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Synthesis of a Thermally Reversible Cross-Linked System Using Electrophilic Cleavage/Functionalization of Poly(isobutylene-co-isoprene)

Savannah H. Steadman

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Synthesis of a Thermally Reversible Cross-Linked System Using Electrophilic
Cleavage/Functionalization of Poly(isobutylene-*co*-isoprene)

by

Savannah H. Steadman

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Submitted to the Honors College of
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of the Requirement for the Degree of
Bachelor of Science
in the School of Polymers and High Performance Materials

May 2017

Approved by

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Abstract

Multifunctional polyisobutylenes (PIBs) are of great academic and commercial interest. Current methods to create these materials currently utilize prohibitively expensive synthetic strategies. Recently, Storey *et al.* reported a novel method for the synthesis of multifunctional PIB which is more commercially viable than the current methods. For this research, the material produced via this technique was utilized to create a thermally reversible crosslinked system using Diels-Alder chemistry. To achieve this, a bromide-functional polyisobutylene obtained via electrophilic cleavage and functionalization of butyl rubber was split into two portions and further functionalized. The first portion of the bromide-functional PIB was reacted with furfuryl mercaptan to create a furfuryl-functional PIB. The second portion of the bromide-functional PIB was reacted with furan-protected maleimide, to create a maleimide-functional polyisobutylene. These two products were mixed and cast as thin films. The films were heated to 125°C to allow deprotection of the maleimide-functional material followed by annealing at 75°C to cure the network by the Diels-Alder reaction. Mechanical testing indicated an average percent elongation of ~300%, suggesting that the material possesses the desired elastomeric properties.

Dedication

To my parents, Garland and Susan Steadman, for your constant, unwavering love, support, and encouragement. Without everything you both have done for me, this document would never have been possible.

Acknowledgments

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Chapter I: Objective Statement and Introduction

Objective Statement

The purpose of this research is to demonstrate the synthesis of a thermally-reversible crosslinked polymer system, containing reversible Diels-Alder crosslinks, from multifunctional polyisobutylene (PIB) made via electrophilic cleavage/functionalization. The latter process involves the breakdown of a high-molecular-weight isobutylene-based copolymer, such as butyl rubber, into smaller chain segments, which are simultaneously functionalized along their backbone and at their terminal ends. This new chemistry allows for the production of multifunctional PIBs in a manner which is more commercially friendly than any method which currently exists.The goal is to synthesize a thermally-reversible crosslinked system utilizing this chemistry. Ideally, the material will act as a thermosetting rubber at low temperatures, however will be able to be processed as a thermoplastic at higher temperatures. The butyl-rubber-based system described herein has the potential to be used for self-healing and/or sensing sealants and coatings.

Introduction

Thermoset Rubbers vs Thermoplastic Elastomers

A thermosetting material is defined by IUPAC as a "prepolymer in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing."[1] Thermosets are widely known as being non-reversible crosslinked systems that must go through either vulcanization or another method of curing. Rigid thermosets are those that have a high crosslink density, whereas flexible thermosets have a lower crosslink density and are comprised of polymer backbones with low glass transition temperatures (Tg).[2] Thermoset rubbers, specifically, are natural or synthetic single-phase materials typically characterized by glass transition temperatures under 25-27°C. Typically, these materials are crosslinked via vulcanization and their precursors include rubbers such as natural rubber, polyisoprene rubber, and butyl rubber. Thermosetting rubbers such as these are advantageous compared to thermoplastic elastomers (TPEs) because they impart more strength and durability.[3]

Thermoplastic elastomers are typically comprised of high-T_g linear polymer segments linked together by low-T_g linear difunctional polymer segments. Thermoplastic elastomers first became commercially available in 1959, and are characterized as flexible materials, which even though free of covalent crosslinks, are capable of returning to their original state after multiple deformations, within reasonable limitations. One of the main advantages of using thermoplastic elastomers is their ability to be processed multiple times. TPEs can be processed through several different methods, including injection molding and extrusion, and are significantly more recyclable than thermosetting materials. Thermoplastic elastomers have replaced thermosetting rubbers for many

industrial applications.[4,5] An additional property exhibited by thermoplastic elastomers is phase separation, driven by the Gibbs' free energy of the system. The phase separation exhibited by polymers allows for the properties of each polymer in the blend to be exhibited by the final product.[6,7] For the purpose of this research, the goal is to create a thermosetting rubber from polyisobutylene that has the ability to melt and flow when temperatures are raised above the retro-Diels-Alder reaction temperature, allowing the material to be reformed much like a thermoplastic elastomer.[8]

Polyisobutylene

Polyisobutylene (PIB)-base polymers have a wide range of uses for the synthesis of graft copolymers,[9] lubricating oil additives,[10] amphiphilic conetworks,[11] and photocurable adhesives, coatings, and sealants.[12] The largest volume commercial product is butyl rubber, which is a copolymer composed of 97-98% isobutylene repeat units, with 2-3% isoprene repeat units to provide unsaturations which act as reactive sites during sulfur vulcanization.

$$\left[\!\!-CH_2-\!\!\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\!\!-\!\!\right]_n$$
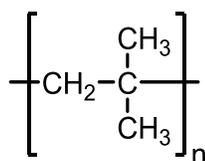
Figure 1: Structure of the polyisobutylene monomer repeat unit.[13]

Figure 1 above shows the polyisobutylene repeat unit. Polyisobutylene is a highly amorphous, low-T_g polyolefin which can only be synthesized by cationic polymerization.[13] Cationic polymerization is a chain-growth process involving positively charged propagating chain ends. A common technique for the synthesis of polyisobutylene utilizes a tertiary alkyl halide as the initiator and titanium tetrachloride as

the co-initiator. The advantage of this technique is that it can be used to create multifunctional PIBs when using an initiator that has multiple tertiary alkyl halide sites. When using a weak Lewis acid such as $TiCl_4$ to catalyze the reaction, the polymerization exhibits minimal chain transfer to monomer, resulting in a living polymerization for target molecular weights within certain limits. Thus, every initiating site results in a functional chain end which can be later modified. Once the polymerization is completed and the monomer has been exhausted, various additives can be added to the reaction to simultaneously modify the chain end and end the polymerization, a process known as quenching. Previously, Storey *et al.* have reported that alkoxybenzenes function as very efficient quenchers to impart a variety of functional groups to the chain end, the most important of which, at least as it pertains to this work, is a primary bromide functionality.[14]

