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Monomer and Polyimide Production for Radiation Shielding Purposes in Manned Space Exploration

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**Monomer and Polyimide Production for Radiation Shielding Purposes in Manned
Space Exploration.**

A thesis submitted in partial fulfillment of the requirement
for the degree of Bachelor of Sciences in Chemistry from
The College of William and Mary

by

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Accepted for _____

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Abstract

Deep space radiation poses a major threat to personnel and equipment on long-range and long-term manned expeditions to other planets in our solar system and beyond. Current forms of shielding are inadequate when faced with radiations such as galactic cosmic radiation, neutrons, and high energy electromagnetic radiation. In light of this, it is necessary to produce new lightweight shielding materials which are both structurally functional and effective in blocking these dangerous forms of radiation.

High-performance polymers such as polyimides provide the thermal and structural stability necessary for this application, properties which can be enhanced through increased aromatic character of the polymer backbone. In addition, methods for monomer synthesis provide a convenient route for increasing hydrogen content in the monomer and thereby increasing the polymer's radiation shielding capabilities.

This research has concentrated primarily on the synthesis of bisphenol monomers as well as subsequent steps toward polyimidization. Tungsten additives and their effects on thermal and mechanical properties were also explored. These syntheses as well as future research into similar compounds will advance the search for more effective shielding materials

Acknowledgements

First and foremost, I would like to thank Dr. Robert Orwoll for being my advisor, for his willingness to help in lab, and for his support in my endeavors. I would like to extend special thanks to Dr. Christopher Abelt for his assistance in characterization and synthesis and for his patience. Thank you to Dr. Elizabeth Harbron for setting me on the right track from the beginning of this work. Finally, I would like to thank Emily Harbert for her assistance in polymerization and both Jordan Walk and Elise Dennis for their help in characterization.

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I. Introduction

Technological advances in the areas of rocket propulsion and navigation continually expand our ability to explore the further reaches of our galaxy. NASA has successfully launched monitoring satellites to Saturn, has landed surveying instruments on Mars, and there are now the beginnings of commercial space flights. The problems of long-term space travel and habitation are receiving increasing levels of consideration.

A. Barriers to Long-Range Space Travel

In light of recent interest in lunar habitats as well as manned exploratory missions to Mars, NASA has identified a need for more efficient forms of radiation shielding. Traditional aluminum shielding has proved to be not only ineffective in blocking deep space radiation, but in fact to worsen its effects through nuclear fragmentation.

Several forms of radiation which are deflected by the Earth's magnetic field or absorbed by the atmosphere are of great concern for human travel beyond the van Allen belts. These include galactic cosmic radiation (GCR), ultraviolet light, X-rays, gamma rays, electrons, and protons. In addition, neutrons, which are generally of little concern due to their short half-life, become a problem when these other forms of radiation affect elements in the space craft. On short expeditions, the accumulated radiation is relatively harmless to humans. On longer expeditions, however, exposure to these radiations can cause measurable damage to both biological and electrical systems. Those radiations with which this research is most concerned are galactic cosmic radiation, neutrons, and high-energy electromagnetic radiation.

1. Galactic Cosmic Radiation (GCR)

GCR consists of the bare nuclei of every element, but is largely composed of both hydrogen (85%) and helium (14%). There is also a significant iron presence. GCR nuclei can travel at enormous velocities, sometimes nearing the speed of light, and in the absence of effective shielding are detrimental to both biological and electrical systems.

Those nuclei with high atomic number and high energy are referred to as HZE nuclei. These nuclei represent the greatest threat to astronauts due to their increased biological effects. HZE particles have the capacity to completely penetrate current shielding materials. In the process, the HZE nuclei interact with shielding nuclei to create a cascade of nuclear fragments, resulting in higher levels of radiation behind the shielding material.¹

Shielding from GCR is effectively accomplished through Coulombic interactions enacted on the GCR nucleus by the electrons and nuclei of the target material. These interactions reduce the kinetic energy of a GCR nucleus. The energy loss enacted upon the GCR by the shielding material increases with the charge-to-mass ratio of the shield. It then follows that, on a per gram basis, hydrogen is the most effective element in protecting against GCR. This is due to hydrogen's lack of neutrons, which add to the mass of an atom without affecting the charge.

2. Neutrons

Neutrons have a short half life ($t_{1/2}=10$ min) and so are not free-floating in space, as is GCR. Instead, they become a problem when GCR strikes nuclei in the space craft and nuclear fission causes nuclei from both sources to fragment, scattering subatomic

particles which cause further damage. Because the neutrons lack electrical charge, they are immune to the Coulombic interactions that shield against other types of atomic particles and against GCR.

Certain elements, such as boron, gadolinium, and tungsten, have isotopes with large neutron cross-sections. Embedding such materials in the body of the ship can assist in shielding both the ship and the astronauts from neutron-related damage. The neutron shielding system is completed through the usage of hydrogen, which slows the neutrons, thereby facilitating the capture process.

3. High-Energy Electromagnetic (EM) Radiation

High-energy electromagnetic radiations are chargeless forms of radiation, consisting of ultraviolet (UV) radiation, X-rays, and gamma rays. These radiations are of great concern in space travel. UV radiation can cause ionization and radical production through bond cleavage in chemical compounds, which readily absorb the radiation. However, this form of radiation can be dealt with relatively easily through the addition of carbon black or other similar fillers.

X-rays and gamma rays interact with shielding materials in three ways: through the photoelectric effect, through Compton scattering, and through pair production. In the photoelectric effect, a quantum of radiation is completely absorbed by the shielding molecule or atom. This absorption is followed by the ejection of a bound electron with energy equal to the quantum energy minus the electron's binding energy. The probability for this effect to occur is directly proportional to the absorbing species' atomic number raised to the fifth power and is inversely proportional to the quantum energy raised to the

3.5 power. This process is most efficient (and therefore most likely to occur) for low-energy photons impacting a high atomic number absorber.

Compton scattering is a process in which a photon with medium energy (generally gamma rays with energies of 0.6-4 MeV) impacts an atom or molecule. The photon transfers only a portion of its energy to the ejected electron. The reduced energy photon is then scattered from its original path. The probability of this process occurring is directly proportional to the absorbing material's atomic number and is inversely proportional to the energy of the photon.

Pair-production results in the fabrication of a positron-electron pair. The process requires a photon with energy of at least 1.02 MeV. The probability of pair-production increases with increasing atomic number of the absorbing species and with the logarithm of the photon energy. Any energy in excess of the required 1.02 MeV is distributed equally to increase the kinetic energies of both the positron and electron. Eventually, the positron will annihilate an electron, producing two photons of equal energy radiating in opposite directions.¹

Due to the correlation between all three processes and increasing atomic number, elements with high atomic number serve best in shielding against gamma rays. A nanocomposite of one of the neutron-absorbing elements listed above [tungsten ($Z=74$) or gadolinium ($Z=64$)] can serve the dual purpose of shielding against gamma rays and against neutrons.

B. The Proposed Solution

In order to provide protection for both astronauts and electrical equipment, it is necessary to develop effective shielding. The problem becomes complicated by weight restrictions. Lead and concrete are the traditional forms of radiation shielding, but a craft constructed from these materials would never leave the ground.

Ideally, the shielding material should have a high hydrogen content to provide both impedance of neutrons and adequate protection from GCR. The developed material should also contain the heavy elements necessary for neutron capture and shielding from high-energy EM radiation. Above all, the material must be lightweight while simultaneously maintaining the thermal and mechanical stability necessary to withstand the extreme conditions present during space travel.

Strong, lightweight shielding materials could be provided by high-performance polymers. Such polymers are durable and can be produced in a myriad of forms with a high level of structural integrity. The polymers could be used as everything from load-bearing structures to plumbing materials to fibers for space suits. The multifunctional nature of the compounds is extremely useful in reducing costs as well as weight in the spacecraft.

