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The synthesis and characterization of selected copolyoxamides with special emphasis on their complexation behavior.

Allan Howard Beeber
University of Massachusetts Amherst

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THE SYNTHESIS AND CHARACTERIZATION OF SELECTED COPOLYOXAMIDES WITH SPECIAL EMPHASIS ON THEIR COMPLEXATION BEHAVIOR

A Dissertation Presented
by
ALLAN HOWARD BEEBER

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY
February 1977
Polymer Science and Engineering
THE SYNTHESIS AND CHARACTERIZATION OF SELECTED COPOLYOXAMIDES WITH SPECIAL EMPHASIS ON THEIR COMPLEXATION BEHAVIOR

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ALLAN HOWARD BEEBER

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To the Lord Jesus Christ

"There is a way which seems right to a man, but its end is the way to death." Prov. 14:12

"Trust in the Lord with all your heart, and do not rely on your own insight. In all your ways acknowledge Him, and He will make straight yours paths." Prov. 3:5,6

"For what does it profit a man, to gain the whole world and forfeit his life." Mk 8:36
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I would like to also thank my family and friends, especially my mother, John and Joannie Fittz, and Calvin Layton, for their steadfast love, encouragement, and prayers.

Most important of all I thank my Lord and Savior Jesus Christ, to whom this thesis is dedicated, and without whose help it would not have been possible. The growing realization of His character, truth, and love gently constrains me to "live no longer for myself, but for Him who died and was raised again". (II Cor. 5:15).
ABSTRACT

The Synthesis and Characterization of Selected Copolyoxamides with Special Emphasis on Their Complexation Behavior

(February, 1977)

Allan H. Beeber, B.S., Muhlenberg College M.S. and Ph.D., University of Massachusetts

Directed by: Professors Otto Vogl and Sidney Siggia

Regular aliphatic/aliphatic and aliphatic/aromatic copolyoxamides were prepared from aliphatic diamine-oxamides (A-B-A type) and diacid chlorides by interfacial polymerization. N,N'-bis(2-aminoethyl)oxamide was primarily used; however, diamine-oxamides with more than one oxamide unit in the molecule have also been synthesized and in one case a polymer was prepared with isophthaloyl chloride. The aliphatic diacid chlorides used included the 1,1-cyclobutane, cis- and trans-1,4-cyclohexane, and sebacic dicarboxylic acid derivatives. The aromatic diacid chlorides used included the isophthalic, terephthalic, 2,6-pyridine, and 1,6- and 2,6-naphthalic dicarboxylic acid derivatives. Both 1,8- and 1,5-anthraquinone and anthracene dicarboxylic acid chlorides were also synthesized, but their insolubility and low reactivity prohibited the formation of high molecular weight polymer.

Oligooxamides and precursors have been characterized by
infrared and proton magnetic resonance spectroscopy, and by elemental and thermal analysis. The majority melt with decomposition and char formation at temperatures above 250°C. The 1,8- and 1,5-anthraquinone and anthracene dicarboxylic acid chlorides and precursors have been characterized by infrared spectroscopy and melting point determinations. All diacid chlorides melt above 200°C.

Most of the polymers form films and are soluble in concentrated sulfuric acid, trifluoroacetic acid, and dimethylacetamide (containing LiCl), are high melting (over 360°C, usually) and decompose during the melting process. The polymers were further characterized by measurements of elemental analysis, inherent viscosity, and infrared and PMR spectra.

Investigations were made into the general complexation behavior of copolyoxamides in contact with aqueous solutions of metal ions or with aromatic acids or bases using one-plate batch equilibration techniques. The results indicate the discovery of a complexation resin for metals which can be converted from a chelating resin into a general ion exchange resin simply by increasing the basicity of the solution. The copolyoxamides also show appreciable uptake of aromatic acids and bases.
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CHAPTER I
INTRODUCTION

Polyoxamides

Polyoxamides, such as the poly(hexamethylene oxamide) shown below, are of interest because of their high melting points, chemical resistance, stiffness, and low moisture sensitivity relative to common nylon resins.\(^1,2\)

\[
\begin{align*}
\text{HOOH} & \text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N-C-C-N} & \text{n} \\
\text{oxamide portion}
\end{align*}
\]

Several methods of preparation by step growth poly-condensation are the reactions of oxalic acid with diamine, oxalate ester with diamine, and interfacial, emulsion, or gas-liquid polymerization of oxalyl chloride with diamine.\(^3\)

In the case of the reaction of oxalic acid with diamine, high molecular weight polymer cannot be obtained because the temperature required for the dehydration of the polymeric oxalic salt is higher than the decomposition temperature of the oxamide group. In fact, polyoxamides often exhibit thermal instability at their melting points or lower. Significant degradation can occur as low as 250°C. with accompanying gas evolution and loss of molecular weight. The reaction of oxalate ester with diamine, the most frequently used method for the synthesis of polyoxamides, is similarly effected.\(^4\)
An example of the synthesis of an aliphatic polyoxamide by solution polymerization is found in Stamatoff's work. Recently, T.A. Sorokina and coworkers described a melt polycondensation with hexa-, octa-, nona-, and decamethylene diamines which yielded high molecular weight polymers.

Aliphatic polyoxamides display greater insolubility than do common aliphatic polyamides, which are soluble in phenols, formic acid, and various types of halogenated alcohols, among others. This is a result of the greater polarity and hydrogen bonding effects exhibited by the oxamide linkage relative to simple amide bonds. One way to increase solubility is to incorporate aromatic groups into the polymer chain backbone. One case where aromatic polyoxamides were obtained in sufficiently high molecular weights, yet were soluble enough to be cast into tough, clear films, was reported by Hall and Berge.

Interfacial, emulsion, and gas-liquid polymerizations of oxalyl chloride with diamine are adversely affected by the rapid hydrolysis of the short-chain diacid chloride, which limits the molecular weight that can be obtained. This results from the much greater reactivity of the oxalyl chlorides. The highest molecular weights that have been obtained were those resulting from the gas-liquid polymerizations. Gaseous oxalyl chloride is bubbled in with the carrier gas nitrogen into an aqueous solution of diamine. Even here the reduced viscosities were often not much higher than 0.6.
A novel route to polyoxamides was worked out by Ellingboe, who reacted chlorinated esters with diamines, which involves acid chloride intermediates.\textsuperscript{11,12}

Working from a different direction, Vogl and Knight attempted the ring opening addition-type polymerization of cyclic oxamides.\textsuperscript{1-3} It was expected that the cyclic monomer would melt lower than the region of thermal instability of the respective polymer. Therefore, high molecular weight material should be obtained.

To prepare the cyclic oxamides they employed a high dilution method.\textsuperscript{1} Figure 1 shows the synthetic route that was used.\textsuperscript{4} The monomer, c-62, melted at 232°C, which was indeed lower than the polymer's region of thermal instability.

The cyclic oxamides resembled lactams in their polymerization behavior. Polymerization began almost immediately when anionic initiators such as sodium methoxide were added in the melt. A number of other bases or basic salts and even cationic initiators are effective including acetate and stearate salts of alkali and transition earth metals. The initiating ability of the latter two types of salts are especially interesting, since under comparable conditions lactams do not polymerize. However, in all cases of polymerization, concurrent evolution of carbon monoxide and dioxide were observed.
FIGURE 1
Formation of Cyclic Oxamides

\[
\begin{align*}
\text{NH}_2 (CH_2)_6 \text{NH}_2 + \text{Cl-C-C-Cl} & \rightarrow (CH_2)_6 \text{C}=O + \text{I, c-62*} \\
\text{II, c-6262} \\
\text{III, c-626262} \\
\text{IV, p-62}
\end{align*}
\]

* c = cyclic, p = polymer
This showed that decomposition was occurring along with polymerization and inherent viscosities above 0.5 dl/g (0.5 % m-cresol) could not be obtained.

During their investigations Vogl and Knight synthesized a cyclic tetraamide, c-6266. Experiments showed that when this compound was polymerized it occurred primarily through the oxamide bond and not through the simple amide bonds. The resulting polymer was not a polyoxamide, though. Rather, it was now a copolyoxamide, a regular alternating copolyamide of the (A-B-A-D)\textsubscript{n} type. Since copolyoxamides would exhibit properties similar to simple polyoxamides, the next step was to determine the best method of introducing the oxamide group into a copolyamide.

Preparative Methods of Introducing Regularity

Use of Preformed Regular Intermediates. To circumvent the problems posed by the instability of the oxamide unit at high temperatures, including the previous case of c-6266, different methods of introducing the oxamide unit in a regular manner into the polymer backbone were investigated. One of the best ways in which one can introduce regularity into a polymer backbone is to polymerize a difunctional monomer such as the diamine-oxamide prepared by Vogl and Knight. Several methods have been previously developed for the preparation of amide-containing difunctional monomers.
A. Conversion of Functional Groups

H. Zahn and coworkers have done the majority of investigations into the formation of A-B-A type oligoamide compounds. One method he studied extensively was that whereby a difunctional compound B is reacted with two moles of a difunctional compound A, in which one of the latter's groups is protected. A completely aromatic diamine-diamide A-B-A monomer was synthesized by Shigeyoshi and coworkers.

B. Use of Protecting Groups

G.M. van der Want and coworkers used the well-known concept of protecting groups in their synthesis of oligo-\(\omega\)-peptides. They first condensed a \(\omega\)-phtalimido acid chloride with an \(\omega\)-amino acid and then removed the phthali-mido group, as shown in Figure 2.

Stepwise synthesis of oligomers by means of a polymer carrier is another interesting use of protecting groups. Several homologous series of oligoamides were synthesized by Kusch and by Rothe and coworkers.

Ring Opening of Cyclic Precursors. Little has been done in this area, but one of the best examples is found in the work by Wang and Bauman. They synthesized several bi-imidazolines with which they studied metal ion complexations. However, they discovered that the compounds readily hydrolyzed in water; a quantitative yield of N,N'-bis(2-aminoethyl)oxamide was obtained.
FIGURE 2

Synthesis of Oligo-$\omega$-peptides

\[
\begin{align*}
\text{CO} & + \text{H}_2\text{N}(\text{CH}_2)_5\text{COOH} \rightarrow \text{N-}(\text{CH}_2)_5\text{COOH} \\
\text{SOCl}_2 & \rightarrow \text{N-}(\text{CH}_2)_5\text{COCl} & \text{H}_2\text{N}(\text{CH}_2)_5\text{COOH} \\
\rightarrow & \text{N}(\text{CH}_2)_5\text{CONH-}(\text{CH}_2)_5\text{COOH} \\
\text{N}_2\text{H}_4 & \rightarrow \text{H}_2\text{N}(\text{CH}_2)_5\text{CONH-}(\text{CH}_2)_5\text{COOH} \\
+ & \text{H}_2\text{N}(\text{CH}_2)_5\text{CONH-}(\text{CH}_2)_5\text{COOH} \\
\end{align*}
\]

repeat to obtain higher oligomers
Direct Condensation. This last method proved to be the one of choice. The first report in the literature of the use of aliphatic diamine-oxamides synthesized by direct condensation was in 1963. Rio and Robin linked prepolymer of isocyanate and polyesters or polyethers together with the ethyl, propyl, and hexyl diamine-oxamides to form elastomers which contained oxamide groups. The same workers have also synthesized aromatic diacid-oxamides and diol-oxamides.25,26

Vogl and Knight had previously formed a diamine-oxamide by the direct condensation of hexamethylene diamine with diethyl oxalate to make N,N'-bis-(6-aminohexyl)oxamide. Yields were modest due to the competing side reaction of polymer formation.1

Chang set out to improve the yield and in the course of his investigations he developed the techniques for the synthesis of a number of A-2-A aliphatic diamine-oxamides in good yields.4,27,28 Specifically, he used diamines containing from two to twelve methylene units (the "A" portion) in condensation with diethyl oxalate (the "B" portion, referring to the number of carbons in the oxalyl unit). He found that the optimal conditions were those in which the
diamine had a limited solubility in the solvent system (specifically, those solvents with low dielectric constants) and where it was used in at least a two-fold excess. To this excess of diamine the diethyl oxalate was slowly added, while the temperature was kept below 10°C. The A-2-A monomer itself tended to have limited solubility, also, and would precipitate out of the reaction mixture when formed. A combination of these factors allowed him to reduce oligomer and polymer formation to between 5 and 10 % of the reaction mixture. Under these reaction conditions he found no evidence of cyclization.

Along with these improvements he developed an effective separation method of A-2-A monomer from the accompanying oligomers and polymers. Simple recrystallization could be used, but was accompanied by some yield losses and large volumes of solvent were required. These problems were circumvented by the use of Soxhlet extraction techniques.

The compounds obtained were crystalline. As the number of methylene units increased, the melting points increased in a regular odd-even alternation from A=2, 107°C, to A=12, 127°C. Also, as the number of units increased, the solubility of the diamine-oxamides became more similar to the alkylene diamine precursors. They exhibited solubility behavior which allowed polymerization by either interfacial or solution techniques using polar solvents. In the case where the diamine portion contained more than six methylene groups
(A > 6), only solution polymerization is possible. Further discussion regarding polymerization behavior will be given later on in this chapter.

Regular Condensation Polymers

The basic theory regarding the formation of regular copolyamides had been worked out as early as 1944 by Schlack, yet it was not until this last decade that any systematic investigations were carried out.

\[ \text{H}_2\text{N}-\text{R'}-\text{HNO}-\text{CONH}-\text{R'-NH}_2 + \text{Cl-CC-R''-CO-Cl} \rightarrow \]

Several examples are given of types of regular alternating copolyamides.

Pisanchyn has recently reported one of the few studies on the preparation of an ordered, alternating, aliphatic copolyamide. He formed a copolyamide consisting of 6-amino-hexanoic acid and 11-aminoundecanoic acid residues.

Preston and coworkers have done considerable work in the area of the synthesis of regular aromatic copolyamides. Several symmetrical A-B-A diamine-diamides have been synthesized and polymerizations carried out to form \((\text{A-B-A-D})_n\) copolyamides. One example is the reaction of \(\text{N,N'}-\text{m-phenylenebis-(m-aminobenzamide)}\) with isophthaloyl chloride.
The regular copolymers prepared in this manner have significantly higher melting points and decomposition temperatures than those prepared randomly.

General Methods of Polyamide Preparation

There are several methods used for synthesizing high molecular weight polyamides. A brief review of the most common types follows, with emphasis given to those which permit the formation of regular copolyamides.

A. Ring Opening Polymerization of Lactams

A typical example is that of the preparation of Nylon 6 from ε-caprolactam.

The polymerization can take place either by addition or step-growth mechanisms. Both are random reactions in the sense that in a comonomer mixture the active species can
attack either monomer. Hence, one cannot readily obtain regular alternating copolyamides. Also, only strained rings (8 > 5 and 6 membered) give sufficiently high molecular weights. This greatly restricts the variety of polyamides which can be synthesized by this method.

B. Polycondensation Reactions

The four most commonly used methods are the following: 1) diacid with diamine, 2) amino acid, 3) diester with diamine, and 4) diacid chloride with diamine. The last one is shown below.

\[
\begin{align*}
\text{n Cl-CO-R-CO-Cl + n H}_2\text{N-R'-NH}_2 \xrightarrow{\text{low temp.}} & \rightarrow \left[\text{CO-R-CONH-R'-NH}\right]_{n-m} + m \text{CO} \text{N-R'-NH}_2 + 2n \text{HCl}
\end{align*}
\]

All four reaction mechanisms are step-growth. All require exact equivalence of reactants in order to attain high molecular weights, though reaction \#4 is more tolerant to imbalances. This point will be discussed in more detail further on.

The first three reaction methods require high temperatures, especially in the final stages when the reaction actually occurs in the melt state. However, the fourth reaction occurs at moderate temperatures (ambient or lower) in solution, due to the much greater reactivity of the acid chloride groups. Reactions \#1-3 occur under near-equilibrium conditions, while \#4 is a non-equilibrium, irreversible,
reaction. Those polymerizations involving amide bonds in which high temperatures must be employed, suffer from trans-amidization reactions. Hence, regular copolyamides usually cannot be obtained by the first three methods. However, case \#4, an extension of the familiar Schotten-Bauman reaction, does not have this drawback and is commonly used for the synthesis of regular copolyamides.

Low-Temperature Methods

A. General Description

Low-temperature methods do have some specific disadvantages over other methods such as melt polycondensation. Oftentimes, formation of large quantities of by-product salt occurs, one must use large volumes of solvent, the finely divided form of the polymer makes handling difficult, the diacid chlorides are expensive, etc. Nevertheless, many times the low-temperature method provides the best route to obtain high molecular weight regular copolymers. This is the case for the preparation of the copolyoxamides.

Polymerization can be carried out either interfacially or by solution polycondensation. In the interfacial method the diamine and usually the acid acceptor are dissolved in water and the diacid chloride is dissolved in an immiscible organic solvent such as chloroform or benzene. The two phases normally are brought together very rapidly with stirring in a blender. Polymerization takes place at the liquid-liquid interface, the organic phase being diffused in the
aqueous phase as small droplets. High molecular weight polymer is formed almost immediately and usually precipitates out.

In the solution method the reaction is carried out in only one liquid which is an inert solvent for both intermediates, and sometimes in the presence of an acid acceptor such as a soluble tertiary amine. Polymer usually precipitates out as medium to high molecular weight is attained. Higher molecular weights are more frequently obtained by interfacial polymerization than by solution.

A brief comparison of certain features of the two methods follows because they were both extensively employed in the general investigation of the preparation of regular copolyoxamides. This is a brief comparison; the interested reader is referred to the review by Morgan. 37

B. Reaction Rate

In order to obtain high molecular weights, interfacial polycondensations should have rate constants which are much greater than any side reactions, such as hydrolysis, and the polymerization must be complete before the polymer precipitates out of the reaction medium. The actual chemical mechanism is an $S_N^2$ nucleophilic displacement.
Here, $k_{H^+} > k_2 > k_{\text{reactant mixing}}$, where the last term reflects the rate of competitive hydrolysis versus that of actual amide formation. Some absolute reaction rates of unhindered aliphatic acid chlorides with primary diamines are estimated to be as high as $10^4 - 10^6$ liters/mole-sec in homogeneous solution.\footnote{37}

Solution polycondensations involve the same reaction mechanism and have similar rates but are affected by several different factors and limitations, which will be discussed later.

C. Stirring and Concentration Effects

A high rate of stirring is desired in interfacial polymerizations in order to provide a rapidly renewable fresh interface on the acid chloride droplets. Oftentimes the polymer precipitates out of solution in a highly swollen, finely divided form, and this gel can be so thick that stirring is stopped. Therefore, concentrations are usually kept below 1%. Other factors include the shape and size of the blades and vessel, and the nature of the reaction mixture.
Solution polymerizations are affected similarly by stirring rate and concentration in that it affects stir-ability and temperature control. In both methods, too low a concentration can have negative effects in that there would be a relatively higher degree of impurities present compared to the amount of reactant. These variables must be individually determined for each polymer.

D. Temperature

In stirred interfacial and solution polymerizations the reactants are usually added at room temperature or lower. Suitable cooling is provided to remove the heat generated during the reaction, which improves the yield and molecular weight. Increasing the temperature will change the solubility of the intermediates and increases the rate of polymerization. Yet the rate of competing side reactions can be also increased, with a resulting reduction in molecular weight.

E. Method of Reactant Addition

Quick addition of the organic phase to the rapidly stirring aqueous phase usually leads to the highest molecular weight materials rather than in the reverse order. This is especially true in the case of polymers which precipitate out of the reaction medium quickly.

Fast solution polymerizations are again similar to interfacial polymerizations. The sooner the reaction is completed, the less time there is for interfering side reactions;
hence, additions should be done quickly. However, if the reactants are added together too fast, a large amount of heat can be generated, which causes side reactions. It has been found to be better to add the diacid chloride to the diamine; higher concentration of amine groups counterbalances the tendency to cyclize.

F. Reactants Ratio

Interfacial polymerization is much less sensitive to the need for exact equivalence of reactants than is solution polycondensation. This is due to the different reaction environments. Whereas in the solution method the reactants are homogeneously mixed, interfacial polymerization occurs at or within droplets of the organic phase. One can think of the organic droplets as static and the aqueous phase as very mobile, rapidly removing the by-product hydrogen halide and bringing fresh diamine to the reaction site. High molecular weights can be obtained in small areas of the reaction medium, though the overall yield may be low. In solution polymerization the reactants are evenly distributed throughout the reaction medium, and any imbalance, however small, exerts a greater effect on the reaction as a whole.

G. Variation of Acid Acceptors

In interfacial systems strong bases, such as sodium carbonate, are usually the best acid acceptors and normally function best in a 2:1 ratio. The degree of basicity is important since increasing the alkalinity of the solution
can greatly accelerate the rate of hydrolysis of the acid chloride groups. As the basicity of the amine groups increases, so must the acid acceptor’s strength be increased in order to keep the amine from forming a salt.

In solution polymerizations the hydrogen halide must be removed from the reaction site to prevent salt formation, also. Inorganic bases display poor solubility and therefore are slow to function. Usually the basic amide solvent often used is sufficient, but tertiary amines have also been found to be good acid acceptors. Ordinarily the salt will actually precipitate out of solution during the polymerization.

H. Solvent Choice

In both the interfacial and solution systems one usually must use trial and error to determine exactly which solvent system is best. The choice of polar solvents is usually much larger for solution polymerizations because there is no longer the restriction of water immiscibility. Factors which are important are that they be inert to the reactants while providing good solubility both for reactants and acid acceptor, and preferably for the polymer itself.

I. Effect of Impurities

The non-homogeneous nature of interfacial polymerization allows for the tolerance of many types of impurities without affecting the molecular weight too greatly. Inert impurities in the reactants simply lead to a non-equivalence of difunctional groups. Monofunctional groups will obviously
reduce the molecular weight obtainable. Stabilizers or other impurities, such as the ethanol in chloroform, can react with and deactivate the acid chloride groups. The addition of neutral salts, such as NaCl, to the aqueous phase is an interesting case of added electrolytes. The availability of the diamine should be increased and the hydrolysis of the acid chloride decreased because the salt both reduces the miscibility of both phases and reduces the solubility of both reactants in the aqueous phase. However, this technique does not work for all systems.\(^8\)

Solution polymerization is much more dependent on the exact equivalence of functional groups since the reaction takes place in a homogeneous medium; hence, reactant purity must be high. Likewise, reactive impurities in the solvent and acid acceptor must be rigorously excluded. One of the most harmful is the presence of small amounts of water which causes hydrolysis, the next subject of discussion. Even the influence of the atmosphere under which the reaction is carried out is important, as demonstrated in the reaction of carbon dioxide with amines to form salts.\(^9\)

\[
2 \text{RNH}_2 + \text{CO}_2 \rightarrow \left[ \text{RNH}_3^+ \overset{\text{OCNHR}}{\text{O}} \right]
\]

J. Hydrolysis of Acid Chlorides

The hydrolysis of acid chloride groups is the most important interfering side reaction in the interfacial syn-
thesis of the copolyoxamides. The rate of hydrolysis can be affected by such variables as temperature, the type of organic solvent, how strongly basic the acid acceptor is, concentration of acid chloride, and rate of stirring.

As previously mentioned, in solution polymerization, water must be rigorously excluded from the system and this always requires elaborate techniques. Yet this method would seem to be the logical route of choice if one encounters hydrolysis problems in the other, and it is the logical choice for commercial processes. Sometimes, however, the polymers which are formed precipitate out prematurely in a low molecular weight state which usually prohibits further polymerization.

Preparation of Copolyoxamides

Kagiya and coworkers and Wang and Bauman discovered that bis-imidazolines were readily hydrolyzed by heating the aqueous solution to yield diamine-diamide compounds.

\[
\begin{align*}
\text{H}_2\text{C} \quad \text{N} & \quad \text{C}-\text{R}-\text{C} \quad \text{N} & \quad \text{CH}_2 & + & 2 \text{H}_2\text{O} & \rightarrow \\
\text{H}_2\text{C} \quad \text{N} & \quad \text{C}-\text{R}-\text{C} \quad \text{N} & \quad \text{CH}_2 & \quad & \\
\text{H}_2\text{N}-(\text{CH}_2)_2-\text{N}-\text{C}-\text{R}-\text{C}-\text{N}-(\text{CH}_2)_2-\text{NH}_2 & \\
\text{A} & \quad \text{B} & \quad \text{C}
\end{align*}
\]

In the case of \( R=0 \), the compound obtained is \( N,N'\text{bis}(2\text{-aminoethyl})\text{oxamide} \). It was quite soluble in water and interfacial
polycondensation reactions could be carried out with some diacid chlorides to yield \((A-B-A-D)\_n\) copolyamides of inherent viscosities of ca. 1.0 (TFAA, 70°C).

Regular copolyoxamides were previously studied by Chang, Stevenson and Gaudiana in our laboratories.\(^{4,28,41,118-121}\) Chang investigated the polymerization behavior of a number of A-2-A monomers, where A ranged from two to twelve methylenic units in the diamine portion, with aliphatic diacid chlorides (D), which had between four and eight methylene units in the polymer chain. For those diamine-oxamides containing from two to five methylene units, both interfacial and solution polymerizations could be carried out, sometimes at elevated temperatures \((\sim 60\degree C)\). Above five methylene units only solution polymerizations could be run because the diamine-oxamides were no longer readily soluble in water.

When there was a choice between interfacial and solution polymerization, the former almost invariably yielded materials with greater inherent viscosities. When used in a two-fold excess, sodium carbonate proved to be generally the most effective base. Chloroform displayed the best behavior for use in the organic phase. The concentration of \(m-A-2-A\) (where "m" signifies monomer) and diacid chloride was kept at low concentrations.

One of the greatest problems faced was that of the hydrolysis of the acid chloride during the reaction with a resulting loss in molecular weight. As the number of methyl-
ene groups was increased in either the diamine-oxamide or diacid chloride monomers, they became more hydrophobic and thus more resistant to hydrolysis. This led to the formation of higher molecular weight polymers. Not only the diacid chloride but also the acid chloride-terminated oligomer was affected by the hydrolysis reaction. Therefore, the more hydrophobic the monomers were, the less interaction there was with the aqueous layer at the reaction interface. There was thus less hydrolysis and higher molecular weights were obtained.

Thermal characterization of the polymers showed that as the number of methylene groups decreased in either monomer, the melting point increased up to where the polymer would start decomposing (300 to 360°C). This reflected the greater degree of polarity and interchain interaction. The more polar polymers also showed the greatest amount of remaining char after programmed degradation on the TGA.

Stevenson and Gaudiana investigated copolyoxamides with the goal of synthesizing and testing polymers potentially suitable for reverse osmosis desalination applications.\(^{42,43}\) A membrane suitable for such work must exhibit a high permeability to water and low permeability to dissolved ions. This can be achieved by increasing the amount of hydrogen-bonding groups or hydrophilic regions in the polymer matrix. High mechanical strength and low creep when wet are two other necessary prerequisites. These can be obtained by
incorporating certain structures in the polymer chain which either have a high glass transition temperature or allow for light crosslinking.

