

**The Syntheses and Characterizations of Organometallic
Polymers from Chromium and Molybdenum Complexes**

by

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Polymers from Chromium and Molybdenum Complexes**

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Abstract

Derivatives of benzene chromium tricarbonyl, (η^6 -arene)chromiumtricarbonyl, and a molybdenum complex, trans-bis(1,2-bis(diphenylphosphinoethane)bis(p-isocyanoaniline) molybdenum (0), were polymerized to form rigid organometallic polymer systems are reported. The resulting polymers were characterized systematically. The organochromium monomers were prepared by reacting the arene with chromium hexacarbonyl in refluxing dibutyl ether/tetrahydrofuran under inert conditions. There were several steps in the synthesis of the organomolybdenum monomer. p-Phenylenediamine was converted to p-isocyanoaniline in the presence of potassium hydroxide. Trans-bis(1,2-bis(diphenylphosphinoethane)bis(dinitrogen) molybdenum (0) was prepared by reducing molybdenum (V) chloride with a sodium/mercury amalgam in the presence of dinitrogen gas and bis(diphenylphosphinoethane) in tetrahydrofuran. Trans-bis(1,2-bis(diphenylphosphinoethane)bis(dinitrogen) molybdenum (0) and p-isocyanoaniline were reacted in tetrahydrofuran to prepare the organomolybdenum monomer, trans-bis(1,2-bis(diphenylphosphinoethane)bis(p-isocyanoaniline) molybdenum (0). The syntheses and characterizations of model compounds and related organic polymers were attempted. Analogous model compounds and organic polymers were synthesized from isocyanates and acid chlorides in either dimethylacetamide or tetrahydrofuran. A series of organic polymers was synthesized via low temperature solution polycondensation from reacting diisocyanates and acid chlorides with the organometallic monomers in solution. An attempt to set up a gel permeation chromatography lab to determine the molecular weight of the polymers was unsuccessful.

It is believed that the compounds formed from m-phenylenediamine, except for the monomer, have not been previously reported. The molybdenum polymers have not been reported. The organometallic polymers reduce the amount of hydrogen bonding of the polymers and increases the solubility of the polymers.

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List of Abbreviations

δ - chemical shift

η - eta

Σ - sum

Bu₂O - dibutylether

bz - benzene

CH₂Cl₂ - dichloromethane

cm⁻¹ - reciprocal centimeters, wave numbers

CNR - isocyanide ligand

"CN" - coordination number

CO - carbonyl ligand

dppe - 1,2-bis(diphenylphosphino)ethane

EAN - effective atomic number

EtOH - ethanol

DMAc - dimethylacetamide

FT - fourier transform

g - grams

GC/MS - gas chromatography/ mass spectrometry

GFC - gel filtration chromatography

GPC - gel permeation chromatography

i - series of all of the molecular weights that are present

IR - infrared (as in spectroscopy)

IUPAC - International Union of Pure and Applied Chemistry

KOH - potassium hydroxide

m - *meta*

\bar{M}_i - specific molecular weight

\bar{M}_n - number average molecular weight

\bar{M}_v - viscosity average molecular weight

\bar{M}_w - weight average molecular weight

mL - milliliters

mmol - millimoles

N_i - number of molecules at a given molecular weight

NMR - nuclear magnetic resonance (as in spectroscopy)

p - *para*

P^+ - parent ion peak in mass spectrometry

R - alkyl group

SEC - size exclusion chromatography

S_N2 - bimolecular nucleophilic substitution

UV-VIS - Ultraviolet-visible (as in spectroscopy)

THF - tetrahydrofuran

Part One

An Introduction to Elementary Organometallic Chemistry, Polyamides, and Gel Permeation Chromatography

Chapter One

An Introduction to Elementary Organometallic Chemistry

1. Ligands and bonding theories.

Organometallic chemistry combines features of inorganic and organic chemistry. Research in this area began to flourish about forty years ago. Much of the interest in organometallic compounds has been due to their efficiency as catalysts for organic or polymer syntheses.¹ It is also believed that there may be advantages in the properties of polymers with inorganic fragments in their repeating unit. In particular, inorganic elements are expected to induce properties in polymers that can not easily be induced using conventional organic fragments. Polyphosphazenes, polysiloxanes, and polysilanes are among the inorganic polymers that have been produced commercially because of their novel properties.² Understanding polymers that contain organometallic fragments requires an understanding of organometallic chemistry.

Organometallic chemistry has been studied over the last few decades because of the seemingly infinite number of derivatives obtained by varying the ligands and metals of organometallic compounds. A transition metal organometallic compound is composed

of one or more metal centers surrounded by a set of ligands. The ligands may be thought of as Lewis bases that donate electrons to the central metal atom which acts as a Lewis acid site. The relative stability of each complex is related to the valence electron count of the metal. The 18-electron rule predicts that a complex will be stable if it has 18 valence electrons associated with each metal center in the non-bonding orbitals of the metal and in the metal-ligand bonds. When the rule is obeyed, such complexes often display increased stabilities. There are some exceptions to the rule, but metals in the middle of the transition series in low formal oxidation states, such as the complexes that will be discussed in this thesis containing chromium and molybdenum, generally obey the rule.^{1,3}

The complexes may vary in the manner in which electron pairs interact with the metal. For π -complexes, one or more π bonds on the ligand may donate electrons to a single metal atom. The hapticity (*i.e.* its η^n number) of the ligand is the number of atoms that are within bonding distance of the metal atom. Arenes are typically η^6 (*i.e.* six carbons within bonding distance of the metal) and in this structure donate six electrons to a metal. The total number and nature of ligands that are coordinated to a metal determines the coordination number, "CN", of the metal. The number of coordination positions that a ligand occupies generally refers to the number of electron pairs donated to the metal. Different ligands may vary in formal charge, the number of electrons that may donate to the metal atom, and the number of coordination positions around the metal as shown in Table 1.1.1.³

Table 1.1.1. Oxidation state formalism for common ligands.

| <u>Ligand</u> | <u>Formal Charge</u> | <u>Number of Electrons Donated</u> | <u>Number of Coordination Positions around Metal</u> |
|------------------|----------------------|------------------------------------|--|
| acyl | -1 | 2 | 1 |
| η^2 -alkene | 0 | 2 | 1 |
| alkyl | -1 | 2 | 1 |
| η^2 -alkyne | 0 | 2 | 1 |
| η^2 -arene | -1 | 2 | 1 |
| η^6 -arene | 0 | 6 | 3 |
| carbene | -2 | 4 | 1 |
| carbonyl | 0 | 2 | 1 |
| carbyne | -3 | 6 | 1 |
| dinitrogen | 0 | 2 | 1 |
| ethylenediamine | 0 | 4 | 2 |
| halide | -1 | 2 | 1 |
| hydride | -1 | 2 | 1 |
| isocyanide | 0 | 2 | 1 |
| nitrosyl | +1 | 2 | 1 |
| phosphite | 0 | 2 | 1 |
| phosphine | 0 | 2 | 1 |
| pyridine | 0 | 2 | 1 |

Details for the bonding of the classes of organometallic compounds synthesized in this thesis have been reported previously. The carbonyl ligand is a common ligand in transition metal organometallic compounds. Its bonding is typical of π -acid ligands (*i.e.* N_2 , NO, CNR). For octahedral compounds, a sigma bond is formed from overlap of one lobe of an unfilled metal hybrid orbital (*i.e.* d^2sp^3) of σ -symmetry with a filled sp hybrid orbital on carbon. There is also π -back-bonding from a pair of filled π symmetry d orbital on the metal (*i.e.* d_{xy} , d_{xz} , d_{yz}) and a pair of empty π^* anti-bonding orbital on the carbonyl. These two components are synergic. Thus, the overall metal-carbonyl bond is stronger than a linear sum of the two components. The π symmetry interaction is referred to as π back-bonding and results in electron transfer from the metal to the carbonyl.

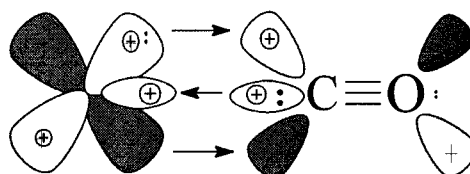


Figure 1.1.1. A "Dewar-Chatt-Ducanson" representation of the bonding of a carbonyl ligand to a transition metal.⁴

An alternate explanation of the bonding of metal carbonyls is provided by Valence Bond Theory. Valence Bond Theory represents the bonding from several resonance forms.

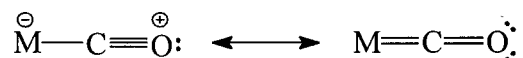


Figure 1.1.2. Valence Bond Theory representation of the bonding of the carbonyl ligand.

Spectroscopy and x-ray diffraction may be used to study the metal-carbonyl interaction. Infrared spectroscopy may be used to measure the amount of back-bonding

of the metal to the ligand. The IR stretching frequencies of carbonyls decrease from 2100 cm^{-1} to below 1700 cm^{-1} as the metal becomes more electron rich and consequently, as the amount of back-bonding increases. As the amount of backbonding increases, the CO bond order decreases and the carbon-metal bond order increases. Various studies have shown carbonyl ligands are poor σ -donors and strong π acceptors. Nuclear magnetic resonance spectroscopy may also be used to examine the electron richness of the complex. As the amount of back-bonding increases, the chemical shift of the carbonyl carbon correlates with the electron richness of the complex (*i.e.* shifting either downfield or upfield for a series of related complexes). X-ray diffraction may be used to examine metal-ligand interactions. The bond order of the carbon-metal bond increases and the bond length decreases with a higher degree of back-bonding. Simultaneously, the carbon-oxygen bond order decreases and its bond length increases with more backbonding.⁵

The bonding of the isocyanide ligands is isoelectronic to bonding of the carbonyl ligands. The isocyanides are less electronegative and are therefore better electron donors than carbonyls. In terms of the Dewar-Chatt-Duncanson model, there is σ -donation from the lone pair of electrons of the carbon (*i.e.* sp) to an empty σ -symmetry (*i.e.* d^2sp^3) orbital of the metal. There is also π -back donation from a pair of filled d orbitals of π symmetry on the metal to a pair of empty π^* orbitals on the carbon and nitrogen atoms of the aryl isocyanide.^{4,5}

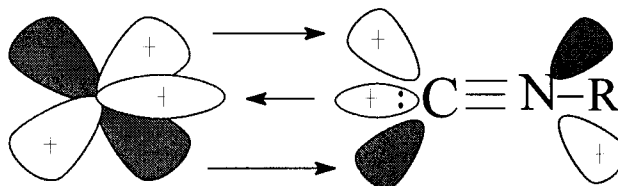


Figure 1.1.3. A Dewar-Chatt-Duncanson model representation of the bonding of an isocyanide ligand to a transition metal.

Valence bond theory represents another explanation of the bonding that occurs during the coordination of an isocyanide to a transition metal. In Valence Bond Theory, the coordination is explained via resonance.⁶

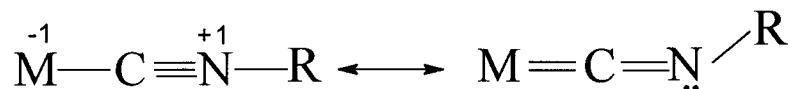


Figure 1.1.4. Valence Bond Theory model for the isocyanide ligand.

Both of the models produce the same conclusions through different depictions. The electron richness of the metal center affects the bond orders for the metal-carbon and carbon to nitrogen bonds. If the electron richness of the metal is increased, there is more backbonding and the second resonance form is favored. The metal-carbon bond order increases and the carbon-nitrogen bond order decreases. The electron richness may be measured through infrared spectroscopy. The CN stretching frequency for the complex is 250-350 wavenumbers lower than the stretching frequency for the free isocyanide.^{4,5,7}

Olefins are also common ligands. The bonding of olefins involves a forward donation of π -electron density from the occupied pi bonding orbitals of the alkene to the valence orbitals of the metal atom (*i.e.* d^2sp^3 orbitals). Back donation occurs from filled d orbitals on the metal into an empty π^* molecular orbital on the ligand.

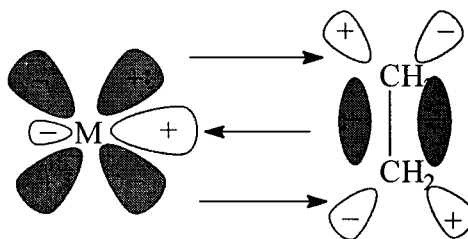


Figure 1.1.5. A Dewar-Chatt-Ducanson model representation for the bonding of an alkene ligand to a transition metal.

The electron richness of the metal may be measured through spectroscopy and x-ray diffraction. Back donation has the largest effect in the bonding of the olefin to the metal atom. Increasing the electron richness on the metal produces increased back bonding and therefore, the bond order of the carbon-carbon double bond decreases. X-ray diffraction has shown that the increased electron richness on the metal and the subsequent backbonding decreases the metal to ligand bond distance, increase in the carbon-carbon bond length, and decreases the H-C-H bond angles from 120 to 109°. π -bonded hydrocarbons such as olefins and eta-six arenes generally increase the net electron density on the metal while π acid ligands such as carbonyls and isocyanates decrease the net electron density on the metal.

The 1,2-bis-diphenylphosphinoethane, dppe, ligand is a bidentate ligand. Each phosphorous atom has a lone pair of electrons from a sp^3 hybrid orbital that is donated to an empty d^2sp^3 orbital on the octahedral metal centers. For phosphine ligands such as this, back bonding plays little or no role.²

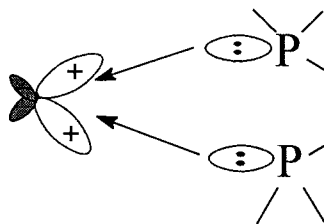


Figure 1.1.6. A Dewar-Chatt-Ducanson model representation for the bidentate dppe ligand to a transition metal.

The dinitrogen ligand is a monodentate ligand because only one pair of electrons from the dinitrogen molecule coordinates to the metal. However, its bonding is much like that of CO or ArCN.^{2,3}

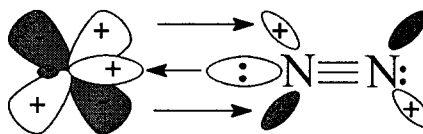
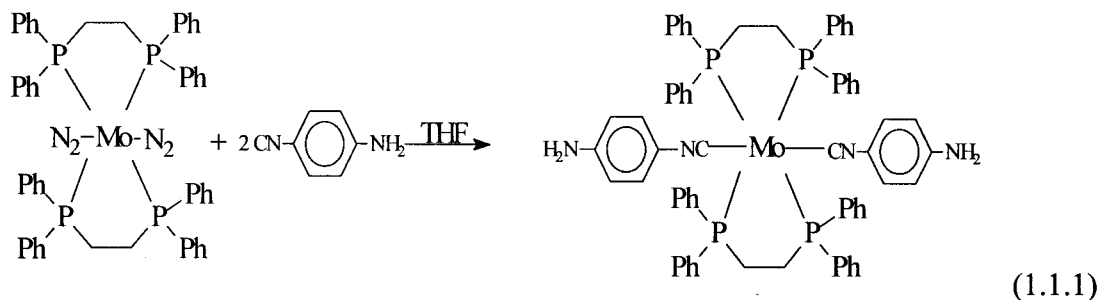


Figure 1.1.7. A Dewar-Chatt-Ducanson model representation for the bonding of a dinitrogen ligand to transition metal.

Free dinitrogen is IR inactive due to its lack of a dipole moment, but it is Raman active. Nitrogen complexed to a metal results in a strong polarization of the molecule. There is sigma donation from a filled sp^3 hybrid orbital of one of the nitrogens to an unfilled metal hybrid orbital (*i.e.* d^2sp^3) similar to the bonding of the carbonyl ligand. There is also π -back-bonding from a pair of filled π symmetry d orbitals on the metal (*i.e.* d_{xy} , d_{xz} , d_{yz}) to a pair of empty π^* anti-bonding orbitals on the nitrogens. The polarization leads to the observation of a N-N stretch between $1920\text{-}2150\text{ cm}^{-1}$ and to chemical activation of the dinitrogen ligand. However, the net σ or π interactions are weaker than for most other ligands, such as carbonyls and isocyanides, so that dinitrogen ligands often may be readily displaced from the complex.



The types of metal-ligand interactions that have been described and other metal-ligand interactions observed in organometallic chemistry may be incorporated into polymer science to produce new classes of polymers and derivatives of existing polymers. The bonds formed between inorganics are longer, stronger, and more resistant to free radical cleavage than for organics. Many inorganic elements have a higher

coordination number than carbon and intrinsically longer bonds. This allows inorganic elements to have more sidegroups. The differences in bonding and valencies between carbon and inorganics produce different bond angles, internuclear distances, and backbone rigidities. Polyphosphazenes and polysiloxanes are among the inorganic polymers that have been produced commercially.²

2. Inorganic Polymers

Polyphosphazenes are the largest class of inorganic polymers. The backbone of polyphosphazenes contain alternating nitrogen and phosphorous atoms with two side groups on each phosphorous. The groups attached to the phosphorous may be organic or inorganic.

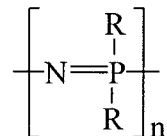


Figure 1.1.8. Repeating unit of a polyphosphazene.

Useful molecular weights range from two to ten million. Although the backbone is represented as alternating double and single bonds, structural measurements indicate that the bonds are all nearly the same length. The importance of the polyphosphazenes stems from the wide variety of side groups that may be utilized. By changing the side groups, a wide range of properties were developed. The properties lend to utilization as elastomers, hydrophilic, hydrophobic, bioinert or bioactive polymers, and to applications as insulators, conductors, flame resistance, membranes, and controlled drug delivery systems.

Polysiloxanes have many commercial applications in which they exhibit a wide range of properties. There is a silicon-oxygen bond in the backbone of the polysiloxanes with two side groups bonded to each silicon atom. The side groups bonded to the silicon atom may also be either organic or inorganic.

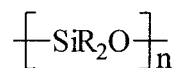


Figure 1.1.9. Repeating unit of a polysiloxane.

The strength of the bonds in the polysiloxane backbone makes this class of polymers useful for applications requiring high thermal stabilities (*i.e.* heat-transfer agents, biomedical materials, waterproofing agents, coatings, contact lenses, and separation membranes).

The discovery of inorganic and organometallic polymers has created new classes of polymers and has extended functionalization of existing classes of polymers. The utilization of many different ligands as sidegroups of an inorganic polymer or in the backbone, itself, dramatically changes the properties within the class of polymers synthesized. To understand the new organometallic polymers that are presented in this paper, related organic analogues will be studied in parallel to the organometallic polymers. Polyamides and polyureas are the classes of polymers that correlate closest to the organometallic polymers. A discussion of polyamides and polyureas is presented in Chapter Two.

Chapter Two

An Introduction to Polyamides and Polyureas

1. A general introduction to polyamides.

There are two commercial aryl amide (*i.e.* Aramid) polymers of significant importance in the United States. They are synthesized from reactions producing amide linkages between aromatic rings. Researchers at Du Pont discovered the first viable method of producing a polymer chain with enhanced properties.⁶ The outstanding physical properties of the aromatic polyamides led to the commercialization of the polymers. At the request of the Du Pont Company in 1971, the United States Federal Trade Commission termed Aramids the generic name to the class of aromatic polyamide fibers. Aramids were defined by the Federal Trade Commission as a "manufactured fiber in which the fiber-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide (-CO-NH-) linkages are attached directly to two aromatic rings."⁹

Aramids may be named by the IUPAC nomenclature system or by trade names. Acronyms or the initial letters of the monomers are often combined with the initials of the diamines preceding the other bifunctional moieties. Alternately, they are named by using the names of the monomers. An example repeating unit is shown in Figure 1.2.1.

