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The Production of Novel Poly(arylene ethers) for Use as Radiation Shielding in Outer Space

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The Production of Novel Poly(arylene ethers) for Use as Radiation Shielding in Outer Space

A thesis submitted in partial fulfillment of the requirements for the degree of Bachelor of Science with Honors in Chemistry from the College of William and Mary in Virginia.

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Accepted for Honors

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Abstract:

Current radiation shielding materials are not effective for shielding astronauts and equipment for long missions. Radiation threats include galactic cosmic radiation, solar energetic particles, neutrons, and electromagnetic radiation. Novel, lightweight materials must be developed that have the appropriate radiation shielding capabilities and the thermal and mechanical abilities to be used for a wide variety of applications. Poly(arylene ethers) have excellent mechanical and thermal properties, and may be engineered to include radiation shielding components. In this research, four different high hydrogen-content poly(arylene ethers) were synthesized. A gadolinium salt and modified tungsten nanoparticles were produced to be incorporated into the polymers to provide enhanced shielding capabilities. Both thin films and a thick bar were produced. The polymers mostly showed good resistance to thermal degradation. These initial findings and future research may lead to the successful development of new materials for radiation shielding on long-term outer space missions.
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I would like to thank Dr. Orwoll for his wisdom and mentoring. He has taught me so much, and has been a wonderful guide throughout my academic career. I would also like to thank Emily Harbert and Norah Bate for taking me under their wings and showing me the ropes. This research only builds on the foundations that they have set. Lastly, I would like to thank my parents, Jim and Lucinda Speers, for loving and supporting me in all that I do.
I. Introduction

The exploration of space continually advances and builds to new heights. The Voyager space probes have passed beyond the orbit of Pluto, and the Huygens probe successfully landed on Titan, a moon of Saturn. With the increasing interest in manned space travel and possible lunar and Martian bases, new considerations for radiation shielding have arisen.

A. Radiation Barriers to Long-Range Space Travel

As long-term space missions are planned, the need for better forms of shielding has come to the fore. Near-Earth space missions are protected by the Earth’s magnetic field, which deflects many of the charged particles in radiation. However, this protection ends beyond the Van Allen belts, and more shielding is required.¹

Space radiation comes in several forms, including galactic cosmic radiation (GCR), solar energetic particles, and electromagnetic radiation. Neutrons, though short-lived, are also formed from the interactions of other types of radiation with space craft materials. On short-term missions, such as the Apollo missions to the moon, the exposure to radiation is not of much concern. However, the accumulated exposure experienced on long term missions can be detrimental to both astronauts’ health and equipment.

1. Galactic Cosmic Radiation (GCR)

GCR includes energetic, bare nuclei of all natural elements, primarily hydrogen and helium (85% and 14%, respectively), with a significant minority of elements near iron. These particles originate from outside the solar system. Nuclei with a high atomic
number and high energy, called HZE particles, are particularly dangerous because of their very high energies, sometimes exceeding 1 GeV per nucleon. Current shielding materials, such as the aluminum walls of the Apollo spacecraft, are unable to completely stop HZE particles; the shielding needed to completely halt these particles would be prohibitively heavy. Such shields may even worsen the problem when the particles hit nuclei and fragment into smaller nuclei and neutrons. The resulting particles may even entail a higher dosage behind the shield than the incident radiation would have caused.

Besides collisions with nuclei, HZE and other GCR nuclei interact with shielding materials through Coulombic interactions. Attraction between the positively charged nuclei and negatively charged electrons and repulsion with positively charged protons in the shielding material slows down incoming nuclei and lowers their kinetic energy. Hydrogen, with the highest concentration of charge per unit mass, is thus the most effective shielding material, as the most abundant isotope has no neutrons, which add to the mass without contributing to the charge. In addition, per unit mass, incoming nuclei lose more kinetic energy upon interacting Coulombically with hydrogen nuclei and electrons than in interactions with larger atoms.

2. Solar Energetic Particles

Solar energetic particles are similar to GCR in that they consist of bare nuclei. These particles are almost exclusively hydrogen and helium nuclei. They present the same type of dangers as GCR. However, the average and maximum energies of solar energetic particles are less than those of GCR, and so effective shielding for GCR would also take care of these particles.
3. Neutrons

Neutrons have short half lives (on the order of $t_{1/2} = 10$ min), but they are generated when GCR nuclei collide with and fragment shielding material nuclei. Neutrons cannot be stopped by Coulombic interactions because they are not charged, so they are highly penetrating. Neutrons are dangerous because they may be absorbed by nuclei and render them unstable and prone to fragmentation, possibly producing a cascading effect as more neutrons are released. Short wavelength, high-energy electromagnetic radiation, such as gamma rays, often accompanies these nuclear events. Fortunately, several isotopes have large neutron-capture cross-sections, such as some isotopes of boron and gadolinium. These elements would be too heavy to use as shielding material by themselves, but embedded in a lightweight organic polymer they would be effective neutron absorbers. Hydrogen is also effective at slowing down incident neutrons.\(^2\)

4. Electromagnetic Radiation

Electromagnetic (EM) radiation comes in a wide range of energies, ranging from fractions of an electron volt to millions of electron volts. The higher energy radiation, encompassing ultraviolet, X-rays, and gamma rays, is the most dangerous and important for shielding purposes.\(^2\) UV radiation is able to produce radicals through homolytic bond cleavage as well as ionization. UV radiation is readily absorbed by additives such as carbon black. X-rays and gamma rays are ionizing radiations.

