Polyarylenes: Synthesis and Characterization Towards Advanced Applications

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POLYARYLENES:
SYNTHESIS AND CHARACTERIZATION TOWARDS ADVANCED APPLICATIONS

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POLYARYLENES:
SYNTHESIS AND CHARACTERIZATION TOWARDS ADVANCED APPLICATIONS

A Dissertation Presented to the Graduate Faculty of the

Dedman College

Southern Methodist University

in

Partial Fulfillment of the Requirements

for the degree of

Doctor of Philosophy

with a

Major in Chemistry

by

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December 21, 2019
ACKNOWLEDGEMENTS

I would like to thank my advisor, Professor David Son, for his guidance and support during my four years here. He was great in terms of providing whatever I needed to accomplish my goals and to be successful. I was always so busy, and he was always willing to help and encouraged me to continue working hard.

I would also like to thank my committee members, Professors David Son, John Buynak, Scott Iacono, Nicolay Tsarevsky, and Brian Zoltowski. Their comments, guidance, and advice were valuable. Their reviewing of my synopsis, proposal, this work, and all my writings was very much appreciated.

Special thanks to the faculty and staff in the chemistry and outside departments of Southern Methodist University, University of Texas, Dallas, University of Northern Texas, Texas Christian University, and the University of Arizona. I’m grateful to Buynak’s laboratory for advice, Garcia-Bosch’s laboratory for dry solvents, Alan Humason for everything and the teaching laboratory for the ATR–FTIR spectrometer, Lippert’s laboratory for the UV-Vis and fluorescence spectrometer, Runčevski’s laboratory for the TGA and DSC instruments, Tsarevsky’s laboratory for the GPC and light scattering instruments, and Zoltowski’s laboratory for friends.

I am most grateful to my family, friends, and girlfriend for their love, support, and help along the way. My train family on the DART were consistent and supportive. My gym friends were great. My golf, fishing, and shooting buddies have been great fun. And my collaborators,
and undergraduate and high school students, and community college staff and students have been very helpful and supportive. Thanks!!!
A series of semi-fluorinated and non-fluorinated Diels–Alder step-growth polyarylene polymers and co-polymers were synthesized via typical oil bath heating (days/weeks) and more rapid microwave-assisted polymerization (hours). The polymers were characterized by multinuclear (¹H, ¹³C, and ¹⁹F) NMR and ATR–FTIR spectroscopy, thermal analysis (TGA, DSC, and DMA), GPC, XRD, water contact analysis (WCA), and refractive index (RI) measurements. The NMR spectra indicated a mixture of para and meta conformations through the polymer backbone increasing to more para with greater fluorine content. Thermal gravimetric analysis revealed the fluorine-containing polyarylenes possessed the highest char yields at almost 80% at 1000 °C under nitrogen, and all the polyarylenes possessed onset of degradation temperatures above 550 °C under nitrogen and air atmospheres. XRD analysis showed more ordering for the fluorine-containing polyarylenes which afforded the high char yields. DMA gave storage moduli values in the range of 1-10 GPa for the polyarylenes. GPC results indicated molecular weights for all samples were above 100 kg/mol. Water contact angles did not change with fluorine content due to the shielding effect of the pendant phenyl groups. However, the refractive index decreased to 1.6497 at 632.8 nm for the polyarylene with the highest fluorine content.
A series of six new polyarylene polyimides (PAPI) were prepared from a new diamino-phenylated-phenylene synthesized via a Diels–Alder reaction, followed by a one-step microwave-assisted step-growth polycondensation reaction with a variety of dianhydrides. The polymerizations were optimized from 10 to 30 minutes in reaction time with isoquinoline as catalyst. Yields as high as 99% were achieved using nitrobenzene as the solvent. Semi-fluorinated dianhydrides were included to compare polyimide properties to the non-fluorinated materials. Full characterization was carried out via $^1$H and $^{19}$F nuclear magnetic resonance and attenuated total reflectance Fourier transform infrared spectroscopy. Thermal properties were characterized via thermal gravimetric analysis and differential scanning calorimetry. The onset of thermal degradation was approximately 550 °C in nitrogen and air atmospheres while the char yield at 1000 °C in nitrogen was almost 70%. The semi-fluorinated polyarylene polyimide exhibited the highest char yield. The glass transition temperatures were in the range of 355 to 387 °C, with the semi-fluorinated material possessed the highest $T_g$. The optical transparency was good in all the materials, with the semi-fluorinated material having the largest optical window in the UV-Vis region. The polymers were colorless or pale-yellow solids. Solubility was excellent in chloroform, tetrahydrofuran, toluene, and cyclohexanone.

The new diamino-phenylated-phenylene (PDA) was synthesized utilizing a Diels-Alder reaction affording a mixture of para and meta conformations. This new hardener was cured with bisphenol A diglycidyl ether (BADGE). To investigate the conformation mixture, pure 1,4-benzenediamine and 1,3-benzenediamine were cured with BADGE. DSC was employed to observe cure curves affording the onset, peak, and enthalpy change, as well as the glass transition temperature. ATR–FTIR spectroscopy was used to elucidate the structures of the cured network.
samples. TGA was used to determine thermal stability, and DMA was used to obtain thermal mechanical properties including storage and loss modulus and tan delta.

Diels–Alder reactions were utilized to end-cap small molecule phenylated phenylene with ethynyl and phenylethynyl end-groups, resulting in the synthesis of two new resins. An oligomeric phenylated polyphenylene was prepared with terminal phenylethynyl groups producing a third new resin. Melting points were in the range of 80 to 150 °C and curing temperatures in the range of 160 to 400 °C.

Boron nitride nanotubes (BNNTs) were successfully functionalized with acetylene end-groups using hypervalent iodine. High molecular weight polyarylene was synthesized via microwave-assisted polymerization. Polyarylene-boron nitride nanotube nanocomposite materials were prepared and characterized.
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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ATR</td>
<td>attenuated total reflection</td>
</tr>
<tr>
<td>BPA</td>
<td>bisphenol A</td>
</tr>
<tr>
<td>C</td>
<td>Celsius</td>
</tr>
<tr>
<td>$^{13}$C NMR</td>
<td>carbon nuclear magnetic resonance</td>
</tr>
<tr>
<td>$\delta$</td>
<td>NMR chemical shift in parts per million</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DGEBA</td>
<td>diglycidyl ether of bisphenol A</td>
</tr>
<tr>
<td>DMA</td>
<td>dynamic mechanical analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>EI</td>
<td>electron impact</td>
</tr>
<tr>
<td>EM</td>
<td>electron microscopy</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>fluorine nuclear magnetic resonance</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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</table>

XX
GC-MS ............................................................ gas chromatography-mass spectrometry

GPC/SEC .................................................. gel permeation chromatography/size-exclusion chromatography

$^1$H NMR ........................................................ proton nuclear magnetic resonance

HETCOR ........................................................ heteronuclear correlation spectroscopy

HMBC ........................................................ heteronuclear multiple bond correlation spectroscopy

HSQC ........................................................ heteronuclear single quantum coherence

$J$ ..................................................................................... joule (kg⋅m$^2$⋅s$^{-2}$)

$J$ ................................................................ coupling constant (NMR spectroscopy)

$m$ ..................................................................................... meta

m/z ................................................................ mass-to-charge ratio

MHz ........................................................ megahertz

$M_n$ ........................................................ number-average molecular weight

$M_w$ ........................................................ weight-average molecular weight

$M_w/M_n$ ........................................................ molar mass dispersity, $D_M$

$\nu$ .......................................................... wavenumber (cm$^{-1}$)
nm……………………………………………………………………………….. nanometer

NMR…………………………………………………………………………… nuclear magnetic resonance

o………………………………………………………………………………… ortho

p………………………………………………………………………………… para

%………………………………………………………………………………… percent

ppm……………………………………………………………………………. parts per million

pXRD…………………………………………………………………………… powder X-ray diffraction

$R_f$……………………………………………………………………………… retention factor

rt ………………………………………………………………………….. room temperature

T……………………………………………………………………………… temperature

$\text{Tan } \delta_{\text{max}}$……………………………………………………………… tan delta max

TBAF…………………………………………………………………………… tetrabutylammonium fluoride

$T_d$……………………………………………………………………… onset of thermal decomposition temperature

TEA…………………………………………………………………………… triethylamine (NEt$_3$)

$T_g$……………………………………………………………………………… glass transition temperature
TGA………………………………………………………………………… thermal gravimetric analysis

TLC………………………………………………………………………… thin layer chromatography

THF………………………………………………………………………… tetrahydrofuran

UV-Vis…………………………………………………………………… ultraviolet-visible

wt%………………………………………………………………………… weight percent
DEDICATION

I would like to dedicate this work to my father, Michael Budy, my grandfather, Ted Budy, my aunt and uncle, Tamara and Fred Kenniston, my uncle Leonard Rosson, and uncle Milt “Donkey Bop” Minter.

You know, I'm just a regular guy who grew up with the posters of these guys on my wall... and now I'm one of them! That's right, I'm standing here, living proof that if you work hard enough, and you want it bad enough... dreams do come true. So, follow your dreams... - Izzy
Chapter 1

INTRODUCTION

1.1. Background

Fluorinated polymers were initially based on fluorine modified vinyl monomers, but the desirable chemical and thermal stability and low surface energy from having fluoride substituents was applied to high performance polymers starting in the 1950's. High performance, or more specifically, high temperature organic polymer research was initiated in the late 1950’s primarily to meet the needs of the aerospace and electronics industry. Along with the development in aerospace technology and space exploration, came an increased demand for new materials which would be able to withstand severe environmental conditions.

Most of the compounds that display good thermal stability contain aromatics, which is the simplest organic structure resistant to thermal decomposition or oxidation. Benzene has been reported to be stable up to 530 °C. The linear combination of benzene rings linked directly together along the backbone produces polyphenylene, the simplest, totally aromatic polymer. The melting points increase as the number of phenyl units increases, and there is a strong dependence on whether the linkage is ortho, meta, or para.

Further evidence supporting the use of polyphenylenes as high temperature polymers is that oligophenyls (terphenyls to sexiphenyls) have been used as high temperature lubricants, hydraulic fluids, heat-transfer agents, and coolants for nuclear reactors. Polyarylenes are formally described as those polymers composed of macromolecules containing exclusively arenediyil
(formerly arylene) or heteroarenediyi (formerly heteroarylene) units in the backbone; polyphenylenes are a subclass of polyarylenes.

1.2. Synthesis of Polyarylenes

1.2.1. Dehydration of Poly(1,3-Cyclohexadiene)

Cationic, anionic, and Ziegler-Natta-type catalysts have been used to polymerize 1,3-cyclohexadiene (Figure 1), as well as more exotic examples. The best conversions were seen under anionic conditions with organolithium compounds. The polymerization of 1,3-cyclohexadiene with Ziegler-Natta catalysts (e.g., triisobutylaluminum-titanium tetrachloride ($i$-Bu$_3$Al-TiCl$_4$), vanadium trichloride (VCl$_3$), or tetrabutyl titanate (Bu$_4$Ti)) lead to low molecular weight amorphous materials. The product polymers contained only 1,4-bonds with no 1,2-structures.

![Figure 1](image)

**Figure 1.** Cationic, anionic, and Ziegler-Natta-type catalytic polymerization of 1,3-cyclohexadiene followed by dehydrogenation to afford polyphenylene.

Interestingly, anionic polymerization of 1,3-cyclohexadiene using alkyl lithium/amine in hydrocarbon solvent leads to predominate formation of 1,2-product. Bergman cycloaromatization of enediynes leads to the formation of substituted polyphenylenes. The use
of cationic initiators such as boron triflouride (BF$_3$), phosphorus pentafluoride (PF$_5$), and titanium tetrachloride (TiCl$_4$) lead primarily to mixtures of 1,2- and 1,4-linked poly(1,3-cyclohexadiene). Anionic conditions using $n$-butyllithium or sec-butyllithium lead to polymers with up to 98% conversion.\textsuperscript{23} Attempted radical polymerization of 1,3-cyclohexadiene initiated thermally or by benzoyl peroxide resulted in two competing reactions; dimerization and polymerization. Polymers obtained under these conditions were of low molecular weight. Substituted poly(cyclohexene) was prepared by radical polymerization of cyclohexadiene-1,2-diol derivatives, and then thermal treatment or exposure by deep-UV energy in the presence of a photoacid generator afforded polyphenylene.\textsuperscript{24}

The aromatization of poly(1,3-cyclohexadiene) to the desired polyphenylene was accomplished by a variety of catalytic and chemical methods. For example, $p$-chloranil (2,3,5,6-tetrachloro-$p$-benzoquinone) in refluxing xylene for 48 h lead to a tan product with 30% nonaromatic poly(1,3-cyclohexadiene). Further aromatization at 450 °C for 5 h under an inert atmosphere lead to 90% polyphenylene.\textsuperscript{25} Alternatively, aromatization can be carried out by halogenation of the remaining double bound with either chlorine or bromine followed by pyrolysis ($>300$ °C).\textsuperscript{26} A disadvantage of this method is the obtained polymer may contain residual amounts of halogen.
1.2.2. Oxidative-Cationic Polymerization

The very readily available precursor benzene can be polymerized to poly($p$-phenylene) through the use of a Lewis acid, a co-catalyst, and an oxidizing agent (Figure 2). The first method involved aluminum chloride (AlCl$_3$), ferric chloride (FeCl$_3$), and a co-catalyst (e.g., water hydrogen sulfide, acetic acid, and nitroethane).$^{27-31}$

![Figure 2](image)

**Figure 2.** Oxidative-cationic polymerization of benzene via Lewis acid, co-catalyst, and oxidant.

The product was obtained (2 hr at 80 °C) as a rust-colored, crystalline material with possible chlorination of the ring. The reaction of benzene with an aluminum chloride-cupric chloride-water system was the first example of a well-defined polymerization of an aromatic backbone to give a homopolymer.$^{32-33}$ The product was obtained under mild conditions (30 min at 37 °C) as a brown material containing minor amounts of chloride. Other Lewis acid combinations were found to be effective as well; molybdenum pentachloride-water$^{34}$ and antimony pentachloride-cupric chloride.$^{35}$ The ratio and amounts of each reactant were also studied. In the aluminum chloride-cupric chloride-water system, an aluminum chloride to cupric chloride ratio greater than 2:1 lead
to nearly quantitative yields of poly($p$-phenylene) while the use of lower ratios resulted in a
decrease in yield (ca. 20%).

Studies were carried out to determine the effect of the catalyst-co-catalyst in the benzene-
ferric chloride-water system\textsuperscript{31} and the aluminum-cupric chloride-water system.\textsuperscript{36} When water was
added as a co-catalyst, the rate of polymerization was enhanced, but the effect was less important
at longer reaction times; the most active catalyst-co-catalyst complex was ferric chloride-water
(1:1 ratio).\textsuperscript{31} However, any additional amounts of water to the aluminum chloride-cupric chloride-
water reduced the amount of poly($p$-phenylene) obtained.\textsuperscript{35} The molecular weight also decreases
at higher reaction temperatures and lower concentration of benzene in all the solvents investigated
($p$-dichlorobenzene, 1,2,4-trichlorobenzene, and $o$-dichlorobenzene). In addition, the
polymerization will not take place with the Lewis acid alone, so the oxidation is necessary for the
formation of polymer. The polymerization must also take place stepwise and not by random
coupling.\textsuperscript{37}

Important disadvantages of these polymerization systems for the synthesis of poly($p$-
phenylene) are the formation of polynuclear segments, branching along the main chain, and the
incorporation of chlorine or other heteroatoms into the polymer backbone. The formation of
polynuclear segments and branching occur during the chain growth process, while the chlorination
or halogenation occurs during termination of the growing cation chain end with a free halogen
ion.\textsuperscript{38}

1.2.3 Metal-Catalyzed Coupling Reactions

The Wurtz-Fittig\textsuperscript{39-40} reaction, Ullmann\textsuperscript{41-42} synthesis, and coupling of Grignard\textsuperscript{43} reagents
and organolithium compounds have been used to synthesize polyphenylene (Figure 3).\textsuperscript{44-52} Direct
synthesis of polyphenylene by oxidation of benzene or nickel(0) coupling of dihalobenzenes leads to insoluble material with low molecular weight or soluble (pyridine, quinoline, and aqueous sodium hydroxide) with a degree of polymerization (DP) less than 100. The direct oxidation method contains a large amount of defects due to the 1,2-coupling and formation of condensation polyaromatic units, while the nickel coupling of the dihalobenzene method affords solely a 1,4-coupling. In order to increase the solubility of the polymers, pendant groups were utilized.

Figure 3. Metal-catalyzed coupling reaction with substituted and unsubstituted benzene to afford polyphenylene.

The Ullmann condensation of 3,3’-dinitro-4,4’-diidodiphenyl yielded a yellow, crystalline solid. The average degree of polymerization was determined to be 52. The presence of the nitro substituents increased the solubility in polar solvents (e.g., nitrobenzene, dimethyl formamide), but the material was generally insoluble in other solvents. The reactions of 1,4-dibromo or diidoperfluorobenzene under Ullmann conditions lead to a polymer that had low molecular weight and contained residual amounts of bromine or iodine. Similarly, poly(perfluorophenylene) was prepared from dichlorotetrafluorobenzene (80% meta and 20% ortho isomer) over copper powder in a sealed ampoule. Other transition metal catalysts (e.g., palladium) have been successful as well. The Ullmann synthesis has been useful for the preparation of many substituted...
polyphenylenes as well. Typically, higher molecular weights and melting points are found from the Ullmann reactions.

The first reported synthesis of polyphenylene was a Wurtz-Fittig reaction using 1,4-dichlorobenzene employing metallic sodium or sodium-potassium alloy in dioxane. The afforded polymer was tan, amorphous, and soluble in benzene. The product was obtained in ca. 50% yield with a molecular weight of 2700. Chlorine analysis showed the polymer contained approximately one chlorine atom per five to seven aryl units. The backbone was thought to be primarily connected in the 1,4-position due to ultraviolet-visible (UV-vis) spectroscopy results. Little has been explored since the synthesis and mechanism were announced. However, organometallic synthesis continues in niche areas along with dechlorination of chlorobenzene.

The Grignard method of polymerization has been successful in the preparation of meta-linked and substituted polyphenylenes. Grignard reactions typically yield higher molecular weight polymers compared to the Wurtz-Fittig method, but lower molecular weights than the Ullmann synthesis. The preparation of a homopolymer containing 1,3-bonds was carried out by heating a solution of the mono-Grignard reagent of m-dibromobenzene in refluxing benzene in the presence of ferric chloride or cobaltous chloride. The polymer had a molecular weight of 2000. The Grignard reaction was also used to prepare poly(perfluorophenylene) by refluxing pentafluorophenylmagnesium bromide or chlorine in tetrahydrofuran, with o-chloroperfluorotoluene. Polymers with melting points between 230 and 350 °C were obtained. The poly(perfluorotoluene) adduct was more soluble than the poly(perfluorophenylene) and had high molecular weights. This can be assumed to be from the higher solubility of the monomer allowing higher diffusion while being polymerized.
Also noteworthy are some multi-step synthetic schemes to arrive at polyphenylene. One method starts with microbial (*Pseudomonas putida*) oxidation of benzene to afford cyclohexadienediol. Radical-initiated polymerization (i.e., using 2,2'-azobisisobutyronitrile, AIBN) of the diacetate gives the precursor polymer, which is then thermally converted into polyphenylene.\(^9\) This material, however, is not stereoregular and contains 10-15% of 1,2-linkages. Totally regioregular polyphenylene has been prepared by Grubbs *et al.* by a stereospecific nickel-catalyzed polymerization of a cyclohexanediol disilylether, followed by conversion of the resulting polymer to poly(*p*-phenylene) via the acetoxy-precursor.\(^70-73\) Another method for preparing poly(*p*-phenylene) is nickel catalyzed polycondensation of methyl 2,5-bromobenzoate, which was hydrolyzed to the polyacid, and then decarboxylated to give only 1,4-linkages.\(^54,\ 74\) Electropolymerization can also be utilized under reductive or oxidative conditions from metal surfaces (i.e., conductive surfaces) to prepare polyphenylene films.\(^75\)

### 1.2.4. Diels–Alder Polymerization

One of the most successful synthetic methods of polyphenylenes has been the Diels–Alder\(^76-78\) reaction of bistetracyclone with bisacytlenes (Figure 4).\(^79\) All the obtained polymers were an off-white, amorphous phenylated polyphenylene,\(^80-86\) which will be referred to as polyarylene. The reaction was carried out in toluene at 180–250 °C for 24 h to afford quantitative yields of high molecular weight polymers (20–100 kg/mol). Surprisingly, these polymers are soluble up to *ca.* 15 wt% in common organic solvents (e.g., benzene, toluene, tetrahydrofuran, chloroform,
Figure 4. Diels-Alder polymerization of bistetraphenylcyclopentadienone (bistetracyclone) with diacetylenes to afford polyarylene.

e.g.) at 25 °C, which can be attributed to the presence of the pendant phenyl groups, as well as a portion of the backbone containing meta linkages. The intermediate adduct decomposes with the loss of carbon monoxide to yield the substituted polyarylene. Due to the asymmetric nature of the intermediate which can be formed during polymerization, the resulting polyarylenes may contain a mixture of meta- and para-linkages along the backbone.

