SAUNDERS, JOSHUA DANIEL. Novel Supramolecular Polyamides. (Under the supervision of Richard Kotek)

Abstract

The objective of this research is to use low DP poly(p-benzamide) (PBA) segments, terminated by units forming supramolecular bonds, able to extend the overall DP of the aromatic polyamide. PBA fibers, and the related industrially produced PPTA (Kevlar), exhibit their most interesting ultra-high strength properties only when a considerably large DP (>100) is attained. Use of cumbersome and expensive syntheses and solvents are required to attain DP in the range (~200-300) of industrial interest. Moreover, the fully covalent polymers thus far produced are highly insoluble in common organic solvents. On the other hand, easier processing becomes feasible if the DP of conventional PBA (prepared by the Yamazaki reaction) is increased by supramolecular bonding through ionic or hydrogen bond interactions. The effects of three different binding methods were first investigated on short rigid monomers with promising results the same binding was then used on rigid segments of PBA. The binding methods used two diamine binders triethylenediame (TED) and bipiperidine (Bipip) to form ionic bonds with the monomer, and polymer segments. The last method utilized a 2(6-iso cyanato hexylamino carbonyl amino)-6-methyl-4[1H]pyrimidinone (Upy) end group covalently bonded to the PBA polymer. This end group has the ability to form 4 hydrogen bonds with itself and thus could be used to increase the overall DP of the polymer starting material. This is believed to be the first recorded hydrogen bonded supramolecular interaction in amide type solvents. The novel and revolutionary idea of using low DP segments of PBA to increase the overall DP of polymer could be an industrially viable way to produce the highly sought after industrial polyamides.

Novel Supramolecular Polyamides

By

Joshua D. Saunders

A Thesis Submitted to the Graduate Faculty of

NORTH CAROLINA STATE UNIVERSITY

in Partial Fulfillment of the Requirements for the Degree of

Master of Science in

Textile Chemistry

June 2005

APPROVED BY

Chair of Advisory Committee

Committee Member

Committee Member

Committee Member

Biography:

Joshua Saunders was born in Gastonia, North Carolina on 2nd of February, 1980. Graduating from North Gaston high school, he was accepted to the Textile Engineering, Chemistry, and Science Department as well as Chemistry Department at North Carolina State University in 1999. Graduating in 2003, he received his bachelor of science in both Textile Chemistry and Chemistry.

He was admitted to the graduate school of North Carolina State University in 2003 and began his master's work at North Carolina State University, in Textile Chemistry (Polymer Chemistry) degree program.

Acknowledgements:

I am thankful to my advisor, Dr. Richard Kotek, who has advised me during the different steps of my work and who always encouraged me to push the research during the difficult times. My sincere and deep thanks to Dr. Samuel Hudson, whose many discussions on the research helped to create solutions to difficult problems that arose during the work along with the many rousing conversations about politics and science. I am thankful to Kyeong Pang, for the many things that I learned from the time spent working with her in the lab. I would like to thank Dr. Christian Melander, for agreeing to be a representative of my committee and for his insightful comments. I would like to thank my family members who have supported me through out my colligate career: My father Joel Saunders, who has been there through the good and bad times, and always knows how to make me smile; My mother, for her caring and concern during the many years of my collegiate education. I want to thank all of my friends from home and those I met in college for their support and understanding. I, furthermore, would like to thank my dearest friends: Daniel Pope, who was there lending support to my research; Tim and Julie Bollinger, who gave me encouragement while I completed my research; Svetlana Verenich and Hooman Vahedi Tafreshi for their valuable insights into the many different aspects of my work. I would last like to thank the most important person in my life: My beautiful and immensely sweet wife for her love, support, and understanding during the difficult process of completing this thesis, without whom I would have never been able to complete my work.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. Introduction and Definitions Associated with Supramolecular Polymers

1.1. Introduction

Over the years much work [1-8] has been done on supramolecular polymerization [1]. Supramolecular polymerization is defined as the process of using bifunctional unimers to form long chain sequences held together by only non-covalent forces [1]. The term supramolecular polymer can be loosely defined as a network or system made up of non-covalent interactions through out the chain [1]. The aims of this chemistry are to produce highly complex chemical systems and advanced materials emphasizing an array with its components held together by only intermolecular forces instead of the conventional covalent bonding seen in synthetic materials. This allows for a new and exciting class of materials to emerge into commercial production. In most of the literature in this area, it is suggested that the properties of such materials are highly reliant on the interaction and relationship of the components used to form such networks and arrays [9]. Using the definition of supramolecular chemistry, it can easily be seen how this can be seen as a dynamic chemistry and the interaction of the molecules that make up a supramolecular entity [3]. This is because the supramolecular interactions associated with this type of chemistry allow for the discovery of compounds that can interact without side stimuli from surroundings and environment, which incorporate many novel features to such systems [9].

Also a series of classifications are needed to properly describe and understand such novel materials. This can be achieved by dividing supramolecular polymers into four classes,

which define the different systems, used to form the complex arrays of supramolecular polymeric materials and example arrays can be seen in Figure 1.1.

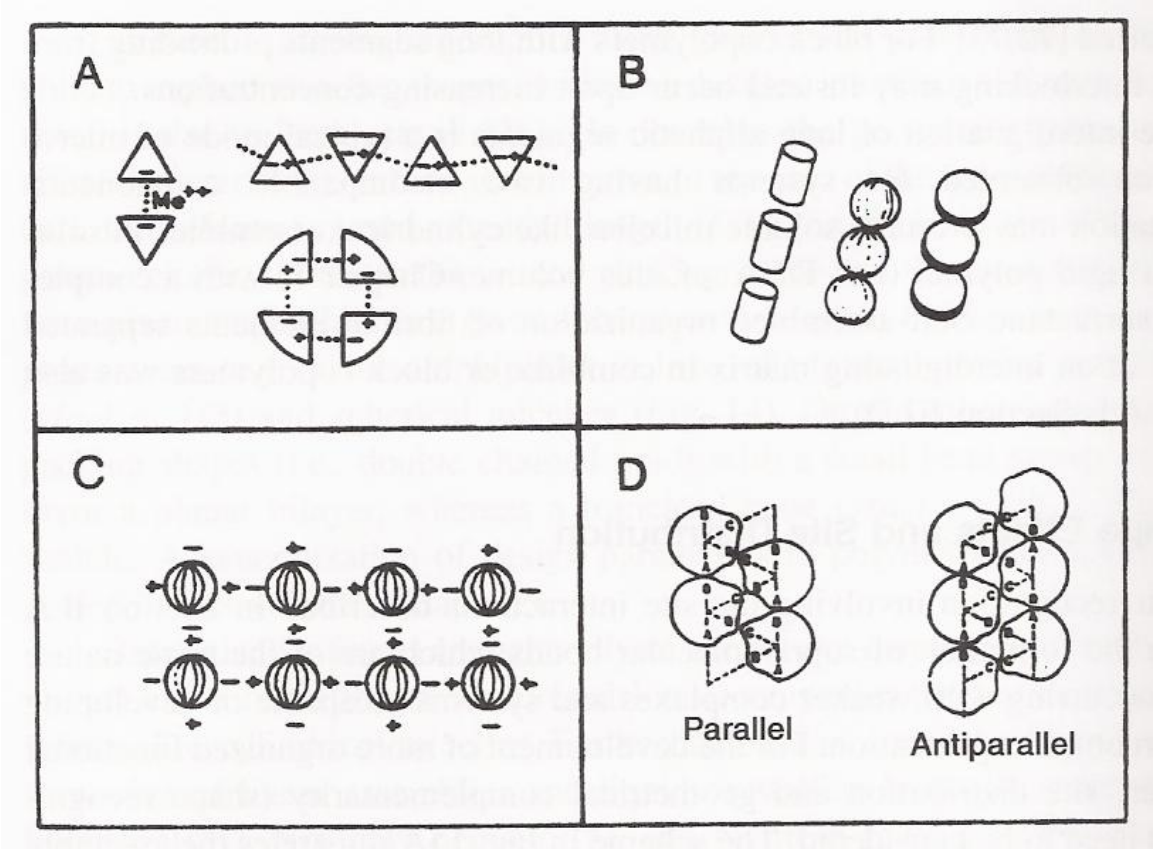


Figure 1.1. Geometric Arrays

Schematic assemblies of (A) triangular units with monofunctional and bifunctional binding sites; (B) cylindrical, spherical, disklike units forming linear sequences; (C) spherical units with and equatorial distribution of binding sites forming a planar assembly; (D) asymmetrical site distribution generating helical assemblies. (from [7])

1.1.1. Class A. It can be defined as systems that use equilibrium to form polymers. This class can include unimers with functionality greater than 2 and examples can include hydrogen bonded, coordination, and micelles [1]. Examples of complex geometries included in this class are those with helical, columnar, and tubular type geometry (Figure 1.1). Composites made up of block copolymers are also included within this class [1].

1.1.2. Class B represents those with self-assembling structures containing monofunctional unimers utilizing noncovalent forces for binding [1]. This includes the host/guest species as well as those possessing side chain bindings of the monofunctional unimer to that of a covalent polymer chain. Other examples of this would be double and triple chain assemblies from side group interactions as shown in Figure 1.2.

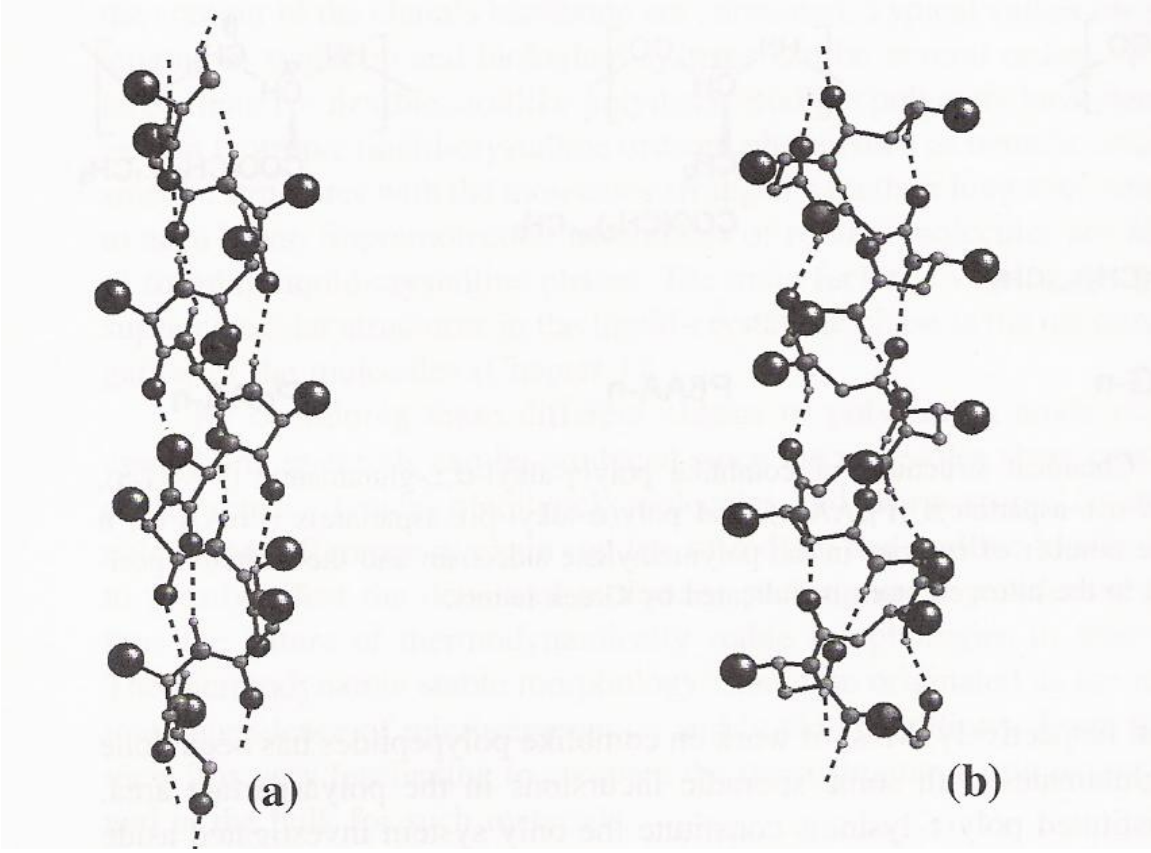


Figure 1.2. Helical Arrays

(a) The 18/5 right-handed α helix typical of poly(α,L-peptide)s. (b) The 13/4 right-handed pseudo-α-helix observed in poly(α-alkyl-β,L-aspartate)s. In both helices the hydrogen bond scheme is set between every third amide group but counted at opposite directions with respect to the directionality of the main chain. The larger spheres represent the side chains and hydrogen bonds are indicated as dotted lines (from [7]).

1.1.3. Class C includes the supramolecular polymers utilizing superimposition of covalent and supramolecular bonds [1]. These systems are shown to be self-assembling but contain irreversible interactions. This includes both assemblies that form supramolecular bonds and then subsequently form covalent bonds and those that form covalent bonding before the supramolecular bonding [1].

1.1.4. Class D. The fourth and the last are those in which the assemblies do not spontaneously form ordered structures under normal conditions, but rely on synthesis or a set of controlled methods of deposition to finally form supramolecular interactions [1].

All the following topics include details either directly or indirectly related to supramolecular chemistry and supramolecular polymerizations. This dissertation discusses many theories and demonstrates the varying classes and gives many unique applications in which supramolecular materials could be utilized. Supramolecular chemistry could provide powerful contributions and solutions to the fields of nanoscience and nanotechnology. This could then lead to the development of novel nanomaterials and smart materials. There are many expectations that could one day be met with the marriage of supramolecular chemistry with that of polymer chemistry.

This dissertation consists of six chapters. Chapter two is an overview of previous works related to supramolecular arrays. Chapter three discusses the results related to the experimental work utilizing N,N'-bis(p-carboxylphenyl) terephthamide monomer with treatment of diamine binders to form supramolecular polymers consisting of rigid rod segments. In Chapter four, the work with poly(p-benzamide) as the starting component of a supramolecular polymer made up of short chain polyamide segments combined with

various binders is discussed. In Chapter five, conclusions are presented. Chapter six contains communications for future work.

1.2. References

1. Cavalleri P., Ciferri A., Dell'Erba C., Marino N., Purevsuren B., *Macromolecules,* 30, 3513-3518,(1997)
2. Aharoni S. H., Hammond W. B., Szobota J. S., Masilamani D., *J. Polym. Sci. Polym. Chem. Ed.,* 22, 2579-2599, (1984)
3. Balbi C., Bianchi E., Ciferri A., Tealdi A., *J. Polym. Sci. Poly. Phy. Ed.,* 18, 2037-2053, (1980)
4. Brunsveld L., Folmer B. J. B., Meijer E. W., Sijbesma R. P., *Chem. Rev.,* 101, 4071-4097, (2001)
5. Ciferri A, *Macromol. Rapid Commun.,* 23, 511-529, (2002)
6. Ciferri A., *Recent Res. Devel. Macromol.,* 6, 129-147, (2002)
7. Ciferri A. Ed., *Supramolecular Polymers,* Marcel Dekker Inc., 2000,
8. Tessa ten Cate A., Sijbesma R. P., *Macromol. Rapid Commun.,*23, 1094-1112, (2002)
9. Sellens R. J., Runciman J. I., Griffon A. C., Bryant E. S., Hughes W. E., *Mol. Cryst. Liq. Cryst.,* 166, 123-129, (1989)
10. Kotek R., Krigbaum W. R., Preston J., *J. Polym. Sci. Chem. Ed.,* 20, 3241-3249, (1982)
11. Higashi F., Ogata S., Aoki Y., *J. Polym. Sci. Chem. Ed.,* 20, 2081-2087, (1982)

II. Literature Review

2.1. Introduction to Binding Methods and Theories

The classical noncovalent forces that are involved in the formation of supramolecular bonds are those associated with van der Waals interactions, coulombic interactions, hydrogen bonds. Since supramolecular interactions are composed of two complementary segments, the shapes of segments are of great importance when determining the best fit of complimentary sites, and in favoring the assembly of supramolecular systems. There is detailed quantitative analysis of the relative roles of the noncovalent forces in the literature dealing with the supramolecular chemistry and organic host-guest complexes [1-4]. General conclusions that can be obtained from the literature on noncovalent bonding forces show that stabilization of supramolecular polymers can be obtained by combination of several noncovalent interactions. This can be used to show that the occurrence of several sites for complimentary interaction can magnify the effect of weak singular interactions. Different interactions used in supramolecular polymers are as follows:

2.1.1. Coulombic Bonds

Interaction of the permanent charge type might be of the ion-ion, ion dipole, or ion-quadruple type. These types of interactions have been used to increase the stability of host guest complexes and are commonly seen in biological supramolecular polymers.

Attraction between ion pairs occurs between fixed and complementary ionizable groups and is modulated by co and counter ions (Figure 2.1).

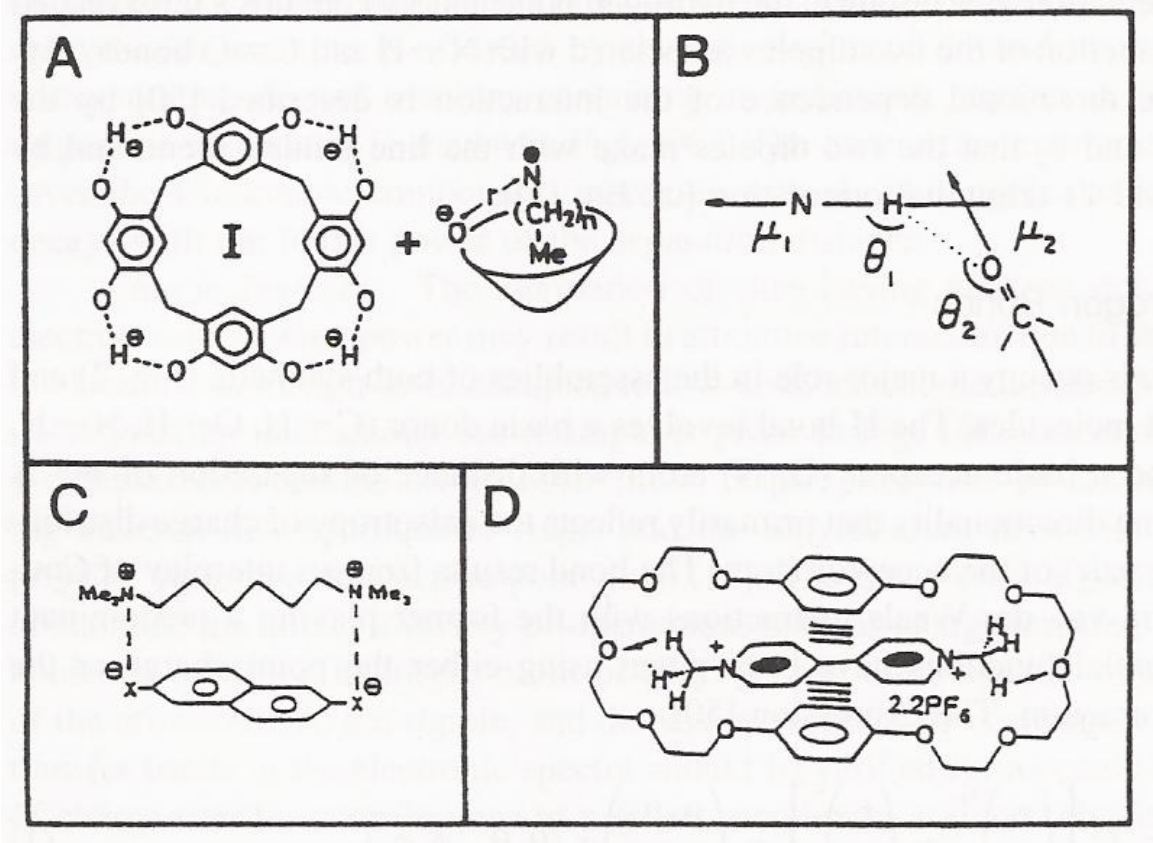


Figure 2.1. Counter Ion Arrays

(A) The ion pair $I^- N^+R_4$[R = (CH_2)Me]. An increase of n causes an increase of the separation distance and decrease of ΔF of formation. (B) Dipol-dipol interaction parameters for H-bonds. (C) Induced dipoles. ΔF for ion pair formation increases not only with the number of salt bridges but also with the number of aromatic rings in a series of di- and trications and di- and trianions. (D) π-π stacking interactions plus H-bonds contribute to the stabilization of a complex between paraquat $[PQT]^{2+}$ and a cylclophane-like macrocyclic polyether with hydroquinal rings (from [9]).

2.1.2. Hydrogen Bonds

These bonds are the major forces in the supramolecular assemblies in both synthetic and biological supramolecular molecules. The H-bond is from the basic donor (O-H, N-H, F-H) in combination with the basic acceptors (O, N). These bonds exhibit the principle of

additive binding, allowing for a great stabilization supramolecular interactions (Figure 2.2).

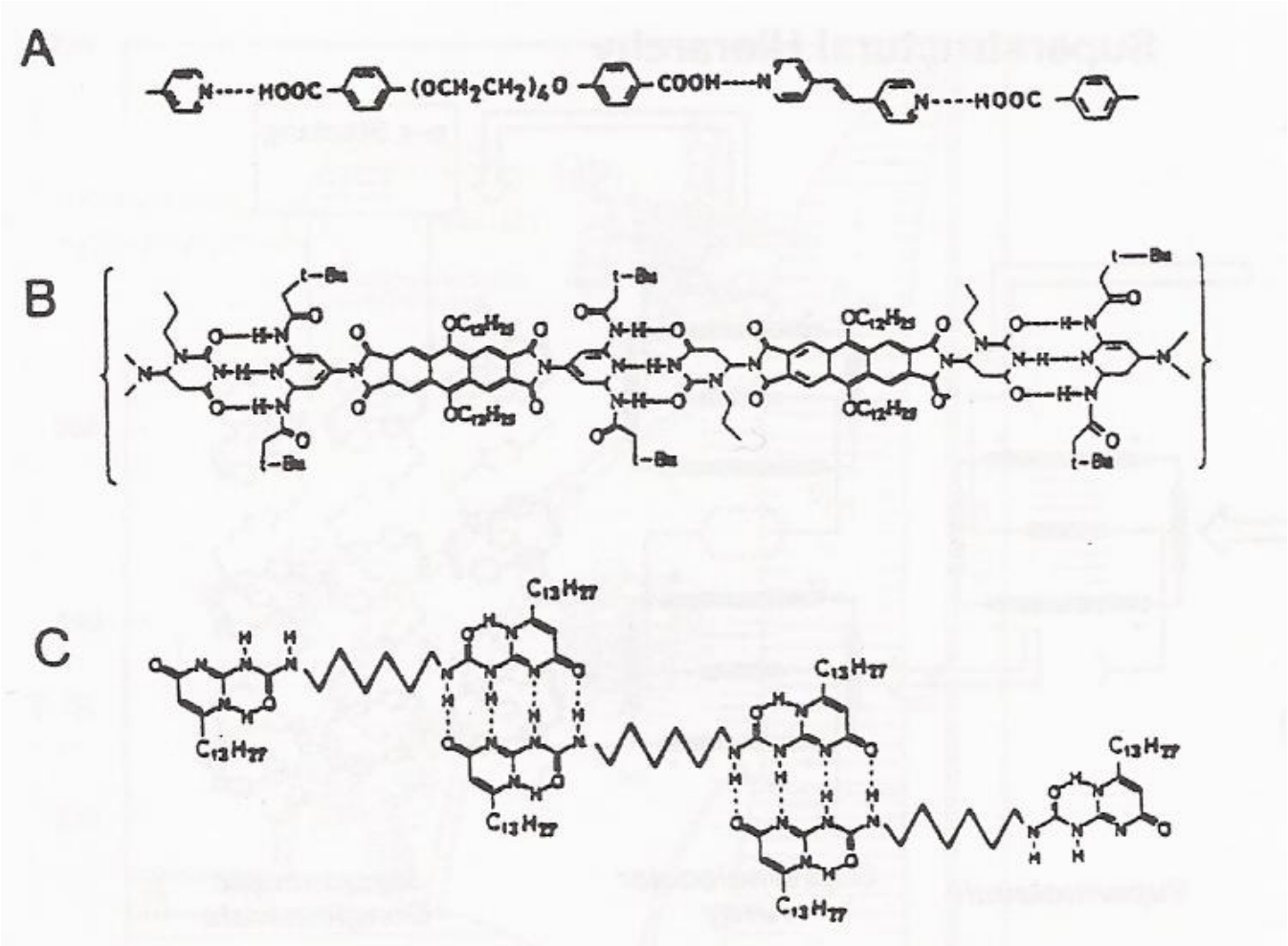


Figure 2.2. Hydrogen Bonded Arrays

Supramolecular polymers stabilized by one, three, and four, hydrogen bonds for repeating unit. Polymer A exhibits thermotropic liquid crystalline behavior. Polymer B forms a nematic lyotropic phase in 1,1,2,2-tetrachloroethane at RT. Polymer C is stable in isotropic solutions of chloroform (from [9]).