In terms of hydrogen content, aliphatic polymers are the preferable material. Polyethylene and polypropylene, both aliphatic polymers, have 0.143 moles of hydrogen per gram of polymer. However, this type of polymer lacks the thermal and mechanical stability necessary for space travel. Given the need for durability in this application, it is evident that aromatic polymers are preferable to their aliphatic counterparts.

Polymers with aromatic backbones have high strength and thermal stability, making it possible to integrate the shielding materials into the structural components of the space craft. Aromatic polymers are already routinely used in space travel. The drawback to aromatic polymers as shielding materials is their relatively low hydrogen content. For instance, polyetherimide has a hydrogen content of 0.0405 moles per gram of polymer. Thus, the question becomes that of forming hydrogen-rich monomers from which to construct the polymers. Elements with high neutron-capture radii can then be embedded in the polymers to provide the desired protection against neutrons.

This research has concentrated, in large part, on the production of bisphenol monomers as polyimide precursors. Polyimides provide good thermal stability, chemical resistance, and excellent mechanical properties. These properties are enhanced by the usage of aromatic-based monomers. The emphasis on monomer synthesis has led to the production of several feasible high hydrogen content monomers with clear routes to polymerization.

The feasibility of tungsten additives and their impact on the mechanical and thermal properties are also under investigation.

C. Background Research

1. Polyimides

a. Properties

Polyimides are high performance polymers with inherent radiation shielding properties². Additionally, polyimides have high thermal and dimensional stability, high compressive strength, and high flexural modulus, making them extremely useful for this

application³. They are known to be resistant to solvents, acids, and alkalis, are flame retardant, and maintain their excellent mechanical properties even at high temperatures⁴. Hydrogen content of the polyimides can be altered by varying the chemical structure of the monomer. Polyimides can be fabricated into a wide range of composites, films, coatings, and a variety of other forms to provide the needed materials.

b. Polymer Synthetic Method

Polyimides are most commonly produced following preparation of the poly(amic acid). The poly(amic acid) is produced by reaction of a dianhydride and a diamine in polar, aprotic solvents. Commonly used solvents include *N*-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc), and dimethylformamide (DMF). The poly(amic acid) is converted to the polyimide through either thermal or chemical dehydration.² An example reaction is detailed in the experimental methods section.

A thin film can be produced using the poly(amic acid), which can be poured onto a glass plate and pulled to a desired thickness using a doctor blade. Ideally, the solution should be clear and without bubbles. Bubbles in the film interrupt the structural integrity of the film and therefore weaken its mechanical stability. Similarly, lack of film clarity makes it difficult to determine the uniformity of additive distribution following tungsten addition.

In the context of this research, the pulled film is cured at elevated temperatures. This step not only evaporates the solvent from the poly(amic acid) but also converts the amide linkage of the acid to an imide linkage, thereby completing the polymerization (Figures #8 and #9).

Following curing, the film should be clear and even in both thickness and color. Most importantly, the film should be creasable. The creasability of the film is an indication of both high molecular weight and general mechanical stability. Thus, those films which were capable of being creased without snapping were judged to be appropriate for the aims of this research.

c. Method for Bisphenol Monomer Synthesis

Bisphenol monomers such as 2,2-bis(4-hydroxy-3,5-dimethylphenyl)cyclohexane, shown here as Figure #1, were chosen for production due to their aromatic character and ease of conversion to the dinitro and eventually diamine derivatives. Bisphenols were produced via reaction between a ketone and a phenol following a procedure by Weber et al⁵. The most commonly used methods for this condensation are generally acid-catalyzed although base-catalyzed reactions appear to yield the same or similar products.

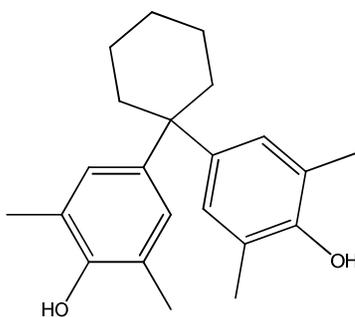


Figure #1: 2,2-bis(4-hydroxy-3,5-dimethylphenyl)cyclohexane

V. Braun postulated mechanisms for both the acid and base catalyzed reactions for the condensation of acetone with phenol. In both cases, the reaction proceeds through a *p*-isopropenylphenol intermediate⁶. An illustration of the acid-catalyzed reaction is

shown below in Figure #2. The acid-catalyzed reaction proceeds in the same manner regardless of the nature of the ketone⁷.

In the first step of the condensation, the phenol adds to the carbonyl group. This addition is followed by an intermolecular loss of one molecule of water between one molecule of the phenol-hydrin formed in step one and one molecule of phenol.

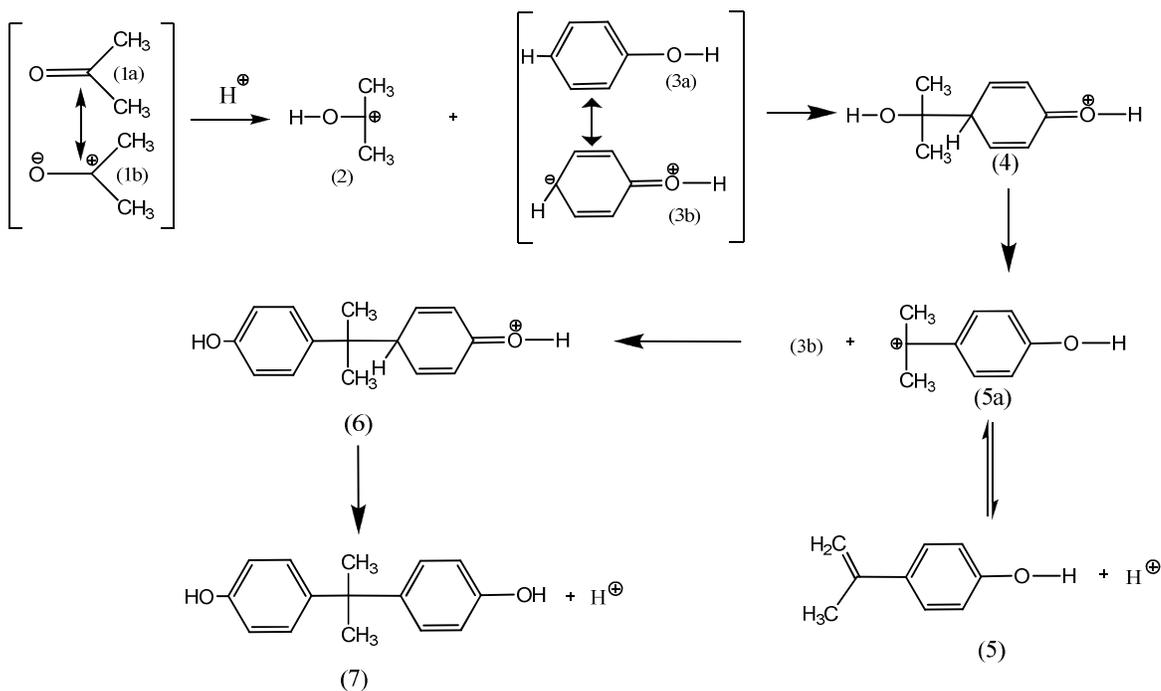


Figure #2: Acid-Catalyzed Mechanism for Synthesis of Bisphenol-A

A general schematic for full synthesis of the polymer from the phenol and ketone starting materials is shown below in Figure #3.