The Diels−Alder reaction has been successful as a step-growth reaction in the formation of linear, ladder, and step-ladder polymers. Polymer formation is particularly effective when a small molecule such as carbon monoxide, carbon dioxide, or sulfur dioxide is lost during the polymerization, thereby driving the reaction forward and preventing the retro-Diels−Alder reaction from occurring. High molecular weight polymers can be produced from either the monomer containing both the diene and dienophile (AB-type monomer) or from the reaction of equal molar equivalents of a bisdiene (AA-type monomer) with a bisdienophile (BB-type monomer).
In addition to the typical Diels–Alder reaction to afford polyarylenes, more exotic examples have been prepared.\textsuperscript{4, 81-83, 94-97} Starting from 1-ethynyl-3-(2,3,4,5-tetraphenylphenyl)azulene a synthesis of dumb-bell shaped alkynyl-bridged diazulenyl compounds and a triazulenylbenzene derivative was accomplished.\textsuperscript{98} A series of polyarylenes containing short alkylene chains (i.e., (CH\textsubscript{2})\textsubscript{n} with n = 3, 4, 6, 10, and 14) in between the phenylated phenylene units was also prepared.\textsuperscript{99} 2-Cyanopyridine has also been shown to be an effective dienophile in a Diels–Alder cycloaddition reaction with tetraphenylcyclopenta-2,4-dien-1-one to form 2-(2’-pyridyl)-3,4,5,6-tetraphenylpyridine.\textsuperscript{100} These interesting heteroatom adducts were not polymerized, but were complexed with rhodium and palladium for new possible catalysis. Tetracyclone was reacted with lithiopentafluorobenzene (C\textsubscript{6}F\textsubscript{5}Li) to form 2-pentafluorophenyl-2,3,4,5-tetraphenylcyclopent-3-en-1-one and 5-hydroxy-5-pentafluorophenyl-1,2,3,4-tetraphenylcyclopentadiene as the results of 1,6- and 1,2-additions, respectively. Interestingly, the reaction of 3-ferrocenyl-2,4,5-triphenylcyclopentadienone with C\textsubscript{6}F\textsubscript{5}Li leads to 4-ferrocenyl-4-pentafluorophenyl-2,3,5-triphenylcyclopent-2-en-1-one and 5-hydroxy-5-pentafluorophenyl-2-ferrocenyl-1,3,4-triphenylcyclopentadiene, the products of 1,4- and 1,2-addition, respectively.\textsuperscript{101}

1.3. Properties

1.3.1. Solubility and Solution Properties

The properties of polyarylenes are as diverse as the methods for their synthesis. The effects of ortho, meta, and para linkages, as well as the various substituents, vary considerably with the method of preparation. Due to the early work on unsubstituted polyphenylene being intractable and insoluble, the polymer characterization has been very poor. However, the presence of ortho linkages in polyphenylene prepared by dehydrogenation of poly(1,3-cyclohexadiene) has been
ruled out and the rings are believed to be nearly coplanar. X-ray analysis showed a strong band present at 4.54 Å due to the lateral packing of the polymer chains, and not due to the repeat d spacing of one poly(p-phenylene) unit (expected to be 4.20–4.30 Å).\textsuperscript{102} The polyphenylene prepared by the Wurtz-Fittig method showed no crystallinity upon X-ray analysis.\textsuperscript{26} Molecular dynamic (MD) calculations have also been used to study the behavior of polyphenylene, once thought to be completely a rigid rod. The MD calculations showed the backbone to be surprisingly flexible with changes in end-to-end distances as large as 16%. An examination of the energies (calculated by various methods) associated with out-of-plane bending deformation, suggests that the rigid rod polymers may in fact be even more flexible than the simulations indicate. The results provide rationalizations for the relatively short persistence lengths measured in solution and for bending observed in high-resolution electron micrographs of these materials.\textsuperscript{103}

There are a number of approaches for improving the solubility of polyarylenes.\textsuperscript{104} Semi-fluorinated polyarylenes have been synthesized by incorporating fluorine into either the bis(cyclopentadienone)\textsuperscript{105-107} or the diethynyl.\textsuperscript{108-109} However, the most efficient method of attaining greater solubility is by the incorporation of phenyl substituents into polyarylenes.\textsuperscript{86} Another method that will assist in solubility is the control and amount of metal/para linkages in the backbone.\textsuperscript{4} Thus, the random arrangement of metal/para linkages within the polymer backbone, a high degree of branching at irregular intervals, and varying chain lengths should lead to amorphous polyarylenes with high solubility. Stille and Noren used a model reaction (3-(4-biphenylyl)-2,4,5-triphenylcyclopentadienone with 4-ethynylbiphenyl) to produce the meta and para-linked isomers (Figure 5).\textsuperscript{110} The biphenyl moiety was chosen to represent the growing chain. The reaction was carried out at 200 °C in order to obtain a sufficient quantity for characterization.
Figure 5. Scheme of the Diels–Alder step-growth model reaction studied by Stille and Noren to obtain meta/para linkages.

The pure isomers were separated by fractional crystallization; two isomers were recovered with melting points of 278 and 200 °C. An independent synthesis of the alleged para product was accomplished by a Diels-Alder reaction performed at 200 °C, which led to a product with a melting point of 275–277 °C. The assignment of the meta structure being the lower melting isomer was
presumed to be due to the lack of symmetry, because the unsubstituted *meta*-linked oligophenylene had a low melting point which slowly increased as the number of phenylene units increased. However, more recently, Mullen *et al.* performed another model reaction (1,4-bis(2,4,5-triphenylcyclopentadienone-3-yl)benzene with 4-ethynylbiphenyl), but this time used more modern tools (high resolution NMR including C–H correlation in 2D-NMR spectra and NOE measurements, IR spectroscopy, and single-crystal X-ray analysis) to characterize the products (Figure 6).\(^ {111}\) The Diels-Alder reaction was carried out at 240 °C and the isomers were separated by crystallization. One product was obtained in 83% yield and had a melting point of ca. 350 °C. NMR analysis suggested the main product was the \((m,m)\) isomer, which was confirmed by X-ray analysis. The authors claimed to correct Stille and Noren’s previous conclusion that no more than 50% of the *meta* isomer was produced in the Diels–Alder reaction. However, both model reactions used different monomers, solvents, and conditions, and therefore should not be compared. Mullen’s model monomer was closer to the typical polyarylene system, but only was performed at 240 °C with 80% yield. According to Stille’s model reaction study, increasing reaction temperatures resulted in increasing *para* linkages. Obviously, more work in this area is necessary to understand and control the Diels-Alder synthesis for polyarylenes.
Figure 6. Scheme of the Diels–Alder step-growth model reaction studied by Mullen et al. to obtain \((m,m), (p,p), (m,p),\) and/or \((p,m)\) linkages.
1.3.2. Thermal Stability

The types of degradation mechanisms vary depending upon the environmental conditions in which the polymer is used and the structure of the polymer. The changes which occur in a polymer during degradation are manifested in a number of ways depending upon the type of degradation process involved. The types of property changes may be divided into chemical or physical. Degradation/oxidation reactions are dependent on the presence of oxygen, temperature, and the structure of the polymer. One of the most interesting properties of polyarylenes is their thermal stability. Unfortunately, the thermal stability was only reported in terms of melting point early in the literature, while more recently thermal gravimetric analysis has been used. This makes comparison of the effects of the method of preparation, environment, true molecular structure, or any other parameter very difficult.

The relative stability of different polymer systems has long been the subject of much discussion and debate in search for the ultimate question regarding the inherent instability of polymers. The degradation and oxidation of polymers leads to chain scission; therefore, the most important factor controlling polymer stability is the stability of their primary bonds. Thus, the stronger the chemical bond, the more stable the polymer (Table 1). Molecular rigidity and the absence of oxidizable groups (e.g., C–H bonds) will contribute significantly to their stability. More specifically, the incorporation of aromatic rings induces a high degree of rigidity and reduces chain flexibility; stability increases in the order poly(phenylene sulfide) < poly(phenylene oxide) < poly(p-xylene) < poly(p-phenylene).
Table 1. Bond strength values (kJ/mol)\textsuperscript{114}

<table>
<thead>
<tr>
<th>Bond</th>
<th>Strength (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—S</td>
<td>273</td>
</tr>
<tr>
<td>B—H</td>
<td>294</td>
</tr>
<tr>
<td>Si—H</td>
<td>319</td>
</tr>
<tr>
<td>P—O</td>
<td>528</td>
</tr>
<tr>
<td>C═C</td>
<td>609</td>
</tr>
<tr>
<td>C—N</td>
<td>307</td>
</tr>
<tr>
<td>B—C</td>
<td>374</td>
</tr>
<tr>
<td>Si—C</td>
<td>328</td>
</tr>
<tr>
<td>P—C</td>
<td>580</td>
</tr>
<tr>
<td>C═N</td>
<td>617</td>
</tr>
<tr>
<td>C—Cl</td>
<td>340</td>
</tr>
<tr>
<td>B—N</td>
<td>386</td>
</tr>
<tr>
<td>Si—N</td>
<td>437</td>
</tr>
<tr>
<td>Ti—O</td>
<td>672</td>
</tr>
<tr>
<td>C—C</td>
<td>349</td>
</tr>
<tr>
<td>B—O</td>
<td>777</td>
</tr>
<tr>
<td>Si—O</td>
<td>445</td>
</tr>
<tr>
<td>C—O</td>
<td>361</td>
</tr>
<tr>
<td>C—H</td>
<td>416</td>
</tr>
<tr>
<td>C—F</td>
<td>428</td>
</tr>
</tbody>
</table>

Polyphenylene produced from poly(1,3-cyclohexadiene) showed no weight loss via thermal gravimetric analysis for periods up to 72 h at 230 °C in air and gradual weight loss in air at 400 °C, and a major loss at 450 °C.\textsuperscript{9,10} Polyphenylene obtained from the polymerization of benzene showed a major weight loss in air at 508 °C.\textsuperscript{115} An analysis of the pyrolysis byproducts of these polymers by gas chromatography showed the presence of five components;\textsuperscript{116} the first component was a 20:1 molar mixture of hydrogen and methane, followed by benzene (4.1% w/w), biphenyl (2.5%), \textit{p}-terphenyl (0.4%), and \textit{p}-quaterphenyl (0.8%). The thermo-oxidative degradation of poly(\textit{p}-phenylene) produced from the dehydropolymerization of benzene from aluminum chloride-cupric chloride and the Wurtz-Fittig reaction was investigated under isothermal conditions at 50 °C intervals.\textsuperscript{25} The thermal stability in air of the polyphenylene from benzene was in the range of 400-450 °C, while the thermal stability from the Wurtz-Fittig reaction was 350-400 °C. Polyphenylenes from the oxidative polymerization of Grignard reagents exhibited a weight loss of 7% at 500 °C in air.\textsuperscript{25} Polyphenylenes from the Diels–Alder reaction showed degradation at \textit{ca}. 500 °C in air.\textsuperscript{117} Polyarylenes prepared by the reaction of bis-
tetracyclones with diethynyl benzene degrades in air at 550 °C.\textsuperscript{82,83} Surprisingly, \textit{meta-} and \textit{para-}
linked poly(perfluorophenylene) under inert conditions were comparable to polyphenylene, but
inferior under an oxygen atmosphere. Thermal studies on high molecular weight (DP ≈ 100)
poly(perfluorophenylene) showed a gradual weight loss of 10% up to 600 °C, while a low
molecular weight sample (DP ≈ 25) had a major degradation at 380 °C.\textsuperscript{118} The rate of
decomposition was found to obey the typical Arrhenius equation $k = 10^9 e^{-39,000/RT}$.

1.4. Applications

1.4.1. Coatings

Polymer coatings have many properties such as corrosion protection, insulation against
heat and noise, and wear resistance. Steel constructions exposed in harsh environments are often
protected against corrosion by solvent-borne organic coatings.\textsuperscript{119} Polymeric films that are
synthesized by electrochemical methods can find a variety of applications in electrochemical
sensors, solar cells, and electro-chromic devices. The replacement of these polymeric films for
chromium (VI)-containing coatings for iron alloys will have a desirable impact on the
environment.\textsuperscript{120} As mentioned previously, electropolymerization of polyphenylenes has been
successful and may show desirable properties in this field.

Carbon fiber reinforced polyphenylene sulfide (PPS) composite coatings were successfully
prepared via flame spraying.\textsuperscript{121} Flame drying has been attracting increased attention due to its
advantages of low cost, low pollution, and portability. The interface between the substrate and
polymer coating must be taken into account. Polyphenylene sulfide was deposited on the surface
of cold-rolled, stainless and galvanized steels under nitrogen and oxygen atmosphere at 350 °C.
The PPS/steel interface was determined to be dependent on the bond strength species of sulfur-related iron compounds (e.g., Fe$_2$(SO$_4$)$_3$ > FeSO$_4$ > FeS).\textsuperscript{122}

The grafting of polymer films on various substrates (e.g., metal, glass, etc) has attracted considerable attention for many applications. Surface modification plays a pivotal role in controlling such properties as adhesive properties, wettability, corrosion protection, or biocompatibility. The major problem to be overcome is the typical weak adhesion between organic polymers and substrate. Many routes include drop casting, spin coating, spray coating, vacuum evaporation, or Langmuir-Blodgett technique. The most desirable situation is by far the covalent bonding of the thin film by methods such as plasma polymerization, self-assembled mono- and multi-layers, and cathodic, anodic, and electropolymerization.\textsuperscript{123} A new technique called diazonium-induced anchoring process (DIAP) using an aryl diazonium salt proved to be an efficient way of forming a covalent polyphenylene-like adhesion to inorganic or organic surfaces without any conductivity required.

1.4.2 Membranes

1.4.2.1 Proton Exchange Membranes for Fuel Cells

Proton exchange, or more specifically, polymer electrolyte membrane (PEM) fuel cells have attracted a great deal of attention as alternative and environmentally friendly energy sources for transportation, portable devices, and stationary power.\textsuperscript{124} A successful commercial product, Nafion\textsuperscript{TM}, is a popular proton exchange membrane for fuel cell applications due to its excellent conductivity and chemical stability.\textsuperscript{125} Proton exchange membranes require high proton conductivity, sufficient thermal stability, low permeability to fuel and oxidant, and long-term stability and durability.\textsuperscript{126} However, their high cost and relatively low operation temperatures limit
applications into the future. Sulfonated aromatic polymers, such as poly(arylene ether),\textsuperscript{127} poly(arylene ether ether ketone),\textsuperscript{128} perfluorocyclobutyl (PFCB) aryl ether polymer,\textsuperscript{129,130} polyimide,\textsuperscript{131} poly(phenylene sulfide),\textsuperscript{132} poly(\textit{p}-phenylene),\textsuperscript{133} polyarylenes,\textsuperscript{134} and polybenzimidazole\textsuperscript{135} have been investigated as PEM materials. The sulfonated versions of these polymers were chosen for their good proton conductivity, thermal stability, and low cost, however, most of them have a crucial problem with long-term stability under high operating temperatures and conditions of fuel cells. Oxygen diffusion is also a problem, but methanol diffusion in most of the polymers are superior to the Nafion\textsuperscript{TM} for direct methanol fuel cell (DMFC) applications. Much work has been investigated with these polymer systems, including copolymers, block copolymers, cross-linked polymers, and more exotic examples. However, increased control and stability, as well as complete understanding of these materials under fuel cell working conditions are of current interest.

1.4.2.2. Gas Separation Membranes

Membrane science and technology is recognized as a powerful tool in solving some important global problems and developing new industrial processes needed for a sustainable industrial world.\textsuperscript{136} Membrane gas separation is a pressure-driven process with different industrial applications that represent only a small fraction of the potential applications in refineries and chemical industries. Since 1980, when the production of commercial polymeric membranes was implemented, gas separation membranes have rapidly become a competitive separation technology.\textsuperscript{137} It is expected that gas separation membranes will play an increasingly important role in reducing the environmental impact and costs of industrial processes,\textsuperscript{138} especially in the global hydrocarbon reservoirs. There continues to be many opportunities to extend markets for gas
separation membranes; the membrane materials, membrane configuration, and the preparation routes are inadequate to fully exploit all the goals in this area.

Poly(phenylene sulfone)s are one class of polyphenylenes commonly used as a membrane material in processes such as ultrafiltration, reverse osmosis, and gas separation. Gas transport studies have been performed on silicon derivatives of poly(phenylene sulfone)s. Sulfonated polyether sulfone (SPES)-based membranes have been used for hydrogen recovery and natural gas separation. Different degrees of sulfonation exhibited a decrease in permeability and an increase in the selectivity due to the effect of electrostatic cross-linking. Poly(phenylene oxide) (PPO) membranes have a somewhat high gas permeability among aromatic polymeric membranes. Therefore, blends and carbon membranes prepared on a tubular ceramic support represent some of the techniques used to enhance the gas separation properties. The challenge in gas separation membrane technology is to improve upon the current technology. Promising results thus far are still in their infancy and time will tell whether they are significant.

1.4.2.3 Reverse Osmosis Membranes

The world-wide need for fresh water requires more and more plants for the treatment of non-conventional water sources. During the last decades, seawater has become an important source of fresh water in many regions. The traditional desalination processes (i.e., reverse osmosis, etc.) have evolved into reliable methods; the current technology focuses on process improvements in terms of lower cost membranes and a more environmentally friendly operation. Ground water and/or surface water is not always sufficiently available, and the availability is expected to decrease in the future. Therefore, alternative sources of water such as waste water, brackish water, and seawater will gain importance and become more valuable.
The reverse osmosis performance of thin-film composite membranes prepared from sulfonated polyphenylene oxide polymer with different ion-exchange capacities (IEC) was studied using various electrolyte solutes. It was found that the preparation of thin-film composite membranes with high selectivities and high fluxes was possible by adjusting the IEC values and the solvent. The membrane performance was primarily dependent on the ion-exchange reaction between the solute cation and the proton in the sulfonic acid group (–SO₃H), and the Donnan equilibrium. Composite membranes with sulfonated poly(phenylene oxide) showed better performances when high molecular weight polymers were utilized. New polymers continue to represent a great area of research, as well as the development of membrane modules with improved designs. Composite membranes continue to improve and spread beyond the field of reverse osmosis membranes.
2.1. Introduction

High performance plastics, thermoplastics, or polymers (e.g., polyaramides, polyimides, and polybenzimidazoles) typically possess good thermal and chemical stability, excellent mechanical properties, and high glass transition temperatures.\textsuperscript{148-150} Beginning in the 1960s, an increase in need, and therefore research and development, was driven by aerospace and nuclear applications.\textsuperscript{151} High performance polymers must exceed the requirements for standard and engineering polymers, however, these polymers have many disadvantages due to these properties such as the need for special equipment for processing due to the polymers’ insolubility in common organic solvents and lack of a melting temperature.\textsuperscript{152-153} The addition of fluorine substituents has been shown to increase the processability due to increased solubility.\textsuperscript{154-156} Fluorine-containing polymers are also known to contain unique properties due to the low surface energy, as well as high thermal stability, improved chemical stability, and superior oxidative stability.\textsuperscript{155} The bond strength of the carbon-fluorine (C–F) bond is 490 kJ/mol.\textsuperscript{157} Fluorine addition also leads to low dielectric constant, hydrophobicity, and low surface energy due to its small size and high electronegativity.\textsuperscript{158} Due to these improved properties, fluorine-containing polymers are attractive for a wide variety of applications,\textsuperscript{159} including positron emission tomography (PET),\textsuperscript{160} pharmaceuticals,\textsuperscript{161} pesticides,\textsuperscript{162} organic field-effect transistors,\textsuperscript{163} photovoltaics (PVs),\textsuperscript{164}
polymer light emitting diodes (LEDs), polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), and gas separation membranes.

Diels–Alder step-growth polymerization has been utilized for the synthesis of a variety of polymers. More specifically, reacting bistetracyclone dienes, containing the cyclopentadienone moieties, with phenylethlenic dienophiles affording phenylated polyphenylenes or polyarylenes and carbon monoxide. In these Diels–Alder reactions, both meta and para products are possible, and early model compounds pointed toward meta being preferred. Then with more advanced characterization techniques a new model system showed meta was almost exclusively present. And finally most recent a sulfo-phenylated polymer was characterized, as well as model compounds to determine a 50:50 mixture of para and meta is present. Fluorine-containing bistetracyclone and polyarylenes have been studied previously. The 1,3-diethyl-2,4,5,6-tetrafluorobenzene and diphenyl ether bistetracyclone polyarylene possessed the highest molecular weight among the series being studied but the thermal properties were in the middle or toward the lower end of the other polymers studied. The 4,4′-hexafluoroisopropylidene bistetracyclone and bis(4-ethynylphenyl)methanone polyarylene showed relatively low molecular weight and thermal properties compared to the other polymers investigated.

Herein, we discovered and optimized the microwave-assisted synthesis of fluorine-containing polyarylene. The polymers were fully characterized to elucidate the structure-property relationships between the fluorine and non-fluorine-containing polyarylenes. The morphology of the polymers was studied using X-ray diffraction. The thermal properties were investigated using thermal gravimetric analysis in nitrogen and air atmospheres, differential scanning calorimetry, and dynamic mechanical analysis. The polymer molecular weights were determined by gel
permeation chromatography and films could be formed from all samples above 60-75 kg/mol. The optical properties were measured in terms of refractive index, and as expected the fluorine-containing polyarylene had the lowest values.

2.2 Results and Discussion

Six non-fluorinated and semi-fluorinated polymers were synthesized from bistetracyclone and diethynyl aromatic compounds, as shown in Scheme 1. Bistetracyclone and the other six monomers were synthesized according to Scheme 2 and 3, respectively. 1,4-Bisbenzil and diphenyl acetone afforded bistetracyclone under basic conditions in excellent yields (90%) and large scales (up to 50 g). Purification via crystallization afforded very pure materials. 1,4-(1) and 1,3-diethynylnbenzene (2) are commercially available but were sublimed and distilled, respectively, to purify. The other monomers were prepared from dibromo aromatic benzyl precursors reacted under Sonogashira conditions using bis(benzonitrile)palladium(II) dichloride, triphenylphosphine, copper(I) iodide, anhydrous triethylamine, and either trimethylsilylacetylene (TMSA) or 2-methylbut-3-yn-2-ol. The alkyne with alcohol functionalization allowed for crystallization of the protected precursors and no column purification. Deprotection under reflux and basic conditions afforded the products (3, 4, and 6). Purification of the final compounds were accomplished using sublimation giving highly pure monomers. The synthesis of 1,4-diethynyl-2,3,5,6-tetrafluorobenzene (4) which was a liquid required the more typical TMSA protecting group, deprotection using tetra-n-butylammonium fluoride (TBAF, 1 M in tetrahydrofuran), and purification via distillation. Great care must be taken in the distillation as self-polymerization
begins to occur as the last amounts of solvent is removed under reduced pressure. The monomers were characterized via NMR and FTIR spectroscopy.

Scheme 1. Synthesis of semi-fluorinated and non-fluorinated polyarylenes.

