2005

Novel polyimides based on 2,2-BIS(3-amino-4-hydroxyphenyl)hexafluoropropane, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, and mellitic acid dianhydride, and their NLO pendent polymers

Eugene Galperin

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(HEXAFLUOROISOPROPYLIDENE)DIPHTHALIC ANHYDRIDE, AND MELLITIC
ACID DIANHYDRIDE, AND THEIR NLO PENDENT POLYMERS

Eugene Galperin

Thesis

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

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NOVEL POLYIMIDES BASED ON 2,2-BIS(3-AMINO-4-HYDROXYPHENYL)HEXAFLUOROPROPANE, 4,4'-(HEXAFLUROISOPROPYLIDENE)DIPHTHALIC ANHYDRIDE, AND MELLITIC ACID DIANHYDRIDE, AND THEIR NLO PENDENT POLYMERS

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Title of thesis **NOVEL POLYIMIDES BASED ON 2,2-BIS(3-AMINO-4-
HYDROXYPHENYL)HEXAFLUOROPROPANE, 4,4’-
(HEXAFLUOROISOPROPYLIDENE)DIPHTHALIC ANHYDRIDE, AND MELLITIC
ACID DIANHYDRIDE, AND THEIR NLO PENDENT POLYMERS**

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Eugene Galperin
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<td>MA</td>
<td>Mellitic acid</td>
</tr>
<tr>
<td>MADA</td>
<td>Mellitic acid dianhydride</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>APAF</td>
<td>2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane</td>
</tr>
<tr>
<td>6FDA</td>
<td>4,4' (Hexafluoro-isopropylidene)diphthalic Anhydride</td>
</tr>
<tr>
<td>NLO</td>
<td>Nonlinear Optical</td>
</tr>
<tr>
<td>alt-PAA</td>
<td>Alternating polyamic acid, Alt-poly[4,4'-(Hexafluoroisopropylidene)diphthalic anhydride --- 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane --- Mellitic dianhydride --- 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane]amic acid, Alt-PAA[ 6FDA --- APAF --- MADA --- APAF], (Alt-PAA)</td>
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<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>DMAc</td>
<td>N, N-dimethylacetamide</td>
</tr>
<tr>
<td>DCC</td>
<td>Dicyclohexylcarbodiimide</td>
</tr>
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<td>Polymer-based BCC</td>
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<td>Bis(an)MADA</td>
<td>1,3-Bis(aminobenzene)benzene hexacarboxylic acid</td>
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<td>Nitro-NLO</td>
<td>(E)-2-[2-(4-nitrophenyl)ethenyl]thiophene</td>
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<td>Amino-NLO</td>
<td>(E)-2-[2-(4-aminophenyl)ethenyl]thiophene</td>
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<td>Trimer</td>
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<td>NLO bis(an)MADA</td>
<td>1,3-Bis(N-aminobenzene)-5-[N-aminobenzene-4-(2-yl-vinyl)-2-thiophene]-benzene hexacarboxylic acid</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>H&lt;sup&gt;1&lt;/sup&gt;NMR</td>
<td>Proton nuclear magnetic resonance</td>
</tr>
<tr>
<td>2-D H&lt;sup&gt;1&lt;/sup&gt;NMR</td>
<td>Two-dimensional proton nuclear magnetic resonance</td>
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<td>TGA</td>
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The goals of this research are the synthesis of novel three-component polyamic acids and polyimides, and corresponding pendant polymers where nonlinear optical (NLO) "chromophores" have been attached. Synthesis of a corresponding guest molecule is also sought to facilitate structural and NLO property comparisons. All synthesized materials were characterized with TLC, NMR, FTIR, and UV-VIS. Polymers were characterized by TGA. The average molecular weight of one polymer was determined by ebulliometry and dilute solution viscosity. Starting materials were chosen to increase the flexibility, lower hydrophilicity, and achieve colorlessness of the polymer backbone by incorporating additional C-F bonds between the aromatic rings of the diamines and dianhydrides.

The novel three component polyamic acid (alt-PAA) based on 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (APAF), 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and mellitic acid dianhydride (MADA) are synthesized under nitrogen gas in freshly dried solvent tetrahydrofuran (THF). The NLO pendent group is attached to the alt-PAA in presence dicyclohexylcarbodiimide (DCC) or N-benzyl-N′-cyclohexylcarbodiimide (polymer-based BCC). Alternatively, NLO reacts with the anhydride ring of previously imidized alt-PAA without any additional catalyst. TLC results indicate the completion of the reaction to make polymers and the attachment of NLO molecule.

The appearance of an IR band at approximately 1650 cm\(^{-1}\) in the initial product which disappears upon heating at temperatures above 160°C is consistent with initial
formation of amide and subsequent imidization. The appearance of peaks near 13 and 10 ppm in the $^1$H NMR of the initial polymer product, and their disappearance upon high temperature treatment provides further support that the proposed polymerization and imidization is occurring. Proton coupling data from 2-D $^1$H NMR verifies that the NLO moiety has been attached to alt-PAA. The absorption properties of synthesized materials (at wavelengths less then 350, 280, 390, and 395 for alt-PAA, alt-PI (solution imidized), NLO alt-PAA and NLO alt-PI, respectively) indicate that a high degree of transparency in the visible region has been achieved. TGA shows that the onset of weight loss due to decomposition occurs at temperatures over 200°C.

The molecule bis(an)MADA based on aniline and MADA is synthesized in freshly dried solvent, THF. The NLO pendant group is attached to the bis(an)MADA in presence of DCC to make a “guest”. Both molecules are characterized by TLC, FTIR, $^1$H NMR and UV-VIS spectroscopy. TLC was used to determine the completion of the reaction while FTIR and $^1$H NMR were employed to prove that the product has the proposed structure. Spectral changes analogous to those for the alt-PAA polymerization and NLO attachment were observed. UV-VIS spectroscopy showed much higher degree of light absorbance of NLO guest molecule compared to the NLO polymer.
1. INTRODUCTION

The field of nonlinear optics has many important applications such as frequency doubling, optical storage and electro-optical modulation and switching.\textsuperscript{[1-3]}

The application of an electric filed across the dielectric medium induces polarization. When the electric field is larger than the atoms internal electric field of 109 volts/cm, nonlinear effects can occur. Mathematically, the nonlinear relationship of polarizability and electric field can be expressed as:

\[ P_x = \alpha E_x + \beta E_x^2 + \gamma E_x^3 \]

Where \( P_x \) is optically induced polarization

\( E \) is an electric field

\( \beta \) is the first molecular hyperpolarizability (second order effect)

\( \gamma \) is the second molecular hyperpolarizability (third order effect)

Typically \( \alpha \gg \beta \gg \gamma \).\textsuperscript{[2]}

Another way of interpreting this expression is that it is a measure of how easy it is to polarize the electronic structure of a molecule. Ideally, highly polarizable molecules are needed for second order nonlinear applications, which means that higher coefficients are desirable. During this research, second order nonlinear optical (NLO) molecules were used because they are more studied and are easier to manipulate as compared to the third-order NLO.\textsuperscript{[1]}
Table 1.1 Effects and Uses of Second-Order NLO Molecules

<table>
<thead>
<tr>
<th>Susceptibility</th>
<th>Effects</th>
<th>Possible Uses</th>
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<tr>
<td>$\alpha$</td>
<td>Refraction</td>
<td>Optical Fibers</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Second Harmonic Generation (SHG)</td>
<td>Frequency Doublers</td>
</tr>
<tr>
<td></td>
<td>Frequency Mixing</td>
<td>Optical Mixers</td>
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<tr>
<td></td>
<td>Parametric Amplification</td>
<td>Optical Parametric Oscillators</td>
</tr>
<tr>
<td></td>
<td>Pockels Effects</td>
<td>Electro-Optical Modulators</td>
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One of the more useful NLO effects is SHG. When light with frequency $\omega$ is passed through a medium possessing second-order NLO properties, light with the frequency $2\omega$ is emitted.

$$P = \alpha E^1 \sin^1 \omega t + \beta E^2 \sin^2 \omega t$$

$$\sin^2 \omega t = \left(\frac{1}{2}\right)(1 - \cos 2\omega t)$$

$$P = \alpha E^1 \sin \omega t + ((\beta E^2)/2) (1 - \cos 2\omega t)$$

where the first term of this equation is linear and dominates at low radiation intensity, and the second term represents second-order nonlinear behavior which becomes more significant at high radiation intensity. The SHG is also called “three way mixing” process due to the fact that two photons with frequency $\omega$ combine to make a single photon with frequency $2\omega$. [2]
Classically, inorganic materials have been used to obtain the NLO effect. However, the cost, processability and poor optical quality problems of inorganic semiconductors and crystals have fueled the need for other kinds of NLO materials. In the nineteen eighties it became apparent that organic NLO-functionized polymers could be those materials. Unlike inorganic materials they are cheap, have good optical properties, are easy to fabricate, and can be optimized by molecular engineering. [5]

Over the years the criteria for design of second-order NLO materials which exhibit large hyperpolarizability has been established. First of all, the material must be polarizable, meaning that it is capable of significant displacement of electrons from their equilibrium positions producing charge separation. An asymmetric charge distribution is achieved by incorporation of donor and acceptor functional groups with a bridge of π-conjugated electrons. Finally, these NLO moieties (or chromophores) need to be arranged in acentric crystal packing which is usually achieved with the introduction of a chiral center. [6, 7]

However, applicability of the organic NLO materials is limited due to the problems of low NLO activity and poor temporal stability. The methods used to address these problems include guest-host, main chain and pendant polymer approaches. In the
guest-host system NLO material is dissolved in the polymer matrix. The main-chain approach incorporates the NLO chromophore in the backbone of the polymer. Finally, the pendant polymer system has NLO moieties covalently attached to the polymer backbone. The latter system could have several advantages over the others including higher concentration of chromophores without phase separation, and increased temporal stability if high glass transition temperatures ($T_g$) polymer backbone is used.\cite{8-12}