2.1.3. Van der Waals Bonds

Bonding through the van der Waals forces occurs through weak dipole interactions. Dipole molecules are the types of molecules involved in this type of bonding. In dipolar molecules, the electronegativity difference between the covalently bonded atoms exceeds or equals 0.4 but is less than or equal to 2.0 [1]. This difference in electronegativity causes the electrons of the molecule to become unequally distributed. The atoms within the molecule that have the higher electronegativity attract the electrons from those with less electronegativity. This makes the atom with the higher electronegativity acquire a slightly negative charge, denoted by δ^-. The atoms with less electronegativity acquire a slightly positive charge, denoted by δ^+. These regions of the molecules are attracted to the oppositely charged regions of other dipolar molecules. In this way, the dipolar molecules are bonded to one another, and it is this bonding that constitutes van der Waals bonding [5].

2.2. Binding Methods in Supramolecular Assembly

There is a detailed chemistry involved in reversible interactions and noncovalent forces that make up supramolecular assemblies. The polymers that can be formed through recognition controlled intermolecular connections between the different molecular components could be used to produce new and revolutionary materials. This is a primary goal to design procedures for creating dynamic materials with inherent abilities to respond to environmental stimuli [6]. These can be achieved by using heterocomplementary monomers to form supramolecular polymers which have the ability to respond to outside stimuli. This can be more easily seen as two-keyed end groups are designed to complement one another like a lock and key mechanism (Figure 2.3).

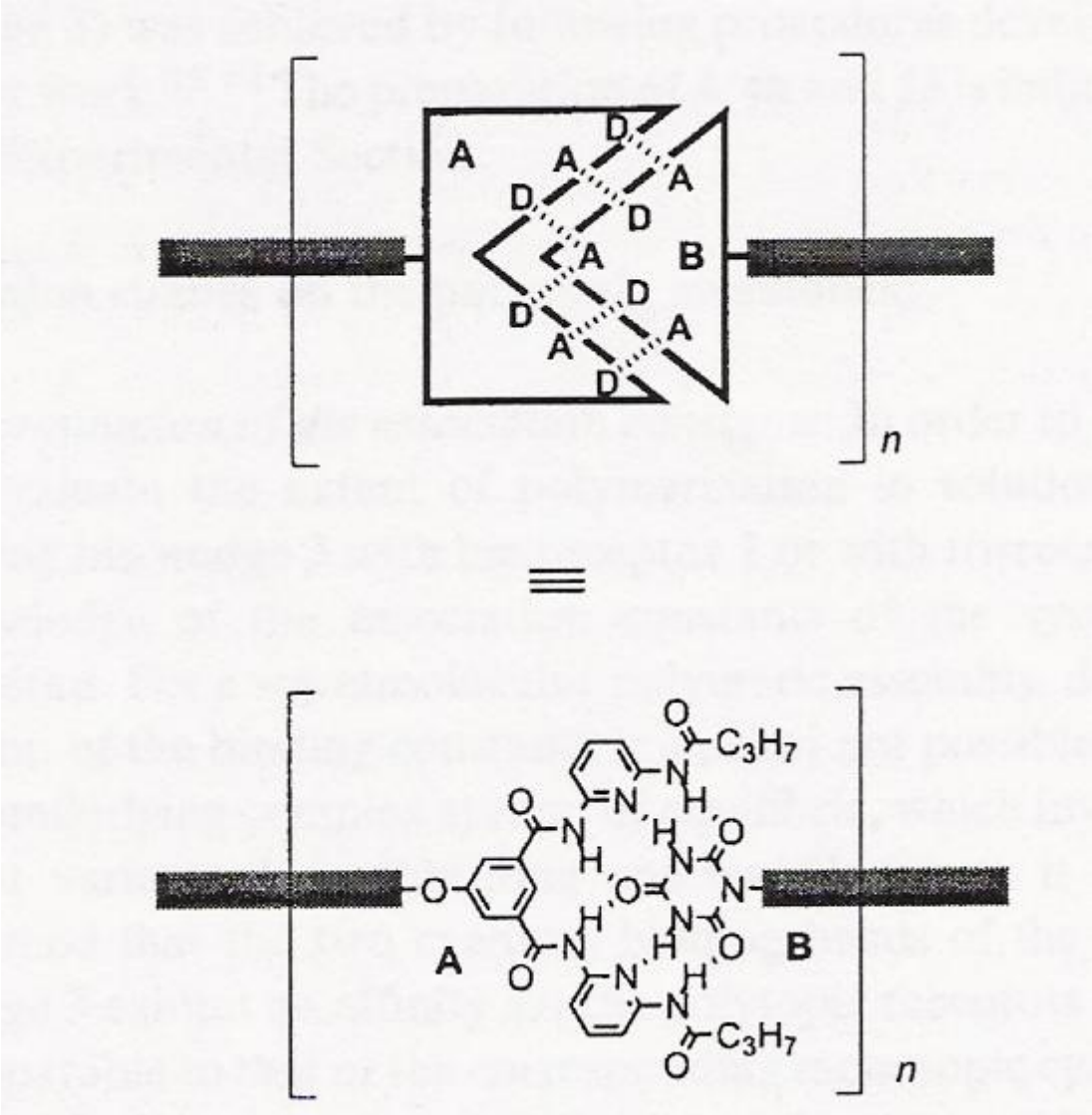
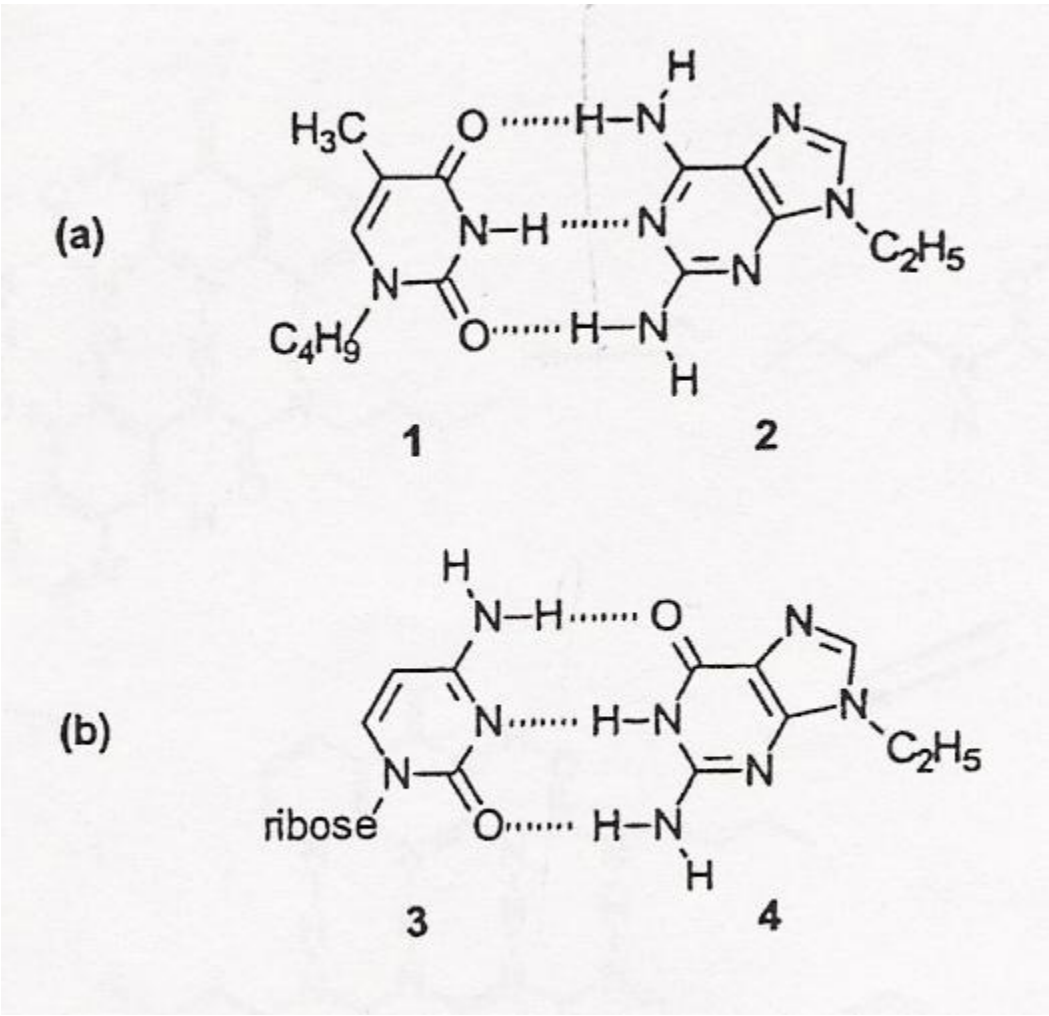


Figure 2.3. Example of Complimentary Components (from [6])

2.2.1. Hydrogen Bonding in Supramolecular Assembly

The literature shows the formation of supramolecular polymers in which hydrogen bonding is used to form the assembly [7]. Several examples are given to explain the chemistry and strength of different compounds used to form hydrogen bond linkages in supramolecular assemblies (Figure 2.4). The three examples exhibit two of the donor and

acceptor relationships of H-bonding commonly found in supramolecular polymers utilizing such attractions.



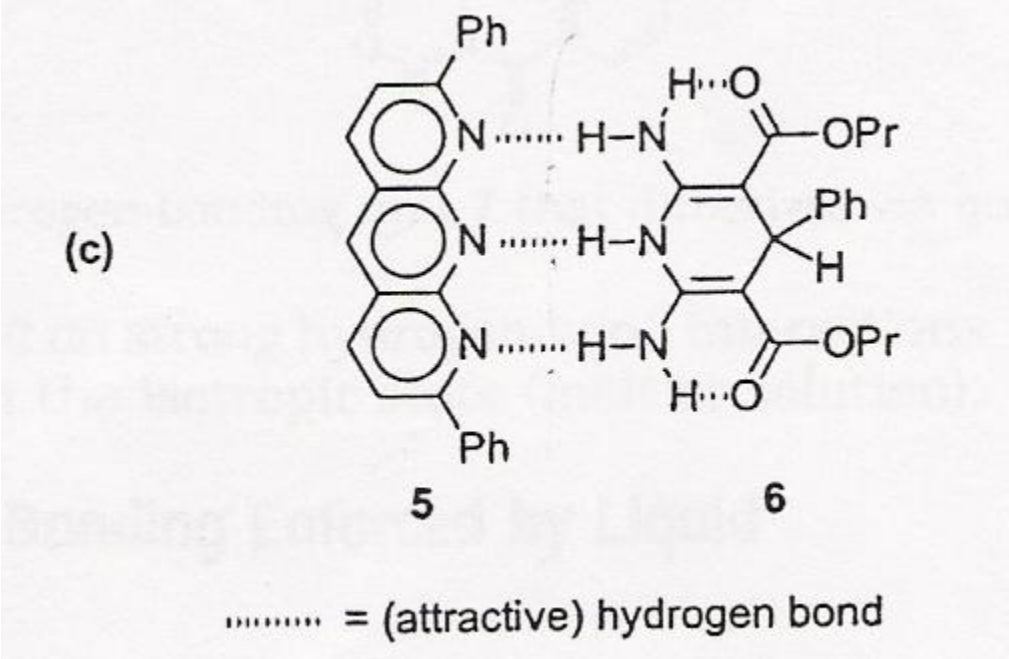


Figure 2.4. Examples of biological molecules exhibiting multiple hydrogen bonds (from [7])

The assembly of supramolecular assemblies from ureidopyrimidinone (Upy) end groups Figure 2.5 based components is directly related to the work of this research. The use of Upy as a terminating group for poly(p-benzamide) PBA in hopes of creating a supramolecular polyamide is on the key points of research of this project. This research makes use the concept of additive site interactions. Because the UPy components have the ability to form five separate H-bonds with itself after being bound to a model compound terminated with OH groups as shown in the literature [7]. The chemistries involved with this work based on pyrimidines such as UPy are shown schematically below in Figure 2.5.

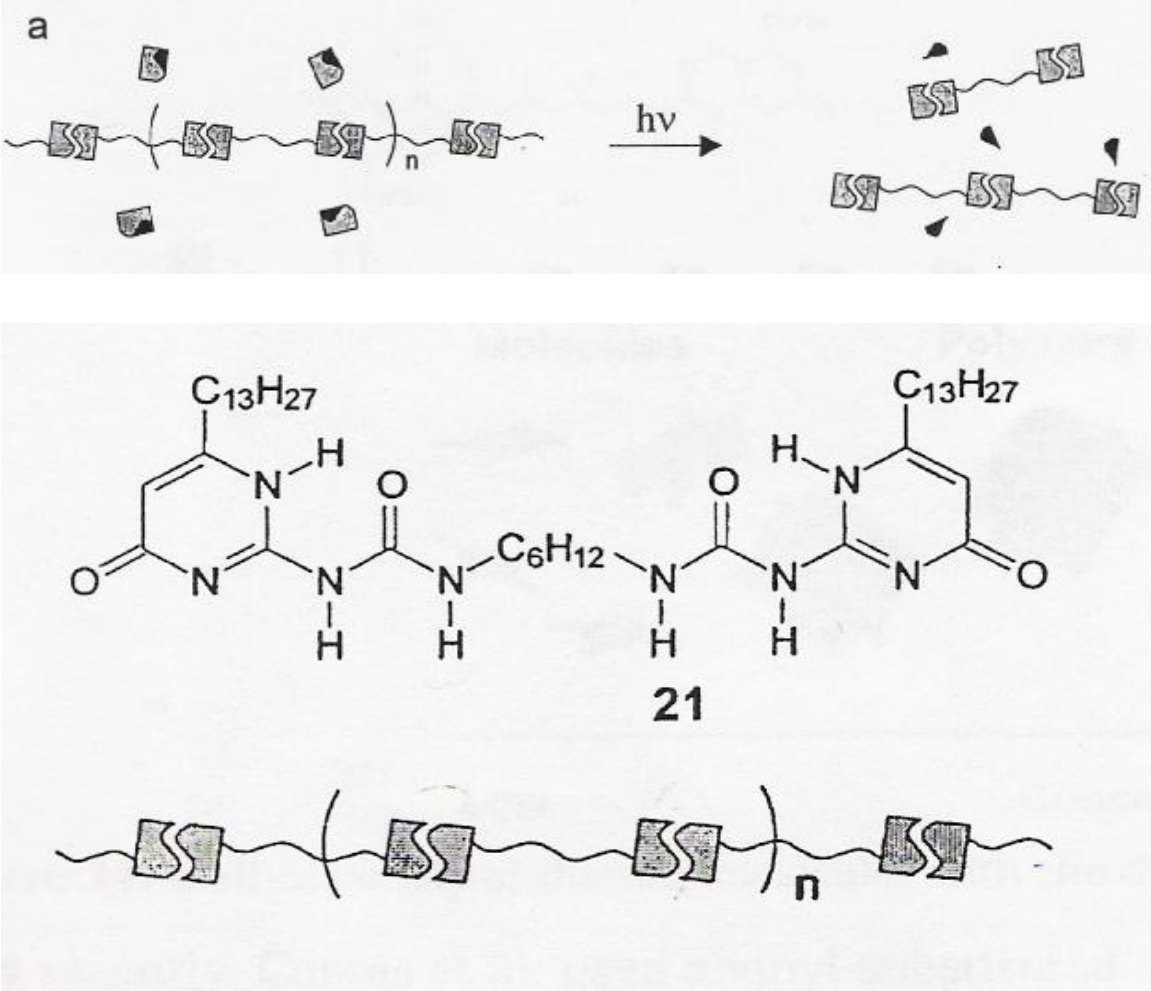


Figure 2.5. Example Supramolecular Polymer Array Utilizing UPy

(a) The concept of the binding mechanism of a supramolecular polymer (from [7]).

A main source of the literature discusses the classic binding principles of supramolecular polymers. An example of one the mechanisms utilizing multiple H-bonds that results in a polymer via supramolecular polymerization is shown in Figure 2.6 [8].

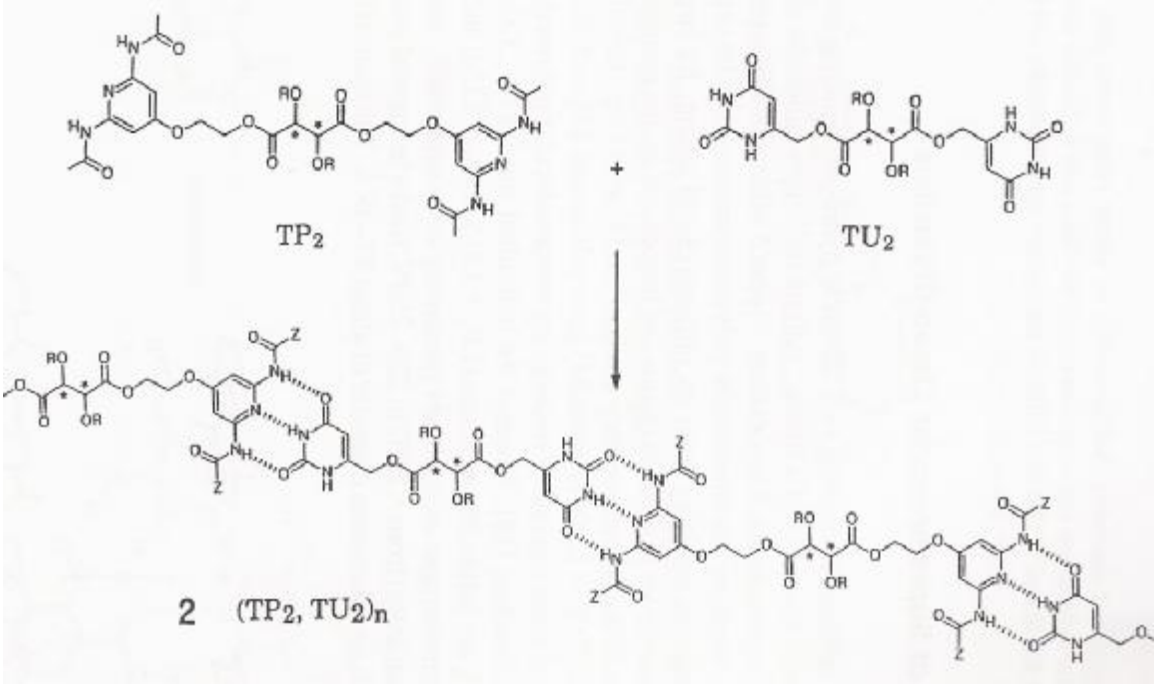


Figure 2.6. Hydrogen Bonded Array Utilizing Multiple H-Bonds

Self assembly of the polymolecular supramolecular species $(TP_2, TU_2)_n$ from the complementary chiral components TP_2 and TU_2 via hydrogen bonding; T represents L-, D-, or meso(M)- tartaric acid; R = $C_{12}H_{25}$.

One of the new and novel ideas is the idea of producing supramolecular polymeric materials that use the chain extension of telechelic polymers via reactive hydrogen bonding synthon [7]. This is accomplished by using low molecular weight telechelic polymers and functionalizing the ends with pre-chosen associating end groups. Association can be from many forms including van der Waals forces, ionic interactions, or hydrogen bonding. The suggested mechanism for the reaction of supramolecular forming endgroup, utilizes a Upy unit linked to a reactive isocyanate group from this it is able to form noncovalent interactions with itself. This was used to functionalize the hydroxy-telechelic copolymer of ethylene oxide and propylene oxide. Synthon was chosen since it is completely amorphous and apolar which strengthens the hydrogen bonds. It is shown in the literature that a similar technique can be used to make telechelic

polyesters, polyethers, and polycarbonates, which would lead to the ability to produce new supramolecular polymeric materials.

Other literature shows one of the more common ways to obtain supramolecular polymer networks [9]. This work investigates the chemistry involved in using strong dimerizing quadruple hydrogen bonded ureido-pyrimidone units to obtain a reversible polymer network. This supramolecular network is prepared using 3(4)-isocyanatomethyl-1-methylcyclohexyl-isocyanate in a coupling reaction utilizing multihydroxy functionalized polymer with isocytosines. The strongly hydrogen bonded ureido-pyrimidone network was then compared to that of a conventional covalently bonded polymer network which was comprised of a multidirectional hydrogen bonded network of urea units. The hydrogen bonded supramolecular network was found to form more favorable thermodynamic products due to the reversibility of the bonding over that of the irreversible covalently bonded polymer network. The ureido-pyrimidone network possessed many unique properties including the additional stabilization without the need for crystallinity or other types of phase separation. The ureido-pyrimidone network reported in this work is the first reversible network to exhibit such properties and due to the strength of the dimerization is able to form supramolecular materials with unique mechanical abilities.

Many supramolecular polymers utilize rod like geometries comprised of different geometric segments [11]. Supramolecular polymers comprised of coils, rods, and rings and those using hydrogen bonding within their assemblies are often mentioned in the literature. Tessa ten Cate and Sijbesma [11] focused on multi-hydrogen bonded

supramolecular polymer networks. They introduced a theoretical relationship between the association constant and the degree of polymerization of supramolecular polymers. This goes along with the suggestion that the easiest way to strengthen the interaction between hydrogen bonding groups is by increasing the number of hydrogen bonds. The authors mention ureidotriazine and ureidopyrimidinone (both structures are shown in Figure 2.6) to prove the point going along with aforementioned papers emphasizing this type of chemistry. They discuss ureidopyrimidinone derivatives used in supramolecular polymerizations along with the description of the determination of DP of these types of materials to support the theory of higher DP in networks containing multiple hydrogen bonds. The possible preparation of such materials via the reaction of telechelic poly(ethylene/butylene) synthon in the same fashion would be of a great help in producing novel materials. The order of polymer chains directly affects the properties of polymers since most polymers are random coil configuration. This poses a problem due to the fact smart materials need a more structured architecture than that of the randomly coiled conventional polymer. This leads to the need to use rod-like supramolecular polymers that would allow for use as foundation for nanoelectronic and nanooptical applications. These polymers would need to possess a secondary and perhaps a tertiary structure very similar to those in biopolymers. Tessa ten Cate and Sijbesma [11] also use disc shaped molecules to form columnar stacks like those mentioned by other authors and explain how the columnar architecture could be improved via various stabilizing methods and properties.

The literature also discusses cyclization and its inevitable influence on the properties of polymeric materials and reasons why such cyclization exists in hydrogen-bonded assemblies along with the mechanisms and the of determination of cyclization within polymer samples via H-NMR. Their is evidence in the literature of conformational preorganization by rigid building blocks of dypyridone with rigid linkers and their success of application of rigid linkers and cyclic chemistry, which contain quadruple hydrogen bonds. The use of tuneable ring and chain equilibriums can often be seen in supramolecular polymers the literature suggests theories of how to control both using UPy and changes in temperature. It has been shown that high bonding constants are directly related to the synthetic accessibility in formation of reversible polymers possessing high degrees of polymerization which are a direct result of possessing quadruple hydrogen bonds within their networks which allows for additional control over the architecture of supramolecular polymers and provides and setups a hierarchy of organization. The literature also suggests arguments that could be used to produce scaffolds for use in supramolecular photonics and electronics. This will require the use of a well-defined helical columnar secondary and tertiary structures. The underlying arguments on the unique features of ring/chain equilibrium that include critical concentrations and critical temperatures. This can only be observed when interaction is strengthen via a quadruple hydrogen bond, and consider this a promising means for future use in production of smart materials.

2.2.2. Metal Compound Coordination in Supramolecular Assembly

The coordination of certain metal compounds has been known for some years to allow for the assembly of a wide range of supramolecular complexes that range from cages to cyclic dimers [7]. A lot of the metal chemistry has been used that involves the coordinate interactions of copper and silver (Figure 2.7) [7]. Also, the use of porphyrin complexes has been reported.