The non-fluorinated and semi-fluorinated polyarylene synthesis was optimized using microwave-assistance. Typical oil bath heating was utilized as a comparison (Figure 7). Microwaves can reduce heating effects or hot spots when using sand or aluminum heating blocks, provide more efficient energy to the compounds of interest and not the solvent if desired, and allow faster heating thereby reducing byproducts, increasing yield, and reducing reaction times.\textsuperscript{179-180} Approximately one month of heating in an oil bath is necessary to achieve a molecular weight of over 100 kg/mol. However, using a normal synthetic microwave, the same molecular weight, and even higher, could be achieved in approximately one day. Diphenyl ether proved to be a good
solvent using oil bath techniques due to the high boiling point and ease of removal when precipitating the polymer product in acetone. When optimizing the synthesis using microwaves, diphenyl ether was a poor solvent due to its small dipole moment. A variety of solvents were used to optimize the polymerization (Figure 8). Anhydrous para-xylene, nitrobenzene, toluene, N,N’-dimethylformamide (DMF), tetrahydrofuran (THF), chloroform (CHCl₃), and ACS grade-nitrobenzene were used. The monomers and polymer are soluble in all of the solvents except DMF. All solvents led to measurable molecular weights including DMF, which surprisingly even though the polymer was not soluble still led to oligomeric material. THF produced product with the second
**Figure 7.** Number average molecular weight versus microwave-assisted polymerization time (solvent = anhydrous nitrobenzene; pressure = open due to mechanical stirrer use; 300 W; 180 ± 10 °C) compared to conventional oil bath heating time (solvent = anhydrous diphenyl ether; mechanical stirrer use; 180 °C); (P1).
Figure 8. Number average molecular weights and $M_w/M_n$ ratio versus time optimizing multiple solvents (diphenyl ether, *para*-xylene, ACS-grade nitrobenzene, toluene, $N,N'$-dimethylformamide, tetrahydrofuran, chloroform, and anhydrous nitrobenzene) for the microwave-assisted polymerization of P1 at 0.12 M concentration.
highest molecular weight but also produced the highest polydispersity in the molecular weights. Anhydrous nitrobenzene was the best solvent affording a number molecular weight close to 300 kg/mol in 24 hr, whereas ACS grade-nitrobenzene was one of the worst solvents due to impurities preventing step growth polymerization. Next, different monomer concentrations were varied to increase the molecular weight quicker (Figure 9). Nitrobenzene and THF were the top two solvent systems so a concentration of 0.24 and 0.36 M were used. THF did not show a significant concentration effect but slightly lower dispersities were achieved. Nitrobenzene increased to almost 175 kg/mol in only 5 hr at 0.24 M while at 0.36 M at only 2 hr almost reached 150 kg/mol molecular weight. The polydispersity did increase with concentration as well. Higher concentrations were not possible due to the increase in viscosity and the microwave stirring mechanism not being able to stir. The microwave did have an “open” setting whereby a reflux condenser was attached and a mechanical stirrer with glass stir rod and plastic paddle was utilized during the microwave polymerization (Figure 7). In this case, the molecular weight increased to approximately 350 kg/mol in 35 hr. An ideal microwave system would consist of a mechanical stirrer kept under pressure and including the possibility of large-scale setups.
Figure 9. Number average molecular weights and $M_w/M_n$ ratio versus time optimizing two concentrations (0.24 M and 0.36 M) for the microwave-assisted polymerization of P1 using anhydrous THF and nitrobenzene.
Once optimal polymerization conditions were established, polyarylenes \textbf{P1-P6} were prepared from the corresponding monomers \textbf{1-6} via Diels–Alder microwave-assisted polymerization. Proton NMR spectroscopic analysis of 1,4-diethynylbenzene polyarylenes has been confirmed previously via 2D NMR\textsuperscript{176} and was used in this study to confirm the successful formation of polyarylene and also provided additional morphology elucidation (\textbf{Figure 10}). The \textsuperscript{1}H NMR peaks are all confined to the aromatic region between approximately 6.0–7.5 ppm. The CDCl\textsubscript{3} peak is present at 7.26 ppm in all spectra. The central aromatic peak from the starting material bistetracyclone is preserved in the polymer and gives a triplet-like peak found between 6.0–6.5 ppm. This peak shows the ratio between the three possible conformations: \textit{meta-meta} (\textit{m-m}), \textit{para-para} (\textit{p-p}), and \textit{para-meta} (\textit{p-m}).
Figure 10. Proton NMR spectra (CDCl$_3$, 500 MHz) of non- and semi-fluorinated polyarylene (P1-P6).
For P1 (Figure 11), the aromatic hydrogen atoms of the 1,4-diehtynylbenzene monomer are present at 7.43 ppm. The pendant phenyl group hydrogen atoms are present between 6.79–7.24 ppm. The hydrogen atoms at each end of the newly formed phenyl groups from the Diels–Alder polymerization, which are a mixture of para and meta isomers, are found between 6.54–6.78 ppm.

In the signals assigned to the central aromatic ring of the bistetrycylcone monomer, the m-m peak is present at 6.34 ppm, the p-p peak is present at 6.27 ppm, and the p-m peak is present at 6.20 ppm. The m-m and p-m peaks are similar in height indicating a roughly equal mixture while the p-p peak has the largest height and thereby is the primary component in the polymer conformation.

Figure 11. Proton NMR spectrum (CDCl₃, 500 MHz) of the non-fluorinated polyarylene (P1).
For **P2** (Figure 12), the aromatic hydrogen atoms of the 1,3-diethynylbenzene monomer have shifted upfield to 7.09–7.24 ppm. The pendant phenyl group hydrogens are found at 6.73–7.08 ppm. The *para/meta* mixture hydrogen atoms are between 6.50–6.71 ppm. Interestingly, the *m-m* peak at 6.33 ppm and the *p-p* peak at 6.26 ppm are of similar height indicating more *meta* conformation than **P1**. The *p-m* peak at 6.16 ppm is smaller than either peak. Additional splitting and shoulders indicate further conformation ordering beyond pure *para* or *meta*.

![Figure 12. Proton NMR spectrum (CDCl₃, 500 MHz) of the non-fluorinated polyarylene (P2).](image-url)
For P3 (Figure 13), the biphenyl hydrogen atoms are observed at 7.50 and 7.32 ppm. The pendant phenyl group hydrogens appear between 6.84–7.24 ppm. The para and meta hydrogen atoms of the newly formed aromatic ring are observed between 6.58–6.85 ppm. In the signals assigned to the central aromatic ring of the bistetracyclone monomer, the m-m peak at 6.38 ppm is the smallest, indicating the biphenyl moiety is too bulky for substantial meta conformation, but not eliminated completely. The p-p peak is the largest at 6.31 ppm while the p-m peak at 6.24 ppm is between the two others in height.

Figure 13. Proton NMR spectrum (CDCl₃, 500 MHz) of the non-fluorinated polyarylene (P3).
For the semi-fluorinated $\text{P4}$ (Figure 14), there are no hydrogen atoms from the diethynyl phenyl group monomer since they are all replaced with fluorine. The pendant phenyl group hydrogen atoms are downfield between 6.76–7.42 ppm. The para and meta mixture hydrogen atoms of the newly formed aromatic ring are observed at 6.52–6.75 ppm. The meta and para content was found to be similar to the non-fluorinated analog. The $m$-$m$ peak at 6.37 ppm and the $p$-$m$ peak at 6.21 ppm are of similar height with the $m$-$m$ peak being slightly larger. However, the $p$-$p$ peak at 6.31 ppm is significantly larger and indicates the predominant configuration.

Figure 14. Proton NMR spectrum (CDCl$_3$, 500 MHz) of the semi-fluorinated polyarylene ($\text{P4}$).
For P5 (Figure 15), the pendant phenyl group hydrogen atoms have shifted downfield slightly further to 6.81–7.42 ppm. The para/meta mixture hydrogen atoms of the newly formed aromatic ring appear at 6.62–6.81 ppm. The m-m and p-m peaks (6.41 and 6.22 ppm, respectively) are of more similar intensity as compared to the analogous non-fluorinated polymer, with the p-p peak at 6.33 ppm still being the largest. Again, shouldering and splitting are present as seen in both 1,3 monomers. The greater amount of para conformation could be due to the fluorine being bulkier than hydrogen.

Figure 15. Proton NMR spectrum (CDCl₃, 500 MHz) of the semi-fluorinated polyarylene (P5).
For P6 (Figure 16), the pendant phenyl group protons have shifted even further downfield to 7.50–6.92 ppm. The \textit{para} and \textit{meta} mixed protons are intermixed with the pendant phenyl group protons at 6.90–6.67 ppm. The \textit{m-m} peak is the smallest even more so like the analog but even more bulky found at 6.47 ppm. The \textit{p-m} peak is significantly more intense at 6.33 ppm while the \textit{p-p} peak is the largest found at 6.40 ppm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure16.png}
\caption{Proton NMR spectrum (CDCl$_3$, 500 MHz) of the semi-fluorinated polyarylene (P6).}
\end{figure}
$^{19}$F NMR spectroscopy ([Figure 17] is a very sensitive technique to elucidate the electronic and local environment when fluorine is present in a small molecule, polymer, or mixture.\textsuperscript{181-182} Due to the fluorinated aromatic ring being close to 90° out-of-plane (model compounds)\textsuperscript{183} and no other fluorine atoms being present, no long-range order is observed in the $^{19}$F NMR spectra except for the P5 which contains $^{19}$F-$^{19}$F coupling. However, as was seen in the $^1$H NMR spectra, clear distinctions between the $\text{para-para}$, $\text{meta-meta}$, and $\text{para-meta}$ conformations are also detected, and more easily observed with fluorine sensitivity and no fluorine background.\textsuperscript{177, 184-185}

![Figure 17. Fluorine NMR spectra (CDCl$_3$, 470 MHz) of semi-fluorinated polyarylene (P4-P6).]
Semi-fluorinated polyarylene P4 (Figure 18) shows a singlet at −140.84 ppm due to the symmetric fluorine in the \textit{para-para} conformation. The \textit{para-meta} conformation now shows two distinct environments at −139.19 and −137.40 ppm. The \textit{meta-meta} conformation is similar with two peaks present at −138.41 and −135.73 ppm indicating only the \textit{para-para} conformation is symmetric with a single peak.

\textbf{Figure 18.} Fluorine NMR spectrum (CDCl$_3$, 470 MHz) of the semi-fluorinated polyarylene (P4).
Semi-fluorinated polyarylene P5 (Figure 19) has three distinct fluorine environments in the para-para position; −165.88 (a), −134.05 (b), −116.81 and −112.88 (c), and −132.49 ppm (d). The para-meta conformation shows a singlet at −164.20 (a), −130.34 (b), −111.36 (c), and −128.38 ppm (d). The meta-meta conformation is present at −162.17 (a), −126.29 (b/d), and −108.71 ppm (c).

Figure 19. Fluorine NMR spectrum (CDCl$_3$, 470 MHz) of the semi-fluorinated polyarylene (P5).
Semi-fluorinated polyarylene P6 (Figure 20) has two symmetric fluorine locations at \(-139.38\) ppm (a/d) and \(-138.60\) ppm (b/c) due to the \textit{para-para} conformation. The \textit{para-meta} conformation shows two peaks present at \(-136.53\) (a/d) and \(-131.87\) ppm (b/c).

![Fluorine NMR spectrum (CDCl\(_3\), 470 MHz) of the semi-fluorinated polyarylene (P6).]

\textbf{Figure 20.} Fluorine NMR spectrum (CDCl\(_3\), 470 MHz) of the semi-fluorinated polyarylene (P6).

Attenuated total reflectance Fourier transform infrared (ATR–FTIR) spectroscopy data for the polyarylenes (Figure 21) showed similar results. The semi-fluorinated polyarylenes were distinct in showing a strong C–F stretching vibration at 1234 cm\(^{-1}\). All the polyarylene polymers showed aromatic C–H (sp\(^2\)) stretches at approximately 3080, 3060, and 3020 cm\(^{-1}\), aromatic C–C vibrations at 1599, 1495, 1442, and 1383 cm\(^{-1}\), aromatic C–H \(\delta\) in-plane vibrations at 1254, 1183,
1158, 1111, 1074, and 1024 cm\(^{-1}\), and aromatic C–H \(\delta\) out-of-plane vibrations at 901, 844, 760, 696, and 570 cm\(^{-1}\).

**Figure 21.** ATR–FTIR spectra (neat, 32 scans, 4 wavenumber resolution) of non- and semi-fluorinated polyarylene (P1-P6).

Gel permeation chromatography (GPC) analyses indicated high molecular weight polyarylene was afforded (Table 2). The advantages of the microwave-assisted polymerization were the production of high molecular weight polyarylene in hours instead of days/weeks, and lower dispersities compared to polymers from traditional oil bath reactions. Reprecipitation of the
polymers was carried out twice. One difficulty with the microwave synthesis was the increase in viscosity as the molecular weight increased during the reaction.

Table 2. Thermal properties, molecular weights, water contact angles, and refractive index results for non- and semi-fluorinated polyarylene (P1-P6).

<table>
<thead>
<tr>
<th>entry</th>
<th>$T_d$; N$_2$/Air (°C)$^a$</th>
<th>Char Yield (%)$^b$</th>
<th>$T_g$ (°C)$^c$</th>
<th>$T_g$ (°C)$^d$</th>
<th>$M_n$ (kg/mol)$^e$</th>
<th>$M_w$ (kg/mol)$^e$</th>
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<tr>
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<td>567/594</td>
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<td>345</td>
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<td>564/593</td>
<td>62</td>
<td>327</td>
<td>327</td>
<td>105</td>
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<td>48</td>
<td>417</td>
<td>417</td>
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<td>219</td>
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<td>439</td>
<td>169</td>
<td>473</td>
<td>2.8</td>
<td>87.9</td>
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<tr>
<td>P6</td>
<td>559/609</td>
<td>72</td>
<td>397</td>
<td>397</td>
<td>244</td>
<td>732</td>
<td>3.0</td>
<td>88.8</td>
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</table>

$^a$Onset of thermal degradation determined from TGA under N$_2$; $^b$char yield determined from TGA at 1000 °C under N$_2$; $^c$glass transition temperature determined from 3rd scan in DSC under N$_2$; $^d$mechanical glass transition temperature determined from tan delta peak in DMA, tension, 2 °C/min, 1 Hz; $^e$number and weight average molecular weight determined from GPC using THF; $^f$water contact angle determined with a goniometer using spin cast films; $^g$refractive index measured on thin film at 632.8 nm.
The molecular weight can also have an effect on the physical properties of polyarylenes, and most polymers in general. However, we determined for these polyarylenes the film forming properties occurs at approximately 60–75 kg/mol, and all the polymers in this study were well above that threshold so the properties investigated should help elucidate structure-property relationships. Glass transition temperatures ($T_g$) were determined via differential scanning calorimetry (DSC), and were found to be greater than 300°C for all the polyarylenes (Figure 22, Table 2). The $T_g$ was determined from the third heating scan of each cycle, affording values of 384 ($P_1$), 327 ($P_2$), 417 ($P_3$), 453 ($P_4$), 439 ($P_5$), and 397 °C ($P_6$). As shown in Figure S13, the mechanical properties of the polyarylenes were similar to each other. The storage moduli at room temperature were in the range of 1210–1540 MPa, with loss moduli in the range of 330–540 MPa. The tan delta peaks increased slightly as the frequency increased but the values at 1 Hz using a 2 °C/min heating rate were 397 ($P_1$), 354 ($P_2$), 433 ($P_3$), 469 ($P_4$), 473 ($P_5$), and 431 °C ($P_6$).
Figure 22. DSC results of non- and semi-fluorinated polyarylene (P1-P6) at a heating rate of 10 °C/min; 3rd heating scan.
Figure 23. Tan δ DMA results of polyarylene (P1) at 1, 3, 5, 7, and 10 Hz and storage/loss modulus at 1 Hz using a heating rate of 2 °C/min on films under tension.
Table 3. Dynamic mechanical analysis (DMA) results (tension; 2 °C/min; 1 Hz) for semi-fluorinated and non-fluorinated polyarylene (P1-P6).

<table>
<thead>
<tr>
<th>P#</th>
<th>$E'$ (MPa)$^a$</th>
<th>$E''$ (MPa)$^a$</th>
<th>Tan $\delta^a$</th>
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<tr>
<td>6</td>
<td>1330</td>
<td>500</td>
<td>431</td>
</tr>
</tbody>
</table>

$^a$DMA results of polyarylene (P1-P6) at 1 Hz using a heating rate of 2 °C/min on films under tension; storage modulus and loss modulus reported at 25 °C and tan delta reported at peak maximum.

Thermal gravimetric analyses (TGA) for the polyarylenes under nitrogen and air indicated similar onsets of thermal degradation ($T_d$) and a single step mechanism (Figure 24, Table 2). Under a nitrogen atmosphere, the polyarylenes had $T_d$’s of 567 (P1), 564 (P2), 568 (P3), 556 (P4), 552 (P5), and 559 °C (P6). The char yields at 1000 °C were surprisingly high, with values of 56 (P1), 62 (P2), 48 (P3), 74 (P4), 78 (P5), and 72% (P6). The semi-fluorinated polyarylenes possessed the highest char yields, with the 1,3-diethynyl-2,4,5,6-tetrafluorobenzene polyarylene (P5) possessing the highest char yield overall. Interestingly, the 1,3-diethynylbenzene polyarylene (P2) possessed the highest char yield among the non-fluorinated variants indicating both meta
conformations are important for the structure-property relationships. Under an air atmosphere, the polyarylenes had $T_d$'s somewhat higher as compared to the nitrogen atmosphere with values of 594 (P1), 593 (P2), 603 (P3), 619 (P4), 585 (P5), and 609 °C (P6). However, the char yields at 1000 °C under air were 0% for all the polyarylenes. The weight loss reached 0% between 655 and 740 °C. Investigation of thermal degradation is essential for understanding flame retardancy and material properties. Other studies have included cone calorimetry, thermogravimetric analysis coupled with Fourier transform infrared spectrometry (TGA-FTIR), and thermogravimetric analysis coupled with mass spectrometry (TGA-MS). Carbon, hydrogen, and fluorine were shown to produce different but relatively simple mass fragment patterns in similar semi-fluorinated polymers under nitrogen and air atmospheres.\textsuperscript{186-187}

![Figure 24](image-url) Figure 24. TGA results of non- and semi-fluorinated polyarylene (P1-P6) under an atmosphere of (left) nitrogen and (right) air at a heating rate of 10 °C/min from 25 to 1000 °C.
The surprisingly high char yields, especially for the fluorinated polyarylenes, required
further investigation. X-ray diffraction (XRD) analysis showed typical amorphous characteristics
for all the polyarylenes, but the fluorinated polyarylenes (P4-P6) appeared to exhibit more ordered
conformations that helped increase the char yield (Figure 25). The non-fluorinated polyarylenes
(P1-P3) were relatively unstructured with a peak intensity at approximately 3.11 Å, according to
Bragg’s law. However, the fluorinated 1,4-tetrafluorobenzene (P4) and octafluorobiphenyl (P6)
polyarylene exhibited two well-organized peaks at 5.47 and 4.02 Å, and 5.42 and 4.00 Å, respectively. The 1,3-tetrafluorobenzene (P5) polyarylene only showed a single peak at 5.34 Å.
The charred TGA samples were also analyzed via XRD analysis. The non-fluorinated polyarylene
showed broad unstructured, amorphous results (not shown) whereas the fluorinated polyarylenes
were shiny black materials that seemed to exhibit the typical graphitic carbon (002) and (100)
peaks (Figure 26).
Figure 25. XRD results of non- and semi-fluorinated polyarylene (P1-P6) of drop cast films.
Figure 26. XRD results of semi-fluorinated polyarylene (P4-P6) char yields after TGA runs under nitrogen atmosphere at 1000 °C.
With the addition of fluorine into a polymer structure, hydrophobicity would typically be expected. However, polyarylenes possess pendant phenyl groups which can protect or block the backbone, in which case the fluorine atoms are prevented from coming to the surface. The water contact angle for all the polyarylenes, including the semi-fluorinated, samples were between 81.1 and 88.8° (Table 2). No changing the surface energy may actually be important when making multi-layer films since it is necessary to have good adhesion between polymer or composite layers. The other benefit of adding fluorine to materials is lowering the refractive index (RI) for optical materials. The refractive index was measured at 632.8 nm for each polyarylene. A series of co-polymers (P1-co-P4) was also synthesized and it was demonstrated that the RI could be tailored according to the feed ratio, fitting to a Sellmeier equation (Figure 27). The RI measured using thin films at 632.8 nm was 1.6584 (P1), 1.6579 (P2), 1.6588 (P3), 1.6539 (P4), 1.6536 (P5), and 1.6497 (P6). The non-fluorinated polyarylenes possessed similarly high RI values while the fluorinated polyarylenes possessed somewhat lower values. The octafluorobiphenyl polyarylene (P6) has the most fluorine content and accordingly had the lowest refractive index.
Figure 27. Refractive index versus wavelength results of non- and semi-fluorinated copolymer polyarylene (P1-co-P4).

<table>
<thead>
<tr>
<th>P#</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<td>RI&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.6584</td>
<td>1.6579</td>
<td>1.6588</td>
<td>1.6539</td>
<td>1.6536</td>
<td>1.6497</td>
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</table>

<sup>a</sup>Refractive index (RI) measured using thin films at 632.8 nm.
2.3 Conclusions

Polyarylenes continue to be of great interest among various polymer fields for an ever-increasing number of applications. This study demonstrates the relative ease of synthesis for both fluorinated and non-fluorinated monomers. The Diels-Alder step-growth polymerization is advantageous due to lack of catalysis or initiator, and the formation of carbon monoxide gas as a by-product, preventing the retro-Diels–Alder reaction from occurring. The use of microwaves for polymerization reduces reaction times and improves yields even further. Three fluorine-containing polyarylenes were synthesized and compared to the non-fluorinated polyarylene systems. Elucidation of the structure-property relationships in these materials will lead to further development of tailored materials for future applications. Polyarylenes are excellent high-temperature and high-performance materials due to their outstanding thermal and mechanical properties, as well as tailorable optical properties.

2.4 Experimental

General. All solvents, starting materials, and reagents were purchased from Alfa Aesar, Fisher Scientific, Sigma-Aldrich, TCI America, or VWR as reagent grade and used as received, unless otherwise mentioned. Reactions were carried out under an argon atmosphere, unless otherwise noted. All glassware was oven-dried prior to use and cooled in a desiccator. HPLC-grade tetrahydrofuran and \(N,N'\)-dimethylformamide (DMF) was dried and deoxygenated by passage through a Pure-Solv solvent system equipped with Cu/Al columns from Innovative Technologies. Anhydrous nitrobenzene was purchased from EMD Millipore. Toluene was dried using calcium hydride (CaH₂) and then distilled, discarding the first 5% of the distillate, and then stored over 4
Å molecular sieves under argon. Triethylamine was dried using CaH₂, distilled, and then stored over potassium hydroxide (KOH) under argon, as molecular sieves typically leads to a yellow color over time. Chloroform was dried and purified by passing through a column of alumina, stirring overnight over molecular sieves, distilling, and storing over molecular sieves under argon. Ethanol was dried over magnesium turnings, refluxed with iodine crystals for a few hours, distilled, and then stored over molecular sieves under argon.

