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Synthesis and Characterization of Interpenetrating Polymer Networks for Applications in Extraterrestrial Radiation Shielding

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College of William and Mary

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Synthesis and Characterization of Interpenetrating Polymer Networks for Applications in Extraterrestrial Radiation Shielding

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

By

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May 5, 2016
Abstract

During interplanetary voyages spacecraft are exposed to a variety of ionizing radiations, including high intensity electromagnetic radiation and galactic cosmic rays, creating conditions that are harmful to both instrumentation and human passengers. Current shielding methods offer a degree of protection, but they are not suitable for long term missions or for habitation on extraterrestrial environments, and traditional terrestrial shields are too heavy to be carried on these missions. Organic polymers offer a versatile, lightweight solution to many of the difficulties in shielding, however they also present difficulties establishing a sufficiently high hydrogen content while maintaining high mechanical and thermal stability. By mixing two polymer species together it is possible to produce a material that combines the properties of both polymers, yet due to the immiscible nature of most polymeric materials, using polymer blends is not a practical solution. However it is possible to bypass the issue of immiscibility by dissolving different polymer species together and crosslinking like chains together, forming an interpenetrating polymer network (IPN).

This research focuses on the synthesis and characterization of IPNs consisting of aliphatic and aromatic polymer species, containing a high hydrogen content and good mechanical properties, respectively, to be used in extraterrestrial environments to provide protection from ionizing radiation for humans and instrumentation alike.
# Table of Contents

**Abstract** ........................................................................... iii
**List of Common Abbreviations** ........................................ i

## Introduction

- 1) Space Exploration and Radiation Shielding ...................... 1
- 2) Types of Interplanetary Radiation .................................. 1
- 3) The Issues of Extraterrestrial Radiation .......................... 3
- 4) Considerations of Shielding Solutions ............................ 5
- 5) Organic Composites: Polymer Blends and Interpenetrating Networks ......................................................... 7

## Synthetic Methodologies

- 1) Basis for Research Approach ......................................... 8
- 2) Preparation and Crosslinking of PPO ............................. 9
- 3) Preparation and Crosslinking of PB ............................... 13
- 4) Preparation and Crosslinking of PiP .............................. 16
- 5) Synthesis of Binary Systems with BrPPO and PB .......... 18
- 6) Synthesis of Binary Systems with BrPPO and PiP ......... 19

## Material Characterization

- 1) Overview of Polymer Characterization Methods .......... 21
- 2) Differential Scanning Calorimetry ............................... 21
- 3) Attenuated Total Reflectance Fourier Transform Infrared Spectrometry .......................................................... 24
- 4) Swell Testing and Extraction ......................................... 25
- 5) Elemental Analysis ................................................... 27

## Discussion

- 1) Synthetic Efforts .......................................................... 28
- 2) Characterization Efforts ............................................... 30
- 2) Conclusions ................................................................ 35

## Proposed Future Research

- 1) Final Goals of the Project ............................................ 36
- 2) Continuing Current Research Efforts ........................... 36
- 3) Expanding Research Efforts: New Materials and Studies .......................................................... 42

## Appendices of Collected Analytical Results

- 1) DSC Thermographs .................................................... 46
- 2) ATR-FTIR Spectra and their Corresponding Peaks ....... 52
- 3) Galbraith Results ..................................................... 59

## References ........................................................................ 61

## Acknowledgements ............................................................ 64
List of Common Abbreviations

BPO – Benzoyl Peroxide
BrPPO – Brominated Poly(2,6-dimethyl-1,4-phenylene oxide)
DSC – Differential Scanning Calorimetry
EDA – Ethylene Diamine
EGDMA – Ethylene Glycol Dimethacrylate
GCR – Galactic Cosmic Radiation
HZE – High charge, high energy
IPN – Interpenetrating Polymer Network
\( \bar{M}_w \) – Weight Average Molecular Wight
PB – Polybutadiene
PiP – Polyisoprene
PPO – Poly(2,6-dimethyl-1,4-phenylene oxide)
SIN – Simultaneous Interpenetrating Network
SPEs – Solar Particle Events
\( T_g \) – Glass transition temperature
Introduction

Space Exploration and Radiation

One of the greatest hindrances to interplanetary space travel has consistently been the effects of ionizing radiation on both instrumental and biological components, including humans, during the missions. This creates several challenges when attempting travel in space. On the earth’s surface the environment enjoys higher degrees of protection from these conditions due to the natural shielding provided by the planet’s magnetic fields and atmosphere. Furthermore terrestrial radiation shields are often reliant on heavy components, such as concrete and lead, which exceed the weight carrying capacities of spacecraft. Due to these restrictions new, light-weight materials capable of withstanding these harsh conditions to shield spacecraft must be developed. Additionally these materials must be able to withstand extended exposure to a wide array of high energy charged particle species, different from radiation encountered in terrestrial environments.  

Types of Interplanetary Radiation

Trapped Radiation

On the surface of the earth, the geomagnetic fields provide a large degree of protection from the conditions in space. However these fields are capable of trapping charged species, predominately protons and electrons, within regions known as the Van Allen belts (Fig. 1). These radiation belts form two distinct regions between 400 km and 18,400 km above the earth’s surface, though this region

*Figure 1 – Van Allen radiation belts*
changes in response to solar weather\textsuperscript{10,14}. Particles trapped within these belts have a wide array of energies associated with them, and travel between “mirror points” located at either end of the belt limits\textsuperscript{10,16}. Despite the seemingly sizable range of these belts, they fill only a small region of the space between the earth and the moon\textsuperscript{10}.

\textbf{Solar Particle Events (SPEs)}

Solar weather accounts for a large amount of low-mass particles in the interplanetary space within the solar system. During solar flares energetic particulates – including electrons, protons, alpha particles, and trace quantities of heavier elements – are jettisoned into space. While the earth’s geomagnetic fields provide surface protection from these particles, larger solar events are capable of producing high energy species capable of causing significant damage to any mission traveling within or beyond the magnetic fields\textsuperscript{10}. However SPEs are difficult to predict, throwing random amounts of radiation of varying energies into space directionally\textsuperscript{10}. Due to the uncertainties associated with these events, SPEs present a significant challenge to protecting sensitive instrumentation and crew members during extended missions. Fortunately, most events do not last for long periods of time, and therefore the spikes in radiation do not persist for much longer than a few days\textsuperscript{10}.

\textbf{Galactic Cosmic Radiation (GCR)}

Galactic cosmic radiation consists of highly energetic ionized atomic nuclei and gamma rays originating outside the solar system. GCR is made up of about 87\% hydrogen nuclei, 12\% helium nuclei, and 1\% all other naturally occurring nuclei, all without electrons resulting in very high charge, high mass (HZE) particles for some components\textsuperscript{2,4,10,18}. These nuclei are commonly believed to have originated in supernovae, in part due to the massive kinetic energies they can attain, which can achieve thousands of GeV per Da, though this theory does
not necessarily explain the presence of ultra-high energy radiation that can exceed energies up to 100 TeV\textsuperscript{10,18}. Though elemental ions up to uranium have been detected, nuclei larger than iron-56 become progressively less common\textsuperscript{2,4,10}. Although GCR can be attenuated by geomagnetic fields, particles with higher kinetic energy are capable of reaching the earth’s surface. Because of the large amount of damage these rays can inflict on biological and technological materials, they pose special risk to missions traveling beyond the earth’s magnetic fields and have been subject to a great deal of research regarding their attenuation\textsuperscript{2,3,4,10,13}.

**The Issues of Extraterrestrial Radiation**

Although the presence of the particulate radiation, including HZE nuclei, has long been known by astronomers, they continue to represent a significant barrier to space exploration due to their effects on vital components of missions through interplanetary space, most notably the detrimental effects on human health. In terrestrial environments, radiation exposure is well known to damage human cells and cause cancers through damage of DNA helices (Fig. 2), most often by exposure to high energy electromagnetic radiation sources, such as the sun and medical x-rays\textsuperscript{14,17}. However, beyond the earth’s atmosphere and geomagnetic fields, high energy ionizing radiation, especially HZE ions, are

![Figure 2 – Comparison of damage to DNA helix by X-Ray and HZE ion\textsuperscript{12}](image-url)
capable of devastating living cells and destroying DNA helices (Fig. 2). Additionally, extended exposure to these ionizing heavy ions can result in charge accumulation in technological components of space craft, potentially causing severe damage to internal portions of vital hardware. Without sufficient protection for these aspects any mission through interplanetary space will be risking disaster.

Although a wide array of radiation shielding materials have been developed for use in terrestrial environments, several restrictions prevent these from being adapted for use in space. The predominate restriction, as indicated earlier, is the extreme weight that many of these shields, often comprised of dense materials such as water and concrete, whose masses exceed the weight carrying capacities of craft intended to be launched into space. Additionally, there is such a significant difference between the radiation energies experienced on earth’s surface and in space that it results in a complication of attenuation physics. Strong terrestrial radiation sources, such as reactors, typically generate ionizing radiation in the MeV range which can be deflected through collisional interactions, modeled as semi-elastic collisions, with bound electrons and nuclei, resulting in limited loss of kinetic energy for each collision.