Polyimides are a great choice for NLO pendant system. They have high $T_g$s, high temperature stability, low dielectric constants, good mechanical properties (low stress, high modulus) and fluorinated varieties have low optical loss. Polymers with high $T_g$ should stabilize the dipolar orientation of the NLO chromophores at high device operating temperatures. High thermal stability of the polyimides enables them to survive at elevated temperatures during the manufacture and operation of the photonic devices.\cite{13} One of the most famous polyimides is Kapton\textsuperscript{TM} by Dupont. It is prepared from polycondensation of pyromellitic dianhydride and 4,4-oxydianiline followed by either thermal or chemical cyclodehydration of the polyamic acid.
Kapton™ is strongly colored (brown-orange) due to the charge transfer interactions between the electron-rich diamine and the electron-poor dianhydride. In 1999 the NASA invention of the year was a colorless polyimide thin film which is optically transparent at 400 – 900 nm wavelengths and has a low dielectric constant. [14]

Figure 1.3 Structure of NASA Colorless Polyimide
It was noted that positioning a bulky hexafluoro-isopropylidene group (---CF\_\_---) between the aromatic rings disrupts the conjugated π system resulting in decrease of color. In addition, incorporation of C-F bonds, in the polyimide repeating unit, increases the T\_g and flame resistance while decreasing water absorption and dielectric constant of the polymer. Using a colorless polyimide backbone as a part of a NLO pendant polyimide system is advantageous because absorbance of laser light would decompose the material. [15-17]

Growing experimental evidence and common logic suggests that using a polymer with high T\_g for pendently attaching NLO should increase the thermal stability of a NLO pendant polymer system. [18-20]

In 1995, Dr. Illingworth began investigating Mellitic Dianhydride (MADA) as site for pendant group attachment. Previous graduate students, working under Dr. Illingworth, have used MADA as a point of attachment to the polyimide backbone. In all cases dicyclohexylcarbodiimide (DCC) was used as dehydrating agent to facilitate the attachment of pendant groups. [21-23]
**Figure 1.4 Synthesis of Zirconium Complex Pendant Polyimide (made by Wei Cheng)**
The broad objectives of my research are to synthesize and characterize a novel three-component polyamic acid, and then attach NLO pendants to the polymer backbone. (see Figures 5 and 6) The characterization is to be performed using TLC, NMR, FTIR and GPC. In addition, the polyamic acid is to be imidized and characterized as above.

Figure 1.5 Structure of NLO Pendant Polyamic Acid to be Made

Figure 1.6 Structure of NLO Pendant Polyimide to be Made
Further, a NLO guest molecule is to be made and characterized for future comparison between pendant and guest-host NLO systems (see Figure 1.7).

![Figure 1.7 Structure of NLO Pendant Guest Molecule to be Made](image)

The focus of this work is to increase the flexibility and decrease the visible light absorbance of the polymer backbone by introducing additional C-F bonds between the aromatic rings of the diamines and dianhydrides. Also, high boiling, polar solvent NMP, which was used in previous polymerizations of polyimides, is to be replaced with THF, which is relatively low boiling and therefore is easier to get rid from the formed polymer.
2. EXPERIMENTAL

2.1 Chemicals

All of 2-Thiophenecarboxaldehyde, sodium ethoxide (21wt% solution in denatured ethyl alcohol), dicyclohexylcarbodiimide (DCC), polymer-bound N-benzyl-N'-cyclohexylcarbodiimide (polymer – bound BCC), p-cresol, (4-nitrobenzyl)triphenylphosphonium bromide, d6-methyl sulfoxide, N, N-dimethylacetamide (DMAc) were obtained from Aldrich. Methylene chloride, silica gel Celite 545, methyl ethyl ketone, toluene and methanol were obtained from J. T. Baker. Acetone was obtained from Fisher ChemAlert®. Mellitic acid was obtained from TCI, Tokyo KASEI. All of these chemicals were used as received.

Both 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (APAF) (Chriskev Company, Inc) and 4,4’-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (Aldrich) were purified by subliming under vacuum at 245 to 250°C, and 244 to 251°C, respectively, and stored in a desiccator containing P2O5 to prevent the absorption of moisture. Ice was used in the cold finger of the sublimation apparatus. Tetrahydrofuran, THF, used for polymerization and DCC reactions, obtained from Aldrich, was dried by vacuum distillation over calcium hydride, CaH2 just prior to use.

Silica chromatogram sheets with fluorescent indicator used for thin layer chromatograms were obtained from Eastman Kodak Co. Silica gel for separation of NLO (mesh 200-400, 60 Å) was obtained from Aldrich.

2.2 Mellitic Acid Dianhydride (MADA)

Mellitic acid dianhydride, a light gray-brown powder, is prepared form mellitic acid (MA) by controlled cyclodehydration,
Two ways of making MADA were used. During the first method 3.0 g of well grounded MA was placed on the inner surface of a 20 mL Pyrex test tube. The test tube with MA equipped with nitrogen inlet, outlet, and thermometer embedded in the rubber stopper was placed horizontally in a drying pistol. It was heated at 190°C, generated by ethylene glycol at reflux under a nitrogen flow of 20mL/min. Preparation of MADA from MA took 24 hours with rotation of the test tube every hour for the first 8 hours. Rotation of the test tube, and therefore MA, allowed for uniform heating and hence purer MADA.\(^{[22]}\) See Figure 2.2.

\[\text{Mellitic Acid} \xrightarrow{10.5 \text{ hours heating in } \text{N}_2} \text{Mellitic Acid Dianhydride (MADA)}\]
Figure 2.2 Previously Used Apparatus for Making MADA[22]

For the second method of preparing MADA 10.0 g of well grounded MA was placed uniformly on the bottom of 125 mL filter flask. A thermocouple was inserted through the septum so that it touches the bottom of the filter flask thus measuring the temperature to which the MA was being exposed. Vacuum pump evacuation was applied to the filter flask through its sidearm. The heating of the filter flask was done by a variac-controlled heating mantle filled with sand. This method of making MADA takes 10 hours, providing for greater convenience and less sources of human error. Also, 5.0 - 15.0 g of MADA can be prepared in one vessel versus a maximum of only 3.0 g for method one. See Figure 2.3.
After comparing the two methods, the latter one was found to be more practical for the research work planned. The purity of the product was confirmed using thermogravimetric analysis (TGA). Upon further heating, MADA loses 1 molecule of water and turns into trianhydride, see Figure 2.4. Therefore, a 5.8% mass loss on TGA curve (which corresponds to 1 molecule of water, per molecule of MADA) is expected if the MADA sample is pure.

Figure 2.3 Alternative Apparatus for Making MADA

Figure 2.4 Conversion of MADA to Trianhydride During TGA
2.3 Synthesis of Nonlinear Optical Materials (NLO)

2.3.1 (E)-2-[2-(4-nitrophenyl)ethenyl]thiophene (nitro-NLO)

(4-Nitrobenzyl)triphenylphosphonium bromide (9.57 g, 0.0200 moles) was dissolved in 25 mL of ethanol. 2-Thiophenecarboxaldehyde (2.24 g, 0.0200 moles) and 7.46 mL (0.0200 moles, 21 wt% solution) sodium ethoxide in ethanol was added to the stirring solution in the nitrogen glove bag and flask was rinsed with 5 mL of ethanol. After stirring for 60 minutes the red reaction mixture turned to brownish and finally a yellow powder (cis and trans nitro-NLO) formed, see Figure 2.5. The yield of the product was 2.596 g, 56.13%.

![Chemical structure of reaction products](image)

Figure 2.5 Synthesis of cis and trans-Nitro-NLO
After extraction with petroleum ether (flash point 35-62°C), the yellow solid was collected. Crystallization from hot ethanol gave 0.5532 g, 21.31% trans-nitro-NLO, m.p. 169-173°C (literature value of 174°C). See Figure 3.6.

![Figure 2.6 Recrystallization of trans-Nitro-NLO](image)

2.3.2 (E)-2-[2-(4-aminophenyl)ethenyl]thiophene (amino-NLO)

Nitro-NLO (0.8000 g, 0.003463 moles), triiron dodecacarbonyl Fe₃(CO)₁₂ (2.2231 g, 0.0034593 moles), and 6 mL methanol were placed in 30 mL of benzene in a nitrogen glove bag. The solution was heated at reflux overnight. After filtration with a 2 cm thick cellite in a glove bag, column chromatography was performed under N₂ atmosphere with ethyl ether and hexane (v/v, 1:1) as the eluent. Vacuum evaporation was used to dry the final pale yellow product, trans-amino-NLO, see Figure 2.7. The product was made in 0.1523 g, 27.53 % yield and had a 119°C-123°C melting point (literature value of 119-127°C).
The final pale yellow product, trans-amino-NLO in benzene was spotted onto silica gel TLC plate and eluted with ethyl ether and hexane (v/v, 2:8) solution to verify the completion of the reaction. The $R_f$ of the nitro-NLO (0.875) was larger then amino-trans-NLO (0.675).

2.4 Synthesis of Polyamic Acid

2.4.1 1,3-di[N-{4'-(2''',2'''-(1''',1''',3''',3''',3'''-hexafluoropropylene))-bis(1'-hydroxy-2’aminobenzene)]benzene hexacarboxylic acid (Trimer)

In a 100 mL round bottom flask containing a magnetic stirring bar, APAF (1.832 g, 0.005001 moles) was added to recently dried 5.00 mL THF. The flask was capped with a rubber septum with needle inlet and outlet for N$_2$ flow and injected with MADA (0.7654 g, 0.002500 mole) in 4.00 mL of THF. The resulting solution was stirred for 3 hours at ambient temperature. The reaction was followed with TLC in which APAF was spotted versus the product. The mobile system consisted of ethyl ether and hexane (v/v, 2:8) and when the product did not show any APAF, colorless spot with $R_f$ 0.235, the reaction was complete. See Figure 2.8.
2.4.2 Alt-poly[4,4’-(Hexafluoroisopropylidene)diphthalic anhydride --- 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane --- Mellitic dianhydride --- 2,2-Bis(3-amino-4-hydroxyphenyl) hexafluoropropane]amic acid, Alt-PAA[ 6FDA ---APAF --- MADA --- APAF], (Alt-PAA)

In a 250 mL round bottom flask containing a magnetic stirring bar, the trimer solution (prepared in section 2.4.1) was added to recently dried 50 mL THF. The flask was capped with a rubber septum with needle inlet and outlet for N2 flow, and injected with 6FDA (1.111g, 0.002500moles) in 5.43 mL of THF over three hour period at 24°C. The reaction was followed with TLC, using mobile system consisting of ethyl ether and hexane (v/v, 2:8), in which trimer was spotted versus the product. When light yellow product Rf 0.000 did not show any trimer Rf 0.236, it verified that all monomer had
reacted. However due to the step growth nature of the polymerization, the reaction was left stirring overnight. The additional THF was needed to suppress gelation of the solution. The resulting polymer (alt-PAA) was isolated by evaporation of the THF and grinding into light yellow powder, see Figure 2.9.