Instrumentation.

All ¹H, ¹³C, and ¹⁹F NMR spectra were obtained under ambient conditions using a JEOL ECA 500 MHz instrument, and chemical shifts were reported in parts per million (δ ppm). Proton (¹H), fluorine (¹⁹F), and carbon (¹³C) NMR spectra were referenced using the residual solvent peak for CHCl₃ (δ = 7.26 ppm), CFCI₃ (δ = 0.0 ppm), and the center of the multiplet peak for CDCl₃ (δ = 77.16 ppm), respectively. ATR–FTIR analysis was performed on a Thermo Nicolet FTIR Spectrometer iS10 with a diamond ATR crystal (Spetra-Tech) using neat samples with 16 scans and 4 cm⁻¹ resolution. Molecular weights and molecular weight dispersities (Mₘ/Mₙ) were determined by gel permeation chromatography (GPC) on a Tosoh EcoSEC system equipped with a series of 4 columns (TSK gel guard Super HZ-L, Super HZ-M, Super HZM-N, and Super HZ2000) at 40 °C, and using refractive index detector. HPLC-grade tetrahydrofuran was used as the eluent at a flow rate of 0.35 mL/min. The GPC calibration was based on linear polystyrene (PS) standards. Polymer samples were dissolved in THF (1 mg/mL) and filtered through a 0.2-µm PTFE syringe filter before injection. The onset of thermal degradation temperature (T_d) was obtained from thermal gravimetric analysis (TGA) using a SDT 2960 Simultaneous DTA-TGA (TA Instruments) at a heating rate of 10 °C/min under a N₂ or air atmosphere, and typical sample
sizes of approximately 5-10 mg. The glass transition temperature ($T_g$) was determined from differential scanning calorimetry (DSC) using a DSC 2010 (TA Instruments) at a heating rate of 10 °C/min under a nitrogen atmosphere, and sample sizes were approximately 5-10 mg. Each sample was heated and cooled through three cycles, and the third heating was used to calculate the $T_g$. Dynamic mechanical analysis (DMA) using a DMA 2980 (TA Instruments) was used to measure storage and loss modulus and tan δ. Samples were tested at a heating rate of 2 °C/min at a frequency between 1-10 Hz in tension mode. Powder X-ray diffraction (XRD) was performed on a PANalytical X'Pert Pro instrument. The X-ray source is a ceramic sealed tube (3 kW) with a wavelength of 1.5406 Å (Cu Kα). Measurements were taken on a zero diffraction background sample holder. The samples were continuously scanned in the range 20–130 2θ with a 0.017° step size and 10.2 s per step with a 2.1° slit size. Data were collected using PANalytical X'Pert HighScore suite software and processed using Origin Pro 2019.

1,4-Diethynylbenzene.

1,4-Diethynylbenzene was purchased from Sigma-Aldrich. To purify the compound the solid was sublimed at 60 °C (2-3 Torr) before use to afford a crystalline white solid.

1,3-Diethynylbenzene.

1,3-Diethynylbenzene was purchased from Sigma-Aldrich. To purify the compound the liquid was distilled at 65 °C (5 Torr) before use to afford a clear colorless liquid.
**4,4'-Diethynyl-1,1'-biphenyl.**

To a solution of 4,4'-dibromobiphenyl (10.00 g, 32.1 mmol), Pd(PhCN)$_2$Cl$_2$ (51.7 mg, 1.135 mmol), PPh$_3$ (298.1 mg, 1.14 mmol), and Cu(I) iodide (97.2 mg, 0.510 mmol) in triethylamine (150 mL) was added 2-methyl-3-butyne-2-ol (6.73 g, 7.83 mL, 80.1 mmol) dropwise over 30 min. The solution was refluxed overnight under an argon atmosphere. The reaction was cooled to room temperature and the solid brown precipitate was removed by filtration. The filtrate was evaporated, dissolved in CHCl$_3$, and then washed with HCl (1 M), H$_2$O, NaHCO$_3$ (sat’d), and H$_2$O. The combined organic layers were dried with MgSO$_4$, filtered, and evaporated under reduced pressure. The crude protected product was crystallized from DCM at 0 °C. The colorless needles were filtered and dried (5.79 g, 51.8%). **Deprotection.** To a solution of protected product (5.00 g, 14.26 mmol) in anhydrous toluene (200 mL) was added sodium hydroxide (685 mg, 17.12 mmol) and potassium carbonate (710 mg, 5.13 mmol). The solution was refluxed for 3 h. The solids were removed via filtration. The solvent, acetone and toluene, were removed under reduced pressure. No further purification was necessary to afford the product as a white solid (3.15 g, 49%). $^1$H NMR (500 MHz, CDCl$_3$): 3.16 (s, 2H), 7.54–7.60 (m, 8H); FTIR (neat): 3277, 2104, 1488, 857, 826 cm$^{-1}$.

**Scheme 2.** Dibromo aromatic precursor (4,4'-dibromobiphenyl) reacted under palladium and copper conditions with acetylic protecting group (2-methyl-3-butyne-2-ol), followed by deprotection to afford final compound (4,4'-diethynyl-1,1'-biphenyl).
**1,4-Diethynyl-2,3,5,6-tetrafluorobenzene.**

1,4-Diiodo-2,3,5,6-tetrafluorobenzene (5.0 g, 12.4 mmol) was added to 100 mL of freshly distilled triethylamine (Et$_3$N) under a stream of argon gas. Bis(benzonitrile)palladium chloride (Pd(PhCN)$_2$Cl$_2$) (20.0 mg, 52.2 µmol), triphenylphosphine (PPh$_3$) (116 mg, 0.44 mmol), and copper(I) iodide (CuI) (37.7 mg, 0.20 mmol) were added and were kept under an argon atmosphere. The solution was left to stir at room temperature for 30–60 min. 2-Methyl-3-butyne-2-ol (3.0 mL, 2.6 g, 31.1 mmol) was added slowly over 30 min. The solution was stirred for an additional 4 h at room temperature and then at refluxed overnight. Upon cooling to room temperature, dichloromethane (DCM) was added and the bromide salts were filtered. The solvent was reduced under reduced pressure. DCM was added and the solution washed with 1 M HCl, water, saturated sodium bicarbonate (NaHCO$_3$), and water to remove the metal impurities. The organic layer was dried with anhydrous magnesium sulfate (MgSO$_4$), filtered, and the solvent evaporated under reduced pressure. The crude protected product was purified by recrystallization from dichloromethane (DCM) at 0 °C. The colorless needles were filtered and dried (1.6 g, 42%). The protected product (1.5 g, 4.8 mmol) was dissolved in anhydrous toluene (60 mL), and sodium hydroxide (NaOH) (229 mg, 5.7 mmol) and potassium carbonate (K$_2$CO$_3$) (238 mg, 1.7 mmol) were added and refluxed for 3 hr under argon atmosphere. The solids were removed using filtration and the solvents, acetone and toluene, were removed under reduced pressure. The final product was purified via sublimation (385 mg, 41%). $^1$H NMR (500 MHz, CDCl$_3$): δ 3.45 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 147.1, 105.8, 82.6, 78.7; $^{19}$F (470 MHz, CDCl$_3$): −76.9; FTIR (neat), 3295, 2120, 1480 cm$^{-1}$. 

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Scheme 3. Dibromo aromatic precursor (1,4-diiodo-2,3,5,6-tetrafluorobenzene) reacted under palladium and copper conditions with acetylic protecting group (2-methyl-3-butyne-2-ol), followed by deprotection to afford final compound (1,4-diethynyl-2,3,5,6-tetrafluorobenzene).

1,3-Diethynyl-2,4,5,6-tetrafluorobenzene.

1,3-Dibromo-2,4,5,6-tetrafluorobenzene (3.0 g, 9.7 mmol) was added to 100 mL of freshly distilled triethylamine (Et₃N) under a stream of argon gas. Bis(benzonitrile)palladium chloride (Pd(PhCN)₂Cl₂) (112 mg, 292 µmol), triphenylphosphine (PPh₃) (383 mg, 1.5 mmol), and copper(I) iodide (CuI) (186 mg, 974 µmol) were added and kept under an argon atmosphere. The solution was refluxed for 30–60 min and then cooled to room temperature. Trimethylsilacetylene (TMSA, 2.8 mL, 1.9 g, 19.5 mmol) was added slowly over 30 min. The solution was freeze/pump/thawed and degassed with argon. The solution was refluxed and followed via GC-MS until starting material and mono-functionalized material disappeared (24-72 hrs). Upon cooling to room temperature, anhydrous diethyl ether (Et₂O) was added and the bromide salts were filtered. The solvent was reduced under reduced pressure. Et₂O was added and the solution washed with 1 M HCl, saturated sodium bicarbonate (NaHCO₃), and brine to remove the metal impurities. The organic layer was dried with anhydrous magnesium sulfate (MgSO₄) and filtered. The crude protected product was purified by distillation from impurities at 25 °C. The colorless liquid still contained diethyl ether (1.6 g, 49% via GC). To the protected product (1.6 g, 4.8 mmol) dissolved in Et₂O (60 mL), tetrabutylammonium fluoride (TBAF, 10 mL, 10 mmol, 1 M in THF) was added and stirred at room temperature for 1 hr under argon atmosphere and followed via GC-
MS. Calcium carbonate (10 g) was added, then while stirring sulfuric acid (25 mL, 1 M) was added slowly. The solution bubbled vigorously and was stirred for an additional hour at room temperature. A saturated solution of ammonium chloride (150 mL) was added and stirred overnight at room temperature. The aqueous layer was removed, and the organic layer was washed with 1 M H₂SO₄, saturated sodium bicarbonate, and brine and then dried with magnesium sulfate. The ether was distilled at 25 °C under house vacuum and then the product was distilled at 40 °C at 1.20 Torr affording a colorless liquid product or liquid nitrogen cooled distillation trap which freezes the product into a solid (1.1 g, 56%). ¹H NMR (500 MHz, CDCl₃): δ 3.57 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 158.63, 153.43, 151.36, 132.33, 129.27, 99.20, 89.20, 68.22; ¹⁹F (470 MHz, CDCl₃): δ −107.75, −126.05, −162.67; FTIR (neat), 3297, 2126, 1237 cm⁻¹.

**Scheme 4.** Dibromo aromatic precursor (1,3-dibromo-2,4,5,6-tetrafluorobenzene) reacted under palladium and copper conditions with acetylic protecting group (trimethylsilacetylene), followed by deprotection to afford final compound (1,3-diethynyl-2,4,5,6-tetrafluorobenzene).

**4,4'-Diethynyl-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl.**

To a solution of 4,4'-dibromo-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (3.0 g, 6.6 mmol) in triethylamine (100 mL) was added 2-methyl-3-butyn-2-ol (1.6 mL, 1.4 g, 16.5 mmol) dropwise over 30 min. The solution was refluxed for 30-60 min under an argon atmosphere. The reaction was cooled to room temperature and Pd(PhCN)₂Cl₂ (10.6 mg, 27.6 µmol), PPh₃ (58.0 mg, 22.1
µmol), and copper(I) iodide (18.8 mg, 98.7 µmol) were added. The solution was freeze/pump/thawed and degassed with argon. The solution was refluxed and followed via GC-MS 24-48 hr until 100% conversion. The reaction was cooled to room temperature before the solid brown precipitate was removed by filtration. The filtrate was evaporated, dissolved in Et₂O, and then washed with HCl (1 M), brine, NaHCO₃ (sat’d), and H₂O. The combined organic layers were dried with MgSO₄, filtered, and evaporated under reduced pressure. The crude protected product was crystallized from DCM at 0 °C. The colorless needles were filtered and dried (1.4 g, 47%). **Deprotection:** To a solution of protected-product (1.4 g, 2.9 mmol) in anhydrous toluene (75 mL) was added sodium hydroxide (140 mg, 3.5 mmol) and potassium carbonate (145 mg, 1.1 mmol). The solution was refluxed for 1 h and followed via GC-MS. The solution was cooled to room temperature and the solids were removed via filtration. The solvents, acetone and toluene, were removed under reduced pressure. The crude product was sublimed at 65 °C (1.4 Torr) to afford the product as a white solid (504 mg, 22%). ¹H NMR (500 MHz, CDCl₃): δ 3.75 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 146.73, 143.03, 108.28, 105.72, 91.70, 68.49.; ¹⁹F (470 MHz, CDCl₃): δ −137.31, −137.74; FTIR (neat): 3277, 2104, 1488, 1209, 857, 825 cm⁻¹.

**Scheme 5.** Dibromo aromatic precursor (2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl) reacted under palladium and copper conditions with acetylic protecting group (2-methyl-3-butyn-2-ol), followed by deprotection to afford final compound (4,4'-diethynyl-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl).
1,4-Bis(tetraphenylcyclopentadienonyl)benzene (Bistetracyclone)\textsuperscript{176}

1,4-Bis(tetraphenylcyclopentadienonyl)benzene was prepared from the condensation of 2,2-(1,4-phenylene)bis(1-phenylethane-1,2-dione) with 1,3-diphenylacetone. To a 500 mL two-necked, round-bottomed flask equipped with a condenser, a stir bar and a septum, containing 275 mL of freshly distilled ethanol was added 1,3-(diphenyl)propan-2-one (12.3 g, 58.4 mmol, 2.1 eq), and 1,4-bisbenzyl (10.0 g, 29.2 mmol, 1 eq), the solution was then refluxed. After 1 h, KOH (3.3 g, 58.4 mmol, 2.0 eq) was dissolved in 10 mL ethanol and added drop-wise to the refluxed solution. The solution was refluxed for 45-60 min, then the solution was cooled at 0 °C for 2 h using an ice bath. The solution was filtered, the precipitate was dissolved in boiling DCM, and then crystallized affording purple needles at 0 °C. (17.1 g, 85%) $^1$H NMR (500 MHz, CDCl\textsubscript{3}): $\delta$ 6.78 (s), 6.92 (d, $J$ = 7.06 Hz, 4 H), 7.19-7.30 (m, 26 H). $^{13}$C NMR (125 MHz, CDCl\textsubscript{3}): $\delta$ 200.60, 154.93, 154.66, 134.11, 133.50, 130.65, 130.59, 129.77, 129.51, 129.05, 128.53, 128.12, 128.07.

\begin{center}
\textbf{Scheme 6.} 1,4-Bisbenzil and 1,3-diphenylacetone react under basic conditions to afford bistetracycline.
\end{center}
Polyarylene (Conventional oil-bath heating) (P1).

Polyarylene was synthesized using bistetracyclone and 1,4-diethynyl-benzene. 1,4-Diethynylbenzene was purchased from Aldrich and sublimed before use. Bistetracyclone was synthesized according to literature and crystallized before use. To a dry round-bottomed flask with stir bar, bistetracyclone (5.0 g, 7.2 mmol) and 1,4-diethynylbenzene (0.9 g, 7.2 mmol) were added. Polymerizations were performed using 100 mL diphenyl ether (Ph$_2$O) as solvent. The reaction vessel was equipped with a reflex condenser and added to a preheated oil bath at 180 °C for four weeks under an argon atmosphere. The reaction was cooled to room temperature and precipitated in acetone (1000 mL), filtered, and dried. The dry polymer was dissolved in minimal amounts of THF and precipitated in methanol (MeOH), then repeated three times. The tan/off-white powder (94% yield) was collected by filtration and dried in a vacuum oven at 80 °C for 24 h. Soluble in CHCl$_3$, THF, toluene, and cyclohexanone. $^1$H NMR (500 MHz, CDCl$_3$): 7.6–6.1 (m, 40 H); ATR–FTIR (neat): 1600, 1496, 1430, 1441, 1380, 1107, 1073, 1023, 1008, 898, 843, 759, and 696 cm$^{-1}$; GPC in THF relative to polystyrene, $M_n = 174$ kg/mol ($M_w/M_n = 2.82$).

Polyarylene (microwave-assisted polymerization) (P1).

1,4-Diethynylbenzene (9.1 mg, 72.4 µmol) and bistetracyclone (50.0 mg, 72.4 µmol) were carefully added to a 10-mL microwave vessel with stir bar and the sides were rinsed down with anhydrous nitrobenzene (0.6 mL). The vial was covered with a septum, freeze/pump/thawed, and purged with argon three times. Then the septum was removed, and the microwave cap was quickly added. The vessel was carefully inserted into the CEM Discovery microwave reactor trying to keep solids under solvent. The following parameters were set: method = Standard, stir speed =
High, pressure limit = 300 psi, power = 300 W, temperature 180 °C, and time = 2 hr. After the desired time period the polymer solution was viscous orange. The crude polymer was precipitated by added slowly to stirring MeOH (200 mL), filtered and dried to afford a tan/off-white solid product (40 mg, 73%).

**Polyarylene (microwave-assisted polymerization) (P2).**

1,3-Diethynylbenzene (201 mg, 1.59 mmol) and bistetracyclone (1.00 g, 1.59 mmol) were carefully added to a 10-mL microwave vessel with stir bar and the sides were rinsed down with anhydrous nitrobenzene (0.6 mL). The vial was covered with a septum, freeze/pump/thawed, and purged with argon three times. Then the septum was removed, and the microwave cap was quickly added. The vessel was carefully inserted into the CEM Discovery microwave reactor trying to keep solids under solvent. The following parameters were set: method = Standard, stir speed = High, pressure limit = 300 psi, power = 300 W, temperature 180 °C, and time = 5 hr. After the desired time period the polymer solution was viscous orange. The crude polymer was precipitated by added slowly to stirring MeOH (200 mL), filtered and dried to afford a tan/off-white solid product (995 mg, 79%).

**Polyarylene (microwave-assisted polymerization) (P3).**

4,4’-Diethynyl-1,1’-biphenyl (14.6 mg, 72.3 µmol) and bistetracyclone (50.0 mg, 72.3 µmol) were carefully added to a 10-mL microwave vessel with stir bar and the sides were rinsed down with anhydrous nitrobenzene (0.6 mL). The vial was covered with a septum, freeze/pump/thawed, and purged with argon three times. Then the septum was removed, and the
microwave cap was quickly added. The vessel was carefully inserted into the CEM Discovery microwave reactor trying to keep solids under solvent. The following parameters were set: method = Standard, stir speed = High, pressure limit = 300 psi, power = 300 W, temperature 180 °C, and time = 5 hr. After the desired time period the polymer solution was viscous orange. The crude polymer was precipitated by added slowly to stirring MeOH (200 mL), filtered and dried to afford a tan/off-white solid product (46 mg, 76%).

Polyarylene (microwave-assisted polymerization) (P4).

2,3,5,6-Tetrafluoro-1,4-diethynylbenzene (14.3 mg, 72.3 µmol) and bistetracyclone (50.0 mg, 72.3 µmol) were carefully added to a 10-mL microwave vessel with stir bar and the sides were rinsed down with anhydrous nitrobenzene (0.6 mL). The vial was covered with a septum, freeze/pump/thawed, and purged with argon three times. Then the septum was removed, and the microwave cap was quickly added. The vessel was carefully inserted into the CEM Discovery microwave reactor trying to keep solids under solvent. The following parameters were set: method = Standard, stir speed = High, pressure limit = 300 psi, power = 300 W, temperature 180 °C, and time = 5 hr. After the desired time period the polymer solution was viscous orange. The crude polymer was precipitated by added slowly to stirring MeOH (200 mL), filtered and dried to afford a tan/off-white solid product (51 mg, 85%).

Polyarylene (microwave-assisted polymerization) (P5).

1,3-Diethynyl-2,4,5,6-tetrafluorobenzene (222 mg, 1.1 mmol) and bistetracyclone (774 mg, 1.1 mmol) were carefully added to a 35-mL microwave vessel with stir bar and the sides were
rinsed down with anhydrous nitrobenzene (5.0 mL). The vial was covered with a septum, freeze/pump/thawed, and purged with argon three times. The septum was removed, and the microwave cap was quickly attached. The vessel was carefully inserted into the CEM Discovery microwave reactor trying to keep solids under solvent. The following parameters were set: method = Standard, stir speed = High, pressure limit = 300 psi, power = 300 W, temperature 180 °C, and time = 5 hr. After the desired time period the polymer solution was viscous orange. The crude polymer was precipitated by added slowly to stirring MeOH (900 mL), filtered, and dried to afford a tan/off-white solid product (889 mg, 90%).

**Polyarylene (microwave-assisted polymerization) (P6).**

4,4'-Diethynyl-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (208 mg, 0.6 mmol) and bistetracyclone (415 mg, 0.6 mmol) were carefully added to a 35-mL microwave vessel with stir bar and the sides were rinsed down with anhydrous nitrobenzene (5.0 mL). The vial was covered with a septum, freeze/pump/thawed, and purged with argon three times. The septum was removed, and the microwave cap was quickly added. The vessel was carefully inserted into the CEM Discovery microwave reactor trying to keep solids under solvent. The following parameters were set: method = Standard, stir speed = Slow/High, pressure limit = 300 psi, power = 300 W, temperature 180 °C, and time = 0-99 hr. After the desired time period the polymer solution was viscous orange. The crude polymer was precipitated by added slowly to stirring MeOH (200 mL), filtered, and dried to afford a tan/off-white solid product (476 mg, 81%).
Chapter 3

POLYARYLENE POLYIMIDE POLYMERS

3.1 Introduction

Aromatic polyimides were first produced in 1908 by Bogert. In 1955, high molecular weight aromatic polyimides were synthesized via a two-stage polycondensation of pyromelletic dianhydride with diamines. The interest in polyimides has increased since then due to thermo-oxidative stability, unique electrical properties, high radiation, better solvent resistance, and high mechanical strength. However, polyimides often have low solubility in common organic solvents and have high softening temperatures thereby making processing difficult and expensive. The most common technique used to fabricate polyimides uses a soluble poly(amic acid) as a precursor. Films are cast, and then they are thermally dehydrated to produce the final imide. However, inefficient imidization, removal of water, and defect-free films are some of the difficulties. Polyimides are among the most heat-resistant polymers and widely used in high temperature plastics, adhesives, dielectrics, photoresists, nonlinear optical materials, membrane materials for separation, and films. The aerospace, defense, and opto-electronics fields use polyimides in a range of applications, such as liquid crystals, composites, electroluminescent devices, electrochromic materials, polymer electrolyte membrane fuel cells, polymer membranes, and fiber optics. Polyimides derived from monomers with non-planar, cyclic aliphatic, bulky, fluorinated, hetero, carbazole, perylene, chiral, non-linear optical, and unsymmetrical structures have been reported. Various other monomers, including diamines
and dianhydrides, were synthesized to make novel polyimides with unique properties. Polyimides with tailored functional groups, and even dendritic structures, have allowed researchers to tune properties for specific applications. A drawback of polyimides is that they often are poorly soluble in common organic solvents and have high softening temperatures, thereby making processing difficult and expensive. The most common technique used to fabricate polyimides uses a soluble poly(amic acid) as a precursor. Films are cast and then thermally dehydrated to produce the final imide. However, inefficient imidization, difficulty in removing water, and film defects are some of the difficulties encountered in this process.

