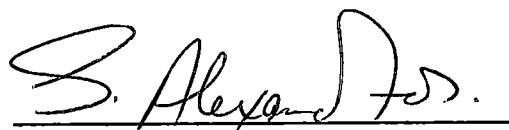


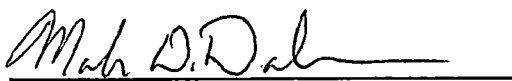
To the Graduate Council:

I am submitting herewith a thesis written by Minjeong Hong entitled " Synthesis of Novel Bifunctional Polymers for Selective Metal Ion Separation." I have examined the final copy of this thesis for form an content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.



Spiro D. Alexandratos, Major Professor

We have read this thesis
and recommend its acceptance:



Accepted for the council:



Associate Vice Chancellor and
Dean of The Graduate School

**SYNTHESIS OF NOVEL BIFUNCTIONAL POLYMERS FOR SELECTIVE
METAL ION COMPLEXATION**

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Minjeong Hong

December 1999

To my husband Suhwan and my family

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ABSTRACT

Polymer supported reagents were synthesized by functionalization of polymer supports for the purpose of selective metal ion separation. Three categories of polymer supports with different microenvironments were prepared. Vinylbenzyl chloride (VBC) crosslinked with 2% divinylbenzene was copolymerized with either methyl methacrylate (MMA) to give a polar environment or styrene (STY) to give a hydrophobic environment. Different ethyleneimines and phosphonic acid were used as ligands in the synthesis of monofunctional resins. Bifunctional aminophosphonic acid resins were prepared by phosphorylation of ethyleneimine ligands. The characterization of the resins shows that as the length of the ethyleneimine ligand increases, more crosslinking takes place. Metal ion studies of Cu^{2+} , Pb^{2+} , Cd^{2+} and Eu^{3+} were performed in pH 5 sodium-acetate buffer solution at a 24 hour contact time. The microenvironmental effect plays an important role in the degree of functionalization as well as in metal ion complexation. Bifunctional aminophosphonic acid resins outperformed the amine or phosphonic acid monofunctional resins in metal ion complexation.

The Mannich reaction of a polystyrene-based primary amine resin with diethylmalonate(DEM), tetraisopropylmethylene diphosphonate (TIPP), triethylphosphonoacetate (TEPAc) and phosphorous acid (PhA) were carried out varying the acid amount, reaction time and temperature.

The Fries rearrangement of poly(4-acetoxystyrene) was successfully achieved with aluminum chloride-nitrobenzene under moisture-free reaction conditions. The Fries-rearranged resin and its phosphorylated analogue were studied with several metal ions.

TABLE OF CONTENTS

CHAPTER	PAGE
1. Introduction	1
2. Immobilized Polyamines and Polyaminphosphonates : First Report of Polymer-supported Synergistic Complexation in Bifunctional Resins and Identification of a Microenvironmental Effect	
Introduction	8
Experimental	13
A. Synthesis and Characterization	13
1. Amination of Copolymers	14
2. Phosphorylation of Amine Resins	16
3. Monofunctional Phosphonic Acid Resins	16
B. Metal Ion Studies	16
Results	20
A. Characterization of Resins	20
1. Amine Resins	20
1.1 Primary Amine (PA) Resins	21
1.2 Ethylenediamine (EDA) Resins	21
1.3 Diethylenetriamine (DETA) Resins	25
1.4 Tetraethylenepentamine (TEPA) Resins	27

2. Aminophosphonic acid Resins	27
4. Monofunctional Phosphonic acid Resins	31
B. Metal Ion Studies	34
Discussion	44
1. The Monofunctional Resins	44
2. The Bifunctional Effect	47
3. The Microenvironmental Effect	53
4. Counter Ion effect	54
Conclusion	56
3. Immobilization of Ligands on Crosslinked Polymers via Mannich Reaction	
Introduction	57
Experimental	61
Poly(glycidyl methacrylate)	61
Reactions of GMA polymer with nitrogen-containing compounds ..	62
Mannich reactions	62
Results and Discussion	64
GMA Resins	64
Mannich reactions	68
Conclusion	73
4. Synthesis of Novel Polymer Ligands Using the Fries Rearrangement	

Introduction	77
Experimental	82
1. Resins preparations	82
Poly(4-acetoxystyrene)	82
Fries rearrangement of poly(4-acetoxystyrene)	82
Phosphorylation of poly(acylhydroxystyrene)	85
Polyhydroxystyrene	86
Phosphorylation of polyhydroxystyrene	86
2. Metal Ion studies	86
Results and Discussion	87
1. Synthesis and characterization	87
Fries rearrangement	87
Phosphorylation of poly(acylhydroxystyrene)	89
Poly(hydroxystyrene) and Phosphorylation	97
2. Metal ion studies	99
Conclusion	103
5. Experimental Procedures	104
Copolymer synthesis	104
Poly(vinylbenzylchloride)	104
Poly(vinylbenzylchloride-co-styrene)(0.18/0.82)	105
Poly(vinylbenzylchloride-co-methylmethacrylate)(0.18/0.82)	106

Chlorine Capacity	117
Infrared Spectroscopy	119
Metal Ion Studies	119
List of References	121
Appendix	132
VITA	139

LIST OF TABLES

Table	Page
2.1.1 Characterization of Amine Resins (2% DVB Crosslinked VBC)	22
2.1.2 Characterization of Amine Resins (2% DVB Crosslinked VBC/STY)	23
2.1.3 Characterization of Amine Resins (2% DVB Crosslinked VBC/MMA)	24
2.2.1 Characterization of Aminophosphonic acid Resins (2% DVB Crosslinked VBC)	28
2.2.2 Characterization of Aminophosphonic acid Resins (2% DVB Crosslinked VBC/STY)	29
2.2.3 Characterization of Aminophosphonic acid Resins (2% DVB Crosslinked VBC/MMA)	30
2.3 Monofunctional Phosphonic Acid Resins	33
2.4.1 Metal Ion Uptake of $\text{Cu}(\text{NO}_3)_2$ from pH5 Acetate Buffer Solution by Amine Resins	35
2.4.2. Metal Ion Uptake of $\text{Pb}(\text{NO}_3)_2$ from pH5 Acetate Buffer Solution by Amine Resins	36
2.4.3 Metal Ion Uptake of $\text{Cd}(\text{NO}_3)_2$ from pH5 Acetate Buffer Solution by Amine Resins	37
2.4.4 Metal Ion Uptake of $\text{Eu}(\text{NO}_3)_3$ from pH5 Acetate Buffer Solution by Amine Resins	38

2.5.1	Metal Ion Uptake of $\text{Cu}(\text{NO}_3)_2$ from pH5 Acetate Buffer Solution by Aminophosphonic Acid Resins	39
2.5.2	Metal Ion Uptake of $\text{Pb}(\text{NO}_3)_2$ from pH5 Acetate Buffer Solution by Aminophosphonic Acid Resins	40
2.5.3	Metal Ion Uptake of $\text{Cd}(\text{NO}_3)_2$ from pH5 Acetate Buffer Solution by Aminophosphonic Acid Resins	41
2.5.4	Metal Ion Uptake of $\text{Eu}(\text{NO}_3)_3$ from pH5 Acetate Buffer Solution by Aminophosphonic Acid Resins	42
2.6	Metal Ion Uptake from pH 5 Acetate Buffer Solution by Monophosphonic Acid Resins	43
2.7	Complexation Stability Constants of Ethylenediamine Ligand with Metals	46
2.8.1	Metal Ion Uptake from pH 5 Acetate Buffer Solution by Monofunctional and Bifunctional Resins (PA)	49
2.8.2	Metal Ion Uptake in pH 5 Acetate Buffer Solution by Monofunctional and Bifunctional Resins (EDA)	50
2.8.3	Metal Ion Uptake in pH 5 Acetate Buffer Solution by Monofunctional and Bifunctional Resins (DETA)	51
2.8.4	Metal Ion Uptake in pH 5 Acetate Buffer Solution by Monofunctional and Bifunctional Resins (TEPA)	52
2.9	Resin Particla Size Effect of VBC/STY gel on Metal Ion Uptake	55

3.1	Reactions of GMA Polymer	66
3.2	Phosphorylation of Aminated GMA Polymer	67
3.3	Primary Amine Polystyrene-Based Gel with Diethylmalonate	69
3.4	Primary Amine Polystyrene-based Gel with TIPP (acid-catalyzed)	71
3.5	Primary Amine Polystyrene-based Gel with TIPP (base-catalyzed)	72
3.6	Primary Amine Polystyrene-Based Gel with TEPAc	74
3.7	Primary Amine Polystyrene-Based Gel with Phosphorous acid	75
4.1	Characterization of Polyacylhydroxystyrene; Fries Rearrangement	88
4.2	Poly(acylhydroxystyrene) from Second Fries Rearrangement	90
4.3	Characterization of Phosphorylated Polyacylhydroxystyrene(ester)	91
4.4	Characterization of Phosphorylated Poly(acylhydroxystyrene)(acid)	92
4.5	Characterization of Ploy(hydroxystyrene) and Phosphorylated Poly(hydroxystyrene)	98
4.6	Cs ⁺ Ion Uptake in 0.1N/ 1N NaOH by Polyhydroxystyrene and Poly(acylhydroxystyrene)	100
4.7	Metal Ion Uptake by Phosphorylated Polyacylhydroxystyrene(acid)	101
4.8	Metal Ion Uptake by Phosphorylated Polyhydroxystyrene(acid)	102
5.1	Atomic Absorption(AA)/ Emission(AE) Spectroscopy Parameters	120
6.1.1	Metal Ion Uptake of Cr(NO ₃) ₃ from pH5 Acetate Buffer Solution by Amine Resins	133

6.1.2	Metal Ion Uptake of $\text{Co}(\text{NO}_3)_2$ in pH5 Acetate Buffer Solution by Amine Resins	134
6.2.1	Metal Ion Uptake of $\text{Cr}(\text{NO}_3)_3$ from pH5 Acetate Buffer Solution by Aminophosphonic Acids	135
6.2.2	Metal Ion Uptake of $\text{Co}(\text{NO}_3)_2$ from pH5 Acetate Buffer Solution by Aminophosphonic Acids	136
6.3	Metal Ion Uptake in pH 5 Acetate Buffer Solution by Monophosphonic Acids	137
6.4	Standard Sieve Sizes	138

LIST OF FIGURES

FIGURE	PAGE
2.1 Polymer Supports	12
2.2 Gabriel Synthesis	15
2.3 Phosphorylation of EDA Resins	17
2.4 Arbuzov Reaction	18
2.5 Possible Crosslinking Configuration of DETA Resins	26
2.6 Structures of Phosphorylated Amine Resins	32
3.1 Mechanism of Mannich Reaction	60
3.2 Reactions of GMA Polymer	63
3.3 Active Hydrogen Compounds Used in Mannich Reaction	65
4.1 Fries Rearrangement and Phosphorylation	83
4.2 Poly(hydroxystyrene) and Phosphorylation	84
4.3 IR Spectrum of Poly(4-oxacetoxystyrene) (MH-3-050)	93
4.4 IR Spectrum of Poly(acylhydroxystyrene) (MH-3-062)	94
4.5 IR Spectrum of Poly(acylhydroxystyrene) (MH-3-092)	95
4.6 IR Spectrum of Poly(hydroxystyrene) (MH-3-038)	96

CHAPTER 1

Introduction

The use of polymer-supported reagents has been widespread in organic synthesis¹, catalysis² and ion exchange³. The interest in ion exchange polymers for the recovery of toxic metal ions from water has grown significantly, as indicated in numerous publications⁴ over the last thirty years. It has been reported that thousands of hazardous waste sites exist all over the world and they are threatening our environment.⁵ For example, the Hanford Reservation in Washington State has 177 underground storage tanks, containing more than 65 million gallons of radioactive waste.^{5a} These wastes were generated from the nuclear experiments for national defense for the past half century. Suitable separation technologies for purification of toxic waste water in a safe, cost-effective and environmentally friendly manner needs to be developed.

Two techniques have been developed for the recovery and purification of toxic metal ions from water : solvent extraction and ion exchange. The principle⁶ of solvent extraction is liquid-liquid distribution. Soluble complexing agents dissolved in organic solvents interact with metal ions in an aqueous phase and concentrate the metal ions in the water-immiscible phase. The complexant can be regenerated by removing from it the metal ions and recycled. The solvent extraction technique is versatile and displays rapid kinetics. However, several

problems such as the handling of large volumes of liquid produced during processing and the loss of complexants into the aqueous phase through dissolution and incomplete phase separation still exist as disadvantages.⁷

The principle of ion exchange resins is that the ligands immobilized onto the polymer matrix complex the metal ions. Further, eluting cation exchange resins with an acidic solution allows recovery of the metal ions and regenerates the polymer for continuous use. The ion exchange resins have a disadvantage in kinetics. The time to equilibrium can be long with ion exchange resins compared to the solvent extraction process.⁸ As our research has shown, however, this problem can be solved by applying the principle of bifunctionality.⁹

Ion exchange resins are defined as insoluble solid materials that can carry exchangeable cations (cation exchangers) or anions (anion exchangers). Two types of polymeric ion exchange resins have been developed : inorganic and organic. Inorganic supports have high mechanical strength, high thermal stability and good ability to withstand organic solvents.¹⁰ However, there are several disadvantages including difficulty in functionalization and low ion exchange capacity.¹¹

The organic ion exchange resins can be either natural polymers (for example, cellulose and chitin) or synthetic polymers. As synthetic polymers, styrene-based polymers are in wide use due to the wide range of versatility in reactions which can be performed such as nucleophilic and electrophilic aromatic substitution. They also have physical and chemical stability.¹

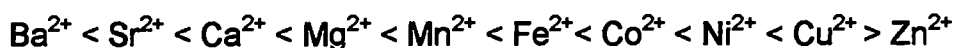
Ion exchange resins were introduced by Adams and Holmes, who sulphonated phenol-formaldehyde condensation polymers.¹² Later, better ion exchange resins containing functionalized styrene-divinylbenzene copolymers were introduced by D'Alelio.¹³

Among many kinds of polymer-supported ligands found to be selective to specific metal ions, polystyrene-supported sulfonic acid resin is in use for the recovery of Ca^{2+} , Mg^{2+} and Mn^{2+} from acidic solutions.¹⁴ It does not have good selectivity among many ions, however, due to its narrow range of reaction free energy values for ion exchange.¹⁵ The carboxylic acid resin is more selective than sulfonic acid but has a limitation in solution pH (which needs to exceed 3).¹⁶

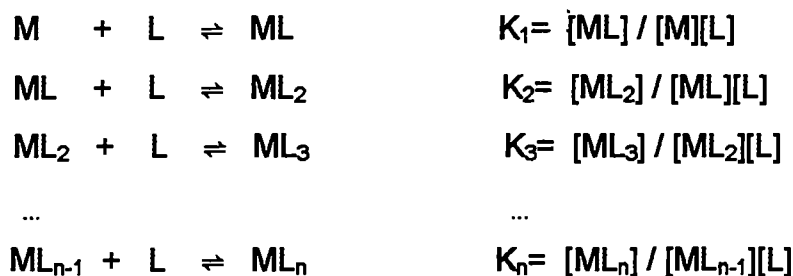
Oxygen-based ligands such as phenol/ formaldehyde¹⁷ copolymers show higher selectivity toward Rb^+ and Cs^+ while sulfur-based ligands such as 4-thiomethylpolystyrene¹⁸, thioglycolate¹⁹ or dithiocarbamate²⁰ are known to complex or precipitate most of the heavy metals such as Ag^+ , Hg^{2+} , etc. The phosphorus-based ligands such as phosphonic acids, esters and phosphine oxides are very good extractants for uranium, gold and transition metals like Zn^{2+} , Ni^{2+} or Co^{2+} .^{20,21} The polymers carrying nitrogen ligands such as polybenzylamine²², aminomethylpyridine²³ and polyethyleneimine²⁴ are found to have a high selectivity toward Cu^{2+} . Crown ethers are well known to have a high selectivity toward alkali metals.²⁵

The selectivity of ion exchange resins toward a targeted metal ion is a very important issue because they become useful when they can recover only

targeted metal ions. Therefore, in designing a selective polymer, the selection of a suitable ligand is a major task. In the selection of a chelating ligand, both theoretical background and experimental evidence should be considered. The Irving-Williams series^{26,27} helps in understanding ligand-metal complex formation. It is the order of stability constants of metal ion complexes :



The formation constants (K_n) of ethylenediamine show a uniform trend of slightly increasing stability constants toward the end of the series.²⁷ For the general case of the complex ML_n (M: metal, L: ligand), the stepwise formation constants (K_n) are



The overall formation constant β_n are

$$\beta_n = K_1 K_2 K_3 \dots K_n \quad \beta_n = [\text{ML}_n] / [\text{M}][\text{L}]^n$$

Pearson suggested a simple rule for predicting the stability of complexes formed between acids (metal ions) and bases (ligands)²⁸ : Hard acids prefer to bind hard bases and soft acids prefer to bind soft bases. Hard species tend to be small in size with low polarizability while soft acids and bases tend to be larger in size and more polarizable.

Metal ion complexation with polymeric ligands could be different from theoretical expectations based on small molecule analogues.²⁹ Some ligands known to show selectivity for a certain metal ion sometimes lose their selectivity when they are applied in polymeric system. The large local concentration of ligands in the macromolecular framework may not allow the same behavior of polymeric ligands as with monomeric ligands.^{4c} However, it is usually assumed that the complexation behavior of a chelating ion exchange resin is similar to that of corresponding monomeric functional units in aqueous solution.³⁰ Eger, *et al.*, evaluated this assumption by comparing the coordination behavior of monomeric N-benzyl iminodiacetic acid and its cross-linked polymer analogue toward some divalent transition metal ions.³¹ The thermodynamic properties of these monomeric and polymeric compounds were similar showing good agreement between experimental and calculated results. Kennedy, *et al.*, investigated the complex stability constants over a suitable range of metal ions for monomeric, dimeric and oligomeric compounds before being incorporated into polymeric supports.³²

There are some considerations that need to be made besides the successful choice of ligands. Selective ion exchange polymers should be stable and resistant to normal operating conditions such as temperature and pressure changes while maintaining their physical and chemical properties.³³ They also should allow a quantitative and fairly fast ion exchange process.

The variables thought to affect the complexation rate of polymer supported ligands are polymer matrix rigidity, macroporosity and resin particle size. A polymer which does not have sufficient *rigidity* may collapse in ionic solution. When the polymer matrix is too rigid, however, it does not allow the metal ions access into the matrix as well as resulting in a low degree of functionalization on the polymer matrix. Therefore, an appropriate polymer matrix rigidity needs to be decided that balances strength against polymer collapse and sufficient accessibility of metal ions.^{9b} Rigidity in the polymer matrix can be controlled by the cross-linking level in polymerization.

There are two types of polymers in terms of *porosity*. One type is macroporous, in which the polymerization is carried out with an inert solvent solvating the monomers and polymer, and the other is microporous (gel), in which the polymerization is carried out in the presence of only monomers. The pores in the macroporous resin ($\sim 0.05\mu\text{m}$) are much larger than in the microporous gel resin ($\sim 0.005\mu\text{m}$). Metal complexation with macroporous resins usually outperforms that of microporous gel resins at a short contact time, where accessibility into the matrix is the controlling variable.^{9c,22} Compared to gels, higher crosslinking is needed for macroporous resins to prevent the collapse of the macro channels but it might restrict accessibility of the functional groups as well as metal ions.

Resin *particle size* is also a factor affecting the metal complexation rate. The smaller size of the resin allows greater access by the metal ions due to the

large surface area of the resin. However, small particle size resin can not always be used because of pressure drop in real industrial processes. The proper particle size of a resin needs to be decided in terms of both maximum performance of metal complexation and process efficiency.

There are two methods of introducing ligands into polymers. One way is making the polymer supports first and functionalizing with ligands. The other way is to pre-functionalize the monomers and then polymerize. The polymerization of pre-functionalized monomers can avoid many drawbacks associated with multistep chemical modification processes in which side reactions can bring impurities into the polymer.³⁴ However, copolymerization of functionalized monomers, in fact, depends on the relative reactivity ratios of those monomers.³⁵ Some functional groups can act as inhibitors or retarders in polymerization, limiting copolymerization. The post- functionalization method is thought to be ideal because it provides flexibility in the selection of functional groups. Designing a minimal number of steps is critical to ensure the formation of the functional groups and to avoid interference of the chelating behavior from other nondiscriminative functional groups.

The goal of this research is to design and synthesize polymer-supported ligands for the purpose of selective metal ion complexation. This work involves the influence of bifunctionality, resin particle size, ligand effect and the microenvironmental effect on the metal ion complexation.

CHAPTER 2

Immobilized Polyamines and Polyaminophosphonates : First Report of Polymer-Supported Synergistic Complexation in Bifunctional Resins and Identification of a Microenvironmental Effect

Polyethyleneimine is known to be ideal for complexation with certain metal ions.^{36,37} However, the complex of polyethyleneimine with metal ions is usually soluble in water and hard to isolate.^{38,39} In order to overcome this limitation, insolubilization of polyethyleneimine was tried by crosslinking with proper agents or by grafting to cross-linked polymers.^{40,41,42} Poly(styrene-g-ethyleneimine) has been found effective for the complexation of heavy metal ions and the higher the content of polyethyleneimine in the graft copolymer, the better the resins complexed the metal ions.⁴² The selectivity was in the order of $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$, which is in agreement with the stability constants of the amine:metal ion complexes.⁴³

A resin formed from reaction of polyethyleneimine with poly(vinyl benzaldehyde) gives a highly selective resin for Fe^{2+} over various other metal ions.⁴⁴ The resin containing polyethyleneimine and mercapto groups shows various metal ion selectivities in different pH.⁴⁵ The 2-pyridylmethylamine and *N*-2-(2-pyridyl)ethylenediamine ligands incorporated into chloromethylated polystyrene have been reported to chelate transition metal ions in the order $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+}$.⁴⁶ Nishide *et al.* separated metal ions including Cu^{2+} ,

Fe^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} and Hg^{+} by using crosslinked poly(ethyleneimine) or poly(vinylpyridine) resins.⁴⁷ Several transition metal ions were complexed with water-soluble polymeric binder made from polyethyleneimine and polyacrylic acid and the metal ions were separated by ultrafiltration from the mixture.⁴⁸ Polyethyleneimine-cellulose copolymer showed selectivity for Cu^{2+} over other transition metal ions at pH 3.5~4.5.⁴⁹

In the study of polyethyleneimine binding with Cu^{2+} and Ni^{2+} ions in solution, it was found that polymeric ethyleneimine more strongly complexed metal ions than monomeric ethyleneimine.⁵⁰ The overall formation constant (β_2) of the polyethylenediamine- Cu^{2+} ion complex was about 10^6 times greater than the formation constant (K_1) of the ethylenediamine- Cu^{2+} ion complex. This great increase in the stability of polyethyleneimine, as explained by the authors, was due to the greater concentration of ligands within the polymer relative to the concentration in solution. A chelate effect can be used to explain the differences in behavior of ammonia vs. ethylenediamine and other polyethyleneimine ligands (see page 45).⁵¹ It is noted that 5-or 6- membered ring systems are ideal for chelation while larger rings do not show the chelate effect.^{52,53} When the ring becomes sufficiently large, the possibility increases that one end of the ligand will contact another metal ion and not come around to the first metal ion attached at the other end of the molecule.

