Segmented Aromatic Polymers Containing Thermally Reversible Linkages

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**Segmented Aromatic Polymers Containing Thermally Reversible Linkages**

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**Abstract**

This dissertation describes a general synthetic platform for segmented polymers that have main-chain reversible linkages based on cyclopentadiene-maleimide Diels-Alder chemistry.

Research in the area of thermally reversible (self-healing) polymers has been an ever-expanding area of interest in the current scientific literature. However, most of the emphasis has been on systems containing furan-maleimide linkages. While inexpensive and synthetically accessible, furan chemistry is mostly limited to crosslinked and hyperbranched architectures due to its relatively weak binding with maleimides at suitable propagation temperatures.

Following a general review of the literature in this area (Chapter 1) the first stage of our research (Chapter 2) entails the synthesis of 2-substituted hydroquinones, which are needed as monomers in the later stages. The novelty of our hydroquinone synthesis stems from the use of allylic and other alkenyl ethers as the source of the ring substituent, and from the utilization of catalytic hydroboration to improve atom-efficiency. We showed that hydroquinones with widely varying functionality can be prepared efficiently by our method; these findings were published in the journal *Tetrahedron* in 2018.

The second stage (Chapter 3) involves the use of the new hydroquinones in step-growth syntheses of hydroquinone-terminated telechelic and chain-extension of these telomers via Diels-Alder chemistry to form segmented polymers having thermally reversible linkages. The novelty of our approach rests with the use of cyclopentadiene-maleimide chemistry for the linkages, while the overall physical properties such as the glass transition temperature were established by using well-defined aromatic polymers – poly(ether ether ketones) or PEEK and poly(aryl ether sulfones).
or PAES – as segments. This approach represents an important departure from earlier work in our group in which reversible linkages were present in every repeat unit of a step-growth Diels-Alder polymer that showed thermal reversibility in solution but not in the bulk, owing to glass transition temperatures that were too high. Using scratch-healing and mechanical (tensile) tests, we show that our new segmented polymers exhibit self-healing characteristics that are competitive with or superior to previously reported systems based on different Diels-Alder chemistry.

The third stage (Chapter 4) aims to explore new application areas for some of the more novel functionalized hydroquinones reported in Chapter 2. First we developed an efficient synthesis of a PAES derivative bearing 5-phenoxypentyl groups on the hydroquinone moiety. Then we showed that the 5-phenoxyl group can be cleanly cleaved, post-polymerization, to afford a PAES having 5-bromopentyl substituents. The promise of our method rests with the potential of the pendant electrophiles to undergo reactions with nucleophilic reagents to post-modify these polymers further. As proof of concept, we showed that substitution of the pendant bromides with furfuryloxy groups enabled thermally reversible crosslinking with a bis-maleimide reagent to form a polymeric material that demonstrates partial scratch healing. Finally we are exploring the synthesis of new ion-containing polymers by substituting the pendant bromides with tertiary amines.
Segmented Aromatic Polymers Containing Thermally Reversible Linkages

Kevin Joseph Kaurich

General Audience Abstract

This dissertation describes a new synthetic approach to polymeric materials that can heal themselves (for example, repair small cracks that may have formed due to stress or aging) simply by heating the damaged area. Our approach uses a thermally reversible chemical reaction (called the Diels-Alder reaction) to connect several shorter polymer segments into longer chains. Upon heating, the segments can come apart, diffuse into and through the damaged area, and then rejoin. The first chapter is a review of background in the published literature as well as previous not-yet-published work in our laboratory. The second chapter describes the creation of new building-block molecules (monomers) that will help control the temperature range necessary to induce self-healing after incorporation into the polymer segments. The third chapter details the process of forming the segments, the incorporation of self-healing functionalities on the ends of the segments, the joining of the segments into longer polymeric chains, and the testing of all of the physical properties of these new materials, including their self-healing capabilities. The fourth chapter represents a preliminary study of a new method of preparing ion-containing polymers. The latter materials have potential use in various membrane technologies including fuel cell devices for the harnessing of renewable energy.
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# Table of Contents

Abstract .......................................................................................................................... ii

General Audience Abstract ......................................................................................... iv

Acknowledgements ........................................................................................................ v

Table of Contents ......................................................................................................... vi

Common Abbreviations ............................................................................................... vii

Chapter 1 Introduction to Self-Healing Chemistry in Macromolecular Systems ........... 1

Chapter 2 Synthesis of 2-substituted hydroquinone derivatives from 1,4-benzoquinone and allyl ethers ........................................................................................................... 23

Chapter 3 Synthesis and Characterization of Linear Segmented Aromatic Polymers Containing Thermally Reversible Linkages ........................................................................... 40

Chapter 4 Rapid, Selective Introduction of Electrophilic Side-Groups in Poly(aryl ether sulfone)s .............................................................................................................................. 65

Chapter 5 Overall Conclusions and Future Work ........................................................... 91

Appendix A Supporting Information for: Synthesis of 2-substituted hydroquinone derivatives from 1,4-benzoquinone and allyl ethers ........................................................................ 92

Appendix B Supporting Information for: Synthesis and Characterization of Linear Segmented Aromatic Polymers Containing Thermally Reversible Linkages .................... 119

Appendix C Supporting Information for: Rapid, Selective Introduction of Electrophilic Side-Groups in Poly(aryl ether sulfone)s ............................................................................. 188

References ..................................................................................................................... 205
**Common Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>DA</td>
<td>Diels-Alder</td>
</tr>
<tr>
<td>RDA</td>
<td>Retro-Diels-Alder</td>
</tr>
<tr>
<td>CPD</td>
<td>Cyclopentadiene</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methylpyrrolidone</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal Gravimetric Analysis</td>
</tr>
<tr>
<td>SEC</td>
<td>Size Exclusion Chromatography</td>
</tr>
<tr>
<td>$DP_n$</td>
<td>Degrees of Polymerization</td>
</tr>
<tr>
<td>PEEK</td>
<td>Poly(ether ether ketone)</td>
</tr>
<tr>
<td>PAES</td>
<td>Poly(aryl ether sulfone)</td>
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Chapter 1  Introduction to Self-Healing Chemistry in Macromolecular Systems

The everyday use of polymeric materials makes them susceptible to damage from chemical, mechanical, and thermal stresses. Damage generally begins with the formation of microcracks in the polymer matrix, which upon further stress lead eventually to the failure of the material. Repairing polymeric material objects via welding, patching, or splicing is typically ineffective.¹ The most obvious alternative, of course, is replacement of the failed item. The less obvious alternative is to impart self-healing characteristics into the polymer. Considerable research has been applied to this problem, because self-healing behavior often causes significant, offsetting losses in the areas of cost and initial mechanical performance of the polymer.

When considering materials science in a broad context, the ability of biological systems to undergo self-healing is enviable indeed.² When damage occurs in a biological system, natural processes act to close the crack and prevent further crack propagation, thus extending the life of the tissue – and the entire organism.³ As the science of self-healing materials has developed, however, needless to say it has moved very far from its biomimetic origins.

Self-healing chemistry can be divided into two distinct approaches: “Extrinsic” self-healing implies the introduction of an additional material – an adhesive, or a catalyst, or some other agent that can be released upon demand to heal some form of damage. The trick is to engineer a good mechanism for the release of the agent. White and co-workers⁴ created an epoxy having Grubbs-type ROMP catalyst molecules and microencapsulated dicyclopentadiene dispersed throughout the resin. Strain on the material (i.e., cracking) forces the capsules open and the monomer spills out, diffuses into the matrix, and heals the material. The advantage of extrinsic self-healing is that an external stimulus is not required to initiate or induce the healing process. The main drawback is that healing might be limited to one or two cycles at the same damage site.
The other type of self-healing is called “intrinsic” self-healing. This approach is based on incorporating co-reactive moieties into the polymer structure itself instead of dispersing them in the polymer matrix. The disadvantage of intrinsic self-healing is that it requires an external stimulus (e.g., heat, light) to induce healing, and it is not always easy for the stimulus to penetrate inside a material. In this respect, heating is more generally applicable.

The Diels-Alder (DA) reaction is the most thoroughly studied and commonly employed reaction in intrinsic self-healing chemistry. As a concerted cycloaddition, the DA reaction is entirely thermal, requires no catalyst (although it can be catalyzed), and involves no by-products. The most important aspect of this reaction, with regards to self-healing, is that the reaction is thermally reversible. The most typical reaction used in Diels-Alder self-healing chemistry is the furan-maleimide reaction (Scheme 1-1).

Scheme 1-1. Furan and maleimide: A Diels-Alder reaction used in self-healing chemistry.

A key feature of any DA chemistry for self-healing is the influence of temperature on the equilibrium constant of the reaction. As an addition reaction, the overall reaction entropy is strongly negative, so lower temperatures favor the adduct, whereas higher temperatures favor the reactants. Throughout the literature of self-healing chemistries, the effects of temperature are often described as a “window.” The low-temperature end of the window represents the “onset” of adduct formation, while the upper end of the window represents the “onset” of the retrograde process. All of this language is used very loosely throughout the literature without rigorous definitions.
Arrhenius theory does not allow for reactions to have “onset temperatures,” but rather the rate of a reaction is a smooth (exponential) function of temperature.

As we will describe below, our approach to self-healing polymers uses the DA reaction as the means of propagation of the polymer. Therefore, for us the practical low-temperature end of the “window” corresponds to a useful propagation temperature. The high-temperature end of the window corresponds to RDA, or reversion to the diene and dienophile. In particular, the “onset” of RDA (the high end of the window) is really just the temperature at which there is some appreciable formation of diene and dienophile components sufficient to realize a self-healing process. Importantly, the “onset” of RDA should not be construed to mean that the diene and dienophile are present in higher concentration than the adduct.

The synthetic challenge of Diels-Alder self-healing chemistry is to incorporate the reactive groups – the diene and the dienophile – into a macromolecular framework. The polymeric architecture employed also needs to consider the particular strengths and limitations of a given chemical system – especially its “temperature window.” The literature of this subject is large, and an exhaustive review of it would not be possible in this space. There are many published reviews already available, and a colleague, Dr. Jeremy Stegall, also reviewed this subject in his doctoral dissertation, and I do not wish to retread the same ground, preferring to emphasize the systems that are most relevant to the development of my own chemistry. As mentioned above, the most commonly-employed system is furan and maleimide. This area will be summarized below before moving on to the chemistry that I intend to use, which will represent an improvement on furan-maleimide chemistry in at least some ways.

One of the pioneering studies on self-healing systems was reported by Wudl. They created a hyperbranched polymer from a diene monomer with four furans and a dienophile monomer with
three maleimide groups (Scheme 1-2). The monomers were dissolved in dichloromethane (in a ratio corresponding to 1:1 furan:maleimide), cast into a mold, and with heating, the solvent was evaporated and polymerization ensued (Scheme 1-2) to afford a transparent solid, effectively a reversible thermoset material. They showed recovery of mechanical properties using fracture toughness testing as follows: A specimen, that was damaged and then healed by treating at 150 °C for several hours, recovered 50% of its original performance under fracture toughness testing (Figure 1-1), and 40% after a second cycle. Only slightly lower recovery (41%) was obtained in another specimen during its first cycle at 120 °C. They noted several reasons for the reduced performance. For example, uniform healing cannot be achieved just by pressing the damaged sample together. They also showed microscope images of crack healing -- surface scratches that re-mended upon heating the sample. Notably though, there are no length scales on the SEM micrographs to assist in quantifying the size of the cracks.

**Scheme 1-2.** The 3M4F hyperbranched, reversible polymer prepared by Wudl and coworkers.\textsuperscript{11}
Follow-up work (published in *The Journal of Chemical Education* by Weizman et al.) illustrate a more typical approach in this field. Like Wudl, they prepared a hyperbranched polymer using a similar tetrafunctional furan along with a commercially available difunctional maleimide (Figure 1-2). They did not perform mechanical recovery tests on their polymer; however, they carried out a more comprehensive study of the visualization of healing using optical microscopy. Instead of forming a bulk object, they solution-cast a film of the monomers on a glass plate, evaporated the solvent, and then heated the residue for several hours at 120 °C to obtain a robust film. The film was then slit with a scalpel and an image was taken. Three more images were then taken at time intervals of 15 minutes, 30 minutes, and 2 h of heating at 120 °C in an oven (Figure 1-3).
Figure 1-2. Furan and maleimide monomers used by Weizman to prepare self-healing films.\textsuperscript{12}

Figure 1-3. Optical micrographs of thermally self-healing, hyperbranched furan-maleimide polymer films prepared by Weizman et al. Cut film was heated for different time intervals at 120 °C. (a) t = 0 (b) t = 15 min (c) t = 30 min (d) t = 2 h.\textsuperscript{12}

Another approach to incorporation of DA linkages within polymeric networks starts with the adduct already formed within a reactive monomer. For example, Tian and co-workers created a tetrafunctional epoxy monomer with a DA linkage built into its core (Scheme 1-3).\textsuperscript{13} Curing with an aliphatic anhydride gave an epoxy resin. While they tested the mechanical properties of the initial Diels-Alder network, they did not re-test the mechanical properties after a healing cycle. Crack-healing, demonstrated the usual way with optical microscopy, is shown in Figure 1-4. Tian’s approach to thermal crack-healing is more advanced than that of his predecessors. After an initial high-temperature interval (100–125 °C for 20 min), presumably to induce some RDA, they
transferred the sample to an 80 °C oven, presumably to anneal the sample and allow DA healing reactions to occur. Importantly, they also showed that the initial thermal treatment at 125 °C was the most effective, whereas initial treatment at 100 °C afforded essentially no healing. They surmised that this difference owes to the fact that the initial RDA reactions cannot occur much below the glass transition temperature of the material (\(T_g = 128\) °C), where there is not enough molecular motion to enable the reactive groups to collide. This effect is evident by the visual difference in the crack healing behavior, where crack closure is realized for the sample treated above RDA (> 120 °C) and not for the sample treated well below RDA (100 °C).

