|---|---|
| | | | | Primary Acid Capacity | |
| Resin | % Solids | P Capacity | Acid Capacity | $I_2$ Oxidation | $Ag^+$ Oxidation |
| DC-01-022 | 54.5 | 5.13 | 5.16 | 1.33[a] | 2.88[b] |
| DC-01-067 | 53.6 | 5.46 | 5.22 | 1.90 | 3.26[b] |
| DC-01-101 | 49.9 | 5.36 | 5.15 | 1.33 | 3.29 |
| DC-01-198 | 53.1 | 5.26 | 5.37 | 1.70 | 2.59 |

[a]average of three determinations
[b]average of two determinations

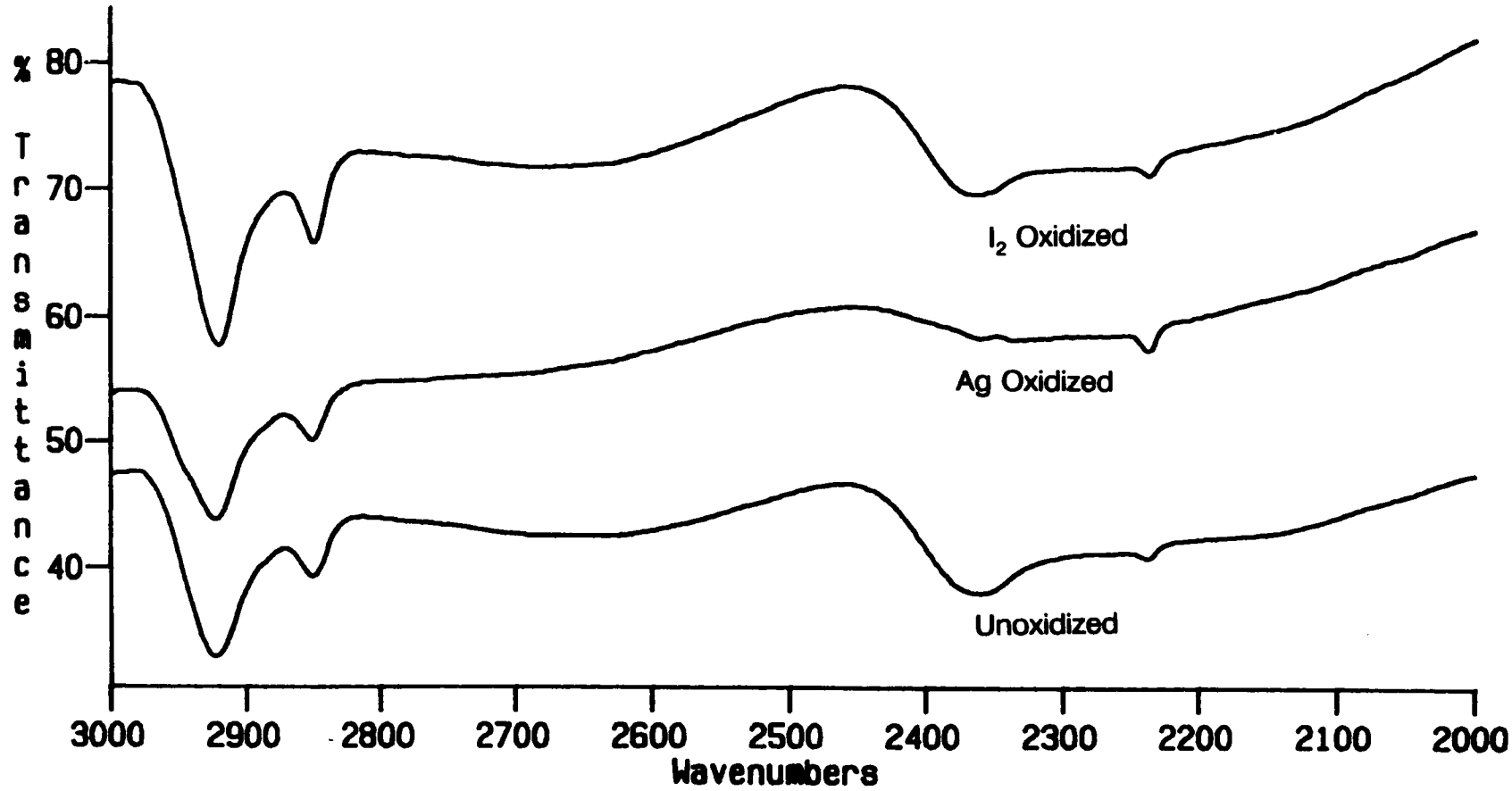



Figure 48. FTIR spectra of oxidized phosphinic acid resin.

the first quench solution had been added, the mixture was allowed to stir for one hour after which a second, identical quench solution was quickly added. A 16 hour reflux served to hydrolyze the diester sites which had formed to the desired monoester.

During the course of the quench, pyridinium chloride forms as a result of the neutralization of liberated HCl by pyridine. This compound is present as a white solid which causes a thickening of the mixture necessitating the periodic addition of small amounts of toluene in order to maintain efficient mixing. It quickly became apparent that removing the pyridinium chloride formed during the addition of the first quench solution prior to the addition of the second dramatically affected the amount of monoester sites which formed. When the pyridinium chloride was removed the percentage of monoester sites fell to an average value of 56% with the remainder of the sites being primarily diester groups. The pyridinium chloride was removed by the repeated addition of small amounts of absolute ethanol to dissolve the solid and removal of the solution by siphoning. Repeated additions were necessary because the pyridinium chloride clogged the sintered glass wand normally used for siphoning, forcing the use of a Pasteur pipette for removal of the liquid. Only small amounts of liquid could be removed each time in order to avoid the loss of beads since the mixture was too viscous to allow the beads to settle until most of the pyridinium chloride was removed. No study was undertaken to fully characterize the key variables responsible for the lower

percentage of monoester sites formed when the beads were washed extensively, but it is likely that the ethanol washes resulted in a larger fraction of ethanol being present in the bead during the hydrolysis step. This is supported by the results of the DC-01-129 series of resins which were synthesized without removal of the pyridinium chloride and with varying ethanol/pyridine ratios in the quench solution. The study showed that a 1:1 ratio was best for the production of high capacities of monoester sites and that the percentage of monoester found on the resin is strongly dependent upon the ethanol/pyridine ratio present during the hydrolysis reaction. No study was performed to investigate the effect of pyridinium chloride itself.

By whatever mechanism, removal of the pyridinium chloride provided a simple way of obtaining resins containing large amounts of both mono- and diester sites. As will be shown by the metal ion studies, such bifunctional resins possess superior extraction abilities relative to their monofunctional counterparts. The properties of the phosphonate monoethyl ester resins synthesized are shown in Table 3.

The phosphonate dialkyl ester resins synthesized for this research were prepared by functionalizing poly(vinylbenzyl chloride) with $FeCl_3$ and $PCl_3$ in the same manner as described for both the phosphonic acid and phosphonate monoethyl ester resins. $FeCl_3$ was used instead of $AlCl_3$ due to the extremely exothermic quench provided by residual $AlCl_3$.[95] The milder

## Table 3

### Characterization of Phosphonate Monoethyl Ester Resins

| Resin | PyHCl Removal | EtOH:Py Ratio | % Solids | Capacities (mequiv/g) | | % Diester | % Monoester | % Diacid |
|---|---|---|---|---|---|---|---|---|
| | | | | P Capacity | Acid Capacity | | | |
| DC-01-023 | Yes | 1:1 | 41.5 | 4.00 | 3.57 | 19 | 72 | 9 |
| DC-01-069A | Yes | 1:1 | 42.5 | 3.93 | 2.25 | 42 | 58 | 0 |
| DC-01-069B | Yes | 1:1 | 45.8 | 3.78 | 2.46 | 35 | 65 | 0 |
| DC-01-102 | Yes | 1:1 | 46.1 | 3.87 | 2.36 | 49 | 42 | 9 |
| DC-01-109 | Yes | 1:1[a] | 52.3 | 3.95 | 2.64 | 35 | 64 | 2 |
| DC-01-116 | No | 1:1[b] | 45.8[c] | 4.11[c] | 4.10[c] | 7[d] | 86[d] | 7[d] |
| DC-01-129A | No | 1:1 | 49.3[c] | 4.19[c] | 4.20[c] | 7[c] | 86[c] | 7[c] |
| DC-01-129B | No | 3:1 | 58.4[c] | 4.04[c] | 2.94[c] | 29[c] | 68[c] | 2[c] |
| DC-01-129C | No | 1:3 | 39.8[c] | 3.52[c] | 4.96[c] | 12[c] | 35[c] | 53[c] |
| DC-01-202A | No | 1:1 | 47.9 | 4.14 | 4.37 | 1 | 92 | 7 |
| DC-01-202B | No | 1:1 | 47.0 | 4.01 | 4.46 | 1 | 88 | 11 |
| DC-02-120A | Yes | 1:1 | 50.5 | 4.09 | 2.38 | 49 | 44 | 7 |
| DC-02-120B | Yes | 1:1 | 48.1 | 4.06 | 2.44 | 45 | 49 | 5 |

[a] quench temperature ≤ 50 °C [b] quench temperature ≤ 15 °C [c] average of two values taken before and after Soxhlet extraction with water
[d] average of three determinations taken before (1 value) and after (2 values) Soxhlet extraction with water

quench afforded by $FeCl_3$ allows a higher percentage of diester groups to form.

Quenching of the intermediate was accomplished with a mixture of the appropriate alcohol and an equal weight of toluene. A nitrogen sweep was employed to remove the HCl which forms and no pyridine was used in order to avoid ester cleavage. The percent esterification was obtained by comparing the measured acid and phosphorus capacities assuming no monoester formation. Characteristics of the phosphonate dialkyl esters are shown in Table 4. Syntheses of the amine-containing resins used for these studies are described in Chapter 2.

Effect of Soxhlet Extraction

A procedure developed earlier in this laboratory involved Soxhlet extraction of the resins with water and reconditioning them prior to metal ion contact studies. In order to be certain that the resin was not degrading during this procedure, a number of the phosphonate monoethyl ester resins were analyzed both before and after Soxhlet extraction. The results, presented in Table 5, show that no significant changes occurred within the resin.

Solution pH

In order to evaluate the performance of the resins, it was necessary to know to final pH of the solutions accurately. Direct measurement of the pH

Table 4

Characterization of Phosphonate Dialkyl Ester Resins

| Resin | Alkyl Group | % Solids | Capacities (mequiv/g) | | % Esterification |
|---|---|---|---|---|---|
| | | | P Capacity | Acid Capacity | |
| DC-01-027 | Ethyl | 60.3 | 3.31 | 0.40 | 94 |
| DC-01-199 | Ethyl | 53.0 | 3.41 | 0.44 | 94 |
| DC-01-247A | Methyl | 55.7 | 3.69 | 0.63 | 91 |
| DC-01-247B | n-Butyl | 69.0 | 3.31 | 0.17 | 97 |

Table 5

Effect of Soxhlet Extraction on the Phosphonate Monoethyl Ester Resin

| Resin | % Solids | Capacities (mequiv/g) | | % Diester | % Monoester | % Diacid |
|---|---|---|---|---|---|---|
| | | P Capacity | Acid Capacity | | | |
| DC-01-116 | [a]44.6/46.9 | 4.13/4.09 | 4.11/4.09 | 11/5[a] | 78/89[a] | 11/5[a] |
| DC-01-129A | 49.3/49.4 | 4.19/4.18 | 4.16/4.24 | 7/6 | 87/86 | 6/8 |
| DC-01-129B | 53.7/63.2 | 4.08/4.00 | 2.95/2.92 | 31/28 | 65/72 | 3/1 |
| DC-01-129C | 31.1/48.4 | 3.66/3.37 | 5.14/4.78 | 11/13 | 38/33 | 51/54 |

[a]Values are given as before/after extraction. For DC-01-116 the value after extraction is an average of two determinations.

after contact was not feasible due to their radioactive nature. In addition, approximately half of the samples contained a large excess of sodium ions leading to measured values lower than the actual solution pH due to response of the electrode to $Na^+$. Knowing the pH of the stock metal solution and the composition of the background solution, it is possible to calculate the theoretical pH of the contact solution. The true final pH can be obtained if one knows the extent to which the resin affects the solution. For this reason, a study was undertaken to determine the extent to which the most commonly used resins exchange or absorb protons from the contact solution.

The resins were contacted with 10 mL of $1x\ 10^{-4}$ N $Hg(NO_3)_2$ in background solutions of varying initial pH. After a 17 hour contact period, the pH of the solution was determined by titration with sodium hydroxide. For comparison, the pH was also determined with a standard pH meter. The results show a close agreement between the measured and titrated pH values in cases where no sodium ions are present. The differences between the initial pH, calculated from the pH of the stock metal solution and the background acid strength, and the measured pH are shown in Tables 6-9. Absorption of protons occurs through protonation of the phosphoryl oxygen at low pH. Clearly, the phosphoryl oxygen of the esters is more basic than that of the parent acid as would be expected from inductive effects.

The values obtained from this study were used to calculate the resin's contribution to the final pH of the contacted solutions which, together with

Table 6

Effect of Phosphinic Acid Resin on Solution pH

| Solution ($N\ HNO_3/N\ NaNO_3$) | Initial pH | Final pH | % of Ligands Exchanged [% of Ligands Protonated] |
|---|---|---|---|
| 4/0 | -0.60 | -0.59 | [40.8] |
| 2/2 | -0.30 | -0.29 | [21.1] |
| 1/3 | 0.00 | 0.01 | [10.9] |
| 0.2/3.8 | 0.70 | 0.68 | 4.2 |
| 0.1/3.9 | 0.99 | 0.93 | 7.4 |
| 0.01/3.99 | 1.90 | 1.37 | 13.7 |
| 0.001/3.999 | 2.44 | 1.41 | 15.5 |
| 0.0001/3.9999 | 2.56 | 1.45 | 15.4 |
| 4/0 | -0.60 | -0.59 | [42.3] |
| 2/0 | -0.30 | -0.30 | 0.0 |
| 1/0 | 0.00 | 0.00 | 0.0 |
| 0.2/0 | 0.70 | 0.69 | 2.1 |
| 0.1/0 | 0.99 | 0.97 | 2.2 |
| 0.01/0 | 1.90 | 1.96[a] | [0.7] |
| 0.001/0 | 2.44 | 2.44[a] | 0.0 |
| 0.0001/0 | 2.56 | 2.53[a] | 0.1 |

[a] The solutions were too dilute to titrate accurately. The values measured with a pH meter have been used.

Table 7

Effect of Phosphonic Acid Resin on Solution pH

| Solution ($N\ HNO_3/N\ NaNO_3$) | Initial pH | Final pH | % of Ligands Exchanged[a] [% of Ligands Protonated] |
|---|---|---|---|
| 4/0 | -0.60 | -0.59 | [38.4] |
| 2/2 | -0.30 | -0.29 | [19.4] |
| 1/3 | 0.00 | 0.01 | [9.3] |
| 0.2/3.8 | 0.70 | 0.69 | 2.0 |
| 0.1/3.9 | 0.99 | 0.91 | 8.6 |
| 0.01/3.99 | 1.90 | 1.34 | 14.1 |
| 0.001/3.999 | 2.44 | 1.39 | 15.5 |
| 0.0001/3.9999 | 2.56 | 1.40 | 15.5 |
| 4/0 | -0.60 | -0.59 | [31.8] |
| 2/0 | -0.30 | -0.29 | [19.7] |
| 1/0 | 0.00 | 0.01 | [9.6] |
| 0.2/0 | 0.70 | 0.69 | 1.9 |
| 0.1/0 | 0.99 | 0.97 | 2.0 |
| 0.01/0 | 1.90 | 1.95[b] | [0.6] |
| 0.001/0 | 2.44 | 2.33[b] | 0.4 |
| 0.0001/0 | 2.56 | 2.51[b] | 0.2 |

[a] Assuming monodeprotonation

[b] The solutions were too dilute to titrate accurately. The values measured with a pH meter have been used.

Table 8

Effect of Phosphonate Monoethyl Ester Resin on Solution pH

| Solution ($N HNO_3$/$N NaNO_3$) | Initial pH | Final pH | % of Ligands Exchanged [% of Ligands Protonated] |
|---|---|---|---|
| 4/0 | -0.60 | -0.58 | [101.5[a]] |
| 2/2 | -0.30 | -0.28 | [51.4] |
| 1/3 | 0.00 | 0.03 | [38.4] |
| 0.2/3.8 | 0.70 | 0.71 | [2.6] |
| 0.1/3.9 | 0.99 | 1.00 | [1.3] |
| 0.01/3.99 | 1.90 | b | -- |
| 0.001/3.999 | 2.44 | b | -- |
| 0.0001/3.9999 | 2.56 | b | -- |
| 4/0 | -0.60 | -0.58 | [102.5[a]] |
| 2/0 | -0.30 | -0.28 | [54.5] |
| 1/0 | 0.00 | 0.02 | [24.8] |
| 0.2/0 | 0.70 | 0.71 | [2.6] |
| 0.1/0 | 0.99 | 0.99 | 0.0 |
| 0.01/0 | 1.90 | 1.96[c] | [0.9] |
| 0.001/0 | 2.44 | 2.43[c] | 0.05 |
| 0.0001/0 | 2.56 | 2.57[c] | [0.04] |

[a] Only monoprotonation is thought to occur. The slight deviation from 100% is believed to be experimental error.
[b] The solutions were too dilute to titrate accurately. The presence of sodium prohibited the use of values measured with a pH meter.
[c] The solutions were too dilute to titrate accurately. The values measured with a pH meter have been used.

Table 9

Effect of Phosphonate Diethyl Ester Resin on Solution pH

| Solution ($N HNO_3$/$N NaNO_3$) | Initial pH | Final pH | % of Ligands Exchanged [% of Ligands Protonated] |
|---|---|---|---|
| 4/0 | -0.60 | -0.59 | [40.2] |
| 2/2 | -0.30 | -0.27 | [58.5] |
| 1/3 | 0.00 | 0.05 | [48.0] |
| 0.2/3.8 | 0.70 | 0.81 | [19.6] |
| 0.1/3.9 | 0.99 | 1.13 | [12.5] |
| 0.01/3.99 | 1.90 | a | -- |
| 0.001/3.999 | 2.44 | a | -- |
| 0.0001/3.9999 | 2.56 | a | -- |
| 4/0 | -0.60 | -0.58 | [79.8] |
| 2/0 | -0.30 | -0.28 | [39.1] |
| 1/0 | 0.00 | 0.02 | [19.7] |
| 0.2/0 | 0.70 | 0.71 | [1.9] |
| 0.1/0 | 0.99 | 1.00 | [1.0] |
| 0.01/0 | 1.90 | 2.00[b] | [1.1] |
| 0.001/0 | 2.44 | 2.46[b] | [0.1] |
| 0.0001/0 | 2.56 | 2.57[b] | 0.0 |

[a] The solutions were too dilute to titrate accurately. The presence of sodium prohibited the use of values obtained with a pH meter.
[b] The solutions were too dilute to titrate accurately. The values measured with a pH meter have been used.

knowledge of the initial pH of the solution, allowed for the calculation of the final pH value.

Metal Ion Studies

All metal ion studies were conducted using $10^{-4}$ N metal nitrate solutions. The low metal concentration is used to prevent loading effects which can alter the inherent affinity of the resin for the ion in question as a large number of the ligands are complexed.

Two series of studies were completed. In the first, the behavior of the phosphonate monoethyl and diethyl ester resins in the extraction of $Fe^{3+}$, $Mn^{2+}$, and $Hg^{2+}$ was compared to that of the phosphinic and phosphonic acid resins over a relatively wide pH range (nitric acid concentrations from $10^{-4}$ to 4 N) both with and without adjustment of the ionic strength to a constant level with $NaNO_3$.

The second series of experiments involved the study of a large number of resins with $Ag^{+}$, $Hg^{2+}$, $Mn^{2+}$, $Fe^{3+}$, and $Zn^{2+}$ over a narrower pH range in solutions of constant ionic strength. In both studies, the results have been analyzed by examining the value of the logarithm of the distribution coefficient, D, as a function of pH.

$$D = \frac{(meq\ M^{n+}/g\ resin)}{(meq\ M^{n+}/mL\ solution)}$$

The wide pH range study revealed no unusual behavior from the phosphonate ester resins. The log D values for $Mn^{2+}$ (Figures 49 and 50) rise smoothly from near 0.00 to 1.00-2.00 in solutions containing sodium ions and to 4.00-5.00 in those solutions without sodium for all resins except the diester. The log D values remain near zero regardless of the pH with the diester. These results indicate that $Mn^{2+}$ is absorbed primarily via an ion exchange mechanism. Competition from sodium, seen as a drop in the log D value, and the apparent lack of interaction with the diester indicate that little or no coordination to the phosphoryl oxygen has occurred. This is to be expected given that $Mn^{2+}$ is a hard divalent ion while the phosphoryl oxygen is a soft ligand.

In agreement with hard-soft acid-base theory, the soft $Hg^{2+}$ ion is readily extracted by the resins under study (Figures 51 and 52). Log D values with the phosphinic acid resin range from 3.3 to 3.9 regardless of the pH or the presence of sodium. This high level of mercury extraction by the phosphinic acid is a result of both a strong coordinative interaction with the phosphoryl oxygen and the ability of the polymer to reduce the $Hg^{2+}$ ions to mercury metal once they are brought into close proximity with the P-H bond.[96] Both the phosphonic acid and the phosphonate monoester resins show a

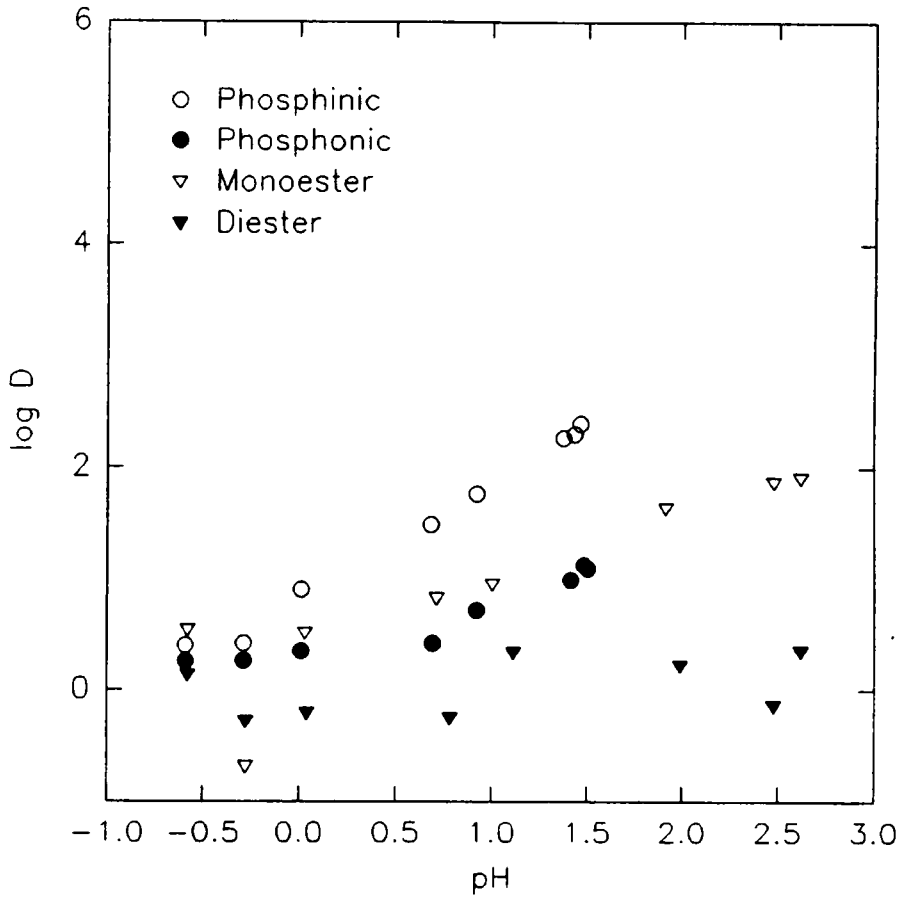



Figure 49. Extraction of $Mn^{2+}$ in the presence of excess sodium nitrate.

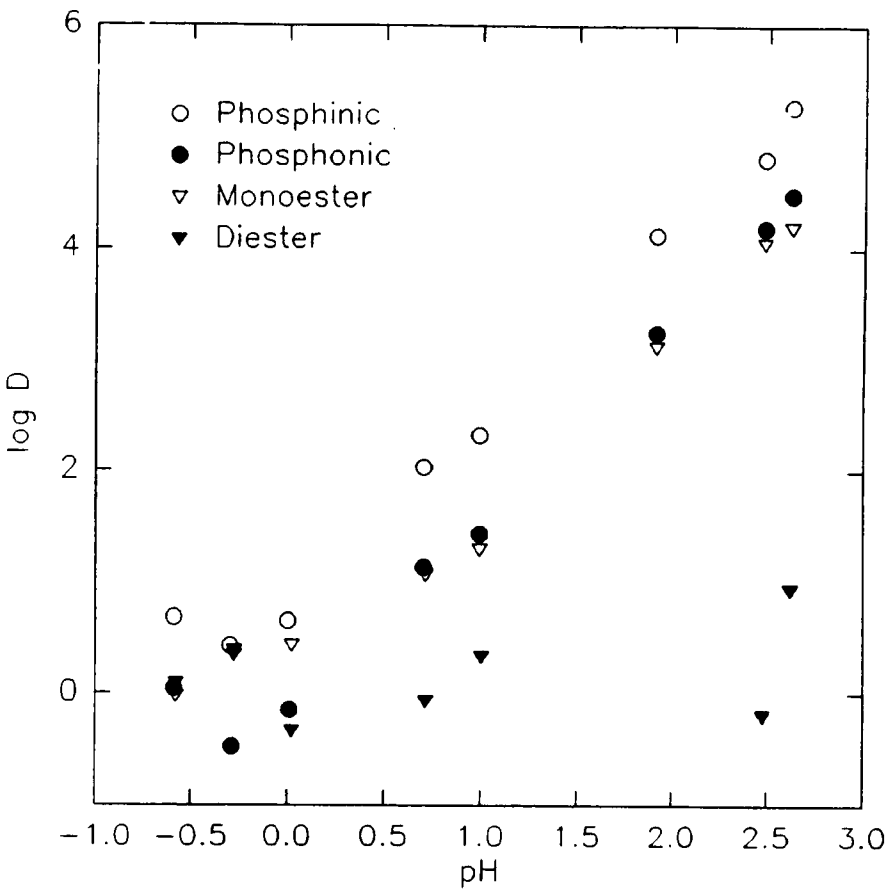



Figure 50. Extraction of $Mn^{2+}$ from solutions without added sodium nitrate.

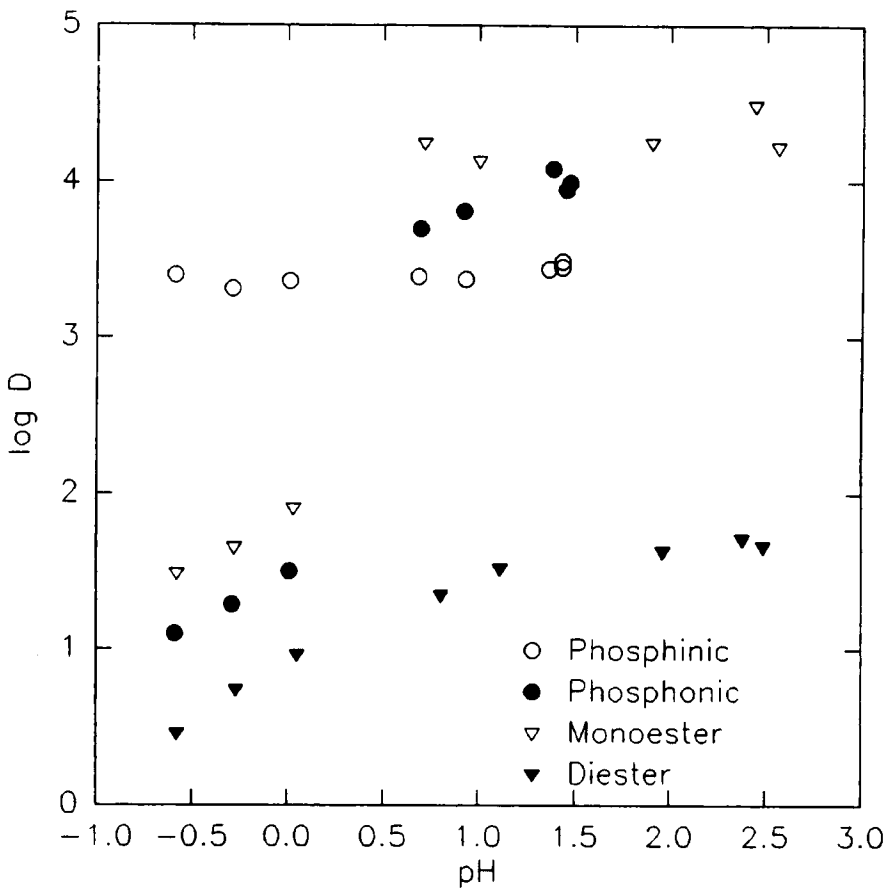



Figure 51. Extraction of $Hg^{2+}$ in the presence of excess sodium nitrate.

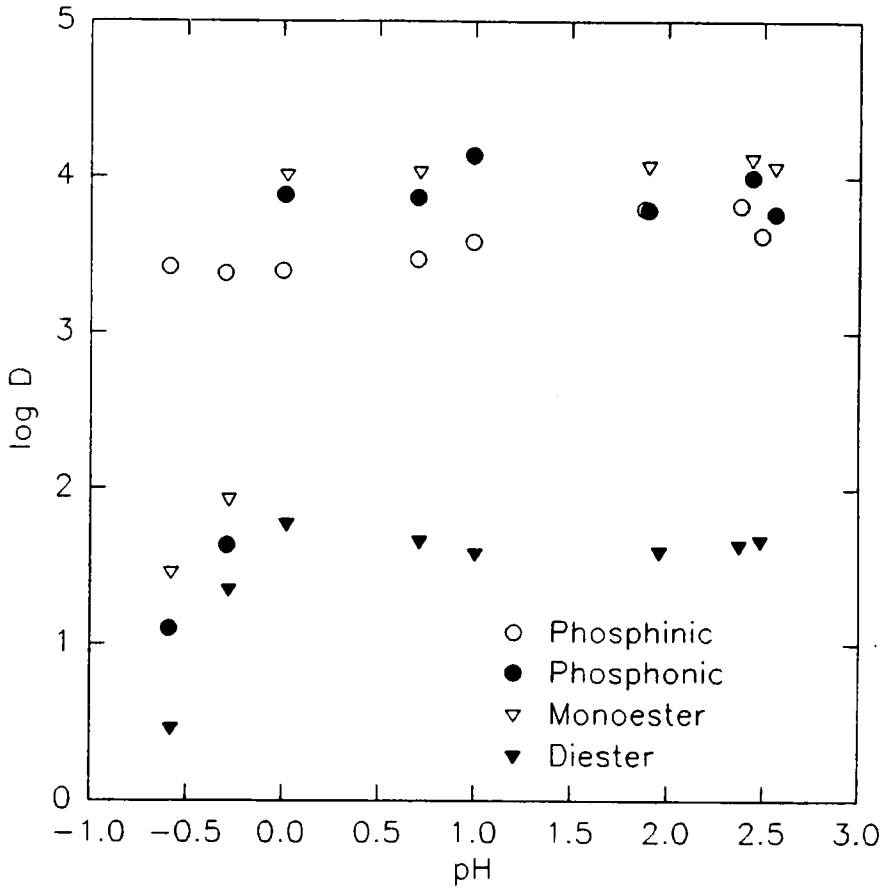



Figure 52. Extraction of $Hg^{2+}$ from solutions without added sodium nitrate.

rapid rise in the log D value with increasing pH until a value of approximately 4 is reached. The log D remains relatively constant after this point regardless of pH. It should be noted that a log D of 4 corresponds to greater than 99% absorption of the target metal ion. The presence of sodium does not alter the overall appearance of the log D vs. pH plots, but it changes the pH at which the maximum value is reached. In the absence of sodium nitrate, the maximum log D value is achieved at a pH of approximately zero. The maximum value is not reached until the pH is approximately 0.7 in the presence of sodium. The results indicate that the monoester, like the phosphonic acid resin, behaves primarily as an ion exchanger. The effect of sodium shows that a limited amount of competition for the ion exchange sites exists although in all but the most acidic solution, sodium is present in at least a 5000:1 excess. The diester behaves in a similar manner although the maximum log D value reached is between 1.5 and 2.0. While the diester does not have an acidic hydrogen capable of ion exchange, the results of the pH study indicate that the phosphoryl oxygen is protonated to a large extent in the lowest pH solutions used. The behavior seen may result from a competition of the mercury ion with protons for the phosphoryl oxygen.

All resins except the diester show a marked affinity for the iron (III) ion which is little affected by pH (Figure 53 and 54). This indicates that $Fe^{3+}$ is not sorbed via an ion exchange process. Given that $Fe^{3+}$ is a hard ion it would not be expected to have a great deal of interaction with the soft phosphorus

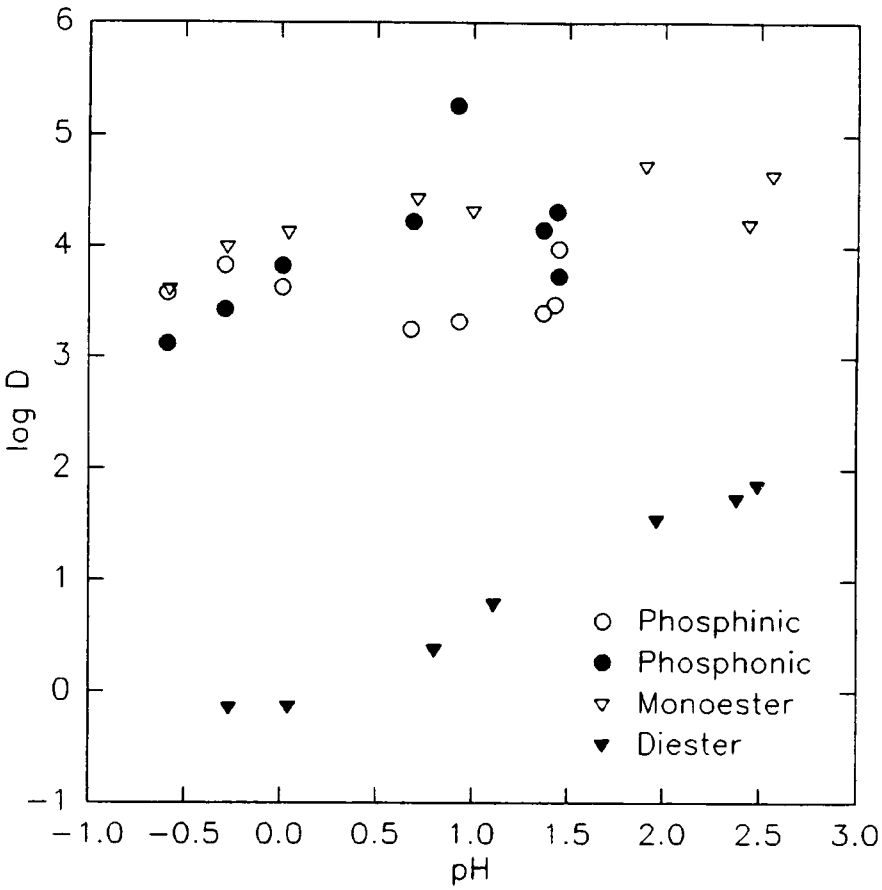



Figure 53. Extraction of $Fe^{3+}$ in the presence of excess sodium nitrate.

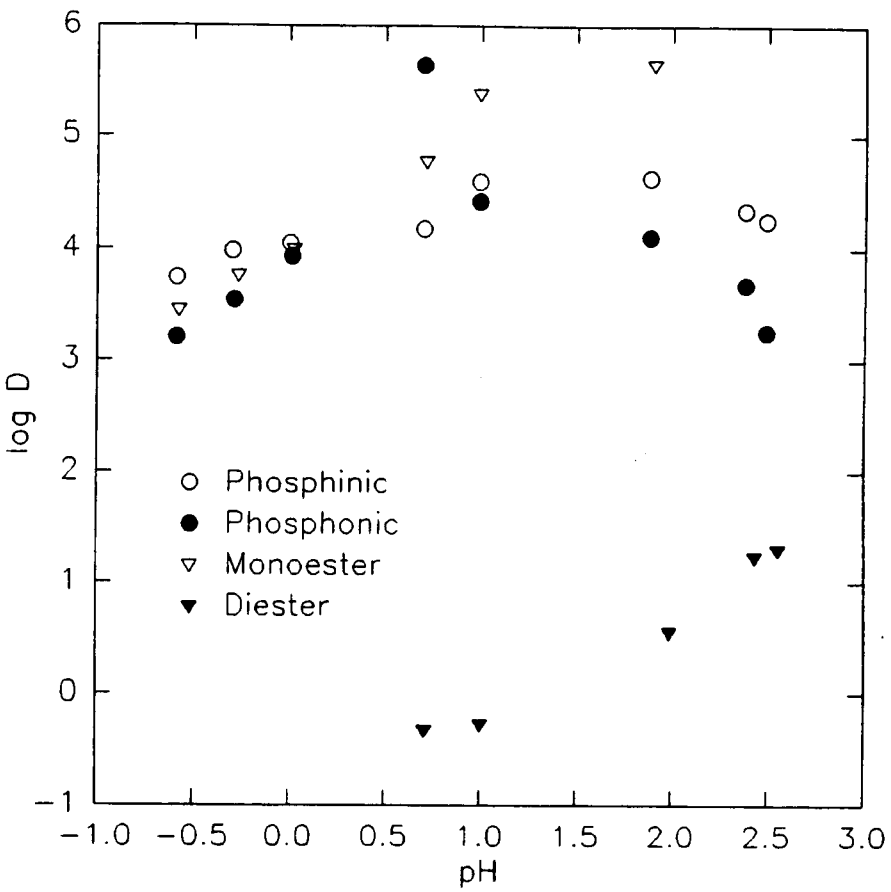



Figure 54. Extraction of $Fe^{3+}$ from solutions without added sodium nitrate.

acid ligands used here. However, it has been postulated that the extraction of $Fe^{3+}$ is favorable due to the increase in entropy which occurs with the loss of water from the ion upon coordination by the phosphoryl oxygen.[96,100] The lack of interaction with the diester can be explained as a result of the steric hindrance provided by the ethyl groups (vide infra).

A more complete set of data was obtained over a narrower pH range. Again, the metal ion concentration was 1 X $10^{-4}$ N to obviate any loading effects and sodium nitrate was added to maintain a constant nitrate background of 4 N. Uptake of the nitrate salts of $Ag^{+}$, $Hg^{2+}$, $Fe^{3+}$, $Mn^{2+}$, and $Zn^{2+}$ from solutions containing $HNO_3/NaNO_3$ at concentrations of 4.0 N /0.0N, 2.0 N/2.0 N, 1.0 N/3.0 N, and 0.2 N/3.8 N was examined. The polymers used in this study were the phosphinic acid, phosphonic acid, phosphonate monoethyl, dimethyl, diethyl, and dibutyl esters, bifunctional phosphonate mono/diester, dimethylamine, and dimethylamine/phosphonic acid resins. The results of an identical study with the sulfonic acid resin are presented for comparison (Figure 55).[95]

The most obvious result is that all of the resins studied displayed a greater degree of selectivity than the sulfonic acid resin. The phosphinic acid resin showed a well-defined selectivity series of Fe>Hg>Ag>Mn>Zn in the solutions studied (Figure 56). Note that the pH was low enough to prevent a significant amount of ion exchange from occurring, meaning that the metals were sorbed via coordination with the phosphoryl oxygen. In addition to

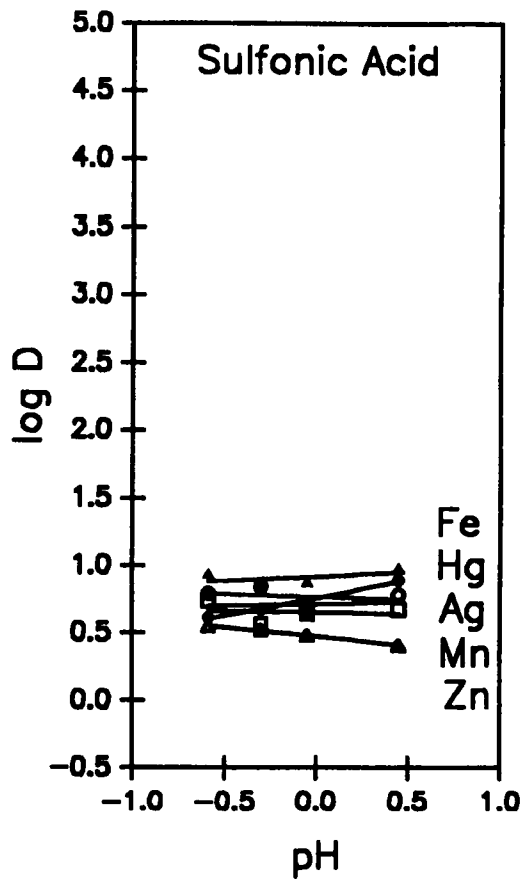



Figure 55. Log D/pH correlations with sulfonic acid resin.

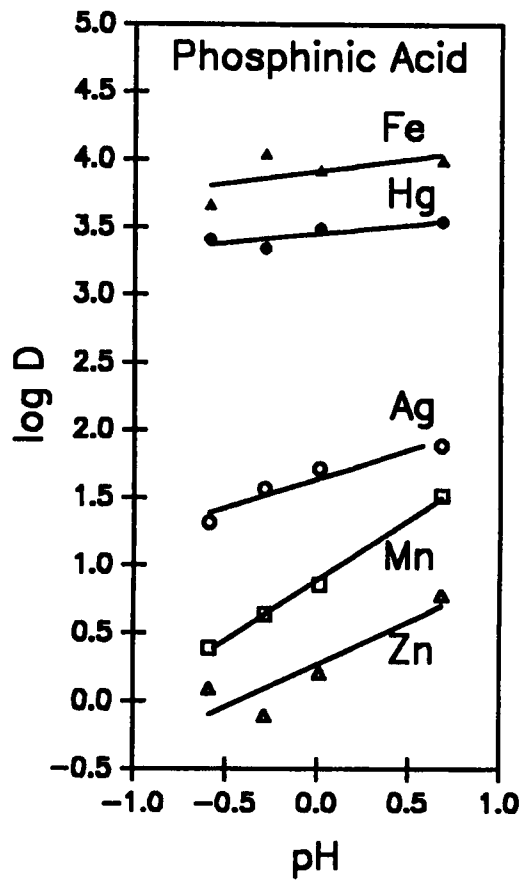



Figure 56. Log D/pH correlations with phosphinic acid resin.

coordination, it has been previously shown that both mercury (II) and silver (I) can be reduced to the zero-valent metal under these conditions.[88] The phosphonic acid resin (Figure 57) showed a lower degree of selectivity than did the phosphinic acid resin and the log D values for both silver and mercury dropped as a result of the inability of the phosphonic acid ligand to reduce the ions. The large increase in the amount of mercury sorbed from the highest pH solution (relative to the other three) is almost surely the result of the onset of ion exchange. The monoethyl ester showed a very similar behavior with the exception of higher log D values for the silver ion (Figure 58). This increase in affinity for the soft silver ion is thought to arise from the increased availability (softness) of the phosphoryl oxygen of the monoester for complexation. The diethyl ester displayed a stronger affinity for silver than for any other metal ion studied (Figure 59). Given that the diester ligand should be even softer than the monoester, this result is expected. The diester showed rather low affinities for all ions except silver and mercury. The bifunctional ester resin, containing approximately 60% monoester and 40% diester sites, showed a diminished affinity for iron and a similar affinity for mercury when compared with the monofunctional monoester resin (Figure 60). Somewhat surprisingly, the bifunctional ester resin showed a higher affinity for the silver ion than either monofunctional resin, indicating that a synergistic interaction is present between the two ligands. In order to verify that the increased uptake of silver was indeed due to a cooperative extraction mechanism, a mixed bed of pure

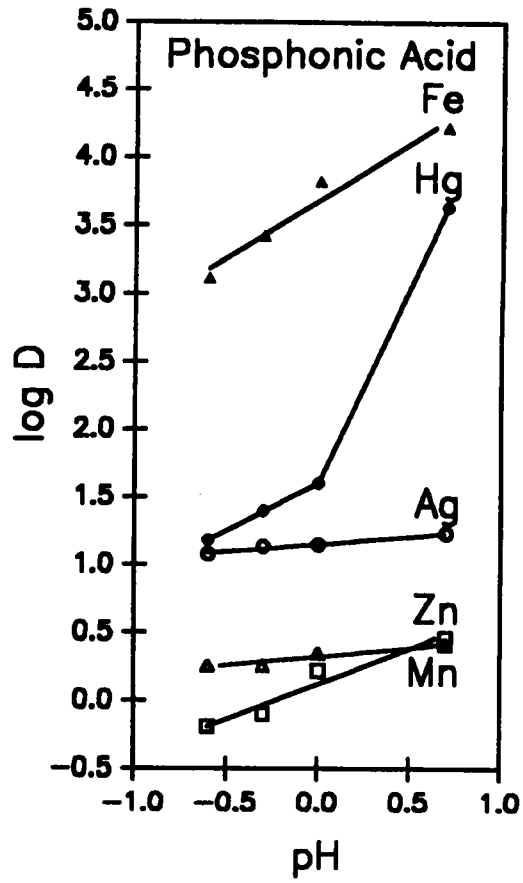



Figure 57. Log D/pH correlations with phosphonic acid resin.

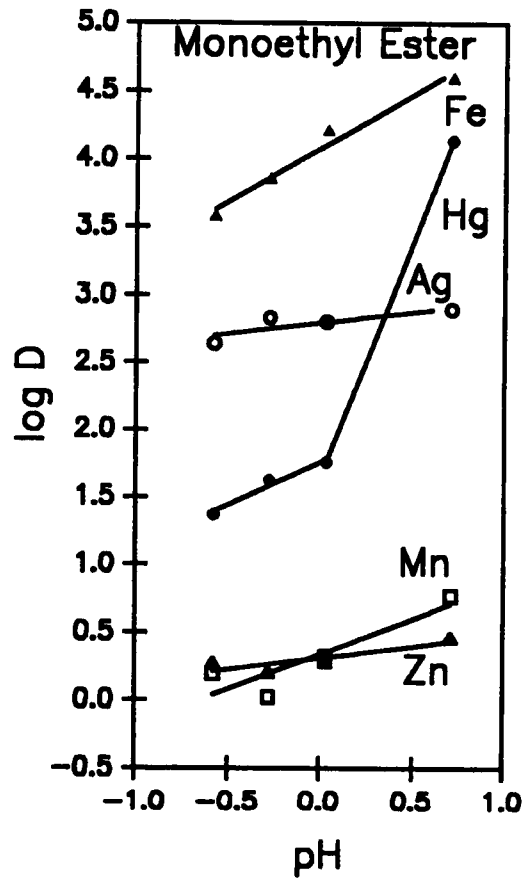



Figure 58. Log D/pH correlations with monoethyl ester resin.

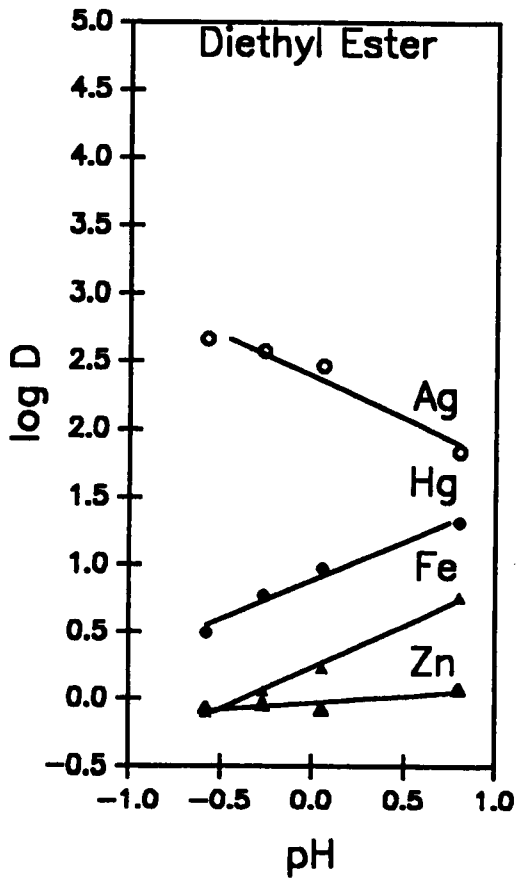



Figure 59. Log D/pH correlations with diethyl ester resin.

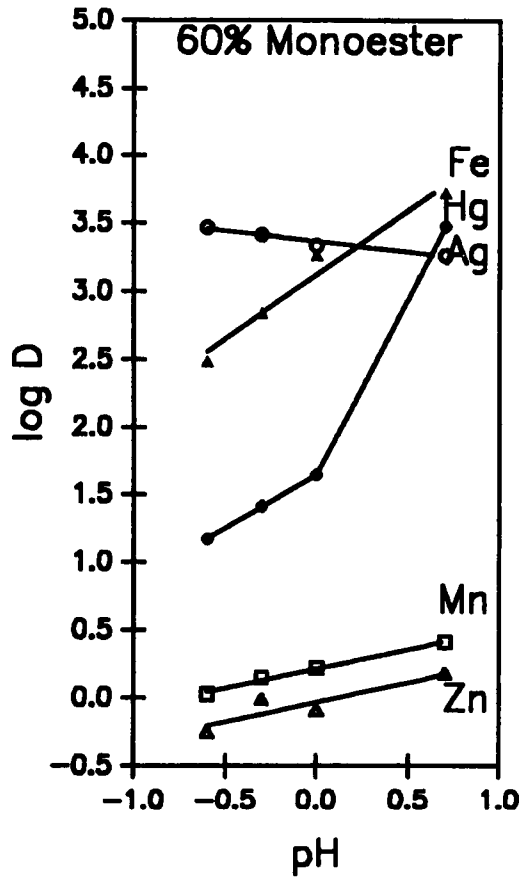



Figure 60. Log D/pH correlations with monoester/diester resin.

monoester and pure diester resins (mixed in the same proportions as found on the resin) was examined. The results (Figure 61) show that a synergistic interaction is indeed operative. The bifunctional resin extracts far more silver than either the monofunctional resins or the mixed bed. While synergism has been reported in liquid extractants,[101] it is believed that this is the first example of such synergism on a synthetic resin and the phenomenon has been termed *supported ligand synergistic interaction.*[102] In this particular case, it is believed that the more hydrophilic monoester sites allow access to the more strongly coordinating, but very hydrophobic, diester sites.

An examination of the extraction ability of the dimethyl and dibutyl ester resins (Figures 62 and 63) reveals another factor influencing the selectivity of the polymer. As expected, given the lack of an ion exchange site, the resins perform poorly with the hard, divalent manganese and zinc ions. The softer silver and mercury ions are extracted to high levels as a result of favorable interactions with the phosphoryl oxygen. In fact, in all but one solution (highest pH with the dimethyl ester) the diester resins display the strongest affinity for the silver ion. On the other hand, the iron ion is extracted to a much lesser extent than with the phosphorus acids. Only the dimethyl ester extracts the iron ion to a great extent and then only at the highest pH. This lack of affinity can be explained by considering the extraction mechanism. The diester resins are purely coordinating materials. Thus, upon entry into the polymer network, an ion must be accompanied by its counterion in order to

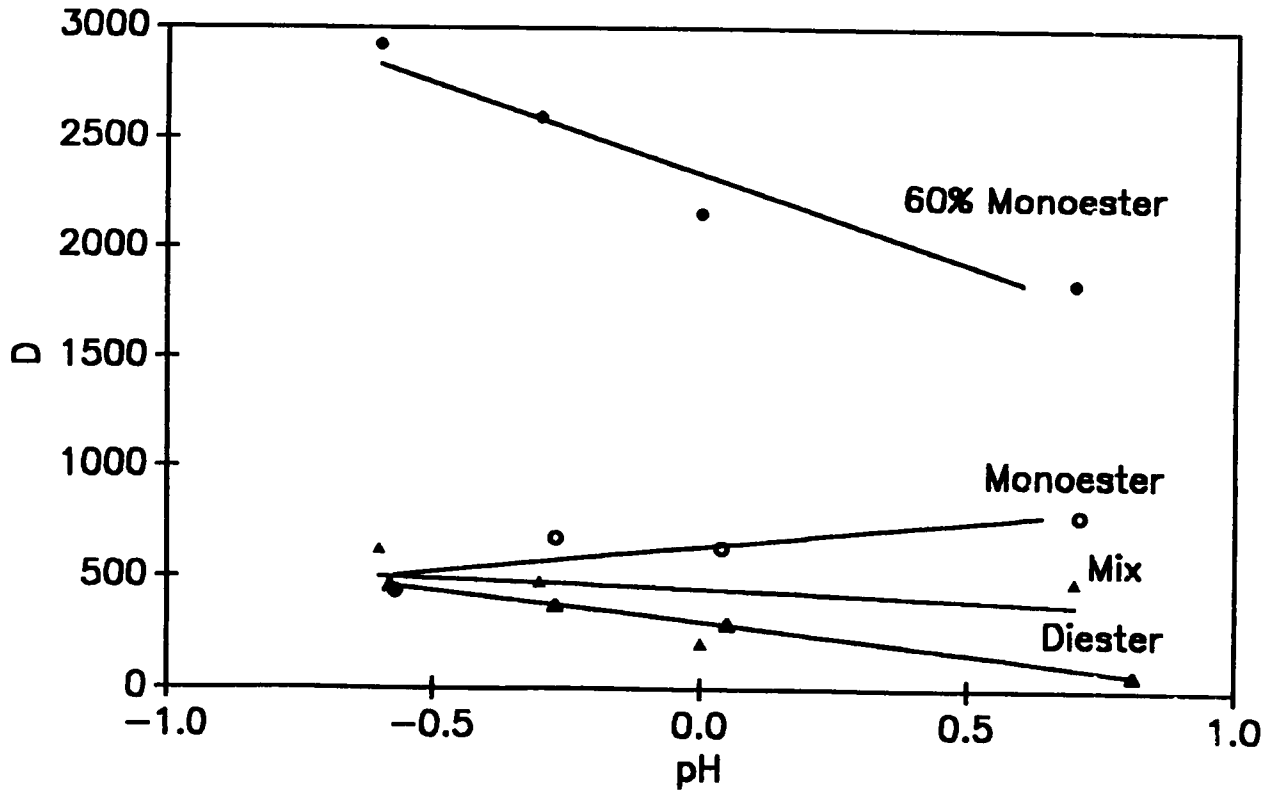



Figure 61. Uptake of $AgNO_3$ by monoester/diester, diester, monoester, and mixed-bed resins.

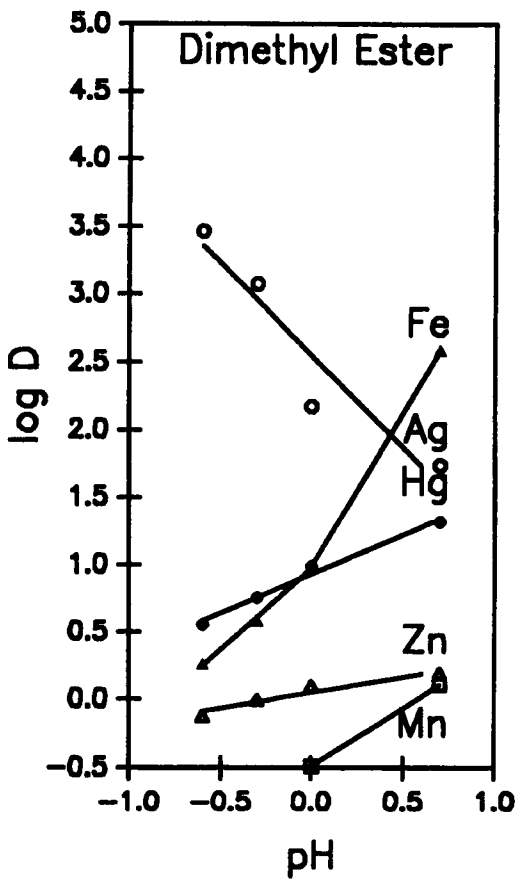



Figure 62. Log D/pH correlations with dimethyl ester resin.

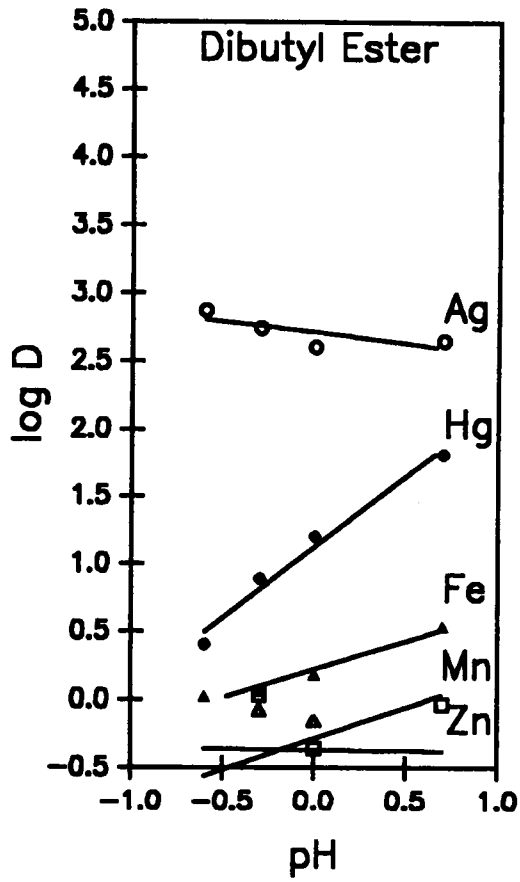



Figure 63. Log D/pH correlations with dibutyl ester resin.

maintain charge neutrality between the phases. This in turn means that the counterions (nitrate in this case) are present during coordination. It is postulated that coordination of the iron trinitrate salt is hindered by the presence of the bulky alkyl groups present on the phosphorus ligand. Notice that the sorption of iron drops as the size of the alkyl substituent increases from methyl to ethyl to butyl. It is apparent that the ethyl group is already large enough to severely hinder the uptake of iron. The resins also display selectivity for silver nitrate over mercury dinitrate. While not examined, it is believed that the negative slope found with the silver extractions is a result of the extraction of a protonated complex.

The dimethylamine resin (synthesized as a control) was found to extract much more silver and mercury than expected (Figure 64). Extraction of mercury (II) by amines at low pH has been reported[103] and it is thought that the same mechanism is in effect here. The mixed functionality dimethylamine/phosphonic acid resin shows a selectivity series similar to the monofunctional phosphonic acid resin although mercury is sorbed at the lower levels of the amine resin (Figure 65). This indicates that the mixed functionality resin operates primarily through the phosphonic acid sites with little interaction from the tertiary amine centers.

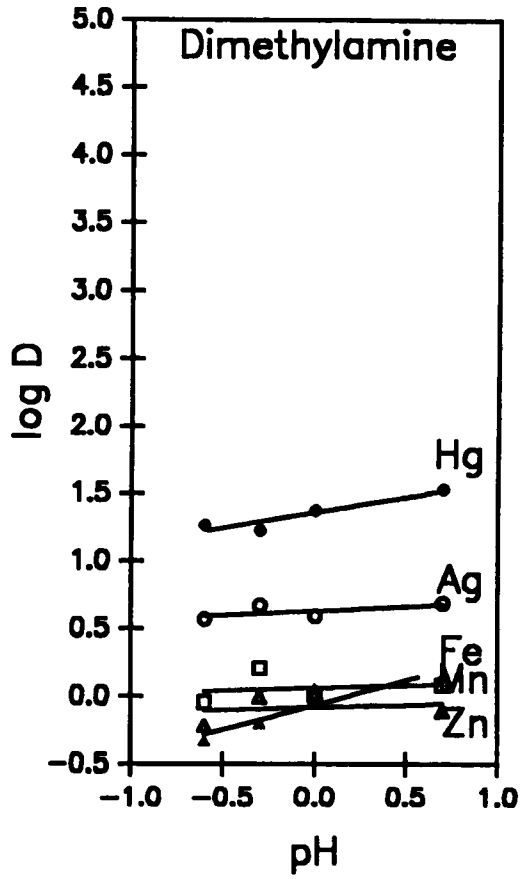



Figure 64. Log D/pH correlations with dimethylamine resin.

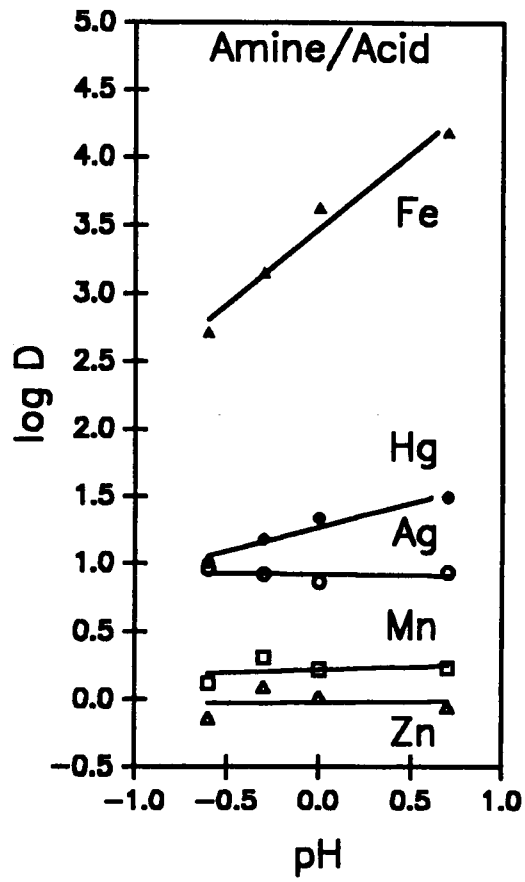



Figure 65. Log D/pH correlations with dimethylamine/phosphonic acid resin.