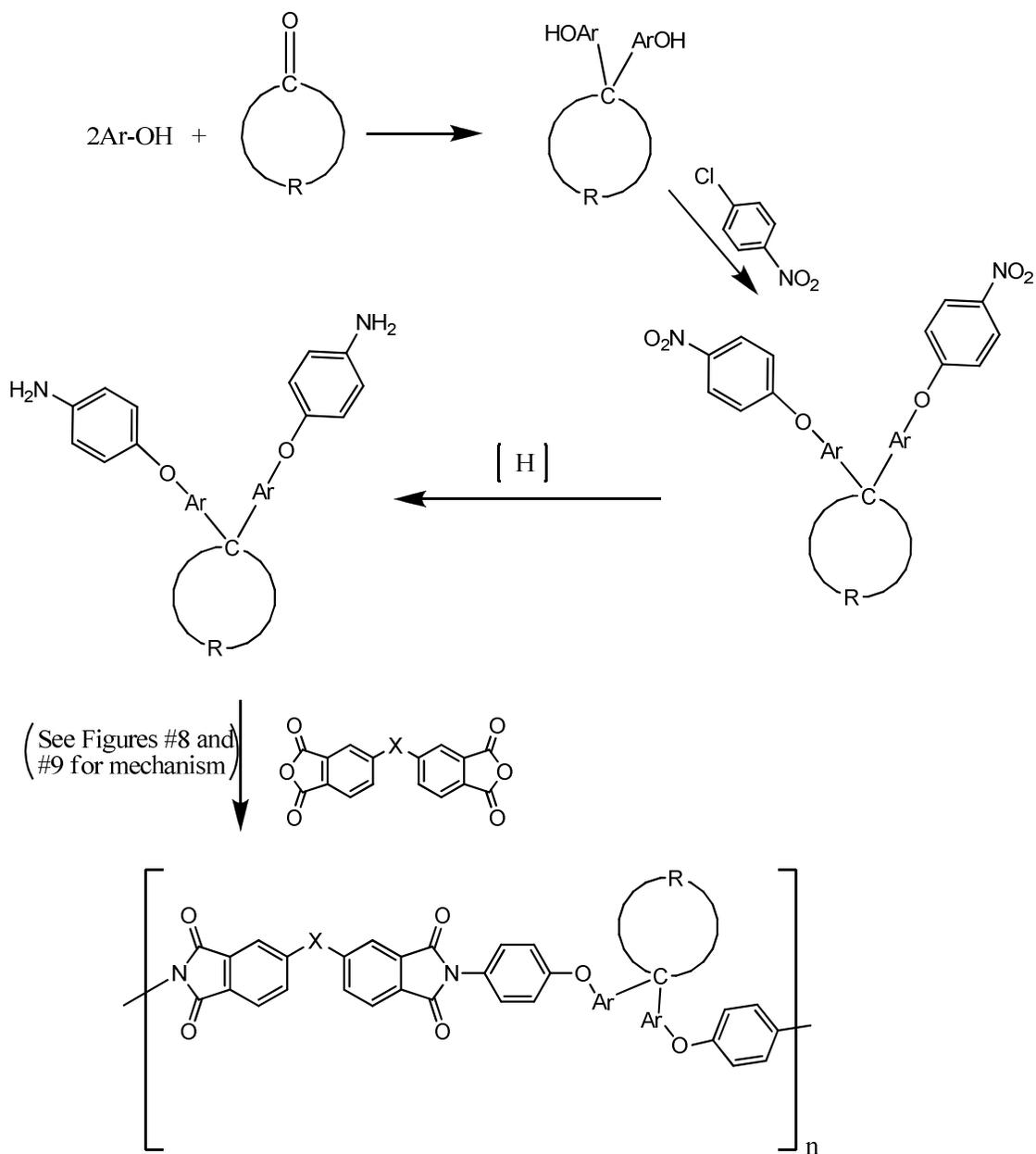


Figure #3: Polymer Formation

One of the main concerns associated with any reaction centers around efficiency and increasing yield of the desired product. There are several concerns specific to this category of condensation including selection of the acid catalyst and ketone reactant, appropriate solvent selection, and reaction temperature.

The acid-catalyzed reaction requires a strong mineral acid. Concentrated sulfuric acid would be most efficient except that it has a tendency to cause sulfonation of the phenols and bisphenols in the reaction⁶. Due to this problem, HCl or concentrated hydrochloric acid is sometimes the most efficient acid with which to carry out the condensation.

The research of Schnell and Krimm found that reactions using acetone or cyclic ketones are most efficient in these condensations and that the reactivity in this context decreases with increasing alkyl chain length⁶. It is plausible that the longer alkyl chains inhibit the reaction because of steric hindrance. By using cyclic ketones, the reacting carbon is less sterically hindered, thereby increasing the reaction rate.

Another important structural concern is choosing between an aldehyde and a ketone for this condensation. It is evident from the proposed mechanism that the carbonyl unit is necessary to the reaction. Ketones generally give better yields than do aldehydes⁶. This may be due to greater stabilization of the carbonyl carbon during the first step of the reaction. The secondary cation resulting from a ketone would be much more stable than the primary cation from an aldehyde, meaning that the first step of the reaction is more likely to take place with a ketone than with an aldehyde.

Further increase of yields is accomplished by minimizing the production of byproducts. The condensation should be carried out at the lowest possible temperature due to increased byproduct formation with increased temperature. If the reaction can be carried out at a temperature which allows the product to crystallize out of solution as it is formed, the presence of byproducts is greatly reduced⁶.

Since two moles of phenol are required for every mole of ketone, the reaction should be carried out using a large excess of phenol. A molar ratio of 2:1 phenol to ketone is the minimum required for the reaction to proceed. A ratio of at least 4:1 should provide more favorable product yields. Depending on the solubility of the phenol, however, this excess can render complete solvation of the phenol in the ketone impossible. Without full solvation, the ketone, which is often a liquid, will be more available for reaction than the phenol (a solid), causing increased byproduct formation. Fortunately in this case, glacial acetic acid provides an efficient solvent for the combination of ketone and phenol.

The final step of the reaction involves neutralization of the reaction mixture and purification of the product. This can be easily accomplished using sodium carbonate or bicarbonate solutions to neutralize the acid followed by washing and fractional distillation of the products under vacuum. This method may cause decomposition of the bisphenol due to the high temperatures required. Decomposition is also accelerated by alkaline impurities and metal ions. To avoid decomposition, secondary or tertiary alkaline-earth phosphates are often added to inactivate the impurities present. Decomposition can be minimized if, instead of using distillation, the condensation product is purified by recrystallization from organic solvents such as benzene or toluene⁶.

2. Tungsten

Tungsten is a heavy transition metal with atomic number $Z=74$ and a melting point of 3422°C . The isotopes of tungsten range in molecular weight from 158 to 190 amu. The neutron-capture cross section, assuming no isotopic enrichment, is 18 barns

per atom⁸. The high atomic number and relatively large neutron-capture radius make this element appropriate for absorption of both high energy EM radiation and slow-moving neutrons.

In this study tungsten nanoparticles were added to the polymer. For the tungsten to be effective, even distribution throughout the polymer must be achieved. To this end, it is necessary to use nanoparticles whose surfaces have been modified with some organic reagent. For this research, the tungsten was treated with benzyl mercaptan. This aromatic compound is believed to associate with tungsten through surface interactions, thereby helping to render the metal particles more compatible with the organic polymer matrix. Without the modification, the tungsten has a tendency to form clumps in the polymer.

II. Experimental Methods

A. Synthesis

All reactants were procured from Sigma-Aldrich Co. and were used with no additional purification.

1. Bisphenol Monomers

Three bisphenol monomers were prepared in this study. Their chemical structures are shown in Figures #4(a)-(c).