Some aromatic polyamides have been demonstrated to perform well as reverse osmosis membranes. As it was pointed out, the chemical structure of copolyoxamides offers three advantages over cellulose and aromatic polyamide-hydrazide membrane materials.

1. They contain only the amide function, which is more resistant to both hydrolysis and oxidative attack than are the cellulose (CA) and the hydrazide groups. Thus, membranes made from the regular copolyamides should be useable over a broader pH range, and should not be subject to attack by oxidants such as Cl₂, as the CA and the polyamide-hydrazones are.

2. Regular copolyamides can produce greater inter-chain hydrogen-bonding because of regularity of structure. This will effect the physical structure in the solid and gelled state, favorably influence the water permeability, and make these membranes more resistant to plastic flow and hence lessen compaction when used under pressure reverse osmosis conditions.

3. Chain length and composition of all the amine and acid residues can be varied independently, which should make it possible to "tailor" the structures for optimum water and salt permeability.
Investigation into the use of copolyoxamides showed that those formed from aliphatic diacid chlorides did not exhibit a good permeability to water, as compared with the standard, commercially used, cellulose acetate. However, much better results were obtained when aromatic diacid chlorides, such as isophthaloyl, were used. Table I shows a portion of the data obtained with different diamine-oxamides and aromatic diacid chlorides.43

**TABLE I**

Desalination Data for Selected Copolyoxamides

<table>
<thead>
<tr>
<th></th>
<th>Inherent Viscosity 30°C, H₂SO₄</th>
<th>Water Flux** D₁C₁ (g/cm-sec)</th>
<th>Salt Flux** D₂K (g/cm-sec, 10⁸)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate</td>
<td>---</td>
<td>1.20 X 10⁻⁷</td>
<td>0.468</td>
</tr>
<tr>
<td>p-2-2-2-I*</td>
<td>1.10</td>
<td>1.92 X 10⁻⁷</td>
<td>1.06</td>
</tr>
<tr>
<td>p-3-2-3-I</td>
<td>1.90</td>
<td>0.782 X 10⁻⁷</td>
<td>0.463</td>
</tr>
<tr>
<td>p-4-2-4-I</td>
<td>1.62</td>
<td>0.048 X 10⁻⁷</td>
<td>0.025</td>
</tr>
<tr>
<td>p-4-2-4-P</td>
<td>0.88</td>
<td>0.148 X 10⁻⁷</td>
<td>0.098</td>
</tr>
<tr>
<td>p-2-2-2-P</td>
<td>0.33</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

* "p" indicates polymer, 2-2-2 indicates the diamine-oxamide monomer used, I=isophthaloyl, and P=2,6-pyridinyl
** a measure of permeability

One notes that with increasing number of methylene units, from 2-2-2 to 4-2-4, the inherent viscosity increases. This reflects the lower solubility of the m-4-2-4 and respective oligomers in the aqueous phase during polymerization. Also, as the number of methylene groups is decreased in the oxamide residue, the resulting membranes exhibit greater water permeability, though not quite as good as cellulose acetate.
Therefore, the m-2-2-2 diamine-oxamide became the monomer around which most of the further investigations centered.

Several approaches were investigated by Stevenson and Guadiana to improve the water permeability of the copolyoxamides. One approach was that of varying the hydrophilicity of the diacid chlorides used in the polymerization. Aromatic diacid chlorides were more hydrophobic than aliphatic ones of equal carbon number and thus the molecular weights obtained were higher. Aromatic diacid chlorides which had nitrogen in the ring displayed greater hydrophilicity than those without, due primarily to the increased amount of hydrogen-bonding possible with the nitrogen atom. Also one observed a several-fold increase in permeability of the membranes. However, attempts to synthesize a high molecular weight, film-forming polymer from 2,6-pyridinedicarboxylic acid chloride and m-2-2-2, the most hydrophilic diamine-oxamide, failed. The hydrophilicity of both the diamine-oxamide and the acid chloride resulted in the growing oligomers having too great an affinity for the aqueous layer at the reaction interface. Moreover, the nitrogen-containing diacid chlorides are more reactive to proton donors such as water due to the electron-withdrawing effect of the nitrogen on the carbonyl groups.

Stevenson tried varying the concentration ratios of diamine-oxamide to diacid chloride in interfacial polymerizations, and later, Guadiana attempted solution polymerization
in polyphosphoric acid and in 4% LiCl/DMAc, but there was no improvement. Similar to Chang's observations, interfacial polymerizations almost invariably gave higher molecular weights than solution ones.

Due to the presence of the amide and aromatic residues all the polymers exhibited high melting temperatures (ca. 360°C.) along with decomposition and char formation. All the copolyoxamides gave normal infrared and proton magnetic resonance (PMR) spectra.

Complexation Resins

A. Synopsis

Chang reported that freshly prepared copolyoxamides would react with a stainless steel spatula and he suggested that these polymers be studied for their uses as complexation resins. The white polymer would turn grey-black and the metal tip corroded when they were in contact for several hours during workup. Also, work done on the amide group-containing polymer, polyvinylpyrrolidone, indicated that the polar oxamide group within copolyoxamides might exhibit good uptake for aromatic acids and bases as well.

The following three sections are intended to provide a brief background and description of ion-exchange, complexation, and non-ionic resins as sorbents for metals and organic compounds. A literature review concerning the interaction of the oxamide group with metals and organics in various solutions is given at the end of this chapter.
B. Ion-Exchange Resins

Ion-exchange resins can be either an insoluble acid or base which remains insoluble when converted to its salt form. Cationic-exchange polyelectrolytes contain fixed negative charges; anionic-exchangers contain fixed positive charges. Mobile counterions of opposite charge which may be exchanged stoichiometrically with other ions of like charge permit the ion exchange phenomenon to occur.

The beginning of modern ion-exchange technology is credited to Adams and Holmes with their studies of water treatment in the late 1930's. Weak-acid cationic-exchange resins were prepared by condensing phenol (and/or its derivatives) with formaldehyde. Weak-base anion-exchange resins were likewise obtained by condensing aromatic amines with formaldehyde. Later, it was found that a sulfonic acid group greatly increased the acidity of cation-exchangers. Similarly, replacement of the aromatic amines with aliphatic amines increased the basicity of anion-exchangers. Since then there have been many modifications and improvements and a general classification scheme has developed. This scheme is shown in Table II. Both cation- and anion-exchangers are generally divided into strong, moderate and weak types.

Most cation-exchange resins are prepared from styrene-divinylbenzene copolymers. Those containing sulfonic acid groups are strong-acid resins, while those containing carboxylic groups are weak-acid resins. Phosphoric acid deri-
# TABLE II

Chemical Classification of Ion-Exchange Resins

<table>
<thead>
<tr>
<th>Classification</th>
<th>Active Group</th>
<th>Typical Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation-exchange</td>
<td></td>
<td></td>
</tr>
<tr>
<td>strong acid</td>
<td>sulfonic acid</td>
<td><img src="image" alt="Sulfonic Acid" /></td>
</tr>
<tr>
<td>weak acid</td>
<td>carboxylic acid</td>
<td><img src="image" alt="Carboxylic Acid" /></td>
</tr>
<tr>
<td>weak acid</td>
<td>phosphonic acid</td>
<td><img src="image" alt="Phosphonic Acid" /></td>
</tr>
<tr>
<td>Anion-exchange</td>
<td></td>
<td></td>
</tr>
<tr>
<td>strong base</td>
<td>quaternary</td>
<td><img src="image" alt="Quaternary Ammonium" /></td>
</tr>
<tr>
<td>amonium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>weak base</td>
<td>secondary amine</td>
<td><img src="image" alt="Secondary Amine" /></td>
</tr>
<tr>
<td>weak base</td>
<td>tertiary amine</td>
<td><img src="image" alt="Tertiary Amine" /></td>
</tr>
<tr>
<td>(aromatic matrix)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>weak base</td>
<td>tertiary amine</td>
<td><img src="image" alt="Tertiary Amine" /></td>
</tr>
<tr>
<td>(aliphatic matrix)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Derivatives are between sulfonic and carboxylic groups in acidity.

Most strong-base anion-exchange resins are quaternary ammonium derivatives of styrene-divinylbenzene copolymers, but the chemical structure of weak-base resins vary greatly, depending on the application and environment. Styrene polymers are used to provide a rigid, slightly hydrophilic, aromatic matrix having secondary or tertiary amine groups. Condensation of polyamines, such as tetraethylene tetraamine, with epichlorohydrin yields aliphatic matrixes similar to that shown below.

\[
\begin{align*}
\text{N-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-N-} \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 \\
\text{N-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-N}^+ \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 \\
\text{N-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-N}^+ \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2 \\
\text{N-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-N}^+ \\
\end{align*}
\]

The resin is polyfunctional, containing both weak base (\(\text{3}^\circ\) ammonium) and strong bases (quaternary ammonium). In combination with the hydroxymethyl groups the resin is very hydrophilic. The high nitrogen content gives it a high total exchange capacity.

The hydrogen atoms of the oxamide group can be ionized and this classifies it as a cation-exchange resin. Abrams
and Benezra have listed several characteristics peculiar to strong and weak cation-exchangers which will be useful in later discussions.44

1. Strong-Acid Cation-Exchange Resins. a) Acid forms hydrolyze neutral salts, converting the salt to its corresponding acid and the resin to the corresponding salt. b) Chemical activity of the resin is similar to that of sulfuric acid. c) In very dilute solutions, the selectivity of the sulfonate group for a given ion increases with increasing valence of the \((\text{Na}^+ < \text{Ca}^{2+} < \text{Ce}^{3+} < \text{Th}^{4+})\). d) In dilute aqueous solutions, relative affinities for ions of a given valence increase with increasing atomic number \((\text{Li}^+ < \text{Na}^+ < \text{K}^+, \text{etc.})\). e) At high concentrations, the influence of both valence and atomic number disappears and, in fact, may be reversed. f) A large excess of strong acid in relatively high concentration is required to achieve complete conversion to the hydrogen form. g) Nitrogenous bases, including amines, amino acids, polypeptides, and proteins are readily absorbed, but the larger molecules are sometimes difficult to elute.

2. Weak-Acid Cation-Exchange Resins. a) Chemical properties are analogous to those of acetic acid. b) Monovalent salts are hydrolyzed like salts of weak acids, and give alkaline reactions. c) Acid forms are most effective at pH above 6. d) These resins can be converted to the hydrogen form with little more than the stoichiometric quantities of strong acid. e) Resins are highly selective for
multivalent cations. Chelate complexes are formed with copper, cobalt, nickel, and other metal cations.

There are a number of factors and problems involved in choosing, preparing, and utilizing a resin. These include hydrophilicity, ion-exchange capacity, density, moisture-retention capacity, fouling, particle size, osmotic shock, and mechanical, thermal, and chemical stability, among others. 45-47

A review of the literature over the past seventy years shows a rapidly accelerating interest in the use of ion-exchange resins. 44, 48, 49 Only a limited number of examples are cited herein to show the scope of the area.

For Metals: Condensation of polyhydric phenols yielded a product highly selective for germanium. 50 Chitan and chitosan, natural amino sugar polymers, are fairly resistant to radiation and have been used to treat radioactive wastes. 51, 52 Chitosan is a selective absorbent for copper 53 and other transition metal ions. 54, 55 Cellulose with sulphydryl groups is selective for mercury. 56 A guanidine resin has been used to absorb trace metals such as silver and mercury. 57-59 A similar resin has been used to separate palladium from platinum. 60, 61 Acrylic acid resins are widely used for alkali reduction in water treatment. 44 Vinylpyridine resins showed selective absorption for copper and other heavy metals. 62, 63 Polyamine-urea resins absorb trace heavy metals from sea water. 64
For organic compounds: The use here has been much more limited, which is due to the wider range of variation and interferences with weak or non-electrolytes such as organic compounds. Nevertheless, a combination of anionic- and cationic-exchange resins were studied in the recovery of low concentrations of amino acids. Anion-exchangers have been used to absorb acidic contaminate such as phenols and chlorophenoxyacetic acid.

C. Chelating Resins

A large number of ion-exchangers belong to the subclass termed "chelating resins". They combine the two processes of ion-exchange and chelation in one material, which are both different types of complexation. If two or more donor groups form a ring upon complexation, this species is known as a metal chelate. This is schematically shown below. The donor is termed a "chelating agent". In a chelating resin the chelating agent may be incorporated either into or onto the polymer chain.

\[
M + 4A \rightarrow A-M-\bar{A} \quad \text{Metal Complex}
\]

\[
M + 2A-A \rightarrow A-\overline{M-A} \quad \text{Metal Chelate}
\]

The formation of the rings leads to several advantages.
"1) **High selectivity.** The affinity of particular metal ions to a certain chelating ion-exchanger depends mainly on the chelating group and not on the size of the ion, its charge, or other physical properties which determine the order of preference in the case of the ordinary ion-exchanger.

2) **Bond Strength.** In ordinary ion-exchangers the binding is electrostatic with a strength of 2-3 kcal/mole, while in the resins dealt with here the binding is of the order of 15-25 kcal/mole.

3) **Kinetics.** While in the ordinary type of exchanger, exchange processes are more rapid and controlled by diffusion only, which is itself a function of the mobility and the concentration gradient of the ions entering and leaving, the exchange process in a chelating exchanger is slower and controlled either by a particle diffusion mechanism or by a second order chemical reaction."

The much greater selectivity of chelating resins over that of simple ion-exchangers has led to wide use of these materials in separations and concentrations of trace metals. As with simple ion-exchangers, they can be used in the substitution of ions, non-ionic sorption, elimination of ionic impurities, and other reactions. They also have basically the same physical requirements as do the ion-exchange resins discussed previously.

However, the types of chelating resins are quite varied, because potentially any chelating agent can be used if it can
be attached to the polymer chain. Several examples are given to demonstrate the chelating effect.

Chelex 100 (or Dowex A-1) is the commercial polymeric analog of EDTA and shows specificity for certain multivalent elements such as Cu, Ni, Co, Ca, Mg, etc. \(^{44,70}\)

Bayer constructed chelating resins from glyoxal-phenol derivatives which were tailor-made for specific ions such as gold. \(^{71}\)

Crown ethers were condensed with formaldehyde to form resins exhibiting uptake for alkali and alkaline-earth metal ions. \(^{72}\)

Considerable work has been done in our laboratories by Dingman\(^ {73}\) on crosslinked polyamino-urea polymers, and by Gloss and Milano\(^ {74}\) and Hackett\(^ {75}\) who converted them to the
more specific and powerful poly(dithiocarbamate) chelating resins, shown below.

\[
\begin{align*}
&\text{Transition metal ions, but not alkali and alkaline-earth metal ions, form dithiocarbamate complexes. The complexes} \\
&\text{are strong and ion uptake is very efficient and the total capacity is high. Hackett used columns of the material in} \\
&\text{measuring trace metal concentrations in sea water and the complexation is essentially irreversible, because the di-} \\
&\text{thiocarbamate is destroyed at low pHs. Hence the resin cannot be renewed, an important economic consideration.} \\
&\text{D. Non-Ionic Resins} \\
&\text{There are many organic polymers which are made up of covalent bonds which are not very polar or relatively ionizable. However, many will absorb both organic acids and bases and some forms of electrolyte complexes.} \\
&\text{Probably one of the most familiar examples of organic}
\end{align*}
\]
uptake is that of dying of fibers. In fact, polyoxamides have been used to enhance the dye uptake in compositions with cellulose triacetate. Polyurethane foams have been used to absorb dissolved pesticides and chlorinated biphenyls from contaminated water. It has also effectively absorbed gold at concentrations below 1.0 ppb because the gold forms uncharged ion pairs in hydrochloric acid. Other types of non-ionic absorbents include polymethylmethacrylate and styrene-divinylbenzene copolymers, and polyamides.

Specifically in regards to uptake of trace amounts of organic compounds some interesting work has been performed in our laboratories on polyvinylpyrrolidone (PVP).

\[
\begin{array}{c}
\text{CH}_2-\text{CH}_2 \\
\text{N} \\
\text{H}_2\text{C} \quad \text{C} \equiv \text{O} \\
\text{H}_2\text{C} - \text{CH}_2
\end{array}
\]

Carpenter concentrated trace levels of organic acids and bases such as phenols and catechol amines on columns of PVP and then released them with ethanol. Binding was determined to be through hydrogen-bonding effects. Mourey later extended this work to azo dyes. However, he found that in this case the binding mechanism was due to interactions such as charge transfer between the amide bond and the unsaturated molecule. This is a good illustration of the fact that with trace organic analysis and uptake one usually
encounters more complexities than with metal ions in ion-exchange. Binding in the polymer matrix cannot be easily elucidated by the study of model compounds as is often possible with metals.

The Chemical Behavior of the Oxamide Group

A number of investigations indicate that many amides coordinate with metals through the oxygen atom. However, there are some amides, notably diamides such as those shown below, in which the close proximity of the two amide groups changes the coordination behavior so that it is now through the nitrogen atom. Examples would be oxamides, malonamides, and their sulphur analogs.

\[
\text{H}_2\text{C}O \quad \text{O} \quad \text{H} \\
\text{X-(CH}_2\text{)}_n\text{N-C-(Q)-C-N-(CH}_2\text{)}_n\text{-X} \\
\text{where } Q = -\text{NH or } -(\text{CH}_2)_n- \quad n = 0,1 \\
\text{X} = -\text{CH}_3, -\text{NH}_2, -\text{NHR}, -\text{NR}_2
\]

Though such diamides have been known for three-quarters of a century, there were few studies into their complexation behavior until the 1930's, and then only a little until the late 1950's.

Oxamide itself (H\text{$_2$}N\text{COCONH}_2) can act as a bidentate ligand. It may coordinate through either or both the oxygen and nitrogen atoms depending on the solution environment. In non-aqueous solvents such as dichloromethane, 1:1 complexes may be formed between oxamide and Ti\text{Cl}_4, where the
oxygens of the carbonyl group are the donor atoms. However, in the case of dithiooxamide the donor atoms appear to be the nitrogens. The reversal appears to be due to electronegativity and steric differences. \(^8^9\) The complexes are weak since they are rapidly hydrolyzed in water; hence the use of non-aqueous solvents in many cases.

Replacing the amine hydrogens with alkyl groups leads to several changes. Working with \(N,N'\)-dimethyloxamide, Kruss and Ziegler\(^9^0\) reported complexes with \(\text{SbCl}_4\) involving \(N,O\)-bonding. This was later confirmed by Izakenaite and coworkers.\(^9^1\) Desseyn et al.\(^9^2\) found that with \(\text{Hg}^{2+}, \text{Pb}^{2+}, \text{Pd}^{2+}\), and \(\text{Ag}^+\) in 50% alcoholic solutions there was metal to sulphur bonding when \(N,N'\)-monosubstituted dithiooxamides were employed. However, in \(\text{Cu}^{2+}\) and \(\text{Ni}^{2+}\) complexes the bonding was between the metal and nitrogen.

Good and Siddall\(^9^3\) have studied the bonding of \(\text{Cu}^{2+}\) and \(\text{Ni}^{2+}\) with tetramethylenoxamide in nitromethane.

\[
\begin{array}{c}
\text{CH}_3 & \text{O} & \text{O} & \text{CH}_3 \\
\text{N} & \text{C} & \text{C} & \text{N} \\
\text{CH}_3 & & & \text{CH}_3
\end{array}
\]

They determined that bonding occurred through the carbonyl oxygens. Note that there are no hydrogens on the nitrogens. The malonamide analog showed stronger bonding, apparently due to the formation of a less-strained, six-membered rather than a five-membered ring. The effect is not as great with metal ions of larger ionic radii, such as \(\text{Mn}^{2+}, \text{Pb}^{2+},\) and \(\text{Cd}^{2+}\).
This appears to be due to better accommodation of the larger ions in the ring. Hart and coworkers\textsuperscript{94} found that tetraethylidithiooxamide coordinated with various divalent transition metals through the sulphur atoms in non-complexing solvents.

In highly polar, alkaline media, whether it be aqueous or in DMSO, the bonding is very different and much simpler. Several workers, notably Kuroda et al.,\textsuperscript{95} Armendarez and Nakamoto,\textsuperscript{96} and Bour et al.,\textsuperscript{97} have concluded that in aqueous solutions of high alkaline concentration the complex with Cu\textsuperscript{2+}, Ni\textsuperscript{2+}, and Pb\textsuperscript{2+} is a square planar diimido structure.

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{C} = \text{C} \\
\text{H} \\
\text{H} \\
\text{M} \\
\text{N} = \text{C} = \text{O} \\
\text{N} \\
\text{H} \\
\text{H} \\
\text{O} = \text{C} \\
\end{array}
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{C} = \text{C} \\
\text{H} \\
\text{H} \\
\text{M} \\
\text{N} = \text{C} = \text{O} \\
\text{N} \\
\text{H} \\
\text{H} \\
\text{O} = \text{C} \\
\end{array}
\]

Investigations into dithiooxamide showed that in alkaline media the amide groups reacted with divalent transition metals to form neutral, inner 1:1 complexes, each nitrogen atom losing one hydrogen. This effect appears to be due to the lower electronegativity of sulphur atoms.\textsuperscript{94}
N,N'-diethyloxamide undergoes the biuret reaction to form the following complex, whereas N,N-diethyloxamide (un-symmetrical) and N,N,N'-triethyloxamide show no reaction.\(^9\)

\[
\begin{align*}
\text{[} & \quad \quad -O \quad C_2H_5 \quad H_5C_2 \quad O^- \\
\text{\quad Cu}^{2+} \quad \text{N=C} \quad \text{N=C} \\
\text{\quad C=\quad H} \quad \text{H} \\
\text{\quad -O} \quad N \quad C \quad H \quad \text{NH}_2
\end{align*}
\]

This shows that the diimido (di-anion) structure must be formed in order for there to be complexation through the nitrogens in aqueous media.

In 1959, Jacobs and Yoe\(^9\) synthesized N,N'-bis(3-di-methylaminopropyl) dithiooxamide and found that it was a better chelating agent than the simple dithiooxamide. In 1967, Zuberbuhler and Fallab were the first of a number of investigators to study the chelating ability of diamine-diamides in depth.\(^1\) They began with the reaction of N,N'-diglycyl-1,2,-diaminoethane (whose close analog, triethyl-tetraamine, was a well-known complexing agent) and higher homologs with CuSO\(_4\) in alkaline solutions.

\[
\begin{align*}
\text{C} & \quad \text{H} \\
\text{H}_2\text{N-CH}_2-\text{C-}\text{N-CH}_2(\text{CH}_2)_n-\text{N-C-CH}_2-\text{NH}_2 & \quad n = 1-5 \\
\text{H}_2\text{O}
\end{align*}
\]

These diamine-diamides formed 5-, 6-, 7-, 8-, and 9-membered rings between the two amide groups, such as diagrammed below. There was no evidence of binuclear species.
In 1968, Grieser and Fallab\textsuperscript{101} worked with analogous diamides, except that now the -CO-NH- order was reversed.

\[
\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-N-C-(\text{CH}_2)_x-N-C-\text{CH}_2-\text{CH}_2-\text{NH}_2
\]
\[x = 1-3\]

Along with other investigators\textsuperscript{102} they found that oxamide \((x=0)\) and malonamide \((x=1)\) compounds formed tridentate mononuclear chelates in slightly acidic media. The malonamide derivative exhibited greater stability.

These compounds were more stable in alkaline media because the amide hydrogens were abstracted, resulting in a strong electron donor.

If the concentration of Cu\textsuperscript{2+} ions was high, a bidentate binuclear chelate was formed, as illustrated in the case of
Several variations have been made by replacing the amino groups with other groups such as 2-pyridylmethyl, but otherwise there was little else that was new in the literature regarding metal chelation or complexation by oxamides.

Wang and Bauman measured the ionization constants of \( \text{N,N'-bis(2-aminoethyl)oxamide} \) in 1.0 \( \text{M KNO}_3 \) solution at 25\(^\circ\)C. and determined that \( pK_{a1} = 8.30 \) and \( pK_{a2} = 9.54 \) for the oxamide hydrogens.

There is only one report pertaining to organic complexation with oxamides. In studies with \( \text{o-,m-, and p-nitrophenols with oxamide, N,N'-dimethyloxamide, and N,N,N',N'-tetramethyloxamide} \) in aqueous systems, Tronov and coworkers found that the stability of the complexes decreases with increasing number of methyl groups.
CHAPTER II
EXPERIMENTAL PART - SYNTHESIS

Preparation of Diamine-Oxamides

Description of Starting Materials.

A. Diethyl oxalate (DEC): obtained from Aldrich Chemical Co., Inc., Metuchen, New Jersey, was stored over activated molecular sieves (5Å) before use.

B. Ethylenediamine: obtained from Aldrich Chemical Co., Inc., Metuchen, New Jersey, was stirred over barium oxide overnight, decanted, and then distilled over sodium metal under a nitrogen atmosphere, center cut at 113°C, before use. It was stored in the dark over activated molecular sieves (3Å).

C. Solvents: Diethyl ether (anhydrous): obtained from Fisher Scientific Co., Fair Lawn, New Jersey, was used without further purification.

Tetrahydrofuran (THF): obtained from Fisher Scientific Co., Fair Lawn, New Jersey, was distilled from LiAlH₄, center cut at 65°C, before use.

Hexafluoroisopropanol (HFIP): obtained from E.I. du Pont de Nemours and Co., Inc., was used without further purification.

Trifluoroacetic acid (TFAA) and o-dichlorobenzene: obtained from Eastman Kodak Co., Rochester, New York, were used without further purification.
Dimethyl sulfoxide (DMSO): obtained from Eastman Kodak Co., Rochester, New York, was stored over activated molecular sieves (3A) before use.

D. Miscellaneous: Molecular sieves (3A): obtained from MCB Manufacturing Chemists, East Rutherford, New Jersey, were activated at 320°C under a stream of nitrogen gas.

Molecular sieves (5A): obtained from J.T. Baker Chemical Co., Phillipsburg, New Jersey, were used as received.

Preparation of Individual Diamine-Oxamides.