High performance polymers, such as polyimides, poly(arylene ether)s, poly(ether ketone)s, poly(ether sulfone)s, and polyarylenes, possess a high glass transition ($T_g$), high thermal stability, and good mechanical properties and, therefore, have been identified for a variety of applications in government, industry, and academia. However, despite possessing these excellent properties, most of these high performance polymers have major drawbacks, such as insolubility in common organic solvents, intractability, infusibility, and opaqueness. It has been observed in some instances that introduction of fluorine can impart many desirable properties making them suitable for a much wider range of applications including pharmaceuticals, crop protection agents, tracers for positron emission tomography (PET), transistors, light emitting diodes (LEDs), photovoltaic (PV) cells, gas separation membranes, and proton exchange membranes (PEMs) for fuel cells. Most of the compounds that display good thermal stability contain aromatics, which is the simplest organic structure resistant to thermal decomposition or oxidation. For example, benzene has been reported to be stable up to 530 °C. The linear combination of benzene rings linked directly together along the backbone produces polyphenylene, the simplest totally aromatic polymer. The melting points increase as the number
of phenyl units increases, and there is a strong dependence on whether the linkage is ortho, meta, or para. Further evidence supporting the use of polyphenylenes as high performance polymers is that oligophenyls have been used as high temperature lubricants, hydraulic fluids, heat-transfer agents, and coolants for nuclear reactors. Polyarylenes are formally described as macromolecules containing exclusively arylene units in the backbone; highly phenylated polyphenylenes are a subclass of polyarylenes that contain pendant phenyl groups in addition to arylene units in the backbone. One of the most successful synthetic methods has been the Diels–Alder reaction of bistetracyclone and diethynylbenzenes. The obtained polymer requires no catalyst or initiator, and the only by-product is carbon monoxide, affording an off-white, amorphous polyarylene. The reaction can be carried out in a high boiling solvent (e.g., diphenyl ether) at 180 °C for days/weeks to produce quantitative yields of high molecular weight polymers (>100 kg/mol). These polyarylenes are soluble up to 15-20 wt% in common organic solvents (e.g., benzene, toluene, tetrahydrofuran, chloroform, and cyclohexanone). We have used polyarylenes to investigate fuel cell and asymmetric gas separation membranes.

Herein, we combine the polyarylene repeat unit backbone utilizing a newly synthesized phenylene diamine, with a series of six dianhydrides to produce new polyarylene polyimides with excellent solubility and processability, as well as the combination of the two materials properties. The properties of the polyarylene polyimides were characterized to show synthesis was achieved and thermal properties were comparable to other polyimide materials, but the solubility was better which will allow for greater processability.
3.2 Results and discussion

Monomer synthesis

The synthesis of the new diamino-phenylated-phenylene monomer started with the synthesis of bistetracyclone (Scheme 7). Initially, 1,3-diphenylacetone and 1,4-bisbenzil were dissolved in anhydrous ethanol. Two equivalents of potassium hydroxide were added to afford a dark purple powder.

Scheme 7. Synthesis of diamino-phenylated-phenylene from bistetracyclone and 4-ethynyl aniline.

Upon crystallization from dichloromethane dark purple crystals were obtained in 85% yield. A Diels–Alder reaction was utilized with bistetracyclone and two equivalents of 4-ethynyl aniline at 150 °C in ortho-xylene (Scheme 8). The orange solution was precipitated into hexane. The tan powder was filtered and dried under vacuum at 75 °C overnight to afford 84% yield. Because of the Diels–Alder reaction between the diene and dienophile there are two possible configurations on each end group; para and meta. Diamino-phenylated-phenylene was fully characterized though melting point, Fourier transform infrared (FTIR), and $^1$H/$^{13}$C nuclear magnetic resonance (NMR) spectroscopy (Figure 27 and 28). The singlet at 3.54 ppm corresponds to the two amine end groups. The aromatic peaks from 7.5 to 6.0 ppm correspond to the pendant and backbone phenyl groups. The three peaks at 6.37 (mm), 6.30 (pp), and 6.23 (pm) ppm correspond to the
central backbone phenyl group and indicates \textit{paralpara (pp)}, \textit{paralmeta (pm)}, and \textit{metalmeta (mm)}.\textsuperscript{176} The conformation with the highest concentration is \textit{pp}, then \textit{mm}, and finally \textit{pm}. We have crystallized model compounds previously to observe the backbone phenyl groups rotating out of plane.\textsuperscript{183} This mixture in conformation reduced rigidity due to backbone twisting will afford extra solubility in the new polyarylene polyimides.

\textbf{Polymer synthesis}

A four-step thermal cycle was attempted for these new polyarylene polyimides heating in an oil bath using \textit{N,N}-dimethylacetamide (DMAc) as the solvent heating at 50 °C for 2 hr, adding triethylamine (TEA) and acetic anhydride (Ac$_2$O) at 50 °C and heating for 1 hr, 75 °C for 1 hr, and 100 °C for 1 hr.\textsuperscript{210} This method worked well and afforded polyarylene polyimides approximately 30 kg/mol molecular weights and clean FTIR and NMR spectra. However, to reduce the reaction time and increase the number of reactions reacted easily at one time, we optimized the microwave-assisted polymerization technique using a multi-mode system with a 36-vessel carousel sample holder. Reaction times as low as ten minutes resulted in molecular weights up to 30 kg/mol. And to prevent having to open the vessels we switched to a one-step method in nitrobenzene using isoquinoline. No benzoic acid was used which should have increased the molecular weight even further. Attempts were tried without any catalyst and molecular weights did increase to 20 kg/mol. The optimized procedure consisted of adding both monomers, five drops of distilled isoquinoline, and enough distilled nitrobenzene for a 10 wt% solution (\textbf{Scheme 9}). The microwave vessel with stir bar was freeze/pump/thawed and de-gassed.
Scheme 8. Synthesis of polyarylene polyimides (PAPI 1-6) from diamino-phenylated-phenylene and six dianhydrides.
with argon. The microwave vessel top was quickly changed and inserted into the microwave carousel. As many as ten reactions were run at one time and blank nitrobenzene was filled to the same volume to balance the heating. The power was set at 1600 W but would change to maintain the temperature at 200 °C. The reaction time was changed from 10, 20, and 30 min. The vessel was cooled to room temperature and slowly added dropwise to large excess of stirring acetone: methanol (50/50) to precipitate the polymers. Isoquinoline was sometimes still observed in the NMR spectra after drying so a second precipitation was typically carried out by dissolving in minimal amounts of tetrahydrofuran (THF) and precipitating into acetone. Drying at 100 °C in a vacuum oven overnight afforded clean samples in 87-99% yield.

**Properties of polyarylene polyimides**

**Characterization**

The $^1$H NMR spectra of all the polyarylene polyimides (PAPI 1-6) are shown in Figure 29. The peaks from phenylated phenylenediamine between 6.0–7.5 ppm stay relatively constant for all the polymers. The peak at 8.42 ppm is from the pyromellitic dianhydride phenyl group (PAPI 1, Figure 30). The peaks at 7.50, 7.52, and 7.96 ppm are from the 3,3’,4,4’-biphenyltetraarboxylic dianhydride phenyl groups (PAPI 2, Figure 31). The peaks at 8.11, 8.21, and 8.26 ppm are from the benzophenone-3,3’,4,4’-tetracarboxylic dianhydride phenyl groups (PAPI 3, Figure 32). The peaks at 7.39, 7.50, and 7.85 ppm are from the 4,4’-oxydiphthalic dianhydride phenyl groups (PAPI 4, Figure 33). The peaks at 7.83, 7.89, and 8.00 ppm are from the 4,4’-(hexafluoroisopropylidene)diphthalic dianhydride phenyl groups (PAPI 5, Figure 34). The $^{19}$F NMR for PAPI 5 shows a singlet at −63.17 ppm from the hexafluoroisopropylidene group.
Figure 30. Proton NMR (500 MHz, CDCl$_3$) spectra of PAPI 1-6.

(Figure 35). The $^1$H NMR peaks at 1.74, 7.20, 7.32, 7.39, and 7.85 ppm are from the 4,4’-(4,4’-isopropylidene diphenoxy) bis(phthalic anhydride) phenyl groups (PAPI 6, Figure 36).

In the FTIR spectra (Figure 37), the characteristic peaks at 3050 and 3025 cm$^{-1}$ were assigned to the C–H (sp$^2$) stretching vibration in all the polymers. The peak at 2966 cm$^{-1}$ was assigned to the C–H (sp$^3$) stretching vibration in PAPI 6. The peaks at 1720 and 1365 cm$^{-1}$ were
assigned to C=O and C–N vibrations, respectively, from the imide ring. The peak at 1785 cm\(^{-1}\) is from the anhydride end group vibrations. The peak at 530 cm\(^{-1}\) was assigned to the C–F vibration in PAPI 5. The absence of the peaks at 3500 cm\(^{-1}\) corresponding to the amine vibration and the peaks at 1650 and 1550 cm\(^{-1}\) corresponding to the amic acid vibrations further confirms imidization ring closure.

Figure 38. ATR–FTIR spectra (neat, 32 scans, 4 wavenumber resolution) of PAPI 1-6.
Thermal properties

Thermal gravimetric analysis (TGA) of the polyarylene polyimides are shown in Figure 38 and 39. The onset of thermal degradation ($T_d$) under a nitrogen atmosphere shows values of 553 (PAPI 1), 562 (PAPI 2), 530 (PAPI 3), 544 (PAPI 4), 519 (PAPI 5), and 517 °C (PAPI 6). PAPI 1 and 2 are the most aromatic and rigid polyimide and showed the highest $T_d$ values. PAPI 6 showed the lowest value due to the methyl (CH$_3$) groups which are not very thermally stable.

Figure 39. Thermal gravimetric analysis (TGA; 25 to 1000 °C; 10 °C/min; nitrogen atmosphere) results for PAPI 1-6.
These polyimides are not extremely high molecular weight (<50 kg/mol) and not cross-linked, yet they already are showing very stable thermal properties. Another thermal property of interest is the char yield at 1000 °C under nitrogen for these polyimides: 61 (PAPI 1), 59 (PAPI 2), 63 (PAPI 3), 64 (PAPI 4), 68 (PAPI 5), and 55% (PAPI 6). The lowest char yield is again PAPI 6 due to the labile methyl group. The relatively high char yield of PAPI 5 can be attributed to the fluorine atoms in the structure. The $T_d$ under air atmosphere for all the polyimides were approximately 550 °C while the char yields were 0%. Other studies have included more
quantitative studies utilizing pyrolysis mass spectrometry to elucidate polymerization and degradation pathways of aromatic and semi-fluorinated polyimides showing simple degradation and thermal rearrangement.\textsuperscript{212-213}

The third heating cycle of the differential scanning calorimetry (DSC) results were used to determine the glass transition temperatures ($T_g$) (Figure 40, Table 4); 369 (PAPI 1), 355 (PAPI 2), 364 (PAPI 3), 374 (PAPI 4), 387 (PAPI 5), and 373 °C (PAPI 6). The $T_g$ values of the polyarylene polyimides were dictated by the chain rigidity, whereby more rigid backbones showed higher glass transition temperatures. Electron-withdrawing dianhydride groups and electron-donating diamine residues will also interact via inter- and intra-molecular interactions. The CF\textsubscript{3} groups are bulkier than the CH\textsubscript{3} groups which is indicated by PAPI 5 having the highest $T_g$. PAPI 6 contains two phenyl ether groups while PAPI 4 only contains one, but their $T_g$’s are approximately the same. PAPI 2 contains the lowest glass transition temperature. Structurally, PAPI 1 appears to be the most rigid but the determined $T_g$ was in the middle of all the polyimides measured. The mixed para and meta configuration from the polyarylene repeat unit affords all the polyimides more flexibility and solubility. PAPI 1 has the lowest meta-meta conformation. PAPI 2 has the majority para-para. PAPI 3-6 have lower meta-meta conformation but similar para-para and para-meta conformations. PAPI 6 has almost similar conformations amongst the three, which also has the most flexible dianhydride group.
Figure 41. Differential scanning calorimetry (DSC, 25 to 500 °C; 10 °C/min; nitrogen atmosphere; 3rd heating scan) results for PAPI 1-6.
Table 4. Reaction times, number and weight molecular weight, polydispersity, onset of thermal degradation in nitrogen and air atmosphere, char yield, and glass transition temperature results for PAPI 1-6.

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<th>$M_w$ (kg/mol)</th>
<th>$M_w/M_n$</th>
<th>$T_d$ (°C) N2/Air</th>
<th>Char yield (%)</th>
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**Solubility**

The solubility of the polyarylene polyimides were tested in a variety of organic solvents. An issue with most polyimides is their insolubility in low boiling point solvents such as chloroform (CHCl₃) and tetrahydrofuran (THF). Typically, only high boiling point polar aprotic solvents (e.g., N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and N-methyl-2-pyrrolidone (NMP)) can be used to dissolve most polyimides which are difficult to remove after processing. Due to the para and meta mixed conformation of the polyarylene repeat unit in these polyimides, all the samples dissolved at room temperature in CHCl₃, THF, DMAc, NMP, toluene, and cyclohexanone. The samples were only slightly soluble in DMSO but were soluble at elevated temperatures. The samples were not soluble in water, hexane, ether, or alcohols.

**Water contact angle analysis**

The polyarylene polyimides were spin cast onto glass slides as thin films (~50 nm) from 10 wt% THF solutions after filtering with 0.2-µm PTFE syringe filters. The spin coater was spun at 800–1000 rpm for 30 seconds. The films were dried in a vacuum oven at 100 °C for 48 hrs. Contact angles for each film were measured individually using a goniometer and filtered HPLC-grade water, and the measurements were repeated three times. Contact angle values were approximately 80° for all the samples; 79.5 (PAPI 1), 80.7 (PAPI 2), 79.2 (PAPI 3), 85.9 (PAPI 4), 82.3 (PAPI 5), and 82.9° (PAPI 6). PAPI 5 is the only fluorine-containing polyimide but it did not show an extraordinarily high value, suggesting the phenyl groups shield the fluorinated backbone and dominate the surface interactions.
3.3. **Conclusions**

In this work, a new diamino-phenylated-phenylene was synthesized via a Diels–Alder synthesis between bistetrayclclone and two equivalents of 4-ethynylaniline. The phenyl groups twist out of plane and the conformation is mixed with para and meta connectivity, thereby giving increased solubility and processability. The new diamino-phenylated-phenylene was used to make six new polyarylene polyimides via microwave-assisted polymerization in 10-30 minutes. The synthetic methods were optimized, and the new materials were fully characterized. Excellent thermal properties were observed in all the materials with the semi-fluorinated polyimide being the most thermally stable. All the materials possessed good optical transparency, with the semi-fluorinated polymer having the largest optical window in the UV-Vis region. This study focused on the synthesis of these new materials and preliminary characterization. Future studies will include more detailed characterization of the polyimides and cross-linking to further improve thermal properties. Suitable applications will be identified after these investigations are complete.

3.4. **Experimental**

*Materials*

All solvents, starting materials, and reagents were purchased from Alfa Aesar, Fisher Scientific, Sigma-Aldrich, TCI America, or VWR as reagent grade and used as received, unless otherwise mentioned. Reactions were carried out under an argon atmosphere, unless otherwise noted. All glassware was oven-dried prior to use and cooled in a desiccator. Dichloromethane (DCM) was dried and deoxygenated by passage through a Pure-Solv solvent system equipped with Cu/Al columns from Innovative Technologies. Nitrobenzene was purified by extraction with
aqueous sodium hydroxide (2 M), deionized water, dilute hydrochloride acid (1 M), deionized water, and then dried with anhydrous magnesium sulfate, and finally fractional distilled under reduced pressure and stored under argon in aluminum foil covered flask. Ortho-xylene was dried using calcium hydride (CaH₂) and then fractionally distilled, discarding the first 5% of the distillate, and then stored under argon in aluminum foil covered flask. Ethanol was dried using magnesium turnings, refluxed with iodine crystals for a few hours, distilled, and then stored over 4 Å molecular sieves under argon in aluminum foil covered flask.

Measurements

All ¹H, ¹³C, and ¹⁹F NMR spectra were obtained under ambient conditions using a JEOL ECA 500 MHz instrument, and chemical shifts were reported in parts per million (δ ppm). Proton (¹H), fluorine (¹⁹F), and carbon (¹³C) NMR spectra were referenced using the residual solvent peak for CHCl₃ (δ = 7.26 ppm), CFCl₃ (δ = 0.0 ppm), and the center of the multiplet peak for CDCl₃ (δ = 77.16 ppm), respectively. ATR–FTIR analysis was performed on a Thermo Nicolet FTIR Spectrometer iS10 with a diamond ATR crystal (Spetra-Tech) using neat samples with 16 scans and 4 cm⁻¹ resolution. Molecular weights and molecular weight dispersities (Mₘ/Mₙ) were determined by gel permeation chromatography (GPC) on a Tosoh EcoSEC system equipped with a series of 4 columns (TSK gel guard Super HZ-L, Super HZM-M, Super HZM-N, and Super HZ2000) at 40 °C, and using refractive index detector. HPLC-grade tetrahydrofuran was used as the eluent at a flow rate of 0.35 mL/min. The GPC calibration was based on linear polystyrene (PS) standards. Polymer samples were dissolved in THF (1 mg/mL) and filtered through a 0.2-μm PTFE syringe filter before injection. The onset of thermal degradation temperature (T_d) was obtained from thermal gravimetric analysis (TGA) using a TG209F3 (NETZSCH) at a heating
rate of 10 °C/min under a N₂ or air atmosphere, and typical sample sizes of approximately 5-10 mg. The glass transition temperature (\( T_g \)) was determined from differential scanning calorimetry (DSC) using a DSC 214 Polyma (NETZSCH) at a heating rate of 10 °C/min under a nitrogen atmosphere, and sample sizes were approximately 5-10 mg. Each sample was heated and cooled through three cycles, and the third heating was used to calculate the \( T_g \). Thin films were prepared using a spin coater (Laurell Technologies Corporation). Water contact angles were measured on a goniometer (Rame-Hart). Data were processed using Origin Pro 2019.

**Synthesis of monomer**

**Bistetracyclone.**

1,4-Bisbenzil (10.0 g, 29.2 mmol) and 1,3-diphenylacetone (12.3 g, 58.4 mmol) were added to a 1-L two-neck round bottom flask. Freshly distilled ethanol (455 mL) was added to the flask. The mixture was stirred and heated until it dissolved into a homogenous yellow solution. Potassium hydroxide (3.3 g, 58.4 mmol) was dissolved in distilled ethanol (5 mL) and added dropwise. The black solution was refluxed for 2-3 hrs. The reaction was cooled to room temperature and half the solvent was evaporated under reduced pressure. The reaction was cooled to 0 °C overnight. The dark black/purple solid was filtered, washed with cold ethanol, and dried with air. The crude product was crystallized from minimal amounts of hot anhydrous dichloromethane, cooled to room temperature, and storied at 0 °C. The dark purple needle-like crystals were filtered, washed with cold DCM, and dried under vacuum at room temperature for 24 hr (17.4 g, 86%). \(^1\)H NMR (500 MHz, CDCl₃): \( \delta \) 6.78 (s), 6.92 (d, \( J = 7.06 \) Hz, 4 H), 7.19-7.30
Diamino-Phenylated-Phenylene.

Bistetracyclone (5.0 g, 7.2 mmol) and 4-ethynylaniline (1.8 g, 15.2 mmol) were dissolved in o-xylene (250 mL). The solution was freeze/pump/thawed and de-gassed with argon. The reaction was refluxed for 24 hrs. The orange solution was cooled to room temperature and reduced to minimal solvent (~10 mL). The solution was added dropwise to stirring hexane (50 mL). The precipitated product was filtered, washed with hexane, and dried under vacuum at 50 °C for 24 hr to afford a tan/off-white powder (5.3 g, 84%). ¹H NMR (500 MHz, CDCl₃): δ 7.49–7.47 (2H), 7.24–6.84 (27H), 6.83–6.61 (8H), 6.51–6.42 (4H), 6.40–6.20, 3.54 (4H); ¹³C NMR (125 MHz, CDCl₃): δ 144.71, 142.25, 141.54, 140.97, 140.70, 140.55, 139.34, 137.89, 137.13, 136.23, 132.00, 131.90, 131.87, 131.72, 130.95, 130.77, 130.59, 130.29, 130.07, 127.60, 126.99, 126.64, 126.19, 125.43, 125.30, 114.51; ATR–FTIR (neat): ν 3053, 3035, 1606, 1506, 1229, 1180, 1033, 828, 699, 554.
Figure 28. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of diamino-phenylated-phenylene.
Figure 29. $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of diamino-phenylated-phenylene.

Synthesis of polymers

In separate experiments, diamino-phenylated-phenylene and one of six commercial dianhydrides (1-6) were added to a 35-mL microwave vial with stir bar. Anhydrous nitrobenzene (5.0 mL, 10 wt%) and isoquinoline (0.1 mL) were slowly added down the sides of the vial to rinse the solid keeping it all immersed below the solvent level. The solution was freeze/pump/thawed and de-gassed with argon. The microwave vial was inserted into a CEM MarsX carousel with nitrobenzene in every other slot to balance the heat. The microwave cycle was heated to 200 °C in 2 min at high stir rate and maximum power (1600 W) for 10-30 min total reaction time. The dark purple solution turned to a brown-red color. The reaction was cooled to room temperature.
The viscous solution was slowly precipitated into stirring methanol and acetone (50:50). The tan/off-white solid polymer was filtered, washed with acetone, and dried under vacuum at 75 °C for 72 hr.

**PAPI 1.**

Pyromellitic dianhydride (100 mg, 460 µmol), diamino-phenylated-phenylene (400 mg, 460 µmol), and isoquinoline (0.1 mL) catalyst were combined with 5.0 mL nitrobenzene in a microwave vial. The reaction afforded a tan solid product (477 mg, 99%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 8.42 (2H), 7.50 (2H), 7.38–6.86 (29H), 6.86–6.55 (9H), 6.51–6.18 (4H); ATR–FTIR (neat): ν 3051, 3024, 1777, 1724, 1600, 1513, 1359, 1090, 964, 945, 819, 758, 696, 553.