Self-Healing and Self-Sensing Polymers

The development of smart polymers has been the subject of intense interest in recent years. Smart polymers are polymers that are able to respond to a small change in stimuli or revert back to their original state under a stimulus. These materials encompass self-healing polymers.[15] Self-healing polymers, more accurately defined as reversibly crosslinked systems, can be autonomous or stimuli-responsive, and would include systems that are reversible by application of some stimulus such as heat, light, electricity, and/or magnetism.[16] A popular type of thermally reversible system utilizes Diels-Alder chemistry, which involves the breaking and forming of covalent bonds without the gain or loss of any small molecule, a characteristic essential to a reversible system.[16] Specifically, the use of furan and maleimide derivatives in self-healing materials has been

extensively researched and is highly favored because the retro Diels-Alder temperature is

sufficiently low to allow for the relatively simple decoupling or de-crosslinking processes

that are necessary.[17] Further, utilizing furan has the potential to lead to not only self-

healing polymers, but recyclable materials for more sustainable industries.[17]

Chapter II: Synthetic Strategies Towards Multifunctional PIB

For the first portion... This research involved electrophilic cleavage/functionalization of

poly(isobutylene-*co*-isoprene) (i.e., butyl rubber), using (3-bromopropoxy)benzene as a

Friedel-Crafts substrate. This method provided the product shown in Figure 2, consisting

of degraded chain segments with primary bromide functionality in both pendent and

terminal positions. This functional polymer was divided into two equal portions, and

each portion was further functionalized separately to create two mutually reactive

polymers.
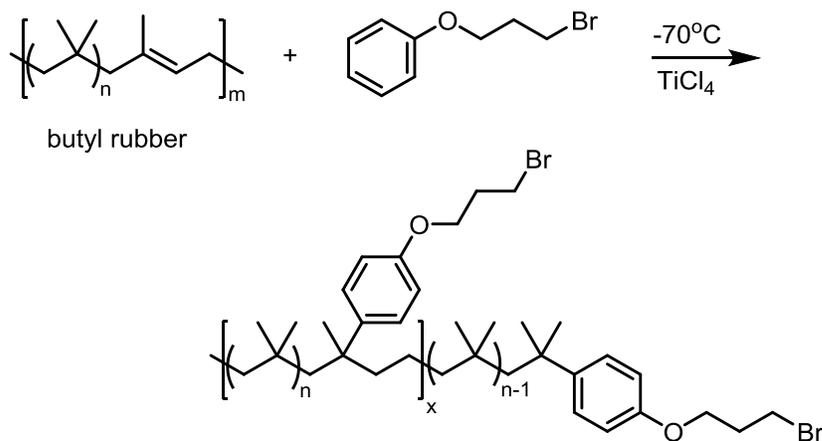
Figure 2: Electrophilic cleavage/functionalization of butyl rubber in the presence of (3-bromopropoxy)benzene.

For the first portion, a furan-protected maleimide was synthesized. Following

successful synthesis, the small molecule was reacted with the bromide-functional

polyisobutylene in the presence of excess potassium carbonate, which removed the

bromide functional groups and replaced them with the furan-protected maleimide. This

is shown in Figures 3 and 4 below.
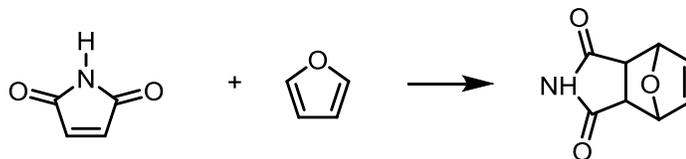
Figure 3. Synthesis of furan-protected maleimide small molecule.
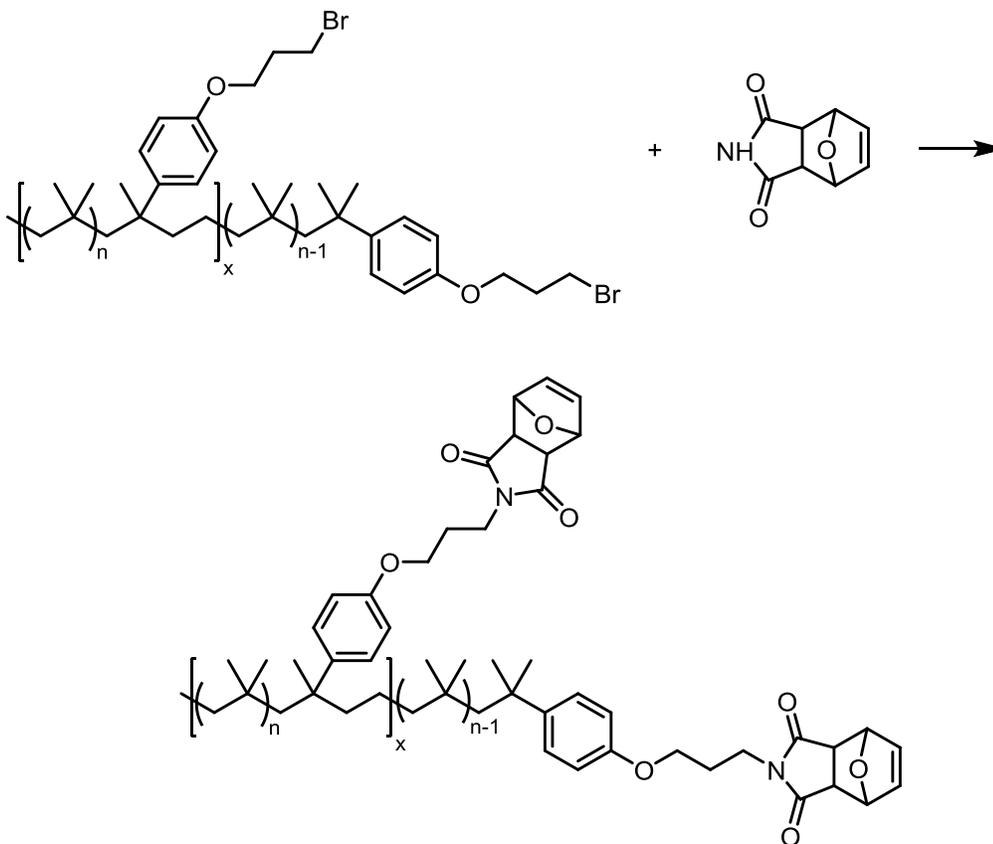
Figure 4. Reaction of first portion of bromide-functional PIB with furan-protected maleimide.