Phosphinic and phosphonic acid groups are known to exhibit high selectivity toward hard Lewis acid cations including uranyl and ferric ions.^{54,55}

Kennedy and co-workers synthesized a phosphorylated polystyrene-divinylbenzene copolymer and found it to be selective for uranyl and ferric ions due to strong coordination by the electron donating phosphoryl oxygen.^{56,57} Egawa, *et al.*, investigated the uptake of trivalent lanthanides by various polystyrene based phosphinic and phosphonic acids at different crosslink levels, porosity, contact times and acidity of solutions.⁵⁸ Bis(phosphonic acid) functionalized polystyrene is also found to be a good coordinator for transition metals used as catalysts in hydrogenation.⁵⁹ There are many other phosphoryl compounds showing excellent metal ion recovery such as tributylphosphate⁶⁰ and trioctylphosphine oxide.⁶¹ Phosphonic acid ligands are also excellent complexing agents by combining ion exchange with coordination.⁶²

Dual mechanism bifunctional polymers have been developed by Alexandratos *et al.* which utilize both an access mechanism to bring metal ions into the polymer matrix and a recognition mechanism to selectively react with the metal ions.⁶³ A phosphinic acid resin, which operates via ion-exchange and redox mechanisms has been used to reduce Ag^+ and Hg^{2+} to Ag^0 and Hg^0 , respectively.⁶³ The bifunctional phosphonate monoester/diester resin utilizes coordination as the recognition mechanism.⁶⁴ The bifunctional phosphonic acid/quaternary ammonium chloride resin removes Ag^+ as its insoluble chloride salt by means of precipitation as the recognition mechanism.⁶⁵ The aminophosphonic acid resin is prepared in the present research for study as a dual mechanism ion exchange/ coordination resin.

The microenvironmental effect⁶⁶ can be defined as the influence of non-reactive groups surrounding an active ligand on the interaction between that ligand and incoming molecules or metal ions. For example, it was reported⁶⁷ that (dialkylamino)pyridine ligands covalently bound to a polystyrene support worked better as an acylation catalyst when the degree of functionalization was less than 50%. This was due to a more hydrophobic environment around the ligands. In recent research, it was found that as the polarity of the microenvironment surrounding active ligands in the Mitsunobu reaction decreased, the kinetics improved by lowering the energy of the transition state.⁶⁶

The microenvironmental effect is also observed in metal ion complexation by ion exchange resins. Alexandratos, *et al.*, found that different microenvironments surrounding an active ligand on a polymer can affect the metal ion complexation and the results were quantified by the corresponding binding constants.⁶⁸ The equimolar imidazole:ester IPN (Interpenetrating Polymer Network) binds Cu^{2+} almost 100 times more strongly than the imidazole IPN because the polymeric microenvironment becomes less polar with the ester content in the polymer.

In this research, vinylbenzyl chloride (VBC) was polymerized with divinylbenzene (DVB) as the cross-linking agent and either styrene (STY) or methyl methacrylate (MMA) to give different microenvironments in the polymer support (Figure 2.1). The VBC / STY copolymer creates a hydrophobic

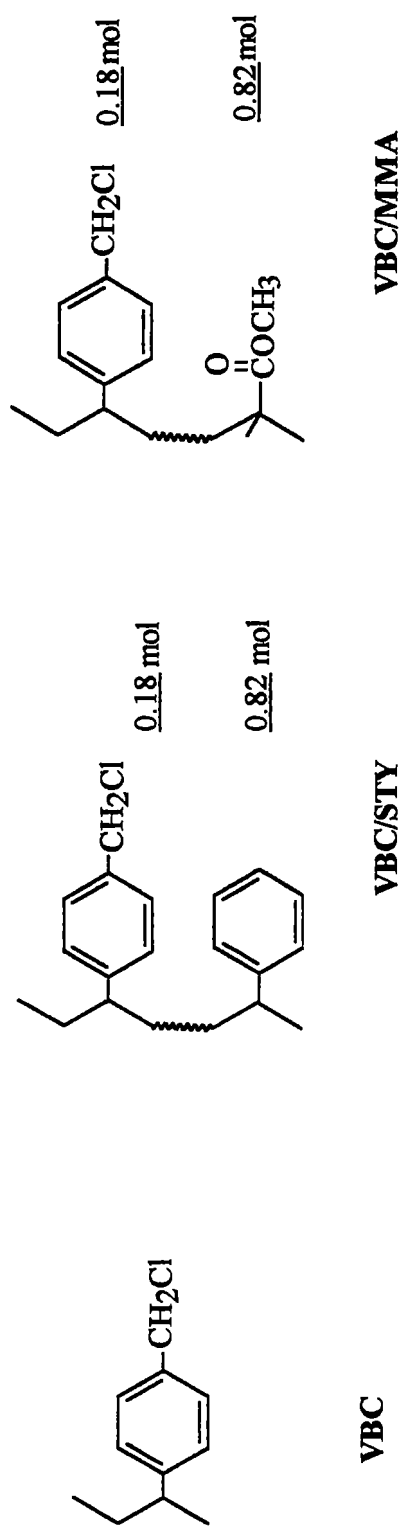


figure 2.1
Polymer Supports

environment around the active ligands while the VBC / MMA copolymer creates a more polar environment. Each copolymer was prepared with a molar ratio of VBC to STY or MMA of 0.18/0.82. The molar ratio in the copolymers was based on performance determined from previous research.⁶⁶

Monofunctional resins with various lengths of ethyleneimine and phosphonic acid groups were introduced into the polymeric supports. Aminophosphonic acid resins were prepared to study the effect of bifunctionality on metal ion complexation.

Experimental

A. Synthesis and Characterization

The three copolymer supports being used in metal ion studies are 2% DVB cross-linked VBC, VBC/STY (0.18/0.82 mole ratio) and VBC/MMA (0.18/0.82 mole ratio) copolymers. Each copolymer is prepared by suspension polymerization with bead sizes of -40 +60 mesh (0.250-0.425mm) for the VBC and VBC/STY resins and -60+80 mesh size (0.180-0.250mm) for the VBC/MMA resin beads. The relationship of bead diameter with standard sieve sizes is summarized in Table 6.4 of the Appendix.

Each polymer support has three different types of ligands: amine, aminophosphonic acid, and phosphonic acid. A variety of amines are introduced on the copolymer : primary amine(PA), ethylenediamine (EDA),

diethylenetriamine (DETA) and tetraethylenepentamine (TEPA). The aminated copolymers are further phosphorylated to prepare the aminophosphonic acid bifunctional resins. The reaction procedures are briefly described below and more detail given in Chapter 5.

1. Amination of Copolymers

The primary amine (PA) resins were prepared by the Gabriel reaction (Figure 2.2).⁶⁹ The beads containing VBC moieties were reacted with excess potassium phthalimide in DMF followed by hydrogenation with hydrazine and hydrolysis. The functionalized beads were washed with distilled water and conditioned by eluting with 1L H₂O, 4wt% NaOH, H₂O, 4wt% HCl and H₂O until neutral. The ethylenediamine (EDA) resins were prepared by reaction of the VBC, VBC/STY or VBC/MMA gels with excess ethylenediamine (99% purity) in dioxane at reflux. The beads were conditioned as above. The diethylenetriamine (DETA) resins were prepared using the same procedure as the EDA resins from diethylenetriamine (99% purity) and conditioned as above.

Tetraethylenepentamine (TEPA) resins were prepared with tetraethylenepentamine (technical grade:60% purity, includes tris(aminoethyl)amine, diaminoethylpiperazine, and piperazinoethylenediamine according to technical personnel at the Aldrich Chemical Co.). All resins were characterized by their percent solids (g dry resin/ g wet resin x 100) and nitrogen elemental analysis.

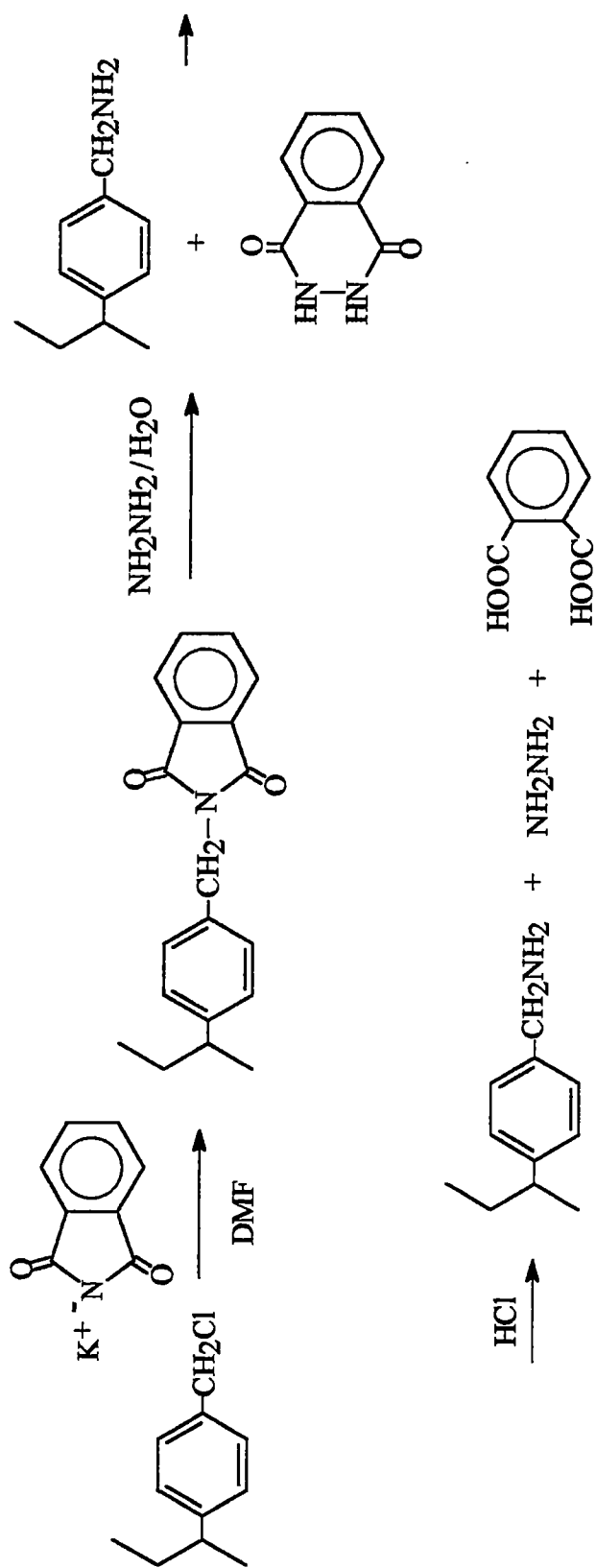


figure 2.2

Gabriel Synthesis

2. Phosphorylation of Amine Resins

In order to prepare bifunctional resins, the amine resins were phosphorylated via the Mannich reaction using formaldehyde and phosphorous acid with an acid catalyst (Figure 2.3). The functionalized resins were conditioned by eluting with 1L H₂O, 4wt% HCl, H₂O, 4wt% NaOH and H₂O until neutral. The aminophosphonic acid resins were characterized by their percent solids, nitrogen, phosphorus and acid capacities.

3. Monofunctional Phosphonic Acid Resins

Monofunctional phosphonic acid resins were prepared by the Arbuzov reaction on each copolymer using an excess of triisopropyl phosphite. The phosphonate ester was hydrolyzed to the phosphonic acid by refluxing with concentrated HCl (Figure 2.4). The functionalized resins are washed and conditioned with 1L H₂O, 4wt% NaOH, H₂O, 4wt% HCl and H₂O until neutral. The phosphonic acid resins were characterized by percent solids, phosphorus analysis and acid capacity.

B. Metal Ion Studies

The metal ion complexing abilities of the amine, aminophosphonic and phosphonic acid resins from 2 % DVB crosslinked VBC, VBC/STY and VBC/MMA copolymers are investigated using 1×10^{-4} N Cu(NO₃)₂, Pb(NO₃)₂,

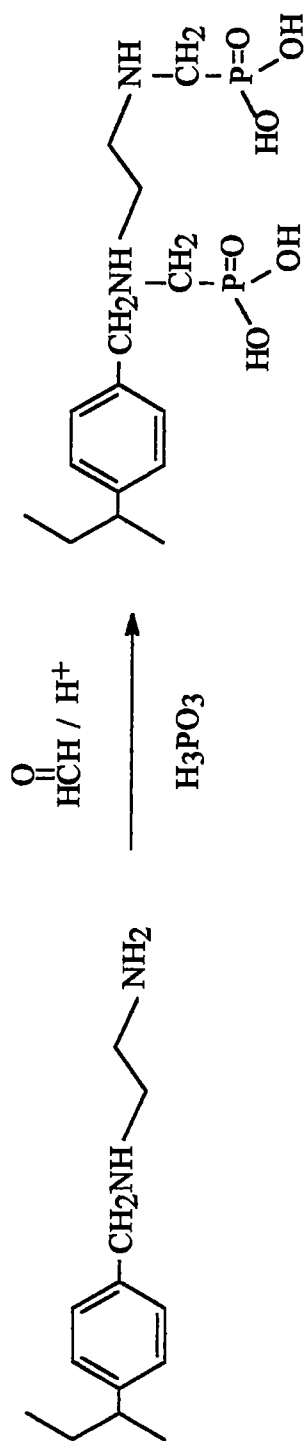


figure 2.3
Phosphorylation of EDA Resin

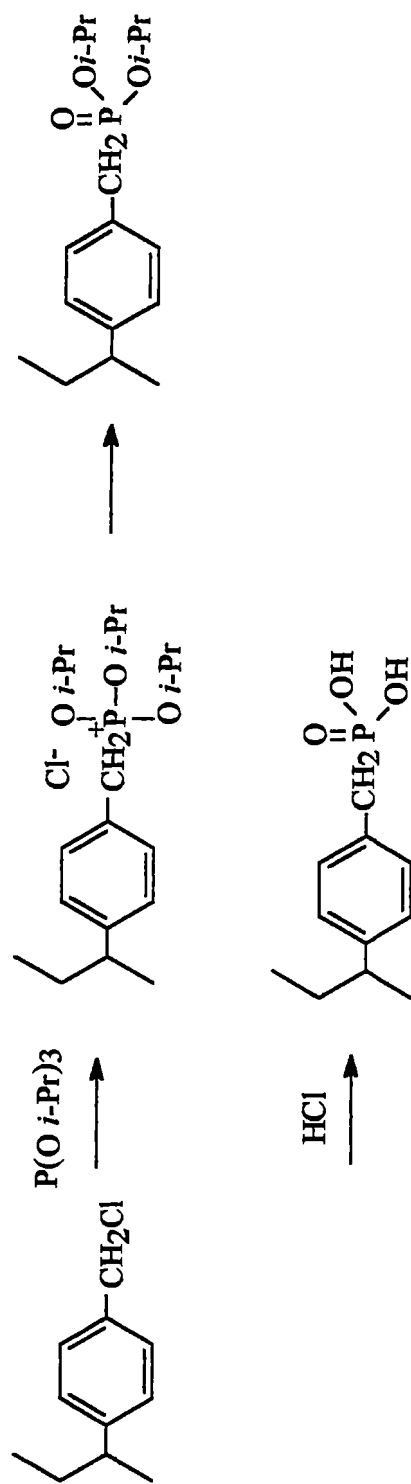


figure 2.4
Arbuzov Reaction

$\text{Cd}(\text{NO}_3)_2$, $\text{Eu}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$, and $\text{Co}(\text{NO}_3)_2$ in solutions buffered to pH5 with 0.6N acetate.

A buffer solution was used in the metal ion studies because the amine functional groups can be easily protonated from acid solutions. It was found that the pH of acidic solutions kept changing irregularly after each solvent exchange with amine resins due to protonation of the amine ligands. The protonated amine resins did not give reproducible results in the metal ion studies.

An amount of resin corresponding to either 0.5 or 1 milliequivalent of functional groups (nitrogen capacity for amine resins, phosphorus capacity for phosphonic acid resins, and either nitrogen or phosphorus capacity (see Tables) for aminophosphonic acid resins) were weighed and solvent exchanged four times with pH 5 acetate buffer solution. (The former amount was used when the resin was in short supply.) This is indicated as (0.5) and (1) for 0.5 and 1 mequiv in the Tables. Metal complexation results using the different amounts of resins can not be compared in terms of percent complexed, but distribution coefficients can be compared. After solvent exchange, the resins were contacted with 10 ml of the 10^{-4} N metal ion solution for 24 hour to allow enough time to reach equilibrium. The metal ion solutions were then filtered from the resins and the final concentrations were measured with a Perkin-Elmer Model 3100 atomic absorbance spectrometer. The results are reported in terms of percent M^{n+} complexed and distribution coefficients (D) defined as

$$D = \text{milliequivalents } M^{n+} \text{ per g polymer} / \text{milliequivalents } M^{n+} \text{ per ml solution}$$

It should be noted that a small difference in percent M^{n+} complexed at high complexation levels can give a large difference in the distribution coefficient. For example, in studies with the same resin, 14.00% complexed has a D value of 6.0 and 20.32% complexed has a D value of 9.3 but 93.46% complexed has a D value of 612 while 99.00% complexed has a D value of 4242.

In order to evaluate whether complexation by the polyamine resins is simply an additive effect of having more than one nitrogen in the ligand, a new distribution coefficient (D') is introduced to compare the results in terms of milliequivalents of functional group (nitrogen capacity for the amine resins, phosphorus capacity for the phosphonic acid resins, and either nitrogen or phosphorus capacity for the bifunctional resins (as specified in the Tables)).

$$D' = \frac{\text{milliequivalents } M^{n+} \text{ per milliequivalent functional group in the polymer}}{\text{milliequivalents } M^{n+} \text{ per ml solution}}$$

Results

A. Characterization of resins

1. Amine Resins

1.1. Primary Amine (PA) Resins

The properties of the PA resins prepared from the Gabriel reaction (Figure 2.2) are listed in Tables 2.1.1, 2.1.2 and 2.1.3. The percent solids of the VBC/STY resin (MH-1-233) was higher than the VBC(MH-1-173) or VBC/MMA (MH-1-253) resins due to the hydrophobic character of the styrene. The nitrogen capacities of all three PA resins show that the aminations are successful. MH-1-173 is 81 % functionalized while MH-1-233 and MH-1-253 are 76% and 100% functionalized, respectively.

That the VBC and VBC/STY resins are less functionalized than the VBC/MMA resin may be due to the crowded environment between the ligands in the former polymers. The VBC and phenyl groups in the 2% cross-linked polymers may be so close to each other that they interfere in the phthalimide functionalization. The VBC/MMA resin, with a molar ratio of 0.18/0.82, was functionalized to 100% perhaps due to the less crowded surroundings between the VBC ligands.

1.2. Ethylenediamine (EDA) Resins

The EDA resins were successfully prepared and the characterization results are reported in Table 2.1.1, 2.1.2 and 2.1.3. The percent solids of the VBC/STY EDA resin (MH-1-110) was higher than the VBC and VBC/MMA EDA resins (MH-1-032 and -142). The experimental nitrogen capacity of MH-1-032

Table 2.1.1
Characterization of Amine Resins (2% DVB Crosslinked VBC gel, 0.250-0.425mm)

Resins	Functional group	% Solids (%)	Nitrogen capacity (mequiv/g)	% Functionalization^b
MH-1-173	PA	60.23	5.79 (7.12) ^a	81.32
MH-1-032	EDA	46.99	7.54 (11.13)	67.74
MH-1-037	DETA	46.94	8.89 (13.56)	65.56
MH-1-041	TEPA	44.61	10.88 (16.30)	66.75

^a Theoretical

^b Apparent functionalization for all but the PA resin; used as a measure of internal crosslinking by the polyamines (see text)

PA : primary amine EDA: ethylenediamine

DETA: diethylenetriamine TEPA: tetraethylenepentamine

Table 2.1.2
Characterization of Amine Resins (2% DVB Crosslinked VBC/STY gel, 0.250-0.425mm)

Resins	Functional group	% Solids (%)	Nitrogen capacity (mequiv/g)	% Functionalization^b
MH-1-233	PA	87.20	1.21 (1.60) ^a	75.63
MH-1-110	EDA	73.86	2.50 (2.91)	85.91
MH-1-116	DETA	73.66	2.55 (4.14)	61.59
MH-1-120	TEPA	67.87	4.08 (6.17)	66.13

^aTheoretical

^b Apparent functionalization for all but the PA resin; used as a measure of internal crosslinking by the polyamines (see text)

PA : primary amine EDA: ethylenediamine
DETA: diethylenetriamine TEPA: tetraethylenepentamine

Table 2.1.3
Characterization of Amine Resins (2% DVB Crosslinked VBC/MMA gel, 0.180-0.250mm)

Resins	Functional group	% Solids (%)	Nitrogen capacity (mequiv/g)	% Functionalization ^b
MH-1-253	PA	68.87	1.82 (1.58) ^a	100
MH-1-142	EDA	66.82	2.45 (2.96)	82.77
MH-1-146	DETA	59.99	3.48 (4.18)	83.25
MH-1-150	TEPA	57.11	4.42 (6.22)	71.06

^aTheoretical

^b Apparent functionalization for all but the PA resin; used as a measure of internal crosslinking by the polyamines (see text)

PA : primary amine EDA: ethylenediamine
DETA: diethylenetriamine TEPA: tetraethylenepentamine

was 7.54mequiv/g. This was not attributed to incomplete functionalization of the copolymer because the phosphorylated EDA resin (MH-1-009) was subsequently examined by chlorine elemental analysis and showed a very low chlorine capacity (0.4 mequiv/g), which implies that all $\text{-CH}_2\text{Cl}$ groups are functionalized. It is noted that for, this and all other resins, the experimental nitrogen capacity is considerably less than the theoretical value. The most likely explanation is internal crosslinking by the polyamines. Possible crosslinking reactions of diethylenetriamine(DETA) with VBC are illustrated in Figure 2.5. The percent functionalization can be used as a measure of the degree of crosslinking because the theoretical nitrogen capacity is obtained by assigning a non-crosslinked structure and the lower the apparent percent functionalization, the greater the crosslinking. The phenomenon is prominent only in the VBC resins, not in the VBC/STY and VBC/MMA resins. In the case of EDA, compared to the 68% functionalization of the VBC resin, the VBC/STY resin was 86% functionalized and the VBC/MMA resin was 83% functionalized. This is because the greater number of $\text{-CH}_2\text{Cl}$ groups present in the VBC copolymer give a greater chance for bridge formation. The VBC/STY or VBC/MMA copolymers give less bridge formation due to a lower concentration of $\text{-CH}_2\text{Cl}$ groups.