Conclusions

The phosphonate monoethyl ester resin operates primarily via an ion exchange mechanism in a manner similar to the parent acid while the diester has a limited affinity for the ions studied which results from a poor match between the hard-soft acid-base characteristics of the ligand and the ions studied.

It has been shown that the bifunctional phosphonate mono/diethyl ester resin displays a unique supported ligand synergistic interaction in the extraction of $Ag^+$ from low pH solutions. The bifunctional resin extracted far more silver than either monofunctional resin. In addition to other factors which affect selectivity, the results of the metal ion studies with various phosphonate dialkyl esters indicate that the steric bulk of the alkyl groups can have a subtle influence on the extraction ability of the resin.

# CHAPTER 2

## CLASS III DUAL MECHANISM BIFUNCTIONAL POLYMERS: SYNTHESIS AND AMINATION OF PARTIALLY FUNCTIONALIZED PHOSPHONIC ACID RESIN

### Introduction

Initial research on the ion exchange/precipitation resins resulted in the production of resins possessing both phosphonic acid and quaternary amine sites. These polymers displayed selectivity for those cations which formed insoluble compounds with the counterions present on the amine sites,[93,104] but were not as uniformly bifunctional as desired due to an inhomogeneous initial functionalization (introduction of phosphonic acid sites). A method for synthesizing a more uniform partially functionalized phosphonic acid resin was developed in preparation for the production of Class III resins with a high degree of bifunctionality. Several polymers were produced from the uniformly functionalized resin but extensive metal ion studies were not conducted with well characterized materials.[105]

The goal of this research was to investigate the feasibility of producing a series of uniform Class III resins differing only in the size of the alkyl substituents on the nitrogen atom and to examine what effects this change would have on the extraction abilities of the polymer. Once synthesized, the

performance of the Class III resins was to be compared with the monofunctional amine and phosphonic acid polymers in order to determine if the ligands behaved synergistically in the extraction of metals.

A report is given here of the attempts made to synthesize the desired polymers and the characterization of the materials produced. In addition, given their similarity to the Class III resins, the synthesis and characterization of the dimethylamine and the Class II dimethylamine/phosphonic acid resins introduced in Chapter 1 will be described here.

Amine Resins

Fully aminated polymers were prepared from poly(vinylbenzyl chloride) by nucleophilic displacement with a number of amines in order to serve as monofunctional controls for the Class III resins. The general technique was similar for all amines used and consisted of a 4 to 17 hour reflux of a mixture of poly(vinylbenzyl chloride) and the amine. The solvent for the reaction varied. Both dimethyl and trimethylamine were present as aqueous solutions, triethylamine was saturated with water, and tributylamine was dissolved in dioxane. All aminations yielded resins with high capacities, measured as total anion exchange capacities (TAEC), regardless of whether the exchange sites were exclusively from quaternary sites (from tertiary amines) or a mixture of quaternary and protonated tertiary groups (from secondary amines).

Additional cross-linking via reaction of a polymer-supported tertiary amine site with a nearby benzyl chloride site is possible in resins functionalized with secondary amines. The presence of such sites can be quantitatively measured by eluting the resin with a sodium hydroxide solution which deprotonates the tertiary centers and replaces the anion on the quaternary centers with hydroxide. Displacement of hydroxide with nitrate followed by titration of the hydroxide allows the number of anion exchange sites due to quaternary centers to be determined. This quantity is called the salt-splitting anion exchange capacity (SSAC). For polymers containing only quaternary groups, the TAEC and SSAC are equivalent.

Functionalization of the polymer is accompanied by a considerable increase in size. Given that the polymers used were only 2% cross-linked, this increase in size was accompanied by a large amount of splitting. Shortening the reflux period with dimethylamine from 10 to 4 hours was shown to have no effect on the number of split beads (essentially 100%). For the purposes of these studies, it was thought that the presence of split beads would not affect the equilibrium sorption capacity of the resin, but the effect of split beads must be taken into account should kinetic measurements ever be performed. The properties of the fully functionalized amine resins are shown in Table 10.

Table 10

Characterization of Monofunctional Amine Resins

| Resin | Amine | % Solids | Capacities (mequiv/g) | | |
|---|---|---|---|---|---|
| | | | Cl Capacity | TAEC | SSAC |
| DC-01-121B | Dimethylamine | 43.4 | 3.82 | 4.13 | 0.39 |
| DC-01-127 | Dimethylamine | 42.8 | 3.58 | 4.29 | 0.47 |
| DC-02-282[a] | Trimethylamine | 21.0[b] | 3.97 | 4.03[b] | -- |
| DC-02-187A | Triethylamine | 22.4 | -- | 3.80 | -- |
| DC-02-166 | Tributylamine | 23.6 | -- | 3.01 | -- |

[a]5% cross-linked macroporous resin
[b]average of two values

Partially Functionalized Phosphonic Acid Resin

Using previously developed procedures, the phosphonic acid ligand was introduced onto the network prior to amination. In order to limit the degree of functionalization, lower reaction temperatures and a less active Friedel-Crafts catalyst ($FeCl_3$) were used than in the synthesis of the fully functionalized phosphonic acid resin described in the previous chapter. Two variations of the procedure were employed. In the first, poly(vinylbenzyl chloride) cross-linked with 2 wt% divinylbenzene was allowed to swell in a mixture of $PCl_3$ and $FeCl_3$ (1.2 mole/mole $-CH_2Cl$ sites) for 18 hours at room temperature. This was to insure uniform distribution of the catalyst throughout the bead and thus uniform functionalization. Following the swelling period, the functionalization was accomplished by heating the mixture at 40 °C for 4 hours prior to quenching in ice. The properties of the resins made in this manner are shown in Table 11.

Notice that the measured acid capacity is less than twice the value of the phosphorus capacity as is expected for a phosphonic acid group. Chemical causes for this behavior could include the presence of unhydrolyzed P-Cl bonds or the formation of anhydride linkages due to the reaction of these sites with phosphonic acid groups. The resin was further hydrolyzed in refluxing 12 M HCl for 17 hours. No increase in the measured acid capacity (1.67 mequiv/g before versus 1.61 mequiv/g after) was noted and no change in the IR spectrum was seen. It seems very unlikely that any

Table 11

Characterization of Partially Functionalized Phosphonic Acid Resins Made Without a Co-solvent

| Resin | % Solids | Capacities (mequiv/g) | | | g/g |
|---|---|---|---|---|---|
| | | Acid Capacity | P Capacity | Cl Capacity | |
| DC-01-105 | 39.4 | 1.67 | 1.38 | 4.23 | 0.92 |
| DC-02-012 | 41.9 | 1.92 | 1.65 | 3.85 | 0.95 |
| DC-02-037 | 44.0 | 1.94 | 1.55 | 3.88 | 0.93 |
| DC-03-026 | 46.9 | 2.28 | 1.67 | 3.75 | 0.94 |

residual P-Cl or P-O-P bonds would remain unhydrolyzed after this harsh treatment indicating that such structures were not responsible for the low acid capacities measured. A more plausible explanation is that the resin retains its original hydrophobic character (since it is functionalized to a low degree) making many of the sites inaccessible to the base during the acid capacity determination. The phosphorus capacity is a much more reliable measure of the degree of functionalization since the resin is solubilized during the course of the analysis.

At this time a useful quantity, the g/g value, must be introduced. The g/g value provides a measure of the extent of any otherwise undetected side reactions. The concept is that the measured capacities of a given resin should account for all possible mass in the sample. For example, consider a resin thought to contain only phosphonic acid and benzyl chloride sites. If the measured capacities (P and Cl as mequiv/g) are converted into masses then the sum of these masses should equal 1.00. The presence of cross-linking lowers this value since, in general, the divinylbenzene sites will not undergo functionalization. Thus one gram of 2% cross-linked poly(vinylbenzyl chloride) resin made with 55.4% pure DVB would contain 0.9639 g of functionalizable material. If only phosphonic acid (MW of repeat unit = 0.198152 g/mequiv) and benzyl chloride (MW of repeat unit = 0.152612 g/mequiv) groups are present then the quantity

$$\frac{(P\ capacity)(0.198152) + (Cl\ capacity)(0.152612)}{0.9639}$$

should equal 1.00. In practice, a g/g value of 1.00 is almost never achieved but values higher than about 0.90 indicate that an acceptable portion of the resin has been characterized. In contrast, a low g/g value indicates the presence of side reactions which are forming an undetected product. The g/g value is therefore a useful tool for detecting the presence of secondary cross-linking reactions.

Two of these partially functionalized resins were converted to bifunctional amine/acid resins. The amines used were dimethyl and trimethylamine and the final properties of the resins are shown in Table 12. DC-01-121A was used for radiotracer experiments described in Chapter 1, but unfortunately, DC-02-012 was unusable as the amination resulted in a large amount of swelling which left only small bead fragments.

Evidence from other studies had suggested that the partially functionalized phosphonic acid resin synthesized as described earlier were not uniformly functionalized leading to amine/acid resins which were not truly bifunctional.[105] This idea was later shown to be true through the use of solid-state $^{31}P$ NMR spectroscopy (Chapter 6).

An alternative method of producing the partially functionalized resin was developed which incorporated a swelling solvent (1,4-dioxane) into the

Table 12

Characterization of Amine/Phosphonic Acid Resins

| Resin | Amine | % Solids | Capacities (mequiv/g) | | | | g/g |
|---|---|---|---|---|---|---|---|
| | | | P Capacity | Cl Capacity | TAEC | SSAC | |
| DC-01-121A | Dimethylamine | 37.1 | 0.74 | 3.12 | 3.25 | 0.03 | 0.82 |
| DC-02-012 | Trimethylamine | 17.8 | 0.78 | 3.10 | 3.21 | -- | 0.87 |

reaction mixture allowing greater access of the reagent to the interior of the bead.[105] Also, dioxane dissolves the $FeCl_3$ quite readily which enhances its accessibility to the interior of the bead to an even greater degree. Thus, an equal volume of dioxane was used in addition to the $PCl_3$, the catalyst level was decreased to 0.77 mole $FeCl_3$ per mole $-CH_2Cl$ sites and the reaction was conducted as before. During the course of the synthetic studies on the amine/acid polymers and the PEG containing polymers (described in Chapter 3) a large number of partially functionalized phosphonic acid resins were produced and their properties are summarized in Table 13.

Attempted Amination

Amination of these partially functionalized resin proved to be more challenging than expected based on the earlier results with resins made without dioxane. An initial attempt to produce a bifunctional tributylamine/phosphonic acid resin used a procedure developed earlier in this laboratory.[105] The partially functionalized phosphonic acid in the base form was eluted first with 95% and then with 100% ethanol to remove the water present in the resin. The resin was then allowed to reflux with a solution of tri-n-butylamine in ethanol for eighteen hours. Surprisingly, the resin (DC-02-169) showed no anion exchange capacity indicating that no amination occurred. The resin was again placed into the base form and reacted with tributylamine using a stronger swelling solvent (80% aqueous

Table 13

Characterization of Partially Functionalized Phosphonic Acid Resins Made With Dioxane

| Resin | % Solids | Capacities (mequiv/g) | | | g/g |
|---|---|---|---|---|---|
| | | Acid Capacity | P Capacity | Cl Capacity | |
| DC-02-075 | 67.0 | 3.06 | 1.68 | 2.98 | 0.82 |
| DC-02-158 | 63.9 | 3.24 | 1.82 | 3.04 | 0.86 |
| DC-02-191 | 61.7 | 3.42 | 1.77 | 2.91 | 0.83 |
| DC-02-214 | 55.5 | 3.30 | 1.83 | 2.98 | 0.85 |
| DC-02-225 | 61.8 | 3.86 | 1.95 | 2.57 | 0.81 |
| DC-02-238[a] | 30.3 | 1.22 | 0.85 | 4.53 | 0.95 |
| DC-02-255[b] | 32.6 | 3.95 | 1.93 | 2.71 | 0.88 |
| DC-03-007 | 62.6 | 3.38 | 1.73 | 3.45 | 0.90 |
| DC-03-194 | 68.8 | 3.34 | 1.68 | 2.96 | 0.81 |
| DC-04-091 | 67.7 | 3.34/3.44[c] | 1.81 | 3.16 | 0.87 |
| DC-04-117[b] | 40.6 | 3.46 | 1.74 | 2.71 | 0.83 |

[a]10% cross-linked macroporous resin
[b]5% cross-linked macroporous resin
[c]second value was obtained in 60% aqueous dioxane rather than water

dioxane, DC-02-175) instead of ethanol, but no anion exchange capacity was measurable. It was thought that the lack of amination was due to limited accessibility of the bulky tributylamine into the resin. A swelling technique developed for the reswelling of dry resins[106] was then employed to try to obviate this problem. The technique involves stirring the resin in dioxane for two hours at room temperature, followed by replacement with fresh dioxane and swelling for 24 hours at 50°C. Partially functionalized phosphonic acid resin (acid form) was so treated and refluxed in a 50:50 mixture of tributylamine and dioxane (DC-02-183). Once again, the resin did not aminate. An older technique which had given aminated polymers in the past[104] was employed. The base form of the polymer was refluxed with a 37 wt% solution of tributylamine in dioxane for 18 hours leading, yet again, to a resin (DC-02-197) containing no anion exchange sites.

Attention then turned to less bulky amines. An initial attempt with triethylamine lead to material which appeared to have aminated (DC-02-202). Due to a mechanical problem, the solvent escaped during the course of the reaction and the beads crushed making a complete analysis difficult. However, a Cl elemental analysis of material eluted with sodium nitrate (replacing any $Cl^-$ counterions with $NO_3^-$) revealed no chlorine. At the time, this was taken as evidence of complete amination (an idea later discounted). A second attempt was made with triethylamine in addition to tripropylamine (DC-02-219A&B). The procedure used was developed earlier[104] and

involved refluxing the base form of the partially functionalized resin with the appropriate amine dissolved in an alcohol (triethylamine in ethanol, tri-n-propylamine in isopropanol). Again, no anion exchange capacity was noted. Even more surprising, Cl elemental analysis revealed that the partially functionalized resins no longer contained chlorine. A side reaction was leading to the destruction of the benzyl chloride sites before the amination could occur.

Since amination with trimethylamine had occurred quite readily in the past (DC-02-012), the reaction was repeated (DC-02-243A) using partially functionalized resin prepared by the modified method in conjunction with another attempt with triethylamine (DC-02-243B). Both reactions were allowed to run at room temperature to decrease the likelihood of side reactions for periods of 44 ($Me_3N$) and 120 ($Et_3N$) hours. No amination occurred with triethylamine and no chlorine remained on the resin. Only a small amount of functionalization occurred with trimethylamine (TAEC = 0.56 mequiv/g). Given that partially functionalized resins prepared by the older method aminate easily, these results indicated that the newer method of partially functionalizing the network yields resins with significantly altered accessibility. This was supported by the fact that the less bulky dimethylamine also failed to aminate the partially functionalized phosphonic acid resin (DC-02-248B).

A 10% cross-linked macroporous polymer (rather than 2% cross-linked gel) was partially functionalized and reacted with trimethylamine to yield a resin (DC-02-248A) with a suitable TAEC but a low phosphorus capacity (3.07 and 0.55 mequiv/g respectively). The lower degree of functionalization of this resin prior to amination made it difficult to compare its behavior with that of the previous polymers. Using partially functionalized resin in the acid rather than the base form made little difference in the properties of the resin when aminated with trimethylamine (compare DC-02-243A and DC-02-249). A 5% cross-linked partially functionalized phosphonic acid resin was prepared and reacted with both trimethyl and tributylamine leading to only a low level of amination with trimethylamine (DC-02-257) and none with tributylamine (DC-02-259). The trimethylamine resin had a suitable phosphorus capacity but also possessed a very low g/g value of 0.65.

In order to determine if hydroxide present in the aqueous amine solution ($Me_3N$ is 25wt% in $H_2O$) was attacking the benzyl chloride sites to form benzyl alcohol groups, DC-02-257 was reacted with $PCl_5$ in dioxane, rinsed with nitric acid to remove chloride counterions and analyzed for Cl. No Cl was found on the resin indicating that benzyl alcohol sites were not formed.

Despite this, it was shown that hydroxide can displace the chloride present on the resin by allowing poly(vinylbenzyl chloride) to stir in water

adjusted to pH 12.52 (the approximate pH of 25% $Me_3N$) for 24 hours. The pH of the water dropped to 6.49 and the Cl capacity of the resin decreased from 6.32 to 3.13 mequiv/g. A control experiment with polystyrene beads showed no decrease in pH.

Two additional aminations were conducted under conditions which would decrease the amount of hydroxide present. In the first (DC-03-019) the pH of the trimethylamine solution was adjusted to 5 prior to reaction with the partially functionalized resin. It was thought that the equilibrium present between amine and ammonium ions would be sufficient to supply enough unprotonated amine to complete the reaction. No amination occurred, but the chlorine capacity was not reduced to zero as before. In the second experiment (DC-02-030) the trimethylamine solution was saturated with NaCl prior to the reaction in order to increase the ionic strength of the solution and thus decrease the amount of hydroxide produced. A large number of the beads fragmented during this experiment, but a moderate degree of amination did occur (TAEC = 1.47 mequiv/g). The characteristics of the resins produced by these reactions have been summarized in Table 14.

Since the phosphonic acid sites are deprotonated, either with sodium hydroxide in a separate step prior to amination or by the amine itself during the reaction, the possibility that the polymer was too hydrophilic to allow the less water soluble amine access to the reactive center was investigated. To increase the hydrophobicity of the network, the resin was partially

Table 14
Characterization of Partially Functionalized Phosphonic Acid Resins
After Attempted Amination

| Resin | Amine | % Solids | Capacities (mequiv/g) | | | |
|---|---|---|---|---|---|---|
| | | | TAEC | Cl Capacity | P Capacity | g/g |
| DC-02-248B | Dimethyl | 56.9 | 0.00 | -- | -- | -- |
| DC-02-243A | Trimethyl | 50.0 | 0.56 | -- | -- | -- |
| DC-02-248A | " | 28.8 | 3.07 | 3.17 | 0.55 | 0.95 |
| DC-02-249 | " | 49.4 | 0.54 | -- | -- | -- |
| DC-02-257 | " | 25.5[a] | 0.85[a] | 1.03[a] | 1.85[a] | 0.66 |
| DC-03-019 | " | 63.9 | 0.00 | 3.29 | -- | -- |
| DC-03-030 | " | 38.9 | 1.47 | -- | -- | -- |
| DC-02-202 | Triethyl | -- | 0.00 | -- | -- | -- |
| DC-02-219A | " | 47.3 | 0.00 | 0.00 | 1.59 | |
| DC-02-243B | " | 50.8 | 0.00 | -- | -- | -- |
| DC-02-219B | Tri-n-propyl | 49.9 | 0.00 | 0.00 | 1.87 | |
| DC-02-169 | Tri-n-butyl | 68.7 | 0.00 | -- | -- | -- |
| DC-02-175 | " | 58.8 | 0.00 | -- | -- | -- |
| DC-02-183 | " | 62.0 | 0.00 | -- | -- | -- |
| DC-02-197 | " | 58.9 | 0.00 | -- | -- | -- |
| DC-02-259 | " | 31.2 | 0.00 | 0.62 | -- | -- |

[a]average of two values

functionalized with dibutylphosphonate sites rather than the parent acid. This was accomplished by quenching the reaction with n-butanol instead of water as described in Chapter 1 for the fully functionalized dibutylphosphonate ester. The resin prepared in this manner was found to have a phosphorus capacity of 1.23 mequiv/g and an acid capacity of 0.07 mequiv/g in accordance with the formation of diester sites, but repeated Cl elemental analyses showed the absence of benzyl chloride sites. Not surprisingly, no amination occurred when this material was treated with tributylamine. This proved to be a key factor in understanding the behavior of this type of resin. The synthesis of the dibutyl ester proceeds under acidic conditions so it is not possible that hydroxide replaced the chlorine on the resin. The functionalized polymer was subjected to an extensive toluene wash (including an overnight stir) prior to the butanol quench and to another extensive wash with butanol after formation of the ester sites. The synthesis was repeated and samples were taken at various points in the procedure in order to determine at what point chlorine was lost from the resin. Samples were taken prior to quenching both before and after the toluene wash, after the first and second quench solutions had been added, and after the butanol washes and conditioning (finished resin). The results of the chlorine elemental analyses were quite surprising. Prior to the toluene wash the resin had a Cl capacity of 3.72 mequiv/g. After the overnight toluene wash the capacity had fallen to 0.54 mequiv/g. No significant decrease was noted

after this point (finished product: 0.51 mequiv Cl/g). In order to show that the Cl capacity of the resin prior to washing with toluene was due to covalently bound chlorine, the resin was Soxhlet extracted with water and reanalyzed. The Cl capacity decreased slightly to 3.36 mequiv/g indicating that a large portion of the measured Cl capacity was due to covalently bound chlorine.

Based on this experiment and the behavior of the partially functionalized phosphonic acid resin during attempted aminations and Williamson ether formations (see Chapter 3), it was hypothesized that the iron trichloride catalyst led to secondary cross-linking via the reaction shown in Figure 66. The formation of benzyl cations during the reaction of benzyl chloride, $PCl_3$, and $FeCl_3$ has been reported[107] and it is thought that dioxane promotes this reaction by solubilizing the $FeCl_3$ and allowing ready access to all available sites. Given the cross-linked nature of the material, spectroscopic evidence ($^{13}C$ NMR spectroscopy for example) was not easily obtainable as the structures formed would not give rise to well-resolved peaks. Standard wet chemical techniques (% Solids and capacity determinations) strongly suggest that this secondary cross-linking reaction is responsible for the lower reactivity/accessibility of the partially functionalized resins made with dioxane. A comparison of the two types of partially functionalized resin shows that those made in the presence of dioxane generally have higher percent solids values, indicating higher cross-link

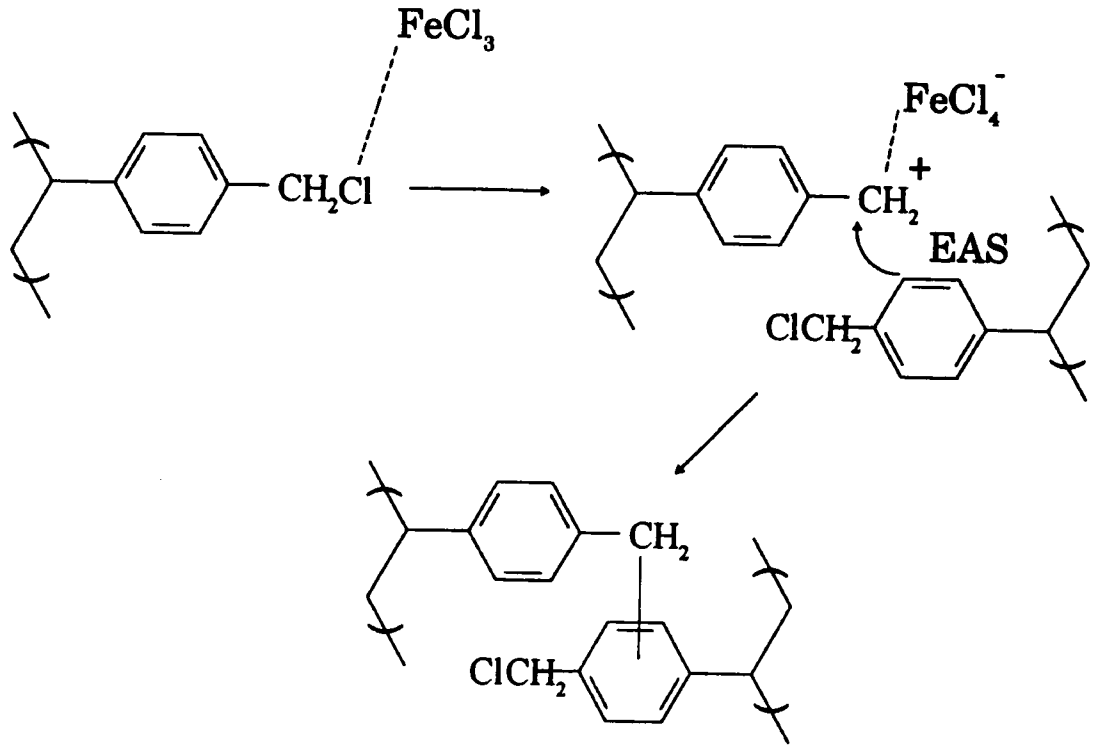



Figure 66. $FeCl_3$ promoted secondary cross-linking.

levels, and lower g/g values, indicating that unanalyzed sites are being formed on the polymer.

Reduction of Secondary Cross-linking

If this hypothesis is correct, then reducing the amount of secondary cross-linking would facilitate further reaction of the network. The possibility of using solvents other than dioxane was investigated in order to see if the solvent had a strong affect on the amount of secondary cross-linking which occurred. Resins were synthesized using standard conditions and either 1,2-dichloroethane, THF, or chlorobenzene as the swelling solvent. Of these, only THF dissolved the iron trichloride. The interaction between THF and $FeCl_3$ was quite strong. After the 18 hour swelling period, a sticky solid had formed in the reaction flask and the beads were imbedded in what was believed to be poly(tetrahydrofuran) formed by Lewis acid ($FeCl_3$) catalyzed ring opening polymerization. The properties of the other two resins are shown in Table 15. Although additional work is needed to determine optimum conditions for production of resins with the desired capacity, both 1,2-dichloroethane and chlorobenzene produced resins with good properties. The only adverse affect discovered was the presence of a peak at -1.84 ppm in the solid-state $^{31}P$ NMR spectrum of the resin made with chlorobenzene. This is believed to be a small molecule phosphate species,

Table 15

Characterization of Partially Functionalized Phosphonic Acid Resin Made with 1,2-Dichloroethane and Chlorobenzene

| Resin | Solvent | % Solids | Capacities (mequiv/g) | | | g/g |
|---|---|---|---|---|---|---|
| | | | Acid Capacity | P Capacity | Cl Capacity | |
| DC-04-126 | 1,2-dichloroethane | 47.5 | 5.94 | 3.52 | 1.40 | 0.94 |
| DC-04-134B | chlorobenzene | 55.1 | 1.53 | 1.02 | 5.01 | 1.00 |

but it was decided not to continue work with this resin until other possible routes of synthesis had been examined.

It was thought that the secondary cross-linking could be limited by shortening either the swelling or the functionalization period. In order to see if this could be accomplished without a severe decrease in the degree of functionalization, a study was undertaken with shortened swelling and reaction periods. DC-04-156 was synthesized using a standard 18 hour swelling period followed by a one, rather than four, hour functionalization at 40 °C. The analyses show that the resin is functionalized to almost the same degree as with a four hour functionalization, but the high g/g value (0.95) indicates that little secondary cross-linking has occurred. In order to determine if functionalization was occurring only on the surface, a second reaction was completed under identical conditions using smaller copolymer (-100+200 mesh rather than -60+100 mesh). If the reaction was occurring only on the surface, then the smaller resin would show a higher weight capacity since the surface area per gram is increased for the smaller resin. The results of this experiment were inconclusive in that a higher phosphorus capacity was obtained with the smaller resin but the acid capacity remained unchanged.

The effect of shortening the swelling period was also investigated. A synthesis was performed (DC-04-172) in which the swelling period was shortened to 2 hours. This was followed by a standard 4 hour, 40 °C

functionalization. The results indicated that a considerable portion of the functionalization occurs during the swelling period. The phosphorus capacity of the resin is diminished by 0.36 mequiv/g when compared with a typical resin prepared with an 18 hour swell and a 4 hour reaction period (DC-04-091). The g/g value of 0.90 is higher than that of polymers prepared with a full swelling period but it is not as high as that of the polymer prepared with a shortened reaction time.

Next, the effect of shortening both the swelling and the reaction periods was investigated. Two different size fractions (-60+100 and -100+200) of the same copolymer were functionalized using a 2 hour swelling period followed by a 1 hour reaction at 40 °C. The resins had similar % solids values, phosphorus and chlorine capacities, and had high g/g values. The acid capacities differed however, with the smaller resin having the higher acid capacity. It was thought that perhaps the resins were not very accessible to the base solution used to determine the acid capacity due to the low level of functionalization (≈0.90 mequiv/g). The larger surface area of the smaller resin would then result in a higher measured acid capacity. To test this, the capacities were redetermined in a swelling solvent (60% aqueous dioxane) using KOH as the base. In agreement with uniform functionalization, the acid capacities of the two resins were equivalent. Several other partially functionalized resins were synthesized with shortened reaction and swelling times. In an attempt to

produce a resin with a higher phosphorus capacity, the reaction period was increased to two hours in some cases. Unfortunately, the g/g levels, while higher than those of resins produced at longer reaction times, were not consistently as high as in the preliminary experiments. Attempts at further functionalization of these resins met with mixed success as is described in Chapter 3, and no further work was done on the production of a partially functionalized phosphonic acid resin. The properties of those resins produced are shown in Table 16.

In order to determine if the partially functionalized phosphonic acid resins with high g/g values would indeed react more readily with amines, two samples of DC-05-116 were reacted with trimethyl and tributylamine. The results, shown in Table 17, reveal that amination occurred quite readily.

The nitrogen analysis of DC-05-134 was thought to be in error since it was higher than both the TAEC and the Cl capacity. This would indicate that not all amine sites have chloride as their counterion. Since the resin was conditioned with 1 N HCl prior to analysis, this was thought to be very unlikely. The nitrogen analysis was repeated and gave essentially the same result (2.18 mequiv/g). Since the resin was eluted with water after conversion to the chloride form, it was thought that perhaps some $Cl^-$ was being lost during the water wash. Elution with only 250 mL of water rather than 1 L did not result in a significant change in the TAEC (1.77 mequiv/g). It was determined that no additional $Cl^-$ was eluted when 2 L of $NaNO_{3(aq)}$

Table 16

Characterization of Partially Functionalized Phosphonic Acid Resins
Made with Shortened Swelling and Reaction Times

| Resin | Swelling Period (hrs) | Reaction Period (hrs) | % Solids | Capacities (mequiv/g) | | | g/g |
|---|---|---|---|---|---|---|---|
| | | | | Acid Capacity | P Capacity | Cl Capacity | |
| DC-04-156 | 18 | 1 | 64.1 | 2.66 | 1.41 | 4.19 | 0.953 |
| DC-04-172 | 2 | 4 | 63.9 | 2.58 | 1.45 | 3.82 | 0.903 |
| DC-04-177[a] | 18 | 1 | 58.5 | 2.68 | 1.59 | 3.43 | 0.870 |
| DC-04-184A | 2 | 1 | 52.9 | 1.33[b]/1.66[c] | 0.92 | 5.00 | 0.981 |
| DC-04-184B[a] | 2 | 1 | 49.5 | 1.59[b]/1.66[c] | 0.89 | 4.99 | 0.973 |
| DC-04-216 | 2 | 1 | 53.1 | 1.58[c] | 0.91 | 4.82 | 0.950 |
| DC-05-094 | 2 | 1 | 57.5 | 2.04[c] | 0.99 | 4.98 | 0.992 |
| DC-05-116 | 2 | 1 | 49.9 | 1.61[c] | 0.76 | 5.07 | 0.959 |
| DC-05-132 | 2 | 1 | 55.9 | 1.20[c] | 0.69 | 5.13 | 0.954 |
| DC-05-207 | 2 | 2 | 68.2 | 2.55[c] | 1.40 | 3.87 | 0.901 |
| DC-05-253 | 2 | 2 | 68.1 | 2.53[c] | 1.44 | 3.49 | 0.849 |
| DC-05-264 | 2 | 2 | 68.5 | 2.38[c] | 1.26 | 3.84 | 0.867 |

[a]-100+200 mesh resin
[b]measured in water
[c]measured in 60% aqueous dioxane

Table 17

Characterization of Aminated Partially Functionalized Phosphonic Acid Resin

| Resin | Amine | % Solids | Capacities (mequiv/g) | | | | g/g[a] |
|---|---|---|---|---|---|---|---|
| | | | P Capacity | Cl Capacity | N Capacity | TAEC | |
| DC-05-124 | Trimethyl | 27.6 | 0.39 | 3.61 | 3.76 | 3.52 | 0.91 |
| DC-05-134 | Tributyl | 49.3 | 0.58 | 1.74 | 2.17 | 1.70 | 0.88 |

[a]Based on phosphorus and nitrogen capacities

was used in the TAEC analysis and no increase in the exchange capacity was noted when 2 L of HCl were used to convert the resin to the chloride form. These results indicate that all sites capable of having chloride as a counterion are converted to that form by the procedure used and that the chloride is quantitatively removed during the TAEC analysis. Finally, the nitrogen and chlorine capacities were redetermined yielding essentially the same values (2.06 and 1.72 mequiv/g, respectively). Later, it was determined that a portion of the amine sites have the phosphonate anion as the counterion through the use of solid-state $^{31}P$ NMR spectroscopy (Chapter 6), explaining the discrepancy in the exchange and elemental nitrogen capacities.

## Conclusions

While some success has been achieved in the synthesis of bifunctional Class III resins, the project is still hindered by the lack of a well-characterized partially functionalized phosphonic acid resin. It is felt that an alternate method of producing the resin will have to be developed, possibly copolymerization of vinylbenzylphosphonic acid with vinylbenzyl chloride, before satisfactory results will be obtained. In addition, the feasibility of controlling the degree of amination should be investigated so that the Class III resins could be made by partial amination followed by phosphorylation of the remaining sites.

# CHAPTER 3

## CLASS II DUAL MECHANISM BIFUNCTIONAL POLYMERS CONTAINING PENTA(ETHYLENE GLYCOL) GROUPS

### Introduction

Yet to be discussed are those Class II polymers which utilize a penta(ethylene glycol) (PEG) group as the coordinating ligand. Warshawsky and co-workers, building on the work of Pederson[108], first published the concept and synthesis of polymer supported "pseudocrown ether" ligands and characterized the affinity of these polymers toward anionic transition metal halogen complexes and both protic and Lewis acids.[109-111] Similar resins have been used for the separation of alkali and alkaline earth metal cations,[112] the extraction of mercuric chloride,[113] and as phase transfer catalysts.[114] While most researchers have used polystyrene as the support for such ligands, a report has appeared[115] in which the attachment of ethylene glycol oligomers to a polyphosphazene backbone is described.

As a method of enhancing the utility of crown ethers, Bartsch and co-workers have investigated the incorporation of an acidic group into the crown ether structure.[116-119] The presence of an ionizable group resulted in compounds which displayed both enhanced efficiencies and selectivities in the extraction of alkali and alkaline earth metal cations. In subsequent work,[120-122]

the extraction properties of polymers formed by condensation polymerization of formaldehyde with dibenzo-crown ethers containing a carboxylic group were examined.

While a report has appeared[123] describing the thermal generation of carboxylic acid sites from linear, polystyrene-supported ethylene glycol oligomers, no study of the properties of polymers which contain both acidic groups and pseudocrown ether structures has been completed. An investigation of polymers of this type was warranted due to the enhanced properties of crown ethers which contain ionizable groups and the lower expense of pseudocrown ether resins in comparison to polymers which contain well defined crown ether units. The work reported here is an extension (and reexamination of selected portions) of research initiated in this laboratory.[106] The synthesis and characterization of bifunctional pseudocrown ether resins containing penta(ethylene glycol) ligands and either carboxylic or phosphonic acid groups as well as their monofunctional counterparts are described. The results of an initial set of contact studies are also reported.

Synthesis of Penta(Ethylene Glycol) Resins

The synthesis of penta(ethylene glycol) resins (PEG resins) was achieved using the method developed by Warshawsky and co-workers[109] and later used in this laboratory to produce similar resins for use in metal ion extractions.[106] Briefly, poly(vinylbenzyl chloride) cross-linked with

divinylbenzene is swollen in dioxane and allowed to react with the anion of penta(ethylene glycol) which is formed *in situ* by treatment of PEG with sodium hydride (Figure 67). It is known[109] that synthesis of PEG resins via this method leads to a mixture of linear PEG groups and pseudocrown PEG sites as shown in Figure 68. Due to the extreme expense of commercial penta(ethylene glycol), it was necessary to isolate the needed material from a mixture of low molecular weight poly(ethylene glycols). This isolation was accomplished by vacuum distillation of commercial poly(ethylene glycol) with an average molecular weight of either 200 or 300.

As a result of a discrepancy in the reported values of the boiling point of the pentamer,[106,109] it was necessary to verify that the results obtained previously with this class of resins were correct. Many of the synthetic conditions and analyses techniques were reexamined with material known to be the pentamer. The effect of both the PEG/Cl ratio and the length of the reaction were studied as was the effect of the purity of the dioxane. The analysis for total PEG capacity by chromic acid oxidation and the analysis for -OH groups (and thus linear PEG capacity) by reaction with $PCl_5$ were extensively examined. An alternate method for the analysis of the linear PEG sites was also investigated and later adopted as an improved method for the analysis.

First, the purity of the material obtained via vacuum distillation was verified. A sample of the distilled material (boiling point = 152-160 °C at 0.25

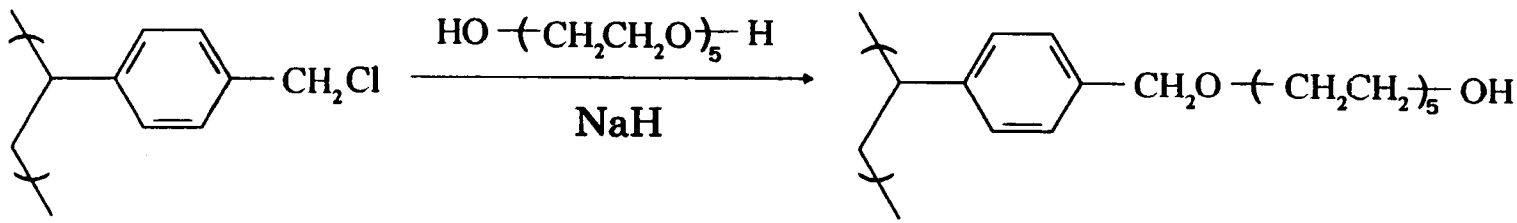



Figure 67. Synthesis of penta(ethylene glycol) resin.

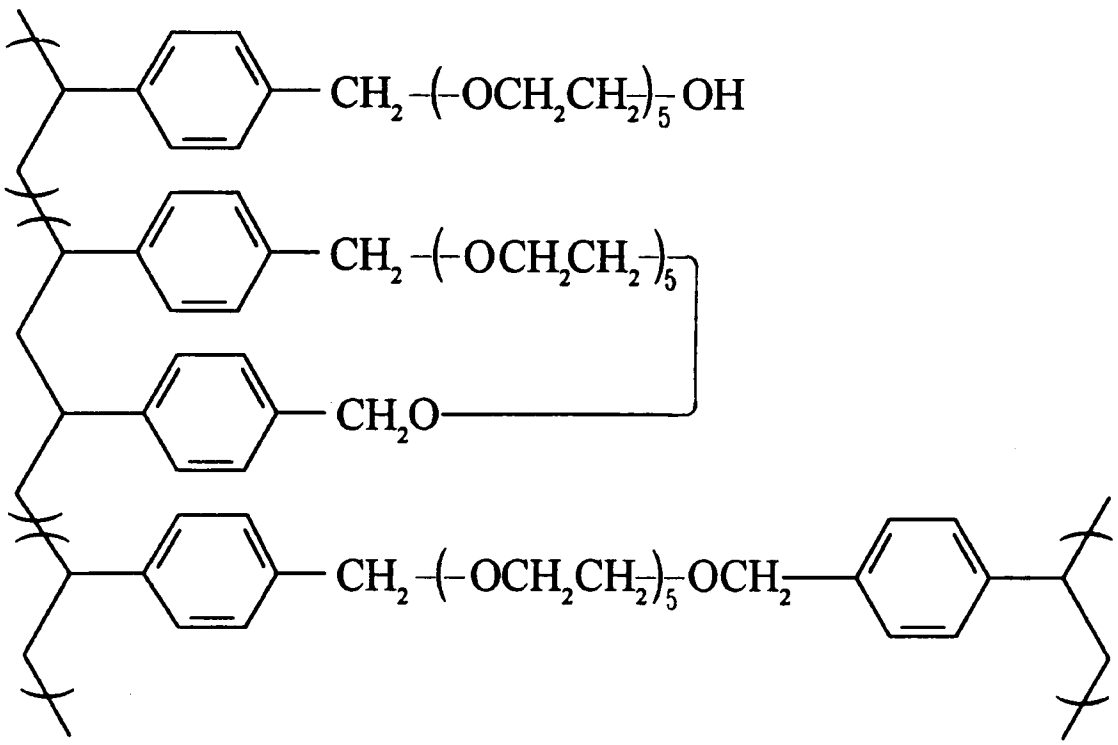



Figure 68. Structure of penta(ethylene glycol) resin.

torr, literature boiling point = 178-182 °C at 1.5 torr[109] ) was submitted for mass spectrometric analysis along with a sample of the commercially purified pentamer (Aldrich). The spectra reveal that a single vacuum distillation yields pentamer with a purity comparable to that of the commercial product. Close inspection of the mass spectra (Figure 69) shows the presence of other oligomers ranging from the trimer up through the nonamer in both samples. Note that all peaks appear one unit higher than their true molecular mass due to the addition of a proton during ionization. Due to the close similarity of the samples, all of the pentamer used in this project was purified with a single vacuum distillation.

The effect of the PEG/Cl ratio was studied by varying the amount of PEG which was allowed to react with a constant amount of 2% cross-linked poly(vinylbenzyl chloride) (VBC). The VBC used was prepared in-house by suspension polymerization of vinylbenzyl chloride and technical grade divinylbenzene. All resins used for these studies were Soxhlet extracted with toluene and sieved to isolate the -60+100 mesh cut.

The copolymer was suspended in dioxane and allowed to swell for one hour. Following this, a solution of the appropriate amount of penta(ethylene glycol) (PEG) dissolved in dioxane was quickly added and the required amount of NaH (60% in mineral oil) was slowly added to the mixture. Contrary to previous work,[106] no clumping of the resin was noted even when the PEG solution was added quickly. The VBC used in these studies was

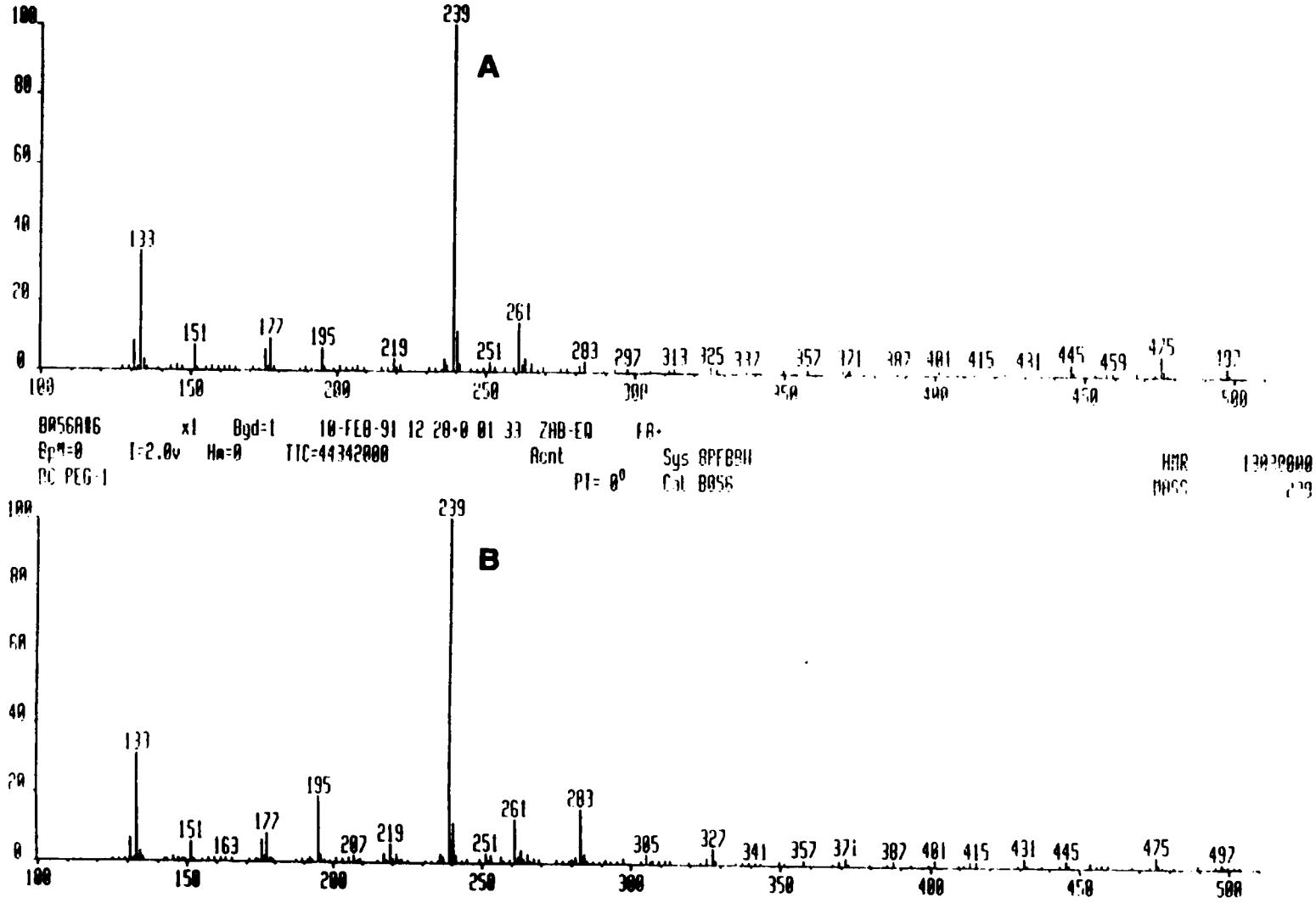



Figure 69. Mass spectra of commercial (A) and distilled (B) penta(ethylene glycol).

Soxhlet extracted with toluene prior to the reaction to remove the small amount of linear VBC present after the polymerization. The presence of these oligomeric impurities is thought to have been responsible for the clumping observed previously. The mixtures were heated to reflux over a one hour period and held at that temperature for 48 hours. The resins were then carefully rinsed with a small amount of $H_2O$ to remove any unreacted NaH. Following this the resins were conditioned by elution with 1 L of dioxane followed by 2 L of $H_2O$. Later, it was discovered that a 17 hour Soxhlet extraction with dioxane could replace the 1 L elution and had the advantage of consuming much less dioxane. After conditioning, the resins were characterized by determining their % solids values along with their linear PEG and residual Cl capacities.

An unusual property of the PEG resins was noted during the course of these analyses. After drying in a 110 °C oven, the resins were soft and sticky rather than sandy as expected. At first, it was thought that unbound PEG remained trapped within the resin leading to the observed softening. The resins were Soxhlet extracted with dioxane and reanalyzed. However, this procedure resulted in little change in the resin. In order to determine if Soxhlet extraction could remove unbound PEG, a sample of VBC was shaken with a solution of PEG in dioxane. The resin was rubbery after drying, but returned to its original state after Soxhlet extraction. It is now thought that the softness of the dried resin was due to the plasticization of the bead by PEG chains

which were thermally cleaved from the resin during the percent solids determination.[123] Results of the various analyses are presented in Table 18. Not surprisingly, the Cl capacities of the resins clearly indicate that a PEG/Cl ratio of at least 1.00/1.00 is necessary for complete reaction. From the values of the total and linear PEG capacities it is possible to calculate the pseudocrown PEG capacity and the ratio of linear to pseudocrown PEG sites. The linear/pseudocrown ratio was essentially unchanged after a 0.50/1.0 ratio of PEG/Cl was reached but, as expected, the lowest PEG/Cl ratio resulted in the formation of a greater percentage of pseudocrown sites.

For these reactions, the dioxane (99+%, Aldrich) was used without further purification. Any traces of water present would form hydroxide ion when treated with NaH. Hydroxide could then replace chlorine on the resin, leading to the measurement of elevated linear PEG capacities. Warshawsky[109] reports that distilled dioxane, dried over anhydrous sodium sulfate, performed as well as "superdry distilled dioxane" in the synthesis of resins of this type. In order to determine if the distillation was necessary, a reaction was performed using distilled dioxane which had been dried with anhydrous sodium sulfate overnight. The results are compared with those obtained from an identical reaction which utilized the Aldrich material as received. The PEG/Cl ratio was 1.0/1.0, the NaH/PEG ratio was 1.1/1.0, and a 48 hour reflux was employed. The results of the analyses are presented in Table 19. Notice that while the linear PEG capacity of the resin made with dry dioxane is slightly lower than that

Table 18

Characterization of PEG Resins Produced with Varying PEG/Cl Ratios

| Resin | PEG/Cl Ratio | % Solids[a] | Capacities (mequiv/g) | | | | Linear/PC Ratio |
|---|---|---|---|---|---|---|---|
| | | | Cl Capacity[a] | Total PEG Capacity | Linear PEG[a] Capacity | Pseudocrown PEG Capacity | |
| DC-03-187A | 0.25/1.0 | 74.6 | 3.56 | 1.27 | 0.30 | 0.97 | 24/76 |
| DC-03-187B | 0.50/1.0 | 68.9 | 2.01 | 1.78 | 0.87 | 0.91 | 49/51 |
| DC-03-187C | 1.0/1.0 | 50.9 | 0.00 | 2.46 | 1.29 | 1.17 | 52/48 |
| DC-03-187D | 2.0/1.0 | 47.6 | 0.00 | 2.58 | 1.22 | 1.36 | 47/53 |

[a] Average of two determinations

Table 19

Comparison of PEG Resins Made with Dry and Unpurified Dioxane

| Resin | Dioxane Purity | % Solids | Capacities (mequiv/g) | | | | Linear/PC Ratio |
|---|---|---|---|---|---|---|---|
| | | | Cl Capacity | Total PEG Capacity | Linear PEG Capacity | Pseudocrown PEG Capacity | |
| DC-04-141 | As Received | 59.8 | 0.00 | 2.04 | 1.34 | 0.70 | 66/34 |
| DC-04-174 | Distilled, Dry | 55.2 | 0.00 | 2.20 | 1.26 | 0.94 | 57/43 |

of the resin made with unpurified dioxane, it is still higher than those of the DC-03-187 series of resins, which were also made with unpurified material. Therefore, removal of any water present did not lead to a lower number of -OH groups on the resin. The differences which are present are not significant enough to warrant the extra purification step in future work. All other PEG resins were made using dioxane (99+ %) as received from Aldrich.

The effect of the length of reaction was studied using a constant PEG/Cl ratio of 1.0/1.0 and NaH/PEG ratio of 1.1/1.0. All reactions were conducted at reflux in a constant volume of dioxane (150 mL). Following functionalization, the resins were treated as before except that a 17 hour Soxhlet extraction with dioxane replaced the dioxane elution. The results of the analyses are shown in Table 20. The data indicate that the reaction is complete within twelve hours and that little difference exists among the resins. This being the case, it was decided that all future PEG resin syntheses would be conducted using a 24 hour reaction period to insure complete functionalization.

Several other PEG resins were synthesized for the purpose of providing material for contact studies. A summary of their properties is presented in Table 21. Of interest is that both DC-05-189 and DC-06-130 were large batches (40.00 g). Prior attempts to synthesize large batches of PEG resin had proven unsuccessful.[106]

Table 20

Characterization of PEG Resins Produced with Varying Reaction Lengths

| Resin | Reaction Length (hrs) | % Solids | Capacities (mequiv/g) | | | | Linear/PC Ratio |
|---|---|---|---|---|---|---|---|
| | | | Cl Capacity | Total PEG Capacity | Linear PEG Capacity | Pseudocrown PEG Capacity | |
| DC-04-224A | 12 | 58.2 | 0.00 | 2.03 | 1.35 | 0.68 | 67/33 |
| DC-04-224B | 24 | 55.1 | 0.00 | 2.11 | 1.32 | 0.79 | 63/37 |
| DC-04-224C | 48 | 55.4 | 0.00 | 2.15 | 1.51 | 0.64 | 70/30 |
| DC-04-224D | 96 | 56.8 | 0.00 | 2.13 | 1.34 | 0.79 | 63/37 |

Table 21

Characterization of PEG Resins Produced for Contact Studies

| Resin | % Solids | Capacities (mequiv/g) | | | | Linear/PC Ratio |
|---|---|---|---|---|---|---|
| | | Cl Capacity | Total PEG Capacity | Linear PEG Capacity | Pseudocrown PEG Capacity | |
| DC-02-040[a] | 50.9 | 0.00 | 2.37 | 1.24 | 1.13 | 52/48 |
| DC-05-109[b] | 45.5 | 0.00 | 2.03 | 0.97 | 1.06 | 48/52 |
| DC-05-189 | 59.8 | 0.00 | 2.11 | 1.29[c] | 0.82[c] | 61/39 |
| DC-06-130 | 58.5 | 0.00 | 2.06 | 1.00 | 1.06 | 49/51 |

[a] Synthesized using a 48 hour reflux and material now believed to be predominantly hexamer and heptamer

[b] Synthesized using 5% cross-linked MR VBC

[c] Average of two determinations

Characterization of PEG Resins: Total PEG Capacity

Characterization of the PEG resins presented a challenge due to the absence of directly titratable groups. Others in the field have reported capacities based on the increase in mass which occurs during functionalization.[109] While this method is effective, one must assume that no side reactions occur and the necessity of isolating all of the functionalized resin can result in complications during the work up of the resin. A method has been reported[124] which utilizes $BBr_3$ to cleave polyglycol chains and GC analysis to quantify the fragments. While promising, $BBr_3$ is very hazardous and difficult to handle. A safe, effective procedure was desired. A method was developed in this laboratory which utilizes an oxidation of the PEG chains with chromic acid followed by a potentiometric titration of the resulting solution to determine the residual chromic acid concentration. Analysis conditions have been extensively studied prior to this work.[106] It was found that oxidation of the resin at room temperature for five days with 0.6000 N $K_2Cr_2O_7$ in 5.4 M sulfuric acid allowed for determination of the PEG capacity using the following expression:

$$\frac{(Vol.\ chromic\ acid)(N\ chromic\ acid) - 10(Vol.\ FeSO_4)(N\ FeSO_4)}{52(wt.\ dry\ resin)}$$

In this case 10 % of the total volume of chromic acid has been titrated with $FeSO_4$ and the 52 is an empirically determined value[106] which represents the

number of electrons transferred to each PEG chain. Given the earlier discrepancy in the boiling points it was suspected that this constant had been determined using material which was predominantly hexamer or heptamer rather than pentamer. Also, assuming that the polyglycol and the point of attachment to the backbone are oxidized to oxalic acid and a carboxylic acid site, respectively, the theoretical number of electrons transferred is 44 for a linear PEG unit and 48 for a pseudocrown unit. This is complicated by the fact that the technical divinylbenzene used as a cross-linking agent is only 55.4% DVB with the remainder being mainly ethylvinylbenzene. These impurities are oxidizable and will increase the observed number of electrons transferred. Also, as seen in the mass spectrum of the distilled material, the PEG has a small degree of polydispersity which will further complicate the analysis. Due to these problems, it was decided that the chromic acid oxidation technique should be reexamined to verify that correct capacities were being obtained.

The first variable to be reexamined was the length of time required for complete oxidation of the PEG groups. A sample of fully functionalized PEG resin (DC-03-187D) was treated with chromic acid at room temperature for periods of 30, 72, 120, and 240 hours. As shown in Figure 70, the measured PEG capacity (assuming 52 electrons transferred per unit) increases slowly at contact times longer than 30 hours. Doubling the contact time from 120 to 240 hours resulted in an increase of only 0.15 mequiv/g in the measured capacity. From these results, it has been concluded (in agreement with previous results

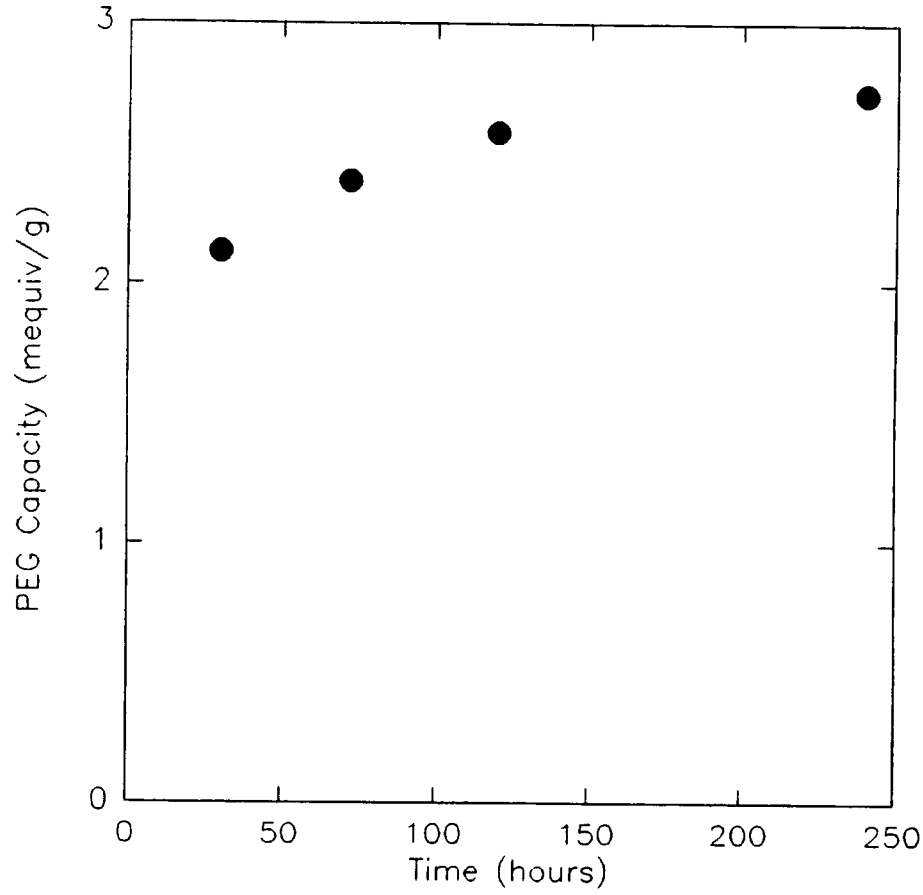



Figure 70. Time dependence of the PEG capacity as measured by chromic acid oxidation.

from this lab) that the optimum contact time is 120 hours. This provides an accurate measure of the capacity of the resins without requiring an inconveniently long period of time.

The DC-03-187 series of resins were each oxidized for a period of 120 hours and the capacities were calculated using values of 52 (previously determined empirically) and 44 (theoretical value for a linear PEG unit) for the number of electrons transferred to each PEG unit (Table 22). The maximum theoretical capacity (assuming that all of the PEG sites are linear) is 2.72 mequiv/g. Clearly, more than 44 electrons are being transferred to each PEG chain since the capacities of the two fully functionalized resins are higher than the theoretical value.

As control experiments for the basic oxidation technique, a series of small molecules were oxidized with chromic acid and the number of electrons consumed per milliequivalent of compound was determined as a function of time (Table 23). Both penta(ethylene glycol) and 1,4-dioxane show values very close to the theoretical number of electrons transferred after 24 hours. At long reaction times it is possible for the oxalic acid which forms to be further oxidized to carbon dioxide. Only the 120 hour oxidation of 1,4-dioxane showed any increase in pressure inside the Erlenmeyer flask which would indicate the formation of $CO_2$. It should be noted that no buildup of pressure was ever noted when PEG resin was oxidized. The oxidation of both toluene and ethylbenzene was hindered by the fact that neither was soluble in the chromic

Table 22

Calculated PEG Capacities Using Varying Values for the Number of Electrons Transferred to Each PEG Unit

| Resin | Capacity (mequiv/g) | |
|---|---|---|
| | Using 44 $e^-$ | Using 52 $e^-$ |
| DC-03-187A | 1.50 | 1.27 |
| DC-03-187B | 2.10 | 1.78 |
| DC-03-187C | 2.91 | 2.46 |
| DC-03-187D | 3.05 | 2.58 |

Table 23

Oxidation of Small Molecules with Chromic Acid

| Compound | Theoretical Value ($e^-$/mequiv compound) | Reaction Length (hours) | | | |
|---|---|---|---|---|---|
| | | 1 | 6 | 24 | 120 |
| penta(ethylene glycol) | 40 | 28.85 | -- | 39.38 | 42.86 |
| 1,4-dioxane | 16 | -- | 7.20 | 14.25 | 17.27 |
| toluene | 6 | -- | 0.22 | 1.44 | 4.66 |
| ethylbenzene | 10 | -- | 0.31 | 2.20 | 5.42 |

acid solution. Two layers were visible even after five days and the odor of the unoxidized compounds was present in both samples, along with colorless crystals assumed to be benzoic acid (no characterization was attempted). It is thought that ethyl groups present on the resin (from ethylvinylbenzene) will be more readily oxidized due to the presence of hydrophilic PEG groups which will increase the accessibility of the resin to chromic acid.