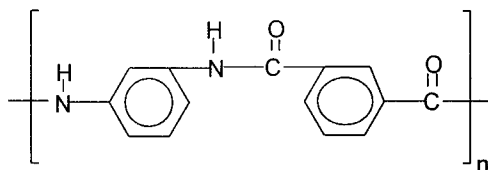


Figure 1.2.1. The repeating unit of poly(m-phenylenediamine isophthalamide).

The repeating unit of this polymer would be named either (MPD-I) or poly(m-phenylene isophthalamide). Trade names are also commonly used to refer to such polymers. The polymer that is shown on the previous page was named Nomex[®] by the Du Pont Company for its aramid fiber prepared from m-phenylenediamine and isophthalic acid while Teijin, a Japanese company, refers to it as Conex[®].⁹ Similarly, The Du Pont polyarylamide Kevlar[®] involves *para* amide linkages for the repeating unit and is named (PPD-T) or poly(p-phenylene terephthalamide).⁸

2. Liquid crystalline solutions.

Some aromatic polyarylamides have liquid crystalline structures in solution. Liquid crystallinity occurs when the polymer chains become aligned in a highly ordered array while retaining fluid-like intermolecular motions. Liquid crystals are neither true solids nor liquids because they are ordered while retaining rapid translational motion. Lyotropic crystals form under the influence of a solvent. For Kevlar[®] and Nomex[®], liquid crystalline behavior may be attributed to the hydrogen bonding between the hydrogen of the amide nitrogens and the lone pair of electrons on the oxygen of the carbonyl.^{8,9}

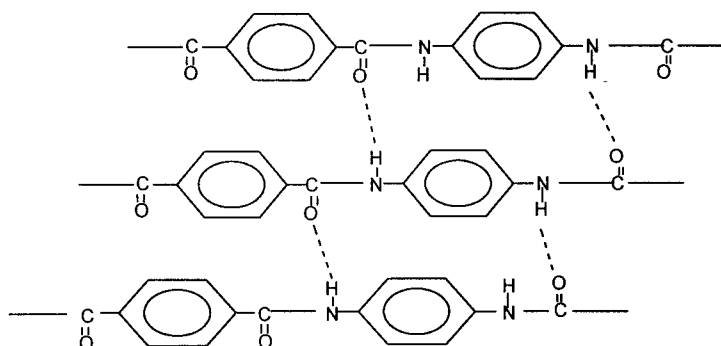


Figure 1.2.2. Hydrogen bonding of the backbone of a polyamide.

These liquid crystalline polymers exhibit rod-like microstructures which possess a nearly perfect polymer chain extension and exhibit a higher tenacity, initial modulus, and degree of crystallinity than related amorphous polymers. The polyamides were the first man-made rod-like polymer. There is a distinct advantage to rod-like polymers compared to flexible polymers. Due to their ordered orientation, rod-like polymers have superior physical properties compared to flexible polymers with the exception of their solubilities, viscosities, and flexibilities. The chains of the rod-like fibers tend to self-orient to produce enhanced properties while the flexible polymers do not tend to naturally align.⁸

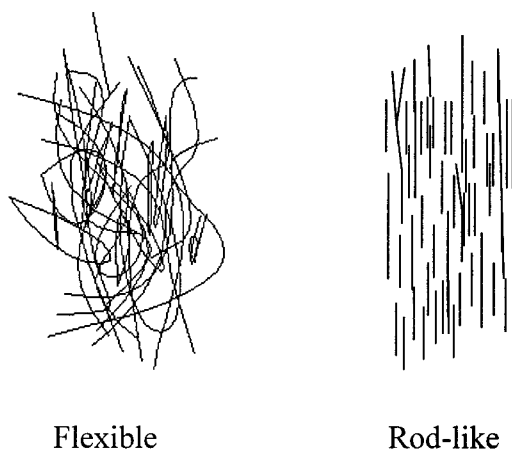
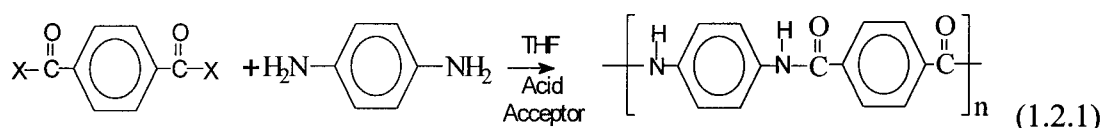


Figure 1.2.3. A comparison of flexible and rigid rod polymers.

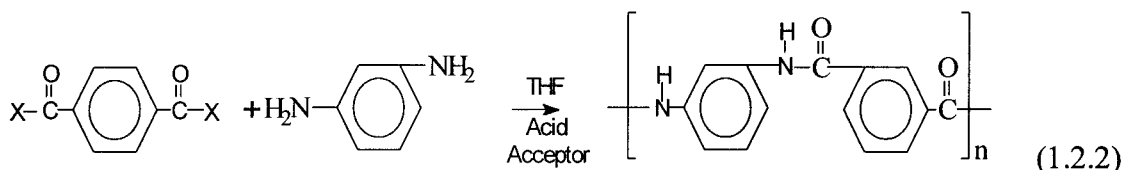
The degree of liquid crystallinity and rigid rod character differ for *para*- and *meta*-substituted polymers. The *para*-substituted polymer will form liquid crystals better because the polymer is more linear and rod-like. The *meta*-substituted polymer will also be rigid due to the phenyl groups, but it will not be able to pack as efficiently as the *para* polymer and it will therefore be more flexible.

3. Synthesis of polyamides.

There are two commercial Aramides polymers of significant commercial importance in the United States. They are Kevlar[®] and Nomex[®]. Both are registered by Du Pont. The two aramides differ only by the position of the amines of the diamine. The aromatic polyamides are formed by reacting an aromatic dicarboxylic acid or a derivative of an aromatic dicarboxylic acid (*i.e.* where X= OH, Cl) with a diamine. 8,12



The reaction, which is shown directly above is for the synthesis of poly(*p*-phenylene terephthalamide) and it is commercially known by the Du Pont trade name of Kevlar[®]. The amino groups of the diamine monomer as well as the functional groups on the terephthalate are in the *para* position.



The synthesis of the previously discussed Nomex[®] was shown in the above reaction. The two polymers may be synthesized under the same reaction conditions and have the same empirical formulas, but they have different structures and slightly different properties. Polyamides may be synthesized from interfacial or solution condensation reactions.

The interfacial polymerization of aramids is conducted in a binary phase system. The diacid, or its derivative is dissolved in an inert, water immiscible organic solvent, (*i.e.* toluene or dichloromethane), and the diamine is dissolved with the acid acceptor in an aqueous solvent. The solvents are combined to produce a two-phase system in which

the bifunctional monomers react to form a polymer film at the interface of the binary system. The phases are stirred to increase the amount of monomers at the interface, the yield, and the molecular weights. The polymer is separated, washed, dried and then dissolved in a suitable solvent for fabrication.^{10,11}

The low-temperature solution polycondensation method involves reacting diacid chlorides or dicarboxylic acids, with diamines. It is the most important process to synthesize aramid fibers. The solution method is important because often a solvent may be used in the reaction that is suitable for direct fabrication of fibers. The solvent must dissolve at least one of the monomers and either be capable of dissolving the polymer or act as a swelling agent. There is not a known organic solvent with the solvating power to keep these polymers in solution as the molecular weight increases. Once the polymer has formed and the reaction has gone to completion the polymer is processed by methods similar to those used for the interfacial method.¹¹

4. Reaction conditions for the polymerization.

There are many variables that may affect the polycondensation methods. Every system does not maximize every variable. There is a trade-off to customize the reaction as desired. The purity of the reactants and solvents must be higher for the interfacial method. In a single phase system, all of the reagents are in the polymerization area. Nonreactive impurities may depress the solubility of the polymer or disrupt the stoichiometric balance with respect to the intermediate and lower the reaction rate. Unsubstituted diamines have high reaction rates and the reaction may be completed in a manner of minutes. However, slower rates usually lead to higher molecular weights and substitution reduces the rates. The reactions are carried out at room temperature or slightly below. An increase in temperature causes the viscosity and yield to significantly decrease. This occurs even though the reaction rate increases with higher temperatures

because there is a relatively greater increase in interfering side reactions. Solution polycondensation is more tolerant to unbalanced stoichiometry than the interfacial method because the interfacial method generally has faster reacting intermediates. The choice of a solvent is also a factor because the solvent dissolves the intermediates and provides mixing and contact. It also dissolves or causes the resulting polymer to swell which aids in maintaining the reaction process. The solvent also carries the acid acceptor. It affects the formation of byproducts and the reaction by its inherent polarity or solvent effects. Also, the solvent may absorb heat from the reaction as the reactions are generally exothermic.^{9,11}

5. Mechanism of the Polymerization.

The aramids are generally synthesized through a low temperature polycondensation processes (*i.e.* under 100 °C). Interfacial and solution polycondensation methods provide a method to synthesize a large variety of high molecular weight aromatic polyamides. Interfacial and solution polymerization react following the same mechanism but under different reaction conditions. The preparations are an adaptation of the Schotten-Bauman Reaction:¹⁰

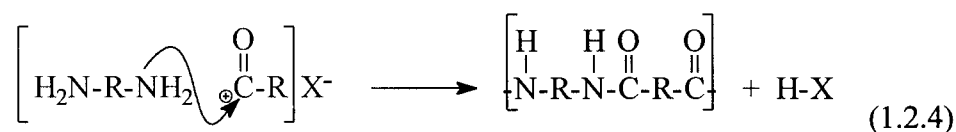
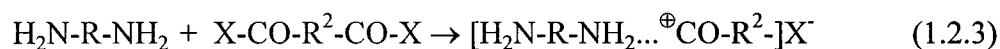
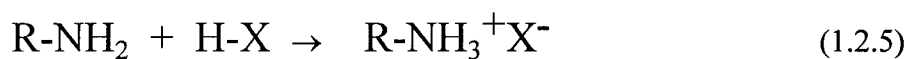


Figure 1.2.4. Mechanism from the Schotten-Bauman Reaction

The reaction is irreversible and proceeds through a second order rate expression. The reaction for diacid halides and dicarboxylic acids follows a bimolecular nucleophilic acyl substitution mechanism (S_N2). In the first stage, an intermediate forms and the formation of the intermediate is more rapid than its decomposition which forms the product and HX. When X represents a halogen, usually Cl, the byproduct HX may react with amino groups to produce unreactive salts of the amines under the synthesis conditions.¹¹



An acid acceptor is necessary to remove the hydrogen halide that evolves so the hydrogen halide does not react with one of the diamine sites and block the formation of high molecular weight chains. Substituted amines are most commonly used to neutralize the resulting acid because they are inexpensive and do not interfere in the polymerization.^{9,11}



6. Processing polyamide fibers.

The aramid fibers are usually spun from liquid crystalline solutions of the polymers. Nomex[®] and Kevlar[®] are insoluble in common organic solvents so they are spun from concentrated sulfuric acid at ambient temperatures into water. After being spun, the average molecular weight should be sixty thousand or higher for the polymers to be useful in conventional applications. After spinning, the fibers are dried and usually hot-drawn. Rod-like polymers, such as poly(m-phenylene terephthalamide) and poly(p-phenylene terephthalamide), produce anisotropic solutions. The anisotropic solutions

result from lyotropic liquid crystals that result from preferential orientation of the polymer chains. The orientation of the liquid crystals eliminates the requirement for hot drawing. However, hot drawing may be used where it results in an increase in the initial modulus and a decrease in the property of elongation to breaking of the fiber. In summary, to process Kevlar[®], the fibers are dissolved in concentrated sulfuric acid, passed through a spinneret, and passed through water to dilute the acid. The randomly oriented chains become fully oriented in the direction of the shear. This process is a cost effective method to highly orient and achieve very strong fibers with little energy input.^{7,9,11,13}

7. Properties of polyamides.

The liquid crystalline behavior of the aramids produces a wide range of enhanced properties compared to flexible polymers such as nylon that also has amide linkages. Polyarylamides have thermal stabilities, high tensile strengths, excellent flame resistance, good electrical properties, and excellent chemical resistance. Generally, the *meta*- and *para*-substituted isomers have similar properties, but the properties of the *para*-substituted polymers are typically slightly better than those of the *meta* substituted materials because of their higher degree of ordering.

Aramid fibers tend not to give measurable melting points. Instead, they decompose at elevated temperatures. It has been reported from thermogravimetric analysis, (TGA), that weight loss for flexible alkylamide polymers, such as nylon, begins to occur around four hundred and twenty-five degrees Celcius, while the rod-like arylamide polymers starting to lose weight at nearly five hundred and fifty degrees Celcius. The rod-like polymers have enhanced thermal characteristics because of their higher degrees of orientation and crystallinity. The aramid fibers also tend to have good tensile strength, low elongation, high modulus, and a relatively high density (1.45 g /mL for Kevlar[®]). Plastics containing the *meta*-substituted polymers utilize these properties

for applications as heat and flame-resistant fibers. Plastics containing the *para*-substituted polymers are generally used for polymers with high strength fibers. The heat resistance allows the fibers to be used in filter bags for hot stack gases, press cloths for industrial presses, home ironing board covers, sewing thread for high-speed sewing, insulation paper for electrical motors and transformers, braided tubing for the insulation of wires, and paper-makers dryer belts.^{7,8,9}

The aramid fibers have tensile strengths at two hundred and fifty degrees Celcius that conventional fibers have at ambient temperatures (*i.e.* Nylon 6,6 loses almost all of its strength by two hundred and five degrees Celcius). The tensile modulus of an aramid fiber will begin to significantly decrease between three hundred and three hundred and fifty degrees Celcius. The aramids retain their tensile properties at three hundred degrees Celcius for one to two weeks. The fibers retain their properties better at lower temperatures in air. Paper made from Nomex[®] has a lifetime of forty hours at three hundred degrees Celcius, fourteen hundred hours at two hundred degrees Celcius, and may retain eighty percent of its strength for several thousand hours in air at one hundred and seventy-seven degrees Celcius. Heat aging also results in the decrease of elongation which is nearly proportional to the decrease in tensile properties. The utility of the fiber usually depends more on elongation than tenacity. Along with wiring applications, the properties lends to reinforcement of fire hoses and V-belts.^{7,9,12}

Aramid fibers tend not to burn easily. As a result, they are suitable fibers for use in flame resistant materials. When the aramids burn, the fibers produce a thick char which forms a thermal insulating barrier which may protect skin from serious burns. Some aramids, such as Nomex[®], shrink away from the flame or the heat source. Additives may be applied to promote surface crosslinking to further stabilize the fibers. An example would be a polymer from Du Pont, in which, poly(*p*-phenylene terephthalamide) is spun from sulfuric acid with THPC, tetrakis(hydroxymethyl)phosphonium chloride. Then the THPC is further crosslinked with melamine,

1,3,5-triamino-2,4,6-azabenzene. Nomex[®] may also be modified by such a process. The flame resistance allows the fibers to be used for industrial protective clothing, welder's clothing, fire department turnout coats, jump suits for forest fighters, flight suits for Armed Services pilots, mailbags, carpets, upholstery, drapes, cargo covers, boat covers, and tents.^{7,9,12,14}

The fibers have high volume resistivities, high dielectric strengths, and are capable of maintaining their electrical properties at elevated temperatures. They exhibit breakdown voltages of 3000 V/ mil up to one hundred and eighty degrees Celsius compared to Teflon's 2250 V/ mil at one hundred and fifty degrees Celsius, and Nylon-6,6's 120 V/ mil also at one hundred and fifty degrees Celsius. For example, paper made of Nomex[®] has nearly twice the dielectric strength of high quality rag paper and the Nomex will retain useful electrical properties at higher operating conditions than one hundred and five degrees Celsius, which is the upper operating limit for the high quality rag paper.^{7,9,12}

Aramid fibers have good resistance to chemicals, ultraviolet light, and ionizing radiation. The fibers are typically more resistant to acid than nylons but not as resistant as polyester fibers. Their resistance to strong bases is also superior to nylon. The aramids probably have such a high chemical resistance due to the orientation of the backbone chains and because adjacent polymer chains are tightly bound by hydrogen bonding. Unfortunately, the fibers are difficult to dye due to their high glass transition temperatures. The fibers may be dyed by using a dye carrier at elevated temperatures in pressurized beam machines and in jet-dyeing machines. Aramids, as well as nylons, are susceptible to degradation by ultraviolet light. The phenyl groups do not provide for any enhanced resistance to the ultraviolet light. Photoquenchers or screening agents may be added (at concentrations less than one percent of the polymer) to reduce this photodegradation. Aramids have a very large advantage over nylons in terms of resistance to ionizing radiation. For the same exposure, Nylon-6,6 was reduced to no

strength while Nomex[®] retained seventy-six percent of its strength. Similar results were obtained upon exposure of the fibers to gamma radiation and x-rays.^{7,9,12}

Rod-like polymers have a high strength and a high modulus with high intrinsic and inherent viscosities even when molecular weights are moderate. This is due to the rod-like polymers having a high effective volume in solution. The high strength and high modulus of the aramids make the aramids stronger and stiffer than glass and steel on a weight per weight basis of comparison. The enhanced properties lead to the use of aramids to reinforce rigid and flexible composites. Kevlar[®] reinforces rubber as tire cord and may be used as an alternative to lower modulus types of graphite. Fibers are also used for cables, body armor, rigid reinforced plastics specifically aircraft, antenna components, circuit boards, filament wound vessels, fan blades, and in sporting goods.^{7,8,9,11,12}

8. Characterization of polyamides.

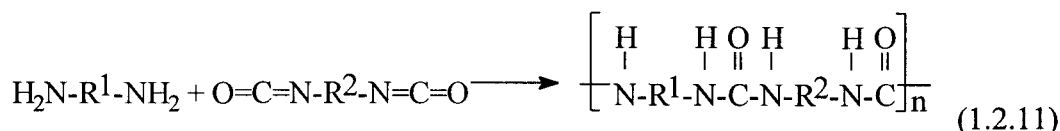
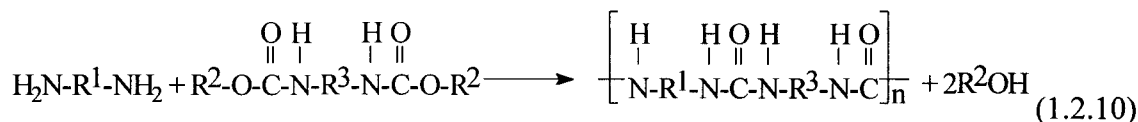
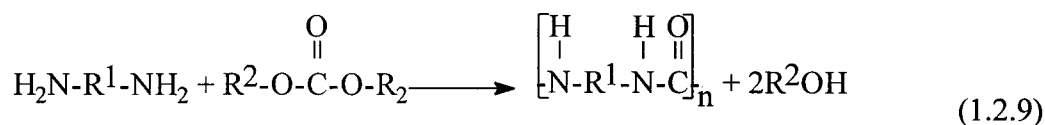
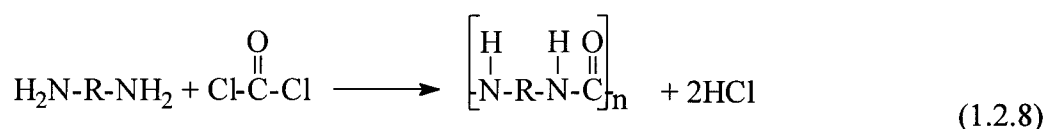
The polymers may be characterized through colligative properties or through end group analysis. Viscosity measurements are the most common characterization performed in industry. It is quick, does not require any expensive instruments, and it allows for quick determination of molecular weight. Other colligative properties, such as membrane osmometry, boiling point elevation, etc., may also be applied to the aramids. Elemental analysis and spectroscopic methods, such as FT-NMR, FTIR, and UV-VIS, may be used to study the polymers through end group analysis. X-ray and electron diffraction are important for studying their liquid crystallinity.¹⁵ The colligative properties and end group analyses are used to confirm the structure of the fibers and correlate molecular weight and structure to the properties of the fibers.