1.3. Diethylenetriamine (DETA) Resins

The properties of the DETA resins are summarized in Table 2.1.1, 2.1.2 and 2.1.3. The percent solids in the VBC/STY resin (MH-1-116) was higher than

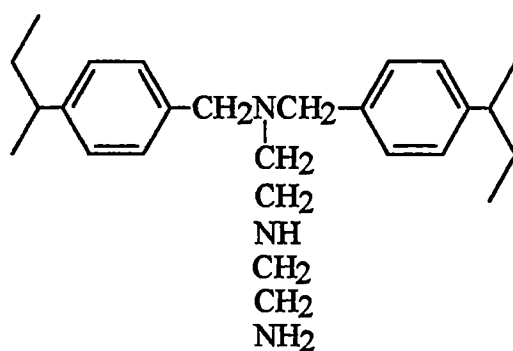
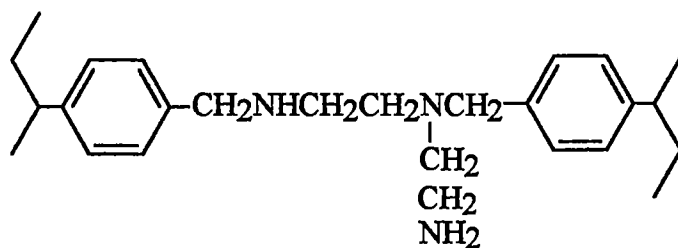
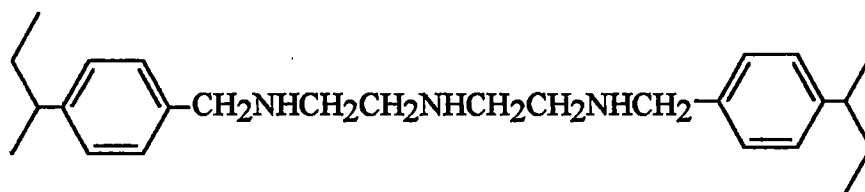
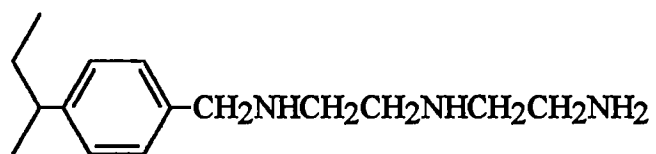


figure 2.5

Possible Crosslinking Configurations of DETA Resins

the VBC and VBC/MMA resins (MH-1-037 and MH-1-146), as expected. The experimental nitrogen capacities for the three DETA resins were again less than the theoretical values due to crosslinking. However, it should be noted that the VBC resin and the VBC/STY resin showed greatly decreased functionalization. It was found that VBC has 66%, VBC/STY has 62% and VBC/MMA has 83% functionalization, indicating a high level crosslinking. The reason the VBC/STY resin is highly crosslinked is probably because diethylenetriamine is long enough to reach another $-CH_2Cl$ group. It is unclear, however, why the VBC/MMA resin shows less crosslinking than the VBC/STY resin.

1.4. Tetraethylenepentamine (TEPA) Resins

The properties of the TEPA resins are listed in Tables 2.1.1, 2.1.2 and 2.1.3. They show the same trend in percent solids and nitrogen capacities as the DETA resins. Given the low TEPA purity, the precise composition of the resins is unclear. The metal ion studies are reported as indicators of what can be expected using commercially available TEPA, but can not be used for comparative conclusions.

2. Aminophosphonic acid resins

The data for the aminophosphonic acid resins are summarized in Tables 2.2.1, 2.2.2 and 2.2.3. The primary amine phosphonic acid resins from VBC (MH-1-180) and VBC/MMA polymers (MH-1-270) showed a nitrogen to phosphorus

Table 2.2.1
Characterization of Aminophosphonic acid Resins (2% DVB Crosslinked VBC gel, 0.250-0.425mm)

Resins	Functional group	% Solids (%)	N capacity (mequiv/g)	P capacity (mequiv/g)	Acid capacity (mequiv/g)	N:P ratio	P:Acid ratio
MH-1-180	PA /PhA	63.18	3.14	4.85	9.55	1 : 1.54	1 : 1.97
MH-1-070	EDA /PhA	49.23	4.71	3.81	7.38	1 : 0.81	1 : 1.94
MH-1-073	DETA/PhA	53.96	5.71	3.77	7.46	1 : 0.66	1 : 1.98
MH-1-094	TEPA/PhA	50.66	6.92	3.56	8.40	1 : 0.51	1 : 2.35
PA : primary amine		EDA: ethylenediamine		DETA: diethylenetriamine			
TEPA: tetraethylenepentamine		PhA : phosphonic acid					

Table 2.2.2
Characterization of Aminophosphonic acid Resins (2% DVB Crosslinked VBC/STY gel, 0.250-0.425mm)

Resins	Functional groups	% Solids (%)	N capacity (mequiv/g)	P capacity (mequiv/g)	Acid capacity (mequiv/g)	N:P ratio	P: Acid ratio
MH-1-286	PA / PhA	77.94	1.21	0.81	0.90	1 : 0.66	1 : 1.12
MH-1-130	EDA / PhA	82.30	1.75	1.29	3.62	1 : 0.74	1 : 2.80
MH-1-134	DETA/ PhA	76.93	4.53	1.59	3.14	1 : 0.35	1 : 1.98
MH-1-138	TEPA/ PhA	67.65	2.90	1.78	3.44	1 : 0.61	1 : 1.93
PA : primary amine		EDA: ethylenediamine		DETA: diethylenetriamine			
TEPA: tetraethylenepentamine		PhA : phosphonic acid					

Table 2.2.3
Characterization of Aminophosphonic acid Resins (2% DVB Crosslinked VBC/MMA gel, 0.180-0.250mm)

Resins	Functional group	% Solids (%)	N capacity (mequiv/g)	P capacity (mequiv/g)	Acid capacity (mequiv/g)	N:P ratio	P:Acid ratio
MH-1-270	PA / PhA	59.31	1.44	2.13	4.62	1 : 1.48	1 : 2.16
MH-1-154	EDA / PhA	66.60	2.00	1.79	3.44	1 : 0.89	1 : 1.93
MH-1-158	DETA/ PhA	63.81	3.60	2.03	4.25	1 : 0.56	1 : 2.09
MH-1-162	TEPA/ PhA	57.70	3.76	2.27	4.42	1 : 0.60	1 : 1.95
PA : primary amine		EDA: ethylenediamine		DETA: diethylenetriamine			
TEPA: tetraethylenepentamine		PhA: phosphonic acid					

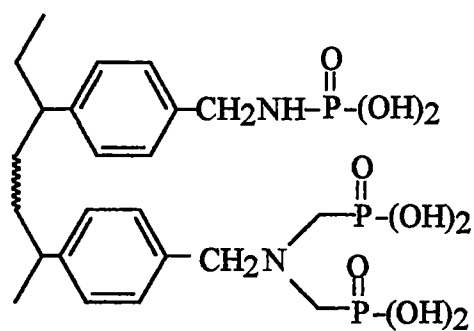
capacity ratio of approximately 1:1.5. This indicates that some of the nitrogen in the amine resins reacted with more than one phosphorous acid (Figure 2.6).

However, the VBC/STY resin (MH-1-286) was not phosphorylated as much as the VBC or VBC/MMA resins, showing a nitrogen to phosphorus capacity ratio of 1:0.66.

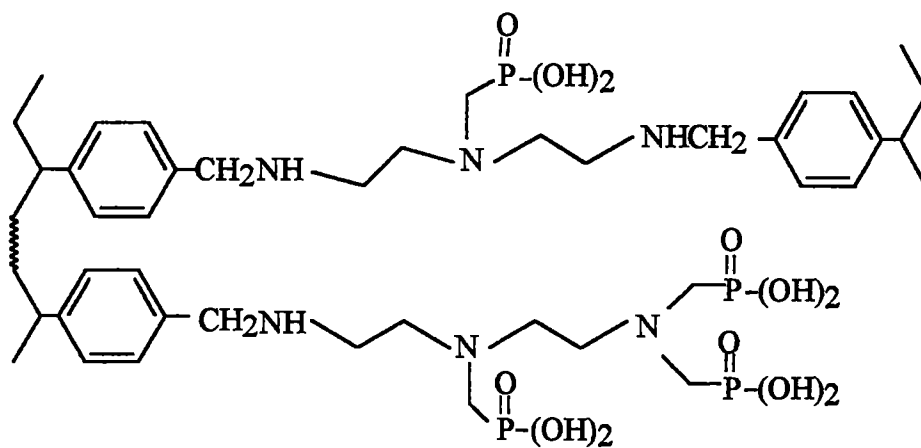
The remaining phosphorylations achieved nitrogen to phosphorus ratios in the range 1:0.35 to 1:0.89. It is thought that a 1:1 ratio could not be achieved because of steric hindrance. As the length of the amine group increases, more crosslinking causes steric hindrance and may hinder access of the phosphorous acid.⁴² For all aminophosphonic acid resins, the acid capacities are almost exactly twice the phosphorus capacities, indicating complete hydrolysis to the acid.

3. Monofunctional Phosphonic acid Resins

The properties of the phosphonic acid resins are summarized in Table 2.3. The phosphorus capacity of each resin is in good agreement with the theoretical value. The acid capacities are supposed to be twice the phosphorus capacities after ester hydrolysis. However, the VBC/STY resin is not completely hydrolyzed perhaps because of the hydrophobic environment. The VBC/MMA resin shows an acid capacity that is larger than the theoretical value, and this may indicate that the methacrylate is being partially hydrolyzed.



PA/PhA



DETA/PhA

figure 2.6

Structures of Phosphorylated Amine Resins

Table 2.3
Monofunctional Phosphonic acid Resins

Resins	Copolymers	Functional Group	bead size (mm)	% solid (%)	phosphorus cap. (mequiv/g)	Acid cap. (mequiv/g)	P: Acid ratio
MH-1-034	VBC	PhA	0.250-0.425	53.91	4.51 (4.82) ^a	8.86	1 : 1.96
MH-1-256	VBC/STY	PhA	0.250-0.425	64.44	1.65 (1.42)	1.82	1 : 1.10
MH-2-002	VBC/MMA	PhA	0.180-0.250	58.12	1.69 (1.25)	4.47	1 : 2.64

^a theoretical

PhA : phosphonic acid

B. Metal Ion Studies

The amine, aminophosphonic acid and phosphonic acid resins were contacted with metal ion solutions for 24 hours. The amine resin studies with Cu^{2+} , Pb^{2+} , Cd^{2+} and Eu^{3+} are summarized in Tables 2.4.1, 2.4.2, 2.4.3 and 2.4.4. The aminophosphonic acid resins were also studied with Cu^{2+} , Pb^{2+} , Cd^{2+} and Eu^{3+} and the results are in Tables 2.5.1, 2.5.2, 2.5.3 and 2.5.4. Since the Co^{2+} and Cr^{3+} solutions did not give good reproducibility, only Cu^{2+} , Pb^{2+} , Cd^{2+} and Eu^{3+} studies will be emphasized. The Co^{2+} (Tables 6.1.2 and 6.2.2) and Cr^{3+} (Tables 6.1.1 and 6.2.1) results will be listed separately in the appendix. Studies with the monophosphonic acid resins are reported in Table 2.6.

Generally, as the length of ligand in the amine resins increases from PA to EDA, the level of Cu^{2+} complexation increases indicating a chelate effect by multidentate ligands. There is no further increase from EDA to TEPA and PEHA resins.

The VBC /STY resins show less complexation than the VBC or VBC/MMA resins due to the hydrophobic character of the styrene. This indicates a microenvironmental effect that will be discussed in more detail below. The PA resin of the VBC/STY copolymer was the poorest complexing resin due to not only the short length of ligand but also its hydrophobicity.

Through all the metal ion studies, the aminophosphonic acid resins show better complexing ability than amine resins except for Cu^{2+} which complexes well with both amine and aminophosphonic acid resins.

Table 2.4.1
Metal Ion Uptake of $\text{Cu}(\text{NO}_3)_2$ from pH 5 Acetate Buffer Solution by Amine Resins

	PA	EDA	DETA	TEPA
VBC	MH-1-173	MH-1-032	MH-1-037	MH-1-041
% M complexed	32.5% (1)	100% (1)	98.4% (1)	96.9% (1)
D	14	infinite	5469	3368
D'	4.8	infinite	615	313
VBC/STY	MH-1-233	MH-1-110	MH-1-116	MH-1-120
% M complexed	5.40% (0.5)	99.20% (1)	99.20% (1)	99.20% (1)
D	1.37	3102	3166	5033
D'	1.14	1240	1240	1240
VBC/MMA	MH-1-253	MH-1-142	MH-1-146	MH-1-150
% M complexed	20.32% (0.5)	99.20% (1)	100% (1)	100% (1)
D	9.3	3040	infinite	infinite
D'	5.1	1240	infinite	infinite

PA : primary amine EDA: ethylenediamine DETA: diethylenetriamine
 TEPA: tetraethylenepentamine (1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.

Table 2.4.2
Metal Ion Uptake of Pb(NO₃)₂ from pH 5 Acetate Buffer Solution by Amine Resins

	PA	EDA	DETA	TEPA
VBC	MH-1-173	MH-1-032	MH-1-037	MH-1-041
% M complexed	10.93% (1)	15.31% (1)	3.35% (1)	10.45% (1)
D	3.6	13.6	3.0	12.6
D'	1.2	1.8	0.3	1.2
VBC/STY	MH-1-233	MH-1-110	MH-1-116	MH-1-120
% M complexed	12.06% (0.5)	20.53% (1)	23.43% (1)	23.43% (1)
D	3.3	6.5	7.8	12.5
D'	2.7	2.6	3.1	3.1
VBC/MMA	MH-1-253	MH-1-142	MH-1-146	MH-1-150
% M complexed	14.00% (0.5)	10.98% (0.5)	2.70% (0.5)	6.80% (0.5)
D	6.0	6.1	1.9	6.4
D'	3.3	2.5	0.1	1.5
PA : primary amine	EDA: ethylenediamine		DETA: diethylenetriamine	
TEPA: tetraethylenepentamine	(1) : weight based on 1 mequiv.		(0.5) : weight based on 0.5 mequiv.	

Table 2.4.3
Metal Ion Uptake of $\text{Cd}(\text{NO}_3)_2$ from pH 5 Acetate Buffer Solution by Amine Resins

	PA	EDA	DETA	TEPA
VBC	MH-1-173	MH-1-032	MH-1-037	MH-1-041
% M complexed	23.30% (1)	26.00% (1)	24.00% (1)	35.00% (1)
D	8.8	26.4	28.8	57.8
D'	3.1	3.5	3.2	5.4
VBC/STY	MH-1-233	MH-1-110	MH-1-116	MH-1-120
% M complexed	12.78% (0.5)	16.01% (0.5)	18.66% (0.5)	27.26% (0.5)
D	3.36	9.5	11.7	30.6
D'	2.9	3.8	4.6	7.6
VBC/MMA	MH-1-253	MH-1-142	MH-1-146	MH-1-150
% M complexed	16.09% (0.5)	15.02% (0.5)	14.36% (0.5)	19.98% (0.5)
D	7.0	8.7	11.7	22.0
D'	3.8	3.5	3.4	5.0

PA : primary amine

EDA: ethylenediamine

DETA: diethylenetriamine

TEPA: tetraethylenepentamine (1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.

Table 2.4.4
Metal Ion Uptake of $\text{Eu}(\text{NO}_3)_3$ from pH 5 Acetate Buffer Solution by Amine Resins

	PA	EDA	DETA	TEPA
VBC	MH-1-173	MH-1-032	MH-1-037	MH-1-041
% M complexed	4.45% (1)	0.00% (1)	3.00% (1)	0.00% (1)
D	0.1	0	2.7	0
D'	0.5	0	0.3	0
VBC/STY	MH-1-233	MH-1-110	MH-1-116	MH-1-120
% M complexed	0.00% (0.5)	6.70% (0.5)	8.20% (0.5)	10.40% (0.5)
D	0	3.4	4.6	9.5
D'	0	1.4	1.8	2.3
VBC/MMA	MH-1-253	MH-1-142	MH-1-146	MH-1-150
% M complexed	0.00% (0.5)	6.40% (0.5)	5.10% (0.5)	7.50% (0.5)
D	0	3.4	3.7	7.2
D'	0	1.4	1.1	1.6

PA : primary amine EDA: ethylenediamine DETA: diethylenetriamine
 TEPA: tetraethylenepentamine (1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.

Table 2.5.1

Metal Ion Uptake of $\text{Cu}(\text{NO}_3)_2$ from pH 5 Acetate Buffer Solution by Aminophosphonic Acid Resins

	PA/PhA	EDA /PhA	DETA/PhA	TEPA/PhA
VBC	MH-1-180	MH-1-070	MH-1-073	MH-1-094
% M complexed	98.40% (1)	100% (0.8)	100% (1)	96.90% (1)
D	2958	infinite	infinite	1099
D'	615 ^a (940) ^b	infinite	infinite	312 (159)
VBC/STY	MH-1-286	MH-1-130	MH-1-134	MH-1-138
% M complexed	91.40% (0.5)	97.44% (1)	99.20% (1)	99.20% (1)
D	171	491	1971	2208
D'	212 (142)	381 (281)	1240 (435)	1240 (761)
VBC/MMA	MH-1-270	MH-1-154	MH-1-158	MH-1-162
% M complexed	99.00% (0.5)	100% (1)	100% (1)	100% (1)
D	4242	infinite	infinite	infinite
D'	1980 (2946)	infinite	infinite	infinite
PA : primary amine	EDA: ethylenediamine	DETA: diethylenetriamine		
TEPA: tetraethylenepentamine	PhA : phosphonic acid			

(1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.

^a calculated based on P capacity ^bcalculated based on N capacity

Table 2.5.2

Metal Ion Uptake of $Pb(NO_3)_2$ from pH 5 Acetate Buffer Solution by Aminophosphonic Acid Resins

	PA/PhA	EDA /PhA	DETA/PhA	TEPA/PhA
VBC	MH-1-180	MH-1-070	MH-1-073	MH-1-094
% M complexed	98.12% (1)	100% (0.8)	98.12% (1)	100% (1)
D	2505	infinite	1968	infinite
D'	522 ^a (798) ^b	infinite	522 (343)	infinite
VBC/STY	MH-1-286	MH-1-130	MH-1-134	MH-1-138
% M complexed	93.23% (0.5)	100% (1)	100% (1)	100% (1)
D	222	infinite	infinite	infinite
D'	275 (183)	infinite	infinite	infinite
VBC/MMA	MH-1-270	MH-1-154	MH-1-158	MH-1-162
% M complexed	93.46% (0.5)	100% (0.5)	93.80% (0.5)	93.80% (0.5)
D	612	infinite	614	687
D'	286 (425)	infinite	303 (170)	303 (183)

PA : primary amine EDA: ethylenediamine DETA: diethylenetriamine

TEPA: tetraethylenepentamine PhA : phosphonic acid

(1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.

^a calculated based on P capacity ^bcalculated based on N capacity

Table 2.5.3

Metal Ion Uptake of $\text{Cd}(\text{NO}_3)_2$ from pH 5 Acetate Buffer Solution by Aminophosphonic Acid Resins

	PA/PhA	EDA /PhA	DETA/PhA	TEPA/PhA
VBC	MH-1-180	MH-1-070	MH-1-073	MH-1-094
% M complexed	92.00% (1)	98.00% (0.8)	98.00% (1)	99.60% (1)
D	550	2305	1840	8745
D'	115 ^a (176) ^b	605 (490)	490 (322)	2490 (1264)
VBC/STY	MH-1-286	MH-1-130	MH-1-134	MH-1-138
% M complexed	53.11% (0.5)	89.15% (0.5)	96.77% (0.5)	95.11% (0.5)
D	18	212	1101	689
D'	22 (15)	164 (121)	599 (244)	389 (238)
VBC/MMA	MH-1-270	MH-1-154	MH-1-158	MH-1-162
% M complexed	83.00% (0.5)	96.10% (0.5)	97.43% (0.5)	96.10 % (0.5)
D	209	880	1536	1119
D'	98 (145)	493 (440)	758 (427)	493 (297)

PA : primary amine EDA: ethylenediamine DETA: diethylenetriamine

TEPA: tetraethylenepentamine PhA : phosphonic acid

(1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.

^a calculated based on P capacity ^bcalculated based on N capacity

Table 2.5.4

Metal Ion Uptake of $Eu(NO_3)_3$ from pH 5 Acetate Buffer Solution by Aminophosphonic Acid Resins

	PA/PhA	EDA /PhA	DETA/PhA	TEPA/PhA
VBC	MH-1-180	MH-1-070	MH-1-073	MH-1-094
% M complexed	92.41% (1)	90.50% (0.8)	90.23% (1)	92.25% (1)
D	585	447	347	419
D'	121 ^a (186) ^b	117 (95)	92 (61)	119 (60)
VBC/STY	MH-1-286	MH-1-260	MH-1-263	MH-1-138
% M complexed	3.22% (0.5)	92.25% (0.5)	91.80% (0.5)	91.30% (0.5)
D	0.54	459	321	374
D'	0.67 (0.44)	247 (-)	224 (-)	210 (137)
VBC/MMA	MH-1-270	MH-1-154	MH-1-158	MH-1-162
% M complexed	81.81% (0.5)	91.50% (0.5)	91.20% (0.5)	91.32% (0.5)
D	193	384	420	478
D'	90 (134)	215 (192)	207 (117)	210 (127)

PA : primary amine EDA: ethylenediamine DETA: diethylenetriamine

TEPA: tetraethylenepentamine PhA : phosphonic acid

(1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.

^a calculated based on P capacity^b calculated based on N capacity

Table 2.6
Metal Ion Uptake from pH 5 Acetate Buffer Solution by MonoPhosphonic Acid resins

VBC PhA resin (MH-1-034)				
	Cu(NO₃)₂	Pb(NO₃)₂	Cd(NO₃)₂	Eu(NO₃)₃
% M complexed	98.06% (1)	100% (1)	49.20% (1)	92.30% (1)
D	3144	infinite	48	588
D'	704	infinite	9.7	120
VBC/STY PhA resin (MH-1-256)				
	Cu(NO₃)₂	Pb(NO₃)₂	Cd(NO₃)₂	Eu(NO₃)₃
% M complexed	76.41% (0.5)	100% (0.5)	30.19% (0.5)	2.33% (0.5)
D	96.3	infinite	13	0.7
D'	65	infinite	8.6	0.5
VBC/MMA PhA resin (MH-2-002)				
	Cu(NO₃)₂	Pb(NO₃)₂	Cd(NO₃)₂	Eu(NO₃)₃
% M complexed	51.52% (0.5)	64.39% (0.5)	21.66% (0.5)	74.48% (0.5)
D	36	62	9.3	98
D'	21	36	5.5	58
PhA : phosphonic acid (1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.				

Discussion

The metal ion studies are reported in terms of percent M complexed and distribution coefficients D and D'. The former (D) value was calculated per one gram of resin used. The later (D') value was calculated per one milliequivalent of nitrogen for amine resins ; either per one milliequivalent of phosphorus or one milliequivalent of nitrogen, as specified in the Tables, for the aminophosphonic acid resins; and per one milliequivalent of phosphorus for the phosphonic acid resins. Since the degree of functionalization of VBC/STY or VBC/MMA resins are lower than that of VBC resins, D values of VBC/STY and VBC/MMA resins are much smaller than that of VBC resins for the same percent M complexed. The D' value, which is based on the number of functional groups, decreases this gap which arise from the different degrees of functionalization between resins. The metal ion studies will be discussed mainly in terms of D' because it lets us compare the metal study results purely in terms of the type and the length of the ligand without being affected by the degree of functionalization.

