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High Performance Co-Polyimide Synthesis for Cosmic Radiation Shielding

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

by

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Abstract:

Space radiation continues to be a problem for sustained space travel, harming humans and sensitive machinery. Overcoming this barrier is crucial to NASA's goals for manned missions to asteroids and Mars. Therefore, more research is needed in order to safely protect our missions. Passive shielding through high performance polymers shows promise in providing lightweight shielding and strength for spacecraft. This thesis focused on the novel synthesis of aromatic, hydrogen rich co-polyimides. It was shown that through thermal co-polymerization, favorable physical and chemical properties increased due to the presence of branching and/or crosslinking chains in the polymer matrix.

Acknowledgements:

I would like to thank Dr. Robert Owoil for being my mentor and advisor over my college career. Your patience and love of teaching continues to amaze me, and I will always fondly remember working in the lab. I again am grateful to Dr. Richard Kiefer, who allowed a freshman undergraduate the opportunity to work a summer in his lab, eventually leading to this project. A large thank you is in order for Joe Auslander, who mentored me and showed me the many techniques used for this thesis. I'd like to thank Mr. Jeffery Molloy, for teaching me how to use the many instruments open to undergraduates, and dealing with my incessant questions. Funding for this research was provided by NASA through International Scientific Technologies in Radford, VA, as well as Ken Updike. Thank you to those at IST, especially Dr. Eugene Aquino, and Mr. Updike, for giving back to your alma mater. Finally, to my parents, for always pushing me and providing me with unlimited opportunity.

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I: Introduction

One of the National Aeronautics and Space Administration's (NASA) goals for 2015 is continuing research towards the 2025 and 2030 deadline for sending manned missions to an asteroid and Mars, respectively. With manned missions however, comes the problem with sustained levels of space radiation. NASA states that, "Radiation protection for crew members remains one of the key technological issues which must be resolved."¹ The purpose of this honors thesis is to undertake further research on high-performance polyimides for space radiation shielding. The thesis mainly focuses on characterization of co-polymers, containing different ratios of dianhydrides to a constant amount of relative diamine. The major question that was addressed was, "Could co-polymer combinations show increased physical strength and temperature resistance while still providing comparable radiation shielding?" The thesis will explore the problem of radiation, then discuss polymerization methods and characterization, and then results. Finally, a discussion of implications of data and future studies will conclude the thesis.

¹ NASA, 2014

II: Assessment of Problem: Radiation

The Earth experiences two major sources of primary radiation: Galactic Cosmic Radiation (GCR) and Solar Particle Events (SPE). Due to the magnetic belt shielding of the Van Allen Radiation Belts, humans on Earth experience relatively little to none of the

damaging radiation. However, once outside of the belts, astronauts can suffer from a host of health problems similar to acute radiation poisoning from nuclear

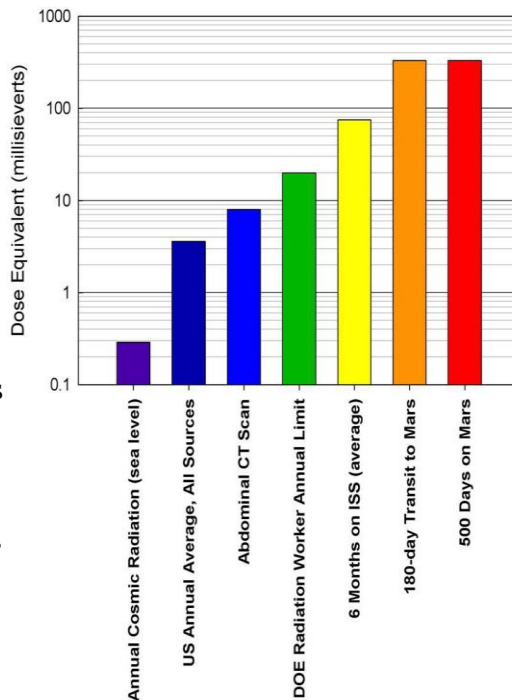


Figure 1: Dose Equivalents from Various Sources

accidents and explosions. There is little literature on the effects of chronic radiation poisoning, due to the paucity of cases seen on Earth, and the lack of human test subjects in space. Shielding is needed to stop or slow the particles from GCR and SPE.

A) Galactic Cosmic Radiation and Solar Particle Events (Primary Radiation

Sources)

Galactic Cosmic Radiation consists of 85% protons, 14% helium, and 1% other high energy nuclei.² GCR particles have been observed to have energies as high as 3×10^{20} eV, or around 40 million times more energetic than ones found from the Large Hadron Collider in Switzerland.³ To put things in perspective, at 50 J, a particle with the highest energy would have energy comparable to the kinetic energy of a baseball thrown at 56 mph. This amount of energy would have severely adverse health effects on astronauts. Radiation is measured in two main

² Schimmerling, 2011

³ CERN, 2015

units, Grays and Sieverts. Grays refer to the absorbed dose of radiation, defined as 1 Joule/kilogram. Sieverts refer to the dose equivalent. Since not all radiation particles are the same, the absorbed dose of a particular type of

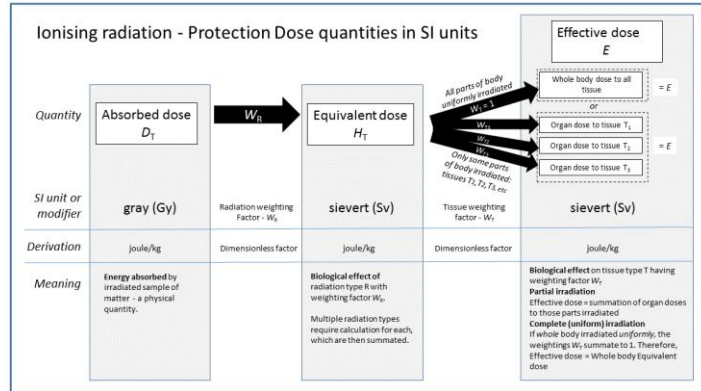


Figure 2: Explanation of Radiation

radiation can be multiplied by a quality factor to obtain the dose equivalent.⁴ (See Figure 2 for clarification) When the recent Mars Rover Curiosity landed on Mars, it showed a dose equivalent of 300 millisieverts, which is close to obtaining 24 CAT scans on Earth.⁵ As shown in Figure 1, radiation from traveling to Mars on a 500 day mission would be detrimental for the astronauts' health with current shielding technology.

Solar Particle Events (SPE) occur when solar flares on the surface of the sun cause a large emission of protons and other high energy nuclei. One major difference between the two types of radiation is duration. GCR occurs constantly, and so radiation doses accumulate over time. GCR events occur light-years away from Earth, so the dose received from events is essentially constant. However, since the sun is so close to the Earth, SPE can cause massive amounts of radiation during a short period of time. The amounts of radiation can be lethal. In a measurement between the Apollo 16 and 17 missions by NASA, a SPE was recorded that would have caused astronauts to absorb lethal doses of radiation. It was only by chance that no mission was currently on its way to the Moon. Currently, the best way to shield against these high spikes of radiation is to provide the astronauts with heavily shielded “bunkers” to stay in while the SPE

⁴ USRNC, 2014

⁵ Gifford, 2014

occurs. Another difference between GCR and SPE is the range of energized particles. GCR, due to the different types of galactic events, large and small, has a wider range of energized particles. GCR, as stated earlier, can have highly energized particles, more so than SPE. Although not covered in this thesis, SPE and GCR can cause electronic malfunctions and reduce the usage of electronic devices while in space. Shielding electronics is also a problem that NASA continues to research. Current research for shielding for GCR and SPE includes passive shielding: hydrocarbon materials, liquid hydrogen, water, and active shielding including magnetic deflection techniques analogous to the Earth's magnetic field. Passive shielding works by providing a physical barrier to stop radiation. In the case of GCR or SPE, passive shielding negates radiation through Coulombic interactions with electrons and nuclei in the shield. Additionally, collisions with shield nuclei can cause fragmentation, decreasing the overall harm of the radiation. Hydrogen has the highest charge/mass ratio due to the lack of neutrons. Therefore, it is the best element to slow and fragment the charged particles of GCR and SPE.