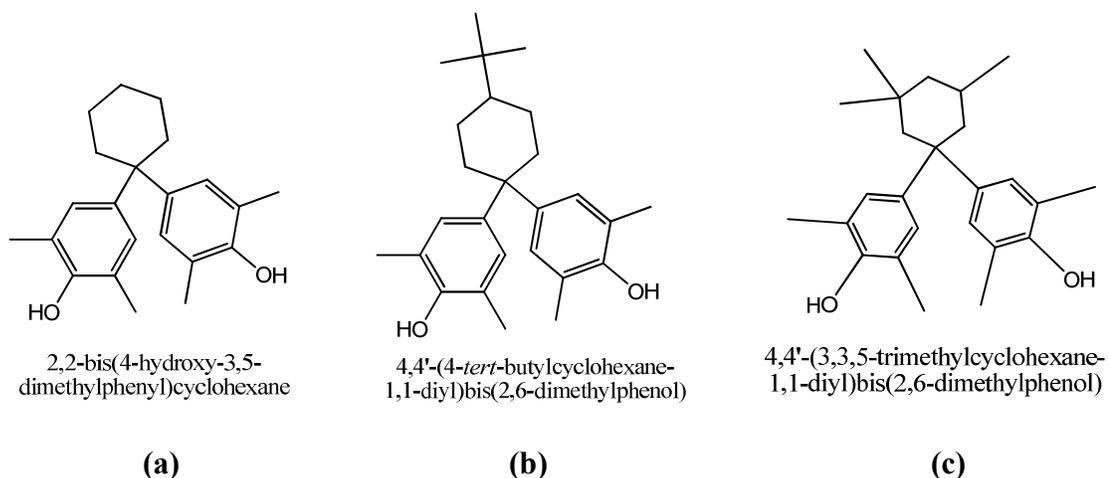


Figure #4: Synthesized Bisphenol Monomers

Preparation of 2,2-bis(4-hydroxy-3,5-dimethylphenyl)cyclohexane

Following a procedure outlined by Weber et al⁵, 2,2-bis(4-hydroxy-3,5-dimethylphenyl) cyclohexane (Figure 4a) was prepared by combining 38mL of glacial acetic acid, 20mL of concentrated sulfuric acid, and 0.5mL of dimethyl sulfoxide at 15°C. A mixture of 114.53g (0.94mol) of 2,6-dimethylphenol and 20mL of cyclohexanone was heated until all solids were dissolved. The solution was then added drop-by-drop to the acidic mixture and allowed to react under stirring for 90 minutes. The resulting mixture was a brown paste. The paste was transferred into 0.5L of distilled

water and heated to 30°C with stirring. The resulting blue substance was collected by vacuum filtration, washed with water and then added to a solution made of 250mL of distilled water and 1.25g sodium acetate. The mixture was heated to 90°C with stirring and then allowed to cool to room temperature before recrystallization from chlorobenzene. Percent yield was 33%.

Preparation of 4,4'-(4-*tert*-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol)

In a procedure similar to that outlined above, 2,6-dimethylphenol was reacted with 4-*tert*-butylcyclohexanone to form 4,4'-(4-*tert*-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol) (Figure 4b). 28mL of sulfuric acid was combined with 1mL dimethyl sulfoxide at 6°C. 114.53g (0.94mol) 2,6-dimethylphenol was combined with 28.92g (0.19mol) 4-*tert*-butylcyclohexanone and 38.2mL of glacial acetic acid and heated slightly to ensure full dissolution of the solids. The ketone/phenol/acetic acid solution was then added drop-by-drop to the concentrated sulfuric acid/DMSO solution, under stirring. The reaction was allowed to continue overnight. The resulting red product was substantially more solid than the product from 2,2-bis(4-hydroxy-3,5-dimethylphenyl)cyclohexane preparation. Workup and purification was accomplished using a process identical to that outlined above.

Preparation of 4,4'-(3,3,5-trimethylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol)

The procedure for the preparation of 4,4'-(3,3,5-trimethylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol) (Figure 4c) is similar to that for the preparation of 4,4'-(4-

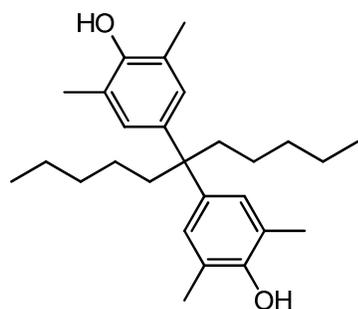
tert-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol) listed above, with 3,3,5-trimethylcyclohexanone in place of the 4-*tert*-butylcyclohexanone. In this case, however, the reaction mixture was allowed to continue under stirring for five days and then was placed into the refrigerator for an additional three to allow for more complete reaction before the addition to water. Recrystallization from chlorobenzene yielded an impure product. Product was subsequently recrystallized using methanol.

Preparation of 4,4'-(undecane-6,6-diyl)bis(2,6-dimethylphenol)

The preparation proceeded as with 4,4'-(4-*tert*-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol), with 6-undecanone in place of 4-*tert*-butylcyclohexanone. The structure for this compound is shown below in Figure #5a.

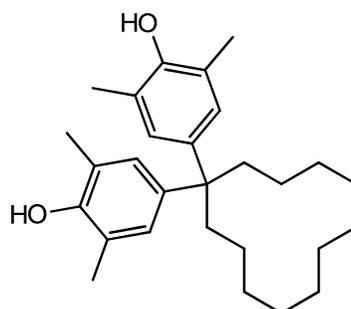
Preparation of 4,4'-(cyclododecane-1,1-diyl)bis(2,6-dimethylphenol)

The preparation proceeded as with 4,4'-(4-*tert*-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol), with cyclododecanone in place of 4-*tert*-butylcyclohexanone. The structure for this compound is shown below in Figure #5b.



4,4'-(undecane-6,6-diyl)bis(2,6-dimethylphenol)

(a)



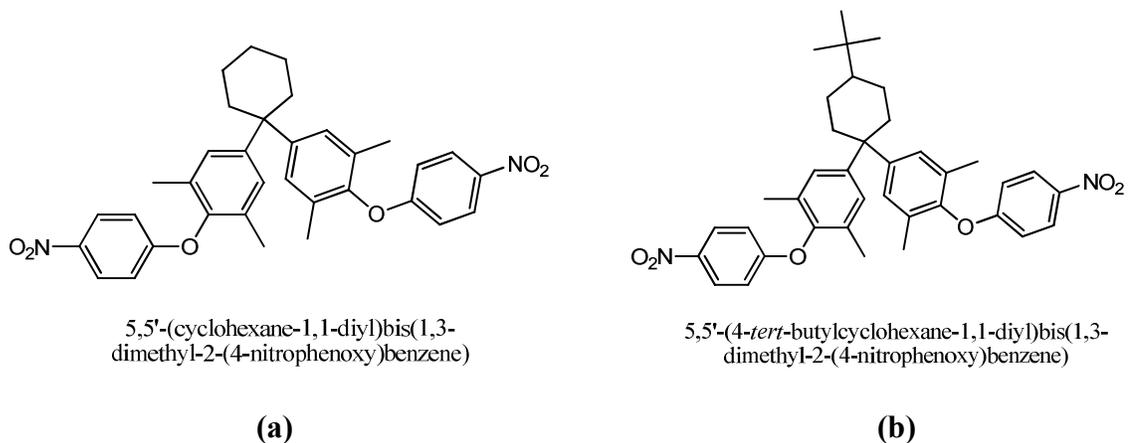
4,4'-(cyclododecane-1,1-diyl)bis(2,6-dimethylphenol)

(b)

Figure #5: Additional Attempted Bisphenol Monomers

2. Dinitro Derivatives

Two dinitro derivative compounds were prepared in this study. Their chemical structures are shown below in Figure #6:



Figure#6: Synthesized Dinitro Derivatives

Synthesis of 5,5'-(cyclohexane-1,1-diyl)bis(1,3-dimethyl-2-(4-nitrophenoxy)benzene)

5,5'-(cyclohexane-1,1-diyl)bis(1,3-dimethyl-2-(4-nitrophenoxy)benzene) (Figure 5a) was prepared following a procedure outlined by Hu et al⁹. 24.98g (0.077 mol) of 2,2-bis(4-hydroxy-3,5-dimethylphenyl)cyclohexane, 26g (0.166 mol) of 4-chloronitrobenzene, and 25.133g (0.184 mol) of anhydrous potassium carbonate were combined with 116 mL of *N,N*-dimethylformamide and refluxed at 170°C for 21 hours. The solution was then precipitated in a 1:1 (v/v) methanol-water mixture. The yellow product was collected and recrystallized from glacial acetic acid and washed with water. Typical yield of this dinitro product was 92%.