For the second portion, the bromide functional groups were reacted with furfuryl

mercaptan in the presence of excess potassium carbonate, which displaced the bromide

groups and functionalized the polyisobutylene with furan rings via a thio-ether linkage

(Figure 5).
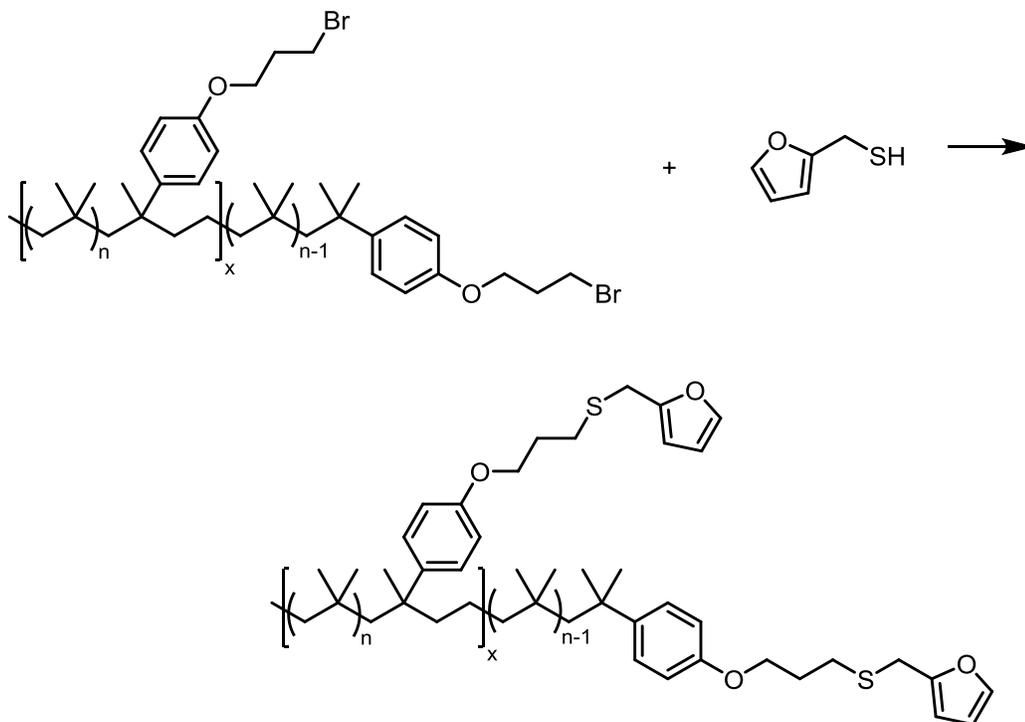
Figure 5: Reaction of second portion of bromide-functional PIB with furfuryl mercaptan.

Following successful synthesis, the two functionalized polyisobutylenes were

reacted together. Heat under vacuum was utilized to remove the furan from the

maleimide functionalized polyisobutylene, allowing the two materials to react together.

Chapter III: Literature Review

Diels-Alder Chemistry

A Diels-Alder reaction is defined as a [4+2]-cycloaddition between a diene and a

dienophile. The reaction is driven by the formation of stable σ bonds and is commonly

employed as a synthetic route toward unsaturated six-membered rings.[18] When applied

to polymeric systems, Diels-Alder chemistry is considered to be a type of "click"

chemistry.**Error! Bookmark not defined.** As discussed by Liu and Chuo in a review article, Diels-

Alder chemistry is popular for thermally-reversible systems due to the thermal instability

of the Diels-Alder bond. Furan-maleimide Diels-Alder reactions have previously been used to prepare thermally-responsive micelles and macromolecular networks. Additionally, polymethacrylate was modified with furan and maleimide. This polymer was shown to have high flexibility, unlike the crosslinked resins from small molecule precursors. Other research reviewed by Liu and Chuo reported that mechanical properties of a furan-maleimide polymer were comparable to commercially available thermosetting resins. One of the noted downsides of using these two molecules in a "self-healing" polymer was the limitation due to chain mobility.[19]

The use of a furan-protected maleimide small molecule was documented by Lacerda et al. In this research, Diels-Alder chemistry was chosen because of the versatility and recyclability caused by the thermally reversible crosslink obtained. They reported that during curing of the network, both the *endo-* and *exo-* stereoisomers of the Diels-Alder linkage were formed. The final material was used to create a rigid thermally-reversible system.[20] Further, review of work utilizing Diels-Alder networks done by Gandini showed that potential interactions caused by having both the *endo-* and *exo-* forms of the material can mostly be ignored for the formation and reversal of bonds.**Error! Bookmark not defined.**

According to work done by Ji and Zhang *et al.*, the use of furan-protected maleimide is preferable due to the ease of deprotection. Heating at 110°C was found to be sufficient to remove the furan protecting group without further catalysis, allowing the maleimide to readily react with additional monomers. Specifically, styrene was used as the primary monomer and was reacted with the furan-modified maleimide as the so called latent, or secondary, monomer, and the rate of incorporation of maleimide was controlled

by the rate of deprotection of the maleimide. It was found that when using the furan-protected maleimide, the placement of the maleimide groups was slightly different than the placement found when utilizing maleimide. The polymerization of styrene with furan-protected maleimide at 100°C was found to result in a polymer with random sequencing, yet indicated an incomplete release of furan from the system. The researchers found that the temperature the removal of furan occurred at, as well as the concentrations of each monomer, played an important role on the sequence distribution of the final polymer.[21]

Electrophilic Cleavage/Functionalization of Butyl Rubber

The simultaneous electrophilic cleavage and functionalization of butyl rubber by alkoxybenzenes in a superacidic environment is a new synthetic technique, pioneered by the Storey Research Group, for the synthesis of multifunctional polyisobutylenes. In this process, butyl rubber was dissolved in *n*-hexane overnight; the polarity of the solution was increased by the addition of methylene chloride, and the mixture was chilled to -70°C. Then, (3-bromopropoxy)benzene, concentrated sulfuric acid, and titanium tetrachloride were added to initiate the reaction. The resulting polyisobutylenes were found to be of low molecular weight and multifunctional.[22]

Characterization Methods

Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance spectroscopy (NMR) is an analytical technique used for determining the structure of small molecules and polymers. This technique uses magnetization to study the nuclei present in a system.[23] For the study of polymers, the

two most useful nuclei are[13]C and [1]H.[24] For this study, ^{1}H NMR spectroscopy was used to determine polymer structure and composition, and for end group identification.