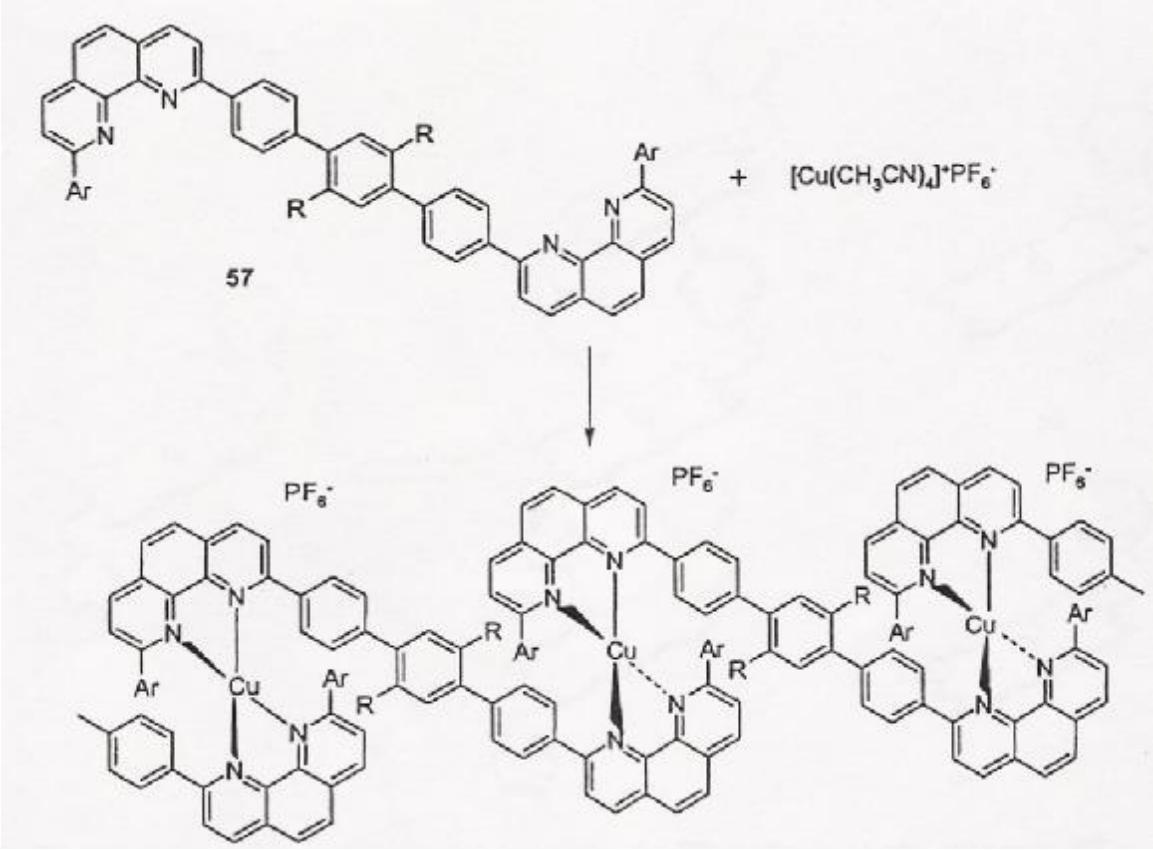


Figure 2.7. Examples of Supramolecular Array Utilizing Coordinate Chemistry

Ciferri [8] also discusses polymers produced via coordination chemistry mentioning many metal binding groups, which could be used to form reversible coordination polymers including functionalized porphyrins in Figure 2.8 [8].

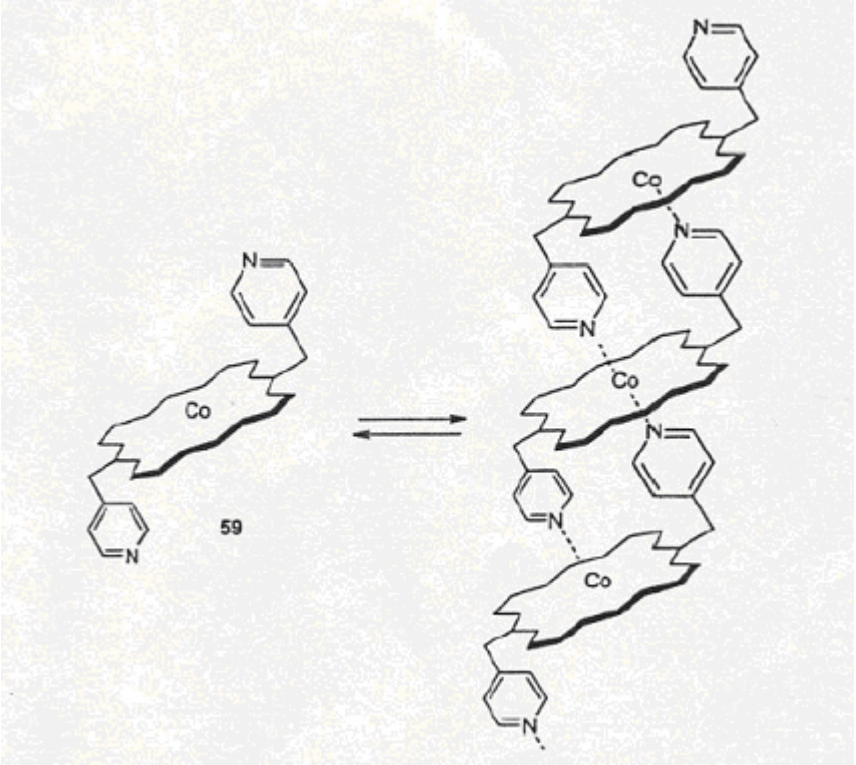


Figure 2.8. Formation of Coordination Polymers from Porphyrin (from [7]).

2.2.3. Cyclodextrins in Supramolecular Assembly

The use of cyclodextrins in supramolecular chemistry to form nanotube architecture is possible since the inclusion of the guest groups allows a polyfunctional polymer to form with a unique cavity architecture (Figure 2.9) [7].

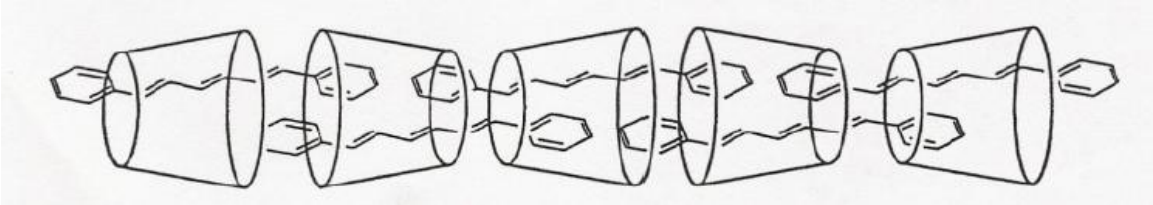


Figure 2.9. Supramolecular Polymer Consisting of β-cyclodextrin (from [7]).

The theories pertaining to the uses of helical chains and functional systems that mimic mechanical properties of biological systems are given in the literature [8]. Assemblies formed by columnar and micellar chemistry can also be used to form supramolecular networks (Figure 2.10).

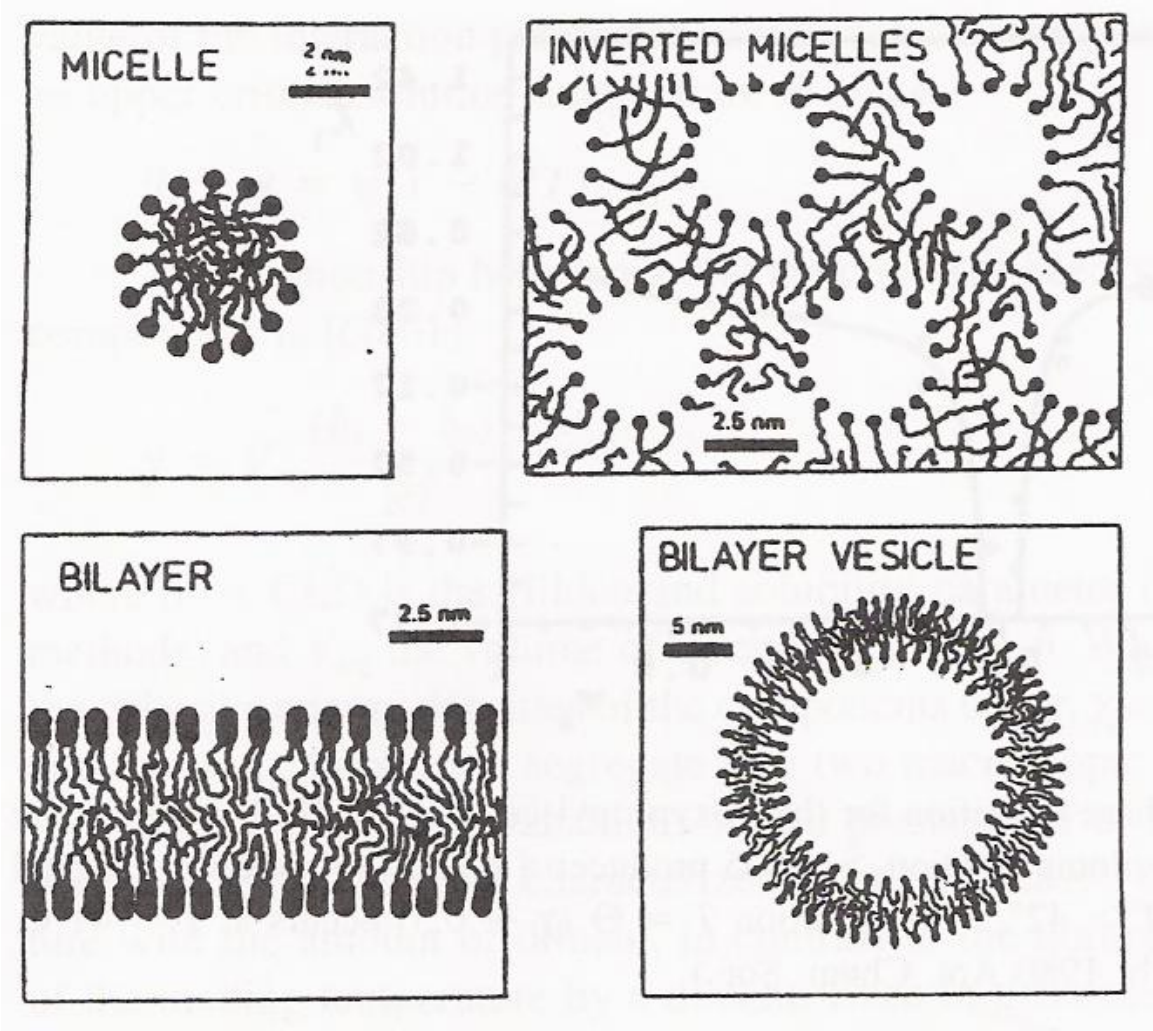


Figure 2.10. Micelles, Bilayers, and Vesicles Formed by Single- or Double-chained Surfactants in Water (from [9]).

2.2.4. Combinational Bonding in Supramolecular Assembly

Several works of literature [13-17] have been done that show evidence of growth-coupled-to-orientation resulting from discotic molecules that possess a disc shape made of rigid alkyl chains. A combination of two of the previous mentioned chemistries have been used into helical-columnar growth mechanisms, which involves disc shaped molecules that assemble into columnar stacks via hydrogen bonding and arene-arene

interactions. This paves the way for the introduction of supramolecular polymers using a tubular assembly Figure 2.11.

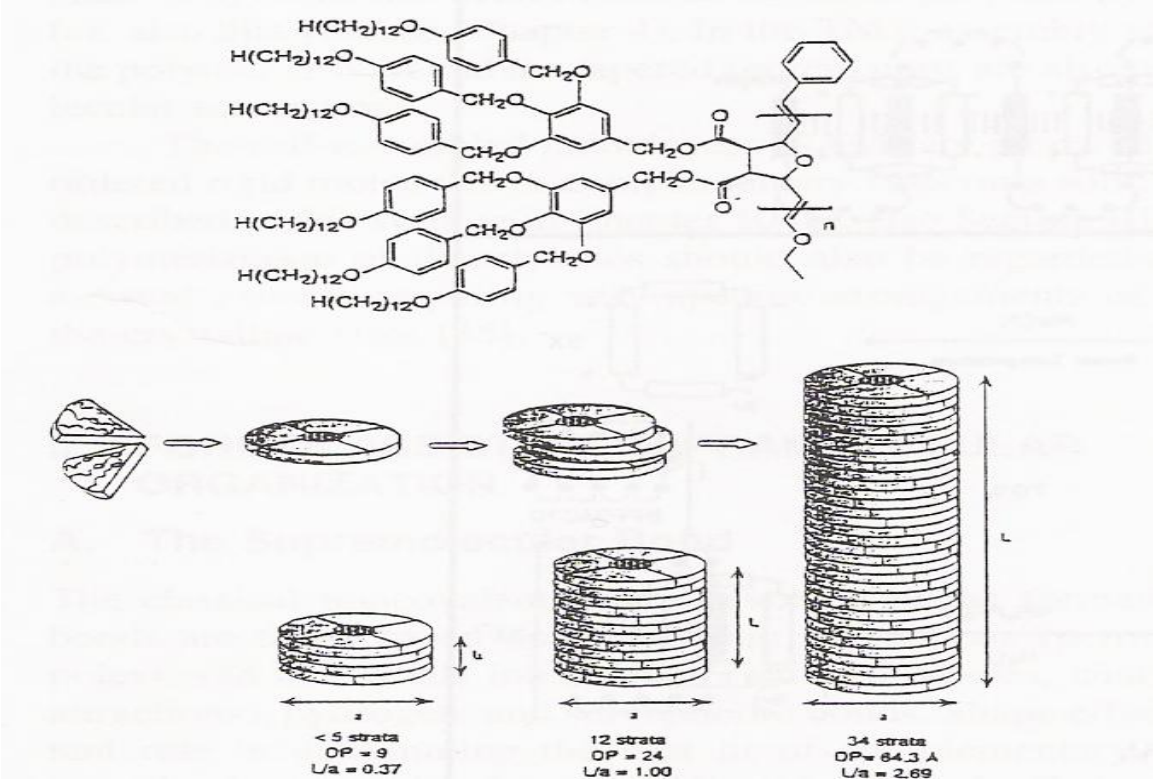


Figure 2.11. Example of a Supramolecular Polymer Utilizing Columnar Assembly

Top: polymer resulting from living ring opening metathesis polymerization of a 7-oxanorbornene monomer substituted with two tapered monodendrons. Bottom: schematization of the assembly of four monodendrons (two monomers) in strata and in columns for polymers with DP = 24 and 64 (from [9]

Using again disc shaped supermolecules, which exhibit liquid crystalline behavior and can form columnar stacking via the use of discotic molecules has been mentioned in the literature and is shown in the Figure 2.11 earlier. This allows the formation of host/guest polymeric assemblies in which covalent polymers can be formed within the cavity of the columnar-stacked supramolecular system. This would allow for a variety of different

applications for orienting and screening single polymers from similar neighborhood interactions.

The use of self-assembly and designing building blocks that would result in supramolecular polymerizations has been discussed through the literature [1-8]. Future research topics proposed by the literature, includes investigating and determining a way to accurately assess the DP of supramolecular polymers. Also, the assessment of mechanical strength of supramolecular bond with linear hydrogen bonding was one of the major concerns. It has been mentioned in the literature [17-26] that there is a need for a detailed investigation of the growth mechanisms associated with supramolecular polymers.

2.2.5 References

1. Schneider H-J, *Angew Chem Int Ed Engl*,30,1417, (1991)
2. Hobza P., Zahradnik, *Intermolecular Complexes.* Amsterdam:Elsevier, (1988)
3. Chem Rev 88: 813-988, (1988)
4. Jorgensen WJ, *Acc Chem Res* 22:184, (1989)
5. Fyfe MCT, Stoddart JF, *Acc Chem Res,* 30, 393, (1997)
6. Berl V., Schmutz M., Krische M. J., Khoury R. G., Lehn J.,*Chem. Eur.J.,* 8, No. 5, (2002)
7. Brunsveld L., Folmer B. J. B., Meijer E. W., Sijbesma R. P., *Chem. Rev.,* 101, 4071-4097, (2001)
8. Ciferri A, *Macromol. Rapid Commun.,*23, 511-529, (2002)
9. Ciferri A. Ed., *Supramolecular Polymers,* Marcel Dekker Inc., 2000,
10. Lange R. F. M., Van Gurp M., Meijer E. W., *J. Polym. Sci. Chem. Ed.,*37, 3657-3670, (1999)
12. Tessa ten Cate A., Sijbesma R. P., *Macromol. Rapid Commun.,*23, 1094-1112, (2002)
13. Aharoni S. H., Hammond W. B., Szobota J. S., Masilamani D., *J. Polym. Sci. Polym. Chem. Ed.,* 22, 2579-2599, (1984)
14. Balbi C., Bianchi E., Ciferri A., Tealdi A., *J. Polym. Sci. Polym. Phy. Ed.,* 18, 2037-2053, (1980)

15. Berl V., Schmutz M., Krische M. J., Khoury R. G., Lehn J.,*Chem. Eur.J.,* 8, No. 5, (2002)
16. Bladon P., Griffon A. C., *Macromolecules,* 26, 6604-6610, (1993)
17. Burchell C. J., Ferguson G., Lough A. J., Gregson R. M., Glidwell C., *Acta Cryst.,* B57, 329-338, (2000)
18. Cavalleri P., Ciferri A., Dell'Erba C., Marino N., Purevsuren B., *Macromolecules,* 30, 3513-3518,(1997)
19. Ciferri A. Ed., *Supramolecular Polymers,* Marcel Dekker Inc., 2000,
20. Ciferri A., *Recent Res. Devel. Macromol.,* 6, 129-147, (2002)
21. Folmer B. R. B., Sijbesma R. P., Versteegen R. M., Vander Rijt J. A. J., Meijer E. W., *Advanced Materials,* (2000)
22. Hoshino H., Jin J. I., Lenz R. W., *J. App. Polym. Sci.,* 29, 547-554, (1984)
23. Kotera M., Lehn J-M, Vigneron J-P, *J.Chem. Soc. Chem. Commun.,*197-198, (1994)
24. Kwolek S. L., Morgan P. W. , Schaefgen J.R., Gulrich L. W., *Macromolecules,* 10, 1390-1396, (1977)
25. Lehn J., *Macromol. Symp.,* 174, 5-6, (2001)
26. Killian F. L., *American Chemical Society Polym. Div.,*17, 69-74, (1969)
27. Sellens R. J., Runciman J. I., Griffon A. C., Bryant E. S., Hughes W. E., *Mol. Cryst. Liq. Cryst.,* 166, 123-129, (1989)
28. Ying Q., Benjamin C., *Macromolecules,* 20, 871-877, (1987)

2.3 Conventional Methods of Synthesis

This chapter discusses the conventional methods used in polyamides synthesis. The literature was consulted to find the best method to produced the rigid rods for the foundation of the supramolecular polyamides.

2.3.1. Synthesis via Polycondensation

Yamazaki [1] used direct polycondensation to synthesize PBA structure shown in Figure 2.12 The investigators used p-aminobenzoic acid (p-ABA) and diphenyl and triaryl phosphites in N-methylpyrrolidone (NMP)/pyridine solution containing lithium chlorides.

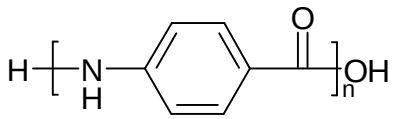
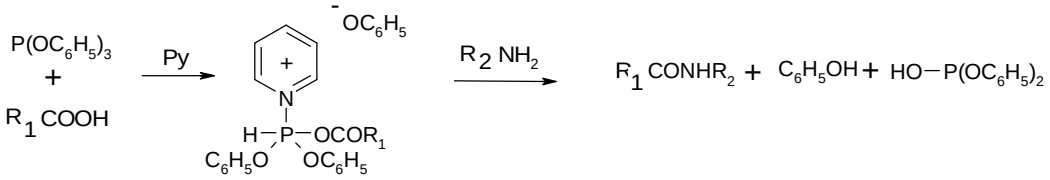


Figure 2.12 The Structural Repeat Unit of Poly(p-benzamide)

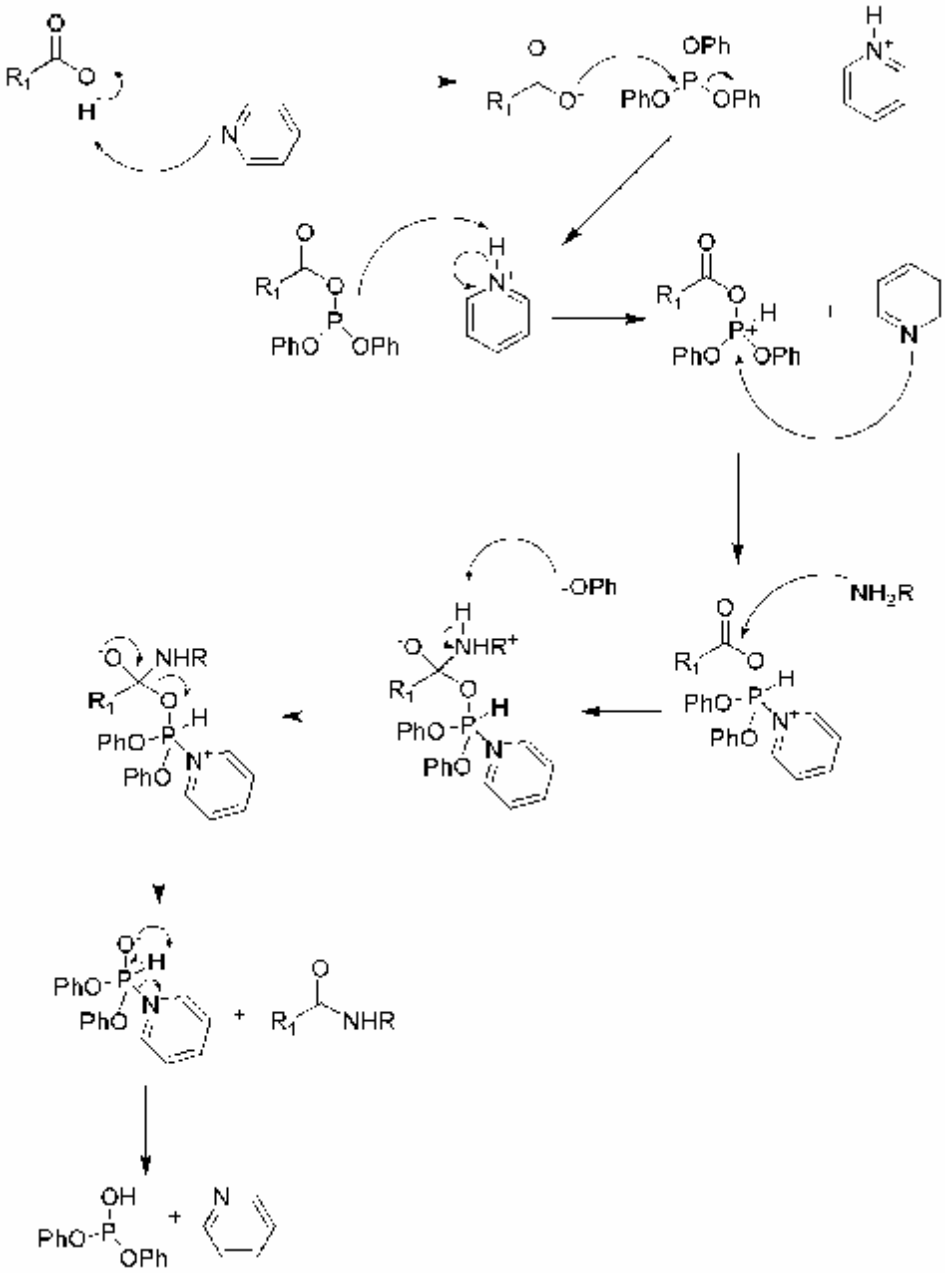
Molecular weights of polymers were shown to vary with the amount of salts added to the mixed solvent. The polycondensation was shown to be strongly affected by the monomer concentration, solvents, and tertiary amines such as pyridine.

The literature gives one method that can be used to improve the solubility of rigid polyamides. This can done by alternating the sequence of a block copolymer with rigid and semiflexible units. The synthesized rigid blocks of poly-(p-benzamide) and semiflexible blocks of polyamide-hydrazide make a good combination for improving the solubility of the copolymer. The prepolymer of PBA was synthesized using both p-aminobenzoic acid and triphenyl phosphite under the Yamazaki conditions. The Yamazaki reaction mechanism is shown in Scheme 2.1. proceeds through the following mechanism forming the amide linkage in the end product. The acid and complexes with triphenyl phosphite and pyridine kicking anion phenyl group, this allows for the attack of the carbonyl by the amines lone pair. After a rearrangement the newly form amide is kicked off leaving diphenyl phosphite.

Scheme 2.1. The scheme depicts the mechanism of the amide linkage formation in the Yamazaki reaction

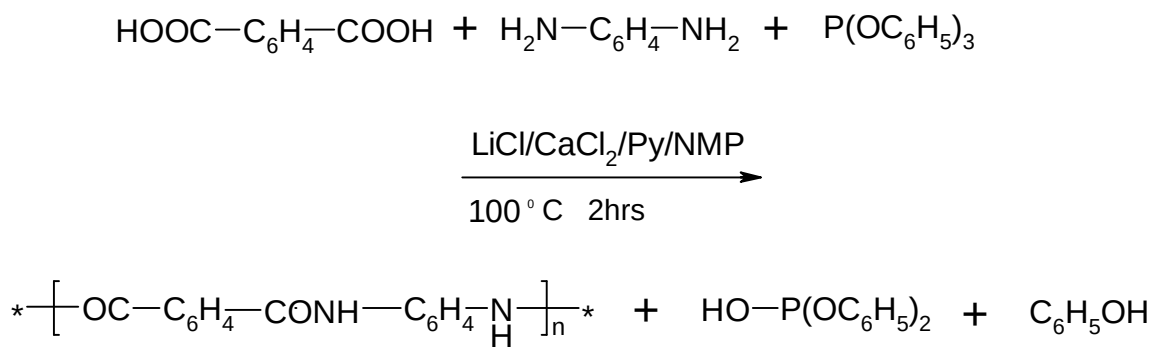


Hypothetical mechanism.