Synthesis of 5,5'-(4-*tert*-butylcyclohexane-1,1-diyl)bis(1,3-dimethyl-2-(4-nitrophenoxy)benzene)

The synthesis of 5,5'-(4-*tert*-butylcyclohexane-1,1-diyl)bis(1,3-dimethyl-2-(4-nitrophenoxy)benzene) (Figure 5b) was accomplished following the same procedure detailed above by replacing 2,2-bis(4-hydroxy-3,5-dimethylphenyl)cyclohexane with 4,4'-(4-*tert*-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol).

3. Diamine Derivatives

The syntheses of two diamine derivative compounds were attempted during the course of this research. The structures for both are shown below as Figure #7. The first (4,4'-(4,4'-(cyclohexane-1,1-diyl)bis(2,6-dimethyl-4,1-phenylene))bis(oxy) dianiline) was verifiably synthesized. The product of the second reaction is still under examination.

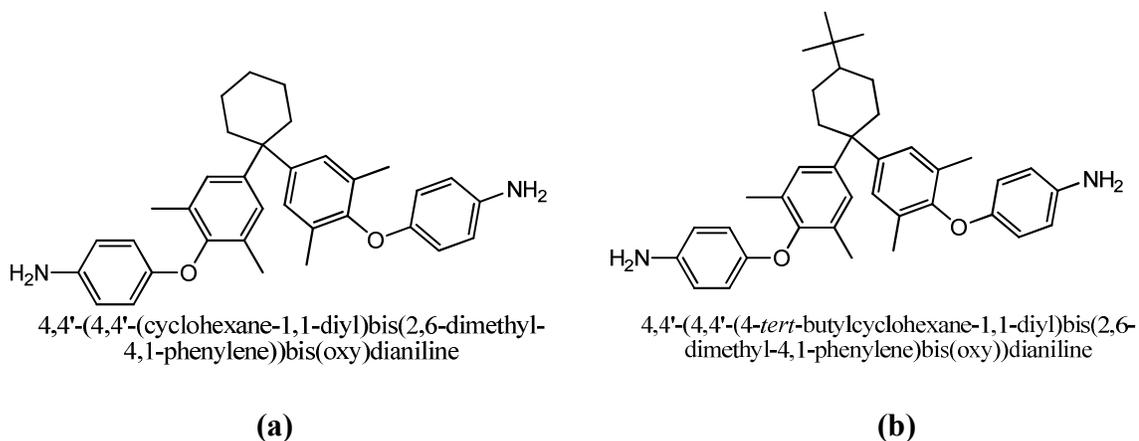


Figure #7: Synthesized Diamine Derivatives

Synthesis of 4,4'-(4,4'-(cyclohexane-1,1-diyl)bis(2,6-dimethyl-4,1-phenylene))bis(oxy) dianiline

The synthesis of 4,4'-(4,4'-(cyclohexane-1,1-diyl)bis(2,6-dimethyl-4,1-phenylene))bis(oxy)dianiline (Figure 6a) began with combination of 54.98g (0.097mol) of 5,5'-(cyclohexane-1,1-diyl)bis(1,3-dimethyl-2-(4-nitrophenoxy)benzene) and 0.3884g of 10% Pd on active carbon in 258 mL of ethanol. 194 mL of hydrazine monohydrate was added drop wise and the mixture was refluxed for 22 hours⁹. The initial product of this reaction was a grey solid. Following hot filtration, the product was recrystallized from ethanol. The final product was a tan solid.

Synthesis of 4,4'-(4,4'-(4-tert-butylcyclohexane-1,1-diyl)bis(2,6-dimethyl-4,1-phenylene))bis(oxy)dianiline

Synthesis of 4,4'-(4,4'-(4-tert-butylcyclohexane-1,1-diyl)bis(2,6-dimethyl-4,1-phenylene))bis(oxy)dianiline (Figure 6b) proceeded as detailed above. Little product was observed.

Alternate Synthesis of 4,4'-(4,4'-(4-tert-butylcyclohexane-1,1-diyl)bis(2,6-dimethyl-4,1-phenylene))bis(oxy)dianiline.

This alternate synthesis involved the use of a hydrogenator. 10.033g of 5,5'-(4-tert-butylcyclohexane-1,1-diyl)bis(1,3-dimethyl-2-(4-nitrophenoxy)benzene) was placed in a wrapped vessel along with 0.9956g of 10% Pd/C catalyst and combined with 250mL of ethanol. The reaction mixture was placed on the apparatus, charged to 10 psi with hydrogen gas, shaken and purged. The vessel was then charged to 15 psi, shaken, and

purged, then to 20 psi, shaken, and purged, before finally being charged to 47psi and was allowed to shake for two days.

The reaction was incomplete at this point so an additional 0.1045g catalyst was added before the charge and purge cycle was repeated. The reaction was allowed to continue overnight. The reaction remained unfinished so an additional 0.1056g catalyst was added and the procedure was repeated¹⁰.

4. Polymer Synthesis

Poly(amic acid) production

To produce 3g of polymer, 1.834g of 4,4'-(4,4'-(cyclohexane-1,1-diyl)bis(2,6-dimethyl-4,1-phenylene))bis(oxy)dianiline was combined with 8.7mL *N*-methylpyrrolidone in a flask with stirring. 1.166g of 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA) was completely dissolved in 5.5mL of *N*-methylpyrrolidone before the mixture was added drop wise to the diamine/NMP mixture. The mixture was allowed to react at 0°C overnight and then heated to 45°C to complete the reaction. This addition is shown below in Figure #8.

Tungsten preparation

Tungsten nanoparticles were first combined with toluene or chloroform to give one mole tungsten per liter of liquid. For every five moles of tungsten, one mole of benzyl mercaptan was added to the mixture. The mixture was stirred and then allowed to sit for three hours before being centrifuged. Afterward, the liquid was decanted and the solid was allowed to dry before addition to the polymer.

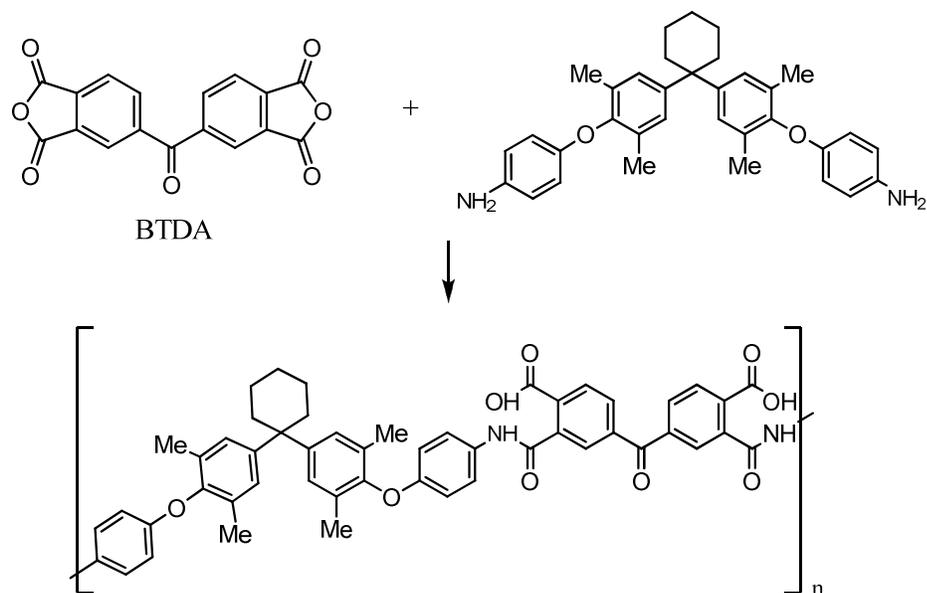


Figure #8: Poly(amic acid) Production

Polyimidization

Polyimides were produced containing 0%, 5%, 10%, and 15% tungsten nanoparticles. After creation of the poly(amic acid), 0g, 0.1579g, 0.3333g, and 0.5294g, respectively, of the tungsten/mercaptan product were added to each of four 3g poly(amic acid) batches. The resulting mixtures were stirred for 3 hours before being poured out onto glass plates.