The small molecule results indicate that accurate values for the number of electrons transferred per molecule can be obtained in cases where the reagent has accessibility to the substrate. The chromic acid oxidation technique is therefore an accurate measure of the number of electrons transferred to the PEG chains. The only variable which had not been confirmed at this point was the number of electrons transferred per PEG unit.

Since it was clear that more than 44 electrons are transferred to each unit and the use of 52 electrons per PEG unit yielded capacities close to the theoretical values, it was decided to compare the results obtained using the chromic acid oxidation technique and those from a careful measurement of the increase in mass during functionalization.

The resin was synthesized using a PEG/Cl ratio of 1.0/1.0 and a 48 hour functionalization at reflux and treated as described earlier. Great care was taken at each step to transfer all of the resin to the next container. The resin was Büchner dried and the mass of the entire sample was recorded prior to removing a sample for a percent solids determination. The final weight of the

resin was determined by multiplying the Büchner dried weight by the percent solids value. The amount of PEG incorporated was then calculated as described by Warshawsky.[109]

$$\frac{(W_p - W_s) + (aW_s - bW_p) \times 10^{-2}}{(MW\ of\ PEG)} \times 10^3$$

$W_p$ = wt. product
$W_s$ = wt. starting resin
a = % Cl of starting resin
b = % Cl of product

The capacity is then simply the number of milliequivalents of PEG introduced divided by the weight of the product. Using this method one obtains a value of 2.12 mequiv/g. This compares favorably with the value of 2.04 mequiv/g found via chromic acid oxidation using 52 as the average number of electrons transferred per PEG unit. Therefore, it appears that the analysis techniques were developed using material which was predominantly pentamer rather than the larger oligomers as was suspected. All PEG capacities were determined using a 5 day, room temperature oxidation with chromic acid using a value of 52 for the number of electrons transferred to each unit.

A single attempt to determine the capacity of a PEG resin via an oxygen elemental analysis was made. The resin (DC-03-187C) was vacuum dried (0.5 torr, 30 °C) over $P_2O_5$ until a constant weight was obtained. The sample was sent to Galbraith Labs for an elemental analysis which revealed that the resin contained 27.94% O. Conversion of this value to milliequivalents and division by six (the number of oxygen atoms in a PEG chain) yields a PEG capacity of 2.91

mequiv/g. This value exceeds the maximum theoretical capacity of 2.72 mequiv/g. It is believed that trace amounts of water remained trapped in the resin elevating the observed oxygen content. Since the chromic acid analysis technique yields accurate values, the time and expense associated with oxygen elemental analysis is not warranted (even if one assumes that removal of water can be accomplished easily).

It had been thought that the chromic acid analysis would not be feasible for resins which contained acidic ligands in addition to PEG units due to the uptake of chromium by the ion exchange site. However, given the low pH of the chromic acid solution, it was possible that chromium would not exchange with the proton, particularly when the $pK_a$ of the ligand is high, as is the case with carboxylic acid groups. In order to determine if the chromic acid analysis could be used to characterize the bifunctional PEG/carboxylic acid and PEG/phosphonic acid resins which were to be produced, a study was undertaken to evaluate the apparent number of electrons consumed by acidic resins containing no PEG groups. No attempt was made to determine if the observed values were due to ion exchange of the chromium ions or to actual oxidation of the resin. To measure to what extent the PEG capacities would be affected, all values were calculated using the same equation used for the monofunctional PEG resin.

As shown in Table 24, treatment of a partially functionalized carboxylic acid resin with chromic acid leads to very low measured capacities. Even a

Table 24

Chromic Acid Analysis of Acidic Resins

| Resin | Degree of Functionalization | Physical Form | "PEG Capacity" (mequiv/g) |
|---|---|---|---|
| Carboxylic Acid | Partial | Oven Dried | 0.02 |
| Carboxylic Acid | Partial | Büchner Dried | 0.10 |
| Phosphonic Acid | Partial | Oven Dried | 0.10 |
| Phosphonic Acid | Partial | Büchner Dried | 0.58 |
| Carboxylic Acid | Complete | Büchner Dried | 0.36 |
| Phosphonic Acid | Complete | Büchner Dried | 1.22 |

fully functional carboxylic resin yields a "PEG" capacity which is low in relation to the capacity of the acidic ligands (acid capacity = 5.53 mequiv/g). This is in contrast to the behavior of the phosphonic acid resin. Analysis of the partially functionalized resin reveals an apparent capacity of 0.58 mequiv/g while that of the fully functionalized resin is 1.22 mequiv/g. Both of these values are too large to permit use of the chromic acid oxidation technique to determine PEG capacity in the presence of phosphonic acid sites. Attempts to correlate the observed capacity with the acid capacities of the resins were unsuccessful. The effect of ligand accessibility is clearly evident in the values obtained for the oven dried, partially functionalized resins. The oven dried resins do not reswell to a sufficient degree in the chromic acid solution leading to lower capacities than those observed with the Büchner dried material. This factor must be taken into account when resins with high percent solids are analyzed. The data clearly demonstrate that only the PEG/carboxylic acid resin can be accurately analyzed via a chromic acid oxidation.

Linear PEG Capacity

In order to completely characterize the PEG resins, it was necessary to determine the amount of PEG present as linear units. Previously, these groups have been quantified by reacting the resin with 3,5-dinitrobenzoyl chloride followed by a nitrogen analysis.[109] The number of -OH groups (and thus the number of linear PEG groups) can then be calculated from the nitrogen

capacity of the resin. In this laboratory, the analysis was carried out in a different manner due to the lack of a quick, inexpensive method of determining the nitrogen capacity. The method used was reaction of the resin with $PCl_5$ in the presence of pyridine followed by a chlorine elemental analysis. The linear PEG capacity can then be calculated from the change in chlorine capacity. Initially, all analyses were performed using the chlorination method. However, it quickly became apparent that the current resins were yielding linear PEG capacities higher than those obtained previously in both this laboratory and by Warshawsky.[106,109] In order to determine if reaction with $PCl_5$ was producing reliable capacities, a limited study of the analysis conditions was performed.

The presence of pyridine in this analysis serves to neutralize the acid produced and thus avoid acid catalyzed cleavage of the polyether chains. Should such a cleavage occur, additional -OH sites would be produced, leading to the measurement of an artificially elevated linear PEG capacity. It was decided to examine the PEG content of a resin via oxidation with chromic acid after reaction with $PCl_5$. The resin was subjected to the normal chlorination conditions: 2.00 g of resin contacted with 2.50 g $PCl_5$ and 1.00 g pyridine in 50 mL dioxane for 48 hours at room temperature. This procedure was followed by an extensive conditioning procedure which removes any unbound chlorine. The chlorinated resin was analyzed for PEG content via a 120 hour chromic acid oxidation and was found to have lost 0.63 mequiv/g. However, it was noted that the percent solids of the chlorinated resin was over 20% higher than

the initial PEG resin. As was shown with the comparison between oven and Büchner dried acidic resins, the accessibility of the resin has a profound impact on the measured capacity. It was therefore felt that the change in PEG capacity could not be relied upon as a true measure of the loss of glycol units from the resin.

Since pyridine was present to prevent the destruction of the PEG chains, a study was undertaken to determine the optimum amount of pyridine. Five 1.00 gram samples of DC-04-224D were contacted with 1.25 g $PCl_5$ and a varying amount of pyridine in 25 mL dioxane. The sample with 0.5 g pyridine represents the usual reaction mixture (Table 25). Obviously, the absence of pyridine leads to a linear PEG capacity which is higher that the theoretical maximum. It appears that at least one gram of pyridine is needed for each gram of resin, but the linear capacities for all samples containing pyridine are very similar given the amount of error associated with the chlorine elemental analysis technique. Nonetheless, the amount of pyridine used in the previous analyses was large enough to prevent excessive chain cleavage.

A subtle point which was examined was the order of reagent addition. Normally, the resin was suspended in dioxane and the $PCl_5$ was added, followed by pyridine. Even though only a few moments passed between the addition of the $PCl_5$ and that of pyridine, the slight chance that some chain cleavage occurred during this period was examined by repeating the analysis for one resin and inverting the order of reagent addition. DC-03-187C was used

Table 25

Effect of Pyridine Level on the Measured Linear PEG Capacity

| Amount of Pyridine | Linear PEG Capacity (mequiv/g) |
|---|---|
| None | 3.28 |
| 0.50 g | 1.37 |
| 1.00 g | 1.11 |
| 2.00 g | 1.23 |
| 10.00 g | 1.03 |

and yielded a linear PEG capacity of 1.15 mmole/g. Previous analyses with the usual order of reagent addition had given values of 1.33 and 1.21 mmole/g. These values are within the experimental error of the chlorine elemental analysis leading to the conclusion that no significant chain cleavage occurred prior to the addition of pyridine.

One other means of testing the analysis would be to prepare resins which should have a high linear capacity due to the synthetic conditions. A corresponding increase in the measured capacity would then support the use of the chlorination technique. A single attempt to produce a resin functionalized with ethylene glycol rather that the pentamer failed.

The results of the studies described above served to support the idea that the chlorination of the glycol chain was a reliable method of obtaining the linear PEG capacity. However, the chlorine elemental analysis was not always well controlled. The technique consists of a sodium fusion followed by destruction of the excess sodium, dissolution of the solids in water, and titration of the chloride in the resulting solution via the Mohr method.[106] While analysis by this method usually proceeded without any difficulty, occasionally the final solution was too dark to titrate accurately. The color is caused by extremely small carbon particles which pass through the filter paper and form a suspension which is colloidal in appearance. Various methods of reducing the amount of carbon present in the solution have been investigated by other members of the group, but no method has been found which produces clear

solutions in all cases. The chlorinated PEG resins were particularly prone to this problem. In some cases, the solution was too dark to titrate and a second analysis was completed. In those samples which could be titrated, the color of the solution varied, leading to the possibility that the final number was strongly affected by the blank value of the solution. Titration of a separate blank solution was not possible due to the continuous variation in color.

These problems led to the search for an alternate way of analyzing for the -OH group. The development of an extremely accurate, inexpensive method of analyzing resins for nitrogen (a modified Kjeldahl analysis)[125] now made it possible to use the method described by Warshawsky.[109] Due to the reported resistance of the nitro group to the Kjeldahl digestion,[126] the quantities of all reagents were increased by twenty percent. In some cases, heating was continued for a longer period of time than normal in order to achieve complete digestion. A control experiment was performed with 3,5-dinitrobenzoyl chloride itself. Analysis of freshly recrystallized material showed a nitrogen capacity of 8.70 mequiv/g in excellent agreement with the theoretical value of 8.67 mequiv/g.

The general procedure described by Warshawsky was used for the reaction of PEG resins and 3,5-dinitrobenzoyl chloride (DNB). Briefly, 1.00 g of oven dried resin was reacted with 2.31 g (10.0 mmoles) of 3,5-dinitrobenzoyl chloride in 10 mL of chloroform. Chloroform was purified by passage through a column of silica gel and the DNB was recrystallized from $CCl_4$.[127] The mixture

was refluxed for one hour and the resin was washed several times with chloroform and acetone to remove unreacted DNB. For resins which also contained acidic groups, a water wash was inserted into the series of acetone washes in order to hydrolyze any anhydride linkages which might have formed. The resin was then dried overnight at 60 °C and analyzed for nitrogen content.

Initially, a PEG resin (DC-05-109) was examined and found have a nitrogen capacity of 1.77 mequiv/g, in close agreement with the 1.60 mequiv/g which had been estimated by monitoring the weight change of the resin upon treatment with DNB. This change in mass must be taken into account when calculating the final -OH group capacity. After such a correction, DC-05-109 was found to have a linear PEG capacity of 1.07 mequiv/g compared with a value of 0.97 mequiv/g found via chlorination with $PCl_5$.

Warshawsky reports that "freshly recrystallized" DNB was used. In response to a low value obtained with material which had been recrystallized ten days prior to analysis, DC-05-271C (a PEG/carboxylic acid resin) was analyzed using material recrystallized at varying times. All of the DNB samples had been recrystallized from $CCl_4$ and were stored under a nitrogen atmosphere in a round bottom flask sealed with a rubber septum. The material had also been protected from light with aluminum foil. The measured capacities are shown in Table 26. Based on these results, it was decided that all analyses should be conducted with DNB which had been recrystallized on the day of use.

Table 26

Effect of DNB Age on the Measured Linear PEG Capacity

| Time Since Recrystallization | Linear PEG Capacity (mequiv/g) |
|---|---|
| 4.5 Months | 0.67 |
| 10 Days | 0.84 |
| 0 Days | 1.33 |

In order to verify that the presence of carboxylic or phosphonic acid groups would not interfere with the analysis, samples of fully functionalized phosphonic and carboxylic acid resins were subjected to the procedure. After reaction with DNB the phosphonic and carboxylic acid resins showed nitrogen capacities of 0.06 and 0.18 mequiv/q, respectively. These values are low enough to permit the analysis of resins which contain a significant number of -OH groups in addition to the acidic ligands.

The use of DNB has several advantages over $PCl_5$. First, the analysis can be completed in less time (48 versus 72 hours) when DNB is used. Second, the nitrogen analysis appears to give more accurate numbers than does the sodium fusion analysis for chlorine.[106, 125] Finally, the likelihood of having to repeat the analysis due the inherent difficulties of the method (dark solutions in the chlorine analysis) is greatly diminished when using the DNB method. For all of these reasons, it is strongly suggested that all future analyses of this type be performed using DNB. One area which should be modified is the purification of the DNB. A less environmentally toxic solvent should be employed for the recrystallization. Also, a study of the effect of the method used to dry the resin is in order. It has been reported[123] that PEG chains can be thermally cleaved at the benzyl carbon to form carboxylic acid sites on the resin and free PEG. Such cleavage could increase the number of -OH groups present on the resin. This degradation could be the cause of the discrepancy in the amount of pseudocrown ether sites cited earlier, but further

investigation is warranted since the previous studies also utilized resins dried at elevated temperatures. It is recommended that PEG resins be dried at room temperature in a vacuum oven.

Synthesis of Carboxylic Acid Resins

The development of a synthetic method to produce well characterized partially and fully functionalized carboxylic acid resins was initiated earlier in this laboratory.[106] Further development of the multistep synthetic method has been accomplished and the products of the reactions have been characterized spectroscopically.

The initial step is the production of a benzyl ethyl ether resin from VBC in which a portion of the chlorine atoms have been replaced by ethoxy groups. This is accomplished by heating VBC in a 1:1 mixture of toluene (a swelling solvent) and 25 wt% KOH in 95% ethanol. The degree of functionalization is controlled by both the temperature and the length of reaction. Based on earlier results,[106] 60 °C was chosen as an initial reaction temperature for these studies. The degree of functionalization (measured as residual chlorine capacity) was monitored as a function of the length of reaction (Table 27).

The difference in chlorine capacity seen after Soxhlet extraction is due to the removal of KCl from the resin. Initially, the resins were eluted with 1 L 95% EtOH and 2 L $H_2O$. During determination of the percent solids of the resins, the appearance of a white solid was noted in the vial. Soxhlet extraction with water

Table 27

Characterization of Benzyl Ethyl Ether Resins Synthesized at 60 °C

| Resin | Reaction Length (hrs) | % Solids | | Cl Capacities (mequiv/g) | |
|---|---|---|---|---|---|
| | | Before Extraction | After Extraction | Before Extraction | After Extraction |
| DC-03-028A | 4 | 71.0 | -- | 5.29 | -- |
| DC-03-170 | 4 | 76.9 | 40.0 | 4.94 | 4.65 |
| DC-03-028B | 8 | 75.5 | 36.3 | 4.78 | 3.52 |
| DC-03-028C | 12 | 77.6 | 35.9 | 4.54 | 3.11 |
| DC-03-028D | 48 | 46.5 | 42.4 | 2.72 | 1.31 |

resulted in polymers which had a lower percent solids, were slightly lighter in color and greatly increased in volume. The extracted resins did not release a white solid upon drying. Addition of silver nitrate to the water used for extraction caused the formation of a white precipitate and a flame test was positive for potassium, confirming the presence of KCl.

In order to determine if the changes observed in the resins were solely due to the removal of KCl, the resins were analyzed by IR spectroscopy. No degradation of the resin was observed after extraction (Figure 71). The resins were treated with $PCl_5$ and the chlorine capacity was reexamined in order to determine if any ether groups had been cleaved to yield benzyl alcohol sites. No increase in the chlorine capacities were noted, indicating that no benzyl alcohol groups were present.

Since the resin was not completely functionalized at 60 °C (even after long reaction times) a reaction was conducted using a 48 hour reflux. The polymer (DC-03-065) displayed a chlorine capacity of 1.34 mequiv/g before Soxhlet extraction and 0.56 mequiv/g (91.1% functionalization) afterwards. In contrast to the other benzyl ethyl ether resins, DC-03-065 showed an increase (0.37 mequiv/g) in the chlorine capacity when treated with $PCl_5$ indicating that a small number of benzyl alcohol sites were formed. It should be noted that the presence of benzyl alcohol sites on the resin is not disadvantageous in terms of producing the target resin. The next step in the synthesis involves the cleavage

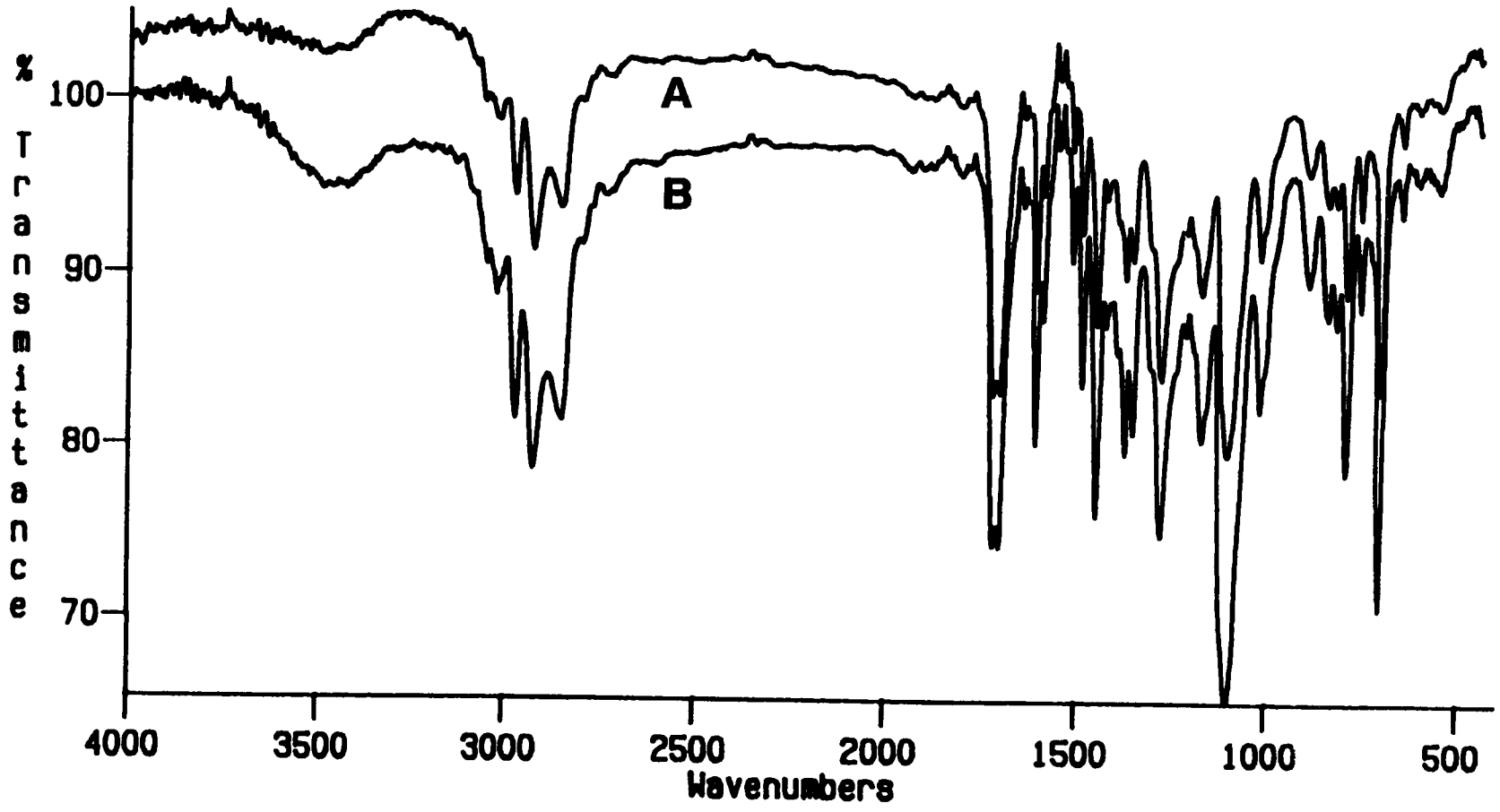



Figure 71. IR spectra of benzyl ethyl ether resin before (A) and after (B) Soxhlet extraction.

of the ether groups and the subsequent oxidation of the resulting alcohol sites to aldehyde and carboxylic acid groups.

The capacity of the final resin is determined by the degree of functionalization of the initial benzyl ethyl ether resin. Thus, for a fully functionalized carboxylic acid resin, the benzyl ethyl ether resin is produced using a 48 hour reflux. Following Soxhlet extraction of the resin, as described above, the polymer is hydrolyzed/oxidized by a 24 hour reflux in a mixture of 70% aqueous dioxane and 3 M nitric acid (5:3).[128] The resulting solution is 7 wt% nitric acid. The product of this reaction contains aldehyde sites in addition to carboxylic acid groups as evidenced by the IR spectrum. An aldehyde peak is clearly visible at 2731 $cm^{-1}$ in addition to a carbonyl peak at 1698 $cm^{-1}$. The final step in the production of a carboxylic acid resin is reaction with hydrogen peroxide in dioxane which converts the remaining aldehyde groups to the desired carboxylic acid. The aldehyde peak present in the IR spectrum disappears upon reaction with $H_2O_2$ and a characteristically broad -OH peak appears around 3000 $cm^{-1}$ (Figure 72).

The production of a partially functionalized resin was similar. Following partial conversion of VBC to benzyl ethyl ether resin and hydrolysis/oxidation with nitric acid, the resin was dried and then treated with $PCl_5$ and pyridine. Any remaining alcohol sites were reconverted to the chloride and the aldehyde groups were transformed to acid chloride sites which were readily hydrolyzed to the carboxylic acid upon treatment with water. Additional reaction with $PCl_5$

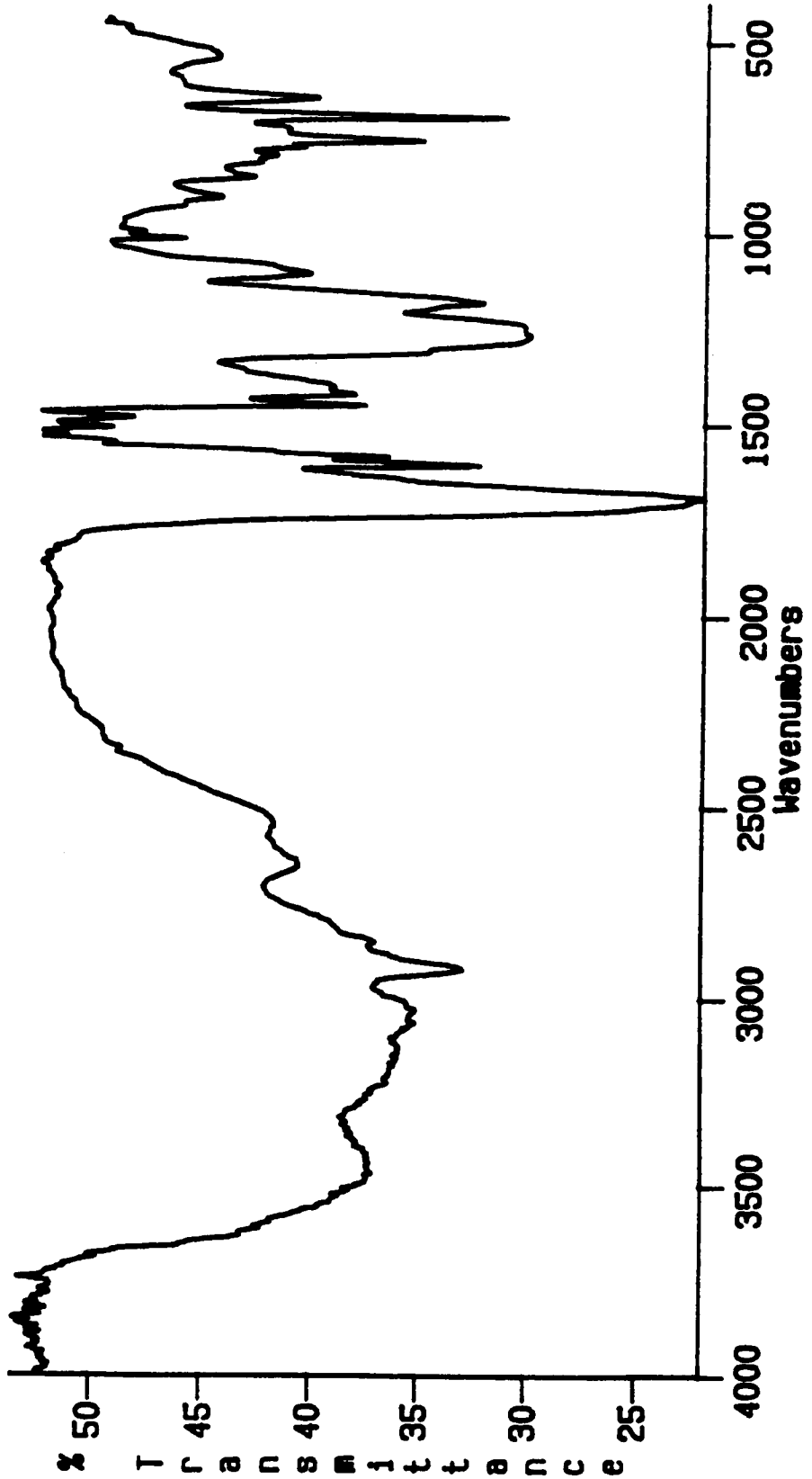



Figure 72. IR spectrum of carboxylic acid resin.

revealed no residual alcohol or aldehyde groups. The syntheses of partially and fully functionalized carboxylic acid resins are summarized in Figures 73 and 74, respectively. The characteristics of carboxylic acid resins produced for this project are shown in Table 28. All acid capacities were measured in a partially non-aqueous environment (60% dioxane) in order to increase the accessibility of the hydrophobic resins to the hydroxide ion. The necessity of performing the analysis in a swelling solvent was demonstrated by the measured capacities of DC-04-088: 1.94 mequiv/g in 60% dioxane and 0.38 mequiv/g in water.

Synthesis of PEG/Carboxylic Acid Resins

The synthesis of PEG/carboxylic acid resins from the partially functionalized carboxylic acid resins proved to be rather straightforward. The procedures described in a previous dissertation[106] were reexamined (again due to the discrepancy in boiling points) and were found to be effective for the synthesis.

Water was removed from partially functionalized carboxylic acid resin by an azeotropic distillation with heptane. The water was collected in a Dean-Stark trap and the heptane was removed from the resin by evaporation. In the course of other studies related to this project an alternate method of drying the resin was employed. The alternate method involved eluting the wet resin with absolute ethanol followed by 2,2,4-trimethylpentane. The 2,2,4-trimethylpentane

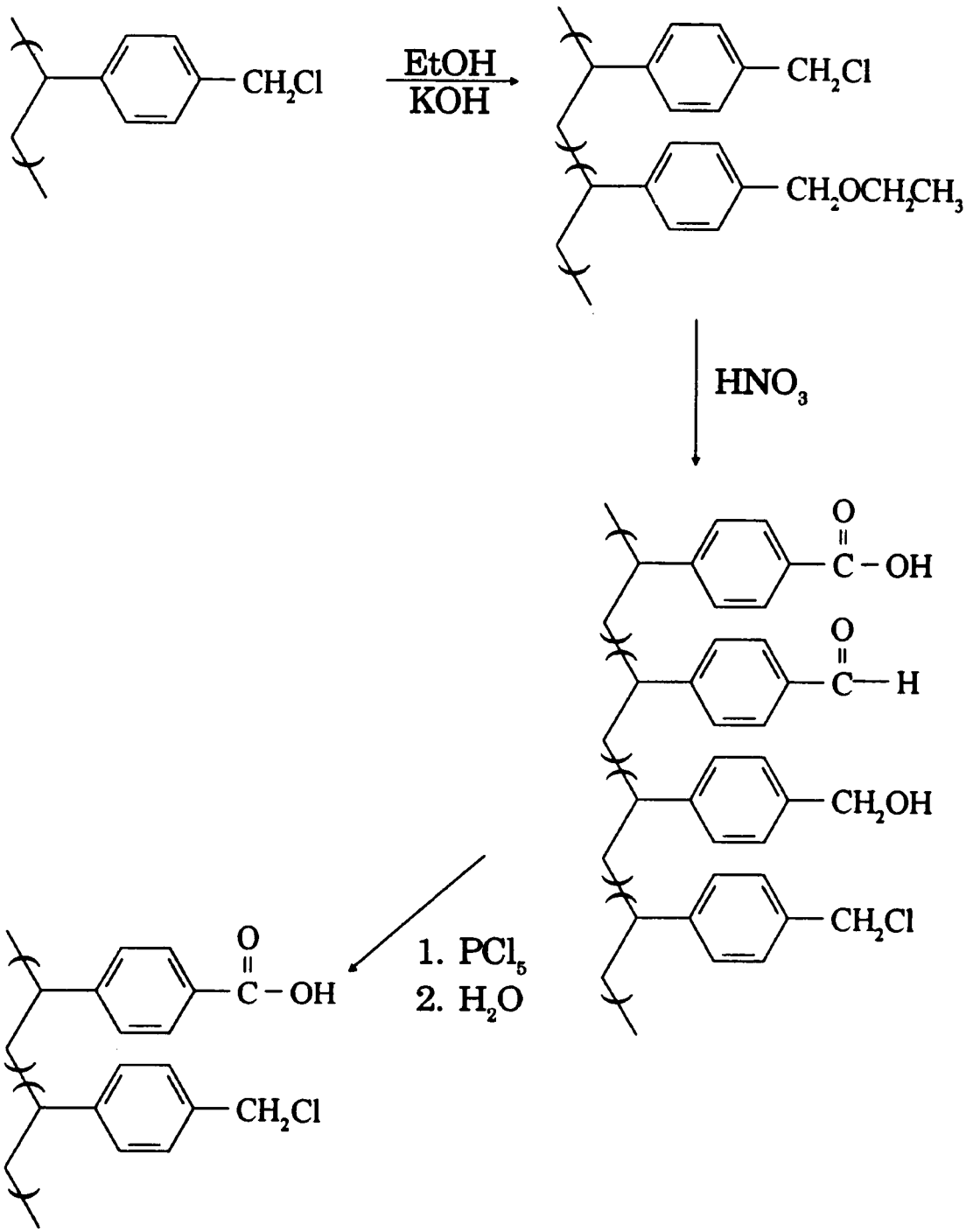



Figure 73. Synthesis of partially functionalized carboxylic acid resin.

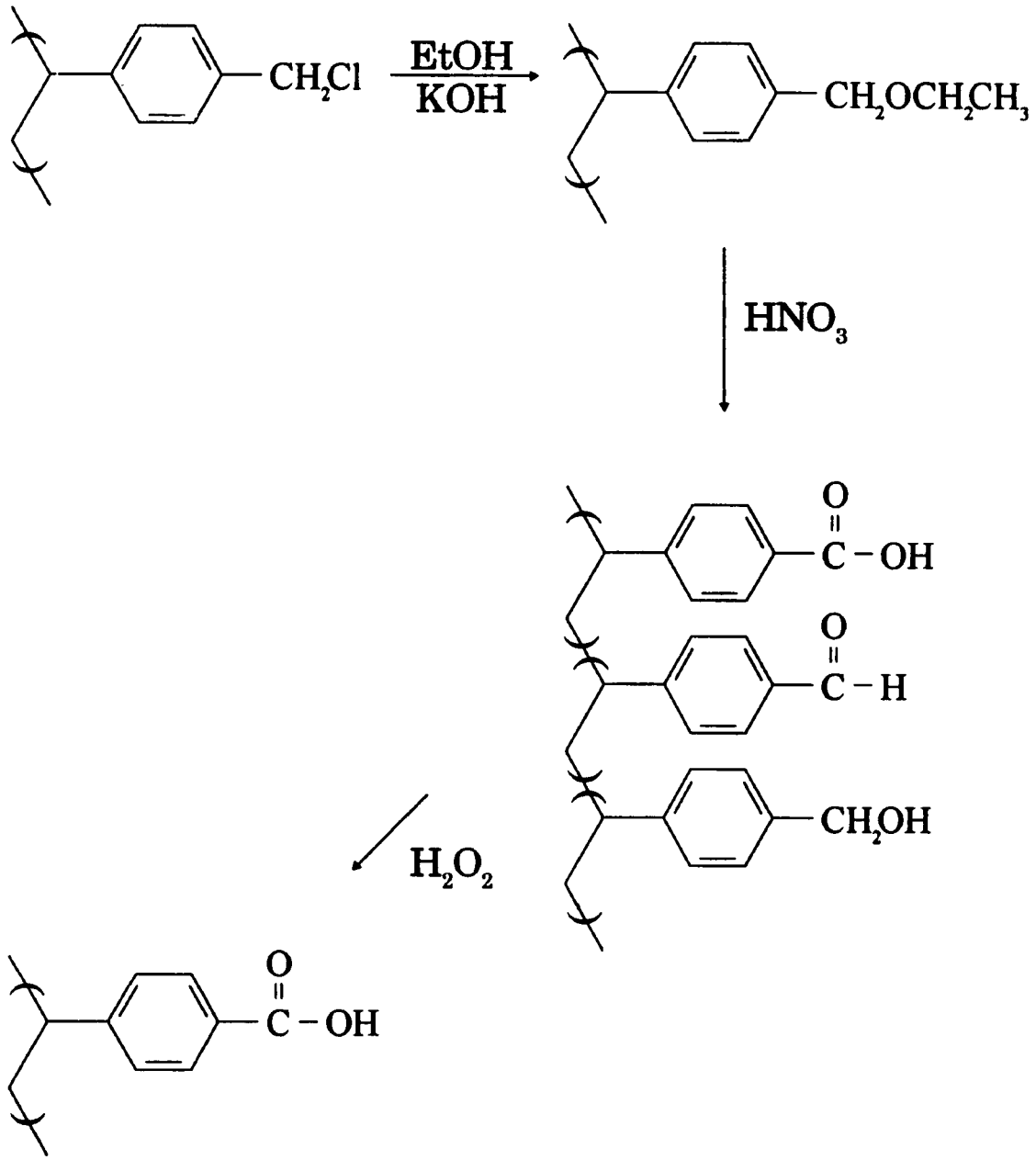



Figure 74. Synthesis of fully functionalized carboxylic acid resin.

Table 28

Characterization of Carboxylic Acid Resins

| Resin | % Solids | Acid Capacity (mequiv/g) | Cl Capacity (mequiv/g) |
|---|---|---|---|
| DC-03-226 | 41.5 | 5.94 | -- |
| DC-04-076 | 45.7 | 5.53 | -- |
| DC-04-088 | 70.9 | 1.94 | 5.10 |
| DC-04-097 | 69.2 | 1.86 | 5.28 |
| DC-04-211 | 68.1 | 1.59 | 5.08 |
| DC-06-072 | 64.8 | 2.08 | 4.56 |

was also removed by evaporation. The newer method had the advantage of causing less collapse of the resin, therefore increasing the accessibility of the beads.

First, the effect of the PEG/Cl ratio was studied. The dry (heptane azeotrope) resin was reswollen via an elaborate technique developed earlier.[106] The resin (10.00 g) was suspended in 50 mL of dioxane and the mixture was stirred for two hours at room temperature. The dioxane was replaced with 100 mL of fresh dioxane and the mixture was heated at 50 °C for 24 hours. Following this, the dioxane was removed and the resin treated in the same manner as VBC (monofunctional PEG resin synthesis). The amount of sodium hydride was adjusted for the presence of the acidic groups. The amount of 60% NaH needed was calculated using the following expression.

$$\frac{[(mmole\ PEG + (wt.\ resin)(acid\ capacity)][0.023998][1.1]}{0.6}$$

For the initial study, the mixtures were refluxed for 48 hours. After a careful rinse with $H_2O$, the polymers were Soxhlet extracted with dioxane and conditioned with successive 1 L/1 hr elutions of $H_2O$, 1 N NaOH, $H_2O$, 1 N $HNO_3$, and $H_2O$. Nitric acid replaced hydrochloric acid due the reported ability of these resins to retain acids.[110] Uptake of HCl would lead to incorrect chlorine elemental analyses. Analysis of the resins led to the results shown in

Table 29. A C-O-C band at 1100 $cm^{-1}$ was present in the IR spectrum of all of the resins.

The results indicate that a PEG/Cl ratio of at least 1.0/1.0 is required for complete functionalization. Also, the carboxylic acid sites seem to hinder the formation of pseudocrown units as indicated by the elevated linear/pseudocrown PEG ratio relative to the monofunctional PEG resin. One unexpected result was the behavior of the acid capacity. Rather than decreasing as the mass of the resin increased with functionalization, the first three resins show a steady increase in acid capacity. At first it was thought that a number of the PEG chains were being protonated during conditioning. Thus, a higher PEG capacity would lead to a higher acid capacity. To test this idea, a sample of DC-04-192 was eluted with 1 L of 1 N HCl followed by 1 L $H_2O$ and the resin was analyzed for chlorine content. No increase in the chlorine capacity was noted indicating that no HCl had been absorbed. It is now believed that some of the PEG chains were cleaved to form additional carboxylic acid sites. No experimental verification of this idea has been attempted yet, but such studies are in order, particularly since earlier work[123] indicated that thermal cleavage of PEG benzyl ethers occurs only in dry resins.

As with the monofunctional PEG resin, a study of the length of time needed to complete the reaction was performed. For this study, the partially functionalized carboxylic acid resin was freed of water by elution with absolute ethanol followed by 2,2,4-trimethylpentane. In addition, because work with the

Table 29

Characterization of PEG/Carboxylic Acid Resins Produced with Varying PEG/Cl Ratios
(Precursor Resin Dried via Heptane Azeotrope)

| Resin | PEG/Cl Ratio | % Solids | Capacities (mequiv/g) | | | | | Linear/PC Ratio |
|---|---|---|---|---|---|---|---|---|
| | | | Cl Capacity | Acid Capacity | Total PEG Capacity | Linear PEG Capacity | Pseudocrown PEG Capacity | |
| DC-04-112A | 0.25/1.0 | 70.9 | 2.75 | 0.78 | 0.76 | 0.63 | 0.13 | 83/17 |
| DC-04-112B | 0.50/1.0 | 70.9 | 1.60 | 1.10 | 1.15 | 1.00 | 0.15 | 87/13 |
| DC-04-192 | 1.0/1.0 | 67.6 | 0.00 | 1.31 | 1.53 | 1.32 | 0.21 | 86/14 |
| DC-04-197 | 2.0/1.0 | 68.9 | 0.00 | 1.12 | 1.63 | 1.24 | 0.39 | 76/24 |

partially functionalized phosphonic acid indicated that the elaborate swelling procedure was undesirable (vide infra), these resins were synthesized after a 1 hour swell with dioxane at room temperature instead. A PEG/Cl ratio of 1.0/1.0 was employed and the amount of sodium hydride was calculated as previously described for the study of the PEG level. Four identical mixtures were refluxed for periods of 12, 24, 48, and 96 hours. Following a normal work up, the properties shown in Table 30 were measured.

As with the monofunctional PEG resin, it appears that the reaction is complete after 12 hours. To insure complete reaction, it was decided that all future reactions of this type would be allowed to continue for 24 hours.

Since the method of removing water from the partially functionalized resin had changed during the period in which these studies were conducted and the reswelling procedure had been abandoned, it was decided to repeat the study of the effect of PEG/Cl ratio. Three additional reactions were completed and, together with the DC-05-271B, yield a complete view of the effect of the PEG/Cl level (Table 31).

Comparison of the two series of resins (Tables 29 and 31) reveals little difference. The linear PEG capacity is slightly higher in the second series of resins but all other parameters are very similar. Standard conditions for synthesizing the PEG/carboxylic acid resin were determined to be a PEG/Cl ratio of 1.0/1.0 and a 24 hour reflux.

Table 30

Characterization of PEG/Carboxylic Acid Resins Produced with Varying Reaction Lengths

| Resin | Reaction Length (hours) | % Solids | Capacities (mequiv/g) | | | | | Linear/PC Ratio |
|---|---|---|---|---|---|---|---|---|
| | | | Cl Capacity | Acid Capacity | Total PEG Capacity | Linear PEG Capacity | Pseudocrown PEG Capacity | |
| DC-05-271A | 12 | 68.8 | 0.00 | 1.33 | 1.49 | 1.03 | 0.46 | 69/31 |
| DC-05-271B | 24 | 69.4 | 0.00 | 1.39 | 1.45 | 1.00 | 0.45 | 69/31 |
| DC-05-271C | 48 | 65.3 | 0.00 | 1.36 | 1.50 | 0.84 | 0.66 | 56/44 |
| DC-05-271D | 96 | 63.9 | 0.00 | 1.37 | 1.53 | 1.18 | 0.35 | 77/23 |

Table 31

Characterization of PEG/Carboxylic Acid Resins Produced with Varying PEG/Cl Ratios
(Precursor Resin Dried via Solvent Elution)

| Resin | PEG/Cl Ratio | % Solids | Capacities (mequiv/g) | | | | | Linear/PC Ratio |
|---|---|---|---|---|---|---|---|---|
| | | | Cl Capacity | Acid Capacity | Total PEG Capacity | Linear PEG Capacity | Pseudocrown PEG Capacity | |
| DC-06-064A | 0.25/1.0 | 61.2 | 2.90 | 0.81 | 0.76 | 0.76 | 0.00 | 100/0 |
| DC-06-064B | 0.50/1.0 | 66.5 | 1.59 | 1.04 | 1.01 | 1.18 | 0.00 | 100/0 |
| DC-05-271B | 1.0/1.0 | 69.4 | 0.00 | 1.39 | 1.45 | 1.27 | 0.18 | 88/12 |
| DC-06-064C | 2.0/1.0 | 69.4 | 0.00 | 1.49 | 1.53 | 1.21 | 0.32 | 79/21 |

Synthesis of PEG/Phosphonic Acid Resins

The PEG/phosphonic acid resins produced previously[106] were thought to be inadequate for contact studies since later work[105] had called the uniformity of the initial functionalization with phosphonic acid groups into question. In contrast to the synthesis of PEG/carboxylic acid resins, the production of bifunctional PEG/phosphonic acid resins proved to be considerably more challenging. An initial attempt to study the effect of the PEG/Cl ratio on the properties of the resin produced polymers which contained no PEG groups. The reactions were performed as described for the PEG/carboxylic acid synthesis (Figure 75). The extensive reswelling procedure was employed and the mixtures were allowed to reflux for 48 hours. In order to compensate for the presence of acidic groups, the following expression was used to calculated the amount of 60% sodium hydride needed.

$$\frac{[mmole\ PEG + 2(phosphorus\ capacity)(wt.\ resin)][0.023998][1.1]}{0.6}$$

Following the reaction, no ether band was observed in the IR spectrum of any of the polymers and wet chemical analysis showed little change. The analytical data are shown in Table 32. No improvement was noted when another sample was allowed to reflux for 120 hours. The lack of functionalization was thought to be due to limited accessibility of the resin to the anion of PEG. As a means of verifying this, a small amount of partially

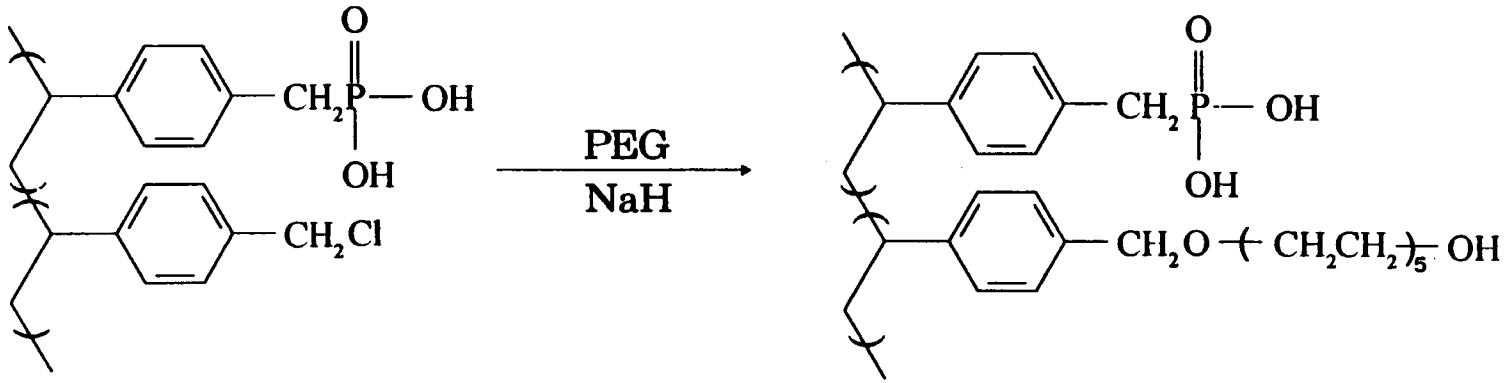



Figure 75. Synthesis of PEG/phosphonic acid resin.

Table 32

Characterization of Partially Functionalized Phosphonic Acid Resin Reacted with Varying Levels of PEG

| Resin | PEG/Cl Ratio | % Solids | Capacities (mequiv/g) | | |
|---|---|---|---|---|---|
| | | | Cl Capacity | Acid Capacity | Phosphorus Capacity |
| DC-04-091 | a | 67.7 | 3.16 | 3.34 | 1.81 |
| DC-04-099A | 0.25/1.0 | 73.1 | 2.61 | 2.88 | 1.81 |
| DC-04-099B | 0.50/1.0 | 74.6 | 2.96 | 2.91 | 1.80 |
| DC-04-099C | 1.0/1.0 | 73.0 | 2.31 | 2.76 | 1.83 |
| DC-04-099D | 2.0/1.0 | 76.2 | 2.48 | 2.93 | 1.80 |

[a] Precursor resin (partially functionalized phosphonic acid resin)

functionalized phosphonic acid was synthesized using 5% cross-linked, macroporous VBC as starting material. However, when this polymer was subjected to the same reaction conditions as the -099 series, it also failed to react with PEG. It is now believed that a side reaction leading to secondary cross-linking occurs during attachment of the phosphonic acid groups, resulting in a polymer which is not accessible to PEG (see Chapter 2). The use of a macroporous resin did not facilitate the reaction because it too had undergone a significant amount of secondary cross-linking.

The next approach taken was reaction of PEG with partially functionalized phosphonic acids synthesized with shorter preswell and reaction lengths. As described earlier, these resins have a higher g/g value (and thus a lower amount of secondary cross-linking) at the expense of a decrease in the phosphonic acid capacity. The initial reaction (DC-04-181), which used resin synthesized with a shortened reaction period only (DC-04-156), appeared to be successful in that the chlorine capacity of the resin dropped significantly (4.19 to 1.56 mequiv/g) and reaction with $PCl_5$ caused an increase in the chlorine capacity of 0.27 mequiv/g. However, the phosphorus capacity decreased only slightly (from 1.41 to 1.24 mequiv/g) and no ether peak was visible in the IR spectrum. This region is masked by phosphoryl bands so it is possible that the band was present but not visible. The solid-state $^{13}C$ NMR spectrum of the resin did show a peak at 71 ppm as would be expected for a resin containing PEG. A second sample of partially functionalized phosphonic acid (DC-04-

184A) in which both the preswell and the reaction time had been shortened was treated in the same manner. The resin showed decreases in both the phosphorus (0.92 to 0.66 mequiv/g) and chlorine capacities (5.00 to 1.68 mequiv/g) and displayed a peak at 1098 $cm^{-1}$ in the IR spectrum.

Given the conflicting nature of the evidence found with DC-04-181, it was strongly suspected that reaction with PEG was not the only process by which Cl was being lost from the resin. As shown earlier with the synthesis of partially functionalized dibutyl phosphonate resin, contact of this type of resin with dioxane for extended periods of time can lead to a loss of Cl, presumably due to secondary cross-linking. In order to investigate if the lengthy reswelling procedure used in these reactions was leading to a decrease in the Cl capacity prior to the addition of PEG, a sample of DC-04-184B (partially functionalized phosphonic acid) was subjected to the reswelling procedure, conditioned, and analyzed for Cl content. The chlorine capacity decreased by 0.60 mequiv/g revealing that a small amount of secondary cross-linking occurred during the reswell. Given this observation, it was decided that all future reactions would be conducted with only a one hour, room temperature swelling period as is used for VBC in the production of monofunctional PEG resin.

Two samples of partially functionalized resin were allowed to swell in dioxane at room temperature for one hour after which the penta(ethylene glycol) and sodium hydride were added and the mixtures heated to reflux. One mixture (DC-05-136) was refluxed for 24 hours while the other (DC-05-148)

continued for 96 hours. As shown in Table 33, the phosphorus and chlorine capacities of both resins decreased relative to those of the starting material (DC-05-094). However, only DC-05-148 displayed an ether peak in the IR spectrum.

It appeared that longer reaction times increased the amount of PEG incorporated, but it was noted that the long reaction times led to a greater number (approximately 10%) of cracked beads. Since it still appeared that a lack of accessibility was hindering the reaction despite the advances made in the synthesis of partially functionalized resins, other barriers to the penetration of PEG were considered. One which can be dismissed is electronic repulsion. During the reaction, PEG anions must penetrate a bead which contains numerous anionic sites (from deprotonation of the acid ligands). While some electronic repulsion must exist, it should not be greater in the phosphonic acid than in the carboxylic acid given that both contain approximately the same number of acidic protons. The ease with which the partially functionalized carboxylic acid reacts with PEG indicates that any electronic repulsion present is not significant.

The possibility of damage to the resin during the drying procedure was examined and it was found that resins dried via a heptane azeotrope appeared to be collapsed when viewed with a microscope. An alternate method of drying the resin was investigated. The Büchner dried beads were eluted with absolute ethanol followed by 2,2,4-trimethylpentane which was then removed by slow

Table 33

Characterization of PEG/Phosphonic Acid Resins
Synthesized without an Extensive Reswelling Period

| Resin | Reaction Length (hours) | % Solids | Capacities (mequiv/g) | | |
|---|---|---|---|---|---|
| | | | Cl Capacity | Acid Capacity | Phosphorus Capacity |
| DC-05-094 | a | 57.5 | 4.98 | 2.04 | 0.99 |
| DC-05-136 | 24 | 76.6 | 3.73 | 1.14 | 0.84 |
| DC-05-148 | 96 | 77.7 | 2.09 | 0.73 | 0.73 |

[a] Precursor resin (partially functionalized phosphonic acid)

evaporation in a fume hood. When viewed with a microscope, resins dried in this manner exhibited less collapse than did those dried via azeotropic distillation with heptane.

A sample of partially functionalized resin (DC-05-116) dried in this manner was reacted with PEG. A PEG/Cl ratio of 1.0/1.0 was used and the reaction was refluxed for 24 hours. Analysis indicated that a significant amount of PEG was incorporated. The phosphorus capacity had decreased from 0.76 to 0.40 mequiv/g and the chlorine capacity was 0.00 mequiv/g after the reaction compared with 5.07 mequiv/g before. The IR spectrum displayed a prominent peak at 1100 $cm^{-1}$.

The success of this reaction prompted further study into the production of a PEG/phosphonic acid resin with a higher phosphorus capacity. Resins with a higher phosphorus capacity were necessary in order to have a truly bifunctional resin because the partially functionalized resin had less than 20% of its chlorine atoms replaced. The production of these partially functionalized resins was described in the preceding chapter. A 24 hour reflux with PEG anion produced a polymer (DC-05-213) with both phosphorus and chlorine capacities of 1.18 mequiv/g. This represents a decrease of 0.22 mequiv/g in phosphorus content and a drop of 2.69 mequiv/g in chlorine capacity. Because the incomplete reaction was attributed to an insufficient reaction length, a second sample was treated in an identical manner and the reflux was allowed to continue for 96 hours (DC-05-235). The chlorine capacity of the

resin was 0.00 mequiv/g, but the phosphorus capacity only dropped to 1.16 mequiv/g, little different from that found after a 24 hour reflux. A single attempt to produce a PEG/phosphonic acid resin with the dianion of PEG (NaH/PEG ratio = 2.2/1.0) yielded a resin which was essentially unchanged from the starting material. This indicated that accessibility of the polymer to the dianion is severely hindered, possibly as a result of the limited solubility of the dianion.

An attempt to complete the study of the effect of reaction length (begun with DC-05-213 and -235) was made by reacting a sample for 48 hours and led to a polymer in which a limited number of PEG units had been introduced. The starting material for this reaction had been a polymer with a lower g/g value (and therefore a higher degree of secondary cross-linking) than the one used for -213 and -235. This indicated that accessibility of the PEG anion was strongly affected by slight variations in the physical nature of the precursor polymer. Extending the length of reaction to 96 hours led to no further improvement in the final properties of the resin.

Given the extreme sensitivity of this reaction to the properties of the partially functionalized resin and the difficulties associated with producing such a resin in a reproducible manner, it became clear that this approach to producing a bifunctional PEG/phosphonic acid resin was not feasible. A more reliable method had to be found.

Previous work in this laboratory had shown that esters of phosphonic acid resins could be produced by converting a phosphonic acid resin to the

phosphonic dichloride and then quenching the acid chloride with the appropriate alcohol.[125] Since well characterized fully functional phosphonic acid resins could be easily synthesized, this approach was tried.

A sample of Büchner dried resin (10.00 g) was freed of water by three solvent exchanges (15 min. shake) with DMF. The resin was then converted to the dichloride with a mixture of thionyl chloride and DMF. The dichloride was then quenched with a solution of PEG in anhydrous pyridine. The amount of PEG used in this case was quite high. A 2.0/1.0 ratio of PEG/Cl was used as recommended,[125] but it must be noted that since each PEG chain has two -OH groups the actual alcohol/Cl ratio was 4.0/1.0. Due to time limitations, the effect of the PEG/Cl ratio was not investigated, but it is felt that a 1.0/1.0 ratio would have been sufficient. Any future work with this resin should include a study of this variable in order to conserve the use of reagents.

The initial reaction produced a resin with an acid capacity of 1.52 mequiv/g and a phosphorus capacity of 2.77 mequiv/g compared with values of 8.75 and 4.49 mequiv/g, respectively, in the initial phosphonic acid resin. The IR spectrum contained strong bands at 1112 $cm^{-1}$ (C-O-C) and 2800-2950 $cm^{-1}$ (C-H from PEG). All analyses indicated that a PEG diester had been formed. It is well known that mild, base catalyzed hydrolysis of phosphonic acid diester leads predominantly to the phosphonate monoester.[129] This reaction was thought to be ideal for producing a bifunctional PEG/phosphonic acid resin since all PEG units would have an acidic proton in close proximity.

Hydrolysis of the diester with 0.5 N KOH in 50% ethanol produced a resin with a percent solids value of 59.3, and acid and phosphorus capacities of 3.49 and 3.01 mequiv/g, respectively. Titration of the resin with 0.1 N NaOH revealed that 80% of the sites were PEG monoester (Figure 76). The remaining sites consisted of 18% diacid and 2% diester. Reaction with 3,5-dinitrobenzoyl chloride indicated that 2.22 mequiv/g of linear PEG units were present on the resin.

Two more batches of PEG monoester resin were synthesized for use in contact studies. Since it was not known if conversion to the dichloride would proceed smoothly when large amounts of resin were used, both batches were made by functionalizing and quenching two 20.00 g samples of phosphonic acid resin. In one case (DC-06-080) the batches were combined prior to hydrolysis of the monoester while in the other case (DC-06-163) the batches were hydrolyzed separately due to a slight difference in appearance of the quenched resins. The resins were all cracked to a greater degree than the initial phosphonic acid and an examination of DC-06-163B revealed that most of the cracking took place during the hydrolysis. Future work should include a study of the hydrolysis conditions in order to preserve the mechanical integrity of the resins. The characteristics of these large batches are shown in Table 34.

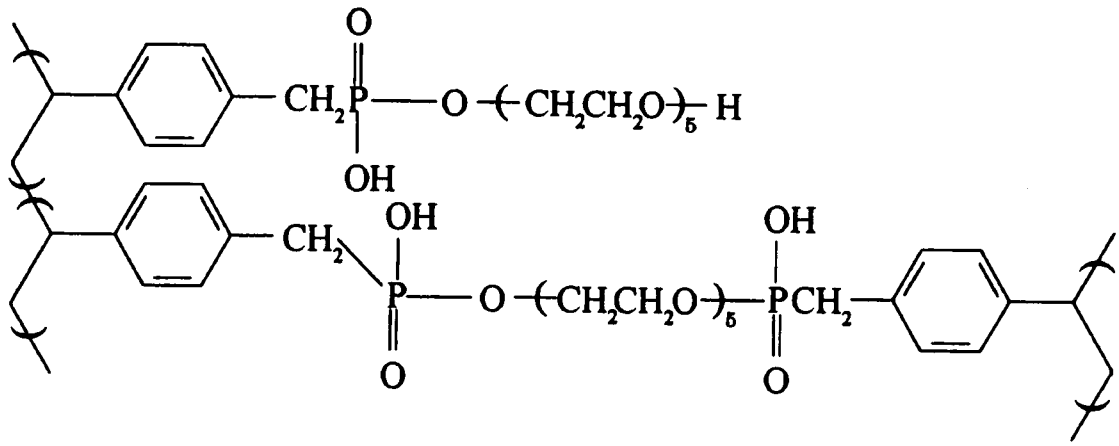


Figure 76. PEG phosphonate monoester resin.

Table 34

Characterization of PEG Phosphonate Monoester Resins

| Resin | % Solids | Capacities (mequiv/g) | | | % Diacid | % Monoester | % Diester |
|---|---|---|---|---|---|---|---|
| | | Acid Capacity | Phosphorus Capacity | Linear PEG Capacity | | | |
| DC-06-080 | 57.5 | 3.35 | 3.00 | 2.20 | 10 | 90 | -- |
| DC-06-163A | 55.2 | 4.02 | 3.28 | 2.00 | 19 | 81 | -- |
| DC-06-163B | 55.5 | 4.01 | 3.28 | 2.18 | 24 | 74 | 2 |

Contact Studies

Prior to the initiation of large scale contact studies with metal ions, a brief investigation was made of the affinity of the PEG resin for various organic acids. The purpose of this was to determine if the microenvironment of the polymer could be probed with molecules, such as aromatic acids, which can have the electron density of their functional group controlled through substitution. The results of the initial studies are shown in Table 35.

No significant interactions were observed, leading to the conclusion that molecules of this type cannot be used to investigate the microenvironment of the PEG resin. The data do show a clear hydrophobic effect in that as the aqueous character of the solvent is increased, more of the target molecule is absorbed by the resin.

Given the known affinity of crown ethers for alkali and alkaline earth metals,[108] it was expected that the PEG resins would display a significant interaction with these cations as well. Attempts were made to define the conditions under which accurate binding constants (see appendix 1) between the PEG resin and metal ions could be determined.

Strontium(II) was chosen as the first cation to be examined due to its presence as an environmental pollutant[1] and the ease with which low concentrations are detected via atomic emission spectroscopy.

Since a constant pH is necessary when measuring binding constants (see Chapter 4), the metal solutions were buffered, initially with 0.6 N acetic

Table 35

Uptake of Organic Acids by PEG Resin

| Compound | Solvent | $R_i$ | Percent Absorbed |
|---|---|---|---|
| Benzenesulfonic Acid | Methanol | 0.10 | 16.92 |
| | | 1.0 | 9.13 |
| 3,5-dinitrobenzoic Acid | Methanol | 0.10 | 21.43 |
| | | 1.0 | 18.90 |
| | 75% Methanol | 0.10 | 38.15 |
| | | 1.0 | 35.72, 36.98[a] |
| m-chlorobenzoic acid | Methanol | 0.10 | 11.51 |
| | | 1.0 | 17.60 |
| | 75% Methanol | 0.10 | 33.91 |
| | | 1.0 | 27.56 |
| sodium benzoate | Methanol | 0.075 | 25.98[b] |
| | | 0.75 | 22.67[b] |

[a] Duplicate runs

[b] Blurred endpoint

acid/sodium acetate at pH 5, and the resin samples were solvent exchanged (10 mL, 15 min. shake, 4X) prior to contact. Samples of carboxylic and phosphonic acid resins, in addition to the PEG resin, were contacted with $Sr(NO_3)_2$ at $R_i$ values ($R_i$ = milliequivalents target species/milliequivalents supported ligand) of 0.10 and 1.0 for periods of one and three days. The results, shown in Table 36, clearly indicate that the systems had reached equilibrium after one day. The low percent absorbed found with the PEG resins was not expected and was initially thought to be due to the presence of an excess of sodium ions (from the buffer). However, little increase in the percent absorbed was noted when the study was repeated in doubly distilled water (pH 5.3-5.6) where the PEG resin absorbed 10.20 and 4.47% at $R_i$ values of 0.10 and 1.0, respectively.