2.5 Solid-State Imidization of alt-PAA

2.5.1 Imidization at 195°C at Vacuum and Air

A sample of alt-PAA was exposed to 195°C in air for one hour. Another sample of alt-PAA was exposed to 195°C in vacuum for one hour. In both cases the product
changed color from pale yellow to yellow-orange and the degree of imidization was established using FTIR. Additional heating did not give a noticeable increase in the extent of imidization. The resulting imidized product proved to be insoluble in common solvents, see Figure 2.10.

2.5.2 Imidization with Mesitylene

A sample of alt-PAA was mixed with 50 mL of mesitylene in a 150 mL round bottom flask with a boiling stone and stirring bar. Distillation of that mixture using a Dean Stark trap was performed at 180°C and took 2 hours. The FTIR spectra after 4 hours of distillation with mesitylene did not show any difference compared to the product after 2 hours of distillation. The remaining mesitylene was separated by means of vacuum filtration, see Figure 2.10. The color of the final product was yellow-orange.
2.6 Solution Imidization of alt-PAA

In a 250 mL round bottom flask containing a magnetic stirring bar, alt-PAA (5 g) was added to 25 g of deuterated dimethylsulfoxide (DMSO-d₆). The resulting solution flask was fitted with a condenser tube which was capped off with a drying tube, and heated at reflux for 6 hours. The FTIR spectra after 8 hours of reflux with DMSO-d₆ did not show any difference compared to the one after 6 hours. The solid product was isolated by solvent evaporation using a combination of vacuum and temperature of 70°C.
The final product was yellow-orange in color and was soluble with common solvents, such as methanol, acetone and acetonitrile, see Figure 2.10.

2.7 NLO Pendant alt-PAA

2.7.1 Synthesis NLO Pendant alt-PAA via DCC

Amino-NLO (0.5032 g, 0.002500 moles) and excess DCC (6.231 g, 0.03020 moles) were added to the alt-PAA (3.708 g, 0.002500 moles) solution flask containing recently dried THF (10 mL). The reaction was monitored by TLC, consisting of ethyl ether and hexane (v/v, 1:8), where amino-NLO was spotted against the reaction product. Once the reaction solution did not show any free amino-NLO the reaction was stopped. The solid NLO pendant PAA was isolated by evaporation of the THF and grinding to a powder. The product was purified with ethyl ether using the Soxhlet extraction apparatus overnight and dried in a vacuum oven at room temperature. The final polymer stood at 0.675 g, 99.1 % yield and appeared dark brown in color. See Figure 2.11
2.7.2 Synthesis NLO Pendant alt-PAA via Polymer–Bound BCC

Amino-NLO (0.5032g, 0.002500 moles) and 2.5 g (0.00425 moles of BCC) of polymer-bound N-Benzyl-N’-cyclohexylcarbodiimide (polymer-bound BCC) were added to the alt-PAA (3.708 g, 0.002500 moles) solution containing recently dried THF (10 mL). The reaction was monitored by TLC, using ethyl ether and hexane (v/v, 2:8) as an eluent, were amino-NLO was spotted against the product. After verifying the completion of the reaction, the polymer-bound urea byproduct was filtered off. The solid product was isolated by evaporation of solvent, grinding to a powder, and washing with ice cold THF, see Figure 2.11. The final light-to-medium brown product was produced 3.533 g, 95.3 % yield before washing with cold THF and 1.97g, 53.4 % yield after the wash.

![Diagram of Synthesis of NLO Pendant alt-PAA](image-url)

*Figure 2.11 Synthesis of NLO Pendant alt-PAA*
2.8 Synthesis NLO Pendant alt-PI via Solution Imidized alt-PI

Solution imidized alt-PAA (1.00 g, 0.000952 moles) was added to the d₆-DMSO (15 mL) in a flask. Amino-NLO was added in increments of 0.05 g and tested with TLC for the reaction completion. After TLC, using ethyl ether and hexane (v/v, 2:8) as an eluent, showed that free amino-NLO remains in the solution unreacted, the final product was isolated by solvent removal using a combination of vacuum and temperature (100°C). The resulting solid product was washed with cold THF. The final product after washing was medium brown in color and 0.513 g was produced, 51.3% yield. See Figure 2.12.

![Figure 2.12 Synthesis of NLO Pendant alt-PI](image)
2.9 Synthesis of Guest NLO

2.9.1 1,3-Bis(aminobenzene)benzene hexacarboxylic acid, (Bis(an)MADA)

In a 250 mL round bottom flask containing a magnetic stirring bar, aniline (0.457 mL, 0.00500 moles) and MADA (0.7654 g, 0.002500 moles) were added to recently dried 10.0 mL THF. The flask was capped with a rubber septum with N₂ flow as before and stirred for 3 hours at ambient temperature. The MADA completely dissolved in the aniline and THF solution, and the reaction was monitored by TLC as in previous reactions, see Figure 2.13. The product was synthesized 0.744 g, 97.3 % yield and was pale-yellow in color.

![Diagram of Synthesis of (Bis(an)MADA)](image)

Figure 2.13 Syntheses of Bis(an)MADA

2.9.2 Synthesis of 1,3-Bis(N-aminobenzene)-5-[N-aminobenzene-4-(2-yl-vinyl)-2-thiophene]-benzene hexacarboxylic acid, (NLO pendant Bis(an)MADA)

Amino-NLO (0.5032g, 0.002500 moles) and excess DCC (6.231 g, 0.03020 moles) was added to a flask containing bis(an)MADA (0.7447 g, 0.001512 moles) and 10 mL of freshly dried THF. The reaction was monitored by TLC as in previous reactions where amino-NLO was spotted against the product. The Rᵣ of the product (0.25) was lower then that of amino-NLO (0.675). After verifying the completion of the reaction, the NLO
pendant bis(an)MADA was purified with ethyl ether using the Soxhlet extraction apparatus overnight. See Figure 2.14. The final black-brown product stood at 0.00147 g, 97.3 % yield.

![Figure 2.14Synthesis of NLO Bis(an)MADA](image)

### 2.10 Characterization Methods

#### 2.10.1 Proton Nuclear Magnetic Resonance Spectroscopy (1-D $^1H$ NMR)

Precipitated alt-PAA, NLO pendant alt-PAA, solution imidized alt-PAA, Bis(an)MADA and NLO Bis(an)MADA powders were separately dissolved in deuterated dimethylsulfoxide (d$_6$-DMSO). TMS was used as internal standard. The one-dimensional $^1H$-NMR spectra were recorded on a 300 MHz Bruker NMR Spectrometer by using Bruker’s 1.1 version software at room temperature.
2.10.2 Proton Nuclear Magnetic Resonance Spectroscopy (2-D $^1$H NMR)

Precipitated alt-PAA and NLO pendant alt-PAA were separately dissolved in deuterated dimethylsulfoxide (DMSO-d$_6$). TMS was used as internal standard. The two-dimensional $^1$H-NMR spectra were recorded on a 300 MHz Bruker NMR Spectrometer by using Bruker’s 1.1 version software at room temperature.

2.10.3 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared spectra were recorded on a BIO-RAD Excalibur Series FTS 3000. The IR spectra were obtained from 600 cm$^{-1}$ to 3800 cm$^{-1}$. IR spectra of precipitated alt-PAA, NLO pendant alt-PAA, solid and solution imidized alt-PAA, Bis(an)MADA and NLO Bis(an)MADA powders obtained above were analyzed directly using a Pike Miracle HATR attachment.

2.10.4 Thermogravimetric Analysis (TGA)

TGA were performed on TGA 2050 Thermogravimetric Analyzer (TA instruments Inc.). The amount of sample used in each measurement was 10-20mg. MADA, alt-PAA and NLO pendant alt-PAA were measured separately in platinum pans under nitrogen atmosphere with a flow rate of 30 mL/min. MADA samples were heated from 30 to 150°C with a heating rate of 10°C/min, and then from 150 to 500°C with a heating rate of 1°C/min. Alt-PAA and NLO pendant alt-PAA samples were heated from 30 to 600°C with heating rate of 10°C/min. The results were plotted as percentage of weight loss versus temperature. The change in slope of percent weight loss versus temperature was determined by plotting the derivative of percent weight loss versus the derivative of temperature.
2.10.5 Solubility Testing

Alt-PAA, bis(an)MADA, NLO bis(an)MADA, all of the alt-PI and NLO pendant alt-PAA were tested for solubility in various solvent. The solvents included THF, 1-methyl-2-pyrrolidone (NMP), methanol, acetone, 2-methoxyethanol, methyl ethyl ketone, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), acetonitrile, 2-propanol, petroleum ether, toluene, methylene chloride, ethyl ether, and xylene.

2.10.6 Casting of Film

Alt-PAA, NLO Pendant alt-PAA made via DCC, NLO Pendant PAA made via polymer-bounded DCC were dissolved in DMSO and cast on glass slides. Commercial scotch tape with thickness of 0.055mm was applied to the long sides of a glass slide. The above solutions were cast between the stripes of tapes. The resulting films of polymer were dried at 100°C in air oven. Alt-PAA was spin coated on silica wafer for 30 seconds at 500 rpm after which the wafer with a polymer was dried at 100°C in air oven.

2.10.7 Absorption of Light by Ultraviolet and Visible (UV-VIS) Spectroscopy of Various Polymers and Guest Molecule

Alt-PAA, NLO Pendant alt-PAA made via DCC, NLO Pendant PAA made via polymer-bounded DCC, bis(an)MADA and NLO Bis(an)MADA were dissolved in THF. Absorbance of all of those solutions was obtained with a double beam SHIMADZU UV-2401PC UV-Vis Recording Spectrophotometer using THF in the reference beam. Each solution was diluted to the same concentration, 0.00578 mmoles/L, in THF and the absorbance was obtained between 200-600 nm.
2.10.8 Ebulliometry

The molecular weight of alt-PAA was analyzed using ebulliometry apparatus as shown in Figure 2.15.