**Figure 31.** \(^1\)H NMR (500 MHz, CDCl\(_3\)) spectrum of PAPI 1.
PAPI 2.

3,3′,4,4′-Biphenyltetracarboxylic dianhydride (127 mg, 430 µmol), diamino-phenylated-phenylene (374 mg, 430 µmol), and isoquinoline (0.1 mL) catalyst were combined with 5.0 mL nitrobenzene in a microwave vial. The reaction afforded a tan solid product (476 mg, 98%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \textsuperscript{δ} 7.85 (2H), 7.50 (2H), 7.38 (2H), 7.31 (5H), 7.24–6.85 (29H), 6.84–6.58 (7H), 6.41–6.21 (3H); ATR–FTIR (neat): \textnu 3054, 3023, 1775, 1716, 1559, 1513, 1361, 1072, 970, 948, 835, 759, 738, 695, 551.

\textbf{Figure 32.} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) spectrum of PAPI 2.
PAPI 3.

Benzophenone-3,3’,4,4’-tetracarboxylic dianhydride (135 mg, 420 µmol), diamino-phenylated-phenylene (365 mg, 420 µmol), and isoquinoline (0.1 mL) catalyst were combined with 5.0 mL nitrobenzene in a microwave vial. The reaction afforded a tan solid product (468 mg, 97%). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.34–8.03 (6H), 7.57–7.46 (2H), 7.28–6.87 (31H), 6.85–6.58 (8H), 6.44–6.21 (3H); ATR–FTIR (neat): ν 3051, 3023, 1779, 1719, 1513, 1363, 1293, 1089, 1073, 1021, 979, 966, 927, 911, 899, 835, 758, 695, 558.

Figure 33. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of PAPI 3.
PAPI 4.

4,4’-Oxydiphthalic dianhydride (132 mg, 424 µmol), diamino-phenylated-phenylene (369 mg, 424 µmol), and isoquinoline (0.1 mL) catalyst were combined with 5.0 mL nitrobenzene in a microwave vial. The reaction afforded a tan solid product (452 mg, 93%). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.06–7.88 (2H), 7.61–7.36 (6H), 7.35–6.85 (30H), 6.85–6.58 (8H), 6.45–6.19 (4H); ATR–FTIR (neat): ν 3053, 3024, 1779, 1723, 1601, 1515, 1474, 1441, 1366, 1273, 1236, 1074, 1022, 1008, 958, 898, 837, 818, 764, 761, 697, 558.

Figure 34. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of PAPI 4.
PAPI 5.

4,4’-(Hexafluoroisopropylidene)dipthalic dianhydride (169 mg, 381 µmol), diamino-phenylated-phenylene (331 mg, 381 µmol), and isoquinoline (0.1 mL) catalyst were combined with 5.0 mL nitrobenzene in a microwave vial. The reaction afforded a tan solid product (422 mg, 87%). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.07–7.75 (6H), 7.57–7.44 (2H), 7.34–6.86 (29H), 6.86–6.54 (9H), 6.44–6.19 (4H); $^{19}$F NMR (470 MHz, CDCl$_3$): δ –63.17; ATR–FTIR (neat): ν 3054, 3026, 1785, 1722, 1600, 1514, 1441, 1367, 1254, 1209, 1192, 1101, 1023, 983, 963, 912, 893, 878, 836, 758, 697, 560.

**Figure 35.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of PAPI 5.
Figure 36. $^{19}$F NMR (470 MHz, CDCl$_3$) spectrum of PAPI 5.
4,4’-(4,4’-Isopropylidene diphenoxy) bis(phthalic anhydride) (187 mg, 360 µmol), diamino-phenylated-phenylene (313 mg, 360 µmol), and isoquinoline (0.1 mL) catalyst were combined with 5.0 mL nitrobenzene in a microwave vial. The reaction afforded a tan solid product (467 mg, 96%). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.92−7.80 (2H), 7.55−7.46 (2H), 7.43−7.26 (8H), 7.26−6.85 (34H), 6.85−6.57 (9H), 6.42−6.19 (4H), 1.74 (6H); ATR–FTIR (neat): ν 3051, 3024, 2966, 1777, 1720, 1599, 1503, 1477, 1441, 1364, 1271, 1173, 1074, 1014, 950, 896, 834, 760, 745, 697, 552.

Figure 37. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of PAPI 6.
Chapter 4

DIAMINO-PHENYLATED-PHENYLENE AND BISPHENOL A DIGLYCIDYL ETHER EPOXY NETWORKS

4.1 Introduction

Epoxy resins are one of the most important and heavily used thermoset materials in applications including high-performance coatings, adhesives, and composites, due to excellent thermal, mechanical, and electrical properties. The current problems in epoxy resins not being used in even more applications include low stiffness and strength, and heat being produced in the curing reaction that leads to processing difficulties. Vitrification has been observed in many bisphenol A diglycidyl ether resins caused when the glass transition temperature reaches the curing temperature, the mobility of the molecules is reduced. The curing process proceeds due to diffusion. The reaction mechanism and the kinetics of the curing process for an epoxy resin determine the morphology of the three-dimensional network, thus defining its physical and mechanical properties. The techniques employed to monitor the curing reaction can be grouped into two methods. The direct methods allow the evaluation of the concentration of one or more reactive groups as a function of time. They include attenuated total reflectance-Fourier transform infrared spectroscopy. Indirect analysis gives only an assessment of the degree of cure by monitoring, as a function of time, a physical property directly correlated with the conversion of the reactants. The most typical technique in this area is differential scanning calorimetry, which is based on the rate of heat evolution being proportional to the rate of polymerization.
Diels–Alder polymerization between bistetracyclone and diethynyl compounds has led to high molecular polyphenylated polymers.\textsuperscript{172-173, 178} During the step-growth polymerization, carbon monoxide is lost, which prevents the retro-Diels–Alder reaction from occurring and results in a formation of a stable phenyl ring. Depending on the approach of the reactants, the possible Diels–Alder products can exist in either \textit{para} and \textit{meta} conformation.\textsuperscript{110, 174} Of particular interest typically is the enhanced solubility of the phenylated materials in common organic solvents (e.g., toluene, chloroform, tetrahydrofuran, etc.) due to the mixture in conformation throughout the backbone,\textsuperscript{94, 99} and twisting of phenyl groups.\textsuperscript{183}

In this study, the mixed conformation backbone of the Diels–Alder diamino-phenylated-phenylene was utilized. A new diamino-phenylated-phenylene was synthesized, mixed, and cured with bisphenol A diglycidyl ether. Two model systems with pure 1,4-benzene diamine and 1,3-benzene diamine conformations were also cured with bisphenol A diglycidyl ether in an attempt to compare the conformation morphology. The size and shape were not perfect, but efforts were made to understand all the systems involved using careful characterization.

4.2 Results and Discussion

The synthesis of bistetracyclone is a straightforward one step base-catalyzed reaction between 1,4-bisbenzil and 1,3-diphenylacetone. After crystallization and drying, bistetracyclone was reacted via Diels–Alder with 4-ethynylaniline to afford the new hardener, diamino-phenylated-phenylene (PDA), in 84\% yield (Scheme 10). The new monomer was fully characterized via $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The Diels–Alder reaction is not regioselective, resulting
in a mixture of \textit{para} and \textit{meta} conformations in the product; the highest concentration is \textit{para-para}, then \textit{meta-meta}, and finally \textit{para-meta}. The conformational mixture affords more flexibility and better solubility than if it were just a single conformation. One drawback is that diamino-phenylated-phenylene is a solid, so mixing with the epoxy resin is more difficult. Future synthetic strategies will involve new liquid hardeners. Bisphenol A diglycidyl ether (BADGE) was chosen as the resin in this preliminary study because of its ready availability and widespread use in epoxy applications.

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\end{center}

\textbf{Scheme 10.} Synthesis of diamino-phenylated-phenylene (PDA) from bistetracyclone and 4-ethynylaniline.

Due to the mixed conformation of diamino-phenylated-phenylene, two pure conformation model compounds were compared: 1,4-benzenediamine (1,4-BDA) and 1,3-benzenediamine (1,3-BDA). Both of these compounds are solids so proper mixing techniques were optimized with these commercial compounds before attempting the reaction with PDA. The model compounds were ground in a mortar and pestle and carefully weighed and mixed with BADGE at a 1:2 molar ratio for 3-5 minutes with continuous stirring. PDA and BADGE were mixed in a 1:8 mole ratio, respectively (\textbf{Scheme 11}). PDA is a high molecular weight solid and attempts to mix in a 1:2 mole ratio did not afford a consistent mixture.
Scheme 11. Synthesis of diamino-phenylated-phenylene bisphenol A diglycidyl ether epoxy network from diamino-phenylated-phenylene (PDA) and bisphenol A diglycidyl ether (BADGE).
The homogenously mixed samples (5-10 mg) were immediately sealed in hermetic convex differential scanning calorimetry (DSC) aluminum pans. The reference pan was an empty sealed DSC pan. For FTIR and thermal gravimetric analysis (TGA), the samples were removed from the DSC pans after DSC analysis, or samples were cured in an oven separately on aluminum foil. Different surfaces were studied for curing including glass slides, aluminum foil, silicone baking molds, and teflon-coated silicone baking sheets. The glass slides afforded clean network samples with flat surfaces ideal for ATR–FTIR analysis, but typically a razor blade was necessary to release the sample from the glass substrate. Aluminum foil afforded the cleanest samples, and because the aluminum foil can be easily folded, the network samples could be removed like an adhesive sticker. The silicone baking molds worked equally well and were flexible, but attempts to prepare larger samples for dynamic mechanical analysis (DMA) resulted in air bubbles being formed in higher occurrences. The Teflon coated silicone baking sheet was the easiest to remove; however, it appeared that a reaction occurred between the Teflon and the network, resulting in discoloration of all the network samples.

DSC scans were obtained at a heating rate of 10 °C/min. The first heating scan illustrated the curing curve while the second heating curve indicated the glass transition temperature of the cured epoxy network (Figure 41). The 1,4-BDA BADGE network showed an onset of cure at 73 °C and a peak max at 128 °C. The enthalpy change (ΔH) was determined to be 385 J/g. The second heating scan indicated the glass transition temperature (Tg) to be 103 °C. The 1,3-BDA BADGE network showed an onset of cure at 74 °C and a peak max at 151 °C. The enthalpy change was determined to be significantly higher than the 1,4-benzenediamine network at 526 J/g. The second heating scan indicated the glass transition temperature was significantly higher at 151 °C. The onset of cure in the PDA BADGE network was at a much higher temperature (146 °C) with a
peak max at 206 °C. The lowest glass transition temperature \( T_g = 103 \, ^\circ C \) was found in the 1,4-BDA BADGE network due to more linear chains being formed. The highest enthalpy change \( \Delta H = 526 \, J/g \) was measured in the 1,3-BDA BADGE network because it was the most reactive.\(^{217}\) The PDA BADGE network had the highest glass transition temperature \( T_g = 206 \, ^\circ C \) due to the mixture of para and meta conformations, higher molecular weight, and more bulky than 1,4- and 1,3-BDA, and therefore presumably density and compressive modulus. The extra phenyl groups also lead to secondary intermolecular aromatic interactions, reducing chain mobility. The PDA BADGE network possessed the lowest enthalpy change \( \Delta H = 238 \, J/g \), reflecting lower reactivity and slower diffusion due to the size and bulk of PDA.
1,3-BDA

Heat Flow (W/g)

Temperature (°C)

1st:
- Onset = 74 °C
- Area = 526 J/g

2nd:
- $T_g = 151 °C$

Peak = 151 °C
Figure 42. Differential scanning calorimetry (DSC) results for 1,4-benzenediamine (1,4-BDA) BADGE network, 1,3-benzenediamine (1,3-BDA) BADGE network, and diamino-phenylated-phenylene (PDA) BADGE network; 1st heating scan shows curing curve with onset, peak, and ΔH area; 2nd heating scan shows glass transition temperature ($T_g$); heating rate = 10 °C/min under nitrogen atmosphere.
Attenuated total reflectance Fourier transform infrared (ATR–FTIR) spectroscopy characterization of the cured network materials shows the loss of peaks corresponding to the epoxy or oxirane group (910 cm\(^{-1}\)) and primary amine (between 3500 and 3300 cm\(^{-1}\) stretching and 1650-1500 cm\(^{-1}\) deformation). All the samples are aromatic and possess similar functionality, and therefore possess similar spectra (Figure 42). Substitution patterns in the aromatic rings should be different between the 1,4- (para) and 1,3- (meta) benzenediamine at 2000-1600 and 900-600 cm\(^{-1}\), but there is no significant change. However, the PDA network sample does show new or strong peaks in that region due to multiple aromatic ring substitution. The O-H stretching from the opening of the epoxy ring occurs for all the samples between 3437-3300 cm\(^{-1}\). The C–H (sp\(^2\)) vibrations at 3036-3030 cm\(^{-1}\) are from the aromatic rings in both the resin and hardener. The C–H (sp\(^3\)) stretching vibrations of the ring-opened epoxy rings are present at 2963-2869 cm\(^{-1}\). The C=C stretching occurs at 1606 and 1603 cm\(^{-1}\). Aromatic C–C stretching occurs at 1507-1505 cm\(^{-1}\). The methyl (-CH\(_3\)) deformation occurs at 1361 and 1362 cm\(^{-1}\). The C–O stretching occurs at 1235-1229 and 1181-1179 cm\(^{-1}\). The C–N vibration occurs at 826-821 cm\(^{-1}\). Literature has shown examples of qualitative information about the chemical makeup of the network using mid-infrared spectroscopy, and quantitative analysis of residual epoxy and amine groups using near-infrared spectroscopy and a calibration curve using model compounds (e.g., anisole, aniline, and 1-aminophenyl-3-phenoxy-propan-2-ol).\(^{217}\)
**Figure 43.** ATR–FTIR spectra of 1,4-benzenediamine (1,4-BDA) BADGE network, 1,3-benzenediamine (1,3-BDA) BADGE network, and diamino-phenylated-phenylene (PDA) BADGE network; 32 scans; 4 cm⁻¹ resolution.
Thermal gravimetric analyses (TGA) of the cured networks were performed in nitrogen and air atmospheres (Figure 43). The onset for thermal degradation ($T_d$) was similar for all the network samples. The 1,4-BDA BADGE network had a $T_d$ equal to 332 °C and a char yield at 1000 °C in nitrogen atmosphere of 26%. The 1,3-BDA BADGE network had a slightly higher $T_d$ of 367 °C and a slightly lower char yield at 1000 °C in nitrogen atmosphere at 12%. The PDA BADGE network had the highest $T_d$ at 380 °C and a char yield at 1000 °C in nitrogen atmosphere of 25%. Under an air atmosphere, the networks showed a bi-modal degradation at 332 and 575 °C (1,4-BDA), 364 and 542 °C (1,3-BDA), and 387 and 536 °C (PDA). The char yields at 1000 °C in air for all the networks were 0%.
Figure 44. Thermal gravimetric analysis (TGA) results for 1,4-benzenediamine (1,4-BDA) BADGE network, 1,3-benzenediamine (1,3-BDA) BADGE network, and diamino-phenylated-phenylene (PDA) BADGE network; nitrogen (top) and air (bottom) atmosphere; heating rate = 10 °C/min.
The thermal mechanical properties of the network properties were measured using dynamic mechanical analysis (DMA) (Figure 44). The 1,4-BDA BADGE network possessed a storage and loss modulus at room temperature of approximately 200 and 10 MPa, respectively. The tan delta indicated the mechanical glass transition temperature to be 102 °C. The 1,3-BDA BADGE network possessed a storage and loss modulus at room temperature of approximately 150 and 10 MPa, respectively. The tan delta indicated the mechanical glass transition temperature to be 180 °C. The meta isomer in a variety of epoxy networks as compared to the para isomer affects thermal mechanical properties due to a combination of changes in packing efficiency, reaction kinetics, and conformational freedom.\textsuperscript{217} The PDA BADGE network possessed a storage and loss modulus at room temperature of approximately 350 and 40 MPa, respectively, indicating this network to have a higher strength or mechanical rigidity than the two model networks. The tan delta indicated the mechanical glass transition temperature to be 209 °C. This showed the thermal mechanical properties to be greater than either model compound, with higher storage and loss moduli and a higher tan delta peak temperature. Sample preparation was more difficult for the PDA BADGE network as bubbles can act as defect sites and reduce the mechanical properties. Also, a 1:2 molar ratio could not be used due to the PDA being a higher molecular weight and not dissolving or mixing efficiently in the BADGE. Future work will entail further optimization and use in adhesive and composite applications.
Figure 45. Dynamic mechanical analysis (DMA) data for 1,4-benzenediamine (1,4-BDA) BADGE network, 1,3-benzenediamine (1,3-BDA) BADGE network, and diamino-phenylated-phenylene (PDA) BADGE network; E’ = storage modulus, E” = loss modulus, and E”/E’ = tan delta (δ); heating rate = 2 °C/min; frequency = 1 Hz.
4.3 Conclusions

Two model epoxy networks were prepared from the reaction of 1,4- or 1,3-benzenediamine with bisphenol A diglycidyl ether and compared to a network prepared from a newly synthesized hardener, diamino-phenylated-phenylene, with a mixed para and meta conformation. Curing and glass transition temperature curves were studied with DSC. ATR–FTIR was used to characterize the cured networks’ structures. Thermal stability was elucidated using TGA and thermal mechanical analysis data was obtained using DMA. The mixture of the para and meta isomer configuration leads toward further tailoring of chemical and thermomechanical properties. This new diamino-phenylated-phenylene hardener shows great promise for the development of new and improved high-performance epoxy resins for use in the aerospace and automotive industries due to its increased thermal stability and improved mechanical properties. Future studies will focus on property optimization of these systems and advanced applications.

4.4 Experimental

Materials and methods

All solvents, starting materials, and reagents were purchased from Alfa Aesar, Fisher Scientific, Sigma-Aldrich, TCI America, or VWR as reagent grade and used as received, unless otherwise mentioned. Bisphenol A diglycidyl ether (BADGE, 340.42 g/mol) was purchased from TCI. 1,3-Benzenediamine was purchased from TCI. 1,4-Benzenediamine was purchased from Alfa Aesar. Reactions were carried out under an argon atmosphere, unless otherwise noted. All glassware was oven-dried prior to use and cooled in a desiccator. Dichloromethane (DCM) was dried and deoxygenated by passage through a Pure-Solv solvent system equipped with Cu/Al
columns from Innovative Technologies. *Ortho*-xylene was dried using calcium hydride (CaH₂) and then fractionally distilled, discarding the first 5% of the distillate, and then stored under argon in aluminum foil covered flask. Ethanol was dried using magnesium turning, refluxed with iodine crystals for a few hours, distilled, and then stored over 4 Å molecular sieves under argon in aluminum foil covered flask.

**Instrumentation**

All ¹H and ¹³C NMR spectra were obtained under ambient conditions using a JEOL ECA 500 MHz instrument, and chemical shifts were reported in parts per million (δ ppm). Proton (¹H) and carbon (¹³C) NMR spectra were referenced using the residual solvent peak for CHCl₃ (δ = 7.26 ppm) and the center of the multiplet peak for CDCl₃ (δ = 77.16 ppm), respectively. ATR–FTIR analysis was performed on a Thermo Nicolet FTIR Spectrometer iS10 with a diamond ATR crystal (Spectra-Tech) using neat samples with 16 scans and 4 cm⁻¹ resolution. The onset of thermal degradation temperature (T_d) was obtained from thermal gravimetric analysis (TGA) using a Tarsus TG 209 (Netzsch) at a heating rate of 10 °C/min under a N₂ or air atmosphere, and typical sample sizes of approximately 5-10 mg. The glass transition temperature (T_g) was determined from differential scanning calorimetry (DSC) using a Polyma DSC 214 (Netzsch) at a heating rate of 10 °C/min under a nitrogen atmosphere, and sample sizes were approximately 5-10 mg. Each sample was heated and cooled through three cycles, and the third heating was used to calculate the T_g. Dynamic mechanical analysis (DMA) using a DMA 2980 (TA Instruments) was used to measure storage and loss modulus and tan δ. Samples were tested at a heating rate of 2 °C/min at a frequency of 1 Hz in compression mode. Data were processed using Origin Pro 2019.
**Bistetracyclone.**

1,4-Bisbenzil (10.0 g, 29.2 mmol) and 1,3-diphenylacetone (12.3 g, 58.4 mmol) were added to a 1-L two-neck round bottom flask. Freshly distilled ethanol (455 mL) was added to the flask. The mixture was stirred and heated until it dissolved into a homogenous yellow solution. Potassium hydroxide (3.3 g, 58.4 mmol) was dissolved in distilled ethanol (5 mL) and added dropwise. The black solution was refluxed for 2-3 hrs. The reaction was cooled to room temperature and half the solvent was evaporated under reduced pressure. The reaction was cooled to 0 °C overnight. The dark black/purple solid was filtered, washed with cold ethanol, and dried with air. The fairly pure product was crystallized from minimal amounts of hot anhydrous dichloromethane, cooled to room temperature, and stored at 0 °C. The dark purple crystals were filtered, washed with cold DCM, and under vacuum at room temperature for 24 hr affording 17.4 g (86%). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.11 (10H), 7.98–7.96 (9H), 7.96–7.67 (5H), 7.67–7.52 (10H).

**Diamino-Phenylated-Phenylene (PDA).**

Bistetracyclone (5.0 g, 7.2 mmol) and 4-ethynylaniline (1.8 g, 15.2 mmol) were dissolved in o-xylene (250 mL). The solution was freeze/pump/thawed and de-gassed with argon. The reaction was refluxed for 24 hrs. The orange solution was cooled to room temperature and reduced to minimal solvent (~10 mL). The solution was added dropwise to stirring hexane (50 mL). The precipitated product was filtered, washed with hexane, and dried under vacuum at 50 °C for 24 hr to afford a tan/off-white powder (5.3 g, 84%). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.49–7.47 (2H), 7.24–6.84 (27H), 6.83–6.61 (8H), 6.51–6.42 (4H), 6.40–6.20, 3.54 (4H); $^{13}$C NMR (125 MHz,
CDCl₃): δ 144.71, 142.25, 141.54, 140.97, 140.70, 140.55, 139.34, 137.89, 137.13, 136.23, 132.00, 131.90, 131.87, 131.72, 130.95, 130.77, 130.59, 130.29, 130.07, 127.60, 126.99, 126.64, 126.19, 125.43, 125.30, 114.51; ATR–FTIR (neat): ν 3053, 3035, 1606, 1506, 1229, 1180, 1033, 828, 699, 554.