Gel Permeation Chromatography (GPC)

Gel permeation chromatography is a common method for separating polymer molecules according to their size and for determining molecular weight and molecular weight distribution (PDI) of a polymer system. The use of multiple detectors, including differential refractive index (RI), UV absorbance, and multi-angle laser light scattering (MALLS), confers additional analytical capabilities. RI and MALLS detection used together allows absolute molecular weight determination without need for calibration standards. Combining RI and UV absorbance detectors yields compositional information as a function of molecular weight.[25] For this study, GPC with RI and MALLS detection was used to determine the number average molecular weight and polydispersity of the polymer samples.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis measures the mass lost from a sample as a function of increasing temperature. It is useful for determining the wt% volatile organic compounds in a sample as well as a sample's degradation temperature. Additionally, thermogravimetric analysis is a useful way to determine the temperature to which a material must be heated to remove all traces of solvent from the material.[26] For this work, TGA was utilized to determine the temperature at which all *n*-hexane solvent has been removed from the samples and to quantify the amount of furan removed from the polymer matrices during deprotection of the maleimide moieties.

Chapter IV: Materials and Methods

Synthesis Methods

Electrophilic Cleavage/Functionalization of Butyl Rubber

Multifunctional polyisobutylene was synthesized via electrophilic cleavage and functionalization of butyl rubber according to a recently published procedure.[22] An example synthesis was as follows: 59.724g of butyl rubber (Exxon™ Butyl 365) was dissolved in 600 mL of *n*-hexane overnight (Acros Organics, 99%) in a 1L round-bottom flask, and 400 mL of methylene chloride (MeCl$_2$, Fisher Chemical 99.9%) was later added. The reaction flask, which was equipped with a magnetic stir bar, was cooled to -70°C using a methanol bath. Then, 20 mL of titanium tetrachloride (TiCl$_4$, Sigma-Aldrich 99.9%, stored under N$_2$), 0.46 mL of deionized water, and 12 mL of (3-bromopropoxy)benzene (PPB, AK Scientific 98%) were added to the reaction flask to initiate the reaction. The reaction was allowed to proceed overnight with continuous stirring. At 18.5 h, an aliquot was taken and terminated into excess methanol in a scintillation vial. This vial was then centrifuged at 4000 rpm for 5 min. The methanol was decanted; the precipitate was re-dissolved into fresh *n*-hexane, and the solution was re-precipitated into excess methanol. The system was centrifuged at 4000 rpm for 5 min and the methanol was decanted. The precipitate was re-dissolved in fresh hexane. The resulting solution was washed three times with deionized water, dried over magnesium sulfate (MgSO$_4$), and filtered using a filtering pipette. Nuclear Magnetic Resonance spectroscopy was performed. The sample was returned to a tared scintillation vial and dried with nitrogen before being placed in the vacuum oven at room temperature overnight. The sample was then prepared for Gel Permeation Chromatography.

Synthesis of Furan-Protected Maleimide Small Molecule

The purpose of this reaction was to use furan to protect maleimide prior to reaction with bromide-functional polyisobutylene. In the reaction, 0.991 g of maleimide (Ark Pharm, 98%) was dissolved into 10 mL of THF in a 25 mL round bottom flask. After the maleimide dissolved, 1.5 mL of furan (Sigma Aldrich, >99%) was added, and the reaction was allowed to proceed at reflux with constant stirring overnight. An additional 10 mL of THF and 1.5 mL of furan were added. Following verification of reaction completion via NMR, the protected maleimide was set aside for later use.

Synthesis of Furan-Protected Maleimide-Functional PIB

The purpose of this stage of the synthesis was to react the first portion of the bromide-functional polyisobutylene with the furan-protected maleimide small molecule to create a maleimide-functional polyisobutylene that would not self-crosslink prior to removal of the furan. In this reaction, 10.051 g of the polyisobutylene synthesized via electrophilic cleavage and functionalization was dissolved in 45 mL of tetrahydrofuran in a 250 mL round bottom flask. To this, 1.181 g of potassium carbonate (K_2CO_3), 5mL of furan (Sigma Aldrich, >99%), and the small molecule obtained in the previous reaction were added. The reaction was allowed to proceed at reflux for 14 h under nitrogen blanket while stirring. Then, 2.009 g of tetrabutylammonium bromide (Sigma-Aldrich, >99%) was added, and the reaction was allowed to proceed under the same conditions overnight. An aliquot was taken and precipitated into a scintillation vial containing excess methanol. This vial was centrifuged for 5 min and the methanol was decanted. The polymer was then re-dissolved into fresh *n*-hexane and re-precipitated into excess methanol. The vial was centrifuged for 5 min and the methanol was decanted. This

process was repeated a third time. The sample was dried with nitrogen before NMR

spectroscopy experiments were performed. The sample was returned to a tared

scintillation vial and dried in a vacuum oven at room temperature. The sample was then

prepared for GPC analysis. The remaining sample was purified twice over chilled

methanol, re-dissolving in THF between purifications. After cloudiness was observed

during the purification process, the polymer was dissolved in 145 mL of hexane, and

methanol washes were performed using a solution of methanol and deionized water

(10%) in a 250 mL separatory funnel. The product was dried with magnesium sulfate

overnight. To remove the excess magnesium sulfate from the material, the product was

centrifuged in batches and the organic solution was decanted into a 200 mL flask. Rotary

evaporation was performed to remove the excess solvent from the system. When not in

use, the material was stored in a freezer at -19 °C to prevent oxidative degradation.

Synthesis of Furfuryl-Functionalized PIB

This reaction proceeded as shown in Figure 5. In a 250 mL flask fitted with a stir

bar, 10.183 g of the bromide-functional PIB synthesized via electrophilic cleavage and

functionalization was dissolved in 50 mL of THF. Then, 1.313 mL of furfuryl mercaptan

(Alfa Aesar, 98$^+$%) and 2.394 g of potassium carbonate (K_2CO_3) were added to displace

the bromides and replace them with furfuryl groups. The reaction proceeded using a

condenser under a nitrogen blanket overnight at THF reflux with constant stirring. An

aliquot was taken and terminated into excess methanol in a scintillation vial. This vial

was then placed in a centrifuge and run at 4000 rpm for 5 min. The methanol was

decanted; the precipitate was re-dissolved into fresh n-hexane, and the solution was re-

precipitated into excess methanol. This was centrifuged at 4000 rpm for 5 min and the

methanol was decanted. The precipitate was re-dissolved in fresh hexane. The remaining product was purified over chilled methanol twice, re-dissolving in THF between purifications. Due to cloudiness observed during purification, the polymer was dissolved in 200 mL of n-hexane and a wash was performed with methanol and distilled water (10%) in a 500 mL separatory funnel. The product was then dried with magnesium sulfate overnight. To remove the magnesium sulfate, the solution was centrifuged in batches, and the n-hexane was decanted into a 200 mL flask. Rotary evaporation was then performed to remove the remaining solvent.