1. The Monofunctional Resins

The monofunctional amine resins have the highest affinity for Cu^{2+} with the most dramatic increase being from PA to EDA. The affinities displayed by EDA, DETA and TEPA are similar and all microenvironments have the same affinities. That the very high Cu^{2+} affinities indicate that accessibility into the matrix is not a limiting factor. All amine resins have very low affinities for Pb^{2+} ,

Cd^{2+} and Eu^{3+} with a possible order of $\text{Cd}^{2+} > \text{Pb}^{2+} > \text{Eu}^{3+}$. The different microenvironments have similarly low affinities.

The fully functionalized monofunctional phosphonic acid resin has very high affinities for Cu^{2+} and Pb^{2+} , a high affinity for Eu^{3+} , and a lower affinity for Cd^{2+} . The affinity for all ions decreases significantly in the MMA microenvironment and the affinity is still not significant in the STY microenvironment for all ions except for Pb^{2+} where complexation is quantitative.

The fact that the PA resin performs poorly relative to other resins can be explained with the coordination stability constants. The table of overall stability constants (β_n) (Table 2.7) shows how the stability of the Cu^{2+} complex with ammonia in low coordination number is poor compared to that of EDA. The overall complexation constant β_3 of ammonia is almost similar to that of the β_1 of EDA. This means that Cu^{2+} needs three ammonia ligands to be as stable as Cu^{2+} complex with one EDA ligand. This enhanced stability of the EDA complex is due to stable chelate ring formation, which is the coordination between the metal ion and a multidentate ligand. Thermodynamically, the entropy of the chelated complex (EDA) is higher than that of the nonchelated complex (ammonia) and the stability of the metal ion complex is enhanced by the formation of the chelate ring.⁵¹ The increases in D' values from the PA resin as the length of the amine ligand increases, indicates that this may be attributed to an increase in ligand length, not the total number of nitrogens in the resin sample. For the amine resins, the D' values for metal ions other than Cu^{2+} were

Table 2.7
Complexation Stability Constants of Ethyleneimine Ligands with Metals ^a

	Cu^{2+}	Cd^{2+}	Co^{2+}	Pb^{2+}
ammonia				
log β_1	4.04	2.62	1.99	
log β_2	7.47	4.56	3.50	
log β_3	10.27	5.90	4.43	
EDA				
log β_1	10.54	5.45	5.6	7.0
log β_2	19.6	9.98	10.5	8.45
DETA				
log β_1	15.9	8.4	8.0	8.5
log β_2	20.9	13.8	13.9	10.37
TETA				
log β_1	20.1	20.63	10.95	10.4
TEPA				
log β_1	22.8	14.0	13.3	10.5

^a Kotly, S.; Sucha, L., *Handbook of Chemical Equilibria in Analytical Chemistry*, Ellis Horwood Limited. (1985), p 114, 115 and pp 143-149.

EDA: ethylenediamine

TETA: triethylenetetramine

DETA: diethylenetriamine

TEPA: tetraethylenepentamine

hard to be compare in terms of length of amine because the extent of complexation was extremely low and without much difference.

Table 2.7 also indicates that all amines have higher selectivity for Cu^{2+} over Cd^{2+} , Co^{2+} and Pb^{2+} . The complexation stability constant (β_1) of ammonia with Cu^{2+} is 10^2 times greater than Cd^{2+} or Co^{2+} . The β_1 of EDA with Cu^{2+} is 10^5 times greater than Cd^{2+} and Co^{2+} and 10^3 times greater than Pb^{2+} . This explains the fact that Cu^{2+} is complexed with amines readily even though other metal ions are poorly complexed with amines.

2. The Bifunctional Effect

The incorporation of phosphonic acid groups in amine resins allowed for the preparation of bifunctional resins. The effect of increasing the length of the polyamine evident with the monofunctional resins is evident here as well. Most significant, however, is the observation of synergism under certain conditions where both groups operating together complex more metal than either one alone. Ion exchange ability by the phosphonic acid ligand and coordination by the amine ligand cooperate as a dual mechanism for metal ion complexation. In synergistic solvent extraction, the combination of certain pairs of extractants gives enhanced complexation for certain metals relative to what could be calculated based on the distribution coefficients of each extractant alone.⁷⁰ For example, thenoylfluoroacetate(HTTA)-tributylphosphate (1:1) solution showed the

synergistic enhancement in zinc with D values of 10^4 times higher than HTTA and 10^2 higher than tributylphosphate.⁷¹

Comparisons of the metal ion complex abilities of the amine, aminophosphonic acid and phosphonic acid resins quantified in Tables 2.8.1, 2.8.2, 2.8.3 and 2.8.4 show the first clear examples of the bifunctional effect. As a general statement, the results indicate synergistic complexation for Cd^{2+} by all of the bifunctional aminophosphonic acid resins (i.e., regardless of microenvironment) and with all of the metal ions for all the bifunctional resins within the MMA microenvironment (though, for Cu^{2+} , this is pronounced only with the PA/PhA and EDA/PhA resins). For the remaining conditions, the bifunctional resin performed like the monofunctional amine or phosphonic acid resin, depending on which had the higher affinity for the metal ion. For example, within the STY microenvironment, the bifunctional resin behaved like the EDA, DETA and TEPA resins when complexing Cu^{2+} and like the phosphonic acid resin when complexing Pb^{2+} (the PA resin has such a low affinity for Cu^{2+} , that the bifunctional resin behaves more like the phosphonic acid resin for this metal though some synergism may be evident).

Cadmium shows the most evident bifunctional effect. For example, it is complexed by the EDA(VBC) resin to 26% (D' value of 3.5) and to 49% (D' value of 9.7) by the PhA resin, but the bifunctional resin complexes 98% Cd^{2+} (D' value of 490) which far exceeds the combined D' values of the monofunctional resin. Additionally, Eu^{3+} shows a strong synergistic interaction with the three

Table 2.8.1
Metal Ion Uptake from pH 5 Buffer Solution by Monofunctional and Bifunctional Resins (PA)

	Cu²⁺	Pb²⁺	Cd²⁺	Eu³⁺
<u>VBC (1)</u>				
PA	32.5% ^a (14) ^b 4.8 °	10.9% (3.6) 1.2	23.3% (8.8) 3.1	4.45% (0.1) 0.5
PA/PhA	98.4% (2958) 615	98.1% (2505) 522	92.0% (550) 115	92.4% (585) 585
PhA	98.1% (3144) 704	100%	49.2% (48) 9.7	92.3% (588) 120
<u>VBC/STY (0.5)</u>				
PA	5.4% (1.4) 1.1	12.1% (3.3) 2.7	12.8% (3.3) 2.9	0%
PA/PhA	91.4% (171) 212	93.2% (222) 275	53.1% (18.3) 23	3.2% (0.5) 0.7
PhA	76.4% (96) 65	100%	30.2% (13) 8.6	2.3% (0.7) 0.5
<u>VBC/MMA (0.5)</u>				
PA	20.3% (9.3) 5.1	14.0% (6.0) 3.3	16.1% (7) 3.8	0%
PA/PhA	99.0% (4242) 1980	93.5% (612) 286	83.0% (209) 97.7	81.8% (193) 90
PhA	51.5% (36) 21.2	64.4% (62) 36	21.7% (9.3) 5.5	74.5% (98) 58

^a % M complexed ^b D ° D' (based on nitrogen capacity for PA and phosphorus capacity for PA/PhA and PhA)

PA : primary amine PhA : phosphonic acid

(1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.

Table 2.8.2
Metal Ion Uptake from pH 5 Buffer Solution by Monofunctional and Bifunctional Resins (EDA)

	Cu^{2+}	Pb^{2+}	Cd^{2+}	Eu^{3+}
<u>VBC</u>	(1)	(1)	(1)	(1)
EDA	100%	15.31% ^a (13.6) ^b 1.8 ^c	26.0% (26.4) 3.5	0%
EDA/PhA	98.4% (2958) 615	100%	98.0% (2305) 605	90.50% (447) 117
PhA	98.1% (3144) 704	100%	49.2% (48) 9.7	92.3% (588) 120
<u>VBC/STY</u>	(1)	(1)	(0.5)	(0.5)
EDA	99.2% (3102) 1240	20.53% (6.5) 2.6	16.0% (9.5) 3.8	6.7% (3.4) 1.4
EDA/PhA	91.4% (171) 212	100%	89.6% (212) 164	92.3% (459) 247
PhA	76.4% (96) 65	100%	30.2% (13) 8.6	2.3% (0.7) 0.5
<u>VBC/MMA</u>	(1)	(0.5)	(0.5)	(0.5)
EDA	99.2% (3040) 1240	11.0% (6.1) 2.5	15.0% (8.7) 3.5	6.4% (3.4) 1.4
EDA/PhA	99.0% (4242) 1980	100%	96.1% (880) 493	91.5% (384) 215
PhA	51.5% (36) 21.2	64.4% (62) 36	21.7% (9.3) 5.5	74.5% (98) 58

^a % M complexed ^b D ^c D' (based on nitrogen capacity for EDA and phosphorus capacity for EDA/PhA and PhA) EDA : ethylenediamine PhA : phosphonic acid

(1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.

Table 2.8.3
Metal Ion Uptake from pH 5 Buffer Solution by Monofunctional and Bifunctional Resins (DETA)

	Cu²⁺	Pb²⁺	Cd²⁺	Eu³⁺
<u>VBC</u>	(1)	(1)	(1)	(1)
DETA	98.4% ^a (5469) ^b 316 ^c	3.4% (3.0) 0.3	24.0% (29) 3.2	3.0% (2.7) 0.3
DETA/PhA	100%	98.1% (1968) 522	98.0% (1840) 490	90.2% (347) 92
PhA	98.1% (3144) 704	100%	49.2% (48) 9.7	92.3% (588) 120
<u>VBC/STY</u>	(1)	(1)	(0.5)	(0.5)
DETA	99.2% (3166) 1240	23.4% (7.8) 3.1	18.7% (11.7) 4.6	8.2% (4.6) 1.8
DETA/PhA	99.2% (1971) 1240	100%	96.8% (1100) 599	91.8% (321) 224
PhA	76.4% (96) 65	100%	30.2% (13) 8.6	2.3% (0.7) 0.5
<u>VBC/MMA</u>	(1)	(0.5)	(0.5)	(0.5)
DETA	100%	2.7% (1.9) 0.1	14.4% (11.7) 3.4	5.1% (3.7) 1.1
DETA/PhA	100%	93.8% (613) 303	97.4% (1536) 758	91.2% (420) 207
PhA	51.5% (36) 21.2	64.4% (62) 36	21.7% (9.3) 5.5	74.5% (98) 58

^a % M complexed ^b D ^c D' (based on nitrogen capacity for DETA and phosphorus capacity for

DETA/PhA and PhA) DETA : diethylenetriamine PhA : phosphonic acid

(1) : weight based on 1 mequiv.

(0.5) : weight based on 0.5 mequiv.

Table 2.8.4
Metal Ion Uptake from pH 5 Buffer Solution by Monofunctional and Bifunctional Resins (TEPA)

	Cu²⁺	Pb²⁺	Cd²⁺	Eu³⁺
<u>VBC</u>	(1)	(1)	(1)	(1)
TEPA	96.9% ^a (3368) ^b 313 ^c	10.4% (12.6) 1.2	35.0% (58) 5.4	0%
TEPA/PhA	96.9% (1099) 312	100%	99.6% (8745) 2490	92.3% (419) 119
PhA	98.1% (3144) 704	100%	49.2% (48) 9.7	92.3% (588) 120
<u>VBC/STY</u>	(1)	(1)	(0.5)	(0.5)
TEPA	99.2% (5033) 1240	23.4% (12.5) 3.1	27.3% (31) 7.6	10.4% (9.5) 2.3
TEPA/PhA	99.2% (2208) 1240	100%	95.1% (689) 389	91.3% (374) 210
PhA	76.4% (96) 65	100%	30.2% (13) 8.6	2.3% (0.7) 0.5
<u>VBC/MMA</u>	(1)	(0.5)	(0.5)	(0.5)
TEPA	100%	6.8% (6.4) 1.5	20.0% (22) 5.0	7.5% (7.2) 1.6
TEPA/PhA	100%	93.8% (687) 303	96.1% (1119) 493	91.3% (374) 210
PhA	51.5% (36) 21.2	64.4% (62) 36	21.7% (9.3) 5.5	74.5% (98) 58

^a % M complexed ^b D ^c D' (based on nitrogen capacity for TEPA and phosphorus capacity for

TEPA/PhA and PhA) TEPA : tetraethylenepentamine PhA : phosphonic acid

(1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.

polyamine/PhA resins in the STY microenvironment : while the DETA (VBC /STY) resin has 8.2% complexed (D' value of 1.8) and the PhA resin has 2.3% complexed (D' value of 0.5), the DETA/PhA resin complexed 91.8% Eu^{3+} (D' value of 224).

3. The Microenvironmental Effect

The different polymer matrices supporting the ligands affect complexation of the metal. This microenvironmental effect is the influence of inert groups adjacent to the main ligand on the interaction between the ligand and the substrate. As shown in Tables 2.8.1~4, the same ligands contacted with the same metal ion show different complexing abilities depending on whether they are immobilized on VBC, VBC/STY or VBC/MMA copolymers. The fully functionalized phosphonic acid resin either outperforms the resins with the STY microenvironment (for Cu^{2+} , Cd^{2+} and Eu^{3+}) or gives results that are comparable (for Pb^{2+}); the lowest level of complexation is in the MMA microenvironment for the divalent ions though the MMA resin outperforms the STY resin with Eu^{3+} . Whereas there is no significant microenvironmental effect with any of the amine resins, this is not the case for the aminophosphonic acid resins. It is clear that a microenvironmental effect exists. For Cd^{2+} when interacting with the PA/PhA resins with the fully functionalized resin outperforming the MMA resin which, in turn, outperforms the STY resin. The same trend is evident with Eu^{3+} interacting with PA/PhA resin. The microenvironmental effect is less important with the other

ions and with remaining two resins. Why Cd^{2+} should more sensitive to the microenvironment and why the bifunctional PA and EDA resins should display this effect and not the other amines is the object of continuing investigation .

In order to show that the poor metal ion complex ability of the PA and PA/PhA in VBC/STY resins are caused by its hydrophobicity, smaller size bead (0.045-0.075mm) of PA and PA/PhA resins were examined. These beads were contacted with Cu^{2+} , Pb^{2+} and Eu^{3+} ion in pH5 acetate buffer solutions and the results are summarized in Table 2.9. Generally, the percent complexed increased somewhat with the smaller size of the resins, with Eu^{3+} showing a large increase from ~3% to ~80% with the PA/PhA resin. This indicates that the poor performance of the VBC/STY resin is due to the presence of hydrophobic styrene which limits ionic accessibility. The smaller beads have higher surface area and the ligands are thus more accessible to the metal ions.

4. Counter Ion Effect

In this research, all metal ion solutions are made from nitrate salts in pH 5 sodium-acetate buffer solution. Two anions, acetate and nitrate, are always present with the metal ions and are thought to affect metal ion complexation. It was reported that the anion can influence the selectivity when coordination is the sole mechanism of complexation.⁷² In the study of $\text{Cu}(\text{NO}_3)_2$ with polymer-supported imidazole in pH 5 acetate buffer solution, it was found that the acetate ion is brought into the polymer matrix along with the Cu^{2+} ion because $\text{Cu}(\text{OAc})_2$

Table 2.9
Resin Particle Size Effect of VBC/STY gel on Metal Ion Uptake

VBC/STY	PA resins	MH-2-182 (0.045-0.075mm)	MH-1-233 (0.250-0.425mm)
	Cu²⁺	41.3% ^a (23) ^b	5.40% (1.37)
(0.5)	Pb²⁺	30.0% (14)	12.06% (3.3)
	Eu³⁺	17.49% (7)	0%
VBC/STY	PA/PhA resins	MH-2-202 (0.045-0.075mm)	MH-1-286 (0.250-0.425mm)
	Cu²⁺	100% ^a (infinite) ^b	91.4% (171)
(0.5)	Pb²⁺	82.07% (113)	93.23% (222)
	Eu³⁺	79.60% (97)	3.22% (0.54)
^a % M complexed	^b D	PA : primary amine	PhA : phosphonic acid
			(0.5) : weight based on 0.5 mequiv.

has a higher formation constant than $\text{Cu}(\text{NO}_3)_2$.^{68,73} The effect of coexisting counter anions (Br^- , Cl^- , SO_4^{2-} , SO_3^- , CH_3COO^- and etc) on the extraction of rare earth metal ions (Lu^{3+} , Ho^{3+} , La^{3+} , Eu^{3+} and etc) using styrene-vinylbenzene copolymer containing CYANEX 272 was studied.⁷⁴ In the metal study with poly(amido-amine) resin, it was reported that the metal ion complexation was affected by the nature and concentration of counterions in the aqueous phase.⁷⁵

In the present research, the amount of acetate ion is far greater than nitrate ion and the results are applicable to it as the counter ion.

Conclusions

The various lengths of ethyleneimine and phosphorylated ethyleneimine ligands were incorporated into 2% cross-linked VBC, VBC/STY and VBC/MMA polymer matrices and their ability to complex with metal ions was evaluated. A bifunctional effect has been identified. The aminophosphonic acid resins showed better results than amine or phosphonic acid resins generally. A microenvironmental effect was also identified for the complexation of Cd^{2+} by ligands in fully functionalized STY and MMA matrices. The nature of the ligand, bifunctionality, the microenvironmental can be used to affect separations of targeted metal ions from other ions. Having established the experimental results, further research will have to establish the theoretical foundation of these results.

CHAPTER 3

Immobilization of Ligands on Crosslinked Polymers via the Mannich Reaction

Introduction

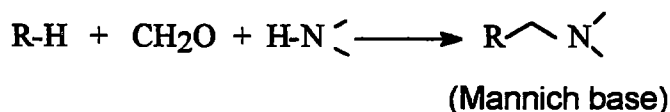
Poly(glycidyl methacrylate) polymer (GMA) and its derivatives have been studied for ion exchange applicability.^{76,77} While most commercial ion-exchange resins⁷⁸ show slow kinetics due to their hydrophobicity and poor selectivities for metal ions, hydrophilic GMA polymers have better kinetics as well as the possibility to introduce numerous ligands via a ring opening reaction of the epoxy group. N,N'-bis(2-benzimidazolmethyl)amine resin immobilized on GMA polymer⁷⁹ showed better kinetic performance than the same ligand on polystyrene⁸⁰.

Resins containing amine groups have a number of applications such as immobilization of biologically active compounds and as ion exchangers.⁸¹ GMA polymers have been reacted with various amines including ammonia, hydroxyalkylamine, aminoalkylamine, imidazol and pyrazole.^{77,82,83} The amine ligands show good metal ion complexing ability. Immobilization of ethylenediamine and iminodiacetic groups onto GMA-ethylenedimethacrylate copolymers produce resins selective for Ag^+ and Hg^{2+} .⁸⁴ GMA polymers withazole-containing amine ligands are reported to show high selectivity for Cu^{2+} over other divalent transition metal ions.⁸⁵ The pyrazole-containing ligand, 5-(3,5-

dimethylpyrazol-1-yl)-3-thiapentyl amine, was found to be selective for Cu^{2+} at pH 6 and for Cd^{2+} and Zn^{2+} ions at $\text{pH} < 2.5$.⁸⁶ The 2-(aminomethyl)pyridine ligand anchored onto GMA-ethylene glycol dimethacrylate copolymer shows good selectivity for Cu^{2+} from a large excess of Zn^{2+} .⁸⁷ Triethylenetetramine and methylphosphonic acid groups were introduced onto GMA polymers and showed selectivity in the order of $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$.⁸⁸

The reactivity of the epoxide in GMA is affected by the solvent, the reactants' nucleophilicity, the temperature, etc.⁸⁹ In the reaction with amines (RNH_2), the type and size of the substituent R as well as the basicity of the amines affect the reaction rate.⁸² The type of comonomer in the GMA copolymer was also found to affect the reactivity of the epoxide ring.⁹⁰ An increase in the reactivity of the epoxide ring of the glycidyl acrylate-acrylonitrile copolymer was observed due to an interaction between the amino and nitrile groups.⁹¹

The Mannich reaction is the condensation reaction of amines, formaldehyde and a compound containing an active hydrogen with an acid or



base catalyst. Interest in the Mannich reaction has increased since its first study in 1942⁹² and numerous studies have been reported. The great reactivity of Mannich bases produces numerous other compounds, which can lead to various applications.^{93,94} One of the most important applications is pharmaceutical uses

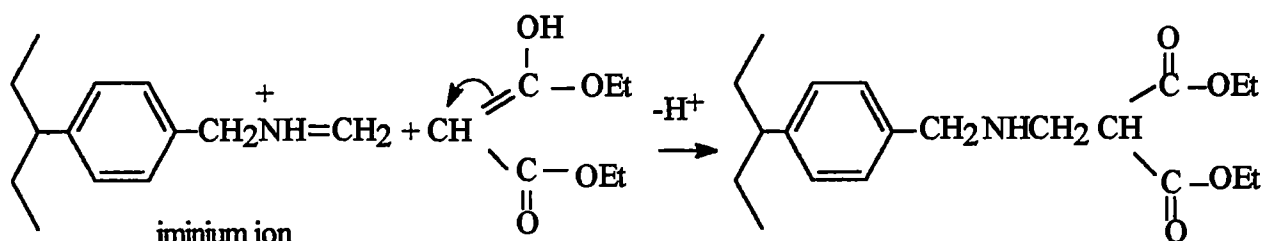
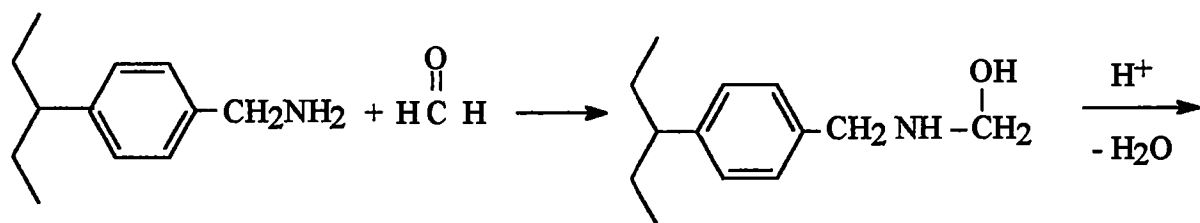
including antineoplastic drugs, analgesics and antibiotics.^{95,96} They are also applied in fine chemicals⁹⁷, polymers⁹⁸, antifoulants⁹⁹ and fuel additives¹⁰⁰.