A. N,N'-bis(2-aminoethyl)oxamide (m-2-2-2): The synthesis of m-2-2-2 was similar to that described by Chang.110

B. 1) Bis-(2-ethoxyoxalylimino)ethane: To a 1000 ml. three-neck round bottom flask equipped with a mechanical stirrer at the center neck, a Claisen adapter on a side neck with a thermometer and a Liebig condenser, and a 250 ml. pressure-equalizing addition funnel on the remaining neck, were added, under dry nitrogen, DEO (140.40g, 0.96 mole) and 650 ml. of anhydrous diethyl ether. The addition funnel contained ethylenediamine (14.40g, 0.24 mole) in 115 ml. of anhydrous diethyl ether. The three-neck flask was cooled to keep the temperature below 15°C by means of an ice-water bath. The ethylenediamine solution was slowly added over a period of four hours and the reaction mixture which consisted of a white solid was filtered through a Buchner funnel, washed in a one gallon blender with ether, and refiltered. The material was dried in a vacuum oven overnight at room temperature; yield 57.80g(93%).
The solid was extracted in a Soxhlet extractor with anhydrous THF. After cooling a white solid deposited from the extract which was filtered, dried, and melted at 128-129°C (capillary). It was soluble in o-dichlorobenzene, hexafluoroisopropanol, and water. The infrared spectrum (KBr disc) showed absorptions at: 3290 cm\(^{-1}\) (N\text{HCO} stretching), 2965 cm\(^{-1}\) (asym. stretching of CH\(_2\)), 2925 cm\(^{-1}\) (sym. stretching of CH\(_2\)), 1735 cm\(^{-1}\) (ester stretching), 1665 cm\(^{-1}\) (CO stretching), 1547 cm\(^{-1}\) (NH bending), 1465 cm\(^{-1}\) (CN stretching), and 722 cm\(^{-1}\) (NH out of plane bending). The proton magnetic resonance (PMR) spectrum (DMSO) showed \(\delta : 8.89\) (N\text{HCO}CO, 2), 4.25 (CH\(_3\)-CH\(_2\), 4), 3.28 (N-CH\(_2\), 4) and 1.29 (CH\(_3\), 6). Anal. Calcd. for C\(_{10}\)H\(_{16}\)N\(_2\)O\(_6\): C, 46.15%; H, 6.20%; N, 10.76%. Found: C, 46.31%; H, 6.41%; N, 10.65%.

B. 2) Bis(2-aminoethyliminooxalylimino)ethane (m-2-2-2-2-2): To a 1000ml three-neck round bottom flask were added ethylenediamine (23.10g, 0.38 mole) and 300 ml of THF. Bis(2-ethoxyoxalylimino) ethane (5.00g, 0.019 mole) was dissolved in 200 ml of hot THF. The reaction was run under a slow nitrogen flow while the flask contents were kept boiling (4 hrs.). The white precipitate was filtered through a coarse glass-sintered funnel and dried in a vacuum oven overnight at room temperature; yield 5.30g (96%); decomposed 250°C (DSC). It was soluble in TFAA and boiling water. Infrared spectrum (KBr disc): 3290 cm\(^{-1}\) (N\text{HCO} stretching), 2945 cm\(^{-1}\) (asym. stretching of CH\(_2\)), 2870 cm\(^{-1}\) (sym. stretch-
ing of CH₂, 1650 cm⁻¹ (CO stretching), 1530 cm⁻¹ (NH bending), 1460 cm⁻¹ (CN stretching), and 750 cm⁻¹ (NH out of plane bending). The PMR (CF₃COOH) spectrum showed δ: 8.22 (NHCO, 4), 6.75 (H₂N, 6), and 3.29 (CH₂, 12). Anal. Calcd. for C₁₀H₂₀N₆O₄: C, 41.66%; H, 6.99%; N, 29.15%. Found: C, 41.76%; H, 7.03%; N, 29.00%.

E. 3) Bis(2-aminoethyliminooxalylimino) ethane dihydrochloride salt(m-2-2-2-2-2 • 2 HCl): m-2-2-2-2-2 was dissolved in boiling water and a large excess of concentrated hydrochloric acid was quickly added, whereupon the salt precipitated out immediately. The solution was cooled rapidly, filtered, and dried. The white powder decomposed >290°C(DSC). Infrared spectrum (KBr disc): 3260 cm⁻¹ (NHCO stretching), 2970 to 2900 cm⁻¹ (asym. and sym. stretching of CH₂), 1650 cm⁻¹ (CO stretching), 1590 cm⁻¹ (amine salt bending), 1520 cm⁻¹ (NH bending), 1445 cm⁻¹ (CN stretching), and 742 cm⁻¹ (NH out of plane bending). Anal. Calcd. for C₁₀H₂₂N₆O₄Cl₂: C, 33.25%; H, 6.14%. Found: C, 33.42%; H, 6.35%.

C. 1) N,N'-bis(2-ethoxyoxalyliminoethylene)oxamide: To a 2000 ml. three-neck round bottom flask were added diethyl oxalate (83.90g, 0.57 mole) in 400 ml. tetrahydrofuran. N,N'-bis(2-aminoethyl)oxamide (5.00g, 0.029 mole) was dissolved in 1000 ml. of hot THF and added during a period of six hours to the boiling solution of DEO. The precipitate was filtered and dried at 1 mm. overnight at room temperature; yield 9.21g (86%). The white powder is soluble only in
hexafluoroisopropanol; m.p. 249°C. (DSC). Infrared spectrum (KBr disc): 3300 cm\(^{-1}\) (\(\text{NHCO}\) stretching), 2990 cm\(^{-1}\) (asym. stretching of \(\text{CH}_2\)), 2950 cm\(^{-1}\) (sym. stretching of \(\text{CH}_2\)), 1740 to 1655 cm\(^{-1}\) (broad, ester and CO stretching), 1555 cm\(^{-1}\) (NH bending), 1455 cm\(^{-1}\) (CN stretching), and 740 cm\(^{-1}\) (NH out of plane bending). The PMR (HFIP) spectrum showed:

\[ \delta: 8.84 \text{ (NHCOO, 4), 4.23 (CH}_3\text{CH}_2\text{, 4), 3.26 (N-CH}_2\text{, 8), and 1.35 (CH}_3\text{, 6).} \]

Anal. Calcd. for \(\text{C}_{14}\text{H}_{22}\text{N}_4\text{O}_8\): C, 44.92%; H, 5.92%. Found: C, 44.93%; H, 5.99%.

C. 2) \(\text{N,N'}\)-bis(2-aminooxaliminooxaliminoethylene)oxamide dihydrochloride salt (m-2-2-2-2-2-2-2-HCl):

To a 50 ml. three-neck round bottom flask were added ethylenediamine (1.61g, 0.027 mole) and 15 ml. of hexafluoroisopropanol. \(\text{N,N'}\)-bis(2-ethoxyoxaliminoethylene)oxamide (2.00g, 0.0053 mole) was dissolved in 24 ml. of hexafluoroisopropanol, gravity filtered from undissolved material and added over a period of six hours to the ethylenediamine while the solution was refluxing. The mixture was chilled overnight and the precipitate was suction filtered, washed, and dried at 100°C. and 1 mm pressure overnight; yield 1.11 g (51%). The compound had very low solubility and could only be purified through the formation of the dihydrochloride salt which decomposed > 270°C. (DSC). Infrared spectrum (KBr disc): 3300 cm\(^{-1}\) (\(\text{NHCO}\) stretching), 3000 to 2900 cm\(^{-1}\) (asym. and sym. stretching of \(\text{CH}_2\)), 1657 cm\(^{-1}\) (CO stretching), 1600 cm\(^{-1}\) (amine salt bending, weak), 1505 cm\(^{-1}\) (NH bending), 1457 cm\(^{-1}\) (amine salt bending, weak).
cm⁻¹ (CN stretching), and 750 cm⁻¹ (NH out of plane bending). The PMR (CF₃COOH) spectrum showed δ: 8.34 (NHCOCO, 6), 6.79 (⁺H₂N, 6), and 3.22 (CH₂, 16). Anal. Calcd. for C₁₄H₂₈N₆O₆Cl₂: C, 35.38%; H, 5.94%. Found: C, 35.12%; H, 5.94%.

Characterization of Diamine-Oxamides and Their Precursors.

Every compound was characterized by melting point determination, infrared and proton magnetic resonance spectra, and elemental analyses.

A. Melting Point Determinations: The melting point of those compounds which visually melted were measured in an open-end capillary tube on a Melt-Temp Apparatus at a heating rate of between 1-2°C. per minute and are uncorrected. Differential scanning calorimetry (DSC) was employed for all those materials which degraded or did not show a clear melt. A Perkin-Elmer Differential Scanning Calorimeter DSC-1B was used at a heating rate of 20°C. per minute under a nitrogen flow of 25 lb/in².

B. Infrared Spectra: Infrared spectra of the compounds were determined using a Perkin-Elmer 727 spectrometer. Samples were prepared by mixing the vacuum-dried material with anhydrous KBr in a 1-3% by weight concentration and pressing the mixture into a disc.
C. PMR Spectra: Proton magnetic resonance spectra of the compounds were obtained either in a Hitachi/Perkin-Elmer PMR spectrometer R-24 (60 MHz) or in a Perkin-Elmer R-32 (90 MHz) in concentrations ranging from 5-20%. Tetramethylsilane or hexamethyldisiloxane was used as an internal standard and the spectra were measured at the instrument's normal operating temperature (ca. 37°C.). For each specific compound the solvent that was used for the PMR determination is noted in parentheses preceding the actual PMR data.

D. Elemental Analyses: The elemental analyses for each material were performed by the Microanalysis Laboratories of the University of Massachusetts, Amherst, Mass.

Preparation of Diacid Chlorides.

Description of Starting Materials

1) Diacid chlorides or precursors: 1,1-cyclobutanedicarboxylic acid (1,1-CBT): obtained from Pfaltz and Bauer, Inc., Flushing, New York, was recrystallized from 1,2-dichloroethane to give white crystals, m.p. 158-160°C.

Dimethyl-1,4-cyclohexanedicarboxylate (DM-1,4-CHX) (cis, trans mixture): obtained from Eastman Kodak Co., Rochester, New York, was used without further purification.

Sebacyl chloride: obtained from Eastman Kodak Co., Rochester, New York, was redistilled in a Bantam-ware vacuum-jacketed column at 0.1 mm pressure, at a center cut of 96.8°C, before use.
Isophthaloyl chloride and 2,6-pyridinedicarboxylic acid chloride, obtained from Aldrich Chemical Co., Inc., Metuchen, New Jersey, and terephthaloyl chloride, obtained from Eastman Kodak Co., Rochester, New York, were recrystallized three times from n-hexane under a dry nitrogen atmosphere before use.

1,6-naphthalenedicarboxylic acid: obtained from Pfaltz and Bauer, Inc., Flushing, New York, was recrystallized from glacial acetic acid to yield a beige powdery material, m.p. 298-299.5°C.

Dimethyl-2,6-naphthalenedicarboxylate: obtained from Aldrich Chemical Co., Inc., Metuchen, New Jersey, was recrystallized from 100% ethanol to yield beige, mica-like crystals, m.p. 188-190°C.

1,8-dichloroanthraquinone: obtained from Pfaltz and Bauer, Inc., Flushing, New York, was recrystallized from glacial acetic acid to yield a dark yellow powder, m.p. 201-202.5°C. The infrared spectra was in agreement with the Sadtler reference.

1,5-dichloroanthraquinone: obtained from Pfaltz and Bauer, Inc., Flushing, New York, was recrystallized from benzene to yield short, fluffy, yellow needles, m.p. 247-252°C. The infrared spectra was in agreement with the Sadtler reference.

2) Solvents: n-Hexane: obtained from Fisher Scientific Co., Fair Lawn, New Jersey, was distilled from freshly
cut sodium and stored over sodium wire in the dark.

Chloroform: obtained from Fisher scientific Co., Fair Lawn, New Jersey, was washed three times with equal volumes of water, pre-dried over anhydrous CaCl₂, and then over activated molecular sieves (3Å).

1,2-dichloroethane: obtained from Fisher Scientific Co. Fair Lawn, New Jersey, was stirred over NaOH pellets overnight, decanted, and distilled from P₂O₅ under a nitrogen atmosphere. It was stored over activated molecular sieves (3Å) in the dark.

Benzene, toluene, 100% ethanol, acetone, and glacial acetic acid: obtained from Fisher Scientific Co., Fair Lawn, New Jersey, were used without further purification.

Chlorobenzene: obtained from Eastman Kodak Co., Rochester, New York, was stored over anhydrous CaCl₂ before use.

Benzyl cyanide and dimethylformamide (DMF): obtained from Aldrich Chemical Co., Inc., Metuchen, New Jersey, were used without further purification.

Dimethylacetamide (DMAc): obtained from Aldrich Chemical Co., Inc., Metuchen, New Jersey, was distilled from barium oxide at 30 mm through a fractionation column, at a center cut of 85°C, and stored over a column of activated molecular sieves (3Å) before use.

Dimethyl sulphoxide (DMSO): obtained from Eastman Kodak Co., Rochester, New York, was vacuum distilled at 2 mm, at a center cut of 54°C, before use.
3) Miscellaneous: Nitric, sulfuric, hydrochloric, and glacial acetic acid, and ammonium hydroxide: obtained from Fisher Scientific Co., Fair Lawn, New Jersey, were used without further purification.

Thionyl chloride: obtained from Aldrich Chemical Co., Inc., Metuchen, New Jersey, was purified according to the procedure outlined in Fieser.\textsuperscript{111} It could then be stored indefinitely in the freezer in a flask sealed with Parafilm.

Zinc powder, CaCl\textsubscript{2}, and barium oxide, obtained from J. T. Baker Chemical Co., Phillipsburg, New Jersey, were used without further purification.

Molecular sieves (3A): obtained from MCB Manufacturing Chemists, East Rutherford, New Jersey, were activated at 320°C. under a stream of nitrogen gas.

**Preparation of Individual Diacid Chlorides**

1) 1,1-Cyclobutanedicarboxylic acid chloride: To a 100 ml. one-neck round bottom flask equipped with a Liebig condenser to which a CaCl\textsubscript{2} drying tube was attached were added 1,1-CBT (19.40g, 0.27 mole), four drops DMF as catalyst, and some boiling stones. The mixture was refluxed eight hours and then the excess thionyl chloride was removed by simple atmospheric distillation. The 1,1-cyclobutanedicarboxylic acid chloride was distilled at 59 mm pressure, at a center cut of 108°C., before use.

2) Trans-1,4-cyclohexanedicarboxylic acid chloride: (a) Separation of the trans isomer from the cis, trans mixture
of dimethyl-1,4-cyclohexanedicarboxylate: The cis, trans mixture (225 ml) was cooled to 0°C. Mostly trans-isomer precipitated out. The precipitate was recrystallized five times from technical grade n-hexane to yield white crystals; m.p. 67°C.

(b) Hydrolysis of trans-dimethyl-1,4-cyclohexanedicarboxylate: To a 100 ml. one-neck round bottom flask equipped with a magnetic stirrer and Liebig condenser were added trans-DM-1,4-CHX (7.00g, 0.036 mole) and 42.00g of a 36% HCl solution. The solution was stirred and refluxed for eight hours and then allowed to cool to room temperature. The white precipitate was filtered by Buchner, recrystallized from distilled water, and dried in a vacuum oven at 64°C for 12 hours to give a nearly quantitative yield of shiny white crystals of trans-1,4-cyclohexanedicarboxylic acid; m.p. 312-317°C.

(c) Synthesis of the diacid chloride: To a 50 ml. one-neck round bottom flask equipped with a magnetic stirrer and a Liebig condenser to which a CaCl₂ drying tube was attached were added trans-1,4-cyclohexanedicarboxylic acid (4.78g, 0.028 mole), thionyl chloride (6.61g, 0.11 mole), and four drops of DMF as catalyst. The mixture was refluxed for nine hours and the diacid chloride precipitated out upon cooling. Later, the excess thionyl chloride was removed by simple atmospheric distillation, and the trans-1,4-cyclohexanedicarboxylic acid chloride was recrystallized from purified n-hexane under a dry nitrogen atmosphere to give white,
short needles; m.p. 66-67°C.

3) Cis-1,4-cyclohexanedicarboxylic acid chloride: (a) Hydrolysis of cis-dimethyl-1,4-cyclohexanedicarboxylate: To a 500 ml. one-neck round bottom flask equipped with a magnetic stirrer and a Liebig condenser were added 50 ml. of a mostly cis-isomer mixture of dimethyl-1,4-cyclohexanedicarboxylate and 150.0 g of a 36% HCl solution. The solution was stirred and refluxed for eight hours and then allowed to cool to room temperature. The white precipitate was filtered with a Buchner funnel, recrystallized from 1,2-dichloroethane, and dried in a vacuum oven at 65°C overnight to give a nearly quantitative yield of white, shiny crystals of cis-1,4-cyclohexanedicarboxylic acid; m.p. 165-167°C.

(b) Synthesis of the diacid chloride: To a 100 ml. one-neck round bottom flask equipped with a magnetic stirrer and a Liebig condenser to which a CaCl₂ drying tube was attached were added cis-1,4-cyclohexanedicarboxylic acid (14.63 g, 0.085 mole), thionyl chloride (40.44 g, 0.26 mole), and four drops DMF as catalyst. The mixture was refluxed for nine hours and then the excess thionyl chloride was removed by simple atmospheric distillation. The cis-1,4-cyclohexanedicarboxylic acid chloride was then purified by vacuum distillation at 0.4 mm, and a center cut of 86°C, was collected.

4) 1,6-Naphthalenedicarboxylic acid chloride: Synthesis of the diacid chloride: To a 50 ml. one-neck round bottom flask equipped with a Liebig condenser to which a CaCl₂
drying tube was attached were added 1,5-naphthalenedicarboxylic acid (6.50g, 0.030 mole), thionyl chloride (42.93g, 0.18 mole), four drops DMF as catalyst, and some marble boiling chips. The solution was refluxed for seven hours and then the excess thionyl chloride was removed by simple atmospheric distillation. The diacid chloride was recrystallized from n-hexane to yield white crystals; m.p. 84-87°C.

5) 2,6-Naphthalenedicarboxylic acid chloride: (a) Hydrolysis of dimethyl-2,6-naphthalenedicarboxylate: To a 1000 ml. three-neck round bottom flask equipped with a mechanical stirrer and a Liebig condenser were added dimethyl-2,6-naphthalenedicarboxylate (22.70g, 0.093 mole) and 210 ml. of a 10% KOH/100% ethanol solution. The solution was refluxed for eight hours with a steam bath, poured into an equal volume of distilled water and gravity filtered. The filtrate was warmed and dilute HCl was added until the solution was at pH=2. The white precipitate was filtered, washed with water, and dried in a vacuum oven at 60°C. overnight. The 2,6-naphthalenedicarboxylic acid decomposed over 380°C.

(b) Synthesis of the diacid chloride: To a 100 ml. one-neck round bottom flask equipped with a Liebig condenser to which a CaCl₂ drying tube was attached were added 2,6-naphthalenedicarboxylic acid (19.20g, 0.089 mole), thionyl chloride (120.78g, 0.27 mole), four drops DMF as catalyst, and some marble boiling chips. The solution was refluxed four hours and then the excess thionyl chloride was removed by
simple atmospheric distillation. The 2,6-naphthalenedicarboxylic acid chloride was recrystallized from 1,2-dichloroethane to yield short, yellow needles; m.p. 186–190°C.

6) 1,8-Anthraquinonedicarboxylic acid chloride: (a) Synthesis of 1,8-dicyanoanthraquinone: To a 250 ml. one-neck round bottom flask equipped with a Liebig condenser through which pressurized air was blown, on top of which was a 10" air condenser, was added 1,8-dichloroanthraquinone (20.00 g, 0.072 mole), then cuprous cyanide (16.00 g, 0.18 mole), then 181 ml. of benzyl cyanide. The mixture was heated to 230°C. by means of a silicone oil bath placed on a hot plate. After 30 minutes the black solution was allowed to cool, and then filtered through a coarse glass-sintered funnel. The black tarry material was washed with 250 ml. benzene, followed by 350 ml. of 100% ethanol. It was then refluxed four days in 10% HNO₃ solution, which was renewed every day. A trap of aqueous KMnO₄ solution was used to oxidize any HCN given off. A fine blackish-brown powder was obtained which was washed with water and acetone before vacuum drying at 65°C. overnight; yield 12.38 g (67%). The material was then extracted one day with distilled water, and one day with acetone, using a Soxhlet apparatus. It was dried in the vacuum oven overnight at 60°C. and then recrystallized from dimethylacetamide to give a dark reddish-brown powder; dec. > 350°C. Infrared spectrum (KBr disc) showed absorptions at: 2250 cm⁻¹ (nitrile) and 1665 cm⁻¹ (quinone).
(b) Hydrolysis of 1,8-dicyanoanthraquinone: To a 500 ml. standard-taper Erlenmeyer flask equipped with a magnetic stirrer and a Liebig condenser were added 1,8-dicyanoanthraquinone (5.00g, 0.019 mole), 278 ml. of conc. H$_2$SO$_4$, and 123 ml. of distilled water. The mixture was refluxed 30 minutes, and then the dark yellow, clear solution was transferred to a 1000 ml. Erlenmeyer. 400 ml. of distilled water was then added and after five minutes long golden needles precipitated out. The diacid was purified by first dissolving it in hot ammoniacal solution, and then slowly adding dilute HCl solution until the long golden needles would begin to precipitate out again. Dried in a vacuum oven overnight to 60°C; yield 5.69g (100%); dec. > 305°C. Infrared spectrum (KBr disc): 3550 to 2400 cm$^{-1}$ (broad, -COOH), and 1660 cm$^{-1}$ (broad, -COOH and quinone).

(c) Synthesis of the diacid chloride: To a 1000 ml. one-neck round bottom flask equipped with a magnetic stirrer and a Liebig condenser to which a CaCl$_2$ drying tube was attached were added 1,8-anthraquinonenedicarboxylic acid (8.00g, 0.027 mole), thionyl chloride (12.83g, 0.054 mole), 480 ml. of chlorobenzene, and four drops of DMF as catalyst. The solution was refluxed for five hours, then cooled in the freezer. Yellow platelets precipitated out. The 1,8-anthraquinonenedicarboxylic acid chloride had limited solubility in chloroform; hence, it was recrystallized from chlorobenzene under a dry nitrogen atmosphere to yield whitish-yellow short
needles; m.p. 208-211°C (literature unknown). Infrared spectrum (KBr disc): 1782 cm\(^{-1}\) (CO-C\(_1\)) and 1675 cm\(^{-1}\) (quinone).

7) 1,8-Anthracenedicarboxylic acid chloride: (a) Synthesis of 1,8-anthracenedicarboxylic acid: To a 1000 ml. three-neck round bottom flask equipped with a mechanical stirrer and a Liebig condenser were added 1,8-anthraquinonedicarboxylic acid (11.00g, 0.037 mole), zinc powder (22.00g, 0.015 mole), and 550 ml. of a 1N NH\(_4\)OH solution. It was refluxed 3 hours and then the solution was allowed to cool and suction filtered by Buchner funnel. The filtrate was yellowish-olive green. It was brought to a boil and HCl added until it almost would not go back into solution. It was cooled in the refrigerator overnight; a small amount of olive green precipitate was then suction filtered off. The filtrate was then brought to a boil and HCl was added until pH = 2; one obtained a yellow, fluffy precipitate. This was purified by reprecipitation from NH\(_4\)OH/HCl; yield 10.76g (98\%) of 1,8-anthracenedicarboxylic acid; dec. > 310\(^0\)C.\(^{112}\) Infrared spectrum (KBr disc): 3400 to 2400 cm\(^{-1}\) (broad, -COOH) and 1730 to 1640 cm\(^{-1}\) (broad, -COOH).

(b) Synthesis of the diacid chloride: To a 100 ml. one-neck round bottom flask equipped with a magnetic stirrer and a Liebig condenser to which a CaCl\(_2\) drying tube was attached were added 1,8-anthracenedicarboxylic acid (4.00g, 0.015 mole) thionyl chloride (10.71g, 0.090 mole), 62 ml. of chlorobenzene, and four drops DMP as catalyst. The mixture was re-
fluxed ten hours and cooled in the freezer. Orangish-yellow crystals precipitated out. Later, the excess thionyl chloride and chlorobenzene were removed by simple atmospheric distillation. The 1,8-anthracenedicarboxylic acid chloride had very limited solubility in chloroform; hence, it was recrystallized from chlorobenzene under a dry nitrogen atmosphere to yield pink crystals; m.p. 267-275°C. $^{113,114}$ Infrared spectrum (KBr disc): 1780 cm$^{-1}$ (C=O-Cl).

8) 1,5-Anthraquinonenedicarboxylic acid chloride: (a) Synthesis of 1,5-dicyanoanthraquinone: To a 250 ml. one-neck round bottom flask equipped with a Liebig condenser through which pressurized air was blown, on top of which was a 10" air condenser, were added 1,5-dichloroanthraquinone (40.00g, 0.14 mole), then cuprous cyanide (32.00g, 0.36 mole), then 120 ml. of benzyl cyanide. The mixture was heated to 230°C by means of a silicone oil bath placed on a hot plate. After 30 minutes the solution was allowed to cool, and then filtered through a coarse glass-sintered funnel. The black tarry material was washed with 350 ml. of benzene, followed by 500 ml. of 100% ethanol. It was then refluxed for four days in 10% HNO$_3$ solution, which was renewed every day. A trap of aqueous KMnO$_4$ solution was used to oxidize any HCN given off. A granular dark brown material was obtained which was washed with water and acetone before vacuum drying at 65°C overnight; yield 29.5g (79%). The material was then extracted for one day with distilled water, and one day with acetone,
using a Soxhlet apparatus. It was dried in the vacuum oven overnight at 60°C. and then recrystallized from DMAC to give brownish-gold short needles; dec. > 390°C. Infrared spectrum (KBr disc): 2250 cm\(^{-1}\) (nitrile) and 1670 cm\(^{-1}\) (quinone).

(b) Hydrolysis of 1,5-dicyanoanthraquinone: To a 125 ml. standard-taper Erlenmeyer equipped with a magnetic stirrer and a Liebig condenser were added 1,5-dicyanoanthraquinone (15.90 g, 0.062 mole), 54.1 g of conc. H\(_2\)SO\(_4\), and 9.70 g distilled water. The solution was quickly brought to a boil on a hot plate. It first became clear and deep red, and later the orange diacid precipitated out. The solution was transferred to a 250 ml. Erlenmeyer and 60 ml. of distilled water was added. NaOH pellets were added at boiling until the diacid was in solution. The dark reddish-brown mixture was then gravity filtered while hot. 3N HCl was slowly added to the filtrate until all the diacid had precipitated out, and then it was filtered. This technique was repeated twice; the last time, animal charcoal was introduced to remove colored impurities. Dried in a vacuum oven overnight at 60°C; one obtained a whitish-yellow, talc-like material; yield 10.50 g (58%); dec. > 390°C. Infrared spectrum (KBr disc): 3300 cm\(^{-1}\) (broad, -COOH) and 1670 cm\(^{-1}\) (broad, -COOH and quinone).