Reaction of Furan-Protected-Maleimide-Functionalized Polyisobutylene with Furfuryl-Functionalized PIB

The maleimide and furfuryl-functionalized PIBs were separately dissolved in hexane, and a small aliquot from each solution was used to determine wt% solids by drying under vacuum until a constant weight was achieved. The furfuryl-functional PIB was found to be 29.77% solids, and the furan-protected-maleimide-functiontionalized PIB was found to be 18.91% solids. Utilizing the functional equivalent weights and percent solids of the two functionalized polyisobutylene solutions, a 1:1 stoichiometric mixture was achieved by mixing 36.528 g of the furan-protected maleimide-functional polyisobutylene solution with 25.825 g of furfuryl-functionalized polyisobutylene solution. Rotary evaporation was performed to remove most of the excess *n*-hexane; although some *n*-hexane was left to ensure flow of the material. Approximately 2 mL of the sample was placed onto a glass slide, which had previously been washed with acetone, and put under vacuum at 75°C for 4h to remove any remaining *n*-hexane from the system. This sample was allowed to cure for 4h at 125°C under vacuum, and then the

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temperature was lowered to 75°C to activate the forward Diels-Alder reaction overnight. Bars were then cut for use in tensile testing.

Characterization Methods

Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy was used to determine the structure of the copolymer system. Specifically, we tracked the disappearance of the primary alkyl halide of the PIB chain to monitor reaction progress during the coupling reaction outlined in Chapter II. NMR data were acquired following the procedure outlined by Morgan *et al.*[27]

Gel Permeation Chromatography

Gel permeation chromatography was used to determine number average molecular weight, weight average molecular weight, and polydispersity index of the copolymers using methods outlined by Morgan, et al.[27]

Thermogravimetric Analysis

Using a TGA Q-50, along with TA Instruments Open Analysis software to analyze data, thermogravimetric analysis was run with the following parameters: 5 to 15 mg of sample were placed into an instrument weighed platinum hanging pan. The temperature was ramped from 30°C to 400°C at a rate of 2.5°C per minute under an inert nitrogen atmosphere.

Tensile Testing

Tensile tests were performed using a MTS Alliance RT/10 system and MTS Testworks 4 software. Testing was performed on 2 bars, one measuring 28.65 (gauge

length) x 10.07 x 1.05 mm and the second measuring 23.62 x 8.58 x 0.89 mm. The

samples were clamped using a 100N load cell and tested at a crosshead speed of 5

mm/min at room temperature.

Chapter V: Data and Discussion

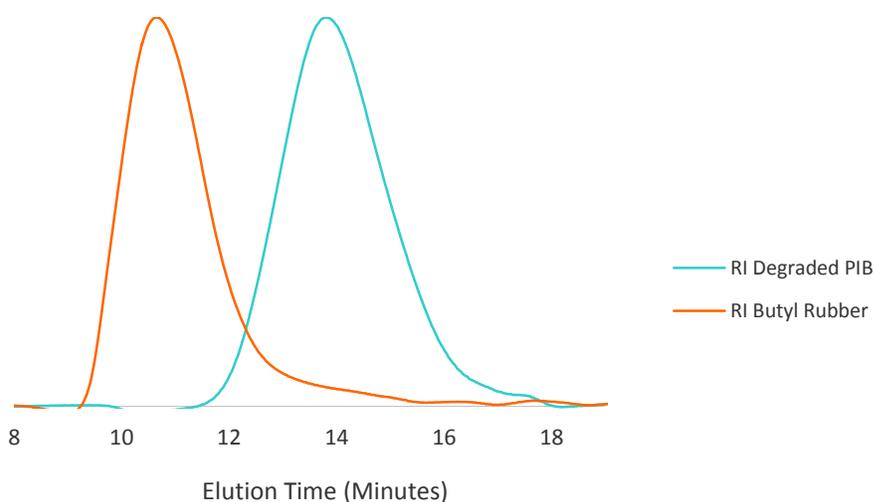*Gel Permeation Chromatography*

Figure 6. GPC traces of starting butyl rubber and PIB obtained via electrophilic cleavage and functionalization.

Figure 6 above shows the gel permeation chromatography (GPC) traces for the

original starting material as well as for the PIB synthesized via electrophilic cleavage and

functionalization. GPC/MALLS data for the original butyl rubber material indicated M_n

= 225,100 g/mol and polydispersity (M_w/M_n) = 1.5. GPC/MALLS data after electrophilic

cleavage/functionalization indicated M_n = 12,450 g/mol and polydispersity (M_w/M_n) =
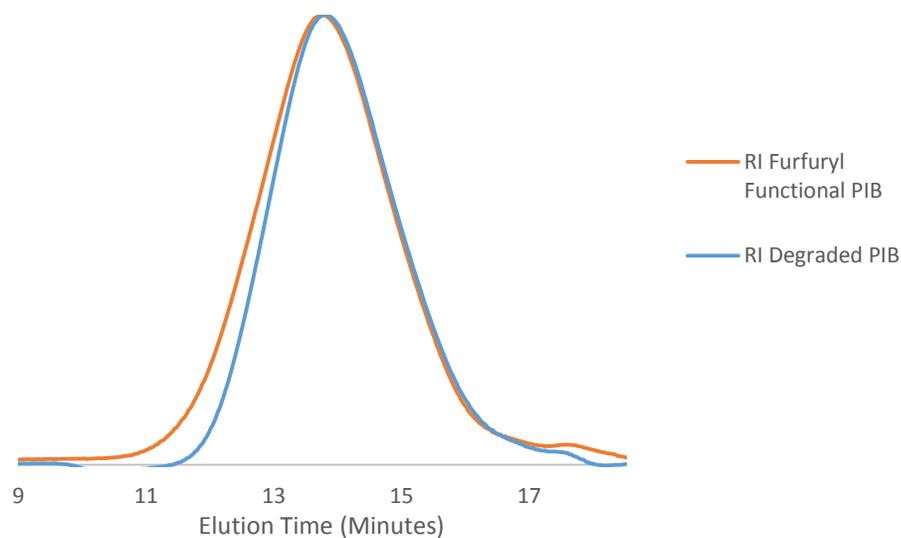
1.4.

Figure 7. GPC traces of starting electrophilically cleaved and functionalized PIB and furfuryl-functionalized PIB.