B) Secondary Radiation

Secondary radiation occurs when a primary cosmic ray, whether it be GCR or SPE radiation, strikes an object, causing more radiation. Among others, neutrons, secondary charged particles, and secondary electromagnetic wave radiation are cause enough to be addressed in shielding.

The effect of neutron radiation on the human body cannot be overlooked. Neutrons can catalyze other nuclear reactions in the body, causing damage, especially in soft tissues. Neutrons are characteristically neutral, so electromagnetic fields do not influence their trajectory. Thus, only isotopes with high "neutron capture cross-section" properties are able to capture neutrons

by use of the Nuclear Strong Force. Elements such as gadolinium and boron which have a high neutron capture cross-section are some of the isotopes used as nanoparticles in shielding to protect against neutrons. Also, hydrogen atoms slow down high energy neutrons for easier capture. Current shielding for secondary radiation includes hydrocarbon materials, such as polyethylene, concrete, or water. Secondary charged particles are usually addressed with the same shielding for GCR and SPE.

III: Current Shielding and High Performance Polymers

The problem with current aerospace shielding is the functionality associated with shielding properties. The best physical shielding would need to be: lightweight enough to justify the weight while being transported, physically resistant enough to endure space travel, and designed to adequately shield the astronauts from radiation. Current shielding does not meet these metrics. Materials such as concrete or liquid hydrogen are too heavy or too dangerous to line a spacecraft. Hydrocarbon materials such as polyethylene shield properly and are lightweight, but cannot withstand high temperature changes and are structurally weak and malleable. Research on high-performance polymers for radiation shielding proposes an answer to radiation shielding by providing physically strong, lightweight, and effective materials to be used on spacecraft.

High-performance polymers (HPPs) are defined by their resistance to temperature changes, their chemical stability, and their favorable mechanical properties. Hydrocarbon high-performance polymers are used for radiation shielding for all of these characteristics, and also the shielding properties that they can provide. HPPs with nanoparticles of heavy metal elements

or boron can help shield against neutrons as discussed above. For charged particles, the high hydrogen content helps to reduce the harmful effects due to primary and secondary collisions.

IV: Polyimides, Imidization, and

Crosslinking

Polyimides are used as HPP in this thesis. Polyimides are characterized by the imide bond between two monomers, in this case a dianhydride and a diamine (Figure 3). Polyimides are currently used in high temperature military materials, fuel cells, and

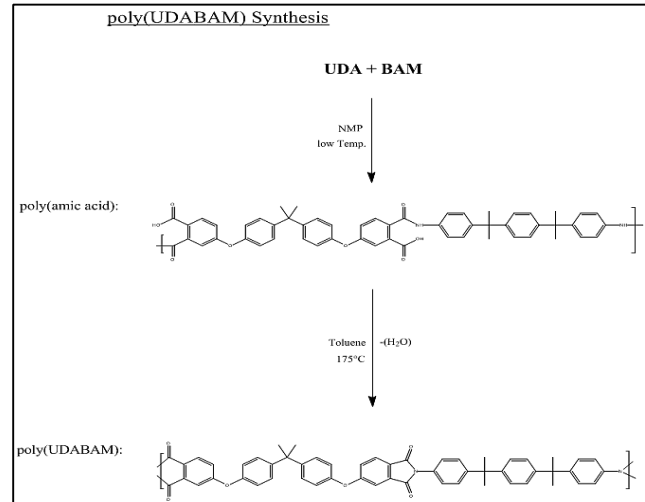


Figure 3: Example of Polyimide Synthesis

even reverse osmosis treatment of water. Polyimides serve as a good subject for aerospace shielding material because the carbon backbone provides strength, but is light. Aromatic polyimides function particularly well in this role, providing more strength for the material while contributing more sites for hydrogen atoms. The glass transition temperature, T_g , of a polyimides is known to be higher than that of the most common plastics (The glass transition temperature of a polymer is when the polymer changes from the glassy state to a more malleable state).

There are two mechanisms of imidization. The first is through azeotropic removal of water using toluene and heating the solution until imidization occurs. This process will be called thermal imidization for the rest of the thesis. The second process requires addition of acetic anhydride and pyridine. The solution is mildly heated, which causes imidization through chemical rearrangement. This process will be called chemical imidization for the rest of the thesis.

Crosslinked and branched polymers provide increased mechanical and chemical stability for polymeric materials. Crosslinking occurs when chains are connected through ionic, chemical, or photo-radiative mechanisms, usually through a crosslinking agent or active site. Branching occurs when side chains are added to a polymer backbone. In this thesis, a crosslink/branching mechanism is proposed to explain the difference in mechanical and chemical properties found in co-polymers which are made up of different combinations of monomer. In the system studied here, the co-polymerization of an added third monomer creates a ketone as an active site that

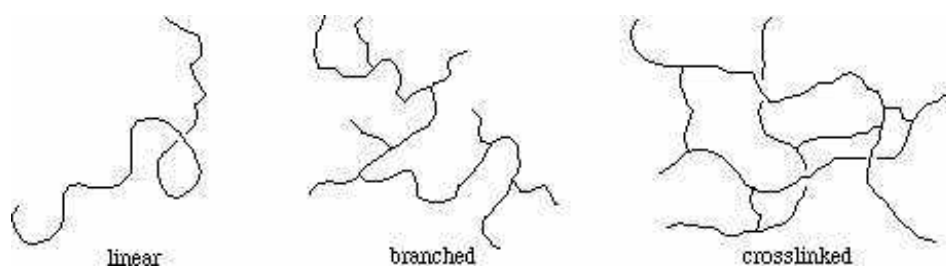


Figure 4: Visual Examples of Linear, Branched, and Crosslinked Polymer Chains

promotes branching. This will be discussed in depth later in the methods section.

In the interest of improving radiation shielding, HPPs co-polyimide in this work have attempted to increase the amount of hydrogen atoms while simultaneously increasing thermal, chemical, and mechanical properties.

III: Experimental Section:

A) Materials:

Three monomers were used for this thesis. The dianhydrides used were: 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (UDA) which was purchased from Sigma Aldrich with a given 97% purity and also benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) also purchased from Sigma Aldrich with a labeled purity of 96%. Finally, the diamine

used was 4,4'-(1,3-phenylenediisopropylidene)bisaniline (BAM) and was purchased from Sigma Aldrich with a 98% purity.

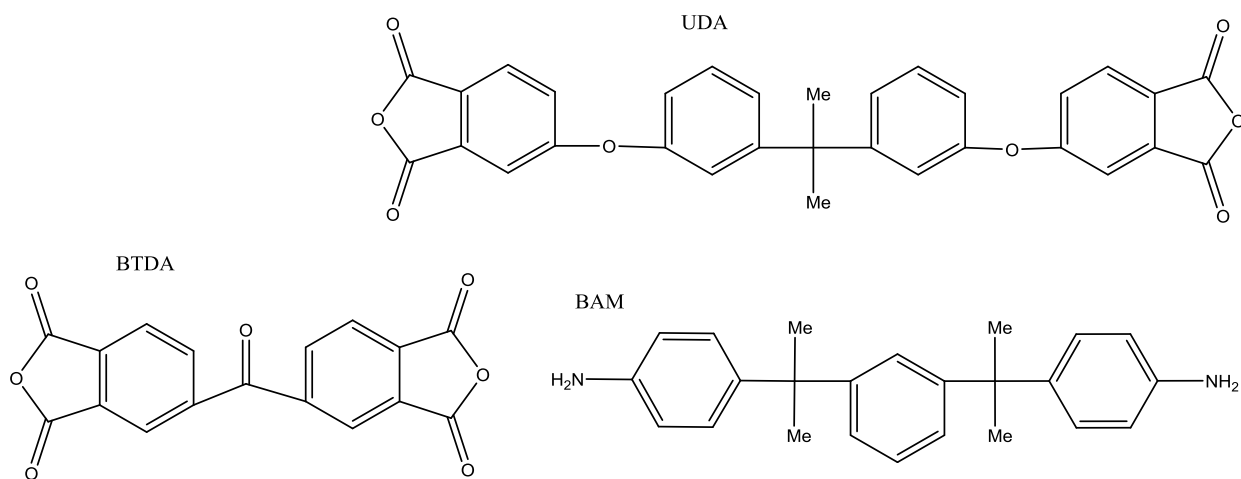


Figure 5: 3 Monomers Used

Polymerizations were carried out in N-methyl-2-pyrrolidinone (NMP) purchased from Sigma Aldrich with a 99% purity. Toluene was used as a washing agent and an azeotrope for water removal, and was purchased from Fisher Scientific at 99.9% purity. Ethanol was used as a washing agent and recrystallization solvent, labeled at 95% purity. Methanol was used as a polymer washing agent labeled at 99.8% from Fisher Scientific. Acetic anhydride was used as a chemical imidization reactant, washing agent, and recrystallization solvent, and was purchased from Fisher Scientific. Pyridine was used as a chemical imidization reactant and was purchased from Sigma Aldrich at 99% purity.