X-rays and gamma rays interact with shielding materials in three ways: the photoelectric effect, Compton scattering, and pair production. In the photoelectric effect,
a quantum of radiation is absorbed completely by an atom or molecule, and a bound electron is ejected with energy equal to the quantum energy minus the binding energy of the electron. The photoelectric effect has a probability inversely proportional to the quantum energy raised to the 3.5 power and directly proportional to the absorbing species’ atomic number raised to the fifth power. This process is thus most efficient for low-energy photons colliding with a high atomic number absorber.

In Compton scattering, the photon gives up only a portion of its original energy to the ejected electron, and the photon is reemitted with reduced energy in a random direction. This process occurs with photons of a medium energy, usually gamma rays with energies of 0.6 – 4 MeV. Compton scattering has a probability inversely proportional to the energy of the photon and directly proportional to the absorbing material’s atomic number. Again, the absorption process is most efficient for materials with a high atomic number.

Pair-production is the highest energy process, requiring a photon with energy in excess of 1.02 MeV. This process results in the production of a positron-electron pair. This process occurs with a probability increasing with the logarithm of the photon energy and with increasing atomic number. The energy in excess of 1.02 MeV is distributed equally between the kinetic energies of the positron and electron. The positron eventually collides and annihilates with an electron, producing two photons of equal energy radiating in opposite directions.

Since all three processes correlate positively with increasing atomic number, elements with high atomic number serve as the best shielding material against X-rays and gamma rays. Nanocomposite particles of neutron-absorbing elements, such as tungsten
and gadolinium, can serve a dual purpose of shielding against high energy EM radiation and against neutrons.³

**B. The Proposed Solution**

From the above discussion, it is clear that an effective shielding material will have a high hydrogen content (to slow down GCR, solar energetic particles, and neutrons), as well as heavy atoms such as tungsten or gadolinium (to absorb neutrons and high energy EM radiation). In addition, the shielding material must be structurally strong and able to withstand high temperatures, in order to be used for a variety of purposes. The material must also be lightweight in order for the spacecraft to be able to get off the ground.

High performance polymers are excellent materials to fulfill the structural, thermal, and weight requirements of shielding material. These polymers can withstand rugged use and be molded into a vast variety of shapes. They may be used for everything from space suit fibers to dashboard consoles to structural supports. The myriad possible uses will reduce cost as well as weight in space missions.⁴

For shielding purposes, hydrogen-rich aliphatic polymers are preferable. The aliphatic polymers polypropylene and polyethylene contain 0.143 moles of hydrogen per gram. However, these polymers have limited thermal and mechanical capabilities that curtail their usefulness. Aromatic polymers, on the other hand, are more thermally durable and thus useful. However, they have limited hydrogen content; Kapton, for example, has only 0.026 moles of hydrogen per gram.¹

The solution to this problem is to use hybrid polymers that retain the desirable mechanical and thermal properties of aromatic polymers with the high hydrogen content
of aliphatic polymers. This can be accomplished by using hybrid monomers with both aromatic and aliphatic components. Hybrid poly(arylene ethers) combine these useful properties. Heavy atoms may be added to the polymer in the form of nanoparticles to complete the shielding material.

This research has focused on the production of poly(arylene ethers) with hydrogen-rich bisphenol monomers utilized by Norah Bate.\(^4\) Poly(arylene ethers) are high performance polymers, with excellent thermal and mechanical properties and chemical stability.\(^5\) Both thin films and a thick (3 mm) bar were thermally investigated, and the feasibility of adding tungsten nanoparticles or gadolinium was examined.

C. Background Research

1. Poly(arylene ethers)

a. Properties

Poly(arylene ethers) are high performance polymers. Their good mechanical properties, thermal stability, and resistance to chemical degradation make these polymers useful in a wide variety of applications, and their good processability and low cost make them economically attractive. Poly(arylene ethers) have been used as composite matrices, adhesives, fibers, films, coatings, moldings, and membranes.\(^5\) High hydrogen content may be achieved by varying the monomers used in their manufacture.

b. Polymer synthetic method

Poly(arylene ethers) are commonly synthesized by the reaction of a bisphenol with a dihalide with potassium carbonate, as illustrated in Figure 1. A polar, aprotic
solvent such as dimethylacetamide (DMAc) is used. The resulting white powder is collected and purified, and then can be redissolved in a polar, aprotic solvent such as DMAc or N-methyl-2-pyrrolidinone (NMP). Metal nanoparticles can be added to the solution at this point.

Thin films can be produced by pouring the polymer solution onto a clean, dry glass plate and pulling the solution with a doctor blade to ensure uniform thickness. The film is then cured in an oven at high temperatures to evaporate the solvent. Ideally, the film should be transparent and without bubbles. Bubbles interrupt the structural integrity of the film and weaken its mechanical stability. Also, an opaque film renders it difficult to determine if the metal nanoparticles are distributed evenly in the film.