The more flexible polyamide-hydrazide was synthesized using p-aminobenzhydrazide and terephthalic acid and the active reagent diphenyl phosphite. The evidence used to prove the copolymer existence was the increase in inherent viscosity during the second step of the polymerization. Also, the solubility of the copolymer was compared to that of the homopolymers used in the synthesis. This work demonstrates a novel way for improving the solubility and compatibility of aromatic polyamides with other polymers using a copolymer made of rigid and semiflexible blocks via synthesis by the Yamazaki reaction by a two-step process. The use of the Yamazaki reaction in this paper gives vital information needed if one is inclined to synthesize PBA using either of the two monomers mentioned above.

Higashi [2] synthesized high molecular weight poly(p-phenyleneterephthalamide) via a polycondensation reaction similar to the one used by the Yamazaki, mentioned earlier and shown in Scheme 2.2.



Scheme 2.2

The reaction promoted by use of triphenyl phosphite and pyridine was successfully used to synthesize p-aminobenzoic acid and isophthalic acid and diamines. High yields were reported except when terephthalic acid was used as a monomer. The reaction relies on the presence of the metal salts LiCl and $CaCl_2$ in a mixed solvent of NMP and pyridine. This

work shows the effectiveness of metal salts in overcoming the difficulties of modifying polyterephthalamides due to the polyamide monomers and solvents.

The reaction involving the use of p-benzamide units is the work by Kotek et al. [3-4], which uses both the Higashi reaction and the Yamazaki reaction mentioned above. Both methods use metal salts LiCl and $CaCl_2$ in the same mixed solvent mixture of NMP and pyridine with promotion of the reaction by triphenyl phosphite. The authors demonstrate the first preparation of rod like polymers by use of a phosphorylation reaction containing p-benzamide units resulting in polymers of molecular weights comparable to industrial grade fibers. This work also shows the synthesis of copolymers containing the rigid and semiflexible units much like papers mentioned before. The copolymer contained the rigid p-benzamide and m-benzamide and was synthesized via use of a rigid prepolymer added to a preformed amide linkage under Yamazaki conditions and resulted in a block copolymer with a relatively high inherent viscosity. In another effort by [3-5], the authors expanded the research using the same phosphorylation and polycondensation reactions of Yamazaki and Higashi to synthesize poly-(p-phenyleneoxamide) in quantitative yields, although it was found that the polyoxamides synthesized via the phosphorylation tended to have lower inherent viscosities than those produced using the polycondensation reaction due to the poor solubility of the polyoxamides in the phosphorylation medium.

2.3.2 References

1. Yamazaki N., Matsumoto M., Higashi F., *J. Polym. Sci. Chem. Ed.,*13, 1373-1380, (1975)
2. Higashi F., Ogata S., Aoki Y., *J. Polym. Sci. Chem. Ed.,* 20, 2081-2087, (1982)
3. Kotek R., Krigbaum W. R., Preston J., *J. Polym. Sci. Chem. Ed.,* 21, 2837-2841, (1983)
4. Kotek R., Krigbaum W.R., Preston J., *J. Polym. Sci. Chem. Ed.,* 22, 873-876 (1984)
5. Kotek R., Krigbaum W.R., Preston J., *J. Polym. Sci. Chem. Ed.,* 22, 873-876 (1984)

2.4 Motivation of Research

The purpose of this work is to investigate the possibility of the production of novel supramolecular polyamide. We propose that the use of low DP poly(p-benzamide) (PBA) segments, terminated by units able to form supramolecular bonds to form a supramolecular polymamide. Another method that this work investigates is the use of diamine binders in order to be able to extend the overall DP of the aromatic polyamide via a series of ionic bonds. There could be a great interest in this system from both a technological and a fundamental point of view. The fact that PBA fiber, and the related industrially produced PPTA (Kevlar), exhibit their most interesting ultra-high strength properties only when a considerably large DP (>100) is attained. Along with the interesting fact that the considerably large DP cannot be obtained using simple polymerization techniques such as the well-known Yamazaki's reaction. Use of cumbersome and expensive syntheses and solvents is required to attain DP in the range (~200-300) of industrial interest. This research offers two methods of obtaining our objectives.

(a) N, N’-bis(p-carboxylphenyl)terephthalamide monomer

- TED binding
- Bipip binding

(b) PBA binding in amide solvents

- TED binding
- Bipip binding
- UPy binding

Moreover, the fully covalent polymers thus far produced are highly insoluble in common organic solvents; On the other hand, easier processing becomes feasible if the DP of conventional PBA (prepared by the Yamazaki reaction) is increased by supramolecular bonding in polyamide solvent mediums.

2.5 Acknowledgments

I would like to thank Dr. Melander for providing the mechanism of the Yamazaki phosphorylation reaction used in this chapter.

III. N, N'-bis(p-carboxylphenyl)terephthalamide Monomer Synthesis and Binding

3.1 Introduction

Molecular recognition induced from polyassociation of complementary molecular components through noncovalent forces such as hydrogen bonding has been shown to yield polymeric species of the supramolecular type, which may even have liquid crystalline properties. The use of supramolecular chemistry allows the creation of materials comprised of rigid blocks. The assembly of such species would require the design of molecular components endowed with the ability to spontaneously assembly such species through molecular recognition-directed self-assembly. Many studies have been carried out concerning the controlled formation of various superstructures through hydrogen bonding in solid state or solution. The theory if two complementary units are combined in the presence of an organic solvent may lead to the self-assembly of a linear polymeric rigid rod is seen throughout the literature. This may result in a new material which may possess novel properties and liquid crystalline properties. In the present study the N,N'-bis(p-carboxylphenyl)terephthalamide (JPM) monomer was chosen as the rigid rod core component and triethylene diamine as the complimentary unit used for formation of the supramolecular array. Due to the weak nature of the hydrogen bond in comparison to that of the covalent bond, molecules formed by hydrogen bonding rapidly break and recombine. Bonding from smaller fragments will have different populations of each of the constituent components both bound and unbound.

3.2 Experimental

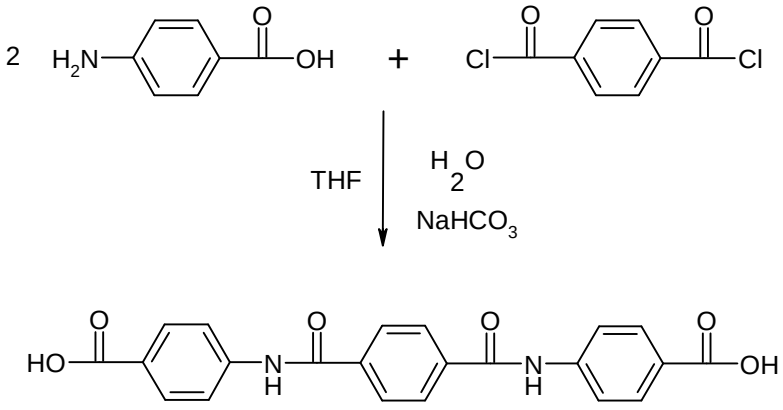
3.2.1 Materials

Commercially available anhydrous LiCl (Aldrich) was dried in an oven at 400 ^{o}C and kept in a vacuum desiccator containing NaOH. N,N-dimethylacetamide (DMAC), anhydrous, 99.0% (Aldrich), sodium bicarbonate (Aldrich), tetrahydrofuran (THF) (Aldrich) , hydrochloric acid (Aldrich), p-aminobenzoic acid (p-ABA) (Aldrich), triethylenediamine, bipiperidine dihydrochloride (Aldrich), chloroform (Aldrich), sodium hydroxide pellets (NaOH) (Fischer), pentane (Aldrich), 2-amino-4-hydroxy-6-methylpyrimidine (Aldrich), hexyldiisocyanate, and terephthaloyl chloride (TCL) (Aldrich) were used with out further purification.

3.2.2 Monomer Synthesis

The p-aminobenzoic acid (Aldrich) was used as received and was reacted with terephthaloyl chloride to produce N, N'-bis(p-carboxylphenyl)terephthalamide (JPM) monomer according to the Scheme 3.1 [1-3].

Scheme 3.1



The procedure is as follow $2.4x10^{-2}$ mol of TCL were added to 100mL of THF and allowed to dissolve. A second solution containing $4.7x10^{-2}$ mol of sodium bicarbonate and $5.2x10^{-2}$ mol p-ABA was added to 100 ml of water and allowed to dissolve. Once both solutions were dissolved completely the solution were mixed together in a blender and allowed to mix for 10 min. The filtered product was washed with diluted HCl. The product was collected and dried in vacuum at 80^{o}C. A percent yield of 90% was recorded from the synthesis.

Anal. Calcd. for $C_{22}H_{16}O_6N_2$: C = 65.44 % H = 3.96% O = 23.34% N = 6.94% Found: C = 63.32% H = 4.36% O = 24.28% N = 6.31%

Galbraith Laboritories, Inc carried out the elemental analyses.

The melting points of N, N'-bis(p-carboxylphenyl)terephthalamide monomers used were experimentally determined using a Perkin-Elmer differential scanning calorimeter (DSC) and recorded in Table 3.1.

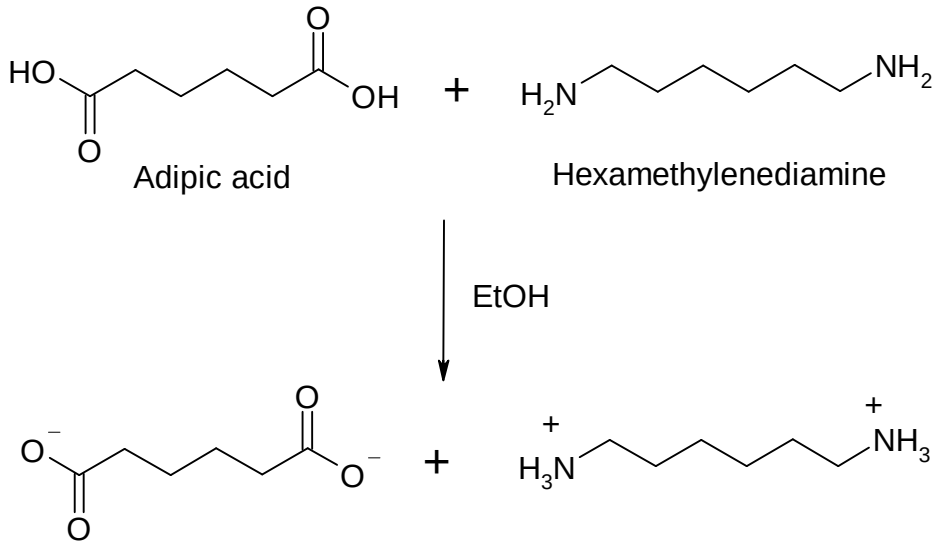
Table 3.1. Melting Points of JP Monomers

Monomer	DSC Mp (^{o}C)
JPM-1	404.87
JPM-2	398.86
JPM-3	399.92
JPM-4	402.35
JPM-5	399.34

3.2.3 Binding Methods

Three different binding methods used in the investigation utilized workable chemistries with the acid groups of the monomer to create ionic bond formations between the monomer and binders. The theoretical idea that diamines could form hydrogen or ionic bonds interlinking the acid groups of the monomer in self-assembling supramolecular polymer led to the choice to use diamines. Perhaps the way nylon salts are formed in the following Scheme 3.2.

Scheme 3.2



The purpose of using both secondary and tertiary amines shown in Figure 3.1 was to investigate which would produce the most optimal binding. The monomer was used because of its rigid rod construction and its termination with acid groups [1-3].

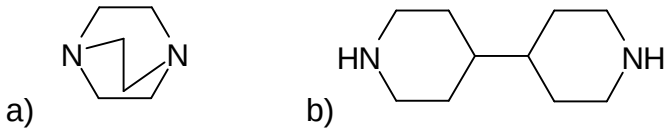


Figure 3.1. Diamine Binder Structures: (a) Triethylenediamine (b) 4,4'-bipiperidine

3.2.3.1 Binding with Triethylenediamine (TED)

At Room Temperature

Two solutions were made by adding $1.93x10^{-3}$ mol of monomer to 10 ml of DMAC containing 4% LiCl along with $1.93x10^{-3}$ mol TED to 10 ml of DMAC containing 4% LiCl. The solutions were then added together and mixed at room temperature. The resulting precipitate was filtered via vacuum, and collected and dried under reduced pressure at 60^{o}C. A percent yield of 96% was recorded.

At Elevated Temperature

Two solutions were made by adding $1.93x10^{-3}$mol of monomer to 10 ml of DMAC containing 4% LiCl along with $1.93x10^{-3}$mol TED to 10 ml of DMAC containing 4% LiCl. The solutions were then added together mixed and heated to 100^{o}C for 1h. The resulting precipitate was vacuum filtered, and collected and dried under reduced pressure at 60^{o}C. A percent yield of 94% was recorded.

3.2.3.2 Binding with Bipiperidine (Bipip)

Bipiperidine (Bipip) was obtained from simple organic separation by adding 0.01 mol bipiperidine dihydrochloride (Aldrich) to 100 ml water containing an excess of NaOH pellets. The solution was then added to a separation funnel containing 100ml chloroform (Aldrich). The organic layer was collected and distilled off and the product was dried in vacuum at 80^{o}C. A percent yield of 94% was recorded.

At Room Temperature

Two solutions were made by adding $1.73x10^{-3}$ mol of monomer to 10 ml of DMAC containing 4% LiCl along with $1.78x10^{-3}$ mol Bipip to 10 ml of DMAC containing 4% LiCl. The solutions were then added together and mixed at room temperature. The resulting precipitate was filtered via vacuum, collected and dried under reduced pressure at 60^{o}C. A percent yield of 95% was recorded.

At Elevated Temperature

Two solutions were made by adding $1.73x10^{-3}$ mol of monomer to10 ml of DMAC containing 4% LiCl along with $1.78x10^{-3}$ mol Bipip to 10 ml of DMAC containing 4% LiCl the solutions were then added together mixed and heated to 100^{o}C for 1h. The resulting precipitate was vacuum filtered, collected and dried under reduced pressure at 60^{o}C. A percent yield of 96% was recorded.

3.2.4 Analytical Measurements

3.2.4.1 Differential Scanning Calorimetry (DSC)

DSC was conducted on 3-10 mg samples in a Diamond DSC Perkin Elmer with Pyris software. An indium standard was used for calibration, a heating rate of 20^{o}C/min. was employed, and nitrogen was used as the purge gas.

3.2.4.2 Fourier Transform Infrared (FTIR)

Absorbance FTIR spectra were recorded on a Thermo Electron Nexus 470 bench with OMNIC software. Frequencies from 400-4000 cm^{-1} were covered and 64 scans were recorded with a gain =1 on samples mixed with KBr and pressed into pellets.

3.2.4.3 Thermogravimetric Analysis (TGA)

TGA scans of 5-10 mg samples were obtained using a PerkinElmer Pyris 1 thermogravimetric analyzer. The samples were placed in platinum pans that were hung in the heating furnace. The weight percentage of the material remaining in the pan was recorded while heating 25-800^{o}C a heating rate of 20^{o}C/min. Nitrogen was used as the purge gas.

3.2.4.4 Elemental Analysis

Galbraith labs determined the hydrogen, nitrogen, oxygen and carbon content of the JPM samples for verification of the purity and structure.

3.3 Results and Discussion

The FTIR spectra of the original JPM samples and samples treated with TED are presented in Figures 3.2 thru 3.5 Comparing the original samples with those treated with diamines shows structural changes from the original monomer. The original sample spectrum in Figure 3.2 shows N-H amide peak at 3300 cm^{-1}, which is expected from the amide linkages in the starting monomer. The three peaks at 2995, 2663, and 2547 cm^{-1} are from the OH group of the acid. The peak at 1680 cm^{-1} is related to the carbonyl stretch of the acid endgroups. The peaks from the 800-500 cm^{-1} represent the aromatic ring stretching. This goes along with the structural make up of the N,N'-bis(p-

carboxylphenyl)terephthalamide monomer synthesized using the method in section 3.2.2 The structure the monomer can be seen in Scheme 3.3.

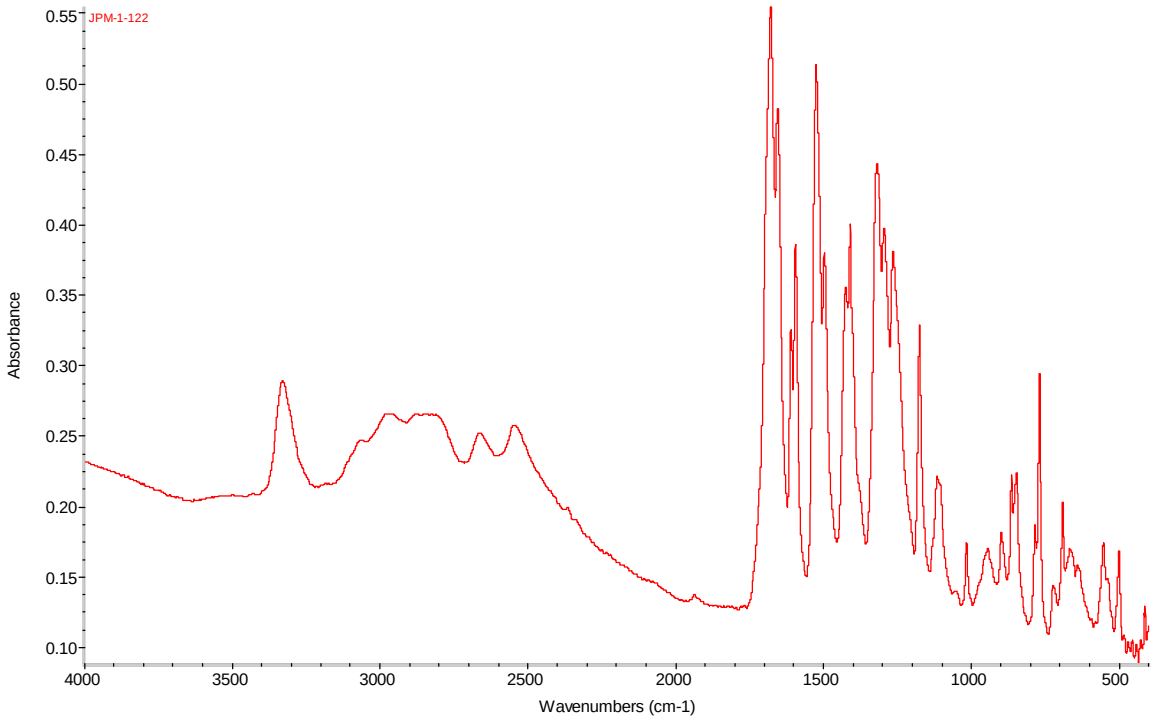
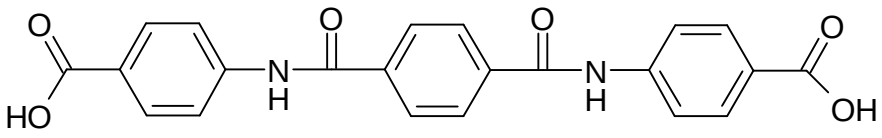


Figure 3.2 IR of JPM Monomer Sample JPM-1-122

Scheme 3.3



The spectra of the monomer treated with TED shown in Figure 3.3 shows a similar peak to the starting material at 3300 cm^{-1} corresponding to the amide linkage of the monomer. While the three peaks at 2995, 2663, and 2547 cm^{-1} are from the OH group of the acid are

not seen in the spectra of the sample treated with TED, it does show a peak at 1680 related to a carbonyl stretch. Some peaks appear in the treated sample that do not appear in the original untreated sample. These peaks at 1523, 1493, 1430 cm^{-1} correspond to CH_2 stretching. The starting monomer does not contain CH_2 so this can be assumed to be from triethylenediamine. The spectrum shown in Figure 3.3 supports the reaction scheme shown in Scheme 3.4.

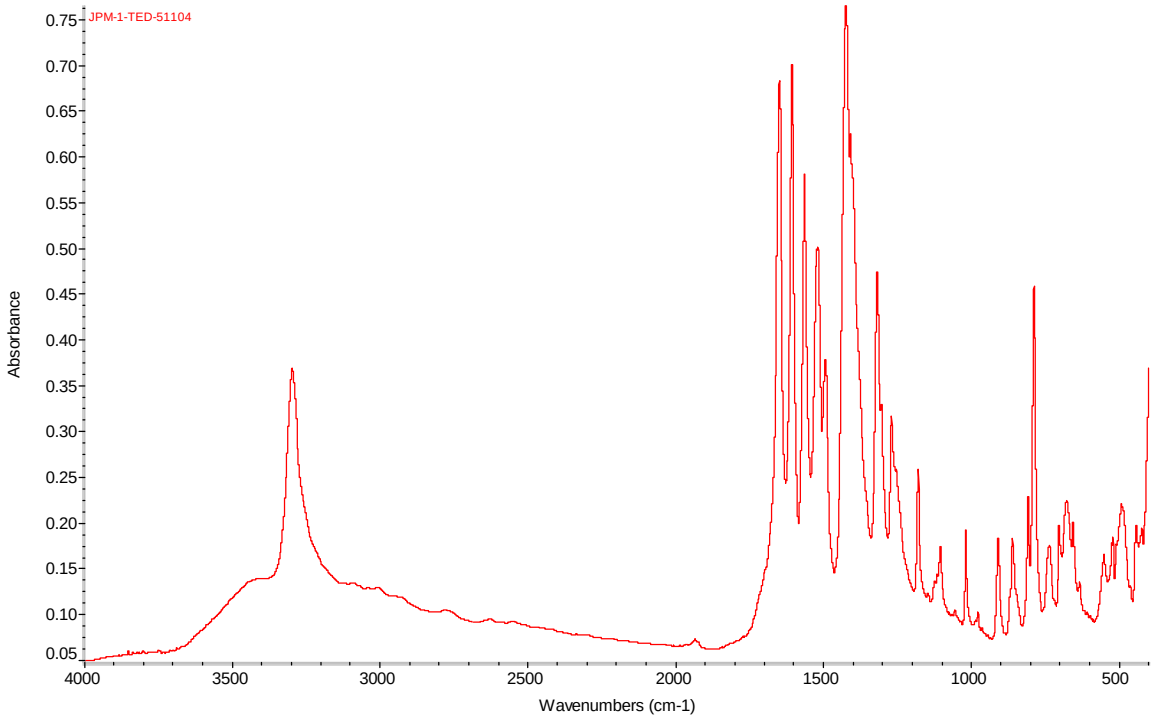
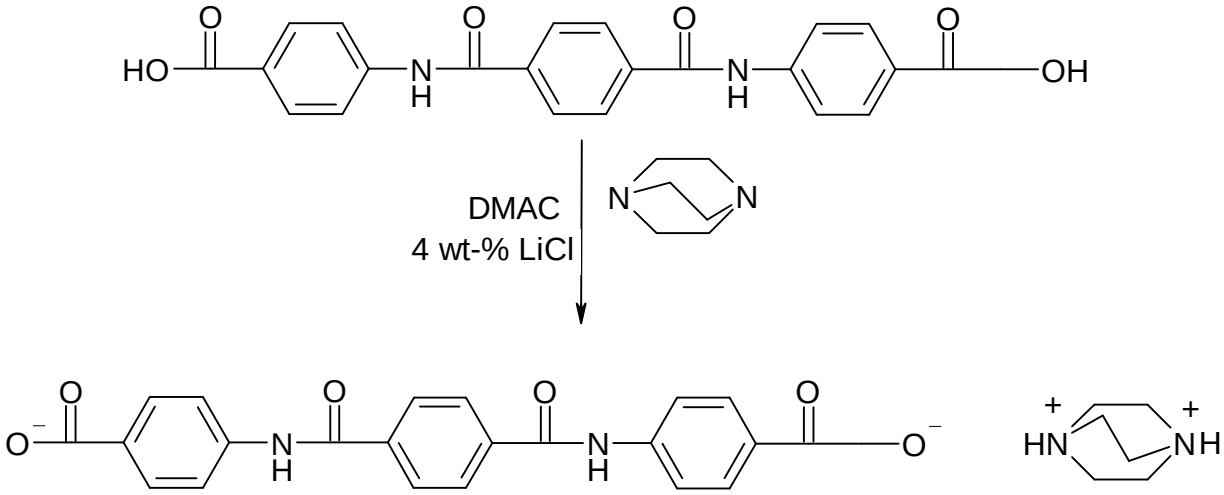