(c) Synthesis of the diacid chloride: To a 200 ml. one-neck round bottom flask equipped with a magnetic stirrer and a Liebig condenser to which a CaCl\(_2\) drying tube was attached
were added 1,5-anthraquinonedicarboxylic acid (4.00g, 0.014 mole), thionyl chloride (9.74g, 0.082 mole), 70 ml. of chlorobenzene, and four drops of DMF as catalyst. The solution was refluxed for eight hours, then cooled to room temperature; red crystals precipitated out. The 1,5-anthraquinonedicarboxylic acid chloride was recrystallized from chlorobenzene under a dry nitrogen atmosphere to yield red, short needles; m.p. 275-283°C. Infrared spectrum (KBr disc): 1775 cm\(^{-1}\) (CO-Cl) and 1665 cm\(^{-1}\) (quinone).

9) 1,5-Anthracenedicarboxylic acid chloride: (a) Synthesis of 1,5-anthracenedicarboxylic acid: To a 500 ml. three-neck round bottom flask equipped with a mechanical stirrer and a Liebig condenser were added 1,5-anthraquinonedicarboxylic acid (1.00g, 0.0034 mole), zinc powder (3.00g, 0.046 mole), and 300 ml. of 15% NH\(_4\)OH solution. The solution was refluxed for four hours and then allowed to cool and suction filtered with a Buchner funnel. The filtrate was yellowish-olive green. It was brought to a boil and HCl added until it almost would not go back into solution. It was cooled in the refrigerator overnight, and a small amount of olive green precipitate was suction-filtered off. The filtrate was brought to a boil and HCl was added until pH=2, and one obtained a yellowish-olive green precipitate. This was purified by reprecipitation from NH\(_4\)OH/HCl several times; yield 0.73g (73%) of 1,5-anthracenedicarboxylic acid; dec. > 370°C. Infrared spectrum (KBr disc): 3300 to 2400 cm\(^{-1}\)
(broad, -COCH₃) and 1675 cm⁻¹ (broad, -COOH).

(b) Synthesis of the diacid chloride: To a 200 ml. one-neck round bottom flask equipped with a magnetic stirrer and a Liebig condenser to which a CaCl₂ drying tube was attached were added 1,5-anthracenedicarboxylic acid (4.00g, 0.015 mole), thionyl chloride (9.96g, 0.048 mole), 70 ml. of chlorobenzene, and four drops of DMF as catalyst. The solution was refluxed seven hours, then cooled to room temperature; needles precipitated out quickly from the dark green solution. The 1,5-anthracenedicarboxylic acid chloride was recrystallized from chlorobenzene under a dry nitrogen atmosphere to yield dark yellow long needles; m.p. 259-261°C. Infrared spectrum (KBr disc): 1740 cm⁻¹ (CO-Cl).

Characterization of Diacid Chlorides and Precursors:
All the anthraquinone and anthracene compounds were characterized by melting point determinations and infrared spectra. While the other, simpler, diacid chlorides are well-known, the anthraquinone and anthracene diacid chlorides have not been reported extensively.

1) Melting Point Determinations: The melting points of the compounds were measured in an open-end capillary tube on a Melt-Temp Apparatus at a heating rate of between 1-2°C per minute and are uncorrected.

2) Infrared Spectra: The infrared spectrum of the compounds were obtained using a Perkin-Elmer 727 spectrometer. Samples were prepared by mixing the purified, vacuum dried
material with anhydrous KBr in a 1-3% concentration and pressing the mixture into a disc.

**Preparation of Copolyoxamides.**

**A. Description of Starting Materials**

1) Aqueous solutions were prepared with distilled water. Sodium carbonate was the best base to use for the interfacial synthesis of copolyoxamides. This was totally dissolved before the diamine-oxamide was added and brought into solution. The diamine-oxamides which were used for polymerization were recrystallized three times before use and dried at 0.1 mm pressure over P2O5 at 78°C in an Alberhalde apparatus with a liquid nitrogen trap overnight.

2) The best organic solvent was determined to be chloroform, obtained from Fisher Scientific Co., Fair Lawn, New Jersey. It was washed three times with an equivolume amount of distilled water, dried over anhydrous calcium chloride, filtered, and then dried over molecular sieves (3Å), before use. It was stored in the dark. All diacid chlorides which were used for polymerization were recrystallized three times immediately before use.

3) Dimethylacetamide: see page 50.

4) Lithium chloride: obtained from Fisher Scientific Co., Fair Lawn, New Jersey, was dried at 0.1 mm at 140°C for 40 hours before use.

5) Apparatus: Either a one-quart or one-gallon Waring blender (Cat. No. 700 and CB-6, respectively) was used for
interfacial polymerizations. They were obtained from Waring Products Division, Dynamic Corporation of America, New Hartford, Connecticut.

B. Preparation of Individual Polymers

Most of the polymers were synthesized by interfacial polymerization at least two times; one representative run is described.

1) New Polymers

Poly(iminoethyleneiminooxalyliminoethyleneiminocarbonyl-1,1-cyclobutylene carbonyl) (p-2-2-1-1-cyclobut.)

An aqueous solution of N,N'-bis(2-aminoethyl)oxamide (2.47g, 0.014 mole) and sodium carbonate (1.51g, 0.028 mole) in 168 ml. of distilled water was placed into a one-quart Waring blender and the proper blending speed was obtained using a 140 V Variac. The solution of 1,1-cyclobutanedicarboxylic acid chloride (2.57g, 0.014 mole) in 100 ml. of chloroform was added at once. White polymer was formed as soon as the organic solution was added and blending was continued for five minutes. The resulting white mass was filtered through a coarse glass-sintered funnel, washed twice with 200 ml. of distilled water, then 250 ml. of acetone, and finally dried at 60°C. at 30 mm for twelve hours. The polymer weighed 3.39g (85%), and melted at 286°C., and decomposed above 327°C (DSC). The polymer was soluble in sulfuric acid, TFAA, and DMAC containing 4% LiCl. Infrared spectrum (film on KBr disc) showed absorptions at: 3300 cm⁻¹
(NHCO stretching), 2950 cm\(^{-1}\) (asym. stretching of CH\(_2\)), 2880 cm\(^{-1}\) (sym. stretching of CH\(_2\)), 1650 cm\(^{-1}\) (CO stretching), 1520 cm\(^{-1}\) (NH bending), 1440 cm\(^{-1}\) (CN stretching), and 710 cm\(^{-1}\) (NH out of plane bending). The FNR (CF\(_3\)COOH) showed \(\delta\) : 8.71 (NHCOO, 2), 7.82 (NHCO, 2), 3.71 (acyclic CH\(_2\), 8), and 2.67 to 2.09 (broad, cyclic CH\(_2\), 6). The inherent viscosity of a 0.5\% H\(_2\)SO\(_4\) solution of this polymer was 0.50 dl/g. Anal. calcd. for (C\(_{12}\)H\(_{18}\)N\(_4\)O\(_4\))\(_n\): N, 19.85%; Found: N, 19.13%.

Poly(iminoethyleneiminooxalyliminoethyleniminocarbonyltrons-1,4-cyclohexylenecarbonyl) (p-2-2-2-trans-1,4):

N,N'-bis(2-aminoethyl)oxamide (9.17g, 0.053 mole) and Na\(_2\)CO\(_3\) (11.15g, 0.11 mole) in 625 ml. of distilled water; trans-1,4-cyclohexanediacarboxylic acid chloride (11.00g, 0.053 mole) in 375 ml. of chloroform; reaction time 5 minutes; polymer yield 12.00g (74%); decomposed >370°C (DSC). Infra-red spectrum (film on KBr disc): 3280 cm\(^{-1}\) (NHCO stretching), 2935 cm\(^{-1}\) (asym. stretching of CH\(_2\)), 2860 cm\(^{-1}\) (sym. stretching of CH\(_2\)), 1654 cm\(^{-1}\) (CO stretching), 1524 cm\(^{-1}\) (NH bending) 1448 cm\(^{-1}\) (CN stretching), and 717 cm\(^{-1}\) (NH out of plane bending). The FNR (CF\(_3\)COOH) showed \(\delta\) : 8.87 (NHCOO, 2), 7.84 (NHCO, 2), 3.68 (acyclic CH\(_2\), 8), and 2.55 to 1.60 (broad, cyclic CH and CH\(_2\), 10). The inherent viscosity of a 0.5\% H\(_2\)SO\(_4\) solution of this polymer was 0.51 dl/g. Anal. Calcd. for (C\(_{14}\)H\(_{22}\)N\(_4\)O\(_4\))\(_n\): N, 18.05%; Found: N, 17.94%.
1,4-cyclohexylenecarbonyl) (p-2-2-2-cis-1,4):

N,N′-bis(2-aminoethyl)oxamide (9.55 g, 0.055 mole) and Na₂CO₃ (11.62 g, 0.11 mole) in 650 ml of distilled water; cis-1,4-cyclohexanedicarboxylic acid chloride (11.46 g, 0.055 mole) in 390 ml of chloroform; reaction time 5 minutes; polymer yield 12.90 g (76%); decomposed > 370°C (DSC). Infrared spectrum (film on KBr disc): 3280 cm⁻¹ (NHCO stretching), 2940 cm⁻¹ (asym. stretching of CH₂), 2870 cm⁻¹ (sym. stretching of CH₂), 1645 cm⁻¹ (CO stretching), 1527 cm⁻¹ (NH bending), 1447 cm⁻¹ (CN stretching), and 716 cm⁻¹ (NH out of plane bending). The PMR (CF₃COOH) showed δ: 8.71 (NHCOCO, 2), 7.85 (NHCO, 2), 3.69 (acyclic CH₂, 8), and 2.75 to 1.98 (broad, cyclic CH and CH₂, 10). The inherent viscosity of a 0.5% H₂SO₄ solution of this polymer was 0.48 dl/g. Anal. Calcd. for (C₁₄H₂₂N₄O₄)ₙ: N, 18.05%; Found: N, 17.59%.

Poly(iminoethyleneiminoxyalyliminoethyleneiminoterephthaloyl) (p-2-2-2-T):

N,N′-bis(2-aminoethyl)oxamide (5.00 g, 0.029 mole) and Na₂CO₃ (6.02 g, 0.057 mole) in 340 ml of distilled water; terephthaloyl chloride (5.83 g, 0.029 mole) in 200 ml of chloroform; reaction time 5 minutes; polymer yield 7.90 g (91%); decomposed > 400°C (DSC). Infrared spectrum (film on KBr disc): 3270 cm⁻¹ (NHCO stretching), 2945 cm⁻¹ (asym. stretching of CH₂), 2860 cm⁻¹ (sym. stretching of CH₂), 1650 cm⁻¹ (CO stretching), 1520 cm⁻¹ (NH bending), 1425 cm⁻¹ (CN stretching), and 710 cm⁻¹ (NH out of plane bending). The PMR (CF₃COOH) showed δ:
8.90 (NHCOCO, 2), 8.30 to 7.64 (irresolvable; aromatic H, 4; and NHCO, 2), and 3.89 (CH₂, 8). The inherent viscosity of a 0.5% H₂SO₄ solution of this polymer was 0.63 dl/g. Anal. Calcd. for \( \text{C}_{14}\text{H}_{16}\text{N}_{4}\text{O}_4 \): N, 18.41%; Found: N, 18.08%.

Poly(iminoethyleneiminooxalyliminoethyleneiminocarbonyl-1,6-naphthylencarbonyl) (p-2-2-2-1,6-N):

\[ \text{N,N'-bis(2-aminoethyl)oxamide (0.82g, 0.0047 mole) and Na}_2\text{CO}_3 \text{(1.00g, 0.0094 mole) in 56 ml. of distilled water; 1,6-naphthalenedicarboxylic acid chloride (1.19g, 0.0047 mole) in 34 ml. of chloroform; reaction time 5 minutes; polymer yield 1.38g (83%); decomposed >370°C (DSC). Infrared spectrum (film on KBr disc): 3300 cm⁻¹ (NHCOCO stretching), 2948 to 2865 cm⁻¹ (asym. and sym stretching of CH₂), 1670 cm⁻¹ (CO stretching), 1520 cm⁻¹ (NH bending), 1427 cm⁻¹ (CN stretching), and 730 cm⁻¹ (NH out of plane bending). The PMR (CF₃COOH) showed δ: 8.86 (NHCOCO, 2), 8.30 to 7.60 (irresolvable, broad; NHCO, 2, and aromatic H, 6), and 3.87 (CH₂, 8). The inherent viscosity of a 0.5% H₂SO₄ solution of this polymer was 0.78 dl/g. Anal. Calcd. for \( \text{C}_{18}\text{H}_{18}\text{N}_{4}\text{O}_4 \): N, 15.81%; Found: N, 15.24%.

Poly(iminoethyleneiminooxalyliminoethyleneiminocarbonyl-2,6-naphthylencarbonyl) (p-2-2-2,6-N):

\[ \text{N,N'-bis(2-aminoethyl)oxamide (2.06g, 0.012 mole) and Na}_2\text{CO}_3 \text{(2.52g, 0.024 mole) in 350 ml. of distilled water; 2,6-naphthalenedicarboxylic acid chloride (3.00g, 0.012 mole)
in 210 ml. of chloroform; reaction time 5 minutes; polymer yield 4.24 g (100%); decomposed > 370°C (DSC). Infrared spectrum (film on KBr disc): 3300 cm\(^{-1}\) (NH\(_2\) stretching), 2950 cm\(^{-1}\) (asym. stretching of CH\(_2\)), 2880 cm\(^{-1}\) (sym. stretching of CH\(_2\)), 1660 cm\(^{-1}\) (CO stretching), 1520 cm\(^{-1}\) (NH bending), 1440 cm\(^{-1}\) (CN stretching), and 717 cm\(^{-1}\) (NH out of plane bending). The PMR (CF\(_3\)COOH) showed \(\delta\): 8.91 (NH\(_2\)CO, 2), 8.36 (aromatic H, 6), 7.94 (NH\(_2\)CO, 2), and 3.94 (CH\(_2\), 8). The inherent viscosity of a 0.5\% H\(_2\)SO\(_4\) solution of this polymer was 0.58 dL/g. Anal. Calcd. for (C\(_{18}\)H\(_{18}\)N\(_4\)O\(_4\))\(_n\): N, 15.81%; Found: N, 15.51%.

Poly(iminoethyleniminooxalyliminoethyleniminooxalylimino-
ethyleniminoisophthaloyl) (n-2-2-2-2-2-1): Bis(2-aminoethyliminooxalylimino)ethane dihydrochloride salt (1.78 g, 0.0049 mole) and Na\(_2\)CO\(_3\) (1.57 g, 0.015 mole) dissolved in 90 ml. of hot (85°C) distilled water: isophthaloyl chloride (1.00 g, 0.0049 mole) in 75 ml. of warm chloroform; warm blender (65°C); reaction time 5 minutes; polymer yield 1.89 g (92%); decomposes > 370°C (DSC). Infrared spectrum (film on KBr disc): 3300 cm\(^{-1}\) (NH\(_2\)CO stretching), 3080 cm\(^{-1}\) (asym. stretching of CH\(_2\)), 2960 cm\(^{-1}\) (sym. stretching of CH\(_2\)), 1655 cm\(^{-1}\) (CO stretching), 1525 cm\(^{-1}\) (NH bending), 1440 cm\(^{-1}\) (CN stretching), and 710 cm\(^{-1}\) (NH out of plane bending). The PMR (CF\(_3\)COOH) showed \(\delta\): 8.74 (NH\(_2\)CO, 2), 8.40 to 7.60 (irresolvable, broad; aromatic H, 4, and NH\(_2\)CO, 2), and 3.79
(CH₂, 12). The inherent viscosity of a 0.5% H₂SO₄ solution of this polymer was 0.45 dl/g. Anal. Calcd. for \((C_{16}H_{22}N_{6}C_{6})_n\); N, 20.09%; Found: N, 18.96%.

2) Compounds made before but mentioned here for convenience.

**Poly(iminoethyleniminooxalyliminoethyleneiminosobacetyl) (p-2-2-2-10):**

N,N'-bis(2-aminoethyl)oxamide (10.00 g, 0.14 mole) and Na₂CO₃ (12.17 g, 0.29 mole) in 680 ml. of distilled water; sebacyl chloride (13.72 g, 0.14 mole) in 400 ml. of chloroform; reaction time 5 minutes; polymer yield 15.37 g (79%); m.p. 349°C, (decomposed > 355°C) (DSC). Infrared spectrum (film): 3290 cm⁻¹ (NHCO stretching), 2940 cm⁻¹ (asym. stretching of CH₂), 2855 cm⁻¹ (sym. stretching of CH₂), 1640 cm⁻¹ (CO stretching), 1530 cm⁻¹ (NH bending), 1450 cm⁻¹ (CN stretching), and 740 cm⁻¹ (NH out of plane bending). The PMR (CF₃COOH) showed δ: 8.78 (NHCCO, 2), 8.45 (NHCO, 2), 3.80 (N-CH₂, 8), and 2.15 to 1.42 (broad, C-CH₂-C, 16). The inherent viscosity of a 0.5% H₂SO₄ solution of this polymer was 0.76 dl/g. Anal. Calcd. for \((C_{16}H_{20}N_{4}O_{4})_n\); N, 16.46%; Found: N, 16.33%.

**Poly(iminoethyleneiminooxalyliminoethyleneminoisophthaloyl) (p-2-2-2-1):**

N,N'-bis(2-aminoethyl)oxamide (32.05 g, 0.18 mole) and Na₂CO₃ (39.01 g, 0.37 mole) in 1600 ml. of distilled water;
isophthaloyl chloride (37.36g, 0.18 mole) in 1000 ml. of chloroform; reaction time 3 minutes; polymer yield 55.00g (99%); m.p. 367°C.; decomposed 370°C. (DSC). The polymer was soluble in sulfuric and trifluoroacetic acid and warm dimethylacetamide containing 4% LiCl. Infrared spectrum (film): 3290 cm\(^{-1}\) (\(\text{NHCO}\) stretching), 2940 cm\(^{-1}\) (asym. stretching of \(\text{CH}_2\)), 2880 cm\(^{-1}\) (sym. stretching of \(\text{CH}_2\)), 1655 cm\(^{-1}\) (CO stretching), 1518 cm\(^{-1}\) (NH bending), 1440 cm\(^{-1}\) (CN stretching), and 728 and 708 cm\(^{-1}\) (NH out of plane bending). The \(\text{PMR}\) (\(\text{CF}_3\text{COOH}\)) showed \(\delta\): 8.85 (NHCCCO, 2), 8.38 to 7.60 (irresolvable; aromatic H, 4, and NHCCO, 2), and 3.86 (CH\(_2\), 8). The inherent viscosity of a 0.5% \(\text{H}_2\text{SO}_4\) solution of this polymer was 1.06 dl/g. Anal. Calcd. for \(\text{C}_{14}\text{H}_{16}\text{N}_4\text{O}_4\)\(_n\): N, 18.40%; Found: N, 18.41%.

C. Characterization of Polymers

Each polymer was characterized by elemental analysis, thermal analysis, infrared and \(\text{PMR}\) spectra, and viscosity measurements.

1) Thermal Analysis: For measuring the endothermic and exothermic transitions, including melting behavior, a Perkin-Elmer Differential Scanning Calorimeter DSC-1B was used at a 20°C per minute heating rate under a nitrogen flow of 25 lb/in\(^2\).

Thermal degradation of the copolyoxamides was monitored by a DuPont 950 Thermogravimetric Analyzer (TGA) and DuPont 900 Analyzer (temperature programmer) at a 20°C per minute heating rate under a nitrogen flow of 25 lb/in\(^2\).
2) Infrared Spectra: Infrared spectra were obtained from either a Perkin-Elmer 727 or 283 spectrometer. All spectra were measured on films when feasible. If films could not be cast directly, 5% solutions in trifluoroacetic acid were dropped on preformed KBr discs and the solvent evaporated before measurements were made.

3) PMR Spectra: Proton magnetic resonance spectra of the polymers were obtained either by a Hitachi/Perkin-Elmer PMR R-24 (60 MHz) spectrometer or in a Perkin-Elmer R-32 (90 MHz) spectrometer in concentrations ranging from 5-20%. Tetramethylsilane was used as an internal standard and the spectra were measured at the instrument's normal operating temperature (ca. 37°C).

4) Viscosity Measurements: The viscosities of the polymers were measured in a Cannon-Fenske viscometer. Measurements were made in a constant temperature bath at 30.00°C ± 0.02°C. All solutions were 0.5 weight percent in sulfuric acid.

5) Elemental Analysis: The elemental analyses for the copolyoxamides were performed by Instranal Laboratories, Inc., Rensselaer, New York, and by the Microanalysis Laboratories of the University of Massachusetts, Amherst, Massachusetts.
CHAPTER III
RESULTS AND DISCUSSION - SYNTHESIS

Objective

In this part of the thesis the basic objective was to synthesize new and improved polymer candidates for use in reverse osmosis desalination, which actually consisted of three objectives.

The first was to make higher homologs of m-2-2-2, specifically m-2-2-2-2-2 and m-2-2-2-2-2-2-2, and polymerize them with appropriate diacid chlorides to high molecular weight polymers. The second objective was to incorporate bulky diacid chlorides into the polymer backbone in an attempt to increase the amorphous content of the polymers so that water transport in reverse osmosis applications would be improved and also to increase $T_g$. The m-2-2-2 monomer exhibited optimal behavior when compared with all other diamine-oxamides. This was to be polymerized with 1,1-cyclobutane-, cis- and trans-1,4-cyclohexane-, 1,6- and 2,6-naphthalene-, and 1,8- and 1,5-anthraquinone- and anthracenedicarboxylic acid chlorides, and sebacyl, isophthaloyl, and terephthaloyl chlorides. The third objective was to increase the inherent viscosity of p-2-2-2-P, a polymer which had great potential for use in reverse osmosis desalination applications, but had not been obtained in high molecular weight form.

In total, altogether 21 precursors, two diamine-oligo-
oxamide, nine diacid chlorides, and nine linear copolyoxamides were synthesized and characterized.

Monomer Preparation

**Diamine-Oxamides.** The synthesis of both the m-2-2-2-2-2 and m-2-2-2-2-2-2 had been attempted previously. However, good elemental analyses were not obtained and other measurements and identification by spectral methods such as infrared and proton magnetic resonance had to be repeated.

(a) Bis(2-aminooethyliminooxalylimino)ethane (m-2-2-2-2-2): In the case of the preparation of m-2-2-2-2-2, one approach was to react m-2-2-2 with ethyl N-(2-aminoethyl) oxamate hydrochloride.

\[
\begin{align*}
\text{HOOH} & \quad \text{HOOH} \\
1 \quad \text{H}_2\text{NCH}_2\text{CH}_2\text{N-C-C-N-CH}_2\text{CH}_2\text{NH}_2 + 1 \quad \text{EtO-C-C-N-CH}_2\text{CH}_2\text{NH}_3^+ \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{HOOH} & \quad \text{HOOH} \\
1 \quad \text{H}_2\text{NCH}_2\text{CH}_2\text{N-C-C-N-CH}_2\text{CH}_2\text{N-C-C-N-CH}_2\text{CH}_2\text{NH}_3^+ \quad \text{Cl} + 1 \quad \text{EtOH}
\end{align*}
\]

m-2-2-2-2-2·(HCl)

In principal, another approach would be to react ethyl N-(2-aminoethyl) oxamate with ethylenediamine.

\[
\begin{align*}
\text{HOO} & \quad \text{HOO} \\
2 \quad \text{H}_2\text{NCH}_2\text{CH}_2\text{N-C-C-OEt} + 1 \quad \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \\
\text{HOO} & \quad \text{HOO} \\
1 \quad \text{H}_2\text{NCH}_2\text{CH}_2\text{N-C-C-N-CH}_2\text{CH}_2\text{N-C-C-N-CH}_2\text{CH}_2\text{NH}_2 + 2 \quad \text{EtOH}
\end{align*}
\]

m-2-2-2-2-2
The third approach is to react bis(ethoxyoxalylimino)-ethane with ethylenediamine, shown below.

\[
\begin{align*}
1 & \text{EtO-C-C-N-CH}_2\text{CH}_2\text{-N-C-C-OEt} + 2 \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \\
\rightarrow & \text{boiling THF} \\
1 & \text{H}_2\text{NCH}_2\text{CH}_2\text{-N-C-C-N-CH}_2\text{CH}_2\text{-N-C-C-N-CH}_2\text{CH}_2\text{NH}_2 + 2 \text{EtOH}
\end{align*}
\]

The first two reactions involve unsymmetrical intermediates which are difficult to synthesize and purify. The third route was chosen for three reasons. First, it involved symmetrical intermediates which were easy to prepare from available starting materials. Secondly, the ethylenediamine could be used in larger excess, thus reducing the possibility of polymer and oligomer formation. Thirdly, because the reagent used in excess was a liquid and not a solid, it was much easier to separate and purify from the m-2-2-2-2-2. This reaction was carried out in boiling tetrahydrofuran and high yields of m-2-2-2-2-2 were obtained.

The solubility of m-2-2-2-2-2 was much lower than m-2-2-2 and was only soluble in TFAA and boiling water, and the latter solvent was chosen for purification of large quantities of the compound. The dihydrochloride salt was much more soluble in boiling water than the free-amine.

(b) N,N'-bis(2-aminoethyloxalyliminoethyl)oxamide, (m-2-2-2-2-2-2-2-2-2): In principle it is possible to form m-2-2-2-2-2-2-2-2-2 from two moles of m-2-2-2 and one mole of diethyl oxal-
ate. This synthesis had been previously attempted in DMSO, but had failed because the compound was not very soluble.\(^{117}\)

\[
\begin{align*}
2 \text{H}_2\text{NCH}_2\text{CH}_2-\text{N}-\text{C}-\text{C}-\text{N}-\text{CH}_2\text{CH}_2\text{NH}_2 &+ 1 \text{EtO-C-C-OEt} \rightarrow \\
\text{HOOH} &\quad \text{HOOH} &\quad \text{HOOH} \\
1 \text{H}_2\text{NCH}_2\text{CH}_2-\text{N}-\text{C}-\text{C}-\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{N}-\text{C}-\text{C}-\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 &+ 2 \text{EtOH} \\
&= \text{m-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2}
\end{align*}
\]

Thus, a different route was investigated, similar to that used in the synthesis of m-2-2-2-2-2. A precursor to m-2-2-2-2-2-2-2, which had ethoxy end groups, was made by reacting two moles of diethyl oxalate and one mole of m-2-2-2 in boiling THF.

\[
\begin{align*}
2 \text{EtO-C-C-OEt} &+ 1 \text{H}_2\text{NCH}_2\text{CH}_2-\text{N}-\text{C}-\text{C}-\text{N}-\text{CH}_2\text{CH}_2\text{NH}_2 \\
\text{boiling THF} &\rightarrow \\
1 \text{EtO-C-C-N-CH}_2\text{CH}_2-\text{N}-\text{C}-\text{C}-\text{N-CH}_2\text{CH}_2-\text{N}-\text{C}-\text{C}-\text{OEt} &+ 2 \text{EtOH} \\
&= \text{m-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2}
\end{align*}
\]

The resulting N,N'-bis(2-ethoxyoxalyliminoethyl)oxamide was only appreciably soluble in hot HFIP. Hence, the subsequent reaction with ethylenediamine was carried out in this solvent, to give a modest yield of m-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2.
As in the case of the synthesis of m-2-2-2-2-2, the excess reagent was a liquid and could be easily removed. The use of a highly polar protic solvent, such as HFIP, over an aprotic one, such as DMSO, appeared to be a key in the successful synthesis because the m-2-2-2-2-2-2-2 is more soluble in HFIP. Yet the m-2-2-2-2-2-2-2-2 exhibited such poor solubility that it could only be satisfactorily purified as the dihydrochloride salt.