**Scheme 1-3.** Diels-Alder functionalization of epoxy resin for curing by Tian.\(^{13}\)
Figure 1-4. Initial crack healing at (a) 100 °C (b) 119 °C (c) 125 °C for 20 min followed by heating at 80 °C for (1) 0 h (2) 12 h (3) 72 h reported by Tian.\textsuperscript{13}

Kotteritzsch and co-workers devised a synthesis of a single-component (multifunctional) polymer with built-in furan-maleimide self-healing chemistry.\textsuperscript{14} His design involved a block copolymer prepared using ATRP (Scheme 1-4), which enabled the variation of block lengths. During polymerization ($T_p = 70$–90 °C) the maleimide monomer was well-protected as a furan adduct. After polymerization, the resin was solvent cast and then cured for 5 h at 160 °C. At this temperature, the furan was released from the maleimide monomer and evaporated, and the authors
report the formation of a “very hard film.” Note that a temperature of 160 °C could be sufficient to induce free-radical self-polymerization of the maleimide functionalities or generate an alternating furan/maleimide co-polymer, especially in a film with a high surface area. Self-healing studies used AFM and SEM (see below). Scratches of 100 microns in width were made with a knife, and healing was observed by SEM while annealing at 160 °C. This temperature was chosen to match DSC endotherms that the authors assigned to RDA events. Loss of the maleimide-protecting-group furan moiety was also observed in the DSC, at temperatures that ranged quite widely (100–200 °C) and didn’t correlate well to the T_g of the polymers. In other literature the RDA “onset” temperature for furan-maleimide systems is typically around 120 °C, but many reports indicate self-healing tests in the range of 150 °C, which obviously accelerates the RDA reaction. We note also that the T_g of their successful polymers (P5 and P7) are much lower in temperature (50 °C and –16 °C) compared to the other block co-polymers. Examples having T_g > 150 °C displayed no signs of healing behavior. While they studied initial mechanical properties for one of the copolymers, they did not report mechanical properties after any healing cycles. In self-healing tests, the authors found that the polymer with a longer methacrylate backbone (P7) was able to heal scratches on the millimeter range compared to P5, which was limited to healing on the nanometer range. They attributed the increase in the healing range to the more flexible co-monomer which allows for a better ability of the polymer to reflow into the scratch. They also found that healing at a higher temperature (160 °C vs. 110 °C) allowed for a faster and more complete healing of the scratched surface (Figure 1-5 and Figure 1-6).
Scheme 1-4  Free radical polymerization resulting in a terblock copolymer containing furan-maleimide functionality as reported by Kotteritzsch.\textsuperscript{14}

Figure 1-5.  Self-healing behavior of a terblock copolymer containing furan-maleimide functionality as reported by Kotteritzsch. SEM images of (a) initial film (b) scratch before healing (c) heating at 160 °C for 1 min (d) heating at 160 °C for 3 min.\textsuperscript{14}
Figure 1-6. Scratch-healing tests conducted on a terblock copolymer containing furan-maleimide functionality as reported by Kotteritzsch. SEM image of (a) scratch before healing; (b) after 30 min at 110 °C; (c) after 1 h at 110 °C; (d) after 4 h at 110 °C. The temperature is too low to induce thermal healing in these polymers.\textsuperscript{14}

So far, all of the examples involving furan-maleimide DA reactions have involved cross-linked or hyperbranched polymeric architectures. One might imagine constructing a linear polymer by step-growth polymerization of simple bis-furan and bis-maleimide monomers. However, a main issue with furan and maleimide is that the DA/RDA temperature “window” is relatively narrow. In other words, the equilibrium constant for adduct formation at a temperature high enough to realize rapid propagation by DA is actually very low. (In as-yet unpublished work, co-workers in our laboratory have studied these reactions using NMR spectroscopy and found that the formation of an adduct from furfuryl alcohol and N-4-fluorophenylmaleimide exhibits a binding constant of about 50.) In order to reach a high molecular weight in a linear polymer, using a thermally reversible propagation reaction, one needs a high equilibrium binding constant \textit{at the}
polymerization temperature. As shown in eq 1, molecular weight of a step-growth polymer at unit monomer stoichiometry is limited by the equilibrium constant for adduct formation, also called the equilibrium constant of binding \((K_{eq})\), and the initial monomer concentration. Moreover, development of “polymer properties” such as the ability to form a creaseable film or realize acceptable mechanical strength depends on reaching the critical molecular weight for entanglement. And in systems that contain several aromatic moieties, these molecular weights often need to exceed 20 kDa. For these reasons, examples of linear polymers built on the furan-maleimide platform as a propagation reaction, are quite sparse.

\[
DP_n = \sqrt{(K_{eq})[M]}
\]

(1)

Du and co-workers reported a linear polyurethane containing Diels-Alder linkages that was able to undergo healing (Scheme 1-5).\(^{15}\) Their work actually provides a reasonable model for what I will describe in subsequent chapters using an alternative (perhaps complementary) cyclopentadiene-maleimide platform. Du and co-workers started with hydroxyl-terminated poly(1,4-butylen adipate) (1 kDa) and end-capped it with isocyanates. As a control, they polymerized this polyurethane prepolymer using 1,4-butanediol to obtain a polymer with \(M_n = 18\) kDa. To create a bis-furan segment they reacted their polyurethane prepolymer with furfurylamine and polymerized the resulting bis-furan segment with a typical bis-maleimide, also resulting in a polymer having \(M_n = 18\) kDa (\(DP_n = \text{ca. 8}\)). They characterized the healing capability of their system using both tensile testing and scratch-heal testing. They found that even after two damage and healing cycles their system was able retain 66% of its mechanical properties under tensile testing (Figure 1-7). To demonstrate scratch healing a cut was made on the surface of a film with a surgical blade. The film was then placed on a heating stage under an optical microscope and
heated at 120 °C until all evidence of the crack disappeared. Again, they chose this temperature to align with features in the DSC thermogram assigned to RDA events. They noted that after 1 minute the crack was already showing signs of disappearing and after 3 minutes the crack was completely gone (Figure 1-8). They also used a linear polyurethane without Diels-Alder linkages as a control to demonstrate that the crack healing was actually due to the reversible linkages and not other external factors. It should be pointed out here, though, that these authors do not report any T_g data for their polymers (which is known to affect healing capabilities¹). Other than the endotherm assigned to RDA events at ca. 120 °C, their DSC data does not show any features above –60 °C except in the case of their model polymer which shows a possible T_g at around –40 °C. Thus, when these polymers are “self-healed” at 120 °C, it seems likely that much of this self-healing could be ascribed to bulk flow of the polymer itself. Their model polymer (non-DA-linked) does not exhibit this behavior due to its permanent thermoset nature, arising from the combination of soft-segments and hard-segments.

**Scheme 1-5** Diels-Alder polymerization of furan functionalized polyurethane and bismaleimide to produce a linear, Diels-Alder-linked, segmented polyurethane as reported by Du.¹⁵
Figure 1-7. Tensile results from a linear, Diels-Alder-linked, segmented polyurethane as reported by Du. Comparison of virgin sample (PU-DA0), samples after healing (PU-DA1 and PU-DA2), and control sample having no DA linkages (PU-BDO). PU-DA displays better initial mechanical properties and the ability to recover 80% breaking tensile strength after the 1\textsuperscript{st} heal cycle and 66% breaking tensile strength after the 2\textsuperscript{nd} heal cycle.\textsuperscript{15}

Figure 1-8. Optical micrographs of a linear, segmented polyurethanes as reported by Du. Crack healing is evident in the sample containing furan-maleimide DA linkages (top), but not in the control sample lacking Diels-Alder linkages (bottom).\textsuperscript{15}
Moving away from the furan/maleimide system, Murphy and co-workers explored the use of cyclopentadiene for reversible linkages.\textsuperscript{16} Their monomer is a macrocyclic diester of Thiele’s Acid. This monomer then undergoes RDA/DA (ring-opening) polymerization (Scheme 1-6) to afford a solid polymer of unknown molecular weight (owing to its poor solubility). The new polymer contained Diels-Alder linkages that could undergo thermal remending in the bulk. They characterized the healing properties of the polymer by fracture tests (tensile tests) and SEM. They found their best recovery of mechanical properties was around 46\% of the original performance (Figure 1-9). SEM analysis of a fractured polymer film before and after thermal treatment shows closure of the crack with a scar taking its place (Figure 1-10).

**Scheme 1-6.** Synthesis of bis-CPD-based DA polymer as reported by Murphy and co-workers.\textsuperscript{16}

![Scheme 1-6](image)

**Figure 1-9.** Fracture testing of bis-CPD-based DA polymer as reported by Murphy and co-workers: Initial film sample (blue diamonds), film after the 1\textsuperscript{st} healing cycle (magenta squares), and film after the 2\textsuperscript{nd} healing cycle (yellow triangles).\textsuperscript{16}
Some of the issues pertaining to the use of cyclopentadiene dimerization as a platform for reversible chemistry are evident in the work described above. The polymer resulting from ROP of the cyclic monomer is insoluble, and this feature has been ascribed to the formation of cross-links. Evidently the double bond of the adduct norbornene moiety can react with the diene end group to form significant amounts of polycyclic species. This finding also explains observations on bis-cyclopentadiene polymers that reach back to the work of John Stille in the early 1960s.\textsuperscript{17}

The preceding review shows that there are several possible platforms for Diels-Alder-based self-healing polymers. The furan-maleimide system is the most commonly employed, but it seems best suited to cross-linked or hyperbranched polymers, which do not depend on high conversion in the DA event. However, linear step-growth polymerization is demanding when it comes to reaching high conversion, so there are relatively few instances of polymers that are \textit{propagated} by the DA reaction. Furans also have other limitations such as hydrolytic instability, especially under acidic conditions.\textsuperscript{18}

\textbf{Figure 1-10.} SEM image of crack healing in the bis-CPD-based DA polymer reported by Murphy and co-workers, (a) before thermal treatment (b) after thermal treatment.\textsuperscript{16}
Our research group has focused on developing a *cyclopentadiene-maleimide platform* for reversible DA polymerization with the goal of synthesizing linear polymers having reversible linkages that will exhibit useful physical properties at room temperature, thermal stability (including with respect to RDA) up to a reasonable temperature such as 80 °C, and self-healing properties at higher temperature still (ideally around 120 °C, a temperature chosen, rather arbitrarily, to be in direct competition with the furan-maleimide system). Our “first generation” synthetic plan was to find a bis-maleimide monomer and a bis-cyclopentadiene monomer that would polymerize at a reasonable temperature (say, 60-80 °C) to a high molecular weight (say, 25 kDa) and exhibit RDA reactions, ideally at ca. 120 °C (Scheme 1-7).

**Scheme 1-7.** General Diels-Alder Polymerization of Biscyclopentadienes and Bismaleimides

![General Diels-Alder Polymerization of Biscyclopentadienes and Bismaleimides](image)

This plan encountered two fundamental problems. These were discussed in detail in Jeremy Stegall’s dissertation and will be highlighted only briefly here. One of the key difficulties that we had to overcome at the outset was the tendency for bis-cyclopentadiene monomers to self-polymerize. Almost all monosubstituted cyclopentadienes self-dimerize, which means that one cannot merely attach cyclopentadiene to the ends of a molecular chain and use that as a monomer. Sanghamitra Sen in our group found that disubstituted cyclopentadienes undergo self-dimerization much more reluctantly. For example, in Scheme 1-8, when R = H the compound self-polymerizes slowly at 25 °C and within minutes at 60 °C, whereas when R = CH₃, the compound only starts to polymerize around 120 °C; when R = CMe₃, no reaction whatsoever is observed below 180 °C.
**Scheme 1-8.** Self-polymerization of bis-cyclopentadienes as reported by Sen and co-workers.\(^{20}\)

![Scheme 1-8](image_url)

The other fundamental problem we had to solve was the characteristically high temperature needed for RDA to occur in a cyclopentadiene-maleimide adduct (ordinarily ca. 180 °C). Dr. Jeremy Stegall studied the effects of cyclopentadiene substitution on the RDA “onset” temperatures of several cyclopentadiene-maleimide adducts (Figure 1-11). Dr. Stegall showed that having either a bulky group (CMe\(_3\)) or an electron-withdrawing group (C\(_6\)F\(_5\)) in the *bridgehead* position of the bicyclic adduct destabilizes the adduct, leading to a more facile RDA process (ground state effect). As one can see from Figure 1-11, one additional compounding problem is the tendency for cyclopentadienes to isomerize (tautomerize). Thus, monoalkylated or monoarylated cyclopentadienes are really inseparable mixtures of the 1-substituted and 2-substituted isomers.