Figure 3.3 IR of Salt of JPM with TED Synthesized at Room Temperature

Scheme 3.4



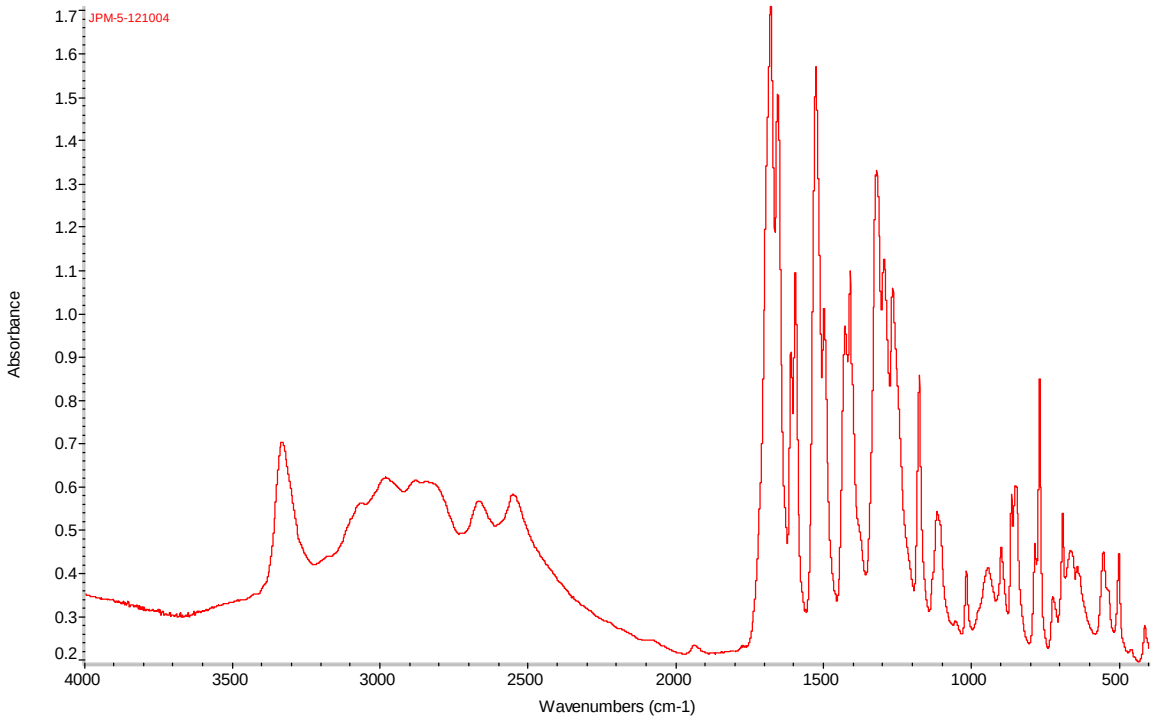


Figure 3.4 IR of JPM Monomer Sample JPM-5-121004

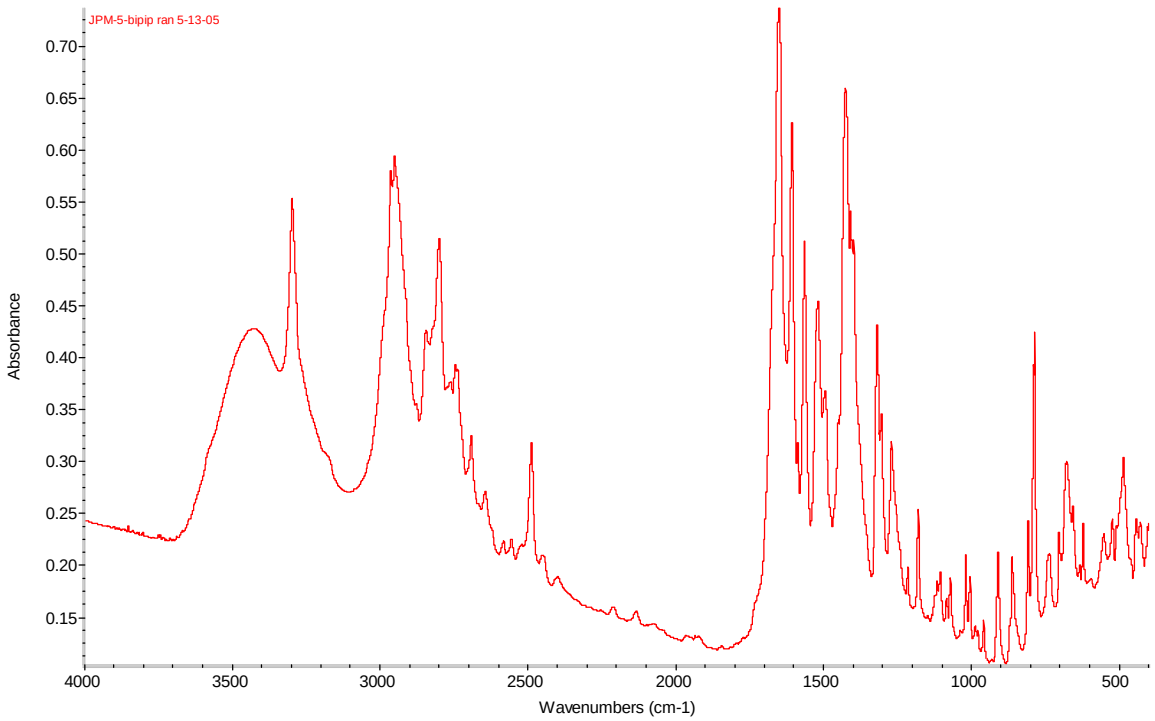
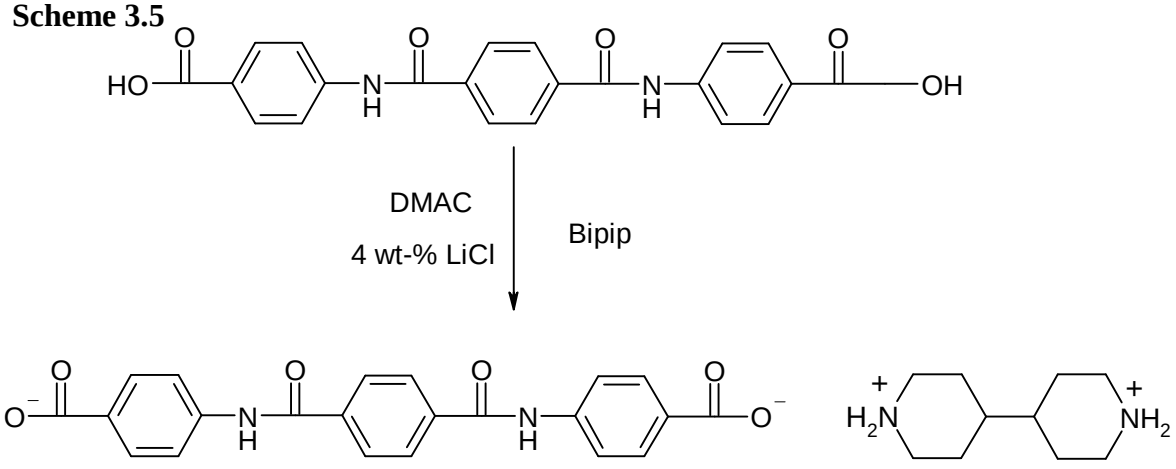


Figure 3.5 IR of Salt of JPM with Bipip Synthesized at Room Temperature

The JPM sample treated with the Bipip shows the expected peak at 3300 cm^{-1} corresponding to NH from the formation of the salt with the binder and the monomer. This salt formation after reaction of Bipip with the OH portion of the acid group of the monomer as shown in the reaction schematic in Scheme 3.5.

Scheme 3.5



The peaks and doublets from 2600 to 3000 cm^{-1} relate to CH_2 from the saturated rings of the Bipip diamine. The peak at 1680 cm^{-1} comes from the carbonyl groups of the monomer. The peaks from the 800-500 cm^{-1} represent the aromatic ring stretching of the starting monomer.

The thermo-gravimetric analysis (TGA) was performed in nitrogen to ensure the test was administered in an inert environment. The amount of weight loss during the experiments was recorded. The thermal degradation of the JPM monomer (Figure 3.6) shows a two-step weight loss confirming that it is a stable compound. The second stage of weight loss seems to be from the aromatic rings breaking apart at the amide linkages. The TGA of the sample treated with TED is shown in Figure 3.7 and shows a three-step weight loss the latter two steps is exactly like that of the weight loss seen in the monomer. The first weight loss can be explained as the TED component of the sample this can due to similar weight loss being seen in Figure 3.11 of the TGA of the TED component. The weight loss for the samples treated with the Bipip diamine show vastly different weight loss between the sample prepared at room temperature and the one prepared and heated to 100^{o}C. The weight loss graphs shown in Figures 3.9 and 3.10 show three step weight loss much like that seen in the samples treated with TED.

The first step of weight loss is from the Bipip diamine and the last two from the monomer starting material.

Elemental analysis was conducted on N,N'-bis(p-carboxylphenyl)terephthalamide monomer and the monomer treated with TED. The results are presented in Table 3.2. The calculated values for both the monomer and the treated sample were a match proving that

the monomer was structurally correct and that the monomer treated with TED retained the diamine after treatment.

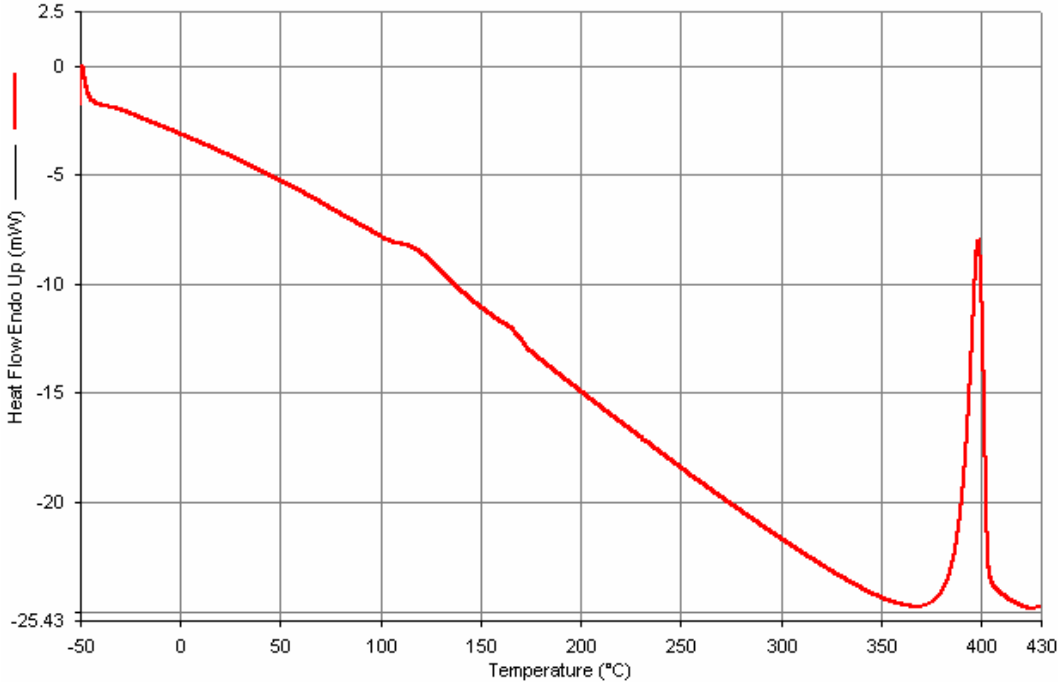


Figure 3.6 DSC of JPM Monomer sample JPM-1-122

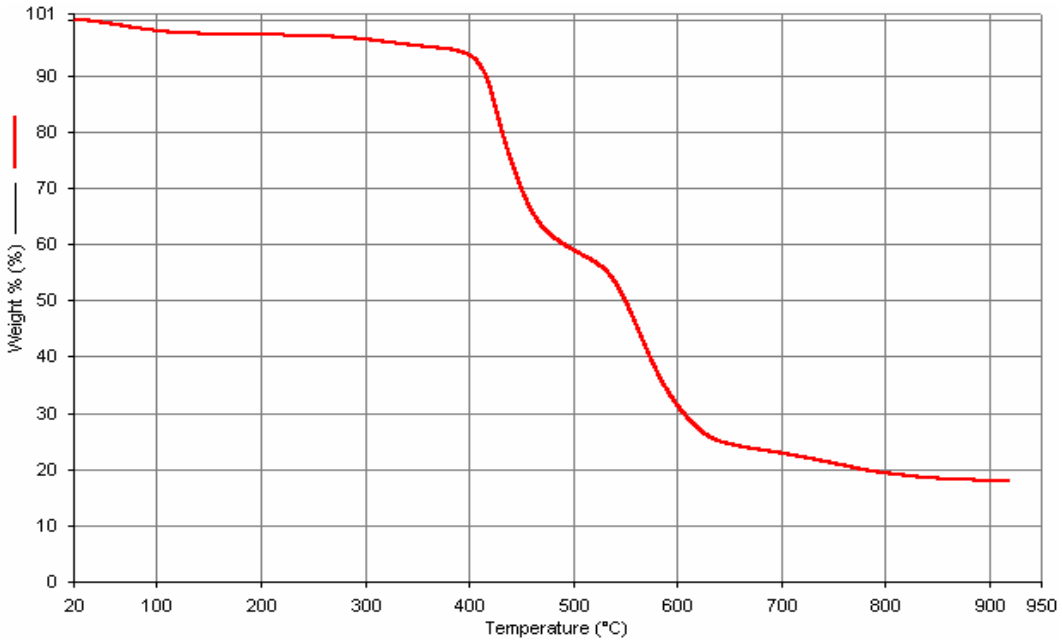


Figure 3.7 TGA of JPM Monomer sample JPM-1-122

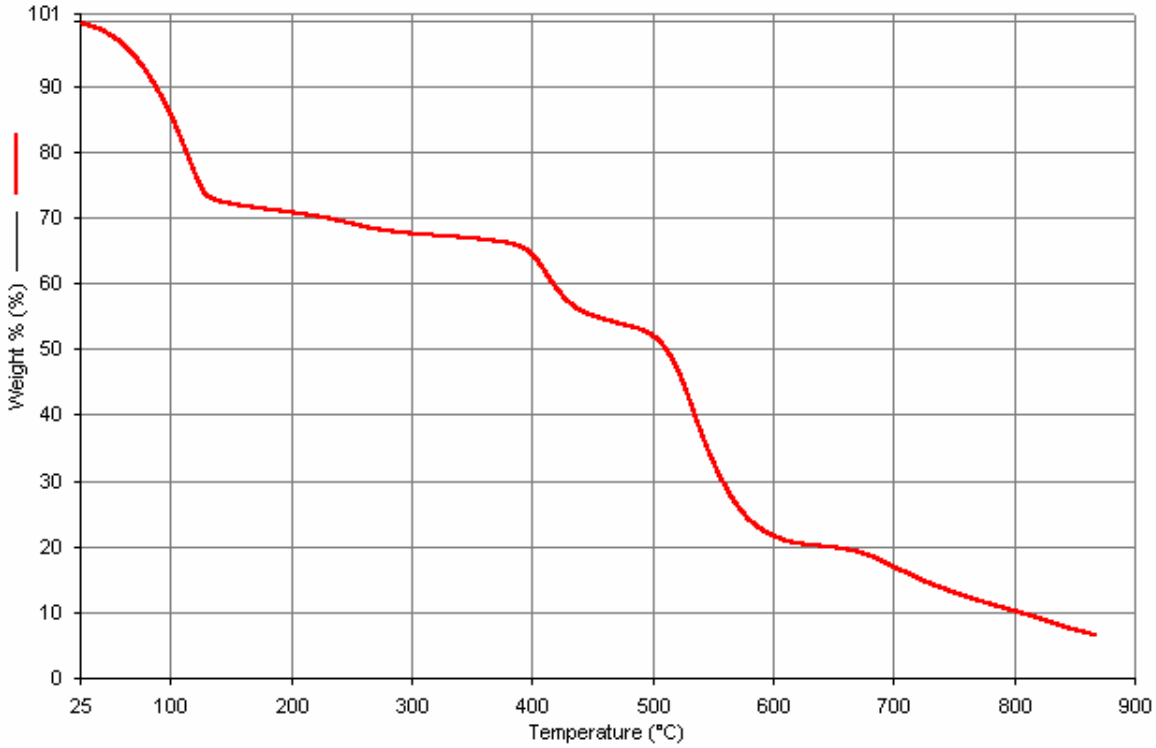


Figure 3.8 TGA of Salt of JPM with TED Synthesized at Room Temperature

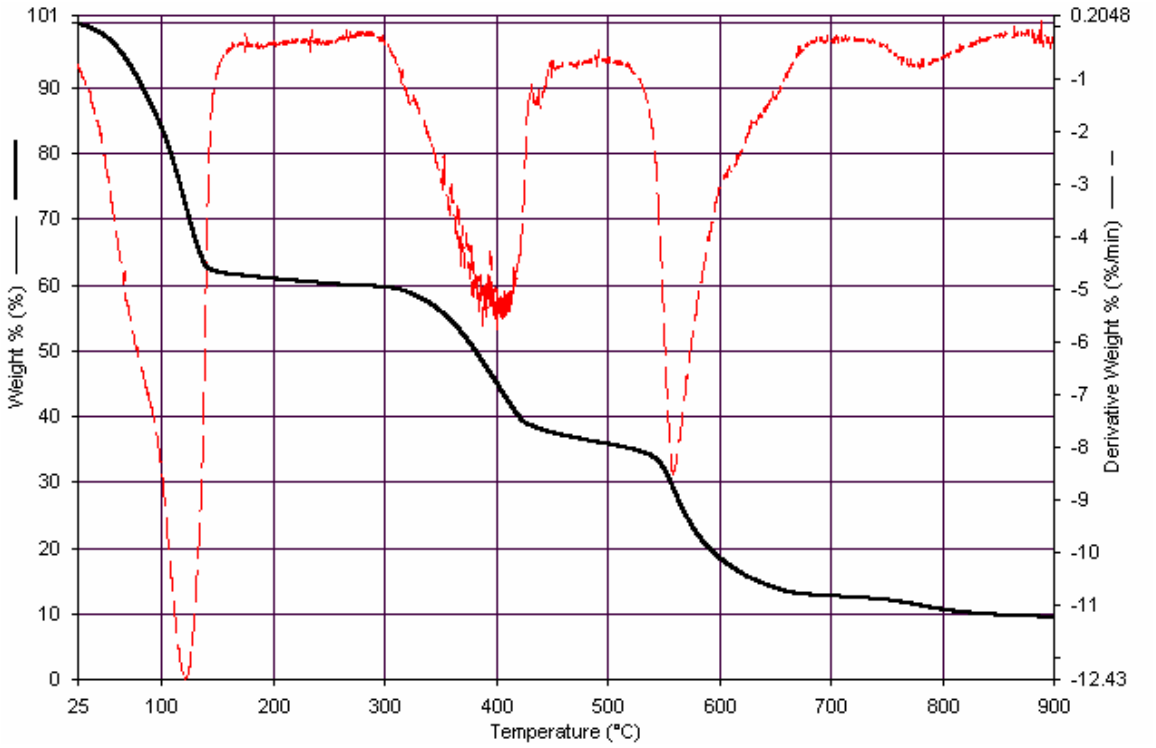


Figure 3.9 TGA of Salt of JPM with Bipip Synthesized at Room Temperatu**re**

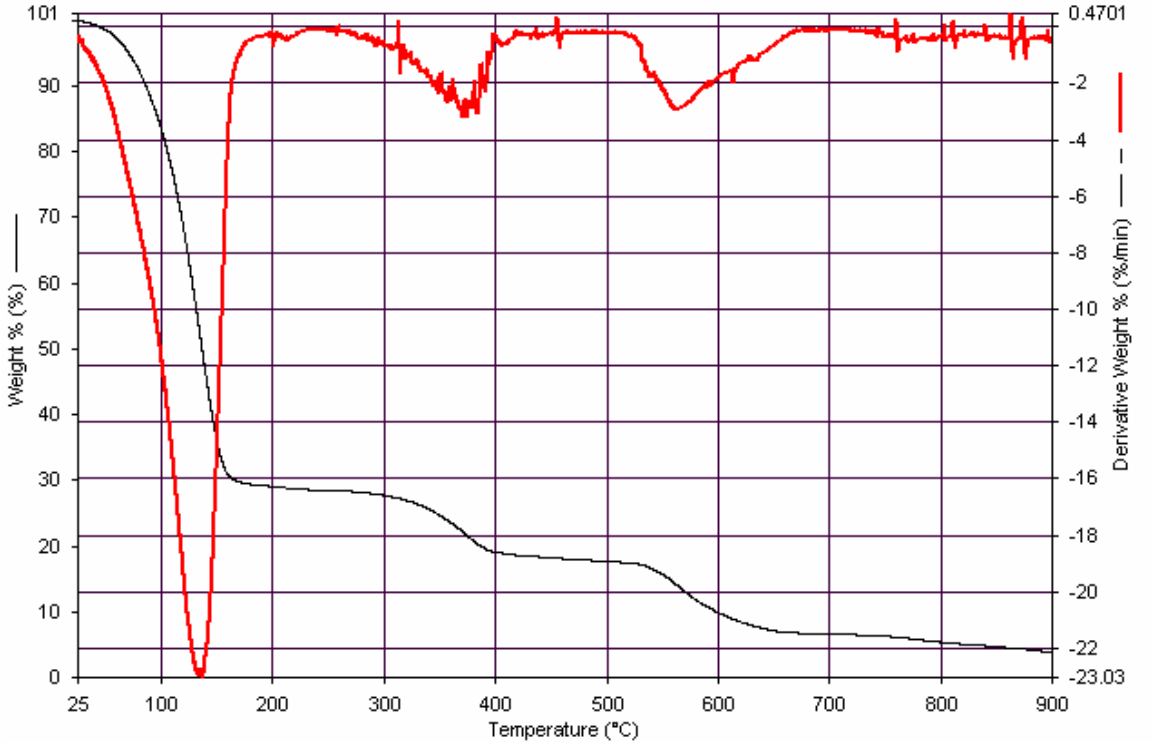


Figure 3.10 TGA of Salt of JPM with Bipip Synthesized at Elevated Temperature

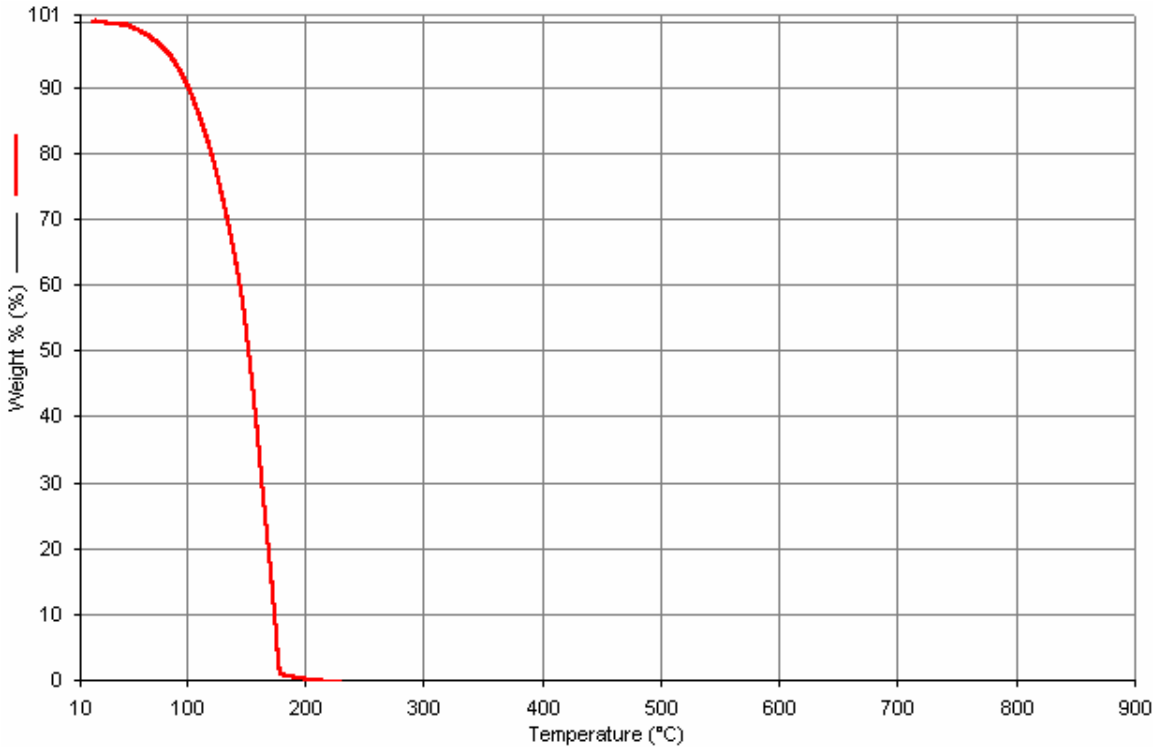


Figure 3.11 TGA of TED Binding Component

Table 3.2 Elemental Analysis of JP Monomer and JPM Salt with TED

JP Monomer[a)]

Analysis For	Calculated (%)	Found (%)
Oxygen	23.64	24.28
Carbon	65.44	63.37
Hydrogen	3.96	4.36
Nitrogen	6.94	6.32

a) $C_{22}H_{16}O_6N_2$

JP Monomer/ TED[b)] Salt

Analysis For	Calculated (%)	Found (%)
Oxygen	18.52	19.21
Carbon	65.19	64.41
Hydrogen	5.43	5.63
Nitrogen	10.87	10.79

b) $N_2C_6H_{12}$.