A. Physical Properties

1) Solubility: The diamine-oxamides are white solids which are hygroscopic. Table III lists the solvents in which the diamine-oxamides and their precursors are soluble and their relative solubility.

As the number of oxamide units increased, the solubility of the compounds decreased. Ethoxy derivatives were more soluble in aprotic solvents than the corresponding amine ones. Yet in highly polar protic solvents the reverse case is true, probably because of the better hydrogen-bonding which is possible through the amino group. Formation of the dihydrochloride salts gave the diamine-oxamides much greater solubility in water.

2) Thermal Behavior: Table IV lists the thermal behavior of the diamine-oxamides and their precursors.

As the number of oxamide groups and molecular weight increases, so does the melting point or decomposition temperature. This is a common observation in oligomer characterization studies. Converting from the ethoxy group to
# TABLE III

Solubility Behavior of Oxamides

<table>
<thead>
<tr>
<th>Oxamide</th>
<th>Solvents</th>
<th>THF</th>
<th>H₂O</th>
<th>HFIP</th>
<th>DMF</th>
<th>DMAC/4% LiCl</th>
<th>TFAA</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O (H₂N(CH₂)₂-N-C-)₂</td>
<td>m-2-2-2</td>
<td>1(3*)</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>O O H (EtO-C-C-N-CH₂-)₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>room temperature</strong></td>
<td></td>
<td>2(4*)</td>
<td>--</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>--</td>
</tr>
<tr>
<td>H O O H (H₂N(CH₂)₂-N-C-N-CH₂-)₂</td>
<td>m-2-2-2-2</td>
<td>1</td>
<td>3(5**)</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>O O H H O (EtO-C-C-N(CH₂)₂-N-C-)₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>boiling</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H O O H H O (H₂N(CH₂)₂-N-C-C-N(CH₂)₂-N-C-)₂</td>
<td>m-2-2-2-2-2</td>
<td>0</td>
<td>3**</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>0 = insoluble; 5 = good solubility</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* at boiling point
** dihydrochloride salt
<table>
<thead>
<tr>
<th>Oxamide</th>
<th>M.W. (g/mole)</th>
<th>Phys. Appearance</th>
<th>M.P. in °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>174.20</td>
<td>shiny, long needles</td>
<td>106-7 (cap.)</td>
</tr>
<tr>
<td>$(\text{H}_2\text{N(\text{CH}_2)_2-N-C-')_2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-2-2-2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{O-OH}$</td>
<td>260.25</td>
<td>shiny, mica-like, talc</td>
<td>128-9 (cap.)</td>
</tr>
<tr>
<td>$(\text{EtO-C-C-N-CH}_2-')_2$</td>
<td></td>
<td>consistency</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>288.30</td>
<td>powder, talc consistency</td>
<td>dec.$&gt;250$ (DSC)</td>
</tr>
<tr>
<td>$(\text{H}_2\text{N(\text{CH}_2)_2-N-C-C-N-CH}_2-')_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-2-2-2-2-2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>361.24</td>
<td>very fine powder</td>
<td>dec.$&gt;290$ (DSC)</td>
</tr>
<tr>
<td>$(\text{Cl}^+\text{H}_2\text{N(\text{CH}_2)_2-N-C-C-NCH}_2-')_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-2-2-2-2-2$\cdot2\text{HCl}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{O-OH}$</td>
<td>374.36</td>
<td>shiny, powder</td>
<td>249 (DSC)</td>
</tr>
<tr>
<td>$(\text{EtO-C-C-N(\text{CH}_2)_2-N-C-')_2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>475.34</td>
<td>powder</td>
<td>dec.$&gt;270$ (DSC)</td>
</tr>
<tr>
<td>$(\text{Cl}^+\text{H}_2\text{N(\text{CH}_2)_2-N-C-C-N-(\text{CH}_2)_2-N-C-')}_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the aminoethylimino-group, which is more polar and can hydrogen-bond, results in a further increase. The dihydrochloride salts are more stable than the free-amine.

3) Spectral Interpretations: Both infrared and proton magnetic resonance (PMR) spectra have been obtained for all the diamine-oxamides and precursors studied in this project.

(a) Infrared spectra: The compounds all show normal infrared absorptions for the various functional groups. The IR spectra of all the compounds are tabulated in Appendix C.

Table V lists several of the characteristic absorptions of the diamine-oxamides and their respective precursors which have been synthesized in this work.

One observes that in going from m-2-2-2 to m-2-2-2-2-2, the frequencies of absorption increase for the NHCO, asym., sym., and C=O stretching and N-H bending vibrations. In going from m-2-2-2-2•2HCl to m-2-2-2-2-2-2•2HCl the NHCO and C=O stretching frequencies increase; the N-H bending decreases while that of the amine salt bending increases. Likewise, as one moves from bis(2-ethoxyoxalylimino)ethane to m-2-2-2-2-2-2, the NHCO, asym., and sym. stretching frequencies and the N-H bending frequencies increase.

Apparently these changes are occurring for two main reasons. As one progresses to a greater number of oxamide groups, or changes the end groups from the ethoxy to the aminoethylimino analog, the compounds become much more "rigid" due to the large increase in polarity. Chains have
<table>
<thead>
<tr>
<th>Formula</th>
<th>NHCO</th>
<th>asym.</th>
<th>sym.</th>
<th>C=O</th>
<th>N-H</th>
<th>NH$_3^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H$_2$N(CH$_2$)$_2$-N-C-)$_2$</td>
<td>3290</td>
<td>2937</td>
<td>2860</td>
<td>1648</td>
<td>1515</td>
<td>--</td>
</tr>
<tr>
<td>m-2-2-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EtO-C-C-N-CH$_2$-)$_2$</td>
<td>3290</td>
<td>2965</td>
<td>2925</td>
<td>1665</td>
<td>1547</td>
<td>--</td>
</tr>
<tr>
<td>H$_2$O H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H$_2$N(CH$_2$)$_2$-N-C-C-N-CH$_2$-)$_2$</td>
<td>3290</td>
<td>2945</td>
<td>2870</td>
<td>1650</td>
<td>1530</td>
<td>--</td>
</tr>
<tr>
<td>m-2-2-2-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Cl$^+$H$_3$N(CH$_2$)$_2$-N-C-C-N-CH$_2$-)$_2$</td>
<td>3260</td>
<td>2970</td>
<td>2900</td>
<td>1650</td>
<td>1520</td>
<td>1590</td>
</tr>
<tr>
<td>m-2-2-2-2-2HCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EtO-C-C-N(CH$_2$)$_2$-N-C-)$_2$</td>
<td>3300</td>
<td>2990</td>
<td>2950</td>
<td>--</td>
<td>1555</td>
<td>--</td>
</tr>
<tr>
<td>H$_2$O H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Cl$^+$H$_3$N(CH$_2$)$_2$-N-C-C-N(CH$_2$)$_2$-N-C-)$_2$</td>
<td>3300</td>
<td>3000</td>
<td>2900</td>
<td>1657</td>
<td>1505</td>
<td>1600</td>
</tr>
<tr>
<td>m-2-2-2-2-2-2-2-2-2-2HCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
less freedom of movement and hence the methylene groups experience some degree of strain, resulting in shifts to higher frequency absorptions.

The increase in the NHCO and C=O stretching and N-H and NH$_3^+$ bending frequencies indicates that there is a decrease in the degree of hydrogen-bonding, although the higher homologs are much more polar. A possible explanation of this behavior may be given when one takes into account the observed increase in frequency of the methylene group absorptions. This increase in frequency indicates that the methylene groups are in strained positions. The increased strain caused by the rigid chains of the compounds may result in reduced freedom of mobility and in less possible ordering of N-H and C=O groups. This in turn prohibits hydrogen-bond formation and lowers the frequency of absorption.

(b) PMR spectra: The diamine-oxamides and their precursors all show normal absorptions. The PMR spectra are tabulated in Appendix C.

Table VI lists several of the characteristic chemical absorptions of the diamine-oxamides and their respective precursors which have been synthesized in this work.

The largest change occurs in the amide absorption in converting from the ethoxy group of the oxamide precursor to the corresponding aminooethylimino analog. The ethoxy group
<table>
<thead>
<tr>
<th></th>
<th>NHCO</th>
<th>$^2H_2N$</th>
<th>CH$_2$CH$_2O$</th>
<th>CH$_2$N-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td>3.39</td>
</tr>
<tr>
<td>(H$_2$N(CH$_2$)$_2$N-C-)$_2$</td>
<td>8.29</td>
<td>6.88</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>m-2-2-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EtO-C-C-N-CH$_2$-</td>
<td>8.89</td>
<td>------</td>
<td>4.25</td>
<td>3.28</td>
</tr>
<tr>
<td>H$_2$N(CH$_2$)$_2$N-C-N-CH$_2$-</td>
<td>8.22</td>
<td>6.75</td>
<td>------</td>
<td>3.29</td>
</tr>
<tr>
<td>m-2-2-2-2-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EtO-C-C-N(CH$_2$)$_2$N-C-</td>
<td>8.84</td>
<td>------</td>
<td>4.23</td>
<td>3.26</td>
</tr>
<tr>
<td>H$_2$N(CH$_2$)$_2$N-C-N(CH$_2$)$_2$N-C-</td>
<td>8.27</td>
<td>6.70</td>
<td>------</td>
<td>3.25</td>
</tr>
<tr>
<td>m-2-2-2-2-2-2-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) = TFAA, (b) = DMSO, (c) = HFIP
is more electronegative than the secondary amide group and hence deshields the amide proton in question to a greater extent. The use of different solvents complicates any absolute comparisons, though.

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{O} & \quad \text{C}-\text{C}-\text{N}- \\
\text{H} & \quad \text{O} \quad \text{O} \quad \text{H} \\
\text{Cl}^+\text{H}_2\text{NCH}_2\text{CH}_2\text{N} & \quad \text{C}-\text{C}-\text{N}-
\end{align*}
\]

There are only small changes in the absorption regions of other hydrogens. The protonated amine and the methylene groups near the O and NH absorb at lower frequency as the molecular weight increases. Also, the oxamide units may affect each other since they are only separated by two methylene groups.

**Diacid Chlorides.** A number of alicyclic and aromatic diacid chlorides have been prepared from the diacids and thionyl chloride, including the little-known 1,8- and 1,5-anthraquinone- and anthracenedicarboxylic acid chlorides. Figure 3 schematically diagrams the synthetic route used to synthesize the 1,8-anthraquinone- and anthracenedicarboxylic acid chlorides. The case of the 1,5-isomer is similar. Several general observations have been made. The synthesis of the dicyano-derivatives was time consuming. However, replacement of the benzyl cyanide or nitrobenzene, which had been previously recommended for workup, with DMac resulted in an improved workup. The hydrolysis reactions proceeded smoothly. Reprecipitation from alkaline solu-
tions with HCl was a satisfactory method of purification. However, this technique worked better for the 1,8-anthraquinonedicarboxylic acid than for the 1,5-isomer; the latter was more insoluble. Conversion from the anthraquinone to the anthracenedicarboxylic acids went smoothly. The compounds were difficult to purify by reprecipitation because they were not very soluble, especially the 1,5-isomer. With increasing aromaticity and symmetry, separation and purification becomes more difficult. The dicarboxylic acid derivatives did not melt, but decomposed at high temperatures. Therefore, melting points could not be used to determine the purity of these compounds.

A. Physical Properties

1) Solubility: The diacid chlorides are crystalline solids which are soluble in aromatic hydrocarbons. Their relative solubilities in boiling chlorobenzene are shown in Table VII.

1,8-anthraquinonedicarboxylic acid chloride (the most soluble of the four) was only one-sixth as soluble as 2,6-naphthalenedicarboxylic acid chloride, while the latter is virtually insoluble in boiling hexane, a good solvent for the 1,6-isomer. Solubility appears to depend on several factors. First is the symmetry of the molecule. The 1,5- and 2,6-isomers are more symmetric than the 1,8- and 1,6-isomers, respectively, so it is more difficult for solvent molecules to break up the crystal lattice of the former two.
FIGURE 3

Synthetic Route for 1,8-Anthraquinone- and 1,8-Anthracenedicarboxylic Acid Chlorides

1,8-dichloroanthraquinone

1,8-dicyanoanthraquinone

1,8-anthraquinonenedicarboxylic acid

1,8-anthraquinonenedicarboxylic acid chloride

1,8-anthracenedicarboxylic acid chloride
### TABLE VII

Physical Properties of Large Diacid Chlorides

<table>
<thead>
<tr>
<th>Diacid Chloride</th>
<th>Solubility in boiling chlorobenzene</th>
<th>M.P. (°C) (cap.)</th>
<th>lit. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>&gt; than 1.8</td>
<td>208-211</td>
<td>unknown</td>
</tr>
<tr>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>&gt; than 1.5</td>
<td>267-275</td>
<td>dec. 220 (144)</td>
</tr>
<tr>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>&gt; than 1.8</td>
<td>275-283</td>
<td>255-257 (145)</td>
</tr>
<tr>
<td><img src="image4" alt="Chemical Structure" /></td>
<td>least soluble 1.5</td>
<td>259-261</td>
<td>dec. 330 (146)</td>
</tr>
</tbody>
</table>
Second, the presence of the quinone oxygens makes the anthraquinone molecules more soluble than the anthracene ones because of the greater degree of polar interactions possible in solution. Third, with increasing degree of aromaticity and molecular weight, solubility decreases and purification becomes much more difficult, as evidenced by the melting ranges for the diacid chlorides.

2) Thermal Behavior: Table VII indicates that the melting points of the diacid chlorides appear to increase with the decreasing solubility behavior, except for the 1,5-anthracene case. Though each compound was recrystallized at least several times, the melting ranges sometimes were spread out up to eight degrees.

3) Spectral Interpretations: Infrared spectra were obtained for all the diacid chlorides and precursors, and are tabulated in Appendix C. The compounds show normal infrared absorptions for the various functional groups.

Polymer Preparation

Regular copolyoxamides of the general formula \((A-B-A-D)_n\) and in one case \((A-B-A-B-A-D)_n\), where \(A\) is an ethylenediamine unit, \(B\) an oxalyl unit, and \(D\) is a dicarboxylic group which is aliphatic, aromatic, or heteroaromatic, have been prepared by interfacial polymerizations. In the large majority of cases \(N,N'-\text{bis(2-aminoethyl)}\)oxamide was used as the diamine reactant.
They have been characterized by inherent viscosity and thermal measurements and by infrared and proton magnetic resonance spectra.

Regular aliphatic/aicyclic copolyoxamides were formed from m-2-2-2 and 1,1-cyclobutanedicarboxylic acid chloride, both the cis- and trans-1,4-cyclohexanedicarboxylic acid chlorides, and sebacyl chloride. Sebacyl chloride would not be considered to have a bulky structure such as a cyclohexane ring has, for example, but was included for means of several comparisons.

Regular aliphatic/aromatic and aliphatic/heteroaromatic copolyoxamides were formed from m-2-2-2 and isophthaloyl and terephthaloyl chloride, and 2,6-pyridine-, 1,6- and 2,6-naphthalenedicarboxylic acid chlorides. In one case, m-2-2-2-2 was polymerized with isophthaloyl chloride. Polymerizations with 1,8-anthraquinonedicarboxylic acid chloride, the most soluble of the very large diacid chlorides, failed to give high molecular weight material.

Physical Properties.

A. Inherent Viscosities and Mechanical Strength of Films: Table VIII lists the inherent viscosity of each poly-
### TABLE VIII

Inherent Viscosities and Mechanical Strength of Films

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>η (30^\circ\text{C.}, \text{ in } \text{H}_2\text{SO}_4)</th>
<th>Qualitative Mech. Strength of Films*</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-2-2-2-1,1-cylicobut.</td>
<td>0.50</td>
<td>brittle</td>
</tr>
<tr>
<td>p-2-2-2-cis-1,4</td>
<td>0.48</td>
<td>brittle</td>
</tr>
<tr>
<td>p-2-2-2-trans-1,4</td>
<td>0.51</td>
<td>brittle</td>
</tr>
<tr>
<td>p-2-2-2-10</td>
<td>0.76</td>
<td>flexible, some toughness</td>
</tr>
<tr>
<td>p-2-2-2-I</td>
<td>1.06</td>
<td>flexible, tough</td>
</tr>
<tr>
<td>p-2-2-2-2-2-I</td>
<td>0.45</td>
<td>flexible, some toughness</td>
</tr>
<tr>
<td>p-2-2-2-T</td>
<td>0.63</td>
<td>flexible, little toughness</td>
</tr>
<tr>
<td>p-2-2-2-P</td>
<td>0.40</td>
<td>brittle</td>
</tr>
<tr>
<td>p-2-2-2-1,6N</td>
<td>0.78</td>
<td>flexible, some toughness</td>
</tr>
<tr>
<td>p-2-2-2-2-,6N</td>
<td>0.58</td>
<td>flexible, little toughness</td>
</tr>
</tbody>
</table>

* = 5-10% TFAA solutions, cast on microscope slides, dried one minute with gentle heating, then gelled in water.
mer in sulfuric acid at 30°C and the qualitative mechanical strength of films cast from trifluoroacetic acid. The inherent viscosity of the polymer is largely determined by the relative degree of interaction of the growing oligomer with the aqueous phase during interfacial polymerization. Of the aliphatic diacid chlorides the 1,1-cyclobutane group has the fewest number of methylene groups, three, and one of the lowest viscosities. However, the sebacyl unit, which has eight methylene groups, exhibits the highest viscosity.

Of all the aromatic and heteroaromatic diacid chlorides, 2,6-pyridinedicarboxylic acid chloride yields the polymer with the lowest viscosity. The presence of the nitrogen atoms leads to increased hydrogen-bonding and hence, its more hydrophilic than isophthaloyl chloride, as noted by Gaudiana and others. The effects are seen in the respective polymer viscosities, 0.40 and 1.06. A number of efforts have been made to increase the molecular weight of p-2-2-2-P. Several of these have been discussed in the Introduction. Two new approaches were studied in these investigations. One was to conduct the interfacial polymerization at lower temperatures (5-10°C vs. 25-30°C) in order to retard the hydrolysis reaction. However, inherent viscosities of less than 0.30 were obtained. The second approach was to try "salting out" the growing oligomer from the aqueous phase by increasing the concentration of sodium hydroxide (used in place of sodium carbonate as the acid acceptor). Table IX lists the
results which were obtained by varying the concentration of NaOH.

**TABLE IX**

<table>
<thead>
<tr>
<th>Amt. of Base (moles)</th>
<th>( \eta ), ( 30^\circ C ), in H(_2)SO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Na}_2\text{CO}_3 )</td>
<td>1X</td>
</tr>
<tr>
<td>NaOH</td>
<td>1X</td>
</tr>
<tr>
<td>1.1X</td>
<td>0.41</td>
</tr>
<tr>
<td>2X</td>
<td>0.34</td>
</tr>
<tr>
<td>10%</td>
<td>0.23</td>
</tr>
<tr>
<td>30%</td>
<td>0.17</td>
</tr>
<tr>
<td>50%</td>
<td>0.14</td>
</tr>
</tbody>
</table>

One observes that there is little positive effect resulting from the extra NaOH and it apparently does not "salt out" the growing oligomer as hoped. Attempts to synthesize the polymer by solution polymerization failed because it precipitates out of solution in a low molecular weight state which prohibits further polymerization. In our hands, the solution polymerization methods formed copolyoxamides with lower inherent viscosity than if interfacial polymerization methods were used.

As it has been shown before, m-2-2-2 reacted with isophthaloyl chloride yielded a polymer exhibiting the greatest inherent viscosity and best film properties of all the di-acid chlorides tried. Apparently the copolyoxamide p-2-2-2-I has the best swellability in chloroform. In the case of terephthaloyl chloride, a polymer with lower inherent viscosity is obtained. This is a reflection of the much poorer
swellability of the polymer in chloroform.

A similar situation exists in the case of the 1,6- and 2,6-isomers of naphthalenedicarboxylic acid chlorides. The 1,6-isomer is similar in solubility to isophthaloyl chloride, while the 2,6-isomer is relatively less soluble than the terephthaloyl chloride. p-2-2-2-1,6N exhibits a greater inherent viscosity (0.78) than p-2-2-2-2,6N (0.58). As expected, more dilute solutions had to be used for the terephthaloyl chloride and the 2,6-naphthalenedicarboxylic acid chlorides. The growing oligomers have a lower swellability in the organic phase than those resulting from the more soluble diacid chlorides. Thus there is more interaction with the aqueous phase and hydrolysis is more probable. Moreover, the acid chloride groups on the larger diacid chlorides are less reactive due to increased resonance and delocalization effects. Conducting the polymerizations at higher temperatures did not improve the inherent viscosity of the resulting polymers.

The polymerization of m-2-2-2-2-2 with isophthaloyl chloride does not proceed as effectively to high molecular weight because the oligooxamide is less soluble in the aqueous phase, and even less soluble in the organic phase. Thus the oligooxamide probably cannot diffuse effectively into the interface.

Both interfacial and solution methods (DMAc) were used in a number of attempts to form high molecular weight polymers of m-2-2-2 reacted with 1,8-anthraquinonedicarboxylic
acid chloride. However, inherent viscosities above 0.10 could not be obtained. There are two main reasons which account for this. First, though this particular diacid chloride was the most soluble of the four anthraquinone and anthracene derivatives, it had very poor solubility in chloroform, even when hot. Second, the reactivity of the acid chloride groups was reduced even further than the naphthalene derivatives due to greater aromaticity. Thus, no attempts were made to polymerize the remaining three diacid chlorides.

The physical properties of the films of the copolyoxamides from m-2-2-2 parallels their inherent viscosities. Only p-2-2-2-I has been studied carefully enough that molecular weights have been obtained which, after solution casting, produced films which exhibit sufficiently good mechanical strength to be used in reverse osmosis membrane work. An interesting observation was noted in that p-2-2-2-2-2-1, though having an inherent viscosity of only 0.45, yields a flexible film which exhibits some degree of toughness. Polymers from m-2-2-2 must have inherent viscosities over 0.60 before exhibiting similar behavior.

B. Thermal Measurements: Table X lists the DSC measurements performed on each polymer. As was stated previously, one of the objectives of this work was to incorporate bulky diacid chlorides into the polymer backbone with the intention that this would introduce a greater degree of amorphous character into the polymer matrix in order to improve
TABLE X

Melting and Decomposition Temperatures of Copolyoxamides Measured by DSC

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>$T_m$ in °C</th>
<th>Initial Decomp. Temp. in °C.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-2-2-2-1,1-cyclobut.</td>
<td>286</td>
<td>325</td>
</tr>
<tr>
<td>p-2-2-2-cis-1,4</td>
<td>---</td>
<td>370</td>
</tr>
<tr>
<td>p-2-2-2-trans-1,4</td>
<td>---</td>
<td>370</td>
</tr>
<tr>
<td>p-2-2-2-10</td>
<td>350</td>
<td>370</td>
</tr>
<tr>
<td>p-2-2-2-I</td>
<td>367</td>
<td>370</td>
</tr>
<tr>
<td>p-2-2-2-2-2-I</td>
<td>---</td>
<td>370</td>
</tr>
<tr>
<td>p-2-2-2-T</td>
<td>---</td>
<td>400</td>
</tr>
<tr>
<td>p-2-2-2-P</td>
<td>---</td>
<td>340</td>
</tr>
<tr>
<td>p-2-2-2-1,6N</td>
<td>---</td>
<td>370</td>
</tr>
<tr>
<td>p-2-2-2-2,6N</td>
<td>---</td>
<td>370</td>
</tr>
</tbody>
</table>

* = taken as the point at which the line began diverging from a constant slope.
water transport in the resulting membranes. DSC was used to
measure any changes which arose from glass transitions. How-
ever, no definite glass transition was observed in any case,
though experimental conditions were varied and a more sensi-
tive instrument (DSC-IIIB) was tried. Studies were done on
quenched samples but they yielded similar negative results.
They were prepared by gelling TFAA solutions of polymer in
ice cold distilled water using a Waring blender into which
the dilute solutions were slowly dropped. Yet, though DSC
does not show any definite $T_g$, wide angle X-ray measurements
indicate only a small amount of large scale crystallinity
(see Chapter IV). The solution to this particular inconsist-
tency will require further study.

The DSC measurements give an indication of thermal sta-
bility, along with the TGA measurements listed in Table XI.
Only three of the copolyoxamides show any definite melting
behavior, and two of those, the p-2-2-2-10 and p-2-2-2-1, are
followed closely by decomposition. The fact that the p-2-2-
2-1,1-cyclobut. polymer does melt, and at a relatively low
temperature, is interesting. Chang noted that with decreas-
ing methylene units the polymers became more polar, and the
melting temperature increased.$^{41}$ P-2-2-2-1,1-cyclobut. should
be even more polar, yet it melts lower than the latter two.
It is possible that the bulkiness of the ring disrupts hy-
drogen-bonding and prevents close-order packing.

The DSC and TGA data indicates that all the copolyoxamides
### TABLE XI

Decomposition Temperature of Regular Copolyoxamides
Measured by TGA

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>10% Weight Loss in °C.</th>
<th>Maximum Rate of Decomposition in °C.*</th>
<th>Residue at 500°C. in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-2-2-2-1,1-cyclobut.</td>
<td>354</td>
<td>402</td>
<td>18.9</td>
</tr>
<tr>
<td>p-2-2-2-cis-1,4</td>
<td>379</td>
<td>418</td>
<td>5.7</td>
</tr>
<tr>
<td>p-2-2-2-trans-1,4</td>
<td>394</td>
<td>430</td>
<td>9.7</td>
</tr>
<tr>
<td>p-2-2-2-I</td>
<td>389</td>
<td>412</td>
<td>31.0</td>
</tr>
<tr>
<td>p-2-2-2-2-2-I</td>
<td>347</td>
<td>399</td>
<td>24.9</td>
</tr>
<tr>
<td>p-2-2-2-T</td>
<td>394</td>
<td>450</td>
<td>35.6</td>
</tr>
<tr>
<td>p-2-2-2-P</td>
<td>359</td>
<td>397</td>
<td>27.5</td>
</tr>
<tr>
<td>p-2-2-2-1,6N</td>
<td>370</td>
<td>408</td>
<td>35.7</td>
</tr>
<tr>
<td>p-2-2-2-2,6N</td>
<td>356</td>
<td>434</td>
<td>42.4</td>
</tr>
</tbody>
</table>

* = taken as the midway point of a straight line drawn on the constant slope portion of the graph in the area of the highest rate of decomposition.
decompose at high temperatures. The maximum rate of decomposition ranged over only 37 degrees, indicating that it probably was the region where the oxamide group was rapidly breaking apart. The amount of char residue that remained at 500 °C increased as the amount of aromatic- and nitrogen-containing groups increased. Good elemental analyses were difficult to obtain for these reasons. Combustion had to be carried out in an oxygen atmosphere to cut down on char formation.