Figure 1: Synthesis of poly(arylene ethers)\(^1\)

After curing, the film should be transparent and have even thickness and color. Importantly, the film should be creasable. Creasability indicates that the film has high
molecular weight and good mechanical stability. Thus, those films that were able to be creased without snapping were judged to be fit for the aims of this research.\textsuperscript{4}

c. Bisphenol monomer synthetic method

Bisphenol monomers such as 4,4’-(cyclohexane-1,1-diyl)bis(2,6-dimethylphenol), shown in Figure 2, used by Norah Bate, were chosen for their aromatic character and high hydrogen content. The bisphenols were produced in a reaction between a ketone and a phenol following a procedure developed by Weber et al.\textsuperscript{6} This condensation is most often acid-catalyzed, but base-catalyzed reactions seem to yield similar or identical products.

![Figure 2: 4,4’-(cyclohexane-1,1-diyl)bis(2,6-dimethylphenol)](image)

V. Braun postulated two-step mechanisms for both the acid and base catalyzed condensations of phenol with acetone. In both cases, the reaction proceeds through a $p$-isopropenylphenol intermediate. An illustration of the acid-catalyzed reaction is shown below in Figure 3. The acid-catalyzed reaction proceeds in the same way, whatever the nature of the ketone.\textsuperscript{7}
In the first step of the condensation, the phenol adds to the carbonyl group. This addition is followed by an intramolecular loss of one molecule of water, and the addition of the phenol-hydrid formed in step one to another phenol.

![Chemical Reaction Diagram](image)

**Figure 3: Acid-catalyzed mechanism for the synthesis of Bisphenol A**

Some of the main concerns involved in any reaction are efficiency and increasing the yield of the desired product. There are several concerns specific to this category of condensation, including selection of the acid catalyst and ketone reactant, reaction temperature, and appropriate solvent selection.

The acid catalyzed reaction requires a strong acid such as a hydrogen halide or sulfuric acid. Concentrated sulfuric acid would be the most efficient catalyst, but it has a
tendency to cause unwanted sulfonation of phenols and bisphenol derivatives. Because of this, a 70% sulfuric acid solution may be used instead. Hydrogen chloride and concentrated hydrochloric acid are also effective catalysts.

In this reaction, the most reactive ketones are acetone and aliphatic cyclic compounds such as cyclohexanone. Dialkyl ketones condense less efficiently with increasing chain length.\(^8\) This may be due to steric hindrance. With cyclic ketones, the reacting carbon is less sterically hindered because the alkyl chain is not flopping about so much, and the rate of reaction is thus increased.\(^4\)

Another consideration that arises is the choice between a ketone and an aldehyde for the condensation reaction. The proposed mechanism demonstrates that the carbonyl is necessary for the reaction. It would seem that aldehydes would be less sterically hindered than ketones, and would thus be preferable. However, Schnell and Krimm found that ketones tend to give better yields of the desired product than aldehydes do.\(^8\) This effect may be due to the greater stabilization of the carbonyl carbon in ketones during the first step of the reaction. The tertiary cation produced from a ketone would be more stable than the secondary cation produced from an aldehyde, so the first step of the reaction is more likely to occur with a ketone than with an aldehyde.\(^4\)

Yields of the desired product are increased by decreasing the formation of byproducts. Since there is increased byproduct formation at higher temperatures, the condensation should be carried out at a low temperature. Ideally, the reaction should be performed at such a temperature that the product crystallizes out of solution as it is formed, reducing the production of byproducts and preventing the desired product from reacting further.\(^8\)
Since the reaction requires two moles of phenol for every mole of ketone, the reaction should be performed with a large excess of phenol. A molar ratio of at least 4:1 should provide more favorable product yields than the minimal 2:1 ratio. However, such a large excess of phenol may not be fully soluble in the ketone. If the phenol is not fully solvated, the ketone, often in liquid form, will be more available for reaction than the phenol (a solid), causing increased byproduct formation. Fortunately, glacial acetic acid provides an effective solvent for combining the phenol and ketone.4

The final step of the reaction sequence is to neutralize the reaction mixture and purify the product. This may be accomplished by using sodium bicarbonate or carbonate solutions to neutralize the acid, followed by washing and fractional distillation of the products under vacuum. However, the high temperatures used in this method may result in the decomposition of the bisphenol. The decomposition is also accelerated by metal ions and alkaline impurities. To prevent this decomposition, secondary or tertiary alkaline-earth phosphates are often added to inactivate the impurities present. Decomposition may also be minimized by recrystallizing the bisphenol from organic solvents such as toluene or chlorobenzene rather than distilling it; this method was used in this experiment.8

2. Tungsten and Gadolinium

Tungsten is a transition metal with atomic number $Z = 74$ and a melting point of 3422°C. It has naturally-occurring isotopes ranging from 180 amu to 186 amu. At natural isotopic frequencies, tungsten has a decent neutron-capture cross-section, at 18 barns per atom.9 Because of its high atomic number and good neutron-capture radius,
tungsten is an appropriate element for absorbing both high-energy EM radiation and neutrons.

Gadolinium is a lanthanide metal with atomic number Z = 64 and a melting point of 1313°C. It has naturally occurring isotopes ranging from 152 amu to 160 amu. At natural isotopic frequencies, gadolinium has an excellent neutron-capture cross-section, at 49,000 barns per atom. According to the previous discussion of properties conferring shielding status, gadolinium should be a slightly worse absorber of high-energy EM radiation than tungsten, but it should be a much better neutron absorber.