![Figure 1-11](image_url)

**Figure 1-11.** Effects of bridgehead substituents on RDA “onset” temperatures as observed by Stegall.

We rationalized that the design of Dr. Sen’s monomer could solve this problem by forcing either the perfluoroaryl or the CMe\(_3\) group to reside at the bridgehead, for all three of the observed
isomers of the cyclopentadiene. Dr. Stegall took up this challenge by preparing a model cyclopentadiene bearing one CMe$_3$ group and one perfluoroaryl group (E = C$_6$F$_4$C$_6$F$_5$), reacting the compound with a model maleimide, characterizing all of the products (five of the six possible isomers were observed), and studying the product ratios observed at several different reaction temperatures (Scheme 1-9).

**Scheme 1-9.** Effects of cyclopentadiene tautomerization on Diels-Alder adduct formation as reported by Stegall (E = perfluoroaryl).

Dr. Stegall then demonstrated that variations of Dr. Sen’s monomer (Scheme 1-8) with R = CHMe$_2$, CMe$_3$, or CMe$_2$Ph (cumyl) polymerized well with several different bis-maleimide monomers at polymerization temperatures within our targeted range (60–80 °C) to high molecular weights (above 25 kDa). The resulting polymers were soluble in chloroform and THF. No self-polymerization of any of the bis-cyclopentadiene monomers was observed. Moreover, Dr. Stegall
found that treatment of the polymers with an excess of the monofunctional maleimide (FMI) resulted in complete disassembly of the polymer with essentially quantitative recovery of the bis-maleimide monomer and the FMI-capped bis-cyclopentadiene monomer. As a model system Dr. Stegall’s results were a great success.

The main drawback of Dr. Stegall’s polymers were the inability to show self-healing in the bulk. While RDA was possible in the bulk under forcing conditions (heating at 250 °C in a tube furnace under vacuum recovered about 50% of the bis-cyclopentadiene monomer), these conditions are not practical for thermal self-healing. Our rationale for these difficulties rests with their glass transition temperatures. Stegall’s glass transition temperatures ($T_g$) were typically 160 °C or higher.21 Because RDA and self-healing require at least some local mobility within the polymer, RDA cannot occur below $T_g$.6 Thus, it is perhaps most accurate to say that Dr. Stegall laid the important groundwork for the chemistry that I will use, but his polymer properties were not in an appropriate range to demonstrate self-healing capabilities.

Based on previous work,19 it was not feasible to modify previous monomers further to bring the $T_g$ down below RDA. Dr. Stegall had already explored most of the parameter space of his monomers within the limits of what could reasonably be synthesized. This conclusion led us to re-think our polymer design more fundamentally. First, if self-healing properties in a linear polymer require chain scission, then we shouldn’t need 20+ linkages per chain, which is about how many were present in Dr. Stegall’s polymers based on his observed $M_n$ values and monomer structures. Second, if most of the polymer chain comprised some type of “known” structure, then we would be able to predict and control the $T_g$ much better. Dr. Stegall’s polymers are composed entirely of DA reactive groups, the properties of which (prior to his work) were entirely unknown.
Moreover, the DA adduct structure is quite rigid, so a polymer containing mostly DA adduct structures will have a high $T_g$.

_We realized that we could solve all of these problems simultaneously by switching to a segmented polymer design._ Ideally we would choose a “garden variety” step growth polymer, with molecular weight and end-group chemistry under synthetic control, and fit the ends with DA reactive groups. This strategy is essentially the same as that of Du and co-workers, except that we arrived at this plan from a different logical direction, namely our need to decrease and tune the polymer $T_g$, whereas Du and co-workers were primarily interested in the compatibility of their polymers with urethane-based paints and coatings. Despite the different reasons, the approaches are strikingly similar. We chose aromatic polymers as the basis for the telechelic segments. We wanted a polymer that would be well-controlled synthetically, thermally stable (so that all thermal events could be ascribed to DA/RDA chemistry), and ideally _phenol-terminated_. The latter constraint (determined in as of yet unpublished work by a co-worker in our laboratory) is intended to facilitate the attachment of our cyclopentadiene (CPD) end groups using nucleophilic aromatic substitution chemistry. Probably telechelic segments terminated with other functional groups might have worked, but we chose phenols for their convenience. This choice led us to hydroquinone-based polymers, especially poly(ether ether ketone) (PEEK) and poly (aryl ether sulfone) (PAES). We had precedent for the substitution chemistry in other work within our group (reported in the dissertation of Charles Carfagna), so we knew the basic chemistry would work.

However, traditional PEEK and PAES have $T_g$’s that are far above the RDA onset temperature ($> 120 \, ^\circ\text{C}$), which as seen above would serve to limit any thermally driven healing capabilities. Rather than search for a completely different polymer platform, we decided to try modifying the $T_g$ through monomer chemistry. One of the easiest solutions is to incorporate side chain
substituents that can effectively manipulate the $T_g$ to our desired temperature range. Small substituents like methyl groups have no real effect on $T_g^{22}$ and bulky groups like tert-butyl and phenyl only serve to increase the $T_g$ (175 °C and 154 °C respectively).$^{23}$ Methyl substituted PEEK can however be brominated to generate a benzylic bromide which can then be converted into many other substituents (Table 1-1).$^{24}$ Of particular note are the methoxymethyl and acetoxy methyl functional groups which display $T_g$’s that are lower than the parent polymer. The introduction of these substituents increases the free volume of the system without impeding backbone rotation (unlike tert-butyl and phenyl) which overall lead to a reduction in the $T_g$. Thus our approach to incorporating self-healing capability in PEEK and PAES will be by incorporating long, flexible side chains on the polymer backbone.

**Table 1-1. Effect of Side Chain Substituent on $T_g$ of poly(arylene ether ketone)$^{24}$**

<table>
<thead>
<tr>
<th>R</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$Br</td>
<td>149</td>
</tr>
<tr>
<td>CH$_2$OCH$_3$</td>
<td>136</td>
</tr>
<tr>
<td>COOCH$_3$</td>
<td>197</td>
</tr>
<tr>
<td>CH$_2$OH</td>
<td>183</td>
</tr>
<tr>
<td>CH$_2$N(C$_2$H$_5$)$_2$Br</td>
<td>178</td>
</tr>
<tr>
<td>CH$_2$N(C$_2$H$_5$)$_2$</td>
<td>166</td>
</tr>
<tr>
<td>CH$_2$OCOCH$_3$</td>
<td>134</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>159</td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>189</td>
</tr>
</tbody>
</table>

Chapter 2 of this dissertation will describe our approach to 2-substituted hydroquinones. Chapter 3 will describe their incorporation into thermally self-healing, DA-linked, segmented aromatic polymers. Chapter 4 will describe post-polymerization modification of phenoxyalkyl-substituted PAES derivatives toward reversible crosslinking and novel ionomers. Chapter 5 will summarize our overall findings and describe our future plans.
Chapter 2. Synthesis of 2-substituted hydroquinone derivatives from 1,4-benzoquinone and allyl ethers

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Foreward. This chapter represents a study published in the journal Tetrahedron and is reproduced here with permission from Elsevier. I performed all of the work reported in this chapter except as follows: Mehdi Ashraf-Khorassani performed the mass spectroscopic analyses; Atlantic Microlab, Inc. (Norcross, GA) performed the microanalyses, and Prof. Paul A. Deck supervised my work.

Graphical Abstract

Abstract

B-Alkylpinacolboranes, derived from rhodium-catalyzed hydroboration of allyl ethers with pinacolborane, react with 1,4-benzoquinone under acidic, oxidizing conditions, to afford, after subsequent hydrogenation, 2-substituted hydroquinones in isolated, purified yields of about 50% based on 1,4-benzoquinone. The product hydroquinones have potential use as precursors to poly(arylene ether) and related aromatic polymers.

Keywords

Hydroboration, hydroquinone, benzoquinone, Wilkinson’s catalyst
2.1. Introduction

Alkylated hydroquinones and benzoquinones are found in nature and can have important cytotoxic and antioxidant activities. Hydroquinones are also important constituents of aromatic polymers such as poly(arylene ether)s and polyesters. Traditional synthetic approaches to alkylated hydroquinones include Friedel Crafts and free-radical alkylations as well as oxidation of substituted phenols. While procedurally simple, these methods often afford low yields or complex mixtures of products.

Trialkylboranes, conveniently generated by alkene hydroboration, can transfer one alkyl group to 1,4-benzoquinone to afford alkylated hydroquinones, usually in the presence of dioxygen. Either primary or secondary alkyl groups may be transferred, and the method tolerates functional groups that are compatible with BH₃ (halogens, esters, ethers, and nitriles). Although overall yields in these reactions are usually high, there are three frustrating complications. First, only one alkyl group from the trialkylborane is transferred, thereby wasting two equivalents of the starting alkene. Second, the borinic acid byproduct (R₂BOH) is difficult to separate from the desired hydroquinone. When R is relatively small (i.e., C₆ or less), the borinic acid can be removed by steam distillation, but with larger R groups, researchers have resorted to derivatizing the hydroquinone to enable a separation. Third, alkene hydroboration with BH₃ (or with BH₃•SMe₂) is not highly regioselective, especially for alkenes having electron-withdrawing substituents near the double bond. Although the initial hydroboration may afford mostly primary borane, the higher migratory aptitude of secondary radicals can lead to significant contamination by the branched alkyl group in the hydroquinone, and then recrystallization is needed to obtain a pure regioisomer.
Recent advances in the preparation of organoboranes have partly alleviated these problems. Using catecholborane instead of BH$_3$ should, in principle, eliminate the problem of wasting two thirds of the alkene.$^{36}$ B-Alkylcatecholboranes derived from various unfunctionalized alkenes will transfer a primary or secondary alkyl group to 1,4-benzoquinone. A recently reported method of preparing B-alkyl catecholboranes uses catecholborane in the presence of $N,N$-dimethylacetamide (DMAC), however this method has about the same regioselectivity for simple terminal alkenes as one would obtain using BH$_3$. Moreover, the optimized conditions for alkyl transfer to 1,4-benzoquinone requires a twofold excess of the B-alkyl catecholborane, ostensibly to outpace the natural tendency of the alkylated hydroquinone product to reduce the 1,4-benzoquinone reactant in situ. In this case the product hydroquinone must be separated from by-product catechol derivatives, likely including catecholboronic acid, $o$-$C_6H_4O_2BOH$. In preliminary experiments we found these kinds of separations difficult and inefficient.

The challenge of product isolation in these procedures is not to be underestimated. Renaud developed a tetrahydroisoquinoline-derived catecholborane that facilitated removal of the byproducts by acidic aqueous extraction upon workup; however, the needed catechol derivative is not commercially available and the overall procedure is complicated.$^{38}$ Cole and co-workers generated trialkylboranes having the formula RBMe$_2$, which transfer primary and secondary alkyl groups to benzoquinone in strong preference to the methyl groups.$^{39}$ However, preparing those trialkylboranes requires hydroboration with HBCl$_2$ (generated in situ from HSiEt$_3$ and BCl$_3$) followed by substitution of the BCl$_2$ moiety with MeMgBr, a pathway that excludes most other functional groups because of reagent incompatibilities.$^{40}$ In another recent advance, alkyl- and arylboronic acids were combined with 1,4-benzoquinone to give 2-substituted 1,4-benzoquinones.
in moderate to high yields.\textsuperscript{41} Boronic acids are not always the most conveniently prepared synthetic intermediates.

In the course of our ongoing work on functionalized aromatic polymers we wanted to develop a general synthetic method for monosubstituted hydroquinones that would start with selective anti-Markovnikov hydroboration of an allyl ether and then transfer the 3-alkoxypropyl group to 1,4-benzoquinone. Because allyl ethers are readily prepared by Williamson synthesis, such a method would give us rapid access to a wide range of functional 2-substituted hydroquinone derivatives.