DMAc (8.7 mL) was added to the two-neck flask and the solvent was brought to boiling. After the temperature stabilized, it was recorded. Alt-PAA (1.0 g) was dissolved in 8.7 mL of DMAc and the boiling point of the resulting solution was determined the same way as for pure DMAc. Ethylene glycol (1.0000 g, 0.00029851 moles) and p-cresol (1.0000 g, 0.0092517 moles) were dissolved separately in 8.7 mL of DMAc and, as before, the boiling point of each solution was determined.
2.10.9 *Dilute Solution Viscosity*

The molecular weight of alt-PAA was also analyzed by viscometry. Six solutions 0.0250, 0.0375, 0.0500, 0.0625, 0.0750, 0.0875 g/25 mL of DMAc were made up. An Ubbelohde viscometer was used to measure the time it took for 16 mL of the solution to drop from one mark to the other, see Figure 2.16. The viscometer, as well as solutions were kept in 30.2 +/-0.1 °C water bath and were allowed 40 minutes to equilibrate to the desired temperature. Each time measurement was repeated until three coincident readings with a standard deviation of +/- 0.2%.

![Figure 2.16 Solution Drop Levels of Viscometer](image)

The Mark-Houwink-Sakurada equation is used to estimate the viscosity average molecular weight of the alt-PAA.
3. RESULTS

3.1 Synthesis of Mellitic Acid Dianhydride (MADA)

When MADA is analyzed using TGA, the curve of percent weight loss versus the temperature is obtained. The result is shown in Figure 3.1. The only weight loss, before the decomposition, is consistent with the formation of mellitic acid trianhydride. That weight loss agrees with the calculated value of the loss of one molecule of water per molecule of MADA, 5.8%.

3.2 Synthesis NLO

3.2.1 Synthesis of nitro-NLO

The melting point range of synthesized bright yellow product was 169-173°C which is in good agreement with reported color and melting point of 174°C for nitro-NLO. [24]

3.2.2 Synthesis of amino-NLO

The melting point range of this product was at 123-129°C and its pale yellow color both agree with those of amino-NLO from previously done work. [25]

3.2.2.1 $^1$H Nuclear Magnetic Resonance (NMR)

3.2.2.1.1 1-D $^1$H Nuclear Magnetic Resonance (NMR)

NMR of the amino-NLO was taken and compared to Wei Cheng’s. See Figure 3.2. The currently made spectrum agrees with Wei’s spectrum. [25] Chemical shifts and
Figure 3.1 TGA of MADA
Figure 3.2: H-NMR of Amino-NLO
ratio of integrations consistent with expected structure.

3.2.2.1.2 2-D $^1$H Nuclear Magnetic Resonance (NMR)

The 2-D NMR of phthalic anhydride NLO was taken using the NMR technique called 2-D cosy90sw which involves the application of two 90 degree pulses to a spin system, and the results after Fourier transform give proton assignments. The spin-spin coupling between the hydrogens appear in 2-D cosy90sw spectrum as a cross peaks. The coupling is displayed as squares. See Figure 3.3. The spectrum is consistent with the proposed structure of NLO.

3.2.2.2 UV-VIS Spectroscopy

Absorbance of amino-NLO was performed in 200-600 nm region. The result was plotted on Figure 3.4. It shows no light absorption in visible region of the spectrum. The solvent THF absorbed light at wavelengths less than 210 nm.

3.3 Synthesis and Characterization of Polymers

3.3.1 Alt-PAA

The alt-PAA was prepared by adding APAF to the trimer in freshly dried THF over a three hour period. Excess solvent THF had to be used to stop the gelation of the resulting polymer. The resulting step-growth polymerization was allowed 24 hours to complete.
Figure 3.3 2-D $^1H$ NMR of Phthalic Anhydride NLO (courtesy of Julie Lieston)
Figure 3.4 UV-VIS Absorbance Spectra of amino-NLO
3.3.1.1 Infrared Spectrometry (FTIR)

The FT-IR spectrum of alt-PAA is shown in Figure 3.5. The major characteristic bands are 1656, 1608, 1245 and 1187 cm\(^{-1}\) which correspond to C=O (amide), C=C (aromatic), CF\(_3\) (two) stretches, respectively. The IR spectrum of the polymer is consistent with the proposed structure. All assignments for FTIR stretches are summarized in section 3.5.

3.3.1.2 \(^1\)H Nuclear Magnetic Resonance (NMR)

3.3.1.2.1 1-D \(^1\)H Nuclear Magnetic Resonance (NMR)

NMR was performed to verify the structures of the polyamic acid. See Figure 3.6. The large peaks at 6-8 ppm correspond to aromatic protons while the smaller peaks around 10 ppm correspond to the amide and hydroxy protons. In addition, the peaks for amino group of APAF are no longer visible. The broad peaks around 13 ppm are assigned to carboxylic acid protons. Chemical shifts and ratio of integrations consistent with expected structure. All the assignments for NMR spectra are summarized in section 3.5.

3.3.1.2.2 2-D \(^1\)H Nuclear Magnetic Resonance (NMR)

Proton coupling is displayed as squares. See Figure 3.7. The number of squares is consistent with the proposed structure of the polymer considering the possibility of isomerization.
Figure 3.5 FTIR of alt-PAA
Figure 3.6 $^1H$ NMR of alt-PAA
Figure 3.7 2-D $^1$H NMR of alt-PAA
3.3.1.3 UV-VIS Spectroscopy

Absorbance of alt-PAA was analyzed in 200-600 nm region. Alt-PAA spectrum showed minimal absorption in the visible region. See Figure 3.8.

3.3.1.4 Solubility

Solubility of alt-PAA was tested in different solvents including alcohols, ketones and hydrocarbons. The solubility rankings were:

VS - Very soluble
S – Soluble
SS – Slightly soluble
NS – Not soluble

Table 3.1 Solubility of alt-PAA

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Alt-PAA</th>
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<tbody>
<tr>
<td>Tetrahydrofuran</td>
<td>vs</td>
</tr>
<tr>
<td>Acetone</td>
<td>vs</td>
</tr>
<tr>
<td>Methanol</td>
<td>vs</td>
</tr>
<tr>
<td>2-Methoxyethanol</td>
<td>vs</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>vs</td>
</tr>
<tr>
<td>DMSO</td>
<td>vs</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>s</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>s</td>
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<td>ns</td>
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<td>Xylene</td>
<td>ns</td>
</tr>
</tbody>
</table>
Figure 3.8 UV-VIS Absorbance Spectra of alt-PAA versus NLO Pendant alt-PAA
3.3.1.5 Thermogravimetric Analysis (TGA)

Thermal stability of alt-PAA was studied using TGA. See Figure 3.9. The first weight loss feature is consistent with the imidization of the polymer. That weight loss (5.912 %) is comparable with the calculated value for the loss of five molecules of water per repeating unit of alt-PAA, (90.07 g / 1483 g = 6.07%). The onset point was 242.2°C.

3.3.1.6 Molecular Weight Determination

3.3.1.6.1 Ebulliometry

Ebulliometry was performed on two samples with known molecular weight p-cresol and poly(ethylene glycol) and on the alt-PAA. For all samples DMAc was used as a solvent.

\[ \Delta T_b = K_b \times m \]

\[ 0.02 = 3.32 \times \left( \frac{(1.0000 \text{ g alt-PAA} / \text{MW})}{0.00815 \text{ kg DMAc}} \right) \]

MW = 20,368 g/mole (alt-PAA)

where \( m \) is the molality (moles of solute per kilogram of solvent) and \( K_b \) is the Ebullioscopic Constant, a characteristic property of the solvent.

The \( K_b \) of DMAc was determined using p-cresol and poly(ethylene glycol):

Polyethylene Glycol => \( K_b = 0.12 \ ^\circ\text{C} / [(1.0000g / 3350 \text{ g/mole}) / 0.00815 \text{ kg DMAc}] = 3.27 \)

p-Cresol => \( K_b = 3.83 \ ^\circ\text{C} / [(1.0000g / 108.1 \text{ g/mole}) / 0.00815 \text{ kg DMAc}] = 3.37 \)

\( K_b \) (average) = \( (3.27 + 3.37) / 2 = 3.32 \),

and plugged in to the formula to find molecular weight of alt-PAA as shown above to give the molecular weight of \( 20 \times 10^3 \) g/mole.
### 3.3.1.6.2 Viscometry

Viscometry is an indirect technique of measuring molecular weight. Mark-Houwink-Sakurada (MHS) equation $\eta = K[M_v]^a$ is employed to convert the relative viscosity data to the viscosity average molecular weight, $M_v$. Since alt-PAA is a novel polymer, its $K$ and $a$ values are not known. Therefore values of Kapton were used to calculate $M_v$. \[^{26}\] The viscosity experiment for alt-PAA was performed in DMAc, see Table 3.2. The plot of Viscosity versus Concentration of alt-PAA was performed, see Figure 3.10. The viscosity average molecular weight was calculated to be 25,528 g/mole.

#### Table 3.2 Viscosity Data for alt-PAA

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<th>Concentration of Solution g/mL</th>
<th>Density g/mL</th>
<th>Time (sec)</th>
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<th>$\eta_{\text{inh}}$</th>
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<td>0.9427</td>
<td>102.55</td>
<td>15.27</td>
<td>14.94</td>
</tr>
</tbody>
</table>

### 3.3.2 Synthesis and Characterization of Solid-State Imidized alt-PAA

A sample of alt-PAA was imidized in 195°C for 1 hour in air oven. A second sample of polyamic acid was imidized at 195°C for 1 hour in vacuum by means of a stoppered filter flask apparatus similar to that used to prepare MADA. Finally, a sample of alt-PAA was mixed in with mesitylene and distilled. Due to insolubility of all the solid-state imidized polyamic acids, only FTIR spectra of them were obtained,
Figure 3.10 Plot of Viscosity vs. Concentration of alt-PAA
see Figures 3.11-3.13. The major bands are 1857, 1783, 1726, 1378, 719 cm\(^{-1}\), which are due to C=O (anhydride), C=O (imide sym. and asym.), C-N and C-H (aromatic, out of plane bending)\(^9\), respectively. The absence of a peak at 1656 cm\(^{-1}\) C=O (amide) signifies a high degree of imidization. The lessening intensity of absorption bands at 3000 - 3500 cm\(^{-1}\) in imidized material is due to disappearance of OH stretches of carboxylic acids and N-H stretches of amido groups. The IR spectrum of the product is consistent with the proposed polyimide structure. All assignments for FTIR stretches are summarized in section 3.5.