Because of this, terrestrial shielding materials around strong sources can rely on highly dense materials, such as concrete with special additives, to sufficiently lower the kinetic energies. However, for GCR, which – as previously stated – can readily achieve several thousand GeV across a far greater range of masses, the primary energy-loss mechanism results from Coulombic interactions between the completely ionized nuclei and the electron density and nuclei within the material it strikes. Therefore protium, possessing a 1:1 charge-to-mass ratio, is the best atomic species for shielding against extraterrestrial radiation, as all interactions...
with HZE particles will result in energy-reducing Coulombic interactions$^{2,4}$. This differs from interactions between GCR and atomic species with larger nuclei, such as Carbon-12, which has a reduced charge: mass ratio due to the presence of neutrons. Therefore interactions between HZE radiation and one gram of hydrogen atoms will result in greater reduction of the particulate radiation's kinetic energy than interactions between a particle of the same energy and one gram of carbon atoms, as half the mass of $^{12}$C is comprised of neutrons.

Additionally, protium will not undergo nuclear fragmentation if impacted with HZE particles, reducing the amount of secondary radiation$^{2,4}$. This is contrasted with Carbon-12, which can fragment into secondary radiation (that is, alpha-, beta-particles and neutrons). These fragmentations will actually produce a net increase in radiative species in shielding materials that are too thin, resulting in additional considerations that are beyond the scope of this study.

**Consideration of Shielding Solutions**

With the aforementioned considerations in mind, the most straightforward and best theoretical solution would be liquid hydrogen$^{3}$. However this presents a host of practical issues, and therefore it becomes necessary to consider other desirable qualities that are necessary for the material to be readily transported into space. The need for high hydrogen content has been established, and additionally high thermal stability and good mechanical strength is necessary for the shield to withstand the various conditions it will experience in outer space. The need for this mechanical strength arises from the need for components on spacecraft to be multifunctional for the purpose of simultaneously maximizing

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>-85</td>
</tr>
<tr>
<td>Polyisoprene (cis)</td>
<td>-73</td>
</tr>
<tr>
<td>Polyisoprene (trans)</td>
<td>-53</td>
</tr>
<tr>
<td>Polybutadiene (cis)</td>
<td>-108</td>
</tr>
<tr>
<td>Polybutadiene (trans)</td>
<td>-18</td>
</tr>
</tbody>
</table>

*Table 1 - Glass transitions of common aliphatic polymers$^{22}$.*
space conservation and reducing weight by making it unnecessary to attach many single-purpose components. Organic polymeric materials present a readily available class of lightweight materials that are relatively easy to manipulate, and can be designed to be high performance, and to hold large amounts of hydrogen.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>100</td>
</tr>
<tr>
<td>Poly(Phenylene oxide)</td>
<td>210</td>
</tr>
<tr>
<td>LARC-TPI</td>
<td>246</td>
</tr>
</tbody>
</table>

*Table 2 – Glass transitions of organic polymers with aromatic moieties*.

Unfortunately, despite the large degree of control synthetic chemistry provides over organic polymers and their properties, aliphatic polymers that provide the highest percent mass of hydrogen are also generally not high performance materials. Table 1 lists polyethylene

![Images of polymers](image1.png)

*Figure 3 – Examples of organic polymers with aliphatic (A) and aromatic (B) character.*
which, along with polypropylene, is the organic polymer with the highest hydrogen concentration, as well as other aliphatic polymers (Fig. 3), along with their glass transition temperatures. While higher $T_g$ values indicate a material is better able to retain mechanical properties at higher temperatures (with the exception of crystalline polyethylene, which has increased mechanical properties arising from its crystallinity despite its low $T_g$), these aliphatic polymers consistently display glass transitions below 0°C, indicating significantly decreased mechanical behavior even at standard temperature and pressure. In order to gain the desired increase in thermal stability and mechanical strength, moieties with characteristics such as resonance stabilization and intermolecular forces are necessary. For applications in radiation shielding, it is preferable to have increased bond strength to better withstand the high linear energy transfer imparted by HZE ions, and therefore resonance stabilization provided by aromaticity is necessary, despite most often coming at the expense of hydrogen content.

Some examples of glass transition temperatures of organic polymers with aromatic regions (Fig. 3) are given in Table 2. It is immediately clear that these aromatic-containing polymers possess significantly stronger structural properties than the listed aliphatic materials. By combining the structural capacities of aromatic polymers with the hydrogen content of aliphatic polymers, it becomes possible to develop materials which are structurally functional components of the craft while providing radiation protection.

*Organic Composites: Polymer Blends and Interpenetrating Networks*

The most straightforward approach to synthesizing a material with the combined properties of each type of material is to mix together an aliphatic and an aromatic polymer to generate an organic composite material. Indeed this is the logical underpinning behind the
concept of polymer blends, which, in a few instances, are materials used in commercial and industrial applications to achieve combinations of desirable bulk properties with the benefit of the lightweight nature of organic materials. Unfortunately most polymer pairs are immiscible, greatly restricting the combinations of blends that can be produced.

An approach to bypassing this innate restriction on polymer mixing is the synthesis of an interpenetrating polymer network (IPN). IPNs are synthesized by dissolving two different polymer species together in a common solvent, and crosslinking like chains together simultaneously to entangle the two different polymers together and physically prevent phase separation on a molecular level. Although often difficult to synthesize, IPNs present a viable solution in specialty applications that require specific combinations of polymeric materials’ properties.

This research proposes the synthesis of IPNs combining aromatic and aliphatic polymer species for application as lightweight radiation shielding from GCR and from other forms of ionizing radiation found in extraterrestrial environments.

**Synthetic Methodology**

*Basis for Research Methods*

An example of an IPN of aromatic and aliphatic polymers was found in a publication by Frisch and Hua in 1989. This article outlines the synthesis and characterization of full and semi-IPNs of poly(2,6-dimethyl-1,4-phenylene oxide) (hereafter referred to simply as ‘poly(phenylene oxide)’ or PPO) and polybutadiene (Fig. 3), seemingly as an intellectual exercise. However this work is noteworthy for a few district reasons. It features relatively simple crosslinking reactions between commercially available polymer chains both of which exhibit properties desirable for radiation shields. Because of this the authors are spared the challenge of attempting
simultaneous polymerizations, and are able to go almost directly into synthesizing a simultaneous IPN (SIN)\textsuperscript{23}. Despite the apparent straightforward nature of this synthesis the combination of a scarcity of details and the age of the publication itself allowed for challenges in the synthetic methodologies. Thus research efforts were based on developing a modified synthetic methodology focused on using modern procedures to achieve the same results that Frisch reported.

*Preparation and Crosslinking of Brominated Poly(Phenylene Oxide)*

![Conversion of PPO (A) to BrPPO (B), and crosslinking (C).](image)

**Cleaning Procedure**

First, the poly(arylene ether) PPO was prepared following the recommendations made by Frisch and Hua (Fig. 4). The homopolymer was purchased from Sigma Aldrich with $\overline{M}_n = 20,000$ g/mol. The polymer sample was accurately weighed to ±1.0mg, and was dissolved in chloroform (instead of the suggested carbon tetrachloride) to produce a 0.8M PPO/CHCl\textsubscript{3} solution, where the concentration of the solution is expressed as the molarity of the PPO repeat unit (120.144 g/mol). The polymer was then precipitated in alcohol via blender to purify it.

Early experiments followed literature guidelines and used methanol for precipitation, but it was discovered that using ethanol instead returns approximately 99% PPO, an improvement over
MeOH, which generally returned between 92-96%. Both EtOH and MeOH were found to be strongly preferable to other solvents, such as MeOH/H₂O/Acetonitrile (2:1:1 ratio) mixed solutions, which were insufficient for precipitation and generally returned 70-73% PPO, despite the strongly polar nature of acetonitrile. The collected PPO was rinsed with chilled EtOH, and allowed to dry on a Büchner funnel.

**Bromination Procedure**

Once the PPO sample was dried, it was prepared for bromination. This was achieved using a photochemical activation of N-bromosuccinimide (NBS) to produce a free radical bromination of the allylic methyl substituents (Fig. 5). As this reaction is relatively straightforward, the procedure outlined by Frisch and Hua was utilized without complication.

The homopolymer was added to a four-neck round-bottom flask - fitted with a nitrogen inlet, condensing tube, drying tube, and thermometer - and once again dissolved in chloroform to achieve a 0.8M solution. The flask was placed in a water bath and its temperature was raised to 50°C. The solution was stirred vigorously to facilitate dissolution of PPO, which is inclined to stick together in chloroform. After the polymer was completely dissolved, the corresponding mass of

![Figure 5 – Primary mechanism of Radical Allylic Bromination of PPO to BrPPO (B) using NBS (A)](image-url)
NBS was added to the solution with a reagent: repeat unit ratio of 1mol NBS: 10mol PPO repeat units. The reacting solution was then illuminated with a 100W tungsten bulb and stirred. After three hours the light was turned off, and the solution was allowed to return to room temperature. Then the brominated polymer was precipitated by mixing the solution with MeOH in a blender, as with the cleaning procedure. The brominated polymer was then rinsed with cold MeOH and allowed to dry.