The versatility of Mannich bases comes from the diversity of the functional groups in Mannich condensates. For example, in epoxy applications, the phenol groups in Mannich condensates have advantages in terms of providing further active sites.¹⁰¹ Phenol-containing compounds such as poly(*p*-vinylphenol) or 2,3,6-tris(dimethylaminomethyl)phenol can function as epoxy curing accelerators.¹⁰²

In recent years, the Mannich bases have been applied to polymer chemistry, especially paints and surface-active agents.⁹³ Cationic flocculants used in paper manufacture was prepared by the Mannich reaction of polyacrylamide with dimethylamine and formaldehyde.¹⁰³ Phenolic resin obtained from the Mannich reaction of polyphenol with formaldehyde and amine was applicable as a corrosion-resistant coating material that also prevented discoloration.¹⁰⁴ A water-soluble Mannich base resin for use in electrocoating was prepared by the reaction of bisphenol diepoxide with formaldehyde and amine.¹⁰⁵

The Mannich reaction can be carried out in both acidic and basic conditions. The two types of catalysts in the Mannich reaction give rise to the different mechanisms.⁹⁷ The mechanisms with diethylmalonate (DEM) in acid and base are illustrated in Figure 3.1. In the acid catalyzed reaction, the iminium ion is formed as an intermediate from the reaction of aldehyde and amine. The

Acid-catalyzed



Base-catalyzed

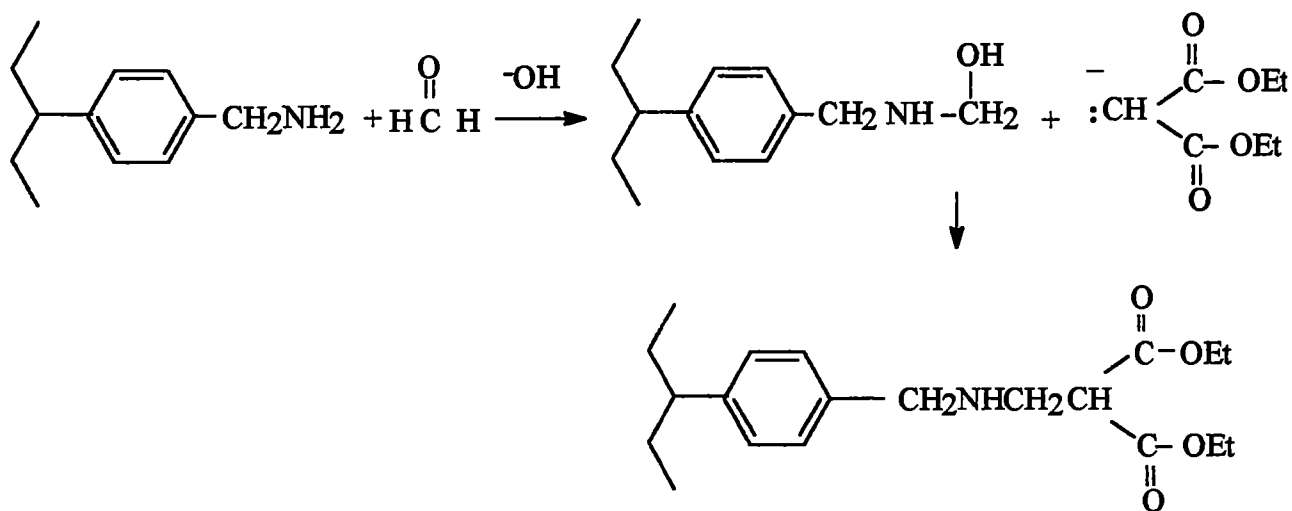


Figure 3.1

Mechanism of Mannich Reaction

active-hydrogen compound reacts as an enol and electrophilic attack of the iminium ion on the enol takes place. In basic medium, the reactant is thought to be a hydroxymethylamine and the active hydrogen compound reacts as a carbanion.

The aim of this research is to phosphorylate a primary amine ligand immobilized onto crosslinked polystyrene beads using active hydrogen compounds, tetraisopropylmethylenediphosphonate (TIPP) and triethylphosphonoacetate (TEPAc) under Mannich reaction conditions. Exploratory runs were done with diethylmalonate (DEM). Comparative phosphorylations were carried out with formaldehyde and phosphorous acid (PhA). Due to the hydrophilicity of the latter system, that reaction was also run on amine immobilized on 2% DVB crosslinked GMA polymers. Variables including the amount of acid catalyst, reaction time and reaction temperature identify mild reaction condition.

Experimental

Poly(glycidyl methacrylate)

The 2% DVB cross-linked poly(glycidyl methacrylate) (GMA) was prepared by suspension polymerization. An organic phase containing GMA, AIBN and DVB was combined with an aqueous phase containing poly(vinylalcohol), sodium chloride and distilled water, then heated to 90°C. The

beads were washed with distilled water, soxhlet extracted with dioxane and dried in a 60°C oven.

Reactions of GMA polymer with nitrogen-containing compounds

The GMA polymer was reacted with four different compounds : *p*-nitrophenol, sodium *p*-nitrophenoxide, aniline and ethylenediamine (Figure 3.2). The GMA polymer was reacted with a ten-fold stoichiometric excess of each compound in aqueous medium either at room temperature or at 80°C. The products were characterized by nitrogen capacity.

Phosphorylations of aniline and ethylenediamine GMA polymers were achieved by the reaction with phosphorous acid, formaldehyde and acid catalyst either at room temperature or with heating. The beads were washed with distilled water and characterized by nitrogen and phosphorus capacity.

Mannich Reactions

A 2% DVB cross-linked VBC primary amine resin (PA) was reacted with four different active hydrogen compounds : diethylmalonate (DEM), tetra isopropyl methylene diphosphonate (TIPP), triethylphosphonoacetate (TEPAc) and phosphorous acid (PhA). A nine-fold stoichiometric excess of each active-hydrogen compound was reacted with the resin. Many experimental sets that varied in terms of the catalyst amount, reaction time and reaction temperature were attempted and the products were characterized by nitrogen capacity. The

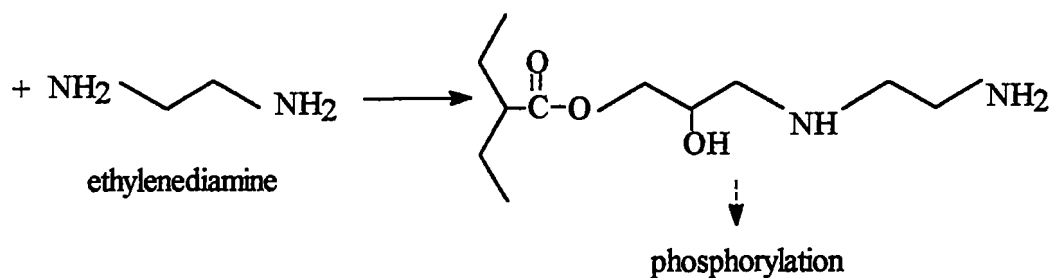
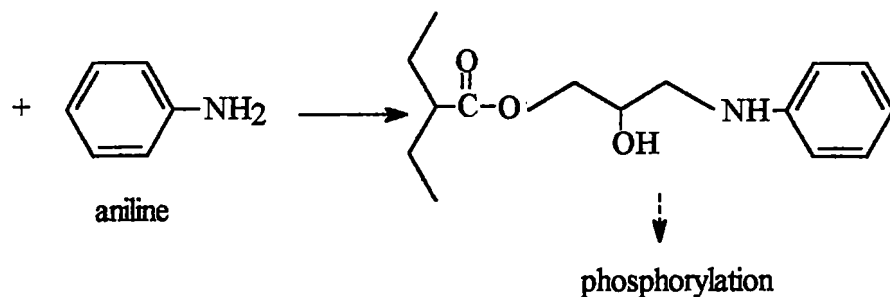
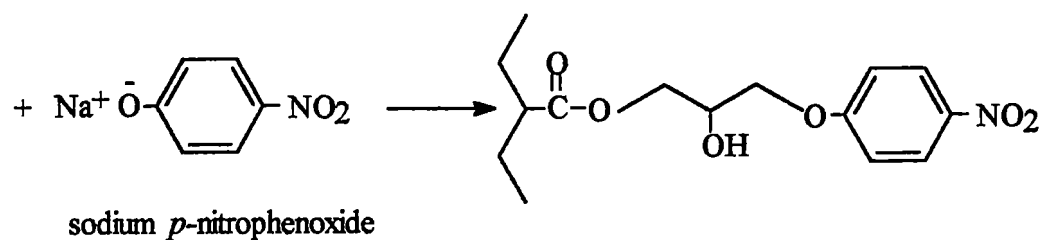
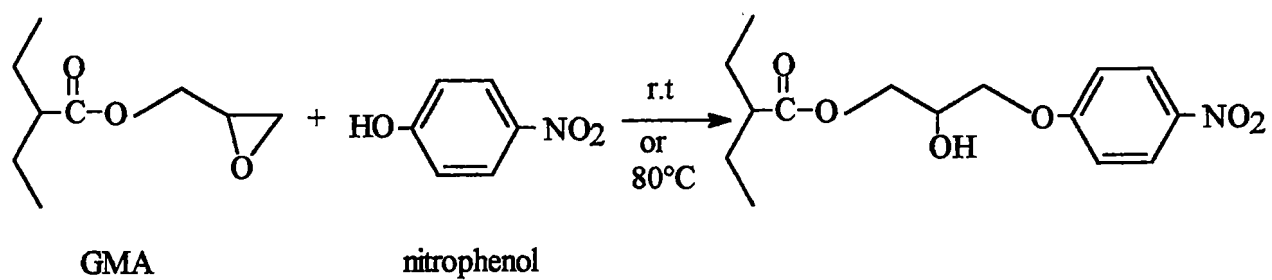


Figure 3.2
Reactions of GMA Polymers

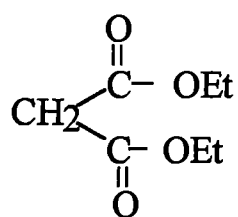
structures of the four different active hydrogen compounds are illustrated in Figure 3.3.

Results and Discussion

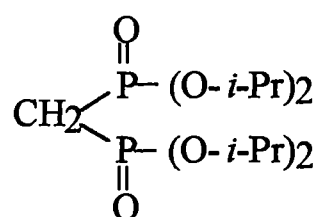
GMA Resins

The progress of the each reaction can be evaluated by the nitrogen elemental analysis of the products since all the products contain nitrogen. According to the results in Table 3.1, nitrophenol seems a poor nucleophile for GMA attack both at room temperature and at 80°C. The reaction of sodium *p*-nitrophenoxide gives a good nitrogen capacity (63% functionalization) when it is carried out at 80°C but the reaction did not go at room temperature. The aniline reaction shows good results, achieving over 77% functionalization not only at room temperature but at 80°C also. The reaction with ethylenediamine (EDA) was performed only at room temperature because the reaction with heating had been performed successfully earlier (Chapter 2). The ethylenediamine (EDA) product shows a nitrogen capacity 66% of the theoretical value. All theoretical nitrogen capacities of aminated GMA compounds were calculated based on the assumption of 1:1 (GMA:amine) reaction ratio.

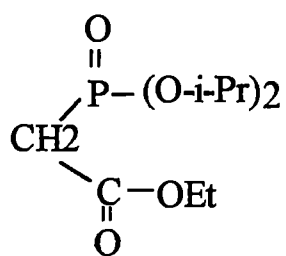
The two GMA polymers aminated by aniline and EDA at room temperature were phosphorylated with phosphorous acid. The properties of these phosphorylated products are summarized in Table 3.2. The



DEM



TIPP



TEPAc

H₃PO₃

PhA

Figure 3.3

Active Hydrogen Compounds Used in Mannich Reaction

Table 3.1
Reactions of GMA Polymer

Resin	Reactant	Nitrogen capacity (mequiv/g)		
		<u>room temperature</u>	<u>80°C</u>	<u>theoretical</u>
MH-2-222	<i>p</i> -nitrophenol	0.65 (18.73%) ^a	0.34 (9.8%) ^a	3.47
MH-2-223	sodium <i>p</i> -nitrophenoxide	-0.19 (0 %)	2.20 (63.40%)	3.47
MH-2-221	aniline	3.21 (77.35%)	3.28 (79.04%)	4.15
MH-2-228	ethylenediamine	6.31 (66.40%)	-	9.50

^a % functionalization

Table 3.2
Phosphorylation of Aminated GMA Polymer

Resin	Amine type	temperature	% solid (%)	Nitrogen capacity (mequiv/g)	Phosphorus capacity (mequiv/g)
MH-2-238	aniline ^a	r.t. ^c	69.54	3.49 (2.39) ^d	0.01 (2.39) ^e
MH-2-230		heat	74.88	2.80	0.46
MH-2-239	ethylenediamine ^b	r.t	51.96	6.61	0.73
MH-2-233		heat	60.02	4.49	2.80

^aMH-2-227, original nitrogen capacity : 3.35 mequiv/g ^c room temperature
^bMH-2-228, original nitrogen capacity : 6.31 mequiv/g ^d theoretical

phosphorylation of the aniline:GMA polymer was not successful both at room temperature and with heating, giving very low phosphorus capacities.

The EDA:GMA polymer could be phosphorylated comparatively well when it was heated, but the reaction did not take place at room temperature. Not all nitrogens in the EDA resin were phosphorylated in MH-2-233, but a 1.6:1 ratio of nitrogen to phosphorus capacity was achieved.

Mannich reactions

The purpose of the control reactions is to find the ideal reaction time, catalyst amount and lowest reaction temperature as possible, maintaining the maximum extent of reaction. The extent of reaction can be measured by the nitrogen capacity of the products since they all contain nitrogen. After completion of the reaction, the nitrogen capacity per g polymer should be decreased to 1.92 milliequivalents/g from the original nitrogen capacity, 4.40 mequiv/g, of the primary amine resin (MH-2-244, 0.180-0.250mm).

According to Table 3.3, in the first reaction set with DEM in which the acid catalyst amount was varied, not much difference in nitrogen capacity was found when using 0.1 to 0.5ml acid. With 0.1ml acid catalyst maintained, reaction time and temperature were then controlled. An 80°C reaction temperature gave results that were remarkably independent of reaction time though, in retrospect, it would have been interesting to determine what the results would have been with a 0.5 h reaction time. The lowest temperature that we could get reaction was

Table 3.3**Primary amine Polystyrene-Based Gel Reaction with Diethylmalonate(DEM)**

resin	H ₂ SO ₄	rxn time	rxn temp	N cap(mequiv/g)
MH-2-250 ^a	0.1 ml	16 hrs	80°C	2.92
	0.25	"	"	2.70
	0.5	"	"	2.97
	1.0	"	"	3.13
MH-2-260 ^a	0.1	2	80	2.56
	"	4	"	2.79
	"	8	"	2.84
	"	24	"	2.88
	"	48	"	2.88
MH-2-268 ^a	"	8	60	2.88
	"	8	40	3.99
	"	24	r.t	4.27
MH-2-272 ^a	"	8	50	3.56
	"	24	40	3.42
MH-2-281 ^b	"	9	60	2.95
	"	25	50	2.69

^a bead size 0.180-0.250mm, theoretical nitrogen capacity : 1.92 mequiv/g^b bead size 0.075-0.150mm, theoretical nitrogen capacity : 2.53 mequiv/g

60°C at 8 hours (MH-2-268, 0.180-0.250 mm) or 50°C at 25 hours reaction time (MH-2-281, 0.075-0.150 mm). Reactions with smaller size beads (MH-2-281, 0.075-0.150 mm) resulted in a nitrogen capacity closer to the theoretical value (note: the smaller size beads had a higher -NH_2 capacity than the larger beads which leads to a higher final theoretical capacity after reaction with DEM).

In Tables 3.4 and 3.5, the results of the Mannich reaction with TIPP carried out with acid or base catalyst are summarized. When the reaction is complete, the nitrogen capacity should decrease to 3.16 milliequivalent/g from the original nitrogen capacity of 5.8 mequiv/g of the amine resin (MH-2-264, 0.075-0.150 mm).

The TIPP does not seem to react well with acid catalyst regardless of the catalyst amount or reaction temperature. According to Table 3.4, all phosphorus capacities are very low. If experimental error in the phosphorus elemental analysis were considered, the phosphorus capacities of all reactions seem to be almost zero, meaning no TIPP has reacted. It is thought that the TIPP cannot form the enol, which is the intermediate in the acid-catalyzed Mannich reaction. This is because the $2p$ orbital of the carbon and the $3p$ orbital of the phosphorus can not overlap as much as the $2p$ orbitals overlap in DEM due to their size difference.

The base-catalyzed Mannich reaction of TIPP, in which a carbanion but no enol forms was done using the NaOH, piperidine and DABCO. As can be seen in Table 3.5, better phosphorus capacities than in the acid-catalyzed

Table 3.4
Primary amine Polystyrene-Based Gel with TIPP^a (Acid-catalyzed)

resin ^b	H ₂ SO ₄	rxn time	rxn temp	Nitrogen cap. (mequiv/g)	Phosphorus cap. (mequiv/g)
MH-2-286	0.1 ml	8 hrs	60°C	3.78 (3.16) ^c	0.10(1.58)
MH-3-002	1 ml	"	80	3.40	0.29
	"	"	60	3.02	0.29
MH-3-010	"	"	80	3.56	0.16
	"	"	60	3.49	0.13

^a tetraisopropylmethylenediphosphonate

^b bead size : 0.075-0.150 mm

^c theoretical

Table 3.5
Primary amine Polystyrene-Based Gel with TIPP^a (Base-catalyzed)

resin ^b	base (g)	rxn time	rxn temp	nitrogen capacity (mequiv/g)	phosphorus capacity (mequiv/g)
MH-3-014	0.15 ^c	25 hrs	60°C	- (3.16) ^f	0.73(1.58)
MH-3-016	0.26 ^c	24	"	3.46	0.34
MH-3-018	1.54 ^c	"	"	4.59	0.18
MH-3-022-1	3.27 ^c	22	80	5.16	0.41
MH-3-022-2	0.30 ^d	"	"	4.55	0.60
MH-3-028	0.24 ^e	"	"	4.51	0.51

^a tetraisopropyl methylene diphosphonate

^b bead size : 0.075-0.150 mm

^c 50% NaOH

^d piperidine

^e DABCO

^f theoretical

reaction were achieved but still they were far from the theoretical value. The stronger bases, piperidine and DABCO, seem to work somewhat better as a catalyst than 50%NaOH.

As an alternative, TEPAc, which bears both the carbonyl and phosphoryl groups, was reacted with the amine resins with an acid catalyst. Despite the presence of the carbonyl group in TEPAc, the results were not successful as shown in Table 3.6. It is unclear why the reactions do not work well and this will be the subject of the future studies.

Phosphorous acid was reacted with the amine resin using varying conditions such as the acid amount, reaction time and temperature. The reaction went well with sulfuric acid and it was found that most of the amine groups reacted with two moles of phosphorous acid. The theoretical nitrogen and phosphorus capacities were calculated based on the structures assuming a 1:1 N:P ratio. As can be seen in Table 3.7, ratios of 1:1.4 to 1:1.9 were achieved under various reaction conditions. The lowest temperature to give reaction was 40°C and it gave a N:P ratio of 1:1.38 in the product.

Conclusion

The reactions of GMA polymer with aniline and ethylenediamine were successfully achieved with or without heating. Due to the poor nucleophilicity of *p*-nitrophenol, its reaction with GMA polymer could not be accomplished, but the reaction of sodium *p*-nitrophenoxide succeeded when it was heated.

Table 3.6
Primary amine VBC Gel with TEPAc^a

resin ^b	H ₂ SO ₄	rxn time	rxn temp	Nitrogen cap. (mequiv/g)	Phosphorus cap. (mequiv/g)
MH-3-080	1 ml	8 hrs	80°C	3.76(2.10) ^c	0.12(2.10)
	"	"	60°C	3.97	0.08
^a triethyl phosphonoacetate			^b bead size : 0.075-0.150 mm		^c theoretical

Table 3.7
Primary amine VBC Gel with Phosphorous acid

resin ^b	H ₂ SO ₄	rxn time	rxn temp	Ncap. (mequiv/g)	P cap. (mequiv/g)	N:P ratio
MH-3-020	0.5 ml	16 hrs	80°C	3.15 (3.39) ^c	5.58(3.39)	1: 1.77
	1.0	"	"	3.08	4.98	1:1.62
	2.0	"	"	2.98	4.69	1:1.57
	4.0	"	"	-	2.50	-
MH-3-025	0.5	2	"	3.01	5.13	1:1.70
	"	4	"	2.93	5.28	1:1.80
	"	8	"	2.87	5.37	1:1.87
	"	24	"	2.81	5.36	1:1.90
	"	47	"	2.92	5.35	1:1.83
MH-3-030	0.5	18	70	2.94	5.30	1:1.80
	"	"	60	3.19	5.13	1:1.61
MH-3-042	"	"	50	3.17	5.11	1:1.61
MH-3-037	"	24	40	3.34	4.60	1:1.38
	"	"	r.t	-	0.47	-

^b bead size : 0.075-0.150 mm ^c theoretical

The Mannich reactions of a polystyrene-based primary amine resin with DEM, TIPP, TEPAc and PhA were performed in various conditions. The DEM and PhA were successfully bonded to amines with formaldehyde and an acid catalyst. The reaction temperatures with DEM and PhA could be lowered to 50 °C and 40°C, respectively. TIPP was not able to react with the amine resin but is worth studying further in the future.

CHAPTER 4

Synthesis of Novel Polymer Ligands Using the Fries Rearrangement

Introduction

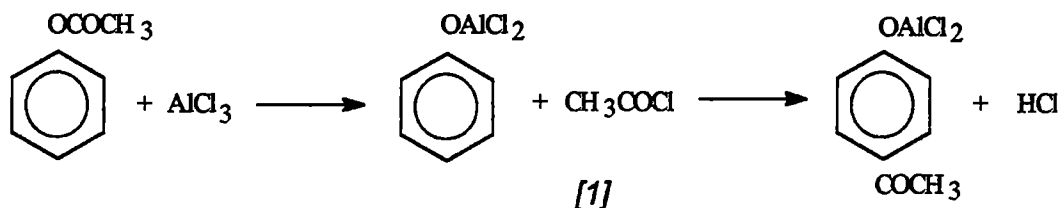
The Fries rearrangement is the acid-catalyzed conversion of a phenolic ester into a hydroxyketone. In the early 1900s, Fries observed the rearrangement of phenolic esters of chloroacetic acid to *o*- and *p*-chloro acetylphenols by using aluminum chloride.^{106,107} There were publications^{108,109,110} preceding those of Fries that reported the rearrangement of phenolic esters under the influence of Lewis acids. However, it was Fries who first recognized that this rearrangement represents a general reaction.

Since the discovery of this reaction, numerous experimental studies have been established in order to understand the mechanism of the Fries rearrangement. Nevertheless, the mechanism has not been completely solved and many attempts to solve the mechanism have resulted in considerable amounts of data, among which there are some contradictions and a fair amount of speculation about the mechanism.

The Fries rearrangement can be conducted thermally in the presence of a Lewis acid catalyst or photochemically¹¹¹ by irradiation with UV light. Among the many Lewis acids, including AlCl_3 ¹¹², TiCl_4 ¹¹³, SnCl_4 ¹¹⁴ and ZnCl_2 ¹¹⁵, the most common acid catalyst used is aluminum chloride. In addition, HF ¹¹⁶, H_3PO_4 ¹¹⁷,

$\text{AlCl}_3 \cdot \text{NaCl}$ ¹¹⁸ and BF_3 ¹¹⁹ are also found to show catalytic activity. Specific catalysts such as a zeolite¹²⁰ and a sulfonated cation exchange resin¹²¹ also have been reported.