3.3.3 Synthesis and Characterization of Solution Imidized alt-PAA

A sample of alt-PAA was heated at reflux in d\(_6\)-DMSO therefore inducing imidization under dilute conditions, unlike solid-state imidization.

3.3.3.1 Infrared Spectrometry (FTIR)

The major bands are 1862, 1793, 1725, 1596, 1371, 1247, 1189, 719 cm\(^{-1}\), which are due to C=O (anhydride), C=O (imide sym. and asym.), C=C, C-N, CF\(_3\) (two), and C-H (imide aromatic, out of plane bending), respectively. A significant decrease in the intensity of 1656 cm\(^{-1}\) C=O (amide) signifies a high degree of imidization (approximately 70% but not as high as solid-state imidization). The lessening intensity of absorption bands at 3000 - 3500 cm\(^{-1}\) in imidized material is due to disappearance of OH stretches of carboxylic acids and N-H stretches of amido groups. The IR spectrum of the polymer is consistent with the proposed structure, see Figure 3.14. All assignments for FTIR stretches are summarized in section 3.5.
Figure 3.11 FTIR of alt-PAA Imidized in 195°C Air
Figure 3.12 FTIR of alt-PAA Imidized in 195°C Vacuum
Figure 3.13 FTIR of alt-PAA Imidized in Mesitylene
Figure 3. FTIR of alt-P44 Imidized in d-DMO
3.3.3.2 $^1$H Nuclear Magnetic Resonance (NMR)

NMR was performed to verify the structures of the solution imidized polyamic acid. Absence of carboxylic acid proton peaks at 13 ppm and significant decrease in intensity of the peaks at 10 ppm signifies imidization occurred. The amide proton signals disappear, but signals due to phenoxy protons around 10 ppm should remain. See Figure 3.15. The NMR spectrum of the polymer is consistent with the proposed structure. All assignments for NMR peaks are summarized in section 3.5.

3.3.3.3 UV-VIS Spectroscopy

Absorbance of solution imidized polyimide was analyzed in 200-600 nm region. The results indicate that alt-PI does not absorb light in the visible region. See Figure 3.16.

3.3.3.4 Solubility

Solubility of alt-PI was tested in different solvents including alcohols, ketones and hydrocarbons. The solubility rankings were:

VS - Very soluble
S – Soluble
SS – Slightly soluble
NS – Not soluble
Figure 3.15 $^1$H NMR of alt-PI Made in $d_6$-DMSO
Figure 3.16 UV-VIS Absorbance Spectra of alt-PI versus NLO Pendant alt-PI
3.3.4 Synthesis and Characterization of NLO Pendant alt-PAA

The NLO pendant alt-PAA was prepared by addition of NLO to alt-PAA in freshly dried solvent THF. Anhydride-like reactivity on the polymer backbone results from activation of the adjacent carboxylic acid groups on MADA with N,N'-dicyclohexylcarbodiimide (DCC) or polymer-based BCC. The progress of the reaction was followed by TLC. The amino-NLO diluted in THF was spotted versus the product. When the product did not show any more of free NLO the reaction was stopped. The reaction mixture turned a shade darker brown color by the end of the reaction. When DCC was used, a byproduct light in color (urea), was clearly seen on the bottom of the reaction flask. However when polymer-based BCC was employed, the solid on the bottom of the flask was red-brown in color (a urea pendant polymer). In both cases the solid was separated from the solution by vacuum filtration.
3.3.4.1 Infrared Spectrometry (FTIR)

The major bands are 1783, 1726, 1607, 1383, 1247, 1189, 708 cm\(^{-1}\), which are due to C=O (imide sym. and asym.), C=C, C-N, CF\(_3\) (two), and C-H (aromatic, out of plane bending), respectively. The lessening intensity of absorption bands at 3000 - 3500 cm\(^{-1}\) is due to disappearance of OH stretches of carboxylic acids and N-H stretches of amido groups. The IR spectrum of polymers is consistent with the proposed structure. However, no NLO stretches were apparent, see Figures 3.17-3.18. All assignments for FTIR stretches are summarized in section 3.5.

3.3.4.2 \(^1\)H Nuclear Magnetic Resonance (NMR)

3.3.4.2.1 1-D \(^1\)H Nuclear Magnetic Resonance (NMR)

NMR was performed to verify the structures of the NLO pendant alt-PAA polymers. The large peaks at 6-8 ppm correspond to aromatic protons while the smaller peaks around 10 ppm correspond to the amide and hydroxy protons. The broad peaks around 13 ppm are assigned to carboxylic acid protons. The amino proton peaks from amino-NLO at around 5.7 ppm have disappeared, while hydroxy groups at 10 ppm remain. The NMR spectra of the NLO pendant polymers are nearly consistent with the proposed structure. See Figure 3.19-3.20. Deviation from the expected integration ratio for the amido and phenoxy proton region (around 10 ppm) to the aromatic region (7 to 8.4 ppm), equal to 9:25 (1:2.8), was greater when the excess of carbodiimide was greater, see page 21 and 22. All assignments for NMR peaks are summarized in section 3.5.
Figure 3.17 FTIR of NLO Pendant alt-PAA (made with DCC)
Figure 3.18 FTIR of NLO Pendant-1-PAA (made with polymer-based BCC)
Figure 3.19 $^1H$ NMR of NLO Pendant alt-PAA (made with DCC)
Figure 3.20 $^1$H NMR of NLO Pendant alt-PAA (made with polymer-based BCC)
3.3.4.2 2-D $^1$H Nuclear Magnetic Resonance (NMR)

The 2-D NMR of NLO pendant alt-PAA was taken to verify the addition of NLO to the alt-PAA backbone. The NMR technique called 2-D cosy90sw involves the application of two 90 degree pulses to a spin system, and the results after Fourier transform give proton assignments. The spin-spin coupling between the hydrogens appear in 2-D cosy90sw spectrum as a cross peaks. The spin-spin coupling of the hydrogens in NLO also emerges in NLO pendant alt-PAA (made with polymer-based BCC). The coupling is displayed as squares that are numbered from 1 to 8, see Figure 3.21. The number of squires is consistent with the proposed structure of NLO. See Figure 3.3.

3.3.4.3 UV-VIS Spectroscopy

Absorbance of NLO Pendant alt-PAA (made with DCC) and NLO pendant alt-PAA (made with polymer-based BCC) was analyzed in 200-600 nm region. See Figure 3.22. Absorbance of NLO pendant alt-PAA is minimal in the visible region of the spectrum.

3.3.4.4 Solubility

Solubility of NLO Pendant alt-PAA was tested in different solvents including alcohols, ketones and hydrocarbons. The solubility rankings were:

VS - Very soluble
S – Soluble
SS – Slightly soluble
Figure 3.2: 2-D J-H NMR of NO Pendant alt-P44 (made with polymer-based BCC)
Figure 3.22 UV-VIS Absorbance Spectra of NLO Pendant alt-PAA (DCC) versus NLO Pendant alt-PAA (polymer-based BCC)
NS – Not soluble

Table 3.4 Solubility of NLO Pendant alt-PAA Polymers via DCC and Polymer-based BCC

<table>
<thead>
<tr>
<th>Solvent</th>
<th>NLO Pendant Alt-PAA (DCC)</th>
<th>NLO Pendant Alt-PAA (p-DCC)</th>
</tr>
</thead>
<tbody>
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<td>vs</td>
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<td>Acetone</td>
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</tr>
<tr>
<td>2-Methoxyethanol</td>
<td>s</td>
<td>vs</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
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<td>vs</td>
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<td>DMSO</td>
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<td>Methylene Chloride</td>
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<tr>
<td>Xylene</td>
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<td>ns</td>
</tr>
</tbody>
</table>

3.3.4.5 Thermogravimetric Analysis (TGA)

Thermal stability of NLO pendant alt-PAA (made with polymer-based BCC) was studied using TGA. See Figure 3.23. The first weight loss feature is consistent with the imidization of the polymer. That weight loss (5.128 %) is comparable with the calculated value of the loss of five molecule of water per repeating unit of NLO pendant alt-PAA, (90.07 g / 1666 g = 5.40 %). The onset point was 236.2°C.
Deriv. Weight (%/C)

Weight (%)

Temperature (°C)

Universal V25 TA Instruments

Figure 3.23: TGA of NLO Pendant alt-PAA (made with polymer-based BCC)

Run Date: 4-Jul-03 17:17
Operator: Eugene
File: A:NL0-alt-PAA J 4-03 001
Sample: NL0-alt-PAA J 4-03 001

236.15°C
(0.6281mg)
5.128%

64
3.3.5 Synthesis and Characterization of NLO Pendant alt-PI

NLO pendant alt-PI was made from solution imidized alt-PI and amino-NLO in d₆-DMSO. Since the anhydride ring of the alt-PI was to react with amide of the amino-NLO, no DCC was used. The progress of the reaction was followed by TLC. The amino-NLO diluted in d₆-DMSO was spotted versus the product. When the product did showed free NLO even after 24 hour period of reacting, the reaction was stopped. The resulting product was washed with cold THF to remove low molecular weight species and excess amino-NLO. The percent of amino-NLO that reacted with solution imidized alt-PI was calculated:

$$0.000952 \text{ moles alt-PI} \times (1.000 \text{ mole NLO} / 1\text{mole alt-PI}) \times (201.29 / 1.000 \text{ mole NLO}) = 0.192 \text{ g of NLO (total grams of NLO per grams of alt-PI for 100\% imidization)}$$

$$0.135 \text{ g NLO (actually reacted)} / 0.192 \text{ g NLO (total)} = 71\% \text{ of NLO reacted with alt-PI}$$

3.3.5.1 Infrared Spectrometry (FTIR)

The major bands are 1781, 1723, 1618, 1374, 1246, 1200, 716 cm⁻¹, which are due to C=O (imide sym. and asym.), C=C, C-N, CF₃ (two), and C-H (imide aromatic, out of plane bending), respectively. The IR spectrum of polymers is consistent with the proposed structure. However, no NLO stretches were apparent, see Figure 3.24. All assignments for FTIR stretches are summarized in section 3.5.
Figure 3.24 FTIR of NLO Pendant alt-PI
3.3.5.2 $^1H$ Nuclear Magnetic Resonance (NMR)

3.3.5.2.1 1-D $^1H$ Nuclear Magnetic Resonance (NMR)

NMR was performed to verify the structures of NLO pendant alt-PI. The large peaks at 6-8 ppm correspond to aromatic protons while the smaller peaks around 10 ppm correspond to hydroxy protons. Absence of carboxylic protons suggests that the product was imidized to a high degree. The amino peaks from amino-NLO have disappeared. The NMR spectrum of the NLO pendant polymers is consistent with the proposed structure. See Figure 3.25. All assignments for NMR peaks are summarized in section 3.5.