Crosslinking

Once the BrPPO sample had been successfully cleaned and dried, it was prepared for the crosslinking reaction. The crosslinking itself is a completely chemical process achieved through alkyl amination by reacting a diamine with the alkyl bromine (Fig. 6). In order to achieve this, Frisch prescribed dissolving BrPPO in toluene with a solute: solvent ratio of 1g BrPPO: 10mL

![Crosslinking mechanism of BrPPO with the crosslinking reagent ethylene diamine](image)

*Figure 6 – Crosslinking mechanism of BrPPO with the crosslinking reagent ethylene diamine*.  

11
toluene in a nitrogen-purged round-bottom flask at 60°C. Then the crosslinking reagent, ethylene diamine (EDA), was added at a ratio of 11.2μL EDA: 1.00 g BrPPO. The reaction was stirred rapidly for 10 minutes, then transferred in a Petri dish to a circulating oven at 70°C for two days. The temperature was then raised to 90°C for three hours, and then the product was allowed to dry at 60°C.

This procedure was tested by submitting a sample of the dried product to Galbraith Laboratories for elemental analysis, and it was determined that the above procedure is sufficient to induce crosslinking in BrPPO samples. Several films were produced via this procedure, some in glass evaporating dishes and others in aluminum weighing pans covered with aluminum foil. It was discovered that BrPPO crosslinked in the weighing dishes had bonded with their container upon drying, and so glass evaporating dishes proved to be the preferable vessels for holding the solution. Additionally, after several tests the drying temperature was reduced to 50°C in order to reduce the amount of sample clinging to the sides of the solution container. After drying at 50°C overnight in a circulating oven, the films were then moved to a vacuum oven at 60°C in order to remove any toluene trapped in the network.

In order to assess whether the crosslinking reaction experienced diminished effectiveness at increased temperatures that would interfere with procedural changes for polybutadiene crosslinking, a sample of BrPPO was crosslinked at 75°C, assessed via mass loss analysis, and determined to be similarly effective at the higher temperature.
Preparation and Crosslinking of Polybutadiene

Linear polybutadiene (PB) was employed as the aliphatic material for the original IPN. Figure 7 shows the main route by which PB is crosslinked, although due to the nature of radical interactions there are a few possible potential products for this reaction. The mechanism for this general reaction is shown in Figure 8, and makes it apparent how other possible products can be formed. The radical initiator, benzoyl peroxide (BPO), dissociates at 70°C and reacts with a terminal alkene on the crosslinking reagent, ethylene glycol dimethacrylate (EGDMA), allowing the newly formed radical EDGMA to react with the alkene moieties within a PB chain. At this point, the radical on the hydrocarbon chain is able to react with a BPO radical (Fig. 7, 8) or an additional radical EGDMA to terminate the reaction. As the reaction repeats, PB chains become linked together to form an aliphatic network.

Figure 7 – Linear PB (A) experiences a reaction between its alkene functionality and radical crosslinking reagents. The radical on the polymer chain (B) can terminate by reacting with additional BPO (C) or with other radical species (not pictured) to complete the reaction. See Fig 8 for more detail.
Initially PB with $\bar{M}_w = 2000\text{g/mol}$ was utilized, however it was determined that the chains in this sample were of insufficient length to produce a sufficient network. Instead PB with $\bar{M}_w = 200,000\text{g/mol}$ was employed for the purpose of this research. Both were purchased from Sigma Aldrich.

**Cleaning**
For the purpose of this reaction, the publication recommends cleaning PB by dissolving it in toluene and precipitating it in methanol\(^1\). However it was determined that the homopolymer can be crosslinked without any special preparation. The linear polymer was stored under vacuum in order to prevent oxidation of the $\pi$-bonds by the atmosphere.

**Crosslinking**
Polybutadiene is dissolved in toluene with a solute: solvent ratio of 1.000g PB: 15.0mL toluene in a round-bottom flask at room temperature. Because linear PB chains are able to pack quite closely the solution was stirred overnight to ensure the chains were sufficiently dissolved. This reaction was run with the same conditions as the crosslinking of BrPPO, as the reactions would be run simultaneously when synthesizing the binary system. The solution was heated to 60°C, and the crosslinking reagents were weighed accurately within ±0.0001g, and added to the stirring solution. BPO was added to the reaction with a reagent: polymer ratio of 0.0050g BPO: 1.0000g PB, and EGDMA was added with a ratio of 24.0μL EDGMA: 1.0000g PB. As with BrPPO, Frisch recommended allowing the reaction to stir for 10 minutes, transferring the reaction solution to a Petri dish – this time with a layer of clean liquid mercury on the bottom to prevent adhesion to the container – and placing the reaction in an oven at 70°C for 48 hours and then 90°C for three hours\(^1\).
Unlike the procedure to crosslink BrPPO, this procedure was determined to be nonviable for crosslinking PB. To produce a material with sufficient crosslinking, a new procedure was developed, addressing a variety of issues with the published method\textsuperscript{1}.

\textit{Figure 8 – Primary radical mechanism for crosslinking of PB.}
As mentioned, PB was dissolved by stirring with toluene overnight at room temperature in a stoppered 3-neck round-bottom flask, purged with nitrogen. To set up the reaction, the round-bottom flask was placed in a water bath, and fitted with a nitrogen inlet, a condenser and drying tube, and a glass stopper. The flask was purged with dry nitrogen as the water bath was heated to 75°C. Both BPO and EGDMA were added in the same ratios described by Frisch and Hua, and the reaction was stirred vigorously for three hours. As with Frisch’s procedure, the reaction solution was then transferred to a glass evaporating dish, covered with aluminum foil, and placed in a circulating oven at 70°C for 48 hours and then for three hours at 90°C.

An adequate substitute for liquid mercury has yet to be found to prevent the polymer from adhering to its container, although experiments with Zyvax® release agents have been carried out in aluminum weighing dishes and have shown promising results. Also it was found that when using glass dishes, the favorable interactions between the glass silicates and water have been exploited to remove samples that became stuck.

Preparation and Crosslinking of Polyisoprene

![Figure 9 – Crosslinking of linear PiP (A) via radical crosslinking](image)
In order to see if these reactions are effective when employing alternative polymeric species, polyisoprene (PiP) was substituted for PB. As shown in Figure 9 the reaction scheme is nearly identical to the crosslinking of PB. While there is not a particularly striking difference between the structures of PB and PiP, the latter possesses bulk properties that make it simpler to work with in laboratory conditions. This polymeric material is widely known to be relatively straightforward to manipulate, and, due to its broad applicability in many commercial and industrial settings, there is ample preexisting research to address issues that may arise. Additionally, PiP can be purchased already polymerized – like PB and PPO – and ordered in pellets, a form that makes it significantly easier to weigh quickly and accurately as compared to PB, which is available in tacky sheets.

**Crosslinking**

As with PB, PiP was used as purchased from Sigma-Aldrich Chemicals. The linear polymer was purchased in the form of dense pellets, and consequently required time and heating to dissolve. Samples were dissolved in the common solvent toluene at a solute: solvent ratio of 1.000g PiP: 20.0mL toluene. This solution was stirred overnight at 60°C in a three-neck round-bottom flask with a condenser and two glass stoppers. To ensure proper crosslinking, the same procedure that was used for PB was also utilized for PiP. As the solution temperature was raised to 70°C, the glass stoppers are replaced with a nitrogen inlet and drying tube. As there was not a significant difference in polymer structure and therefore changes in chemistry are not predicted, the same polymer: reagent ratios – 0.0050g BPO: 1.0000g PiP, and 24.0μL EDGMA:
1.0000g PiP – were utilized for the crosslinking reaction. The reaction solution was allowed to stir vigorously for three hours at 70°C before being transferred into a glass evaporating dish, covered tightly with aluminum foil, and placed in a circulating oven at 70°C for 48 hours. After 48 hours, the temperature was raised to 90°C for three hours, and then the foil cover was removed and the product was allowed to dry at 50°C.

**Synthesis of Binary Systems with BrPPO and PB**

After determining that both BrPPO and PB underwent the reactions described and consistently produced stable products, full IPNs combining the two species were synthesized utilizing the modified reaction conditions described for polybutadiene.