Dianhydride and diamine crystals were dried separately to avoid cross-contamination while drying. The dianhydrides were placed in a Fisher Scientific Isotemp Model 281A Vacuum Oven. The diamines were placed in a Thermo Scientific Lindberg/Blue M Vacuum Oven. Polymerizations occurred with an Electrothermal, EM Series Electromantle Heating Element. Once polymerized, films were pulled on glass plates using a BYK-Gardner Film Casting Knife

(AG-4300 Series), and cured in a Blue M Electric PRO-350 Oven. Differential Scanning Calorimeter (DSC) testing was completed using a TA Instruments DSC Q20. Thermogravimetric analyses (TGA) were completed using a TA Instruments Q500 TGA. Tensile testing was completed using 810 Material Test System.

B) Monomer Workup and Recrystallization:

Three different monomers from commercial sources were recrystallized to ensure their purity rates. Since polymer molecular weights in condensation reactions are heavily dependent on obtaining a 1:1 dianhydride to diamine ratio, any variation in monomer purity affects the final quality of the product. For the dianhydrides known commonly as UDA and BTDA, the crystals were dissolved in acetic anhydride in a 1:1 gram to milliliter ratio. The solution was heated to 130°C and additional monomer was added until saturation. The solution was then placed in a refrigerator to induce crystallization upon cooling. After 12 hours, the solution was filtered using a Büchner funnel. The crystals were washed with chilled acetic anhydride followed by chilled toluene. Once dried to room conditions, the crystals were placed in a vacuum oven at 110°C for further drying. Once dried for 24 hours, melting temperatures were obtained to compare to literature. Melting temperatures of 187-189°C for UDA corresponded well to literature values of 184-187°C.⁶

Diamines were recrystallized using ethanol as solvent. A 1:4 gram to milliliter ratio was used, and the solution was heated to 75°C. Monomer was added until saturation. The solution was left to cool to room temperature, and then placed into a refrigerator for at least 12 hours to induce further crystallization. The solution was then filtered using a Büchner funnel. The crystals caught by the filter were washed with cold ethanol and then placed into the diamine oven at 70°C

⁶ Sigma-Aldrich, 2015

for 12 hours. Melting temperatures were then obtained to compare to literature values. Melting temperatures of 111°C-113°C were found, and compared well to literature values of 110-114°C.

In both cases, if the monomers failed to correspond to literature melting values, the monomers were recrystallized once again using the method discussed above. Again stated, in condensation polymerization reactions, a 1:1 equimolar ratio between dianhydrides and diamines must be maintained. Recrystallization presents a problem because of residual solvent still left in the monomer crystals. Therefore, to achieve the 1:1 ratio, thermogravimetric analysis was used to determine the amount of residual solvent.

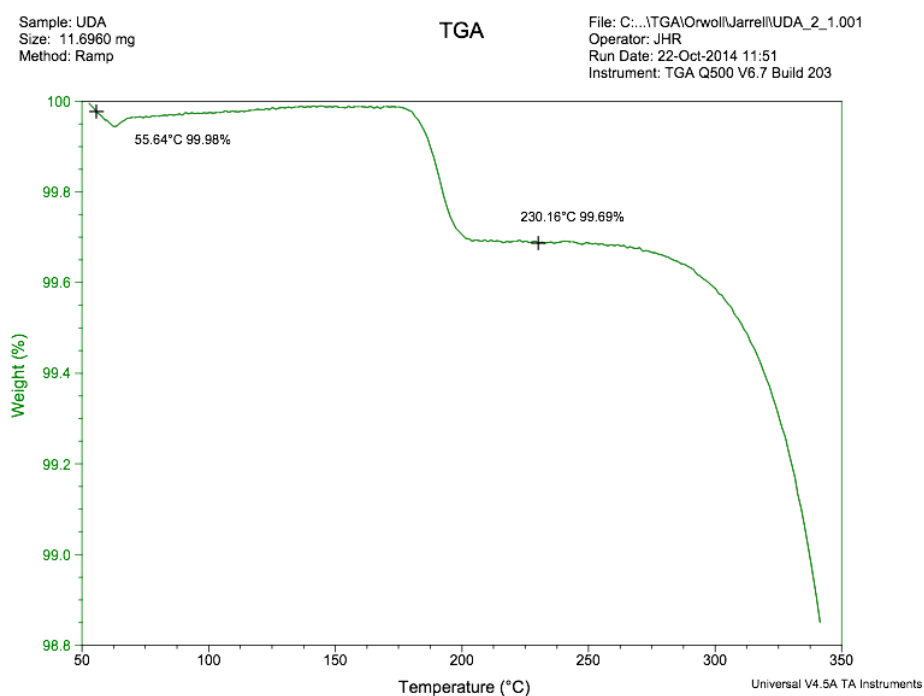


Figure 6: Sample TGA Solvent Analysis

As shown in the graph above, the higher plateau of data was used as the total sample amount, and the lower plateau was taken to be the monomer without solvent residue. Samples usually were 99.2-99.8% pure after two recrystallizations. This purity was taken into account

when determining how much monomer to polymerize. An example of a polymerization is listed below:

Table 1: Example polymerization calculation			
Moles of Anhydride	Moles of Diamine	Moles of Crosslink Monomer	Crosslink Monomer/Anhydride
0.01632	0.03265	0.01632	1
Molecular Weight of Anhydride	Molecular Weight of Diamine	Molecular Weight of Crosslink Monomer	Total Grams of Polymerization
520.49	344.10	322.23	25
Calculated Grams of Anhydride	Calculated Grams of Diamine	Calculated Grams of Crosslink Monomer	Amount of NMP (85% of solution weight)
8.49619	11.2439	5.2599	137.80ml
Purity	Purity	Purity	
0.9970	0.9997	0.9947	
Actual Grams	Actual Grams	Actual Grams	
8.5218	11.2473	5.2880	

First inputting the total amount of polymer needed for the final product, the number of moles were calculated using molecular weights. Calculated grams of each monomer were found, and then taking the purity into account, the actual amount of grams was calculated. The crosslink monomer/anhydride ratio was inputted to determine the molar ratios between the dianhydrides and the diamine.

C) Poly(amic) Acid and Polyimide Polymerization:

Polyimide synthesis occurs in two steps (Figure 3): the formation of the poly(amic) acid and then conversion to polyimide. The poly(amic) acid is formed by addition of equimolar amounts of dianhydride and diamine. A 4 neck 2-L flask consisting of a thermometer, nitrogen inlet, stirring apparatus, and Drierite tube was used for the reaction. After purging the flask with

nitrogen gas for at least 10 minutes, the calculated quantity of diamine dissolved in NMP was added to the flask. The dianhydride was then added with an addition funnel and dripped over 30 minutes to 1 hour depending on the amount of dianhydride. All glassware used during this process was rinsed with excess NMP to make sure all residue monomer was recovered into the 4-neck flask. The total amount of NMP used was measured so that it was 85% by weight of the total solution. The poly(amic) acid solution was stirred at room temperature for 24 hours under nitrogen gas to increase molecular weight. After 24 hours, a sample of the solution was taken for reference purposes and the remaining solution was then ready for imidization.