GPC traces for polyisobutylene synthesized via electrophilic cleavage and functionalization as well as furfuryl-functional polyisobutylene are shown in Figure 7. GPC/MALLS data for furfuryl-functional PIB indicated that the product possessed M_n of 16,780 g/mol and a polydispersity (M_w/M_n) of 1.5.
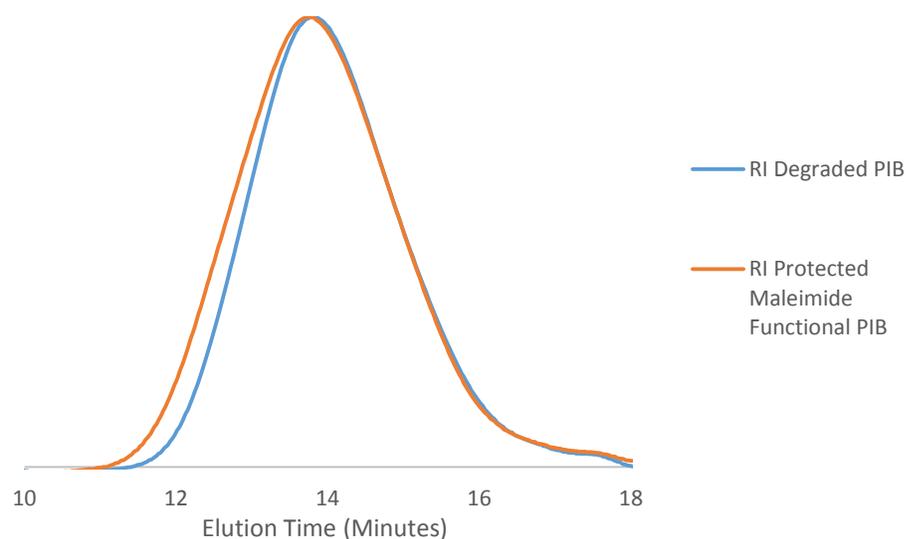

Figure 8. GPC Traces of starting electrophilically cleaved and functionalized PIB and protected maleimide functional PIB.

GPC traces for polyisobutylene synthesized via electrophilic cleavage and functionalization as well as furan-protected maleimide-functional polyisobutylene are shown in Figure 8. GPC/MALLS data for the protected maleimide-functionalized PIB indicated that the product possesses a M_n of 15,910 and a polydispersity (M_w/M_n) of 1.4.
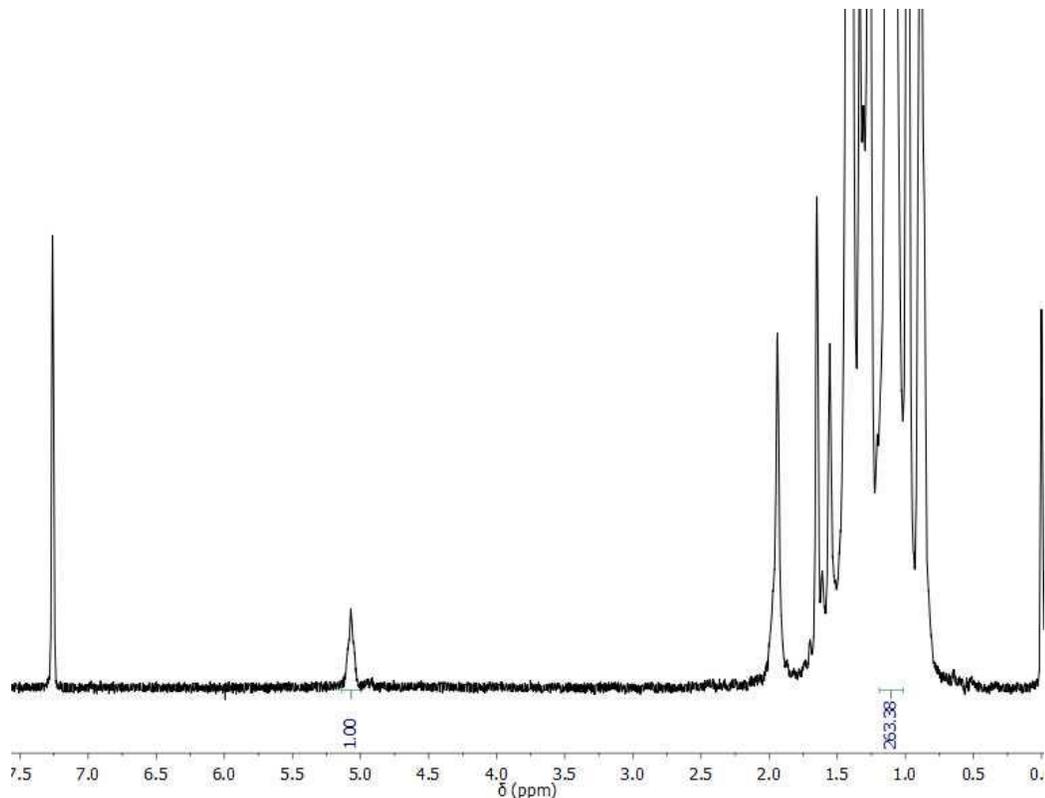
Nuclear Magnetic Resonance Spectroscopy

Figure 9. ^1H NMR spectrum for butyl rubber starting material.

Figure 9 shows the NMR spectrum of the starting butyl rubber material. The mole fraction of isoprene units was calculated to be 0.0266. Additionally, it was determined that there were approximately 37.6 isobutylene units per isoprene unit.
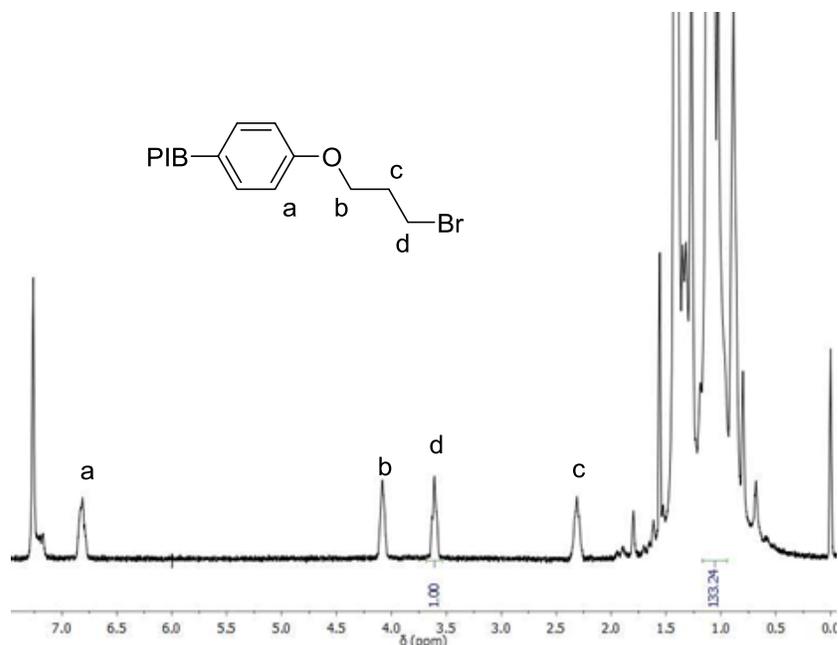
18

Figure 10. ¹H NMR spectrum for bromide-functionalized polyisobutylene obtained via cleavage/functionalization of butyl rubber.