Preliminary efforts using BH$_3$•SMe$_2$ and catecholborane, with allyl ethyl ether as the substrate, afforded poor yields of the desired 2-(3-ethoxypropyl)hydroquinone. We then thought to use pinacolborane, which is not only more stable than catecholborane,\textsuperscript{42} but might also afford better regioselectivity because of its greater steric bulk and lower overall electrophilicity. However, the utility of $B$-alkylpinacolboranes in radical-transfer processes has met with mixed results. In particular, alkyl transfer to 1,4-benzoquinone was shown to be quite sluggish, even in the presence of K$_2$S$_2$O$_8$ and AgNO$_3$.\textsuperscript{41} On the other hand, a related fluorination with SelectFluor\textsuperscript{TM} showed better efficiency in the presence of CF$_3$COOH (TFA). We reasoned that TFA might facilitate the desired alkyl transfer to 1,4-benzoquinone as well. Such a procedure under oxidizing conditions (K$_2$S$_2$O$_8$, AgNO$_3$, and TFA) would ideally give an intermediate 2-substituted 1,4-benzoquinone, which we could then reduce to the corresponding hydroquinone derivative by catalytic hydrogenation, possibly with minimal workup between steps, thereby approaching one-pot efficiency. We now describe our efforts to explore these possibilities.
2.2. Results and Discussion

Our efforts in the area of functionalized aromatic polymers have led us to develop a general synthetic approach to monosubstituted hydroquinones starting with anti-Markovnikov hydroboration of an allyl ether as the origin of the substituent that is then transferred from boron to 1,4-benzoquinone in a free-radical process. Like others before us, we started with BH$_3$·SMe$_2$ because of its simplicity and low cost. Even though we knew we would lose two thirds of our alkene to byproducts, we wanted to ensure that we could reproduce the results of others with our own hands. Table 2-1 shows the results of these preliminary studies. Yields obtained with 1-hexene and 1-octene (1a and 1b, entries 1 and 2, respectively) are for purified products and are consistent with crude yields previously reported.$^{35}$ Cyclooctene (1c, entry 3) gives a higher yield, possibly due to the enhanced migratory aptitude of the secondary alkyl group.$^{34}$

**Table 2-1. Yields of hydroquinones derived from trialkylboranes**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>R</th>
<th>yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-hexene (1a)</td>
<td>(CH$_2$)$_3$CH$_3$</td>
<td>2a 72</td>
</tr>
<tr>
<td>2</td>
<td>1-octene (1b)</td>
<td>(CH$_2$)$_7$CH$_3$</td>
<td>2b 70</td>
</tr>
<tr>
<td>3</td>
<td>cyclooctene (1c)</td>
<td>cyclo-C$<em>8$H$</em>{15}$</td>
<td>2c 88</td>
</tr>
<tr>
<td>4</td>
<td>allyl ethyl ether (1d)</td>
<td>(CH$_2$)$_3$OCH$_2$CH$_3$</td>
<td>2d 33</td>
</tr>
<tr>
<td>5</td>
<td>allyl 2,2,2-trifluoroethyl ether (1e)</td>
<td>(CH$_2$)$_3$OCH$_2$CF$_3$</td>
<td>2e 30</td>
</tr>
<tr>
<td>6</td>
<td>allyl 2,2,3,3,3-pentafluoropropyl ether (1f)</td>
<td>(CH$_2$)$_3$OCH$_2$CF$_3$CF$_3$</td>
<td>2f 29</td>
</tr>
</tbody>
</table>

$^a$Isolated yields based on 1,4-benzoquinone.
Allyl ethers however, gave disappointing results (1d-f, entries 4-6). While a yield of 30% might seem tolerable, one must recall that this yield is based on 1,4-benzoquinone, whereas the allyl ethers are the more precious of the two main reactants. Yields based on the allyl ethers are only about one third of the yields based on benzoquinone because only one alkyl group of the trialkylborane intermediate is transferred.

One factor in the low yields obtained for 2d-f could be the low regioselectivity for hydroboration of allyl ethers noted by Brown and co-workers. Rather than question or repeat their work in this area, we moved on to different hydroboration reagents. Even if we had obtained better yields for 2d-f, the necessity of removing the byproduct borinic acid (R2BOH) by steam distillation would tend to limit the range of usable allyl ethers. Moreover there is still the issue of wasting two-thirds of the alkene reactant.

We next explored monohydroborating agents and their use in generating substituted hydroquinones. As noted above, haloboranes such as HBCl2 were ruled out entirely because they form strong complexes with ethers. Table 2-2 shows the results of our studies using catecholborane and Wilkinson’s catalyst, (Ph3P)3RhCl, to effect hydroboration of four alkene substrates, followed by reductive alkyl transfer from the alkylboron intermediate to 1,4-benzoquinone. Yields are somewhat improved relative to those shown in Table 2-1, but “atom economy” with respect to the alkene is still low (2 equiv of B-alkylcatecholborane is needed), and the chromatographic separation of the product from catecholboronic acid and other by-products required large volumes of eluting solvents. Importantly, using one of our most urgently desired substrates, allyl phenyl ether (1g), the initial hydroboration was extremely sluggish and unpredictable, and in four attempts with the typical adjustments to conditions and isolation procedures, we obtained no yield of the corresponding 3-phenoxypropyl-1,4-hydroquinone (2g)
whatsoever. Analysis of the reaction mixture by NMR spectroscopy after the initial hydroboration step revealed mostly unreacted allyl phenyl ether – an unacceptable result for us.

Table 2-2. Yields of hydroquinones derived from B-alkylcatecholboranes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>R</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-hexene (1a)</td>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2a 58</td>
</tr>
<tr>
<td>2</td>
<td>1-octene (1b)</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;7&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2b 59</td>
</tr>
<tr>
<td>3</td>
<td>allyl ethyl ether (1d)</td>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;OCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2d 59</td>
</tr>
<tr>
<td>4</td>
<td>allyl 2,2,2-trifluoroethyl ether (1e)</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;OCH&lt;sub&gt;2&lt;/sub&gt;CF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2e 52</td>
</tr>
<tr>
<td>5</td>
<td>allyl phenyl ether (1g)</td>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;OPh</td>
<td>2g --</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yields based on 1,4-benzoquinone.

Still hoping to conserve alkene starting materials and improve the scope of our method, we switched to hydroboration with pinacolborane, which gives selective anti-Markovnikov addition to terminal alkenes using Wilkinson’s catalyst.<sup>42</sup> Using 1-hexene (1a) for initial screening (Table 2-3), Rh-catalyzed hydroboration succeeded either in THF or dichloromethane solution, but the subsequent alkylation of benzoquinone entirely failed using aqueous THF (entry 1). Slightly more promising results for the alkylation step were obtained using a water-dichloromethane biphasic mixture (entry 5), but the reaction still afforded a very poor yield. Others have also found that alkyl transfer from B-alkylpinacolboranes to 1,4-benzoquinone is sluggish,<sup>41</sup> so based on related findings<sup>43</sup> in the area of fluorinations of B-alkylpinacolboranes, we reasoned that TFA might help facilitate alkyl transfer (entry 3). In contrast to that prior work, we found that TFA alone, rather than 4:1 TFA:H<sub>3</sub>PO<sub>4</sub> (entry 9), gave the highest yields. Longer reaction time resulted in no improvement (entry 4), so we considered the reaction to be optimized at the yields shown in Table
The final hydrogenation is not yield-limiting, as we optimized hydrogenation conditions separately.

Table 2-3. Yields of hydroquinones derived from $B$-alkylpinacolboranes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>R</th>
<th>Solvent</th>
<th>Yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>(CH$_2$)$_3$CH$_3$</td>
<td>THF/H$_2$O</td>
<td>2a 0</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>(CH$_2$)$_3$CH$_3$</td>
<td>CH$_2$Cl$_2$/H$_2$O</td>
<td>2a 10</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>(CH$_2$)$_3$CH$_3$</td>
<td>CH$_2$Cl$_2$/H$_2$O/TFA</td>
<td>2a 52</td>
</tr>
<tr>
<td>4</td>
<td>1a</td>
<td>(CH$_2$)$_3$CH$_3$</td>
<td>CH$_2$Cl$_2$/H$_2$O/TFA</td>
<td>2a 50</td>
</tr>
<tr>
<td>5</td>
<td>1d</td>
<td>(CH$_2$)$_3$OCH$_2$CH$_3$</td>
<td>CH$_2$Cl$_2$/H$_2$O/TFA</td>
<td>2d 50</td>
</tr>
<tr>
<td>6</td>
<td>1e</td>
<td>(CH$_2$)$_3$OCH$_2$CF$_3$</td>
<td>CH$_2$Cl$_2$/H$_2$O/TFA</td>
<td>2e 49</td>
</tr>
<tr>
<td>7</td>
<td>1f</td>
<td>(CH$_2$)$_3$OCH$_2$CF$_2$CF$_3$</td>
<td>CH$_2$Cl$_2$/H$_2$O/TFA</td>
<td>2f 49</td>
</tr>
<tr>
<td>8</td>
<td>1g</td>
<td>(CH$_2$)$_3$OC$_6$H$_4$H$_5$</td>
<td>CH$_2$Cl$_2$/H$_2$O/TFA</td>
<td>2g 73</td>
</tr>
<tr>
<td>9</td>
<td>1g</td>
<td>(CH$_2$)$_3$OC$_6$H$_4$H$_5$</td>
<td>CH$_2$Cl$_2$/H$_2$O/4:1 TFA:H$_3$PO$_4$</td>
<td>2g 64</td>
</tr>
<tr>
<td>10</td>
<td>1h</td>
<td>(CH$_2$)$_3$OC$_6$H$_4$Br</td>
<td>CH$_2$Cl$_2$/H$_2$O/TFA</td>
<td>2h 44$^b$</td>
</tr>
<tr>
<td>11</td>
<td>1h</td>
<td>(CH$_2$)$_3$OC$_6$H$_4$Br</td>
<td>CH$_2$Cl$_2$/H$_2$O/TFA</td>
<td>2h 54$^c$</td>
</tr>
</tbody>
</table>

$^a$ Yields based on 1,4-benzoquinone after product purification by silica gel chromatography.

$^b$ Total yield of 44% representing a 3:2 mixture of R = 4-$C_6$H$_4$Br (2g) and R = $C_6$H$_5$ (2h).

$^c$ Yield of pure 2h using a dissolving-zinc reduction instead of catalytic hydrogenation.

Next we extended our method to allyl ethers (Table 2-3, entries 5-10). Variations in reaction time, proportions of reagents, etc. were explored, but isolated yields were reliably close to about 50% for the 2-alkylated hydroquinones after chromatographic purification. When we started with allyl 4-bromophenyl ether (1h, R = 4-$C_6$H$_4$Br), $^1$H NMR spectroscopic analysis of the chromatographically purified product showed contamination with about 30% of the debrominated
product (2g, R = C₆H₅), not a surprising result for a sequence that includes a noble-metal-catalyzed hydrogenation.⁴⁴ We found, however, that the 3-aryloxypropyl-substituted 1,4-benzoquinones could be isolated (ca. 73% for R = C₆H₅; 60% for R = 4-C₆H₄Br). They are not especially stable, but reduction of the benzoquinone derivative bearing the pendant 4-bromophenyl group was effected cleanly using dissolving zinc in about 90% isolated yield. For all the other derivatives, both the hydroboration and benzoquinone-alkylation steps were carried out in a single pot, as the organic solvent for the hydroboration step and the alkylation step was the same (dichloromethane). After a short aqueous workup, the crude 2-substituted 1,4-benzoquinone intermediate can be subjected directly to catalytic hydrogenation with Raney nickel (1 atm, 25 °C, 1 h) to afford the desired 2-substituted hydroquinone after silica gel chromatographic purification. While 50% yield is not ordinarily cause for celebration, the improvement in yield with respect to the alkene was improved compared to using BH₃SMe₂. Our yields are comparable to those obtained by Baran and co-workers using boronic acids as the alkylation reagent.⁴¹ We cannot rule out the possibility that our pinacolboranes are hydrolyzed to the corresponding boronic acids in situ, since our reaction conditions include aqueous TFA. Likewise we could imagine converting our pinacolboranes to boronic acids or potassium alkyltrifluoroborates, but based on results obtained by Baran and co-workers, we would not anticipate significant improvements in yield, and those conversions would involve additional synthetic steps. An important feature of our methods is its experimental simplicity, especially starting from allyl ethers as the source of the alkyl group. This feature will allow us to extend the scope of the alkylation agent widely because allyl ethers themselves are easily prepared.
2.3. Conclusion

In summary we have developed a simplified and apparently general method for the synthesis of 2-substituted hydroquinones derived from allyl ethers. Further development of this work, particularly in the formation of derivatives having much longer fluorous substituents attached to the ether oxygen atom are underway, as are studies of these hydroquinone derivatives as monomers for poly(arylene ether)s.