The method for thermal imidization is as follows.⁷ The polyimide was formed by a mechanism shown in Figure 7. The Drierite tube was replaced with a Dean-Stark trap with a condensing tube above it. Toluene was added 15% by volume to induce azeotropic removal of water from the solution. The solution was heated to 165°C - 175°C, which is the temperature of the toluene-water azeotrope. The two evaporate together, up the Dean-Stark trap and into the condensing tube. The cool environment of the condensing tube causes the azeotrope to condense and fall into the top of the Dean-Stark trap, in which toluene and water separate. Since water is denser than toluene, the water sinks to the bottom of the trap, and the toluene is free to return back to the 4-neck flask. The water was removed through a stop cock at the bottom of the trap. The reaction time depends on the amount of polymer, with 25 gram polymerizations taking 2 hours and 250 gram polymerizations taking up to 6 hours. Once there has been 30 minutes without water precipitating, the reaction was considered to be complete. The toluene was removed through the Dean-Stark trap and the polymer is apparently fully thermally imidized. At this point a sample of the polymer was taken for films and FTIR to confirm imidization.

⁷ Auslander, 2013

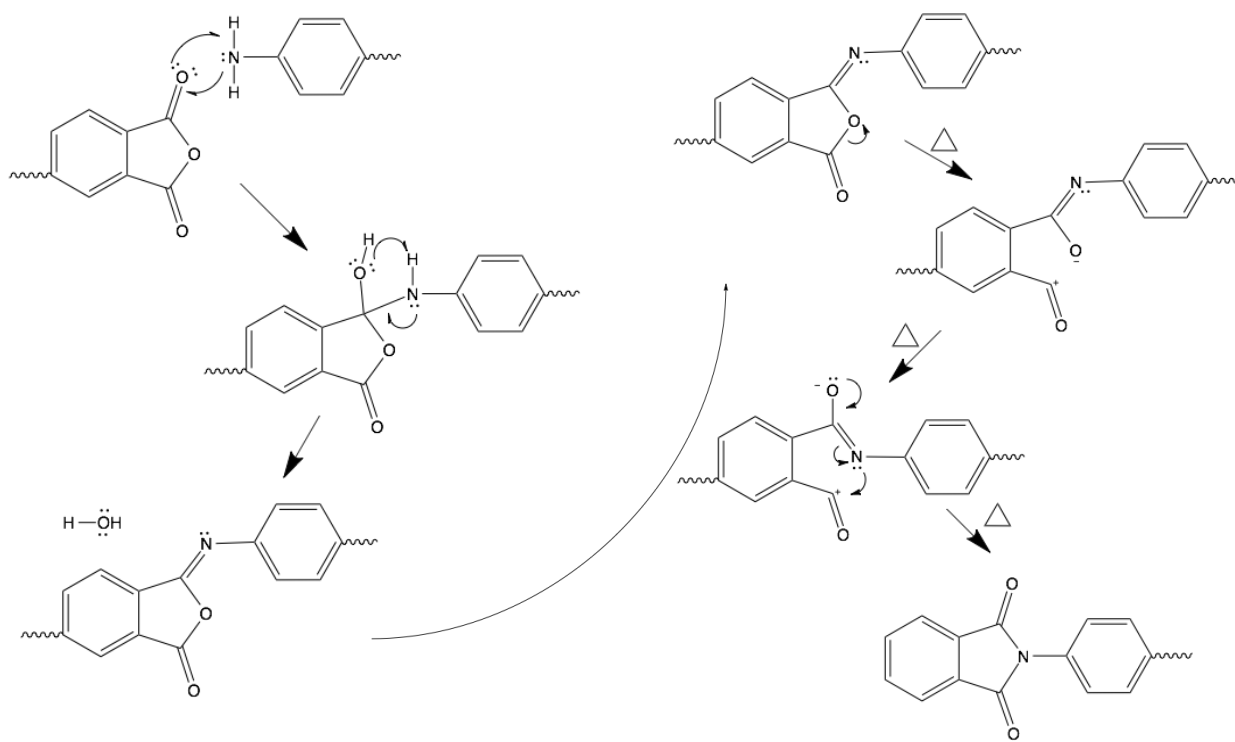


Figure 7: Thermal Imidization Mechanism

Chemical imidization is the second pathway for imidization of the poly(amic) solution. Acetic anhydride was added in an 8.4:1 molar ratio compared to the moles of polymer repeating unit. Pyridine was added in 6.2:1 molar ratio compared to the moles of polymer repeating unit.⁸ The reaction was heated to 100°C for 3 hours. At this point a sample of the polymer was taken for films and FTIR analysis. The waste products from chemical imidization are washed out using organic solvents in the washing and drying stage, outlined below. A mechanism outline is diagramed in the discussion section.

Since atmospheric water is thought to hydrolyze the polyimide and shorten chain length, decreasing overall polymer quantity, it is advantageous to work up polymer into flakes for better storage and for testing purposes. The polymer was first poured into DI water in a household blender at high speeds. This causes the polymer to crash out of solution, as a flocculent material.

⁸ Tsuda, 2009

The flakes were dried using a Büchner funnel and vacuum flask. The polymer was once washed using methanol, and then DI water 2-3 times. The polymer was then placed in a circulating oven at 100°C for further drying.

D) Testing and Characterization:

At this point the polymer was collected in two different forms: powder and liquid. Liquid samples are simply the polymer solution in NMP, and can be used for FTIR, viscometry, and thin film sampling. The liquid samples can be worked up to create polymer powder, which can be used for TGAs, DSCs, polymer pressing, and storage.

Films were pulled pouring 15mL of imidized liquid polymer solution on a glass plate which was cleaned using DI water and acetone. A doctor blade set to 0.15 millimeters was then used to distribute the solution over the glass plate at a constant thickness. The plate was then put into a curing oven, and subjected to the following heating program: 2 hours at 100°C, 4 hours at 200°C, 4 hours at 300°C and then stepped down to 25°C in 2 hours. Each change of temperature was completed over one hour. Once cool, the plate was submerged in a water bath, which removed the film from the plate. The film was dried and then subjected to a crease test. If the film is able to be creased without cracking or breaking, the polymer chains are long enough to span the physical crease, and so the polymerization can be determined successful.

Thermogravimetric analysis was used for two reasons. The first was to determine monomer purity as discussed earlier. The second reason was to further analyze the thermal properties of the polymer. TGAs offer general measures of thermal resistivity by measuring the temperature at which the sample has lost 5 and 10% of its original mass when heated. Comparing these values between polymers can give insight into how the polymers would perform in space,

where temperatures vary drastically. The polymer can also be tested for residual solvent, which can disrupt pressing. TGAs were taken with the polymer in the powder form.

Differential scanning calorimeter testing was used as the main source of thermal and physical testing measure. The glass transition temperature, where the polymer changes from the glassy state to a rubber-like state, is crucial in determining polymer strength and resistivity to temperature. DSC testing can measure glass transition temperatures by determining heat flow changes in polymer substances. In high-performance polymers, a glass transition temperature of 180-220°C shows good resistance and strength. DSCs were taken with the polymer in powder form.

Fourier transform infrared spectroscopy was used to confirm imidization. Films were subjected to scanning to determine if amide stretching was seen around 3100-3500 cm^{-1} . If a sample is imidized correctly, there should be no amide stretching. In general, FTIR spectroscopy should be similar in both imidization processes.

Tensile testing is used to measure the physical capabilities of the polymer. In this thesis, standardized thin films were subjected to tensile testing. Using a constant program of one inch over one minute, the polymer is recorded on its reaction to strain in the amount of force required to move the polymer sample that distance over the given time.