The apparent lack of interaction was attributed to the low pH at which the study was conducted. The study was repeated at pH 8 using 0.6 N TRIS (tris(hydroxymethyl)aminomethane) adjusted to the correct pH with nitric acid. Once again, the data (Table 37) indicate that the systems have reached equilibrium after one day but the PEG resin still did not absorb a significant amount of metal ion. A study conducted at pH 9 both with and without buffer (Table 38) revealed that the buffer was interfering with the uptake of $Sr^{2+}$. The final pH of the unbuffered solutions ranged from 6.8 to 9.1. TRIS most likely interferes with the absorption of strontium by either interacting with the PEG resin via its ammonium group or by interaction with strontium itself through the

Table 36

Uptake of $Sr^{2+}$ from Acetic Acid/Sodium Acetate Buffer at pH 5 by Carboxylic Acid, Phosphonic Acid, and PEG Resins

| Resin | $R_i$ | Contact Time (days) | Percent Absorbed |
|---|---|---|---|
| Carboxylic Acid | 0.10 | 1 | 35.42 |
| | | 3 | 35.20 |
| | 1.0 | 1 | 19.38 |
| | | 3 | 17.91 |
| Phosphonic Acid | 0.10 | 1 | 86.73 |
| | | 3 | 86.98 |
| | 1.0 | 1 | 57.54 |
| | | 3 | 55.87 |
| PEG | 0.10 | 1 | 2.42 |
| | | 3 | 2.57 |
| | 1.0 | 1 | 0.86 |
| | | 3 | 0.00 |

Table 37

Uptake of $Sr^{2+}$ from TRIS Buffer at pH 8
by Carboxylic Acid, Phosphonic Acid, and PEG Resins

| Resin | $R_i$ | Contact Time (days) | Percent Absorbed |
|---|---|---|---|
| Carboxylic Acid | 0.10 | 1 | 80.78 |
| | | 3 | 80.67 |
| | 1.0 | 1 | 57.40 |
| | | 3 | 58.52 |
| Phosphonic Acid | 0.10 | 1 | 96.63 |
| | | 3 | 96.58 |
| | 1.0 | 1 | 82.15 |
| | | 3 | 82.04 |
| PEG | 0.10 | 1 | 7.31 |
| | | 3 | 9.82 |
| | 1.0 | 1 | 2.03 |
| | | 3 | 4.79 |

Table 38

Uptake of $Sr^{2+}$ from Buffered and Unbuffered Solutions at pH 9 by Carboxylic Acid, Phosphonic Acid, and PEG Resins

| Resin | $R_i$ | Buffer | Percent Absorbed |
|---|---|---|---|
| Carboxylic Acid | 0.10 | TRIS | 98.56 |
| | | None | 99.55 |
| | 1.0 | TRIS | 76.76 |
| | | None | 83.67 |
| Phosphonic Acid | 0.10 | Tris | 100[a] |
| | | None | 99.93 |
| | 1.0 | TRIS | 94.09 |
| | | None | 93.73 |
| PEG | 0.10 | TRIS | 10.23 |
| | | None | 32.11 |
| | 1.0 | TRIS | 3.64 |
| | | None | 16.89 |

[a] No AA signal

-OH groups. A search for a better buffer was initiated and, based on structure and $pK_a$ value, it was decided that "EPPS" (N-[2-hydroxyethyl]- piperazine-N'-[3-propanesulfonic acid]) would be investigated despite its high cost.

The contact study was performed at pH 8 in 0.6 N EPPS. Although the pH control provide by EPPS was excellent, this compound made the samples virtually impossible to analyze via atomic emission due to rapid clogging of the burner. Because of this, samples were compared with the AA standards which had been prepared with TRIS. While it appeared that the percent absorbed increased, the validity of the results are in question since the matrices of the samples and standards differed greatly. Both PEG samples ($R_i$ 0.10 and 1.0) showed approximately 27% absorbed. The final buffer to be examined was imidazole. Samples were prepared in 0.6 N imidazole at pH 7 and contacted for 24 hours. The results indicated that imidazole would function well as a buffer in this system as the pH was well controlled, no difficulties were encountered during the AA analysis, and the compound did not seem to seriously inhibit uptake of strontium by the PEG resin. Given these observations, solutions were prepared over a wide concentration range and the binding constants to carboxylic and phosphonic acid resins were evaluated.

Prior to evaluation of the binding constants, the stoichiometry of the interaction between strontium and the phosphonic acid resin was examined. The binding constant analysis depends on the existence of a 1:1 binding and it was of interest to investigate a method of verifying the stoichiometry should

questions arise in future contact studies. The stoichiometry was examined by using the method of continuous variations.[130] Briefly, one performs a contact study in which the sum of milliequivalents of metal and milliequivalents of resin is held constant. The ratio of metal to resin is varied and the amount of complex formed is plotted against the fraction of resin present in the sample (Job plot). The maximum amount of complex will be formed when the ratio of metal to resin equals the stoichiometry of the complex. Thus, for a 1:1 complex, the maximum amount of complex will be formed when the fraction of resin equals 0.5.

Phosphonic acid resin was contacted with strontium using a total of one milliequivalent of metal and resin. The Job plot shown in Figure 77 clearly shows the formation of a 1:1 complex. Given the success of this experiment, it is recommended that future questions of stoichiometry be addressed in this manner rather than through more elaborate spectroscopic means.

Contact of one milliequivalent of resin with 10 mL of strontium nitrate solution of varying concentration resulted in the isotherms shown in Figures 78 and 79. Fitting the experimental curve with a double hyperbolic equation (see Appendix 1) gave the results shown in Table 39. Both resins show modest binding constants to strontium. Unfortunately, when the PEG resin was contacted with the same strontium solutions, no isotherm was obtained. The percent absorbed varied between 3.1 and 6.8 over a wide range of $R_i$ values (0.0025 to 4.0). These results indicate that no significant interaction exists

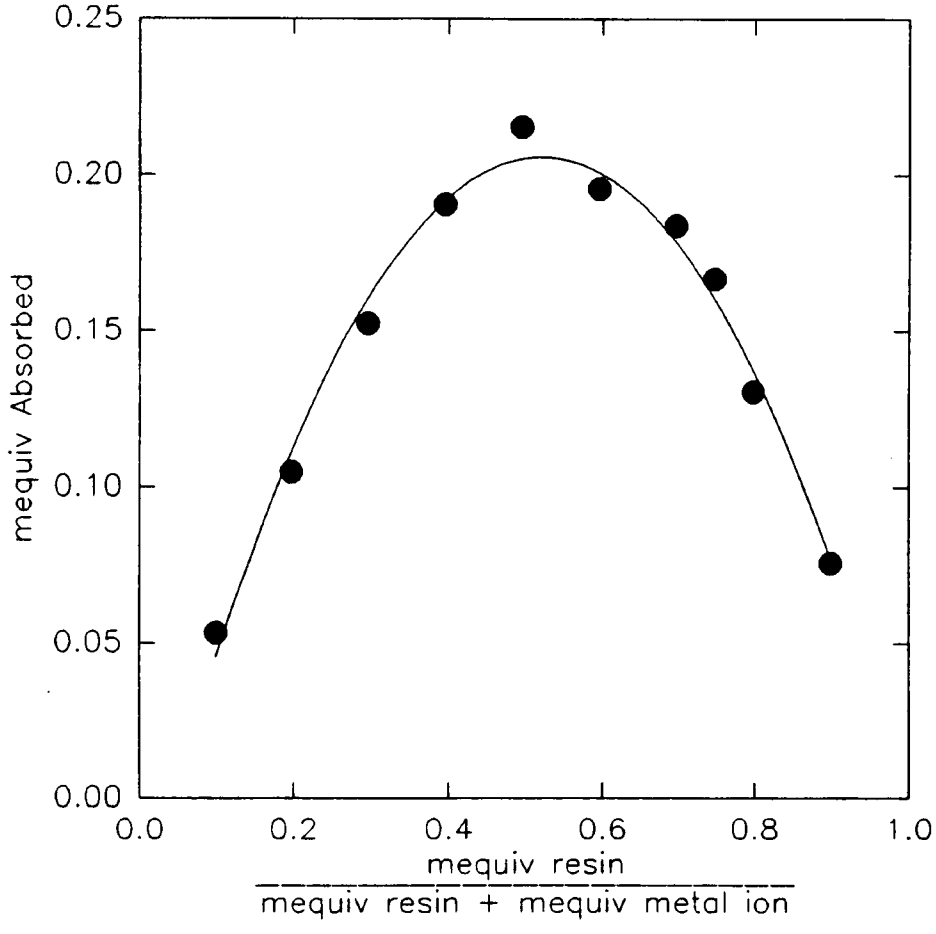



Figure 77. Job plot for the interaction of strontium with phosphonic acid resin.

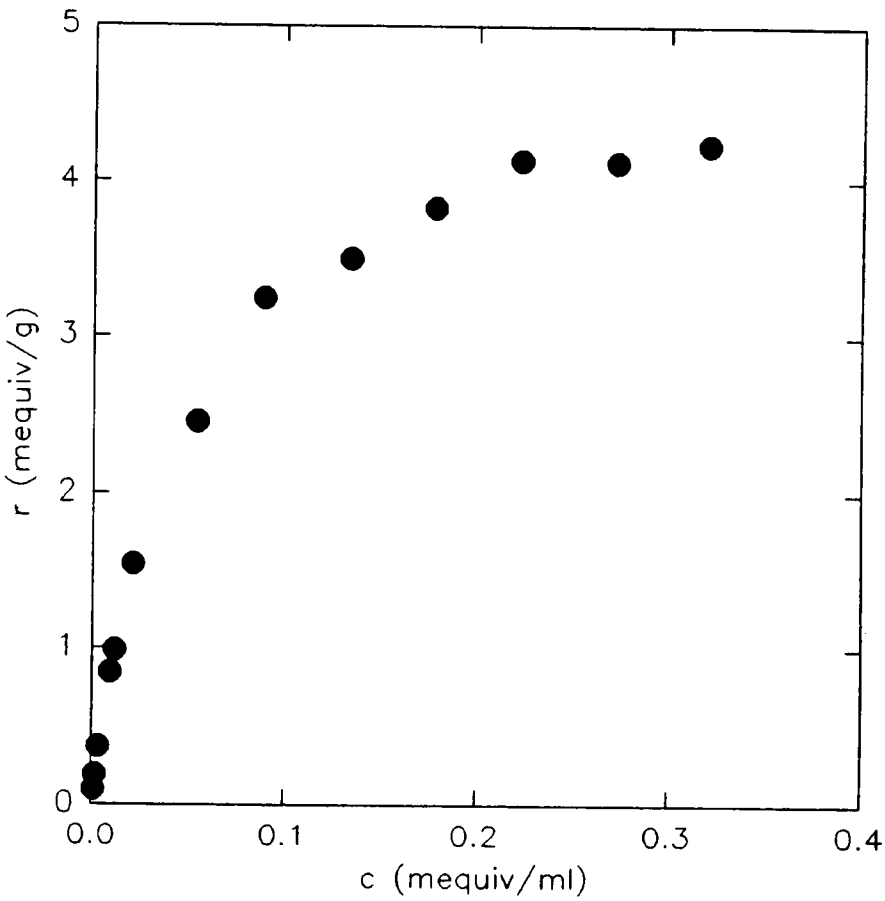



Figure 78. Binding isotherm for the interaction between $Sr^{2+}$ and carboxylic acid resin.

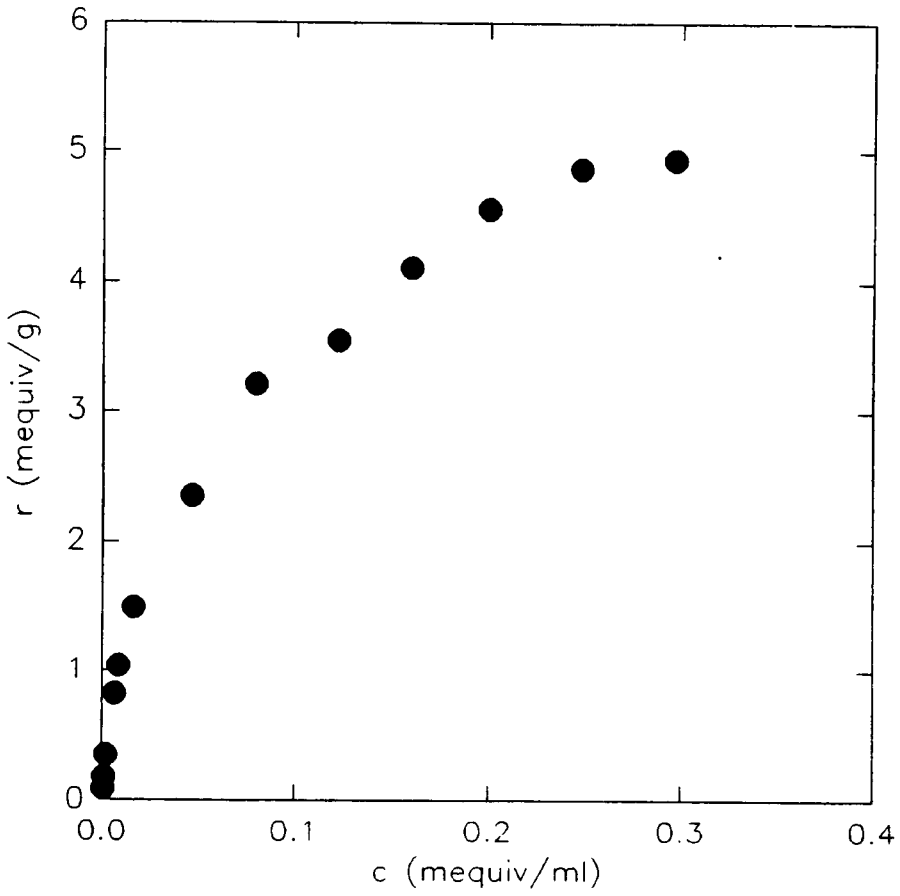



Figure 79. Binding isotherm for the interaction between $Sr^{2+}$ and phosphonic acid resin.

Table 39

Binding Constants Between $Sr^{2+}$ and Carboxylic and Phosphonic Acid Resins

| Resin | Carboxylic Acid | Phosphonic Acid |
|---|---|---|
| a | $9.65 \times 10^{5}$ | 1.47 |
| b | $1.33 \times 10^{7}$ | $7.66 \times 10^{-3}$ |
| 1/b | $7.53 \times 10^{-8}$ | 131 |
| c | 4.58 | 5.91 |
| d | $4.28 \times 10^{-2}$ | 0.189 |
| 1/d | 23.4 | 5.28 |
| Correlation | 0.9983 | 0.9982 |

$$r = \frac{ax}{b + x} + \frac{cx}{d + x}$$

r = mequiv metal/g resin
x = mequiv metal/mL solution
a = saturation capacity 1
b = 1/binding constant 1
c = saturation capacity 2
d = 1/binding constant 2

between strontium and the PEG resin in this system.This was a surprising result considering the interactions which exist between crown ether and the alkaline earth cations. The possibility that the beads were collapsing due to the high ionic strength of the solution was investigated. Three samples were contacted with strontium in 0.2 N imidazole at $R_i$ values of 0.010, 0.10, and 1.0. Once again, less that 7% was absorbed in each sample. Samples were then contacted with unbuffered solutions and the percent absorbed was found to be strongly dependent on the final pH of the system. When the final pH varied from 4.1 to 4.7 the percent absorbed was 14.33, 4.52, and 6.03 at $R_i$ values of 0.010, 0.10, and 1.0. Increasing the final pH (by eluting the resin with 1 N NaOH and $H_2O$ prior to contact) to the range 6.4-7.9 led to 99.67, 20.69, and 4.98 percent absorbed for the same $R_i$ values. A set of polystyrene controls were also contacted and each sample absorbed less than 3% of the strontium present. This data seemed to indicate that the buffer was causing collapse of the gel resins even at a concentration of 0.2 N.

A 5% cross-linked MR PEG resin was synthesized in order to provide a resin less susceptible to collapse at high ionic strength. However, this resin did not absorb a significant amount of strontium from either 0.6 N or 0.2 N imidazole (less than 12% at $R_i$ = 0.010). Once again, the percent absorbed followed the expected trend in the absence of buffer: 79.26, 15.08, and 6.57% at $R_i$ values of 0.010, 0.10, and 1.0 (pH 7.0-7.6). No significant interactions were observed between imidazole and $Sr^{2+}$ (investigated with UV/Vis

spectroscopy) or between imidazole and the PEG resin (investigated via contact studies). The precise mechanism by which imidazole and other buffers inhibit the uptake of strontium is not known but it is believed to be a weak interaction with the resin. This would imply that the interaction of PEG resin with strontium is itself very weak. Given this data, it was decided to abandon the study of the uptake of alkaline earth metals by PEG resins. No bifunctional PEG/Acid resins were examined.

Attention then turned to the uptake of anionic transition metal chloro complexes. These complexes were extensively studied by Warshawsky[109] during the initial synthesis of the PEG resin, forming a large body of control data against which the performance of the bifunctional resins could be compared. In order to verify the similarity of resins produced in this lab to those used in the earlier study, a limited set of samples was contacted with $HFeCl_4$ under similar conditions. The initial study was done in 5 N NaCl at pH 1.5 ($3.16 \times 10^{-2}$ N HCl) which proved to be too concentrated to allow the AA analysis to be completed without clogging of the burner. Nonetheless, the approximate numbers obtained differed little from those of the earlier study prompting more extensive investigations. In order to facilitate the AA analysis, the NaCl concentration was lowered to 4 N. A full set of samples were contacted ($R_i$ 0.001 to 3.0) and the residual Fe concentration was again measured by atomic absorption after dilution to the proper concentration with water. The isotherm generated from the data approached 0.75 mequiv/g as

the maximum value. This is in excellent agreement with the value of 0.73 mequiv/g obtained by Warshawsky. However, the process of diluting the samples with $H_2O$ (necessary to avoid clogging of the burner) led to solutions containing a varying amount of NaCl. This differing matrix resulted in some scatter in the data, especially in the lower concentrations. A better method of analyzing the samples for residual iron was needed.

Since $FeCl_4^-$ is colored, the use of visible spectroscopy to quantify the amount of iron remaining in solution was investigated. The spectrum of a $10^{-4}$ N solution had maxima at 224 and 338 nm. Since the shorter wavelength is out of the range of simple laboratory equipment, a series of standards were prepared and a Beer's law plot was generated using the absorbance values obtained at 338 nm with a Spectronic 21 instrument. The standards ($2.5 \times 10^{-5}$ to $1.0 \times 10^{-4}$ N) yielded a straight line with a linear correlation of 0.99984.

Contact studies were performed with both the PEG and the phosphonic acid resin and the concentration of the contacted solution was measured via visible spectroscopy. The phosphonic acid isotherm continued to have some scatter despite the improved analysis method and it was suspected that this was due to the samples not reaching equilibrium after 24 hours. A limited kinetic study was undertaken and it was found that the PEG reached equilibrium after 24 hours, but the phosphonic acid continued to absorb Fe even after three days. After seven days, the rate of increase in the percent absorbed had slowed considerably, but small increases were seen even at 14 days (Table 40).

Table 40

Kinetic Study of the Uptake of $HFeCl_4$ by Phosphonic Acid Resin

| | % Absorbed | | | | |
|---|---|---|---|---|---|
| $R_I$ | 1 Day | 3 Days | 7 Days | 10 Days | 14 Days |
| 0.10 | 69.53 | 87.55[a] | 97.69[a] | 98.77 | 99.00 |
| 1.0 | 20.70 | 22.06 | 33.11[a] | 35.13 | 41.08 |

[a] Average of two determinations

The fact that the phosphonic acid absorbed a significant amount of iron from this solution was considered uncharacteristic since the iron should be present as an anionic complex. The mechanism by which a cation exchange resin could extract anions was of considerable interest. It is known (Chapter 1) that the phosphoryl oxygen of phosphonic acid and its esters is readily protonated at low pH. It was postulated that the iron was being extracted by a process in which a proton bound to the phosphoryl oxygen was exchanged for a molecule of $HFeCl_4$. This hypothesis was supported by the decrease in the pH of the contacted solution which was as large as 0.35 pH units. However, to my knowledge, no such complex had ever been reported, leading to suspicion that the proposed mechanism was incorrect.

An attempt was made to limit the pH change of the solution by solvent exchanging the resins with 4 N NaCl only (no HCl) in order to avoid the initial protonation of the phosphoryl oxygen. As before, the PEG resin showed little change in pH but the phosphonic acid resin was still undergoing large changes although the final pH values were not as low as those observed earlier. No definite conclusions concerning the mechanism could be drawn from this.

If the proposed mechanism were correct, then an increase in the sodium chloride concentration (and thus a higher concentration of $FeCl_4^-$) should lead to a larger amount of uptake. To investigate this, both the PEG and the phosphonic acid resins were contacted with solutions which varied in sodium chloride concentration. As seen in Table 41, the PEG resin was very sensitive

Table 41

Effect of Sodium Chloride Concentration on the Uptake of $HFeCl_4$

| Resin | $R_i$ | [NaCl] | | |
|---|---|---|---|---|
| | | 3 N | 4 N | 5 N |
| Phosphonic Acid | 0.10 | 97.22 | 97.91 | 98.51 |
| | 1.0 | 30.28 | 34.62 | 36.83 |
| PEG | 0.10 | 33.15 | 69.31 | 94.45 |
| | 1.0 | 14.68 | 31.47 | 45.90 |

to the NaCl concentration. The phosphonic acid resin was much less sensitive, although a slight increase in percent absorbed was noted with increasing sodium chloride concentration implying that the absorbed species was $FeCl_4^-$. However, the magnitude of the increase was too small to draw definitive conclusions.

More direct evidence of the nature of the extracted species was providedby elemental analysis. A sample of phosphonic acid resin was contacted for 7 days with an $HFeCl_4$ solution at an $R_i$ of 3.0. Following contact, the solution was analyzed for residual iron and the resin was divided into two portions. One portion was eluted with 100 mL of 1 N $HNO_3$ while the other remained unwashed. A chlorine elemental analysis of the unwashed sample revealed 2.93 mequiv/g (NaCl) while the washed sample did not contain any chlorine. The resins were also sent to Galbraith Laboratories for an iron elemental analysis and were found to contain 8.21% (unwashed, 1.47 mmole/g) and 8.48% Fe (washed, 1.52 mmole/g). These values are in reasonable agreement with the 1.81 mmole/g found by analysis of the contacted solution. In order to be certain that nitric acid was not destroying the chloro complex, the experiment was repeated (with sulfonic acid resin used as a control) and the resin washed with 100 mL of water instead. Analysis at Galbraith Laboratories revealed that the phosphonic acid contained 8.58% Fe (1.54 mmole/g) and 0.92% Cl (0.26 mmole/g). The sulfonic acid resin did not absorb a significant amount of iron as measured by analysis of the contacted solution and was not

sent for elemental analysis. The elemental analyses demonstrate that $FeCl_4^-$ is not the species being extracted by the phosphonic acid resin. It is believed that the species extracted is trivalent cationic iron which will be present in small quantities in the solution. As the $Fe^{3+}$ is extracted, more is produced via the equilibria which exist. This can explain the unusually long period of time required for the system to reach equilibrium.

The bifunctional PEG/phosphonic acid and PEG/carboxylic acid resins, along with their monofunctional counterparts, were contacted with the chloro complexes of Fe, Zn, Cd, Hg, and Co. While complete isotherms were obtained in some cases, the interactions were small enough in others to permit characterization of only a small portion of the complete curve. As a result, the performance of the resins has been evaluated by comparing the amount of metal absorbed per gram of resin, r (mequiv/g), at selected $R_l$ values. The results of this analysis are presented graphically in Figures 80-82. The PEG resin yields results which are very similar to those obtained by Warshawsky. Neither the carboxylic acid nor the PEG/carboxylic acid resin display a great deal of selectivity or have very high affinities for any of the ions examined.

The phosphonic acid resin displays a high selectivity for Fe due to the fact that the chloro complex formed with iron is the weakest of those examined.[131] This allows iron to exist to a larger extent as a cation, for which phosphonic acid ligands are known to have a high affinity (see Chapters 1 and 5). The high affinity of the phosphonic acid ligand for iron is continued in the

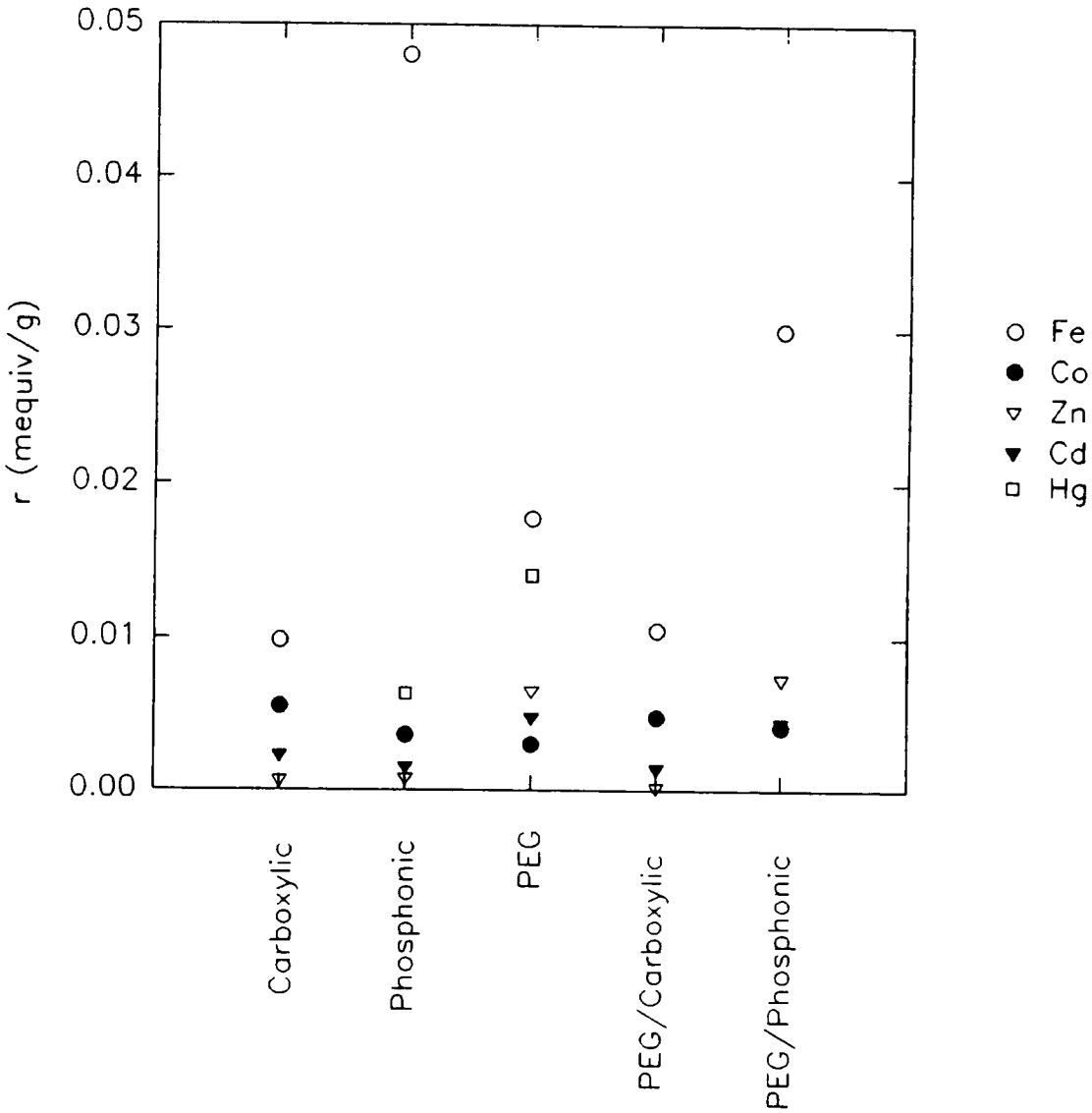



Figure 80. Selectivity of the PEG series of resins at $R_i$ = 0.010.

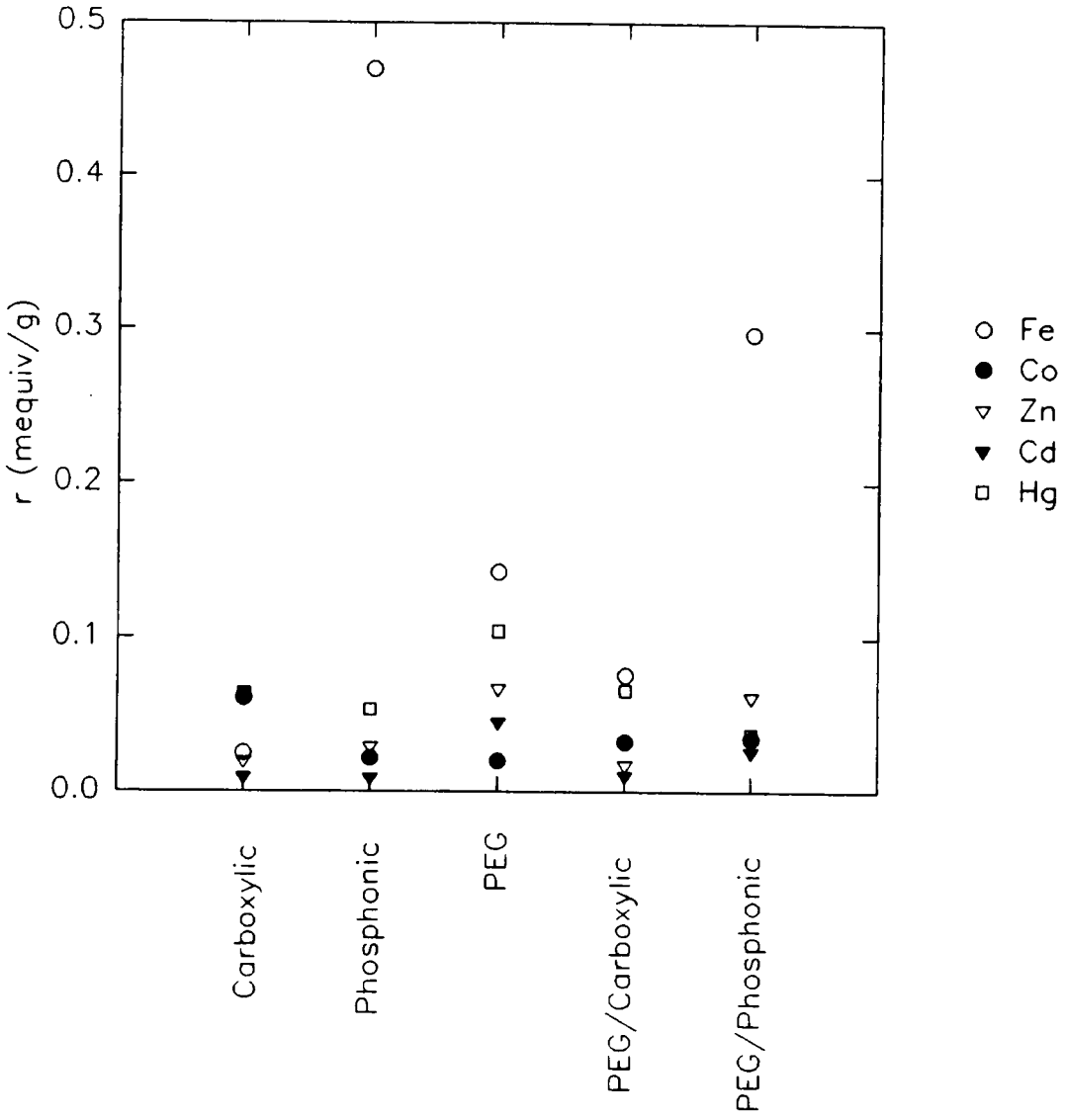



Figure 81. Selectivity of the PEG series of resins at $R_i$ = 0.10.

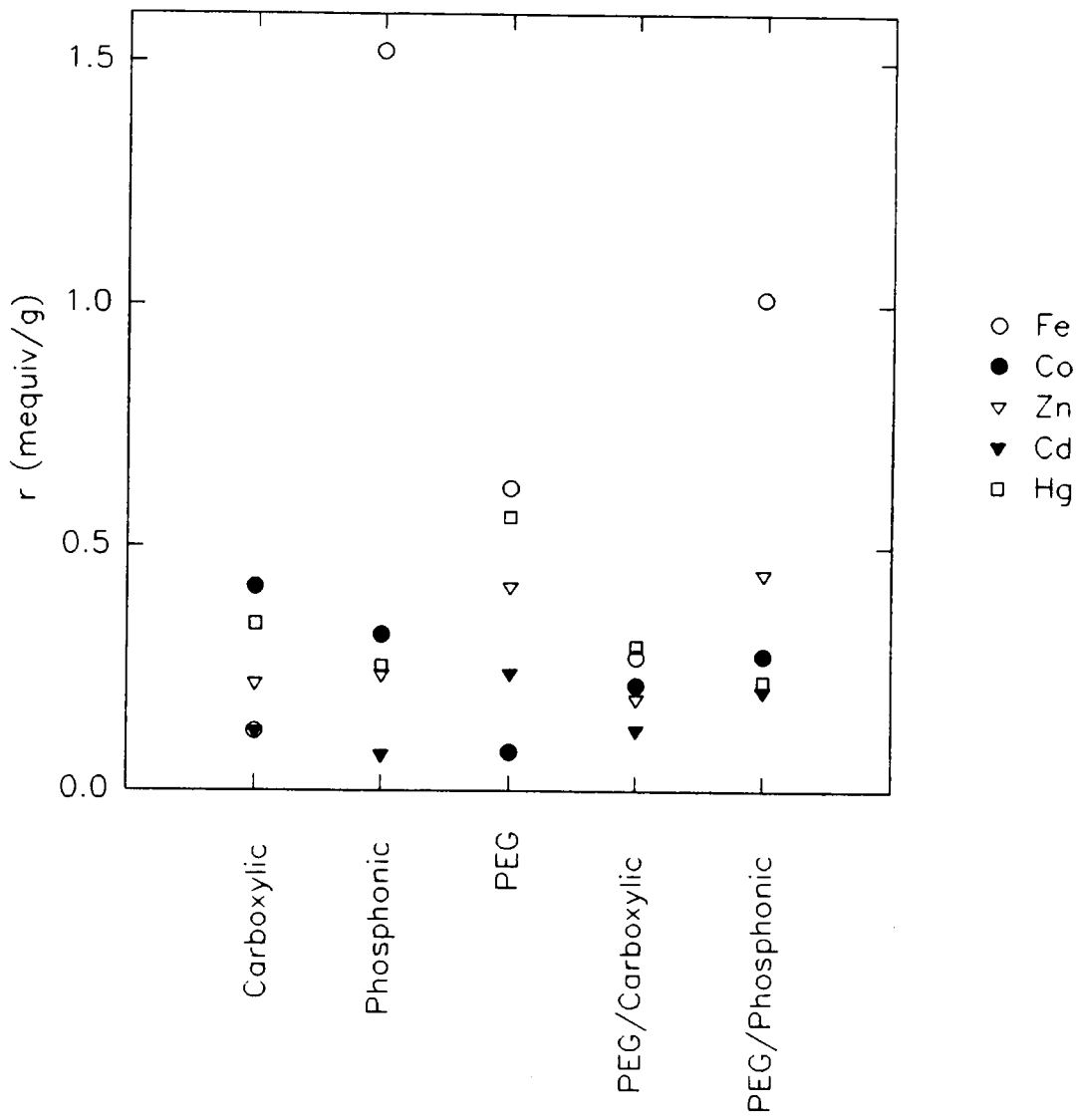



Figure 82. Selectivity of the PEG series of resins at $R_i$ = 1.0.

bifunctional polymer and the selectivity series for the remaining metals is modified from that of either monofunctional resin. In general, a larger amount of metal is absorbed per gram of polymer than with the phosphonic acid resin despite its higher capacity. This indicates that a cooperative extraction is occurring although additional research is necessary in order to determine if synergism is truly present.

The final compound examined was sodium picrate. This molecule was chosen because the PEG chains exhibit a moderate affinity for sodium and its concentration can be easily monitored by visible spectroscopy since the picrate anion is intensely colored. The amount of sodium sorbed by the resin is equal to the amount of picrate lost from the solution since the anion must accompany sodium into the resin in order to maintain charge neutrality. Initial studies in both methanol and tetrahydrofuran (THF) indicated that PEG resin possessed a considerable affinity for the sodium salt which appeared to be greater (higher percent absorbed) in THF. For this reason, THF was chosen as the solvent for further studies.

The binding isotherm was investigated with two different batches of PEG resin in order to evaluate the reproducibility of the determination. The initial portion of the isotherms was not well characterized due to the range of concentrations chosen, but the resins gave almost identical curves in the latter portion. Enough of the initial portion was defined to allow for a calculation of the binding constant by fitting the experimental portion with a double hyperbolic

equation (see Appendix 1). Excellent agreement was obtained with the two resins yielding binding constants of 67.80 $N^{-1}$ and 64.60 $N^{-1}$. This value is within the same order of magnitude as the calculated binding constant of a polystyrene supported linear poly(ethylene glycol) resin containing seven oxygens which was examined by Smid and co-workers.[132-134]

Examining the early portion of the curve required only a decrease in the concentration of the picrate solution. However, due to an incomplete leveling of the binding isotherm, it was also of interest to examine portions of the curve past the last experimental point. This posed a difficulty due to the limited solubility of sodium picrate in THF. Reaching this portion of the curve required an increase in the $R_i$ value which was only possible by decreasing the amount of resin contacted. To examine the feasibility of this procedure, 0.25 milliequivalents of resin were contacted with two series of solutions. One series required that 5 mL of contact solution be added to the resin while the other needed 10 mL in order to reach the desired molecule-to-ligand ratio. This also allowed the effect of the contacted volume on the measured binding constant to be examined. The results were somewhat mixed. The series contacted with 5 mL of solution gave a binding constant of 60.01 $N^{-1}$ while the 10 mL samples gave 41.08 $N^{-1}$. However, a large amount of scatter was present in the data. Later it was observed that the scatter was due to the increased amount of relative error associated with weighing such small samples. For this reason, all other contact studies were performed with 0.5 milliequivalents of resin.

The PEG/carboxylic, PEG/phosphonic, and all three monofunctional resins were examined for their ability to extract sodium picrate from THF over a wide range of concentration. The carboxylic acid resin had little affinity for sodium picrate and did not yield a binding isotherm. The phosphonic acid was little better, although when plotted the data did begin to approximate an isotherm despite the low amount of sodium picrate extracted. The three PEG containing resins all had an affinity for sodium picrate as shown by their binding isotherms (Figures 83-85). The binding constants obtained were 67.54, 40.26, and 30.77 $N^{-1}$ for the PEG, PEG/carboxylic acid, and PEG/phosphonic acid resins, respectively. The presence of an acidic group results in a modest decrease in the binding constant. Such a modification would facilitate the regeneration of the resin following loading with sodium picrate. A full study of the uptake of picrate salts would include the examination of several alkali and alkaline earth picrates in a wide variety of solvents.

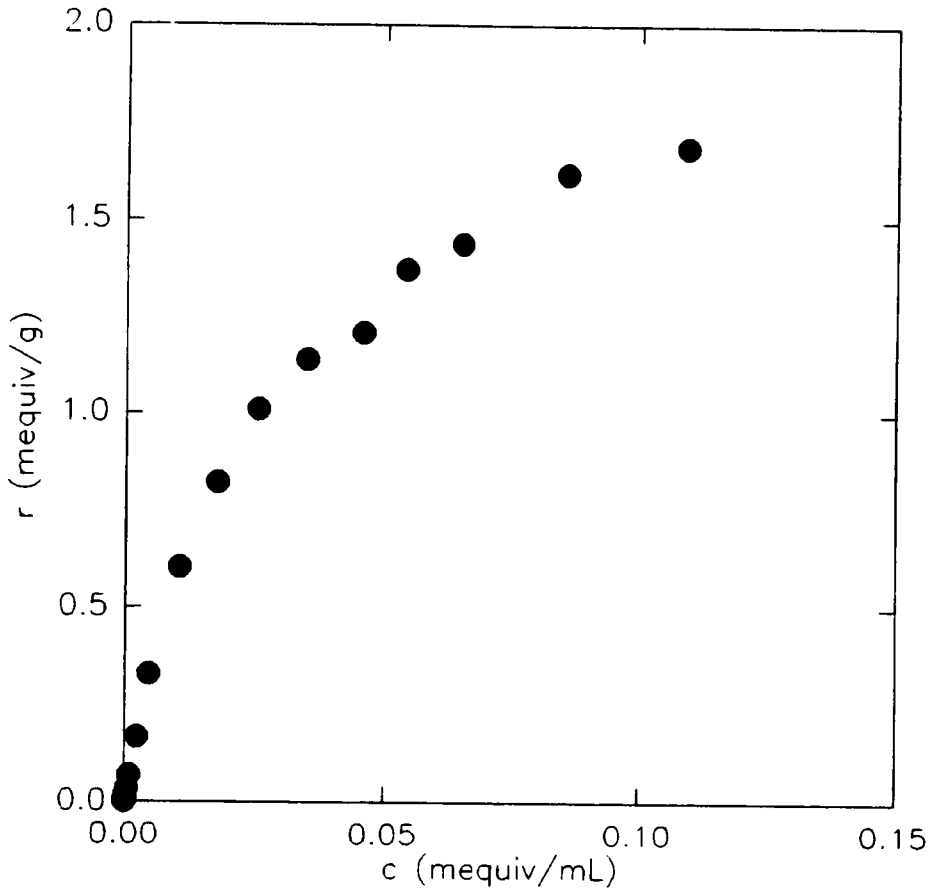



Figure 83. Binding isotherm for the interaction of sodium picrate with PEG resin.

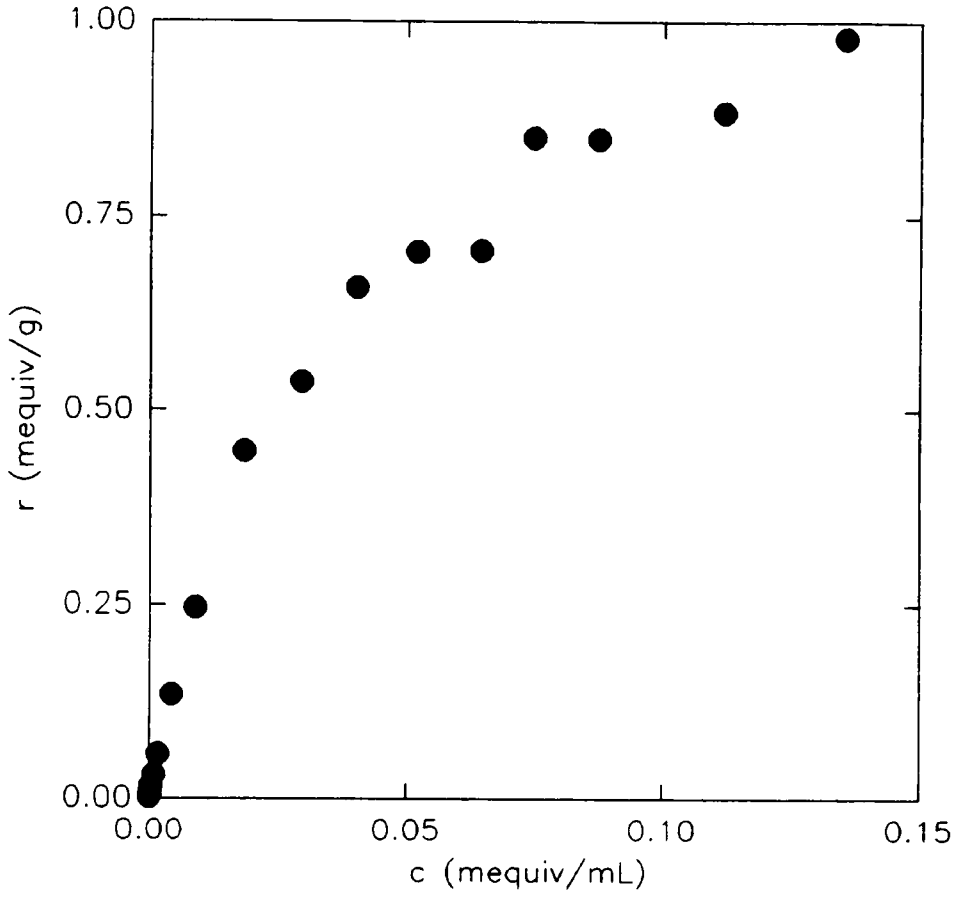



Figure 84. Binding isotherm for the interaction of sodium picrate with PEG/carboxylic acid resin.

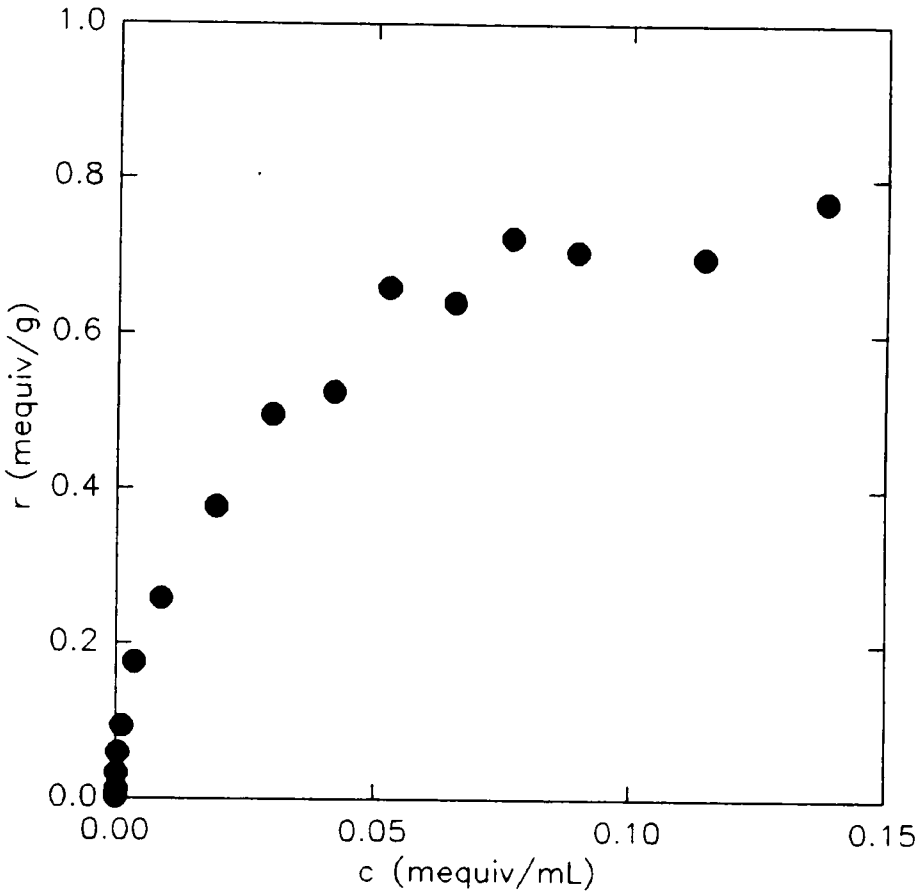



Figure 85. Binding isotherm for the interaction of sodium picrate with PEG/phosphonic acid resin.

## Conclusions

A series of resins containing both pseudocrown ether sites and acidic groups has been synthesized and characterized. The uptake of several classes of compounds has been investigated and binding constants to sodium picrate have been determined. The preliminary data indicate that the presence of the acidic group can modify the binding environment and that further investigation of this class of resins is warranted. In particular, the effect of the acidic groups on the kinetics of absorption should be examined in order to characterize the influence these groups exert on the accessibility of the resin.

# BIFUNCTIONAL ION EXCHANGE RESINS:

# SYNTHESIS AND CHARACTERIZATION

# OF

# ION-SELECTIVE POLYMERS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Darrell W. Crick

May 1994

# CHAPTER 4

# INTERPENETRATING POLYMER NETWORKS

## Introduction

Interpenetrating polymer networks (IPNs) can be defined as materials consisting of two entangled, noncovalently bound networks. In general, these materials are prepared by synthesizing one network in the presence of the other by one of several common techniques described in the extensive IPN literature.[135-139] All IPNs synthesized for these studies were sequential IPNs, meaning that network I was prepared and then swollen in the network II monomers which were polymerized to yield the IPN.

Although many IPNs have found use in a wide variety of fields, a limited number of IPNs have been used for ion exchange. One of the first descriptions of this sort of material was an IPN of polystyrene and poly(vinylbenzyl chloride) in which the styrene was sulfonated and the VBC aminated to yield a polymer containing both cation and anion exchange sites.[140] Other ion-exchanging IPNs have been described, primarily in the patent literature.[141-143]

It was thought that IPNs could provide a novel route to dual mechanism bifunctional polymers, either through functionalization of pre-formed IPNs or by

polymerization of functional monomers. An experimental program was undertaken to study the feasibility of producing IPNs with the desired characteristics. The goals of this experimental program were to establish the conditions under which the desired IPNs could be synthesized and characterized and to define an experimental method for determining their metal ion binding constants.

Synthesis

Initial studies concentrated on the production of IPNs of polystyrene with an ion exchanging network. Polystyrene xerogel beads were synthesized via suspension polymerization as described in the experimental section and were Soxhlet extracted with toluene, dried, and sieved to yield the -40 +60 mesh fraction which was used in all IPN syntheses.

Network II was introduced by allowing network I (polystyrene) to swell in a solution of the network II monomer(s), cross-linking agent, and initiator dissolved in toluene. The concentration of the active monomer(s) was 4.25M (full details of the solution preparation are given in the experimental section). Network I was allowed to swell overnight after which the excess monomer solution was removed from the swollen beads by filtration. Swelling ratios were between 4 and 5. The IPN was then formed by subjecting the swollen beads to a second suspension polymerization. Once formed, the IPNs were washed with hot water to remove the suspension stabilizers and Soxhlet

extracted with methanol to remove any material which was not incorporated into the network.

Due to the ability of pyridine to coordinate certain metal ions, poly(4-vinylpyridine) was chosen as the first candidate for network II. A polystyrene/poly(4-vinylpyridine) IPN was synthesized (PS/VP) in which network I (polystyrene) was cross-linked with 2 wt% divinylbenzene and network II with 10 mole%.

Other IPNs were prepared. In order to provide a bifunctional polymer, polystyrene/poly(4-vinylpyridine-co-ethyl acrylate) was synthesized (PS/VP-EA), and the ester sites hydrolyzed to yield a polymer containing both pyridine and carboxylic acid groups. The monofunctional polystyrene/poly(ethyl acrylate) IPN (PS/EA) was also prepared and hydrolyzed to polystyrene/poly(acrylic acid) (PS/AA) to provide a second control resin against which the performance of the bifunctional IPN could be compared. Polystyrene/poly(methacrylic acid) (PS/MA) was also synthesized as was poly(ethyl acrylate)/polystyrene (EA/PS). The latter is simply the inverse of the PS/EA IPN described above and was produced in order to provide a control resin for an NMR study of the degree of interpenetration (Chapter 6). A single attempt to produce a polystyrene/poly(4-vinylpyridine-co-acrylic acid) IPN by direct polymerization of 4-vinylpyridine and acrylic acid was unsuccessful. The heat of the acid-base reaction which occurred upon mixing of the monomers was sufficient to initiate polymerization before the network II

monomers could be sorbed into the polystyrene beads. A listing of the IPNs produced for this project is given in Table 42. A schematic of the formation of the PS/VP-EA IPN is shown in Figure 86.

All of the IPNs containing ethyl acrylate gave spherical, homogeneous beads with little to no chaff. In contrast, the monofunctional PS/VP IPN contained a large amount of chaff. The chaff was removed from the beads by taking advantage of its lower mechanical strength. The mixture was placed in a beaker and stirred vigorously with a large stir bar overnight which served to break up most of the chaff into very fine particles. These were easily separated from the beads by sieving the mixture. The chaff is believed to be lightly cross-linked poly(4-vinylpyridine) which formed due to leaching of a small amount of monomer from the polystyrene support during the suspension polymerization. Analysis of the material by infrared spectroscopy revealed it to be nearly identical in chemical composition to the beads. Optimization of the aqueous phase for this system would eliminate the formation of chaff and should be performed prior to any future syntheses. The polystyrene/poly(methacrylic acid) IPN also contained a considerable amount of chaff due to extraction of the monomer into the aqueous phase.

Hydrolysis of the ethyl acrylate groups proved to be more challenging than first estimated, most likely due to the high level of cross-linking present. Initial attempts to hydrolyze the network utilized 12 M HCl which had proven very effective in hydrolyzing phosphonic acid esters (see Chapters 1 and 5).

Table 42

Composition of Interpenetrating Polymer Networks

| Resin | Network I | Network II |
|---|---|---|
| DC-03-239 | PS (2 wt% DVB) | VP (10 mol% DVB) |
| DC-03-244 | PS (2 wt% DVB) | EA (10 mol% DVB) |
| DC-03-244H | PS (2 wt% DVB) | AA |
| DC-03-247 | PS (2 wt% DVB) | EA (10 mol% DVB) |
| DC-03-251A | PS (2 wt% DVB) | VP-EA (10 mol% DVB) |
| DC-03-251AH | PS (2 wt% DVB) | VP-AA |
| DC-03-251B | PS (2 wt%DVB) | VP-EA (10 mol% DVB) |
| DC-03-251BH | PS (2 wt% DVB) | VP-AA |
| DC-03-262 | PS (2 wt% DVB) | MA (10 mol% DVB) |
| DC-03-267 | PS (2 wt% DVB) | EA (4 mol% DVB) |
| DC-05-179 | EA (10 mol% DVB) | PS (2 wt% DVB) |

PS = polystyrene

VP = poly(4-vinylpyridine)

EA = poly(ethyl acrylate)

AA = poly(acrylic acid) from hydrolysis of poly(ethyl acrylate)

MA = poly(methacrylic acid)

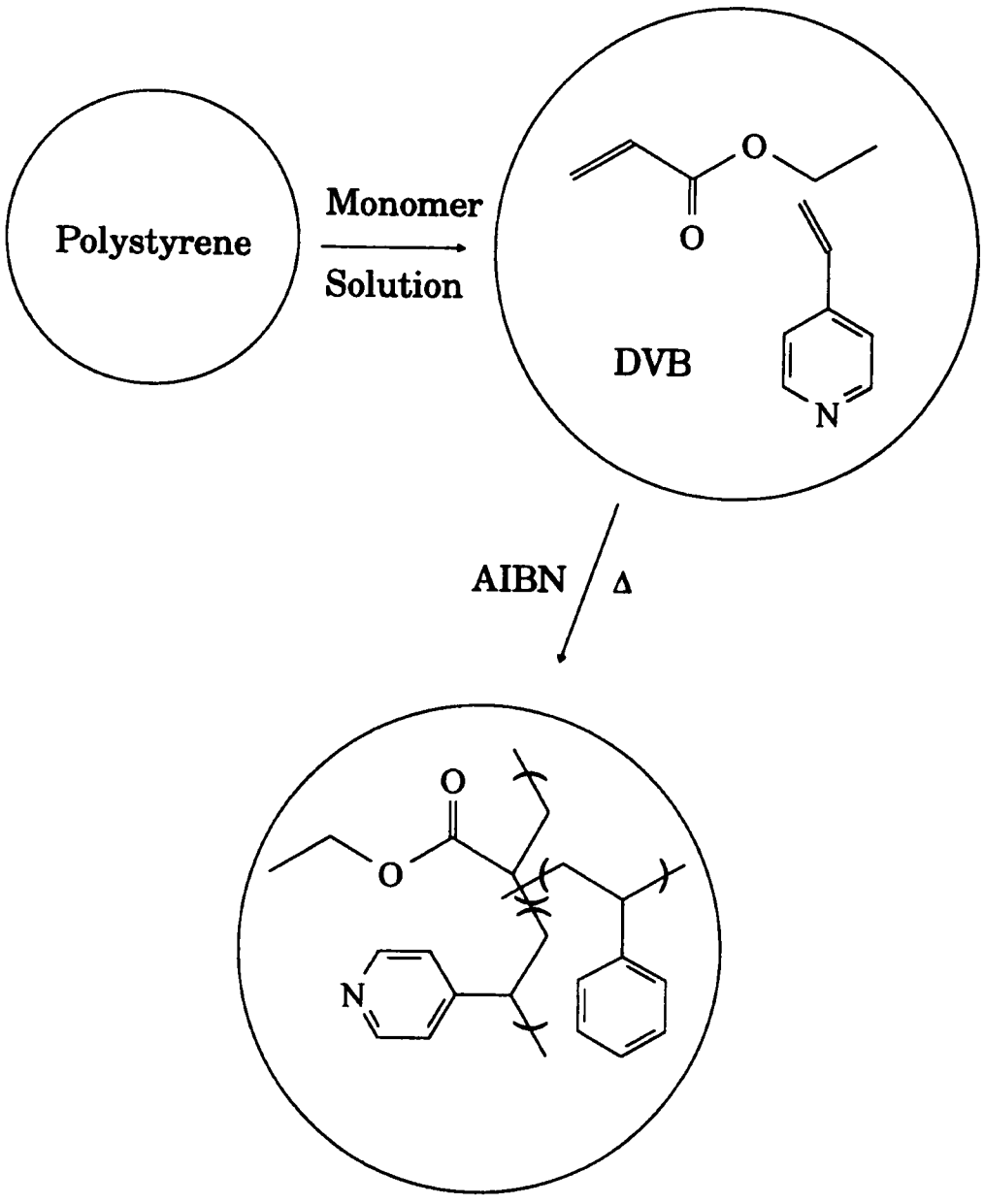



Figure 86. Synthesis of polystyrene/poly(4-vinylpyridine-co-ethyl acrylate) IPN.

For example, two treatments of DC-03-244 (PS/EA) with refluxing 12 M HCl for 18 hours led to a material with an acid capacity of only 3.04 mequiv/g compared with a theoretical capacity of 6.46 mequiv/g (assuming 100% incorporation of the monomer). Hydrolysis with dilute aqueous NaOH or dilute KOH in 60% dioxane also proved ineffective. Finally, it was found that refluxing 2 M KOH in approximately 90% dioxane (a two-phase system) was sufficient to hydrolyze the ester although long reaction times were needed. A PS/EA network hydrolyzed with this solution showed acid capacities of 4.38, 5.30, and 5.32 mequiv/g at reaction lengths of 13, 57, and 98 hours. In order to insure complete hydrolysis, all IPNs were hydrolyzed for 72 hours.

Characterization

A direct measurement of the ester functionality was not possible due to the lack of a good analytical method. However, since a method had been found which was capable of completely hydrolyzing the ester groups, it was possible to calculate the number of ester groups present prior to hydrolysis. This was done by assuming that hydrolysis of the ester group was the only reaction which occurred upon treatment of the IPN with KOH and that the hydrolysis was complete (assumptions supported by solid-state NMR spectroscopy). Since the number of milliequivalents of acidic protons in a given sample must be equal to the number of ester groups originally present, it is a simple matter to obtain the original ester capacity by considering the

change in mass which occurs upon hydrolysis. Thus, the ester capacity was calculated from the acid capacity using the following equation where 0.028052 is the weight difference between the ester and acid groups.

$$\textit{ester capacity} = \frac{\textit{acid capacity}}{1 + (\textit{acid capacity})(0.028052)}$$

The pyridine groups were determined by both acid and base capacity analyses. Due to the intermediate $pK_a$ of pyridine (5.25),[144] normal conditioning of the resin leaves the pyridine units in a mixture of protonated and unprotonated forms. Since HCl was the acid used during the conditioning, the protonated sites have chloride counterions which can be easily quantified by either chlorine elemental analysis or TAEC determination. A standard acid capacity determination will measure both the protonated pyridine sites and any carboxylic acid groups present from ester hydrolysis. The carboxylic acid capacity (and therefore the ester capacity of the unhydrolyzed IPN) was then obtained from the difference between the acid capacity and chlorine elemental analysis. It should be noted that sulfuric acid was used for the base capacity determinations. Later work in this laboratory[145] has indicated that, in some cases, the base capacities obtained with sulfuric acid are too high due to the formation of bisulfate counterions on the protonated pyridine groups. The use of HCl will obviate any difficulties which may arise due to this. The characteristics of the IPNs produced for this

study are given in Table 43. An extensive solid-state NMR investigation was conducted on these materials and is presented in Chapter 6.

Metal Ion Contact Studies

In order to obtain a more fundamental measurement of the metal ion affinity of the IPNs, it had been decided to determine the equilibrium constant for the interaction rather than simply measuring the distribution constant. The details of doing this are presented in appendix 1. The metal ion studies presented here were the first in this laboratory which were directed toward determining the binding constant. As a result, a great deal of effort was expended to determine the experimental techniques which would result in the measurement of accurate binding constants.