Initially the procedure described by Frisch and Hua was set up with the expectation that the conditions described in the publication could be replicated¹. However a variety of issues with the procedure became apparent that prevented reproduction of the original study. The authors described a possible range of solvent volumes that might be used during the synthesis to produce IPNs with varying homopolymer ratio concentrations without specification for any particular combination. Additionally the procedure implied that all polymers and reagents should be added simultaneously, yet both aliphatic crosslinking reagents are thermally sensitive, and EDA is air-sensitive. Therefore, these aspects of the procedure were disregarded to prevent the risk of decreased reactivity during the extended period of time required for the dissolution of high molecular weight PB.

Due to these limitations, IPN synthesis was approached stepwise to ensure proper preparation of starting materials. As before, PB was dissolved by stirring in toluene - 1.000g PB: 15.0mL toluene - overnight in a three-neck flask purged with nitrogen. The flask was placed in a
water bath, heated to 70°C, and fitted with a nitrogen inlet, a condenser with a drying tube, and a glass stopper. Once the flask reached 70°C, the aliphatic crosslinking reagents were added to the solution at the same ratios prescribed for homopolymer crosslinking, and the reaction was allowed to stir vigorously for two hours.

As the aliphatic crosslinking reaction was stirring, the aromatic component was prepared. BrPPO was dissolved in toluene by stirring – 1g BrPPO: 10mL toluene – in a stoppered Erlenmeyer flask. Once the homopolymer was sufficiently dissolved, the solution was transferred to an addition funnel, and set aside until the two hour time-point was reached.

After two hours the glass stopper on the round-bottom flask was removed, and replaced with the addition funnel containing the BrPPO solution. This solution was slowly added to the stirring reaction solution until no solution remained in the addition funnel, and then the glass stopper was replaced and the polymers were allowed to mix in solution for an hour. Once this hour passed, the aromatic crosslinking agent EDA was added with the prescribed reagent-polymer ratio, and this reaction was stirred for an additional 10 minutes.

Once the final 10 minutes passed, the reaction solution was transferred into a glass evaporating dish, covered tightly with aluminum foil, and placed in a circulating oven at 70°C. As with each of the homopolymer reactions, the sample was left in the oven at 70°C for 48 hours, then raised to 90°C for three hours before removing the aluminum foil and allowing the product to dry at 50°C.

**Synthesis of Binary Systems with BrPPO and PiP**

In order to start moving beyond the systems published by Frisch and Hua, networks were synthesized utilizing PiP as the aliphatic species'. It was not noted until later that a
network with similar components had been synthesized by De Barros, Huang and Frisch, yet as
the system reported in that publication utilized different crosslinking chemistry for the aliphatic
polymer this is considered the first test of this particular approach to a PiP-BrPPO IPN.

As with the homopolymer, PiP was dissolved in toluene with a 1.000g PiP: 20.0mL
toluene ratio overnight at 60°C. The solution was mixed in a three-neck round-bottom flask in a
water bath and purged of air. The flask was fitted with a nitrogen inlet, condenser with a drying
tube, and a glass stopper.

To begin the synthesis, the temperature of the solution was increased to 70°C and both
BPO and EGDMA were added to the solution at the same ratios as in the homopolymer
crosslinking. This reaction was allowed to stir vigorously for two hours. During this time, the
BrPPO solution was prepared by dissolving the polymer in toluene within an Erlenmeyer flask
before transferring to an addition funnel.

Once the reaction solution had stirred for two hours the glass stopper was replaced by
the addition funnel, and the BrPPO solution was completely added dropwise to the stirring
reaction solution. Then the addition funnel was replaced with the glass stopper, and the
solution was stirred for another hour before the aromatic crosslinking agent, EDA, was added
to the pot. This reaction was allowed to proceed for an additional 10 minutes.

Once the final 10 minutes had passed, the reaction solution was transferred into a glass
 evaporating dish, covered tightly with aluminum foil, and placed in a circulating oven at 70°C
for 48 hours. After 48 hours, the temperature was raised to 90°C for three hours, and then the
aluminum cover was removed, and the product was dried at 50°C.
**Materials Characterization**

*Overview of Polymer Characterization Methods*

In order to determine the effectiveness of the synthetic methodologies employed, it is of utmost importance to be able to directly and reproducibly characterize the materials produced. However due to the nature of polymeric materials – in particular crosslinked and network materials, which are insoluble – many traditional chemical analysis techniques are unable to provide data that may be realistically interpreted, or do not provide a sufficient amount of data to adequately characterize a binary crosslinked system. Therefore a wide array of techniques – including thermal, spectroscopic, and simple qualitative procedures – were employed to gain a comprehensive understanding of the systems being produced.

*Differential Scanning Calorimetry*

Differential scanning calorimetry (DSC) was utilized as the principal characterization technique due to its versatility and ability to indicate glass transition temperatures. The instrument used was a TA Q20 Series DSC, and data produced by it was analyzed on by the TA 2000 program. For this project, DSC data was utilized for two types of analysis: reagent reactivity testing, and glass transition determination.

**Reagent Reactivity Testing**

As mentioned earlier, both reagents for aliphatic crosslinking, EGDMA and BPO, exhibit thermal and photosensitivity that could potentially cause a decrease in reactivity and prevent higher degrees of crosslinking from being achieved. Additionally, both reagents undergo reactions (polymerization and dissociation, respectively) at higher temperatures. Because of this, it is possible to determine qualitatively whether these compounds are capable of reacting utilizing DSC to view changes in heat flow over increasing temperatures.
For EGDMA (Fig. 10), a 5.9mg aliquot was massed in an aluminum hermetic pan. The instrument was set to run over a temperature range from 10°C to 200°C at a heating rate of 20°C/min. The sample was then cooled to 50°C to ensure that the sample did not exhibit any additional reactivity.

For BPO (Appendix 1), a 1.6mg sample was massed in an aluminum hermetic pan. The instrument was set to run over a temperature range from 10°C to 200°C at a heating rate of 20°C/min. An exotherm beginning just above 100°C indicates dissociation of the peroxide. The sample was then cooled to 50°C to ensure that the sample did not exhibit any additional reactivity.

Figure 10 – DSC graph of EGDMA heated from 10°C to 200°C showing evidence of polymerization.
**Glass Transition Determination**

One of the most important values to obtain for polymeric samples is the $T_g$ value. As mentioned earlier, $T_g$ values give insight into the mechanical properties materials will exhibit at higher temperatures. This transition marks the point at which a heated sample crosses over from a rigid glassy state into a thermodynamically stable amorphous state, and thus typically exhibits diminished mechanical toughness. Additionally, for polymer blends, samples do not exhibit both $T_g$ values of their constituent homopolymers, but rather display a single value that falls between those glass transitions of the two homopolymers. Identification of this transition on the DSC graph allows for an estimation of how thoroughly the polymeric species have been blended, as those composites featuring extensive phase separation exhibit two glass transitions or extensive $T_g$ broadening. However it is important to consider that $T_g$ values are not absolute, but rather are variable and can occur over a wide range depending on the conditions in which the sample is tested.

Samples of polymer, generally having masses between 5-6 mg, were weighed in aluminum hermetic pans. The instrument was programmed to equilibrate at 40°C, then ramp to 220°C at a heating rate of 10°C/min before ramping back down to 40°C at a cooling rate of 25°C/min. The heating and cooling procedures were then both repeated in their respective orders.

The first heating and cooling cycle allows for chains to assume a more regular conformation irrespective of the synthetic conditions, thus making the results more replicable. Therefore, all data obtained from the DSC (See Appendix 1) is determined through analysis of
the second heating cycle. The T_g values were determined by enlarging the heating portion of
the thermograph and examining it for an inflection point.

**Attenuated Total Reflectance Fourier Transform Infrared Spectrometry (ATR-FTIR)**

Vibrational spectroscopies such as FTIR are indispensable techniques for determination
of functional groups. FTIR spectroscopy using attenuated total reflectance is particularly useful
for analysis of polymeric species as it allows for analysis of samples with low transmission,
including powdered and solid samples. This is particularly useful for crosslinked and network
species, as it does not require grinding the insoluble sample and mixing it with KBr crystals. For
the aromatic and both aliphatic species the application of this technique was not to determine
the structure of the polymeric species, as they were purchased from Sigma Aldrich, but rather
to determine the presence and amount of crosslinking agents within the networked systems.
Each crosslinking reagent features a functionality that is very different from any functionality
present in the homopolymer structure; secondary amines from reacted EDA, and carbonyls
from EGDMA (Tables 3, 4).

<table>
<thead>
<tr>
<th>Functionality</th>
<th>Wavenumber</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Br</td>
<td>500-600</td>
</tr>
<tr>
<td>C-O</td>
<td>1000-1300</td>
</tr>
<tr>
<td>C-H (allylic)</td>
<td>1350-1480, 2850-3000</td>
</tr>
<tr>
<td>C-H (aromatic)</td>
<td>3000-3100</td>
</tr>
<tr>
<td>C=C (aromatic)</td>
<td>1400-1600</td>
</tr>
<tr>
<td>N-H</td>
<td>1600, 3300-3500</td>
</tr>
<tr>
<td>R=C-H</td>
<td>3010-3100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Functionality</th>
<th>Wavenumber</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H (allylic)</td>
<td>1350-1480, 2850-3000</td>
</tr>
<tr>
<td>C=O</td>
<td>1700-1725</td>
</tr>
<tr>
<td>C=O</td>
<td>1000-1300</td>
</tr>
<tr>
<td>C=C (aromatic)</td>
<td>1400-1600</td>
</tr>
</tbody>
</table>

*Table 3 - Selected absorptions for functionalities within crosslinked BrPPO*.