The desirable physical properties of the aramids has led to the wide variety of applications that were mentioned. The price of Kevlar[®] ranges from twenty-five to

seventy-five dollars per pound, but it is the only synthetic polymer with such a high strength and modulus. The two aramids, Kevlar[®] and Nomex[®], are commonly used as homopolymers for aviation and military applications. For other applications, they are blended with nylons or polyester elastomers, which have lower costs per pound, to form composites with significant but acceptable losses in their properties. They are each prepared in continuous processes and spun with additives only to enhance the properties of interest.⁷

9. An introduction to polyureas.

Polyureas are a separate class of polymers from polyamides, but polyureas are very similar to polyamides in their properties, structures, and syntheses. Polyureas differ from polyamides in that polyamides have (-CO-NH-) linkages while polyureas have (-NH-CO-NH-) linkages. Polyureas may be prepared by interfacial and solution polycondensation methods by following the same mechanism which was proposed for polyamides. Thus, diamines may be reacted with phosgene, carbonate esters, bisurethanes, and diisocyanates to form polyureas.



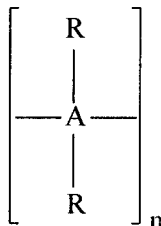
Polyureas have rod-like structures similar to polyamides. They form liquid crystalline solutions by hydrogen bonding between the lone pairs of electrons on the oxygen of the carbonyl with the hydrogens of the (-NH-CO-NH-) linkage. Polyureas are similar in structure and have common properties with polyamides. However, the commercial applications of polyureas have been limited by economic factors.

Chapter Three

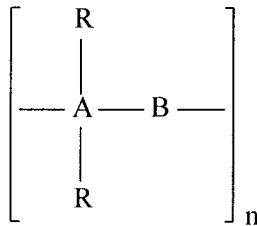
Solution Viscosity and Gel Permeation Chromatography

1. Solution Viscosity.

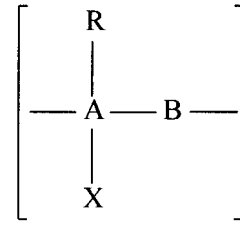
Polymers are composed of long chains of atoms linked together by covalent bonds. The repeating units of the resulting chains may also have side groups attached to their backbones. There may be one type of group in the repeating unit or there may be more than one type of group as depicted in 1.3.1 and 1.3.2, respectively. Polymers may also have variations in their side chains (e.g.1.3.3).²



1.3.1



1.3.2



1.3.3

Polymers can have any number of repeating units in each chain and, as a result, a bulk sample will generally have a wide molecular weight distribution (Figure 1.3.1). Properties vary with both average molecular weight and the width of the molecular weight distribution. In order to get optimum properties out of a polymer, the molecular weight range should generally be narrow. As shown in Figure 1.3.2, there is a tradeoff between the physical properties of a polymer and its viscosity. The optimum molecular weight range for practical applications, known as the working range, lies in the middle.²

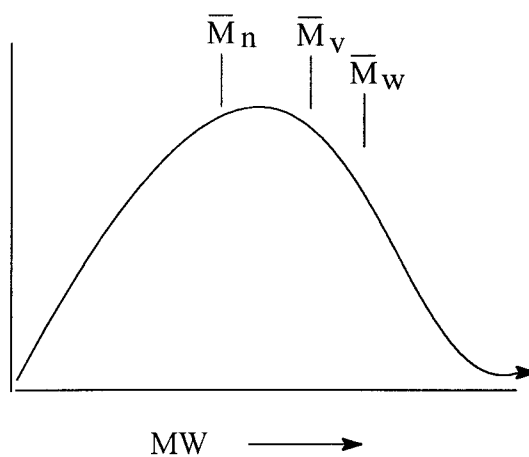


Figure 1.3.1. Molecular weight distribution

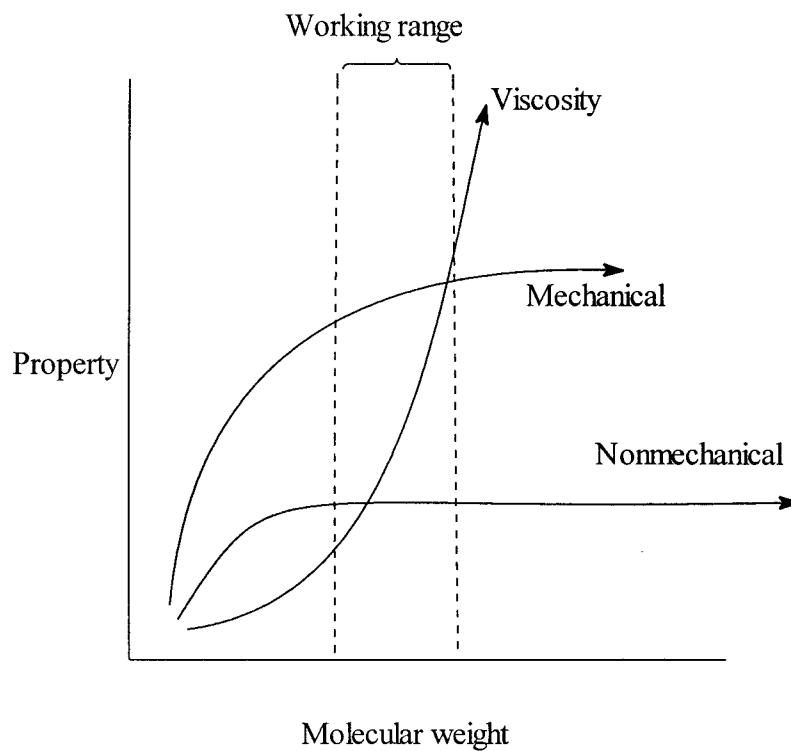


Figure 1.3.2. Dependence of polymer properties on molecular weight.

There are several ways of describing molecular weight distributions, three of the most common are the number average, weight average, and viscosity average molecular weights (\bar{M}_n , \bar{M}_w , and \bar{M}_v , respectively). The number average molecular weight is the summation of the number of moles in each fraction multiplied by the molecular weight of each fraction divided by the summation of the number of moles in each fraction.¹

$$\bar{M}_n = \frac{\sum(N_i M_i)}{N_i} \quad (1.3.4)$$

This average is commonly obtained by measuring colligative properties such as melting point and elevated boiling point, vapor pressure and osmotic pressure, or by end group analysis, all of which depend only on the number of particles present in solution.² Weight average molecular weight is the summation of the number of moles in each fraction multiplied by the square of the molecular weight of each fraction divided by the summation of the number of moles in each fraction multiplied by the molecular weight of each fraction.²

$$\bar{M}_w = \frac{\sum(N_i M_i^2)}{\sum(N_i M_i)} \quad (1.3.5)$$

The viscosity of a solution is related to the molecular weight of the polymer solutes by the Mark-Houwink-Sakurada equation.¹

$$[\eta] = K \bar{M}_v^\alpha \quad (1.3.6)$$

Where $[\eta]$ is the intrinsic viscosity of the solution (*i.e.* measured at infinite dilution), \bar{M}_v is the viscosity average molecular weight, and K and α are the Mark-Houwink constants. These are a function of the temperature, the solvent, and the polymer's structure and do

not vary with chain length for linear polymers except at low molecular weights where end effects become significant. The viscosity average molecular weight is defined as

$$\bar{M}_v = \frac{\sum(N_i M_i^2)}{\sum(N_i M_i)} \quad (1.3.7)$$

The values of K vary widely (typically from 10^{-3} to 0.5) depending strongly on the strengths of the polymer-solvent interactions while the α values typically vary over a narrower range from 0.5 (for a randomly coiled polymer in a Theta solvent) to 0.8 with values over 1.0 for rod shaped polymers. These parameters are evaluated from a plot of the log of $[\eta]$ versus $\log \bar{M}$ (\bar{M}_n , or better \bar{M}_w , values are used for such studies) for a series of isostructural polymers differing only in molecular weight with α and $\log K$ being the measured slope and intercept, respectively.^{1,2,3}

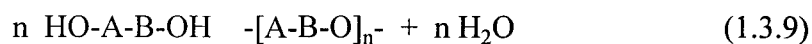
$$\log [\eta] = \log K + \alpha \log \bar{M} \quad (1.3.8)$$

Inspection of equations 1.3.4, 1.3.5, and 1.3.7 indicates that \bar{M}_w will always be greater than or equal to \bar{M}_n , that for non-rod like polymers $\bar{M}_n < \bar{M}_v < \bar{M}_w$, and that generally \bar{M}_v will be closer to \bar{M}_w than to \bar{M}_n . The opposite trend would be true for rod-like polymers. The value for \bar{M}_v would be closer to \bar{M}_n than \bar{M}_w .

Materials having narrow molecular weight distributions have $\bar{M}_n \approx \bar{M}_v \approx \bar{M}_w$, and have polydispersity indices (i.e. M_w / M_n) of close to one. Wider molecular weight distributions give larger \bar{M}_w / \bar{M}_n values ranging up to ten or more. The value of \bar{M}_n is more sensitive to the size of the low molecular weight fraction (i.e. due to their large number of chains per gram) while \bar{M}_w is more sensitive to the size of the high molecular weight fraction.^{4,5}

Two types of polymerization reactions are step-growth and chain-reaction polymerizations. Step-growth polymers grow by the random formation of bonds between monomers, oligomers, and growing chains.³ Often, step growth polymerizations are

condensation reactions in which small molecules such as HCl or H₂O are lost in each bond forming step. For example, both reactive functional groups can be on one molecule.¹

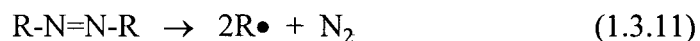


Or the reaction can have two monomers which are each difunctional.¹

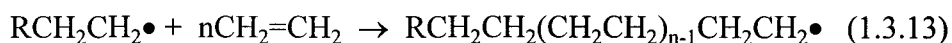
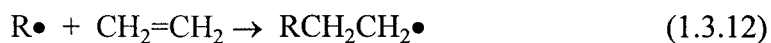


Such reactions generally produce high \bar{M}_w / \bar{M}_n values and broad molecular weight distributions. In contrast, chain-growth polymers are formed via the sequential addition of monomers to reactive chain ends.⁴ The mechanism of such reactions consists of three steps: initiation, propagation, and termination. The initiation step starts the reaction (e. g. 1.3.11). It generally involves the formation of highly reactive free radical, anionic, or cationic species known as the initiator. The propagation step(s) increases the molecular weight via the addition of monomers to the reactive end(s) of the chains. Finally, a termination step ends the chains growth (e. g. equations 1.3.12 and 1.3.13, respectively).¹

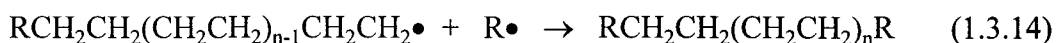
Initiation:



Propagation:



Termination:



Such polymers generally have much higher molecular weights and much narrower molecular weight distributions (*i.e.* their $\overline{M}_w/\overline{M}_n$ values approach one).³ The molecular weight of the polymer may be increased by limiting the termination step. Molecular weight distribution curves such as that shown in Figure 1.3.1 are generally best obtained from gel permeation chromatography, GPC.

2. Gel Permeation Chromatography.

Gel permeation chromatography has been largely attributed to J. C. Moore of the Dow Chemical Company. J. C. Moore used polystyrene gels to separate synthetic polymers in organic solvents.¹⁶ The discovery led to the determination of molecular weight distributions through calibration curves. Gel permeation chromatography, GPC, has developed into a liquid chromatographic system where a wide range of molecules may be separated by molecular size.¹⁷ It is also known as molecular sieving or size exclusion chromatography, SEC. When gels are used to separate biological polymers, it is termed gel filtration chromatography, GFC.¹⁸

For GPC, the molecules are separated by their molecular size by passing a dilute sample through a gel column. The sample is delivered into and through the column by a mobile phase, which is typically an organic solvent, most often THF.¹⁹ The column is the stationary phase and is packed with a gel that has pores. Gels are composed of two components. There is a dispersed, gel forming substance and a dispersing agent which is similar to a solvent. The gel forming substance and the dispersing agent penetrate and stabilize each other. Small molecules may diffuse into the gel with the gel acting as a solvent. The pores of the gel vary in size to separate the molecules.²⁰ The columns may have different pore sizes to separate molecules by size through variations in retention

times. For a given column, the retention times of samples are dependent on the size of the sample. Smaller molecules in the sample can diffuse into the pores of the gel, intermediate molecules diffuse into some of the pores, but the large molecules are excluded from the pores. The small and intermediate molecules constantly diffuse in and out of the pores. Solvent flowing outside of the pores flush molecules through the column.^{20,21} Retention times are correlated directly to the amount of time the molecule spends diffusing in and out of the gel pores. Smaller molecules have longer retention times because it takes a smaller molecule more time to travel in and out of the pores than it would for a larger molecule that does not fit into the pores. After the molecules pass through the column, they reach the detector. Usually, a refractive index or ultraviolet detector is used. The detector produces a signal from the sample with the signal of the solvent as the baseline. A chromatogram may be obtained from the signals through an interface with a personal computer or another outlet, such as a strip chart recorder. The resulting chromatogram displays signal intensity vs. retention time.^{20,22}

The chromatograms may be used to determine the molecular weight of a sample. The number and weight average molecular weights require knowledge of the number of molecules at a certain molecular weight. Standards may be purchased and used for a calibration curve. The standards that are used must vary in molecular weight especially in the expected range of the sample, have narrow and specified molecular weights, and may be used on the same column and under the same conditions. After chromatograms are obtained from the standards, a plot of the molecular weights against the retention times forms the calibration curve. The molecular weights obtained from the calibration curve are relative to the polymer that was used as a standard. Since all polymers are not analogous, a universal calibration curve may be used. The curve is a plot of the logarithms of the product of the intrinsic viscosity of the polymer and the molecular weight relative to the standard against the retention times.^{18,20,21}

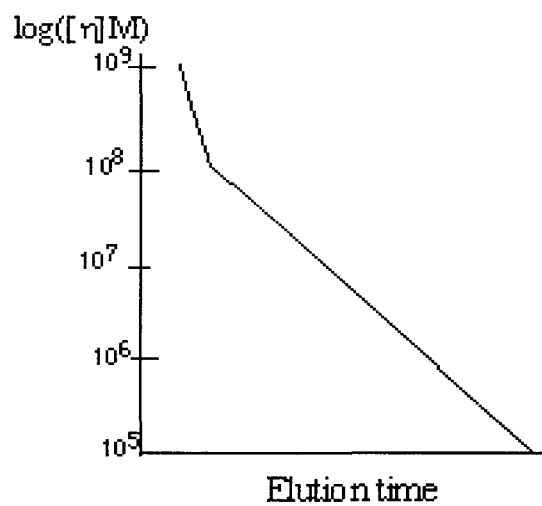


Figure1.3.3. GPC Universal Calibration Curve.

The Universal Calibration Curve, that is shown above, is used to directly determine the molecular weight of a sample from its elution time under the same conditions of the calibration.

Works Cited

- (1) Jenkins, P. R. *Organometallic Reagents in Synthesis*; Oxford University Press: New York, 1992.
- (2) Mark, J. E.; Allcock, H. E.; West, R. *Inorganic Polymers*; Prentice-Hall Inc.: Englewood Cliffs, New Jersey, 1992.
- (3) (a) Douglas, B.; McDaniel, D.; Alexander, J.. *Concepts and Models of Inorganic Chemistry*; John Wiley and Sons Inc.: New York, 1994. (b) Eisch, J. J. *The Chemistry of Organometallic Compounds: The Main Group Elements*; The Macmillan Company: New York, 1967. (c) Huheey, J. E. *Inorganic Chemistry: Principles of structure and reactivity*; HarperCollins Publishers Inc.: New York, 1983.
- (4) Heck, R. F. *Organotransition Metal Chemistry: A Mechanistic Approach*; Academic Press: New York, 1974.
- (5) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole Publishing Company: Monterey, California, 1985.
- (6) (a) Hall Jr., H.K. *J. Amer. Chem. Soc.* **78**, 2717 (1956). (b) Wittbecker, E. L.; Morgan, P.W. *J. Polymer Sci.* **40**, 289 (1959). (c) Mark, H. F.; Atlas, S.M.; Ogata, N. *J. Polymer Sci.* **61**, S49 (1962).
- (7) Kevlar® Aramid Fiber Technical Guide. Du Pont. 1992.
- (8) (a) Stevens, M. P. *Polymer Chemistry: An Introduction*; Oxford University Press: New York, 1990. (b) Mark, J. E., et al. *Physical Properties of Polymers*; American Chemical Society: Washington, D.C., 1984, 207.

- (9) Preston J. *Encyclopedia of Polymer Science and Technology: Supplement Vol. 2*; Interscience Publishers: New York, 1977, 84.
- (10)(a) Herlinger, H., et al. *Appl. Poly. Symp.* **21**, 201 (1973). (b) Millich, F.; Carraher, Jr., C. E. *Interfacial Synthesis Volume II: Polymer Applications and Technology*; Marcel Dekker, Inc.: New York, 1977, 154.
- (11) Morgan, P. W. *Polymer Reviews Volume 10: Condensation Polymers: By Interfacial and Solution Methods*; Interscience Publishers: New York, 1965.
- (12) Properties of Nomex Aramid Filament Yarns. Du Pont. 1981.
- (13) (a) Lenk, R. S. *J. Poly. Sci.: Macro. Rev.* **13**, 355 (1978). (b) Mikhailov, N. V., Maiboroda, V. I.; Nikolaeva, S. S.. *J. Poly. Sci.* **52**, 245 (1961).
- (14) Hathaway, C.E.; Early, C. E.. *Appl. Poly. Symp.* **21**, 101 (1973).
- (15) (a) Campbell, D.; White, J. R.. *Polymer Characterization*; Chapman and Hall: New York, 1989. (b) Crompton, T. R. *Analysis of Polymers: An Introduction*; Pergamom Press: New York, 1989. (c) Silverstein, R. M.; Bassler; G. C.; Morrill, T.C. *Spectroscopic Identification of Organic Compounds*; John Wiley and Sons, Inc.: New York, 1991.
- (16) Moore, J. C. *J. Polym. Sci.; Part A.* **2**, 835 (1964).
- (17) (a) Provder, T. *Chromatography of Polymers: Characterization by SEC and FFF*; Americam Chemical Society: Washington, D.C., 1993. (b) Wolf, F. J. *Separation Methods in Organic Chemistry and Biochemistry*; Academic Press: New York, 1969.
- (18) Stevens, M. P. *Polymer Chemistry: An Introduction*; Oxford University Press: New York, 1990.