2.4. Experimental section

**General:** Pinacolborane (Alfa-Aesar), catecholborane (Sigma-Aldrich), Wilkinson’s catalyst (Strem), borane dimethyl sulfide (Oakwood), allyl ethyl ether (Sigma-Aldrich), allyl phenyl ether (Sigma-Aldrich), potassium persulfate (Oakwood), Raney nickel (Oakwood), and silver nitrate (Sargent Welch) were used as received. 1,4-Benzoquinone was prepared according to literature procedures and sublimed prior to use. Allyl 2,2,2-trifluoroethyl ether, allyl 2,2,3,3,3-pentafluoropropyl ether, and allyl 4-bromophenyl ether were prepared according to literature procedures. Tetrahydrofuran and dichloromethane were distilled from calcium hydride. Melting points were taken on a Buchi Melting Point M-560 and are uncorrected. NMR spectra were collected using Agilent (Varian) U4-DD2 and Agilent (Varian) MR4 spectrometers (1H at 400 MHz, 19F at 376 MHz, and 13C at 101 MHz). A line broadening window function (0.5 Hz) was applied to the FIDs prior to Fourier transformation, and Whittaker baseline corrections were applied to frequency-domain spectra. High-resolution mass spectra were collected using an Agilent 6220 with electrospray ionization (ESI) and time-of-flight (TOF) mass analysis; samples were introduced by direct infusion of a methanol solution containing 1% formic acid.
2.4.1. 2-Alkylhydroquinone synthesis method A (using BH₃SMe₂). The following procedure was adapted from a published procedure.³⁵ A flame-dried three-neck 500-mL round-bottomed flask was charged with 0.050 mol of borane dimethylsulfide (neat liquid) and 50 mL ether. A nitrogen inlet, dropping funnel, magnetic stir bar, and condenser were fitted to the flask. Liquid alkene (0.15 mol) was added to the dropping funnel and added dropwise to the stirred mixture, using 10 mL of ether to rinse the funnel. The reaction can be slightly exothermic, depending on the alkene, and induce reflux. Once all of the alkene was added and reflux had subsided, the solvent was removed by distillation using a steam bath. 1,4-Benzoquinone (4.32 g, 0.040 mol) was then dissolved in 125 mL of ether and added dropwise to the solution using an addition funnel. Upon complete addition of the 1,4-benzoquinone the nitrogen inlet was removed, and the ether was removed by distillation using a steam bath. Water (350 mL) was added to the oil, and steam distillation was used to remove the dialkylborinic acid byproduct (R₂BOH). Several additions of DI water were required for the steam distillation to completely remove the borinic acid byproduct, depending on the alkene, until the distillate showed no signal in an ¹¹B-NMR spectroscopic analysis. The reaction flask was then cooled using an ice bath, causing the oily crude 2-alkylhydroquinone to precipitate as a chunky tan or brown solid. The solid was collected on a Buchner funnel, washed with water (100 mL), and dried briefly under air. Analytically pure samples were obtained as white powders by recrystallization from toluene and hexanes (1:1).

2.4.2. 2-Alkylhydroquinone synthesis method B (using catecholborane). This procedure was adapted from a literature procedure.³⁶ A flame-dried 100-mL Schlenk flask was charged with catecholborane (300 mg, 2.5 mmol) and diluted with 3 mL of THF. Liquid alkene (2.0 mmol) was added to the flask followed by 0.040 mmol (37 mg) Wilkinson’s catalyst. The neck of the flask was rinsed with about 2 mL of THF to ensure that the all of the catalyst entered the reaction.
mixture. The dark red solution was stirred overnight at room temperature. Water (0.1 mL) was then added and the mixture stirred for 15 min to quench any unreacted catecholborane. To the brown mixture was added THF (5 mL), DMPU (2.0 mmol) and 1,4-benzoquinone (1.0 mmol). The dark mixture was stirred for 2 h at room temperature. The reaction was then worked up by diluting with ether (60 mL), washing with water (2 x 20 mL) and brine (20 mL), drying over MgSO₄, filtering, and concentrating by rotary evaporation to afford a dark reddish-brown oil. Silica gel column chromatography eluting with 30% ethyl acetate in hexanes afforded, after evaporation of the eluent, the pure 2-alkylhydroquinone as a white solid.

2.4.3. 2-Alkylhydroquinone synthesis method C (using pinacolborane): A flame-dried 100-mL Schlenk flask was charged with 0.250 g (1.95 mmol) of pinacolborane and 3 mL of dichloromethane. Liquid alkene (1.77 mmol) was added to the flask followed by 0.040 mmol (36 mg) of Wilkinson’s catalyst. The neck of the flask was rinsed with about 2 mL of dichloromethane to ensure that the all of the catalyst entered the reaction mixture. The reddish solution was stirred for about 15 h under a nitrogen atmosphere. Water (5 mL) was then added and stirred for 10 min to quench any unreacted pinacolborane. Then 1,4-benzoquinone (127 mg, 1.18 mmol) was dissolved in 2 mL of dichloromethane and added to the flask. Silver nitrate (40 mg, 0.24 mmol) and potassium persulfate (960 mg, 3.54 mmol) were added and the neck of the flask was rinsed with about 5 mL of water to ensure that the all of the reagents had entered the reaction mixture. Trifluoroacetic acid (5 mL) was then added and the flask was opened to air. The biphasic mixture was stirred under reflux (50 °C) for 24 h. The mixture was then cooled to RT, diluted with 20 mL of dichloromethane, separated, and extracted with additional dichloromethane (2 x 20 mL). The organic layers were combined, washed with water (3 x 20 mL), dried over MgSO₄, filtered, and concentrated by rotary evaporation to afford a dark oil. The crude intermediate 2-alkyl-1,4-
benzoquinone was dissolved in 15 mL of THF and 0.7 g Raney nickel was added. A balloon of hydrogen was fitted, and the mixture was stirred at room temperature under a hydrogen atmosphere for 1 h. The solution was then diluted with 40 mL of ether, filtered through diatomaceous earth, dried over MgSO₄, and concentrated by rotary evaporation to yield a dark brown oil. Silica gel column chromatography using flash-grade absorbent and eluting with 30% ethyl acetate in hexanes, afforded after evaporation of the eluent, the pure 2-alkylhydroquinone as a white solid.

2.4.4. Previously reported compounds. 2-Hexylhydroquinone (2a) was prepared using Methods A (72%), B (58%) and C (52%) as described in Sections 4.1, 4.2, 4.3, respectively; mp 82.1-84.1 °C; lit. mp 81.5-82.7. TLC (silica gel, 30% EtOAc/Hexanes) Rf = 0.43. 2-Octylhydroquinone (2b) was prepared using Methods A (71%) and B (59%); mp 89.2-92.1 °C; lit. mp 92-94 °C. TLC (silica gel, 30% EtOAc/Hexanes) Rf = 0.45. 2-Cyclooctylhydroquinone (2c) was prepared using Method A (88%); mp 144.5-146.3 °C. TLC (silica gel, 30% EtOAc/Hexanes) Rf = 0.36.

2.4.5. Previously unreported compounds.

2.4.5.1. 2-(3-Ethoxypropyl)-1,4-hydroquinone (2d) was prepared using Methods A, B, and C (33%, 53%, and 50%, respectively, mp 115.9-118.9 °C); ¹H NMR (400 MHz, DMSO-d₆) δ 8.50 (s, 1H, OH), 8.46 (s, 1H, OH), 6.55 (d, ³J = 9 Hz, 1H, aromatic CH), 6.44 (d, ⁴J = 3 Hz, 1H, aromatic CH), 6.38 (dd, ³J = 9 Hz, ⁴J = 3 Hz, 1H, aromatic CH), 3.39 (q, ³J = 7 Hz, 2H, CH₂), 3.33 (t, ³J = 7 Hz, 2H), 2.48 – 2.41 (m, 2H), 1.77 – 1.64 (m, 2H), 1.10 (t, ³J = 7 Hz, 3H, CH₃). ¹³C {¹H} NMR (101 MHz, DMSO-d₆) δ 149.6 (aromatic C), 147.5 (aromatic C), 128.5 (aromatic C), 116.3 (aromatic CH), 115.4 (aromatic CH), 112.8 (aromatic CH), 69.4 (CH₂), 65.2 (CH₂), 29.4 (CH₂), 26.5 (CH₂), 15.2 (CH₃). HRMS ESI (+) Calc for C₁₁H₁₆O₃ (M⁺) 196.1094; Found 196.1098. Rf (30% EtOAc/Hexanes) = 0.23.
2.4.5.2. 2-{3-(2,2-Trifluoroethoxy)propyl}1,4-hydroquinone (2e) was prepared using Methods A, B and C (30%, 52%, 49%, respectively; mp 98.2-100.4 °C). \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) δ 8.51 (s, 1H, OH), 8.50 (s, 1H, OH), 6.56 (d, \(^3\)J = 9 Hz, 1H, aromatic CH), 6.45 (d, \(^4\)J = 3 Hz, 1H, aromatic CH), 6.39 (dd, \(^3\)J = 9, \(^4\)J = 3 Hz, 1H, aromatic CH), 4.02 (q, \(^3\)J\(_{HF}\) = 10 Hz, 2H, CH\(_2\)CF\(_3\)), 3.56 (t, J = 7 Hz, 2H, CH\(_2\)), 2.48 – 2.43 (m, 2H, CH\(_2\)), 1.79 – 1.70 (m, 2H, CH\(_2\)). \(^{13}\)C\({^{1}\text{H}}\) NMR (101 MHz, DMSO-d\(_6\)) δ 149.6 (aromatic C), 147.5 (aromatic C), 128.2 (aromatic C), 125.0 (q, \(^1\)J\(_{CF}\) = 278 Hz, CF\(_3\)), 116.3 (aromatic CH), 115.4 (aromatic CH), 113.0 (aromatic CH), 71.4 (CH\(_2\)), 67.0 (q, \(^2\)J\(_{CF}\) = 32 Hz, CH\(_2\)CF\(_3\)), 29.1 (CH\(_2\)), 26.1 (CH\(_2\)). \(^{19}\)F NMR (376 MHz, DMSO-d\(_6\)) δ −72.85 (t, \(^3\)J\(_{HF}\) = 10 Hz, CF\(_3\)). The assignment of the CF\(_3\) group was confirmed by \(^{13}\)C\({^{19}\text{F}}\) NMR (101 MHz, DMSO-d\(_6\)): δ 125.0 (t, \(^3\)J\(_{FH}\) = 5 Hz, CF\(_3\)). HRMS ESI (+) Calc for C\(_{12}\)H\(_{18}\)O\(_3\) (M\(^*\)+) 250.0811; Found 250.0810. \(R_f\) (30% EtOAc/Hexanes) = 0.23.

2.4.5.3. 2-{3-(2,2,3,3,3-Pentafluoropropoxy)propyl}1,4-hydroquinone (2f) was prepared using Methods A and C (29% and 49%, respectively, mp 102.6-103.9 °C); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) δ 8.53 (s, 2H, OH), 6.56 (d, \(^3\)J = 9 Hz, 1H, aromatic CH), 6.45 (d, \(^4\)J = 3 Hz, 1H, aromatic CH), 6.39 (dd, \(^3\)J = 9, \(^4\)J = 3 Hz, 1H, aromatic CH), 4.10 (tq, \(^3\)J\(_{HF}\) = 14 Hz, \(^4\)J\(_{HF}\) = 1 Hz, 2H, CH\(_2\)CF\(_2\)CF\(_3\)), 3.57 (t, \(^3\)J = 7 Hz, 2H, CH\(_2\)), 2.45 (t, \(^3\)J = 7 Hz, 2H, CH\(_2\)), 1.81 – 1.69 (m, 2H). \(^{13}\)C\({^{1}\text{H}}\) NMR (101 MHz, DMSO-d\(_6\)) δ 150.1 (aromatic C), 147.9 (aromatic C), 128.6 (aromatic C), 116.8 (aromatic CH), 115.9 (aromatic CH), 113.4 (aromatic CH), 72.0 (CH\(_2\)), 66.5 (t, \(^2\)J\(_{CF}\) = 26 Hz, CH\(_2\)CF\(_2\)CF\(_3\)), 29.5 (CH\(_2\)), 26.5 (CH\(_2\)). The CF\(_2\) and CF\(_3\) groups were located in the \(^{13}\)C\({^{19}\text{F}}\) NMR (101 MHz, DMSO-d\(_6\)): δ 118.6 (s, CF\(_3\)) and 113.5 (CF\(_2\)). \(^{19}\)F NMR (376 MHz, DMSO-d\(_6\)) δ −82.68 (s, 3F), −122.47 (t, \(^3\)J\(_{HF}\) = 14 Hz, 2F, CF\(_2\)). HRMS ESI (+) Calc for C\(_{12}\)H\(_{13}\)F\(_5\)O\(_3\) (M\(^*\)+) 300.0779; Found 300.0797. \(R_f\) (30% EtOAc/Hexanes) = 0.31.
2.4.5.4. 2-(3-Phenoxypropyl)-1,4-hydroquinonone (2g) was prepared using Method C (73%, mp 102.2-103.4 °C). \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 8.55 (s, 1H, OH), 8.53 (s, 1H, OH), 7.27 (t, 8 Hz, 2H, aromatic CH), 6.96 – 6.87 (m, 3H, aromatic CH), 6.58 (d, \(^3\)J = 9 Hz, 1H, aromatic CH), 6.49 (d, \(^4\)J = 3 Hz, 1H, aromatic CH), 6.41 (dd, \(^3\)J = 9, \(^4\)J = 3 Hz, 1H, aromatic CH), 3.94 (t, \(^3\)J = 7 Hz, 2H, CH\(_2\)), 2.59 (t, \(^3\)J = 7 Hz, 2H, CH\(_2\)), 2.00 – 1.86 (m, 2H, CH\(_2\)). \(^{13}\)C\[^{1}\]H NMR (101 MHz, DMSO-d\(_6\)) \(\delta\) 158.7 (aromatic C), 149.7 (aromatic C), 147.6 (aromatic C), 129.5 (aromatic C), 128.2 (aromatic CH), 120.4 (aromatic CH), 116.4 (aromatic CH), 115.5 (aromatic CH), 114.4 (aromatic CH), 113.0 (aromatic CH), 66.9 (CH\(_2\)), 28.8 (CH\(_2\)), 26.4 (CH\(_2\)). HRMS ESI (+) Calc for C\(_{12}\)H\(_{18}\)O\(_3\) (M\(^+\)) 244.1094; Found 244.1096. R\(_f\) (30% EtOAc/Hexanes) = 0.24.