In this study, tungsten nanoparticles were added to the polymer. For the tungsten to be most effective, it must be evenly distributed throughout the polymer. Therefore, the tungsten nanoparticles were modified with an organic agent to make them more compatible with the polymer. In this research, the tungsten was treated with benzyl mercaptan. The polar thiol group interacts with the tungsten while the aromatic benzyl interacts with the organic polymer matrix. Without modification, the tungsten would tend to clump up in the polymer. In a similar fashion, gadolinium was modified with phenylacetate groups to allow it to dissolve in the organic polymer, though in this case the gadolinium began in the form of gadolinium (III) nitrate rather than as neutral nanoparticles.
II. Experimental Methods

A. Synthesis

All reactants were used from Sigma-Aldrich or Fischer without further purification.

1. Bisphenol Monomers

Three bisphenol monomers were synthesized in this study. Their structures are shown in Figure 4 below.

\[
\begin{align*}
(a) & \quad 4,4'-(\text{cyclohexane-1,1-diyl})\text{bis}(2,6\text{-dimethylphenol}) \\
(b) & \quad 4,4'-(4\text{-tert-butylcyclohexane-1,1-diyl})\text{bis}(2,6\text{-dimethylphenol}) \\
(c) & \quad 4,4'-(3,3,5\text{-trimethylcyclohexane-1,1-diyl})\text{bis}(2,6\text{-dimethylphenol})
\end{align*}
\]

Figure 4: Synthesized Bisphenol Monomers

Synthesis of 4,4'-(cyclohexane-1,1-diyl)bis(2,6-dimethylphenol)

Using a procedure developed by Weber et al\textsuperscript{6} and used by Norah Bate,\textsuperscript{4} 4,4'-(cyclohexane-1,1-diyl)bis(2,6-dimethylphenol) (hereafter CB) (Figure 4a) was prepared by combining 20 mL of concentrated sulfuric acid, 38 mL of glacial acetic acid, and 0.5 mL of dimethyl sulfoxide in a round-bottomed flask in an ice bath. A mixture of 20 mL of cyclohexanone and 114.53 g (0.94 mol) of 2,6-dimethylphenol was heated to dissolve all the solids. This solution was then added drop-wise to the acidic mixture and allowed
to react under stirring for 90 minutes, with the flask still in the ice bath. The resulting mixture, in the form of a paste, was transferred to 500 mL 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 250 mL of distilled water and 1.25 g sodium acetate. The mixture was heated to 90°C with stirring and then allowed to cool to room temperature before the bisphenol was recrystallized from chlorobenzene. The bisphenol was then recrystallized from methanol.

**Synthesis of 4,4’-(4-tert-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol)**

In a procedure similar to the one outlined above, 4-tert-butylcyclohexanone was reacted with 2,6-dimethylphenol to form 4,4’-(4-tert-butylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol) (hereafter TBCB) (Figure 4b). 28 mL of sulfuric acid was combined with 1 mL dimethyl sulfoxide in a flask in an ice bath. 28.92g (0.19 mol) of 4-tert-butylcyclohexanone was combined with 114.53 g (0.94 mol) of 2,6-dimethylphenol and 38.2 mL of glacial acetic acid and heated to ensure that the solids dissolved fully. This solution was then added drop-wise to the sulfuric acid/DMSO solution with stirring. The reaction was allowed to continue overnight, still in the flask in the ice bath, though the thick, red, solid product was formed within an hour. Workup and purification was accomplished using a process identical to the one outlined above.
Synthesis 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) (hereafter TMCB) (Figure 4c) is similar to the procedure for the preparation of 4,4’-(4-tert-buthylcyclohexane-1,1-diyl)bis(2,6-dimethylphenol) outlined above, with 3,3,5-trimethylcyclohexanone in place of the 4-tert-butyldicyclohexanone. In this case, however, the reaction mixture was allowed to continue under stirring for four weeks at room temperature before the addition to water. Workup and purification was accomplished using a process identical to the one outlined above.

2. Poly(arylene ethers)

Synthesis

The poly(arylene ethers) were synthesized according to a procedure used by Emily Harbert. One equivalent of bisphenol and 2.4 equivalents of potassium carbonate were dissolved in a toluene/DMAc mixture in a round-bottomed flask with stirring, under nitrogen, at 60°C. The bisphenol dissolved within minutes, but the K$_2$CO$_3$ did not fully dissolve at this temperature. After mixing for three hours, one equivalent of 4,4-difluorobenzophenone (hereafter BPF) was added and the temperature was raised to 160°C. The amount of DMAc was such that the polymer solution in pure DMAc would be 15% polymer by weight. For every 70 mL DMAc used, 30 mL of toluene was used. The apparatus had a Dean-Stark trap filled with toluene under a condenser. As water formed as a reaction byproduct, it formed an azeotrope with toluene and evaporated off before condensing in the condenser and falling to the bottom of the Dean-Stark trap,
since water is denser than toluene. After 24 hours at 160°C, the temperature was raised to 190°C to drive off the toluene and any remaining water into the Dean-Stark trap, which was emptied periodically. The round-bottom flask had three necks: one attached to a nitrogen tank to keep out oxygen and water from the atmosphere, one with a mechanized stirring rod, and one with the Dean-Stark trap. The flask was partially submerged in a silicone oil bath that was heated to the appropriate temperatures.