It was known from previous work[146] that when the liquid present in the resin differed significantly from the background solution of the contact sample, the amount of material sorbed could be altered. For this reason, it was necessary to insure that the liquid within the bead at the beginning of the experiment was similar to the contact solution. This was accomplished by "solvent exchanging" the resin. The desired amount of resin was placed in the container to be used and the background solution (without the target species) was added and the sample shaken for a period of time. The solution was removed and the process repeated until the liquid within the bead had been replaced with the background solution. In the past, it was found that four 15

Table 43

Characterization of Ion-Exchanging Interpenetrating Polymer Networks

| IPN | Composition | % Solids | Capacities (mequiv/g) | | | |
|---|---|---|---|---|---|---|
| | | | Acid Capacity | Base Capacity | Ester Capacity | Cl Capacity |
| DC-03-239 | PS/VP | 63.2 | 0.91 | 5.72 | – | 1.08 |
| DC-03-244 | PS/EA | 83.6 | 0.04 | – | 4.56 | – |
| DC-03-244H | PS/AA | 61.8 | 5.23 | – | – | – |
| DC-03-247 | PS/EA | 86.3 | 0.10 | – | 4.63 | – |
| DC-03-247H | PS/AA | 59.0 | 5.32 | – | – | – |
| DC-03-251A | PS/VP-EA | 71.9 | – | 2.24 | 2.33 | – |
| DC-03-251B | PS/VP-EA | 76.2 | 0.59 | 2.47 | 2.20 | 0.68 |
| DC-03-251AH | PS/VP-AA | 63.3 | 2.50 | 3.25 | – | 0.00 |
| DC-03-251BH | PS/VP-AA | 63.7 | 2.35 | 3.45 | – | 0.00 |
| DC-03-262 | PS/MA | 62.3 | 5.10 | – | – | – |
| DC-03-267 | PS/EA | 80.0 | 0.01 | – | – | – |

minute contacts with the background solution were sufficient to accomplish this. These studies involved replacing water in the resin with an organic solvent (usually methanol) so it was necessary to verify that the same solvent exchanging technique would be sufficient when replacing one aqueous phase with another of a different pH. This was accomplished by measuring the pH of the exchange solution after each 15 minute contact period. For the solvent exchange of PS/VP IPN with 1 X $10^{-3}$ N $HNO_3$ it was found that the pH changed little after the second solvent exchange and had stabilized after the fourth. Similar behavior was seen with all solutions tested. All resin samples were therefore solvent exchanged four times (15 minute shake) with approximately 10 mL of the background solution.

Despite the solvent exchange, initial metal ion studies with copper at pH 3 were not successful due to the large change in the pH of the metal ion solution during the course of the experiment. The percent absorbed changed little with varying $R_i$ indicating that little interaction was occurring. Using sodium nitrate in the solvent exchange to minimize the change in ionic strength upon contact with the metal ion solution had little effect on the final results as did an attempt to adjust the final pH of the samples to a constant value.

Buffers were not initially considered due to their probable interaction with the target ions. Such interactions would cause the measured binding constants to be relative to the strength of the metal-buffer interaction instead

of being absolute measures of the ion affinity of the network. However, the widely varying final pH values (over 2 pH units from the most to the least concentrated solution in some cases) caused the binding isotherms to be uninformative. The use of buffers in metal ion contact studies did have precedent[51] and so they were considered here. For solutions at pH 5 the buffer system sodium acetate/acetic acid was chosen. Total acetate concentrations of 0.4 and 0.6 N were evaluated. Since the higher buffer concentration afforded better control of the final pH of the solution and did not result in severe clogging of the atomic absorption instrument used to measure the residual metal concentration, it was chosen for all metal ion studies. The effect of buffering the metal is readily apparent in the binding isotherms obtained for the interaction of PS/AA IPN and $Cu^{2+}$ (Figures 87 and 88). The range of final pH values in the unbuffered samples was 2.37-4.55 while that of the buffered sample was 4.89-5.04. The large increase in the amount of metal sorbed in the buffered sample is most likely due to the higher final pH of contact solution compared to the unbuffered samples. However, the possibility that the resin is more accessible to the more hydrophobic metal-buffer complex than it is to the uncomplexed ion cannot be discounted based on these studies.

All initial contact studies were performed in 0.6 N acetate buffer at pH 5 using a 24 hour contact time. The presence of some scatter in the PS/VP--$Cu^{2+}$ binding isotherms led to a limited investigation of the length of

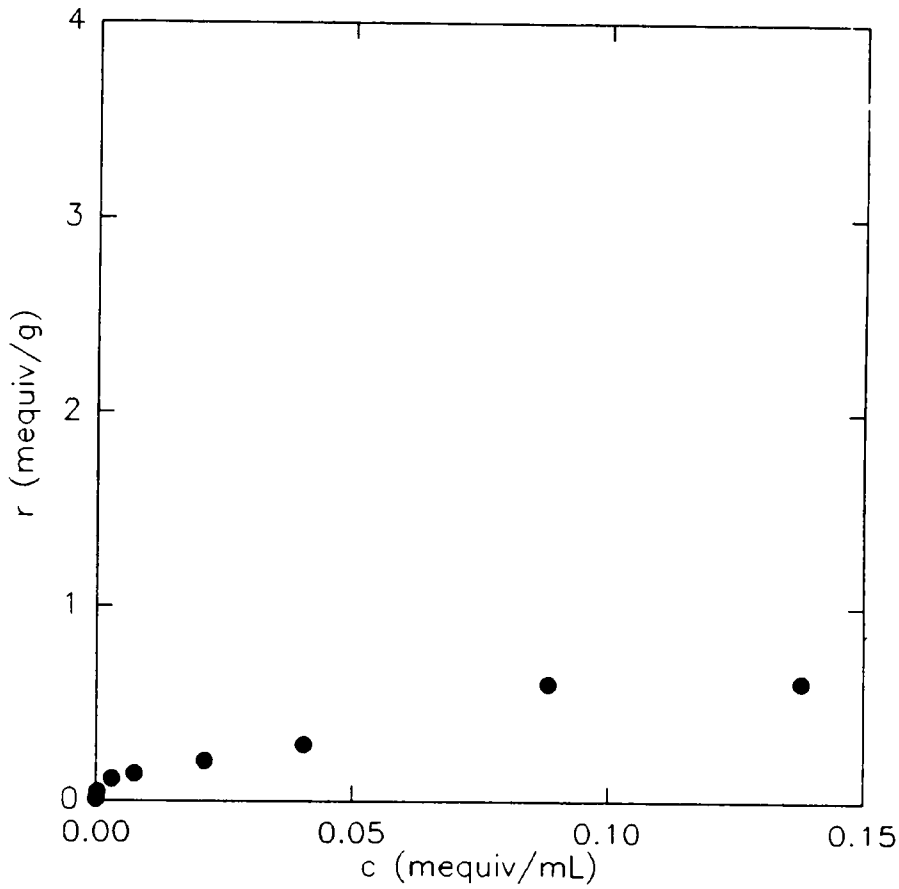



Figure 87. Binding isotherm for PS/AA IPN with $Cu^{2+}$ (no buffer).

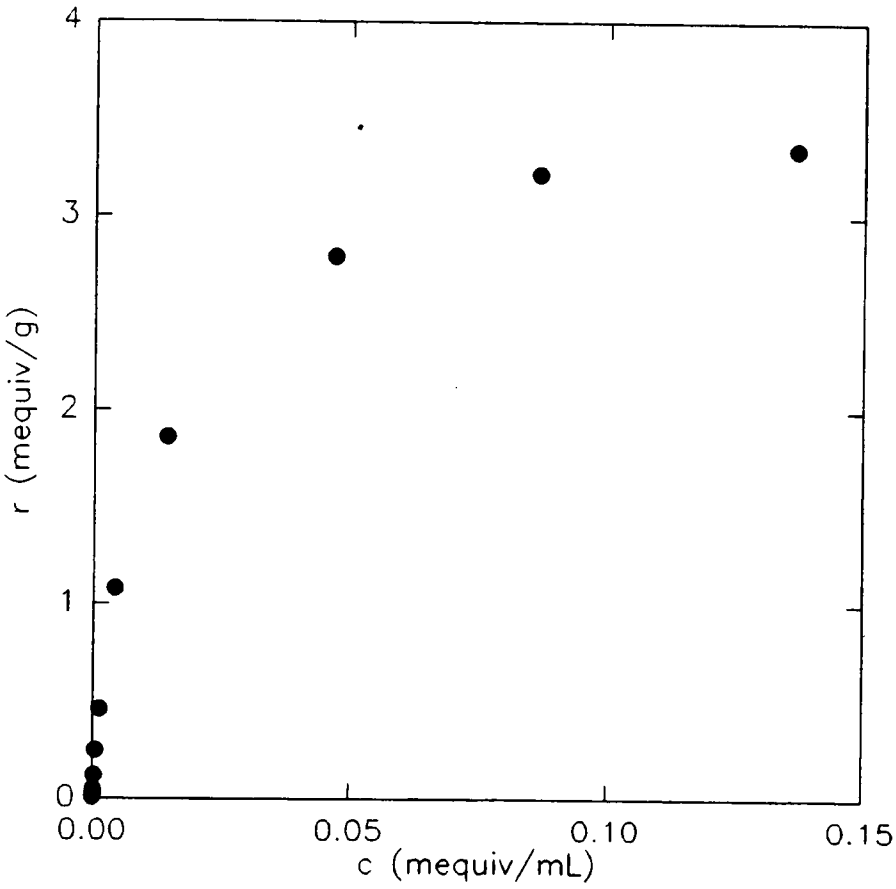



Figure 88. Binding isotherm for PS/AA IPN with $Cu^{2+}$ (0.6 N acetate buffer).

time needed to reach equilibrium. It was found that the percent absorbed increased from 17.73% to 31.10% for the PS/VP--$Cu^{2+}$ at times of 1 and 7 days and from 20.96% to 40.25% for the PS/VP-AA--$Cu^{2+}$ system. Therefore, with the 4-vinylpyridine-containing IPNs at least, the system was not at equilibrium after 24 hours. Given this, it was not possible to extract meaningful binding constants from the 24 hour contact numbers. For comparison purposes, the amount of metal loaded onto the IPNs at an $R_i$ of 1.0 is listed in Table 44. Note that the higher capacity shown by the PS/AA IPN may be a result of increased sorption kinetics rather than an actual affinity difference.

At this point, responsibility for the project shifted to another chemist. The synthetic conditions and analytical techniques had been reasonably well defined as had the method for obtaining reliable values from the metal ion studies.[147] Binding constant determinations were made under equilibrium conditions with polystyrene/poly(N-vinylimidazole-co-ethyl acrylate) and polystyrene/poly(N-vinylimidazole-co-acrylic acid) IPNs synthesized with varying imidazole/acrylate ratios. The binding constant decreased with decreasing imidazole content in the imidazole-acrylic acid IPNs indicating that the two ligands do not cooperate synergistically.[148,149] In contrast, the highest $Cu^{2+}$ binding constant was found with the IPN containing approximately equal numbers of imidazole and ethyl acrylate sites.[150] The binding constant is thus a sensitive measure of the microenvironment surrounding the metal ion binding site.

Table 44

$Cu^{2+}$ and $Co^{2+}$ Capacities of PS/VP, PS/VP-AA, PS/AA, and PS/EA IPNs After 24 Hour Contact at $R_i$ = 1.0

| IPN | $Cu^{2+}$ Capacity (mequiv/g) | $Co^{2+}$ Capacity (mequiv/g) |
|---|---|---|
| PS/VP | 1.16 | 0.97 |
| PS/VP-AA | 1.20 | 1.33 |
| PS/AA | 2.79 | 1.83 |
| PS/EA | 0.12 | 0.39 |

# CHAPTER 5

## POLYMERIZATION OF VINYLIDENE-1,1- DIPHOSPHONIC ACID

### Introduction

A new class of organophosphorus extractants, termed thermally unstable complexants (TUCS), was developed by Dr. E. Philip Horwitz and co-workers at Argonne National Laboratory.[151,152] These extractants have an advantage over conventional organophosphorus compounds in that they are easily decomposed to innocuous materials by either heat or mild chemical reagents and so can be readily eliminated from the aqueous stream after metal complexation has occurred. One of these compounds, vinylidene-1,1-diphosphonic acid (VDPA, Figure 89), had the potential for forming stable polymers via free radical polymerization. Since it was suspected that the presence of geminal diphosphonic acid groups might lead to resins with enhanced extraction abilities relative to the more conventional monophosphonic acid resins, synthesis of these polymers became a top priority. Few reports of resins containing diphosphonic acid groups have appeared, but such materials have been prepared as fire retardant materials and antiplaque dental agents.[153,154]

A study of the polymerization of VDPA was undertaken. The goals of this experimental program were to determine if polymers capable of metal ion

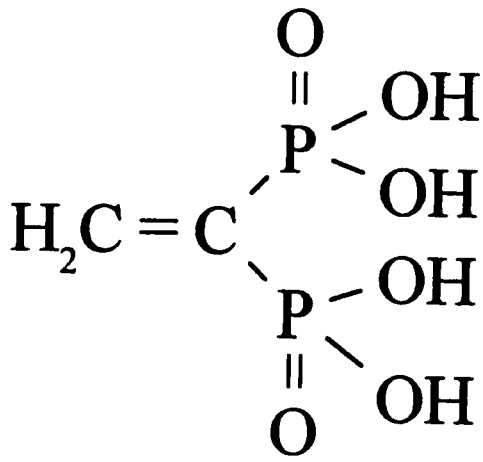



Figure 89. Vinylidene-1,1-diphosphonic acid (VDPA).

extraction could be prepared from VDPA and, if so, to examine the feasibility of producing beads via standard suspension polymerization techniques. A large number of scouting experiments were performed with these goals in mind.

Initial Experiments

VDPA is a white solid which is readily soluble in water. A preliminary experiment indicated that VDPA could polymerize with both acrylic acid and acrylamide from aqueous solutions. A small amount of VDPA was dissolved in water along with the acrylic monomer, and ferrous ammonium sulfate/hydrogen peroxide was used to initiate the polymerization. White solids formed instantly in both mixtures. A more quantitative study was conducted by polymerizing equal weights of VDPA and acrylamide with ferrous ammonium sulfate and $H_2O_2$. A small amount of solid was produced which had a phosphorus capacity of 1.95 mequiv/g, indicating that VDPA could be incorporated into the polymer.

VDPA Copolymers

A series of polymers cross-linked with N,N'-methylene-bis-acrylamide (bis-acrylamide) was prepared from aqueous solutions using both ferrous ammonium sulfate/$H_2O_2$ and potassium persulfate initiators. Acrylamide polymers were prepared as controls as shown in Table 45.

Table 45

Initial VDPA/Acrylamide/bis-Acrylamide Polymers

| Polymer | Wt. VDPA | Wt. Acrylamide | Wt. bis-Acrylamide | Initiator | P Capacity (mequiv/g) |
|---|---|---|---|---|---|
| DC-01-216A | 0.50 g | 0.25 g | 0.25 g | $Fe/H_2O_2$[a] | 3.56 |
| DC-01-216B | – | 0.75 g | 0.25 g | $Fe/H_2O_2$[a] | – |
| DC-01-218A | 0.25 g | – | 0.25 g | $Fe/H_2O_2$[a] | 1.61 |
| DC-01-218B | – | 0.25 g | 0.25 g | $Fe/H_2O_2$[a] | – |
| DC-01-242A | – | 0.25 g | 0.25 g | $K_2S_2O_8$ (2.7 mg) | – |
| DC-01-242B | – | 0.25 g | 0.25 g | $K_2S_2O_8$ (27.0 mg) | – |
| DC-01-243 | 0.25 g | – | 0.25 g | $K_2S_2O_8$ (27.0 mg) | 1.38 |

[a]$Fe/H_2O_2$ = 2.5 mL 0.1 M ferrous ammonium sulfate/2.5 mL 0.1 M $H_2O_2$

The results indicated that VDPA could copolymerize with bis-acrylamide or bis-acrylamide/acrylamide mixtures. The ability of potassium persulfate to initiate the polymerization was important since the iron based initiator system led to polymers contaminated with residual iron. Additionally, it was later discovered that VDPA and other phosphonic acids (phenylphosphonic for example) form precipitates with iron salts. This indicated that the phosphorus capacities found in the iron initiated system may be due to precipitate rather than polymer formation. A preliminary test of the extractive ability of DC-01-218A & B was performed by contacting 0.05 g of the crushed polymers with 5.00 mL of $2 \times 10^{-4}$ N $Cd(NO_3)_2$ in 0.01 N $HNO_3$ for 2 days. The polymer prepared with VDPA (-218A) showed approximately 80% sorption of the Cd while the acrylamide polymer had no affinity for Cd (0% uptake). Similar results were obtained for the uptake of $Fe^{3+}$. VDPA-containing polymer (DC-01-243) showed 97.3% sorption from 0.01 N $HNO_3$ while an acrylamide polymer (DC-01-242B) removed 17.1% and a standard polystyrene-based monophosphonic acid removed greater than 98% of the iron.

Attempts to prepare copolymers of VDPA with p-vinylbenzoic acid and bis-acrylamide were not successful. The polymerization was conducted in 1-butanol due to the limited water solubility of the vinylbenzoic acid and yielded only a small amount of material (P capacity = 1.60 mequiv/g). No further characterization was completed due to lack of sufficient material. Since

polymer was not obtained when VDPA was replaced by acrylamide, no additional studies were conducted with p-vinylbenzoic acid.

An attempt to homopolymerize VDPA using potassium persulfate as the initiator was made (DC-02-030A). Heating 0.25 g VDPA and 25 mg $K_2S_2O_8$ in 5 mL of water at 60 °C for 6 hours resulted in no polymerization. NMR spectroscopy showed only unreacted VDPA in the solution. In contrast, similar mixtures containing 0.25 g bis-acrylamide in addition to VDPA (DC-02-030B) or acrylamide/bis-acrylamide only (DC-02-030C) yielded white polymers. DC-02-030B had a phosphorus capacity of 1.57 mequiv/g after conditioning which corresponds to 30% incorporation of VDPA. The percent incorporation is calculated from the measured and theoretical (assuming complete polymerization of all monomers) phosphorus capacities. Two larger batches of VDPA/bis-acrylamide copolymer were prepared by heating 2.25 g VDPA, 2.50 g bis-acrylamide and 0.25 g potassium persulfate dissolved in 100 mL water at 60 °C for 6 hours (DC-02-143 and -156). The phosphorus capacities of DC-02-143 and -156 were 1.74 and 1.76 mequiv/g, respectively, corresponding to 36% and 37% incorporation of VDPA. DC-02-156 had an acid capacity of 3.75 mequiv/g, in close agreement with the phosphorus analysis. It was noticed that the method of drying had a dramatic effect on the appearance of the polymer. DC-02-143 was oven dried at 110 °C while DC-02-156 was dried at room temperature under vacuum. The polymer dried at an elevated temperature clumped and became somewhat yellow.

Reconditioning the resin failed to reswell the material. The phosphorus capacity of the reconditioned material did not drop significantly (1.70 mequiv/g) indicating that only a limited number of ligands were lost. Despite this, all other polymers of this type were vacuum dried. Both polymers extracted greater than 90% of the metal from a 2 X $10^{-4}$ N solution of $Fe(NO_3)_3$ in 0.01 N $HNO_3$.

It was thought that the low levels of incorporation were perhaps the result of steric hindrance to polymerization caused by the bulky geminal diphosphonic acid groups. In an attempt to reduce the steric barriers to polymerization, a sterically undemanding comonomer, acrylamide, was added to the mixture to function as a spacer.

The results of a study of the effect of the acrylamide level are presented in Table 46 and clearly show that acrylamide does not function as a spacer group. Apparently, acrylamide homopolymerizes to the exclusion of VDPA causing a decrease in the percent of VDPA incorporated with increasing acrylamide levels. No other comonomers were investigated due to a shift in focus to styrene-based systems.

A limited set of experiments was performed in order to produce beads from VDPA/bis-acrylamide polymers by suspension polymerization of an aqueous solution of monomers in an organic continuous phase. Cellulose acetate butyrate dissolved in 1,2-dichloroethane was used as the continuous phase[155] in most cases, although both toluene and heptane were also

Table 46

Effect of Acrylamide Level on VDPA/Acrylamide/bis-Acrylamide Polymers

| Polymer | Wt. VDPA | Wt. Acrylamide | Wt. bis-Acrylamide | P Capacity (mequiv/g) | Theoretical P Capacity (mequiv/g) | % Incorporation |
|---|---|---|---|---|---|---|
| DC-02-194A | 0.90 g | -- | 1.00 g | 1.80 | 4.79 | 38% |
| DC-02-194B | 0.80 g | 0.10 g | 1.00 g | 1.56 | 4.25 | 37% |
| DC-02-194C | 0.65 g | 0.25 g | 1.00 g | 1.03 | 3.46 | 30% |
| DC-02-194D | 0.40 g | 0.50 g | 1.00 g | 0.44 | 2.13 | 21% |

investigated with much less success. The polymerizations were conducted in a 20 mL scintillation vial with a small stir bar in the bottom. The limited study indicated that 0.3 g of cellulose acetate butyrate in 10 mL of 1,2-dichloroethane functioned well as a continuous phase, although further optimization would be necessary for efficient polymerizations. A series of three polymerizations in which the VDPA/acrylamide ratio was varied (Table 47) was completed. The polymerizations were conducted at 70 °C for 19 hours and led to the production of large, soft beads which lost much of their volume and shape upon drying. The VDPA containing beads showed a high affinity for $Fe^{3+}$. Work in this area was abandoned in favor of the styrene-based systems before the polymerization conditions could be optimized.

Styrene-Based Copolymers

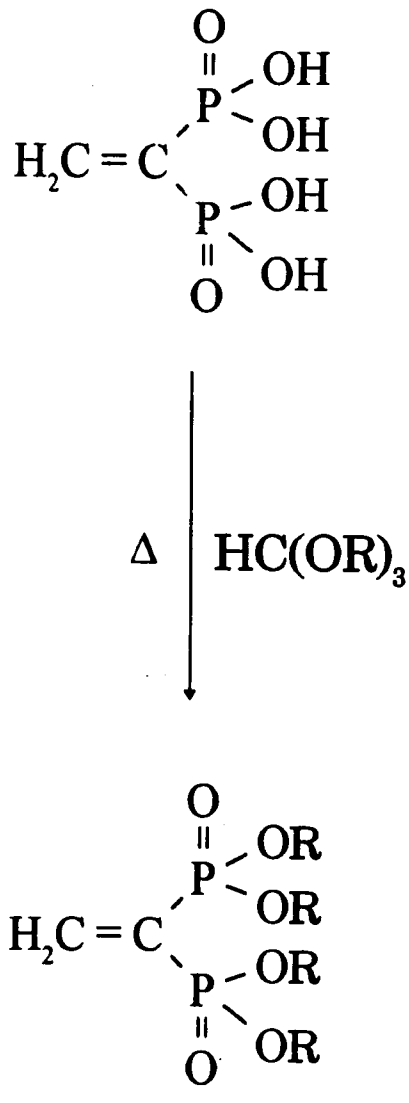
Due to the extreme water solubility of VDPA, it was necessary to modify the molecule prior to conducting standard suspension polymerizations with an aqueous continuous phase. The hydrophilicity of the molecule was decreased by conversion of the parent acid to the tetraalkyl ester via reaction with trialkylorthoformates (Figure 90). The ester linkages could then be hydrolyzed after polymerization to yield the desired diphosphonic acid groups. Synthesis of the esters began with the tetrasodium salt of VDPA (Albright and Wilson) which was converted to the parent acid by contact of an aqueous solution of the sodium salt with an excess of a strong acid (sulfonic) cation exchange

Table 47

Suspension Polymerization of VDPA: Effect of VDPA Level

| Polymer | Monomer Weights[a] | | | P Capacity (mequiv/g) | Fe Uptake[b] |
|---|---|---|---|---|---|
| | VDPA | Acrylamide | bis-Acrylamide | | |
| DC-02-134A | -- | 0.85 g | 0.10 g | 0.00 | 5.0% |
| DC-02-134B | 0.10 g | 0.75 g | 0.10 g | 0.83 | 74.5% |
| DC-02-134C | 0.25 g | 0.60 g | 0.10 g | 2.33 | 77.0% |

[a]Dissolved in 2 mL $H_2O$ and 1 mL dimethylformamide with 0.05 g $K_2S_2O_8$
[b]Uptake by 0.1 mequiv polymer (as P capacity) from 2 X $10^{-4}$ N $Fe(NO_3)_3$ in 0.01 N $HNO_3$




R = Me, Et, Bu

Figure 90. Synthesis of tetraalkyl esters of VDPA.

resin. The acid was washed from the column and the water removed at reduced pressure. The tetramethyl, tetraethyl, and tetra-n-butyl esters of VDPA were then produced via esterification with the appropriate trialkylorthoformate.

Initial polymerizations of tetramethyl VDPA ($Me_4$VDPA) were designed to compare its polymerization behavior with that of VDPA itself. The DC-02-066 series was prepared via bulk (A & B) and solution (C & D) methods using monomer compositions as shown in Table 48. Only A & B produced polymer. The polymers were Soxhlet extracted with toluene to yield material with phosphorus capacities of 2.60 and 3.03 mequiv/g and acid capacities of 0.15 and 0.35 mequiv/g, respectively. The liquid recovered from the Soxhlet was examined by $^{31}P$ NMR spectroscopy and was found to contain $Me_4$VDPA, indicating incomplete polymerization. Both solids were hydrolyzed in refluxing 12 M HCl to produce DC-02-273A & B. As expected, the acid capacities increased. Final capacities were 4.26 and 4.30 mequiv/g while the phosphorus capacities increased slightly due to the loss in mass which accompanies hydrolysis to 2.88 and 3.05 mequiv/g.

The results show that $Me_4$VDPA does not copolymerize well with low levels of DVB without the addition of a comonomer. Again this was attributed to steric hindrance of the polymerization. In order to relieve some of the steric strain, a small monomer was sought to serve as a spacer group. The use of acrylonitrile (AN) was investigated. Polymers cross-linked with 10% DVB were

## Table 48

### Initial $Me_4VDPA$ Polymers

| Polymer | DC-02-066A | DC-02-066B | DC-02-066C[a] | DC-02-066D[b] | DC-02-071A | DC-02-071B |
|---|---|---|---|---|---|---|
| Wt. $Me_4VDPA$ | 0.25 g | 0.25 g | – | 0.25 g | 0.41 g | 0.81 g |
| Wt. VDPA | – | – | 0.16 g | – | – | – |
| Wt. Styrene | 0.25 g | – | 0.16 g | – | 0.41 g | – |
| Wt. DVB | 0.45 g | 0.45 g | – | – | 0.18 g | 0.18 g |
| Wt. bis-acrylamide | – | – | – | 0.25 g | – | – |
| Wt. AIBN[c] | 9.5 mg | 7.0 mg | 3.2 mg | 5.0 mg | 10.0 mg | 10.0 mg |
| P Capacity (mequiv/g) | 2.60 | 3.03 | NO POLYMER | NO POLYMER | 3.87 | 4.78 |
| Acid Capacity (mequiv/g) | 0.15 | 0.35 | – | – | 0.27 | 0.00 |
| P Capacity After Hydrolysis (mequiv/g) | 2.88 | 3.05 | – | – | 4.77 | 5.84 |
| Acid Capacity After Hydrolysis (mequiv/g) | 4.26 | 4.30 | – | – | 6.59 | 7.50 |
| Wt. liquid recovered from Soxhlet | 0.15 g | 0.12 g | – | – | 0.30 g | 0.70 g |

[a]dissolved in 5 mL DMSO [b]dissolved in 5 mL DMSO and 5 mL toluene [c]azo-bis-isobutyronitrile

prepared with 4, 8, 20, and 27 wt% AN with the remaining monomer charge consisting of equal weights of styrene and $Me_4$VDPA. AN seemed to function well as a spacer group as $Me_4$VDPA was incorporated at levels from 82 to 100%. Another scouting study was completed using a wide range of monomer mixtures (Table 49). The results indicated that $Me_4$VDPA copolymerizes best with a mixture of styrene and acrylonitrile.

$Me_4$VDPA was still too water soluble to permit the production of beads via standard suspension polymerization techniques. Therefore, attention turned to the less soluble tetraethyl ester. A mixture containing equal amounts of $Et_4$VDPA and styrene and enough AN and DVB to yield 20 wt% AN and 10% cross-linking was mixed with saturated NaCl. Minimal mixing of the phases was noted. Polymerization of this mixture (initiated with AIBN) failed to produce spherical beads, but a polymer was formed (DC-02-173) which had a phosphorus capacity of 1.43 mequiv/g corresponding to 76% incorporation. Upon hydrolysis in 12 M HCl the polymer contained 1.53 mequiv/g phosphorus and 0.94 mequiv/g acidic sites. The amount of AN and DVB used were too high (and thus the polymer too hydrophobic) to permit complete hydrolysis of the ester groups. Crushing the polymer to improve its accessibility and rehydrolyzing it yielded a material with phosphorus and acid capacities of 1.49 and 3.88 mequiv/g, respectively.

Lower AN and DVB levels were examined. Two bulk polymers were prepared. In the first, the AN level was 10 wt% and the network was cross-

Table 49

Cross-linked $Me_4$VDPA/Styrene/AN Copolymers

| DC-02-105[a] | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| Wt. $Me_4$VDPA | 0.40 g | 0.40 g | 0.40 g | 0.40 g | 0.25 g | 0.25 g |
| Wt. AN | 0.25 g | 0.25 g | 0.25 g | 0.25 g | – | – |
| Wt. Styrene | 0.10 g | 0.10 g | – | – | – | – |
| Wt. DVB | 0.25 g | – | – | 0.10 g | – | 0.10 g |
| Wt. Acrylamide | – | – | 0.10 g | – | 0.38 g | 0.40 g |
| Wt. bis-acrylamide | – | 0.25 g | 0.25 g | 0.25 g | 0.38 g | 0.25 g |
| P Capacity (mequiv/g | 3.27 | NO POLYMER | 1.92 | 2.18 | 1.42 | 1.54 |
| % Incorporation | 100 | – | 59 | 67 | 70 | 76 |

[a]all polymerizations initiated with 10 mg AIBN and were done in 17.5 mL dioxane (except A, bulk polymerization)

linked with 5% DVB while, in the second, the AN and cross-link levels were 15% and 8%. The remainder of the monomer mixture consisted of equal weights of styrene and $Et_4$VDPA and 5 wt% AIBN as initiator. The polymers possessed phosphorus capacities of 2.49 (98% incorporation) and 1.93 mequiv/g (88% incorporation).

A single bulk polymerization was completed using the tetrabutyl ester of VDPA. A monomer mixture consisting of 10% AN, 5% cross-linking (DVB), 5% AIBN, and a $Bu_4$VDPA/styrene ratio of 60/40 was polymerized to give a solid with a phosphorus capacity of 2.39 mequiv/g in 74% yield. The phosphorus capacity is higher than the theoretical value based on the monomer mixture composition indicating that the comonomers did not completely polymerize. Production of this monomer is quite expensive due to the excessive cost of tributylorthoformate. Tributylorthoformate can be easily prepared from the relatively inexpensive lower trialkylorthoformates[156] but it was decided not to pursue the tetrabutyl ester unless the lower esters of VDPA proved unsuitable due to the added time and expense that even a simple synthesis would cause in a commercial setting.

Suspension Polymerization of $Et_4$VDPA

A series of solutions designed as possible aqueous phases for suspension polymerization of the tetraethyl ester were prepared. The solutions consisted of varying amounts of poly(diallyldimethylammonium

chloride) (PADMAC) dissolved in water along with salts such as sodium chloride or sodium acetate. It was found that the tetraethyl ester was soluble in all of these solutions even when 15 g of PADMAC was dissolved in 30 g of concentrated sodium chloride (just below saturation). The addition of gelatin or hydroxyethyl cellulose (two common suspension stabilizers) did not serve to limit the solubility of the ester.

An attempt was made to produce beads using the standard aqueous phase used for poly(vinylbenzyl chloride) beads. The aqueous phase contains both gelatin and PADMAC in addition to a borate buffer at a pH of 10.3 (see experimental section for exact composition) and it appeared that the ester had a limited solubility. However, when the polymerization was conducted in a scintillation vial using an organic:aqueous phase weight ratio of 1.00:1.00 (4.00 g total), few beads were produced and a large amount of ester was lost to the aqueous phase. The addition of sodium chloride to this aqueous phase (5.5 g NaCl in 20 g aqueous phase) served to limit the solubility of the tetraethyl ester to the point where beads could be formed. The polymer (DC-02-228, 20% AN, 10% cross-linked) had a phosphorus capacity of 1.12 mequiv/g which corresponds to 59% incorporation of the ester. After hydrolysis in refluxing 12 M HCl the phosphorus and acid capacities were found to be 1.14 and 5.53 mequiv/g, indicating that a large number of carboxylic acid sites had been formed by hydrolysis of the cyano groups present (from

acrylonitrile). The presence of carboxylic acid groups was supported by the IR spectrum of the hydrolyzed material.

A second suspension polymerization was conducted using lower levels of AN and DVB (DC-02-244A, 10% AN and 5% cross-linking). Beads were formed, although they were somewhat irregular in shape. The phosphorus capacity prior to hydrolysis was 1.89 mequiv/g which is 75% of the maximum value. After hydrolysis the polymer contained 2.04 mequiv/g phosphorus and 3.48 mequiv/g acidic sites. This polymerization was repeated (DC-02-260A) along with an otherwise identical mixture (-260B) containing the tetramethyl rather than the tetraethyl ester. The decreased solubility of the tetraethyl ester was readily apparent. While the tetraethyl ester produced polymer primarily in bead form, the tetermethyl ester led to a product consisting mostly of irregular particles. The phosphorus capacities were 2.05 mequiv/g (81% incorporation of $Et_4$VDPA) and 0.39 mequiv/g (13% incorporation of $Me_4$VDPA). After hydrolysis the $Et_4$VDPA polymer had phosphorus and acid capacities of 2.00 and 5.44 mequiv/g. No further work was done with the tetramethyl ester.

A series (DC-02-270A-C) of suspension polymerizations was completed using the same aqueous phase described above and a varying organic phase as shown in Table 50. Only DC-02-270A produced large quantities of beads.

Table 50

Effect of the Organic Phase Composition on $Et_4VDPA$ Polymers Produced by Suspension Polymerization

| DC-02-270 | A | B | C |
|---|---|---|---|
| Wt. $Et_4VDPA$ | 0.92 g | 0.65 g | 0.83 g |
| Wt. Styrene | 0.31 g | 0.65 g | -- |
| Wt. AN | 0.16 g | 0.08 g | 0.55 g |
| Wt. DVB | 0.14 g | 0.14 g | 0.14 g |
| Wt. AIBN | 0.08 g | 0.08 g | 0.08 g |
| P Capacity (mequiv/g) | 2.27 | 1.90 | 1.38 |
| % Incorporation | 60 | 70 | 40 |
| P Capacity After Hydrolysis (mequiv/g) | 2.43 | 2.03 | 1.18 |
| Acid Capacity After Hydrolysis (mequiv/g) | 7.57 | 4.75 | 11.61 |

Optimization of the Organic Phase

It was thought that the level of ester incorporation could be increased if the polymers could be made to gel prior to loss of a large amount of monomer to the aqueous phase. In order to investigate the variables which might affect the time required for gelation, attention turned once again to bulk polymerizations. Two studies designed to investigate the effects of various levels of AN and $Et_4$VDPA/styrene ratios were completed. In the first (DC-02-295A-E), the polymerizations were conducted after mixing the monomers without any further treatment. In the second (DC-02-297A-E), the monomer mixtures were sparged with $N_2$ for 5 minutes prior to polymerization in order to remove the dissolved oxygen. As shown in Table 51, this procedure had little effect on the final properties of the polymer, but it did strongly affect the length of time required for the polymer to gel. For polymer D, gelation occurred within 2.5 hours for the sparged monomer (DC-02-297D) while the unsparged mixture (DC-02-295D) required more than 8 hours to gel. For this reason, all future polymerizations were conducted only after sparging the monomer mixture with nitrogen.

DC-02-297B & D were hydrolyzed with refluxing 12 M HCl and their ability to extract europium from 0.04 N $HNO_3$ was examined along with other hydrolyzed VDPA polymers. The results, shown in Table 52, reveal that the polymers prepared from $Et_4$VDPA possess a high affinity for europium. This is significant since europium is similar in electronic configuration to the actinides

Table 51

Effect of Nitrogen Sparge on Gelation Time and Final Polymer Properties

| DC-02-295/297[a] | A | B | C | D | E |
|---|---|---|---|---|---|
| Wt. $Et_4$VDPA | 0.57 g | 0.50 g | 0.49 g | 0.46 g | 0.40 g |
| Wt. Styrene | 0.19 g | 0.17 g | 0.32 g | 0.30 g | 0.26 g |
| Wt. AN | 0.10 g | 0.20 g | 0.05 g | 0.10 g | 0.20 g |
| Wt. DVB | 0.09 g | 0.09 g | 0.09 g | 0.09 g | 0.09 g |
| Wt. AIBN | 0.05 g | 0.05 g | 0.05 g | 0.05 g | 0.05 g |
| Gel Point[a] (hours) | 3.0/2.3 | 1.7/1.0 | 6.5/5.7 | >8.0/2.4 | 1.6/1.0 |
| P Capacity[a] (mequiv/g) | 3.20/3.34 | 2.92/2.91 | 3.16/3.16 | 3.01/2.96 | 2.50/2.43 |
| % Incorporation[a] | 84/88 | 89/88 | 97/97 | 98/97 | 97/91 |

[a]unsparged monomer/sparged monomer

Table 52

$Fe^{3+}$ and $Eu^{3+}$ Uptake from 0.04 N $HNO_3$
by Hydrolyzed $Et_4$VDPA Polymers

| Polymer | Solution | % Uptake |
|---|---|---|
| DC-02-270AH[a] | 1 X $10^{-3}$ N $Fe(NO_3)_3$/0.04 N $HNO_3$ | 24.1 |
| DC-02-260AH | " | 6.6 |
| DC-02-119[b] | " | 33.7 |
| DC-01-150A,B,&C[c] | " | 0.0 |
| DC-02-270AH | 1 X $10^{-4}$ N $Eu(NO_3)_3$/0.04 N $HNO_3$ | 100 |
| DC-02-260AH | " | 46.2 |
| DC-02-119[b] | " | 98.3 |
| DC-01-150A,B,&C[c] | " | 11.5[d] |
| DC-02-297BH | " | 98.4 |
| DC-02-297DH | " | 98.5 |

[a]H denotes hydrolyzed polymer
[b]standard polystyrene-supported phosphonic acid resin
[c]poly(vinylbenzyl chloride)
[d]average of two determinations

(particularly americium) and this property is indicative of the possibility of high affinity for the environmentally important actinides.

The effect of the level of initiator was also investigated (DC-03-016A-C). Monomer mixtures containing 10% AN, 5% cross-linking (DVB), and the remainder a 60/40 weight ratio of $Et_4$VDPA to styrene were polymerized with 1, 2 and 5% AIBN as the initiator. Gelation times were 6.0, 4.2, and 3.1 hours, respectively, and the level of incorporation was excellent in all cases (95% for the 1% initiator level, 100% for 2 and 5% initiator). However, the yield of polymer rose from 49%, to 63%, to 69% as the initiator level rose. Given the higher yield and the shorter gelation time (which could limit loss of the monomer to the aqueous phase) it was decided that 5% initiator performed best. This level became the standard level for all other polymerizations.

Benzoyl peroxide (BPO) was substituted for AIBN in a standard monomer mixture (10% AN, 5% cross-linking, 60/40 $Et_4$VDPA/styrene ratio) and the polymerization was conducted at 80 °C rather than 60 °C (used for AIBN). The polymer, which formed in 66% yield, had a phosphorus capacity of 2.77 mequiv/g (91% incorporation). Comparison of two polymerizations (DC-02-090A & B) conducted at 80 °C using both BPO and AIBN showed that the AIBN initiated system gelled in 30-50 minutes as opposed to 60-70 minutes for the BPO initiated system. Given the perceived need for a rapid gelation to lessen loss of the monomer to the aqueous phase, it was decided to continue using AIBN as the initiator.

Other variables were examined. The effect of omission of styrene from the organic phase was studied with the DC-03-046 series of polymers (A-F). As shown in Table 53, the level of $Et_4$VDPA incorporation fell in the absence of styrene, making these formulations unsuitable. The low level of incorporation found with solution polymerization in toluene (DC-03-046D-F) did not improve when benzene was used as the solvent (DC-03-072A-C) indicating that chain transfer to toluene was not the limiting factor in these reactions. Comonomers other than acrylonitrile (methacrylonitrile (MAN) and methyl methacrylate (MMA)) and cross-linking agents other than DVB (diethyleneglycol dimethacrylate (DEGDMA) and trimethylolpropane trimethacrylate (TMPTMA)) were investigated. As shown in Table 54, the new comonomers did not perform better than acrylonitrile and the new cross-linking agents caused the mixtures to gel in less than 4 minutes which, apparently, did not allow $Et_4$VDPA to incorporate.

Lower levels of both trimethylolpropane trimethacrylate (TMPTMA) and diethyleneglycol dimethacrylate (DEGDMA) were compared with DVB and diethyleneglycol diacrylate (DEGDA). The polymers (DC-03-061A-D) were each cross-linked at a level of 5% with 10% AN as a comonomer and had a 60/40 $Et_4$VDPA/styrene ratio. The results (Table 55) indicated that DVB is the most appropriate cross-linking agent in terms of $Et_4$VDPA incorporation. A poorer match between the reactivity ratios of $ET_4$VDPA and the acrylate-based

Table 53

Cross-linked $Et_4$VDPA/AN Copolymers

| DC-03-046 | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| Wt. $Et_4$VDPA | 0.65 g | 0.52 g | 0.34 g | 0.65 g | 0.52 g | 0.34 g |
| Wt. AN | 0.22 g | 0.34 g | 0.52 g | 0.22 g | 0.34 g | 0.52 g |
| Wt. DVB | 0.09 g | 0.09 g | 0.09 g | 0.09 g | 0.09 g | 0.09 g |
| Wt. AIBN | 0.05 g | 0.05 g | 0.05 g | 0.05 g | 0.05 g | 0.05 g |
| Vol. Toluene | -- | -- | -- | 5.0 mL | 5.0 mL | 5.0 mL |
| P Capacity | 3.07 | 2.53 | 1.44 | NO POLYMER | 2.06 | 1.09 |
| % Incorporation | 72 | 73 | 64 | -- | 60 | 48 |

Table 54

Effect of Alternate Comonomers and Cross-linking Agents

| DC-03-053 | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| Wt. $Et_4VDPA$ | 0.50 g | 0.49 g | 0.57 g | 0.50 g | 0.46 g | 0.48 g | 0.48 g |
| Wt. Styrene | 0.17 g | 0.32 g | 0.19 g | 0.17 g | 0.30 g | -- | -- |
| Wt. MMA | 0.20 g | 0.05 g | -- | -- | -- | -- | -- |
| wt. MAN | -- | -- | 0.10 g | 0.20 g | 0.10 g | -- | -- |
| wt. DEGDMA | -- | -- | -- | -- | -- | 0.48 g | -- |
| Wt. TMPTMA | -- | -- | -- | -- | -- | -- | 0.48 g |
| P Capacity (mequiv/g) | 2.78 | 3.13 | 3.08 | 2.39 | 2.69 | 0.57 | 0.80 |
| % Incorporation | 84 | 96 | 81 | 72 | 88 | 18 | 25 |

Table 55

Effect of Various Cross-linking Agents on the Incorporation of $Et_4VDPA$

| Polymer | Cross-linking Agent (5 Wt.%) | P Capacity (mequiv/g) | % Incorporation |
|---|---|---|---|
| DC-03-061A | DVB | 2.86 | 94 |
| DC-03-061B | DEGDMA | 2.64 | 83 |
| DC-03-061C | DEGDA | 2.64 | 83 |
| DC-03-061D | TMPTMA | 2.56 | 80 |

cross-linking agents is a probable cause for this behavior although no studies were undertaken to verify this.

A new set of suspension polymerizations was performed using AIBN as the initiator at 80 °C (DC-03-096, -103A & B, -128A & B). The higher temperature was used to shorten the time to gelation and thus limit loss of the monomer to the aqueous phase. The aqueous phase was once again the one used for poly(vinylbenzyl chloride) with added NaCl. Aqueous:organic phase ratios of 1.00/1.00 did not produce beads, but a ratio of 2.00/1.00 led to the formation of greater than 95% spherical beads with a phosphorus capacity of 2.43 mequiv/g (80% incorporation). After hydrolysis the phosphorus and acid capacities were 2.54 and 7.04 mequiv/g. The ability of this resin to extract $Eu^{3+}$ from 1 X $10^{-4}$ N $Eu(NO_3)_3$ in 0.04 N $HNO_3$ was examined. Europium was extracted at levels of 74.0 and 99.8% at times of 30 minutes and 17 hours. A standard polystyrene-based phosphonic acid resin extracted 99.6 and 100% of the Eu at the same contact times indicating that the presence of the hydrophobic styrene units limited the kinetic performance of the VDPA resin. In response to a query from Argonne National Lab, the effect of drying the resin prior to metal ion extraction was also examined. It was found that DC-03-103BH would only extract 7.8% of the Eu from the solution described above at 17 hour contact times. This indicates that the resin is not capable of rehydrating once it has been dried.

Polymers made with aqueous:organic ratios of 1.25/1.00 and 1.50/1.00 were larger and contained more imperfect beads than the resin made with a 2.00/1.00 ratio, but the phosphorus capacities were 2.63 and 2.54, respectively, corresponding to 87 and 84% incorporation.

Other hydrolyzed polymers were examined. DC-03-016AH & -016CH (both DVB cross-linked) extracted 55.0 and 27.3% of the metal from a 1 X $10^{-4}$ N solution after 30 minutes while DC-03-061DH (cross-linked with trimethylolpropane trimethacrylate) extracted 100% under identical conditions. A series of polymers (DC-03-107A-F) with varying DVB/TMPTMA ratios was synthesized, hydrolyzed, and their Eu extraction abilities measured at 30 minute contact times (Table 56). The total cross-link level was 5%, AN was present at a level of 10%, and the $Et_4$VDPA/Styrene ratio was 60/40. The results indicate that the presence of even small amounts of trimethylolpropane trimethacrylate dramatically increases the kinetic performance of the polymer.

The formulation used for DC-03-107B & D was used to produce polymers via suspension polymerization (DC-03-136A &B). An aqueous:organic phase ratio of 1.50:1.00 was used to yield the polymers described in Table 57.

Finally, two relatively large scale suspension polymerizations were performed using $Et_4$VDPA/Styrene ratios of 60/40, 10% AN, 5% cross-linking (DVB), and 5% AIBN initiator in conjunction with an aqueous:organic phase ratio of 2.00:1.00 (DC-03-143 and -171). The polymerizations were conducted in 3-neck round-bottom flasks equipped with an overhead stirrer. The polymers

Table 56

Characterization of Polymers Cross-linked
with Various DVB/Trimethylolpropane Trimethacrylate Ratios

| Resin | DVB/TMPTMA Ratio | Analysis of Hydrolyzed Polymers | | | |
|---|---|---|---|---|---|
| | | % Solids | P Capacity (mequiv/g) | Acid Capacity (mequiv/g) | % $Eu^{3+}$ Extracted |
| DC-03-107A | 100/0 | 56.4 | 3.53 | 7.60 | 67.6 |
| DC-03-107B | 80/20 | 55.6 | 3.53 | 7.10 | 98.0 |
| DC-03-107C | 60/40 | 50.9 | 3.54 | 7.20 | 100 |
| DC-03-107D | 40/60 | 50.8 | 3.46 | 7.63 | 100 |
| DC-03-107E | 20/80 | 42.5 | 3.33 | 7.51 | 100 |
| DC-03-107F | 0/100 | 37.5 | 3.28 | 7.95 | 100 |

Table 57

Characterization of VDPA Resins Cross-linked with DVB/Trimethylolpropane Trimethacrylate Prepared by Suspension Polymerization

| Resin | DVB/TMPTMA Ratio | Unhydrolyzed Resins | | Hydrolyzed Resins | | % $Eu^{3+}$ Extracted |
|---|---|---|---|---|---|---|
| | | P Capacity (mequiv/g) | % Incorporation | % Solids | Acid Capacity (mequiv/g) | |
| DC-03-136A | 80/20 | 2.54 | 83 | 60.2 | 6.91 | 100 |
| DC-03-136B | 40/60 | 2.42 | 77 | 53.9 | 6.38 | 100 |

consisted of 50-60% spherical beads which were hydrolyzed with 12 M HCl to yield the materials described in Table 58.

Both hydrolyzed resins quantitatively sorbed $Eu^{3+}$ from 1 X $10^{-4}$ N solutions in 0.04 N $HNO_3$. The ability of DC-03-171H to extract $Eu^{3+}$ from 5 N $HNO_3$ was also examined. The VDPA resin sorbed 42.1% of the $Eu^{3+}$ from a 1 X $10^{-4}$ N solution of $Eu(NO_3)_3$ in 5 N $HNO_3$ while a polystyrene-based phosphonic acid sorbed only 4.0%. Other resins tested included a 2% cross-linked phosphinic acid resin (35.2% sorption), 10% cross-linked phosphinic acid (7.2% sorption), and a phosphonate diethyl ester resin (5.9% sorption). Clearly, the VDPA resin, containing geminal diphosphonic acid groups, possesses superior extraction abilities at very low pH.

Table 58

VDPA Resins Prepared by Suspension Polymerization

| Resin | Unhydrolyzed Resin | | | Hydrolyzed Resin | | |
|---|---|---|---|---|---|---|
| | % Solids | P Capacity (mequiv/g) | % Incorporation | % Solids | P Capacity (mequiv/g) | Acid Capacity (mequiv/g) |
| DC-03-143 | 50.6 | 2.43 | 80 | 51.9 | 2.55 | 6.48 |
| DC-03-171 | 52.5 | 2.66 | 88 | 42.9[a] | 3.09[a] | 6.14[a] |

[a]-40+325 mesh

## Conclusions

It was shown that copolymers capable of metal extraction could be produced from VDPA and its tetraalkyl esters in conjunction with the appropriate comonomers. Spherical beads were produced in limited quantities from the tetraethyl ester via standard suspension polymerization techniques. Scale-up of the suspension polymerization and modification of the final polymer has been accomplished by Drs. Andrzej Trochimczuk and Frank Chang (University of Tennessee) to produce the commercial resin Diphonix™ which is available from EIChroM Industries (Darien, IL). Studies at Argonne National Lab have shown that this polymer possesses excellent metal ion uptake abilities.[157,158]

# CHAPTER 6

## SOLID-STATE NMR INVESTIGATIONS

### Introduction

Characterization of the resins produced during these studies presented a challenge due to their cross-linked nature. While wet chemical analyses proved to be very helpful in the characterization of the polymers, in most cases the results obtained were not as descriptive as those obtainable for small molecules by modern spectroscopic techniques. For example, the acid capacity of a resin can be accurately determined using standard wet chemical techniques but no information is gained as to the structure of the acidic site. In cases where the outcome of a synthetic procedure is ambiguous, more information is needed.

Modern NMR spectroscopy has proven to be a very powerful tool in structure elucidation. A wide variety of techniques exist which allow one to determine fundamental properties of molecules in solution including structure, conformation, and molecular motion.[159] Multidimensional NMR spectroscopy has made the determination of the tertiary structure of moderately-sized proteins (approximately 20 kDa) possible, and continued advances in the field appear inevitable.[160] NMR spectroscopy of solids has also advanced greatly in recent years, but the inherent difficulties associated with obtaining solid-

state spectra have prevented its routine use in most laboratories. The difficulties associated with solid-state NMR spectroscopy stem mainly from the limited amount of motion occurring in the sample. The main obstacle to obtaining high resolution solid-state spectra of dilute spins (such as $^{13}C$) is line broadening caused by chemical shift anisotropy and dipolar broadening, both of which are averaged to zero in solution spectra due to rapid tumbling of the molecule. These problems have been partially overcome through magic-angle spinning and high-power proton decoupling. High-power proton decoupling removes the dipolar interactions[161] while spinning the sample at the "magic-angle" ($54^{\circ}\ 44'$) relative to the direction of the magnetic field reduces the chemical shift anisotropy to yield the isotropic chemical shift.[161-164]

Another factor which must be considered is that the lack of molecular motion will inhibit relaxation of the nuclei following an rf pulse. For insensitive nuclei such as $^{13}C$, this greatly increases the time needed to acquire a spectrum since the nuclei must be allowed to relax between pulses and many pulses will be needed to achieve adequate signal-to-noise ratios. This problem has been overcome by utilizing the dipolar interaction to achieve cross-polarization. In cross-polarization, advantage is taken of the shorter $T_1$ relaxation time of the protons relative to the carbon nuclei. Briefly, the technique involves a transfer of polarization from the protons to the carbon nuclei by adjusting the applied fields so that the Hartmann-Hahn[165] condition is met. The Hartmann-Hahn condition is shown by the following equation where

$\gamma$ is the magnetogyric ratio of the nucleus and $B_1$ is the applied field.

$$\gamma_C B_{1C} = \gamma_H B_{1H}$$

The combination of cross-polarization, magic-angle spinning, and high-power proton decoupling comprises the CP/MAS experiment and has been used to acquire high-resolution spectra of solids. The first high-resolution spectrum of a polymer obtained with this technique was reported in 1976[166] and the field has grown rapidly. An excellent monograph[167] has been published and the application of solid-state NMR spectroscopy to characterization of cross-linked polymers in general[168,169] and to polymer-supported reagents[170] has been reviewed extensively.

Narrowing of resonances in polymers has also been achieved through acquiring the spectra of solvent-swollen materials in a standard liquid-state probe.[171,172] True solution-state behavior is not observed in these systems, though, due to restriction of the end-over-end motion caused by the cross-links.[173] As proposed by Doskočilová et al.,[174,175] and elegantly utilized by Fréchet to characterize functionalized polystyrene gels,[173, 176] residual solid-state behavior may be reduced by spinning the solvent-swollen polymer at the magic angle. Since the segmental motions cause the dipolar interactions necessary for cross-polarization to average to zero, such spectra are acquired by standard direct-polarization techniques (DP/MAS). Figure 91 shows the line narrowing achieved by swelling a sample of phosphonic acid resin in

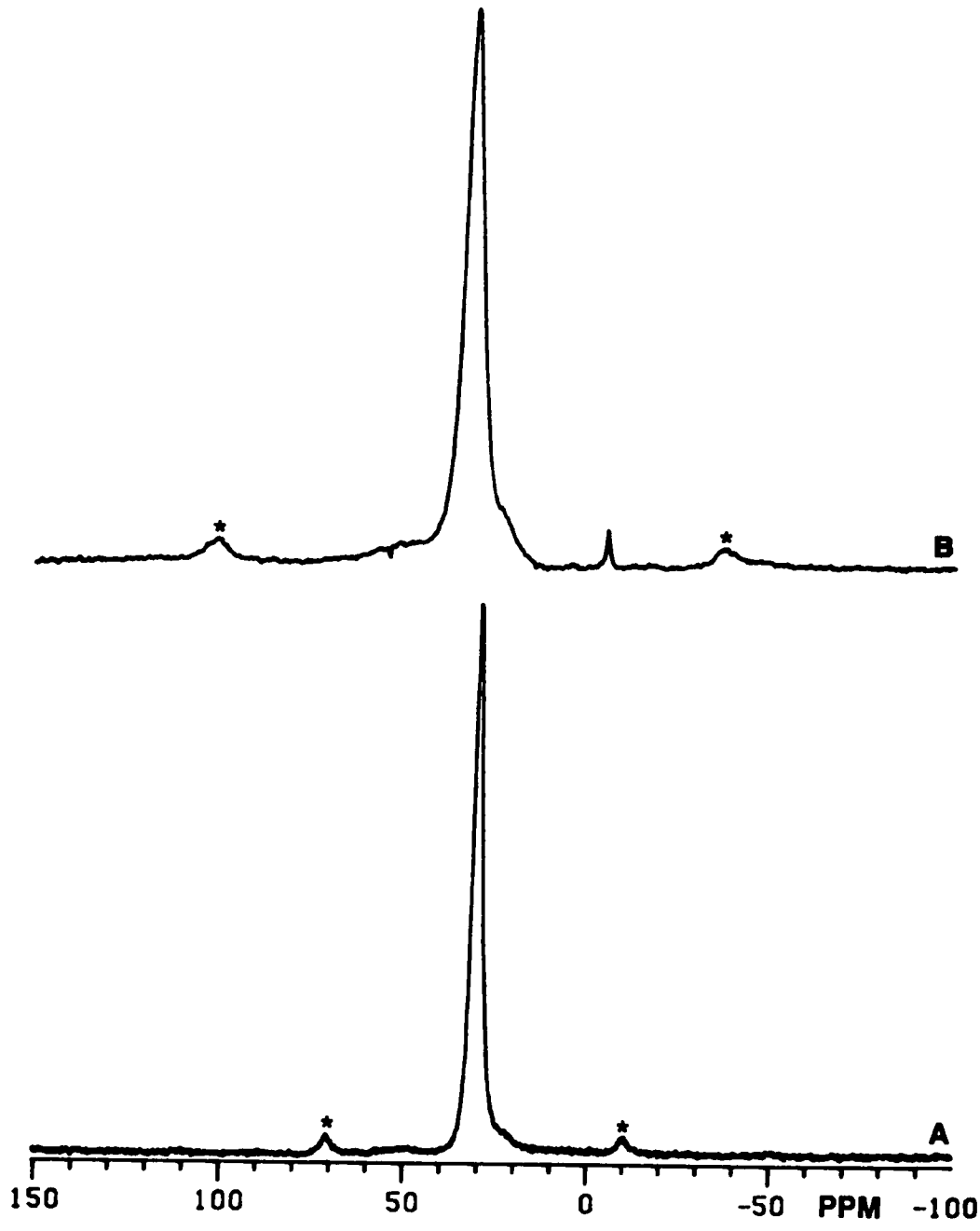



Figure 91. $^{31}P$ spectra of phosphonic acid resin (A) swollen in $H_20$ and (B) dry. Spinning side bands are indicated by asterisks.

water. The resonance at approximately -5.5 ppm in the spectrum of the dry resin is the triphenylphosphine internal standard.

The studies presented here describe the attempts made to apply solid-state NMR spectroscopy to the characterization of resins produced in this laboratory. In many cases, the studies were meant to investigate the feasibility of performing the analysis in the manner indicated and, as such, were not complete studies of the resin under investigation. Given the extensive use of phosphorus-based acids in this laboratory, solid-state $^{31}P$ spectroscopy has been employed in a majority of the cases. Due to the high sensitivity of the $^{31}P$ nucleus, cross-polarization was not necessary to achieve high signal-to-noise ratios, but high-power proton decoupling has still been employed to eliminate the dipolar interactions.

Before useful $^{31}P$ spectra could be acquired, a method for referencing the chemical shift had to be found. Earlier researchers had used both external 85% phosphoric acid and internal triphenylphosphine as a solid-state standard.[177-179] Due to the wide range of reported chemical shift values for triphenylphosphine,[177, 180, 181] it was decided to determine the chemical shift relative to 85% $H_3PO_4$ by using a coaxial tube system (Wilmad Glass Co.). A solution of triphenylphosphine in $CDCl_3$ was placed in the inner tube and a drop of 85% $H_3PO_4$ was placed in the outer tube, forming a thin film surrounding the sample when the tubes were assembled. The signal arising from phosphoric acid was used as the reference (0.00 ppm) yielding a

chemical shift of -5.45 ppm for triphenylphosphine, within the range reported in the literature. This spectrum was measure using a JEOL FX90Q spectrometer since no functioning $^{31}P$ liquid-state probe was available for the instrument used for the solid-state studies (Nicolet NT-200). Initially, triphenylphosphine was added to all samples prior to analysis. However, due to the low percentage of phosphorus in the compound, a large amount of triphenylphosphine had to be added to the samples in order to obtain a suitable reference peak. This, of course, resulted in a smaller amount of resin being present in the sample necessitating longer acquisition times to achieve the desired signal-to-noise ratio. Later it was discovered that the stability of the magnet was such that samples containing no triphenylphosphine could be examined provided that a sample of pure triphenylphosphine had been placed in the rotor, its spectrum acquired, and the resonance set to -5.45 ppm prior to the acquisition of the sample spectrum. In order to yield accurate chemical shift values, all parameters (other than number of acquisitions, line broadening factor, and the pulse lengths) were the same for triphenylphosphine and the resin sample. The reproducibility of the chemical shifts obtained by this method is illustrated by the values obtained for a fully functionalized phosphonic acid resin swollen in water. Three determinations were made with the first being two months prior to the other two which were obtained at the beginning and end of a weekend-long series of acquisitions (with no readjustment of the standard). The values obtained were 30.29, 30.19, and

30.20 ppm. It must be noted that these resonances were narrow in comparison to many of the resonances examined and that the uncertainty in determining the maximum of the peak will increase with increasing line width. For comparison, the broader phosphorus resonance of a sample of Diphonix resin (EIChroM Industries) was observed at 28.29 and 27.93 ppm under identical conditions. To avoid overstating the accuracy of the numbers, all chemical shift values for solid-state spectra will be reported to the nearest ppm.