2.4.5.5. 2-[3-(4-Bromophenoxy)propyl]-1,4-hydroquinone (2h) was prepared using Method C (45%). This compound was formed as a mixture of the desired compound (70%) and the debrominated analogue 2-(3-phenoxypropyl)benzene-1,4-diol (30%). By comparing the NMR spectra of the mixture to the NMR spectra of the pure phenyl derivative, we were able to assign the spectrum of the bromophenyl derivative (pendant aryl group only; all of the other signals were coincident with the signals of the phenyl derivative). \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 8.54 (s, 1H, OH), 8.53 (s, 1H, OH), 7.46 – 7.39 (m, 2H), 6.91 – 6.88 (m, 2H), 6.60 – 6.53 (m, 1H, CH), 6.50 – 6.44 (m, 1H, CH), 6.40 (dd, \(^3\)J = 9 Hz, \(^4\)J = 3 Hz, 1H, CH), 3.98 – 3.89 (m, 2H, CH\(_2\)), 2.62 – 2.52 (m, 2H, CH\(_2\)), 1.99 – 1.87 (m, 2H, CH\(_2\)). \(^{13}\)C\[^{1}\]H NMR (101 MHz, DMSO-d\(_6\)) \(\delta\) 158.0 (aromatic C), 149.6 (aromatic C), 147.5 (aromatic C), 132.1 (aromatic CH), 129.5 (aromatic CH), 128.0 (aromatic CH), 120.4 (aromatic CH), 116.7 (aromatic CH), 116.4 (aromatic CH), 115.4 (aromatic CH), 114.4 (aromatic C), 113.0 (aromatic CH), 111.7 (aromatic CH), 67.3 (CH\(_2\)), 28.6 (CH\(_2\)), 26.3 (CH\(_2\)). R\(_f\) (30% EtOAc/Hexane) = 0.24.
2.4.5.6. 2-[3-(4-Bromophenoxy)propyl]-1,4-hydroquinone (2h) was prepared using Method C, but the intermediate benzoquinone was not subjected to catalytic hydrogenation. Instead, it was directly purified by silica gel chromatography (20% ethyl acetate in hexanes) to obtain the purified 2-[3-(4-bromophenoxy)propyl]-1,4-benzoquinone in 63% yield: mp 80.2 – 82.4 °C. 1H NMR (400 MHz, CDCl3) δ 7.41 – 7.29 (m, 2H, aromatic CH), 6.81 – 6.68 (m, 4H), 6.64 – 6.55 (m, 1H), 3.96 (t, 3J = 6 Hz, 2H), 2.62 (ddd, 3J = 9 Hz, 3J = 6 Hz, 4J = 1 Hz, 2H), 2.06 – 1.94 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 187.7 (CO), 187.4 (CO), 157.9 (aromatic C), 148.8 (alkene C), 136.9 (alkene CH), 136.5 (alkene CH), 132.8 (alkene CH), 132.4 (aromatic CH), 116.3 (aromatic CH), 113.1 (aromatic C), 67.2 (CH2), 27.6 (CH2), 26.2 (CH2). Rf (20% EtOAc/hexanes) = 0.31. We were not able to obtain adequate MS or microanalytical data on this benzoquinone derivative.

A 50-mL round bottom flask was charged with (0.250 g, 0.78 mmol 2-[3-(4-bromophenoxy)propyl]-1,4-benzoquinone dissolved in THF (5 mL). Water (5 mL) was added to the flask followed by the addition of granular zinc (0.31 g, 4.7 mmol) and ammonium chloride (0.21 g, 3.9 mmol). The mixture was stirred for 30 min, during which time the yellow color gradually faded. The reaction was allowed to stir for an additional 30 min. The mixture was diluted with ether (20 mL), washed with water (3 x 10 mL), dried over MgSO4, filtered, and concentrated by rotary evaporation to afford a light brown oil. The light brown oil was recrystallized from toluene and hexanes (1:1) to yield the pure hydroquinone (90% for the reduction, 54% overall from 1,4-benzoquinone): mp 119.0 – 122.6 °C. 1H NMR (400 MHz, DMSO-d6) δ 8.57 (s, 1H, OH), 8.56 (s, 1H, OH), 7.46 – 7.38 (m, 2H, aromatic CH), 6.93 – 6.85 (m, 2H, aromatic CH), 6.57 (d, J = 9 Hz, 1H, CH), 6.47 (d, J = 3 Hz, 1H, CH), 6.40 (dd, J = 9, 3 Hz, 1H, CH), 3.93 (t, J = 3 Hz, 2H, CH2), 2.62 – 2.52 (m, 2H, CH2), 1.98 – 1.87 (m, 2H, CH2). 13C NMR (101 MHz, DMSO-d6) δ 158.0 (aromatic C), 149.7 (aromatic C), 147.6 (aromatic C), 132.2 (aromatic CH), 128.1 (aromatic C), 116.8 (aromatic CH),
116.5 (aromatic CH), 115.5 (aromatic CH), 113.1 (aromatic C), 111.8 (aromatic CH), 67.4 (CH₂), 28.7 (CH₂), 26.3 (CH₂). \( R_f (30\% \text{ EtOAc/Hexane}) = 0.20 \). We were unable to obtain a suitable ESI-MS spectrum of this compound and therefore we sent a sample for microanalysis. Anal. Calcd for \( \text{C}_{15}\text{H}_{15}\text{BrO}_3 \): C, 55.75; H, 4.68. Found: C, 55.69; H, 4.73.

2.4.5.7. 2-(3-Phenoxypropyl)-1,4-benzoquinone (3g) was prepared using Method C, but the intermediate benzoquinone derivative was purified by silica gel chromatography (20% ethyl acetate in hexanes) instead of subjecting it to hydrogenation. A 73% yield was obtained: mp 83.2 – 84.9 °C. \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.30 – 7.24 (m, 2H, aromatic CH), 6.94 (tt, \(^3\)J = 7 Hz, \(^4\)J = 1 Hz, 1H, aromatic CH) 6.89 – 6.83 (m, 2H, aromatic CH), 6.81 – 6.69 (m, 2H, alkene CH), 6.62 (dt, \(^3\)J = 3 Hz, \(^4\)J = 1 Hz, 1H, alkene CH), 4.01 (t, \(^3\)J = 6 Hz, 2H, CH₂), 2.64 (td, \(^3\)J = 8 Hz, \(^4\)J = 1 Hz, 2H, CH₂), 2.07 – 1.97 (m, 2H, CH₂). \(^{13}\)C\(^{1}\)H NMR (101 MHz, CDCl₃) \( \delta \) 187.7 (CO), 187.5 (CO), 158.7 (aromatic C), 149.0 (aromatic C), 136.9 (alkene CH), 136.5 (alkene CH), 132.8 (alkene CH), 129.6 (aromatic CH), 121.0 (aromatic CH), 114.6 (aromatic CH), 66.8 (CH₂), 27.7 (CH₂), 26.3 (CH₂). HRMS-APCI (+) calc for \( \text{C}_{15}\text{H}_{14}\text{O}_3 \) (M⁺+) 242.0937; Found 242.0936. \( R_f \) (20% EtOAc/Hexanes) = 0.48.

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Chapter 3. Synthesis and Characterization of Linear Segmented Aromatic Polymers Containing Thermally Reversible Linkages

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Foreward. With the exception of supporting information relegated to the end of the dissertation, this chapter represents a manuscript in preparation for submission to the journal Macromolecules. I performed all of the work reported in this chapter except as follows: Dana Kazerooni performed uniaxial tensile testing and Prof. Paul A. Deck supervised my work.

Graphical Abstract

Abstract

This article describes a platform for the synthesis of linear, self-healing aromatic polymers using cyclopentadiene-maleimide Diels-Alder as the thermally reversible component. First we
prepared poly(aryl ether sulfone) and poly(ether ether ketone) segments, combining either 4,4-
difluorodiphenyl sulfone or with 4,4-difluorobenzophenone with hydroquinones (HQs) bearing n-
hexyl and n-octyl substituents to match the $T_g$ of the segments to the temperature window of our
self-healing chemistry. Then we capped the HQ-terminated telechelic segments with structurally
tailored cyclopentadienes and extended the telechelic segments into polymers using 1,6-hexane-
bis-$N$-maleimide as the linker to afford Diels-Alder polymers having $M_n$ of ca. 25 kDa that form
creaseable films upon solvent casting. Scratch-heal testing of the Diels-Alder polymers shows that
they have the ability to heal cracks in the same location multiple times. Tensile testing shows a
recovery of 87% of the polymer’s mechanical strength after the first healing cycle and 40% after
the second healing cycle.

**Keywords**

Aromatic polymer, PEEK, PAES, Diels-Alder, Cyclopentadiene-Maleimide, Self-Healing

### 3.1 Introduction

Aromatic polymers, particularly those formed via step-growth polymerization using
nucleophilic aromatic substitution ($S_N$Ar), have many long-standing applications in high-
performance injection-molded parts (i.e., “engineering” polymers), fiber-reinforced
thermoplastic composites, artificial hip joint material, gas separation and reverse osmosis
membranes, and fuel cell proton exchange membranes due to their thermal and chemical
stability as well as their excellent mechanical performance. However, like all materials these
polymers are subject to damage due to prolonged use or to environmental factors. It is desirable
to endow these important materials with the capacity for *self-healing* so that their practical lifetime
could be extended. Moreover, it would be ideal to develop platform chemistry for self-healing that
could be applied to a wide variety of aromatic polymers.
As a thermal cycloaddition, the Diels-Alder reaction is a natural choice for self-healing chemistry.\textsuperscript{9} As shown in eq 1, the reaction between the dienophile and diene form an adduct (a cyclohexene derivative). Because $\Delta S < 0$, the adduct is thermodynamically favored at lower temperatures, and the reactants are favored at higher temperatures. As there is no catalyst required and as no side-products are involved, the reaction can, in principle, be reversed and repeated \textit{ad infinitum}. This principle is the basis for many thermal self-healing technologies whether based on the Diels-Alder reaction or on other chemistries.

$$\text{Diene} + \text{Dienophile} \rightleftharpoons \text{Adduct}$$ (1)

Two general synthetic approaches to self-healing polymers are (a) installing end groups or pendant groups that can engage in reversible cross-linking or hyperbranching, and (b) segmented polymers with thermally reversible linkages between the segments. Of these, the former (a) is far and away the more common. The main issue with the latter (b) option is shown in eq 2.\textsuperscript{21} To obtain a polymer with useful properties such as creaseable film formation, one needs to reach the critical molecular weight for entanglement. However, $M_n$ is governed by the equilibrium constant ($K_{eq}$) for the binding event (eq 2). Thus at a temperature high enough to reach high conversion \textit{kinetically}, one must have a $K_{eq}$ high enough to reach a useful degree of polymerization ($DP_n$), while to achieve thermal reversibility the $K_{eq}$ must be sufficiently \textit{low} at a temperature below the onset of various decomposition processes. This temperature range has often been described as a “window” in the literature of self-healing chemistry.

$$DP_n = \sqrt{(K_{eq})[M]}$$ (2)

Many researchers have used the furan-maleimide Diels-Alder reaction as these moieties are easy to incorporate into macromolecular structures, they have a mild temperature range for Diels-Alder/Retro Diels-Alder reactivity (60 °C to 150 °C),\textsuperscript{11-14,60-61} and they don’t tend to engage in
side-reactions or structural rearrangement under ordinary conditions. However, almost all of these studies have been limited to crosslinking and hyperbranching chemistry as earlier studies using furan/maleimide to create linear polymers resulted in low molecular weights.\textsuperscript{62-64} This is likely due to the equilibrium constant of binding (K\textsubscript{eq}) being too low at the optimal temperature of polymerization for these systems, restricting the polymers to low molecular weights.\textsuperscript{21} Thus, the furan/maleimide system is limited to crosslinking where only a small number of furan/maleimide linkages are needed to achieve the goal of reversible linkages and healing.

We hypothesized that a cyclopentadiene/maleimide (CPD-MI) system could offer a solution to the limited molecular weights of linear Diels-Alder polymers as the CPD-MI reaction has a much higher K\textsubscript{eq} value at temperatures where adduct formation should be fast. However, cyclopentadienes have inherent drawbacks such as self-dimerization, tautomerization, and an unfavorably high temperature required for the Retro Diels-Alder reaction (190 °C) that limits control of healing capabilities.\textsuperscript{16}

We have partly addressed these problems by incorporating substituents on the cyclopentadiene moiety.\textsuperscript{21} Specifically, we showed that the simple bis-cyclopentadiene monomer \textbf{A} reacts with bis-maleimide monomers \textbf{B} at 80 C to afford DA polymers reaching M\textsubscript{n} = 25-40 kDa. The perfluoroarylene linker in monomer \textbf{A} was chosen mostly for synthetic convenience, while the alkyl substituent (\textit{R}) prevents CPD self-dimerization. The monomer \textbf{A} exists as a mixture of three tautomers, but because all three tautomers place at least one of the cyclopentadiene substituents in the bridgehead position of the norbornene moiety in the adduct (which fortuitously destabilizes the adduct and facilitates the RDA process), we have so far tolerated this undesirable complication. These polymers show reversibility in solution above 120 °C, but their bulk self-healing properties
are severely limited by their high glass transition temperatures, despite our attempts to moderate the $T_g$ using long, flexible linking groups (G) in the bis-maleimide monomers.