C. Spectral Measurements: Both infrared and proton magnetic resonance spectra have been obtained for all the copolyoxamides synthesized in this project.

1) The copolyoxamides all show normal infrared absorptions for the various functional groups. The spectra are tabulated in Appendix C.

2) Again, the copolyoxamides exhibit normal behavior for all the protons in the different environments. The PMR spectra are tabulated in Appendix C.
CHAPTER IV
METAL ION UPTAKE STUDIES

Objective

As was mentioned previously in Chapter I, when freshly synthesized copolyoxamides were allowed to remain in contact with a metal spatula, the polymer turned grey or black and the spatula was slowly corroded. This indicated that the resin exhibited the ability to complex with metals. In order to define and characterize this unique property of copolyoxamides, a series of studies were devised. A number of variables were examined, such as type of metal ion, effect of pH, time for uptake, surface area, etc. in order to develop a general picture of the polymers' capabilities.

Experimental

Apparatus. A double beam Perkin-Elmer 403 Atomic Absorption Spectrophotometer was employed for the metal analyses, both for atomic absorption and emission. Standard A-type laboratory pipettes and volumetric flasks were used for dilutions. A Culligan Deionizer provided a continuous supply of distilled deionized water. A Cenco pH meter, Catalog No. 21690, with Cenco glass and saturated calomel electrodes was used for all pH measurements. An International Clinical Centrifuge, Model CL, was used to separate the resin particles
from the solution after equilibration. A New Brunswick Mechanical Shaker, Model No. VS, New Brunswick Scientific Co., was used for all room temperature studies. An AO Model 02156 Water Bath Shaker (American Optical Corp.) was used for elevated temperature studies. Standard 6" Pyrex test tubes were used to contain the resin plus the solution. To decrease the amount of metal leaching and/or absorption with the walls of the test tubes, they were all silanized; the procedure is described on page 101.

Infrared measurements were made using a Perkin-Elmer 283 spectrometer. X-ray measurements were made on a Warkus Flat Film Pinhole Camera used in the wide angle mode, at a 5" sample-to-film distance, using Cu Kα radiation at 35 kilovolts at 20 milliamps. Scanning electron microscopy (SEM) was performed on an Etec Autoscan scanning electron microscope at an accelerating voltage of 20 kilovolts. Surface area measurements using a nitrogen absorption method were performed by Cabot Corp., Concord Rd., Billerica, Mass.

Reagents. Copper, zinc, calcium, lead, nickel, chromium, and silver acetate and lithium chloride; obtained from Fisher Scientific Co., Fair Lawn, New Jersey, were used as received.

Cadmium acetate: obtained from J.T. Baker Chemical Co., Phillipsburg, New Jersey, was used as received.

Technical nitric, hydrochloric, and glacial acetic acid, and ammonium hydroxide: obtained from Fisher Scientific Co.,
Fair Lawn, New Jersey, were used as received.

Trichloromethylsilane: obtained from PCR Inc., Gainesville, Florida, was used as received.

Toluene: obtained from Fisher Scientific Co., Fair Lawn, New Jersey, was dried over CaCl₂ before use.

Pyridine: obtained from Aldrich Chemical Co., Inc., Metuchen, New Jersey, was used as received.

Acetic anhydride: obtained from Eastman Kodak Co., Rochester, New York, was distilled under nitrogen, center cut 136-138°C, before use.

Sodium chloride: obtained from Fisher Scientific Co., Fair Lawn, New Jersey, was used as received.

Miscellaneous: Sea sand (purified): obtained from J.T. Baker Chemical Co., Phillipsburg, New Jersey, was used as received.

Parafilm: obtained from American Can Co., Greenwich, Conn., was used as received.

Buffer solution: obtained from Fisher Scientific Co., Fair Lawn, New Jersey, was used as received.

The metal stock solutions were prepared by weighing the appropriate amount of dried metal acetate salt and dissolving it in a one liter volumetric flask to yield an aqueous solution (distilled, deionized water) which contained 1000 mg/L (ppm) of the metal ion. The stock solutions were stored in polyethylene bottles. In the case of the silver acetate it was stored in the dark. The lower concentrations of metal
ions used for standards and test solutions were prepared fresh for each analysis by making the appropriate dilutions of the metal ion stock solutions in volumetric flasks.

The silanization solution consisted of ten parts toluene, one part trichloromethylsilane, and 0.4 parts pyridine. The test tubes were filled with the solution and allowed to sit for ten minutes. They were then emptied, washed with methanol, then distilled water, and dried prior to use.

General Procedure.

A. Preparation of Resin: The syntheses of the three resins used in these investigations (e.g. p-2-2-2-I, p-2-2-2-2,6N, and p-2-2-2-cis-1,4) have been described in Chapter II. They were chosen for these uptake studies because they exhibited the best mechanical strength of all the polymers synthesized in this project. The remaining polymers would mechanically degrade too rapidly during the washing procedure and one-plate batch equilibration and this made the later separation of the polymer particles from the solution much more difficult.

All three resins were mechanically ground down to ≤60/80 mesh particle size. Each was then magnetically stirred in a large volume of distilled, deionized water for periods of no less than six hours, first at pH = 10.6 (NH₄OH), then at pH = 1.4 (HCl), and finally in plain distilled, deionized water. After each washing step the polymer was filtered through a coarse glass-sintered funnel and washed with large amounts
of water. Each resin was then dried at 100°C. overnight at 0.01 mm pressure over P₂O₅ before beginning the equilibration studies and resieved.

This washing procedure caused little hydrolytic degradation. This was demonstrated in the fact that the inherent viscosity of p-2-2-2-1 (30.0°C., H₂SO₄) before and after washing was 1.06 and 1.02, respectively. This stability, plus the reversibility of metal uptake at low pHs (see page 113), enabled one to recover and renew the resin for further studies.

B. Batch Equilibration Technique: A one-plate batch equilibration technique was use to investigate the metal uptake by the resins. This involved weighing out 50 mg ± 5 mg of sieved, dried resin and adding it to a 6" silanized test tube. To this was added by volumetric pipette 10 ml. ± 0.02 ml. of the aqueous metal ion solution of interest. The test tubes were then sealed closed with a double layer of Parafilm and a rubber band wrapped around it to insure that the Parafilm would not come off during agitation. Usually there were three test tubes without resin (designated henceforth as the "Standard") and three test tubes with resin (designated as the "Sample"). An average value plus a standard deviation could then be calculated for each data point.

The sealed test tubes were then shaken horizontally in plastic test tube shipping trays for a specified period of time, usually 24 hrs., on the mechanical shaker at a moderate
speed at room temperature (unless otherwise noted). After this equilibration period, the test tubes were placed vertically in racks for ten minutes or however long it took for most of the resin to fall to the bottom of the test tube. Aliquots were then carefully pipetted from these solutions into silanized 4" test tubes. Further "clarification" was obtained by spinning down the solutions for 5-10 minutes in a centrifuge. Aliquots of the supernatent metal ion solution were then taken up by volumetric pipet and, where necessary, diluted to the appropriate concentrations with distilled, deionized water, in order that they fall in the linear range for analysis by atomic absorption spectrometry.

C. Analysis of Metals: The metal ions that were studied in these investigations were the following: \( \text{Cu}^{2+}, \text{Pb}^{2+}, \text{Ni}^{2+}, \text{Cd}^{2+}, \text{Zn}^{2+}, \text{Cr}^{3+}, \text{Ag}^{+}, \text{Ca}^{2+}, \text{and Li}^{+} \). In all cases except for lithium, the acetate salt was used to maintain uniformity regarding the type of anion present in the aqueous solutions. All the metals listed, except lithium, were measured by atomic absorption spectrometry (AAS). Lithium was measured by emission spectrometry on the same Perkin-Elmer 403 Spectrometer used for the AAS measurements. All data was taken from the digital readout. As many variables as possible were kept constant, such as wavelength, fuel and oxidant setting, number of readings per sample (or until the values leveled off), and slit size.

Before beginning studies on the resins, standard solutions
were prepared by making the appropriate volumetric dilutions from the stock (1000 ppm) metal solutions and the linear working ranges for the metals were determined. The results are shown below.

\[
\begin{align*}
Cu^{2+} & : 0.0-5.0 \text{ ppm} \\
Pb^{2+} & : 0.0-5.0 \text{ ppm} \\
Zn^{2+} & : 0.0-1.0 \text{ ppm} \\
Cd^{2+} & : 0.0-2.0 \text{ ppm} \\
Ni^{2+} & : 0.0-10.0 \text{ ppm} \\
Cr^{3+} & : 0.0-5.0 \text{ ppm} \\
Ag^{+} & : 0.0-4.0 \text{ ppm} \\
Ca^{2+} & : 0.0-4.0 \text{ ppm} \\
Li^{+} & : 0.0-3.0 \text{ ppm}
\end{align*}
\]

Since there were no interfering ions present in the experimental solutions, no precautions were necessary to guard against them.

D. Data Treatment: The values obtained from the "Sample" solutions were averaged and that value subtracted from the average value of the "Standard" solutions. This difference was then divided by the average value of the Standards and then multiplied by 100 to give the "Percentage Uptake".

\[
\text{Percentage Uptake or } \%U = \frac{(\text{"Standard" avg.} - \text{"Sample" avg.})}{\text{"Standard" avg.}} \times 100
\]
Standard deviations have been calculated for each data point and are listed along with the data.

Studies Performed

A number of variables which affected the percentage uptake were studied and because of the large number are first briefly discussed and then are summarized in the Results and Discussion—Analytical section.

Percent Uptake vs. Metal Concentration.

A. Purpose: to determine at which concentrations it would be most feasible to do the subsequent metal uptake studies.

B. Special Procedure: These initial studies were not done in triplicate. Fresh 60/80 mesh p-2-2-2-I was used along with a 24 hour equilibration period.

C. Results: Table XII shows the percentage uptake versus metal ion concentration for Cu$^{2+}$ and Ni$^{2+}$. Figure 6 shows the same data plotted.

D. Discussion: The highest percentage uptake occurs at low concentrations, and copper is taken up approximately twice as well as nickel. This was very advantageous because the test solutions could be made up in the concentration range over which the atomic absorption readings were linear. Hence, no further dilutions had to be made, and this resulted in less chance for error.

Another significant observation was that at high copper
TABLE XII
Percent Uptake vs. Metal Concentration

<table>
<thead>
<tr>
<th>Initial Cu²⁺ Conc. (ppm)</th>
<th>% U</th>
<th>Initial Ni²⁺ Conc. (ppm)</th>
<th>% U</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>5.5</td>
<td>1000</td>
<td>0.6</td>
</tr>
<tr>
<td>700</td>
<td>10.4</td>
<td>800</td>
<td>16.3</td>
</tr>
<tr>
<td>400</td>
<td>10.6</td>
<td>400</td>
<td>19.1</td>
</tr>
<tr>
<td>200</td>
<td>11.8</td>
<td>200</td>
<td>19.1</td>
</tr>
<tr>
<td>100</td>
<td>15.0</td>
<td>100</td>
<td>17.0</td>
</tr>
<tr>
<td>50</td>
<td>18.5</td>
<td>--</td>
<td>----</td>
</tr>
<tr>
<td>10</td>
<td>28.0</td>
<td>20</td>
<td>22.5</td>
</tr>
<tr>
<td>1</td>
<td>65.0</td>
<td>2</td>
<td>32.5</td>
</tr>
</tbody>
</table>

FIGURE 4
Percent Uptake vs. Metal Concentration
concentrations, the white resins would turn green over a period of several hours. This uptake could be reversed upon addition of HCl, a phenomenon which will be discussed later in this chapter. In other studies, no further color changes were noted for any metal except silver, which turned the resin brown.

Percent Uptake vs. pH for Cu$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, Cr$^{3+}$, Ag$^+$, Ca$^{2+}$, and Li$^+$. 

A. Purpose: The purpose of this study was three-fold. First, the data would give an indication of the relative percentage uptake of the metal ions listed above. Secondly, it would show the effect that varying pH from approximately 5.5 to 7.8 to 10.0 would have on the percentage uptake of the resin. Thirdly, it would give an idea as to whether or not metal hydroxide formation (and possibly precipitation) would be a problem.

B. Special Procedure: In the case of silver, dilute HNO$_3$ was used to vary the pH; in all others, dilute HCl was used. In varying the pH one had to work quickly, otherwise carbon dioxide from the atmosphere would form carbonic acid with the water and lower the pH. This problem was especially evident in the slightly basic, pH = 7.8, range. Fresh 60/80 mesh p-2-2-2-I was used along with a 24 hour equilibration period. In the case of silver, special care was taken to minimize exposure to light.

C. Results: Table XIII shows the data obtained
<table>
<thead>
<tr>
<th>Element</th>
<th>pH</th>
<th>Standard</th>
<th>Sample</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>5.51</td>
<td>0.072 ± 0.004</td>
<td>0.043 ± 0.001</td>
<td>40.3</td>
</tr>
<tr>
<td>2.0 ppm</td>
<td>7.40</td>
<td>0.059 ± 0.008</td>
<td>0.002 ± 0.000</td>
<td>96.6</td>
</tr>
<tr>
<td>10.00</td>
<td>0.068 ± 0.002</td>
<td>0.000 ± 0.000</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>5.84</td>
<td>0.191 ± 0.000</td>
<td>0.153 ± 0.027</td>
<td>19.9</td>
</tr>
<tr>
<td>1.0 ppm</td>
<td>7.95</td>
<td>0.056 ± 0.006</td>
<td>0.039 ± 0.011</td>
<td>75.5</td>
</tr>
<tr>
<td>9.87</td>
<td>0.051 ± 0.004</td>
<td>0.000 ± 0.000</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>5.78</td>
<td>0.286 ± 0.004</td>
<td>0.210 ± 0.009</td>
<td>26.5</td>
</tr>
<tr>
<td>2.0 ppm</td>
<td>7.97</td>
<td>0.284 ± 0.002</td>
<td>0.086 ± 0.005</td>
<td>69.7</td>
</tr>
<tr>
<td>10.05</td>
<td>0.224 ± 0.000</td>
<td>0.000 ± 0.000</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>5.20</td>
<td>0.040 ± 0.002</td>
<td>0.019 ± 0.004</td>
<td>52.5</td>
</tr>
<tr>
<td>4.0 ppm</td>
<td>7.80</td>
<td>0.015 ± 0.003</td>
<td>0.008 ± 0.002</td>
<td>46.7</td>
</tr>
<tr>
<td>10.03</td>
<td>0.037 ± 0.004</td>
<td>0.014 ± 0.003</td>
<td>62.2</td>
<td></td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>5.70</td>
<td>0.068 ± 0.001</td>
<td>0.065 ± 0.001</td>
<td>4.4</td>
</tr>
<tr>
<td>6.0 ppm</td>
<td>7.60</td>
<td>0.069 ± 0.001</td>
<td>0.063 ± 0.001</td>
<td>8.7</td>
</tr>
<tr>
<td>10.15</td>
<td>0.035 ± 0.000</td>
<td>0.008 ± 0.004</td>
<td>77.1</td>
<td></td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>4.60</td>
<td>0.046 ± 0.001</td>
<td>0.042 ± 0.000</td>
<td>8.7</td>
</tr>
<tr>
<td>4.0 ppm</td>
<td>7.80</td>
<td>0.036 ± 0.001</td>
<td>0.031 ± 0.000</td>
<td>13.9</td>
</tr>
<tr>
<td>10.03</td>
<td>0.042 ± 0.000</td>
<td>0.042 ± 0.000</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE XIII (cont.)

<table>
<thead>
<tr>
<th>pH</th>
<th>Standard</th>
<th>Sample</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>5.00</td>
<td>0.177±0.008</td>
<td>0.099±0.013</td>
</tr>
<tr>
<td>4.0 ppm</td>
<td>7.80</td>
<td>0.178±0.008</td>
<td>0.085±0.006</td>
</tr>
<tr>
<td></td>
<td>10.03</td>
<td>0.178±0.003</td>
<td>0.041±0.003</td>
</tr>
</tbody>
</table>

Alkali Metals and Alkaline Earths

| Ca²⁺ | 5.70 | 0.231±0.001 | 0.228±0.005   | 1.3 |
|      | 4.0 ppm | 7.80 | 0.235±0.001 | 0.213±0.003   | 9.4 |
|      | 10.10   | 0.218±0.014 | 0.074±0.005   | 66.1 |

| Li⁺  | 5.97 | 1.969±0.042 | 1.974±0.003   | 0.0 |
|      | 2.0 ppm | 7.60 | 1.976±0.002 | 1.928±0.005   | 2.7 |
|      | 10.05   | 1.993±0.019 | 1.730±0.008   | 13.2 |
for each metal grouped together for ease of overall comparison. Each metal will be dealt with individually in this section, but comparisons will be made with others to show any specific trends.

D. Discussion:

1) Copper: The percentage uptake of Cu$^{2+}$ was high relative to the other metal ions studied at low pHs, i.e. around pH = 5.51 (the pH of the freshly made solution). Note: because of its good detectability by AAS and good percentage uptake, copper was the main ion studied in this project. With increasing pH one observes increased uptake until it was 100% at pH = 10.0. However, the values for the standard fluctuated. With increasing pH it passed through a minimum and then increased to where it was near the original value at pH = 5.51. This type of behavior was observed a number of times during the studies and appeared to be due initially to hydroxide formation of the metal salts with increasing pH. Several times solid particles were noticed along the walls of test tubes. With increasing addition of NH$_4$OH, ammonium ions complexed with the metal ion and/or metal hydroxides and brought the metal back into solution. The standard deviation was usually greater in the cases where hydroxide formation/precipitation interfered.

2) Lead: Lead ion appeared to be taken up to a greater degree than copper, even though the freshly made solution was slightly more acidic. The behavior of Pb$^{2+}$ ion was similar
to Cu$^{2+}$ with respect to the variation of standard values with increasing pH. However, lead ion showed a decrease in uptake at weakly basic pH. Only Cr$^{3+}$ showed such a decrease, and that only at high pH. In the case of lead, uptake increased at higher pH, though less than might be expected when compared with the data for other metal ions. Nonetheless, as the heaviest metal ion studied, lead was taken up the best in the slightly acidic pH range.

3) Cadmium: This metal ion was not taken up by the polymer to the same degree that copper and lead were at slightly acidic pHs. The standard values stayed constant up to moderately high pHs and then started to decrease. This reflected the fact that cadmium hydroxide complexes are usually more soluble than copper ones, for example. The percentage uptake increased in a steady manner. As in the case with copper, there was 100% uptake at high pHs.

4) Zinc: Zn$^{2+}$ was taken up less well than Cu$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$. One observes that the standard values suffered a sharp drop with increasing pH, and this reflected the metal hydroxide's low $K_{sp}$. As in the cases of copper and cadmium, zinc showed a 100% uptake at high pHs, but this should be viewed with caution since there was a concurrent decrease in standard values at basic pHs.

5) Nickel: Nickel exhibited the lowest percentage uptake of all the divalent metal ions studied at slightly acidic pHs. One observes that the behavior of the standard
values for nickel as pH increased is similar to cadmium in that there was no significant change until high pHs. Again, this is an indication of the greater solubility of the nickel hydroxides in slightly basic pHs than in the case of copper, for example. At high pH the jump in percentage uptake was quite large, but so also was the decrease in the standard value.

6) Chromium: This was the only trivalent metal ion studied and its complexation behavior is interesting. It was taken up at slightly acidic pH, similar to the case of nickel. The fluctuation of the standard values is similar to copper. The percentage uptake increased only slightly at pH = 7.80 and then showed zero uptake at pH = 10.0. This was the only metal to display this behavior; in all other cases, percentage uptake was greatest at high pHs.

7) Silver: Silver ion was the only univalent transition metal studied. It exhibited a percent uptake comparable to copper at slightly acidic pHs. The standard value showed little deviation with increasing pH as a result of the relatively high solubility of silver hydroxide complexes. While the maximum uptake did not reach 100% after the 24 hr. equilibration period, it was almost double that obtained at slightly acidic pH.

8) Calcium: This was the only divalent alkaline earth metal studied. At slightly acidic pHs there is virtually no uptake by the polymer for calcium. The behavior of the stan-
Standard values with increasing pH was similar to Cd$^{2+}$ in that there was little interference by hydroxide formation/precipitation until high pHs, and even then the decrease is small. This was advantageous for alkali studies in highly basic solutions. The percent uptake increased a small amount at pH = 7.8, but rose greatly at pH = 10.1.

9) Lithium: Lithium ion was the only univalent alkali metal studied. At slightly acidic pHs, uptake by the p-2-2-2-I is negligible. Standard values showed a slight positive change with increasing pH. As in the case with silver, there appeared to be no precipitation problems. Significant uptake occurred only at high pHs, and even this was relatively low. The uptake was much less than with calcium, a divalent, heavier alkaline earth.

Percent Uptake at Low pH.

A. Purpose: First, to determine whether or not copper would be taken up on the resin in very acidic solutions. Secondly, to determine the percent recovery of copper once it was complexed on the p-2-2-2-I resin.

B. Special Procedure: In the percentage recovery study, two sets of standard and sample test tubes were equilibrated for 24 hours. Then one set was opened and ten drops of concentrated HCl was added to each and they were resealed. After another 24 hours equilibration, both sets were analyzed by AAS. 60/80 mesh p-2-2-2-I was used for the study.
C. Results:

Cu$^{2+}$, 4.0 ppm

<table>
<thead>
<tr>
<th>pH</th>
<th>Standard</th>
<th>Sample</th>
<th>% U</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.97</td>
<td>$0.151 \pm 0.003$</td>
<td>$0.136 \pm 0.003$</td>
<td>0.0=no uptake, 24 hrs.</td>
</tr>
<tr>
<td>5.70</td>
<td>$0.162 \pm 0.002$</td>
<td>$0.097 \pm 0.001$</td>
<td>40.1 -without HCl</td>
</tr>
<tr>
<td>2.00</td>
<td>$0.170 \pm 0.002$</td>
<td>$0.173 \pm 0.001$</td>
<td>0.0 -with HCl</td>
</tr>
</tbody>
</table>

D. Discussion: The data indicates that there was no uptake in highly acidic solutions, as expected. Of greater importance was the 100% recovery of copper, which showed that the p-2-2-2-1 is renewable. When the resin was renewed, however, it was necessary to resieve the material since further mechanical degradation would occur during the magnetic stirring.

Percent Uptake vs. Ionic Strength using Cu$^{2+}$ and Ca$^{2+}$.

A. Special Procedure: A 1000 ppm copper stock solution of ionic strength equal to 0.17 was made by adding glacial acetic acid (10.00g, 0.13 mole) and copper acetate (3.1416 g, 0.015 mole) to a 1000 ml. volumetric flask and diluting to the mark with distilled, deionized water.

To prepare the NaCl-spiked solution, a slightly different route was taken. At first, NaCl (10.00g, 0.17 mole) and copper acetate (3.1416 g, 0.015 mole) was added to a 1000 ml. volumetric flask, and 900 ml.of distilled, deionized water
was added. However, a whitish-green copper chloride precipitate formed which would not go into solution even upon heating. To circumvent this precipitation problem, a 4.0 ppm copper solution was made to which NaCl (0.0400g, 0.00068 mole) was added to yield a solution of 0.17 ionic strength. No observable precipitate was formed and the standard values measured by AAS were only a little lower than normal. 60/80 mesh p-2-2-2-I resin was used in this study, along with a 24 hour equilibration period. Fresh resin was used in the case of copper; renewed resin in the case of calcium.

B. Results: Table XIV shows the results obtained for copper; Table XV shows the results obtained for calcium.

C. Discussion: For copper, in the case of glacial acetic acid, there was definitely an increase in uptake. At pH = 5.60 the percent uptake was only 27.7 in the case of the time studies (see page 132). This is an increase of almost 15%. Similar to previous studies, the uptake was almost 100% in highly basic solutions. Also, there was a similar fluctuation in standard values.

In the case of NaCl the effect of the presence of chloride ions on percent uptake was negligible at slightly acidic pH, and exerted a negative effect as pH increased. In highly basic solutions both the percent uptake appeared to be lower and the precipitation problem to be greater. This was expected since copper chloride complexes are less soluble at higher pHs.
### TABLE XIV

Percent Uptake vs. Ionic Strength Using Cu

<table>
<thead>
<tr>
<th>pH</th>
<th>Standard</th>
<th>Sample</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0 ppm</td>
<td>4.18</td>
<td>0.181 ± 0.001</td>
<td>0.167 ± 0.005</td>
</tr>
<tr>
<td>acetate ion</td>
<td>5.60</td>
<td>0.176 ± 0.001</td>
<td>0.102 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>7.90</td>
<td>0.044 ± 0.009</td>
<td>0.001 ± 0.000</td>
</tr>
<tr>
<td>( \mu = 0.17 )</td>
<td>10.05</td>
<td>0.067 ± 0.003</td>
<td>0.001 ± 0.001</td>
</tr>
</tbody>
</table>

---

### TABLE XV

Percent Uptake vs. Ionic Strength Using Ca

<table>
<thead>
<tr>
<th>pH</th>
<th>Standard</th>
<th>Sample</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0 ppm</td>
<td>5.60</td>
<td>0.166 ± 0.002</td>
<td>0.154 ± 0.001</td>
</tr>
<tr>
<td>acetate ion</td>
<td>5.60</td>
<td>0.168 ± 0.001</td>
<td>0.159 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>7.80</td>
<td>0.173 ± 0.000</td>
<td>0.143 ± 0.003</td>
</tr>
<tr>
<td>( \mu = 0.17 )</td>
<td>9.98</td>
<td>0.149 ± 0.031</td>
<td>0.049 ± 0.003</td>
</tr>
</tbody>
</table>

---

4.0 ppm | 5.60 | 0.166 ± 0.002 | 0.154 ± 0.001 | 7.2 -without; run concurrently 7.0 |
| chloride ion | 5.60 | 0.189 ± 0.002 | 0.174 ± 0.001 | 11.8 |
| | 7.80 | 0.186 ± 0.003 | 0.164 ± 0.000 | 66.7 |
| \( \mu = 0.17 \) | 9.98 | 0.153 ± 0.002 | 0.051 ± 0.003 | 66.7 |
For calcium in both the cases of glacial acetic acid and NaCl, the effect of increased anion concentration appeared to be negligible on percent uptake and the standard values when compared to the data taken in their absence (see page 109).

Percent Uptake vs. Temperature.