3.3.5.2.2 2-D Nuclear Magnetic Resonance (NMR)

The 2-D NMR of NLO pendant alt-PI was taken to verify the addition of NLO to the alt-PI backbone. The spin-spin coupling between the hydrogens appear in 2-D cosy90sw spectrum as a cross peaks. Since the polymer was imidized, its solubility diminished; therefore 300 MHz 2-D NMR did not show all of the expected NLO squares, See Figure 3.26.

3.3.5.3 UV-VIS Spectroscopy

Absorbance of NLO Pendant alt-PI was analyzed in 200-600 nm region. See Figure 3.16. NLO pendant alt-PI does not absorb light in visible region.
Figure 3.25 $^1H$ NMR of NLO Pendant alt-PI
Figure 3.26 2-D $^1$H NMR of NLO Pendant alt-PI
3.3.5.4 Solubility of alt-PAA

Solubility of polymer was tested in different solvents including alcohols, ketones and hydrocarbons. The solubility rankings were:

VS - Very soluble
S – Soluble
SS – Slightly soluble
NS – Not soluble

<table>
<thead>
<tr>
<th>Solvent</th>
<th>NLO Pendant alt-PI</th>
</tr>
</thead>
<tbody>
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<td>Tetrahydrofuran</td>
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<td>Acetone</td>
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<td>2-Methoxyethanol</td>
<td>s</td>
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<td>Methyl Ethyl Ketone</td>
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<td>DMSO</td>
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<td>Acetonitrile</td>
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<td>2-Propanol</td>
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</tr>
<tr>
<td>Xylene</td>
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</tbody>
</table>

3.4 Guest Molecule

3.4.1 Synthesis and Characterization of Bis(an)MADA

Bis(an)MADA was prepared by reaction of aniline and MADA, giving a product which was pale yellow in color.
3.4.1.1 Infrared Spectrometry (FTIR)

The major bands are 1717, 1654, 1598 cm\(^{-1}\), which are due to C=O (carboxylic acid), C=O (amide), and C=C (aromatic), respectively. Absorption bands at 3000 - 3500 cm\(^{-1}\) are due to OH stretches of carboxylic acids and NH stretches of the formed amido groups. The IR spectrum of bis(an)MADA is consistent with the proposed structure, see Figure 3.27. All assignments for FTIR stretches are summarized in section 3.5.

3.4.1.2 1-D \(^1\)H Nuclear Magnetic Resonance (NMR)

NMR was performed to verify the structures of Bis(an)MADA. The large peaks at 6-8 ppm correspond to aromatic protons while the smaller peaks around 10 ppm correspond to amide protons. The broad peaks around 13 ppm are assigned to carboxylic acid protons. Chemical shifts and ratio of integrations consistent with expected structure. See Figure 3.28. All the assignments for NMR spectra are summarized in section 3.5.

3.4.1.3 UV-VIS Spectroscopy

Absorbance of bis(an)MADA was performed in 200-600 nm region. The result was plotted on Figure 3.29. They show no light absorption in visible region of the spectrum.

3.4.1.4 Solubility of Bis(an)MADA

Solubility of bis(an)MADA was tested in different solvents including alcohols, ketones and hydrocarbons. The solubility rankings were:

VS - Very soluble
S – Soluble
Figure 3.27 FTIR of Bis(an)MADA
Figure 3.28 $^1H$ NMR of Bis(an)MADA
3.29 UV-VIS Absorbance Spectra of Bis(an)MADA versus NLO Bis(an)MADA
SS – Slightly soluble
NS – Not soluble

Table 3.6 Solubility of Bis(an)MADA

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Bis(an)MADA</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>Acetone</td>
<td>vs</td>
</tr>
<tr>
<td>Methanol</td>
<td>vs</td>
</tr>
<tr>
<td>2-Methoxyethanol</td>
<td>vs</td>
</tr>
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<td>Methyl Ethyl Ketone</td>
<td>vs</td>
</tr>
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<td>DMSO</td>
<td>vs</td>
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<td>Xylene</td>
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</table>

3.4.2 Synthesis and Characterization of Imidized Bis(an)MADA

A sample of bis(an)MADA was imidized in 210°C for 1 hour in air oven. Due to insolubility of the molecule only FTIR spectra of it was taken. The major bands are 1861, 1787, 1723, 1626, 1362, 718 cm⁻¹, which are due to C=O (anhydride), C=O (imide sym. and asym.), C=C (aromatic), C-N, and C-H (imide aromatic, out of plane bending,) respectively. An important decrease in strength of 1656 cm⁻¹ C=O (amide) signifies a high degree of imidization. The lessening intensity of absorption bands at 3000 - 3500 cm⁻¹ in imidized material is due to disappearance of OH stretches of carboxylic acids and N-H amido groups. The IR spectrum of the imidized bis(an)MADA is consistent with
the proposed structure. See Figure 3.30. All assignments for FTIR stretches are summarized in section 3.5.

3.4.3 Synthesis and Characterization of NLO Pendant Bis(an)MADA

The NLO pendant bis(an)MADA was prepared by addition of NLO to bis(an)MADA in a freshly dried solvent THF. Anhydride-like reactivity on the polymer backbone results from activation of the adjacent carboxylic acid groups on MADA with N,N'-dicyclohexylcarbodiimide (DCC). The progress of the reaction was followed by TLC. The NLO diluted in THF was spotted versus the product. When the product did not show any more of free NLO the reaction was stopped. The reaction mixture turned a dark brown-black color by the end of the reaction, the major byproduct of the reaction being urea.

3.4.3.1 Infrared Spectrometry (FTIR)

The major bands are 1793, 1661, 1596, 1375, 720 cm\(^{-1}\), which are due to C=O (imide), C=O (amide), C=C (aromatic), C-N, and C-H (imide aromatic, out of plane bending), respectively. The lessening intensity of absorption bands at 3000 - 3500 cm\(^{-1}\) is due to disappearance of OH stretches of carboxylic acids and N-H stretches of amido groups. The IR spectrum of bis(an)MADA is consistent with an imidized form of the proposed structure. However, no NLO stretches were apparent, see Figure 3.31. All assignments for FTIR stretches are summarized in section 3.5.
Figure 3.30 FTIR of Imidized Bis(an)MADA in 210°C Air
Figure 3.31 FTIR of NLO Bis(an)MADA (made with DCC)
3.4.3.2 $^1H$ Nuclear Magnetic Resonance (NMR)

NMR was performed to verify the structures of NLO Bis(an)MADA. The large peaks at 6-8 ppm correspond to aromatic protons. Absence of carboxylic protons and small presence of amide protons around 10.5 ppm suggests that the product was imidized to a high degree. The amino peaks from amino-NLO have disappeared. The NMR spectrum of the NLO bis(an)MADA is consistent with the proposed structure. See Figure 3.32. All assignments for NMR peaks are summarized in section 3.5.

3.4.3.3 UV-VIS Spectroscopy

The absorbance of NLO pendant bis(an)MADA was analyzed in 200-600 nm region. See Figure 3.29. Note that its absorbance is large in the visible region of the spectrum.

3.4.3.4 Solubility

Solubility of the guest molecule was tested in different solvents including alcohols, ketones and hydrocarbons. The solubility rankings were:

VS - Very soluble
S - Soluble
SS - Slightly soluble
NS - Not soluble
Figure 3.32 $^1$HNMR of NLO Bis(an)MADA (made with excess DCC)
Table 3.7 Solubility of NLO Pendant Bis(an)MADA

<table>
<thead>
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<th>NLO Pendant Bis(an)MADA</th>
</tr>
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<tbody>
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<td>Xylene</td>
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</table>
To facilitate the comparison of spectral data, see Tables 3.8-3.10 and Figure 3.33.

(a) The integration of amide, hydroxy and carboxylic protons to aromatic protons for al-PAA (1.1.47).

(b) Broad, some integration intensity may be lost.

An integration ratio of (1.4:1.8, = 1:2) is expected for the proposed structure, see Figure 2.9.

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Amido and/or hydroxy

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Table 3.8 Assignments for 1H NMR peaks of Polymer and Guest molecule in d-DMISO
(a) Abbreviations: s = strong, m = medium, w = weak, sh = shoulder.

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Note: The table describes the vibrational modes of a polymer. The frequencies listed are in cm^-1. The modes are identified with different symbols and notes indicating their nature and behavior.
b) Partially masked by excess DC; NLO peaks are not observed (masked).

---

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<td>(cm⁻¹)</td>
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<td>(DCS)</td>
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<td>BIS(AMAD)</td>
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**Table 3.10 FTIR Assignments for Guest Molecule**
4. DISCUSSION

4.1 Synthesis of Mellitic Acid Dianhydride (MADA)

Heated mellitic acid goes from monoanhydride to dianhydride and finally it becomes trianhydride. In its dianhydride state there are two isomer possibilities. See Figure 4.1, and both of them are preferred monomers for the polymerization of alt-PAA.