As an example, a CB/BPF polymer was prepared by combining 20.223 g of CB and 20.692 g of K$_2$CO$_3$ in 192 mL of DMAc and 82 mL of toluene. To this mixture was added 13.736 g of BPF to initiate the polymerization.

**Polymer Purification**

The polymers were purified using a procedure based on the one used by Emily Harbert.$^{10}$ After all the toluene had been driven off (typically after one or two days), the reaction mixture was allowed to cool to room temperature. Then, the reaction mixture was poured into a 4:1 deionized water: glacial acetic acid mixture and blended for 10 to 15 minutes so that the acetic acid would react with any unreacted K$_2$CO$_3$ to form carbon dioxide. If the amount of polymer being produced was large, above 30 g, the reaction mixture was split in two halves, which were blended separately. The resulting white, fluffy polymer powder was then collected on a Büchner funnel, vacuum filtered, and washed five times with boiling deionized water, one time with ethanol, and five times with boiling deionized water to rinse out the acetic acid and various byproducts. After the polymer was dried in an oven at 101-113°C to evaporate the water, it was redissolved in NMP to give a 15% solution and then precipitated, blended, washed, and dried again as
described above. The two purifications were meant to achieve transparent solutions when several grams of polymer were dissolved in NMP to give a 15% solution.

3. **Tungsten Benzyl Mercaptan**

Tungsten benzyl mercaptan was synthesized following a procedure used by Emily Harbert. Tungsten nanoparticles were added to toluene to a concentration of 1 M, and then an amount of benzyl mercaptan was added with a syringe at a ratio of 1 mol benzyl mercaptan to 5 mol tungsten. The suspension was mixed with a stir bar for three hours, and then it was centrifuged and the supernatant decanted and discarded. The solid was dried in an oven at 111°C overnight to drive off the remaining toluene.

4. **Gadolinium Phenylacetate**

Gadolinium phenylacetate was synthesized following a procedure used by Emily Harbert. Gadolinium nitrate was dissolved in water. In a separate beaker, phenylacetic acid was added to water. Ammonium hydroxide and nitric acid were used to adjust the pH of the phenylacetic acid solution to pH 5, at which point the phenylacetic acid dissolved. Gadolinium phenylacetate was made by adding the gadolinium nitrate solution to the phenylacetic acid solution to produce a 1:3 molar ratio of gadolinium nitrate to phenylacetate. The gadolinium phenylacetate precipitated immediately as a white solid. The mixture was refrigerated overnight to fully precipitate the gadolinium phenylacetate. Afterwards, the salt was vacuum filtered on a Büchner funnel and dried in an oven overnight. The gadolinium phenylacetate was found to be soluble in NMP and DMAc.
B. Film Production

1. Thin Films

Thin film samples of polymer were produced following a procedure adapted from that used by Emily Harbert. Samples were prepared by dissolving dry polymer in NMP to give 15% solutions by weight. The samples were dissolved by stirring overnight with a stir bar. After the polymer had fully dissolved, the gadolinium phenylacetate or tungsten benzyl mercaptan was added if desired so that the dried polymer would be 10% metal by weight. Again, the additive was fully dispersed by stirring overnight.

The thin film samples were produced on cleaned glass plates. The plates were cleaned with soap and water and then rinsed sequentially with deionized water, ethanol, and acetone. The glass plate was allowed to dry, and then a razor blade was scraped over the plate to remove any dust that had fallen. The glass plates measured 10 inches x 12 inches x 62.5 mm.

The films were cast using a doctor blade with the thickness set to 0.25 mm. One film was made from each solution. The solution was poured in a line near one end of the plate and then the doctor blade was pulled towards the other end of the plate over the solution line. The films were immediately placed in a programmable oven. The oven ramped up 0.6°C/min to 194°C, held at 194°C for three hours, ramped 0.1°C/min to 202°C, held at 202°C for five hours, and then ramped down at 0.5-1.5°C/min to room temperature.
2. Bar Production

A thick, metal rectangular mold measuring 3.5 in x 0.75 in was assembled and two pieces of thin Kapton film were cut out to fit the mold. The Kapton pieces and the mold pieces were coated with Zvyax release agent twice and dried with a hairdryer to prevent the bar from sticking. One piece of Kapton was put in the bottom of the mold before 5.2 g of the solid polymer powder were poured into the mold, then the other piece of Kapton was put on top of the polymer and the press block was put on top of that. The press block was pounded down with a hammer several times to pack down the polymer so that more could be added.

The press used was a Carver 12-12-H heated press. The mold, with the polymer in it, was placed in the press between the platens and wrapped with insulating material to keep in the heat. The polymer was pressed at 250-400 pounds as it was heated to 440°F (50°F above its glass transition temperature); it was held at that pressure and temperature for one hour before being cooled for one hour under pressure to 330°F. It was then allowed to cool to room temperature overnight under decreasing to no pressure. The pressure was variable because the hydraulic press was hand-pumped and the pressure decayed at a relatively rapid rate, especially as the polymer settled and softened.