The preparation of the glass plate is an important step to the successful production of films. The glass plates were initially soaked in a base bath for at least an hour. The plates were then scrubbed with soap and water and rinsed with deionized water. The plates were then rinsed using acetone, and finally rinsed using ethanol before being allowed to dry completely. Just before pulling the film, a razor blade was used to remove any dust particles which might have deposited during the drying process.

The poly(amic acid) was poured onto a glass plate and pulled to a uniform thickness of 6mm using a doctor blade. The plate was then placed in a programmable curing oven at 30°C. The temperature was elevated from 30°C to 100°C over the course of an hour at constant rate and allowed to maintain a constant temperature for an additional hour. The temperature was then elevated to 200°C over the course of an hour, held isothermally for an hour, elevated to 300°C over an hour and maintained isothermally before being allowed to return to 30°C. This curing process first eliminates excess solvent and then completes the polymerization through a dehydration reaction. The reaction is shown in Figure #9. The cured polymer was then removed from the oven and placed in a water bath to separate it from the glass plate.

Films should not be cured at temperatures exceeding 300°C, as the high temperature produces brittle films which stick too tightly to the glass plate, making recovery of the film difficult at best. At worst, the film will crack as it releases from the glass plate, damaging the plate as it does so. In many cases, glass shards can become embedded in the polymer film due to the superior adherent qualities of polyimides.

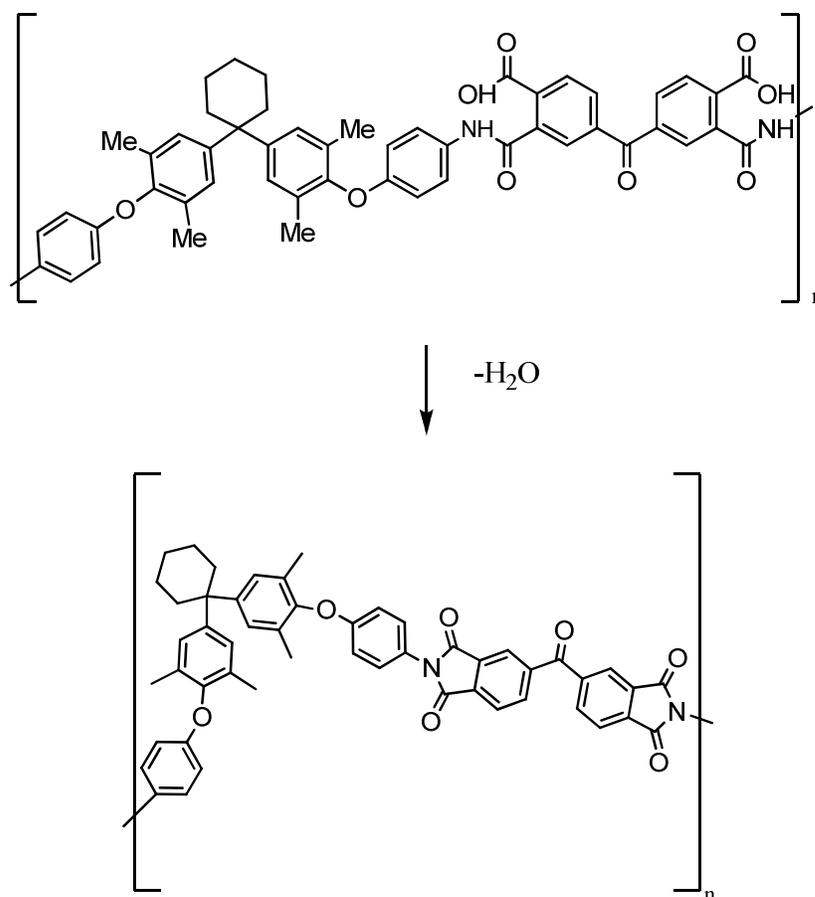


Figure #9: Polyimidization

B. Characterization

1. Bisphenol monomers

Characterization of bisphenol monomers was accomplished using proton nuclear magnetic resonance ($^1\text{H-NMR}$), liquid chromatography-mass spectrometry (LC-MS), and melt-temp techniques. $^1\text{H-NMR}$ scans were accomplished using a Varian 400 MHz Multi-nuclear NMR instrument. The $^1\text{H-NMR}$ solvent was deuterated chloroform for 2,2-bis(4-hydroxy-3,5-dimethylphenyl)cyclohexane and was dimethyl sulfoxide for all other bisphenol monomers.

LC-MS was accomplished using a Finnigan LC-Q DECA ion trap mass spectrometer in negative ion mode using methanol as solvent and ammonium hydroxide to assist in ionization.

2. Dinitro and diamine products

Dinitro and diamine products were characterized using $^1\text{H-NMR}$. The $^1\text{H-NMR}$ solvent for the dinitro and diamine products was deuterated chloroform.

3. DSC

Differential scanning calorimetry (DSC) under an atmosphere of nitrogen was used in determination of the glass transition temperatures of polymer films. A TA 2920 modulated differential scanning calorimeter instrument was used. The procedure used was as follows: the temperature was equilibrated at 60°C and held there for five minutes. The temperature was then elevated to 100°C at a rate of $10^\circ\text{C}/\text{min}$ and held isothermally for five minutes before ramping to 300°C at $10^\circ\text{C}/\text{min}$. The DSC held isothermally for five minutes before ramping back down to 60°C at $10^\circ\text{C}/\text{min}$, held isothermally for five minutes, ramped back up to 300°C , and was allowed to fully cool. The glass transition of the polymer sample was determined on the second heating using the inflection point on a plot of heat flow versus temperature.

4. TGA

Polymer films were tested using thermogravimetric analysis (TGA) in a nitrogen environment. A Shimadzu TGA-50 instrument was used. The analysis was used to

determine the degradation temperature of the films. The sample was placed on the platinum pan and inserted into the instrument. The temperature was ramped from room temperature up to 100°C at a rate of 20°C/min. The temperature was then equilibrated at 100°C and held isothermally for 30 minutes. The temperature was then ramped to 600°C at a rate of 10°C/min.

III. Results and Discussion

A. Bisphenol Monomer Characterization

In the route to the synthesis of polyimides, two bisphenol monomers were prepared according to the methods described above. These monomers were 2,2-bis(4-hydroxy-3,5-dimethylphenyl) cyclohexane and 4,4'-(4-tert-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol). Both monomers were characterized via $^1\text{H-NMR}$.

2,2-bis(4-hydroxy-3,5-dimethylphenyl)cyclohexane was generally a white crystal with m.p.=198-202°C, although a brownish-purple crystal was also achieved in one reaction. The NMR results were the same in both cases. $^1\text{H-NMR}$ (CDCl_3): δ (ppm) = 1.52 (m, 6H, CH_2), 2.2 (m, 16H, CH_2 , CH_3), 4.42 (s, 2H, OH), 6.86 (s, 4H, Ar-H).

4,4'-(4-tert-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol), another white crystal (m.p.=223-226°C) had the following $^1\text{H-NMR}$ peaks (DMSO): δ (ppm) = 0.706 (s, 9H, CH_3), 1.577 (s, 4H, Cyclic- CH_2), 2.067 (m, 12H, Ar- CH_3), 2.475 (m, 5H, Cyclic- CH_2 , Cyclic-CH), 2.62 (s, 2H, OH), 6.67 (d, 2H, Ar-H), 6.83 (d, 2H, Ar-H). The identity of this compound was also corroborated using negative ion LC-MS. The only apparent peak was a parent ion peak at 379 m/z.