Class I and II DMBPs

A limited study was undertaken to examine the nature of the phosphinic acid sites produced during the Friedel-Crafts reaction of polystyrene with $PCl_3$ and $AlCl_3$. Previous results from this laboratory have suggested that secondary (diaryl) as well as primary (monoaryl) phosphinic acid sites are formed during this reaction.[99] The results arise from various wet chemical analyses performed on the beads which, while consistent, lack the degree of certainty desired. To this end, the $^{31}P$ spectrum of a phosphinic acid resin swollen in water was recorded. The resin displayed a peak at 26 ppm in close agreement with the peak at 23 ppm found with a sample of dry phenylphosphinic acid. A dry sample of phosphinic acid resin also had a peak at 23 ppm. It was hoped that the presence of secondary phosphinic acid sites would be readily observable in these resins since a dry sample of

diphenylphosphinic acid showed a single resonance at 33 ppm. However, no peak was present at this position. The line width of the resonance from the dry sample was too large permit inspection of the 30-33 ppm region although no shoulder appeared on the peak. While these results cast doubt on the existence of the secondary sites, the wet chemical evidence is strong, and it was found that diphenylphosphinic acid dissolved in deuterated DMSO displays a peak at 23.3 ppm. The small molecule is not soluble in water, but the secondary phosphinic acid sites present on the resin could be solvated in the water swollen sample due to the close proximity of primary acid sites (phenylphosphinic acid is readily soluble in water). As shown by the solution spectrum, the presence of solvent can have a dramatic effect on the observed chemical shift. Shifts of the magnitude seen in DMSO would make the secondary sites indistinguishable from the primary acid. Due to time limitations further experiments were not conducted, but future studies should include a measurement of the $T_1$ relaxation time of the phosphorus resonance. Since some of the secondary sites will be cross-link points, the motion around them should be restricted, leading to longer relaxation times. A biexponential decay of the signal would indicate the presence of two types of phosphorus atoms relaxing at different rates and would thus be strong evidence in support of the presence of secondary sites.

A preliminary investigation designed to determine the feasibility of studying the interaction between phosphinic acid resin and small molecules via

$^{31}P$ NMR was performed. Phenylphosphinic acid (0.10 M in $D_2O$) was contacted with varying amounts of both aniline and phenol and the interaction was observed by monitoring the chemical shift. The chemical shifts (Table 59) indicated that little interaction was present between the acid and phenol but that aniline interacted to a significant degree, almost surely through salt formation. Binding constant determinations were not attempted but the preliminary results indicate that measurements of this type should be possible in cases where a moderate to strong interaction exists.

A study of the phosphonic acid resin and several of its alkyl esters was completed. The phosphonic acid resin gave rise to a peak at 30 ppm. The methyl, ethyl, and butyl diesters yielded single resonances at 33, 31, and 31 ppm, respectively. These values are within the chemical shift range reported in an early study of phosphonic acids[182] and are similar to the reported chemical shifts of small molecules with analogous structures. For example, benzylphosphonic acid was shown to have a chemical shift of 25.39 ppm[183] while its dimethyl ester exhibited a peak at 29.05 ppm[184] and the diethyl ester has been reported at 25.0-27.0 ppm.[185,186] The dimethyl, diethyl, and di-n-butyl esters of 1-adamantylphosphonic acid yielded resonances at 33.2, 30.9, and 30.6 ppm, respectively,[187] in close agreement with the trend seen in the phosphonates examined here. The monoethyl ester displayed two peaks at 39 and 30 ppm (Figure 92). The appearance of the second peak was unexpected since chemical analysis reveals that greater than 90% of the

Table 59

Interaction of Phenylphosphinic Acid with Aniline and Phenol

| Compound | Target Compound/ Phenylphosphinic Acid Ratio | Chemical Shift (ppm) | ΔChemical Shift (ppm) |
|---|---|---|---|
| Aniline | 0.0/1.0 | 22.5 | -- |
| | 0.2/1.0 | 21.9 | -0.6 |
| | 0.5/1.0 | 20.9 | -1.6 |
| | 1.0/1.0 | 19.0 | -3.5 |
| Phenol | 0.0/1.0 | 22.6 | -- |
| | 0.2/1.0 | 22.6 | 0.0 |
| | 0.5/1.0 | 22.2 | -0.4 |
| | 1.0/1.0 | 22.2 | -0.4 |

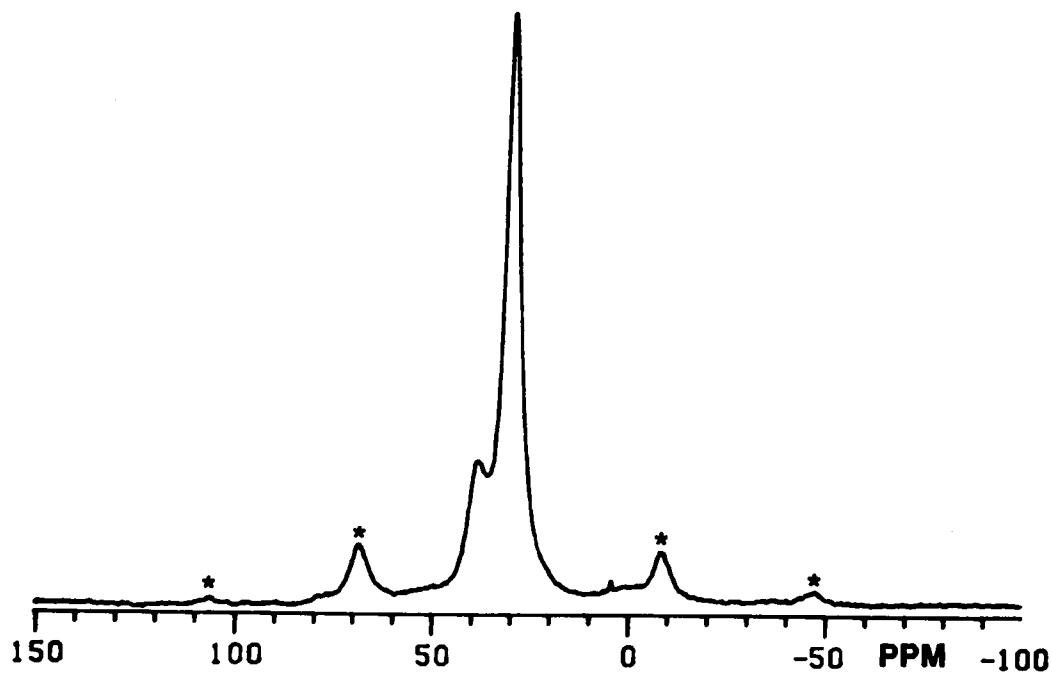



Figure 92. $^{31}P$ spectrum of phosphonate monoethyl ester resin.

ligands are the desired monoethyl ester with the remainder being diacid and diester groups. The single resonances observed in the spectra of the pure diester and diacid resins indicate that the second peak is not due to either ligand. Based on its chemical shift, the resonance at 30 ppm is attributed to the unperturbed monoester site and it is believed that the downfield peak arises from sites in which the phosphoryl oxygen is hydrogen bonded to the acidic proton of another monoester unit. The shift is consistent with that seen with phenylphosphonic acid in the presence of HCl. Dillon and co-workers[188] found that the resonance of phenylphosphonic acid shifted from 18 ppm in an organic solvent to 26.3 ppm in liquid HCl. It is known from studies presented earlier (Chapter 1) that the phosphoryl oxygen of the monoester group is more basic than that of the parent acid. This increased basicity is believed to be responsible for the ability of the monoester ligand to interact in the manner described. However, the monoethyl ester is the only resin in which this resonance is observed. The spectrum of penta(ethylene glycol) monoester resin had a single peak at 30 ppm and that of the bifunctional mono/diethyl ester shows only peaks from those two sites. The absence of the second peak is possibly due to steric hindrance from the large glycol chain and the ethyl groups, respectively. This steric barrier is similar to that seen in the uptake of bulky metal salts by the diester resins (Chapter 1). The absence of the downfield peak in the bifunctional mono/diethyl ester suggests that the diester sites are able to disrupt interactions between the monoester groups,

implying that both sites are distributed in a homogeneous manner throughout the bead.

It is known from wet chemical analyses that the monoethyl ester resin contains some diacid and diester impurities (approximately ten percent). The procedure used to determine the composition of the resin involves a lengthy titration described in the experimental section. It was desired to develop an NMR method which would allow for rapid determination of the composition of the resin. However, even in the swollen state, the line widths of the peaks were large enough to prevent the degree of resolution needed. At best, separate resonances appeared as shoulders as in the case with the 60/40 mono/diethyl ester resin in which the diester peak is clearly visible on the low field side of the main monoester resonance (Figure 93). Determination of the composition of the monoester resin is thus not feasible through a simple integration of the various peaks.

Given the wide chemical shift range of $^{31}P$ and the chemical shifts which were seen with the phenylphosphinic acid/aniline system, a limited investigation was undertaken to determine the effect of complexation with metal ions on the resonant frequency of the 60/40 mono/diethyl ester resin. The resin was contacted with both silver and mercury nitrate in a background of 4 N $HNO_3$. Two studies were conducted. In the first, the resin (1 mequiv) was contacted with 10 mL of both $10^{-4}$ and $10^{-1}$ N metal for 17 hours. Following contact, the resin was dried in a 110 °C oven for 16 hours and

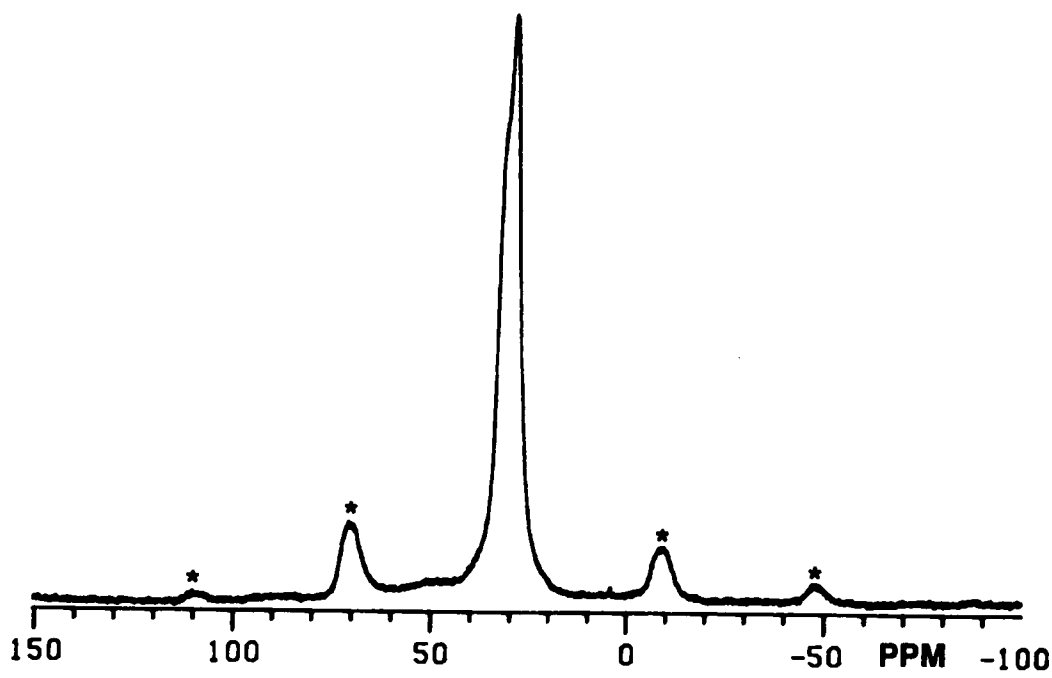



Figure 93. $^{31}P$ spectrum of 60/40 phosphonate mono/diethyl ester resin.

analyzed in the dry state. In the second study, the resins were washed with water prior to being placed in the oven. The unwashed resins all displayed a peak at 30 ppm corresponding to unperturbed phosphonic acid sites and a smaller peak at 4 ppm. Since the intensity was not related to amount of metal contacted, it was strongly suspected that this second peak was due to degradation of the resin caused by the presence of high concentrations of nitric acid during the drying process rather than interaction with the metal. The washed samples confirm this idea. A single resonance at 30 ppm was observed in each case. These studies were conducted before the technique for acquiring spectra was fully developed. As a result, the samples were all dry and triphenylphosphine was present as an internal standard. The use of O-ring sealed rotors enables the acquisition of spectra of contacted samples without washing or drying and would provide a much better measure of any interaction which might occur. Further investigations in this area are warranted.

The structure of partially functionalized phosphonic acid resin was also examined via solid-state $^{31}P$ NMR spectroscopy. IR spectra of such resins were identical regardless of whether dioxane was used as a co-solvent in the reaction or not. Given the different reactivities of these resins (chapter 2), it was thought that a fundamental difference must exist and it was decided to investigate the possibility that the functionalization was proceeding in an abnormal manner during one of the reactions.

As shown in Figure 94, the resin synthesized in the presence of dioxane yields a single peak at 30 ppm while a resin synthesized without dioxane has two resonances at 30 and 9 ppm. Assuming that the relaxation delay used (5 seconds) was long enough to permit complete relaxation between pulses, it appears that the majority of the phosphorus atoms in the resin made without a co-solvent are of the type at 9 ppm. A search of the literature revealed no mechanism by which degradation of the phosphonic acid sites could occur under the conditions present.

It now appears that the upfield peak is due to the formation of an unidentified iron-phosphonic acid complex. The formation of a precipitate from solutions of compounds containing phosphonic acids upon the addition of iron salts (Chapter 5) indicates that a strong complex can be formed between iron and the phosphonic acid group. Such complexes have been synthesized and characterized.[189] The lack of an upfield peak in the spectra of resins made with dioxane could be due to the removal of iron from the resin by the solvent since, in addition to swelling the copolymer, dioxane also dissolves the iron (III) chloride catalyst. In order to investigate the possibility that the upfield peak was due to an iron/phosphonic acid complex, a small (approximately 2 g) sample of DC-03-026 (made without dioxane) was eluted with 500 mL of 0.1 M tetrasodium vinylidenediphosphonate ($Na_4$VDPA) followed by 1 L of 1 N HCl (to reprotonate the resin and remove any insoluble complex) and 1 L $H_2O$. The intensity of the upfield peak was sharply reduced following this procedure

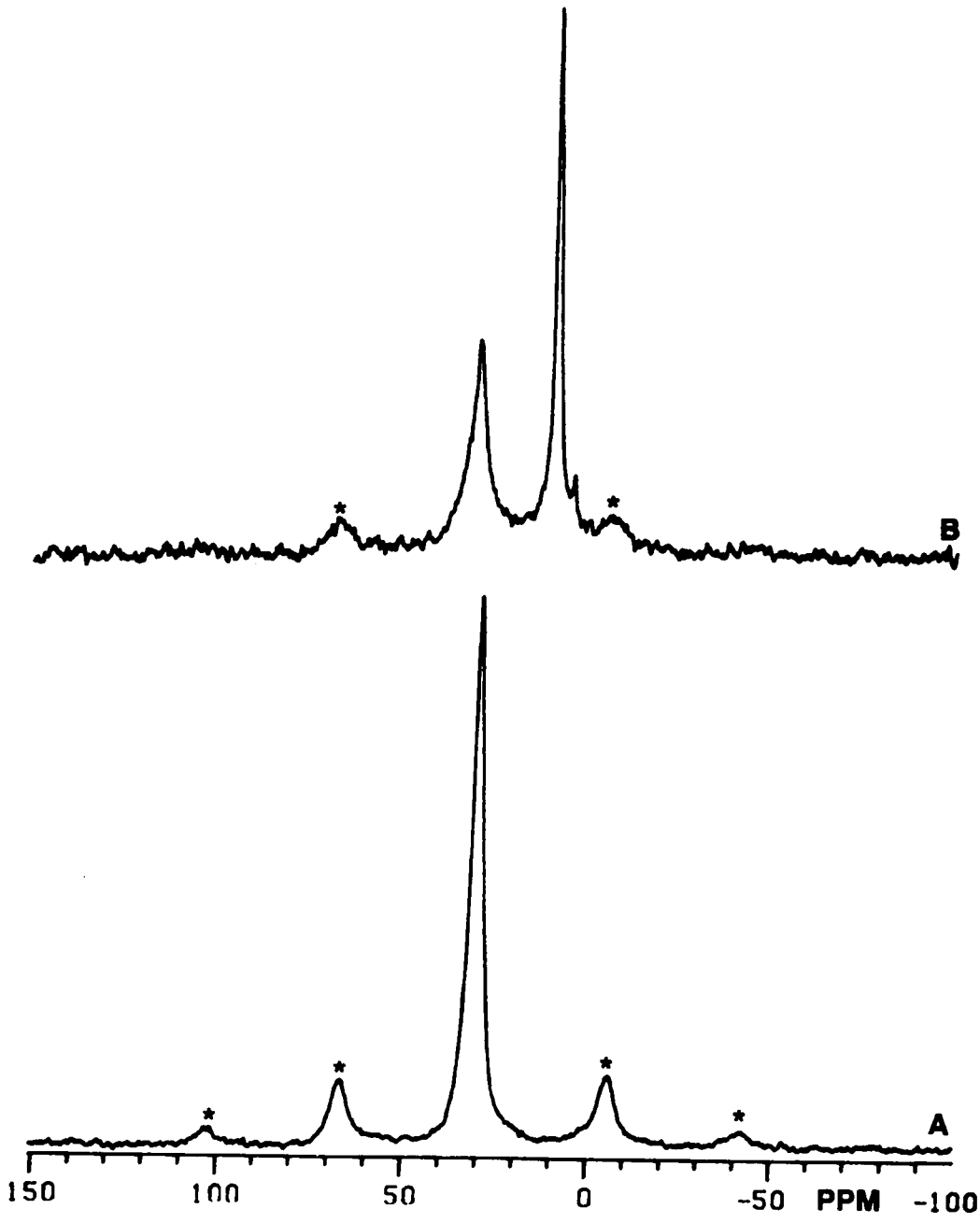



Figure 94. $^{31}P$ spectra of partially functionalized phosphonic acid resins made (A) with and (B) without dioxane.

as shown in Figure 95 (compare with Figure 94B). In addition, a sample of resin made without dioxane which had been refluxed in 12 M HCl (DC-01-119B) showed a very small upfield peak. These results indicated that the peak was due to an iron/phosphonic acid complex which was decomposed, at least partially, by strong stripping agents. However, an attempt to confirm this idea by forming a complex with phenylphosphonic acid and iron (III) chloride yielded a white material which gave no phosphorus signal after almost 8000 scans, possibly due to the paramagnetic nature of the iron. It was later discovered that resins made with dioxane exhibit a resonance (although much smaller) at 9 ppm on occasion. The majority of data obtained to date suggest that an iron complex is responsible for the additional peak but the absence of a resonance in the small molecule phosphonate-iron complex does not allow for confirmation of this hypothesis.

Upon reaction with trimethylamine, the partially functionalized phosphonic acid resins display shifted phosphorus resonances. At this point, a large difference between the resins made with and without dioxane became apparent. Resins made with dioxane display a single peak between 23-24 ppm while in those made without show two peaks at 30 and 23-24 ppm. (Figure 96). Functionalization of resin (made using dioxane) with tributylamine yielded similar results although a peak, present in the precursor resin, is still seen at 9 ppm (Figure 97).

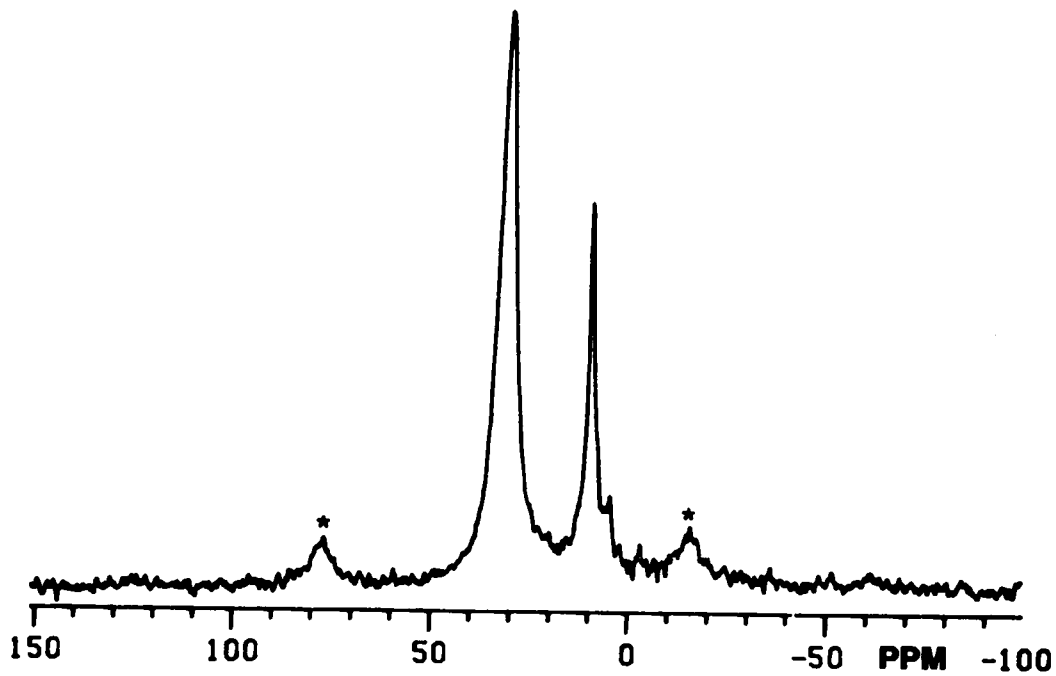



Figure 95. $^{31}P$ spectrum of partially functionalized phosphonic acid resin made without dioxane after treatment with tetrasodium vinylidenediphosphonate ($Na_4VDPA$).

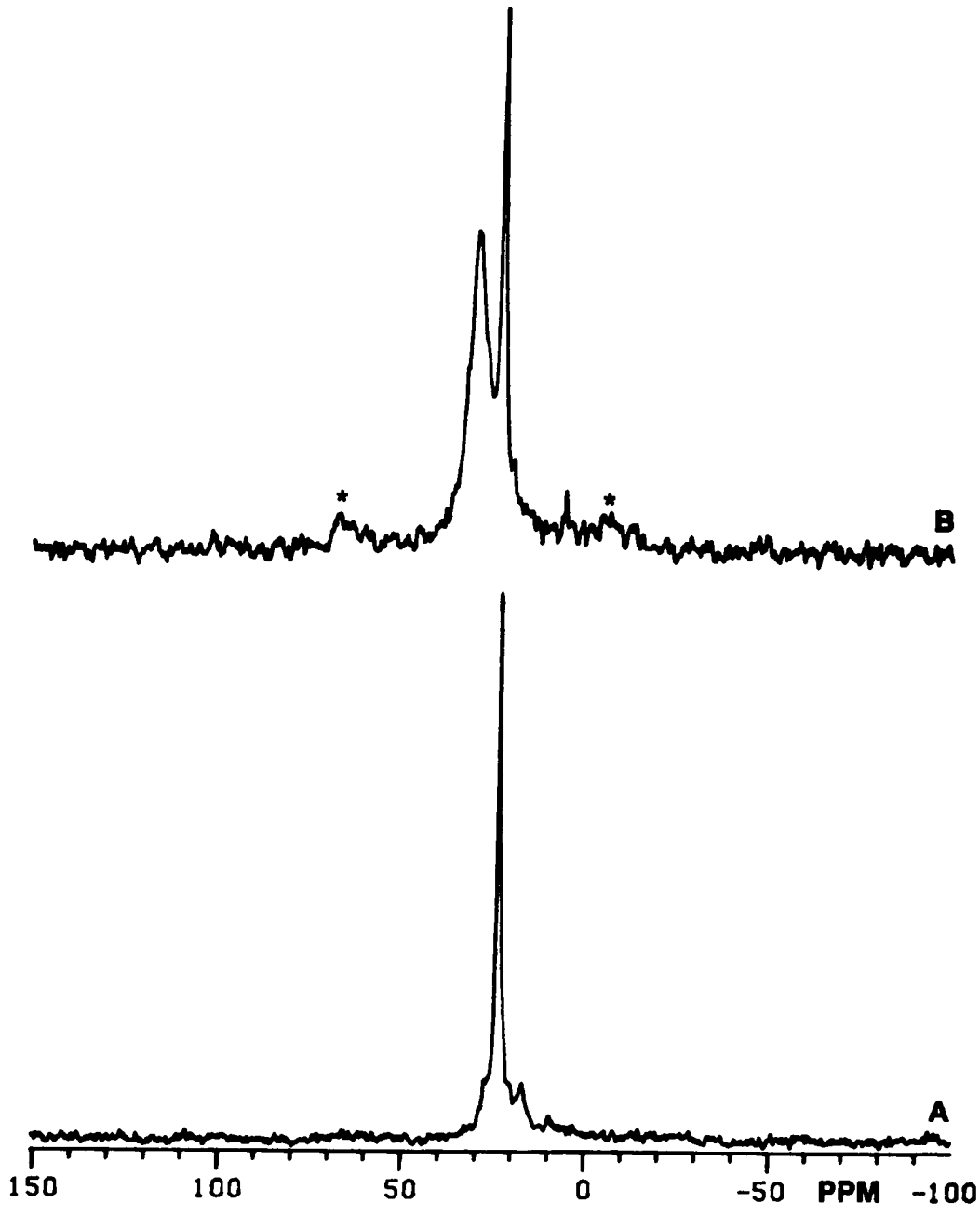



Figure 96. $^{31}P$ spectra of trimethylamine/phosphonic acid resins synthesized from polymers made (A) with and (B) without dioxane.

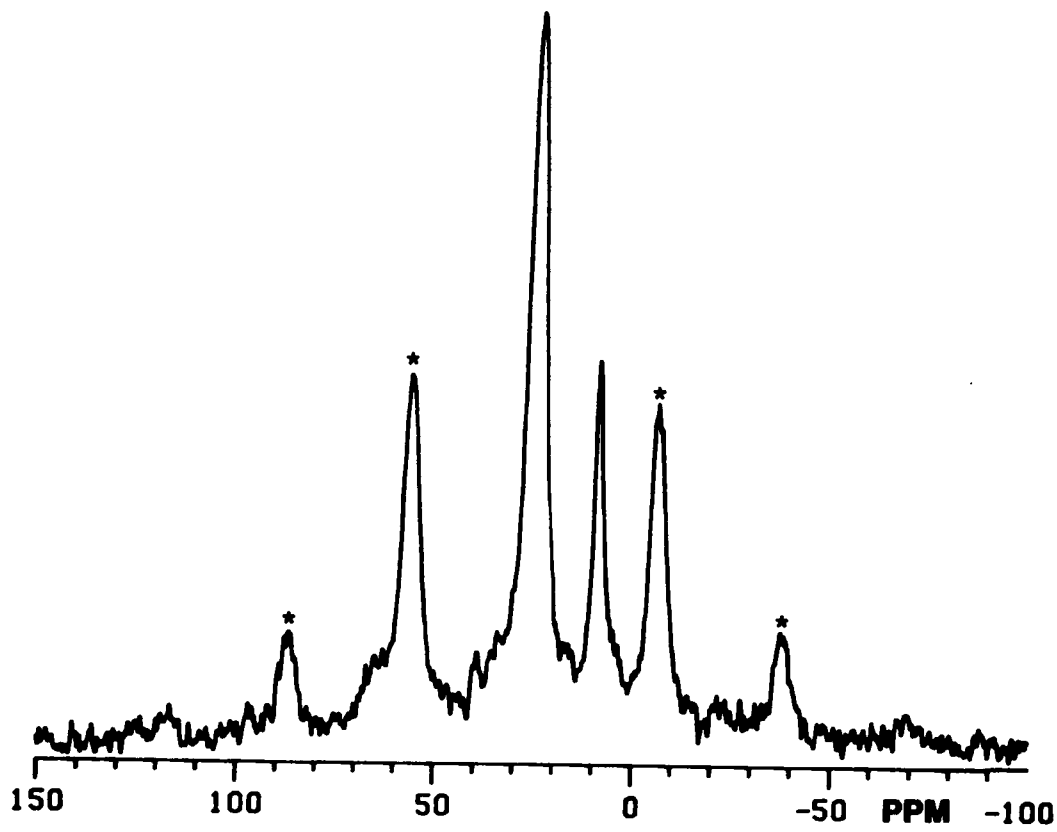



Figure 97. $^{31}P$ spectrum of tributylamine/phosphonic acid resin.

Based on the chemical shift exhibited by the monofunctional phosphonic acid resin, the peak at 30 ppm is thought to result from phosphonic acid groups which are not interactiong with another ligand. The peak shift clearly shows that an interaction exists between the phosphonic acid and the amine groups. At first, it was suspected that the interaction involved electrostatic forces between the phosphonic acid and the quaternary amine sites. However, contacting a sample of phosphonic acid resin with tetrabutylammonium chloride ($R_i$ = 0.10) caused little change in the chemical shift (30 to 29 ppm). The same situation was observed in solution as 0.2 M phenylphosphonic acid shifted from 12.8 ppm in DMSO to 12.7 ppm when the sample was also 0.2 M tetrabutylammonium chloride. All of the results indicate that electrostatic interactions with the quaternary amine groups are not strong enough to cause the magnitude of shift seen in the solid-state spectra.

Shifts of the magnitude seen in the bifunctional resin have been reported upon formation of the phosphonate salt. Benzylphosphonic acid displayed a chemical shift of 17.6 ppm[190] and the $^{31}P$ resonance of cyclohexanephosphonic acid shifted from 32.63 ppm for the fully protonated form to 24.94 ppm upon formation of the disodium salt.[191] Deprotonation of phenylphosphonic acid in $D_2O$ was monitored by the addition of tributylamine. The chemical shifts of phenylphosphonic acid alone, with one equivalent of tributylamine, and with two equivalents of tributylamine were 16.9, 13.1, and

11.9 ppm, respectively. Addition of a single equivalent of trimethylamine produced similar results with a peak at 13.7 ppm. In order to investigate the possibility that the phosphonate anion was the species giving rise to the upfield peak, a sample of fully functionalized phosphonic acid resin was contacted with an excess of 1 N NaOH and rinsed with water. The resin displayed a peak between 23 and 24 ppm, strongly indicating that the phosphonate anion is responsible for the upfield peak seen in the spectra of the bifunctional resins. The interaction between the phosphonate and the quaternary ammonium groups is thus believed to be the formation of an ammonium phosphonate salt by displacement of the chloride counterion. The calculated mass balance (g/g values) and P, N, and Cl elemental analyses are consistent with this idea (see Chapter 2). The conditioning cycle used for these resins involves conversion of the polymer to the base form with 1 N NaOH, elution with water, reprotonation of the acid sites with 1 N HCl, and a final elution with water. Formation of the ammonium phosphonate sites could occur during the initial step but this would imply that the salt can survive the later HCl treatment. Formation of the salt can also occur after conditioning due to the moderate acidity of the phosphonic acid group (the $pK_a$ values of benzylphosphonic acid have been reported as 2.03 and 7.51).[192] At near neutral pH values, the phosphonic acid group will be ionized to a great extent and can then replace the chloride ion as the ammonium counterion.

As discussed at length in a previous thesis,[105] the use of dioxane leads to a more uniform distribution of catalyst throughout the bead and thus to a more uniform functionalization. In contrast, the resins synthesized without dioxane are primarily functionalized on the surface. Upon amination, the resins synthesized in the presence of dioxane possess phosphonic acid groups which are interacting in uniform manner with the quaternary ammonium groups. Two peaks are observed for those resins possessing mainly surface functionalization after the initial step. One peak arises from those groups near the surface of the bead which are surrounded primarily by other phosphonic acid sites while the other is a result of those groups which lie at the boundary of the aminated region within the bead and can interact with the quaternary ammonium sites. The formation of a structure consisting of an aminated core surrounded by a phosphonated shell is thus indicated. In terms of the bifunctionality of the resin, it is clearly advantageous to utilize resins which were initially functionalized in the presence of dioxane. However, the side reaction discussed in chapter 2 renders the partially functionalized resins resistant to further modification. Solid-state $^{31}P$ NMR provides a facile method for monitoring the effect of future synthetic developments with this class of resins.

VDPA Polymers

Several routine $^{13}C$ and $^{31}P$ spectra were recorded of the initial polymers formed with VDPA in order to verify that the desired ligands were being formed. Copolymers of VDPA with N,N'-methylene-bis-acrylamide were examined in the dry state and were found to have a phosphorus resonance at 27 ppm, confirming the presence of phosphonic acid sites on the resin. An additional peak was noted at -2 ppm which, due to its narrow linewidth, appeared to be the result of a small molecule. Its chemical shift suggests that this species is a small molecule phosphate species arising from either decomposition or contamination of the VDPA used to prepare the copolymer. It was not possible to acquire the spectrum of VDPA itself due to its extremely hygroscopic nature. The material quickly absorbed water during an attempt to acquire the spectrum leading to unstable spinning and the threat of severe damage to the probe. No further attempts to characterize VDPA were made. The $^{13}C$ CP/MAS spectrum of the polymer revealed a wide backbone resonance centered at 42 ppm and a carbonyl peak at 178 ppm in agreement with the expected structure. An attempt was made to utilize tetrakis(trimethylsilyl)silane as an internal standard for these $^{13}C$ spectra.[193] However, the compound is hygroscopic, making it difficult to pack into the rotor and to obtain stable spinning. External hexamethylbenzene was found to be a better standard.[194]

The initial styrene-based beads were also characterized. A bead synthesized using the tetraethyl ester of VDPA (DC-02-244A) had a phosphonate ester resonance at 29 ppm which shifted little upon hydrolysis with 12 M HCl. In both cases a small resonance at -2 ppm was present as in the case with the VDPA/bis-acrylamide copolymers. Upon hydrolysis, the ethyl peaks in the $^{13}C$ spectrum disappeared, but no carbonyl (arising from hydrolysis of the cyano groups) was visible. Given the small amount of acrylonitrile present (10%) the resonance was expected to be small but its absence prompted an examination of a polyacrylonitrile bead. After hydrolysis of the acrylonitrile polymer, a carbonyl resonance appeared at 177 ppm. The cyano groups which would appear at approximately 120 ppm are masked in both cases by the aromatic resonances of the divinylbenzene used as a cross-linking agent. This experiment indicated that the hydrolysis conditions used were capable of producing carboxylic acid groups from the cyano units. No further experimentation with VDPA copolymers was performed.

PEG Containing Resins

In order to investigate the attachment of PEG units to both partially functionalized carboxylic and phosphonic acid resins, $^{13}C$ spectra of these resins were acquired in addition to that of the monofunctional PEG resin.

The spectra were acquired with the resins in the dry state using cross-polarization. The monofunctional resin displayed broad peaks at 70 and 62

ppm in good agreement with the spectrum of penta(ethylene glycol) which showed peaks from 58 to 63 and from 67 to 72 ppm. In addition, since the resin had been oven dried prior to analysis, a carbonyl resonance was present at 167 ppm due to carboxylic acid sites formed by thermal cleavage of the PEG chains from the backbone.[123]

These peaks were also present in the spectra of a PEG/carboxylic acid resin (DC-04-192) and a PEG/phosphonic acid resin (DC-04-181). Wet chemical analyses had been ambiguous concerning the incorporation of PEG onto the partially functionalized phosphonic acid resin necessitating the use of NMR spectroscopy. The partially functionalized resins did not display the peaks mentioned above, but did have a resonance at 46 ppm due to the chloromethyl sites.

Interpenetrating Polymer Networks[195]

The formation and subsequent chemical transformation of the interpenetrating polymer networks described earlier was characterized via solid-state $^{13}C$ CP/MAS and DP/MAS (DP = direct polarization) NMR spectroscopy.

Figure 98 presents the DP/MAS spectra of 2% DVB xerogel polystyrene swollen in $CDCl_3$ solutions of 4-vinylpyridine (VP)/ethyl acrylate (EA)/DVB and N-vinylimidazole (VI)/EA/DVB. In addition to the polystyrene signals at 145, 128, 126, and 46-41ppm, spectrum 98A shows the olefinic signals arising from

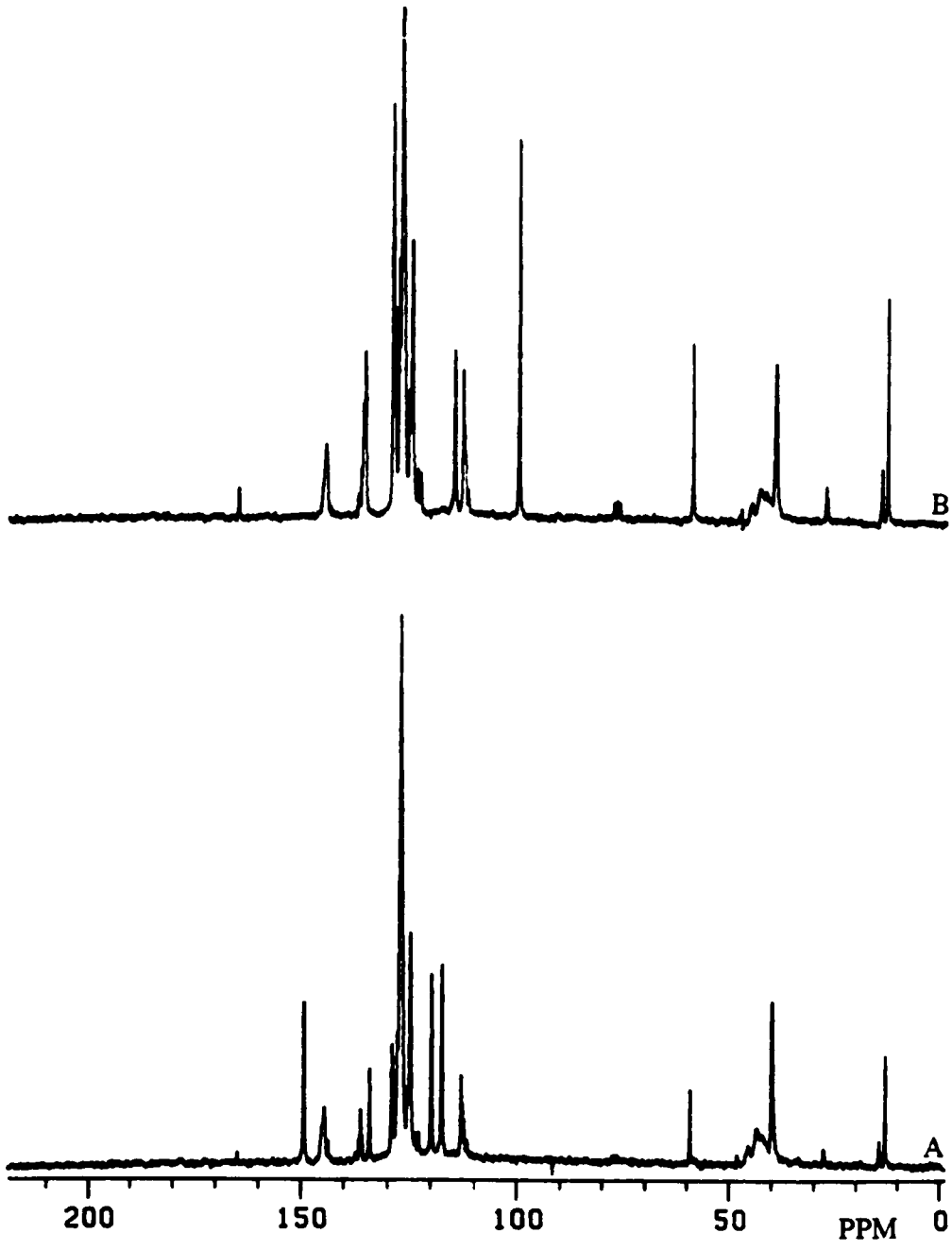



Figure 98. DP/MAS spectra of 2% DVB xerogel polystyrene swollen in $CDCl_3$ solutions of (A) VP/EA/DVB and (B) VI/EA/DVB.

DVB (113 ppm) and VP (117 and 120 ppm). The EA olefinic signals cannot be unambiguously assigned due to overlap with the DVB signal at 129 ppm. The carbons of the ethyl group, however, are visible at 59 and 13 ppm. Other features include the signal from the ester carbonyl at 165 ppm and the quaternary carbon of VP at 149 ppm. All peak assignments were made by comparison with $^{13}C$ spectra of the monomers in $CDCl_3$. The DVB contributes numerous lines to the aromatic region. Spectrum 98B shows the olefinic DVB peak at 113 ppm and additional peaks at 100 and 115 ppm from the VI. The EA resonances seen in Spectrum 98A are also visible as is C-2 of the VI ring at 135 ppm. The small peaks at 28 and 14 ppm arise from the alkyl group of ethylvinylbenzene, which is the principal impurity in technical grade DVB.

Upon sequential IPN formation, the DP/MAS spectra of the IPNs swollen in $CDCl_3$ show only the polystyrene network clearly. At best, weak signals from some of the carbons present in the other network may be seen. Figure 99 shows the PS/VP-EA IPN before and after reflux with hydroxide. Before reaction, small ester resonances are seen at 60 and 14 ppm as well as small peaks from the VP aromatic carbons at 149 and 123 ppm. The small feature at 174 ppm may be due to the carbonyl of the ester group, but its signal-to-noise ratio is too small to permit unambiguous assignment. After reaction, no signals other that those from polystyrene are visible even though titrimetry shows the presence of a second network.[147] Similarly, the DP/MAS spectrum of PS/VI-EA shows only weak resonances in addition to the


Figure 99. DP/MAS spectra of PS/VP-EA IPN swollen in $CDCl_3$ (A) before and (B) after reaction with 2 M KOH in aqueous dioxane.

polystyrene signals. The absence of signals from the second network is explained by the fact that polystyrene (network I) is cross-linked with only 2% DVB while network II has 10% DVB. This 5-fold increase in cross-link level significantly decreases motion in network II relative to that in network I leading to a more rigid network. Two factors may be operative. First, the decreased molecular motion will cause an increase in the observable chemical shift anisotropy and dipolar coupling which will be manifested as broadened lines. Second, the lack of rapid motion will dramatically decrease the relaxation rate. Since the relaxation delay used during the acquisition of the DP/MAS spectra was unusually short, it is probable that many of the resonances were saturated. Increasing the relaxation delay from 0.3 to 20 seconds, however, had little effect on the spectra. The use of $H_2O$ as a swelling solvent with the VP-acid IPN did not enhance the signals from network II, but it did broaden the signals from the polystyrene network, presumably due to lack of good polymer/solvent interactions. Unfortunately, the choice of swelling solvent is extremely limited since it is necessary that the solvent be compatible with the Viton O-rings used to seal the rotor. Acetone, dioxane, and DMSO were found to damage the O-rings.

Since the rigidity of network II in an IPN can render it transparent to DP/MAS, its presence and proof of structure was attempted with CP/MAS. Standard CP/MAS parameters were used to acquire a complete set of spectra using finely ground IPNs packed dry into the rotor.

The CP/MAS spectrum of polystyrene is very similar to the DP/MAS spectrum though the line widths of all resonances are significantly larger in the former. Upon incorporation of a second network, the spectrum becomes more complex. Figure 100 shows the spectra of the PS/EA IPN before and after reaction with hydroxide. Whereas the DP/MAS spectrum shows only polystyrene peaks, the CP/MAS spectrum displays peaks at 175, 61, and 15 ppm in addition to those arising from polystyrene. These peaks are identifiable as the carbonyl and ethyl carbons of the ester by comparison with the linear poly(ethyl acrylate) spectrum.[196] After the IPN is refluxed in a basic solution, the ethyl resonances disappear and a broadened carbonyl peak shifts downfield to approximately 180 ppm, which is consistent with the spectrum of linear poly(acrylic acid).[197,198]

It has been reported that treatment with KOH can convert pyridine and 1-substituted imidazoles into 2-pyridinone and 1-substituted imidazolinones, respectively.[199,200] In addition, treatment with base can cause cleavage of the pyridine ring, leading to poorly characterized, colored compounds,[201,202] and can cleave substituted imidazoles to form alkyl-substituted formamides.[203] In the present study, the NMR spectra confirm that, in spite of the high concentration of KOH, the length of reaction, and the fact that the IPNs darken during hydrolysis, the measured capacities are due to undegraded ligands.

The spectrum of the PS/VP IPN is similar to that of polystyrene with the addition of two unresolved peaks at approximately 150 and 154 ppm. These

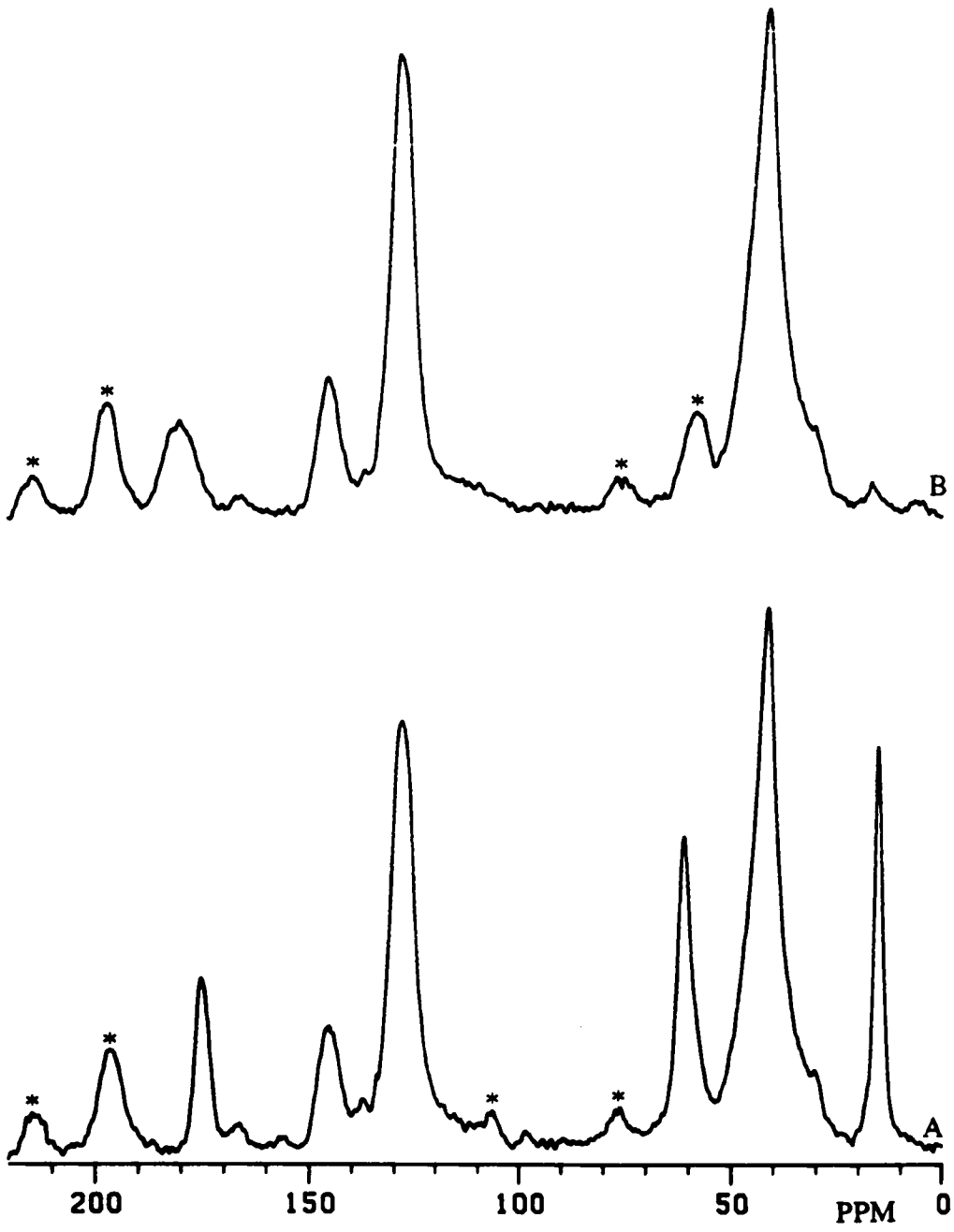



Figure 100. CP/MAS spectra of PS/EA IPN (A) before and (B) after reaction with KOH.

are identified as aromatic VP carbons (C-2 and C-4) by comparison with the linear poly(4-vinylpyridine) spectrum.[204] Figure 101 shows the spectrum of PS/VP-EA before and after reflux with base. The parent sample shows both VP and EA features described above for the monofunctional IPNs. Hydrolysis is the sole reaction after reflux as indicated by a broadening and downfield shift of the carbonyl peak and disappearance of the ethyl peaks. The styrene and pyridine features remain unchanged.

The imidazole networks, in addition to the polystyrene signals, display a peak shoulder at 119 ppm and enhancement of the peak at 137 ppm which, though not well-resolved, are probably due to the VI aromatic carbons. A suspected VI backbone resonance appears at 52 ppm. Definite assignment of these peaks is made by comparison with the spectrum of the linear polymer[205] and by subtraction of the polystyrene spectrum from that of the PS/VI IPN (Figure 102). Although the subtraction does not leave a clean spectrum, it is clear that the peaks at 137 (ring C-2), 123-119 (ring C-4), and 54-52 ppm (backbone $\alpha$-C) are due to the poly(N-vinylimidazole). The PS/VI-EA and PS/VI-acid IPNs (Figure 103) give spectra which display the same pattern found with VP IPNs. No peaks arising from heterocycle degradation products are observed. In particular, peaks associated with conversion of C-2 in both pyridine and imidazole (163 and 152 ppm, respectively)[206,207] are absent.

An attempt to observe the two networks independently was made. A sample of PS/VP-EA was swollen in $CDCl_3$ and its $^{13}C$ spectrum was recorded

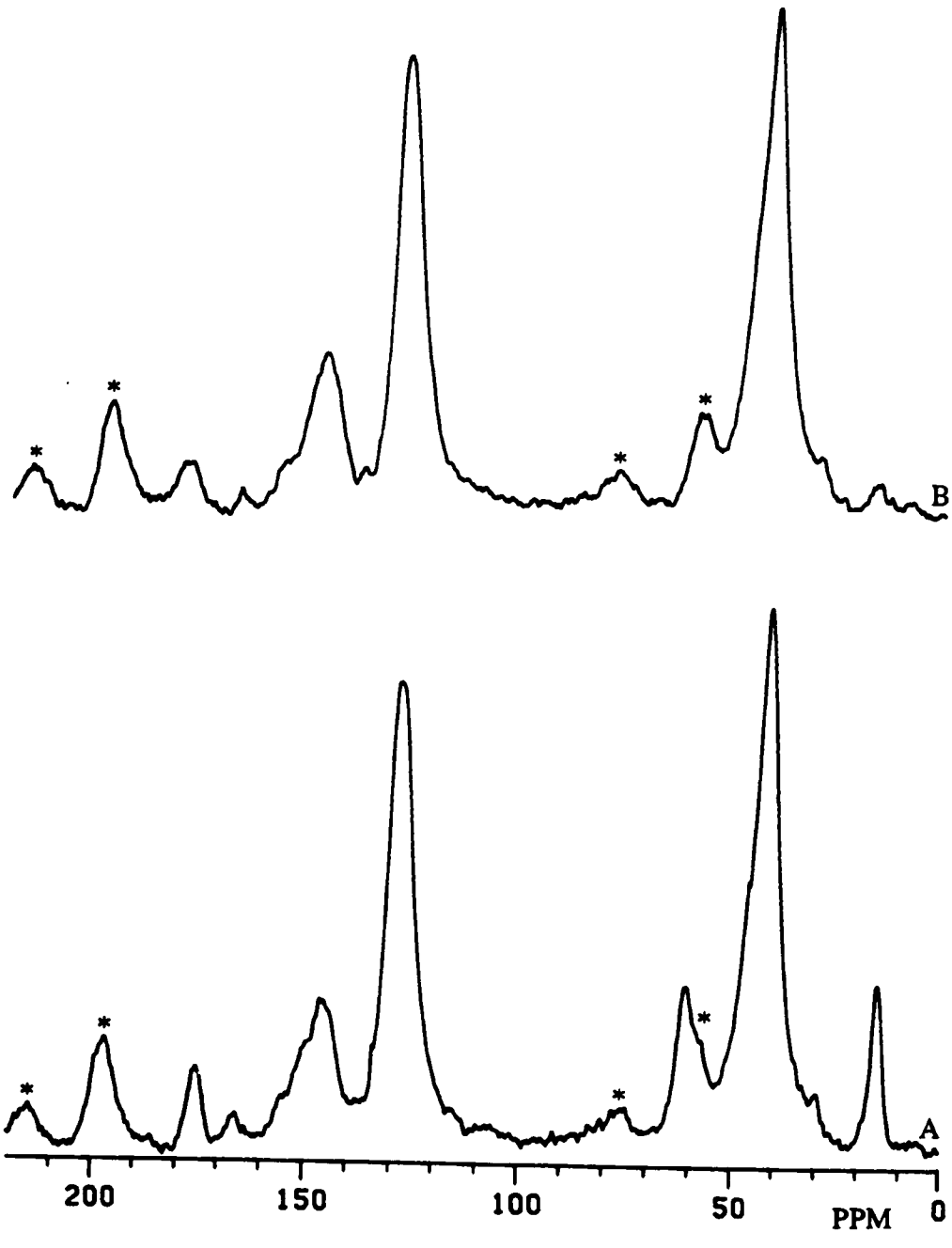



Figure 101. CP/MAS spectra of (A) PS/VP-EA and (B) PS/VP-acid IPNs.

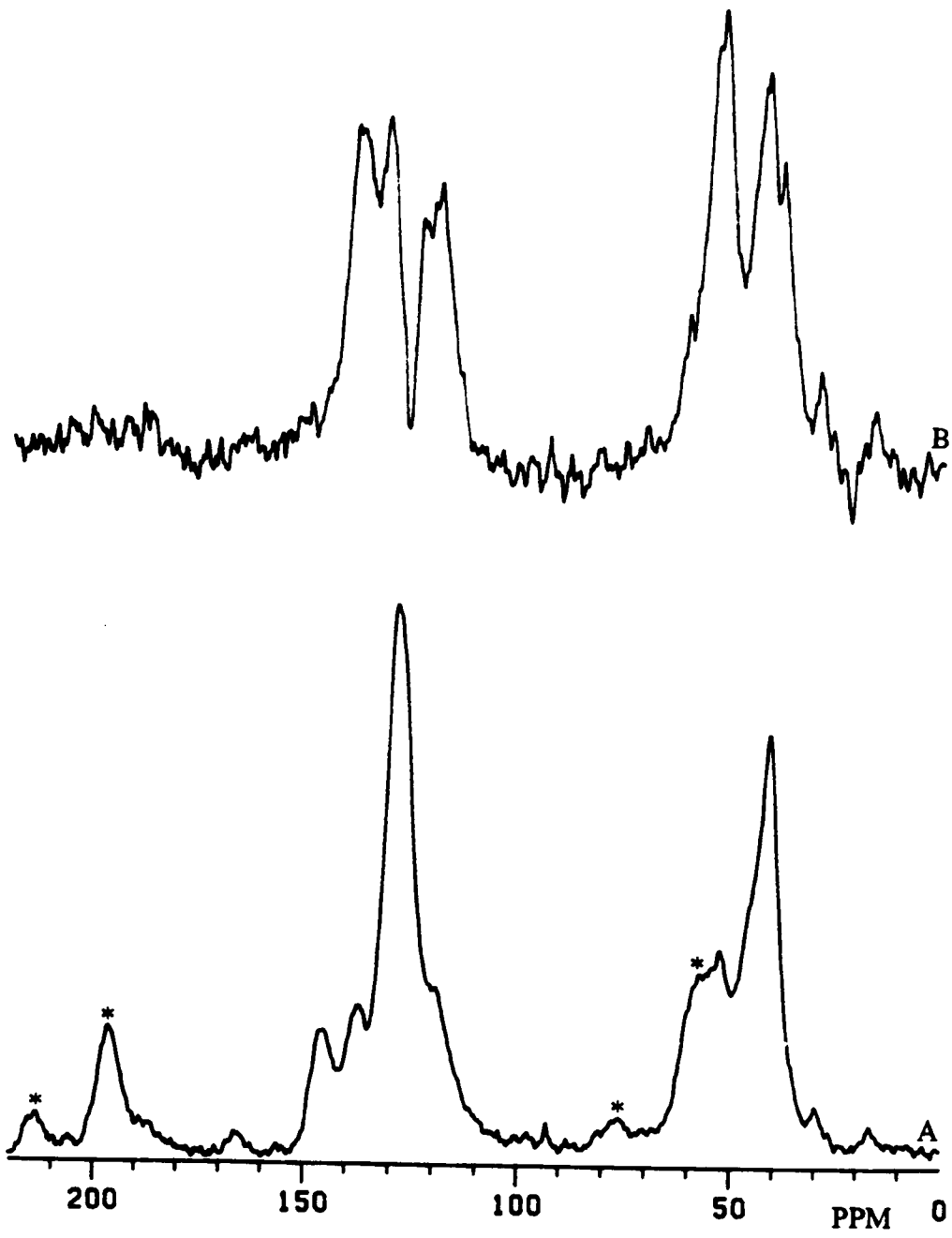



Figure 102. CP/MAS spectra of (A) PS/VI IPN and (B) the subtraction of the spectrum of polystyrene from that of PS/VI IPN.

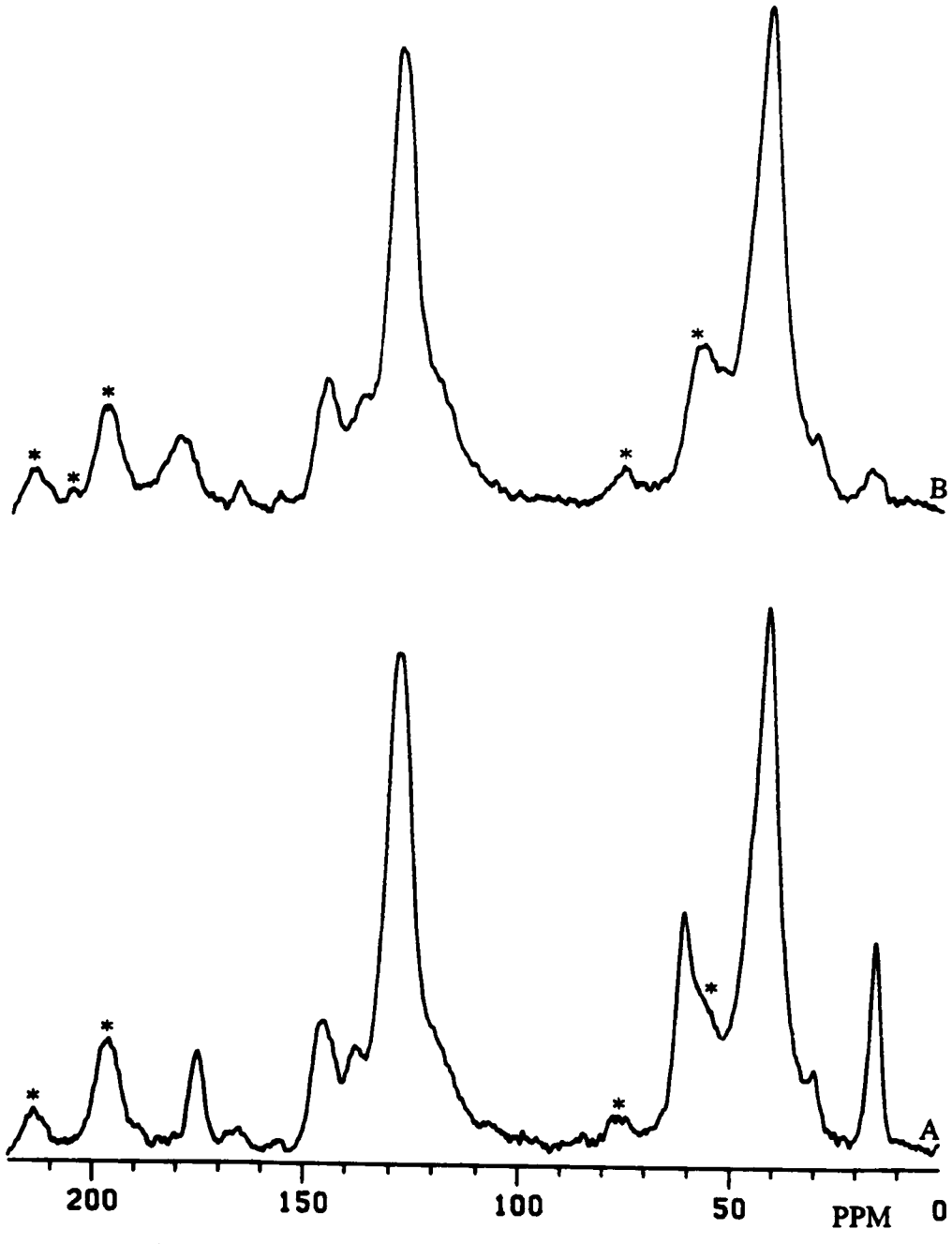



Figure 103. CP/MAS spectra of (A) PS/VI-EA and (B) PS/VI-acid IPNs.

using both CP/MAS and DP/MAS techniques. As described earlier, the DP/MAS spectrum consisted primarily of polystyrene signals. It was thought that the increased segmental motions present in the swollen sample would prevent the polystyrene network from appearing in the CP/MAS spectrum since the dipolar interactions needed for cross-polarization would be averaged to zero. However, both networks are visible in the CP/MAS spectrum. There are two possible explanations for this behavior. First, the segmental motions may not occur to the extent needed to completely average the dipolar interactions to zero. Second, the polystyrene may exist in two regions having differing mobilities. The polystyrene signal seen in the different spectra would then arise from two different regions of the polymer. No experiments were conducted to confirm either possibility and no further attempt to observe the networks independently was made.