![Mellitic Dianhydride Isomer Possibilities](image)

Mellitic monoanhydride and trianhydride are the potential results of insufficient heating or overheating, respectively. Presence of trianhydride would cause cross-linking to produce gel while occurrence of monohydride would initiate early chain termination resulting in low molecular weight. While mellitic trianhydride is an undesirable product, its formation can be used to check for purity of mellitic dianhydride (MADA). As dianhydride turns into trianhydride a molecule of water is lost, which corresponds to 5.8% weight loss. The thermogravimetric analysis of pure MADA would show a curve with on step which corresponds to weight loss of 5.8%. The TGA result confirmed the purity of MADA. See Figure 2.1.

4.2 Preparation of amino-NLO

The purity of amino-NLO obtained from column separation was confirmed by melting point, TLC and also NMR which was compared to the NMR of a previous
research student (Julie Lieston), who obtained a satisfactory elemental analysis on the phthalic anhydride derivative of amino-NLO. All results from the above techniques are consistent with the formation of amino-NLO.

4.3 Synthesis of alt-PAA

Polymerization reaction of alt-PAA is a step growth polymerization. Therefore the molecular weight of the product depends on purity and stoichiometric ratio of the monomers. The alt-PAA is made up of three components, MADA, APAF and 6FDA in 1:2:1 ratio, respectively. The purity of MADA was confirmed as discussed in previous section, APAF and 6FDA were sublimated. Sublimation occurs when the temperature is slightly above the melting point of material to be sublimed. If the temperature is more than 20°C over the melting point, decomposition occurs. It is identified by formation of brownish tint in the sublimed material.

Since two of the monomers are dianhydrides the polymerization is water sensitive and the presence of moisture would open up the anhydride rings. Another monomer is a diamine which is easily oxidizable by the oxygen. Consequently, the presence of moisture or/and oxygen would reduce the reactivities of the monomers and, hence, lower the molecular weight of the polymer.

Addition of dissolved dianhydride (6FDA) to the solution of dianhydride (MADA) and diamine (APAF) is done dropwise in a three hour period. The slow addition and efficient stirring enables the best contact between diamine and dianhydrides, which favors the higher molecular weight polymer. Using excess solvent (THF) retards the formation of gel by impeding the formation of interchain covalent bonding. The
formation of alt-PAA was confirmed by FTIR and NMR. The resulting product is a novel polymer.

4.4 Imidization of alt-PAA

Imidization of alt-PAA was performed four ways, by heating at reflux in mesitylene, 195°C in air, 195°C in vacuum, and refluxing in d₆-DMSO. Imidization in mesitylene proved to be partial as shown by FTIR. Mesitylene has a boiling point of 163°C which apparently did not provide enough activation energy for a complete imidization to take place. It is also worth noting that alt-PAA is not soluble in mesitylene. Imidization at 195°C in air or vacuum provide for nearly complete imidization as can be seen by FTIR. However, the resulting alt-PAA was almost completely insoluble. The solid imidization evidently causes crosslinking between adjacent chains of the polymer. Solvent imidization of alt-PAA was done by dissolving the polymer in d₆-DMSO and heating the resulting solution at reflux (184°C). Since the imidization occurs in solution, the chances of crosslinking are small due to the separation of polymer chains by solvent. FTIR performed on the resulting polymer showed that most of it was imidized, approximately 90% by way of excess DCC and 20% by way of excess polymer-based BCC.

4.5 Synthesis of NLO Pendant alt-PAA

Addition of NLO to the polymer backbone can be done in two ways. The first way is by attaching NLO to the alt-PAA backbone by the reaction between the amino group of NLO with the carboxylic acid groups in the polymer backbone in the presence
of N,N'-dicyclohexylcarbodiimide (DCC). DCC activates the adjacent carboxylic acid groups of MADA, which then react readily with the amino groups of amino-NLO. During the synthesis, vast excess of DCC was added to the polyamic acid followed by the addition of NLO in 1:1 molar ratio to the polymer repeating chain. The byproduct of this reaction, thought to be dicyclohexyl urea, was difficult to get rid off. Therefore, a polymer-based BCC was used which prevents the dissolution of urea in the solvent and allows the byproduct to be easily filtered off. The larger excess of DCC imidized the NLO pendant polyamic acid (approx. 90%), while smaller excess of polymer-based BCC had a smaller imidization effect on the NLO pendant polymer (approx. 20%). The imidization was apparent due to imide stretches in FTIR and decrease in integration ratio of carboxylic and amido protons relative to the aromatic region in $^1$H NMR spectra, see page 55. The completion of NLO attachment to the polymer backbone was confirmed by TLC and verified by 2-D $^1$H NMR. Amino-NLO was spotted versus the product, and when the product showed no more band separation due to amino-NLO, the reaction was presumed completed. In addition 2-D $^1$H NMR of the product was taken which showed coupling attributed to the NLO. This NLO pendent polyamic acid is a novel product.

The second way of attaching the NLO to the polymer backbone is following solution imidization. The alt-PAA was solution imidized in $d_6$-DMSO, and isolated by solution evaporation with combination of vacuum and temperature (100°C). As for solid-state imidization, adjacent carboxylic groups on the MADA form anhydride rings which can react readily (at room temperature) with amino groups on the NLO. However, since the imidization was done in solution, the resulting polyimide retains a measure of solubility in various solvents including THF. Thus, amino-NLO was titrated into a THF solution of
solution-imidized alt-PAA until free NLO became evident with TLC. The resulting product is a novel NLO pendant alt-PAA polyimide.

4.6 Synthesis and Imidization Guest Molecule

4.6.1 Bis(an)MADA

Synthesis of Bis(an)MADA was done by reaction of MADA and aniline in 1:2 stoichiometric ratio, respectively. The synthesis is very water and oxygen sensitive as the reactants have anhydride and amino groups. If dianhydride is exposed to moisture, its anhydride rings would revert to carboxylic acid groups, and oxygen oxidizes the amino groups which would result in lower yield of the product. Therefore, the reaction was performed under nitrogen atmosphere. The resulting product was confirmed by TLC, NMR and FTIR.

4.6.2 Imidized Bis(an)MADA

Bis(an)MADA exposed to 210°C for 1 hour in air produces a nearly complete imidization as can be seen by FTIR. However, the resulting imidized bis(an)MADA was almost completely insoluble. The solid imidization evidently causes intermolecular reactions.

4.6.3 Synthesis of NLO Bis(an)MADA

Addition of NLO to Bis(an)MADA was done in 1:1 molar ratio and through the use of excess DCC. DCC activates the adjacent carboxylic acid groups of MADA which react readily with amino groups of the NLO. The reaction was followed by TLC to check
for unreacted NLO material. Once the NLO material was absent from the reaction solution, the reaction was stopped.

4.7 Characterization of Polymers and Guest Molecule

4.7.1 Infrared Spectrometry (FTIR)

The differences between IR spectrum of polyamic acid and polyimides are due to the formation of imide and anhydride rings which is represented by appearance of 1783, 1726 and 1858 cm\(^{-1}\), respectively.\(^9\) The disappearance of 1656 cm\(^{-1}\) amide stretch is another indication of complete imidization.\(^9\) The IR of imidization by mesitylene shows an amide stretch as well as imide and anhydride stretches which can be attributed to partial imidization. The use of high temperature (195°C) with either vacuum or air atmosphere provides for nearly complete imidization. The IR of high temperature imidized alt-PAA does not show an amide stretch with the corresponding imide and anhydride peaks. However, the loss of product solubility can be attributed to the crosslinking during solid state imidization. The solution imidization via d\(_6\)-DMSO also shows a small amide peak along with imide and anhydrous stretches. However, it is small which suggests that level of imidization was significant. This view was supported by titration results for solution imidized alt-PAA with amino-NLO which showed 71 percent anhydride ring formation (related to imidization). After bis(an)MADA was imidized at 210°C for 1 hour, the large imide peaks at 1786, 1720 cm\(^{-1}\) and the vast reduction of the amide stretch at 1654 cm\(^{-1}\) suggest that imidization is nearly complete.
4.7.2 Nuclear Magnetic Resonance (1-D $^1H$ NMR)

$^1H$ NMR was performed to verify the structures of polyamic acid, polyimides, NLO pendant polyamic acid and NLO pendent polyimide. The NMR spectrum of alt-PAA displays proton peaks that correspond to amido groups, which were predicted to form upon polymerization, as well as carboxylic acid proton peaks. The ratio of carboxylic and amide hydrogens to the aromatic hydrogens in the repeating unit of the proposed polymer was consistent with the ratio of peak areas for the corresponding NMR peaks. Due to almost nonexistent solubility of polyimides produced by mesitylene and solid temperature imidizations, their solution NMR spectra could not be obtained. The NMR spectrum of alt-PI produced by solution imidization in d$_6$-DMSO showed the disappearance of carboxylic and amide peaks as expected. The absences of those peaks are due to the formation of imide (from adjacent amide and carboxylic groups) and anhydride ring (from adjacent carboxylic groups). The NMR spectrum of NLO pendant alt-PAA still shows carboxylic and amide peaks as predicted because the NLO attached via only one carboxylic group. The ratio of different hydrogens in the repeating chain to their corresponding peaks areas was not consistent due to the partial imidization induced by excess DCC or polymer-based BCC. The NMR spectrum of NLO pendant alt-PI does not show carboxylic and amide peaks but shows hydroxyl protons as predicted, due to imidization. The NMR of bis(an)MADA displays proton peaks that correspond to amido groups, as well as carboxylic acid proton peaks. The ratio of carboxylic and amide hydrogens to the aromatic hydrogens in the bis(an)MADA molecule was consistent with the ratio of peak areas for the corresponding NMR peaks. NMR spectrum of imidized bis(an)MADA was not obtained due to inability of imidized material to dissolve. The
ratio of different hydrogens in NMR spectrum of NLO bis(an)MADA ratio of different hydrogens to their corresponding peaks areas was not consistent due to the partial imidization induced by excess DCC.

4.7.3 Nuclear Magnetic Resonance (2-D $^1$H NMR)

2-D $^1$H-NMR spectra of the alt-PAA and NLO pendant alt-PAA were obtained and compared with the one of amino-NLO. Cosy90sw was used in this case, which shows the cross peaks where the spin-spin coupling between the hydrogens occurs. Two 90 degrees pulses were applied to the spin system which gave a signal as a function time between the pulses. Fourier transformation of the results gave proton coupling information for the chemical compound of interest. Squares for coupled protons can be drawn. The series of squares found for the amino-NLO phthalic anhydride derivative were also found in the 2-D NMR of the NLO pendant alt-PAA. This finding verifies the presence of NLO in the NLO pendant alt-PAA.