The attempted synthesis of 4,4'-(3,3,5-trimethylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol) resulted in low yield of a white crystal (m.p.=234-238°C) similar to those of the previously discussed bisphenols above. A $^1\text{H-NMR}$ (DMSO) spectrum was taken to characterize the crystal product. The measured peaks and their proposed assignments are as follows: δ (ppm) = 0.283 (s, 3H, CH_3), 0.902 (s, 6H, CH_3), 1.23 (d, 1H, cyclic CH), 1.65 (d, 1H, cyclic CH_2), 1.82 (m, 1H, cyclic CH), 2.05 (m, 3H, cyclic CH, 12H, Ar- CH_3), 2.4 (d, 1H, cyclic CH), 3.3 (s, 2H, OH), 6.69 (s, 2H, Ar-H), 6.81 (s,

2H, Ar-H). The calculated elemental analysis was 81.92% C, 9.35% H; Percentages found in an elemental analysis carried out by Atlantic Microlab, Inc. were as follows: 81.54% C, 9.26% H. Further characterization is needed to properly determine the structure of this product.

The attempted syntheses of 4,4'-(undecane-6,6-diyl)bis(2,6-dimethylphenol) and 4,4'-(cyclododecane-1,1-diyl)bis(2,6-dimethylphenol) resulted in no detectable product. It is likely that the reactions were too sterically unfavorable under the attempted conditions. The cyclic ketone-based reactions are favorable in part due to the availability of the reaction site as a result of the restricted rotation of the molecule.

Much of the difficulty in monomer production (and therefore eventual production of the polymer) came in making adjustments for reactant mixtures and reaction times in response to altered reactant species. The given amount of phenol was just barely soluble in the stated amount of cyclohexanone, occasionally requiring heating for full dissolution. As the molecular weight of the ketone increased, its solubility decreased, requiring an alteration in the reaction procedure. The acetic acid already being used as solvent in the reaction mixture provided an appropriate solvent when reapplied to the ketone/phenol mixture before addition to the sulfuric acid flask.

Additionally, with several of the monomer syntheses, it became necessary to increase the reaction time. This is most likely due to increased steric interference. In the case of the para-substituted t-butyl cyclohexanone, the reaction seemed to require an extra 24 hours only. In the case of the meta-substituted trimethylcyclohexanone, the reaction required over a week of additional reaction time.

During bisphenol monomer production, percent yields tended to be extremely low. This is likely due either to incomplete reaction times or to large amounts of byproduct formation. The amount of byproduct is expected to increase with increased temperature and so greater attention must be paid to maintaining consistent, low temperatures. Additionally, it may be advantageous to find an appropriate additive which will remove the water produced during reaction without interfering with the overall mechanism and which can then be easily removed following completion.

Characterization of monomers has also proved to be extremely difficult, largely due to inadequacies of recrystallization solvents and difficulties in their removal. Chlorobenzene seems to be the most reliable recrystallization solvent, although complete drying often takes several days, even in a vacuum oven, and occasionally a powder precipitate results alongside full crystals. When this powder occurs, a second recrystallization using methanol has been found to be extremely effective. No trials have been done to verify the effectiveness of methanol as a primary recrystallizing agent. A 72% methanol and toluene azeotrope was also attempted as a recrystallizing agent. The same powder precipitate resulted.

B. Dinitro Derivative Characterization

The dinitro derivatives of both 2,2-bis(4-hydroxy-3,5-dimethylphenyl) cyclohexane and 4,4'-(4-tert-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol) were also successfully prepared and the 2,2-bis(4-hydroxy-3,5-dimethylphenyl) cyclohexane was taken through to its diamine product.

5,5'-(cyclohexane-1,1-diyl)bis(1,3-dimethyl-2-(4-nitrophenoxy)benzene) is a yellow crystal with m.p.=188-190°C and the following ¹H-NMR peaks (CDCl₃): δ (ppm) = 1.6 (d, 6H, cyclic-CH₂), 2.1 (t, 12H, Ar-CH₃), 2.25 (s, 4H, cyclic CH₂), 6.8 (d, 4H, Ar-H), 7.05 (t, 4H, Ar-H), 8.1 (d, 4H, Ar-H).

5,5'-(4-tert-butylcyclohexane-1,1-diyl)bis(1,3-dimethyl-2-(4-nitrophenoxy)benzene) is also a yellow crystal (m.p.=191-194°C). ¹H-NMR (CDCl₃): δ (ppm) = 0.8 (s, 9H, CH₃), 1.2 (s, 3H, cyclic CH₂, cyclic CH), 1.7 (s, 2H, cyclic CH₂), 1.9 (s, 2H, cyclic CH₂), 2.05 (s, 6H, Ar-CH₃), 2.1 (s, 6H, Ar-CH₃), 2.7 (s, 2H, cyclic CH₂), 6.81 (d, 4H, Ar-H), 6.94 (s, 2H, Ar-H), 7.12 (s, 2H, Ar-H), 8.17 (m, 4H, Ar-H).

The initial dinitro derivative product exists as a fine yellow powder before recrystallization. Collection of said product is extremely difficult. Given the large quantity of product generally being dealt with, centrifugation is not a plausible option. The method which results in the best recovery of product involves running the product through the filter multiple times, although this method becomes extremely time consuming.

Following collection of the initial product, the derivative must be purified. The recrystallizing solvent suggested in Hu et al⁹ is acetic acid. For the dinitro products reported in this paper, acetic acid is extremely inefficient as a solvent, requiring large relative volumes to accomplish the recrystallization.

C. Diamine Derivative Characterization

4,4'-(4,4'-(cyclohexane-1,1-diyl)bis(2,6-dimethyl-4,1-phenylene))bis(oxy)dianiline is a tan clay-like solid with m.p.= 159-164°C. The ¹H-

NMR (CDCl₃) data are as follows: δ (ppm) = 1.45 (d, 6H, cyclic CH₂), 2.1 (s, 12H, Ar-CH₃), 2.22 (s, 4H, cyclic CH₂), 3.4 (s, 4H, NH₂), 6.55 (m, 8H, Ar-H), 6.95 (d, 4H, Ar-H).

The 4,4'-(4,4'-(4-tert-butylcyclohexane-1,1-diyl)bis(2,6-dimethyl-4,1-phenylene))bis(oxy)dianiline is still under analysis.

Both the characterization and subsequent reaction of the diamine product to form the polyimide are problematic. Removal of water from the compound is difficult, requiring a vacuum oven and several days' attention. The diamine product must be completely dry before attempted reaction with the dianhydride in order for the polyimidization to proceed.

D. Production and Characterization of Polyimide Films

Two separate batches of polyimide films were produced from the 4,4'-(4,4'-(cyclohexane-1,1-diyl)bis(2,6-dimethyl-4,1-phenylene))bis(oxy)dianiline compound. The hydrogen content of the produced pure (i.e. 0% [W]) polyimide films was 0.0504 moles of hydrogen per gram of polymer.

In each batch, a film was produced with 0%, 5%, 10%, and 15% Tungsten by weight. Both sets of films were transparent, but only the second was both flexible and tough enough for creasing. It is likely that the brittleness of the first set of films was due to improper drying.

The mechanical and thermal properties of produced polyimide films were tested using TGA and DSC techniques under nitrogen. Of particular interest were the effects of the tungsten additive on the properties of the polymers. Glass transition temperatures (T_g) and thermal stability data are presented below in Tables #1 and #2, respectively.