The chemical composition of sequential IPNs has been studied with solid-state $^{13}C$ NMR spectroscopy. Network differences in the cross-link level and swelling characteristics allow DP/MAS and CP/MAS to be used as complementary techniques for identifying both networks: DP/MAS gives the chemical composition of the lightly cross-linked network under conditions where the more heavily cross-linked network is transparent; the latter is then identified by CP/MAS. Combining the spectra with elemental analyses allows for an unambiguous determination of the ligands present.

DP/MAS spectra of network I swollen in the monomers of network II show that both monomers of the second network are sorbed from solution into the polystyrene beads. CP/MAS spectra show that the desired networks have been formed.

Ligand accessibility and completeness of reaction were also defined. Spectra of acrylate-containing IPNs which have been hydrolyzed with KOH indicate that cleavage of all ester sites occurs with no apparent degradation of the network.

While the chemical structure of the IPNs had been well characterized by the solid-state spectra, no information had been gained regarding the physical nature of the IPNs. In order to obtain bifunctionality in the polymer, it is necessary for the differing types of ligands to be in close contact with each other which requires that the two networks be truly interpenetrating rather than existing in phase separated regions. The domain size of the IPNs was expected to be extremely small due to their level of cross-linking. Polymers with a lighter degree of cross-linking using more flexible cross-linking agents show domain sizes of 150 Å and the domain size decreases with increasing cross-linking level.[208,209]

In order to determine the degree of interpenetration, a method of observing the interaction between the two networks was needed. No chemical shift difference was noted for the polystyrene peaks when the second network was added. A model study using benzene and imidazole in equimolar

amounts revealed no change in the chemical shift of either compound. A more sensitive measurement involves characterization of the rotating frame spin-lattice relaxation time, $T_{1\rho}$.[210-214] A closer look the cross-polarization experiment is needed to understand the meaning of $T_{1\rho}$. The initial event in the experiment is a 90° flip of the proton magnetization about the x-axis (in the rotating frame). Following this, the phase of the $B_1$ field is shifted 90° so that the protons are spin-locked along the y-axis ($B_1$ now lies along the y-axis). At this point, the carbon nuclei are pulsed in such a manner that the Hartmann-Hahn condition is met. The build-up of $^{13}C$ magnetization occurs exponentially and is characterized by the time constant $T_{CH}$. Also, the proton magnetization will decay exponentially in the spin-locking field with time constant $T_{1\rho}$. This is due to the fact that the $B_1$ field is smaller than the $B_0$ field. When the initial magnetization due to the $B_0$ field is placed in the smaller $B_1$ field, the population difference decreases until a new equilibrium magnetization is established. It is this approach to the new equilibrium position which $T_{1\rho}$ characterizes.

If the dipolar interactions are strong enough, then, due to spin diffusion, all of the protons in a homogeneous sample will show the same $T_{1\rho}$ value. It is this feature which makes $T_{1\rho}$ useful for studying blends and IPNs. In a completely blended or interpenetrating system, the proton $T_{1\rho}$ values are averaged by spin diffusion. By contrast, a system with separated phases would be characterized by two $T_{1\rho}$ times, one for each type of polymer. In this

case, the spin diffusion process will not be rapid enough to average the $T_{1\rho}$ values between different phases. For example, suppose polymer A and polymer B show different $T_{1\rho}$ values. In an interpenetrating network of A and B, the observed $T_{1\rho}$ would fall somewhere between that of the individual networks. It is common to observe several $T_{1\rho}$ values in systems which are only partially interpenetrating, one arising from the interpenetrating region and the others from the segregated portions.

$T_{1\rho}$ can be measured in two ways.[211] One method is to follow the intensity of the $^{13}C$ signal as a function of the time the nuclei are allowed to cross-polarize. The initial rise in the intensity is characterized by $T_{CH}$ and the slower decline which follows is due to relaxation in the rotating frame ($T_{1\rho}$). It is possible to observe $T_{1\rho}(H)$ by observing the carbon signal since the $^{13}C$ signal intensity is directly proportional to the amount of proton magnetization in the XY plane in a CP experiment. An alternative method is to insert a delay time between the initial spin-lock and the onset of cross-polarization while using a constant cross-polarization time. The $T_{1\rho}$ values are obtained by plotting the log of the signal intensity (integration) as a function of the cross-polarization time, t, or (in cases where a variable delay experiment has been performed) $\tau$ + t, where $\tau$ is the length of the delay.

All experiments were performed at ambient temperature using 8-10 different delay (or contact) times. Plots from the two types of experiments are shown in Figures 104 and 105 and the measured $T_{1\rho}$ values are shown in

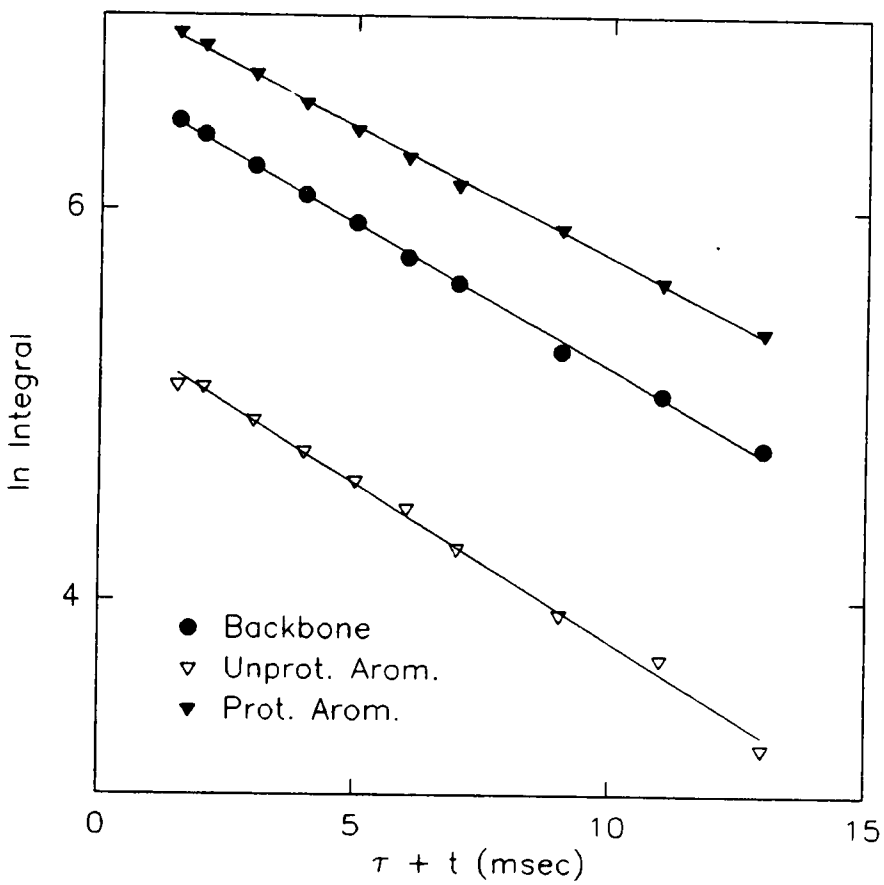



Figure 104. Measurement of $T_{1\rho}$ values of 2% cross-linked polystyrene (DC-03-230A & B) by variable delay times.

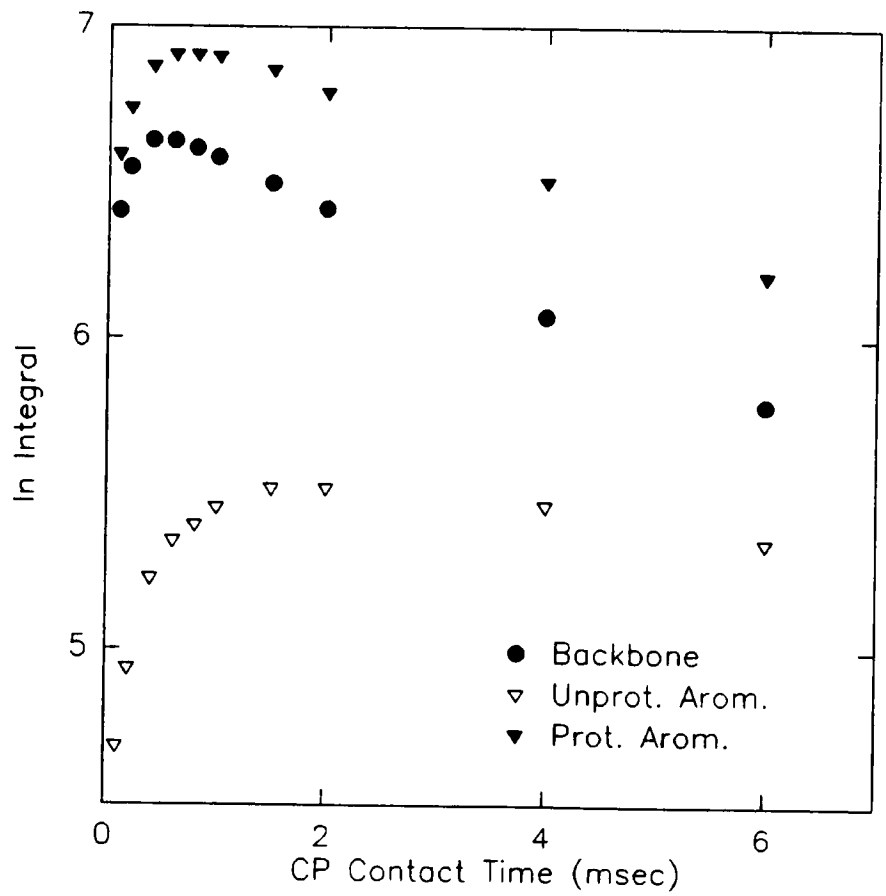



Figure 105. Measurement of $T_{1\rho}$ values of 2% cross-linked polystyrene (DC-03-230A & B) by variable contact times.

Tables 60 and 61. For several resonances, the aromatic peak of the PS/VI IPN for example, the resolution was such that several resonances had to be integrated together. Unfortunately, the $T_{1\rho}$ values of all of the networks are very similar. The experimental accuracy of the technique is shown by the range of values found and is such that values such a 6.5 and 8.0 cannot be assumed to be truly different. No further work was done with these resins, but future work should address the possibility that the $T_{1\rho}$ values will change at different rates with varying temperature. Variable temperature measurements could then yield the desired information concerning the degree of interpenetration.

Table 60

$T_{1\rho}$ Values Measured by Variable Delay Times

| Polymer | Resonance | $T_{1\rho}$ (msec) |
|---|---|---|
| Polystyrene* | Backbone | 6.8, 6.8 |
| | Unprotonated Aromatic | 10.6, 6.2 |
| | Protonated Aromatic | 6.6, 7.5 |
| Poly(ethyl acrylate) | Backbone | 6.6 |
| | Carbonyl | 7.2 |
| | Ethyl $-CH_2-$ | 7.7 |
| | Ethyl $-CH_3$ | 5.8 |
| PS/EA IPN* | Backbone | 8.6, 8.1 |
| | Carbonyl | 11.1, 10.7 |
| | Unprotonated Aromatic | 10.1, 9.6 |
| | Protonated Aromatic | 7.5, 7.4 |
| | Ethyl $-CH_3$ | 10.9, 11.8 |
| EA/PS IPN | Backbone | 8.1 |
| | Carbonyl | 7.8 |
| | Unprotonated Aromatic | 38.8 |
| | Protonated Aromatic | 6.8 |
| | Ethyl $-CH_2-$ | 4.2 |
| | Ethyl $-CH_3$ | 9.2 |
| PS/VI IPN | Backbone | 6.0 |
| | Aromatic | 8.0 |
| PS/VP IPN | Backbone | 7.9 |
| | VP + Unprot. Aromatic | 29.4 |
| | VP + Prot. Aromatic | 7.4 |

* Two determinations were made

Table 61

$T_{1\rho}$ Values Measured by Variable Contact Times

| Polymer | Resonance | $T_{1\rho}$ (msec) |
|---|---|---|
| Polystyrene | Backbone | 6.3 |
| | Protonated Aromatic | 6.9 |
| PS/EA IPN | Backbone | 7.6 |
| | Carbonyl | 8.5 |
| | Protonated Aromatic | 8.2 |
| | Ethyl $-CH_2-$ | 10.6 |
| | Ethyl $-CH_3$ | 12.6 |

## Conclusions

Solid-state NMR spectroscopy has proven to be a useful technique which can be used to augment capacity determinations and elemental analyses in the characterization of cross-linked polymers. Interactions between supported ligands have been examined as has the effect of the synthetic conditions on the bifunctionality of Class III resins. The formation and subsequent chemical transformation of a series of interpenetrating networks has also been explored. Accesibility of the ligands to chemical reagents and the completion of a desired transformation without concurrent side reactions has been demonstrated. Further extensions of the technique (to other nuclei perhaps) would greatly increase its usefulness and could make solid-state NMR spectroscopy the method of choice for the study of interactions between the resin and the targeted molecule or ion.

# EXPERIMENTAL

All materials were obtained from common commercial supply houses and were used without further purification unless otherwise noted. All solutions were prepared using Class A glass transfer pipettes and volumetric flasks.

## Copolymer Synthesis

Beads of poly(vinylbenzyl chloride) cross-linked with 2% divinylbenzene (DVB) were prepared by suspension copolymerization in a standard 1 L three-neck round-bottom flask equipped with a metal double-paddle stir shaft, condenser, and thermometer. The organic phase consisted of 286.2 g vinylbenzyl chloride (Dow), 10.8 g DVB (Dow, technical grade containing 55.4% DVB), and 3.00 g benzoyl peroxide. The aqueous phase was prepared by dissolving 0.96 g gelatin (Pharmagel, Kind & Knox) in 100.0 g $H_2O$ by heating the solution to no more than 50 °C (dissolution normally occurs between 40 and 50 °C). This solution was added to 6.33 g boric acid and 11.90 g poly(diallyldimethylammonium chloride) (Calgon Corp.) dissolved in 216.5 g $H_2O$ and adjusted to a pH of 10.3 with 50 wt% NaOH. After mixing, the pH was readjusted to 10.3 and the aqueous phase transferred to the round-bottom flask. The organic phase was added and the position of the stir shaft was adjusted until the top of the lower blade was at the interface of the

two layers. A nitrogen sweep was started and maintained throughout the polymerization to exclude oxygen. The stir speed was adjusted to a value designed to give beads of the desired size (for example, a stir speed of 525 rpm gave predominantly -60+100 mesh polymer) and the suspension was formed by mixing the phases for two minutes followed by one minute with the stirrer off. This process was repeated three times and the formation of a suspension was verified by observing the stirring mixture in a flashlight beam. The appearance of sparkling particles in the flashlight beam indicated that organic droplets had been suspended in the aqueous layer. The mixture was slowly heated to 80 °C (7° every 15 minutes) and the temperature was maintained there for ten hours with the aid of a Therm-O-Watch temperature control device (Instruments for Research and Industry). The presence of foam was alleviated through the use of a minimal amount of surfactant (CF-32) added as needed. In general, 0-4 drops were required to control foaming. To ensure complete polymerization, the polymer was subjected to a two hour treatment at 100 °C after the addition of 200 mL $H_2O$. After cooling to room temperature, the polymer was washed first with water adjusted to pH 4 with HCl and then with distilled water. The beads were dried at 60 °C and then Soxhlet extracted with toluene for 17 hours in order to remove uncross-linked material. After evaporation of the majority of the toluene in a fume hood, the beads were once again dried at 60 °C. The desired fraction was isolated by sieving the beads through a series of U.S. Standard screens. For most

purposes, the -60+100 fraction was isolated. The designation -60+100 indicates that the beads are small enough to pass through the 60 mesh but are retained by the 100 mesh sieve. A list of mesh sizes and their corresponding diameters is given in Table 62.

In addition to the size distribution obtained by sieving the resins, the polymer was also characterized by determining its swelling ratio in toluene and the amount of extractable material present. The swelling ratio was determined by placing 1.00 mL of beads in a 10 mL graduated cylinder and filling the cylinder with toluene. The polymer was allowed to swell overnight and any bubbles which formed were removed by stirring the mixture and waiting for the beads to settle. The swelling ratio is simply the volume of the swollen beads divided by the volume of the dry polymer. The amount of extractable material was determined by Soxhlet extracting a known amount of polymer with fresh toluene. The toluene used for the extraction was then placed in a tared flask and the solvent removed on a rotary evaporator. The mass of the extracted material was then determined and its percentage of the total mass of polymer calculated.

Polystyrene cross-linked with 2% DVB was prepared in an identical manner except the vinylbenzyl chloride was replaced with an equal weight of styrene and the level of boric acid was reduced to 0.63 g. The aqueous phase was adjusted to a pH of 10.0 and also contained 0.10 g $NaNO_2$ as an aqueous phase polymerization inhibitor. Xerogel polystyrene (2% cross-linked)

Table 62

U.S. Standard Sieve Sizes

| Sieve Number | Diameter of Opening (mm) |
|---|---|
| 16 | 1.19 |
| 20 | 0.84 |
| 40 | 0.42 |
| 60 | 0.25 |
| 100 | 0.149 |
| 200 | 0.074 |
| 325 | 0.044 |

was prepared in an identical manner except that 40% of the organic phase was replaced with toluene which was removed via washing with methanol after the polymerization was complete.

Phosphonic Acid Resin Synthesis

Twenty grams of 2% cross-linked poly(vinylbenzyl chloride) beads were placed in a 500 mL three-neck round-bottom flask equipped with an overhead stirrer, condenser, and thermometer. A drying tube filled with calcium sulfate (Drierite) was attached to the top of the condenser via a tube adapter. One hundred sixty milliliters $PCl_3$ was added and the polymer allowed to swell for 1 hour prior to the addition of 20.97 g $AlCl_3$ (1.2 mole $AlCl_3$/mole copolymer). The mixture was heated to reflux (76 °C) over a period of one hour and the temperature maintained there for four hours. After cooling to room temperature, the reaction was quenched by carefully pouring the mixture into a 4 L plastic beaker containing ice and enough salt to yield a saturated solution once the ice had melted. Additional ice was added as needed during the quench. The resin was conditioned by placing it in a fritted glass column and washing with successive 1L/1 hour elutions of water, 4 wt% NaOH, water, 4 wt% HCl, and water. To further purify the resin for radiotracer experiments, it was Soxhlet extracted for 17 hours with water and reconditioned twice. The resin was analyzed for percent solids, acid capacity and phosphorus capacity.

Phosphinic Acid Resin Synthesis

The apparatus used was identical to that used for the phosphonic acid resin synthesis. Twenty grams of 2% cross-linked polystyrene was swollen in 160 mL $PCl_3$ for 1 hour. Aluminum chloride (19.72 g, 0.77 mole $AlCl_3$/mole copolymer) was added and the mixture heated to reflux (76 °C) over one hour and the temperature maintained there for four hours. The reaction was quenched and the resin conditioned as described for the phosphonic acid resin and analyzed for percent solids, phosphorus, total and primary acid capacities.

Phosphonate Monoethyl Ester and Mono/Diethyl Ester Resin Synthesis

The 60/40 mono/diethyl ester resin was synthesized as follows. Twenty grams of 2% cross-linked poly(vinylbenzyl chloride) was functionalized with $PCl_3$ as described for the phosphonic acid resin. After the reaction had cooled to room temperature, the $PCl_3$ was removed by siphoning through a fritted glass wand. Taking care not to introduce water, the resin was washed three times (30 minutes each) with 200 mL toluene. An overnight wash with toluene, followed by three more 30 minute washes, was conducted prior to quenching the reaction. A small amount of toluene was added to fluidize the mixture and the flask was packed in an ice bath. Quenching was accomplished by the slow addition of a mixture of 64.50 g absolute ethanol

and 110.74 g pyridine (1.4 moles each) via an addition funnel. The rate of addition was controlled so that the temperature did not rise above 10 °C. Small amounts of toluene were added periodically to maintain fluidity. The mixture was allowed to stir for one hour after the quench solution had been added and the first quench solution was removed by siphoning. Due to the formation of pyridinium chloride, this could not be accomplished with a fritted glass wand. A Pasteur pipette was used, taking care not to aspirate beads from the flask. When no more material could be removed without losing resin, portions of absolute ethanol were added and the mixture stirred briefly to dissolve the pyridinium chloride. This procedure was repeated until all of the pyridinium chloride had been removed to leave a bright yellow resin. A second quench solution (identical to the first) was quickly added and the mixture heated to reflux (86 °C) and held there for 16.5 hours. After cooling to room temperature, the resin was washed four times with 95% ethanol, eight times with 50% ethanol, and three times with water prior to conditioning as described for the phosphonic acid resin. The resin was characterized by determination of the percent solids, acid and phosphorus capacities, and by titration with NaOH to determine the monoester capacity.

The monofunctional monoester was synthesized in an identical manner except the reaction was conducted in a 1 L flask and the first quench solution was not removed. After allowing the resin to stir in the first quench solution

for one hour, the second quench solution was added and the resin treated as for the 60/40 mono/diester resin.

Phosphonate Dimethyl, Diethyl, and Dibutyl Ester Synthesis

The diester resins were synthesized using the same apparatus as that for the phosphonic acid resin synthesis. Twenty grams 2% cross-linked poly(vinylbenzyl chloride) was allowed to swell in 160 mL $PCl_3$ for one hour followed by the addition of 42.51 g anhydrous $FeCl_3$ (2.0 mole $FeCl_3$/mole copolymer). The mixture was heated to reflux (76 °C) over one hour and was held there for four hours. After cooling to room temperature, the resin was washed with toluene as described for the phosphonate monoethyl ester resin. Quenching was achieved by the slow addition of 1.4 moles of the appropriate alcohol dissolved in an equal weight of toluene. n-Butyl alcohol was distilled prior to use. The rate of addition was controlled so that the temperature was maintained below 5 °C and a nitrogen sweep was employed to remove the HCl which formed. The mixture was allowed to stir in the quench solution for one hour before it was siphoned off and a second quench solution quickly added. The resin was allowed to stir in the second quench solution overnight after which it was washed with alcohol solutions as described for the monoester. The appropriate alcohol was used for washing (methanol for the dimethyl ester, etc.). The resin was conditioned as described for the

phosphonic acid resin and analyzed for percent solids, acid capacity, and phosphorus capacity.

Hydrolysis of Phosphonate Ester Resins

A small sample (1-5 g) of the phosphonate ester resin was placed in a 250 mL single-neck flask and approximately 200 mL concentrated HCl was added. A condenser was attached and the mixture refluxed for 18 hours. For the VDPA ester resins this procedure was repeated once. The resins were conditioned as described for the phosphonic acid resin and analyzed for percent solids, phosphorus, and acid capacities.

Partially Functionalized Phosphonic Acid Resin Synthesis

Method A: The apparatus used for the fully functionalized phosphonic acid synthesis was employed. Twenty grams of 2% cross-linked poly(vinylbenzyl chloride) was allowed to stir for 18 hours in a mixture of 160 mL $PCl_3$ and 25.51 g anhydrous $FeCl_3$ (1.2 mole $FeCl_3$/mole copolymer). The mixture was heated to 40 °C and the temperature maintained there for 4 hours through the use of a Therm-O-Watch. After this, the resin was quenched and conditioned as described for the phosphonic acid resin with the exception that, at times, more than 1 L of 4 wt% HCl was used in order to remove the iron present. Removal of the iron was monitored by observing the color of the eluate. The resin was analyzed for percent solids, phosphorus,

(non-aqueous) acid, and chlorine capacities.

Method B: The above procedure was modified by the addition of 160 mL dioxane at the beginning of the reaction and the reduction of the catalyst level to 16.37 g (0.77 mole $FeCl_3$/mole copolymer). Later modification used solvents other than dioxane and shorter swelling and reaction periods as described in Chapter 2.

Dimethylamine Resin Synthesis

Twenty grams of 2% cross-linked poly(vinylbenzyl chloride) was placed in a 500 mL three-neck round-bottom flask equipped with an overhead stirrer, stopper, and cold-finger condenser. One hundred sixty milliliters aqueous dimethylamine (40 wt%) and 20 drops 25 wt% NaOH were added and the mixture refluxed for 10 hours. The resin was then placed in a fritted glass column and conditioned with successive 1 L/1 hour elutions of water, 4 wt% HCl, water, 4 wt% NaOH, and water. Prior to radiotracer studies the resin was Soxhlet extracted with water for 17 hours, reconditioned twice, and placed in the nitrate form by elution with 1 L 1 N $HNO_3$ followed by 1 L water. The resin was analyzed for percent solids, TAEC, SSAC, and chlorine capacity.

Trimethylamine Resin Synthesis

A 500 ml three-neck round-bottom flask equipped with an overhead stirrer was used. Twenty grams of cross-linked poly(vinylbenzyl chloride) was placed in the flask along with 360 mL aqueous trimethylamine (25 wt%) and 20 drops 25 wt% NaOH. The mixture was allowed to stir at room temperature overnight and was then placed in a fritted glass column and conditioned as described for the dimethylamine resin with the addition of a second elution with 4 wt% HCl to convert the resin into the chloride form followed by 1 L water. The resin was analyzed for percent solids, TAEC, and chlorine capacity.

Triethylamine Resin Synthesis

Triethylamine was saturated with water by stirring equal volumes of triethylamine and distilled water for 36 hours in a sealed 1 L Erlenmeyer flask. Ten grams of 2% cross-linked poly(vinylbenzyl chloride) was placed in a 250 mL three-neck round-bottom flask equipped with an overhead stirrer, thermometer, and condenser to which was attached a balloon affixed to a tube adapter. The balloon served to limit escape of the amine. The mixture was refluxed (85 °C) for 17 hours. The resin was eluted with 1 L 95% ethanol and conditioned as described for the trimethylamine resin. The resin was analyzed for percent solids, TAEC, and chlorine capacity.

Tributylamine Resin Synthesis

Ten grams of 2% cross-linked poly(vinylbenzyl chloride) was placed in a 500 mL three-neck round-bottom flask equipped as for the triethylamine resin synthesis. One hundred fifty milliliters tributylamine and 150 mL dioxane were added and the resin allowed to swell for 18 hours prior to refluxing the mixture (90 °C) for 8 hours. The resin was conditioned as described for the trimethylamine resin and was analyzed for percent solids, TAEC, and chlorine capacity.

Dimethylamine/Phosphonic Acid Resin Synthesis

Twenty grams of Büchner dried partially functionalized phosphonic acid resin (prepared by method A) was treated as described for the dimethylamine resin synthesis. The resin was conditioned as described for the phosphonic acid resin synthesis and characterized by determining the percent solids, TAEC, SSAC, chlorine and phosphorus capacities.

Trimethylamine/Phosphonic Acid Resin Synthesis

For partially functionalized phosphonic acid resin prepared by method A, the resin was first converted to the base form by elution with 4 wt% NaOH and water. Twenty grams of Büchner dried resin was placed in a 500 mL three-neck round-bottom flask equipped with an overhead stirrer. Three hundred sixty milliliters of 25 wt% trimethylamine was added along with 20

drops of 25 wt% NaOH and the mixture stirred at room temperature for 1 hour. The resin was then conditioned as described for the phosphonic acid resin and analyzed for percent solids, TAEC, chlorine and acid capacities.

For partially functionalized phosphonic acid resin prepared by method B the amination was attempted by extending the contact time to 44 hours. Other attempts utilized an amine solution which had been adjusted to pH 5 with HCl. Eight grams of Büchner dried resin was stirred with 90 mL of this acidified solution for 24 hours at room temperature. Also, the amination was attempted by stirring 2.50 g Büchner dried resin for a period of two days with 90 mL of 25 wt% trimethylamine which had been saturated with NaCl prior to use. These resins were conditioned and analyzed in the same manner as those made from partially functionalized resin prepared by method A.

Attempted Triethylamine/Phosphonic Acid Resin Synthesis

Partially functionalized phosphonic acid resin in the base form (17.73 g, Büchner dried) was placed in the apparatus used for the triethylamine synthesis (a 500 mL flask was used) and the resin was refluxed (78 °C) for 8 hours in a mixture of 192 mL $H_2O$, 89 mL triethylamine, and 130 mL 95% ethanol. The resin was eluted with 1 L 95% ethanol and then conditioned and analyzed as for the trimethylamine/phosphonic acid resin. The synthesis was also attempted by stirring 8.1 g of Büchner dried resin in the base form with

96 mL $H_2O$, 45 mL triethylamine, and 65 mL 95% ethanol for 5 days at room temperature.

Attempted Tripropylamine/Phosphonic Acid Resin Synthesis

Partially functionalized phosphonic acid resin in the base form (17.73 g, Büchner dried) was placed in the apparatus used for the triethylamine synthesis (a 1000 mL flask was used) and the resin was refluxed (85 °C) for 8 hours in a mixture of 192 mL $H_2O$, 122 mL tri-n-propylamine, and 370 mL isopropanol. The resin was eluted with 1 L 95% ethanol and then conditioned and analyzed as for the trimethylamine/phosphonic acid resin.

Attempted Tributylamine/Phosphonic Acid Resin Synthesis

Various methods were tried. 15.65 g Büchner dried (10.00 g dry) partially functionalized phosphonic acid resin in the base form was eluted with 1 L 95% ethanol and 500 mL 100% ethanol to remove the water. The resin was then placed in the apparatus used for the triethylamine synthesis and refluxed in a mixture of 69 mL ethanol and 247 mL tributylamine for 18 hours. Other samples of partially functionalized resin were also refluxed in a mixture of 150 mL dioxane and 150 mL tributylamine for 8 hours and in 375 mL of 37 wt% tributylamine in dioxane for 18 hours. An attempt was made to insure that the resin was fully swollen prior to reflux in 150 mL dioxane/150 mL tributylamine. The resin was stirred in dioxane at room temperature for 2

hours at which time fresh dioxane was added and the mixture held at 50 °C for 24 hours after which the dioxane was removed and the amine solution added. The mixture was refluxed for 8 hours. DC-05-134 was synthesized from partially functionalized phosphonic acid resin prepared by an improved method by refluxing 10.00 g of Büchner dried resin in 183 mL of 37 wt% tributylamine in dioxane for 18 hours. In all cases the resins were eluted with 1 L 95% ethanol and conditioned and analyzed as described for the trimethylamine/phosphonic acid resin.

Partially Functionalized Phosphonate Dibutyl Ester

Twenty grams of 2% cross-linked poly(vinylbenzyl chloride) was partially functionalized as described for the partially functionalized phosphonic acid resin synthesis (method B). After functionalization, the resin was washed with toluene as described for the phosphonate monoethyl ester and was quenched with a mixture of 103.77 g freshly distilled butanol and 103.77 g toluene using the same procedure as for the fully functionalized resin. The resin was washed with butanol (see fully functionalized resin synthesis) and was conditioned in a column with water, 4 wt% NaOH, water, 4 wt% HCl, and water. The resin was analyzed for percent solids, acid, chlorine, and phosphorus capacities.

Carboxylic Acid Resin Synthesis

The fully functionalized carboxylic acid resin was synthesized by first converting 2% cross-linked poly(vinylbenzyl chloride) to the benzyl ethyl ether resin. Sixty grams of polymer was placed in a 1 L three-neck round-bottom flask equipped with an overhead stirrer, condenser, and thermometer. The resin was allowed to swell for 1 hour in 400 mL toluene at which time 400 mL 25 wt% KOH in 95% ethanol was added and the mixture heated to reflux (83 °C) and held at that temperature for 48 hours. After cooling to room temperature, the resin was placed into several fritted glass columns, eluted with 1 L of 95% ethanol and 2 L of $H_2O$ and then Soxhlet extracted with water for 17 hours to completely remove the KCl which forms during the reaction. The resin was characterized by determining its percent solids and chlorine capacity.

The resin was then Büchner dried (yielding 116.2 g) and placed in the same flask used for the production of the benzyl ethyl ether. Five hundred milliliters of 70% aqueous dioxane was added and the resin allowed to swell for one hour. Three hundred milliliters of 3 N $HNO_3$ (yielding 7 wt% $HNO_3$) was added and the mixture refluxed for 24 hours. The resin was eluted with 2 L of $H_2O$ and the percent solids determined. The resin was then returned to the same flask and 250 mL of dioxane was added and the resin allowed to swell for 1 hour. Five hundred milliliters of 30% hydrogen peroxide was added and the mixture heated at 80 °C for 24 hours. The resin was conditioned with

water, 4 wt% NaOH, water, 1 N $HNO_3$, and water prior to being Soxhlet extracted with water for 17 hours and reconditioned twice. The resin was analyzed for percent solids and acid capacity.

Partially Functionalized Carboxylic Acid Resin Synthesis

The partially functionalized carboxylic acid resin was synthesized in a manner similar to that of the fully functionalized polymer. The benzyl ethyl ether reaction was limited to a 4 hour functionalization at 60 °C in order to substitute only a fraction of the benzyl chloride sites. After cooling, the resin was conditioned in an manner identical to that used for the fully functionalized resin.

The resin was Büchner dried (162.0 g) and placed in a 2 L three-neck round-bottom flask equipped with a thermometer, overhead stirrer, and condenser. 810 mL of 70% aqueous dioxane was added and the resin allowed to swell for one hour. 486 mL of 3 N $HNO_3$ was added and the mixture refluxed for 24 hours. The proportions of reagents used in this reaction were obtained from a previous dissertation.[106] The resin was conditioned with 2 L of $H_2O$ and then freed of water by elution with 500 mL of ethanol followed by 500 mL of 2,2,4-trimethylpentane. The solvent was allowed to evaporate in a fume hood. The dry resin was placed in a 2 L three-neck flask equipped with an overhead stirrer. The proportions used[106] were as follows. Dry resin (56.20 g) was combined with 1055 mL dioxane, 21.08 g

pyridine, and 63.24 g $PCl_5$. This mixture was stirred at room temperature for 48 hours and the liquid was decanted from the flask. The resin was conditioned by stirring in 250 mL of the following solutions: dioxane, 80% dioxane, 0.5 N KOH in 50% dioxane, 80% dioxane, 0.5 N $HNO_3$ in 80% dioxane, and 80% dioxane prior to being Soxhlet extracted with 80% dioxane for 17 hours and eluted with 2 L of water. The resin was analyzed for percent solids, and both chlorine and acid capacities.

Penta(ethylene glycol) (PEG) Resin Synthesis

A standard preparation involved placing 10.00 g of 2% cross-linked poly(vinylbenzyl chloride) in a 250 mL three-neck round-bottom flask equipped with a condenser (fitted with a drying tube), a thermometer, and an overhead stirrer. One hundred milliliters of dioxane was added and the resin allowed to swell for 1 hour. Penta(ethylene glycol) (15.06 g, enough to give a 1.0:1.0 mole ratio of penta(ethylene glycol) to benzyl chloride sites on the resin) was dissolved in 30 mL of dioxane and quickly added to the polymer. The flask used to dissolve the penta(ethylene glycol) was then rinsed twice with 10 mL of dioxane and the rinses were added to the reaction mixture (total volume dioxane = 150 mL). The glycol anion was formed by **slow, careful** addition of 2.78 g of NaH (Aldrich, 60% in mineral oil). This is enough hydride to give a 1.1:1.0 mole ratio of NaH to penta(ethylene glycol). The mixture was heated at reflux for a period of 24 hours, cooled to room temperature and the resin

transferred to a Büchner funnel. The resin was then carefully rinsed with a small amount of water in order to destroy any residual NaH. No activity was ever seen at this point, but great care should be taken. Purification of the resin involved a 17 hour Soxhlet extraction with dioxane followed by elution with 2 L of $H_2O$. The resin was analyzed for percent solids, PEG capacity, linear PEG capacity and chlorine content. This reaction was also performed on a 40 gram scale.

Attempted Synthesis of Ethylene Glycol Resin

The synthesis was conducted in a manner identical to that used for the penta(ethylene glycol) resin. Ten grams of 2% cross-linked poly(vinylbenzyl chloride) was reacted with 3.92 g of ethylene glycol and 2.78 g 60% NaH in mineral oil. The resin was purified as described for the penta(ethylene glycol) resin and analyzed for percent solids, chlorine capacity, and glycol capacity by chromic acid oxidation.

Attempted Synthesis of PEG/Phosphonic Acid Resin

Partially functionalized phosphonic acid resin prepared by method B was dried either by azeotropic distillation with heptane or by elution with ethanol and isooctane. For the initial attempts, an elaborate reswelling procedure was used. Ten grams of the dry resin was placed in the apparatus used for the PEG resin synthesis and 50 mL of dioxane was added. This

mixture was stirred at room temperature for 2 hours at which point the dioxane was removed and replaced with 100 mL of fresh dioxane. This mixture was heated at 50 °C for 24 hours after which the solvent was removed and the resin suspended in 100 mL of fresh dioxane. Later it was determined that better results could be obtained with a simple 1 hour contact with dioxane at room temperature. Various PEG/Cl ratios were examined but a 1.0/1.0 ratio was standard. The amount of PEG and NaH added is dependent on the capacities of the starting resin. Enough NaH must be added to completely deprotonate the acid sites on the resin as well as form the PEG anion (a 10% excess is used, as is the case with the monofunctional PEG resin). The amount of PEG is dependent on the chlorine capacity of the resin and the amount of NaH needed is calculated using the following expression.

$$\frac{[mmole\ PEG + 2(phosphorus\ capacity)(wt.\ resin)][0.023998][1.1]}{0.6}$$

For example, DC-04-099C utilized a partially functionalized resin with Cl and P capacities of 3.16 and 1.81 mequiv/g, respectively. For 10.00 grams of this resin, 7.53 g of PEG and 2.98 g 60% NaH were used.

The reaction is conducted exactly as described for the monofunctional PEG resin synthesis. After Soxhlet extraction with dioxane, the resin is conditioned by elution with water, 4 wt% NaOH, water, 1 N $HNO_3$ (twice), and water. The resin is analyzed for percent solids, non-aqueous acid, chlorine

and phosphorus capacities. The linear PEG capacities of some resins were also determined.

PEG/Carboxylic Acid Resin Synthesis

Partially functionalized carboxylic acid resin was dried by either azeotropic distillation with heptane or by elution with ethanol and isooctane. Functionalization with PEG was carried out in a manner identical to that used for the monofunctional PEG resin and the attempted PEG/phosphonic acid resin syntheses. A PEG/Cl ratio of 1.0/1.0 and a reaction length of 24 hours were found to be adequate. Earlier syntheses utilized the extensive reswelling procedure described for the PEG/phosphonic acid resin. Those conducted at later times used only a 1 hour swelling period in 100 mL of dioxane (as used for the monofunctional and PEG/phosphonic resins). Once again, a 10% excess of sodium hydride was used. The amount of NaH required was calculated using the properties of the partially functionalized resin and the following expression.

$$\frac{[(mmole\ PEG + (wt.\ resin)(acid\ capacity)][0.023998][1.1]}{0.6}$$

For example, the synthesis of DC-04-192 involved the use of a partially functionalized resin with Cl and acid capacities of 5.28 and 1.86 mequiv/g, respectively. Thus, for 10.00 g of resin, 12.58 g of PEG and 3.14 g of 60% NaH were used. The reaction was completed as described for the

monofunctional PEG resin and conditioned in the same manner as the PEG/phosphonic acid resin. The resin was analyzed by determining the percent solids, non-aqueous acid, chlorine, total PEG, and linear PEG capacities.

Phosphonate PEG Monoester

The PEG monoester was synthesized using a method developed in this laboratory by Dr. Frank Chang.[125] Fully functionalized phosphonic acid resin, synthesized as described above, was freed of water by solvent exchanging 20.00 g of Büchner dried resin three times with 40 mL of dimethylformamide (DMF). The resin was transferred to a 500 mL three-neck round-bottom flask equipped with an overhead stirrer and suspended in 100 mL of $CH_2Cl_2$. The mixture was cooled with an ice bath and a mixture of 100 mL thionyl chloride and 11 mL DMF was added over a 2 hour period via an addition funnel. The mixture was allowed to stir at room temperature for 3 hours at which point the liquid was removed and replaced with a second solution of thionyl chloride/DMF (100 mL/11 mL, added quickly). This was allowed to stir for 17 hours at which time the liquid was removed and the resin washed with 100 mL of dry $CH_2Cl_2$ and 100 mL of dry toluene under a positive pressure of argon (15 minutes each wash). Following this, the resin was suspended in 50 mL of dry pyridine (smoke is evolved) and cooled in an ice bath. The appropriate amount of PEG was dissolved in dry pyridine and added to the reaction

mixture via an addition funnel over a two hour period. A PEG/Cl ratio of 2.0/1.0 was used. Thus, for 20.00 g of phosphonic acid resin having a percent solids of 51.38 and a phosphorus capacity of 4.73 mequiv/g, 46.33 g (194.42 mmole) of PEG was used. After addition of the quench solution, the mixture was allowed to stir at room temperature for 17 hours. The quench solution was removed and the resin washed 4 times with 75% aqueous dioxane and once with 95% ethanol (100 ml, 15 minutes each wash). The resin was removed, the round-bottom flask washed, and the resin reintroduced into the flask. Three hundred milliliters of 0.5 N NaOH in 50% ethanol was added, a condenser was placed on the round bottom, and the mixture refluxed for 17 hours to hydrolyze diester sites to the monoester. The resin was conditioned as described for the phosphonic acid resin, Soxhlet extracted with 95% ethanol for 17 hours, and reconditioned. The solvents used for this reaction were purified by distillation from calcium hydride and stored over molecular sieves under an argon atmosphere. The bottles were sealed with rubber septa and syringe techniques were used to transfer the solvents. The final resin was characterized by determination of its percent solids, non-aqueous acid capacity, phosphorus capacity, and monoester capacity by titration with NaOH.

IPN Synthesis

The preparation of the monomer solution was quite involved and will be explained in detail here for the synthesis of DC-03-244, a polystyrene/poly(ethyl acrylate) IPN. The amount of solution needed was determined by the amount of polymer to be used and its swelling ratio in the monomer solution. The swelling ratio was different for each monomer solution so the amount needed was sometimes determined by trial and error. To ensure that a maximum capacity had been achieved, it was necessary to have an excess of solution. In cases where an insufficient amount of solution had been prepared, an additional amount was quickly prepared and added to the swollen polymer. In this case, 10.00 g of xerogel polystyrene was used and 90 mL of monomer solution was sufficient to swell the polymer fully. It was desired that the monomer solution have a functional monomer (ethyl acrylate (EA) in this case) concentration of 4.25 M in toluene. The solution also had to contain 10 mole% DVB which was available as a 55.4 wt% (55.8 mole%) product containing primarily ethylvinylbenzene (EVB) as a contaminant.

For 90 mL of a 4.25 M solution of EA, 0.3825 moles of EA would be needed. Letting "x" equal the total number of moles of vinyl monomer then the following equations are true.

$0.100x$ = moles of DVB

$0.079x$ = moles of EVB (from 55.8 mole% DVB)

$0.821x$ = moles of EA = 0.3825 = 38.29 g

Therefore, moles DVB = 0.0466 = 6.07 g

moles EVB = 0.0368 = 4.87 g

total wt. Tech. DVB = 10.94 g

Using densities, one obtains 41.44 mL EA and 12.01 mL technical DVB. Since 90 mL were required, 36.55 mL (31.69 g) of toluene should have been needed assuming the volumes to be additive. The total mass of the organic phase should have been 80.92 g. AIBN was used as the initiator at a level of 2 wt% based on the total mass of the monomer solution. Therefore, 1.62 g of AIBN were needed.

In practice, the solution was prepared by adding the DVB and the EA to a 100 mL graduated cylinder. The AIBN (Polysciences, used as received) was added and the volume was brought to 90 mL with toluene. In general, a slightly different amount of toluene was needed than the preliminary calculation indicated. In this case, 31.83 g, rather than 31.69 g, were used.

The AIBN was dissolved (no volume change was ever seen) and the monomer solution was sparged with nitrogen for 5 minutes. Two grams of xerogel polystyrene (-40+60 mesh) was placed in a 25 mL graduated cylinder and the remaining 8.00 g was placed in a 100 mL beaker. Twenty percent of the monomer solution was added to the cylinder and the remainder was placed in the beaker. The swelling ratio was obtained via the volume change of the beads in the graduated cylinder.

The vessels were covered with Parafilm and the beads were allowed to swell overnight. The amount of liquid on top of the beads in the graduated cylinder was taken as a rough estimate of the amount not absorbed by the beads. For DC-03-244, 6.8 mL remained. Since this represented 20% of the total solution, it was assumed that at least 34.0 mL were unabsorbed. Therefore, a maximum of 56.0 mL had been absorbed corresponding to a maximum of 30.6 g of monomer.

The aqueous phase used consisted of 1.5 wt% poly(vinyl alcohol) (Fluka, 86% hydrolyzed, MW = 15,000) based on the weight of the monomer and 41.7 g $CaCl_2 \bullet 2\ H_2O$ in every 80 mL of solution. Since no more than 30.6 g of monomer were absorbed, the amount of PVA used was (30.6)(0.015) = 0.46 g (per 80 mL). The PVA was allowed to dissolve before the calcium chloride was added. In general, 160 mL of aqueous phase were prepared. For every 5 g of polystyrene used to prepare the IPN, 67.1 g of the aqueous phase was used. All aqueous phases were sparged with nitrogen.

The desired amount of aqueous phase was placed in a 250 mL three-neck round-bottom flask equipped with an overhead stirrer, condenser, and a thermometer. The aqueous phase was heated to 80 °C while the excess monomer was removed from the beads by filtration. The recovered monomer solution was measured in order to provide a basis for the calculation of the theoretical capacities of the network. When the temperature had reached 80 °C, the swollen beads were quickly placed in the flask. The temperature

usually fell 5-10 °C at this point. The mixture was reheated to 80 °C and held at that temperature for 12 hours. Following polymerization, the beads were placed in a beaker and washed with hot water (4 times, 250 mL) to remove the stabilizers. Following Soxhlet extraction with methanol, the IPNs were conditioned as described for the phosphonic acid resin and analyzed for percent solids, acid and base capacities, and, for those IPNs containing pyridine, chlorine capacity. The pyridine-containing IPNs were also rinsed with more than one liter of water at the end of the conditioning sequence in order to deprotonate a larger fraction of the nitrogen atoms.

Synthesis of Cross-linked Poly(Ethyl Acrylate)

A small scale suspension polymerization was conducted by placing an organic phase consisting of 22.85 g EA, 6.52 g technical DVB, and 0.6 g AIBN together with an aqueous phase consisting of 80 mL of an aqueous solution containing 0.45 g poly(vinyl alcohol) and 41.7 g $CaCl_2 \bullet 2H_2O$ in a 100 mL cylindrical polymerization reactor equipped with an overhead stirrer and condenser. The mixture was polymerized at 80 °C for 12 hours and then washed with hot water and Soxhlet extracted with methanol as described for the IPN synthesis. The resin was conditioned as described for the phosphonic acid resin and dried at 110 °C overnight.

Hydrolysis of IPNs with KOH in Dioxane

The KOH solution was prepared by dissolving 28.05 g (0.50 mole) KOH in 25 mL of water and adding enough dioxane to bring the volume to 250 mL. The resulting mixture was not a one-phase system at room temperature. The mixture was placed in a 500 mL single-neck round-bottom flask along with 3.50 g of the IPN to be hydrolyzed. A condenser was added and the mixture refluxed for 72 hours. After cooling to room temperature, the IPN was conditioned with 2 L of $H_2O$, 1 L 4 wt% HCl, and 1 L $H_2O$.

Conversion of the Tetrasodium salt of VDPA into VDPA

In a typical conversion, 13.10 g $Na_4$VDPA was dissolved in 45 mL of $H_2O$ and added to a column containing 100 g of fully functionalized sulfonic acid resin in the protonated form. The solution was allowed to remain in the column for 30-45 minutes and then slowly drained. The column was eluted with water until the eluate was no longer acidic and the eluates combined. The resin was regenerated by passing 1L of 4 wt% HCl through the column in 1 hour followed by 1 L of $H_2O$.

This procedure was repeated several times and the acid eluates were combined and concentrated on a rotary evaporator. Due to the instability of VDPA, the temperature remained at or below 35 °C. When the material crystallized (which can take days unless a seed crystal is added when the solution become viscous) toluene was added and the remaining water

removed as a toluene azeotrope on the rotary evaporator (still at 35 °C). Toluene was added and evaporated repeatedly until the solid became dry. The dried material was very hygroscopic and was stored in the coldroom in a sealed container under a blanket of inert gas.

Solution Polymerization of VDPA

VDPA was copolymerized with various monomers as described in Chapter 5. The weights of the monomers are given there and a typical procedure is described here. DC-02-156 was prepared by dissolving 2.25 g VDPA, 2.50 g N,N'-methylene-bis-acrylamide, and 0.25 g potassium persulfate in 100 mL of water in a 125 mL Erlenmeyer flask. The flask was covered with Parafilm and placed in a 60 °C oil bath for 6 hours. A white solid was visible after 15 minutes. After 6 hours, the solid was recovered by centrifugation and was conditioned by stirring in successive 100 mL portions of the following solutions: $H_2O$, 4 wt% NaOH, $H_2O$, 4 wt% HCl, and $H_2O$ (twice). The solid was isolated from each solution by filtration. When the washings were complete the solid was placed in a beaker covered with a Kimwipe and placed in a vacuum oven. The polymer was dried under vacuum at room temperature and then characterized by determination of the phosphorus and acid capacities.

Earlier work had utilized a ferrous ammonium sulfate/hydrogen peroxide system to initiate the polymerizations. For approximately 1 g of

monomer, 2.5 mL of 0.1 M ferrous ammonium sulfate was added followed immediately by 2.5 mL of 0.1 M $H_2O_2$. The polymerizations were conducted at room temperature. Attempts to remove the iron from the finished polymers by precipitation of the iron with hydroxide were not completely successful. Due to this and the fact that iron salts form insoluble compounds with VDPA, this initiator was abandoned.

Small-Scale Suspension Polymerization of VDPA

VDPA was copolymerized with various monomers under suspension polymerization conditions. The various compositions of the monomer solutions are given in Chapter 5 and an example is given here. DC-02-134C was prepared by dissolving 0.25 g VDPA, 0.60 g acrylamide, 0.10 g N,N'-methylene-bis-acrylamide, and 0.05 g potassium persulfate in 2 mL $H_2O$ and 1 mL dimethylformamide. The continuous phase consisted of 0.3 g cellulose acetate butyrate dissolved in 10 mL 1,2-dichloroethane. The phases were placed into a 20 mL scintillation vial and a small stir bar was placed in the bottom. The vial was placed in an oil bath on a stirring hot plate and the mixture stirred to generate the suspension. The mixture was heated at 60 °C for 19 hours and poured into 100 mL of methanol. The limited amount of solid recovered was washed with water, dried in a 110 °C oven overnight, and characterized by determination of its phosphorus capacity.

Tetraalkyl VDPA Ester Synthesis

The same general method was used to produce all tetraalkyl esters. A standard procedure was to place 5.00 g of VDPA (26.6 mmoles) in a 250 mL three-neck flask equipped with a condenser, spin bar, and a nitrogen inlet. The appropriate trialkylorthoformate was added (319 mmole) and the flask placed under a positive pressure of nitrogen (maintained by an oil bubbler at the outlet). A vigorous flow of nitrogen was maintained. The mixture was stirred and the temperature slowly increased. As the reaction proceeded the VDPA slowly dissolved to yield a yellow solution. The mixture was heated to reflux and maintained there until the reflux temperature reached the boiling point of the trialkylorthoformate (greater than 24 hours in some cases) except in the case of the tetrabutyl ester where the temperature was allowed to rise to 140 °C and was maintained there for 6 hours. Orange to brown solutions were produced. It was found that in cases where the VDPA was not completely dry or where the nitrogen sweep was not fast enough the remove the alkyl formate byproduct, the boiling point of the trialkylorthorformate was not reached. In those cases, the reaction was stopped not less than 24 hours after the time at which the VDPA completely dissolved. The progress of the reaction was easily followed with $^{31}P$ NMR spectroscopy. At this point, the excess trialkylorthoformate was removed using a rotary evaporator (except for tributylorthoformate, which was removed during the subsequent vacuum distillation due to its high boiling point). The residue was primarily tetraalkyl

VDPA. The tetramethyl ester was used without further purification at this point. Both the tetraethyl and the tetrabutyl esters were purified by vacuum distillation (boiling points: $Et_4$VDPA: 133-137 °C at 0.4-0.5 torr, $Bu_4$VDPA: 155-164 °C at 0.015 torr; literature values[215] $Et_4$VDPA: 115-116 °C at 0.05 torr, $Bu_4$VDPA: 155-158 °C at 0.01 torr). The structures of the compounds were verified by $^{31}P$, $^{13}C$, and $^{1}H$ NMR spectroscopy.

Bulk Polymerization of VDPA Esters

A large number of different monomer mixtures were polymerized as described in Chapter 5. The general procedure is exemplified by the polymerization of DC-03-016C. A one dram screw-cap vial was used as the polymerization vessel. The monomer mixture consisted of 0.46 g $Et_4$VDPA, 0.30 g styrene, 0.10 g acrylonitrile, 0.09 g technical grade divinylbenzene (DVB content 55.4%), and 0.05 g AIBN. A small spin bar was added and the monomers thoroughly mixed and then sparged with nitrogen for 2 minutes. The vial was placed in a heated oil bath on a multipoint stir plate (Variomag). The polymerization was conducted at 60 °C (temperature controlled by a Therm-O-Watch) for 20 hours followed by 2 hours at 80 °C. For those polymerizations conducted at 80 °C, the post-heat was carried out at 100 °C. The vial was allowed to cool and was then wrapped in a paper towel and broken with a hammer. The glass was carefully removed and the polymer was again wrapped in the paper towel and crushed to a mesh size of

approximately -40+60. Less polymer is lost using this method than with a mortar and pestle. The solid was Soxhlet extracted with toluene for 17 hours, placed in a fritted glass column, eluted with acetone (500 mL) to remove the toluene, and then conditioned as described for the phosphonic acid resin. The polymer was characterized by determination of its phosphorus capacity.

Suspension Polymerization of $Et_4VDPA$

As before, many different monomer compositions were investigated. DC-02-228 provides an example of the technique. The aqueous phase was prepared by first making a small batch of the standard aqueous phase used for the suspension polymerization of vinylbenzyl chloride (see Copolymer Synthesis). Five and half grams of NaCl was dissolved in 20 g of this aqueous phase. Two grams of this aqueous phase were placed in a 20 mL scintillation vial along with an organic phase consisting of the following: 0.57 g $Et_4VDPA$, 0.57 g styrene, 0.40 g acrylonitrile, 0.36 g technical divinylbenzene (DVB content 55.4%), and 0.10 g AIBN. A small spin bar was added and the vial placed in the same oil bath/stir plate combination used for the bulk polymerizations and heated at 60 °C for 16 hours followed by 2 hours at 80 °C. The resin was Soxhlet extracted with toluene for 17 hours and conditioned in the same manner as the polymers prepared in bulk. The phosphorus capacity was determined.

A large scale suspension polymerization was performed by placing the aqueous and organic phases in a 250 mL three-neck round-bottom flask equipped with an overhead stirrer and a standard paddle, a nitrogen inlet, and a condenser with an oil bubbler attached at the outlet. Seventy grams of the aqueous phase described for the small scale polymerizations were used. The organic phase (35 g total) consisted of 15.94 g $Et_4VDPA$, 10.65 g styrene, 3.50 g acrylonitrile, 3.16 g technical DVB (DVB content 55.4%), and 1.75 g AIBN. The monomers were sparged with nitrogen for 5 minutes. An oil bath was used to heat the flask at 80 °C for 18 hours and 100 °C for 2 hours after which the resin was treated in the same manner as the material prepared in the small scale reactions.

Percent Solids Determination

Excess water was removed from the resin by placing it in a Büchner funnel, covering the funnel with a small piece of rubber sheeting (held in place by rubber bands) and applying a vacuum (720 mmHg) for 5 minutes. Resin treated in this manner is referred to as "Büchner dried resin." A clean, dry 20 mL scintillation vial was obtained and the mass determined using an analytical balance prior to the addition of 1.0 to 1.5 grams of Büchner dried resin. The mass was then accurately redetermined. The sample was heated in a 110 °C oven for 16 hours and then allowed to cool in a desiccator prior to

determination of the mass. The percent solids is calculated as the mass of the oven dried resin divided by the mass of the Büchner dried resin.

Phosphorus Elemental Analysis[216]

Approximately 20 mg of oven dried resin was accurately weighed on an analytical balance and placed in a 125 mL Erlenmeyer flask. The flask was placed on a hot plate in a stainless-steel hood and 5 mL concentrated $HNO_3$ and 10 mL 60-70% $HClO_4$ were added. A blast shield was placed in front of the samples and the resin digested by gently heating the mixtures. When beads were no longer visible (usually 3-4 hours) the mixture was boiled under close supervision for 3-5 minutes. **Under no circumstances should the solution be allowed to boil to dryness due to the explosive nature of perchloric acid.** The hot plate was turned off and the solutions allowed to cool. The liquid was quantitatively transferred to a 100 mL volumetric flask and diluted to the mark with water. A 5 mL aliquot was placed into a 50 mL volumetric flask and the following reagents were added in order: 3.5 mL 70% $HClO_4$, 4.5 mL freshly prepared amidol solution [1 g recrystallized amidol (2,4-diaminophenol dihydrochloride), 10 g $Na_2SO_3$, 2.7 g concentrated sulfuric acid and 90 g $H_2O$] and 3.5 mL ammonium molybdate solution (4.4 g in 50 mL $H_2O$). In order to conserve reagents, only the amount of amidol solution immediately needed was prepared since it is not stable upon standing. The mixture was diluted to 50 mL and allowed to develop for 30 minutes. A blank solution was also prepared

containing all reagents except the phosphorus solution. The absorbance of the solution was measured on a Bausch and Lomb Spectronic 21 which had been zeroed with the blank solution. A series of $K_2HPO_4$ standards was used to calculate the slope of the absorbance vs. concentration curve. The phosphorus capacity was calculated as follows.

$$P\ Capacity = \frac{(Abs)(1000\ mL)}{(g\ resin)(30.974\ mg/mequiv)(slope\ mL/mg)}$$

All determinations were done in duplicate.

Amidol was recrystallized by heating 50 g Amidol and 1 g decolorizing charcoal in 125 mL $H_2O$ until the Amidol dissolved. Boiling should be avoided to prevent decomposition of the Amidol. The solution was filtered and placed in a 500 mL Erlenmeyer flask equipped with a ground glass joint and 100 mL absolute ethanol was added. The mixture was allowed to slowly cool to room temperature and was then placed in a cold room overnight. The white crystals were recovered by filtration, washed with cold, absolute ethanol and dried with a rotary evaporatory.

Acid Capacity

Büchner-dried resin (1.0 to 1.5 g) was accurately weighed on an analytical balance and placed in a 250 mL Erlenmeyer flask sealed with a ground-glass stopper. Two hundred milliliters of standardized 0.10 N NaOH containing 5 weight percent NaCl was then added and the mixture gently stirred

for 17 hours. Two 50 mL aliquots were taken and titrated to a phenolphthalein endpoint with standardized 0.12 N $H_2SO_4$. Potassium hydrogen phthalate (KHP) was used to standardize the NaOH solution which was then used to standardize the $H_2SO_4$ solution. The acid capacity was calculated using the following equation.

$$\textit{Acid Capacity} = \frac{(\textit{Vol. NaOH})(\textit{N NaOH}) - 4(\textit{Vol. } H_2SO_4)(\textit{N } H_2SO_4)}{(\textit{wt. Büchner-dried resin})(\%\textit{Solids})}$$

In cases where the amount of resin available was insufficient to use 1.0 g the amount of NaOH solution used was reduced accordingly.

Base Capacity

Base capacity analysis was conducted in the same manner as the acid capacity analysis except the resin was contacted with $H_2SO_4$ and the aliquots were titrated with NaOH. Evidence exists that bisulfate may be the anion formed rather than sulfate leading to inaccurate base capacities in some instances. It is recommended that all future capacities be conducted using HCl rather than $H_2SO_4$.

Non-Aqueous Acid Capacity

The analysis was conducted as described for the acid capacity analysis except that the basic solution used consisted of freshly prepared, standardized 0.1 N KOH in 60% aqueous dioxane.

Chlorine Elemental Analysis

A sample of oven dried resin (0.3-0.4 g) was accurately weighed on an analytical balance and placed in a 15 X 160 mm test tube. This test tube, along with an empty one, was clamped to a ring stand in a hood. A transfer tube was prepared from 7 mm glass tubing and was designed to protrude slightly into the test tube containing the sample and to reach the bottom of the empty one. Approximately 0.5 g sodium metal was placed in the empty tube and 2 g sodium metal was placed into the tube containing the sample along with 1 mL of xylene. The procedure was conducted behind a blast shield and the experimenter wore an asbestos glove to prevent injury. The sodium in the otherwise empty test tube was melted and the end of the transfer tube heated so that the sodium would not resolidify when it was placed into the tube. A rubber stopper was used to affix the transfer tube to the test tube containing the sample and the other end was inserted into the molten sodium in the second tube. The sodium above the sample was melted, the xylene driven off to insure that the transfer tube was open, and the sample slowly (2-5 minutes) decomposed by heating with a Bunsen burner. The gases produced should bubble through the molten sodium, travel across the tube, and bubble through the second portion of sodium before exiting the open top of the second test tube. After the sample had decomposed, both test tubes were heated strongly for an additional 15 minutes and the carbon was burned from the transfer tube and the top of the test tubes. The tubes were allowed to cool and then were

carefully crushed into approximately 125 mL of dry methanol. Occasionally, the methanol would ignite due to a spark produced by the sodium metal. This was extinguished by placing an asbestos glove over the beaker. The sodium was then allowed to decompose and the methanol was evaporated on a hot plate. The resulting solids were redissolved in water and quantitatively transferred to a 250 ml volumetric flask with filtering. A 50 mL aliquot of this solution was taken and titrated for chloride via the Mohr method. Methyl orange was added to the aliquot which was then acidified with concentrated nitric acid. The solution was then made basic (yellow endpoint) with 0.3 N NaOH. Two milliliters of 5 wt% $K_2CrO_4$ were added and the solution titrated to a brick red endpoint with standard 0.05 N $AgNO_3$. The chlorine capacity was calculated using the following equation.

$$Cl\ capacity = \frac{5(Vol.\ AgNO_3)(N\ AgNO_3)}{g\ resin}$$

When nitrogen was present in the sample, the aliquots were acidified **in a hood** and boiled for 15 minutes to remove the HCN which forms.