Polymer pressing is usually the final stage of workable polymer. Polymer flakes are placed in a steel mold. It is worth noting that the polymer flakes must be dry at this point, or else the solvent will cause bubbles to form in the mold. The flakes are pressed down by a steel block at 1600 psi at 212°C. The polymer is held at 212°C for 1 hour to ensure uniform melting and



Figure 8: Polymer Products - From Left to Right - Pressed Block, Polymer Flakes, Liquid Sample, Film

even distribution of the polymer in the newly formed polymer block. The polymer was heated to 212°C to raise the polymer above the glass transition temperature so the polymer can be molded to the dimensions required by the scientist. The molds can differ in dimension from 1"x4" to 4"x4". These blocks can be used for testing, structure materials, or simply storage.

IV: Results:

Nine polymerizations were completed to determine physical, thermal, and chemical differences between different copolymers. The table below shows the different polymerizations and results from different testing:

Table 2: Results of Co-Polymerizations				
Polymer	5% Degradation, 10% Degradation (°C)	Tg°C	Tensile Testing	Film Crease Testing
UDA-BAM Thermal	519, 534	182	0.3833 lbf/sec 2.6 max force	Creaseable
UDA-BAM Chemical	515, 525	172	N/A	Creaseable
UDA-BAM- BTDA-17% Thermal	511, 526	187	0.4000 lbf/sec 3.10 max force	Creaseable
UDA-BAM- BTDA-17% Chemical	480, N/A	183	N/A	Creaseable
UDA-BAM- BTDA-25% Thermal	516, 533	192	0.6066 lbf/sec 3.97 max force	Creaseable
UDA-BAM- BTDA-25% Chemical	507, 531	177	N/A	Not Creasable
UDA-BAM- BTDA-33% Thermal	549, 577	198	N/A	Creaseable
UDA-BAM- BTDA-33% Chemical	536, 545	191	N/A	Not Creasable
BTDA-BAM Thermal	534, 543	213	N/A	N/A

The percentage associated with each polymer is relative to the polymer chain, for example UDA-BAM-BTDA-25% has the repeating chain unit of:



Figure 9: Example of Polymer Nomenclature

The “chemical” and “thermal” label refers to the imidization process.

5% degradation and 10% degradation temperatures are good measures of how thermally resistant a polymer is. These were measured through TGAs, as shown below:

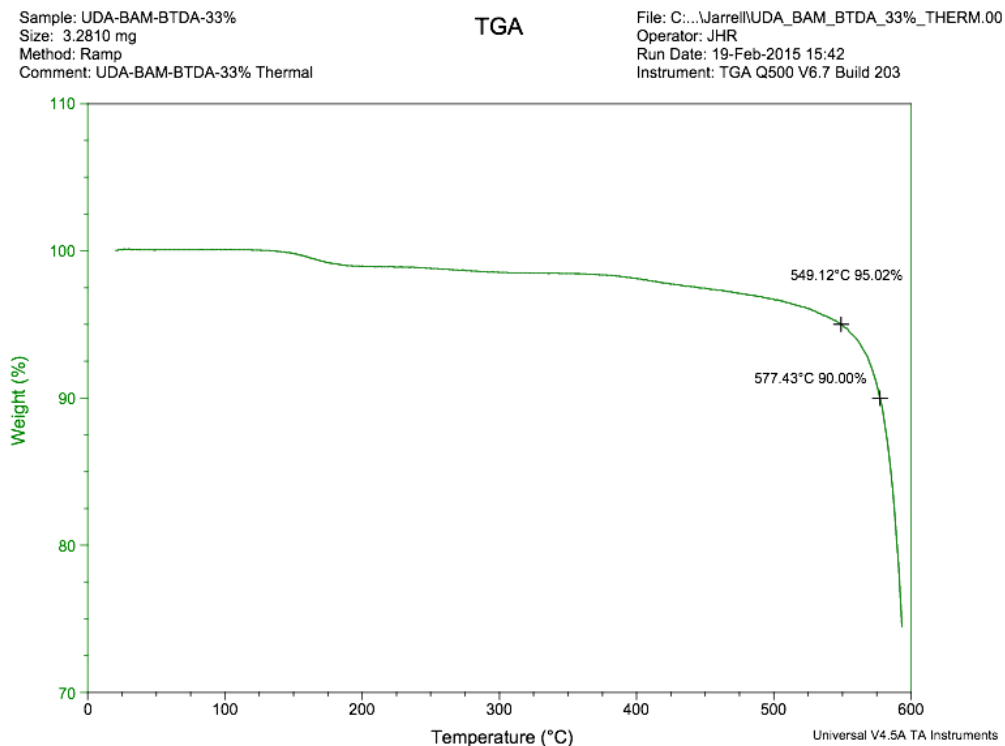


Figure 10: TGA Showing 5% and 10% Degradation Temperatures

There was a positive relationship between the amount of BTDA in the polymer chain and the 5% and 10% degradation temperatures, when comparing the thermally imidized samples. As the amount of BTDA in the polymer chain increased, so did the 5% and 10% degradation temperatures. When looking at the chemical samples, the relationship was positive, but not as strong. This is thought to be due to differences in the imidization process which will be discussed in further detail later.

Glass transition temperatures were obtained using DSC measurements as shown below:

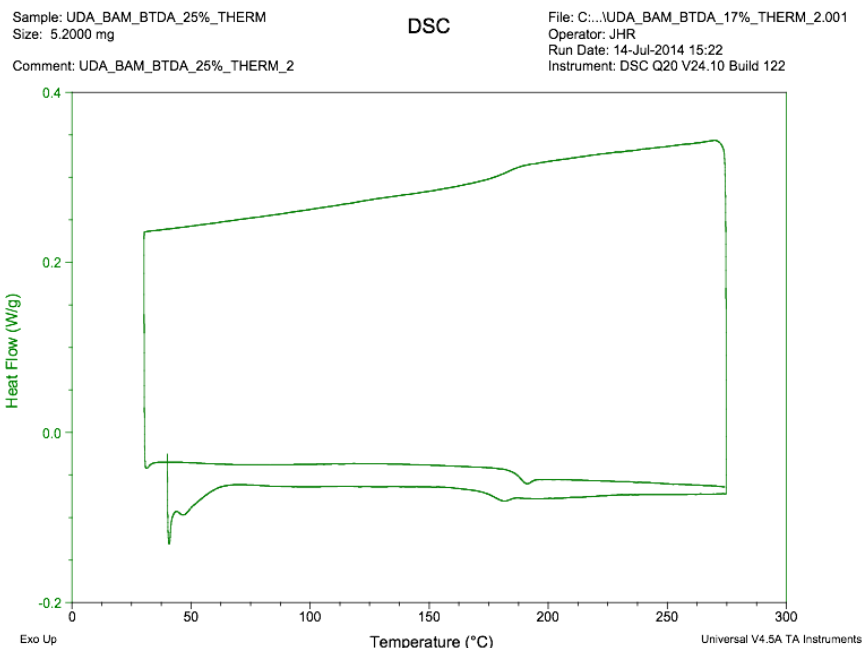
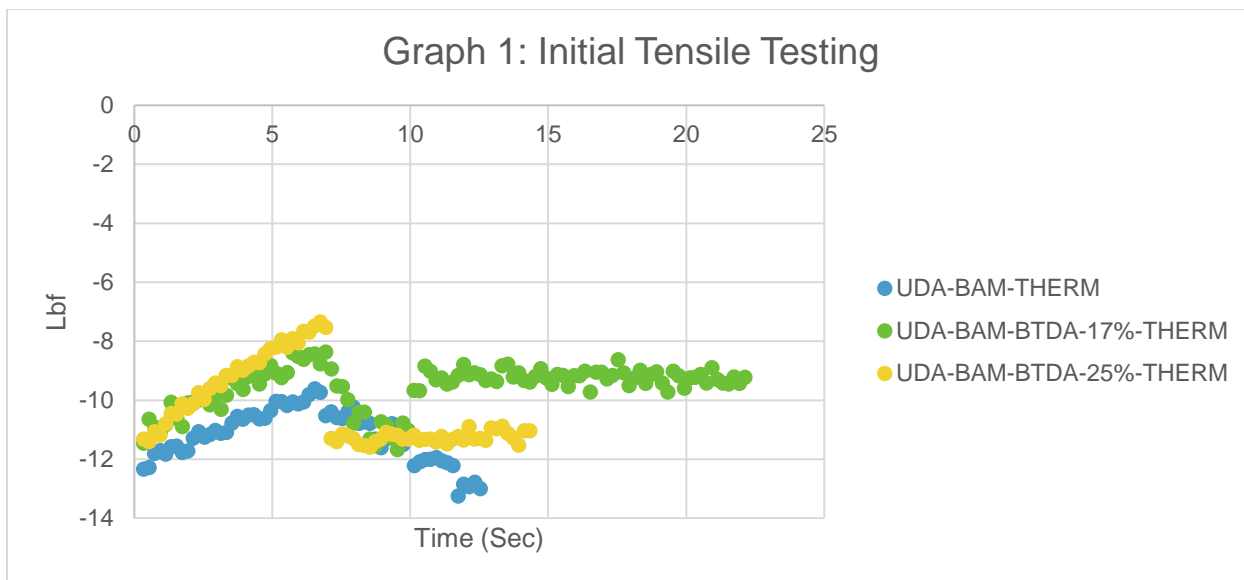