Figure 10 shows the NMR spectrum of cleaved and functionalized PIB. Signal peaks labelled b and d, at 4.08 ppm and 3.61 ppm respectively, are the main indicators of the bromide functionalized chain and indicate methylene groups located next to an oxygen and bromine, respectively. The methylene between these two peaks, at 2.30 ppm, is labelled c. The signal at 6.82 ppm, labelled a, indicates the presence of the phenyl ring in the quencher group. NMR of the degraded polymer indicated a 1:43.25 ratio of bromide functionality to isobutylene units in the final product.
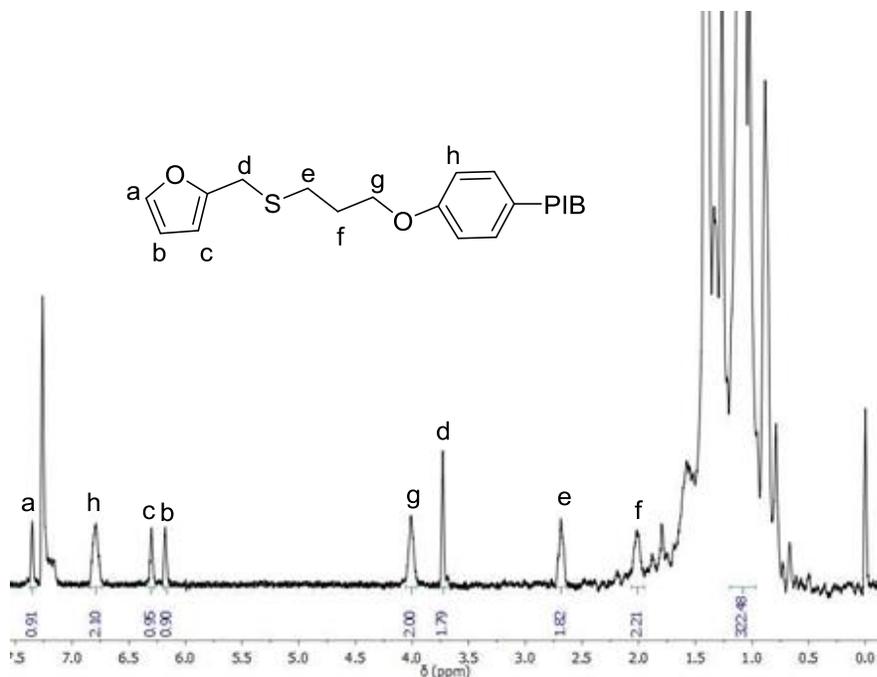
Figure 11. ^{1}H NMR spectrum for fufuryl-functional polyisobutylene.

Figure 11 shows the NMR spectrum for furfuryl-functional polyisobutylene.

Peaks at 6.18 ppm, 6.30 ppm, and 7.38 ppm, represented by letters b, c, and a,

respectively, indicate the presence of the furfuryl ring. Additionally, the peak labeled d

at 3.73 ppm indicates the presence of a methylene group located between the sulfur atom

and the furfuryl ring. This gives further evidence of the successful addition of the

furfuryl group. Peaks labelled e through h indicate the presence of the quencher shown in

Figure 10.
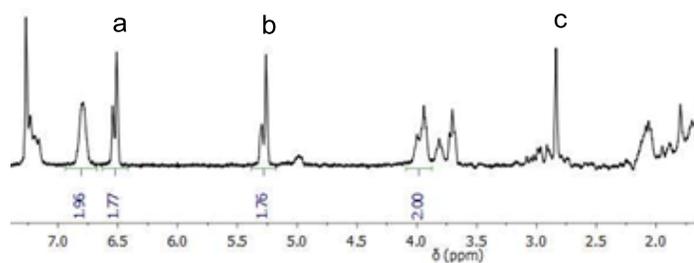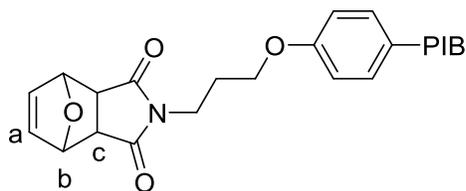
Figure 12. ¹H NMR spectrum for furan-protected maleimide-functional polyisobutylene.

The NMR spectra for the protected maleimide-functional polyisobutylene is

shown in Figure 12. The peak shown at 6.51 ppm, indicated by the letter a, indicates the

presence of the olefinic bond found in the furan-protected maleimide. The peak labelled

b, located at 5.26 ppm, indicates the presence of the methine proton of the oxygen bridge.

The peaks located from 2.71 ppm to 3.10 ppm also indicate the presence of succinimide

peak.
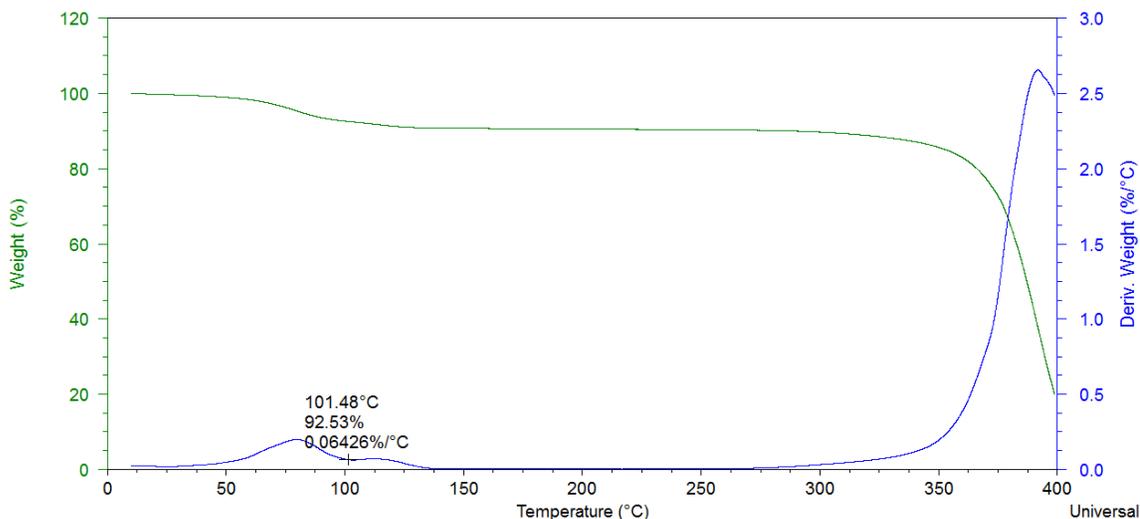
Figure 13. TGA of furan-protected maleimide-functional PIB.