Experiments were conducted using a Shimadzu IRTracer-100 Fourier transform
spectrophotometer with a MIRacle 10 single reflectron ATR accessory. The instrument was set
to take 32 scans and generate absorption spectra from 600 cm\(^{-1}\) to 4000 cm\(^{-1}\). Data generated was analyzed using Shimadzu’s postrun analytical program, LabSolutions IR. To improve the quality of the spectra produced, the data was cleaned using ATR correction, baseline correction and peak normalization before peaks were analyzed.

**Swell Testing and Extraction**

A fundamental property of crosslinked and network polymers is their insolubility, arising from the molecular chains’ physical inability to separate from one another and go into solution due to chemical bonds. This property has been historically used to estimate the degree of crosslinking within a sample by measuring the change in size of polymers before and after swelling them into gels. For the purpose of this research, however, swell testing was utilized for two different purposes: rapid qualitative assessment of crosslinking success and determination of the extent of crosslinking through extraction techniques.

**Rapid Crosslinking Assessment**

The majority of characterization methods utilized in this research tended to be techniques requiring either extended periods of time to conduct the experiments, careful determination by experimenters, or both. In order to quickly assess whether samples have been sufficiently crosslinked and require additional analyses, samples were assessed by their solubilities.

Small sections of the crosslinked sample were excised and placed within beakers. The common solvent toluene was added to the beakers, and light stirring was applied. Polymer samples with sufficient crosslinking typically exhibit swelling within 15 minutes at room temperature, while polymers that were not successfully crosslinked usually dissolve within this time. In order to ensure that swollen samples were in fact crosslinked, the beakers containing
gels were covered with aluminum foil and heated to no higher than 50°C for an additional 15 minutes. The rate of stirring was not increased, as gels became quite fragile and sample tearing by excessive stirring could present difficulty in assessing the effectiveness of crosslinking.

**Extraction Testing**

A more sophisticated application of swell testing was utilized to determine the extent of crosslinking within the samples. Unlike assessments of the degree of crosslinking, these experiments provided information about the mass of non-crosslinked polymer within crosslinked samples, allowing for refined qualitative assessment of the successfulness of crosslinking reactions.

For these experiments Soxhlet extraction was employed to extract non-crosslinked starting materials from bulk samples. A portion of a crosslinked system was excised, accurately massed to ±0.1mg, and placed within a fiberglass Soxhlet thimble. The extraction was then carried out by refluxing toluene for 8 hours. After this, samples were transferred from the thimble onto preweighed aluminum weigh pans and placed in a circulating oven at 80°C for 72 hours, and then reweighed. After this, samples were placed in a vacuum oven at 70°C for 24 hours. The sample was then reweighed, and the percent mass loss was determined through the following calculation:

\[
\text{Mass Loss (\%)} = \left(\frac{\text{Initial Mass} - \text{Final Mass}}{\text{Initial Mass}}\right) \times 100
\]

It was discovered that when analyzing homopolymers, there was a tendency for samples to cling to the walls of the thimble, preventing post-extraction samples from being analyzed accurately. Therefore, a comparable extraction method was utilized for homopolymer analysis. Portions of crosslinked systems were excised, accurately massed to ±0.1mg, and placed within
an Erlenmeyer flask with a ground glass opening. The flask was then filled with toluene, a condenser was inserted, and the sample was refluxed overnight. Gels were separated through gravity filtration, and were rinsed with warm toluene during filtration to prevent filter paper from drying and potentially allowing gels to cling. After this, samples remaining on the filter paper were transferred onto preweighed aluminum weigh pans and placed in a circulating oven at 80°C for 72 hours, and then reweighed. After this, samples were placed in a vacuum oven at 70°C for 24 hours. Extraction data was calculated using the aforementioned formula.

**Elemental Analysis**

In order to quantitatively determine the success of bromination and crosslinking reactions, elemental analysis was employed to measure the amount of bromine and nitrogen within BrPPO samples, and oxygen in PB samples. This analysis was carried out two ways: contracted analysis by Galbraith Laboratories, and $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopic analysis.

Analysis of bromine was conducted to verify the effectiveness of bromination under the conditions described by Frisch and Hua. Nitrogen analysis of crosslinked BrPPO and oxygen analysis provided information about the effectiveness of the crosslinking reactions.

**Galbraith Analysis**

Samples of cleaned PPO, linear and crosslinked BrPPO, as well as linear and crosslinked PB, were accurately weighed to ±0.1mg. Samples of PPO, linear and crosslinked BrPPO were analyzed for bromine, carbon and hydrogen content. Oxygen analysis was omitted from directly requested experimental analysis, instead being determined through differential determination. Percent masses of the atomic species requiring analysis were calculated to provide a theoretical model for comparison with experimentally determined results. Samples
were then submitted to Galbraith for analysis. Both theoretical and experimental data for the analyses of aromatic species is provided in Appendix 3.

Because the key elemental species to be analyzed in aliphatic samples is oxygen, it was decided that this method of elemental analysis would not provide much information, and therefore aliphatic samples were not submitted to Galbraith.

**NMR Analysis**

Although crosslinked and network polymeric species are unable to dissolve, and therefore cannot be tested by traditional NMR analysis, linear polymers can still be analyzed using this technique. Work by Li, Sharma and Frisch indicated that the composition of bromine in linear BrPPO could be estimated using $^1$H NMR chemical shifts. This method was tested on samples with known bromine concentrations – measured by Galbraith – to determine if the method could provide insight into the amount of Br present within these samples.

NMR samples were prepared by dissolving linear BrPPO in deuterated chloroform to give an analyte solution with a concentration of 0.8M PPO structural units per volume of deuterated solvent. The instrument was already set so that $^1$H analyses were run at 400 MHz and $^{13}$C analyses were run at 100 MHz. Collected data was printed, and chemical shifts were determined.

**Discussion**

**Synthetic Efforts**

A variety of samples were produced both through procedures described by Frisch and Hua, and by the modified procedures described earlier. After reacted samples were dried, they were qualitatively assessed using the solubility assessment described to determine whether the reaction had resulted in crosslinking. With the exception of PPO bromination and BrPPO
crosslinking, those samples produced according to the procedure described by Frisch quickly dissolved in toluene. This issue persisted through several procedural variations, including using 5 and 10 times as much aliphatic crosslinking reagents, and decreasing the volume of solvent used to increase the concentration of crosslinking reagents within the reaction solution. Only after allowing aliphatic polymers to stir for three hours at higher temperatures were materials produced that were capable of swelling into gels.

Interestingly, when synthesizing binary IPN samples, the modified three hour procedure was also required, despite the observation that BrPPO successfully crosslinked under the published conditions. The reasons for the failure of BrPPO to crosslink, thus producing a semi-IPN (this is, an IPN consisting of one crosslinked species and one linear species entangled together) is not understood, though this possibly arises from the vastly low concentration of aromatic crosslinking reagent within the total reaction solution. The modified procedure attempts to account for this possibility by using a slightly lower aliphatic homopolymer-to-solvent ratio.

Although indeed the intent of this project is to replicate the work published by Frisch and Hua under modified conditions, the described issues achieving a successful total crosslinking of binary systems were not overcome in a replicable manner for several months. Because of this, there were few efforts to replicate the variety of binary systems with varying homopolymer concentrations described by Frisch. Additionally, due to the possibility of analytical complications with measuring \( T_g \) values for binary systems with aliphatic components exceeding 50% of the total IPN mass, which are reportedly below 0°C, the few binary systems produced with unequal masses were 60:40 BrPPO: PB, and 70:30 BrPPO: PB. Of
these systems only 70:30 was determined to have successfully crosslinked, and therefore is the only unequal system to have been further characterized by DSC, which is shown in Appendix 1. All other systems described are comprised of equivalent aliphatic and aromatic components.