Figure 11: Glass Transition Temperature Calculation Through DSC

Glass transition temperatures were obtained using the second inflection point when transitioning occurs. Glass transition temperatures showed a positive relationship with the amount of BTDA in the polymer backbone when looking at the thermally imidized polymer. For the chemically imidized polymer the same relationship was not as strongly correlated. The polymer samples were taken through a heating and cooling cycle in order to compare different polymers subjected to similar thermal conditions. The polymer powder was heated to 275°C, then cooled to 32°C, then finally heated back up to 275°C.

Tensile testing was completed for some samples, but for some samples it was omitted due to lack of proper film samples, time constraints, or due to mechanical difficulties. Initial tensile testing results hint towards an increasing mechanical resistance as BTDA levels increase in the polymer backbone. Only thermal polymer samples were tested, and most were not completed. The results of preliminary testing is shown in the graph below:



The linear progression of force before breaking was observed to be higher in 25% BTDA samples. The absolute difference between the initial amount of force and the breaking force also was higher in the 25% BTDA sample, which was reported as the max force.

Film crease testing was completed on all samples. Most all samples provided films that creased, indicating that the samples had high enough molecular weight. BTDA-BAM could not be kept in the liquid state, since it had absorbed solvent, and entered the gel state.

VI: Discussion

Stated again, the purpose of this thesis is to further research co-polyimides for space radiation shielding. The thesis focuses on differing levels of BTDA to form polymers with varying chemical, thermal, and physical properties. The majority of the differences between the copolymers is hypothesized to originate from a thermal imidization branching/crosslinking mechanism outlined by Yang and Hsiao.⁹ The mechanism is shown below:

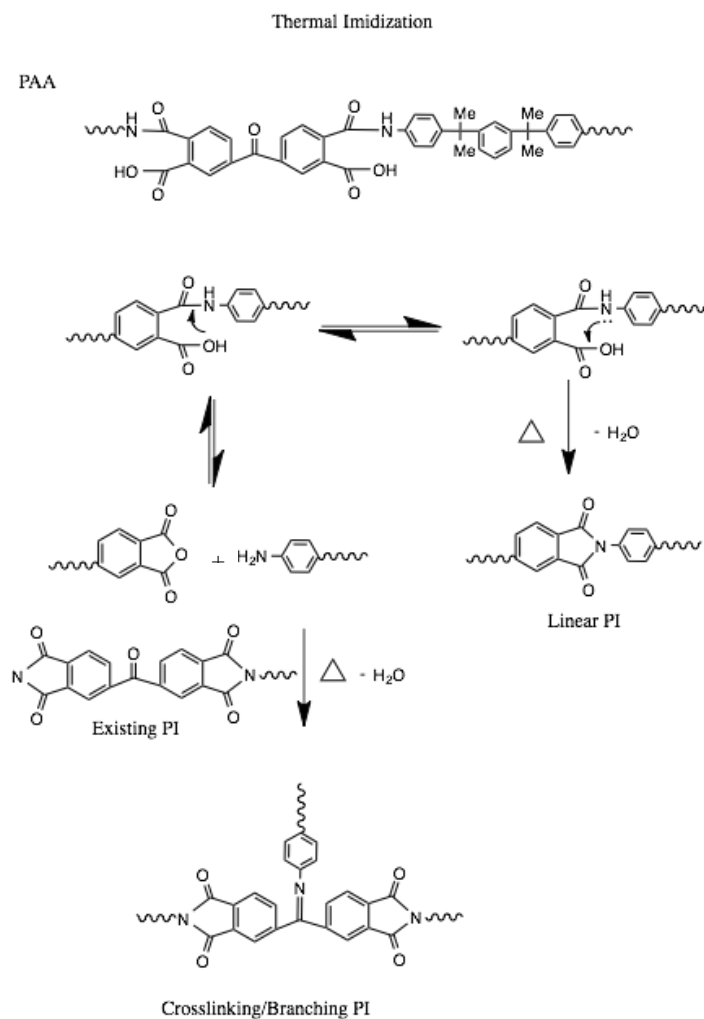


Figure 12: Thermal Imidization Mechanism

⁹ Yang and Hsiao, 2013

However, in the proposed chemical imidization process, this crosslinking/branching does not occur:

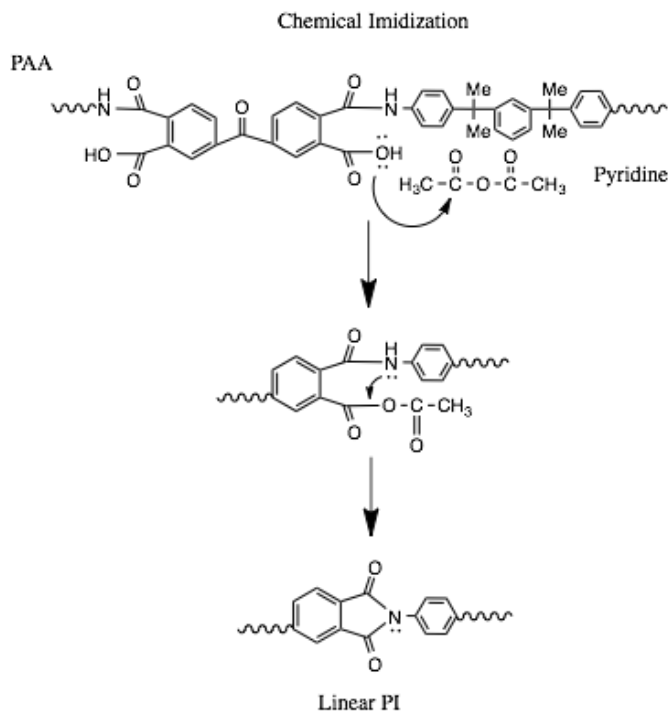


Figure 13: Chemical Imidization Mechanism

The major difference between the two processes is the activation of the carbonyl active site from the BTDA monomer. This carbonyl active site imitates linear imidization by producing water and requiring high temperatures. The imine bond formed between chains can create branching or crosslinking in the polymer matrix. When first starting this thesis, pure BTDA-BAM was thermally polymerized. This resulted in a highly crosslinked network of polymer, which gave a dough-like material that absorbed solvent like a crosslinked network. Similarly, as the co-polymer increased in BTDA content, polymer began to fall out of solution, showing a decreasing solubility.



Figure 14: Polymer Solutions From Left to Right:
UDA-BAM, UDA-BAM-BTDA-17% THERM,
UDA-BAM-BTDA-25% THERM,
UDA-BAM-BTDA-33%THERM

Due to the proposed mechanism above, the thermal imidization polymers showed increases in thermal properties. The addition of BTDA from 0% to 33% showed an increase of 17°C in glass transition temperature, and a 29°C and 43°C increase in 5%, 10% degradation temperatures, respectively.