C. Characterization

1. Thermogravimetric Analysis

All thin polymer films were tested under nitrogen using a TA Instruments Q500 thermogravimetric analyzer (TGA). This test measured thermal stability by measuring the mass loss as a function of temperature as the films were heated. About 5-15 mg of the
film was heated to 200°C at 10°C/min, held at 200°C for 10 min, heated to 500°C at 10°C/min, held at 500°C for 10 min, and heated to 750°C at 10°C/min. The run was sometimes terminated early after the desired information had been obtained. The nitrogen was maintained with a balance purge flow of 40 mL/min and a sample purge flow of 60 mL/min. The 5%, 10%, and 20% degradation temperatures were found from the mass after the 200°C hold. An example TGA graph can be found in Appendix 1.

2. Differential Scanning Calorimetry

Almost all of the thin films were tested in a TA 2920 modulated differential scanning calorimeter (DSC) under nitrogen in order to determine the glass transition temperature of the polymer. 5-15 mg samples were tested. The temperature was ramped 10°C/min to 250°C, held at 250°C for 2 minutes, ramped 10°C/min down to 60°C, held at 60°C for 2 minutes, ramped 10°C/min to 250°C, held at 250°C for 10 min, and then allowed to cool to room temperature. The T_g was found by locating the inflection point of the steep portion of the second heating curve, or the first heating curve if an inflection point was not available on the second curve. An example DSC graph can be found in Appendix 2.
III. Results and Discussion

A. Bisphenol and Polymer Synthesis and Purification

The CB and TBCB monomers were synthesized without any difficulty and in relatively high yield. However, the TMCB proved to be more troublesome. Even after two weeks of reacting, only 5.37g were produced. The methyls meta to the reactive carbonyl in the 3,3,5-trimethylcyclohexanone may slow down the reaction. The monomers were not analyzed for purity due to time constraints.

The first two polymerizations were conducted with CB and 4,4-dichlorobenzophenone (hereafter BPCI) rather than with the fluoro-analog BPF. These reactions did not produce viscous polymer solutions; in fact, when a pure film was made from the first polymerization of CB/BPCI, the solution was not viscous at all and flowed extensively in the dry box before it was heated in the oven. As can be seen in Table 1, this film showed inferior thermal qualities, most likely indicating shorter chain length and lower molecular weight.

This deficiency could be due to two reasons. Firstly, the CB may have had traces of chlorobenzene left even after washing with ethanol and drying; the CB was dried at 113°C, which is below chlorobenzene’s boiling point of 132°C. This remaining chlorobenzene impurity would have thrown off the precise 1:1 molar ratio of bisphenol: dihalide required to achieve high molecular weight. Less bisphenol than dihalide would result in polymer chains end-capped by the dihalide that could not react further with one another to lengthen. To avoid chlorobenzene impurities, the subsequent monomer syntheses had a recrystallization from methanol after the recrystallization from chlorobenzene to remove any remaining traces of chlorobenzene prior to drying;
methanol has a much lower boiling point than chlorobenzene and so is easier to evaporate from a sample. Secondly, BPCI is less reactive than BPF because fluorine has a higher electron affinity than chlorine and so is more susceptible to nucleophilic attack by the deprotonated bisphenol. Thus, the reaction might have gone less to completion with BPCI than with BPF. BPCI was used because BPF was unavailable at the time.

The polymerizations involving a methanol-recrystallized bisphenol and BPF were more successful and tended to yield viscous polymers. In the first few reactions, water was not observed to accumulate in the Dean-Stark trap. This was discovered to be the result of too rapid nitrogen flow, which swept much of the water-toluene azeotrope out of the condenser before it could condense. Lowering the nitrogen flow resulted in the accumulation of water and full recovery of the toluene from the reaction vessel.

The polymer purification process was quite lengthy and tedious. Each purification took up to several days. After blending and washing, the polymer had to be dried at least overnight, and then had to be redissolved in NMP with stirring overnight. The polymers were extraordinarily hygroscopic, able to absorb up to several times their mass in water as they were washed. This water was removed by drying in the oven; the oven had to be periodically wiped with paper towels to absorb all the water that evaporated from the polymer and then condensed on the glass door of the oven. The fluffiness of the polymer was also problematic, as fine particles would waft into the air and be lost whenever the polymer was transferred to another container. The particles that stuck to the previous container and could not easily be removed were also lost. For this reason, the polymer was not always weighed after purification, as each transfer resulted in the loss of polymer.
B. Thin Film Production

Eight films were produced from the polymers, as listed in Table 1. Unfortunately, none of the films produced were of high quality. None were creasable, and all were brittle to varying degrees. A few films cracked extensively while still in the oven. The surfaces were also irregular. However, all films were transparent, even the two CB/BPF films that were poured from opaque white solutions (most polymers, when dissolved in NMP, were transparent or translucent yellow-brown). The tungsten films tended to be darker than the pure films. The irregularities and cracking may have been due to how the glass plates were cleaned. For all but the CB/BPF films, the glass plates were scrubbed with soap and deionized water and then washed sequentially with deionized water, ethanol, and then acetone. According to Emily Harbert,\textsuperscript{10} this procedure can leave a film of acetone on the glass plate. Although the acetone had visibly evaporated, some invisible traces may have remained that would have interfered with the NMP evaporation process. The CB/BPF film plates were cleaned with the ethanol and acetone washes reversed, and then the plates were dried with a hairdryer. These films were still brittle, but they were in better condition than most of the other films, as can be seen by comparing Figures 5 and 6.
Figure 5: TMCB/BPF Pure Film (very crackled)