**Characterization Efforts**

**DSC Analyses**

As stated earlier, the primary characterization technique employed for this research is DSC analysis for $T_g$ determination. An early, recurring mistake in DSC data processing was confusion between the heating and cooling cycles of the graphs. This was due to the fact that the heating cycles of graph were quite nearly linear, while the cooling cycles often produced curves resembling the desired data (See Appendix 1). Though, as described in Volume 1 of the second edition of Edith Turi’s *Thermal Characterization of Polymeric Materials*, it is possible – in some instances even desirable – to collect data about materials’ glass transitions upon cooling, these types of experiments require equilibration at a high temperature and then slow, steady cooling$^{24}$. However the procedure used was designed for determination by heating, and subsequently samples were cooled rapidly. Unfortunately this means that data must be collected from very subtle changes in the nearly linear heating cycle data, and occasionally analyses were conducted that did not produce a detectable $T_g$ slope. Without a distinct inflection point that can be determined on the graph, $T_g$ values cannot be accurately determined. Despite these difficulties several graphs successfully produced visible $T_g$ slopes, and it was noted that these transitions usually occurred significantly higher than those reported – typically in close to 200°C as opposed to the 59°C value reported by Frisch for 50:50 IPNs. These values are closer to the reported glass transition for the crosslinked BrPPO homopolymer ($T_g = 210°C$). Therefore the data potentially indicates that the system is not thoroughly mixed,
although there is an extreme difference in macroscopic behaviors, such as the IPN samples being stronger than the aliphatic polymer yet significantly more flexible than BrPPO. Before this conclusion can be definitively stated, however, additional experiments must be undertaken to verify that this is not simply a byproduct of still-rigid aromatic material experiencing equilibration to the amorphous state.

**ATR-FTIR Spectroscopy**

From a conceptual standpoint, ATR-FTIR spectroscopy is an ideal means of characterizing these crosslinked materials. With the capacity to indicate the presence of the characteristic crosslinking functionalities that are quite different from any aspect of either homopolymer, and with the added benefit of peak intensity being directly related to functionality concentration, this technique is a theoretical ideal. However the combination of those two aspects severely limits the effectiveness of this technique, especially when analyzing IPNs. The small concentration of crosslinking agents combined with the overwhelming amount and regularity of structural moieties within the linear polymer chains means that spectra produced through this technique barely display peaks at characteristic wavenumbers for aliphatic and aromatic crosslinking reagents (See Appendix 2). (The reader is referred back to Figures 6 and 8 for the molecular structures of these reagents.) Additionally, many of those peaks which would best help identify crosslinking reagents fall in the same regions as aliphatic peaks of chain functionalities, making them indistinguishable. Therefore less favorable peaks within the fingerprint region, such as the N-H wag (660-900 cm\(^{-1}\)) on reacted EDA’s secondary amine, are left as the only available peaks for analysis (Appendix 2: Spectrum 2)\(^{33}\). The results of these analyses are collected in Appendix 2.
Another surprising setback encountered during these experiments was the absence of characteristic aliphatic peaks for the BrPPO: PiP system (Appendix 2: Spectrum 7). The cause of this spectroscopic silence is not well-understood, particularly because of the large difference between BrPPO and PiP homopolymer spectra. Currently it is suspected that some interaction between the two components of this system result in a restriction of movement of PiP chains, though a lack of similar behavior in BrPPO: PB systems makes this seem unlikely. A series of experiments designed to shed light on this phenomenon is described later.

Despite this method’s inability to yield the expected analyses at a practical capacity, ATR-FTIR is capable of providing partial confirmation of polymer mixing. While DSC was predominately relied on for this particular type of information, IR spectroscopy is capable of detecting localized mixing on the microscopic scale\textsuperscript{25}. This nicely compliments DSC data by allowing for studies of miscibility within IPNs on molecular levels.

It is worth noting that although this technique provides supporting data, there is a level of unpredictability in this method that prevents it from being utilized as a primary characterization method for the materials used in this research. With IR analysis of polymer composites there is a known tendency for the materials to exhibit various peak shifts according to interactions between polymeric species\textsuperscript{25}. Additionally polymers containing halogens and carbonyls can display minor shifts (\(<10\text{ cm}^{-1}\)), and while the relatively low concentrations of both bromine and carbonyls within the polymeric species utilized in this study will likely prevent this from being a major consideration, the possibility is worth keeping in mind, particularly if the amount of either functionality is increased much farther beyond those reported in this research.
**Elemental Analysis**

**Galbraith Analysis**  
The samples were prepared and submitted to Galbraith for study. It was determined that the bromination procedure results in chains with over 3 wt.% Br (Appendix 3: Tables 2, 5), demonstrating the procedure described by Frisch and Hua is still functional and readily replicable. In one instance, bromination to this degree failed to occur, though the reason why is not understood (Appendix 3: Table 4). See Appendix 3 for the results of this testing.

**NMR Spectroscopic Studies**  
NMR analyses were conducted on cleaned PPO, and then on samples from all batches of BrPPO tested by Galbraith. The intent of this experiment was, as mentioned, to verify claims that some insight into bromine composition could be gained through $^1$H NMR spectroscopy. Additionally, $^{13}$C NMR spectra were collected from the same samples, as this method can theoretically give supporting data by showing if the presence of Br substituents results in an additional peak. However due to unclear guidance in conducting the experiment and very little time to prepare a proper experimental procedure, no usable data was gained through this series of experiments.

**Swell Testing and Extraction Studies**  
Testing using sample swelling was by far the most simplistic method utilized in this study, and yet it was indispensable in guiding procedural development. As mentioned, there were occasional difficulties that arose during interpretation of graphic and spectral data. A sample cannot dissolve if it is crosslinked. This straightforward truth allows for good qualitative assessment of crosslink quality without the uncertainty that pervades analytical judgement calls.
Yet it is important to note that the conditions described must be used to in order to best see the sample swelling. The gels used in this research, particularly the aliphatics, were especially fragile when swollen and would be easily torn apart by even light stirring. Stirring too vigorously easily makes it difficult to determine whether the sample has been crosslinked by shredding them as soon as they begin to swell.

A few preliminary experiments were also conducted to determine which solvents swell a 50:50 BrPPO: PB IPN to determine whether solvents besides toluene could be used to conduct swell testing. The results of these tests are presented in Table 5.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>50:50 BrPPO: PB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>Swelling</td>
</tr>
<tr>
<td>Xylenes</td>
<td>Swelling</td>
</tr>
<tr>
<td>Hexanes</td>
<td>No Swelling</td>
</tr>
<tr>
<td>Chloroform</td>
<td>Swelling</td>
</tr>
<tr>
<td>NMP</td>
<td>No Swelling</td>
</tr>
</tbody>
</table>

*Table 5 – Results of common solvent swell test with IPN samples.*

Unfortunately, as noted in the procedures, when conducting extractions on crosslinked BrPPO the gelled sample clung to the sides of the fiberglass thimble, making it impossible to collect data. An alternative method – also described previously – was employed using Erlenmeyer flasks instead of Soxhlet. However, due to time constraints this method was only tested once, and the gravity filtration employed during the extraction was slowed by the size of the samples. Time constraints likewise prevented extensive testing on IPN samples. The results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Mass (g)</th>
<th>Final Mass (g)</th>
<th>% Not Crosslinked</th>
</tr>
</thead>
<tbody>
<tr>
<td>50:50 BrPPO:PB IPN</td>
<td>1.3023</td>
<td>0.9179</td>
<td>29.50%</td>
</tr>
<tr>
<td>Crosslinked BrPPO</td>
<td>0.6008</td>
<td>0.2243</td>
<td>62.70%</td>
</tr>
</tbody>
</table>

*Table 6 - Experimental results for extraction testing on crosslinked BrPPO and a 50:50 IPN.*
of the two completed extraction analyses are presented in Table 6. Additional applications of this technique are discussed later.

**Conclusions**

The intent of this project from the beginning was to utilize crosslinking chemistry described by Frisch and Hua, and apply it to aliphatic and aromatic polymers to produce radiation shielding\(^1\). However, developing new procedures for crosslinking and finding the means to adequately characterize the produced samples became the central portion of this research. Additionally, the six-month time limit imposed by the Phase I grant from NASA, and the disappearance of data and procedures due to a lack of recorded procedures that a project assistant conducted regarding aliphatic polymer preparation and crosslinking resulted in hurried efforts and a slew of technical difficulties. However, the procedures described here – including the bromination of BrPPO, crosslinking of homopolymers, and the crosslinking of 50:50 systems – have shown great promise in producing IPNs, and it is suspected that little more must be done before the modified procedures are perfected, and thereafter the chemistry can be applied to new materials to produce stronger IPNs with even higher hydrogen content. Additionally, the characterization methods described will be able to provide a comprehensive understanding of the materials being synthesized now that many causes of the unanticipated results, such as the strange behavior of the FTIR results, have been predicted, and further experimentation (described later) is aimed at assessing whether these predictions are accurate.

Once these final preliminary experiments are completed, this project will show great promise for producing organic materials for efficient radiation protection in extraterrestrial environments.
Proposed Future Work

Final Goals of the Project

Because of time limitations imposed upon this research, compounded with a loss of some recorded procedures following the summer research session, the full range of this project was never explored. Originally it was intended that the work by Frisch and Hua would be replicated before the end of summer research, and new IPNs would be synthesized utilizing the seemingly simple crosslinking chemistry\(^1\). However due to the complications discussed, the research presented here became focused solely on the development of new synthetic and characterization procedures to achieve the same results as those published in 1989\(^1\).