- (19) (a) Moore, J. C. *Characterization of Macromolecular Structure*; National Academy of Sciences: Washington, D.C., Publication 1573, 1968. (b) Pearce, E. M.; Wright, C. E.; Bordoloi, B. K. *Laboratory Experiments in Polymer Synthesis and Characterization*; Educational Modules for Materials Science and Engineering Project: University Park, Pennsylvania, 1982.
- (20) (a) Determan, H. *Gel Chromatography*; Springer-Verlag New York, Inc.: New York, 1968. (b) Yan, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; John Wiley and Sons, Inc.: New York, 1979.
- (21) Altgelt, K. H.; Segal, L. *Gel Permeation Chromatography*; Marcel Dekker Inc.: New York, 1971.
- (22) (a) Khopkar, S. M. *Concepts in Analytical Chemistry*; Halsted Press: New York, 1984. (b) Snyder, L. R.; Kirkland, J. J. *Introduction to Modern Liquid Chromatography*; John Wiley and Sons, Inc.: New York, 1979.

Part Two

Organometallic Polymers from Chromium Complexes

Chapter One

Introduction

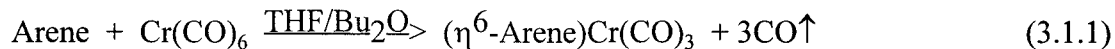
Eta-six benzenechromiumtricarbonyl, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, and its derivatives were one of the first classes of organometallics to be studied and remains under investigation. In $(\eta^6\text{-benzene})\text{chromiumtricarbonyl}$, the benzene ring is planar and the chromium tricarbonyl center is π -bonded to the benzene ring to give a 3-D tripod.²



Figure 2.1.1. Three-dimensional tripod of $(\eta^6\text{-benzene})\text{chromiumtricarbonyl}$

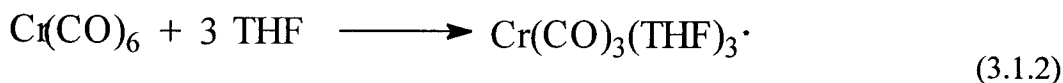
The $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ complex has been reported to have a dipole moment from the benzene ring to the tripod. Due to the carbonyl group's electron-withdrawing effect, the chromium has a partial positive charge.³

Chromium hexacarbonyl, $\text{Cr}(\text{CO})_6$, may be reacted with benzene while being refluxed in mixed solvents such as THF and butyl ether.^{2b,2c,4}



The reagents are reacted under anhydrous and anaerobic conditions to prevent oxidation or hydrolysis of chromium. At room temperature, there is only a partial dissolution of the chromium hexacarbonyl and the loss of CO from $\text{Cr}(\text{CO})_6$ is very slow. The system is heated to

accelerate the reaction. It is believed that the reaction takes place through a THF, tetrahydrofuran, intermediate, $\text{Cr}(\text{CO})_3(\text{THF})_3$. Then a benzene ligand displaces the THF ligands to form $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$.



These reactions are best monitored by Infrared spectroscopy. The carbonyl stretching frequencies of the product and chromium hexacarbonyl may be used to determine the progress of the reaction. Chromium hexacarbonyl has a stretching frequency of 1980 wavenumbers. Two or three stretching frequencies due to the $(\eta^6\text{-arene})\text{chromiumtricarbonyl}$ complexes shift are observed at below 1980 wavenumber with the exact value depending on the electron richness of the complex. The electron richness of the metal and its effect on IR stretching frequencies will be discussed later in this chapter. When the reaction is complete, the solution is cooled to room temperature and the products generally precipitate as yellow to orange crystals. Chromium hexacarbonyl and other complexes may form from decomposition reactions. Many of the undesirable chromium byproducts are green and insoluble.

The bonding of the carbonyl ligand was introduced in Chapter One. The bonding between the carbonyl ligand and the chromium atom may be explained by a Dewar-Chatt-Duncanson model. There is σ -donation from the lone pair of electrons on the carbon to an empty σ -symmetry, d^2sp^3 , hybrid orbital of chromium. Then there is π -back donation from a filled d orbital on chromium to an empty π^* -anti-bonding orbital localized on the carbonyl ligand.^{4b} Substituents which are π -donating to the benzene ring, affect the structure of the benzene ring and the conformation of the $\text{Cr}(\text{CO})_3$ tripod. For example, the strongly π -donating NR_2 groups exhibit structural and spectroscopic effects attributable to contributions from a second resonance

form involving an exocyclic double bond, a positive charge localized on NH_2 , and a negative charge on the $\text{Cr}(\text{CO})_3$ group.^{2c,4}

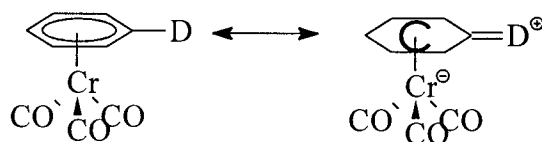


Figure 2.1.2. Resonance forms for the π -donors.

The second resonance form has an 18 electron configuration on the chromium atom that repels the electron density of the exocyclic double bond. This effects the planarity of the benzene ring by bending the *ipso*-carbon atom bonded to the π -donor substituent away from the $\text{Cr}(\text{CO})_3$ center. For polysubstituted arenes, further structural distortions are observed.^{2,3c,4}

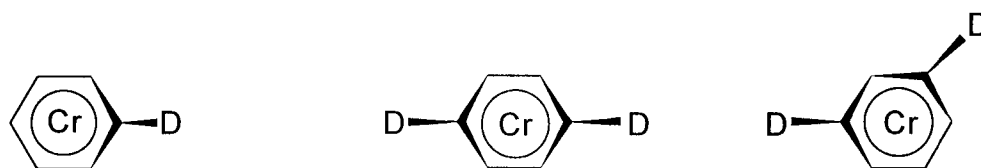


Figure 2.1.3. Planarity of the complexed benzene ring.

The substituents effect the conformation of the $\text{Cr}(\text{CO})_3$ tripod if the arene has π -donor or π -acceptor substituents. The three products that I have prepared have exclusively π -donor substituents. When there is one π -donor group, the tripod generally has an eclipsed conformation. While two *para* substituted donor groups produce a staggered conformation.^{2a,2c,3b,5}



Figure 2.1.4. Conformation of the chromiumtricarbonyl tripod.

π -donor substituents may also effect the electron richness of the organometallic compound. The π -donor substituents increase the net electron transfer from the arene to $\text{Cr}(\text{CO})_3$. As the compound becomes more electron rich, there is a stronger Cr-CO bond and the C-O bond weakens. The net electron transfer may be monitored by IR spectroscopy. As a compound gets more electron rich, the ν_{CO} , the carbonyl stretching frequency, decreases. The electron richness is important in the stabilization of radical cations.²

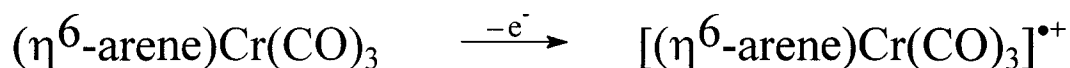
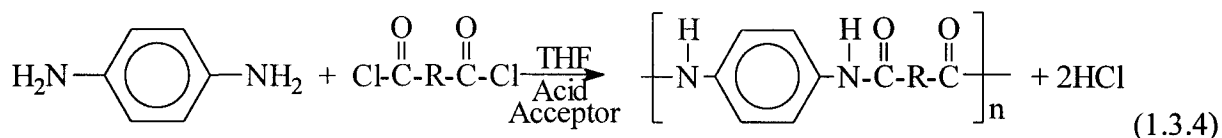


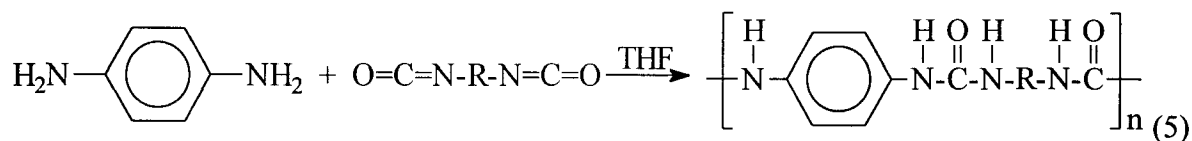
Figure 2.1.5. Formation of radical cations.

Previously the radical cations were thought to be stabilized by the bulk of substituents. For chromium complexes with electron donating substituents, the radical cation also becomes more stable due to the added electron richness of the $\text{Cr}(\text{CO})_3$ center and defense against nucleophilic attack increases which could ultimately reduce decomposition.^{2a,2b}

Organometallic derivatives of $(\eta^6\text{-benzene})\text{chromiumtricarboxyl}$ may be applied in polymerizations. Chromiumtricarboxyl complexes will be used as monomers to synthesize novel organometallic polymers. The organometallic polymers resemble aromatic polyamides and polyureas. The properties of the chromium complexed aromatic polymers will be studied relative to uncomplexed polymers. Both the complexed and uncomplexed polymers may be formed by the same method. A solution polycondensation process will be used for polyamides by reacting a phenylenediamine with an acid chloride in the presence of an acid acceptor.^{1,9}



Solution polycondensation may be used for polyureas. Polyureas are formed by reacting a diisocyanate with a diamine in solution.



Uncomplexed polyamides and polyureas are described in Chapter One in great detail. The polyamides and polyureas have liquid crystalline behavior. Liquid crystallinity occurs when polymer chains become aligned in a highly ordered array while in a liquid state. The liquid crystalline behavior may be attributed to hydrogen bonding between the hydrogen of the amide nitrogens and the lone pair of electrons on the oxygen of the carbonyl. The highly ordered polymers produce enhanced properties. The polymers have enhanced thermal stability, high tensile strength, flame resistance, electrical properties, and chemical resistance. However, the high degree of order limits the solubility of the polymers and makes them harder to process. The uncomplexed polymers are only soluble in 74 % sulfuric acid. The organometallic polymers increases the solubility of the polymers because the chromiumtricarbonyl limits the amount of hydrogen bonding by acting as a spacer.^{6,9}

For the characterization of the polymers, model compounds will be synthesized and their ¹H NMR spectra would provide a quantitative means to determine the molecular weights by the relative ratio of peaks known to correspond to low molecular weight to peaks assigned to the higher molecular weight polymer.⁷ The aromatic models are reacted from solution condensation reactions of monofunctional acid chlorides and diisocyanates with diamines.

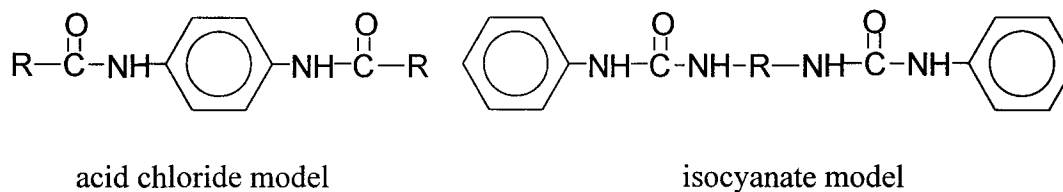


Figure 2.1.6. Representative model compounds for the acid chlorides and isocyanates

Chapter Two

Experimental Section

1. Reagents and reaction conditions.

Reagent grade chemicals were purchased from the Aldrich Chemical Company. The dinitrogen and argon gasses were 99.999 % pure. Tetrahydrofuran, THF, predried over potassium hydroxide, and toluene were dried over sodium/benzophenone and distilled under argon gas. Triethylamine was dried over potassium hydroxide and distilled under dinitrogen gas.⁹ The reactions were conducted under anhydrous and anaerobic conditions by using a vacuum line.¹⁰ The syntheses, collection, and purification were performed carefully to prevent oxidation or hydration. The solvents, reagents, and products were not dried prior to the reaction unless noted. The glassware was dried in an oven above one hundred and ten degrees celcius, assembled, and cooled under nitrogen gas. A mineral oil bubbler was used on the vacuum line to prevent having a closed system and to determine the flow of the nitrogen gas. The reagents and a magnetic stir bar were added through a side neck of the three-necked round bottom flasks that were used in the syntheses under a positive flow of nitrogen. The solution was stirred at a moderate rate with a magnetic stirrer. If heating was required, a condenser was inserted in the center neck of the round bottom flask and cooled with water. Variacs and heating mantles were used to apply heat. Typically, the solid products were filtered and washed and allowed to air dry. The products were recrystallized if needed. The IR spectra were recorded in CH₂Cl₂ on a Perkin-Elmer 1600 FT IR Spectrometer and the mass spectra were obtained from a Finnigan 10-20B GC/MS Spectrometer. ¹H NMR and ¹³C NMR were recorded on a Gemini 2000, 400 Megahertz NMR.

2. Synthesis of the organometallic monomers.

a. Synthesis of (η^6 -aniline)chromiumtricarbonyl.

A 250 mL round-bottom flask with a gas inlet and an air cooled condenser were charged with $N_2(g)$. Then Bu_2O (100 mL), THF (10 mL), aniline (1.60 mL, 13.9 mmol), and chromium hexacarbonyl (3.30g, 15.0 mmol) were added. The reagents were stirred with a magnetic stirrer and stir bar and refluxed for forty-eight hours with the variac set at fifty. The solid product was green. A vacuum pump and solvent trap were used to remove the THF and some of the unreacted chromium hexacarbonyl. The butylether was canulated off and the resulting green solid was washed with dichloromethane (50 mL). The solid was discarded. The dichloromethane extracts were refrigerated resulting in the precipitation of crystals. The white and yellow crystals weighed 0.284g (1.24 mmol) and were a mixture of the desired product and chromium hexacarbonyl based on comparisons to an authentic sample. IR peaks were observed in CH_2Cl_2 at $1959cm^{-1}$, $1872 cm^{-1}$, and $1979 cm^{-1}$

b. Synthesis of (η^6 -p-phenylenediamine)chromiumtricarbonyl.

A 500 mL three-necked round bottom flask fitted with a gas inlet and an air cooled condenser were charged with nitrogen gas and butyl ether (101 mL), THF (10.5 mL), chromium hexacarbonyl (3.36 g, 15.3 mmol), and p-phenylenediamine (1.50 g, 13.9 mmol) . A magnetic stirrer and a variac set at 50 were used to reflux the solution for 41 hours. The yellow product was collected by vacuum filtration in air, washed with hexanes (50 mL) and allowed to air dry for one hour. The weight of the crystals was 4.81 g (19.7 mmol) or 96.6% of the theoretical yield. An IR spectrum was taken in dichloromethane and there were observed carbonyl stretching frequencies at 1949 and $1857 cm^{-1}$.

c. Synthesis of (η^6 -m-phenylenediamine)chromiumtricarbonyl

Butyl ether (101 mL), THF (10 mL), chromium hexacarbonyl (5.00 g, 22.7 mmol), and m-phenylenediamine (2.21 g, 20.4 mmol) were reacted for 96 hours, cooled and the THF was

removed with a vacuum pump and solvent trap. The yellow product was collected by filtration and washed with hexanes. The crystals weighed 4.75 g (19.5 mmol) or a 95.5 % yield. An IR was taken in dichloromethane and the carbonyl stretching frequencies were observed at 1952 and 1864 cm^{-1} .

3. Preparation of the organic model compounds.

a. Reaction of p-phenylenediamine with valeryl chloride.

The glassware was dried overnight in an oven at one hundred and ten degrees celcius. The 300 mL three-necked flask was fitted with an adapter in the central neck leading to an oil bubbler, a gas inlet and a rubber septum were inserted in the side necks of the flask. THF (150 mL), dried from phosphorous pentoxide and distilled under argon, and triethylamine (48 mL), dried from potassium hydroxide and distilled under nitrogen gas, were added to the flask under a positive flow of nitrogen gas. p-Phenylenediamine (5.41 g 50.0 mmol) was added to the flask under a positive flow of nitrogen gas. A magnetic stirrer and stir bar were added and set at a moderate rate. The solution was a dark pink-red in color and clear. The flask was cooled in an ice bath to control the temperature of the reaction flask. Valeryl chloride (4.25 mL, 50.0 mmol) was added dropwise through the rubber septa with a syringe. As more of the valeryl chloride was added to the flask, more white precipitate formed and the color of the solution lightened. The reaction was left for eighteen hours. The white product was filtered and washed with hexane and acetone, air dried, and stored in a schlenk tube.

b. Reaction of aniline with 1,6-diisocyanatohexane.

The glassware was dried in an oven overnight at one hundred and twenty degrees celcius. The glassware was assembled and cooled under nitrogen gas. A stir bar, aniline (0.500 g, 5.36 mmol), and THF (150 mL), dried from calcium hydride and distilled under argon gas, were

added under a positive flow of nitrogen gas. Then 1,6-diisocyanatohexane (0.310 mL, 2.18 mmol) was added with a syringe. A white precipitate was apparent upon addition of the 1,6-diisocyanatohexane. The solution and precipitate were stirred for twenty hours. The white product was filtered and washed with hexanes and acetone and saved in a schlenk tube under nitrogen gas.

c. Reaction of (η^6 -p-phenylenediamine)chromiumtricarbonyl with benzoyl chloride.

A one hundred milliliter three-necked round bottom flask, gas inlet, stoppers and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The apparatus was assembled and cooled under nitrogen gas. Dichloromethane (40 mL) benzoyl chloride (0.110 mL, 8.18 mmol) , and triethylamine (3 mL) were added to the flask under a positive flow of nitrogen gas. (η^6 -p-phenylenediamine)chromiumtricarbonyl (0.100 g, 4.10 mmol) was added under a positive flow of nitrogen gas. The reaction was monitored by IR. After one hour, there was a decrease in the carbonyl stretching by 2 wave numbers. The reaction was continued for eighteen hours. The wavenumber of the carbonyl stretch had decreases by five. The dichloromethane was removed by a vacuum pump and solvent trap. Heat was applied under vacuum to remove the triethylamine. There was a peak at 1980 wavenumbers of the IR spectrum.

d. Reaction of (η^6 -m-phenylenediamine)chromiumtricarbonyl with benzoyl chloride.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degree celcius. The glassware and stir bar were assembled and cooled under nitrogen gas. Dichloromethane (20 mL) and triethylamine (3 mL) were added under a positive flow of nitrogen gas. A magnetic stir plate was added and set at a moderate rate. (η^6 -m-phenylenediamine)chromiumtricarbonyl (0.100 g, 4.10 mmol) followed by benzoyl chloride (0.110 mL, 8.18 mmol) was added under a positive flow of nitrogen gas. IR was used to monitor the reaction. The total time of the reaction

was one hour and forty five minutes. Some of the dichloromethane was boiled off during the exothermic reaction because the level of solvent decreased in the flask. There appeared to be yellow crystals present and a dark yellow-orange solution. The crystals were separated. The solution turned green after a few hours and the yellow crystals also became green. There was an IR peak of 1980 cm^{-1} .

4. Preparation of the organic polymers.

a. Reaction of p-phenylenediamine with sebacoyl chloride.