3.4 Conclusions

Experimental work centered around the treatment of N,N'-bis(p-carboxylphenyl)terephthalamide monomer with diamines in aprotic polyamide solvents containing metal salts. Fourier Transform Infrared spectroscopy was used as the main tool to study the interaction of the diamine binders with the monomer. The results support the theories of ionic supramolecular interaction of the salt formation as depicted in Scheme 3.3. The spectroscopy data also allowed for structural comparison of treated and untreated samples lending support to the structural changes of the monomer after

treatment with the diamine binder. Of the two diamine binders used in the investigation only the TED binder seems to form the supramolecular bonds. Although it seems from the data that TED binder forms a salt with the JP monomer instead of the first theorized hydrogen bonds with the OH components of the acid groups terminating the monomer. The elemental analysis data supports the thermogravimetric analysis of the treated samples retaining the TED after treatment. The TGA data support that the TED binder has some interaction with the JPM monomer.. The data support an interaction due to its persistence of the binder even after repeatable washing with methanol after filtration of the sample. The percentage of weight loss differences between the reaction at room temperature and that of the reaction heated to 100^{o}C. The differences in the treated JPM monomers thermogravimetric analysis graph upon heating the sample after addition of the diamine are possibly due to the added heat forcing the proposed reaction schematic in Scheme 3.4 to more readily go to completion.

3.5 Acknowledgments

I am very grateful for Dr. Jack Preston and his visits during my research from which I gained a great amount of understanding of polyamide synthesis.

3.6 References

1. Kotek R., Krigbaum W. R., Preston J., *J. Polym. Sci. Chem. Ed.*, 20, 3241-3249, (1982)
2. Kotek R., Krigbaum W. R., Preston J., *J. Polym. Sci. Chem. Ed.*, 21, 2837-2841, (1983)
3. Kotek R., Krigbaum W.R., Preston J., *J. Polym. Sci. Chem. Ed.*, 22, 873-876 (1984)

IV. PBA Synthesis and Binding

4.1 Introduction

Aromatic polyamides especially poly-(p-benzamide) have been studied for many years, and have been reported as high-modulus and high-temperature-resistant polymers, and can be produced under the Yamazaki [2, 6] and Higashi [6] reaction conditions. Various attempts have been made to modify the extended-chain aromatic polyamides in order to obtain better mechanical properties. This project involves a novel idea for chain extension of PBA polymers. The PBA segments will be synthesized using the Yamazaki [2] reaction and treated with cyclic aliphatic diamines and pyrimidine derivatives as links in order to ideally form a supramolecular array. Inherent viscosities of the PBA prepared in this manner range from 1-1.7 dL/g with a Mw from 500 to 10000 g/mol respectively in concentrated sulfuric acid. These are only moderately low molecular weight for the polymers to exhibit the high-modulus and high strength properties of industrially produced polyamides. Non-covalent interactions in synthetic systems have increasingly been employed to obtain well-defined aggregates from synthetic molecules through a spontaneous and reversible process indicated with the term self-assembly [3-4]. Linear self-assembled aggregates may be obtained that can be considered as analogs of covalent polymers, but now the monomers are held together by reversible noncovalent interactions, instead of covalent bonds [5].

4.2 Experimental

4.2.1 Materials

Commercially available anhydrous LiCl (Aldrich) was dried in an oven at 400 ^{0}C and kept in a vacuum desiccator containing NaOH. LiCl hydrate (Aldrich), N,N-dimethylacetamide (DMAC), anhydrous, 99.0% (Aldrich), sodium bicarbonate (Aldrich), tetrahydrofuran (THF) (Aldrich) , sulfuric acid (Aldrich), hydrochloric acid (Aldrich), p-aminobenzoic acid (p-ABA) (Aldrich), triethylenediamine, bipiperidine dihydrochloride (Aldrich), chloroform (Aldrich), sodium hydroxide pellets (NaOH) (Fischer), pentane (Aldrich), 2-amino-4-hydroxy-6-methylpyrimidine (Aldrich), hexyldiisocyanate, and terephthaloyl chloride (TCL) (Aldrich) were used with out further purification.

4.2.2 Polycondensation of para-aminobenzoic acid (p-ABA) by Using Triphenyl Phosphite in the Presence of Lithium Chloride

A typical polymerization procedure is shown below.

A mixture of p-ABA (2.74 g, 0.02 mole) and triphenyl phosphite (6.21 g, 0.02 mole) in a mixed solvent of NMP (30 ml) containing lithium chloride (4 wt-%) and pyridine (20 ml) was heated to 100^{o}C for 3 hr with stirring under nitrogen in a three necked conical flask. After cooling, the reaction mixture was poured into methanol (200 ml), and the precipitated polymer was separated by filtration, washed in boiling methanol for 2hr, and dried. Similarly the reaction was carried out by varying the amount of LiCl, using various solvent ratios at different reaction times [2].

4.2.2.1 Polycondensation of p-ABA by Using Triphenyl Phosphite in the Presence of Lithium Chloride Hydrates

Lithium Chloride Hydrate Synthesis

The lithium chloride hydrate was synthesized by making an aqueous saturated solution of LiCl and water. The solution was heated to 60^{o}C until the LiCl was completely dissolved. The solution was allowed to cool until a wet mixture of LiCl reformed and was filtered warm and dried in a desiccator.

Polymerization of PBA with Lithium Chloride Hydrates

A mixture of p-ABA (2.74 g, 0.02 mole) and triphenyl phosphite (6.21 g, 0.02 mole) in a mixed solvent of NMP (30 ml) and pyridine (20 ml) containing lithium chloride hydrates (4 wt-%) was heated to 100^{o}C for 3 hr with stirring under nitrogen. After cooling, the reaction mixture was poured into methanol (200ml), and the precipitated polymer was separated by filtration, washed in boiling methanol for 2hr, and dried.

4.2.3 Binding Methods

4.2.3.1 PBA Solutions

Samples with different molecular weights were synthesized using the Yamazaki reaction conditions. The solvent mixture was prepared by dissolving 4% (g/ml) LiCl, which was dried in an oven at 400 ^{0}C for 24 hrs, and kept in a vacuum desiccator containing NaOH. Solutions of different concentrations were made by adding PBA in (g/ml) to N,N'-dimethylacetamide (DMAC) and kept in a desiccator before use [7].

4.2.3.2 Binding with Triethylenediamine (TED)

Two sets of PBA solutions were prepared using the method in section 4.2.3.1 in different concentrations from 2-4%; one set of solutions was kept as control, while the remaining three solutions were treated with TED which had been dissolved in 0.5ml of the DMAC solvent containing (4 wt-%) in a 2:1 mol ratio of TED: PBA. The solutions were stored in a desiccator for 24 hrs at room temperature. The amount of the components are shown in Table 4.1.

Table 4.1 PBA with TED Binding Solutions Component Amounts

Sample Code	DMAC/LiCl (ml)	PBA (g)	TED (g)
2A	10.5	0.20	0
3A	10.5	0.30	0
4A	10.5	0.40	0
2B	10.5	0.20	7.1×10^{-3}
3B	10.5	0.30	1.1×10^{-2}
4B	10.5	0.40	1.4×10^{-2}

Note: A sample of PBA with inherent viscosity of 1.00 was used for the sample preparation.

4.2.3.3 Binding with Bipiperidine (Bipip)

Bipiperidine (Bipip) was obtained from simple organic separation by adding 0.01 mol bipiperidine dihydrochloride (Aldrich) to 100 ml water containing an excess of NaOH pellets. The solution was then added to a separation funnel containing 100 ml chloroform (Aldrich). The organic layer was collected and distilled off and product was dried in vacuum at 80^{o}C.

Two sets of PBA solutions were prepared using the method in section 4.2.3.1 in different concentrations of (0.5, 1.5, 2.5%); one set of solutions were kept as controls while the remaining three solutions were treated with Bipip which had been dissolved in 0.5ml of the DMAC solvent containing (4 wt-%) in a 2:1 mol ratio of Bipip: PBA. The solutions were stored in a desiccator for 24 hrs at room temperature as shown in Table 4.2.

Table 4.2 PBA with Bipip Binding Solutions Component Amounts

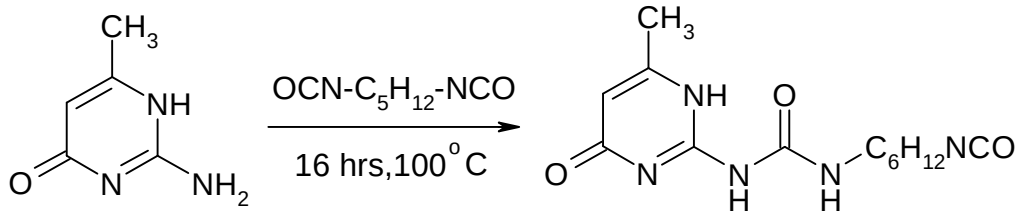
PBA Conc. (wt%)	Sample Code	DMAC/LiCl (ml)	PBA (g)	Bipip (g)
0.5	Control	15.5	0.075	0
1.5.	Control	15.5	0.225	0
2.5.	Control	15.5	0.375	0
0.5.	Exp.	15.5	0.075	$3.0x10^{-3}$
1.5.	Exp.	15.5	0.225	$9.0x10^{-3}$
2.5.	Exp.	15.5	0.375	$1.5x10^{-2}$

Control samples are those without binder added. Exp. samples are those with binder added.

4.2.3.4 Meijer Synthesis

Synthesis of 2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone (Upy) was carried out to the following procedure. 0.04 mol 2-amino-4-hydroxy-6-methylpyrimidine in 0.27 mol hexyldiisocyanate were heated at 100^{o}C for 16 hrs. Pentane was added and the resulting precipitate was filtered and washed with pentane. The white powder was dried at 60^{o}C under reduced pressure. The excess of hexyldiisocyanate was recovered by distillation [11]. The synthesis was carried out by Scheme 4.1.

Scheme 4.1.



Two sets of PBA solutions were prepared using the method in section 4.2.3.1 in different concentrations of (0.5, 1.5 and 2.5%); one set of solutions was kept as control, while the remaining three solutions were treated with Upy which had been dissolved in 0.5ml of the DMAC solvent containing (4 wt-%) in a 2:1 mol ratio of Upy: PBA. The solutions were stored in a desiccator for 24 hrs at room temperature as shown in Table 4.3.

Table 4.3 PBA with Upy Binding Solutions Component Amounts

PBA Conc. (wt%)	Sample Code	DMAC/LiCl (ml)	PBA (g)	Upy (g)
0.5	Control	15.5	0.075	0
1.5	Control	15.5	0.225	0
2.5	Control	15.5	0.375	0
0.5	Exp.	15.5	0.075	5.8×10^{-3}
1.5	Exp.	15.5	0.225	1.7×10^{-2}
2.5	Exp.	15.5	0.375	2.9×10^{-2}

Control samples are those without binder added. Exp. samples are those with binder added.

4.2.3.5 Film Preparation

PBA Solutions

Five PBA solutions were prepared using the method in section 4.2.3.1 of the same concentration of 3.75% (g/ml) using 1.5g PBA in 40ml of DMAC (4 wt-%). Each of the five solutions was split into two 20 ml solutions. One set of solutions was kept as control, while the remaining five solutions were treated with TED that had been dissolved in 0.5 ml of the DMAC solvent containing (4 wt-%) in a 2:1 mol ratio of TED: PBA. The solutions were stored in a desiccator for 24 hrs at room temperature as shown in Table 4.4.

Table 4.4 Addition of TED to PBA Solutions

Sample	Mw (g/mol)	DMAC/LiCl (ml)	PBA (g)	TED (g)
PBA-9-1120 (cont.)	494	40.5	1.5	0
PBA-19-39 (cont.)	839	40.5	1.5	0
PBA-23-716 (cont.)	1046	40.5	1.5	0
PBA-18-226 (cont.)	3348	40.5	1.5	0
PBA-22-630 (cont.)	5812	40.5	1.5	0
PBA-9-1120 (exp.)	494	40.5	1.5	0.0392
PBA-19-39 (exp.)	839	40.5	1.5	0.0439
PBA-23-716 (exp.)	1046	40.5	1.5	0.0477
PBA-18-226 (exp.)	3348	40.5	1.5	0.0334
PBA-22-630 (exp.)	5812	40.5	1.5	0.0289

Cont. samples are those with out binder added Exp. are those with binder added.

Film Preparation

The PBA solutions were added into petri dishes with a diameter of 9.65 cm. The petri dishes were placed in a vacuum oven at 60^{o}C under reduced pressure for 24 hrs.

4.2.4 Analytical Measurements

4.2.4.1 Differential Scanning Calorimetry (DSC)

DSC was conducted on 3-10 mg samples in a Diamond DSC Perkin Elmer with Pyris software. An indium standard was used for calibration, a heating rate of 20^{o}C/min. was employed, and nitrogen was used as the purge gas.

4.2.4.2 Fourier Transform Infrared (FTIR)

Absorbance FTIR spectra were recorded on a Thermo Electron Nexus 470 bench with OMNIC software. Frequencies from 400-4000 cm^{-1} were covered and 64 scans were recorded with a gain =1 on samples mixed with KBr and pressed into pellets.

4.2.4.3 Thermogravimetric Analysis (TGA)

TGA scans of 5-10 mg samples were obtained using a Perkin Elmer Pyris 1 thermogravimetric analyzer. The samples were placed in platinum pans that were hung in the heating furnace. The weight percentage of the mater remaining in the pan was recorded while heating 25-800^{o}C a heating rate of 20^{o}C/min. Nitrogen was used as the purge gas.

4.2.4.4 Elemental Analysis

Galbraith labs determined the hydrogen, nitrogen, oxygen and carbon content of the JPM samples for verification of the purity and structure.

4.2.4.5 Solution Viscosity

Solution viscosities were obtained using Ubbelhode viscometers size 1C and 2 at 25°C. Solvents used were 96% sulfuric acid for PBA; for some portions of the binding experiments dimethylacetamide (DMAC) containing 4% lithium chloride was used in the already prepared PBA solutions. All polymer concentrations were 0.5 g/dL for determining inherent viscosities for intrinsic viscosity calculations. The flow time of the solvent always exceeded 100s. (Note: the concentration of LiCl were grams of salt per 100 mL of solvent.) [8]

Relative viscosity

$$h_{rel} = \frac{t}{t_o} \qquad (1)$$

Specific viscosity

$$h_{spec} = \frac{t}{t_o} - 1 \qquad (2)$$

Reduced viscosity

$$h_{red} = \frac{(\frac{t}{t_o} - 1)}{c} \qquad (3)$$

Inherent viscosity

$$h_{inh} = \frac{\ln(\frac{t}{t_o} - 1)}{c} \qquad (4)$$

Where t_o is the polymer solvent flow time and t is polymer solution flow time.

4.3 Results and Discussion

4.3.1 Binding of PBA

The first step of the research was to master the Yamazaki reaction scheme for making PBA through the polycondensation of p-ABA [2]. The reaction was carried out at 100^{o}C for varying amounts of NMP using triphenyl phosphite in NMP-pyridine in the presence of varying amounts of the LiCl. The viscosity results are given in Figures 4.1 and 4.2 The LiCl was used due to being known to increase the solvating power of aprotic solvents such as NMP [10]. The results of the polycondensation reaction of p-ABA using triphenyl phosphite in the presence of varying amounts of LiCl are shown in Figure 4.2 The addition of the LiCl (1 to 7 wt-%) increased the molecular weight of the polymer considering the maximum values of the viscosity versus the concentration of the salts are more than 2 wt-%. The theory that metal salts may contribute to the improvement of the dissolution power of the resulting polyamide [2]. This improvement seems to be supported by Figure 4.2 there is a increase in viscosity up to 2 wt-% but seems to fall off after making the optimal salt concentration for maximum viscosity build to be around 2-4 wt-% as shown in the work done by Yamazaki [2] and his colleagues. The decrease in molecular weight at higher concentrations of salt maybe due to the salt competing with the polymer for solvent and decreasing the over all polymer solubility [12].

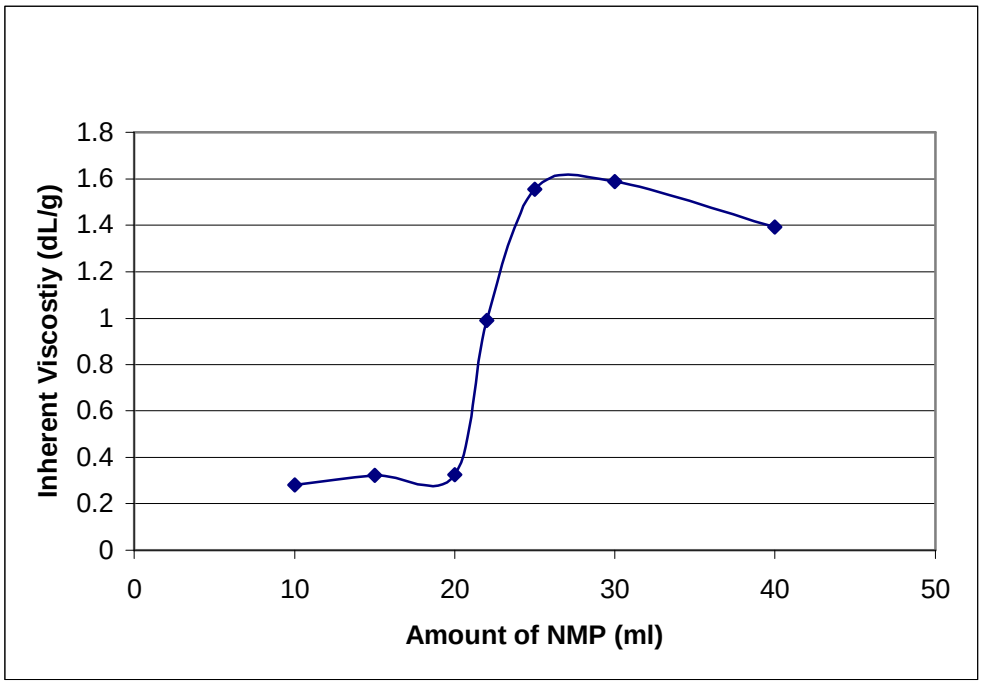


Figure 4.1 Effects of Varying Amount of NMP in the Mixed Solvent Used in the Polycondensation of p-ABA

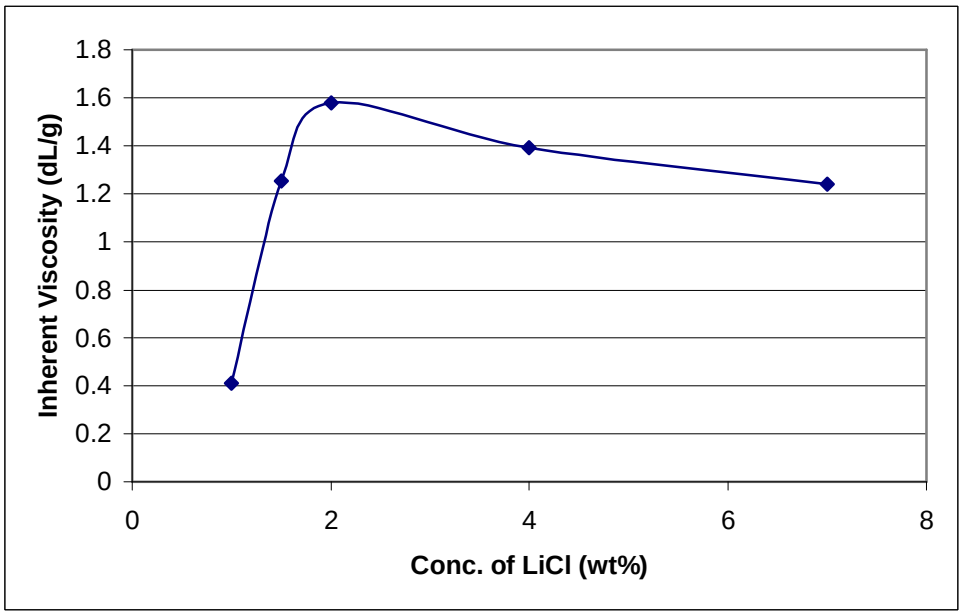


Figure 4.2 Effects of Varying Concentration of LiCl in NMP Used in the Polycondensation of p-ABA

The polycondensation reaction of p-ABA in the presence of 4 wt-% LiCl was examined by varying the amounts of pyridine in NMP as shown in Figure 4.1. By varying the amounts of solvents used during the polycondensation reaction you can vary the molecular weights of the polyamide produced. Another method we tried was to use LiCl hydrates in place of dried LiCl to investigate the effect on the molecular weights of polymers produced. The results are given in Table 4.3. From this table you can see that the hydrates probably inhibit the polymerization resulting in littler or no product. This is supported from the relative viscosity being 1.0. This was thought to be perhaps another option to control the molecular of our PBA samples produced. This was a key factor in our work since the ability to control the size of the PBA segments is key to finding the optimal size for formation of a supramolecular polyamide. Our theory of supramolecular polymerization utilizes small blocks of rigid polyamides bound together by different diamine or pyrimidine binders to increase the over DP and molecular weight. The varying inherent viscosities observed and calculated molecular weights [11] are given in Table 4.5.

Table 4.5 LiCl Hydrates Reaction Conditions and PBA Viscosity Data

Solvent Ratio (NMP/Py)	LiCl (%)	Time (hr)	Type of Hydrate	Relative Viscosity of PBA
30/20	4	3	Aldrich	1.05
30/20	4	3	Synthesized	1.04
30/20	4	3	Aldrich	1.06
30/20	4	3	Synthesized	1.05

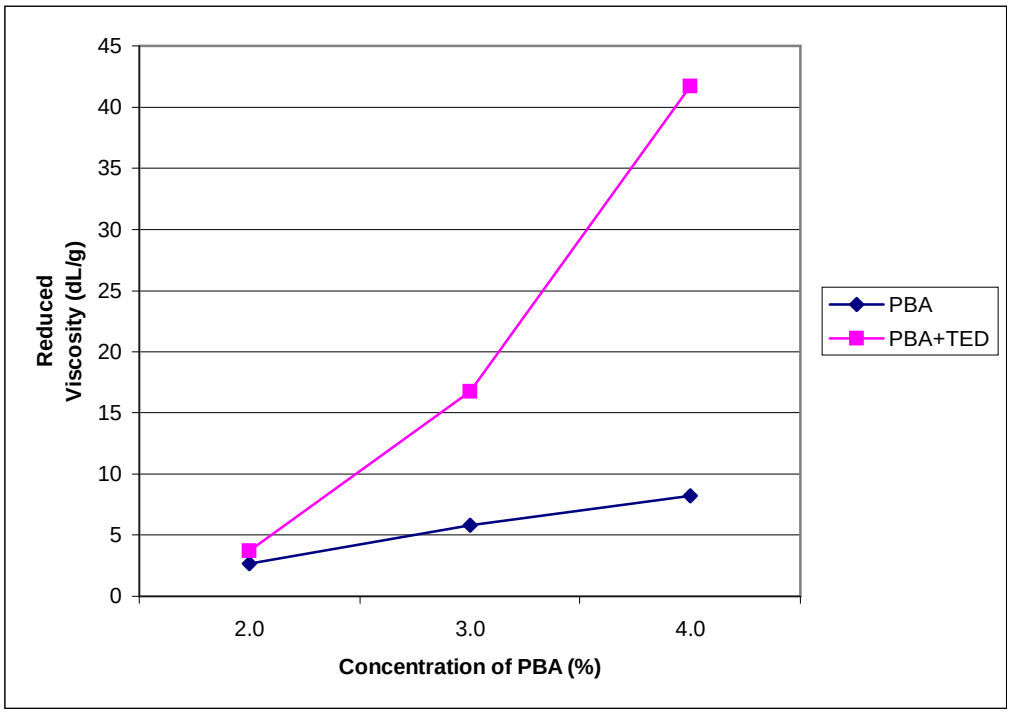


Figure 4.3 Viscometry of PBA Solutions and PBA Solutions Treated with TED Dissolved in DMAC (4 wt% LiCl) Inherent Viscosity 1.24 Mw 6368

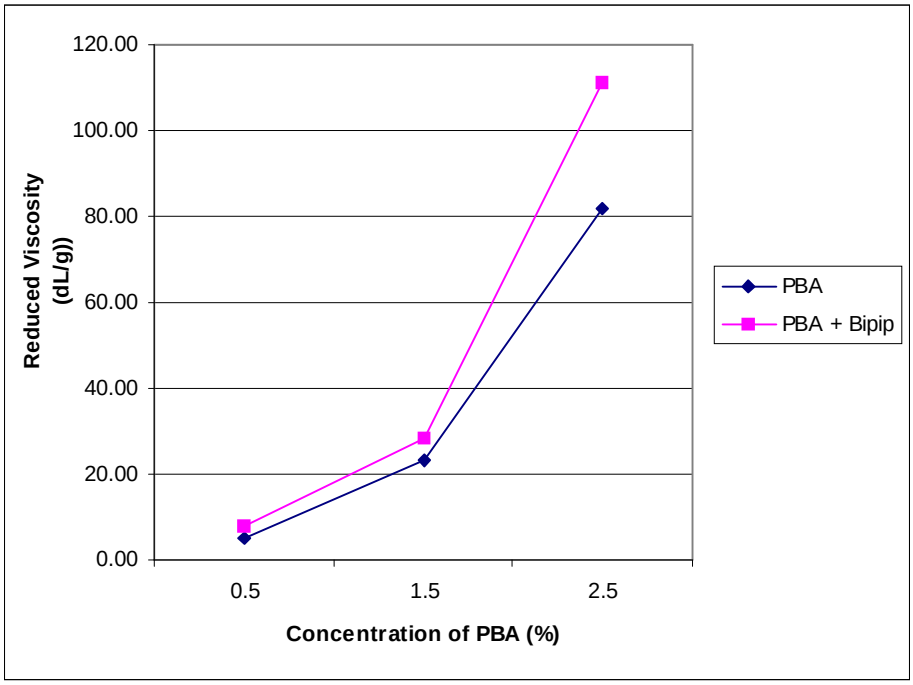


Figure 4.4 Viscometry of PBA Solutions and PBA Solutions Treated with Bipip Dissolved in DMAC (4 wt% LiCl). Inherent viscosity of 1.32 dL/g. Mw of 6891 g/mol.