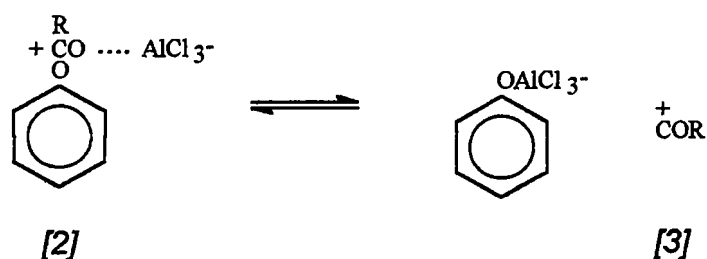
The issue of whether the mechanism of the Fries reaction is intermolecular or intramolecular has been argued for a long time. Skraup¹²² and Cox¹²³ assumed the Fries reaction to involve an intermolecular process in which an acyl chloride [1] is formed from the ester as an intermediate.



Auwers¹²⁴ proposed that the course of the reaction is intramolecular by the fact that a Fries reaction does not lead to the same products as those formed in a Friedel-Crafts acylation. Friedel-Crafts acylations, which are absolutely intermolecular reactions, generally give more *para*- than *ortho*-acylphenols. However, the contrasting fact that the Fries rearrangement can lead to large amounts of the *ortho*-acylphenol suggests the Fries reaction is more intramolecular.

The current proposal for the mechanism of the Fries reaction involves both inter- and intra-molecular paths.¹²⁵ *Para*-rearrangement is thought to be an

intermolecular reaction with the intermediate of the polarized coordination complex of the phenolic ester [2] or the oxocarbonium ion [3].¹²⁶

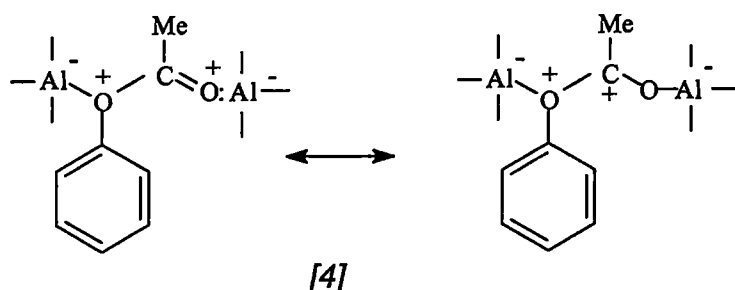


Ortho-rearrangement is thought to proceed by an intramolecular path wherein the intermediate is the polarized coordination complex of the ester and aluminum chloride.^{125,127} Decisive evidence is furnished by the experiments of Baltzly.¹²⁷ *m*-Cresyl acetate was made to rearrange in nitrobenzene containing diphenyl ether in two sets of experiments: one with equal amount of reactants and the other with the same amount of reactants in 5 times more nitrobenzene. The five-fold diluted reactant mixture resulted in a decrease in the yield of *para*-hydroxy ketone from 27% to 6.5%, and acylated diphenyl ether from 20% to 2~5%. In contrast, the yield of *ortho*-hydroxy ketone was maintained, and in fact, even slightly increased from 46% to 51%. The fact that only the *para*-product but not the *ortho*-product was affected by dilution shows that *para*-rearrangement and acylation of ether are intermolecular. It appears that *ortho*-rearrangement proceeds by the intramolecular mechanism.

Fries reactions typically give rise to mixtures of *ortho*- and *para*-substituted products. The proportion of *ortho*- and *para*- products is affected by a number of factors such as the structure of the phenolic ester,¹²⁸ reaction temperature,^{128,129} solvents¹³⁰ and the amount of catalyst.¹³¹ In the Fries reaction carried out at higher temperature, the yield of *ortho*-acetoxy ketone is greater than at lower temperature when other conditions are equal.^{128,129} As additional supporting evidence, 4-hydroxy-2-methylacetophenone (the *para*-isomer) is found to convert into the *ortho*-isomer when it is heated at 170°C with aluminum chloride.^{128b} This trend with temperature is certainly not true for all solvents. Rearrangement of phenyl acetate with aluminum chloride at 80°C gives an *ortho*-/*para*-product ratio of 0.64 in nitrobenzene, 2.4 in ethylene dichloride and 13.0 in petroleum ether.¹³² This illustrates that the polarity of solvent influences the *ortho*-/*para*- ratio in the Fries reaction, and more of the *para*- product is formed in solvents of greater polarity. Ogata attributes the effect of solvent on the *ortho*-/*para*- ratio to steric hindrance by solvation.^{132a} In less polar solvents in which solvation is difficult, rearrangement is predominantly intramolecular, giving the *ortho*-products. In more polar solvents where solvation is easy, the acylium ion is well solvated and attacks the least sterically hindered *para*- position.

The concentration of catalyst is another feature affecting the reaction rate and product distribution in the Fries reaction. It is known that the rate of disappearance of the ester increases with increasing catalyst concentration until

the molar ratio of catalyst to ester is 2.0 and levels off beyond this ratio.¹³¹ This is attributed to repulsion of the positive charges on the adjacent carbon and the oxygen atoms in the 2:1 complex of aluminum to ester [4]. This ratio also yields much more of the *para*- than the *ortho*-products because the *ortho*-position is sterically hindered with the bulky aluminum complex.



The purpose of this research is the synthesis of poly(acyl hydroxystyrene) by the Fries rearrangement of poly (4-acetoxystyrene) for application to metal ion separations. The Fries-rearranged product, poly(acyl hydroxystyrene), is further phosphorylated. As another set of resins for the metal ion study, the poly (4-acetoxystyrene) is hydrolyzed to give poly(hydroxystyrene), which is then further phosphorylated. The two types of poly(hydroxystyrene) resins are studied with Cs^+ in 0.1N and 1N NaOH solutions and the other two phosphorylated poly(hydroxystyrene) resins are studied with Cu^{2+} , Pb^{2+} and Cd^{2+} in 0.1N HNO_3 solutions.

Experimental

1. Resin Preparations

The experimental procedures of the polymerization and the functionalizations are described below and more detail will be given in Chapter 5. The reactions are illustrated in Figure 4.1 and 4.2.

Poly(4-acetoxystyrene)

Poly(4-acetoxystyrene) was prepared by suspension polymerization. The organic phase containing 4-acetoxystyrene, DVB (2 wt%) and BPO was combined with an aqueous phase containing poly(vinylalcohol), calcium chloride and distilled water and heated. The polymer was washed with distilled water and acetone and soxhlet extracted with toluene. The polymer beads were oven-dried to remove moisture and sieved.

Fries Rearrangement of Poly(4-acetoxystyrene) :PAHS

Method 1 : The completely dried poly(4-acetoxystyrene) beads were swelled in carbon disulfide for 3 hours and refluxed at 50°C with aluminum chloride. After reflux, a solution of HCl and water(1:1) were added slowly to break the aluminum complex. The Fries-rearranged beads were washed with water and acetone, soxhlet extracted with dioxane and dried in a 110°C oven. The beads were characterized by phenolic acid capacity and infrared spectroscopy.

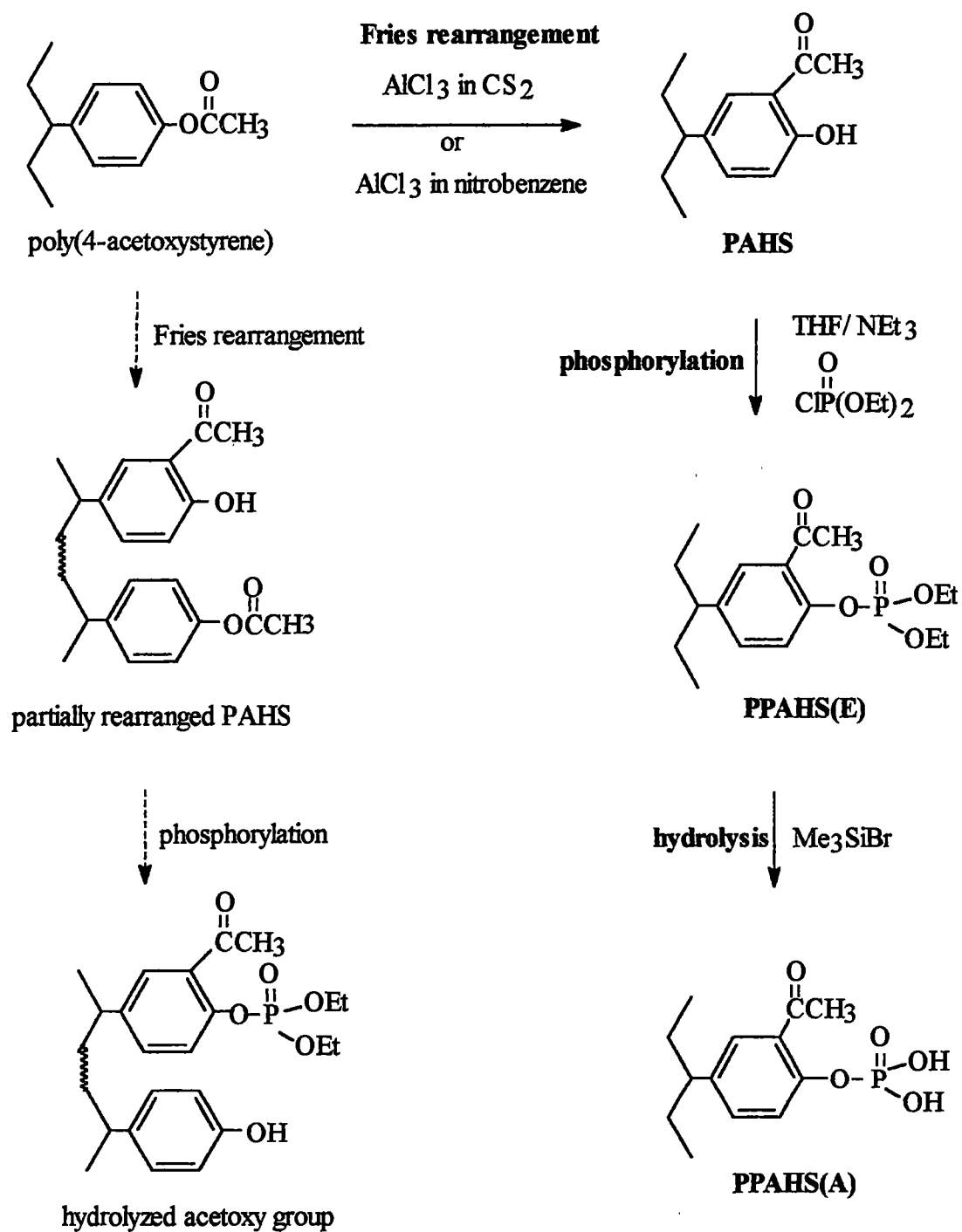


Figure 4.1
Fries Rearrangement and Phosphorylation

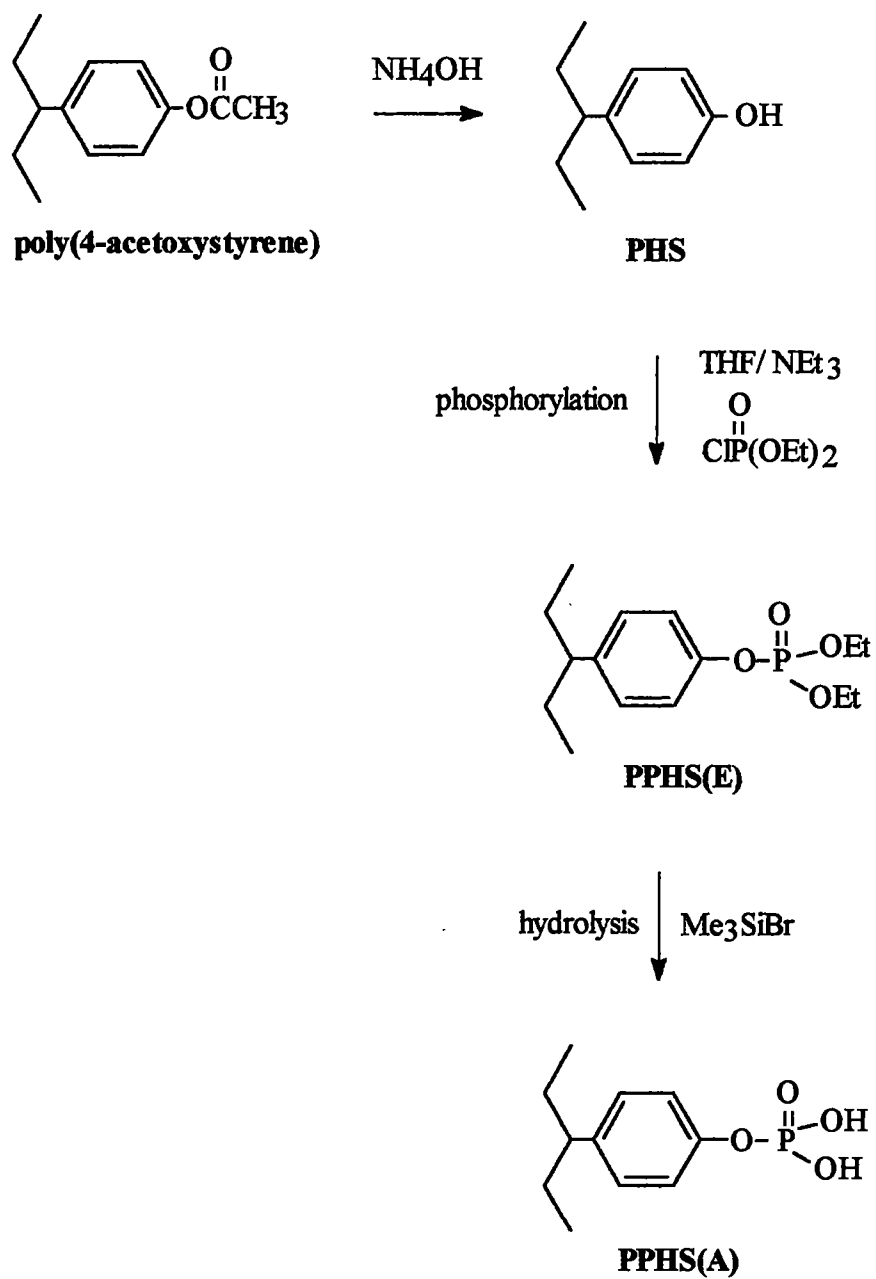


Figure 4.2

Poly(hydroxy styrene) and Phosphorylation

Method 2 : Dried poly(4-acetoxystyrene) beads were swelled in dry 1.5M AlCl_3 -nitrobenzene solution for 2 hours and nitrogen purged for 30 minutes to make sure all the moisture had been removed. After 45 hours of reflux at 70°C , $\text{HCl}/\text{water}(1:1)$ was added to the beads to break the aluminum complex and washed with ethanol, distilled water, acetone and methylene chloride. The beads were dried in the oven and characterized by phenolic acid capacity and infrared spectroscopy.

Phosphorylation of Poly(acylhydroxystyrene) : PPAHS

The Fries rearrangement product, poly(acylhydroxystyrene), was swelled in a solution of anhydrous THF and triethylamine for 1 hour. A solution of anhydrous THF and diethylchlorophosphate was then added over 5 minutes into the swelled beads while cooling in an ice bath. The reaction was performed in an ice bath for 2 hours and at room temperature for 24 hours. The product was washed with dioxane, 2% NaOH , water, ethanol and acetone and dried in the oven.

The phosphonate ester groups of the product were hydrolyzed to phosphonic acid groups by the reaction with trimethylsilylbromide in chloroform at room temperature for 24 hours. The reaction is illustrated in Figure 4.1. The products before and after hydrolysis were characterized by percent solid, phosphorus capacity and acid capacity.

Polyhydroxystyrene : PHS

Dried poly(4-acetoxystyrene) beads (10g) were refluxed with 200 ml ammonium hydroxide (29.7% assay) at 85°C for 7 hours and washed with water two times. Ammonium hydroxide (200 ml) was added to the washed beads and refluxed at 85°C for 17 hours. After reflux, the beads were washed with water three times. The same procedure was repeated one more time and the beads were conditioned with 1L of water, 1N NaOH, water, 1N HCl and water until neutral. The beads were characterized by phenolic acid capacity and infrared spectroscopy.

Phosphorylation of polyhydroxystyrene : PPHS

The phosphorylation of poly(hydroxystyrene) was performed in an identical manner as the phosphorylation of poly(acetyhydroxystyrene). The phosphonate ester and phosphonic acid products were characterized by percent solid, phosphorus capacity, phenolic acid capacity and infrared spectroscopy.

2. Metal ion studies

Metal ion solutions of $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ in 0.1N HNO_3 and $\text{Eu}(\text{NO}_3)_3$ in 1N HNO_3 solutions were prepared. CsNO_3 was also prepared in 0.1 and 1 N NaOH solutions. An amount of resins corresponding to 0.5 milliequivalent of functional group (phenolic acid capacity for hydroxystyrene resins and phosphorus capacity for phosphorylated hydroxystyrene resins) were

weighed and solvent exchanged with blank solutions. The resins were contacted with 10 ml of 10^{-4} N metal ion solutions for 24 hours and the remaining amounts of metal ion in the solutions were measured by atomic spectrometer. The results were reported in terms of % M^{n+} complexed and distribution coefficient (D).

The poly(hydroxystyrene) (PHS) and poly(acylhydroxystyrene) (PAHS) resins were studied with Cs^+ in 0.1 and 1 N NaOH solutions. Phosphorylated poly(hydroxystyrene) (PPHS) and poly(acylhydroxystyrene) (PPAHS) resins were contacted with Cu^{2+} , Pb^{2+} , Cd^{2+} and Eu^{3+} .

Results and Discussion

1. Synthesis and Characterization

Fries Rearrangement

The Fries reaction of poly(4-acetoxystyrene) should always be an *ortho* acyl migration because the *para* position is blocked in the polymeric structure (Figure 4.1). The Fries reaction was carried out in two different experimental procedures. In method 1, $AlCl_3$ is added to the polymer in CS_2 . Since the Fries reaction is very sensitive to moisture, in method 2, the 1.5 M $AlCl_3$ -nitrobenzene solution was prepared and dried over molecular sieves overnight to exclude any moisture before the reaction.

The degree of acyl transfer in the Fries rearrangement was measured by the phenolic acid capacity. According to the results in Table 4.1, method 1 turned out to be not as successful as method 2. Except for the first two resins (MH-2-

Table 4.1
Characterization of Polyacylhydroxystyrene ; Fries Rearrangement

	Resin	phenolic acid capacity (mequiv/g)	bead size (mm)	reaction time
Method 1 ^a	MH-2-217	3.25 ^c	not specified	17 hrs
	MH-2-274	2.76	0.150-0.250	17 hrs
	MH-3-062	1.65	0.075-0.150	20 hrs
	MH-3-066	1.38	0.425-0.840	72 hrs
	MH-3-073	1.83	>0.425	5 days
Method 2 ^b	MH-3-088	3.44	0.250-0.425	45 hrs
	MH-3-091	2.32	0.150-0.250	4 days

^a Method 1 : AlCl_3 in CS_2 , ^b Method 2 : dried 1.5 M AlCl_3 in nitrobenzene

^c theoretical phenolic acid cap. : 5.86 mequiv/g

217and -274), the other three Fries reactions with various bead sizes and reaction times were not successful and their experimental acid capacities were far from the theoretical value. For the purpose of completing the Fries reaction, the partially Fries rearranged polymers were re-reacted with AlCl_3 and excellent phenolic acid capacities were achieved as shown in Table 4.2.

Evidence for the Fries reaction was obtained from infrared spectroscopy. Reaction progress can be easily followed by the disappearance of the ester peak ($\sim 1750\text{cm}^{-1}$) and the appearance of the ketone peak ($1650\sim 1690\text{ cm}^{-1}$) in the IR spectra. The products from method 2 show much larger peaks of ketone than ester. The IR's of MH-088 and -091, which are the second Fries reaction products, indicate almost 100% completion of the reaction (Fig. 4.3 – 4.6).