Figure 6: CB/BPF 10% Tungsten (less crackled)
Adding tungsten benzyl mercaptan proved to be somewhat troublesome. Since the tungsten nanoparticles were quite dense compared to the polymer solution, they had a tendency to sink to the bottom of the beaker even with vigorous stirring; consequently, when the solution was poured on the glass plate, a fair amount of the tungsten was left behind. Thus, the films that were intended to be 10% tungsten in fact had lower amounts of tungsten, except for the CB/BPF tungsten film, where the tungsten was dissolved with very vigorous stirring. Even then, that solution was quite viscous; its companion pure film, made from the same batch of polymer, had solidified into goopy chunks (which subsequently melted in the oven around 90°C to produce a normal film). The viscosity may have made it easier to suspend the tungsten nanoparticles.

The gadolinium phenylacetate was even more intractable than the tungsten benzyl mercaptan. Even after stirring in the polymer solution for two weeks, the gadolinium phenylacetate did not dissolve very much but remained in a white clump. When the film was poured, the gadolinium glop was poured onto the glass as well and heated in the oven to see what would become of it. The glop melted to form an opaque brown mass that was tested by TGA and DSC for its thermal stability and glass transition temperature, respectively. Because of the difficulty of getting the gadolinium phenylacetate to dissolve, no more gadolinium films were made.

C. Bar Production

The heated press was used to make one polypropylene bar and two Ultem bars before a CB/BPF bar was made. To make the first Ultem bar, the polymer was pressed for 30 minutes at 30°F above its glass transition temperature and then allowed to cool
without pressure. This resulted in a bar with only partially melted Ultem pellets; there were lines between the individual pellets, possibly made more visible by dust (the Ultem was used unpurified and unwashed). To rectify this problem, the next Ultem bar was pressed for an hour at 50°F above its glass transition temperature and then allowed to cool under pressure for an hour before the pressure was relaxed. In this bar, the pellets were much better melted (though lines delineating individual pellets were still visible), so this procedure was used to make the CB/BPF bar.

![Figure 7: CB/BPF Bar](image)

The CB/BPF bar (shown in Figure 7) was less than half the thickness of the second Ultem bar (3 mm rather than 7 mm thick) and used a third as much material (5.2 g rather than 15.0 g) because the powder did not pack very well in the mold. Little polymer fit in the mold, even with repeated packings and hammerings of the press block. Of course, the fluffy powder also plumed in to the air and coated the mold, so the mold had
to be wiped off both before going into the press and after it was disassembled. The resulting bar was transparent like the Ultem and polypropylene bars for most of its length, but with many hair like cracks or lines in the interior. At one end, one fifth of the bar was opaque and white, gradually fading into the transparency of the rest of the bar. This white section may have had less polymer in it, so that when the press block was pressed down it exerted less pressure on this end and the polymer melted to a lesser degree than the rest of the polymer. Using a higher pressure may rectify this problem. Temperature unevenness would not have been the problem, because the mold is thick and symmetrical and was wrapped in insulation during the pressing to keep in heat.

<table>
<thead>
<tr>
<th>Film</th>
<th>Additive</th>
<th>Tₜ (°C)</th>
<th>5% Mass Loss (°C)</th>
<th>10% Mass Loss (°C)</th>
<th>20% Mass Loss (°C)</th>
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<tbody>
<tr>
<td>CB/BPCI</td>
<td>None</td>
<td>NA</td>
<td>350.1</td>
<td>395.4</td>
<td>419.5</td>
</tr>
<tr>
<td>TBCB/BPF</td>
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<td>222</td>
<td>417.1</td>
<td>430.3</td>
<td>438.5</td>
</tr>
<tr>
<td>TBCB/BPF</td>
<td>W</td>
<td>223</td>
<td>414.6</td>
<td>427.7</td>
<td>436.2</td>
</tr>
<tr>
<td>TBCB/BPF</td>
<td>Gd</td>
<td>NA</td>
<td>311.7</td>
<td>323.8</td>
<td>336.7</td>
</tr>
<tr>
<td>TBCB/BPF</td>
<td>Gd Glop</td>
<td>215</td>
<td>315.5</td>
<td>354</td>
<td>420.1</td>
</tr>
<tr>
<td>TMCB/BPF</td>
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<td>384.5</td>
<td>423.1</td>
<td>432.2</td>
</tr>
<tr>
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<td>418.6</td>
<td>428.5</td>
<td>435.3</td>
</tr>
<tr>
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<td>192</td>
<td>414.8</td>
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<tr>
<td>CB/BPF</td>
<td>W</td>
<td>194</td>
<td>420.9</td>
<td>435.1</td>
<td>443.6</td>
</tr>
</tbody>
</table>

Table 1: Thermal Film Data

D. Thermogravimetric Analysis

All of the films and the gadolinium glop from the gadolinium TBCB/BPF were subjected to thermogravimetric analysis (TGA). Most of the polymers showed excellent thermal stability, with an average 5% degradation temperature of 392°C, an average 10% degradation temperature of 412°C, and an average 20% degradation temperature of
Most of the films had temperatures above these averages. The tungsten films had similar or slightly better degradation temperatures than the pure films, indicating that adding tungsten nanoparticles does not hinder a polymer’s thermal stability and may even enhance it. The pure films on average performed 6°C worse than the corresponding pure polyimide films made by Norah Bate using the same bisphenols,\textsuperscript{12} which is impressive.