1,4-Benzenediamine (1,4-BDA) and BADGE Epoxy Network.

1,4-Benzenediamine (hardener, 162 mg, 1.5 mmol) and bisphenol A diglycidyl ether (epoxy resin, 1.0 g, 3.0 mmol) were combined neat to create an epoxy network. The hardener is a crystalline solid, so it was crushed into a powder with a mortar and pestle to allow better mixing with the resin. The mixture was stirred for 3-5 minutes and placed in a desiccator at room temperature for 24 hrs. After 24 hrs, the mixture was placed in an oven to cure at 60 °C for 3 hrs, 100 °C for 3 hrs, and 140 °C for 1 hr. This heating cycle would allow it to cure fully. The cured network was characterized using IR spectroscopy, TGA, DSC, and DMA.

1,3-Benzenediamine (1,3-BDA) and BADGE Epoxy Network.

1,3-Benzenediamine (hardener, 150 mg, 1.4 mmol) and bisphenol A diglycidyl ether (epoxy resin, 941 mg, 2.8 mmol) were combined neat to create an epoxy network. The hardener is a crystalline solid, so it was crushed into a powder with a mortar and pestle to allow better mixing with the resin. The mixture was stirred for 3-5 minutes and placed in a desiccator at room temperature for 24 hrs. After 24 hrs, the mixture was placed in an oven to cure at 60 °C for 3 hrs, 100 °C for 3 hrs, and 160 °C for 1 hr. This heating cycle would allow it to cure fully. The cured network was characterized using IR spectroscopy, TGA, DSC, and DMA.
Diamino-Phenylated-Phenylene (PDA) and BADGE Epoxy Network.

Diamino-phenylated-phenylene (hardener, 660.6 mg, 0.8 mmol) and bisphenol A diglycidyl ether (epoxy resin, 2.2 g, 6.4 mmol) were combined neat to create a highly phenylated epoxy networks. Mixing at this particular molar ratio resulted in a homogeneous mixture. Crushing the diamine with a mortar and pestle was not necessary because the hardener is already a powder. The mixture was stirred for 5-7 minutes and placed in a desiccator at room temperature for 24 hours. After 24 hrs, the mixture was placed in an oven to cure at 60 °C for 3 hrs, 100 °C for 3 hrs, and 200 °C for 1 hr. This heating cycle would allow it to cure fully. The cured network was characterized using IR spectroscopy, TGA, DSC, and DMA.
Chapter 5

PHENYLATED POLYPHENYLENE SMALL MOLECULE AND OLIGOMERIC RESINS

5.1 Introduction

High performance polymers are increasingly important in many fields, including the automobile, electronics, and aerospace industries, academics, and government facilities.\(^{218}\) Both thermoplastics and thermosets have been used for high performance applications.\(^{219}\) Thermoplastics have the advantage of minimal to no chemistry changes while processing, and they can be recycled after the assembly process. Some amorphous thermoplastics have poor solvent resistance whereas typical thermosets offer excellent solvent resistance.\(^{220-221}\) However, some of these resins may be too brittle for certain applications and they are difficult to recycle once cross-linked. Network resins for functional and structural applications continue to be of great interest.\(^{222}\) Typical cross-linking functional groups include epoxides,\(^{223}\) cyanate esters,\(^{224}\) ethynyl,\(^{225-226}\) and phenylethynyl end-groups.\(^{227-228}\) As a result, the combination into a single material of thermoplastics’ and thermosets’ beneficial properties which include good processability, mechanical performance, and solvent resistance, is a worthwhile objective.\(^{229-232}\) Liquid monomers or small molecule resins are ideal for melt processing, whereas high molecular weight amorphous polymers typically require solvent processing in which shrinkage and complete removal of the solvent must be addressed.\(^{233-234}\)

Amorphous, high molecular weight Diels–Alder phenylated polyphenylenes have been prepared from dienes, such as bistetracyclone, and dienophiles, such as 1,4- or 1,3-diethynylbenzene.\(^{110,173,175}\) The improved solubility is a result of the pendant aryl substituents, the
mixed para/meta conformations in the backbone, and the ability to utilize a variety of structurally different monomers.\textsuperscript{94, 174, 178} These amorphous, high molecular weight polymers can be manipulated by solvent processing. In order to melt process these polymers, a chain of methylene groups was added to the backbone which lowered the glass transition temperature, but the number average molecular weights were relatively low (30-60 kg/mol).\textsuperscript{99} Lowering the molecular weight allows melt processability even for amorphous polymers. Compared to the para isomer, the meta diethynylbenzene resulted in polymers with better flow properties, which has also been observed in polyimides for some time.\textsuperscript{228, 235-236} Herein, we describe the synthesis of small molecule and oligomeric phenylated phenylene resins with ethynyl and phenylethynyl end-groups that can be thermally cured into network materials.

5.2 Results and Discussion

The synthesis of bistetracyclone is a straightforward reaction that can be scaled up to large scale (Scheme 12) with yields above 85%. Purification leads to dark purple crystals. The base catalyzed reaction between 1,4-bisbenzil and 1,3-diphenylacetone in refluxing anhydrous ethanol is complete in less than five hours. Column chromatography can be used for purification but for large scale reactions, filtration and crystallization from dichloromethane is the preferred technique. Bistetracyclone can be left out in the open air but typically is kept covered and can be stored for months and probably years.
Scheme 12. Synthesis of bistetracyclone (1) from 1,4-bisbenzil and 1,3-diphenylacetone.

Phenylated dibromophenylene 2 is a new compound and can be prepared via a scalable, straight-forward reaction. Twenty-gram reaction scales were performed twice in our laboratory and actually afforded slightly higher yields than the lower scale reported herein. Diels–Alder reactions between bistetracyclone 1 (diene) and two equivalents of 4-bromophenylacetylene (dienophile) were accomplished to afford phenylated dibromophenylene 2 (Scheme 13) with yields above 80%. The end groups are in a mixed para and meta conformation due to the nature of the Diels-Alder reaction mechanism. The purple starting solution was refluxed in anhydrous ortho-xylene which bubbled immediately as carbon monoxide was released, and eventually changed to an orange solution in 24-48 hrs. Evaporation of the solvent under reduced pressure gave a tan solid which was dissolved in minimal amounts of dichloromethane (~10 mL). The solution was added slowly to a stirring solution of hexane (500 mL) to precipitate the product. The precipitated solid was filtered, washed with additional hexane, and dried under vacuum at 50 °C overnight. A pure tan powder was afforded in 81% yield. The $^1$H NMR spectrum displayed typical aromatic protons at approximately 7.5 to 6.2 ppm. The three peaks at 6.4, 6.3, and 6.2 ppm correspond to the possible meta/meta, paral/para, and para/meta conformations$^{174, 176}$ of the end groups, respectively, with a ratio of 1:2:3 (m/m:p/p:p/m) as determined by integration.
Scheme 13. Diels–Alder synthesis of phenylated dibromophenylene (2) from bistetracyclone (1) and two equivalents of 4-bromophenylacetylene.

The phenylated phenylene ethynyl end-capped resin (3) is a new compound and was synthesized using palladium coupling and base deprotection (Scheme 14). Two equivalents of 2-methylbut-3-yn-2-ol were added to phenylated dibromophenylene 2 along with bis(benzonitrile)palladium(II) chloride, triphenylphosphine, copper(I) iodide, and anhydrous triethylamine. The more typical trimethylsilylacetylene (TMSA) was used as well but better results and an easier workup were accomplished with the alcohol protection group. Longer deprotection times were necessary however. Deprotection was accomplished by refluxing with sodium hydroxide and potassium carbonate in toluene for 2-3 days. The product (3) was afforded as a tan solid in 47% yield. The $^1$H NMR spectrum shows a wider range of aromatic signals at approximately 6.2 to 8.3 ppm. The para and meta conformation mixture is preserved. A new peak corresponding to the acetylene proton is observed at 3.4 ppm. The $^{13}$C NMR spectrum shows a broad peak at 91.8 ppm corresponding to the acetylene carbons. In the IR spectrum, a peak at 3350 cm$^{-1}$ corresponds to the C≡C−H vibration and a peak at 2164 cm$^{-1}$ corresponds to the C≡C vibration.
Scheme 14. Synthesis of phenylated phenylene ethynyl end-capped resin (3) from phenylated dibromophenylene (2).

The phenylene phenylethynyl end-capped resin (4) is new and was prepared using a palladium coupling without any deprotection being necessary (Scheme 15). Two equivalents of distilled phenylacetylene were added to phenylated dibromophenylene (2) along with bis(benzonitrile)palladium(II) chloride, triphenylphosphine, copper(I) iodide, and anhydrous triethylamine. The reaction was refluxed for 2-3 days. The light brown solid product was afforded in 69% yield. The $^1$H NMR spectrum shows a slightly wider range of aromatic signals at approximately 8.1 to 6.2 ppm. The para and meta conformations were preserved from 2. There is no proton signal in the acetylene region because a phenyl group is present in place of the hydrogen. The $^{13}$C NMR spectrum does show a peak at 92.9 ppm corresponding to the acetylene carbons. In the FTIR spectrum, a peak at 2161 cm$^{-1}$ corresponds to the C≡C vibration.

Scheme 15. Synthesis of phenylated phenylene phenylethynyl end-capped resin (4) from phenylated dibromophenylene (2).

Br–(Ph–C–Ph)–Br + ≡OH $\xrightarrow{1) \text{Pd(PhCN)$_2$Cl$_2$, PPh$_3$} \quad \text{Cul, NEt$_3$, 90 °C} \quad 2) \text{NaOH, K$_2$CO$_3$} \quad \text{Toluene, reflux}$
The oligomeric phenylated polyphenylene phenylethynyl end-capped resin (5) is new and was synthesized from bistetrayclclone (1) and two equivalents of 1,4-bis(2-phenylethynyl)benzene under microwave-assisted polymerization conditions (Scheme 16). The Diels–Alder polymerization was carried out in anhydrous nitrobenzene at 180 °C with medium stirring at 300 W. The dark purple solution changed to a yellow/orange solution within one to five hours. The yellow color corresponds to the lowest molecular weight ($M_n = 1,500$ g/mol) while the orange color corresponded to longer oligomeric chains ($M_n = 9,800$ g/mol). The tan powder (9.8 kg/mol) product resin was afforded in 86% yield. The $^1$H NMR spectrum shows a range of signals in the aromatic region at approximately 6.7 to 8.1 ppm. The Diels-Alder products are now mostly para-substituted due to steric. The product is oligomeric so the signals are still sharp and not broadened like many polymer signals. The $^{13}$C NMR spectrum shows a peak at 93.9 ppm corresponding to the acetylene carbons. In the FTIR spectrum, a peak at 2169 cm$^{-1}$ corresponds to the C≡C stretch.

Scheme 16. Synthesis of oligomeric phenylated polyphenylene phenylethynyl end-capped resin (5) from bistetrayyclclone (1) and 1,4-bis(2-phenylethynyl)benzene.
The thermal curing properties of these three new resins were characterized via differential scanning calorimetry (DSC) (Figure 45), and show similar curing curves to other ethynyl and phenylethynyl end-capped resins. \(^{225, 228, 237-238}\) The thermogram of phenylated phenylene ethynyl end-capped resin (3) shows a melting point at 83 °C, an onset of thermal curing at 146 °C, and a maximum curing temperature of 207 °C. The thermogram of phenylene phenylethynyl end-capped (4) shows a melting point at 102 °C, an onset of thermal curing at 243 °C, and a maximum curing temperature of 288 °C. The thermogram of oligomeric polyphenylene phenylethynyl end-capped (5) shows a melting point at 128 °C, an onset of thermal curing at 262 °C, and a maximum curing temperature of 318 °C. Depending on molecular weight, the melting point of (5) varied from 120 (1.5 kg/mol) to 150 °C (9.8 kg/mol) but the exothermic curing temperatures were approximately the same. Unsurprisingly, resin 3 possessed the lowest curing temperature due to the reactive ethynyl end-groups. On the other hand, resins 4 and 5 possessed a curing temperature approximately 100 °C due to the lower reactivity of the phenylethynyl end-groups. Oligomeric resin 5 has a higher molecular weight than 4 and a corresponding lower concentration of phenylethynyl groups, which is reflected in its higher curing temperature.
Figure 45. DSC heating curves of compounds 3, 4, and 5 showing melting endotherms and curing exotherms; heating rate = 5 °C/min; nitrogen atmosphere.
5.3 Conclusions

We have synthesized three new thermally cross-linkable small molecule and oligomeric resins with ethynyl and phenylethynyl end-groups. The small molecule resins with ethynyl and phenylethynyl end-groups were synthesized from a phenylated dibromophenylene using palladium coupling. The oligomeric phenylated polyphenylene resin with phenylethynyl end-groups was synthesized by microwave-assisted Diels–Alder polymerization of bistetracyclone and 1,4-bis(2-phenylethynyl)benzene. The melting points for the three new resins ranged from 80–150 °C while the maximum thermal curing temperatures were in the range of 145 to 350 °C. Future work will entail fully characterizing these resins, measuring thermal stability, water absorption properties, and investigating composite applications.

5.4 Experimental Section

General

All solvents, starting materials, and reagents were purchased from Alfa Aesar, Fisher Scientific, Sigma-Aldrich, TCI America, or VWR as reagent grade and used as received, unless otherwise mentioned. Reactions were carried out under an argon atmosphere, unless otherwise noted. All glassware was oven-dried prior to use and cooled in a desiccator. HPLC-grade tetrahydrofuran (THF) was dried and deoxygenated by passage through a Pure-Solv solvent system equipped with Cu/Al columns from Innovative Technologies. Anhydrous nitrobenzene was purchased from EMD Millipore. Ethanol was dried using magnesium turning, refluxed with iodine crystals for a few hours, distilled, and then stored over molecular sieves under argon.
**Instrumentation**

All $^1$H and $^{13}$C NMR spectra were obtained under ambient conditions using a JEOL ECA 500 MHz instrument, and chemical shifts were reported in parts per million ($\delta$ ppm). Proton ($^1$H) and carbon ($^{13}$C) NMR spectra were referenced using the residual solvent peak for CHCl$_3$ ($\delta = 7.26$ ppm) and the center of the multiplet peak for CDCl$_3$ ($\delta = 77.16$ ppm), respectively. ATR–FTIR analysis was performed on a Thermo Nicolet FTIR Spectrometer iS10 with a diamond ATR crystal (Spera-Tech) using neat samples with 16 scans and 4 cm$^{-1}$ resolution. Molecular weights and molecular weight dispersities ($M_w/M_n$) were determined by gel permeation chromatography (GPC) on a Tosoh EcoSEC system equipped with a series of 4 columns (TSK gel guard Super HZ-L, Super HZM-M, Super HZM-N, and Super HZ2000) at 40 °C, and using refractive index detector. HPLC-grade tetrahydrofuran was used as the eluent at a flow rate of 0.35 mL/min. The GPC calibration was based on linear polystyrene (PS) standards. Polymer samples were dissolved in THF (1 mg/mL) and filtered through a 0.2-$\mu$m PTFE syringe filter before injection. The onset of thermal degradation temperature ($T_d$) was obtained from thermal gravimetric analysis (TGA) using a TG209F3 (NETZSCH) at a heating rate of 10 °C/min under a N$_2$ or air atmosphere, and typical sample sizes of approximately 5-10 mg. The glass transition temperature ($T_g$) was determined from differential scanning calorimetry (DSC) using a DSC 214 Polyma (NETZSCH) at a heating rate of 10 °C/min under a nitrogen atmosphere, and sample sizes were approximately 5-10 mg. Each sample was heated and cooled through three cycles, and the third heating was used to calculate the $T_g$. Data were processed using Origin Pro 2019.
To a 500 mL two-necked, round-bottomed flask equipped with a condenser, a stir bar and a septum, were added 275 mL of freshly distilled ethanol, 1,3-diphenylacetone (12.3 g, 58.4 mmol, 2.1 eq), and 1,4-bisbenzil (10.0 g, 29.2 mmol, 1 eq). The solution was refluxed for one hour. Potassium hydroxide (KOH, 3.3 g, 58.4 mmol, 2.0 eq) was dissolved in 10 mL ethanol and added drop-wise to the refluxed solution. The solution was refluxed for an additional 1-2 hrs, and then the solution was cooled at 0 °C overnight. The solution was filtered, the precipitate was dissolved in boiling DCM, and then crystallized affording dark purple needle-like solids at 0 °C. (17.1 g, 85%) \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 6.78 (s), 6.92 (d, \(J = 7.06\) Hz, 4 H), 7.19-7.30 (m, 26 H). \(^1\)C NMR (125 MHz, CDCl\(_3\)): δ 200.60, 154.93, 154.66, 134.11, 133.50, 130.65, 130.59, 129.77, 129.51, 129.05, 128.53, 128.12, 128.07.

**Phenylated Dibromophenylene (2)**

Bistetracyclone (5.0 g, 7.2 mmol) and 4-bromophenylacetylene (2.9 g, 15.9 mmol) were dissolved in anhydrous o-xylene (250 mL). The solution was freeze/pump/thawed and de-gassed with argon, and then refluxed for 12 hrs. The orange solution was cooled to room temperature and reduced to minimal solvent (~10 mL). The solution was added dropwise to stirring hexane (500 mL). The precipitated product was filtered, washed with hexane, and dried under vacuum at 50 °C for 24 hr to afford a tan/off-white powder (5.9 g, 81%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 7.47–7.42 (2H), 7.29–7.18 (7H), 7.17–7.11 (3H), 7.11–7.05 (3H), 7.05–6.88 (17H), 6.80–6.62 (8H), 6.42–6.24 (4H); \(^1\)C NMR (125 MHz, CDCl\(_3\)): δ 141.89, 141.81, 141.77, 141.31, 141.25, 141.07, 140.95, 140.91, 140.74, 140.27, 140.03, 139.88, 139.85, 139.81, 139.62, 139.48, 139.43,
139.41, 139.39, 139.11, 138.96, 138.82, 137.00, 136.52, 136.22, 131.88, 131.77, 131.75, 131.64,
131.61, 131.59, 131.57, 131.54, 131.29, 130.83, 130.73, 130.57, 130.19, 129.98, 127.71, 127.69,
127.24, 127.19, 127.05, 126.75, 126.39, 126.36, 125.91, 125.85, 125.75, 125.50, 120.66, 120.59;
ATR–FTIR (neat): v 3079, 3052, 3022, 1487, 1006, 830, 559 cm$^{-1}$.

Phenylated Phenylene Ethynyl End-capped Resin (3)

Phenylated dibromophenylene 2 (500 mg, 0.5 mmol) and 2-methylbut-3-yn-2-ol (0.1 mL, 1.1 mmol, 2.2 equiv.) were added to a round bottomed flask and dissolved in anhydrous tetrahydrofuran (THF, 50 mL) and anhydrous triethylamine (NEt$_3$, 50 mL). The mixture was refluxed for 30 min and then cooled to room temperature. Bis(benzonitrile)palladium(II) chloride (5.8 mg, 15 µmol, 3 mol%), triphenylphosphine (19.8 mg, 75 µmol, 15 mol%), and copper(I) iodide (10.5 mg, 55 µmol, 11 mol%) were added to the flask and the solution was freeze/pump/thawed and de-gassed with argon. The reaction was refluxed under argon for 24-48 hr. The light brown solution was cooled to room temperature and the solids were separated via filtration. The solvent was evaporated under reduced pressure. The brown solid was dissolved in dichloromethane (DCM), and the solution and washed with hydrochloric acid (1 M), sodium bicarbonate (NaHCO$_3$, saturated), and brine (3x). The DCM layer was dried with anhydrous magnesium sulfate (MgSO$_4$), filtered, and evaporated under reduced pressure affording a tan solid. The protected product was dissolved in anhydrous toluene (50 mL) to which sodium hydroxide (NaOH, 61.3 mg) and potassium carbonate (K$_2$CO$_3$, 70.6 mg) were added. The mixture was freeze/pump/thawed and de-gassed in argon. The solution was refluxed for 24-48 hrs. The dark brown solution was cooled to room temperature, the solids were removed via filtration, and the solvent was evaporated under reduced pressure. The residue was dried under vacuum at 60 °C
for 24 hr to afford a tan powder (211 mg, 47%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.72–7.65 (1H), 7.58–7.39 (3H), 7.28–7.10 (10H), 7.10–6.85 (18H), 6.79–6.59 (8H), 6.42–6.21 (4H), 3.44 (2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 141.88, 141.80, 141.76, 141.30, 141.24, 141.06, 140.94, 140.90, 140.73, 140.26, 140.02, 139.94, 139.87, 139.84, 139.81, 139.80, 139.74, 139.61, 139.47, 139.41, 139.40, 139.37, 139.10, 138.95, 138.81, 136.98, 136.51, 136.20, 132.02, 131.88, 131.87, 131.83, 131.81, 131.76, 131.72, 131.65, 131.62, 131.60, 131.58, 131.54, 131.27, 130.81, 130.80, 130.72, 130.56, 130.18, 130.14, 129.97, 128.65, 128.56, 127.70, 127.67, 127.21, 127.18, 127.03, 127.02, 126.74, 126.73, 126.37, 126.34, 125.89, 125.84, 125.74, 125.49, 120.64, 120.58, 108.20, 91.79; ATR–FTIR (neat): $\nu$ 3350, 3080, 3054, 3025, 2164, 1599, 1440, 1013, 696, 540 cm$^{-1}$.