Phosphorylation of poly(acylhydroxystyrene)

The Fries rearranged poly(acylhydroxystyrene) was phosphorylated to phosphonate ester (PPAHS(E)) and hydrolyzed to phosphonic acid (PPAHA(A)) (Figure 4.1). The characterization results are summarized in Table 4.3 and 4.4. The theoretical phosphorus capacity of the PPAHS(E) was calculated based on the precursor's (PAHS) experimental phenolic acid capacity. After complete phosphorylation of the hydroxy groups in PAHS, the phenolic acid capacity of PPAHS(E) should be zero. The phosphorus capacity of MH-2-278 showed the phosphorylation was successful. However, its phenolic acid capacity was 3.19 milliequivalent/g. This unusually high phenolic acid capacity is thought to occur

Table 4.2
Polyacylhydroxystyrene from Second Fries Rearrangement

Resin	precursor	phenolic acid cap. (mequiv/g)	bead size (mm)	reaction time
Method 2 ^a				
MH-3-082	MH-2-274	5.10 ^b	0.150-0.250	45 hrs
MH-3-092	MH-3-088	5.19	0.250-0.425	45 hrs

^a Method 2 : dried 1.5 M AlCl₃ in nitrobenzene

^b theoretical phenolic acid cap. : 5.86 mequiv/g

Table 4.3
Characterization of Phosphorylated Polyacrylhydroxystyrene (ester)

Resin	precursor	Phosphorus capacity (mequiv/g)	Phenolic acid capacity (mequiv/g)
MH-2-246	MH-2-217	1.21 (1.87) ^a	-
MH-2-278	MH-2-274	1.36 (1.59)	3.19 (zero)

^a theoretical

Table 4.4
Characterization of Phosphorylated Polyacrylhydroxystyrene (acid)

Resin	precursor	% solid	Phosphorus cap. (mequiv/g)	Acid cap. (mequiv/g)	Phenolic acid cap. (mequiv/g)
MH-2-248	MH-2-246	27.19	1.34 (1.51) ^a	8.98 (3.03)	8.98
MH-2-283	MH-2-278	40.20	1.60 (1.70)	7.10 (3.39)	7.97

^a theoretical

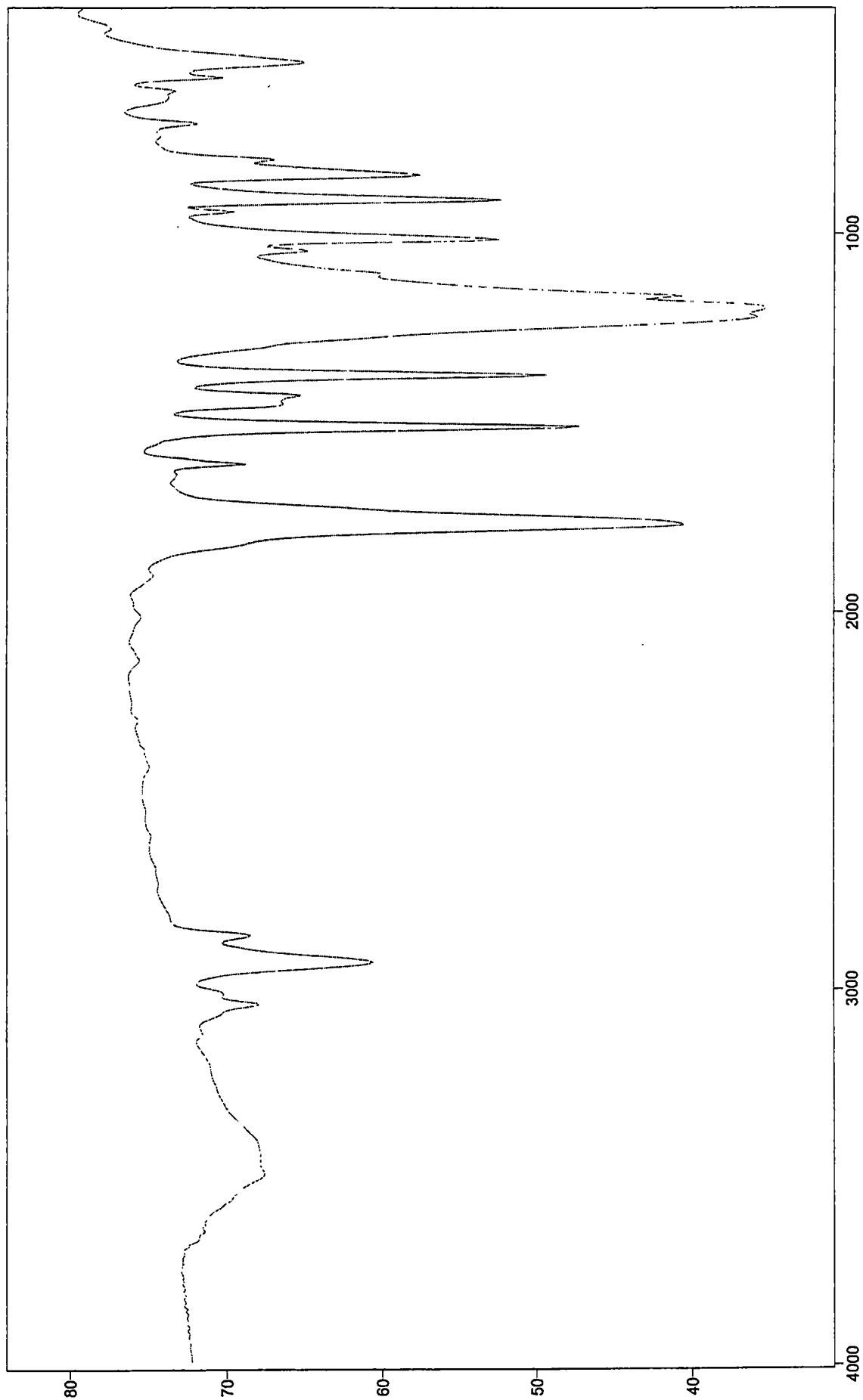


Figure 4.3. IR Spectrum of Poly(4-acetoxystyrene) (MH-3-050)

Transmittance / Wavenumber (cm-1)

Background Peak

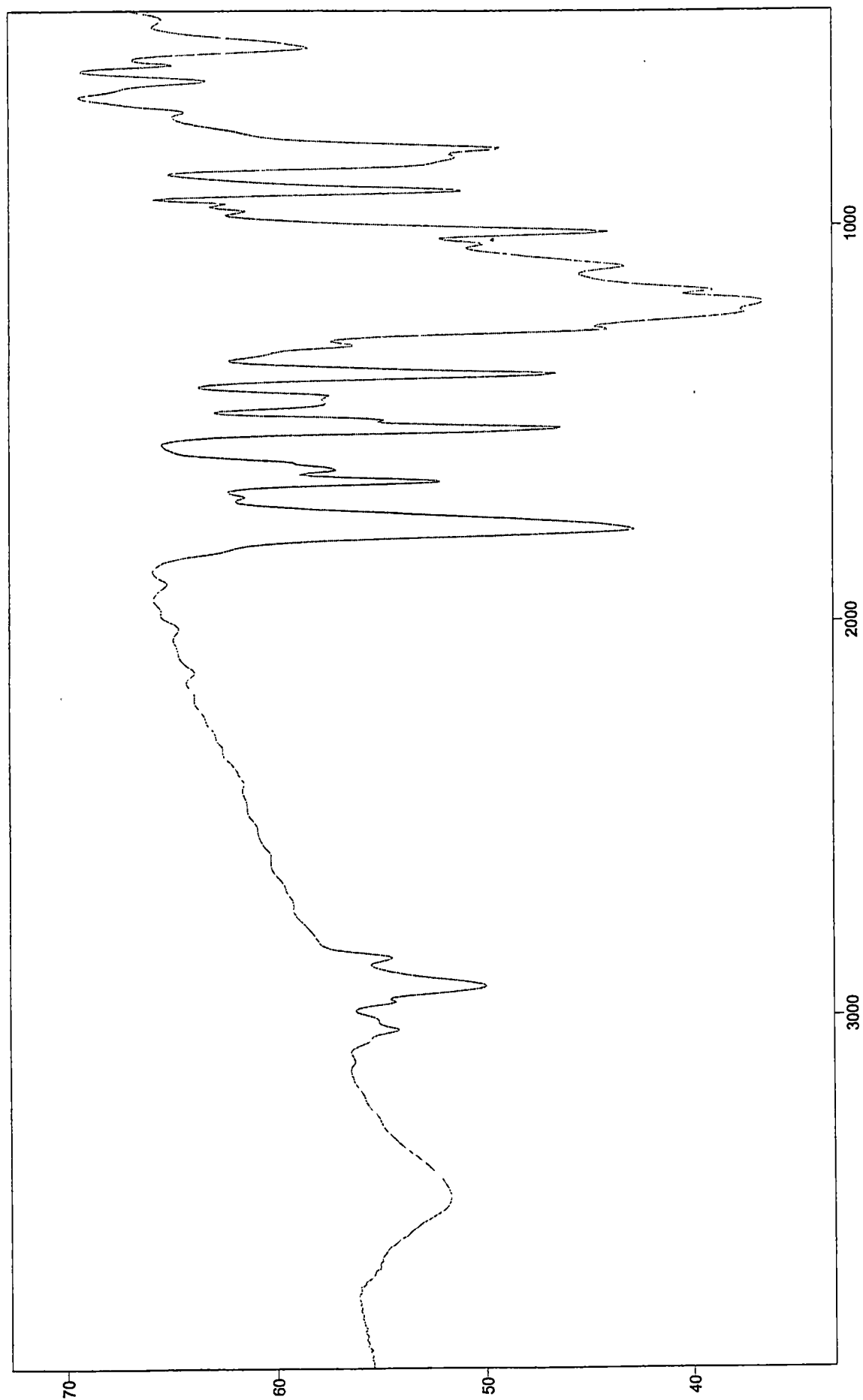


Figure 4.4. IR Spectrum of Poly(acylhydroxystyrene) (MH-3-062)

Transmittance / Wavenumber (cm⁻¹)

Background Peak

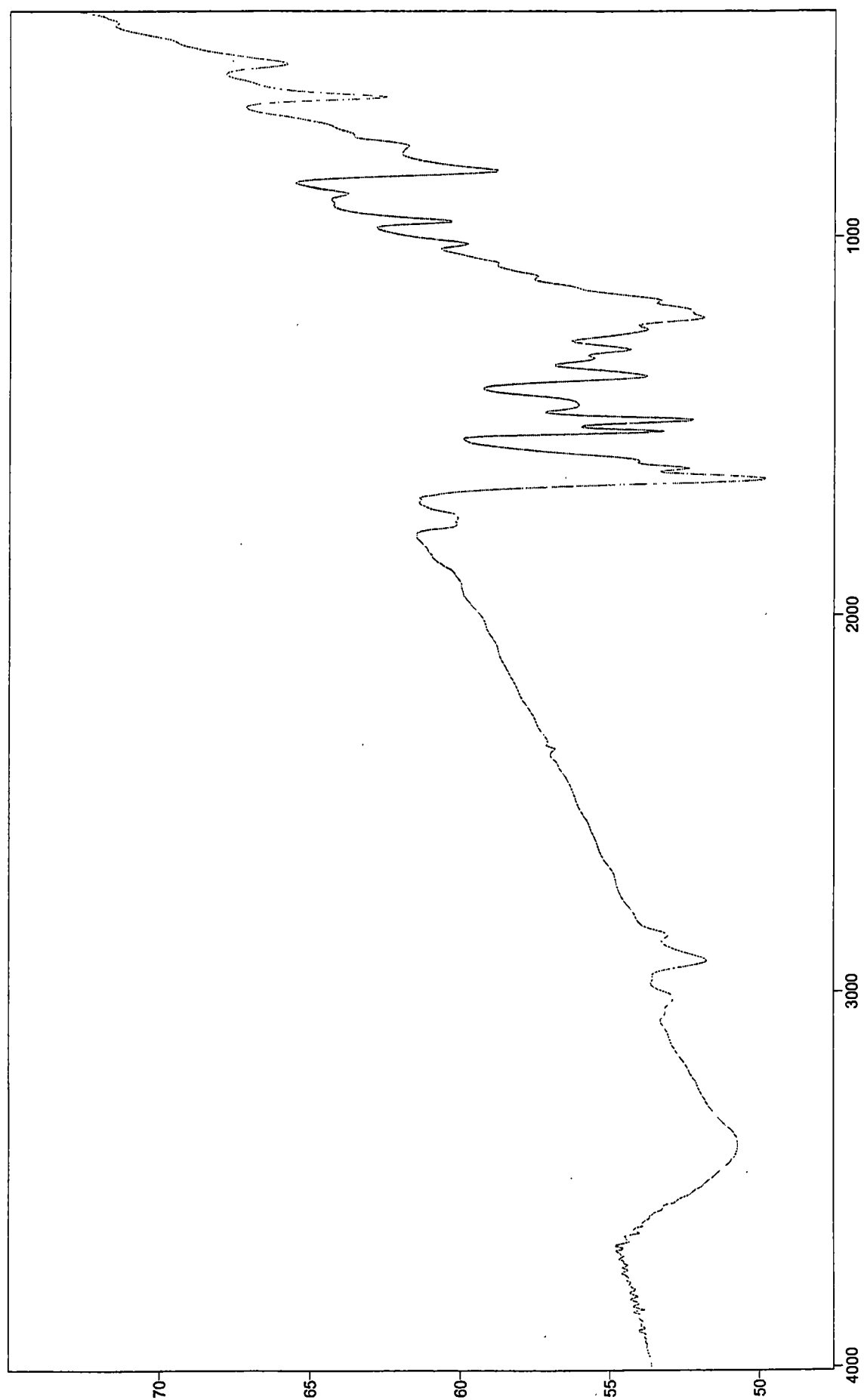


Figure 4.5. IR Spectrum of Poly(acylhydroxystyrene) (MH-3-092)

Transmittance / Wavenumber (cm-1)

Background Peak

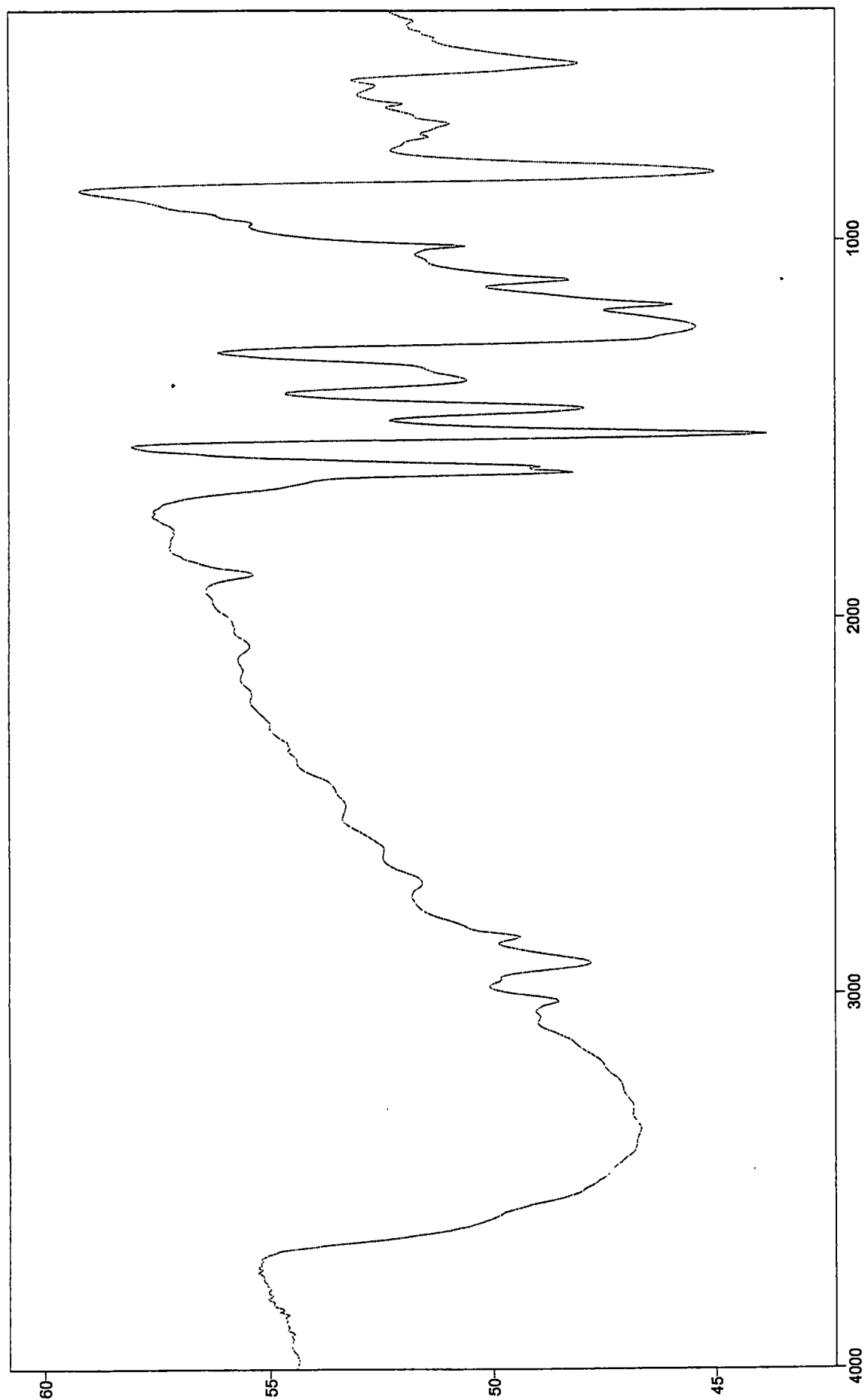


Figure 4.6. IR Spectrum of Poly(hydroxystyrene) (MH-3-038)

Transmittance / Wavenumber (cm⁻¹)

because the precursor of MH-2-278, MH-2-274, is actually partially Fries-rearranged and many of the unrearranged acetoxy groups still remain. The acetoxy groups may be hydrolyzed during the phosphorylation reaction. This is illustrated in Figure 4.1. This assumption can also be supported by the characterization results of PAHS(A) (Table 4.4).

The phenolic acid and regular acid capacities are meant to be different (regular acid capacity is for the characterization of phosphonic acid groups and the phenolic acid capacity is for the hydroxy group in the styrene). However, the experimental phenolic acid and regular acid capacity of the PPAHS(A) resin showed the same value. It seems that either acid capacity includes both the phenolic and phosphonic acid capacities together. After completion of the hydrolysis of the ester groups, the acid capacity of the phosphonic acid group should be double the phosphorus capacity, but the acid capacity of PPASA(A) showed a higher value than expected. This higher acid capacity is thought to come from the hydrolyzed acetoxy groups in polymer.

Poly(hydroxystyrene) and phosphorylation

The properties of poly(hydroxystyrene) prepared by hydrolysis of poly(4-acetoxystyrene) (Figure 4.2) and the phosphorylated poly(hydroxystyrene) are reported in Table 4.5. Successful hydrolysis (82% functionalized) from poly(4-acetoxystyrene) to poly(hydroxystyrene) was accomplished according to the phenolic acid capacity of PHS resin. The low phenolic acid capacity (0.83

Table 4.5
Characterization of Polyhydroxystyrene and Phosphorylated Polyhydroxystyrene

	Resin	%solid	Phenolic acid capacity (mequiv/g)	Phosphorus capacity (mequiv/g)
PHS ^a	MH-3-038	40.55	6.49 (7.88) ^d	-
PPHS(E) ^b	MH-3-076	-	0.83 (0)	3.91 (3.04)
PPHS(A) ^c	MH-3-080	26.20	7.97 (7.78)	4.78 (3.89)

PHS ^a : polyhydroxystyrene

PPHS(E) ^b : phosphorylated polyhydroxystyrene(ester)

PPHS(A) ^c : phosphorylated polyhydroxystyrene(acid)

^d theoretical

mequiv/g) of phosphorylated poly(hydroxystyrene) (PPHS(E)) indicates almost completed phosphorylation of the hydroxy groups. The phosphorus capacity was in good agreement with the theoretical value. The hydrolyzed PPHS(A) also showed good phosphorus and acid capacities.

2. Metal ion studies

A large amount of radioactive Cs^+ produced from nuclear processing has been stored in huge tanks for a long time. Thus, the removal of Cs^+ from water is important and the proper polymeric ligands for the complexation with Cs^+ needs to be studied.

The poly(hydroxystyrene) (PHS) and poly(acylhydroxystyrene) (PAHS) resins were contacted with Cs^+ in 0.1 and 1N NaOH and the results are summarized in Table 4.6. The PHS showed higher complexing ability than PAHS in 1N NaOH, but neither of the two polymers shows good complexation with Cs^+ . Compared to the PHS resin, PAHS (MH-274) showed low complexation ability. The acyl groups adjacent to the hydroxyl groups in PAHS do not seem to help the complexation of hydroxyl groups with Cs^+ .

The phosphorylated poly(acylhydroxystyrene) (Table 4.7) and poly(hydroxystyrene) (Table 4.8) were also contacted with Cu^{2+} , Pb^{2+} and Cd^{2+} . The PPHS(A) shows better complexation with all metal ions than PPAHS(A). Due to the low degree of functionalization of PPAHS(A) resin, the D values of PPAHS(A) were very low even with the comparatively good % M complexed.

Table 4. 6
Cs⁺ ion Uptake in 0.1N/ 1N NaOH by Polyhydroxystyrene and Polyacylhydroxystyrene

	PHS ^a (SN-4-163D)	PAHS ^b (MH-2-274)
1N NaOH	28.76 % ^c (29.61) ^d	8.0% (9)
0.1N NaOH	-	6.57% (7)

^a polyhydroxystyrene ^b polyacylhydroxystyrene
^c % M complexed ^d D

Table 4.7
Metal Ion Uptake by Phosphorylated Polyacrylhydroxystyrene (acid)

	<u>0.1N HNO₃ (MH-2-248)</u>		<u>1N HNO₃ (MH-2-283)</u>
	Cu²⁺	Pb²⁺	Cd²⁺
% M complexed	49.5 %	63.0%	47.31%
D	26.2	45.6	26.4
			Eu³⁺
			34.56%
			17

Table 4.8
Metal Ion Uptake by Phosphorylated Polyhydroxystyrene (acid) (SN-4-178)

0.1N HNO₃	Cu²⁺	Pb²⁺	Cd²⁺
% M complexed	58.29 %	75.10%	62.11%
D	124.3	268.3	145.6

Conclusion

A series of experiments have been performed in order to achieve the Fries rearrangement on the polymer. Unlike in small molecule analogues, the Fries reaction in the polymeric system is affected by many factors including polymer particle size, rigidity of polymer matrix, solvent and so on. The complete removal of moisture from the reaction and the proper selection of solvent are crucial in the Fries rearrangement. Further metal ion studies using the completely Fries-rearranged PAHS need to be done in the future.

CHAPTER 5

EXPERIMENTAL PROCEDURES

Copolymer Synthesis

Every copolymer was synthesized by suspension polymerization with 2%DVB crosslinking and was microporous (gel). All chemicals are reagent grade from Aldrich unless otherwise noted.

Poly(vinylbenzyl chloride) (VBC)

The organic phase was prepared by thoroughly mixing 286.09g VBC, 11.1g DVB (55.4% purity) and 3g benzoyl peroxide(BPO). This solution was sparged with nitrogen for five minutes to remove dissolved oxygen. The aqueous phase was prepared by dissolving 1.44g pharmagel and 158.25g distilled water. Once dissolved, a solution containing 17.85g poly(diallyldimethylammonium chloride) (PADMAC) in 316.5g distilled water was added and mixed thoroughly. The pH was adjusted to 10.3 using 50% NaOH and the aqueous solution was sparged with nitrogen for 10 minutes. The aqueous phase was transferred to a 1000ml round bottom flask which was equipped with a condenser, nitrogen inlet, thermometer with therm-o-watch (a temperature control device) and overhead stir apparatus. The height of the stir blade was adjusted so the top edge was just above the organic layer. The stir motor was started from low stir speed and

increased to the proper speed for proper bead size (stir speed of 390 rpm for beads that sieve between 40 and 60 mesh screens). The stir motor was then turned off for one minute, the bead size was visually inspected and the stir speed adjusted accordingly. This "on/off" cycle was repeated two additional times. The reaction was heated to 80°C over a period of two hours corresponding to an increase of 7°C every 15 minutes. The reaction was further heated at 80°C for 10 hours. In order to finish-off the polymerization, approximately 100ml of distilled water was added and the mixture was allowed to reflux with stirring for two hours. Once cooled, the solution was removed using a glass frit filter tube. The beads were washed with 10^{-4} N HCl while stirring for 15 minutes and then washed with water three more times. The beads were Büchner dried, soxhlet extracted with toluene for 17 hours, placed in a drying dish, and allowed to air dry prior to sieving.

Poly(vinylbenzylchloride-co-styrene) (VBC/STY, 0.18/0.82)

The 2% cross-linked VBC/STY beads were prepared in a manner identical to that of VBC described above. In the organic phase, 69.66g VBC and 216.56g styrene were added instead of VBC. The rest of the procedure was performed as with the VBC gel.

Poly(vinylbenzylchloride-co-methyl methacrylate) (VBC/MMA, 0.18/0.82)

The 2% cross-linked VBC/MMA beads were prepared the same way as VBC except for the organic phase : 71.71g VBC and 216.6g MMA were added as monomers with DVB and BPO in the organic phase.

Poly(4-acetoxystyrene)

The 2% crosslinked acetoxystyrene beads were prepared in a manner identical to that of the VBC with the following exceptions. (This is for the preparation of 10g of beads). In an aqueous phase, 0.42g polyvinylalcohol(PVA), 6.67g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 26.67g distilled water were added. The organic phase contained 9.5g 4-acetoxystyrene, 0.2g DVB and 0.3g BPO. The reaction was heated at 60 °C for 30 minutes, 70 °C for 30 minutes, 80 °C for 1 hour and 85°C for 12 hours. The reaction as further heated at 100°C for 2 hours.