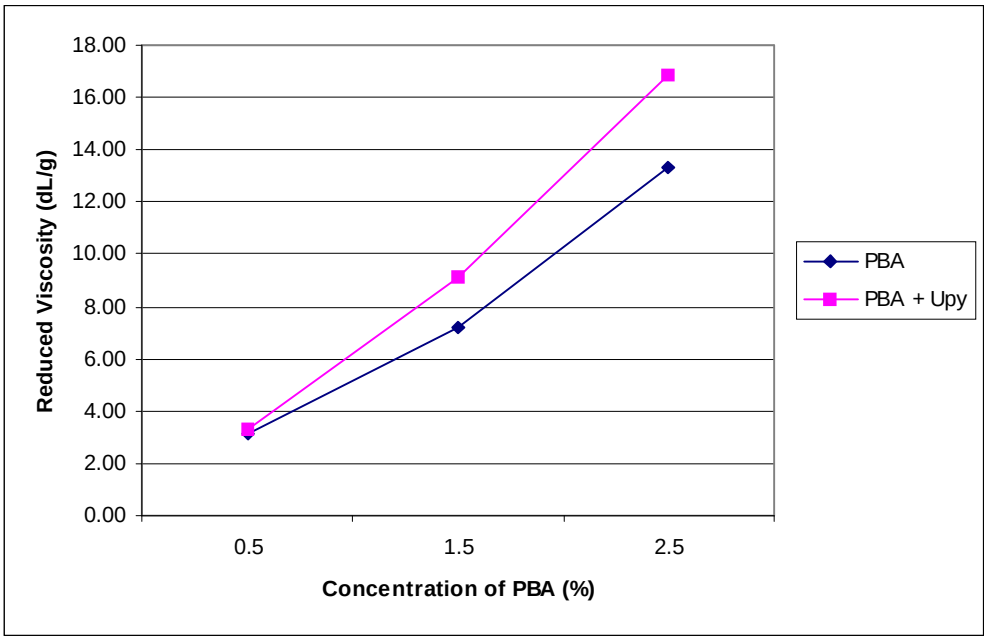


Figure 4.5 Viscometry of PBA Solutions and PBA Solutions Treated with Upy Dissolved in DMAC (4 wt% LiCl). Inherent viscosity 1.42 dL/g. Mw of 7509 g/mol.

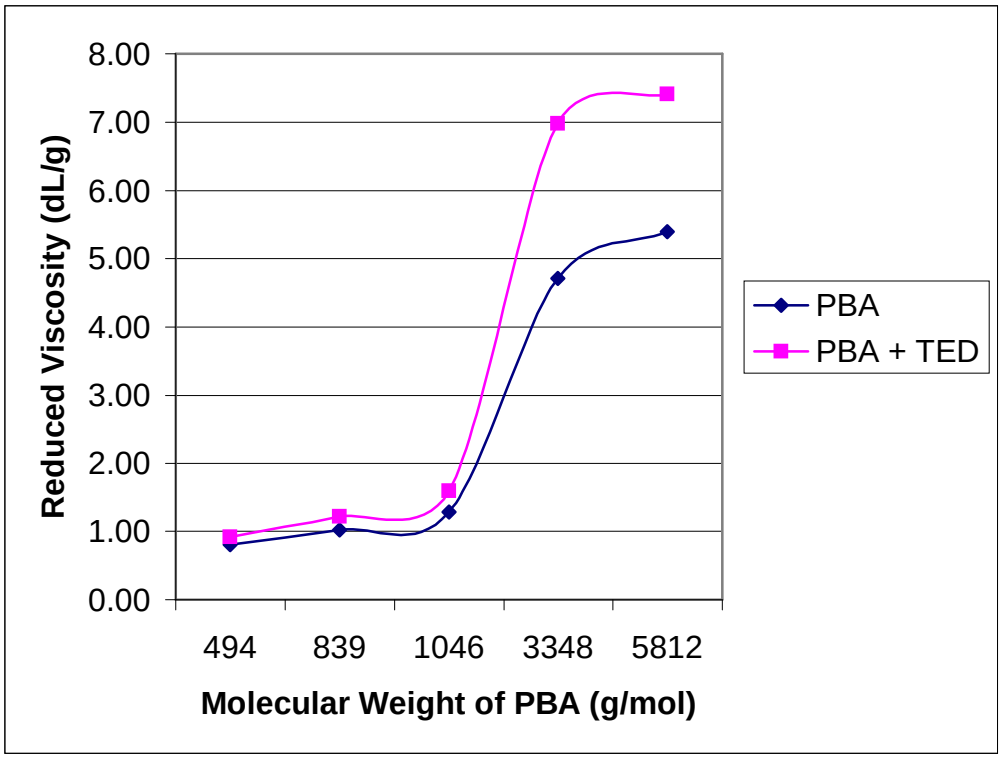


Figure 4.6 Viscometry of PBA Solutions and PBA Solutions with Varying Mw Treated with TED Dissolved in DMAC (4 wt% LiCl).

The molecular weights were calculated using equations from the Schaefgen work on viscosities of PBA. Solution viscometry was preformed on a series of PBA solutions with varying concentrations. The results are shown in Figure 4.7. From these results we were able to use the equations and constants used by Schaefgen [11] to calculate the molecular weight of our polymer samples without a need to do the Huggins plot for every sample. Once a Huggins plot has been done for one sample in a specific solvent, in this case concentrated sulfuric acid, a linear regression can be used to obtain a trend line. Using the equation of the line in the y=mx+b format you may use assume the m or slope of the line will be equivalent for every sample since this is a constant that relates to the solvent interaction with the polymer. Considering *Y* is the inherent viscosity of your sample and *X* is the concentration of that sample it is easy to enough to calculate for the remaining variable b, which is the intercept of, and theoretical intrinsic viscosity of your sample. Using the theoretical intrinsic viscosity coupled with the equations from the Schaefgen paper the molecular weight for any PBA sample can easily be calculated from equations 5 and 6 [11].

$$Mw < 12000 \text{ g/mol} \qquad (5)$$

$$[\eta] = 1.9 \times 10^{-7} Mw^{1.7}$$

$$Mw > 12000 \text{ g/mol} \qquad (6)$$

$$[\eta] = 7.8 \times 10^{-5} Mw^{1.08}$$

The varying molecular weights allowed for the choice of samples with optimal molecular weights for treatment with the binders.

The method for binding was carried out by dissolving PBA in DMAC containing 4 wt-% LiCl at different concentrations below the critical point, where PBA starts to form liquid crystalline phases [12]. The binder was added to the dissolved PBA solutions using the method in section 4.2.3. Solution viscometry was performed on the samples treated with TED and control samples are shown in Figure 4.4. There is a marked increase in viscosity from the control and treated samples when compared when compared with one another. . This increase is possibly due to formation of a salt increasing the molecular weight increases with the TED component as shown in the Scheme 4.2.

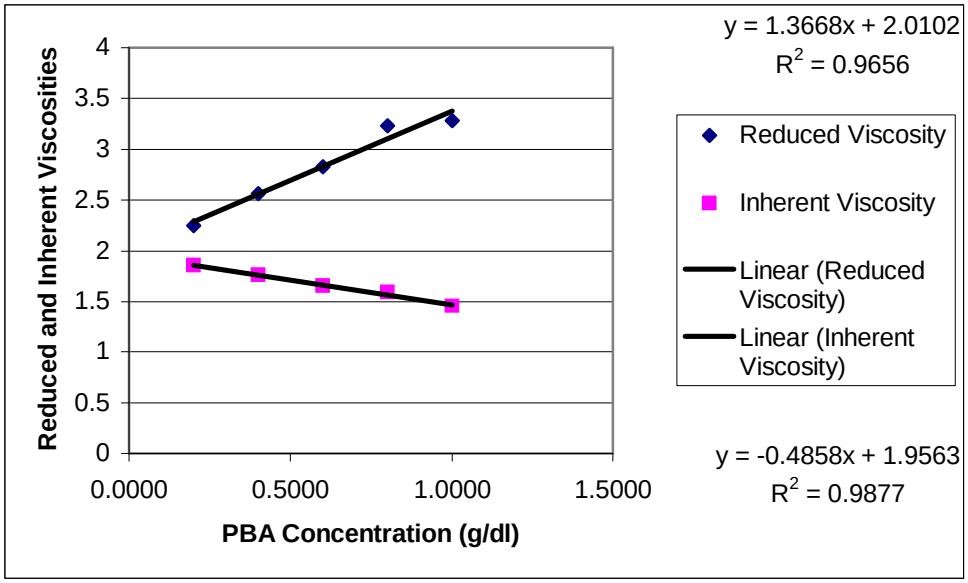
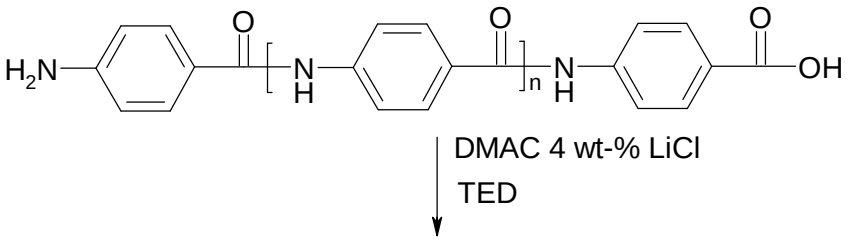
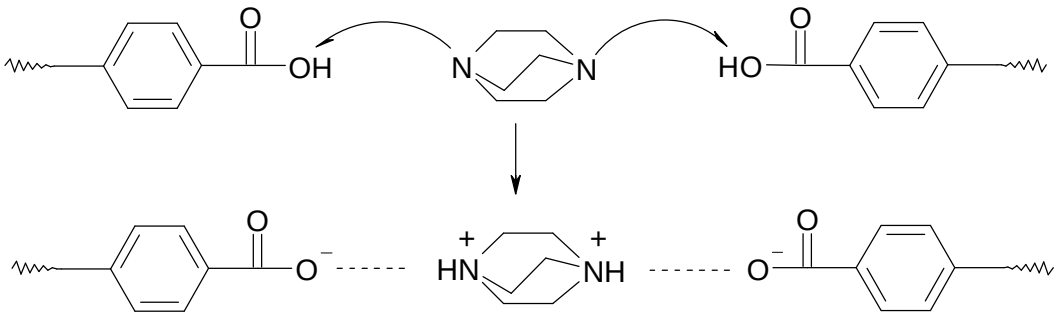


Figure 4.7 Solution Viscometry of PBA-6-1029 in Concentrated Sulfuric Acid

Scheme 4.2. Formation of JPM salt with TED



Scheme for Ideal Salt formation:



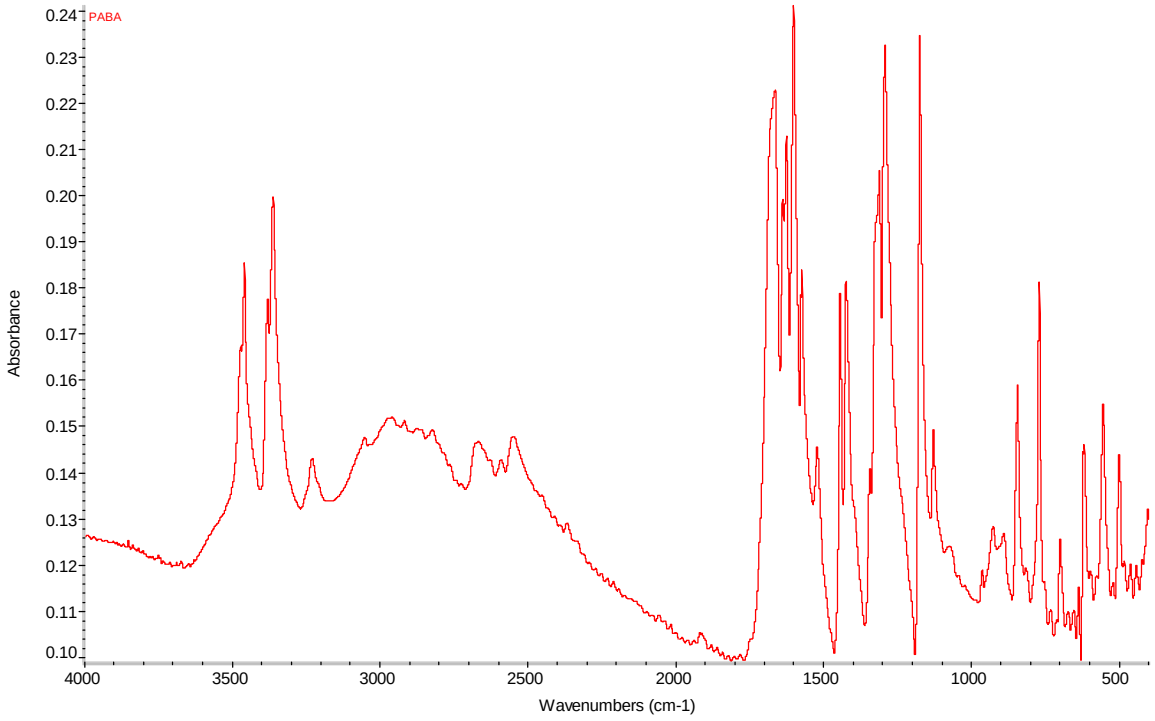


Figure 4.8 IR of p-Aminobenzoic Acid

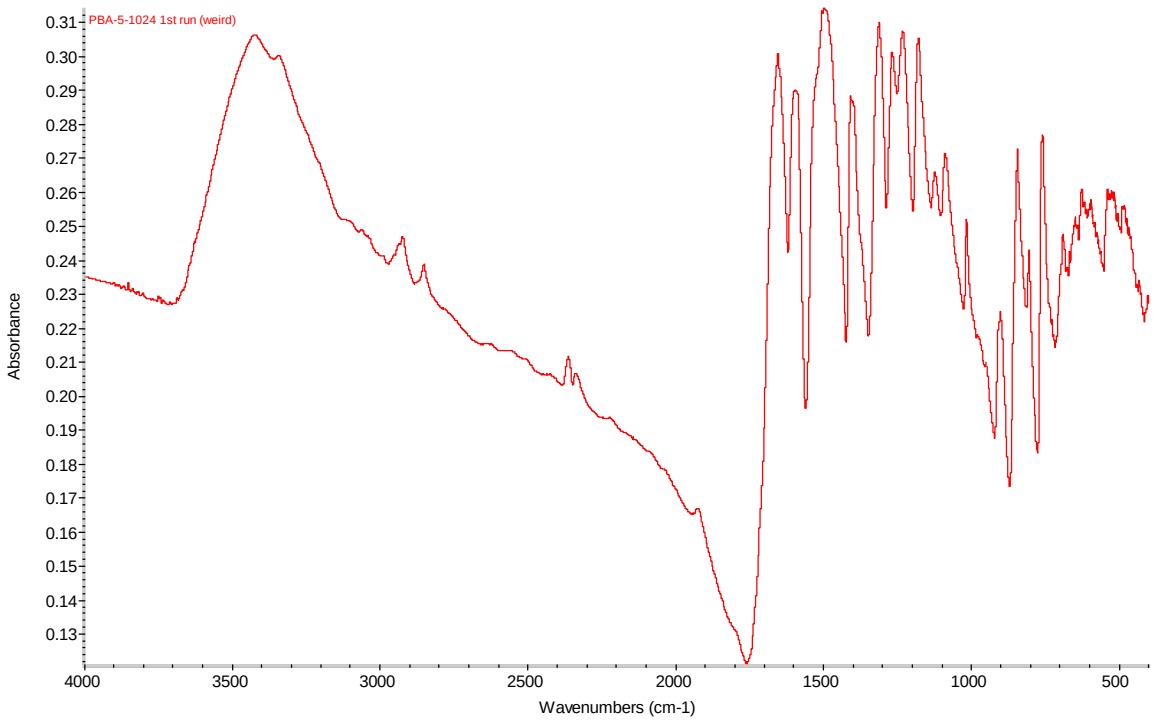


Figure 4.9 IR of PBA-5-1024 PBA Sample

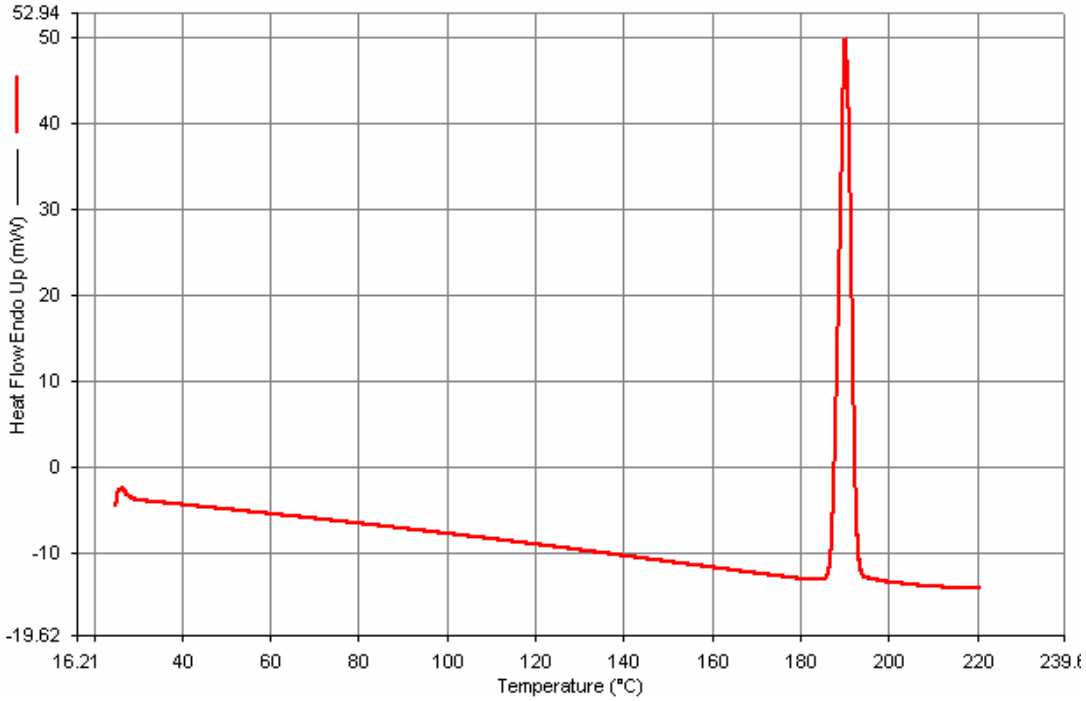


Figure 4.10 DSC Melting Point of p-Aminobenzoic acid

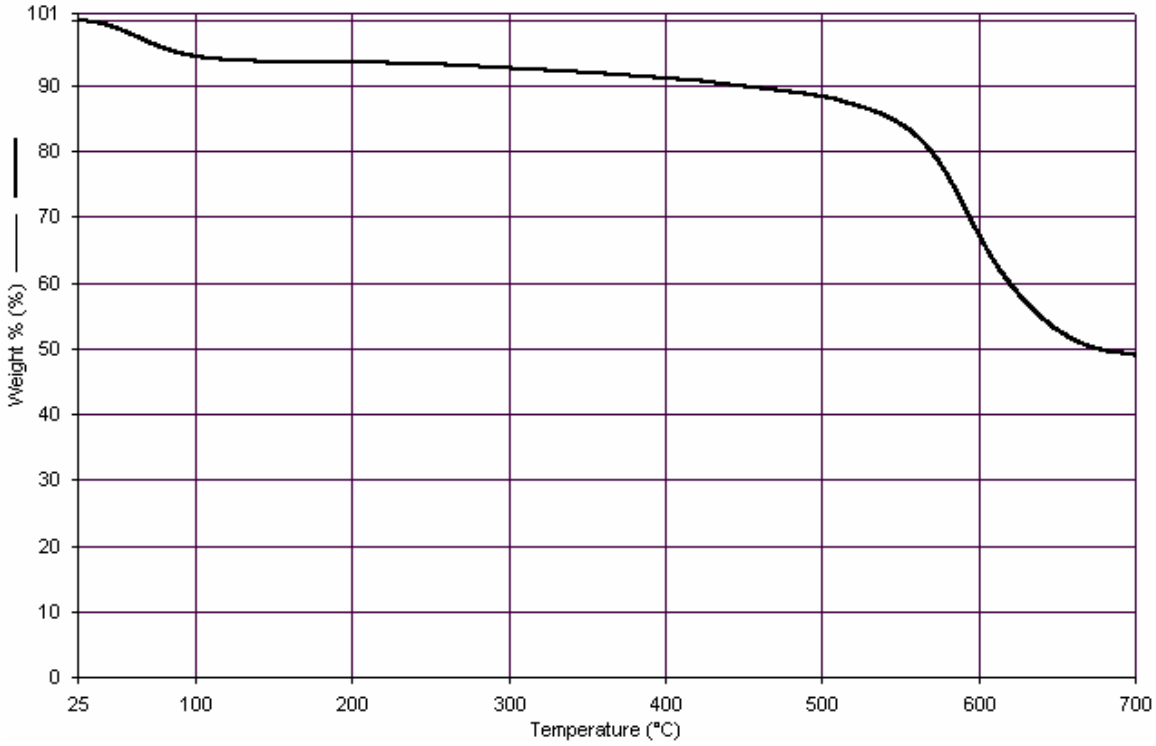


Figure 4.11 TGA of p-Aminobenzoic Acid Monomer PBA-5-1024

The increase in reduced viscosity becomes greater as the concentration of PBA is increased. This could be because a higher concentration of polymer is needed as the molecular weight of the polymer decreases. This is in accordance with concept that more short chains, or chains with lower axial ratio, can be randomly fitted to a given volume of solvent than can longer rodlike chains [12]. This same trend can be observed in Figure 4.4 as the concentration of polymer is increased the difference between the treated and untreated sample begins to become more pronounced. This difference can also be explained by the complexation of the Bipip with the PBA forming a simple salt as depicted in scheme 4.3.

Scheme 4.3 Amide Salt Formation Between JPM and Bipip

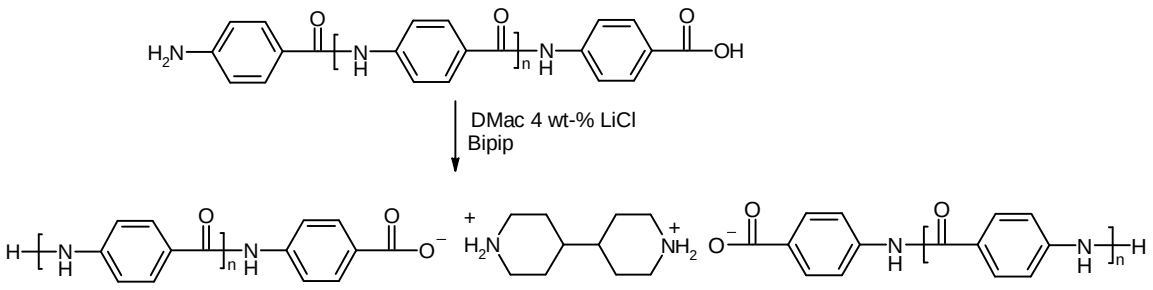


Table 4.6 Molecular Weight of PBA Samples Used for Making Films

Solvent Ratio (NMP/Py)	LiCl (%)	Time (hr)	Mw (g/mol)
30/20	4	3	5812
30/20	4	3	3348
30/20	4	3	1046
30/20	4	3	839
30/20	4	3	494

Like TED, the Bipip NH group could react with the acid group of the PBA to form a simple salt increasing the molecular weight by biding two PBA chains together. This goes along with the basis for the work when this was implemented as a binding agent for PBA it was theorized that it would hydrogen bond with carbonyl group of the acid group of the PBA.