Therefore, this section outlines experimental undertakings that will advance the current research path, as well as proposals for new types of experiments to be undertaken in order to produce stronger, more effective radiation shielding materials.

Continuing Current Research Efforts

Because of time constraints, many types of data were not collected as anticipated at the beginning of this project. The necessary experiments and some proposed procedures are outlined here.

Analysis of IPN and Homopolymer Samples over Large Temp Range DSC Testing

As mentioned earlier, Frisch and Hua report that they measured glass transitions for 50:50 BrPPO: PB IPNs at 59°C\(^1\). No samples produced by the modified procedure have achieved a comparable \(T_g\) value, but instead the DSC thermograms frequently display shallow increases over small temperature ranges that are generally close to 200°C. As was discussed, it is suspected that this may be an artifact resulting from additional changes in BrPPO’s heat capacity as it approaches its own \(T_g\) value. The extreme difference between published and experimentally derived values for this transition is a deeply unpleasant aspect of the current
research. However current experiments aimed at determining this value begin with equilibration at 40°C, which is not significantly below the 59°C literature value (See Table 8). Additionally, near the beginning of each heating cycle it is not uncommon for the graphs of both heating cycles to intersect, complicating analysis at this level.

Therefore, future DSC experiments should be conducted by equilibrating the instrument at -10°C, then ramping to 220°C and repeating the cycle as before. Additionally, the instrument should be programmed to begin data collection following the second heating, and not at the beginning of the initial heating cycle as has been until this point. This will allow the samples to cool well below the reported $T_g$ value and will eliminate the issue of graph intersections, providing data that may be more readily interpreted.

Previously, temperatures below 0°C have been avoided due to concerns of condensing and freezing atmospheric water vapor and severely disrupting data collection. However, after studying the manner in which DSC instrumentation is designed, it has been determined that adequate countermeasures to this possibility have been installed, in no small part due to the fact that the source this decision was based upon was published in 1997 and it is decidedly unlikely that the quality of instrumentation has degraded over time.

**Cleaning of PiP**

During a portion of this study, PiP was used in place of PB as a deviation from published procedures and apply these crosslinking methods to different materials. However, due to time constraints the extent to which PiP was used was quite minimal. Unfortunately a portion of these efforts, including the earliest experiments with PiP crosslinking, were conducted by another researcher whose written procedures could not be located. Therefore the
reactions reported in this research were conducted based on few parts of those early experiments that were directly observed and an understanding of PB crosslinking procedures. Unsurprisingly, this resulted in procedures that were not well-refined, and to this point only one BrPPO: PiP IPN has been successfully synthesized.

However, this network displays greater physical strength than comparable BrPPO: PB networks, so continuing this research is a worthwhile endeavor. A suspected first step is to try cleaning the PiP before the reaction. It was determined through swell testing that crosslinking can occur using PiP without cleaning, however this produces gels that appear more fragile that those produced over summer (which exhibited less degradation upon swelling), possibly indicating diminished reaction success. A cleaning procedure for linear PB is described by Frisch and Hua, and should provide a good starting point for beginning this process.

**IPN Extraction Analyses for the Purpose of Decreasing Procedure Times**

Currently, producing IPN samples takes approximately five days, the bulk of which is heating the sample to ensure the completion of the aliphatic crosslinking. The reason for this is due to the time dependence inherent in BPO’s decomposition rate. The half-life of BPO for forming initiating radicals at 70°C is 7.3 hours. A collection of calculated decomposition rates \( k_d \) and half-lives \( t_{1/2} \) of BPO in benzene at certain temperatures is shown in Table 7.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( k_d ) (s(^{-1}))</th>
<th>( t_{1/2} ) (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>( 2.6\times10^{-5} )</td>
<td>7.3</td>
</tr>
<tr>
<td>85</td>
<td>( 1.4\times10^{-4} )</td>
<td>1.4</td>
</tr>
<tr>
<td>100</td>
<td>( 5.8\times10^{-4} )</td>
<td>20 min</td>
</tr>
</tbody>
</table>

*Table 7 - Rates of decomposition and half-lives of benzoyl peroxide at certain temperatures in toluene.*
Therefore by slightly increasing the temperature, it is possible to decrease the amount of time necessary for the extended heating procedure. Analyzing the results of these increased heating experiments using the crosslinked homopolymer extraction procedure described should allow for fine tuning of the drying procedure, and could potentially result in a more time efficient heating procedure. This was the intended purpose of the extraction experiments conducted, but insufficient time and procedural complications resulted in an inability to complete this series of experiments.

**Determination of Mechanical Properties of Crosslinked Homopolymers and IPNs**
A key aspect of characterization is the study of the materials’ mechanical properties. Studies of stress-strain relationships provide invaluable information about the strength of materials. When dealing with polymer composites, these properties change based on the percent compositions of each material, and those materials’ own properties (Table 8). The chemistry department at William and Mary is equipped to conduct experimental determinations of stress-strain relationships (providing information about toughness, stiffness, strength, etc.) as well as rheological experiments that would provide information on phase separation within the IPN.

As neither of these instruments have been utilized to this point, no experimental procedures can be recommended.

**IPNs of Varying Compositions**
A fundamental aspect of polymer composites is that their properties can be modified by changing the concentration of each polymeric species present within the material. This was demonstrated by Frisch and Hua, who reported data for a series of IPNs with varying percent compositions (Table 8). In order to ascertain which composition possess the best combination of
properties, from total percent hydrogen content to the mechanical properties described above, a
wide variety of IPNs should be synthesized and analyzed.

Additionally, these experiments can be used to investigate the anomalous behavior
exhibited by the 50:50 BrPPO: PiP system during ATR-FTIR analysis. As discussed, this material
failed to display any peaks characteristic of the aliphatic polymer. It was suggested that this
could arise from interactions between the aromatic and aliphatic polymer species resulting in a
reduction of signal from the aliphatic polymer. By producing a series of IPNs starting with
very low aromatic concentrations (ex: 10:90 BrPPO: PiP) and incrementally increasing this
aromatic concentrations, it may be possible to directly observe the degradation of the aliphatic
signals, and potentially gain data allowing for a detailed analysis of molecular behaviors – such
as polymer mixing – within the samples.

**Extension of Crosslinking Reagents**
The attractiveness of the aromatic crosslinking reaction arises from its overwhelming
simplicity. The reaction is mechanistically straightforward, procedurally simple and quick, and
produces samples that are relatively easy to analyze. However the crosslinking reagent utilized
in for this reaction is relatively short, featuring two primary amines connected only by a two-
carbon chain. At the molecular level this connects aliphatic chains close together, potentially

<table>
<thead>
<tr>
<th>sample</th>
<th>comp. wt % PPO-PB</th>
<th>color, transparency</th>
<th>tensile strength, psi</th>
<th>elongation to break, %</th>
<th>T°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>cross-linked PPO</td>
<td>100-0</td>
<td>PY, TP</td>
<td>5880</td>
<td>2.95</td>
<td>210</td>
</tr>
<tr>
<td>FIPN 10</td>
<td>90-10</td>
<td>PY, TP</td>
<td>6434</td>
<td>4.99</td>
<td>205</td>
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<tr>
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<tr>
<td>FIPN 40</td>
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<td>PY, TU</td>
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<tr>
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<td>PY, TU</td>
<td>~75</td>
<td>&gt;87</td>
<td>-82</td>
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<tr>
<td>cross-linked PB</td>
<td>0-100</td>
<td>PY, TU</td>
<td>7</td>
<td>31.4</td>
<td>-85</td>
</tr>
</tbody>
</table>

*PY = pale yellow, TP = transparent, TU = translucent.

Table 8 - Characteristic data of IPNs with varying BrPPO: PB compositions, as well as crosslinked homopolymers. Includes physical and mechanical data for each system.
preventing extensive polymer mixing, especially due to the speed of the reaction. Utilizing other linear diamines with extended hydrocarbon chains could allow for a greater degree of mixing between IPN components, and consequently yield materials with more desirable properties.

A similar principle can be applied to the aromatic crosslinking agent, EGDMA. Although this reagent is slightly longer than EDA, it still does not provide much space for polymer interpenetration. For this crosslinking reagent, it is worth explicitly noting that longer chain glycol dimethacrylates are sold by Sigma-Aldrich\textsuperscript{27,28}. Diamines are likely more commonplace reagents, and therefore this set of experiments is less limited by availability of aromatic crosslinking reagents.

**Nanoparticle Doping Studies**

It is understood that doping materials can be used to alter their properties. In the case of radiation shielding materials, inorganic doping is of particular interest as it allows for an increased shielding capacity by absorbing neutrons produced in secondary radiation\textsuperscript{29}. Therefore being able to dope materials is of considerable interest for this research.