The glassware was dried overnight in an oven at 110 C and cooled under nitrogen gas. The glassware consisted of a three-necked 300 mL round bottom flask, gas inlet, and a glass adaptor connected to a mineral oil bubbler with latex tubing. A magnetic stir bar was also dried, placed in the round bottom flask and cooled under nitrogen gas. The flask was charged with dried and distilled THF (150 mL) and triethylamine (20 mL) under a positive flow of nitrogen gas. p-Phenylenediamine (5.41 g, 22.2 mmol) was weighed and added to the flask under a positive flow of nitrogen. The solution was stirred with a magnetic stirrer and upon the dissolution of the p-phenylenediamine the solution appeared crimson in color. An ice bath was applied surrounding the reaction flask to control the temperature of the exothermic reaction. Sebacoyl chloride (10.7 mL) was added dropwise from a syringe to the stirred solution. A white precipitate immediately formed and white fumes were visible in the reaction flask. As more of the sebacoyl chloride was added more precipitate formed and the color of the solution gradually faded until it was nearly colorless. The reaction was continued overnight under nitrogen gas. The white product was collected by filtration in air and washed with THF (100 mL). The white powder was transferred into a dry schlenk tube. The schlenk tube was evacuated and then filled with nitrogen gas for storage.

b. Reaction of p-phenylenediamine with 1,6-diisocyanatohexane.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The glassware and stir bar were assembled and cooled under nitrogen gas. The flask was charged with dichloromethane (200 mL), dried from phosphorous pentoxide and distilled under argon. A magnetic stirrer was added and set at a moderate rate. p-Phenylenediamine (2.00 g, 18.5 mmol) was added and the solution was clear and crimson in color. 1,6-Diisocyanatohexane (2.10 mL, 18.5 mmol) was added under a positive flow of nitrogen gas. A white precipitate formed. The reaction was stopped after 72 hours of stirring. The solid product was collected by filtration and washed with hexane and acetone and allowed to air dry.

c. Reaction of m-phenylenediamine with 1,6-diisocyanatohexane.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The glassware and stir bar were assembled and cooled under nitrogen gas. THF (150 mL), dried from calcium hydride and distilled under argon, was added under a positive flow of nitrogen gas. A magnetic stirrer was added and set at a moderate rate. m-Phenylenediamine (1.00 g, 9.25 mmol) was added to the flask. The solution was clear and dark pink in color.) 1,6-Diisocyanatohexane (1.10 mL, 9.25 mmol) was added dropwise to the solution. The monomer were reacted for sixteen hours. The white precipitate was collected filtration and washed with hexanes and acetone. An IR of the filtrate did not show any product in solution.

d. Reaction of p-phenylenediamine with methylenedi-p-phenyl diisocyanate.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The apparatus and stir bar were assembled and cooled under nitrogen gas. THF (150 mL), dried from calcium hydride and distilled under argon, was added under a positive flow of nitrogen gas. A magnetic stirrer was added and set at a moderate rate. p-Phenylenediamine

(0.500 g, 4.62 mmol) followed by methylenedi-p-phenyldiisocyanate (1.16 g, 4.62 mmol) were added slowly to the flask under a positive flow of nitrogen gas. A white precipitate formed immediately. The precipitate and the solution were stirred for seventy-two hours. The THF was canulated from the flask and discarded. Any residual THF was removed by vacuum pump. The white product was saved under nitrogen gas.

e. Reaction of m-phenylenediamine with methylenedi-p-phenyl diisocyanate.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The apparatus and stir bar were assembled and cooled under nitrogen gas. The flask was charged with THF (150 mL), dried from calcium hydride and distilled under argon, under a positive flow of nitrogen gas. A magnetic stirrer was added and set at a moderate rate. m-Phenylenediamine (0.500 g, 4.62 mmol) followed by methylenedi-p-phenyl diisocyanate (1.16 g, 4.62 mmol) were added slowly to the flask under a positive flow of nitrogen gas. A white precipitate formed immediately. The precipitate and the solution were stirred for seventy-two hours. The THF was canulated from the flask and discarded. The residual THF was removed by vacuum pump. The white product was saved under nitrogen gas.

5. Preparation of the organochromium polymers.

a. Reaction of (η^6 -p-phenylenediamine)chromiumtricarbonyl with methylenedi-p-diisocyanate.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The apparatus and stir bar were assembled and cooled under nitrogen gas. THF (150 mL), dried from calcium hydride and distilled under argon, was added to the flask under a positive flow of nitrogen gas. A magnetic stirrer was added and set to a moderate rate. (η^6 -p-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) followed by methylenedi-p-

phenyldiisocyanate (1.16 g, 2.05 mmol) were added slowly to the flask under a positive flow of nitrogen gas. The monomers were stirred for seventy-two hours. The THF was canulated from the flask and discarded. Any residual THF was removed by a vacuum pump and solvent trap. The yellow-green product weighed 0.5679 g and was saved under nitrogen gas. The carbonyl stretching frequencies of 1940.9 and 1850.4 cm^{-1} were recorded as a mull.

b. Reaction of (η^6 -m-phenylenediamine)chromiumtricarbonyl with methylenedi-p-diisocyanate.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The apparatus and stir bar were assembled and cooled under nitrogen gas. THF (200 mL), dried from calcium hydride and distilled under argon, was added to the flask under a positive flow of nitrogen gas. A magnetic stirrer was added and set at a moderate rate. (η^6 -m-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) followed by methylenedi-p-phenyldiisocyanate (1.16 g, 2.049 mmol) were added slowly to the flask under a positive flow of nitrogen gas. The monomers were stirred for seventy-two hours. The THF was canulated from the flask and discarded. Any residual THF was removed by a vacuum pump and solvent trap. The yellow-green product weighed 0.6287 g and was saved under nitrogen gas. An IR spectrum was taken as a mull and the carbonyl stretching frequencies were 1939.7 and 1842.1 cm^{-1} .

c. Reaction of (η^6 -p-phenylenediamine)chromiumtricarbonyl with 1,6-diisocyanatohexane.

Method A. The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The glassware and stir bar were assembled and cooled under nitrogen gas. THF (200 mL), dried from calcium hydride and distilled under argon, was added to the flask under a positive flow of nitrogen gas. A magnetic stirrer was added and set at a moderate rate. (η^6 -p-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) followed by 1,6-

diisocyanatohexane (0.500 mL, 2.05 mmol) was added slowly to the flask under a positive flow of nitrogen gas. The monomers were reacted for eighteen hours. The IR spectra after eighteen hours showed a decrease of seven wavenumber for the carbonyl stretching frequency. The THF was removed by rotary evaporation. THF was used to recrystallize the yellow-green product. The yellow crystals weighed 0.5827 g. An IR spectrum was recorded as a mull. The carbonyl stretching frequencies were 1942.3 and 1856.2 cm^{-1} .

Method B. The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The glassware and stir bar were assembled and cooled under nitrogen gas. Anhydrous dimethylacetamide, DMAc, was added with a syringe into the flask under a positive flow of nitrogen gas. A magnetic stirrer was added and set at a moderate rate. (η^6 -p-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) was added to form a yellow solution. The flask was cooled by an ice barh and 1,6-diisocyanatohexane (0.500 mL, 2.05 mmol) was added slowly to the flask under a positive flow of nitrogen gas. The monomers were reacted for two hours. The IR spectra after two hours did not show any change in the carbonyl stretching frequency. The flask was allowed to warm to room temperature. Another IR spectra was taken, but there was still no indication that the monomers reacted. The solution was heated to reflux and allowed to react. An IR was taken after two hours of reflux and there was a shift of two wavenumber. The solution was refluxed overnight. An IR spectra was taken and the solution was cooled. The carbonyl stretching frequencies for the yellow polymer were 1936.2 and 1852.7 cm^{-1} . A five milliliter aliquot was removed for solution viscosity measurements. The viscosity was 0.621 g/dL. The DMAc was removed by a vacuum pump and solvent trap. The yellow crystals weighed 0.7433 g.

d. Reaction of (η^6 -m-phenylenediamine)chromiumtricarbonyl with 1,6-diisocyanatohexane.

Method A. The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The glassware and stir were assembled and cooled under nitrogen gas. The flask was charged with THF (200 mL), dried from calcium hydride and distilled under argon. A magnetic stirrer was added and set at a moderate rate. (η^6 -m-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) followed by 1,6-diisocyanatohexane (0.500 mL, 2.049 mmol), was slowly added to the flask under a positive flow of nitrogen gas. The monomers were reacted for seventy-two hours. The IR spectra showed that after seventy-two hours that the carbonyl stretching frequency had decreased by seven wavenumbers. The THF was removed by rotary evaporation. The crystals were recrystallized from THF. The crystals were washed with hexanes and were air dried. The yellow-green crystals weighed 0.5348 g. The IR spectrum was recorded as a mull and the carbonyl stretching frequencies were 1941.2 and 1850.9 cm^{-1} .

Method B. The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The glassware and stir bar were assembled and cooled under nitrogen gas. Anhydrous dimethylacetamide, DMAc, was added with a syringe into the flask under a positive flow of nitrogen gas. A magnetic stirrer was added and set at a moderate rate. (η^6 -m-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) was added to form a yellow solution. The flask was cooled by an ice barh and 1,6-diisocyanatohexane (0.500 mL, 2.05 mmol) was added slowly to the flask under a positive flow of nitrogen gas. The monomers were reacted for two hours. The IR spectra after two hours did not show any change in the carbonyl stretching frequency. The flask was allowed to warm to room temperature. Another IR spectra was taken, but there was still no indication that the monomers reacted. The solution was heated to reflux and allowed to react. An IR was taken after two hours of reflux and there was a shift of two wavenumber. The solution was refluxed overnight. An IR spectra was taken and the solution was cooled. The carbonyl stretching frequencies were 1932.3 and 1842.2 cm^{-1} . A five milliliter aliquot was removed for solution viscosity measurements. The solution was 0.393

g/dL. The DMAc was removed by a vacuum pump and solvent trap. The yellow solid weighed 0.3127 g.

e. Reaction of (η^6 -p-phenylenediamine)chromiumtricarbonyl with toluene diisocyanate.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The apparatus and stir bar were assembled and cooled under nitrogen gas. THF (100 mL), dried from calcium hydride and distilled under argon, was added to the flask under a positive flow of nitrogen gas. A magnetic stirrer was added and set to a moderate rate. (η^6 -p-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) followed by toluenediisocyanate (0.290 mL, 2.05 mmol) were added slowly to the flask under a positive flow of nitrogen gas. The monomers were stirred for seventy-two hours. The THF was canulated from the flask and discarded. Any residual THF was removed by a vacuum pump. The yellow-green product weighed 0.5169 g and was saved under nitrogen gas. The IR spectrum was recorded as a mull and the carbonyl stretching frequencies were 1942.2 and 1856.2 cm^{-1} .

f. Reaction of (η^6 -m-phenylenediamine)chromiumtricarbonyl with toluene diisocyanate.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The apparatus and stir bar were assembled and cooled under nitrogen gas. THF (100 mL), dried from calcium hydride and distilled under argon, was added under a positive flow of nitrogen gas and a magnetic stirrer was added and set at a moderate rate. (η^6 -m-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) followed by toluenediisocyanate (0.290 mL, 2.05 mmol) were added slowly to the flask under a positive flow of nitrogen gas. The monomers were stirred for seventy-two hours. The THF was canulated from the flask and discarded. Any residual THF was removed by a vacuum pump and solvent trap. The yellow-

green product weighed 0.6911 g and was saved under nitrogen gas. The IR spectrum was recorded as a mull and the carbonyl stretching frequencies were 1941.7 and 1843.6 cm^{-1} .

g. Reaction of (η^6 -p-phenylenediamine)chromiumtricarbonyl with terephthaloyl chloride.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The glassware and stir bar were assembled and cooled under nitrogen gas. Anhydrous dimethylacetamide, DMAc, (75 mL) was added with a syringe into the flask under a positive flow of nitrogen gas. A magnetic stirrer was added and set at a moderate rate. (η^6 -p-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) was added to form a yellow solution. The flask was cooled by an ice bath and terephthaloyl chloride (0.500 mL, 2.05 mmol) was added slowly to the flask under a positive flow of nitrogen gas. The monomers were reacted for two hours. The IR spectra after two hours showed a change in the carbonyl stretching frequency of about 20 cm^{-1} . The flask was allowed to warm to room temperature, stirred for two hours and an IR spectra was taken. During the two hours, IR spectra were taken and the carbonyl stretching frequency did not shift. The IR spectrum of the product had observed carbonyl stretching frequencies at 1954.2 and 1867.8 cm^{-1} . A five milliliter aliquot was removed for solution viscosity measurements. The measured solution viscosity was 0.398 g/dL. The DMAc was removed by a vacuum pump and solvent trap. The yellow crystals weighed 0.6531 g.

h. Reaction of (η^6 -m-phenylenediamine)chromiumtricarbonyl with terephthaloyl chloride.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The glassware and stir bar were assembled and cooled under nitrogen gas. Anhydrous dimethylacetamide, DMAc, was added with a syringe into the flask under a positive flow of nitrogen gas. A magnetic stirrer was added and set at a moderate rate. (η^6 -m-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) was added to form a yellow

solution. The flask was cooled by an ice bath and terephthaloyl chloride (0.500 mL, 2.05 mmol) was added slowly to the flask under a positive flow of nitrogen gas. The monomers were reacted for two hours. The IR spectrum after two hours showed a change of about 20 cm^{-1} in the carbonyl stretching frequency. The flask was allowed to warm to room temperature, stirred for two hours and an IR spectra was taken. During the two hours, IR spectra were taken and the carbonyl stretching frequency did not shift. The final IR spectrum had observed carbonyl stretching frequencies of 1953.7 and 1867.9 cm^{-1} . A five milliliter aliquot was removed for solution viscosity measurements. The measured solution viscosity was 0.273 g/dL . The DMAc was removed by a vacuum pump and solvent trap. The yellow crystals weighed 0.5785 g .

i. Reaction of (η^6 -p-phenylenediamine)chromiumtricarbonyl with sebacoyl chloride.

The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The glassware and stir bar were assembled and cooled under nitrogen gas. Anhydrous dimethylacetamide, DMAc, (75 mL) was added with a syringe into the flask under a positive flow of nitrogen gas. A magnetic stirrer was added and set at a moderate rate. (η^6 -p-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) was added to form a yellow solution. The flask was cooled by an ice barh and sebacoyl chloride (0.500 mL, 2.05 mmol) was added slowly to the flask under a positive flow of nitrogen gas. The monomers were reacted for two hours. The IR spectrum after two hours showed a change of about 20 cm^{-1} in the carbonyl stretching frequency. The flask was allowed to warm to room temperature, stirred for two hours and an IR spectrum was taken. During the two hours, IR spectra were taken and the carbonyl stretching frequency did not shift. The IR spectrum of the product had observed carbonyl stretching frequencies of 1953.6 and 1868.0 cm^{-1} . A five milliliter aliquot was removed for solution viscosity measurements. The measured solution viscosity was 0.981 g/dL . The DMAc was removed by a vacuum pump and solvent trap. The yellow crystals weighed 0.7564 g .

j. Reaction of (η^6 -m-phenylenediamine)chromiumtricarbonyl with sebacoyl chloride.

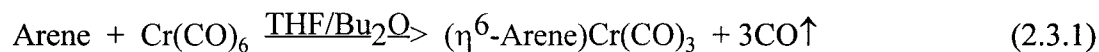
The glassware and stir bar were dried in an oven overnight at one hundred and ten degrees celcius. The glassware and stir bar were assembled and cooled under nitrogen gas. Anhydrous dimethylacetamide, DMAc, (80 mL) was added with a syringe into the flask under a positive flow of nitrogen gas. A magnetic stirrer was added and set at a moderate rate. (η^6 -m-phenylenediamine)chromiumtricarbonyl (0.500 g, 2.05 mmol) was added to form a yellow solution. The flask was cooled by an ice barh and sebacoyl chloride (0.500 mL, 2.05 mmol) was added slowly to the flask under a positive flow of nitrogen gas. The monomers were reacted for two hours. The IR spectrum after two hours showed a change of about 20 cm^{-1} in the carbonyl stretching frequency. The flask was allowed to warm to room temperature, stirred for two hours and an IR spectrum was taken. During the two hours, IR spectra were taken and the carbonyl stretching frequency did not shift. The IR spectrum of the product had observed carbonyl stretching frequencies of 1952.6 and 1868.2 cm^{-1} . A five milliliter aliquot was removed for solution viscosity measurements. The measured solution viscosity was 0.351 g/dL . The DMAc was removed by a vacuum pump and solvent trap. The yellow crystals weighed 0.7082 g .

Chapter Three

Results and Discussion

1. Syntheses and characterizations of the chromium complexed monomers.

Three derivatives of benzenechromiumtricarbonyl were prepared as monomers by the standard reaction methods.^{1b,5} The arenes having two pi-donating substituents, para and meta-phenylenediamines reacted with chromium hexacarbonyl while refluxed in a 10 % THF/Bu₂O solution. It has been proposed that in a solution of Bu₂O/THF a (THF)₃Cr(CO)₃ intermediate forms and which is subsequently converted to (η⁶-arene)Cr(CO)₃.



At room temperature, there was only partial dissolution of the amines and the chromium hexacarbonyl producing a pink solution. As the system was heated, the amines dissolved to produce crimson colored solution and the chromium hexacarbonyl sublimed on the sides and neck of the three-necked flask and eventually in the air condenser. As the mixture approached reflux, the quantity of chromium hexacarbonyl in solution increased and began to react as evident by CO evolution. As the reaction proceeded, the solution slowly changed color from crimson to yellow after several hours. The reactions were monitored by IR spectroscopy and were typically carried out for 40-48 hours. The Cr(CO)₆ has a strong carbonyl stretching at 1980 cm⁻¹ in the infrared region. The reactions were monitored by IR and assumed to be complete when this peak was no longer present. If any unreacted chromium hexacarbonyl was present, it was removed by sublimation into a liquid nitrogen cooled solvent trap under vacuum during

solvent removal or later on the dry solids. The reactions were done under anhydrous conditions under an inert atmosphere of nitrogen gas, 99.999 % pure, to remove carbon monoxide gas that forms as a byproduct. During the reaction, a dynamic flow of dinitrogen gas, approximately 3 mL per minute, was maintained to inhibit air leakage into the system and to prevent inorganic oxide derivatives of chromium from forming. When there was air leaks, oxidation of the chromium produced green chromium complexes. Oxidation, or other decomposition, of the chromium reduces the availability of the chromium hexacarbonyl to produce the arenechromiumtricarbonyl products. The green chromium byproducts may be separated from the product by dissolution in dimethylacetamide, which is weakly polar, and filtering over diatomaceous earth in air.

The quantitative masses for the products, percentage of the theoretical yield, and IR spectra are presented in Table 2.3.1. Each organometallic compound had exclusively NH_2 π -donating substituents coordinated to the arene. As expected the carbonyl stretching frequencies of the phenylenediamine adducts decreased by 20-30 cm^{-1} as expected when compared to (η^6 -benzene)chromiumtricarbonyl's values. The single amino group from the aniline complex produced the smallest change, 22 cm^{-1} , in stretching frequencies while the (η^6 -p-phenylenediamine)complexes decreased the most when compared to the benzene complex. Therefore, (η^6 -p-phenylenediamine)chromiumtricarbonyl is the most electron rich complex and it will have the most stable radical cation. The monomers were also characterized by mass spectrometry.