4.7.4 UV-VIS Spectroscopy

The absorbance spectra of amino-NLO, alt-PAA, alt-PI, NLO pendant alt-PAA, NLO pendant alt-PI, bis(an)MADA and NLO bis(an)MADA were taken between 200-600 nm region. The NLO by itself does not absorb above 250 nm. However, after addition of it to the alt-PAA backbone, the resulting system absorbs up to 400 nm. The alt-PAA as itself does not absorb light above 350 nm. Bis(an)MADA absorbs light to 350 nm, but after addition of NLO molecule the absorption band stretches to 550 nm. The alt-PI does not absorb above 250 nm. However after addition of NLO, the
absorbance band extends to 400 nm. Thus, the addition of NLO to the polymer backbone or to the guest-molecule increases the absorption range and magnitude for the resulting system.

4.7.5 Solubility

The solubility of alt-PAA, alt-PI, NLO pendant alt-PAA, NLO pendant alt-PI, bis(an)MADA and NLO bis(an)MADA were determined in the following solvents: THF, 1-methyl-2-pyrrolidone (NMP), methanol, acetone, 2-methoxyethanol, methyl ethyl ketone, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), acetonitrile, 2-Propanol, petroleum ether, toluene, methylene chloride, ethyl ether, and xylene. The apparent trend is that all of the above polymers and guest molecules are soluble in ketone, alcohols and high boiling polar solvents while insoluble in hydrocarbon solvents. The addition of NLO moiety does not dramatically change the solubility of the polymer or guest molecule, but, imidization does. Solid-imidized polymers and guest molecule apparently do not dissolve at all. Solution-imidized alt-PAA and NLO alt-PAA solubility, while still being soluble, diminishes as compared to the alt-PAA and NLO alt-PAA.

4.7.6 Ebulliometry

Ebulliometry was done on two chemicals with known molecular weight and on alt-PAA. The solvent used for this experiment was DMAC. Change in temperature between the boiling points of pure solvent and alt-PAA was used in conjunction with the formula $\Delta T = K_b \cdot m$ shown that the molecular weight of the alt-PAA was $20 \times 10^3$ g/mole.
4.7.7 Viscometry

The viscosity of alt-PAA was determined with DMAc being the solvent. Using the Mark-Houwink relation and the K and a value of Kapton\textsuperscript{[26]} the molecular weight of the polymer was determined to be 25,528 g/mole. Some difference from the true molecular weight is expected due to “K and a” values being used (from Kapton).
5. CONCLUSIONS

The novel three component alt-PAA[6FDA-APAF-MADA-APAF], and alt-PI[6FDA-APAF-MADA-APAF were synthesized through step growth polymerization. A NLO moiety was pendently attached to the three component polyamic acid to improve the temporal stability of the nonlinear optical effect of the molecule. The produced novel four component polymers were NLO pendant alt-PAA[6FDA-APAF-MADA-APAF] and NLO pendant alt-PI[6FDA-APAF-MADA-APAF]. The techniques TLC, FTIR, 1-D $^1$H NMR and 2-D $^1$H NMR support the proposed structures of polymers.

A guest molecule, bis(an)MADA, was synthesized followed by an attachment of NLO moiety to produce NLO bis(an)MADA. The techniques TLC, FTIR and 1-D $^1$H NMR support the proposed structure of the guest molecule.

Ebulliometry and viscometry testing showed that the novel polymer has a moderate molecular weight. Based on both methods, the average degree of polymerization is 14 ±4. [Average MW for ebulliometry and viscosity (22*10$^3$) / MW of repeat unit (1483 g/ mole)].

TGA of alt-PAA and NLO alt-PAA was taken between 30 and 600°C to check for thermal stabilities of the polymers. Both polymers started to decompose well above 200°C which makes them sufficiently stable for the intended uses.

Addition of the NLO molecule to the alt-PAA polymer backbone increases the region of absorptivity of light but only to 400nm. However, attachment of the NLO moiety to the guest molecule results in absorption up to 550 nm. Solubility testing demonstrates that polyamic acid, NLO polyamic acid and guest molecule are soluble in polar aprotic solvents, ketones, and alcohols, while insoluble in hydrocarbon solvents.
After solution imidization, while still being soluble, the resulting polyimides solubility diminishes in magnitude. Solid state imidization gives insoluble polyimide products.
6. SUGGESTIONS FOR FUTURE WORK

(1) Find a system for precipitating the alt-PAA from solution to allow for higher purity of the polymer.

(2) Investigate the degree of imidization that can be achieved with vast access of polymer-based BCC or/and longer reflux time in d₆-DMSO.

(3) Synthesize an alternative guest-host that does not absorb in 400-600nm wavelength region.

(4) Pole and imidize NLO pendant alt-PAA and guest-host polymer system.

(5) Compare the second-order nonlinearity of NLO pendant alt-PAA and guest-host polymer system.
7. REFERENCES


21. Cheng, W. “Two and Four Component Polyimides Based on Oxydiphthalic Anhydride, 1,3-Aminophenoxybenzene, Mellitic Acid Dianhydride, 3,4’-Oxydianiline, and their Zirconium Pendent Polymers”, *Master Thesis* RIT, December, **2001**


8. APPENDIX

Additional Depictions of Spectra for New and Related Compounds Reported in This Thesis.

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<td>PAA imidized at 195 C in vacuum</td>
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<td>PAA imidized in DMSO-d6</td>
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Digilab Merlin

PAA imidized in Mesitylene

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\begin{align*}
3167.481 & \quad 0.000 \\
2980.990 & \quad 0.000 \\
2518.612 & \quad 0.000 \\
2885.942 & \quad 0.000 \\
1957.592 & \quad 0.000 \\
1763.148 & \quad 0.000 \\
1386.396 & \quad 0.000 \\
879.897 & \quad 0.000 \\
717.577 & \\
1726.637 & \quad 0.000 \\
1610.726 & \quad 0.000 \\
1654.689 & \quad 0.000 \\
1513.107 & \quad 0.000 \\
1246.788 & \quad 0.000 \\
821.911 & 0.00 \\
963.671 & 0.00 \\
1125.194 & 0.00 \\
1181.449 & 0.00 \\
\end{align*}
\]
PAA imidized at 195°C in vacuum
Alp-PI imidized in d6-DMSO

Wavenumber

%Transmittance

3192.204 0.000
3065.343 0.000
1862.161 0.000
1793.423 0.000
1595.699 0.000
1549.120 0.000
1246.780 0.000
1201.528 0.000
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1492.507 0.000

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NLO Pendant paa (DCC)

3401.018 0.000
2929.243 0.000
3319.354 0.000
2854.394 0.000

1783.229 0.000
1620.462 0.000
1437.037 0.000
720.597 1

1727.761 0.000
1513.201 0.000
1368.286 0.000
823.427 0.
961.209 0.000

1247.324 0.000
1202.878 0.000
1182.277 0.000

Wavenumber

%Transmittance
Digilab Merlin

NLO Pendant PAA (p.BCC)

733.322 0.000
3576.302 0.000
3103.907 0.000
2516.336 0.000
2976.242 0.000
2887.536 0.000
1726.232 0.000
1606.779 0.000
2091.559 0.000
1782.734 0.000
901.432 0.000
707.204

%Transmittance

3600 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800

Wavenumber
Digilab Merlin

![Graph of infrared spectra with various wavenumbers and transmittance values.](image)
Digilab Merlin
digilab merlin

bis(an)MADA with NLO

wavenumber

% transmittance

3643.243 0.000
3060.688 0.000
2850.237 0.000
2925.999 0.000
1861.349 0.000
1792.651 0.000
1661.452 0.000
1571.400 0.000
1628.700 0.000
1192.219 0.000
919.954 0.000
1543.324 0.000
753.367 0.000
828.699 0.000
1041.218 0.000
1081.649 0.000
Proton 128, solvent (DMSO), NO pendant PAA. DCC
Product from Phthalic Anhydride and NLO reaction 
done in THF 
Spectrum obtained in DMSO-d6
Product from 4-5-00 after imidization in oven for 1 hr at 200 C
4-7-00
in DMSO-d6

Current Data Parameters
NAME  oven_imid_4-7-0
EXPNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_  500000
Time  17:03
INSTRUM  spect
PROBHDL  5 nm DNP  1H
PULPROG  zg30
TD  32768
SOLVENT  DMSO
NS  15
DS  2
SWH  6172 639 Hz
FPGES  0.188868 Hz
AQ  2.6542580 sec
AG  1149.4
DM  81.000 usec
DE  6.00 usec
TE  300.0 K
B1  1.000000000 sec
P1  9.00 usec
DE  6.00 usec
SF01  300.1318534 MHz
NUC1  1H
P1  -5.00 dB

F2 - Processing parameters
SI  16384
SF  300 1300258 MHz
MDM  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00

1D NMR plot parameters
CX  20.00 cm
F1P  11.000 ppm
F1  3301.43 Hz
F2P  -1.000 ppm
F2  -300.13 Hz
PPNCM  0.60000 ppm/cm
HZCM  180.07802 Hz/cm
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**Diagram:**

- `F1 (ppm)` vs `F2 (ppm)`
- Contour lines indicate spectral peaks
- Data points are plotted on the graph
- Axes range from 6.2 to 8.6 for both `F1` and `F2`

**Note:** The diagram appears to be a 2D NMR spectrum with contour lines indicating chemical shifts. The data points are plotted on the graph, with axes ranging from 6.2 to 8.6 for both `F1` and `F2`. The contour lines suggest different chemical environments or resonances in the sample.
GPC
Attempts to determine average molecular weight for alt-PAA by GPC were performed at E. Kodak. In all cases, the sample adhered strongly to the column material, so GCP results were not obtained.

Light Scattering
Attempts to determine average molecular weight for alt-PAA from light scattering were performed in the RIT physics department under the supervision of Professor M. Kotlarchyk. The polymer in NMP solution appeared to be dynamic and unreliable scattering data were obtained. A literature search using SciFinder did not reveal any articles describing the use of light scattering to determine the average molecular weight of polyamic acids.