Nitrogen Elemental Analysis

A sample of oven-dried resin (0.2 g) was accurately weighed on an analytical balance and transferred to a 500 mL three-neck round-bottom flask equipped with a condenser and two stoppers. Ten grams of $K_2SO_4$, 0.25 g $CuSO_4$, and 25 mL concentrated $H_2SO_4$ were added along with a few boiling

chips. The mixture was heated gently (Variac at 50) with a heating mantle for two hours. The heat was increased (Variac at 85) and the mixture heated until clear (usually occurred within 8 hours). The mixture was cooled and the condenser was rinsed into the flask with a small amount of $H_2O$. A stir bar was added, 100 mL $H_2O$ was slowly introduced with stirring, and the condenser was replaced with a distillation head-condenser combination. A funnel was affixed to the end of the condenser and the large end was allowed to extend below the surface of 50 mL standardized HCl in a 600 mL beaker. One stopper was removed and a stoppered addition funnel containing 150 mL 6 N NaOH was attached. After verifying that the system was closed to the atmosphere, the NaOH was slowly added to the flask with stirring. After the addition was completed, the flask was heated and the liquid allowed to distill into the standardized HCl which neutralized the ammonia present. The distillation was continued for an hour at which time the condensate was tested with pH paper. If the liquid was not basic, the distillation was stopped. The system was partially disassembled prior to removal of the heat source to avoid aspiration of HCl into the distillation flask. The HCl solution was quantitatively transferred to a 250 mL volumetric flask and diluted to 250 mL with $H_2O$. A 100 mL aliquot was removed and titrated to a bromocresol green endpoint with standardized NaOH. To insure accuracy, the HCl used was also standardized to a bromocresol green endpoint (rather than the more conventional phenolphthalein).

The nitrogen capacity was calculated using the following equation.

$$N\ Capacity = \frac{(Vol.\ HCl)(N\ HCl) - 2.5(Vol.\ NaOH)(N\ NaOH)}{g\ resin}$$

Determination of Monoester Capacity by Titration

Approximately 0.25 g Büchner dried resin was placed in a 150 mL beaker and stirred for 1 hour in 5 wt% NaCl. The pH was monitored with a Corning model 150 pH meter equipped with a general purpose combination electrode. One milliliter aliquots of standardized 0.1 N NaOH were added at one hour intervals and the pH recorded at the end of each hour. A plot of pH vs. volume NaOH added was generated and the equivalence point determined. This represented the amount of base required to neutralize the monoester sites and the first proton of the diacid sites. The composition of the resin was calculated as follows.

Diacid Capacity = total acid capacity - capacity at equivalence point

Monoester Capacity = capacity at equivalence point - diacid capacity

Diester Capacity = phosphorus capacity - capacity at equivalence point

Primary Acid Capacity By Iodine Oxidation

The phosphinic acid resin was analyzed for primary acid sites by oxidation of the P-H bond with iodine. The analysis was conducted by placing

0.5 g (dry weight) of Büchner dried resin in a 250 mL brown glass bottle and adding 50 mL 0.2 N $KI_3$ solution (prepared by dissolving 25.4 g $I_2$ and 80 g KI in 1 L $H_2O$) and 2 mL pyridine. The mixture was shaken for 22 hours and 50 mL 0.1 N sodium thiosulfate (prepared by dissolving 25 g $Na_2S_2O_3$ and 0.2 g $Na_2CO_3$ in 1 L $H_2O$) was added. The sample was shaken until the thiosulfate had consumed the $KI_3$. The sample was then titrated for residual thiosulfate with the $KI_3$ solution using a starch indicator. The sodium thiosulfate was standardized against primary standard $KIO_3$ and the $KI_3$ solution was standardized against the sodium thiosulfate solution, both to starch endpoints. The primary acid capacity was calculated as shown in the following equation.

$$1^{o}\ \textit{acid capacity} = \frac{(\textit{Vol. } KI_3)(N\ KI_3) - (\textit{Vol. } Na_2S_2O_3)(N\ Na_2S_2O_3)}{2(\textit{g dry resin})}$$

FTIR analysis revealed that this method did not always result in complete oxidation of the P-H bond.

Primary Acid Capacity By Silver Oxidation

The primary acid capacity of the phosphinic acid resin was also determined by oxidation with silver nitrate. An accurately weighed sample of Büchner dried resin (1-2 g dry weight) was placed in a 250 mL brown glass bottle and a fourfold excess of $AgNO_3$ (based on the phosphorus capacity of the resin) was added along with 100 mL of $H_2O$. The mixture was shaken for 17 hours and then poured into a fritted glass column. The resin was eluted with

1 L $H_2O$, 1 L 4 N $HNO_3$, and 1 L $H_2O$. The acid capacity of the resin was determined and the primary acid capacity was taken as the increase in the total acid capacity.

Total Anion Exchange Capacity (TAEC)

An accurately weighed portion of Büchner dried resin (5-10 g) in the chloride form was placed into a fritted glass column and eluted with 1L 1 N $NaNO_3$ over a 1 hour period. The eluate was collected in a 1 L volumetric flask and a 20 mL aliquot was titrated for chloride via the Mohr method as described for the chlorine elemental analysis. The TAEC was calculated as follows.

$$TAEC = \frac{50(Vol.\ AgNO_3)(N\ AgNO_3)}{(wt.\ dry\ resin)}$$

Salt-Splitting Anion Exchange Capacity (SSAC)

The sample from the TAEC analysis was left in the fritted glass column and was eluted with 1 L of 4 wt% NaOH over a 1 hour period followed by 1 L of water to remove the excess hydroxide. The resin was then eluted with 1 L 1 N $NaNO_3$ as described for the TAEC analysis. The eluate was collected in a 1 L volumetric flask and a 50 mL aliquot was titrated with standardized 0.1 N $H_2SO_4$

to a phenolphthalein endpoint. The SSAC was calculated as follows.

$$SSAC = \frac{20(Vol.H_2SO_4)(N\ H_2SO_4)}{(wt.\ dry\ resin)}$$

PEG Capacity by Chromic Acid Oxidation

Approximately 0.5 g Büchner dried resin was accurately weighed into a 125 mL Erlenmeyer flask with a ground glass stopper and a spin bar. One hundred milliliters of standard 0.6 N $K_2Cr_2O_7$ in 5.4 M $H_2SO_4$ was added and the flask sealed (the ground glass joint was greased). The solution was stirred at room temperature for 5 days and a 10 mL aliquot was titrated potentiometrically with standardized 0.15 N $FeSO_4$ using a Corning model 150 pH meter equipped with a redox combination electrode. The PEG capacity was calculated using the following equation.

$$\frac{(Vol.\ chromic\ acid)(N\ chromic\ acid) - 10(Vol.\ FeSO_4)(N\ FeSO_4)}{52(wt.\ dry\ resin)}$$

The $FeSO_4$ solution was standardized using the standard chromic acid solution.

Linear PEG Capacity

Two methods were used, chlorination with $PCl_5$ and reaction with 3,5-dinitrobenzoylchloride (DNB).

$PCl_5$ Method: The resin was dried overnight at 60 °C prior to analysis. The resin (1.00 g) was placed in a 50 mL brown glass bottle along with 1.25 g

$PCl_5$, 0.50 g pyridine, and 25 mL dioxane. The mixture was shaken for 48 hours at room temperature after which the liquid was decanted. The resin was conditioned by shaking for 1 hour with 25 mL of the following solutions: dioxane, 80% dioxane, 0.5 N KOH in 50% dioxane, 80% dioxane, 0.5 N $HNO_3$ in 80% dioxane, and 80% dioxane. The resin was then transferred to a fritted glass funnel and eluted with 1 L $H_2O$. The resin was oven dried and analyzed for chlorine as previously described. The linear PEG capacity was taken as the increase in the chlorine capacity. The value was corrected for the weight gain which occurred via the following equation where 0.018445 is the weight difference between the chlorine and the -OH group.

$$\textit{linear PEG capacity} = \frac{\Delta \textit{Cl capacity}}{1 - (\Delta \textit{Cl capacity})(0.018445)}$$

DNB method: The resin was dried in a 110 °C oven prior to use. Chloroform was purified by passage through a column of silica gel and the DNB was recrystallized from $CCl_4$.[127] One gram of dry resin was placed in a 50 mL single-neck round-bottom flask equipped with a condenser. DNB (2.31 g, 10.0 mmoles) and 10 mL chloroform were added and the mixture refluxed for one hour. The resin was washed several times with chloroform and acetone to remove the DNB. Resins which had an acidic site present were also washed with water after the first acetone wash in order to hydrolyze any anhydride linkages which might have formed. The resin was dried overnight at 60 °C and

analyzed for nitrogen as previously described. The DNB capacity was taken as one half the nitrogen capacity and the linear PEG capacity calculated by taking the weight gain into account (as before) using the following equation.

$$\textit{linear PEG Capacity} = \frac{\textit{DNB capacity}}{1 - (\textit{DNB capacity})(0.194106)}$$

Elemental Analyses

Analyses for elements other than those described above were performed by Galbraith Laboratories, Inc., Knoxville, TN 37921.

Purification of Penta(ethylene glycol)

Penta(ethylene glycol) was obtained by vacuum distillation of poly(ethylene glycol) of an average molecular weight of either 200 or 300. A tall Vigreux column was used to separate the oligomers. A pressure-boiling point nomograph was used to calculate the temperature at which the pentamer was collected based on the pressure provided by the vacuum pump. The boiling point of the pentamer is 178-182 °C at 1.5 torr.[109]

Removal of Water from Resins

Two methods for drying resins were employed.

Heptane azeotrope: The resin was Büchner dried and placed in a 500 mL single-neck round-bottom flask. The flask was filled to an adequate

capacity with heptane and a Dean-Stark trap and condenser was attached. The water was removed as an azeotrope with heptane and was collected in the Dean-Stark trap. The resin was recovered by filtration and dried at room temperature in a fume hood.

Solvent Elution: A better method (less collapse seemed to occur) was to place the resin in a fritted glass column and elute it with 500 mL of absolute ethanol followed by 500 mL 2,2,4-trimethylpentane (isooctane). The resin was then dried at room temperature in a fume hood.

Metal Ion Solutions

The purity of all metal salts was determined by titration with EDTA using standard techniques.[217] Reagent grade metal salts and acids were used in all cases and the water used was either doubly distilled (the first distillation from $KMnO_4$) or was treated with a Barnstead NANOpure deionization system prior to use.

Solutions for the radiotracer studies were prepared by first making 1 L of a 1 X $10^{-3}$ N stock solution of the desired metal nitrate containing enough nitric acid to yield a pH of approximately 1.5 (to prevent hydrolysis of the metal). Ten milliliters of this stock solution was placed in a volumetric flask and diluted to 100 mL with a nitric acid/sodium nitrate solution of the appropriate concentration to yield the desired final concentration after dilution of the metal stock. For example, 10 mL of 1 X $10^{-3}$ N metal nitrate solution was diluted with

2.22 N $HNO_3$/2.22 N $NaNO_3$ to 100 mL to prepare a solution that was 1 X $10^{-4}$ N in metal nitrate and 2 N in both $HNO_3$ and $NaNO_3$. Recrystallized sodium nitrate was used for all silver solutions to prevent precipitation of the metal by trace amounts of chloride. Sodium nitrate was recrystallized by heating 52 g reagent grade $NaNO_3$ in 1500 mL 95% methanol until the solid dissolved. The material which crystallized upon cooling was recovered, washed with absolute ethanol and dried on a rotary evaporator.

Iron, cadmium, and europium solutions for contact studies with VDPA polymers were prepared by diluting 10 mL each of stock metal and stock acid solutions to 100 mL. Thus, a 1 X $10^{-4}$ N $Eu(NO_3)_3$/0.04 N $HNO_3$ solution was prepared by pipetting 10 mL 1 X $10^{-3}$ N $Eu(NO_3)_3$ and 10 mL 0.4 N $HNO_3$ into a volumetric flask and diluting to 100 mL with purified water. High acid concentrations (such as 5 N) were obtained by weighing an appropriate amount of concentrated nitric acid into the volumetric flask.

Buffered metal ion solutions for the binding constant studies were prepared by one of two methods. The two methods will be described for metal solutions buffered at pH 5 with an acetate buffer.

Method I: All solutions were made with deionized water. The appropriate amount of metal salt was placed in a 150 mL beaker along with 20 mL of 3 N acetic acid (to yield 0.6 N acetate when diluted to 100 mL). The metal was added either as the solid metal salt, for those solutions which require 0.5 g or more, or as an unbuffered stock solution for the more dilute solutions.

Enough deionized water was added to bring the volume to approximately 80 mL and a pH electrode was placed in the solution (Corning model 150 pH/ion meter with a general purpose combination electrode). The pH was adjusted to 4.98-4.99 with 6 N NaOH and the electrode carefully rinsed into the beaker with a small amount of DI water. The solution was quantitatively transferred to a 100 mL volumetric flask and the beaker rinsed into the flask until the solution had been diluted to 100 mL.

Method II: Concentrated solutions were prepared by method I and used to prepare solutions of lower concentration by dilution with 0.6 N acetate buffer (acetic acid/sodium acetate) at pH 5.

Both methods yielded solutions with pH values ranging from 4.95 to 5.05. Method II is preferred due to the smaller number of manipulations and thus the lower chance for error.

Radiotracer Studies

Radiotracer studies were performed by placing 1 milliequivalent of Büchner dried resin (wet sieved to exclude fines) in a 20 mL scintillation vial. Five milliliters of the metal ion solution were placed in the vial and a radioactive spike (10-100 $\mu$L of approximately $10^{-8}$ M metal nitrate) was immediately added. The sample was shaken for 17 hours at room temperature on an Eberbach reciprocating shaker. A 1 mL aliquot was removed, taking great care not to remove beads, and counted in a NaI-Tll well-type scintillation counter equipped

with a multichannel analyzer. Two 1 minute counts were obtained and compared with a blank solution containing only the metal ion solution and the radioactive spike. A ten minute background reading was also obtained with an empty counting tube in the well and was used to correct all observed counts. All of the isotopes used were γ-emitters. The following peaks were counted: $^{59}Fe$ 1.097-1.289 MeV, $^{203}Hg$ 0.279 MeV, $^{110m}Ag$ 0.656-0.885 MeV, $^{65}Zn$ 1.114 MeV, and $^{54}Mn$ 0.835 MeV. Radiotracers were obtained from New England Nuclear with the exception of $^{110m}Ag$ which was obtained from Amersham. The percent absorbed and the distribution coefficient were calculated as shown below where $cpm_i$ is the counts per minute obtained from the blank solution and $cpm_f$ is the counts per minute obtained from the contacted sample.

$$\% \ absorbed = \frac{cpm_i - cpm_f}{cpm_i} (100)$$

$$D = \frac{\frac{5(cpm_i - cpm_f)}{g \ dry \ resin}}{cpm_f}$$

Effect of Resin on Solution pH

One milliequivalent of resin was placed into a 20 mL scintillation vial. Five milliliters of 1 X $10^{-4}$ N $Hg(NO_3)_2$ in a background solution containing a varying amount of nitric acid was placed in the vial and the vial shaken on a Burrell wrist-action shaker for 17 hours. A 1 mL aliquot was removed and titrated with standardized sodium hydroxide to a phenolphthalein endpoint. The pH was also measured with a Corning model 150 pH/ion meter. The effect of the resin on the solution pH was determined by comparing the final pH, as measured by titration, with the initial pH of the solution as calculated from the pH of the stock metal solution and the amount of acid added to prepare the solution.

Metal Ion Uptake of VDPA Polymers

Due to the limited amount of material produced, a full milliequivalent of polymer was not used for these studies. Ten milliliters of the target metal ion solution was placed in a 20 mL scintillation vial along with enough polymer to yield the desired $R_i$ value (0.01 was a common value). The sample was shaken on a Burrell wrist-action shaker for 17 hours in equilibrium studies and for 30 minutes in cases where the kinetic performance of the resin was in question. The liquid was centrifuged and decanted into a clean vial prior to analysis of the solution for residual metal content on a Varian AA-1475 atomic absorption spectrometer. The metals were analyzed by either absorption (AA) or emission (AE) as follows.

Cd AA at 228.8 nm in an air/acetylene flame

Fe AA at 248.3 nm in an air/acetylene flame

Eu AE at 459.4 nm in a nitrous oxide/acetylene flame

The europium samples and standards also contained 4000 ppm $K^+$ (as KCl) as an ionization suppressant. The standards were prepared with added KCl and the contacted samples were spiked with enough 4 N KCl after contact to give the desired concentration. The emission values were corrected for this small amount of dilution.

Contact Studies for Binding Constant Determination

One milliequivalent of the desired resin was placed in a 20 mL scintillation vial and solvent exchanged by contacting it 4 times with 10 mL of the background solution to be used during the contact study. The solution was removed at the end of each contact by aspiration with a Pasteur pipette, taking great care not to remove any resin. Ten milliliters of the target solution was added and the sample shaken for the desired length of time on a Burrell wrist-action shaker. For metal ion solutions, the initial pH was determined by measuring the pH of the contact solution. The final pH of the contacted sample was measured. The contacted solution was then diluted to the appropriate concentration range using glass transfer pipettes and volumetric flasks and its concentration determined as indicated below. Since wide ranges of concentrations were used, it was necessary to dilute all samples with the

background solution used during the contact in order to maintain a constant matrix for the analysis. For metal ion studies conducted in 4 N NaCl and analyzed via atomic absorption or emission, the samples were diluted with 1 N NaCl to avoid clogging the burner. Atomic absorption or emission analyses were performed on either a Varian AA-1475 or a Perkin-Elmer 3100 atomic absorption spectrometer and visible light absorption analyses were conducted with a Bausch & Lomb Spectronic 21. EDTA titrations were conducted using Erio T as the indicator as described in the literature.[217] The methods used to analyze the residual concentration of the target species were as follows.

| | |
|---|---|
| Co | AA at 240.7 nm in an air/acetylene flame |
| Cu | AA at 324.7 nm in an air/acetylene flame |
| Sr | AE at 460.7 nm in a nitrous oxide/acetylene flame |
| Sodium Picrate | Visible light absorption at 353 nm |
| Fe | Visible light absorption at 338 nm |
| Cd | EDTA titration |
| Zn | EDTA titration |

Infrared Spectroscopy

Infrared spectra of the polymers were recorded as KBr pellets on a Bio-Rad FTS-7 FTIR spectrometer. In general, 16 scans were accumulated at a resolution of 4 wavenumbers. The KBr pellet was prepared by first grinding the

polymer in an agate mortar and pestle. Approximately 120 mg of a 1 wt% mixture of polymer in KBr was used to prepare the pellet via standard procedures. The KBr was dried overnight in a 110 °C oven and stored in a desiccator prior to use. The use of commercial plastic vials to grind the polymers was found to be unacceptable since beads with higher mechanical strengths will abrade the poly(methyl methacrylate) ball used to grind the sample leading to the appearance of interfering peaks in the spectrum.

NMR Spectroscopy

Solution $^{13}C$ and $^{1}H$ spectra were recorded on either a JEOL FX90Q spectrometer (operating at 89.55 MHz for $^{1}H$ and 22.49 MHz for $^{13}C$) or a Bruker AC 250 (250 MHz for $^{1}H$) using standard techniques. The proton spectra were referenced to internal tetramethylsilane (TMS) at 0.00 ppm and the carbon spectra were referenced to either internal tetramethylsilane (0.0 ppm) or $CDCl_3$ (77.0 ppm). $^{31}P$ spectra were recorded on a JEOL FX90Q operating at 36.19 MHz. The spectra were proton-decoupled and were referenced to external 85% phosphoric acid at 0.00 ppm. Coaxial tubes were purchased from Wilmad Glass Co. for this purpose. The solution to be examined was placed in the inner tube and a drop of 85% phosphoric acid was placed in the outer. When the tubes were assembled, the phosphoric acid formed a thin film surrounding the inner tube and provided a reference peak.

Solid-state $^{31}P$ and $^{13}C$ NMR spectra were recorded on a Nicolet NT-200 spectrometer operating at 50.310 MHz for $^{13}C$ and 80.988 MHz for $^{31}P$ using a Doty Scientific standard speed, variable temperature 5 mm MAS probe. Sapphire rotors were used and were sealed with either Vespel (for dry samples) or double Viton O-ring equipped Macor (wet samples) end caps. A 100 Hz-400 MHz spectrum analyzer (Marconi Instruments model 2382) was used to tune the probe to the desired frequency and the spinning speed was monitored with both a frequency counter (Simpson model 711) and an oscilloscope (Hitachi model V-422).

Dry samples were ground and the rotors were packed to capacity. Wet samples were placed in the rotor without crushing and the rotor was filled to only 75% capacity to avoid expulsion of the end caps. It was important to determine that the solvent used to swell the polymer sample did not damage the Viton O-rings used to seal the rotor. **Damage to the O-rings could cause leakage of the solvent and severe damage to the probe.** Spinning speeds ranged from 3.0 to 5.0 kHz and spinning sidebands were identified by recording a second set of spectra at a lower spin rate. The data size was 8K which was occasionally zero-filled to either 16K or 32K depending on the degree of resolution needed. All spectra were recorded at ambient temperature.

All $^{13}C$ spectra were recorded with a sweep width of ±15 kHz. Peak positions were referenced to either external hexamethylbenzene or internal $CDCl_3$ (swollen samples). DP/MAS (direct polarization/magic angle spinning)

spectra were recorded with a pulse width of 2.5 $\mu$s (62°), a relaxation delay of 0.3 s, and, in general, 6000 scans. The number of scans was modified to achieve the desired signal-to-noise ratio. The DP/MAS experiment utilized the standard 1PDNA (one-pulse, decoupler on during acquisition) sequence available in the software package provided by Nicolet. CP/MAS spectra were recorded utilizing an initial $^{1}H$ 90° pulse of 5.00 $\mu$s followed by a 1.00 ms cross-polarization contact time and a 10 s relaxation delay. In general, 500 scans were accumulated. The CP/MAS (cross-polarization/magic angle spinning) experiment utilized a standard pulse sequence (SOLIDS or SOLID1) provided by the software package. Exponential line broadenings were 5 Hz for DP/MAS and 30 Hz for CP/MAS spectra and the decoupling levels were 5 W (DP/MAS) and 22 W (CP/MAS). All spectra subtractions were performed using the software package provided by Nicolet.

$^{31}P$ spectra were recorded in either the dry or wet state by utilizing the same pulse sequence used for DP/MAS spectra (1PDNA). A pulse width of 3 $\mu$s was used in conjunction with a 5 s relaxation delay. The decoupling power was 22 W and the sweep width was ±15 kHz. In general, 500 scans were accumulated and exponential line broadening factors of 5 to 30 Hz were employed. All spectra were reference to external triphenylphosphine.

Measurement of $T_{1\rho}$ values was accomplished by recording a series of $^{13}C$ CP/MAS spectra (using the parameters described above) in which either the cross-polarization contact time or the delay between the proton 90° pulse

and the beginning of cross-polarization were varied. Eight to 10 delay (or contact) times were used. For the samples investigated, an appropriate set of delay times was found to be 1.00, 2.00, 4.00, 6.00, 8.00, 10.00, 12.00, 16.00, 20.00, and 24.00 ms. Appropriate contact times were 0.50, 1.00, 2.00, 3.00, 4.00, 5.00, 6.00, 8.00, 10.00, and 12.00 ms. The spectra were acquired by collecting 52 scans at each delay or contact time (these times were in a random order). This process was repeated 10 times to give 520 scans at each contact or delay time. The spectra were all processed using the same scaling factor and the software package provided by Nicolet was used to calculate the peak integrations.

# LIST OF REFERENCES

1. Reed, D. T.; Tasker, I. R.; Cunnane, J. C.; Vandegrift, G. F. In *Environmental Remediation*; Vandegrift, G. F.; Reed, D. T.; Tasker, I. R., Eds.; ACS Symposium Series 509; American Chemical Society: Washington, DC, 1992; Chapter 1.

2. Illman, D. L. *Chem. Eng. News* **1993**, *71*(25), 9.

3. Ritcey, G. M.; Ashbrook, A. W. *Solvent Extraction: Principles and Applications to Process Metallurgy, Part I*; Elsevier: Amsterdam, 1984.

4. Mason, G. W.; Lewey, S.; Peppard, D. F. *J. Inorg. Nucl. Chem.* **1964**, *26*, 2271.

5. Kolařík, Z.; Pánková, H. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2325.

6. McKay, H. A. C. In *Science and Technology of Tributyl Phosphate*; Schulz, W. W.; Navratil, J. D., Eds.; CRC Press: Boca Raton, 1984; Vol. 1, Chapter 1.

7. Walsh, D. J.; Crosby, P.; Dalton, R. F. *Polymer* **1983**, *24*, 423.

8. Helfferich, F. *Ion Exchange*; McGraw-Hill: New York, 1962.

9. Sahni, S. K.; Reedijk, J. *Coord. Chem. Rev.* **1984**, *59*, 1.

10. Tavlarides, L. L.; Bae, J. H.; Lee, C. K. *Sep. Sci. Technol.* **1987**, *22*, 581.

11. Exodus 15:23-25.

12. Kunin, R. *Ion Exchange Resins*, 2nd ed.; Krieger: Malabar, FL, 1990.

13. Simon, G. P. *Ion Exchange Training Manual*; Van Nostrand Reinhold: New York, 1991.

14. Thompson, H. *J. Roy. Soc.* **1850**, *11*, 68.

15. Way, J. T. *J. Roy. Soc.* **1850**, *11*, 313.

16. Adams, B. A.; Holmes, E. L. *J. Soc. Chem. Ind.* **1935**, *54*, 1T; *Chem. Abstr.* **1935**, *29*, 2620[6].

17. D'Alelio, G. F. U.S. Patent 2 340 110, 1944.

18. D'Alelio, G. F. U.S. Patent 2 340 111, 1944.

19. D'Alelio, G. F. U.S. Patent 2 366 007, 1944.

20. D'Alelio, G. F. U.S. Patent 2 366 008, 1944.

21. Juda, W.; McRae, W. A. *J. Am. Chem. Soc.* **1950**, *72*, 1044.

22. Seidl, J.; Malinský, J.; Dušek, K.; Heitz, W. *Advan. Polym. Sci.* **1967**, *5*, 113.

23. Sederel, W. L.; De Jong, G. J. *J. Appl. Polym. Sci.* **1973**, *17*, 2835.

24. Boyd, G. E.; Vaslow, F.; Lindenbaum, S. *J. Phys. Chem.* **1964**, *68*, 590.

25. Boyd, G. E.; Vaslow, F.; Lindenbaum, S. *J. Phys. Chem.* **1967**, *71*, 2214.

26. Warshawsky, A. *Angew. Makromol. Chem.* **1982**, *109/110*, 171.

27. Warshawsky, A. In *Syntheses and Separations Using Functional Polymers*; Sherrington, D. C.; Hodge, P., Eds.; Wiley: New York, 1988, Chapter 10.

28. Kantipuly, C.; Katragadda, S.; Chow, A.; Gesser, H. D. *Talanta* **1990**, *37*, 491.

29. Alexandratos, S. D. *Sep. Purif. Meth.* **1992**, *21*, 1.

30. Mykytiuk, A. P.; Russell, D. S.; Sturgeon, R. E. *Anal. Chem.* **1980**, *52*, 1281.

31. Grinstead, R. R. *J. Metals* **1979**, *31*(3), 13.

32. Koster, G.; Schmuckler, G. *Anal. Chim. Acta.* **1967**, *38*, 179.

33. Majee, S.; Ray, C.; Das, J. *Ind. J. Chem.* **1988**, *27A*, 137.

34. Majee, S.; Das, J. *Ind. J. Chem.* **1989**, *28A*, 538.

35. Patel, C. G.; Patel, D. K.; Parmar, J. S. *React. Polym.* **1993**, *20*, 123.

36. Nayak, P. K.; Lenka, S.; Nayak, P. L. *J. Appl. Polym. Sci.* **1990**, *41*, 2577.

37. Schilde, U.; Uhlemann, E. *React. Polym.* **1992**, *18*, 155.

38. Schilde, U.; Uhlemann, E. *React. Polym.* **1993**, *20*, 181.

39. Kurmanaliev, M; Ergozhin, E. E.; Izteleuova, I. K. *Makromol. Chem.* **1993**, *194*, 2655.

40. Bruening, R. L.; Tarbet, B. J.; Krakowiak, K. E.; Bruening, M. L.; Izatt, R. M.; Bradshaw, J. S. *Anal. Chem.* **1991**, *63*, 1014.

41. Chanda, M.; Rempel, G. L. *React. Polym.* **1993**, *19*, 201.

42. Srivastava, S.; Rao, G. N. *Analyst* **1990**, *115*, 1607.

43. Hsu, J. C.; Huang, H. C.; Liu, C. Y. *Transition Met. Chem.* **1993**, *18*, 453.

44. You, H. J.; Jeon, H. J.; Jeon, D. W. *Han'guk Somyu Konghakhoechi* **1992**, *29*, 328; *Chem. Abstr.* **1993**, *119*, 118001e.

45. Rath, D. K.; Lenka, S.; Nayak, P. L. *J. Appl. Polym. Sci.* **1992**, *46*, 2109.

46. Parija, A.; Nayak, P. L.; Lenka, S. *J. Appl. Polym. Sci.* **1993**, *47*, 367.

47. Fischer, H-J.; Lieser, K. H. *Angew. Makromol. Chem.* **1993**, *208*, 133.

48. Tbal, H.; Maguer, D. L.; Morcellet, J.; Delporte, M. Morcellet, M. *React. Polym.* **1992**, *17*, 207.

49. Chanda, M.; Rempel, G. L. *React. Polym.* **1993**, *19*, 213.

50. Aoi, M.; Matsuda, K. Jpn. Kokai Tokkyo Koho JP 01,215,726 [89,215,726] 29 Aug. 1989; *Chem. Abstr.* **1990**, *112*, 220732m.

51. Egawa, H.; Nonaka, T. *J. Appl. Polym. Sci.* **1986**, *31*, 1677.

52. Harris, W. I.; Stahlbush, J. R.; Pike, W. C.; Stevens, R. R. *React. Polym.* **1992**, *17*, 21.

53. Chanda, M.; Rempel, G. L. *React. Polym.* **1991/1992**, *16*, 149.

54. Chanda, M.; Rempel, G. L. *Ind. Eng. Chem. Res.* **1993**, *32*, 726.

55. Bhattacharya, A.; Davenport, K. G.; Sheehan, M. T.; Sounik, J. R. U.S. Patent 5 210 149, 1993.

56. Lindsay, D.; Sherrington, D. C.; Greig, J. A.; Hancock, R. D. *React. Polym.* **1990**, *12*, 59.

57. Verweij, P. D.; Driessen, W. L.; Reedijk, J.; Rowatt, B.; Sherrington, D. C. *React. Polym.* **1990**, *13*, 83.

58. Kratz, M. R.; Hendricker, D. G. *Polymer* **1986**, *27*, 1641.

59. Moberg, C.; Weber, M.; Högberg, K.; Muhammed, M.; Nilsson, A-C. *React. Polym.* **1990**, *12*, 31.

60. Chessa, G.; Marangoni, G.; Pitteri, B.; Stevanato, N.; Vavasori, A. *React. Polym.* **1991**, *14*, 143.

61. Chessa, G.; Marangoni, G.; Petteri, B. *React. Polym.* **1990**, *12*, 219.

62. Grote, M.; Sandrock, M.; Kettrup, A. *React. Polym.* **1990**, *13*, 267.

63. Verweij, P. D.; Dugué, T.; Driessen, W. L.; Reedijk, J.; Rowatt, B.; Sherrington, D. C. *React. Polym.* **1991**, *14*, 213.

64. Verweij, P. D.; van der Geest, J. S. N.; Driessen, W. L.; Reedijk, J.; Sherrington, D. C. *React. Polym.* **1992**, *18*, 191.

65. Chanda, M.; Rempel, G. L. *React. Polym.* **1992**, *17*, 159.

66. Chanda, M.; Rempel, G. L. *React. Polym.* **1989**, *11*, 165.

67. Chanda, M.; Rempel, G. L. *React. Polym.* **1990**, *12*, 83.

68. Chanda, M.; Rempel, G. L. *React. Polym.* **1990**, *13*, 103.

69. Chanda, M.; Rempel, G. L. *React. Polym.* **1991/1992**, *16*, 29.

70. Kotze, M. H.; Green, B. R.; Ellis, P. *React. Polym.* **1991**, *14*, 129.

71. Lauth, M.; Frere, Y.; Prevost, M.; Gramain, PH. *React. Polym.* **1990**, *13*, 73.

72. Liu, Z. S.; Rempel, G. L. *React. Polym.* **1991**, *14*, 229.

73. Ergozhin, E. E.; Utkelov, V. A.; Rafikov, S. R.; Ashkeeva, R. K. *Dokl. Akad. Nauk SSSR* **1990**, *314*, 1411; *Chem. Abstr.* **1991**, *114*, 103327p.

74. Utkelov, B. A.; Ergozhin, E. E.; Ashkeeva, R. K. *React. Polym.* **1991**, *14*, 187.

75. Yin, J.; Blanch, H. W. *Biotech. & Bioeng.* **1989**, *34*, 180.

76. Siddhanta, S.; Das H. R. *Talanta* **1985**, *32*, 457.

77. Chanda, M.; Rempel, G. L. *React. Polym.* **1991/1992**, *16*, 19.

78. Kennedy, J.; Lane, E. S.; Robinson, B. K. *J. Appl. Chem.* **1958**, *8*, 459.

79. Kennedy, J.; Davies, R. V.; Small, H.; Robinson, B. K. *J. Appl. Chem.* **1959**, *9*, 32.

80. Kennedy, J.; Wheeler, V. J. *Anal. Chim. Acta.* **1959**, *20*, 412.

81. Walsh, E. N.; Beck, T. M.; Toy, A. D. F. *J. Am. Chem. Soc.* **1956**, *78*, 4455.

82. Marhol, M.; Beranová, H.; Cheng, K. L. *J. Radioanal. Chem.* **1974**, *21*, 177.

83. Egawa, H.; Nonaka, T.; Ikari, M. *J. Appl. Poly. Sci.* **1984**, *29*, 2045.

84. Selzer, R. B.; Howery, D. G. *Macromolecules* **1986**, *19*, 2673.

85. *Duolite Ion-Exchange Manual*; Chemical Process Co.; Redwood City, CA, **1960**.

86. Janauer, G. E.; Gibbons, R. E., Jr.; Bernier, W. E. In *Ion Exchange and Solvent Extraction*; Marinsky, J. A.; Marcus, Y., Eds.; Marcel Dekker: New York, 1985; Vol. 9, Chapter 2.

87. Alexandratos, S. D. *Sep. Purif. Meth.* **1988**, *17*, 67.

88. Alexandratos, S. D.; Wilson, D. L. *Macromolecules* **1986**, *19*, 280.

89. Alexandratos, S. D.; Quillen, D. R.; McDowell, W. J. *Sep. Sci. Tech.* **1987**, *22*, 983.

90. Alexandratos, S. D.; Quillen, D. R.; Bates, M. E. *Macromolecules* **1987**, *20*, 1191.

91. Pearson, R. G. *Chemistry in Britain* **1967**, *3*, 103.

92. Pearson, R. G. *Science* **1966**, *151*, 172.

93. Alexandratos, S. D.; Bates, M. E. *Macromolecules* **1988**, *21*, 2905.

94. Akser, M.; Wan, R. Y.; Miller, J. D.; Quillen, D. R.; Alexandratos, S. D. *Metall. Trans. B* **1987**, *18B*, 625.

95. Quillen, D. R. Ph. D. Dissertation, University of Tennessee, Knoxville, December 1989.

96. Alexandratos, S. D.; Quillen, D. R. *Solv. Extr. Ion Exch.* **1989**, *7*, 511.

97. Alexandratos, S. D.; Quillen, D. R. *React. Polym.* **1990**, *13*, 255.

98. Alexandratos, S. D.; Quillen, D. R. *Solv. Extr. Ion Exch.* **1989**, *7*, 1103.

99. Alexandratos, S. D.; Strand, M. A.; Quillen, D. R.; Walder, A. J. *Macromolecules* **1985**, *18*, 829.

100. Nishide, H.; Izushi, T.; Arai, H.; Yoshioka, N.; Tsuchida, E. *J. Macromol. Sci.-Chem.* **1987**, *A24*, 343.

101. Ritcey, G. M. *Sep. Sci. Technol.* **1983**, *18*, 1617.

102. Alexandratos, S. D.; Crick, D. W.; Quillen, D. R. *Ind. Eng. Chem. Res.* **1991**, *30*, 772.

103. Caban, R.; Chapman, T. W. *AIChE J.* **1972**, *18*, 904.

104. Bates, M. E. M.S. Thesis, University of Tennessee, Knoxville, March 1988.

105. Liang, G. M.S. Thesis, University of Tennessee, Knoxville, May 1990.

106. Walder, A. J. Ph.D. Dissertation, University of Tennessee, Knoxville, May 1989.

107. Pokonova, Y. V.; Antonov, P. G.; Kotegov, K. V. *Issled. Obl. Khim. Tekhnol. Prod. Pererab. Goryuch. Iskop.* **1977**, *3*, 124; *Chem. Abstr.* **1980**, *93*, 220091r.

108. Pederson. C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

109. Warshawsky, A.; Kalir, R.; Deshe, A.; Berkovitz, H.; Patchornik, A. *J. Am. Chem. Soc.* **1979**, *101*, 4249.

110. Warshawsky, A.; Borer, B. *Hydrometallurgy* **1979**, *4*, 83.

111. Warshawsky, A.; Patchornik, A.; Kalir, R.; Ehrlich-Rogozinski, S. *Hydrometallurgy* **1979**, *4*, 93.

112. Fujita, H.; Yanagida, S.; Okahara, M. *Anal. Chem.* **1980**, *52*, 869.

113. Lauth, M.; Frère, Y.; Meurer, B.; Gramain, PH.; Prévost, M. *React. Polym.* **1990**, *12*, 155.

114. Tomoi, M.; Suzuki, T.; Kakiuchi, H. *React. Polym.* **1989**, *10*, 27.

115. Janout, V.; Čefelín, P.; Provotorova, N. P.; Tur, D. R.; Vinogradova, S. V. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 3489.

116. Strzelbickl, J.; Bartsch, R. A. *Anal. Chem.* **1981**, *53*, 1894.

117. Strzelbickl, J.; Bartsch, R. A. *Anal. Chem.* **1981**, *53*, 2247.

118. Strzelbickl, J.; Bartsch, R. A. *Anal. Chem.* **1981**, *53*, 2251.

119. Pugia, M. J.; Ndip, G.; Lee, H. K.; Yang, I-W.; Bartsch. R. A. *Anal. Chem.* **1986**, *58*, 2723.

120. Hayashita, T.; Lee, J. H.; Chen, S.; Bartsch, R. A. *Anal. Chem.* **1991**, *63*, 1844.

121. Hayashita, T.; Bartsch, R. A. *Anal. Chem.* **1991**, *63*, 1847.

122. Bartsch, R. A.; Kim, J. S.; Olsher, U.; Purkiss, D. W., Ramesh, V.; Dalley, N. K.; Hayashita, T. *Pure Appl. Chem.* **1993**, *65*, 399.

123. Yanagida, S.; Fujita, H.; Okahara, M. *Chem. Lett.* **1981**, 1617.

124. Drevin, I.; Johansson, B-L. *J. Chromatogr.* **1984**, *295*, 210.

125. Chang, F. W-K. Ph.D. Dissertation, University of Tennessee, Knoxville, August, 1992.

126. Bradstreet, R. B. *The Kjeldahl Method for Organic Nitrogen*; Academic: New York, 1965; pp 115.

127. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.

128. Ogata, Y. In *Oxidation In Organic Chemistry*; Trahanovsky, W. S., Ed.; Academic: New York, 1978; Part C, Chapter 4.

129. Worms, K. H.; Schmidt-Dunker, M. In *Organic Phosphorus Compounds*; Kosolapoff, G. M.; Maier, L., Eds.; Wiley-Interscience: New York, 1976; Vol. 7, Chapter 18.

130. Beck, M. T.; Nagypál, I. *Chemistry of Complex Equilibria*; Ellis Horwood: Chichester, 1990.

131. Haight, G. P., Jr. In *Halogen Chemistry*; Gutman, V., Ed.; Academic: New York, 1967; Vol. 2, p 351.

132. Sinta, R.; Rose, P. S.; Smid, J. *J. Am. Chem. Soc.* **1983**, *105*, 4337.

133. Sinta, R.; Lamb, B.; Smid, J. *Macromolecules* **1983**, *16*, 1382.

134. Xu, W-Y.; Smid, J. *J. Am. Chem. Soc.* **1984**, *106*, 3790.

135. Sperling, L. H. *J. Polym. Sci. Macromol. Rev.* **1977**, *12*, 141.

136. Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum: New York, 1981.

137. Sperling, L. H. *Polym. Eng. Sci.* **1985**, *25*, 517.

138. Frisch, K. C.; Klempner, D.; Xiao, H. X.; Cassidy, E.; Frisch, H. L. *Polym. Eng. Sci.* **1985**, *25*, 758.

139. Sperling, L. H. *CHEMTECH* **1988**, *18*, 104.

140. Solt, G. S. Br. Patent 728 508, 1955.

141. Kolarz, B. N. *J. Polym. Sci., Symposium No. 47* **1974**, 197.

142. Barrett, J. H.; Clemens, D. H. U.S. Patent 3 966 489, 1976.

143. Hatch, M. J. U.S. Patent 3 957 698, 1976.

144. *CRC Handbook of Chemistry and Physics*, 66th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1985, p D-160.

145. Beauvais, R., University of Tennessee, Knoxville, unpublished results.

146. Kaiser, P. T. Ph.D. Dissertation, University of Tennessee, Knoxville, August 1990.

147. Alexandratos, S. D.; Grady, C. E.; Crick, D. W. *Macromolecules* **1991**, *24*, 6365.

148. Alexandratos, S. D.; Ciaccio, C. E.; Crick, D. W.; Beauvais, R. In *Interpenetrating Polymer Networks*; Sperling, L. H., Ed.; ACS Advances in Chemistry Series 239; American Chemical Society: Washington, DC, in press.

149. Ciaccio, C. G. M.S. Thesis, University of Tennessee, Knoxville, December 1992.

150. Alexandratos, S. D.; Ciaccio, C. G.; Beauvais, R. *React. Polym.* **1993**, *19*, 137.

151. Gatrone, R. C.; Horwitz, E. P.; Rickert, P. G.; Nash, K. L. *Sep. Sci. Tech.* **1990**, *25*, 1607.

152. Gatrone, R. C. *J. Org. Chem.* **1989**, *54*, 4272.

153. Carroll, R. L.; Crutchfield, M. M. U.S. Patent 3 576 793, 1971.

154. Degenhardt, C. R.; Kozikowski, B. A. Eur. Pat. Appl. EP 321,233, 1989; *Chem. Abstr.* **1990**, *112*, 164766m.

155. Arshady, R.; Ledwith, A. *React. Polym.* **1983**, *1*, 159.

156. DeWolfe, R. H. *Synthesis* **1974**, 153.

157. Horwitz, E. P.; Chiarizia, R.; Diamond, H.; Gatrone, R. C.; Alexandratos, S. D.; Trochimczuk, A. W.; Crick, D. W. *Solv. Extr. Ion Exch.* **1993**, *11*, 943.

158. Chiarizia, R.; Horwitz, E. P.; Gatrone, R. C.; Alexandratos, S. D.; Trochimczuk, A. W.; Crick, D. W. *Solv. Extr. Ion Exch.* **1993**, *11*, 967.

159. Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon: New York, 1987.

160. Zuiderweg, E. R. P.; Petros, A. M.; Fesik, S. W.; Olejniczak, E. T. *J. Am. Chem. Soc.* **1991**, *113*, 370.

161. Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy, 2nd ed.*; Academic: New York, 1988; Chapter 8.

162. Andrew, E. R.; Bradbury, A.; Eades, R. G. *Nature* **1958**, *182*, 1659.

163. Andrew, E. R.; Bradbury, A.; Eades, R. G. *Nature* **1959**, *183*, 1802.

164. Lowe, I. J. *Phys. Rev. Lett.* **1959**, *2*, 285.

165. Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042.

166. Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031.

167. Fyfe, C. A. *Solid State NMR for Chemists*; C.F.C.: Guelph, Ontario, 1983.

168. Axelson, D. E.; Russell, K. E. *Prog. Polym. Sci.* **1985**, *11*, 221.

169. Andreis, M.; Koenig, J. L. *Adv. Polym. Sci.* **1989**, *89*, 69.

170. Ford, W. T.; Mohanraj, S.; Periyasamy, M. *Brit. Polym. J.* **1984**, *16*, 179.

171. Ford, W. T.; Balakrishnan, T. *Macromolecules* **1981**, *14*, 284.

172. Ford, W. T.; Mohanraj, S.; Blossey, E. C. *Macromol. Synth.* **1990**, *10*, 91.

173. Stöver, H. D. H.; Fréchet, J. M. J. *Macromolecules* **1989**, *22*, 1574.

174. Doskočilová, D.; Schneider, B. *Chem. Phys. Lett.* **1970**, *6*, 381.

175. Doskočilová, D.; Schneider, B.; Jakeš, J. *J. Magn. Reson.* **1978**, *29*, 79.

176. Stöver, H. D. H.; Fréchet, J. M. J. *Macromolecules* **1991**, *24*, 883.

177. Bowmaker, G. A.; Cotton, J. D.; Healy, P. C.; Kildea, J. D.; Silong, S. B.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1989**, *28*, 1462.

178. Turner, G. L.; Smith, K. A.; Kirkpatrick, R. J.; Oldfield, E. *J. Magn. Reson.* **1986**, *70*, 408.

179. Fyfe, C. A.; Clark, H. C.; Davies, J. A.; Hayes, P. J.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1983**, *105*, 6577.

180. Fluck, E.; Heckmann, G. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L. D., Eds.; VCH: Deerfield Beach, Fl, 1987; Chapter 2.

181. Mark, V.; Dungan, C. H.; Crutchfield, M. M.; Van Wazer, J. R. In *$P^{31}$ Nuclear Magnetic Resonance*; Grayson, M.; Griffith, E. J., Eds.; Topics in Phosphorus Chemistry, Vol. 5; Wiley: New York, 1967; Chapter 4.

182. Van Wazer, J. R.; Callis, C. F.; Shoolery, J. N.; Jones, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 5715.

183. Głowacki, Z.; Hoffmann, M.; Topolski, M.; Rachoń, J. *Phosphorus, Sulfur, and Silicon* **1991**, *60*, 67.

184. Lee, S-G.; Bentrude, W. G. *Phosphorus and Sulfur* **1988**, *35*, 219.

185. Bel'skii, V. E.; Kudryavtseva, L. A.; Kurguzova, A. M.; Ivanov, B. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 1047.

186. Bottin-Strzalko, T.; Seyden-Penne, J.; Pouet, M-J.; Simonnin, M-P. *J. Org. Chem.* **1978**, *43*, 4346.

187. Duddeck, H.; Hanna, A. G. *Magn. Reson. Chem.* **1985**, *23*, 41.

188. Dillon, K. B.; Waddington, T. C.; Younger, D. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2665.

189. Puri, R. N.; Asplund, R. O. *Inorg. Chim. Acta* **1982**, *57*, 57.

190. Riess, J. G.; Van Wazer, J. R.; Letcher, J. H. *J. Phys. Chem.* **1967**, *71*, 1925.

191. Ohms, G.; Grossmann, G. *Z. Anorg. Allg. Chem.* **1987**, *544*, 232.

192. Böhmer, V.; Vogt, W.; Chafaa, S.; Meullemeestre, J.; Schwing, M-J.; Vierling, F. *Helv. Chim. Acta* **1993**, *76*, 139.

193. Muntean, J. V.; Stock, L. M. *J. Magn. Reson.* **1988**, *76*, 540.

194. Earl, W. L.; Vanderhart, D. L. *J. Magn. Reson.* **1982**, *48*, 35.

195. Crick, D. W.; Alexandratos, S. D. *Macromolecules* **1993**, *26*, 3267.

196. Ivin, K. J.; Pitchumani, S.; Reddy, C. R.; Rajadurai, S. *Eur. Polym. J.* **1981**, *17*, 341.

197. Watts, D. C. *J. Biomed. Mater. Res.* **1979**, *13*, 423.

198. Prosser, H. J.; Richards, C. P.; Wilson, A. D. *J. Biomed. Mater. Res.* **1982**, *16*, 431.

199. Boulton, A. J.; McKillop, A. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Ed.; Pergamon: New York, 1984; Vol. 2, pp 29-65.

200. Grimmet, M. R. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic: New York, 1980; Vol. 27, pp 241-326.

201. Treibs, A. *Liebigs Ann. Chem.* **1932**, *497*, 297.

202. Kost, A. N.: Gromov, S. P.; Sagitullin, R. S. *Tetrahedron* **1981**, *37*, 3423.

203. Begtrup, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 521.

204. Ghesquiere, D.; Chachaty, C.; Tsutsumi, A. *Macromolecules* **1979**, *12*, 775.

205. Dambatta, B. B.; Ebdon, J. R.; Huckerby, T. N. *Eur. Polym. J.* **1984**, *20*, 645.

206. Konishi, K.; Takahashi, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2512.

207. Begtrup, M. *Acta Chem. Scand., Ser. B* **1974**, *28*, 61.

208. Huelck, V.; Thomas, D. A.; Sperling, L. H. *Macromolecules* **1972**, *5*, 340.

209. Donatelli, A. A.; Sperling, L. H.; Thomas, D. A. In *Recent Advances in Polymer Blends, Grafts and Blocks*; Sperling, L. H., Ed.; Plenum: New York, 1974.

210. Fukushima, E.; Roeder, S. B. W. *Experimental Pulse NMR*; Addison-Wesley: New York, 1981; Chapter 4.

211. Stejskal, E. O.; Schaefer, J.; Sefcik, M. D.; McKay, R. A. *Macromolecules* **1981**, *14*, 275.

212. Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.

213. Voelkel, R. In *Solid State NMR of Polymers*; Mathias, L., Ed.; Plenum: New York, 1991; Chapter 13.

214. Grinsted, R. A.; Koenig, J. L. In *Solid State NMR of Polymers*; Mathias, L., Ed.; Plenum: New York, 1991; Chapter 7.

215. Degenhardt, C. R.; Burdsall, D. C. *J. Org. Chem.* **1986**, *51*, 3488.

216. Arcus, C. L.; Matthews, R. J. S. *J. Chem. Soc.* **1956**, Part IV, 4207.

217. Schwarzenbach, G.; Flaschka, H. *Complexometric Titrations*; Methuen: London, 1969.

218. Langmuir, I. *J. Am. Chem. Soc.* **1916**, *38*, 2221.

219. Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361.

220. Connors, K. A. *Binding Constants*; Wiley: New York, 1987; Chapter 2.

221. Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044.

222. Guyot, A. In *Syntheses and Separations Using Functional Polymers*; Sherrington, D. C.; Hodge, P., Eds.; Wiley: New York, 1988; pp 6-11.

223. Boven, G.; Folkersma, R.; Challa, G.; Schouten, A. J. *Polym. Commun.* **1991**, *32*, 50.

# APPENDICES

# APPENDIX 1

## DETERMINATION OF BINDING CONSTANTS

In order to evaluate the performance of the resins synthesized during the course of these studies, a method of quantitatively describing the interaction between the polymers and the target ions was needed. In earlier studies, the interaction was probed by measuring the distribution coefficient of the metal between the resin and aqueous phases. While this is a valid method of examining the extraction ability of the resins, it fails to provide a measure of the fundamental quantity describing the interaction: the equilibrium constant for the complex formed between the polymer-supported ligand and the metal ion.

The equilibrium constant can be determined by contacting a given amount of resin with a varying amount of target ion.[149] After the system reaches equilibrium, the amount of ion complexed by the resin is obtained by measuring the residual concentration of the metal in solution by an appropriate technique. The interaction can be displayed graphically via an adsorption isotherm. The simplest adsorption isotherm is that developed by Langmuir[218,219] in which all adsorption sites (supported ligands in this case) behave in an identical manner. The isotherm yields curves (r vs. c) of the

form shown in chapter 3 and can be described mathematically[220] by the equation

$$r = \frac{K_{11}c}{1 + K_{11}c}$$

where $K_{11}$ is the equilibrium (binding) constant for a 1:1 complex, r is the amount of metal sorbed per gram of dry polymer (mequiv/g) and c is the concentration of free metal remaining in solution (mequiv/mL). Accurate binding constants can be obtained provided that an adequate portion of the isotherm has been characterized.[221] This isotherm can also be described as a portion of a rectangular hyperbola[220] in which case the equation becomes

$$r = \frac{ac}{b + c}$$

where r and c are as above, a is the saturation capacity (maximum value of r) and b is the dissociation constant ($1/K_{11}$). The binding constant could then be obtained by fitting the experimental points to a rectangular hyperbola and evaluating the constant b. However, analysis of the data by a different technique shows that the interaction involves more than a single binding constant.

The alternative method involves rewritting the equilibrium expression as follows. The equilibrium constant is equal to the concentration of the complex divided by the product of the concentrations of free metal and free ligand. Thus,

$$K_{11} = \frac{r}{[L]c}$$

where [L] is the concentration of free ligand. The saturation capacity of the resin, $S_t$, is equal to the total number of ligands available for binding which will be equal to the sum of the free and bound ligands.

$$S_t = [L] + r$$

Rearranging the equilibrium expression, one obtains

$$\frac{r}{c} = K_{11}[L]$$

Substituting for [L] leads to

$$\frac{r}{c} = K_{11}(S_t - r)$$

or

$$\frac{r}{c} = -K_{11}r + K_{11}S_t$$

Thus a plot of r/c vs. r yields a straight line with a slope of $-K_{11}$ and a saturation capacity equal to -intercept/slope. This is commonly called an Eadie, x-reciprocal, or Scatchard plot.[220]

Deviations from linearity in the Scatchard plot can be caused by non-ideality of the binding sites. This simply means that all sites do not behave in the same manner. The Scatchard plots for most of the polymer/metal systems studied thus far have deviated sharply from linearity as shown by the curve for the interaction of PEG/carboxylic acid resin with sodium picrate (Figure 106). The polymer bead is far from ideal due to several factors. First, it is well known that the degree of cross-linking is not uniform within the bead.[222] This is a result of the differing rates of polymerization of the cross-linking agent (divinylbenzene) and the monomer which allow DVB rich areas to form early in the polymerization. The differing amounts of cross-linking lead to a distribution of microenvironments which cause a range of binding constants. Also, especially in the case of bifunctional resins, the random nature of the

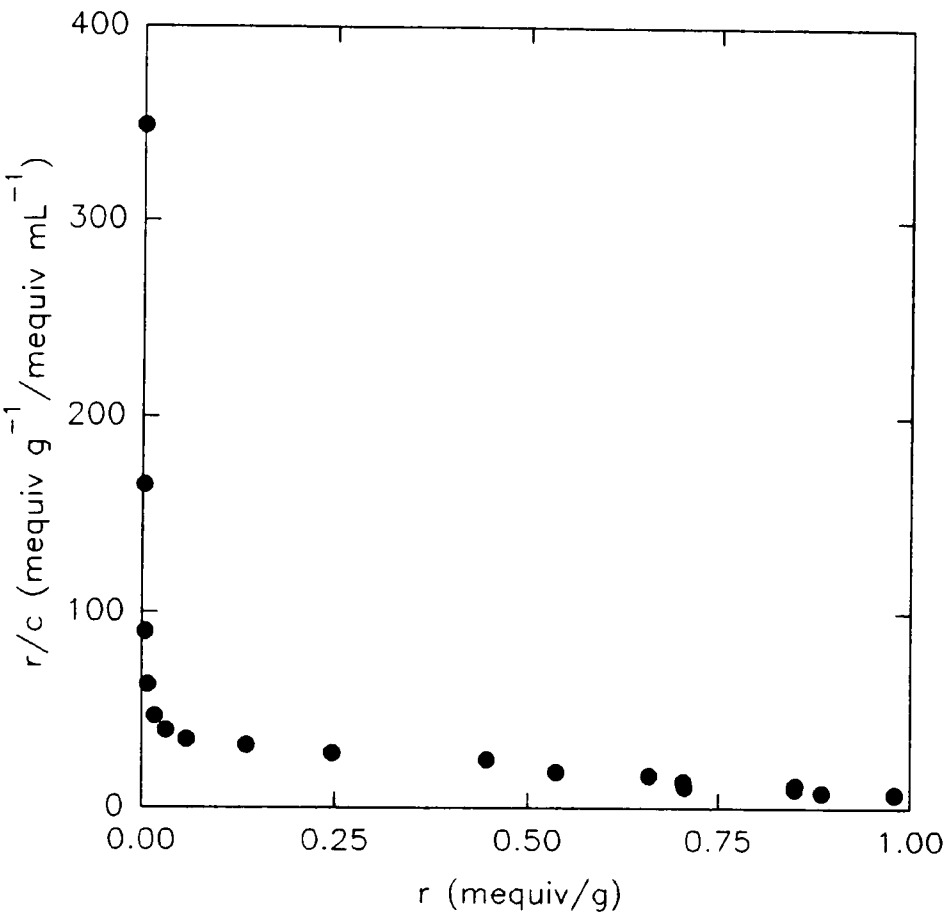



Figure 106. Scatchard plot for the interaction of sodium picrate with PEG/carboxylic acid resin.

functionalization leads to differing microenvironments in the resin. In the extreme case, each ligand in the resin would reside in a slightly different microenvironment, each with its own binding constant. The result of this is a curved Scatchard plot from which an infinite number of binding constants can be extracted by taking tangents to the curve. However, in most cases, there exist two regions with a minimal amount of curvature. This can be explained by considering that most of the ligands fall into two categories, those which bind the ions more tightly and those which, for reasons of limited accessibilty or unfavorable microenvironment, bind the ions to a lesser degree. The region of the Scatchard plot with the greatest curvature corresponds to those ligands which are intermediate in binding ability. Accepting this, one can then characterize the binding behavior of a given system by extracting two binding constants and two saturation capacities from the linear portions of the Scatchard plot. This is readily accomplished by fitting the experimental r vs. c curve with a double hyperbolic function as shown below.

$$r = \frac{ax}{b + x} + \frac{cx}{d + x}$$

In this equation, a and c correspond to the two saturation capacities and b and d are the corresponding dissociation constants ($1/K_{11}$) for the system.

An examination of the results presented in chapter 3 show that, in many cases, one of the saturation capacities is small enough that its binding constant contributes little to the overall behavior of the resin. In other cases, one of the binding constants itself is small enough to contribute little to the extraction ability of the polymer. In these cases, a good approximation of the overall binding ability of the resin is obtained with a single binding constant. This approach has been taken to evaluate the extraction ability of the PEG series of resins. Where appropriate, a single binding constant has been given to characterize the resin. Further discussion of the determination of binding constants is found in the monograph by Connors.[220]

# APPENDIX 2

## ATTEMPTED ATTACHMENT OF POLY(METHYL METHACRYLATE) ONTO GLASS

In response to an outside inquiry, a single attempt was made to attach poly(methyl methacrylate) onto glass by free radical polymerization of methyl methacrylate in the presence of small glass particles.

Methyl methacrylate (71.54 g), DVB (2.71 g) and BPO (0.75 g) were placed into a 250 mL three-neck round-bottom flask equipped with an overhead stirrer, condenser, and thermometer along with 75 g $H_2O$ saturated with NaCl and 7.5 g Rachig rings. The polymerization was conducted at 80 °C to yield a mixture of poly(methyl methacrylate) and Rachig rings. No evidence of polymer attachment to the glass surface was seen. Due to the intractable nature of the material which formed, no further attempts were made.

A recent article reports the grafting of poly(methyl methacrylate) monolayers onto glass by functionalization of the glass surface with a radical initiator which is then used to polymerize methyl methacrylate.[223]

# VITA

Darrell W. Crick was born in Knoxville, Tennessee on December 16, 1965. He attended public schools in Sevierville, Tennessee prior to obtaining a Bachelor of Arts degree with a major in Chemistry from Carson-Newman College in May 1988. In August 1988 he accepted a teaching and research assistantship from the Chemistry Department at the University of Tennessee and began work toward the Ph.D. degree in Polymer Chemistry. The degree was awarded in May 1994.

In July 1993 he accepted a position as a research chemist with Sybron Chemicals, Inc. located in Birmingham, New Jersey where he continued research on ion exchange resins.