Film	sample mass (mg)	T_g (°C)
------	------------------	------------

TED-BTDA 0%W 1.0	4.8	279
TED-BTDA 5%W 1.0	5.2	277
TED-BTDA 10%W 1.0	4.6	278
TED-BTDA 15%W 1.0	4.9	277
TED-BTDA 0%W 2.0	4.3	264
TED-BTDA 5%W 2.0	5.2	269
TED-BTDA 10%W 2.0	6.6	268
TED-BTDA 15%W 2.0	6.1	271

Table #1: DSC Data

Film	Sample mass (mg)	5% loss (°C)	10% loss (°C)	15% loss (°C)
TED-BTDA 0%W 1.0	1.895	412	434	448
TED-BTDA 5%W 1.0	8.627	425	444	457
TED-BTDA 10%W 1.0	12.365	434	450	461
TED-BTDA 15%W 1.0	5.899	431	450	464
TED-BTDA 0%W 2.0	5.051	425	439	448
TED-BTDA 5%W 2.0	5.814	436	452	462
TED-BTDA 10%W 2.0	4.005	442	456	466
TED-BTDA 15%W 2.0	5.711	437	455	467

Table #2: TGA Data

As can be seen from Tables 1 and 2, the tungsten does not interfere with the polymer's thermal and mechanical stability. The TGA data suggest that tungsten may even increase the polymer's ability to withstand thermal stress.

A sample DSC read-out is shown as Figure #10 and a sample TGA read-out as Figure #11.

Sample: TED-BTDA pure
Size: 4.8000 mg
Method: kinetic and Tg

DSC

File: C:\AORWOLL\Norah\CyclohexBTDA pure2.00
Operator: Norah
Run Date: 21-Jul-08 14:28
Instrument: 2920 MDSC V2.6A

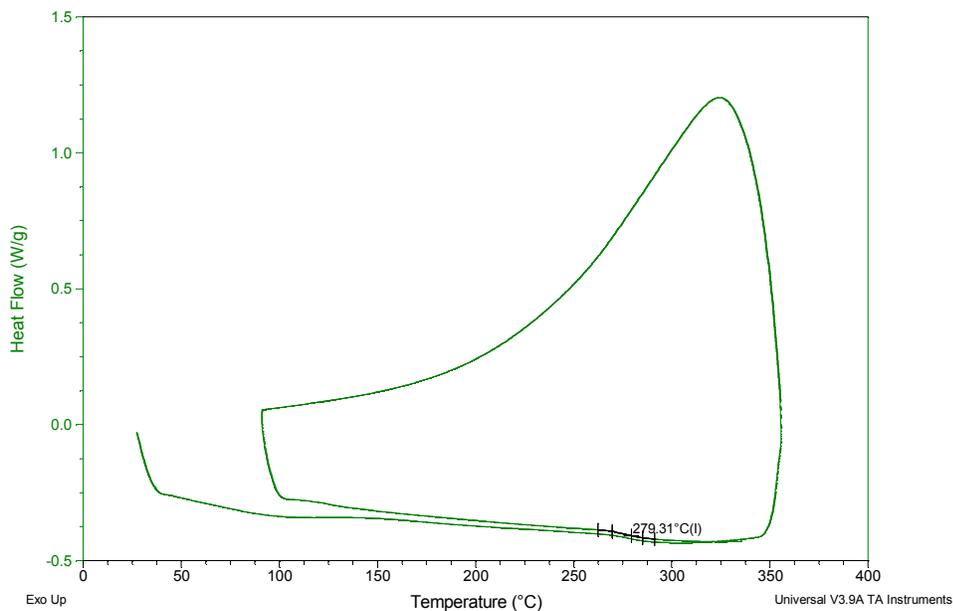


Figure #10: Sample DSC

Sample: CAP-BTDA 0% Tungsten
Size: 1.8950 mg
Method: Stepwise isothermal

TGA

File: C:\aOrwoll\Norah\TED-BTDA 0% W.001
Operator: Norah
Run Date: 2008-07-22 14:10
Instrument: TGA Q500 V6.3 Build 189

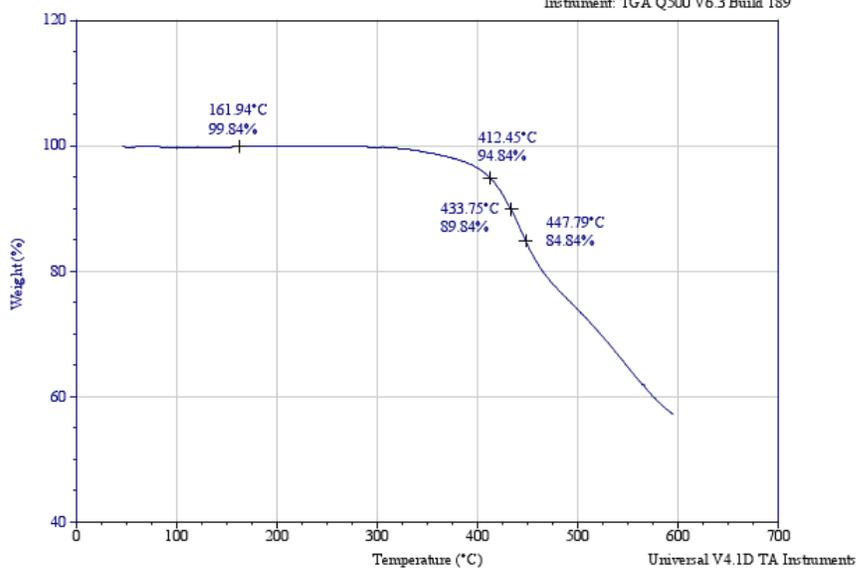


Figure #11: Sample TGA

IV. Conclusion

Dangerous radiation poses a large barrier to deep space exploration. Our relative inexperience with the more energetic forms of radiation has left us at a loss for adequate shielding and therefore leaves both personnel and equipment vulnerable to irreparable damage from these sources.

The research described in this paper has concentrated on the production of polymers which are both structurally functional and efficient in terms of their shielding properties. To this end, high-performance polymers in the form of hydrogen-rich aromatic polyimides have been explored.

Two new bisphenol monomers [2,2-bis(4-hydroxy-3,5-dimethylphenyl)cyclohexane and 4,4'-(4-tert-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol)] were successfully synthesized and characterized along with their dinitro derivatives. Additionally, the diamine derivative of 2,2-bis(4-hydroxy-3,5-dimethylphenyl)cyclohexane was successfully synthesized, characterized, and reacted with BTDA to form the corresponding poly(amic acid).

Polyimide films of varying tungsten concentrations were then created from the poly(amic acid) resulting from the reaction of BTDA and 4,4'-(4,4'-(cyclohexane-1,1-diyl)bis(2,6-dimethyl-4,1-phenylene))bis(oxy)dianiline. While the initial films were too brittle, the second batch passed the creasability test. Additionally, both sets of film had high glass transition temperatures (averages of 278°C and 268°C for batches one and two, respectively) and high decay temperatures (averages of 458°C and 461°C for 15% mass decay for batches one and two, respectively). Addition of modified tungsten

nanoparticles was attempted and monitored for effects to the polyimide films' mechanical and thermal stability. No adverse effects were observed.

The high thermal stability of the developed films makes these materials well suited to space applications. The ease of tungsten addition and the absence of ill effects to the overall stability of the polymer make the heavy metal a promising possibility for increasing the radiation shielding capabilities of the polymer.

V. Current and Future Studies

Current research is concentrated on further characterization of the product resulting from the reaction of 2,6-dimethylphenol and 3,3,5-trimethylcyclohexanone as well as continued exploration of polyimidization using 5,5'-(4-tert-butylcyclohexane-1,1-diyl)bis(1,3-dimethyl-2-(4-nitrophenoxy)benzene). Finally, research into the application of the developed bisphenol monomers to the production of poly(arylene ethers) is currently underway.

Future research will concentrate on several areas including production of additional bisphenol monomers and the usage of alternate dianhydrides in order to increase the hydrogen content of the polyimides. Additionally, the effects of tungsten as well as other additives on both stability and shielding properties will be explored. The polymers will also undergo quantitative testing of shielding capabilities against X-rays and neutrons. Following further polyimidizations, time will be committed to research into the feasibility and effectiveness of thicker films.

VI. Funding

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