Despite the mostly excellent thermal stabilities, there were a few films that performed poorly. The CB/BPCI film has already been discussed. The TBCB/BPF gadolinium film had a thermal degradation temperature nearly 100°C lower than that of the pure film. This anomalous result may be due to the phenylacetate of the gadolinium phenylacetate degrading and leaving the polymer.\textsuperscript{13} However, this seems unlikely, because little of the gadolinium phenylacetate dissolved in the polymer. In addition, the gadolinium glop showed substantially superior 10% and 20% degradation temperatures, with a 20% degradation temperature approaching that of the other polymers (the gadolinium glop likely had some polymer in it). The TBCB/BPF gadolinium film was made from the same bisphenol and polymer as the other TBCB/BPF films.

E. Differential Scanning Calorimetry

At least one DSC experiment was performed on each film. Glass transition temperatures (T\textsubscript{g}’s) were obtained for almost all films and the gadolinium glop, except for the TBCB/BPF gadolinium film; no steep slope was observed for this sample, possibly because the sample was too small. The film itself was very brittle, and it was difficult to get enough material for the DSC pan, so a second pan was not made.
The glass transition temperatures were consistent between the pure and tungsten films, varying between the two by only a few degrees at most. It appears that tungsten nanoparticles have little effect on the glass transition temperature. This makes sense, since the nanoparticles are so large relative to the polymer and spaced relatively far apart so that they do not affect the polymer molecules sliding past one another very much.

The $T_g$’s increased with increasing steric bulk on the cyclohexylene units; the $T_g$ for pure cyclohexylene was less than that of the trimethylcyclohexylene, which in turn was less than that of the tert-butylcyclohexylene. This is reasonable, as the bulky groups extending from the cyclohexylene probably bump into one another on different polymer molecules, preventing the molecules from sliding past one another and increasing the temperature at which the polymer melts. This same order was observed by Norah Bate; her polyimide $T_g$’s were 273°C, 283°C, and 288°C for her CB, TMCB, and TBCB polyimides, respectively.\(^\text{12}\)

Norah Bate’s polyimides showed higher $T_g$’s than the poly(arylene ethers) reported here. As can be seen in Figure 8, her polyimides contain long, rigid 3,3’,4,4’-benzophenone tetracarboxylic dianhydride (BTDA) subunits that provide substantial stiffness and prevent the polymer from moving about freely at lower temperatures, so the melting temperature is higher. The poly(arylene ethers) described here have rigid but substantially shorter BPF subunits. Because BPF is shorter than BTDA, there is more of the flexible bisphenol per milligram of polymer, and so the $T_g$ is lower.\(^\text{12}\)
Figure 8: TED/BTDA vs. CB/BPF

TED/BTDA
$T_g = 273^\circ C$

CB/BPF
$T_g = 192^\circ C$
IV. Conclusion

The materials currently used for radiation shielding are insufficient for deep space applications. The threats of galactic cosmic radiation, solar energetic particles, neutrons, and electromagnetic radiation require the production of novel materials for shielding people and equipment in space.

In this research, high hydrogen-content poly(arylene ethers) were synthesized. In general, poly(arylene ethers) are potentially useful for a wide range of applications. They have excellent thermal and mechanical properties, as well as chemical stability.$^5$ Bisphenol monomers first produced by Norah Bate, namely CB, TMCB, and TBCB,$^4$ were synthesized and incorporated into poly(arylene ethers) using a procedure pioneered by Emily Harbert.$^{10}$

Eight thin films and one thick sample were produced from the poly(arylene ethers). Despite the brittleness of all of the thin films, most of them showed excellent thermal stability, approaching and exceeding 400°C before significant breakdown occurred. If creasable films of higher molecular weight were produced, these thermal properties would only improve. Tungsten and gadolinium proved difficult to integrate into the polymers, but tungsten proved to have no detrimental effect on the thermal stability of the polymer. The bar, though harboring irregularities, provides a promising prototype for future studies.
V. Future Research

Efforts should be made to produce creasable films from the polymers used in this study. Further study into the modification of gadolinium may allow it to be successfully incorporated into polymers, or tungsten may be used instead. Further bars should be made, especially ones containing tungsten or gadolinium. Then, the thin films and bars may be submitted to X-ray and neutron bombardment to determine their shielding properties.

VI. Funding

Funding was provided by International Scientific Technologies, Inc. using a grant from the National Aeronautics and Space Administration.
Sample: TBCB-BPF 10% W
Size: 7.9960 mg
Method: Polyether ramp
Comment: brittle

File: C:\Ellen\TBCB-BPF 10% W TGA.001
Operator: MAJ
Run Date: 2011-04-18 23:33
Instrument: TGA Q500 V6.3 Build 189

Appendix 1: Sample TGA Graph
References:


13. Private conversation with Dr. Robert Orwoll