A. Purpose: To determine whether or not raising the temperature during the equilibration period would have any effect on percent uptake.

B. Special Procedure: The test tubes were doubly sealed to prevent contamination of the metal ion solutions. R.T. means room temperature, which normally averaged out to approximately 25°C. 60/80 mesh p-2-2-2-I was used in this study, along with a 24 hour equilibration period.

C. Results:

<table>
<thead>
<tr>
<th>Cu²⁺</th>
<th>Temp. (°C.)</th>
<th>Standard</th>
<th>Sample</th>
<th>% U</th>
<th>Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.T.</td>
<td>0.155 ± 0.001</td>
<td>0.108 ± 0.001</td>
<td>30.3</td>
<td>9.4%</td>
<td></td>
</tr>
<tr>
<td>pH=5.60</td>
<td>37.5</td>
<td>0.156 ± 0.003</td>
<td>0.094 ± 0.009</td>
<td>39.7</td>
<td></td>
</tr>
<tr>
<td>R.T.</td>
<td>0.151 ± 0.004</td>
<td>0.108 ± 0.003</td>
<td>28.5</td>
<td>15.3%</td>
<td></td>
</tr>
<tr>
<td>50.0</td>
<td>0.146 ± 0.002</td>
<td>0.082 ± 0.001</td>
<td>43.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

D. Discussion: The data shows a clear increase in percent uptake with increasing temperature. There appears to be little significant effect on the standard values.
Competitive Uptake Studies.

A. Purpose: To determine to what degree Cu\(^{2+}\) was taken up by the resin in the presence of similar amounts of Zn\(^{2+}\) or Ag\(^{+}\). The particular combination of Cu/Zn and Cu/Ag was picked for a few reasons. One was that all the metals exhibited good uptake. Also, there were multielement lamps which contained both Cu/Zn and Cu/Ag combinations which allowed one to switch from analyzing for one element to another relatively easily.

B. Special Procedure: For the copper vs. zinc studies, three different solutions were made up in all. A 2.0 ppm copper solution and a 1.0 ppm zinc solution were made up separately. Uptake studies using p-2-2-2-I resin were made on these solutions in order to make a comparison with the uptake of the resin using the third solution, which contained 2.0 ppm copper and 1.0 ppm zinc together. HCl and NH\(_4\)OH were used to vary the pH.

The same general procedure was followed for the copper vs. silver studies, except that concentrations were 4.0 ppm. Also, care was taken to minimize exposure to light. HNO\(_3\) and NH\(_4\)OH were used to vary pH.

Renewed ≤60/80 mesh p-2-2-2-I was used, along with a 24 hour equilibration period.

C. Results: Table XVI shows the results obtained for Cu\(^{2+}\) vs. Zn\(^{2+}\); Table XVII shows the results obtained for Cu\(^{2+}\) vs. Ag\(^{+}\).
### TABLE XVI

Competitive Uptake Study: Cu$^{2+}$ vs. Zn$^{2+}$

<table>
<thead>
<tr>
<th>pH</th>
<th>Standard</th>
<th>Sample</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>5.75</td>
<td>0.075 ± 0.002</td>
<td>0.038 ± 0.001</td>
</tr>
<tr>
<td>2.0 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>5.75</td>
<td>0.154 ± 0.001</td>
<td>0.104 ± 0.005</td>
</tr>
<tr>
<td>1.0 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comb.:

| Cu$^{2+}$ | 0.075 ± 0.001 | 0.041 ± 0.001 | 45.3 |
| 2.0 ppm | | | |
| and | 5.75 | | |
| Zn$^{2+}$ | 0.171 ± 0.002 | 0.165 ± 0.002 | 3.5 |
| 1.0 ppm | | | |

### TABLE XVII

Competitive Uptake Study: Cu$^{2+}$ vs. Ag$^+$

<table>
<thead>
<tr>
<th>pH</th>
<th>Standard</th>
<th>Sample</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>5.75</td>
<td>0.167 ± 0.002</td>
<td>0.116 ± 0.003</td>
</tr>
<tr>
<td>4.0 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>5.72</td>
<td>0.164 ± 0.002</td>
<td>0.128 ± 0.003</td>
</tr>
</tbody>
</table>
| Comb.:
| Cu$^{2+}$ | 0.169 ± 0.003 | 0.115 ± 0.003 | 32.0 |
| 4.0 ppm | | | |
| and | 5.75 | | |
| Ag$^+$ | 0.184 ± 0.002 | 0.165 ± 0.005 | 11.5 |
| 4.0 ppm | | | |
D. Discussion: Copper showed better uptake than silver and silver showed better uptake than zinc. In the Cu/Zn and Cu/Ag solutions the standard values for Zn and Ag were slightly higher when measured separately in solutions, but otherwise there is no negative effect.

Percent Uptake of Cu$^{2+}$ and Cd$^{2+}$ using p-2-2-2-2,6N and p-2-2-2-cis-1,4 Resin.

A. Purpose: To determine whether or not there would be any effect on percent uptake by changing the aromatic content of the polymer. This was accomplished by changing the diacid group in the repeat unit of the polymer backbone from isophthaloyl to cis-1,4-cyclohexyl or to 2,6-naphthyleneyl.

B. Special Procedure: The resins were washed in a manner similar to that of the p-2-2-2-I (see page 101). Due to mechanical degradation of the two resins, ≤60/80 mesh material had to be used for the studies. The increased surface area of the resins were compensated for by using ≤60/80 mesh p-2-2-2-I in the comparison studies. Fresh p-2-2-2-I resin was used in the studies on p-2-2-2-cis-1,4; renewed resin was used in the studies on p-2-2-2-2,6N. The equilibration period lasted 24 hours.

C. Results: Table XVIII shows the results obtained for the p-2-2-2-cis-1,4 resin; Table XIX shows that obtained for p-2-2-2-2,6N.

D. Discussion: Both resins took up both Cu$^{2+}$ and
### TABLE XVIII

<table>
<thead>
<tr>
<th>pH</th>
<th>Standard</th>
<th>p-2-2-2-I</th>
<th>%U</th>
<th>p-2-2-2-cis-1,4</th>
<th>% U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺</td>
<td>5.50</td>
<td>0.152 ± 0.001</td>
<td>0.103 ± 0.003</td>
<td>32.2</td>
<td>0.129 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>4.0 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>5.45</td>
<td>0.254 ± 0.000</td>
<td>0.177 ± 0.002</td>
<td>30.3</td>
<td>0.252 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>2.0 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE XIX

<table>
<thead>
<tr>
<th>pH</th>
<th>Standard</th>
<th>p-2-2-2-I</th>
<th>%U</th>
<th>p-2-2-2-2.6N</th>
<th>% U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺</td>
<td>5.75</td>
<td>0.275 ± 0.005</td>
<td>0.172 ± 0.005</td>
<td>37.5</td>
<td>0.189 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>4.0 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>5.65</td>
<td>0.252 ± 0.002</td>
<td>0.159 ± 0.007</td>
<td>36.9</td>
<td>0.203 ± 0.013</td>
</tr>
<tr>
<td></td>
<td>2.0 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Cd\textsuperscript{2+} to some extent, but not as greatly as did the p-2-2-2-I. The reasons for this behavior are discussed in Chapter VI.

**Percent Uptake on Silanized Sand.**

A. Purpose: To determine if the actual macroscopic structure of a particle would effect uptake. Investigations were performed using copper and cadmium on both sieved (60/80 mesh) and unsieved (larger size) sand in order to determine whether or not the change in surface area might have any effect.

B. Special Procedure: Purified sand was magnetically stirred in a large excess of silanization solution (see Reagents section) for 15 minutes. It was then filtered, washed with methanol, then water, and then dried in the oven. Fresh p-2-2-2-I resin (60/80 mesh) was run simultaneously for a valid comparison. A 24 hour equilibration period was used.

C. Results: Table XX shows the results for copper; Table XXI shows the results for calcium.

D. Discussion: In the case of copper there was definitely some "uptake" by the silanized sand, especially at high pHs, where the hydroxide would tend to precipitate. The type of "uptake" described here for the sand is that in which the sand acts as a filtration bed or as nucleation sites for precipitate formation.

The amphoteric effect is again shown in the lower uptake by the sand at pH = 10.05 than at 7.85. More of the metal is
### TABLE XX

Percent Uptake on Silanized Sand for Cu\(^{2+}\)

<table>
<thead>
<tr>
<th>pH</th>
<th>Standard</th>
<th>p-2-2-2-I</th>
<th>% U</th>
<th>Sand</th>
<th>% U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+}) 4.0 ppm 60/80 sieved sand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.60</td>
<td>0.151 ± 0.003</td>
<td>0.103 ± 0.005</td>
<td>31.8</td>
<td>0.141 ± 0.003</td>
<td>6.6</td>
</tr>
<tr>
<td>non-sieved sand</td>
<td>0.151 ± 0.004</td>
<td>0.108 ± 0.003</td>
<td>28.5</td>
<td>0.145 ± 0.003</td>
<td>4.0</td>
</tr>
<tr>
<td>5.95</td>
<td>0.131 ± 0.002</td>
<td>0.089 ± 0.002</td>
<td>32.1</td>
<td>0.133 ± 0.008</td>
<td>12.8</td>
</tr>
<tr>
<td>7.85</td>
<td>0.012 ± 0.010</td>
<td>--------</td>
<td>----</td>
<td>0.007 ± 0.001</td>
<td>58.3</td>
</tr>
<tr>
<td>10.05</td>
<td>0.018 ± 0.004</td>
<td>--------</td>
<td>----</td>
<td>0.008 ± 0.008</td>
<td>44.4</td>
</tr>
</tbody>
</table>

### TABLE XXI

Percent Uptake on Silanized Sand for Ca\(^{2+}\)

<table>
<thead>
<tr>
<th>pH</th>
<th>Standard</th>
<th>p-2-2-2-I</th>
<th>% U</th>
<th>Sand</th>
<th>% U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+}) 4.0 ppm non-sieved sand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.00</td>
<td>0.219 ± 0.001</td>
<td>0.207 ± 0.001</td>
<td>5.5</td>
<td>0.221 ± 0.002</td>
<td>0.0</td>
</tr>
<tr>
<td>8.10</td>
<td>0.226 ± 0.001</td>
<td>--------</td>
<td>---</td>
<td>0.227 ± 0.002</td>
<td>0.0</td>
</tr>
<tr>
<td>10.05</td>
<td>0.214 ± 0.012</td>
<td>--------</td>
<td>---</td>
<td>0.175 ± 0.001</td>
<td>18.2</td>
</tr>
</tbody>
</table>
in solution due to the higher concentration of ammonium ions at high pH. Also, the sieved sand with its relatively greater surface area showed slightly higher uptake than the non-sieved sand, as would be expected.

In the case of calcium there was no uptake by the sand until high hydroxide concentrations, but then uptake did become significant.

Percent Uptake after Endcapping.

A. Purpose: To determine if the concentration of possible amine and carboxylic end groups was high enough to significantly influence uptake. These end groups would be "deactivated" by end-capping with acetic anhydride.

B. Special Procedure: To a 50ml. one-neck round bottom flask was added 5.0g of p-2-2-2-I (≤60/80 mesh), 35 ml. freshly distilled acetic anhydride, 3 ml. pyridine, and a magnetic stirrer. The flask was stoppered and the solution stirred for 54 hours, during which time it became pink in color. It was then filtered through a coarse glass-sintered funnel and washed with large amounts of distilled, deionized water. Then both it and untreated polymer were extracted with distilled, deionized water in a Soxhlet apparatus for a period of 24 hours. They were then vacuum dried at 100°C. over P₂O₅ at 0.1 mm pressure overnight.

C. Results:

<table>
<thead>
<tr>
<th></th>
<th>Standard</th>
<th>Sample</th>
<th>% U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺ 4.0 ppm pH = 5.70</td>
<td>not endcapped: 0.167 ± 0.001</td>
<td>0.108 ± 0.001</td>
<td>35.3</td>
</tr>
<tr>
<td></td>
<td>endcapped: 0.167 ± 0.001</td>
<td>0.096 ± 0.001</td>
<td>42.5</td>
</tr>
</tbody>
</table>
D. Discussion: Infrared spectra before and after endcapping treatment showed only a small change which indicated a low concentration of end groups and high molecular weight. The data indicates a slightly better uptake for the endcapped than the non-endcapped resin, which is opposite that which one would expect if the end groups were involved in some of the uptake. However, the 54 hour stirring period resulted in further mechanical breakdown and hence the increase in surface area explains the increased uptake. Thus, endcapping had essentially no effect.

Surface Area Measurement and SEM Examination of Particles and Films.

A. Purpose: To determine the area of films and particles of p-2-2-2-I.

B. Special Procedure: Renewed 60/80 mesh p-2-2-2-I was used for the particle studies. Films were cast from 5-10% TFAA solutions onto glass plates, dried one minute in the hood, and then gelled in an ice water bath. Both particles and films were dried under high vacuum at 100°C. over P₂O₅ before use. The films were then cut up into small pieces for ease of handling.

Surface area measurements were determined by use of a nitrogen absorption method. SEM pictures were taken of both the particles and the films.

C. Results: 60/80 mesh p-2-2-2-I particles had a surface area of 4.0 m²/g. Gelled films had a surface area of
Figures 5, 6, and 7 show different magnifications of 60/80 mesh particles. Figures 8, 9, and 10 show comparable magnifications of the surfaces of the films. Figures 11, 12, and 13 show similar magnifications of the interior fracture surfaces of the films after they had been cracked under liquid nitrogen.

D. Discussion: Normally one would expect the surface area of the particles to be larger than that of the films, yet here the reverse case is true. The apparent anomaly is explained by the SEM pictures. While the particles have a much greater "outside" surface area, pictures of the films, particularly those of the fracture surfaces (Figures 11, 12, and 13), show that the "interior" surface area is large and contains many tubular structures, such as those first noted by Tirrell. The fact that nitrogen is being absorbed into the films as well as onto them accounts for the higher surface area of the films over the particles.

Percent Uptake of 60/80 Mesh Particles vs. Films.

A. Purpose: As mentioned in Chapter I, films of p-2-2-2-I have been used as desalination membrane candidates. It was of interest to determine whether or not the percent uptake of films differed from that of 60/80 mesh particles.

B. Special Procedure: Films were prepared as described in the previous study.
SEM Pictures of Particle Surfaces

FIGURE 5

60/80 mesh particles of p-2-2-2-1

mag. = $4 \times 10^2$

FIGURE 6

mag. = $4 \times 10^3$

FIGURE 7

mag. = $9 \times 10^2$
SEM Pictures of Film Surfaces

FIGURE 8
Gelled films of p-2-2-2-I
mag. = $1 \times 10^2$

FIGURE 9
mag. = $5 \times 10^3$

FIGURE 10
mag. = $10 \times 10^3$
SEM Pictures of Film Interior

FIGURE 11

Fracture surfaces of gelled p-2-2-2-1 films.

mag. = 7 \times 10^2

FIGURE 12

mag. = 2 \times 10^2

FIGURE 13

mag. = 9 \times 10^2
C. Results: The results are listed in Table XXII.

D. Discussion: The data clearly shows that the 60/80 mesh particles exhibit much better uptake than the films do. Only those metal ions which display relatively good uptake, such as Cu$^{2+}$, Zn$^{2+}$, and Pb$^{2+}$, are taken up by the films at all.

Percent Uptake vs. Time and Surface Area.

A. Purpose: Though it was initially decided that a 24 hour equilibration time would be employed for most of the studies, it was necessary to determine how the percentage uptake varied versus time. In the course of the investigations it was discovered that much useful data could be obtained by including studies dealing with surface area effects.

B. Special Procedure: Virgin 60/80 mesh p-2-2-2-I resin was initially employed for the copper studies. Later in the project, renewed resin was used for copper, cadmium, and lead investigations. Centrifuging the decanted solutions gave reasonable separations.

C. Results: Table XXIII lists the results for copper; Table XXIV those for cadmium, and Table XXV, those for lead.

D. Discussion: As can be seen from the data in Table XXIII, it appears that there was 100% uptake of copper at slightly basic pHs within only 7.0 hours. Yet this result is somewhat deceptive because the values of the standard solutions fluctuated greatly. Some of the "uptake" was simply
<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Standard</th>
<th>Particles</th>
<th>%U</th>
<th>Film</th>
<th>%U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺</td>
<td>5.03</td>
<td>0.182 ± 0.001</td>
<td>0.133 ± 0.003</td>
<td>26.9</td>
<td>0.153 ± 0.001</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>5.70</td>
<td>0.191 ± 0.008</td>
<td>0.141 ± 0.009</td>
<td>26.2</td>
<td>0.187 ± 0.001</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>5.70</td>
<td>0.188 ± 0.008</td>
<td>0.183 ± 0.001</td>
<td>2.7</td>
<td>0.208 ± 0.007</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li⁺</td>
<td>5.97</td>
<td>1.969 ± 0.042</td>
<td>1.974 ± 0.003</td>
<td>0.0</td>
<td>2.037 ± 0.004</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>5.68</td>
<td>0.069 ± 0.006</td>
<td>0.038 ± 0.003</td>
<td>44.9</td>
<td>0.053 ± 0.004</td>
<td>23.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>5.80</td>
<td>0.215 ± 0.013</td>
<td>0.168 ± 0.002</td>
<td>21.9</td>
<td>0.214 ± 0.001</td>
<td>0.0</td>
</tr>
</tbody>
</table>
### TABLE XXIII

Percent Uptake vs. Time and Surface Area for Cu\(^{2+}\)

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Standard</th>
<th>Sample</th>
<th>%U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH = 7.87</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| fresh resin,
  60/80 mesh |          |        |     |
| 0.8        | 0.071 ± 0.041 | 0.022 ± 0.002 | 69.0 |
| 2.0        | 0.130 ± 0.011 | 0.064 ± 0.005 | 50.8 |
| 4.0        | 0.045 ± 0.016 | 0.004 ± 0.001 | 91.1 |
| 7.0        | 0.060 ± 0.001 | 0.000 ± 0.001 | 100.0 |
| 10.5       | 0.072 ± 0.006 | 0.000 ± 0.001 | 100.0 |
| 24.0       | 0.042 ± 0.014 | 0.000 ± 0.001 | 100.0 |

| Cu\(^{2+}\) |          |        |     |
| 5.5        | 0.171 ± 0.005 | 0.132 ± 0.000 | 22.8 |
| 24.0       | 0.166 ± 0.003 | 0.120 ± 0.004 | 27.7 |
| 48.0       | 0.172 ± 0.005 | 0.115 ± 0.004 | 33.1 |
| 72.0       | 0.172 ± 0.003 | 0.115 ± 0.003 | 33.1 |

| Cu\(^{2+}\) |          |        |     |
| 24.0       | 0.165 ± 0.000 | 0.110 ± 0.001 | 33.3 |
| 48.0       | 0.187 ± 0.000 | 0.115 ± 0.001 | 38.5 |
| 72.0       | 0.171 ± 0.001 | 0.094 ± 0.004 | 45.0 |
due to precipitation resulting from hydroxide formation. Again, this indicated that uptake at even slightly basic pHs can suffer from sparingly soluble hydroxide interferences, which seem to be time dependent, but do not show any definite pattern with increasing time of equilibration.

Further time studies were carried out at a slightly acidic pH (the pH of the freshly made test solutions). At pH=5.60 there was much less fluctuation versus time of the standard values. The uptake of copper at that particular concentration (4.0 ppm) and pH (5.60) began to level off after 24 hours and steadied after 48 hours. The concentration and pH, especially, are emphasized here because these factors exert a great effect on percent uptake, and necessarily, time of uptake.

When renewed ≤60/80 mesh resin was used, percent uptake increased with time. This could be due to the metal slowly diffusing into the (renewed) resin, or to the formation of more surface area by the further mechanical breakdown of the polymer. Not only did the percent uptake increase with time, but uptake for the ≤60/80 mesh resin was significantly greater than for the 60/80 mesh material, the latter having a smaller surface area.

In the case of cadmium, shown in Table XXIV, with both mesh sizes the percent uptake increased with time. The ≤60/80 mesh material exhibited higher uptake, behavior which can be ascribed to its greater surface area.

Another interesting observation was that the renewed resin
### TABLE XXIV

Percent Uptake vs. Time and Surface Area for Cd$^{2+}$

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Standard</th>
<th>Sample</th>
<th>% U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$^{2+}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0 ppm</td>
<td>24.0</td>
<td>0.304 ± 0.011</td>
<td>0.194 ± 0.004</td>
</tr>
<tr>
<td>pH = 5.60</td>
<td>48.0</td>
<td>0.292 ± 0.010</td>
<td>0.178 ± 0.004</td>
</tr>
<tr>
<td>renewed</td>
<td>72.0</td>
<td>0.288 ± 0.009</td>
<td>0.156 ± 0.004</td>
</tr>
<tr>
<td>60/80 mesh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>8.0</td>
<td>0.329 ± 0.003</td>
<td>0.194 ± 0.008</td>
</tr>
<tr>
<td>2.0 ppm</td>
<td>24.5</td>
<td>0.325 ± 0.007</td>
<td>0.189 ± 0.007</td>
</tr>
<tr>
<td>pH = 5.75</td>
<td>48.0</td>
<td>0.326 ± 0.007</td>
<td>0.107 ± 0.015</td>
</tr>
<tr>
<td>renewed</td>
<td>72.0</td>
<td>0.314 ± 0.006</td>
<td>0.080 ± 0.009</td>
</tr>
<tr>
<td>≤ 60/80 mesh</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE XXV

Percent Uptake vs. Time for Pb$^{2+}$

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Standard</th>
<th>Sample</th>
<th>% U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^{2+}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0 ppm</td>
<td>5.5</td>
<td>0.068 ± 0.008</td>
<td>0.021 ± 0.001</td>
</tr>
<tr>
<td>pH = 5.65</td>
<td>24.0</td>
<td>0.074 ± 0.007</td>
<td>0.028 ± 0.002</td>
</tr>
<tr>
<td>renewed</td>
<td>48.0</td>
<td>0.070 ± 0.008</td>
<td>0.015 ± 0.006</td>
</tr>
<tr>
<td>≤ 60/80 mesh</td>
<td>72.0</td>
<td>0.051 ± 0.005</td>
<td>0.007 ± 0.003</td>
</tr>
</tbody>
</table>
had somewhat greater uptake than the virgin material. For example, after 24.0 hours the renewed 60/80 mesh resin had a 36.2% uptake. Virgin material exhibited an uptake of only 26.5% at a comparable pH and concentration (see page 108).

Table XXV shows that there is a general increase in percent uptake of lead with time, as in the cases of copper and cadmium. The standard values fluctuated more in the case of lead than with the two other metal ions. This indicated that studies involving Pb$^{2+}$ would be subject to greater possible error. All three metal ions showed a small decreasing trend in the standard values at slightly acidic pHs.

**Infrared and X-ray Measurements.**

A. Purpose: To determine if the infrared spectra of polymers complexed with Cu$^{2+}$ would show any differences when compared to that of virgin material. Also, to determine if complexation with Cu$^{2+}$ would effect the percent crystallinity in any significant amount as measured by wide-angle X-ray.

B. Special Procedure: ≤60/80 mesh p-2-2-2-I was used for the IR investigations. The complexed polymer was prepared by allowing virgin material to remain in contact with an excess of a 1000 ppm copper acetate solution for 7 days. The green material was then filtered through a coarse glass-sintered funnel, quickly washed with distilled, deionized water, and then vacuum dried at 100°C. at 0.1 mm pressure over $\text{P}_2\text{O}_5$ overnight.
X-ray measurements were obtained on cast films of p-2-2-2-1. Complexation was performed in a manner similar to that for the particles.

C. Results and Discussion: IR spectra indicate some change in NH and C=O absorptions, though the polymeric state of the material obscures much of the quantitative information about the effects of complexation.

X-ray measurements before and after complexation showed no significant amount of crystallinity in the films.
CHAPTER V
ORGANIC ACID AND BASE UPTAKE STUDIES

Objective

Copolyoxamides are quite polar and are composed of appreciable amounts of nitrogen- and aromatic-containing residues in the repeat unit. Because of the results obtained with PVP, discussed in Chapter I, it was of interest to perform similar uptake studies on some of the polymers that were synthesized in this work and to evaluate their behavior. Different organic acids and bases were employed to determine whether or not changing the aromatic content of the acid or base would effect uptake. Also, several polymers were investigated to see what effect a change in aromatic content of the diacid portion of the repeat unit would have on uptake of aromatic acids and bases.

Experimental

Apparatus. Both a Beckman Acta MVI double beam ultraviolet spectrophotometer and a Heath modular double beam scanning spectrophotometer, model EU-707, equipped with a Heath EU-805A DVM were used in these studies. All other instruments and equipment have been previously described in Chapter IV.

Reagents. Phenol: obtained from J.T. Baker Chemical Co., Phillipsburg, New Jersey, was used as received.
\textit{\textbf{\textsuperscript{3}-naphthol:}} obtained from Eastman Kodak Co., Rochester, New York, was used as received.

Aniline: obtained from Fisher Scientific Co., Fair Lawn, New Jersey, was used as received.

All other reagents used have been previously listed in Chapter IV for the metal ion uptake investigations.

The organic compound under study was added in the appropriate amount, either by pipetting or weighing, as was necessary, to a 1000 ml. volumetric flask. This was diluted with distilled, deionized water up to the mark. This yielded a solution which contained 1000 mg/L. (ppm) of the organic compound. The lower concentrations of organic compounds used for standards and test solutions were prepared fresh for each analysis by making the appropriated dilutions of the stock solutions in volumetric flasks.

General Procedure.

A. Preparation of Resins: For the ultraviolet studies it was necessary that the absorbance readings of a blank solution (containing only distilled, deionized water plus polymer) be lower than 0.100 absorbance units. Otherwise, impurities which caused the absorbance would interfere with and/or mask any uptake by the resin. Since the copolyoxamides exhibited good hydrolytic stability, the following wash procedure was devised. After the regular washing described in Chapter IV for the metal ion analyses, the material was put in a coarse glass-sintered thimble and placed
in a Soxhlet extractor with distilled, deionized water, which was renewed twice a day. A period of one to two days was sufficient to obtain blank readings $<<0.100$.

B. Batch Equilibration Technique: The technique used in these analyses was similar to that used in the metal ion uptake studies up to the point where aliquots were withdrawn for analysis by ultraviolet spectroscopy. If the resin did not separate from the solution rapidly, aliquots were pipetted into 4" silanized test tubes which were then centrifuged. Portions of this solution were carefully pipetted from these test tubes into the UV quartz cell, one time to wash the cell (which was previously rinsed several times with distilled, deionized water), and a second time to fill the cell for measurement.

All the test solutions were prepared within the linear working range of the instrument for the particular compound under investigation. Further dilutions were therefore unnecessary.