Figure 13 shows data obtained from the thermogravometric analysis of furan-protected maleimide-functional polyisobutylene. For this sample, *n*-hexane began leaving the sample at 40°C. Furan began to volatilize from the sample at 102°C and was completely removed at 140°C. The maleimide functional polyisobutylene began to degrade just before 300°C. It was found that the sample was 92.53% solids.

Figure 14. TGA of furfuryl-functionalized polyisobutylene.

Thermogravimetric analysis of the furfuryl-functionalized polyisobutylene

yielded the weight percent of polymer as well as the temperature at which n-hexane was

removed from the system. As seen in Figure 14, *n*-hexane begins evolving from the

system around 50°C and was gone by 125°C. The degradation temperature of the

material was 275°C. Based on the data, the sample was 94.24% solids.

Tensile Testing
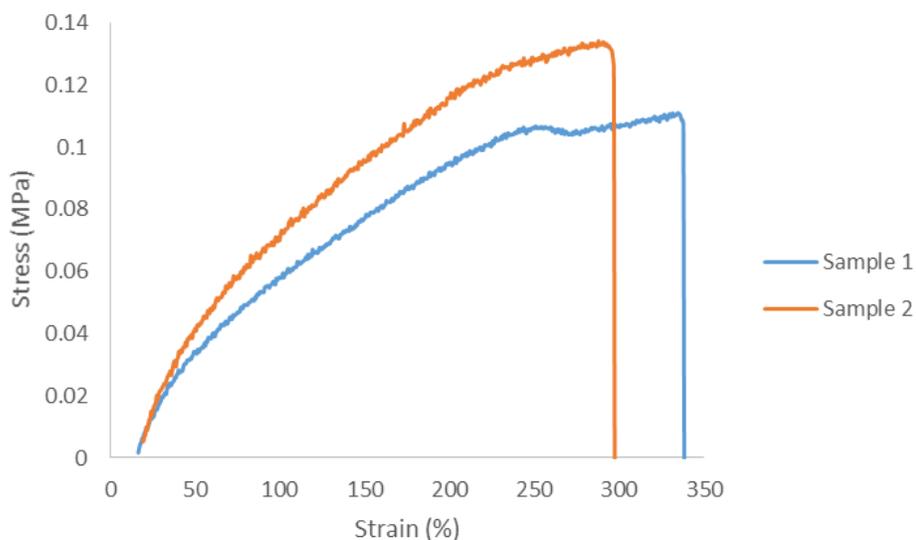
Figure 15: Stress versus strain curves (in duplicate) for the cured final material.

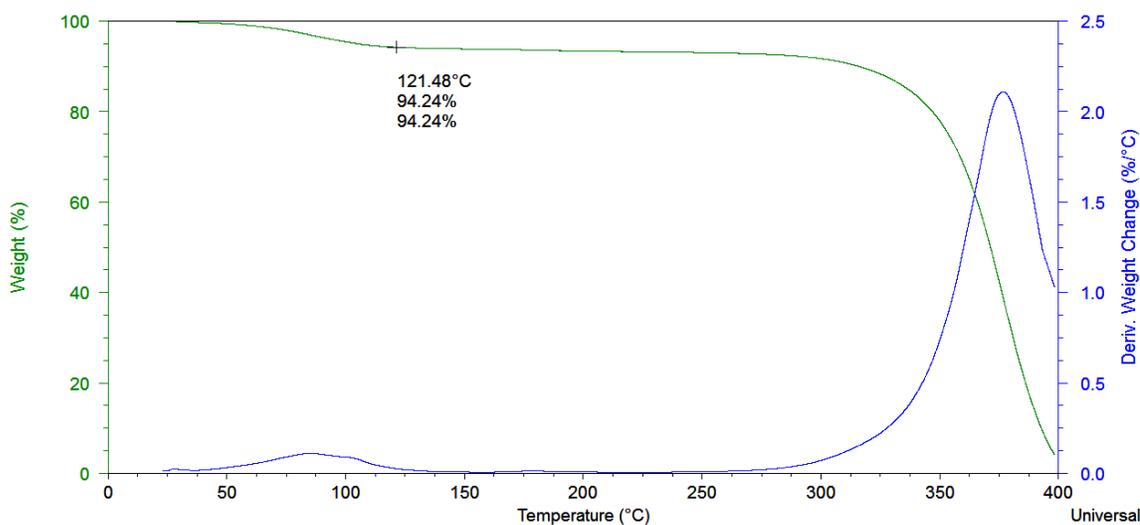Figure 15 shows the stress versus strain curve for two tensile samples of the final

cured material. From the slope of this curve, Young's modulus for Sample 1 was

determined to be 0.122 MPa. For sample 2, Young's modulus was determined to be

0.123 MPa. Elongation to break was not obtained as the samples slipped from the testing

apparatus. For sample 1, failure began to occur at 250% strain, however fully slipped

from the clamps at 334% strain. For sample 2, the clamp released the material at 288%

strain. Percent elongation at fail point was determined to be 275.7% for sample 1 and

288.3% for sample 2. These results show that the materials are weak elastomers.

Chapter VI: Conclusion

In conclusion, we have demonstrated the method of electrolytic cleavage and functionalization of butyl rubber to produce primary bromide-functional PIB. Further, we have demonstrated that this material is a useful starting material from which to synthesize a variety of functional PIBs. In this case specifically, we have shown that we can functionalize the degraded butyl rubber with a furan derivative and a protected maleimide, functional groups commonly used in reversible Diels-Alder Chemistry. Of particular interest is that the first and second samples of the material experienced 275.5 and 288.3 percent elongation respectively before the samples slipped from the testing apparatus. This indicated the successful synthesis of a thermoplastic elastomer. Further, preliminary observations show that the material will reverse when exposed to elevated temperatures in a high boiling solvent. Despite these observations, further research is needed to determine conversion of maleimide and furan groups during the curing reaction. Additional testing would also be required to determine the effect of reprocessing of the material on mechanical properties.

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