The chemical imidization process was used as a control to compare against the thermal products, and imidization was confirmed successful through FTIR.¹⁰ Theoretically, the chemical products would have less difference between the co-polymers compared to the thermal products. This is due to the lack of branching and crosslinking due to the lower temperatures. It was shown that chemical imidization also did increase the thermal properties of the polymers, specifically the glass transition temperatures and the degradation temperatures. The addition of BTDA from 0% to 33% showed a 19°C increase in glass transition temperature, and a 21°C and 20°C increase in 5%, 10% degradation temperatures, respectively.

Comparing similar polymers subjected to the two different imidization processes, thermal imidization products seem to have more favorable thermal properties. The tables below summarize the differences between the imidization processes:

¹⁰ See Appendix for Example FTIR Confirmation

Table 3: 5% degradation Temperatures (°C) for UDA-BAM-BTDA		
% BTDA	Thermal Imidization	Chemical Imidization
0	519.69	515.19
17	511.95	480.73
25	516.27	507.08
33	549.12	536.12

Table 4: 10% Degradation Temperatures (°C) for UDA-BAM-BTDA		
% BTDA	Thermal Imidization	Chemical Imidization
0	534.28	525.45
17	526.33	N/A
25	533.17	531.12
33	577.43	536.12
50	543.22	N/A

Table 5: Glass Transition Temperatures (°C) for UDA-BAM-BTDA		
%BTDA	Thermal Imidization	Chemical Imidization
0	182.38	172.58
17	187.28	183.08
25	192.18	177.69
33	198.01	171.01
50	213.08	N/A

In all cases, the thermal imidization product had higher thermal properties. Again, this is hypothesized to be due to the crosslinking/branching mechanism described at the beginning of the discussion section. Branching and crosslinking would cause the polymer to be more intertwined, requiring more energy to degrade and to soften the polymer matrix.

The tradeoff for adding BTDA monomer to the UDA-BAM backbone is hydrogen content. Since BTDA has fewer hydrogen atoms than UDA, substituting BTDA for UDA

reduces the shielding effectiveness of the polymer. A table below summarizes the differences in hydrogen content, including other sources of commercial shielding for comparison:

Table 6: Hydrogen Content in Co-Polyimides	
Polymer	Hydrogen Content (mol H/g polymer)
Kapton	0.0262
UDA-BAM	0.0531
UDA-BAM-BTDA-17%	0.0516
UDA-BAM-BTDA-25%	0.0507
UDA-BAM-BTDA-33%	0.0498
BTDA-BAM	0.0476
Polyethylene	0.1426
Polypropylene	0.1426

It may seem counterintuitive to add BTDA into the polymer backbone, given the decrease in hydrogen content. However, due to the increasing physical and thermal stability the BTDA crosslinking provides, a copolymer of containing crosslinked polyimides may perform better when placed in the harsh environment of space.

A) Further Research:

One limitation to the research was the long reaction times of the polymerizations. Over 12 polymerizations were conducted, with 3 failing to meet specifications for testing. Because of the nature of these reactions, each sample was only polymerized once. Since polymers are heavily dependent on monomer ratios and atmospheric conditions, it is possible that the results are due to sensitivities in polymerization conditions. The timing also did not allow the completion of tensile testing, as this was the final testing after TGA, DSC, film, and degradation testing.

Water is another source of frustration. Water is a byproduct of the condensation reaction and could be used to determine the success of polymerizations. However, it was discovered early in the research that water levels would greatly differ from calculated values. This could be due to apparatus leaks, allowing water to escape, or due to environmental conditions, specifically the humidity in the lab even when under nitrogen and using Drierite tubes. Measurements of water could be useful, since in the thermal imine reaction, water is given off. Similarly, the extent of imidization cannot be measured well. There are differences in glass transition temperatures and degradation values between UDA-BAM THERM and CHEM. Ideally, there should be little to no difference between the two samples, since both are imidized, just through different means. The difference in properties could signify different rates of imidization. This could undermine the stated increase in thermal properties due to the crosslinking/branching mechanism. Further testing beyond FTIR confirmation would have to be done to determine differences in imidization rates.

Another limitation is the question of molecular weights. Polymers are dependent on their molecular weights for physical and thermal properties. Even though a film crease testing gives the scientist a general idea of molecular weighting, it is not close to the precision needed to truly, quantitatively compare the polymers. Since molecular weight testing is not available at William and Mary, it was assumed in the thesis that the polymers did not differ in molecular weights enough to affect the trends discussed above. Only through molecular weight testing can this be proven.

One final limitation is the extent to which the polymer is crosslinked. Crosslinking is hard to measure, and no quantitative way was used in this thesis to determine how often the polymer crosslinked. In future studies, perhaps a marker could be used to show how often

crosslinks were formed. Also, gel absorption techniques could be used on higher crosslinked networks, but it was not applicable to this thesis outside of the thermal imidization of BTDA-BAM.

VIII: Conclusion

The purpose of this thesis was to further research high performance polyimides for space radiation shielding. Copolymers were synthesized with different amounts of crosslinking monomer, BTDA. Through TGA, DSC, tensile, and film testing, crosslinking co-polymer chains saw improvements to the thermal, physical, and chemical properties. However, this should be weighed with the decrease in hydrogen content. By replacing UDA with BTDA, there is an overall loss in shielding effectiveness. Therefore, an optimal amount of BTDA should be introduced specific to the needs of the material. If the material is to be subjected to higher temperatures or a chemically unstable environment, co-polymers with increased BTDA content could prove useful while still maintaining some level of radiation shielding.

IX: Continuing Studies

There are many implications for this crosslinking/branching mechanism. Theoretically, a polyimide could be imidized chemically, creating linear polymers, and then crosslinked thermally using the carbonyl active site. A highly aliphatic diamine chain like 1,10-diaminodecane could be used to connect polyimide chains while adding hydrogen content to the material. This could make up for the decrease in hydrogen content, while maintaining the increases in stability. Crosslinking polyimides through BTDA also has high potential for metal

introduction into the polymer material. Bonded metals, preferably boron or gadolinium could be added via imine crosslinking.