C. Analysis of Organic Compounds: The organic compounds studied in this investigation were the following: phenol, $\beta$-naphthol, pyridine, and aniline. All measurements were made by ultraviolet spectrometry (UVS). Before beginning studies on the resins, standard solutions were prepared by making appropriate volumetric dilutions from the stock (1000 ppm) solutions. The linear working ranges were determined and are listed below.
<table>
<thead>
<tr>
<th>Compound</th>
<th>(nm)</th>
<th>Working Range (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol</td>
<td>254</td>
<td>0.0 - 30.0</td>
</tr>
<tr>
<td>p-naphthol</td>
<td>274-280</td>
<td>0.0 - 25.0</td>
</tr>
<tr>
<td>pyridine</td>
<td>257</td>
<td>0.0 - 25.0</td>
</tr>
<tr>
<td>aniline</td>
<td>280</td>
<td>0.0 - 50.0</td>
</tr>
</tbody>
</table>

There were no significant impurities present after the washing cycle, so no extra precautions were necessary to guard against them.

All data was taken off the digital readout at the optimal wavelength (~250 nm) for determining the absorbance.

A special procedure was devised to "normalize" the data resulting from the wide range of pHs used for the phenol, pyridine, and aniline studies. In the case of phenol one drop of concentrated HCl was added to the cuvette along with the solution that was to be measured, and the cuvette carefully shaken to insure mixing. For pyridine and aniline, NH₄OH was used rather than HCl. This procedure insured that the compound of interest was in its non-ionic form. Previous tests showed that the non-ionic form gave the highest absorbance values; this made the percent uptake data more accurate. This also insured that one was not on the slope of the absorbance curve for the compound when performing the measurement over a series of pHs. In the case of p-naphthol, this procedure was not used. Rather, both standard and sample solutions were measured at the pH of the test solution.
D. Data Treatment: The data was handled identically to that described in Chapter IV.

Results and Discussion

Seven resins in all were investigated. They are the following:

- p-2-2-2-1
- p-2-2-2-2,6N
- p-2-2-2-cis-1,4
- p-2-2-2-trans-1,4
- p-2-2-1,1-cyclobut.
- p-2-2-2-P
- p-2-2-2-2-1

This first four exhibited acceptable mechanical behavior. However, the last three mechanically degraded during washing into a powder which produced severe light scattering. The results are in question and therefore have not been included.

The four remaining resins will be discussed individually, with comparisons made to each other where applicable. Also, a study was made on silanized sand to see if the sand would show any "uptake".

\[ p-2-2-2-I \]

The data obtained for the p-2-2-2-I resin is listed below, and plotted in Figure 14.

<table>
<thead>
<tr>
<th>pH</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>42.2 ± 0.4</td>
</tr>
<tr>
<td>4.5</td>
<td>41.0 ± 1.3</td>
</tr>
<tr>
<td>5.8</td>
<td>41.8 ± 0.0</td>
</tr>
<tr>
<td>7.0</td>
<td>42.2 ± 0.5</td>
</tr>
<tr>
<td>9.2</td>
<td>36.7 ± 1.8</td>
</tr>
<tr>
<td>10.5</td>
<td>29.3 ± 1.7</td>
</tr>
<tr>
<td>12.0</td>
<td>3.0 ± 1.7</td>
</tr>
</tbody>
</table>
FIGURE 14
Percent Uptake of p-2-2-2-I

FIGURE 15
Percent Uptake of p-2-2-2,6N
pyridine: showed almost zero uptake over the entire pH range from 3.0 to 10.5

aniline: 

<table>
<thead>
<tr>
<th>pH</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>47 ± 2</td>
</tr>
<tr>
<td>5.8</td>
<td>24 ± 2</td>
</tr>
<tr>
<td>8.0</td>
<td>20 ± 1</td>
</tr>
<tr>
<td>10.3</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>12.0</td>
<td>17 ± 1</td>
</tr>
</tbody>
</table>

In these types of analyses any value below 15% uptake is questionable. The resin shows negligible uptake for phenol, but in the case of \( \beta \)-naphthol there was significant uptake (up to approximately 43%) in its non-ionic form. The percent uptake only appears to be influenced by pH at high ammonium ion concentrations.

Pyridine, an organic base, shows no uptake whatsoever, though aniline does. Oddly, percent uptake is better for the protonated form.

Thus, \( \beta \)-naphthol and aniline, with their greater degree of aromatic character than phenol and pyridine, respectively, show greater uptake in spite of increased molecular size.

**p-2-2-2-2,6N.** The data obtained on the p-2-2-2-2,6N resin is listed below, and plotted in Figure 15.

<table>
<thead>
<tr>
<th>phenol:</th>
<th>pH</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.99</td>
<td>13 ± 1</td>
<td></td>
</tr>
<tr>
<td>4.07</td>
<td>13 ± 1</td>
<td></td>
</tr>
<tr>
<td>5.90</td>
<td>13 ± 1</td>
<td></td>
</tr>
<tr>
<td>8.41</td>
<td>13 ± 1</td>
<td></td>
</tr>
<tr>
<td>10.69</td>
<td>11 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>aniline:</th>
<th>pH</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00</td>
<td>50 ± 2</td>
<td></td>
</tr>
<tr>
<td>7.90</td>
<td>48 ± 2</td>
<td></td>
</tr>
<tr>
<td>10.11</td>
<td>35 ± 4</td>
<td></td>
</tr>
</tbody>
</table>
By changing the diacid portion of the repeat unit of the polymer from isophthaloyl to naphthalenyl, one is increasing the aromatic content of the resin. The data displayed above clearly shows that the uptake for phenol and aniline is better for this resin than for p-2-2-2-1. Uptake for phenol, especially, and somewhat for aniline, is highly pH dependent. Again, uptake for phenol is best in its non-ionic form, while that of aniline is best in its protonated form.

p-2-2-2-cis-1,4. The data obtained for the p-2-2-2-cis-1,4 resin is listed below.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol:</td>
<td>2.10</td>
<td>13 ± 1</td>
</tr>
<tr>
<td></td>
<td>3.90</td>
<td>12 ± 1</td>
</tr>
<tr>
<td></td>
<td>6.09</td>
<td>4 ± 3</td>
</tr>
<tr>
<td></td>
<td>8.08</td>
<td>2 ± 1</td>
</tr>
<tr>
<td>aniline:</td>
<td>3.95</td>
<td>2 ± 1</td>
</tr>
<tr>
<td></td>
<td>5.50</td>
<td>6 ± 1</td>
</tr>
<tr>
<td></td>
<td>8.05</td>
<td>11 ± 3</td>
</tr>
<tr>
<td></td>
<td>10.11</td>
<td>9 ± 1</td>
</tr>
<tr>
<td></td>
<td>12.00</td>
<td>7 ± 5</td>
</tr>
</tbody>
</table>

The percent uptake by this resin for both phenol and aniline is below 15%. For this reason one cannot conclude too much from the data. However, uptake for phenol again appears to be better in its non-ionic form, while protonating aniline seems to decrease uptake, unlike before for the previous two resins.

p-2-2-2-trans-1,4. The data obtained for the p-2-2-2-trans resin is listed below.
phenol: showed almost zero uptake over the entire pH range from 1.99 to 10.25

aniline:  

<table>
<thead>
<tr>
<th>pH</th>
<th>% Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.00</td>
<td>21 ± 6</td>
</tr>
<tr>
<td>7.83</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>10.10</td>
<td>21 ± 3</td>
</tr>
<tr>
<td>12.02</td>
<td>9 ± 1</td>
</tr>
</tbody>
</table>

Though phenol uptake is negligible, aniline uptake is significant (almost 20%). Again, aniline appears to exhibit better uptake in its protonated form.

Silanized Sand. An uptake study with phenol over the pH range of 2.00 to 10.00 showed zero uptake. Hence, there does not appear to be any filtration effect exhibited by the sand for this small aromatic molecule.
CHAPTER VI
RESULTS AND DISCUSSION - ANALYTICAL

Objective

The first goal was to investigate the unique property exhibited by copolyoxamides of complexing with metals. This was accomplished through performing one-plate batch equilibrations with aqueous solutions of the metal ion of interest. A number of variables were examined, such as what effect the type of metal ion had on uptake, the effect of pH changes, time for uptake, surface area, possible renewability, etc. They will be summarized and discussed in this section in the same order the studies were presented in the experimental section.

The second goal was to determine whether or not the copolyoxamides were capable of absorbing organic acids and bases. Several variables, such as polymer type, degree of aromaticity, and pH changes, were examined. A brief summary and discussion has been included in this section as well.

Metal Ion Uptake Studies

In the first study, work done at high copper concentrations demonstrated that the p-2-2-2-I was indeed complexing as indicated by the fact that the virgin white resin became progressively more green with time. This could be easily reversed by the addition of HCl. This study also showed that
the percentage uptake was greatest at low metal ion concentrations. Test solutions containing between 1 to 6 ppm of the metal ion of interest could be used, and this simplified analyses, since further dilutions to bring the concentration to within the linear working range of the instrument were unnecessary. It also indicated that the resin was not an especially strong complexer. However, the low capacity of the resin can be circumvented by doing column work, which greatly increases the number of theoretical plates.

The second study, regarding the type of metal ion and pH, was very informative. In general, the relative uptake of p-2-2-2-I at slightly acidic pHs was the following: Pb\(^{2+}\) > Cu\(^{2+}\) > Ag\(^{+}\) > Cd\(^{2+}\) > Zn\(^{2+}\) > Cr\(^{3+}\), Ni\(^{2+}\) > Ca\(^{2+}\) > Li\(^{+}\). Transition metals were taken up better than alkalies and alkaline earth metals, behavior which is characteristic of weak-acid cation-exchange resins. Atomic number was influential in that the heavier metal ions were generally taken up more readily, such as Cd\(^{2+}\) > Zn\(^{2+}\), Ca\(^{2+}\) > Li\(^{+}\), and Pb\(^{2+}\) > all others. Bonding with the soft transition metals, such as Cu\(^{2+}\) and Ag\(^{+}\), was more favorable than with the hard metals, such as Cr\(^{3+}\), because the d orbitals of the former two were more hybridized. Bonding with the alkaline earth and alkali metal ions, Ca\(^{2+}\) and Li\(^{+}\), respectively, could only be ionic since there were no d orbitals for bonding.

Even slight changes in concentration could have significant effects on percent uptake. For example, a 2.0 ppm
copper solution gives an uptake of approximately 40%, while a 4.0 ppm solution shows only a 30% uptake at the same pH. Thus, when comparing the percent uptake by the resin of different metal ions, one should be watchful in noting the different concentrations used.

Increasing the basicity of the solution almost invariably led to greatly increased uptake, sometimes as high as 100%. The reason for this behavior is that the mechanism by which uptake is occurring changes with the rise in hydroxide concentration. In slightly acidic solutions a metal ion approaches an oxamide group in which both hydrogens are essentially non-ionized. For complexation to occur, a reaction must take place in which the two hydrogens are displaced in favor of the metal ion. This is diagrammed schematically below.

As mentioned previously, formation of the ring is favorable in terms of energy considerations. Also, those metal ions which naturally tend to form stronger amine or amide complexes will tend to complex more strongly with the oxamide group, as expected. However, with increasing hydroxide concentration the hydrogens of the oxamide unit begin to
ionize. Wang and Bauman found that the ionization constants for m-2-2-2 was $pK_{a1} = 8.30$ and $pK_{a2} = 9.54$. Thus, at high pHs the oxamide unit becomes a dianion similar to those discussed in the section regarding the chemical behavior of the oxamide group.

The metal ions "see" a cation-exchange resin at high pHs. Where before at slightly acidic pHs the mechanism was one of complexation, it now becomes one of (stronger) ionic bonding. Therefore, alkalies are taken up in highly basic solutions, and almost all metal ions show better uptake. This unique ability of copolyoxamides to undergo conversion from a specific complexing resin to a general cation-exchange resin, has not been previously reported in the literature to the knowledge of the author. This property suggests the potential use of copolyoxamides in separating alkalies from transition metals simply by varying the acid strength of the solutions. This would be very advantageous in work done on saline solutions, where the high alkali and alkaline earth concentrations are usually a large interference in uptake studies.

One problem which was encountered in this second study
was that hydroxide formation of the metal ions in basic solutions interfered with the resin's uptake. Many metal ions, such as Zn$^{2+}$ and Pb$^{2+}$, formed hydroxide precipitates of low solubility in slightly basic solutions. Results were better for NH$_4$OH-adjusted solutions than for NaOH-adjusted ones. The ammonium ions aided the solvation of the metal hydroxides by becoming involved in the solvation shell. This was more evident in highly basic solutions where the concentration of NH$_4^+$ was higher. The standard values would increase from a minimum value at slightly basic pHs, a clear example of an amphoteric effect. Yet, though the prescence of ammonium ions was helpful, one cannot be sure in which form the metal ion was being taken up as, whether by itself, as a hydroxide, or as an ammonium ion-solvated species.

The abnormal behavior of lead and chromium at high hydroxide concentrations may be due to solubility problems. Both metals appear to be in solution at high pHs, which indicates that the ammonium ion complexes may be stronger than the oxamide ones.

The third study, involving the effect of highly acidic solutions on percent uptake, led to two main conclusions. First, there was no uptake at low pHs. Secondly, metal uptake on the resin could be easily reversed by addition of HCl, thereby demonstrating that the resin could be renewed. The solubility of the metal ions in highly acidic
solutions was greater than the strength of the bonds to the oxamide group. Looking at it from a different perspective, hydrogen ion would displace the metal ion as the concentration of the former increased. The relatively easy reversibility of uptake by the copolyoxamides is behavior characteristic of weak-acid cation-exchangers. The renewability of the resin is an important economic consideration.

Study #4 was made to determine if increased ionic strength effected the percent uptake of Cu$^{2+}$ and Ca$^{2+}$. The effects of added chloride ion were either neutral or negative, but the additional acetate led to significantly improved uptake. Again, solubility plays an important role. Chloride salts are less soluble than acetate salts, especially of transition metals. Also, the increased ionic strength has two other effects.$^{75}$ First, ion pair formation such as Cu$^{2+}(X^-)_2$ is promoted (where $X^-$ = acetate ion in this case). Since the anions must accompany the cations into the resin, absorption of the metals by the resin is increased because electroneutrality is more readily preserved in solutions of higher ionic strength. Secondly, the activities of the metal ions are decreased, an effect which is favorable to metal-amide complexation.

The fifth study showed that uptake was significantly increased by increasing the temperature at which the equilibrations were performed. This may be due to a greater and
more rapid mobility of metal ions to complexation sites, or to a greater porosity of the particles themselves, which would make more sites available. Also, the polymer chains would be more flexible and steric restrictions for complexation reduced.

Study #6 was designed to give an idea as to how effective the p-2-2-2-I resin would be in separating two metal ions simultaneously. The results indicate that the metal ion demonstrating the greatest uptake in individual uptake studies (in this case Cu²⁺), exhibited the greatest uptake on the resin. In other words, in competition for the complexing sites, the strongest ion was given preference. This investigation provided further evidence that column work with acidic elution should give good separations of mixtures of metal ions.

The seventh study involved two different resins, p-2-2-2-cis-1,4 and p-2-2-2-2,6N. Both exhibited poorer uptake than p-2-2-2-I. Changing the aromatic content of the polymer did not have a large effect on percent uptake. Rather, the results are explained by the fact that the 2,6-naphthyluenyl and cis-1,4-cyclohexyl acid residues are less hydrophilic than the isophthaloyl one and therefore less wetable. Hence, interaction of the aqueous phase with the polymer surface was reduced, and this resulted in a less favorable environment in which complexation could occur.

Study #8 showed that silanized sand exhibited signifi-
cant uptake even at slightly acidic pH. Apparently the macroscopic structure of the sand particles acted as either or both a filtration bed or as nucleation sites for hydrox-ide precipitates. Therefore, some of the uptake of the copolyoxamid es is partly due to this surface effect; it is not solely due to complexation as one may have assumed. With increasing hydroxide concentration, "uptake" is greater. Very soluble cations, such as calcium, are less effected by this since their hydroxides are still very soluble at high pHs. Silver is one transition metal which forms very soluble hydroxide complexes in the presence of ammonia (see p. 108). In highly basic solutions where most of the other transition metals precipitate out, silver remains in solution. Thus, copolyoxamides show potential for separating silver from a number of other transition metals at high pHs.

The ninth study indicated that the amount of amine and/or carboxylic end groups was low and played little part in uptake by the resin.

The tenth study brought to light another characteristic of copolyoxamides. Gelled films of p-2-2-2-1 had a much higher surface area than did 60/80 mesh particles, using a nitrogen gas absorption technique. This was the reverse of what was expected. Ordinarily a flat film would have a surface area of virtually zero. This anomaly is explained by the SEM pictures of the film surface's interior. As
pointed out previously, they showed many tubular structures whose interior surface area was much larger than the surface area of the outside of the films. If one assumes that the nitrogen gas permeates the interior of the films, then the relatively high value which is obtained for the surface area can be explained. Gelled films were chosen for this and the following study over dense films (which could be formed by simply evaporating the TFAA to dryness from cast films), because the former were more porous. Hence, metal uptake during one-plate batch equilibrations would have a better chance of occurring. Study #1 demonstrated that the gelled films did exhibit some uptake, but only of those metal ions which showed the greatest uptake on the particles. The films, though they possessed a higher overall surface area, did not take up metal ions as well as the particles. One must conclude that complexation occurs on the outer surface of the materials. Therefore, the 60/80 mesh particles, with their higher "outside" surface area (see Figures 7-9), exhibit the greatest uptake.

The twelfth study provided insight as to the effects of pH, time, and surface area on percent uptake. Time studies involving slightly basic solutions again displayed the problem of hydroxide precipitation. The standard values showed great fluctuation and no definite trend was observed. Further investigations were then carried out at slightly acidic pHs, where this problem was minimized. Again, it
was observed that percent uptake was highly dependent on concentration and on pH, especially. Smaller mesh size material exhibited greater uptake, as would be expected due to the greater surface area. Renewed p-2-2-2-I resin exhibited increased uptake over fresh resin, and unlike the latter, percent uptake would increase with time. Renewed resin seemed to mechanically degrade more rapidly than virgin material during the washing procedure. This led to increasing surface area as time progressed, and is the most likely explanation for the observed increases in uptake.

Wide angle X-ray studies showed that films of the copolyoxamides had little crystallinity, whether complexed or not. This result is puzzling since DSC studies on p-2-2-2-I particles showed no definite glass transition temperatures arising from the amorphous material one would expect to be present. Perhaps the highly polar nature of the copolyoxamides restricts the movement of the polymer chains, and any thermal transition is masked or spread over a large region, but further investigations are necessary.

Infrared measurements on complexed and non-complexed films and particles indicated that NH and C=O absorption frequencies were indeed effected by complexation with the metals. However, accurate work can only be performed on model compounds, because the polymeric nature of the resin interferes with and obscures the absorptions of the groups
of interest.

Organic Acid and Base Uptake Studies

The results for the uptake of these organics were quite interesting. Increasing the degree of aromatic character of the acids (e.g. phenol to β-napthol) and the bases (e.g. pyridine to aniline) resulted in increased organic uptake by the p-2-2-2-I. In the case of p-2-2-2-2,6N the uptake of phenol and aniline was greater than for the p-2-2-2-I resin, the latter polymer having a smaller degree of aromatic character. Both the p-2-2-2-cis-1,4 and p-2-2-2-trans-1,4 materials exhibited some uptake of phenol and aniline also. Uptake appears to be more influenced by the degree of aromatic content within the polymer chain than how polar or wetable the resin is. As with the case of PVP (p. 36), the binding mechanism is probably one of charge transfer between the amide bonds and the unsaturated molecule.

As expected, the organic acids were taken up better in their non-ionized form. However, the organic bases showed better uptake in their protonated form, and uptake appeared to level off quickly. This behavior is difficult to explain, but may be due to greater hydrogen bonding with the amide groups in the polymer backbone.
IDEAS FOR FURTHER STUDY

The unique ability of copolyoxamides to be converted from complexation resins to cation-exchange resins should be more fully investigated. The scope of metals examined should be widened and column studies carried out. The same applies for the case of organic uptake.

It is suggested that simple model compounds, such as N,N'-bis(2-benzamidethyl)oxamide be synthesized and metal complexes formed.

\[
\text{Infrared and magnetic susceptibility measurements could be made to accurately determine the type and bond strength of the individual complexes without the interference of the polymeric structure.}
\]

Perhaps the most fruitful area for further investigations would involve the synthesis of diamine-malonamides (and their analogs) and subsequent polymerization.

\[
\text{Metal complexes with these compounds would be more}
\]

\[
\text{Metal complexes with these compounds would be more}
\]
sterically favored due to the formation of a less-strained six-membered ring rather than a five-membered one. The resulting complexes may be stronger and thus the uptake by the polymer would be improved. Also, in the malonamide case, there is the added variable of ionization of a hydrogen from the methylene group situated between the two amide units. Another possible area of investigation is the replacement of the nitrogen or oxygen atoms in the oxamide group with sulphur. Use of dihydrazides would counteract the decrease in electronegativity exhibited by the sulphur atoms.

Applying an electrical potential on either side of a gelled film surface may be an effective way of forcing complexation to occur.

There is the possibility that the oxamide groups may exhibit tautomerism, especially in solutions of high pH.

With proper design one could introduce conjugated groups into the chain backbone which may give the resulting polymer the ability to change color at high pHs, conduct electricity, and even exhibit liquid crystalline behavior.
### APPENDIX A

#### ABBREVIATION NOMENCLATURE OF DIAMINE-OXAMIDES

<table>
<thead>
<tr>
<th>Full Name</th>
<th>Abbreviation Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N,N'$-bis(2-aminoethyl)oxamide</td>
<td>m-2-2-2</td>
</tr>
<tr>
<td>Bis(2-aminoethyliminooxalylimino)ethane</td>
<td>m-2-2-2-2-2</td>
</tr>
<tr>
<td>Bis(2-aminoethyliminooxalylimino)ethane·dihydrochloride salt</td>
<td>m-2-2-2-2·2HCl</td>
</tr>
<tr>
<td>$N,N'$-bis(2-aminoethyliminooxalyliminoethylene)oxamide·dihydrochloride salt</td>
<td>m-2-2-2-2-2·2HCl</td>
</tr>
</tbody>
</table>
### Abbreviation Nomenclature of Copolyoxamides

<table>
<thead>
<tr>
<th>Full Name</th>
<th>Abbreviation Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(iminoethyleneiminooxalyliminoethyleneimino carbonyl-1,1-cyclobutylene-carbonyl)</td>
<td>(p-2-2-2-1,1-cyclobut.)</td>
</tr>
<tr>
<td>Poly(iminoethyleneiminooxalyliminoethylenelaminecarbonyl-trans-1,4-cyclohexylene-carbonyl)</td>
<td>(p-2-2-2-trans-1,4)</td>
</tr>
<tr>
<td>Poly(iminoethyleneiminooxalyliminoethyleneimino carbonyl-cis-1,4-cyclohexylene-carbonyl)</td>
<td>(p-2-2-2-cis-1,4)</td>
</tr>
<tr>
<td>Poly(iminoethyleneiminooxalyliminoethyleneiminosebacyl)</td>
<td>(p-2-2-2-10)</td>
</tr>
<tr>
<td>Poly(iminoethyleneiminooxalyliminoethyleneiminoisophthaloyl)</td>
<td>(p-2-2-2-I)</td>
</tr>
<tr>
<td>Poly(iminoethyleneiminooxalyliminoethyleneimino terephthaloyl)</td>
<td>(p-2-2-2-T)</td>
</tr>
<tr>
<td>Poly(2,6-pyridinediylcarbonylliminoethyleneimino oxalyliminoethylenecarbonyl)</td>
<td>(p-2-2-2-P)</td>
</tr>
<tr>
<td>Poly(iminoethyleneiminooxalyliminoethyleneimino carbonyl-1,6-naphthylene-carbonyl)</td>
<td>(p-2-2-2-1,6N)</td>
</tr>
<tr>
<td>Poly(iminoethyleneiminooxalyliminoethyleneimino carbonyl-2,6-naphthylene-carbonyl)</td>
<td>(p-2-2-2-2,6N)</td>
</tr>
</tbody>
</table>
APPENDIX C

TABLE OF SPECTRA

1. Infrared Spectra

a. Diamine-Diamides

(1) ethylene diamine, diethyl oxalate (DEO),
N,N'-bis(2-aminoethyl)oxamide (m-2-2-2),
bis(2-ethoxyoxalylimino)ethane.

(2) bis(2-aminoethyliminooxalylimino)ethane or (m-2-2-2-2-2),
bis(2-aminoethyliminooxalylimino)ethane •dihydrochloride salt or (m-2-2-2-2-2 •2HCl),
N,N'-bis(2-ethoxyoxalyliminoethylene)-oxamide,
N,N'-bis(2-aminoethyliminooxalylimino-ethylene)oxamide•dihydrochloride salt or (m-2-2-2-2-2-2 •2HCl).

b. Diacid Chlorides

(3) 1,8-dichloroanthraquinone,
1,8-dicyanoanthraquinone,
1,8-anthraquinonedicarboxylic acid,
1,8-anthraquinonedicarboxylic acid chloride.

(4) 1,8-anthracenedicarboxylic acid,
1,8-anthracenedicarboxylic acid chloride,
1,5-dichloroanthraquinone,
1,5-dicyanoanthraquinone.

(5) 1,5-anthraquinonedicarboxylic acid,
1,5-anthraquinonedicarboxylic acid chloride,
1,5-anthracenedicarboxylic acid,
1,5-anthracenedicarboxylic acid chloride.

c. Copolyoxamides

(6) p-2-2-2-1,1-cyclobut.
p-2-2-2-trans-1,4
p-2-2-2-cis-1,4
(8) p-2-2-2-T, p-2-2-2-P, p-2-2-2-1,6N, p-2-2-2-2,6N.

2. PMR Spectra

a. Diamine-Diamides

(9) ethylene diamine, diethyl oxalate (DEO), N,N'-bis(2-aminoethyl)oxamide or (m-2-2-2), bis(2-ethoxyoxalylimino)ethane.

(10) bis(2-aminoethylimino)oxalylimino)ethane or (m-2-2-2-2), N,N'-bis(2-ethoxyoxalyliminoethylene)oxamide, N,N'-bis(2-aminoethylimino)oxalyliminoethylene)oxamide or (m-2-2-2-2-2-2).

b. Copolyoxamides


(13) p-2-2-2-P, p-2-2-2-1,6N, p-2-2-2-2,6N.
1. O. Vogl and A. C. Knight, Macromolecules, 1, 311 (1968).


38. V. V. Korshak, T. M. Frunze, V. V. Kurashev, and K. L. Serova, Vysokomolekul. Soedin., 2, 205 (1961).
70. G. Smuckler, Talenta, 12, 281 (1965).

74. K. Gloss and E. A. Milano, Senior Research Project, University of Massachusetts, Amherst, Massachusetts, unpublished data.