An informal study of this nature was conducted using PB and tungsten nanoparticles (nano-W). After the PB crosslinking reaction solution was transferred into a glass evaporating dish, a small amount of untreated nano-W was mixed into the solution. This was simply intended to test if untreated nano-W separates from the crosslinked polymer. Interestingly it did not, but due to severe time constraints this sample was not analyzed nor was further study performed. Experiments with treated nanoparticles, and with PiP and BrPPO homopolymers should be conducted, as well as with IPNs.
Additionally, boron is known to be a good additive for shielding against neutrons, so attempts to dope these polymeric materials with nano-B should be conducted as well\textsuperscript{26}.

**Expanding Research Efforts: New Materials and Studies**

The long term goal of this project has always been to utilize the crosslinking reactions described by Frisch and Hua in order to synthesize new IPNs consisting of different types of aromatic and aliphatic polymeric materials for the sake of developing advanced radiation shields\textsuperscript{1}. Of particular interest are high performance materials that have been developed in-house, as all necessary procedures are well-documented. Described in this section are proposals for a new IPN using materials that will provide greater hydrogen content and better thermal and mechanical stability, and a series of experiments prompted from observations that may provide insight into new methods of altering properties of the IPNs produced throughout this project.

**High Performance Aromatic Polyimides as Substitutes for PPO**

While the poly(arylene ether) species PPO features good thermal and mechanical stabilities, it is surpassed by many types of polyimides (PIs). PIs are high performance materials widely known to possess excellent thermal and mechanical properties that make them very desirable in for application in harsh environments\textsuperscript{8, 30-31}. However, these materials are also noted to be very difficult to process due to their rigidity and notoriously low solubilities\textsuperscript{8, 30}. Additionally, these materials are also prized for their chemical resistivity which can become a nuisance when trying to carry out reactions with them\textsuperscript{8}.

However, as PIs characteristically possess properties that are extremely desirable in many aspects of industry and academia, there have been countless efforts to improve the solubility of these materials\textsuperscript{30, 31}. Many of these efforts have been centered on counteracting the
rigidity of the chains by way of inserting flexible linkages, such as ethers and sulfones, into the backbone of the polymer, and others have utilized bulky pendant grounds to disrupt interactions between the polar polymer chains\textsuperscript{30,31}.

A previous thesis produced by Norah Bate on the subject of polyimide production describes successful syntheses of PIs containing these desirable functionalities\textsuperscript{29}. In particular, the compound poly(TBD-BTDA) (Fig. 11) contains both ether linkages and a few pendant groups – including a bulky tert-butyl substituent. While solubility studies were not reported for the PIs produced in that research, the structural components of this compound make it a promising candidate for the current research. Additionally this compound has allylic methyl functionalities in addition to the aforementioned tert-butyl group, providing ample sites for bromination with NBS.

Once the solubility of poly(TBD-BTDA) is known for various organic solvents, this compound’s potential to be utilized in an IPN can be more accurately predicted. In the event that this PI is deemed impractical for this purpose, then there are other significant candidates.

Figure 11 - Structure of poly(TBD-BTDA) as synthesized by Norah Bate\textsuperscript{29}.

43
for highly soluble PIs, as shown by Ghosh, et al., in their review on the subject. However it would be particularly desirable to utilize PIs that have been synthesized in-house, as many have been designed with high hydrogen content, and therefore an IPN synthesized from one of these compounds and an aliphatic chain would potentially result in an extremely hydrogen-rich material with even better physical and mechanical properties than materials made with BrPPO.

**Study on the Effects of Release Agents on Crosslinking Materials**

As mentioned briefly, some efforts were made to substitute the release agent Zyvax® for the layer of liquid mercury that Frisch and Hua utilized to prevent crosslinking PB from bonding to the Petri dish it was contained in. Aluminum weighing dishes were coated with a layer of Zyvax® before reaction solutions were poured in, and little consideration was given to amount of release agent – which was allowed to dry before the solution was added – that would be going into the solution, as the relative volume would theoretically be quite small. However various complications, including the facts that Zyvax® refers to a series of release agents and the type available in lab was not indicated, and that the composition of this material was completely unknown, resulted in this series of experiments being shelved.

However, crosslinked samples synthesized in the presence of the release agent were noted to behave slightly differently than those without. In particular a sample of crosslinked BrPPO made using the first attempted batch of brominated polymer from Fall 2015 (See Appendix 3: Table 4) was found to be capable of swelling nearly as well as crosslinked samples produced using BrPPO with significantly higher Br concentrations. Furthermore, even unsuccessful attempts at crosslinking PiP in Zyvax-lined pans resulted in samples that took noticeably longer to dissolve.
While not as necessary a study as the experiments described before this, it could be a worthwhile endeavor to test effects of known release agents on the properties of crosslinked samples. While a specific procedure for analyzing the presence of the release agent within the samples would have to be formulated, there is a possibility that this method could eventually yield a way to introduce beneficial additives into crosslinked and network samples in trace amounts.
Appendices of Collected Analytical Results

Appendix 1: DSC Thermographs

Graph 1 – Reagent reactivity test of BPO. The peak indicates the peroxide has dissociated.
Graphs 2 and 3 – Thermographs of crosslinked BrPPO, crosslinked at 60°C (Top) and 75°C (bottom).
Graph 4 – BrPPO: PB 50:50 Full IPN.
Graph 5 – BrPPO: PB 60:40 Full IPN.
Graph 6 – BrPPO: PB 70:30 Full IPN.
Graph 7 – BrPPO: PiP 50:50 Full IPN.
Appendix 2: ATR-FTIR Spectra and their Corresponding Tables

Spectrum 1 – Cleaned PPO and Selected Peaks
**Spectrum 2 – Crosslinked BrPPO homopolymer**

<table>
<thead>
<tr>
<th>Peak</th>
<th>Intensity</th>
<th>Corr. Intensity</th>
<th>Base (H)</th>
<th>Base (L)</th>
<th>Area</th>
<th>Corr. Area</th>
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</thead>
<tbody>
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<td>5.763</td>
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<td>1.449</td>
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Spectrum 3 – Linear high molecular weight polybutadiene. Due to the delay in getting higher molecular weight PB, there is no reference spectrum for the crosslinked analogue.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Intensity</th>
<th>Corr. Intensity</th>
<th>Base (H)</th>
<th>Base (L)</th>
<th>Area</th>
<th>Corr. Area</th>
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</table>
Spectrum 4 – Linear Polyisoprene
Spectrum 5 – Crosslinked polyisoprene
Spectrum 6 – BrPPO: PB 50:50 Full IPN spectrum.
Spectrum 7 – BrPPO: PiP 50:50 Full IPN spectrum. Note the diminished aliphatic peaks.
Appendix 3: Galbraith Results

<table>
<thead>
<tr>
<th>Atomic Species</th>
<th>Predicted % Mass</th>
<th>Determined % Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>79.97</td>
<td>79.69</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.71</td>
<td>6.64</td>
</tr>
<tr>
<td>Bromine</td>
<td>&lt; 0.1</td>
<td>&lt; 381 ppm</td>
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<tr>
<td>Oxygen</td>
<td>13.32</td>
<td>13.67</td>
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</table>

Table 1 – Elemental composition of clean, non-brominated PPO.

<table>
<thead>
<tr>
<th>Atomic Species</th>
<th>Predicted % Mass</th>
<th>Determined % Mass</th>
</tr>
</thead>
<tbody>
<tr>
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<td>75.5</td>
<td>77.15</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.27</td>
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</tr>
<tr>
<td>Bromine</td>
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<td>3.44</td>
</tr>
<tr>
<td>Oxygen</td>
<td>12.6</td>
<td>13.06</td>
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</table>

Table 2 – Elemental composition of dry BrPPO, brominated during summer 2015.

<table>
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<th>Predicted % Mass</th>
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<td>Oxygen</td>
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<td>&gt; 11.65</td>
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</tbody>
</table>

Table 3 – Elemental composition of crosslinked BrPPO. Composition of linear BrPPO is given in Table 2.

<table>
<thead>
<tr>
<th>Atomic Species</th>
<th>Predicted % Mass</th>
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<td>0.58</td>
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<td>Oxygen</td>
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<td>15.96</td>
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</table>

Table 4 – Elemental composition of dry BrPPO from unsuccessful bromination. Prepared during fall 2015.
### Appendix 3: Galbraith Results (continued)

<table>
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<th>Atomic Species</th>
<th>Predicted % Mass</th>
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<td>Bromine</td>
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<tr>
<td>Oxygen</td>
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<td>13.42</td>
</tr>
</tbody>
</table>

*Table 5 – Elemental composition of dry BrPPO. Second batch prepared during fall 2015.*
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21 Personal communication with Dr. Michael Kelley, College of William and Mary.


28 Sigma-Aldrich Chemicals. *Triethylene glycol dimethacrylate.*


32 University of Puget Sound Chemistry Dept. *IR frequencies.*
  <http://www2.ups.edu/faculty/hanson/Spectroscopy/IR/IRfrequencies.html>.

33 American University of Beirut. *Typical Infrared Absorption Frequencies.*
  <http://staff.aub.edu.lb/~tg02/IR.pdf>.
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