Mass spectrometry and nuclear magnetic resonance were used to confirm the structure of the organometallic compounds and the data is reported in Table 2.3.2 and Table 2.3.3, respectively. The mass spectra confirmed that each product had the desired stoichiometry and are listed. The molecular ion peak, P^+ , and the peaks due to CO loss, ($\text{P}^+ - n28$) for each CO are identical to calculated values. Each of the organochromium complexes had a broad singlet for the N-H shift and had aryl C-H shifts in the ^1H NMR spectra as expected. The ^{13}C NMR displayed the expected aryl C-C and C-O shifts for the complexes.

Table 2.3.1. Quantitative and IR Data for the Organochromium Monomers.

| <u>Product</u> | <u>Solvent</u> | <u>Yield</u> | <u>Theoretical Yield</u> | <u>IR Spectroscopy</u> | |
|--|---------------------------------|--------------|--------------------------|--------------------------|--------|
| | | (in g) | (in %) | A (in cm ⁻¹) | E |
| (η^6 -C ₆ H ₅ NH ₂)Cr(CO) ₃ | CH ₂ Cl ₂ | mixture | mixture | 1958.9 | 1872.1 |
| (η^6 -p-C ₆ H ₄ (NH ₂) ₂)Cr(CO) ₃ | CH ₂ Cl ₂ | 4.809 | 96.65 | 1948.3 | 1857.1 |
| | DMAc | | | 1934.9 | 1842.5 |
| (η^6 -m-C ₆ H ₄ (NH ₂) ₂)Cr(CO) ₃ | CH ₂ Cl ₂ | 4.755 | 95.57 | 1951.5 | 1863.8 |
| | DMAc | | | 1933.6 | 1843.9 |

Table 2.3.2. Mass Spectral Data for the Organochromium Monomers.

| <u>Product</u> | <u>Mass Spectral Data</u> (m/z) | | | |
|--|---------------------------------|--------------------|---------------------|---------------------|
| | P ⁺ | P ⁺ -CO | P ⁺ -2CO | P ⁺ -3CO |
| (η^6 -C ₆ H ₅ NH ₂)Cr(CO) ₃ | 229 | 201 | 173 | 145 |
| (η^6 -p-C ₆ H ₄ (NH ₂) ₂)Cr(CO) ₃ | 244 | 216 | 188 | 160 |
| (η^6 -m-C ₆ H ₄ (NH ₂) ₂)Cr(CO) ₃ | 244 | 216 | 188 | 160 |

Table 2.3.3. NMR Data for the Organochromium Monomers.

| <u>Product</u> | <u>¹H NMR</u> (in ppm) | | <u>¹³C NMR</u> (in ppm) | |
|--|-----------------------------------|-------------|------------------------------------|----------|
| | N-H | aryl C-H | C-O | aryl C-C |
| (η^6 -C ₆ H ₅ NH ₂)Cr(CO) ₃ | 3.553 | 4.821 5.557 | | |
| (η^6 -p-C ₆ H ₄ (NH ₂) ₂)Cr(CO) ₃ | 3.331 | 5.050 | 211.6 | 116.8 |
| | | | | 138.7 |
| (η^6 -m-C ₆ H ₄ (NH ₂) ₂)Cr(CO) ₃ | 3.593 | 6.054 6.131 | 212.2 | 106.1 |
| | | | | 130.5 |
| | | | | 147.9 |

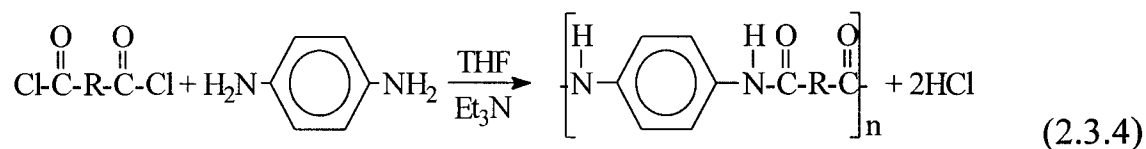
with acid chlorides and isocyanates, but were not characterized because their analogous organic polymers could not be characterized. The uncomplexed model compounds were isolated and proved to be air stable. They precipitated from solution as white precipitates upon addition of the acid chloride. The solutions were stirred for 1-3 hours and filtered in air.

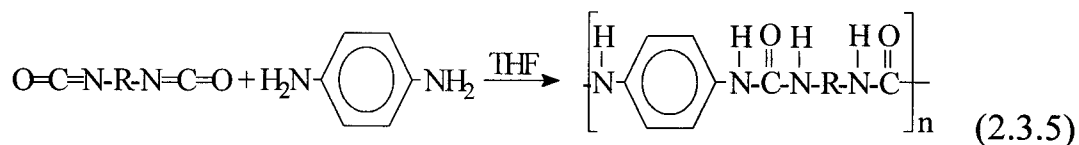
Table 2.3.4. IR Data for the Organochromium Model Compounds.

| <u>Reagents</u> | <u>IR Spectra</u> | |
|--|-------------------|--------|
| | A | E |
| $(\eta^6\text{-p-C}_6\text{H}_4(\text{NH}_2)_2)\text{Cr}(\text{CO})_3 + \text{C}_6\text{H}_5\text{COCl}$ | 1957.8 | 1875.1 |
| $(\eta^6\text{-m-C}_6\text{H}_4(\text{NH}_2)_2)\text{Cr}(\text{CO})_3 + \text{C}_6\text{H}_5\text{COCl}$ | 1959.1 | 1879.4 |
| $(\eta^6\text{-p-C}_6\text{H}_4(\text{NH}_2)_2)\text{Cr}(\text{CO})_3 + \text{C}_6\text{H}_5\text{NCO}$ | 1952.9 | 1869.9 |

3. Syntheses and characterizations of the uncomplexed polymers.

The synthesis of complexed and uncomplexed polymers were done via the low temperature solution polycondensation process by reacting a diamine with a dicarboxylate derivative, (4), or diisocyanate, (5), in solution.¹¹

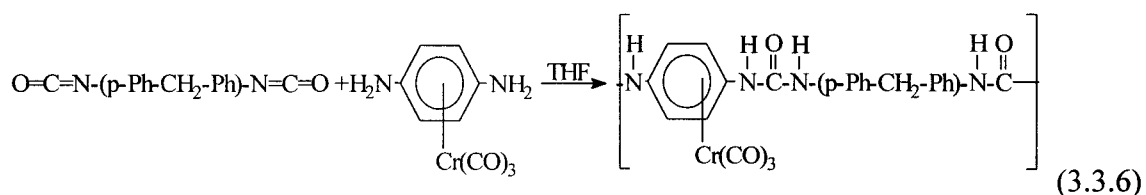




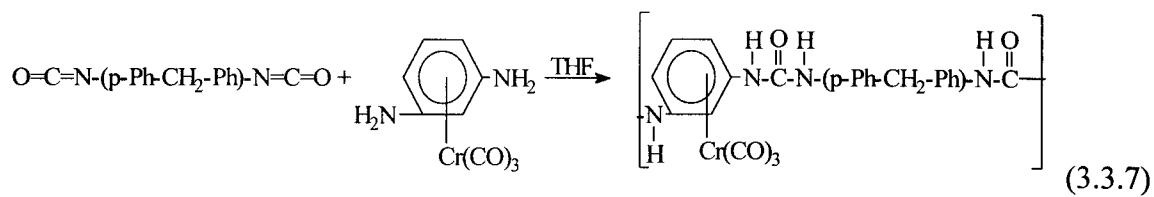
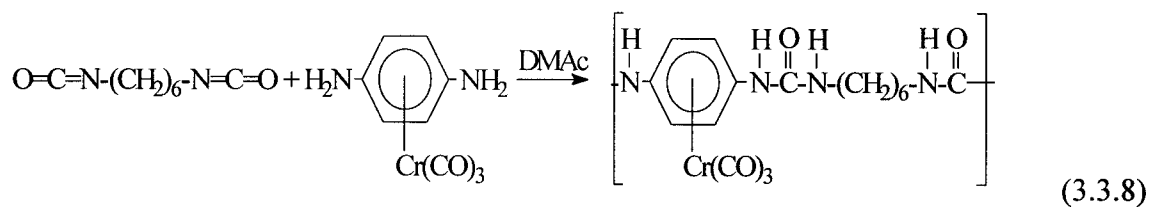
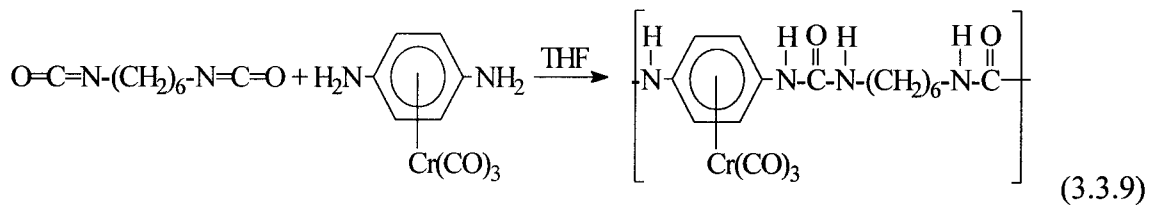
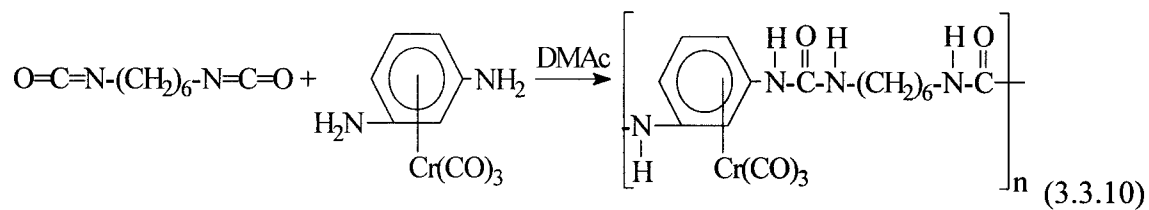
The uncomplexed polymers precipitated from the pink THF solution as a white powder as the diacid chloride or diisocyanate was added dropwise. Gradually, the pink solution became colorless when all of the phenylenediamine reacted. The solution was stirred for 1-3 hours and the white powder was collected by filtration in air. The polymers were insoluble in common organic solvents such as THF, ethanol, dichloromethane, benzene, toluene, carbon disulfide, acetone, and ether. The polymers were slightly soluble in pyridine, dimethylsulfoxide, and dimethylacetamide. The slight solubility was probably due to the low molecular weight fragments that were present. Low molecular weight chains may be expected because the polymer immediately precipitated from solution and limited the capability of the chain to continue to increase in molecular weight. Due to the relative insolubility of the uncomplexed polymers they were not characterized further.

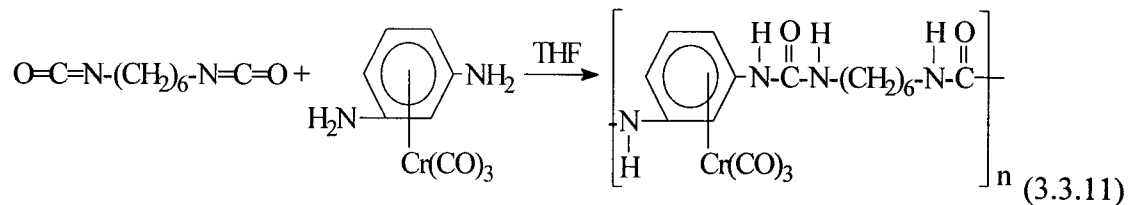
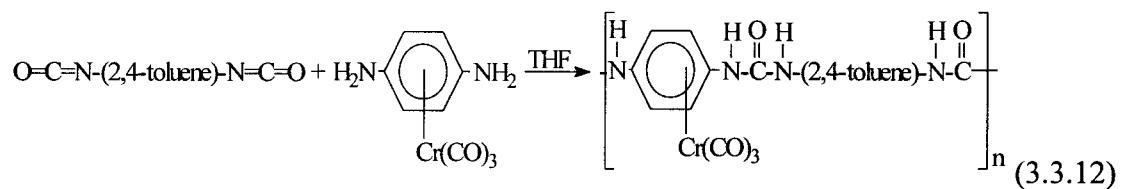
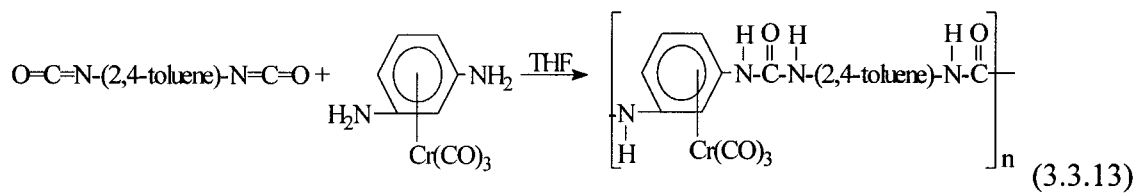
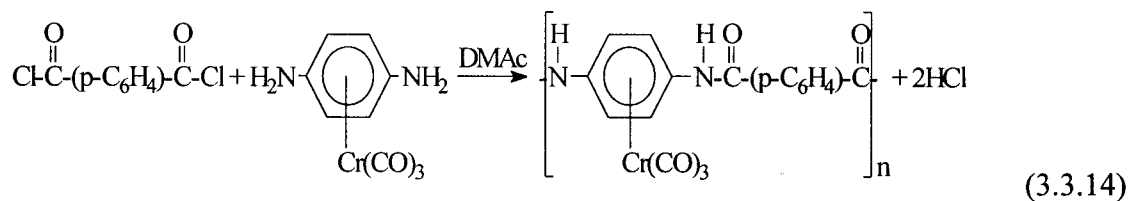
4. Syntheses and characterizations of the chromium complexed polymers.

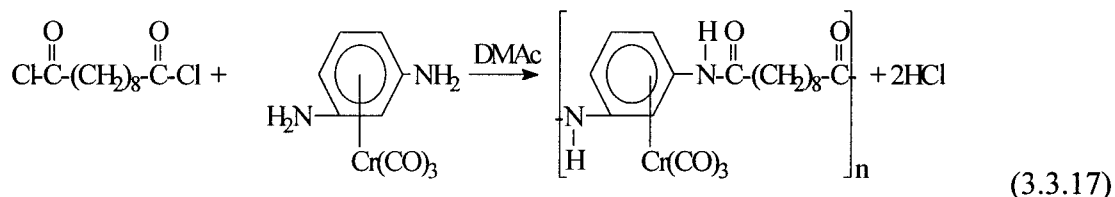
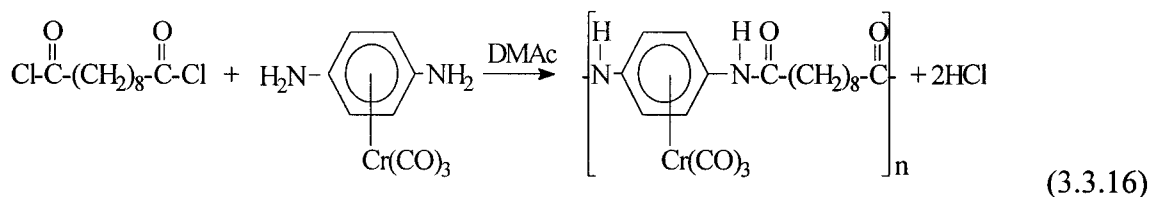
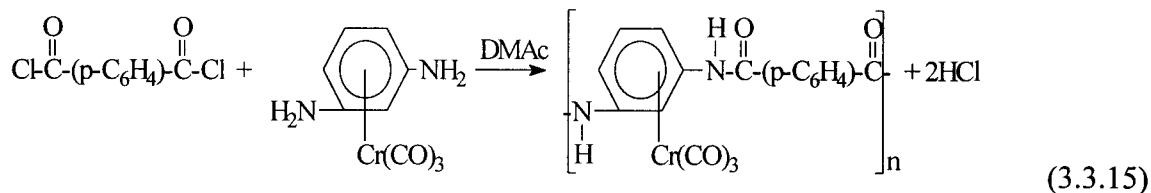
The organochromium polymers were prepared by the solution polycondensation processes that were reported for the uncomplexed polymers, but the polymerizations were done at 0 °C in dimethylacetamide.



Polymer 3.1

**Polymer 3.2****Polymer 3.3****Polymer 3.4****Polymer 3.5**

**Polymer 3.6****Polymer 3.7****Polymer 3.8****Polymer 3.9**



An ice bath was used to regulate the temperature of the reaction because the condensation is an exothermic reaction. The yellow solutions were stirred and the diisocyanate or diacid chloride was added dropwise with a syringe. The reactions were monitored by IR and the polymers were soluble in solution. The diisocyanate reactions were not observed to react at zero degrees celcius so the flasks were allowed to warm to room temperature and then heated to reflux for 12-18 hours to drive the reaction to completion. For the diacid chloride reactions, the carbonyl stretching frequency for chromiumtricarbonyl increased by about 20 wavenumbers. The increase in the carbonyl stretching frequency may be attributed to the newly formed amide linkage, (-NH-CO-). The carbonyl of the

diacid chloride withdraws electron density which reduces the electron richness of chromium. The decrease in electron richness also indicates that there is less back bonding from the metals to the carbonyl group. The diisocyanate reactions exhibited only a slight increase, less than ten wavenumber, in the carbonyl stretching frequency for chromiumtricarbonyl. The smaller shift may be due to a slight stabilization of the diisocyanate carbonyl from an additional secondary amine moiety in the amide linkage, (-NH-CO-NH-). The same trend was evident in the organometallic model compounds. The solubility of the polyamide class of polymers was increased by complexing the polymers with chromium tricarbonyl. The chromiumtricarbonyl may act as a spacer to reduce the amount of intramolecular hydrogen bonding. The organochromium polymers were initially soluble in dimethylacetamide, but they could not be redissolved into solution after they were isolated. The insolubility necessitated removing a ten milliliter aliquot of the solution from the reaction flask and estimating its concentration, based on one hundred percent yield, for viscosity measurements. The viscosity measurements were obtained with a Cannon-Fiske[®] viscometer in a constant temperature bath at 30.0 °C. Workers at Du Pont reported an intrinsic viscosity of 4.52 g/dL with a molecular weight of 78,000. The Mark-Houwink Equation was used to determine the values of K and α through iterations. The iterative values are $\alpha = 1.5$ and $K = 28.5 \times 10^3$. Viscosity measurements were performed only for complexed polymers reacted in DMAc. The iterative values for K and α were extended to all of the polymers for the calculation of the viscosity molecular weights. The reported viscosity molecular weights in Table 2.3.5. were relatively low. The low molecular weights may be attributed to the *in situ* samples used for the viscosity measurements. The solution may contain undesired low molecular weight chains as well as unreacted monomer.