**Scheme 3-1.** Polymerization of disubstituted bis-cyclopentadiene and bis-maleimide with flexible linking groups to generate a linear Diels-Alder polymer.

We hypothesized that we could solve most of the problems inherent to the polymers shown in Scheme 3-1 by redesigning them as reversibly-linked *segmented* polymers.$^{15}$ We first recognized that self-healing properties should be possible with fewer reversible (DA) moieties per polymer chain. Considering melt processing as an example, one chain scission event is sufficient to decrease the viscosity of a polymer by a factor of ca. 10. We also theorized that a segmented design would allow us to tailor the thermal and mechanical properties of the polymer by selecting the chemistry of the segment from a broad array of well-established polymeric systems. We chose step-growth aromatic polymers based on hydroquinone (HQ), partly for their ease of synthesis, partly for their chemical and thermal stability, and partly because they can present phenolic end groups suitable for synthetic elaboration into CPD-terminated telechelic segments using chemistry that we have already developed.$^{21}$ The last remaining issue, the $T_g$ of the telechelic segments, was addressed by using an n-alkyl-substituted HQ monomer. This report therefore describes the synthesis, physical properties, and self-healing behavior of linear, segmented aromatic polymers containing about 5-6 thermally reversible CPD-MI linkages per chain.
3.2 Experimental Section

**General:** Borane dimethyl sulfide (Oakwood) was used as received. NMP (Fisher) was dried and distilled over calcium hydride (80 °C at 10 mmHg). Toluene (Fisher) was used as received. Potassium carbonate (Oakwood) was dried in a vacuum oven at 100 °C for 2 d. THF(Fisher) was dried over molecular sieves. 4,4’-Difluorobenzophenone (Aldrich) was recrystallized from ether. Bis(4-fluorophenyl) sulfone (Oakwood) and 2-methylhydroquinone (Aldrich) were recrystallized from toluene. 2-(Nonafluorobiphenyl-4’-yl)-4-tert-butylcyclopentadiene was prepared according to previous procedures in our laboratory.¹⁹ NMR spectra were collected using Agilent (Varian) U4-DD2 and Agilent (Varian) MR4 spectrometers (¹H at 400 MHz and ¹³C at 101 MHz). A line broadening window function (0.5 Hz) was applied to the FIDs prior to Fourier transformation, and Whittaker baseline corrections were applied to frequency-domain spectra. Thermogravimetric analysis (TGA) was conducted on all of the polymer samples with a TA Instruments Q-50 under a counter stream of nitrogen (40 mL/min for the balance and 60 mL/min for the sample) from RT to 600 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was conducted on all of the polymer samples with a TA Instruments Q-2000 DSC under a counter stream of nitrogen. DSC thermograms analyzed were taken from the second heating cycle which was conducted from 0 °C to 250 °C at a heating rate of 5 °C/min. Molecular weights and dispersity data were obtained using SEC with THF as a solvent at RT on two Agilent PLgel 10 µm MIXED-B columns connected in series with a Wyatt Dawn Helios 2 light scattering detector and a Wyatt Optilab Rex refractive index detector. Molecular weights were calculated by using dn/dc values obtained from the peak assuming 100% mass elution from the columns. Microscopic images were obtained using an AmScope M150C-E5 with 40x magnification. Polymer films of approximately 30 µm thickness were placed on a glass slide and a glass cover was placed on top of the site of
interest. Images were taken of a cross-section and cropped to show the relevant area of interest. Tensile samples were cut from solvent casted films using a Cricut Explore One™ computer controlled cutting machine. Samples were cut in dogbone shapes described by ASTM standard D638-14. Film thickness (25-30 µm) was measured by sampling 5 different points on the film using a Mitutoyo digimatic micrometer model MDSC-1 SXF. Uniaxial tests were performed using an Instron ElectroPuls E1000 testing machine equipped with a 250-N Dyna-cell load cell.

3.2.1. Previously Reported Compounds. 2-Hexylhydroquinone, 2-octylhydroquinone, 2-(3-ethoxypropyl)-1,4-hydroquinone, and 2-[3-(2,2,2-trifluoroethoxy)propyl]-1,4-hydroquinone were all prepared according to Method A from our earlier report.65

3.2.2. Previously Unreported Compounds.

3.2.2.1. Representative Synthesis of 5,000 Mₙ Telomers. A flame dried 100-mL Schlenk flask was charged with hexylhydroquinone (1.50 g, 7.72 mmol), potassium carbonate (1.22 g, 8.80 mmol), and 4,4'-difluorobenzophenone (1.57 g, 7.20 mmol), followed by 14 mL of N-methylpyrrolidone and 10 mL of toluene. The excess of hydroquinone ensured that the oligomers would be hydroquinone-terminated. The mixture was heated to 160 °C to induce reflux. After 4 h the toluene was drained from the Dean-Stark trap and the mixture was allowed to stir for an additional 18 h at 180 °C. The solution was cooled to RT and then precipitated into 300 mL of water. The precipitate was dissolved in chloroform and reprecipitated into methanol, filtered, and dried for 2 d at 40 °C to give a tan powder (2.13 g, 80% yield). This procedure was applied to all of the PEEK and PAES derivatives shown in Table 3-1. Polymers were characterized by ¹H NMR spectrometry as described in the Supporting Information. The spectra typically exhibit signals in the aromatic region arising from the electrophilic monomer (diphenyl sulfone or benzophenone) and the hydroquinone, which are not resolved from one another, and groups of signals in the upfield region.

46
that were assigned to the various side-groups. In each case it was possible to distinguish at least one signal that could be assigned to the benzylic CH$_2$ group of both the repeat unit hydroquinone and the end-group hydroquinones.

3.2.2.2. *Synthesis of High Molecular Weight HexylPEEK.* A flame dried 100 mL Schlenk flask was charged with hexylhydroquinone (0.486 g, 2.50 mmol), 4,4'-difluorobenzophenone (0.545 g, 2.50 mmol), and potassium carbonate (0.394 g, 2.85 mmol) followed by 10 mL of N-methylpyrrolidone and 10 mL of toluene. The mixture was heated to 160 °C to induce reflux. After 4 h, toluene was drained from the Dean-Stark trap and the mixture was allowed to stir for an additional 18 h at 180 °C. The mixture was cooled to RT and then precipitated into 300 mL of water. The precipitate was then dissolved in chloroform and reprecipitated into methanol, filtered, and dried for 2 d at 40 °C to give a white fibrous solid (0.838 g, 90% yield).

3.2.2.3. *Representative Copolymer Polymerization.* A flame dried 100 mL Schlenk flask was charged with methylhydroquinone (0.155 g, 1.25 mmol), hexylhydroquinone (0.243 g, 1.25 mmol), potassium carbonate (0.394 g, 2.85 mmol), and bis(4-fluorophenyl) sulfone (0.636 g, 2.50 mmol), followed by 7 mL of N-methylpyrrolidone and 7 mL of toluene. The mixture was heated to 160 °C to induce reflux. After 4 h, toluene was drained from the Dean-Stark trap and the mixture was allowed to stir for an additional 18 h at 180 °C. The mixture was cooled to RT and then precipitated into 300 mL of water. The precipitate was then dissolved in chloroform and reprecipitated into methanol, filtered, and dried for 2 d at 40 °C to give tan powder (0.841 g, 85% yield).

3.2.2.4. *Representative End-Capping of 5,000 M$_n$ Telomers.* A flame-dried 100-mL Schlenk flask was charged with sodium hydride (0.018 g, 0.750 mmol), THF (12 mL), 5K HePEEK (1.50 g, 0.300 mmol), and CPD linker (0.327 g, 0.750 mmol). The orange solution was stirred at 80 °C for
18 h under N₂. The solution was cooled to RT, quenched with 10% H₂SO₄ (3 mL), and precipitated into a rapidly stirred quench solution. The quench solution comprised methanol (300 mL), water (30 mL) and conc. H₂SO₄ (3 ml). The precipitate was collected on a filter, washed with methanol (3 x 50 mL), and dried for 2 d at 40 °C to yield tan powder (1.35 g, 90% yield).

3.2.2.5. Representative Diels-Alder Polymerization. A flame dried 50-mL Schlenk flask was charged with CPDHePEEK (0.600 g, 0.083 mmol), 1,6-hexane-bis-N-maleimide (0.023 g, 0.083 mmol), and N-methylpyrrolidone (5 mL). The solution was stirred at 80 °C for 18 h under N₂. The solution was cooled to RT and precipitated into methanol (200 mL). The resulting solid was collected on a filter, washed with methanol (3 x 50 mL), and dried under vacuum at 40 °C to yield a brown-orange fibrous solid (0.570 g, 95% yield).

3.2.2.6 Depolymerization using FMI. A flame dried 50-mL Schlenk flask was charged with DAOctylPAES (100 mg), 4-fluorophenyl maleimide (FMI) (0.060 g, 20 mol excess), 1 mL N-methylpyrrolidone and heated at 150 °C for 2 h. Precipitation in methanol yielded a brown solid (90 mg) that was analyzed by SEC and \(^{19}\)F-NMR below.

Results and Discussion

3.3.1 Synthesis of n-alkylated polymers

As described above, our main synthetic goal was to incorporate CPD end-groups in telechelic step-growth aromatic polymers and then chain-extend them using bis(maleimide) linkers. This approach would result in polymers having essentially the same physical properties as the corresponding high-molecular-weight aromatic polymer, but with reversible backbone linkages.

In order to address the high glass transition temperatures which frustrate reversibility in Diels-Alder polymers, we selected two alkylated hydroquinones based on previous work\(^{32,65}\) and
prepared a series of aromatic polymers (Scheme 3-2 and Table 3-1). Since our RDA reactions start at around 120 °C, ideally we would have a polymer with a $T_g$ slightly (perhaps 10-20 °C) lower. The alkyl groups should exert a plasticizing effect and lower the $T_g$ of the poly(arylene ether)s while improving solubility; meanwhile the polymers would still be glassy materials at useful temperatures (i.e., below 80 °C). We targeted $M_n = 5,000$ Da (with HQ end-groups) for the alkylated polymers by controlling monomer stoichiometry. Based on our previous work in which we obtained molecular weights of about 25-40000 Da using CPD-MI chemistry, segments having $M_n = 5000$ Da would afford 5-8 DA linkages per chain, rather than having a reversible linkage in every repeat unit.

**Scheme 3-2.** Step-growth polymerization of n-alkylated hydroquinones and electrophilic monomers to yield poly(arylene ether)s with tailored $T_g$.

![Scheme 3-2](image)

**Table 3-1.** Physical properties of n-alkylated poly(arylene ether)s demonstrating $T_g < 100$ °C and $M_n$ at desired target of around 5000 Da.

<table>
<thead>
<tr>
<th>$G$ =</th>
<th>$R$ =</th>
<th>Yield (%)</th>
<th>$T_d$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$M_{n,NMR}$ (Da)</th>
<th>$M_{n,SEC}$ (Da)</th>
<th>$M_{w,SEC}$ (Da)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>n-Hexyl</td>
<td>92</td>
<td>410</td>
<td>70</td>
<td>5.4k</td>
<td>6.4k</td>
<td>10k</td>
<td>1.6</td>
</tr>
<tr>
<td>CO</td>
<td>n-Hexyl</td>
<td>94</td>
<td>444</td>
<td>76</td>
<td>n/d</td>
<td>24k</td>
<td>32k</td>
<td>1.3</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>n-Hexyl</td>
<td>79</td>
<td>377</td>
<td>93</td>
<td>5.1k</td>
<td>4.4k</td>
<td>5.3k</td>
<td>1.2</td>
</tr>
<tr>
<td>CO</td>
<td>n-Octyl</td>
<td>79</td>
<td>398</td>
<td>55</td>
<td>4.6k</td>
<td>4.5k</td>
<td>5.8k</td>
<td>1.3</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>n-Octyl</td>
<td>85</td>
<td>363</td>
<td>74</td>
<td>4.1k</td>
<td>4.1k</td>
<td>6.0k</td>
<td>1.5</td>
</tr>
</tbody>
</table>

We used a combination of $^1$H NMR spectrometry and SEC to establish molecular weight (Table 3-1). SEC molecular weights were around 5000 Da, consistent with our synthetic targets. Dispersities (Table 3-1) were somewhat lower than the expected value of 2.0 for step-growth
polymerization but at these molecular weights significant fractionation is probably occurring in the reprecipitation step. NMR end group analysis (Figure 3-1) was conducted by analyzing the signals arising from the first CH$_2$ on the aliphatic side chain of the HQ monomer. In Figure 3-1a, corresponding to the sulfone polymer (n-hexyl PAES), the two outside signals are assigned to the two chemically distinct end groups (2-alkyl vs. 3-alkyl), which are present in nearly equal populations, while the central signal is assigned to the repeat unit. (We cannot determine which of the two end group signals corresponds to either specific end-group isomer.) In the case of the ketone polymer (n-hexyl PEEK) only one of the end-group signals is resolved, so we had to assume that the ratio of end groups (2-alkyl vs. 3-alkyl) was the same as in the n-hexyl PAES, and subtract the projected integral of the unresolved end-group signal to obtain the integral of the repeat-unit signal.