X: Bibliography

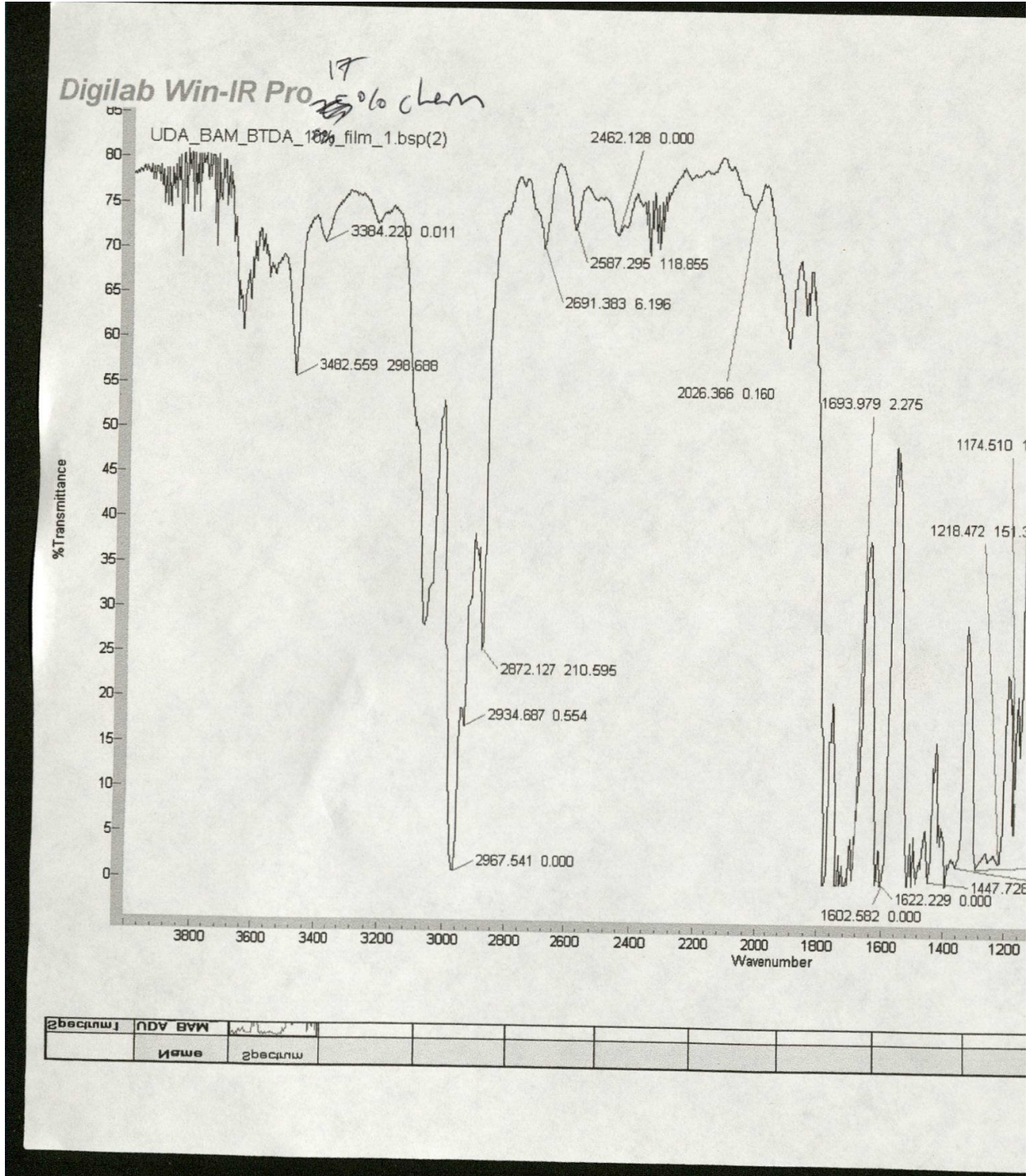
1. "What Is Space Radiation?" NASA. March 4, 2014. Accessed April 4, 2015. <http://srag-nt.jsc.nasa.gov/spaceradiation/what/what.cfm>.
2. Schimmerling, Walter. "The Space Radiation Environment: An Introduction." *The Health Risks of Extraterrestrial Environments*. February 5, 2011. Accessed January 10, 2015. <http://three.usra.edu/concepts/SpaceRadiationEnviron.pdf>.
3. "The Large Hadron Collider." CERN Accelerating Science. January 1, 2015. Accessed April 6, 2015. <http://home.web.cern.ch/topics/large-hadron-collider>.
4. "20.1004 Units of Radiation Dose." United States Nuclear Regulatory Commission. July 10, 2014. Accessed March 27, 2015. <http://www.nrc.gov/reading-rm/doc-collections/cfr/part020/part020-1004.html>.
5. Gifford, Sheyna. "Calculated Risks: How Radiation Rules Manned Mars Exploration." *Space*. February 18, 2014. Accessed March 1, 2015.
6. "Polymer Science." Sigma-Aldrich. January 1, 2015. Accessed February 3, 2015.
7. Auslander, Joseph. *High-Performance Nanocomposites Designed for Radiation Shielding in Space and an Application of GIS for Analyzing Nanopowder Dispersion in Polymer Matrixes*. MS Thesis, Williamsburg: College of William and Mary, 2013.
8. Tsuda, Y. *Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications*. 1st ed. Vol. 5. London: CRC Press, 2009. 17-42.
9. Yang, Chin-Ping, and Feng-Zhi Hsiao. "Synthesis and Properties of Polyimides Based on an Ether Ketone Diamine, 4,4'-Bis(4-aminophenoxy)benzophenone." *Journal of Polymer Research* 10 (2003): 181-93.

10. Sim, Doug. "File:SI Radiation Dose Units.png." Wikipedia.org. November 24, 2013.

Accessed February 21, 2015.

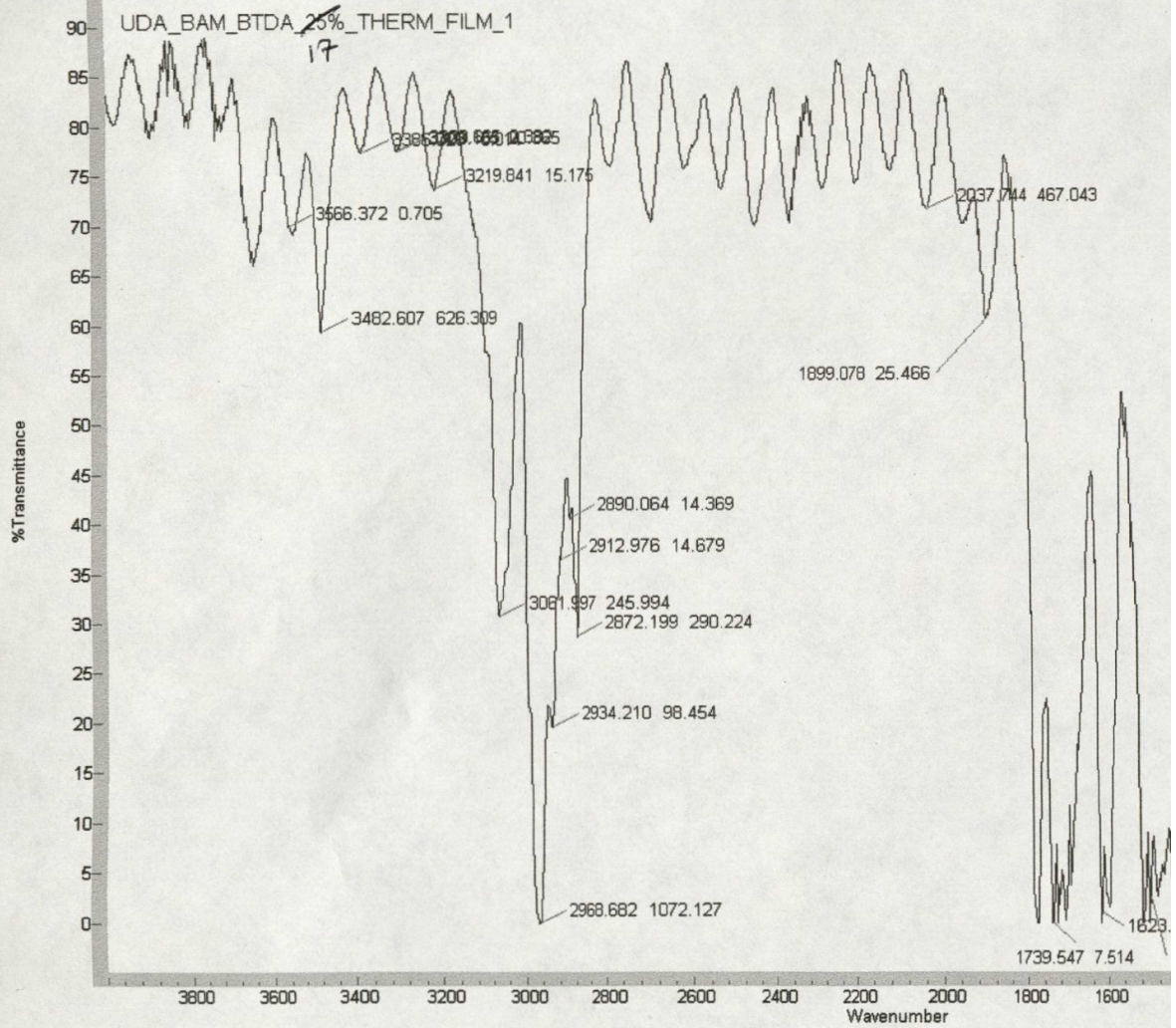
http://commons.wikimedia.org/wiki/File:SI_Radiation_dose_units.png

XI: Appendix



FTIR of UDA-BAM-BTDA-17% CHEM

Digilab Win-IR Pro



3800	3600	3400	3200	3000	2800	2600	2400	2200	2000	1800	1600
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FTIR of UDA-BAM-BTDA-17% THERM