Table 2.3.5. Characterization of the Organochromium Polymers.

| Polymer | IR Sample | Yield (in g) | % Yield (in %) | IR Spectra | | Viscosity (in g/dL) | M_v (in AMU) |
|------------------------------|-----------|-----------------|-------------------|------------|--------------------------|------------------------|-------------------|
| | | | | A | E (in cm^{-1}) | | |
| p-meth Polymer 3.1 | Mul | 0.5679 | 33.24 | 1940.9 | 1850.4 | | |
| m-meth Polymer 3.2 | Mull | 0.6287 | 36.61 | 1939.7 | 1842.1 | | |
| p-hex Polymer 3.3 | DMAc | 0.7433 | 87.96 | 1936.2 | 1842.7 | 0.621 | 13,900 |
| p-hex Polymer 3.4 | Mull | 0.5827 | 68.96 | 1942.3 | 1856.2 | | |
| m-hex Polymer 3.5 | DMAc | 0.3127 | 37.01 | 1932.3 | 1842.4 | 0.393 | 7,000 |
| m-hex Polymer 3.6 | Mull | 0.5348 | 63.29 | 1941.2 | 1850.9 | | |
| p-tol Polymer 3.7 | Mull | 0.5169 | 60.51 | 1942.2 | 1856.2 | | |
| m-tol Polymer 3.8 | Mull | 0.6911 | 80.59 | 1941.7 | 1843.6 | | |
| p-ter Polymer 3.9 | DMAc | 0.6531 | 76.16 | 1954.2 | 1867.8 | .398 | 7,200 |
| m-ter Polymer 3.10 | DMAc | 0.5785 | 67.46 | 1953.7 | 1867.9 | 0.273 | 4,100 |
| p-seb Polymer 3.11 | DMAc | 0.7564 | 76.40 | 1953.6 | 1868.0 | 0.981 | 27,700 |
| m-seb Polymer 3.12 | DMAc | 0.7082 | 71.53 | 1952.6 | 1868.2 | 0.351 | 5,900 |

ter - terephthaloyl chloride

seb - sebacoyl chloride

meth - methylenedi-p-phenyldiisocyanate

tol - toluene diisocyanate

hex - 1,6-diisocyanatohexane

Works Cited

- (1) Jin, J. I.; Kim, R. *Polymer Journal*. **19**, 977-980 (1987).
- (2) (a) Solladie-Cavallo, A. *Polyhedron*. **4**, 901-927 (1985). (b) Hunter, A. D.; Mozol, V.; Tsai, S. D. *Organometallics*. **11**, 2251-2262 (1992). (c) Hunter, A. D.; Shilladay, L.; Furey, W. S.; Zaworotko, M. J. *Organometallics*. **11**, 1550-1560 (1992). (d) Muetterties, E. L. et al. *Chem. Rev.* **82**, 499-525 (1982).
- (3) (a) Lukehart, C. M. *Fundamental Transition Organometallic Chemistry*; Brooks/Cole Publishing, Monterey: California, pp 1-140 (1985). (b) Lumbroso H.; Segard, C.; Roques, B. *Journal of Organometallic Chemistry*. **61**, 249-260 (1973). (c) Neuse, R. W. *Journal of Organometallic Chemistry*. **99**, 287-295 (1975).
- (4) (a) Li, J.; Hunter, A. D.; McDonald, R.; Santarsiero, B. D.; Bott, S. G.; Atwood, J. L. *Organometallics*. **11**, 3050-3055 (1992). (b) Hunter, A. D. Lecture notes, Chemistry 993, Y.S.U., Special Topics in Inorganic Chemistry: Organometallic Chemistry, Spring 1994.
- (5) (a) Solladie-Cavallo, A.; Suffert, J. *Organic Magnetic Resonance*. **14**, 426-430 (1980). (b) Cho, W.; Fernandez, J. L. *Syn. React. Inorg. Metal-Org. Chem.* **4**, 403 (1974).
- (6) (a) Preston, J. *Encyclopedia of Polymer Science and Technology: Supplement Vol. 2*; Interscience Publishers: New York, 1977. (b) Stevens, M. P. *Polymer Chemistry: An Introduction*; Oxford University Press: New York, 1990. (c) Lenk, R. S. *J. Poly. Sci.: Macro. Rev.* **13**, 355 (1978). (d) Mikhailov, N. V.;

- Maiboroda, V. I.; Nikolaeva, S. S. *J. Poly. Sci.* **52**, 245 (1961). (e) Hathaway, C. E.; Early, C. L. *Appl. Poly. Symp.* **21**, 101 (1973).
- (7) (a) Mark, James E. et al. *Physical Properties of Polymers*; American Chemical Society: Washington, D. C., 1984. (b) Campbell, D.; White, J. R. *Polymer Characterization*; Chapman and Hall: New York, 1989. (c) Crompton, T. R. *Analysis of Polymers: An Introduction*; Permamon Press: New York, 1989. (d) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*; John Wiley and Sons Inc.: New York, 1991.
- (8) (a) Dembek, Alexa A. et al. *Polym. Prepr.* **34**, 172 (1993). (b) Dembek Alexa A. et al. US 5,233,004 03 Aug 1993.
- (9) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1987.
- (10) (a) DiMuzio, S. J. *Elementary Inert Atmosphere Techniques*. Compiled and available at Youngstown State University. 1992. (b) Shriver, D. F.; Drezdson, M. A.. *The Manipulation of Air-Sensitive Compounds*; John Wiley and Sons Inc.: New York, 1986. (c) Wayda, A. L.; Darensbourg, M. Y. *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; American Chemical Society: Washington, D. C., 1987.
- (11) Morgan, P. W. *Polymer Reviews Volume 10: Condensation Polymers: By Interfacial and Solution Methods*; Interscience Publishers: New York, 1965.

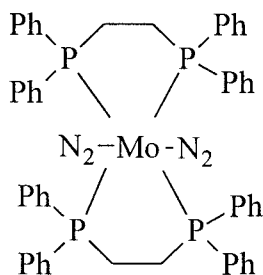
Part Three

Organometallic Polymers From Molybdenum Complexes

Chapter One

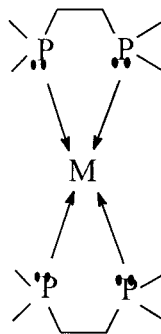
Introduction

Many organometallic compounds containing molybdenum have been reported. In particular dinitrogen-molybdenum complexes have previously been studied because of interest in biological nitrogen fixation. The molybdenum-dinitrogen complex studied in this paper was trans-bis(1,2-bis(diphenylphosphinoethane)dinitrogen) molybdenum (0), trans-[Mo(N₂)₂(dppe)₂].¹



(3.1.1)

This complex has an exclusively trans configuration because both nitrogen and isonitrile ligands are strong trans-directing ligands. The 1,2-bisdiphenylphosphinoethane, dppe, ligand is a bidentate ligand. Each phosphorous atom has a lone pair of electrons in an sp³ hybrid orbital that is donated to the empty σ -symmetry orbital (*i.e.* d²sp³) on the octahedral molybdenum center.²



(3.1.2)

The dinitrogen ligand is a monodentate ligand in these complexes and bonds to the metal in a similar fashion to CO.^{2,3}

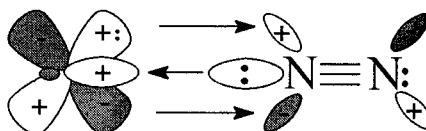
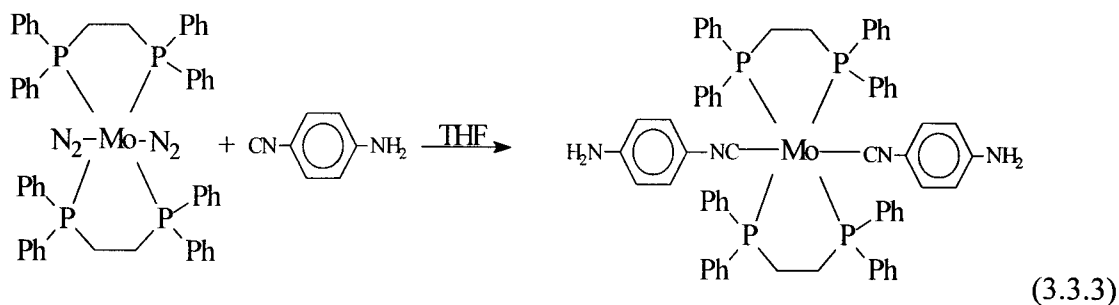


Figure 3.1.1. Dewar-Chatt-Duncanson model for the dinitrogen ligand.

There is sigma donation from a filled sp hybrid orbital of one of the nitrogens to an unfilled metal σ symmetry orbital (*i.e.* d^2sp^3). There is also π -back-bonding from a pair of filled π symmetry d orbital on the metal (*i.e.* d_{xy} , d_{xz} , and d_{yz}) and to a pair of π^* anti-bonding orbitals on the nitrogen. Free dinitrogen is IR inactive, but complexing to a metal results in a strong polarization of the molecule. The polarization leads to the observation of a N-N stretch between $1920\text{-}2150\text{ cm}^{-1}$ and to chemical activation of the dinitrogen ligand. The dinitrogen ligands may be displaced from the complex by refluxing it with stronger complexing ligands such as *p*-isocyananiline under inert atmosphere conditions.^{4,5}



These isocyanide ligands are also isoelectronic to the carbonyl ligands that were described in part 2. The isocyanides are less electronegative than CO and are better σ electron donors and poorer π -acceptors. There is sigma donation from a filled sp hybrid orbital of the isocyanide to an unfilled metal σ symmetry orbital (*i.e.* d^2sp^3). There is also π -back-bonding from a pair of filled π symmetry d orbitals on the metal (*i.e.* d_{xy} , d_{xz} , and d_{yz}) to a pair of π^* anti-bonding orbital on the isocyanide.^{4,5}

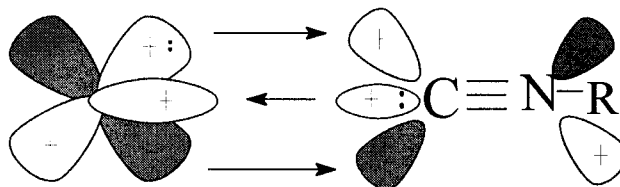


Figure 3.1.2. Dewar-Chatt-Ducanson model of the isocyanide ligand.

In Valence Bond terms, this bonding is again explained through resonance.⁶

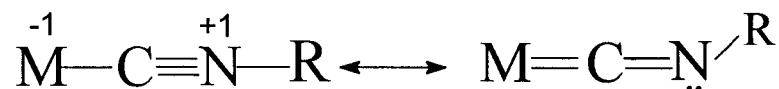


Figure 3.1.6. Valence Bond Theory model for the isocyanide ligand.

Both of the models produce the same conclusions through different depictions. The electron richness of the metal center affects the bond orders for the molybdenum-carbon and carbon to nitrogen bonds. If the electron richness of the metal is increased, there is more π -backbonding and the second resonance form is favored. The molybdenum-carbon bond order increases and the carbon-nitrogen bond order decreases. The electron richness may be measured through infrared spectroscopy.^{4,5,7}

The bifunctional amino complex of molybdenum was used as a monomer in solution condensation reactions. The molybdenum polymers will be compared to its chromium analogues discussed in Part 2. The molybdenum polymers were expected to increase the solubility of the polymers because the bulky dppe ligands would act as intramolecular spacers and limit the amount of hydrogen bonding between chains. The products will be characterized by NMR, IR, and solution viscosity.⁸

Chapter Two

Experimental Section

1. Reagents and reaction conditions.

The reagents and reaction conditions were treated in the same manner as Part 2 in the organochromium section.

2. Syntheses of monomer precursors.

a. Preparation of a 2% sodium/mercury amalgam.

Liquid mercury, Hg, (300 g, 1.50 mol) was poured into a 250 mL filter flask under a flow of nitrogen gas. Sodium (6.01 g, 0.261 mol) was weighed and cut into small pieces. A stir bar was added to the filter flask and a magnetic stirrer was placed below the flask and set at a moderate rate. A safety shield was placed in front of the flask because the addition of the Na is a violently exothermic reaction. The pieces of sodium were each added slowly to the flask. The first few pieces of sodium added resulted in a hissing sound and gas jets appearing as flames. After the first few pieces that were added, there was not any fire but the hissing persisted. After all of the sodium was added the amalgam was stirred until it solidified. The flask was sealed and filled with nitrogen gas and placed in the dark overnight to ensure that it had solidified. The filter flask was placed in a polyethylene bag and cracked to recover the solidified amalgam. The solid was broken apart with a spatula and stored in a schlenk tube until it was used.

b. Synthesis of trans-bis(1,2-bis(diphenylphosphinoethane)dinitrogen) molybdenum (0).

The dppe (10.0 g, 25.1 mmol), and THF (200 mL), were added to the flask under a positive flow of nitrogen gas. The 2 % Na/Hg amalgam (100 g) and molybdenum (V) chloride (3.42 g, 12.52 mmol) were added with magnetic stirring. After 20 hours, the solution was filtered over celite and washed with benzene (200 mL). The solvent was removed by a rotary evaporator. The brown-orange residue was dissolved in benzene (100 mL), filtered through celite and washed with additional benzene (100 mL). Methanol (400 mL) was added to triturate the product, but there were few crystals. The flask was cooled in a freezer. After an hour, many crystals had formed. The benzene and methanol were removed by filtration and the orange crystals (5.463 g, mmol) were dried by vacuum.

c. The formation of p-isocyanoaniline.

p-Phenylenediamine (30.0 g, 0.277 mol), potassium hydroxide (200 g, 3.56 mol), water (800 mL, 44.4 mol), ethanol (120 mL, 2.61 mol), and chloroform (400 mL, 3.35 mol) were mixed in a two liter three-necked round bottom fitted with a condenser in the central neck and glass stoppers in the side necks. A stir bar was added and the joints were greased. The reaction was exothermic, and initially refluxed without heating. After 24 hours, a hot plate was added to maintain the reflux temperature. The solution was allowed to reflux for ninety-six hours. There was an IR peak at 2128 cm^{-1} . The chloroform layer was removed by using a 2 L separatory funnel after the crimson solution had cooled. Three portions of 100 mL each of chloroform was used to extract the aqueous layer. The combined chloroform extracts were dried over anhydrous magnesium sulfate for an hour and the solids were removed by gravity filtration. The chloroform was

concentrated using a rotary evaporator to approximately 200 mL. The residual solution was poured into a 1 L beaker in order for the solvent to evaporate. After five days, a tarry residue remained. A complete yield was not determined because the tar was recrystallized as needed. The tarry residue was recrystallized by a soxhlet extraction using petroleum ether as the solvent. Each portion of the residue was extracted for five days. After extraction, any residue in the extraction thimble that remained was saved for later use. The petroleum ether extract was cooled to zero degrees celcius in a freezer. The white crystals that resulted were collected by filtration. Before use in subsequent reactions, the p-isocyanoaniline was sublimed under vacuum.

3. Synthesis of trans-1,2-bis(diphenylphosphinoethane)bis(p-isocyanoaniline) molybdenum (0)

THF (100 mL) was added under a positive flow of nitrogen gas. $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ was recrystallized and p-isocyaniline was sublimed prior to the reactions. $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ (3.63 g, 3.81 mmol) and p-isocyanoaniline (0.802 g, 6.79 mmol) were added to the flask. Additional THF (100 mL) was added. The solution was stirred for half an hour at a moderate rate. Gradually the solution appeared to gain a red tint. The flask was heated to reflux and left to react overnight under an inert atmosphere. After twenty hours, the red solution with red precipitate was cooled to room temperature. The precipitate was collected by filtration and the red solution also yielded additional crystals after the solvent volume was reduced. The dark red crystals weighed 0.217 g. The IR stretching was 1900.7 cm^{-1} .

4. Syntheses of the organic models.

a. Reaction of 4,4'-methylenedianiline with hexyl isocyanate.

THF (200 mL) and 4,4'-methylenedianiline pellets (3.13 g, 15.8 mmol) were added to a flask under a positive flow of nitrogen gas. The solution was stirred at a moderate rate. Then hexyl isocyanate (3.50 mL, 31.6 mmol) was added. A white precipitate formed after three hours. The solution was stirred for a total of seventy-two hours. Some of the THF was removed by in vacuo and the white precipitate was collected by filtration and washed with hexane and acetone.

b. Reaction of 4,4'-methylenedianiline with phenyl isocyanate.

THF (150 mL) and 4,4'-methylenedianiline (1.82 g, 9.20 mmol) were added and stirred at a moderate rate. Then phenyl isocyanate (2.0 mL, 18.4 mmol) was added dropwise to the solution. A white precipitate formed after ten minutes. The solution was stirred for a duration of twenty hours. The THF was removed by a vacuum pump and the white precipitate was washed with hexane and acetone.

c. Reaction of 4,4'-methylenedianiline with benzoyl chloride.

THF (200 mL) and triethylamine (20 mL) were added to the flask under a positive flow of nitrogen gas. 4,4'-methylenedianiline (1.82 g, 9.20 mmol) was added and stirred at a moderate rate. Then benzoyl chloride (2.15 mL, 18.4 mmol) was added dropwise to the solution. A white precipitate and fumes from the hydrogen chloride gas were apparent upon addition of the benzoyl chloride. The solution was stirred for a duration of twenty hours. The precipitate was collected by filtration, washed with hexanes and acetone, and dried under vacuum.

d. Reaction of 4,4'-methylenedianiline with valeryl chloride.

THF (150 mL) and triethylamine (25 mL) were added to the flask under a positive flow of nitrogen gas. 4,4'-methylenedianiline (1.671 g, 8.43 mmol) was added and stirred at a moderate rate. Then valeryl chloride (2.00 mL, 16.9 mmol) was added dropwise under a positive flow of nitrogen gas. A white precipitate and white fumes from hydrogen gas were visible upon addition of the valeryl chloride. The solution was stirred for twenty hours. There was a slight yellow tint to the solution. The white precipitate was collected by filtration with a Buchner funnel. Then the white solid was washed with hexanes and acetone and dried under vacuum.

5. Syntheses of the organic polymers.

a. Reaction of 4,4'-methylenedianiline with 1,6-diisocyanatohexane.

THF (200 mL) and 4,4'-methylenedianiline (2.461 g, 12.3 mmol) were added and stirred at a moderate rate. Then 1,6-diisocyanatohexane (2.0 mL, 12.4 mmol) was added dropwise. A white precipitate formed immediately. The solution was stirred for a duration of twenty hours. The precipitate was collected by filtration and washed with hexane and acetone.

b. Reaction of 4,4'-methylenedianiline with terephthaloyl chloride.

THF (150 mL) and triethylamine (25 mL) were added to the flask under a positive flow of nitrogen gas. 4,4'-methylenedianiline (2.44 g, 12.3 mmol) was added under a positive flow of nitrogen gas and stirred at a moderate rate. Then 2.50 g (12.3 mmol) of terephthaloyl chloride was added dropwise under a positive flow of nitrogen gas. A white precipitate and white fumes from the hydrogen chloride gas that evolved formed immediately upon addition of terephthaloyl chloride. The solution was stirred for twenty

hours. The precipitate was collected by filtration with a Buchner funnel, washed with hexanes and acetone, and dried under vacuum.

c. Reaction of 4,4'-methylenedianiline with sebacoyl chloride.

THF (200 mL) and triethylamine (15 mL) were added to the flask and stirred at a moderate rate. 4,4'-methylenedianiline (1.859 g, 9.38 mmol) was added under a positive flow of nitrogen gas. Then sebacoyl chloride (2.0 mL, 9.38 mmol) was added dropwise to the solution. The solution was stirred for eighteen hours. The precipitate was collected by filtration with a Buchner funnel, washed with hexanes and acetone, and dried under vacuum.

6. Syntheses of the organometallic polymers.

a. Reaction of trans-1,2-bis(diphenylphosphinoethane)bis(p-isocyanoaniline) molybdenum (0) with sebacoyl chloride.