Poly(glycidyl methacrylate) (GMA)

The 2% cross-linked GMA polymer was prepared in a manner identical to that of the VBC with the following exceptions. 19.51g GMA, 0.42g DVB and 0.16g AIBN (azobisisobutyronitrile) were added in the organic phase and 0.45g PVA (polyvinylalcohol), 4.2g NaCl and 92.5g of distilled water were used in the aqueous phase. The reaction was heated at 50°C for 30 minutes, 60°C for 30 minutes, 70°C for an hour and 80°C for one hour. The reaction was continued at 90°C for 5 hours.

Functionalization of Copolymers

Gabriel Synthesis (primary amine resins)

VBC beads (8 g, 0.052 mol) were swelled in 80 ml of dimethylformamide (DMF) overnight. Next day, 40g (0.216 mol) of potassium phthalimide in 320 ml DMF was added into the swelled beads in a three neck flask fitted with an overhead stirrer, condenser and thermometer. The reaction was heated at 80°C for 17 hours. The solution was removed from the reactor and the beads were stirred with approximately 300ml of distilled water. The solution was removed and washed with water two more times to make sure all the phthalimide dissolved. The beads were solvent exchanged with methanol four times, büchner dried, transferred into a flask with 100ml methanol, and 20ml of hydrazine with 4ml distilled water was added. After refluxing at 65°C for 17 hours, the beads were washed with distilled water four times and 200ml conc. HCl added for the hydrolysis. The hydrolysis was carried out at 90°C for 17 hours and the HCl solution was removed by a glass frit filter tube. The beads were stirred with 300ml 2N NaOH for 2 hours and washed with water four times.

Amine resins

(EDA, DETA, TEPA and PEHA from VBC, VBC/STY and VBC/MMA)

All amine resins were prepared identically. A ten fold stoichiometric excess of the appropriate amine relative to VBC copolymer was used in each

synthesis. In one example, 10g (0.063mol) VBC gel was weighed into a three neck round bottom flask fitted with an overhead stirrer, condenser and stopper. A solution of 40ml (0.6mol) ethylenediamine in 150ml dioxane was added to the flask and the mixture was heated at reflux for 17 hours. Once cooled, the solution was removed by a glass frit filter tube and washed with a dioxane:water (1:1) solution twice and with distilled water twice. The beads were then conditioned with 1L of water, 1N HCl, water, 1N NaOH and water until neutral.

Phosphorylation of Amine Resins

All phosphorylations of the amine resins were performed in an identical manner. In one example, 4.25g (0.017 mol) of beads are weighed into a three neck round bottom flask fitted with an overhead stirrer, condenser and thermometer. 12ml (0.15mol) formaldehyde(37% in water), 8 g (0.098 mol) H_3PO_3 and 40 ml 20% HCl solution were added into the flask and heated at 90°C for 17 hours. The beads were washed four times with water and conditioned with 1L water, 1N NaOH, water, 1N HCl and water until neutral.

Arbuzov Reaction (phosphonic acid resins)

This is the reaction of VBC, VBC/STY or VBC/MMA gel beads to give the phosphonate ester ligand followed by hydrolysis to the phosphonic acid. 20 g of dry VBC resin was weighed into a 500 ml three neck round bottom flask equipped with an overhead stirrer, condenser and stopper. Approximately 300ml

triisopropyl phosphite was added and the mixture was refluxed for 17 hours. The excess phosphite solution was removed and 300 ml of concentrate HCl was added followed by reflux for 24 hours. The beads were washed with water four times and conditioned with 1L water, 1N NaOH, water, 1NHCl and water until neutral.

GMA Polymer with Nitrogen-containing compounds

The reactions of GMA polymer with *p*-nitrophenol, sodium *p*-nitrophenoxide, aniline and ethylenediamine were carried out in an identical manner. The reaction with *p*-nitrophenol was performed as follow. 0.28g (1.92 mmol) GMA polymer, 1.33g (9.57 mmol) *p*-nitrophenol and 10g H₂O were weighed into a flask equipped with an overhead stirrer, condenser and thermometer. Two reaction sets were prepared for each compound. One set was at room temperature with only stirring and the other set was heated at 80°C for 17 hours. The products were washed with methanol four times, oven dried, and characterized by IR and nitrogen capacity.

Phosphorylation of aniline and ethylenediamine/GMA polymers

The phosphorylations of GMA amine resins were carried in the same way as that of the VBC amine resins in Chapter 2. The reactions were carried out at two reaction temperatures: one at room temperature and the other with heating to

90 on the variac. The products were characterized by nitrogen capacity and phosphorus capacity.

Mannich Reactions

Mannich reactions of primary amine VBC resins were performed with diethylmalonate (DEM), tetraisopropylmethylene diphosphonate (TIPP), triethyl phosphonoacetate (TEPAc) and phosphorus acid (PhA) in identical procedures. The reaction of DEM was carried out as follows. The primary amine VBC resin (0.5 g, 2.202 mmol), 1.42g (17.6 mmol) formaldehyde (37% aqueous solution) and 2.82g (17.6 mmol) diethylmalonate were weighed into a vial. The reactions with varying H_2SO_4 , reaction time and reaction temperature were heated in an oil bath. The products were washed with acetone twice and distilled water twice and dried in a 110°C oven. The beads were characterized by nitrogen capacity and IR.

Fries Rearrangement of Poly(4-acetoxy styrene)

Method 1 : 5 g (0.029 mol) oven dried poly(4-acetoxystyrene) beads were swelled in 50 ml CS_2 for 3 hours. 20g (0.145 mol) AlCl_3 was added into the flask containing the swelled beads and equipped with an overhead stirrer, condenser and thermometer. The mixture was heated at reflux for 17 hours. After the reaction was cooled, 80 ml of $\text{HCl}/\text{H}_2\text{O}$ (1:1) solution was very slowly added into the product to break the aluminum complex (very exothermic). The product was

washed with distilled water twice and with acetone twice. The beads were soxhlet extracted with dioxane for 10 hours and dried at room temperature. The products were characterized by phenolic acid capacity and IR.

Method 2 : Oven dried poly(4-acetoxystyrene) beads (4.76 g, 0.028 mol) were swelled in 90 ml (0.14 mol) 1.5 M AlCl_3 -nitrobenzene solution for 2 hours. The mixture was swept with nitrogen for 30 minutes and refluxed at 70°C for 45 hours with a drying tube attached to the end of the condenser. After the reaction was cooled, 80 ml of $\text{HCl}/\text{H}_2\text{O}(1:1)$ solution was very slowly added to the flask to break the aluminum complex (very exothermic). The products were washed twice with ethanol, then distilled water, acetone and methylene chloride and dried in the oven. The products were characterized using IR and phenolic acid capacity.

Poly(hydroxystyrene): PHS

Poly(hydroxystyrene) was obtained by the hydrolysis of poly(4-acetoxystyrene). 10 g poly(4-acetoxystyrene) was added to a flask containing 200 ml NH_4OH (29.7% assay) and the mixture was heated at 85°C for 7 hours. The solution was pulled off and the beads were washed twice with distilled water, followed by the addition of 200 ml NH_4OH and reflux at 85°C for 17 hours. The solution was pulled off and the beads were washed with distilled water three times. These two steps were repeated one more time. The beads were washed with distilled water and conditioned with 1 L water, 1N NaOH , water, 1N HCl and

water until neutral. The products were characterized with the phenolic acid capacity and IR.

Phosphorylation of Poly(acylhydroxystyrene) or Poly(hydroxystyrene)

The phosphorylation methods of the two polymers are identical. The hydroxy group is converted to phosphonate ester and hydrolyzed to phosphonic acid. The reaction procedure from PHS to PPHS is described below.

Poly(hydroxystyrene) 2g was swelled in 49.3ml anhydrous THF and 23 ml dry triethylamine in a three-neck round bottom flask for 2 hours. The swelled beads were swept with nitrogen for 30 minutes and the flask fitted with an overhead stirrer, condenser and addition funnel. A solution of 16 ml anhydrous THF and 13.2 ml diethylchlorophosphate was added to the addition funnel. The solution in the addition funnel was dropped into the flask over 5 minutes with stirring while the flask set in an ice bath. The mixture was held in the ice bath with constant stirring for 2 hours. The ice bath was removed and the reaction was continued at room temperature for 24 hours. The solution was pulled off and the beads were then washed with dioxane twice and 2% NaOH, distilled water, ethanol and acetone each time. The beads were oven dried prior to hydrolysis. The oven dried phosphorylated poly(hydroxystyrene) ester (PPHS(E)) (3g) was swelled in 110ml chloroform for 1 hour and nitrogen swept for 30 minutes. 13ml trimethylsilyl bromide was quickly added into the mixture and nitrogen introduced for 15 minutes with continuous stirring. The nitrogen inlets in the flask were then

replaced by stoppers and the mixture was kept stirring for 22 hours at room temperature. The solution was pulled off from the reaction and the beads were then washed with acetone twice and distilled water twice. The product was characterized by the phenolic acid capacity, phosphorus capacity and IR.

Characterization Method

Percent Solids

An oven dried vial was accurately weighed on the analytical balance. Wet resin was büchner dried at 720 mmHg for 5 minutes and accurately weighed into the vial. The resin was dried in a 110°C oven for 17 hours. The resin was cooled in a desiccator then weighed and the weight of the dried resin obtained.

$$\% \text{ solid} = \frac{\text{dry wt. of sample}}{\text{wet wt. of sample}} \times 100$$

Nitrogen Capacity

A sample of oven dried resins (0.2-0.3g) was accurately weighed into a 500ml three neck round bottom flask equipped with a long jacket condenser and two stoppers. 0.25g CuSO₄, 10g K₂SO₄ and 25 ml conc. H₂SO₄ were added to the flask with some boiling chips. The mixture was heated gently (variac at 50) with a heating mantle for one hour and the heat was increased to 85 on the

variac. The mixture was heated for an additional 16 hours until the mixture became a transparent light blue. After cooling, the inside of the condenser was rinsed into the flask with a small amount of water. A stir bar and 100ml of distilled water were added. The condenser was replaced with a distillation apparatus with a funnel attached at the end and a 250 ml addition funnel. 50.0 ml 0.1N standard HCl solution was pipetted into a 600ml beaker and the beaker was placed right below the funnel in the distillation apparatus. The funnel is placed in the HCl solution in such a way that any gas coming off from the distillation would bubble into the solution. 150ml 6N NaOH was transferred to the addition funnel and the funnel was stoppered. The NaOH solution was added over 5 minutes with stirring. With the stopcock fully open, the mixture was heated at a variac setting of 95. The distillation was continued for an hour at which the distillate was checked with pH paper to confirm a neutral pH. The funnel was rinsed into the beaker with distilled water and the HCl solution was transferred to a 250ml volumetric flask. The solution was diluted to the mark with distilled water and a 50 ml aliquot was pipetted out for the titration with 0.1N standardized NaOH solution using bromocresol green indicator. The nitrogen capacity was calculated using the equation:

$$\text{nitrogen capacity (mequiv/g)} = \frac{(50\text{ml HCl}) (N \text{ HCl}) - 5 (\text{ml NaOH}) (N \text{ NaOH})}{\text{g dry resin}}$$

Phosphorus Capacity

A 0.020 to 0.025g sample of oven dried resin was accurately weighed into a 125 ml Erlmeyer flask. 400 μ L 0.5M CuSO₄ and 10ml conc. H₂SO₄ were added and the mixture was heated on a hot plate setting at 5 for two hours. The mixture was cooled to room temperature at which time 75ml H₂O and 2.0g K₂S₂O₈ were added. The mixture was heated for another two hours on the hot plate setting at 3. The solution was cooled and 50% NaOH solution was added slowly with stirring until it turned light brown. A 2% H₂SO₄ solution was added until the solution was clear again and checked with pH paper to ensure the neutrality of the solution. The solution was transferred quantitatively to a 100 ml volumetric flask and diluted to the mark with distilled water. A 25 ml aliquot was transferred to a 50 ml volumetric flask to which 10 ml vanadate-molybdate solution was added. The solution was diluted to the mark with distilled water and allowed to develop for 15 minutes showing a yellow color. The absorbance was measured on a Baush and Lomb Spectronic 21 which was zeroed at 470 nm with a blank solution containing vanadate-molybdate solution. An absorbance and concentration curve was generated using K₃HPO₄ standard and the slope and y-intercept of the line were calculated. The phosphorus capacity was calculated using the equation :

$$\text{mg P} = \frac{(\text{absorbance}) - (\text{y-intercept})}{(\text{slope})}$$

$$\text{phosphorus capacity (mequiv/g)} = \frac{4 \text{ (mg P)}}{(30.974 \text{ mg/ mequiv}) (\text{g dry resin})}$$

Regular Acid Capacity

A 1.0 to 1.5g sample of Büchner dried resin was accurately weighed into a 250 ml Erlenmeyer flask with a ground glass stopper. 200.0 ml of 0.1 N NaOH standard solution was pipetted into the flask with a stir bar. The mixture was stoppered and stirred on a multipoint stirplate at 350rpm for 17 hours. Two 50.0 ml samples were withdrawn and titrated with 0.1 N HCl standard solution with phenolphthalein indicator. The acid capacity was calculated using the equation:

$$\text{acid capacity (mequiv/g)} = \frac{(\text{ml NaOH}) (\text{N NaOH}) - 4 (\text{ml HCl}) (\text{N HCl})}{\text{g dry resin}}$$

Phenolic Acid Capacity

A 0.5g of Büchner dried resin was accurately weighed into a 250 ml of round bottom flask. 25ml 1N NaOH standard solution was pipetted into the flask and total weight of the flask containing resin and solution was recorded. The flask was set in a rotary evaporator and all solvent was evaporated off. The flask was placed on a balance and water was added to the weight of the original

solution. A 10ml aliquot was withdrawn and titrated with 0.1N HCl standardized solution. The phenolic acid capacity was calculated using the equation:

$$\text{Phenolic Acid Capacity (mequiv/g)} = \frac{(25 \text{ ml NaOH}) (N \text{ NaOH}) - 2.5 (\text{ml HCl}) (N \text{ HCl})}{\text{g dry resin}}$$

Chlorine Capacity

A oven dried sample of 0.05- 0.8 g was accurately weighed into a metal capsule of the Parr-Bomb and an amount of mineral oil was added so the total weight of resin and oil was approximately 0.8g. 5 ml 5% Na₂CO₃ was added to the bomb cylinder and swirled to ensure complete wetting of the inside surface. The capsule was placed in a capsule holder and a 10 cm nickel alloy fuse wire was threaded through the bomb stem holes to make a loop. The bottom of the wire was allowed to touch the sample-oil mixture without touching the capsule. The capsule assembly was then placed into the cylinder while keeping the bleeder open. A security cap was then screwed on the cylinder. The bleeder was closed and attached to the oxygen tank with high pressure tubing. The bomb was filled with oxygen to a pressure of 30 atm and was then degassed with the bleeder. This step was repeated twice to remove any trace of gases other than oxygen. The bomb was filled with oxygen again and connected to a bomb ignition unit. After the connection, the bomb was then placed in a water bath and ignited. The bomb was held in the water bath for 15 minutes then removed and dried.

The pressure of the bomb was released by opening the bleeder very slowly. The solution was quantitatively transferred to a 400 ml beaker. The inside of the cylinder was then washed into the beaker with nanopure water. The solution in the beaker was then filtered into a 250 ml volumetric flask and diluted to the mark with nanopure water. Two 25 ml aliquots were transferred to 125ml Erlenmeyer flasks and 3 ml 3M HNO₃ added to neutralize the carbonate. 10 ml 0.0500 N AgNO₃ was added to each aliquot and another two clean 125ml Erlenmeyer flasks (for standardization of the NH₄SCN). The flask containing aliquots were then placed on a hot plate and allowed to come to a boil to coagulate the precipitate. The solution was then cooled to room temperature in a dark place, filtered and washed with a small amount of 0.01N HNO₃ into clean 125 ml Erlenmeyer flasks. The filtrate was titrated with standard NH₄SCN solution using 3 ml FeNH₄(SO₄)₂ solution as an indicator. The blank containing AgNO₃ was titrated also to standardize the NH₄SCN. The chlorine capacity was calculated in mequiv/g.

Chlorine capacity (mequiv/g)

$$= \frac{10 [(ml \text{ AgNO}_3) (N \text{ AgNO}_3) - (ml \text{ NH}_4\text{SCN}) (N \text{ NH}_4\text{SCN})]}{\text{g dry resin}}$$

Infrared Spectroscopy

IR spectra were obtained using a Bomen MB100 FT-IR spectrometer. An oven dried polymer sample was ground to a fine powder with KBr at a polymer : KBr ratio of 1 : 5 and the sample was pressed into a pellet.

Metal ion Studies

An amount of resin (one mequiv. of functional group) was weighed into a vial and solvent exchanged four times with a solutions at the pH to be studied. The resin was contacted with 10^{-4} N metal ion solution for 24 hours and the solution was filtered. All metal ion solutions were analyzed using a Perkin-Elmer 3100 atomic absorption/emission spectrometer. The parameters used in spectroscopy are listed in table 5.1.

Table 5.1**Atomic Absorption (AA) / Emission (AE) Spectroscopy Parameters**

Metals	mode	wavelength	flame
Cu ²⁺	AA	324.7 nm	air/acetylene
Pb ²⁺	AA	283.3 nm	air/acetylene
Cd ²⁺	AA	228.8 nm	air/acetylene
Cr ³⁺	AA	357.9 nm	air/acetylene
Co ²⁺	AA	240.7 nm	air/acetylene
Eu ³⁺	AE	459.4 nm	N ₂ O/acetylene
Cs ⁺	AE	852.1 nm	N ₂ O/acetylene

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APPENDIX

Table 6.1.1
Metal ion Uptake of $\text{Cr}(\text{NO}_3)_3$ from pH 5 Acetate Buffer Solution by Amine Resins

	PA	EDA	DETA	TEPA
VBC	MH-1-173	MH-1-032	MH-1-037	MH-1-041
% M complexed	21.50% (1)	14.40% (1)	21.50% (1)	28.60% (1)
D	8.0	12.4	24.5	43.1
VBC/STY	MH-1-233	MH-1-110	MH-1-116	MH-1-120
% M complexed	16.85% (0.5)	5.60% (0.5)	11.72% (0.5)	11.72% (0.5)
D	4.8	3.0	9.0	14.0
VBC/MMA	MH-1-253	MH-1-142	MH-1-146	MH-1-150
% M complexed	16.85% (0.5)	7.00% (0.5)	7.00% (0.5)	7.00% (0.5)
D	7.3	3.7	5.2	6.6
PA : primary amine EDA: ethylenediamine DETA: diethylenetriamine TEPA: tetraethylenepentamine (1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.				

Table 6.1.2
Metal ion Uptake of $\text{Co}(\text{NO}_3)_2$ from pH 5 Acetate Buffer Solution by Amine Resins

	PA	EDA	DETA	TEPA
VBC	MH-1-173	MH-1-032	MH-1-037	MH-1-041
% M complexed	13.85% (1)	13.50% (1)	18.00% (1)	94.70% (1)
D	5.0	11.6	19.5	1906
VBC/STY	MH-1-233	MH-1-110	MH-1-116	MH-1-120
% M complexed	0.00% (0.5)	10.43% (0.5)	18.36% (0.5)	90.47% (0.5)
D	0	5.8	11.5	775.6
VBC/MMA	MH-1-253	MH-1-142	MH-1-146	MH-1-150
% M complexed	0.00% (0.5)	10.00% (0.5)	5.00% (0.5)	75.00% (0.5)
D	0	5.4	3.7	265
PA : primary amine EDA: ethylenediamine DETA: diethylenetriamine				
PEHA: pentaethylenhexamine (1) : weight based on 1 mequiv. (0.5) : weight based on 0.5 mequiv.				

Table 6. 2.1
Metal ion Uptake of $Cr(NO_3)_3$ from pH 5 Acetate Buffer Solution by Aminophosphonic Acids

	PA/PhA	EDA /PhA	DETA/PhA	TEPA/PhA
VBC	MH-1-180	MH-1-070	MH-1-073	MH-1-094
% M complexed	64.00% (1)	56.90% (1)	56.90% (1)	64.00% (1)
D	86	62	50	63
VBC/STY	MH-1-286	MH-1-130	MH-1-134	MH-1-138
% M complexed	13.85% (0.5)	14.80% (0.5)	33.25% (0.5)	39.40% (0.5)
D	2.6	4.5	18	23
VBC/MMA	MH-1-270	MH-1-154	MH-1-158	MH-1-162
% M complexed	44.24% (0.5)	39.06% (0.5)	39.06% (0.5)	39.06 % (0.5)
D	34	23	27	29
PA : primary amine	EDA: ethylenediamine			
TEPA: tetraethylenepentamine	PhA : phosphonic acid			
(1) : weight based on 1 mequiv.	(0.5) : weight based on 0.5 mequiv.			
	DETA: diethylenetriamine			

Table 6.2.2
Metal ion Uptake of $\text{Co}(\text{NO}_3)_2$ from pH 5 Acetate Buffer Solution by Aminophosphonic Acids

	PA/PhA	EDA /PhA	DETA/PhA	TEPA/PhA
VBC	MH-1-180	MH-1-070	MH-1-073	MH-1-094
% M complexed	91.00% (1)	94.70% (1)	94.70% (1)	100% (1)
D	489	839	672	infinite
VBC/STY	MH-1-286	MH-1-130	MH-1-134	MH-1-138
% M complexed	49.98% (0.5)	91.26% (0.5)	96.01% (0.5)	96.01% (0.5)
D	16.1	388.9	689.2	855.4
VBC/MMA	MH-1-270	MH-1-154	MH-1-158	MH-1-162
% M complexed	75.00% (0.5)	85.00% (0.5)	75.00% (0.5)	80.00% (0.5)
D	128.4	202	212	182
PA : primary amine	EDA: ethylenediamine		DETA: diethylenetriamine	

(1) : weight based on 1 mequiv. (0.5) : weight based in 0.5 mequiv.

Table 6.3
Metal ion Uptake in pH 5 Acetate Buffer Solution by Monophosphonic Acids

	$\text{Cr}(\text{NO}_3)_2$	$\text{Co}(\text{NO}_3)_2$
VBC PhA (MH-1-034) (1)	56.90% ^a (65) ^b	48.14% (45)
VBC/STY PhA (MH-1-256) (0.5)	13.85% (4.5)	25.36% (10.1)
VBC/MMA PhA (MH-3-002) (0.5)	36.34% (19.4)	3.05% (1.1)
^a % M Complexed	^b D	PhA : Phosphonic acid
(1) : weight based on 1 mequiv.		(0.5) : weight based on 0.5 mequiv.

Table 6.4
Standard Sieve Sizes

Sieve Number	Diameter of Bead (mm)
20	0.84
40	0.425
60	0.250
80	0.180
100	0.150
200	0.075
325	0.045

VITA

Minjeong Hong was born in Chungnam, Korea on October 19, 1971. After graduating from High School in 1990, she joined Chungnam National University, Korea , where she graduated with a Bachelor of Science degree in Chemistry in February 1994. She was an intermediate science teacher in Korea for two years. In August 1996, she came to the Chemistry Department at the University of Tennessee, Knoxville and began her study toward the Master of Science degree in Polymer Chemistry under the guidance of Professor Spiro D. Alexandratos. The degree was awarded in December 1999.