Table 4.7 Comprehensive Viscosity and Reaction Conditions Data for PBA Samples

Solvent Ratio (NMP/Py)	LiCl (%)	Time (hr)	Inherent Viscosity (dL/g)	Mw (g/mol)
40 to10	4	3	1.33	6955
40 to10	4	3	1.40	7388
40 to10	4	3	1.42	7509
40 to10	4	3	1.32	6891
30 to 20	4	3	1.55	8262
30 to 20	4	3	1.73	10016
10 to 40	4	3	0.28	5262
15 to 35	4	3	0.32	4955
40 to10	1	3	0.40	4281
40 to10	1.5	3	1.25	6435
40 to10	2	3	1.57	8374
40 to10	7	3	1.24	6368
20 to 30	4	3	0.32	4955
25 to 25	4	3	1.55	8262
30 to 20	4	1	1.06	5060
30 to 20	4	2	1.56	8318
22 to 28	4	3	0.99	4484
30 to 20	4	0.5	0.87	3348
30 to 20	4	0.5	0.45	3819
10 to 40	4	3	0.22	5717
30 to 20	4	3	1.00	4569
30 to 20	4	3	1.16	5812
30 to 20	4	3	0.48	3522

The synthesis of 2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone (Upy) was carried out using the method described in section 4.2.3.4. Elemental analysis was carried and the results are shown in Table 4.8. The Upy was then added to the dissolved PBA solutions using the method in section 4.2.3. Solution viscometry was preformed on the samples treated with Upy and control samples are shown in Figure 4.5. Similar to the samples treated with the diamine binder, there is a marked improvement in the viscosity of the treated samples. This is probably due to the ability of the Upy to form multiple hydrogen bonds with itself after being attached to a polymer chain segment shown in Figure 4.12.

Table 4.8 Elemental Analysis of UPy Binding Agent

Analysis for	Reported Results (%)[a)]	Laboratory Results %
Oxygen	16.33	16.22
Carbon	53.23	52.86
Hydrogen	6.53	6.65
Nitrogen	23.88	23.76

[a)] The reported results are taken from reference [9].

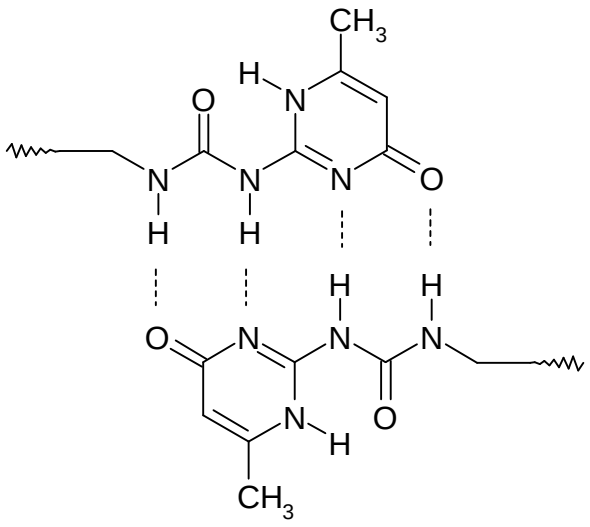
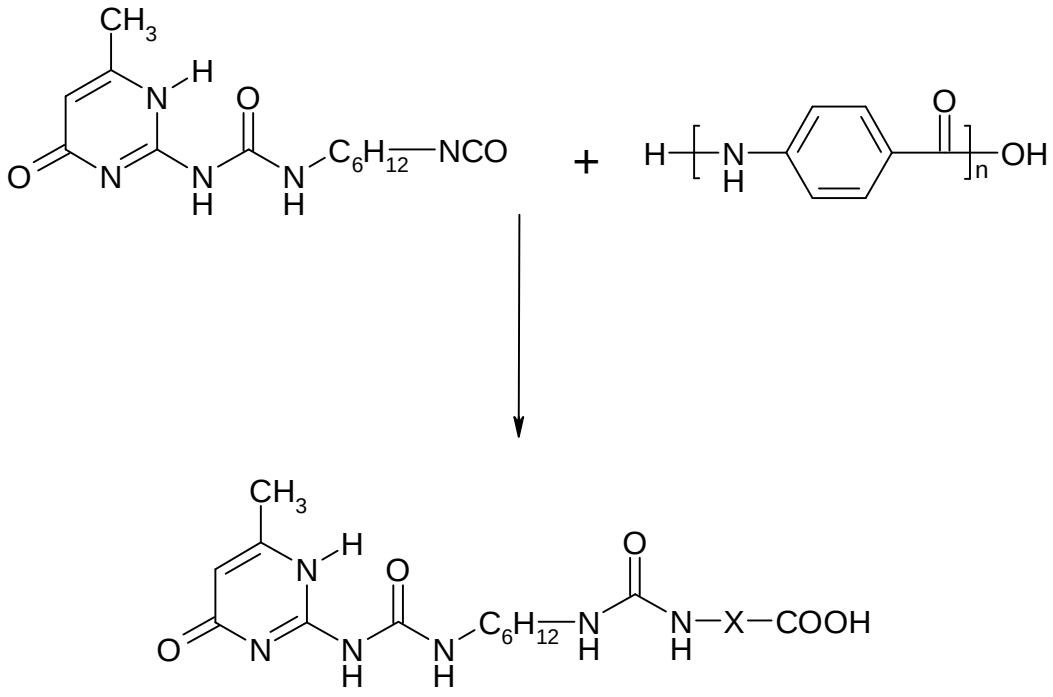


Figure 4.12 Illustration of UPy H-Bonding

Scheme 4.4 Reaction of UPy with Amine groups of PBA



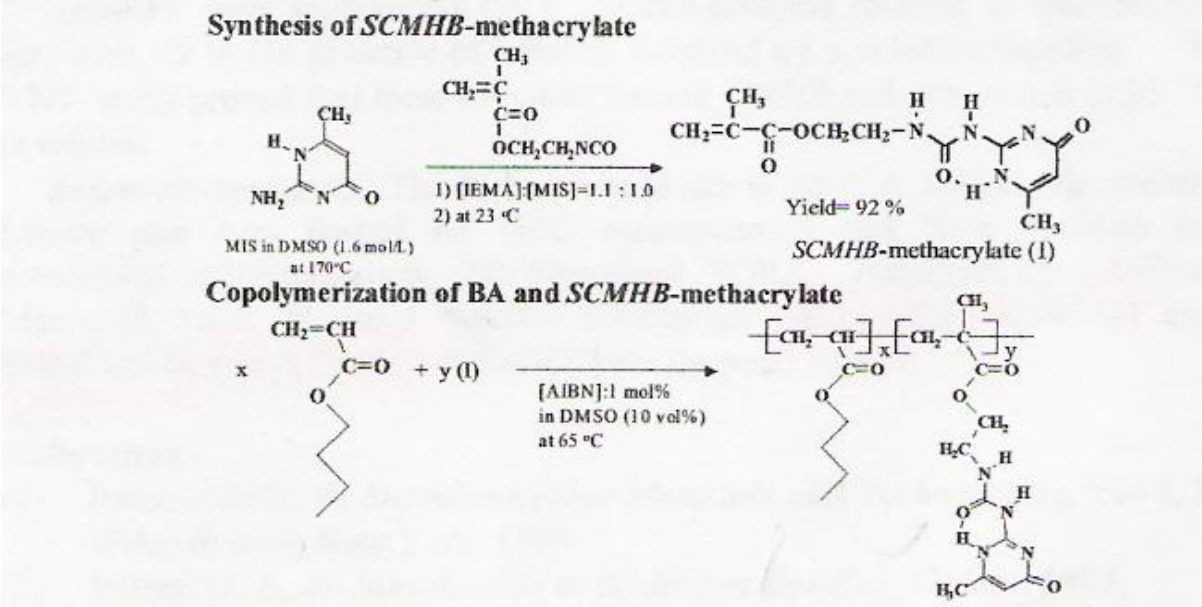
Where X represents the benzamide unit

The theoretical ideas of binding of the Upy to the PBA polymer are supported by the literature. Meijer and his colleagues made use of Upy to form supramolecular molecules with NH_2 terminated model compounds [9].

The binding experiments all show a increase in viscosity as concentration goes up this trend has been seen in the literature and is given below in Scheme 4.5 and Figure 4.13 the scheme shows the polymerization of the methacrylate and the copolymerization that adds the pendants side groups that hang from main chain. These side groups have the ability to interaction with one another in very similar fashion to that of the Upy groups used in our work. The utility of self-complimentary multiple hydrogen bonding (SCMHB) groups

such as the Upy used in this work have been suggested to be sufficiently strong enough to construct novel supramolecular polymers.

Scheme 4.5 Synthetic strategy of novel SCMHB-methacrylate monomer and SCMHB-Copolymers



The trend of increased viscosity with increased concentration of polymer goes along with the same trends that are recorded in our work. The trend is seen in different solvents lending credit to the interaction being a physical change in viscosity over that of a chemical change in viscosity.

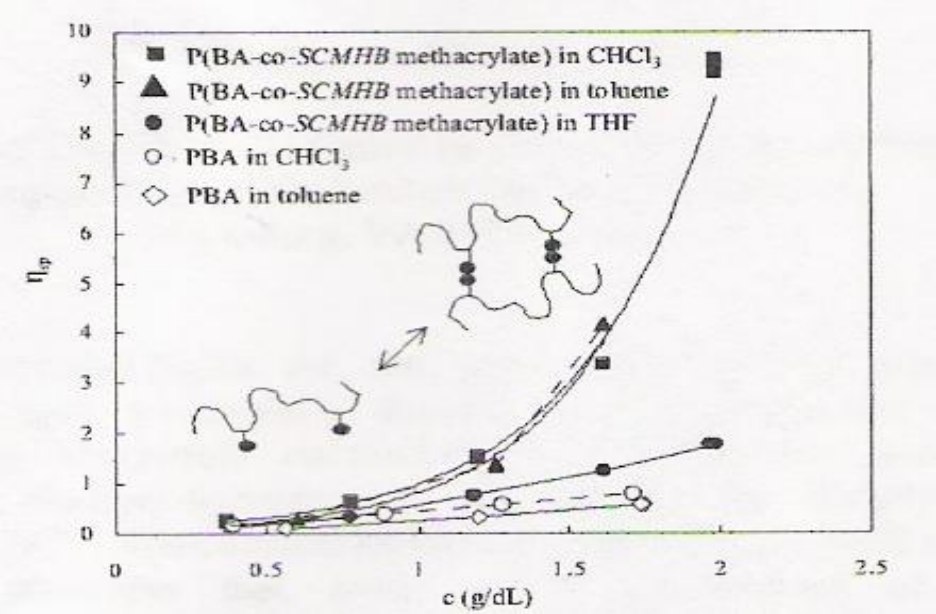


Figure 4.13 Solution viscosity of P(BA-co-SCMHB methacrylate) ([BA]:[SCMHB methacrylate]=91.6:10.4mol%) (II) in different solutions from [13]

The film experiment in section 4.2.3.5 was carried out by making several stock solutions of different polymer samples at the same concentration the stock solutions were split. One set was treated with Upy while one set was kept as controls. Solution viscometry was performed on the samples and the data collected is shown in Figure 4.6. The experiment did not result in actual useable films. This is probably due to the polymer samples used in the experiment being of too low molecular weight to be film forming. The molecular weights used in the production of the films are given in Table 4.6. The highest molecular weight used was still below 10,000 lower molecular weights were used in hopes the diamine treatment would increase the overall DP enough to become film forming.

4.4 Conclusions

Using the Yamazaki reaction conditions polymer samples of varying molecular weights were synthesized. The use of hydrated LiCl was investigated as a method to control the molecular weight of PBA but was found to hinder the polymerization resulting in little or no polymer. Because of the hindrance to the reaction the use of LiCl hydrates as control for the molecular weight of PBA was proven to be unrealistic method. The samples were then treated with two diamines namely triethylenediamine (TED) and bipiperidine (Bipip) and a pyrimidine derivative (Upy) to induce a supramolecular assembly rigid rod polyamide segments. Solution viscometry was used as the main quantitative tool for the analysis of changes in the reduced viscosity of the samples. The viscometric studies completed on the samples shows viscosity increases in the treated samples relating to molecular weight change from the original untreated samples. These same trends are noted in the literature and are given in a similar fashion in Scheme 4.5 and Figure 4.13. The same trend was noted in the literature using a methacrylate copolymer with pendant side groups able to hydrogen bond with one another. This differs from our which utilizes end groups that are more suited for aligning into chain type formations.

Although the production of films for mechanical properties testing would have given greater insight into the mechanical property changes of the treated samples from that of the untreated controls, it was found that the molecular weights ranging from 494-5812 g/mol of the samples used for the production of the films were not high enough to form films even after treatment with diamine binders. Elemental analysis was used as a tool for structural determination of the pyrimidine derivative binder used in the binding portion of the work. The FTIR, DSC, and thermogravimetric analysis was used to gather thermal

stability and thermal properties to compare to known values to insure purity of PBA samples.

4.5 Acknowledgments

I am very grateful for Dr. Jack Preston and his visits during my research from which I gained a great amount of understanding of polyamide synthesis.

4.6 References

1. Asrar J., Preston J., Ciferri A, Krigbaum W. R., *J. Polym. Sci. Chem. Ed.,* 20, 373-381, (1982)
2. N. Yamazaki, M. Matsumoto, F. Higashi, *J. Polym. Sci. Chem. Ed.*, 13, 1373 (1975)
3. Lindsey J. S., *New J. Chem*, 15, 153-180, (1991)
4. Lawrence D. S., Jiang T., Levett M., Chem. Rev., 95, 2229-2260, (1991)
5. Tessa ten Cate A., Sijbesma R. P., *Macromo. Rapid Commun.,*23, 1094-1112, (2002)
6. Higashi F., Ogata S., Aoki Y., *J. Polym. Sci. Chem. Ed.,* 20, 2081-2087, (1982)
7. Ying Q., Benjamin C., *Macromolecules,* 20, 871-877, (1987)
8. Schaefgen J. R., Foldi V. S., Logullo F. M., Good V. H., Gulrich L. W., Killian F. L., *American Chemical Society Polym. Div.,*17, 69-74, (1969)
9. Folmer B. R. B., Sijbesma R. P., Versteegen R. M., Vander Rijt J. A. J., Meijer E. W., *Advanced Materials*, (2000)
10. Ogata N., *Jushukugo,* Kagaku Dojin Press, 1971, pg 39
11. Schaefgen J. R., Foldi V. S., Logullo F. M., Good V. H., Gulrich L. W., Killian F. L., *American Chemical Society Polym. Div.,*17, 69-74, (1969)
12. Kwolek S. L., Morgan P. W., Schaefgen J.R., Gulrich L. W., *Macromolecules,* 10, 1390-1396, (1977)
13. Yamauchi K., Long T, *Polymer Preprints,* 43, 337, (2002)

V. Final Conclusions

In the experiments done on both the N,N'-bis(p-carboxylphenyl)terephthalamide monomer the treatment with TED seemed to form noncovalent bonds with the JPM monomer components via a ionic interaction between the positive charge of the amine and the negative charge of the oxygen terminated monomer. This was what was originally thought would happen and provides the basis of producing a supramolecular polymeric array utilizing rigid rod segments of polyamides. The analytical data collected during the course of the investigation supports this theory. Although the second binder 4,4'-bipiperidine made up amine groups incorporated into two linked saturated rings more likely formed covalent amide linkages with the monomer, it still provides crucial data in the interactive forces of diamines with polyamide monomer segments. This interaction may provide for future work utilizing a two step diamine treatment of the N,N'-bis(p-carboxylphenyl)terephthalamide monomer to form a supramolecular polyamide array discussed more in (Chapter VI).

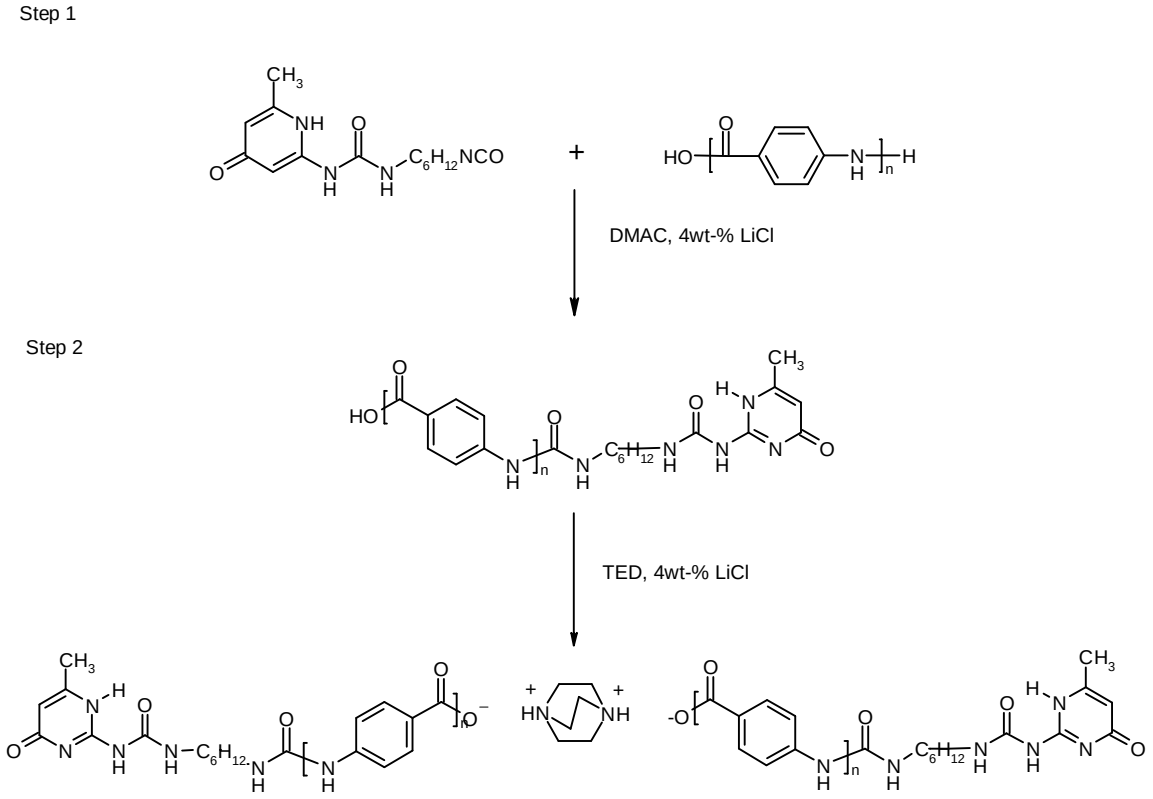
The work done with p-polybenzamide has shown many interesting and promising results. The increases seen in the viscosities of samples treated with TED in an aprotic solvent is a new and novel concept. Most of the literature deals with the use of chloroform and other dangerous solvents to provide a proper solvent medium in which to supramolecularly bind rigid rod systems made up of polyamide components. The data supports the three systems for binding and forming noncovalent bonds with normally associated with supramolecular arrays. 4,4'-bipiperidine and triethylenediamine most likely form simple salts with the acid groups of the PBA components of the system. This system did exhibit the necessary interactions to form a supramolecular system; the

knowledge gained from the experiments could lead to future work discussed more in (Chapter VI). The most promising work done was that utilizing the 2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone (Upy) binder due to its ability to form multiple bonds hydrogen bonds with itself. This molecule could be of great importance in revolutionizing the synthesis of polyamides more work needs to be done to better understand the interaction of the amine groups and the Upy. If it is possible to for the reaction scheme shown in Scheme 4.4 then the knowledge gained from the other binders could be used to create a new novel process for polyamide production. This process would utilize conventional means of polyamide synthesis combined with supramolecular chemistry to produce high molecular weight polymeric materials processing the high modulus high strength properties polyamides industrially produced are known for.

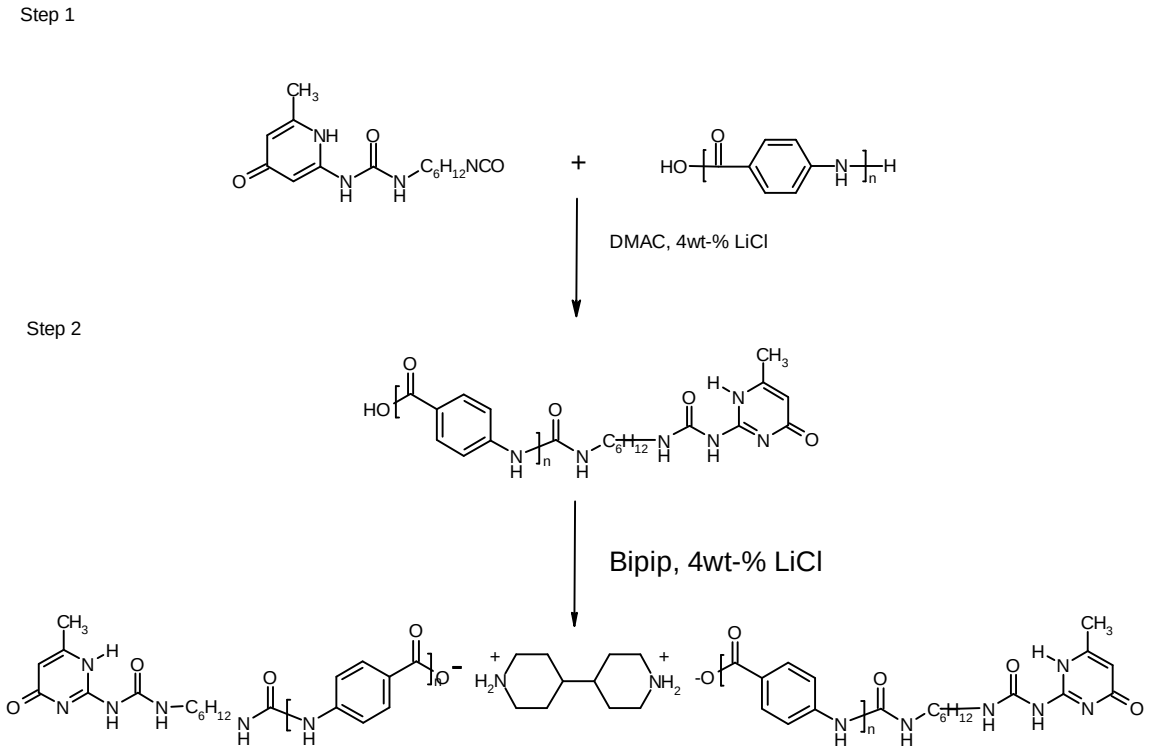
VI. Future Work

In the present work N,N'-bis(p-carboxylphenyl)terephthalamide monomer was treated with diamine binder in the hopes of forming a supramolecular polymeric material. It was shown that the TED and Bipip binder could interact with the acid groups of the monomer to form a polymeric salt comprised of diamine components inonically bonded rigid rod polyamide segments. If this ability of the two diamine binders to form polymeric salts was combined with UPy ability to react with the amine end groups of PBA segments, this could result in a two-step treatment process of the PBA with both could result in a new novel supramolecular polyamide could be produced using the reaction schematic in Scheme 6.1 and Scheme 6.2.

Scheme 6.1



Scheme 6.2



The addition of the TED and Bipip allows for the possible self-assembly of the polymeric salt and supramolecular polyamide to be formed.

This process could be used to produce a new novel supramolecular polyamide with both rigid rod segments. Investigating these two-step systems could provide valuable information on the interaction and properties supramolecular polyamides and would provide basis for the incorporation of supramolecular theories into conventional polymer synthesis techniques. More analytical studies involving other equipment such as gel permeation chromatography, to better understand the molecular weight distribution of the components, would provide more information on the interaction of the systems components with one another and would allow for future development of polymeric synthesis of materials utilizing the binding techniques implemented in this work. Along with carbon nuclear magnetic resonance and hydrogen nuclear magnetic resonance

studies to obtain more structural data on the materials produced from this work, this would add to the knowledge already gained on the interaction, and relationships of the components of the varying systems. The use of higher molecular weight materials in the film experiments would give much needed data on the mechanical properties of the treated samples in comparison with untreated control samples.