**Phenylated Phenylene Phenylethynyl End-capped Resin (4)**

Phenylated dibromophenylene 2 (500 mg, 0.5 mmol) and phenylacetylene (0.1 mL, 1.1 mmol, 2.2 equiv.) were added to a round bottom flask and dissolved in anhydrous tetrahydrofuran (THF, 50 mL) and anhydrous triethylamine (NEt$_3$, 50 mL). The mixture was refluxed for 30 min and then cooled to room temperature. Bis(benzonitrile)palladium(II) chloride (5.8 mg, 15 µmol, 3 mol%), triphenylphosphine (19.8 mg, 75 µmol, 15 mol%), and copper(I) iodide (10.5 mg, 55 µmol, 11 mol%) were added to the flask and the solution was freeze/pump/thawed and de-gassed with argon. The reaction was refluxed under argon for 48-72 hr. The light brown solution was cooled to room temperature and the solids were separated via filtration. The solvent was evaporated under reduced pressure. The brown solid was dissolved in dichloromethane (DCM), and the solution was washed with hydrochloric acid (1 M), sodium bicarbonate (NaHCO$_3$, saturated), and brine (3x). The DCM layer was dried with anhydrous magnesium sulfate (MgSO$_4$), filtered, and evaporated under reduced pressure affording a tan solid. The solid was dried under
Oligomeric Phenylated Polyphenylene Phenylethynyl End-capped Resin (5)

Bistetracyclone (124 mg, 180 µmol) and 1,4-bis(2-phenylethynyl)benzene (100 mg, 360 µmol, 2 equiv.) were added to a microwave vial with a stir bar. Anhydrous nitrobenzene (4 mL) was added, rinsing down the sides to ensure all solid was covered with liquid. The mixture was freeze/pump/thawed and de-gassed with argon. The reaction was microwaved at 180 °C for 30 min segments until the starting purple color changed to yellow-orange, indicating formation of low molecular weight product. The yellow-orange solution was cooled to room temperature, evaporated under reduced pressure, and the solid was washed with acetone. The product was dried under vacuum at 60 °C for 24 hr to afford a tan powder (189 mg, 86%). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.28–8.20 (2H), 7.73–7.67 (1H), 7.60–7.46 (12H), 7.44–7.16 (27H), 6.92–6.70 (20H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 143.13, 142.89, 143.45, 142.07, 141.92, 141.69, 141.31, 141.16, 140.91, 140.84, 140.66, 140.21, 140.05, 139.89, 139.82, 139.77, 139.72, 139.67, 139.49, 139.42, 139.41, 139.36, 139.15, 138.98, 138.87, 137.01, 136.58, 136.20, 135.38, 133.81, 132.91, 129.34,
128.44, 128.41, 127.87, 127.71, 127.54, 126.17, 121.61, 93.89; ATR–FTIR (neat): ν 3081, 3053, 3022, 2169, 1594, 1438, 1016, 698, 539 cm$^{-1}$. 
Chapter 6

POLYARLENE-BORON NITRIDE NANOTUBE NANOCOMPOSITES

6.1 Introduction

The pursuit of lightweight, strong, and high-temperature nanocomposite materials is of significance for a variety of industries, including those with aerospace and automotive interests. The surface interaction between filler and polymer interfaces plays a critical role in the bulk performance of polymer nanocomposites. An acceptable load transfer from polymer to filler demands a strong filler-polymer interface. There has been increased interest in boron nitride nanotubes (BNNTs) since 1995 due to their electronic, thermal, and mechanical properties, which are superior/different as compared to carbon nanotubes (CNTs). BNNTs are electrically insulating, piezoelectric, optically transparent, highly hydrophobic, resistant to neutron radiation, thermally and chemically stable, and considerably more thermo-oxidatively resistant (1000 °C versus 500 °C for CNTs). Furthermore, compared to CNTs, BNNTs bind more strongly to polymeric matrices in composites due to the polarized nature of the B–N bonds. In order to utilize BNNTs in nanocomposites, the nanomaterials must be solubilized or dispersed for processing. It has been shown that BNNTs have a tensile strength up to 30 GPa and a Young’s modulus up to 1000 GPa. It is projected that BNNTs are capable of forming strong binding interfaces with polymers mostly due to their highly polarized electrical properties and the resulting strong Coulombic interactions with polymers. However, the mechanical strength of BNNT-polymer interfaces remains largely unexplored.
The properties of BNNTs make them extremely attractive in the development of high-temperature, lightweight nanocomposites with the potential to impact a range of engineering sectors including aerospace and armored materials.\textsuperscript{243, 247} To accomplish the full potential of BNNT-polymer nanocomposites, it is essential to develop diverse polymer-BNNT nanocomposite systems and architectures, including high weight loadings of BNNTs, which will ultimately require functionalization of the polymers and BNNTs to optimize interactions via bottom-up material design. Polymer wrapping using polyphenylenevinylene (PPV) was introduced to dissolve BNNTs, which afforded thin films;\textsuperscript{248} however, PPV is not thermally or oxidatively stable, thereby diminishing the benefits of polymer-BNNT nanocomposites. It was determined that PPV solubilized BNNTs as a result of the strong affinity between the two components, which was due to $\pi-\pi$ interactions. Highly phenylated polyphenylenes, or polyarylenes,\textsuperscript{94, 99, 110, 172-175, 178} are solely aromatic and therefore hypothesized to perform equally well or better in adhering to and dissolving the BNNTs and forming nanocomposites, with the added critical advantage of being thermally and oxidatively stable ($T_d \approx 550 \degree C$ in air).\textsuperscript{166, 171}
6.2 Results and Discussion

Nuclear magnetic resonance (NMR) and attenuated total reflectance-Fourier transform infrared (ATR–FTIR) spectroscopy were used to characterize the starting materials and polymers. Thermal characterization included thermal gravimetric analysis (TGA) under an atmosphere of air. The functionalization of pure boron nitride nanotubes (BNNTs) was carried out using a hypervalent iodine species to afford triisopropylsilylethynyl groups decorated on the surface of the nanotubes, followed (Scheme 17). Care was taken to keep the reaction under argon after freeze/pump/thaw. Possible reaction mechanisms consist of electrophilic addition of iodosobenzene.257

Scheme 17. Functionalization of boron nitride nanotubes was accomplished using hypervalent iodine species. Deprotection was successful using TBAF (1 M in THF).
Aluminum foil was used to keep light from interfering with the reaction. Anhydrous solvent was used for the reaction, and all glassware was heated and cooled in a desiccator. The pure BNNTs and the hypervalent iodine compound were added to a vial with stir bar, covered in aluminum foil, and anhydrous DMAc was added. The reaction was freeze/pump/thawed and degassed with argon and then heated to 50 °C for 1 hr under argon. Deprotection of the silyl group was accomplished by the addition of tetrabutylammonium fluoride (TBAF, 1 M in tetrahydrofuran (THF)) and stirring at room temperature for 1 hr; however, removing the TBAF salts was problematic. More aggressive methods can be used, but only washing with DI water was used in order to prevent formation of any undesired side products or degradation.

Characterization of the BNNT functionalization was carried out using $^1$H NMR spectroscopy (Figure 46). The samples were not sonicated but were shaken and stirred to increase dissolution; however, there was still significant amounts of sample that did not disperse in CDCl₃. The BNNT functionalized TIPS protected ethynyl groups (BNNT-CC-TIPS) were observed at 1.11–1.26 ppm, which is similar but slightly shifted from the hypervalent iodine starting material species. After deprotection with TBAF, washing with DI water, and drying overnight in a vacuum oven at 60 °C, the BNNT-ethynyl groups (BNNT-CC-H) were observed at 2.84 ppm. TBAF salt impurities were also observed in the spectrum.
Figure 47. $^1$H NMR (500 MHz, CDCl$_3$) spectra of BNNT functionalized with ethynyl-TIPS (BNNT-CC-TIPS) and deprotected ethynyl groups (BNNT-CC-H); tetrabutylammonium salts (arrows).
Characterization of the pure BNNTs and functionalized BNNTs was also carried out using ATR–FTIR (Figure 47). The pure BNNT sample showed two strong B–N vibrations at 1313 and 774 cm\(^{-1}\). The BNNT-CC-TIPS sample showed slightly shifted B–N vibrations at 1341 and 798 cm\(^{-1}\). The C–H(sp\(^3\)) vibrations from the TIPS protecting group are present at 2942 and 2863 cm\(^{-1}\). The ethynyl C-H stretch is weakly shown at 3295 cm\(^{-1}\). The BNNT-CC-H sample showed the B–N vibrations at 1337 and 788 cm\(^{-1}\). The C–H(sp) vibration from the ethynyl group is present at 3296 cm\(^{-1}\). The TBAF salts observed in the NMR spectrum also show C–H(sp\(^3\)) vibrations at approximately 2920 and 2860 cm\(^{-1}\). The C≡C vibration is more easily seen at 2195 cm\(^{-1}\). Elemental analysis and thermal gravimetric analysis have been performed in the literature to determine degree of functionalization, and cytotoxicity studies were performed and shown to decrease cell death as functionalization increased for single-walled carbon nanotubes (SWCNTs).\(^{259}\)
Figure 48. ATR–FTIR spectra (neat, diamond crystal, 32 scans, 4 cm⁻¹ resolution) of pure BNNT, functionalized with ethynyl-TIPS (BNNT-CC-TIPS), and deprotected ethynyl groups (BNNT-CC-H).
To make high performance coatings, thermal stability is of great interest. Typically, an inert atmosphere is used to characterize thermal stability; however, air is a better indication of the material being used in real world applications. Polyarylene (PA) was chosen due to its good processability, high onset of thermal degradation, and high char yield. The monomers for synthesizing polyarylene are 1,4-diethynylbenzene and bistetracyclone. Bistetracyclone was synthesized from 1,4-bisbenzil and 1,3-diphenylacetone, and then reacted with freshly sublimed 1,4-diethynylbenzene using microwave-assisted polymerization to afford high molecular weight ($M_w = 500$ kg/mol) material (Scheme 1).\textsuperscript{260} Thermal gravimetric analysis was used to estimate thermal stability under an atmosphere of air. Pure BNNT lost approximately 7% up to 800 °C and then began oxidizing to increase its mass by approximately 20% at 1000 °C (Figure 48). Pure polyarylene had an onset of thermal degradation ($T_d$) of 550 °C and a char yield at 1000 °C of 0% (Figure 49). When merely blending aromatic polymers with BNNT there is a known π-π interaction.\textsuperscript{248} Polyarylene is solely an aromatic polymer so preliminary studies involved blending studies with polyarylene and BNNT. BNNT was first dispersed in a co-solvent comprised of tetrahydrofuran and N,N’-dimethylacetamide in a 50:50 ratio. This combination was chosen as DMAc is a good solvent for BNNT and THF is a good solvent for polyarylene. Polyarylene (1 wt%) was prepared by dissolving 0.1 g polymer in 10 mL DMAc:THF (50:50), stirring for one week, and filtering through a 0.2-μm syringe filter. BNNT (5 mg) was added to 0.5 mL of 1 wt% polyarylene solution to afford 1 wt% BNNT in 1 wt% PA in DMAc:THF (50:50). The combined mixture was sonicated for 30-60 min to ensure proper mixing. If long sonication times were extended (e.g., 24 hrs to a week), damage to the polymer appeared to occur as observed by immediate mass loss in the TGA (Figure 50). After short sonication times and stirring (which do not seem to affect stability) the mixture was drop cast on a glass petri dish and slowly evaporated.
A thick film (~0.5–1 µm) with obvious white BNNT aggregates was dried in a vacuum oven at 75 °C for 24-48 hrs, scratched with a razor blade to increase surface area, and then dried for a week. The thermal stability of the PA-BNNT nanocomposite sample combined properties of both materials: an onset of thermal degradation of approximately 600-650 °C with 30% weight loss, and then an oxidation mass increase up to almost 120% at 1000 °C (Figure 51). Transmission electron microscopy (TEM) images indicate good π-π interactions between polyarylene and BNNTs as indicated by no free BNNTs (Figure 52). Future work will study this particular nanocomposite in more depth and will include expanded studies into a larger range of functionalized BNNTs.
Figure 52. TGA and DTA results for 1 wt% BNNT in polyarylene nanocomposite sample (1 wt% PA-BNNT); bath sonication for 1 hr; RT to 1000 °C; 10 °C/min; air.
Figure 53. TEM image of the BNNTs and polyarylene nanocomposites.
6.3 Conclusions

Polyarylene-BNNT nanocomposites were prepared and demonstrated excellent thermo-oxidative stability due to π-π interactions. BNNTs were successfully functionalized with ethynyl groups using a hypervalent iodine reagent. These new acetylene-functionalized BNNTs can be polymer grafted from the BNNT surface, polymer end-capped with BNNT, or polymerized with BNNT in the polymer repeat unit (e.g., Glaser coupling, Diels–Alder). Also, acetylene-functionalized BNNTs will allow for adding a variety of functional groups via Diels–Alder reactions, click chemistry, or redox adducts to increase the solubility of the BNNTs.

6.4 Experimental

General. All solvents, starting materials, and reagents were purchased from Alfa Aesar, Fisher Scientific, Sigma-Aldrich, TCI America, or VWR as reagent grade and used as received, unless otherwise mentioned. Reactions were carried out under an argon atmosphere, unless otherwise noted. All glassware was oven-dried prior to use and cooled in a desiccator. Boron nitride nanotubes (BNNTs) were purchased from BNNT.com. 1-[(Triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(1H)-one was purchased from TCI. HPLC-grade tetrahydrofuran (THF) and N-methyl-2-pyrrolidone (NMP) were dried and deoxygenated by passage through a Pure-Solv solvent system equipped with Cu/Al columns from Innovative Technologies. Anhydrous nitrobenzene was purchased from EMD Millipore. Anhydrous N,N’-dimethylacetamide (DMAc) was purchased from EMD Millipore. Ethanol was dried using magnesium turning, refluxed with iodine crystals for a few hours, distilled, and then stored over 4 Å molecular sieves under argon.
**Instrumentation.** All $^1$H and $^{13}$C NMR spectra were obtained under ambient conditions using a JEOL ECA 500 MHz instrument, and chemical shifts were reported in parts per million (δ ppm). Proton ($^1$H) and carbon ($^{13}$C) NMR spectra were referenced using the residual solvent peak for CHCl$_3$ (δ = 7.26 ppm) and the center of the multiplet peak for CDCl$_3$ (δ = 77.16 ppm), respectively. ATR–FTIR analysis was performed on a Thermo Nicolet FTIR Spectrometer iS10 with a diamond ATR crystal (Spetra-Tech) using neat samples with 16 scans and 4 cm$^{-1}$ resolution. Molecular weights and molecular weight dispersities ($M_w/M_n$) were determined by gel permeation chromatography (GPC) on a Tosoh EcoSEC system equipped with a series of 4 columns (TSK gel guard Super HZ-L, Super HZM-M, Super HZM-N, and Super HZ2000) at 40 °C, and using refractive index detector. HPLC-grade tetrahydrofuran was used as the eluent at a flow rate of 0.35 mL/min. The GPC calibration was based on linear polystyrene (PS) standards. Polymer samples were dissolved in THF (1 mg/mL) and filtered through a 0.2-µm PTFE syringe filter before injection. Transmission electron microscopy (TEM) was used to visualize boron nitride nanotubes (BNNTs) and polyarylene-BNNT nanocomposite samples using a JEM-2100F Analytical TEM (JEOL). Samples were drop cast on TEM support grid films, carbon type-B with 200 mesh copper (Prod. No. 01810, Ted Pella). The onset of thermal degradation temperature ($T_d$) was obtained from thermal gravimetric analysis (TGA) using a TG209F3 (NETZSCH) at a heating rate of 10 °C/min under a N$_2$ or air atmosphere, and typical sample sizes of approximately 5-10 mg. The glass transition temperature ($T_g$) was determined from differential scanning calorimetry (DSC) using a DSC 214 Polyma (NETZSCH) at a heating rate of 10 °C/min under a nitrogen atmosphere, and sample sizes were approximately 5-10 mg. Each sample was heated and cooled through three cycles, and the third heating was used to calculate the $T_g$. Data were processed using Origin Pro 2019.
Polyarylene was synthesized via microwave-assisted polymerization of a Diels–Alder step-growth addition from bistetracyclone and 1,4-diethynylbenzene (Scheme S1). Boron nitride nanotubes (BNNTs) were used as received from BNNT.com and appeared as a white powder. BNNT-functionalization was carried out using 1-[(triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(1H)-one in anhydrous N,N′-dimethylacetamide (DMAc). Deprotection was carried out using tetrabutylammonium fluoride (TBAF, 1 M in tetrahydrofuran). Nanocomposite samples were prepared using drop cast and spin cast methods. Anhydrous tetrahydrofuran (THF) and anhydrous N-methyl-2-pyrrolidone (NMP) (50:50) were filtered through a 0.2-µm PTFE syringe filter, degassed with argon, and used for all studies. A stock polyarylene solution (1 wt%) was prepared by dissolving 100 mg polymer in 10 mL solvent mixture. A control BNNT solution (1 wt%) was prepared by dispersing 5 mg BNNT in 0.5 mL solvent mixture. Two different nanocomposite solutions were prepared: 1 wt% consisted of 5 mg BNNT dispersed in 0.5 mL 1 wt% polyarylene solution; 0.5 wt% consisted of 2.5 mg BNNT dispersed in 0.5 mL 1 wt% polyarylene solution. All the samples were exposed to bath sonication times of 1 hr, 24 hrs, or 1 week. All the samples were stirred using a small stir bar at medium stir speed for 30-60 min. The samples were passed through a cotton swab in a glass pipette before drop and spin cast deposition. TEM grids were prepared using the same drop cast method on a TEM grid. All samples were dried in a desiccator for 24 hrs.

1,4-Diethynylbenzene.

1,4-Diethynylbenzene was purchased from Sigma-Aldrich. To purify the compound, the solid was sublimed at 60 °C (2-3 Torr) before use to afford a crystalline white solid.
1,4-Bis(tetraphenylcyclopentadienonyl)benzene (Bistetracyclone)\textsuperscript{175,176}

1,4-Bis(tetraphenylcyclopentadienonyl)benzene was prepared from the condensation of 2,2-(1,4-phenylene)bis(1-phenylethane-1,2-dione) with 1,3-diphenylacetone. To a 500 mL two-necked, round-bottomed flask equipped with a condenser, a stir bar and a septum, containing 275 mL of freshly distilled ethanol was added 1,3-diphenylacetone (12.3 g, 58.4 mmol, 2.1 eq), and 1,4-bisbenzil (10.0 g, 29.2 mmol, 1 eq). The solution was then refluxed for one hour. KOH (3.3 g, 58.4 mmol, 2.0 eq) was dissolved in 10 mL ethanol and added drop-wise to the refluxed solution. The solution was refluxed for 1-2 hrs, and then the solution was cooled at 0 °C overnight. The solution was filtered and dried. The precipitate was dissolved in boiling DCM, and then crystallized affording purple needle-like solids at 0 °C. (17.1 g, 85%) \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 6.78 (s), 6.92 (d, \(J = 7.06\) Hz, 4 H), 7.19-7.30 (m, 26 H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) 200.60, 154.93, 154.66, 134.11, 133.50, 130.65, 130.59, 129.77, 129.51, 129.05, 128.53, 128.12, 128.07.

Polyarylene (microwave-assisted polymerization) (P1).

1,4-Diethynylbenzene (9.1 mg, 72.4 µmol) and bistetracyclone (50.0 mg, 72.4 µmol) were carefully added to a 10-mL microwave vessel with stir bar and the sides were rinsed down with anhydrous nitrobenzene (0.4 mL). The vial was covered with a septum, freeze/pump/thawed, and purged with argon three times. Then the septum was removed, and the microwave cap was quickly added. The vessel was carefully inserted into the CEM Discovery microwave reactor trying to keep solids under solvent. The following parameters were set: method = Standard, stir speed = High, pressure limit = 300 psi, power = 300 W, temperature 180 °C, and time = 2 hr. After the
desired time period the polymer solution was viscous orange. The crude polymer was precipitated by added slowly to stirring MeOH (200 mL), filtered and dried to afford a tan/off-white solid product (40 mg, 73%). Soluble in CHCl₃, THF, toluene, and cyclohexanone. ¹H NMR (500 MHz, CDCl₃): 7.6–6.1 (m, 40 H); ATR–FTIR (neat): 1600, 1496, 1430, 1441, 1380, 1107, 1073, 1023, 1008, 898, 843, 759, and 696 cm⁻¹; GPC in THF relative to polystyrene, \( M_w = 499 \text{ kg/mol} \) (\( M_w/M_n = 2.76 \)).

Scheme 18. The reaction of 1,4-bisbenzil and 1,3-diphenylacetone under basic conditions affords bistetrayclone. The reaction of bistetrayclone and 1,4-diethynylbenzene under microwave conditions affords high molecular weight polyarylene.
BNNT-CC-TIPS.

Pure white powder boron nitride nanotubes (BNNT, 5.0 mg, 201.4 µmol), 1-[(triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(1H)-one (8.6 mg, 20.1 µmol, 10 mol%), and a stir bar were added to a 5-mL test tube covered in aluminium foil. Anhydrous N,N’-dimethylacetamide (DMAc, 1.5 mL) was added rinsing down the sides of the vial. The test tube was capped with a white rubber septum and secured with copper wire. The mixture was freeze/pump/thawed and de-gassed with argon. The reaction was heated to 50 ºC for 1 hr under argon. The mixture was cooled to room temperature and evaporated under reduced pressure. The fluffy white solid was collected via filtration, washed with DI water, and acetone. The protected product was dried in a vacuum oven at 75 ºC overnight. $^1$H NMR (500 MHz, CDCl$_3$): δ 1.26–1.13 (21H); ATR–FTIR (neat): ν 2942, 2890, 2863, 1620, 1340, 1012, 882, 798, 674 cm$^{-1}$.

BNNT-CC-H.

The protected product, BNNT-CC-TIPS, was added to a small beaker. Tetrabutylammonium fluoride (TBAF, 1 M in tetrahydrofuran (THF), 3 mL) was added to the beaker with a stir bar. The mixture immediately turned dark brown, and was stirred at room temperature for 60 min. The solvent was evaporated under reduced pressure. The residual brown solid was added to a beaker with DI water (50 mL) and a stir bar. The mixture was stirred at room temperature for 1 hr. The brown solid product was collected via filtration, washed with DI water and acetone, and then dried in a vacuum oven at 75 ºC overnight affording 6.3 mg (63% recovery). $^1$H NMR (500 MHz, CDCl$_3$): δ 2.84 (1H); ATR–FTIR (neat): ν 3296, 2008, 1710, 1337, 788 cm$^{-1}$.
Scheme 17. Pure boron nitride nanotube (BNNT) was functionalized using hypervalent iodine, 1-[(triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(1H)-one, at 50 °C in anhydrous DMAc for 1 hr. Deprotection was accomplished with TBAF (1 M in THF) at room temperature for 1 hr affording the acetylene-functionalized BNNT product.
Figure 49. Thermal gravimetric analysis (TGA) result of pure BNNT sample; RT to 1000 °C; 10 °C/min; air.
Figure 50. Thermal gravimetric analysis (TGA) result of pure polyarylene sample; RT to 1000 °C; 10 °C/min; air.
Figure 51. Thermal gravimetric analysis (TGA) result of 5 wt% polyarylene-BNNT sample after bath sonication for 24 hr; RT to 1000 °C; 10 °C/min; air.
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