Anhydrous dimethylacetamide, DMAc (20 mL), was added with a syringe into the flask and was stirred at a moderate rate. Trans-1,2-bis(diphenylphosphinoethane)bis(p-isocyanoaniline) molybdenum (0) (0.502 g, 0.445 mmol) was added to form a red solution. The flask was cooled by an ice bath and sebacoyl chloride (0.0949 mL, 0.445 mmol) was added slowly to the flask under a positive flow of nitrogen gas. The monomers were reacted for two hours. The IR spectrum after two hours showed a change, of about 6 cm^{-1} , in the isonitrile stretching frequency. The flask was allowed to warm to room temperature, stirred for two hours with no further change in the IR spectrum. A five milliliter aliquot was removed for solution viscosity measurements.

The measured solution viscosity was 0.117 g/dL. The DMAc was removed in vacuo and the red solid weighed 0.082 g. The IR stretching frequency was 1906.8 cm^{-1} .

b. Attempted Reaction of trans-1,2-bis(diphenylphosphinoethane)bis(p-isocyanobenzene) molybdenum (0) with terephthaloyl chloride.

Anhydrous dimethylacetamide, DMAc (20 mL), was added with a syringe into the flask and was stirred at a moderate rate. Trans-1,2-bis(diphenylphosphinoethane)bis(p-isocyanobenzene) molybdenum (0) (0.500 g, 0.444 mmol) was added to form a red solution. The flask was cooled by an ice bath and terephthaloyl chloride (0.0902 g, 0.444 mmol) was added slowly to the flask under a positive flow of nitrogen gas. The monomers were reacted for two hours. The IR spectrum after two hours did not show a change in the isocyanide stretching frequency. The flask was allowed to warm to room temperature, stirred for two hours and an IR spectra was taken. During the next two hours, IR spectrum were taken and the isocyanide stretching frequency did not shift. The reaction flask was slowly heated to reflux and left to react for eighteen hours. However, the NC stretching did not change. The solution was discarded.

c. Attempted Reaction of trans-1,2-bis(diphenylphosphinoethane)bis(p-isocyanobenzene) molybdenum (0) with 1,6-diisocyanatohexane.

Anhydrous dimethylacetamide, DMAc (20 mL), was added with a syringe into the flask and stirred at a moderate rate. Trans-1,2-bis(diphenylphosphinoethane)bis(p-isocyanobenzene) molybdenum (0) (0.505 g, 0.446 mmol) was added to form a red solution. The flask was cooled by an ice bath and 1,6-diisocyanatohexane (0.0750 mL, 0.446 mmol) was added slowly to the flask under a positive flow of nitrogen gas. The monomers were reacted for two hours. The IR spectrum after two hours did not show a

change in the isonitrile stretching frequency. The flask was allowed to warm to room temperature, stirred for two hours and an IR spectrum was taken. During the next two hours, IR spectra were taken and the isonitrile stretching frequency did not shift. The flask was heated to reflux to accelerate the reaction and left to react overnight. An IR spectrum was taken. There was not a CN peak.

Chapter Three

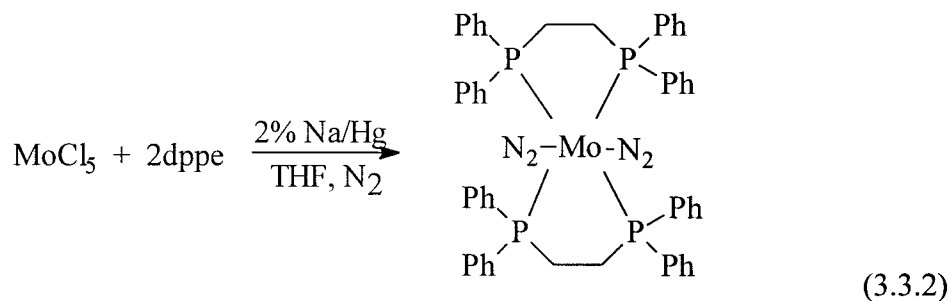
Results and Discussion

1. Syntheses and characterizations of starting reagents.

Reagents had to be synthesized to prepare the monomer, trans-1,2-bis(diphenylphosphinoethane)bis(p-isocyanoaniline) molybdenum (0). A 2 % Na/Hg amalgam was prepared from mercury and sodium metals.

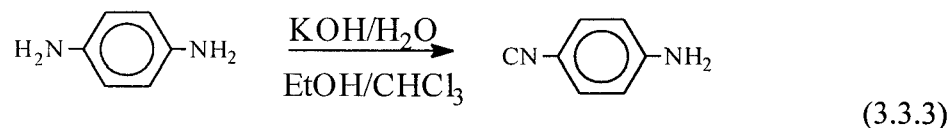


The 2 % Na/Hg amalgam was used as a reducing agent to synthesize trans-1,2-bis(diphenylphosphinoethane)dinitrogen molybdenum (0).



The reagents were added to the flask and stirred to produce a yellow solution. The solution gradually darkened to an orange color over twenty hours. The THF was removed and the product was crystallized from benzene. The solid was separated by filtration and the orange crystals weighed 5.46 g, 22.9% yield. The product was identified by its IR spectrum. There was an observed dinitrogen stretching frequency at 1975.7 cm^{-1} .

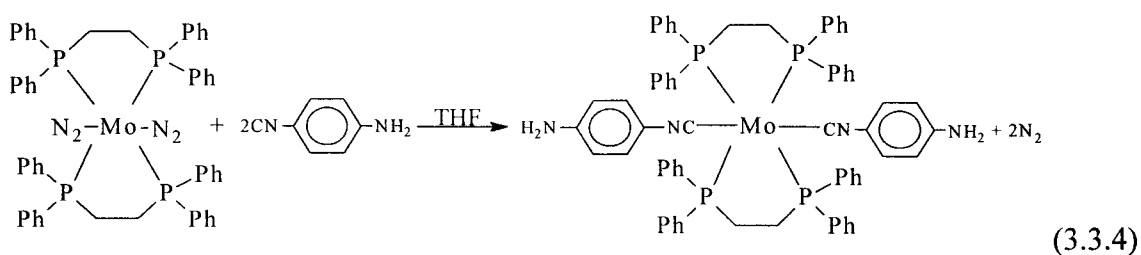
p-Isocyanoaniline was prepared from p-phenylenediamine in the presence of potassium hydroxide.



The reagents were added and there were two visible immiscible layers from the aqueous and organic solvents. The solutions were stirred for 96 hours. IR spectroscopy displayed a characteristic isonitrile stretching frequency of 2128 cm^{-1} . The tarry product was purified by soxhlet extraction using petroleum ether to produce a yellow solution. The petroleum ether was cooled in a freezer and yellow crystals formed. A quantitative yield was not obtained because all of the tarry residue was not recrystallized at once and the p-isocyanoaniline was sublimed prior to use in further reactions as needed. A ^1H NMR spectrum was recorded in CDCl_3 . The N-H shift was a singlet at 3.93 ppm. The aryl C-H shifts were doublets at 6.58 and 7.16 ppm.

2. Synthesis and characterization of trans-1,2-bis(diphenylphosphinoethane)bis(p-isocyanoaniline) molybdenum (0)

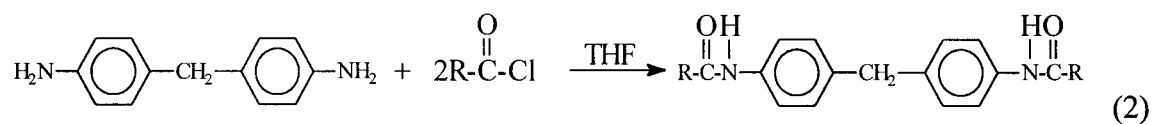
Trans-bis(1,2-bis(diphenylphosphinoethane)dinitrogen) molybdenum (0) was recrystallized and p-isocyanoaniline was sublimed prior to the reaction.



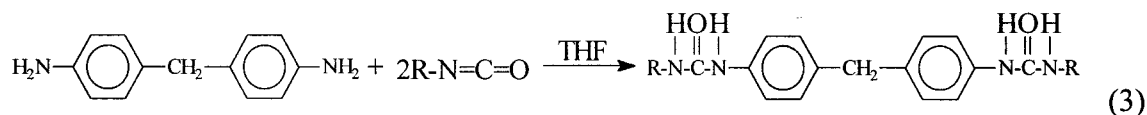
Gradually the orange reaction solution appeared to gain a red tint after half an hour and was heated to reflux. After 20 hours, the red solution was cooled and red crystals formed. The crystals were collected in a yield of 0.217 g, 2.94% yield. The IR stretching for the complex was 1900.7 cm^{-1} . The isonitrile stretching frequency decreased when it complexed because back-bonding to molybdenum increased as the metal became more electron rich.

3. Syntheses of the organic models.

The model compounds were prepared by two different methods. The first method was to react 4,4'-methylenedianiline with an acid chloride in solution under anaerobic and anhydrous conditions. Triethylamine was used in these reactions as an acid acceptor to neutralize the HCl that evolves so that the acid does not attack the product.^{1,6}



The second method to prepare the model compounds involved reacting 4,4'-methylenedianiline with an isocyanate in solution under inert and anhydrous conditions.^{6,7}

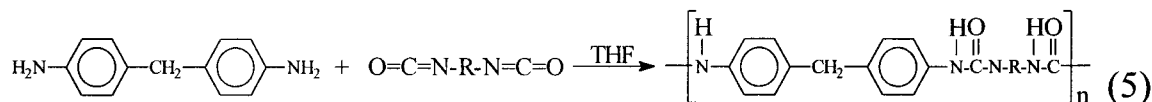
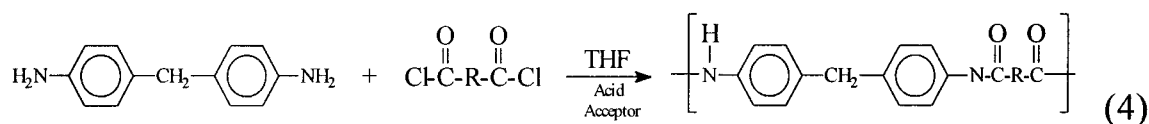


Uncomplexed phenylenediamines were reacted with acid chlorides and isocyanates, but were not further characterized because their analogous organic polymers could not be characterized because of their insolubility in common solvents. The uncomplexed model

compounds were isolated and proved to be air stable. They precipitated from solution as white precipitates upon addition of the acid chloride. The solutions were stirred for 1-3 hours and filtered in air.

4. Syntheses and characterizations of the organic polymers.

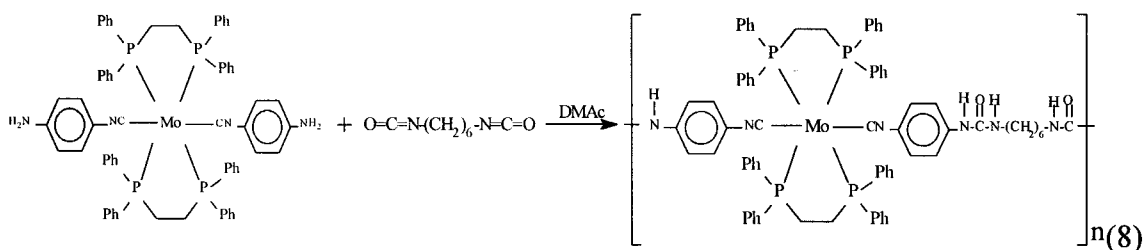
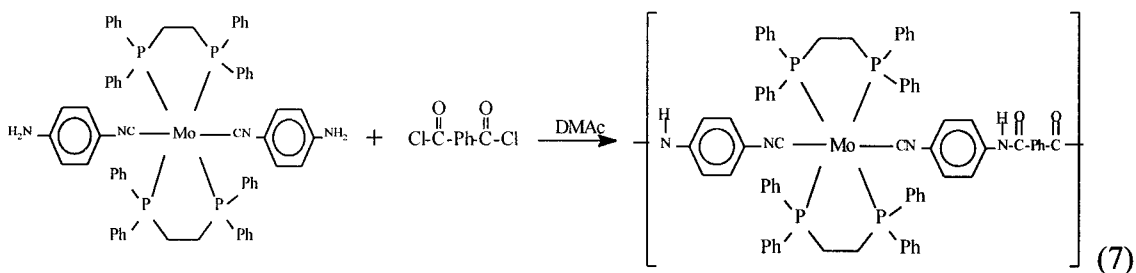
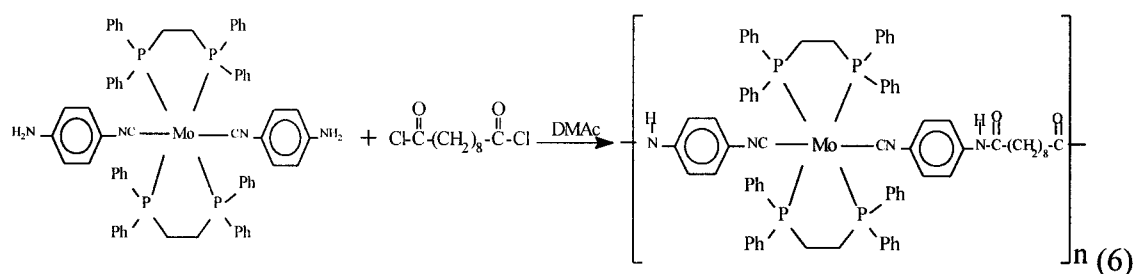
The synthesis of complexed and uncomplexed polymers were done via the low temperature solution polycondensation process by reacting a diamine with a dicarboxylate derivative, (4), or diisocyanate, (5), in solution.¹¹



The uncomplexed polymers precipitated from the THF solution as white powders and were collected by filtration in air. The polymers were insoluble in common organic solvents such as THF, ethanol, dichloromethane, benzene, toluene, carbon disulfide, acetone, and ether. The polymers were slightly soluble in pyridine, dimethylsulfoxide, and dimethylacetamide. The slight solubility was probably due to the low molecular weight fragments that were present. Low molecular weight chains may be expected because the polymer immediately precipitated from solution and limited the capability of the chain to continue to increase in molecular weight. Due to the relative insolubility of the uncomplexed polymers they were not characterized further.

5. Syntheses and characterizations of the molybdenum complexed polymers.

The organomolybdenum polymers were prepared by the solution polycondensation processes that were reported for the uncomplexed polymers, but the polymerizations were done at 0 °C in dimethylacetamide.



An ice bath was used to regulate the temperature of the reaction because the condensation is an exothermic reaction. The red solutions were stirred and the diisocyanate or diacid

chloride was added dropwise with a syringe. The reactions were monitored by IR and the polymers were soluble in solution. The diisocyanate reactions were not observed to react at zero degrees celcius so the flasks were allowed to warm to room temperature and then heated to reflux for 12-18 hours to drive the reaction to completion. For the diacid chloride reaction, the isonitrile stretching frequency for the complex increased by about 6 wavenumbers. The IR stretching frequency was 1906.8 cm^{-1} . The increase in the isonitrile stretching frequency may be attributed to the newly formed amide linkage, (-NH-CO-). The carbonyl of the diacid chloride withdraws electron density which reduces the electron richness of molybdenum. The decrease in electron richness also indicates that there is less back bonding from the metals to the isonitrile group. It was difficult to prepare the molybdenum monomer. Only three polymerizations were attempted because the amount of molybdenum monomer was the limiting factor. Only the reaction with sebacoyl chloride provided data. The organomolybdenum polymers were initially soluble in dimethylacetamide, but they could not be redissolved into solution after they were isolated. The insolubility necessitated removing a ten milliliter aliquot of the solution from the reaction flask and estimating its concentration for viscosity measurements. The viscosity measurements were obtained with a Cannon-Fiske[®] viscometer in a constant temperature bath at $30.0 \text{ }^\circ\text{C}$. Workers at Du Pont reported an intrinsic viscosity of 4.52 g/dL with a molecular weight of 78,000. The Mark-Houwink Equation was used to determine the values of K and α through iterations. The iterative values are $\alpha = 1.5$ and $K = 28.5 \times 10^3$. Viscosity measurements were performed only for complexed polymers reacted in DMAc. The solution viscosity for the molybdenum-sebacate polymer was 0.127 g/dL . The viscosity molecular weight was 7,000 atomic mass units. The low viscosity molecular weight may be attributed to unreacted monomer or low molecular weight chains in the sample because the sample was removed directly from the reaction flask.

Works Cited

- (1) (a) Chatt, J.; Heath, G. A.; Leigh, G. J. *J. Chem. Soc. Chem. Commun.* 534 (1972). (b) George, T. A.; Siebold, C. D. *Inorg. Chem.* **12**, 2548 (1973). (c) George, T.A.; Noble, M. E. *Inorg. Chem.* **117**, 1678-1679 (1978). (d) Hidai, M. et al. *Chem. Commun.* 814 (1969). (e) Wang, Xiaochun.
- (2) (a) Huheey, J. E. *Inorganic Chemistry: Principles of structure and reactivity*; HarperCollins Publishers: New York, 1983. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley and Sons Inc.: New York, 1994.
- (3) Douglas, B.; McDaniel, D.; Alexander, J. *Concepts and Models of Inorganic Chemistry*; John Wiley and Sons Inc.: New York, 1994.
- (4) (a) Chatt, J. et al. *J. Chem. Soc. Chem. Commun.* 708 (1975). (b) Chatt, J. et al. *J. Chem. Soc. Dalton. Trans.* 165 (1978). (c) Pombeiro, A. J. L.; Richards, R. L. *J. Organomet. Chem.* **179**, 459 (1979). (d) Singleton, E.; Oosthuizen, H. E. *Adv. in Organomet. Chem.* **22**, 209-310 (1983).
- (5) Yamamoto, Y.. *Coord. Chem. Rev.* **32**, 193-233 (1983).
- (6) (a) Green II, J. A.; Hoffman, P. T.; Ugi, I. ed. *Isonitrile Chemistry*; Academic Press: New York, 1971. (b) Treichel, P. M. *Adv. in Organomet. Chem.* **11**, 21 (1973).
- (7) Cotton, F. A.; Zingales, F. *J. Amer. Chem. Soc.* **83**, 351 (1961).

- (8) (a) Preston, J. *Encyclopedia of Polymer Science and Technology: Supplement Vol. 2*; Interscience Publishers: New York, 1977. (b) Stevens, M. P. *Polymer Chemistry: An Introduction*; Oxford University Press: New York, 1990. (c) Lenk, R. S. *J. Poly. Sci.: Macro. Rev.* **13**, 355 (1978). (d) Mikhailov, N. V.; Maiboroda, V. I.; Nikolaeva, S. S. *J. Poly. Sci.* **52**, 245 (1961). (e) Hathaway, C. E.; Early, C. L. *Appl. Poly. Symp.* **21**, 101 (1973).

Part Four

Conclusion

The organometallic polymers were synthesized and characterized. The organometallic polymers were not stable in solution when exposed to air and were stable as solids in air for a few days. The organometallic fragments within the polymers increased the solubility of the organometallic polymers compared to their organic analogues. The increased solubility may be attributed to the organometallic moieties role as spacers to hinder hydrogen bonding. The organometallic polymers were slightly soluble in pyridine and soluble in dimethylacetamide when formed. However, the polymers could not be redissolved. The viscosity molecular weights were low, but that may be attributed to the sample itself.

In the future, other organometallic monomers may be used to develop different series of polymers. The work with the organomolybdenum should be extended for a larger range of polymers. Time constraints limited the current work.. Better estimates of molecular weight are needed to characterize the polymers. Gel permeation chromatography or light scattering is needed to produce better estimates of molecular weight as well as determine values for K and α for the Mark-Houwink Equation. Physical properties and their relationship to the molecular weight of the polymer may also be examined in the future.