DSC analysis of the alkylated polymers initially suggested that we might have lowered the T$_g$ too much (<100 °C), as most of the T$_g$ values were in the range 50–100 °C (Table 3-1). However addition of the linking groups (see below) does increase the T$_g$. TGA analysis also showed no negative impact of the flexible side chains with onset of degradation temperatures consistently around 400 °C.
Figure 3-1. End group analysis of hydroquinone-terminated n-hexyl PAES (a) and n-hexyl PEEK (b) segments using $^1$H NMR (CDCl$_3$, 400 MHz). Central signals arise from the benzylic CH$_2$ groups of the repeat unit n-hexylhydroquinone moieties while flanking signals arise from the 2-hexyl and 3-hexyl endgroups (not necessarily respectively).

To further investigate the effects of the alkyl side chains on $T_g$ we synthesized a series of poly(aryl ether sulfone) co-polymers with varying percentages of 2-hexylhydroquinone and 2-methyl hydroquinone. We used 2-methylhydroquinone instead of just hydroquinone so that we could maintain solubility through the entire series. The series should follow a similar trend as established in the Fox equation (eq 3) where the glass transition temperature of the copolymer is a result of the weight percent and glass transition temperature of the two separate homopolymers.

$$\frac{1}{T_g} = \frac{x_1}{T_{g1}} + \frac{1-x_1}{T_{g2}}$$  \hspace{2cm} (3)
Figure 3-2. Experimental (DSC) and theoretical (eq 2) glass transition temperatures of copolymers prepared from 4,4'-difluorodiphenyl sulfone, 2-methylhydroquinone, and increasing fraction of 2-hexylhydroquinone.

We see that these results roughly follow the trend of the Fox equation with each 10% of alkylated hydroquinone incorporated in the polymer decreasing the \( T_g \) of the polymer by approximately 10 °C (Figure 3-2).

3.3.2 Cyclopentadiene End-Capping

In order to end-cap the phenol terminated poly(arylene ether)s we chose a cyclopentadiene linker with two substituents in distal positions (not vicinal).\(^{19}\) The first substituent is a tert-butyl group which helps to prevent dimerization and destabilize the Diels-Alder adduct. The second is a nonafluorobiphenyl group to help further destabilize the Diels-Alder adduct which reduces the temperature needed for the retro-Diels-Alder reaction, and also to provide an electrophilic \( \text{C}_6\text{F}_5 \) moiety which can attach to the phenolic chain ends of the telechelic segments by \( \text{S}_{\text{NAr}} \) chemistry (Scheme 3-3). The resulting polymer was analyzed and characterized in a similar fashion to the previous polymers (Table 3-2). \(^1\)H-NMR analysis showed the disappearance of the end-groups
signals around 2.50 ppm and the appearance of a new end-group signal around 3.50 ppm, which corresponds to the CH$_2$ on the cyclopentadiene (Figure 3-3). Integration indicated the molecular weights increase by about 1000, which corresponds to the molecular weight of the two end-cappers added (416 g/mol for each). $^{19}$F-NMR detected the presence of fluorinated aromatics, further indicating successful attachment of the cyclopentadiene end-capper (Figure 3-4), and there was no signal corresponding to the unique para fluorine of the C$_6$F$_5$ group of the excess unreacted reagent, which was removed upon precipitation of the polymer. The $^{19}$F NMR spectrum was complicated by the presence of three cyclopentadiene tautomers. DSC analysis revealed an increase of approximately 10 °C from the previous hydroquinone-terminated polymers. This is likely due to the more rigid nature of the cyclopentadiene end-capper. TGA analysis displayed no real changes in the onset of degradation.

Scheme 3-3. End-capping reactions of poly(arylene ether)s to incorporate cyclopentadiene functionalities.

Table 3-2. Physical properties of CPD-end-capped n-alkyl PAES and PEEK segments prepared according to Scheme 3-3.

<table>
<thead>
<tr>
<th>G</th>
<th>$R_2$</th>
<th>Yield (%)</th>
<th>$T_d$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$M_n,NMR$ (Da)</th>
<th>$M_n,SEC$ (Da)</th>
<th>$M_w,SEC$ (Da)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>n-Hexyl</td>
<td>84</td>
<td>406</td>
<td>80</td>
<td>7.2k</td>
<td>7.1k</td>
<td>11.2k</td>
<td>1.6</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>n-Hexyl</td>
<td>90</td>
<td>399</td>
<td>103</td>
<td>6.1k</td>
<td>7.0k</td>
<td>9.0k</td>
<td>1.3</td>
</tr>
<tr>
<td>CO</td>
<td>n-Octyl</td>
<td>86</td>
<td>405</td>
<td>61</td>
<td>6.0k</td>
<td>6.4k</td>
<td>9.7k</td>
<td>1.5</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>n-Octyl</td>
<td>83</td>
<td>401</td>
<td>83</td>
<td>6.5k</td>
<td>6.9k</td>
<td>9.3k</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Figure 3-3. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of a CPD-end-capped OctylPAES segment showing integration of the CPD methylene in the end-group and the benzylic methylene of the repeat-unit octylhydroquinones.

Figure 3-4. $^{19}$F-NMR spectrum (CDCl$_3$, 376 MHz) of a CPD-end-capped OctylPAES segment. The upfield signal (-154 ppm) arises from the two fluorines adjacent to the oxygen atom, the downfield signal (-138 ppm) arises from the two fluorine adjacent to the cyclopentadiene moiety, and the rest of the signals arise from the meta fluorines.
3.3.3 Diels-Alder Chain Extension

The cyclopentadiene end-capped polymers were reacted with 1,6-hexanobismaleimide to chain extend the polymer from \( \sim 6,000 \, M_n \) up to \( \sim 25,000 \, M_n \) (Scheme 3-4). Analysis was conducted in the same fashion as for the other polymers (Table 3-3). As this DA polymerization represents an additional step-growth step, it is not surprising that dispersities are now closer to 2.0. With these higher-molecular-weight polymers there is less fractionation during reprecipitation. A useful comparison of size exclusion chromatographs (SEC) is presented in Figure 3-5 for the original HQ-terminated segments, the CPD-end-capped segments, and the DA-chain-extended polymers.

**Figure 3-5.** SEC (light scattering traces) of molecular weights of the HQ-terminated segments (HePAES, blue), the CPD-terminated segments (CPDHePAES, orange), and the segmented polymer after Diels-Alder chain extension (DAHePAES, gray).

\(^1\)H-NMR spectroscopic analysis confirmed a disappearance of the end-group signals at 3.50 ppm and the appearance of multiple adducts signals partially visible on the baseline (Figure 3-6). End-group analysis by NMR spectrometry was not possible. CPD tautomerization gives rise to
six possible DA adducts, and therefore no attempt was made to assign this region of the spectrum.  

$^{19}$F-NMR analysis also displayed minor changes consistent with a chemical reaction having occurred at the cyclopentadiene (Figure 3-7). Again it is not possible to assign this spectrum completely, but we can assign the upfield signal to the two fluorines adjacent to the linking oxygen atom. TGA analysis indicated no major change in the onset of degradation. TGA would not show an RDA event because this would require two adjacent DA linkages to disconnect and an entire 6000-Da segment to be volatized. DSC analysis revealed another increase of approximately 10 °C in $T_g$ likely due to the propagation of the polymer chain and the reduction of the chain ends. Other reports in the field of DA polymers have assigned RDA events to endotherms in their DSC data.  

Those events are likely masked by the broad glass transitions, which are near the temperature of the RDA events by design.

**Scheme 3-4.** Diels-Alder chain extension of CPD end-capped poly(arylene ether)s with 1,6-hexane-bis-N-maleimide as the linker.

![Scheme 3-4](image)

**Table 3-3.** Diels-Alder chain extended polymer properties displaying DP$_n$ of up to 5 starting from CPD-endcapped poly(arylene ether)s.

<table>
<thead>
<tr>
<th>G</th>
<th>R</th>
<th>Yield (%)</th>
<th>$T_d$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$M_{n,NMR}$ (Da)</th>
<th>$M_{n,SEC}$ (Da)</th>
<th>$M_{w,SEC}$ (Da)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>n-Hexyl</td>
<td>95</td>
<td>412</td>
<td>88</td>
<td>-</td>
<td>24.3k</td>
<td>65.0k</td>
<td>2.7</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>n-Hexyl</td>
<td>89</td>
<td>396</td>
<td>113</td>
<td>-</td>
<td>22.8k</td>
<td>40.0k</td>
<td>1.8</td>
</tr>
<tr>
<td>CO</td>
<td>n-Octyl</td>
<td>94</td>
<td>399</td>
<td>69</td>
<td>-</td>
<td>17.2k</td>
<td>39.5k</td>
<td>2.3</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>n-Octyl</td>
<td>76</td>
<td>393</td>
<td>100</td>
<td>-</td>
<td>26.2k</td>
<td>52.1k</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Figure 3-6. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of CPDHexylPAES after chain-extension with bis-maleimide to form DAHexylPAES. The CH$_2$ end group signal assigned to the cyclopentadiene end-capper is absent and broad Diels-Alder adduct signals are apparent near the baseline.

Figure 3-7. $^{19}$F-NMR spectrum of CPDHexylPAES (CDCl$_3$, 376 MHz) after chain-extension with bis-maleimide to form DAHexylPAES displaying new adduct signal present from $-136$ ppm to $-140$ ppm. Complete assignment of the spectrum was not attempted.
3.3.6 Reversibility and Self-Healing Tests

In order to demonstrate that these polymers could undergo smooth RDA chemistry, we first reacted DAOctylPAES with a 20-fold excess of N-4-fluorophenyl maleimide (FMI) at 150 °C (Scheme 3-5) to trap the cyclopentadiene chain ends formed during RDA events.

Scheme 3-5. Depolymerization of DAOctylPAES using FMI as a cyclopentadiene trap to enable analysis by $^{19}$F-NMR spectroscopy

Figure 3-8. $^{19}$F-NMR spectrum (CDCl$_3$, 376 MHz) of FMI reaction with DAOctylPAES. New FMI-end group adduct signals are present at $-112$ ppm which integrate appropriately with the fluorinated signals on the cyclopentadiene to indicate complete endcapping.
\[^{19}\text{F}\]-NMR spectrometry was used for analysis (Figure 3-8). In addition to the expected signals arising from the C\(_{12}\)F\(_{8}\) linking group, the spectrum contains four signals near -112 ppm that we assign (collectively) to isomeric forms of FMI-CPD adducts. The presence of these signals indicates trapping of the cyclopentadiene ends, but we were not able to perform end-group analysis because the main portion of the polymeric segment is not fluorinated. Therefore we turned to SEC (Figure 3-9), which clearly shows essentially complete reversion of the polymer to its segmented form (with allowances for the molecular weight of two FMI units, ca. 400 Da, and additional fractionation during reprecipitation). Analysis of the SEC results yielded a \(M_n\) of 26.2 kDa and a PDI of 1.99 for DAOctylPAES and a \(M_n\) of 8.3 kDa and PDI of 1.33 for the resulting FMI-CPD end-capped segments. These results indicated that at higher temperatures where Retro Diel-Alder is favored the cyclopentadiene-maleimide bonds can be broken \textit{regardless of which isomeric form the adduct assumed during cycloaddition and then reformed with a different maleimide}, both of which are necessary for healing in the bulk to occur.

\[\text{Figure 3-9. SEC (light scattering traces) of DAOctylPAES and FMI reaction. Depolymerization is evidenced by the shift of the trace from 15 min (26 kDa) for the segmented polymer to 18 min (8 Da) for the polymer heated for 2 h at 150 °C in NMP and then quenched.}\]
There are two main ways to test self-healing in polymers: scratch heal testing and the recovery of mechanical properties. To perform the scratch heal test a small piece of DAHePAES film ($T_g \approx 120^\circ C$) was cut on the surface with a razor blade and then placed in a pre-heated oven at 120 °C along with a Hexyl-Methyl PAES copolymer film ($T_g \approx 120^\circ C$). The films were allowed to heal in the oven for 1 h and then analyzed using an optical microscope. The film containing no Diels-Alder linkages showed no significant change in crack size (Figure 3-10), while the film that contained Diels-Alder linkages demonstrated complete crack closure (Figure 3-11), thus showing that self-healing is occurring only when Diels-Alder linkages are present.

**Figure 3-10.** Hexyl-Methyl PAES copolymer control film damaged with a razor blade (left) and after heating at 120 °C for 1 h (right). No evidence of significant healing is observed.

**Figure 3-11.** DAHePAES film damaged with a razor blade (left) and after heating at 120 °C for 1 h (right). Healing is evident by complete crack closure.
In order for the Diels-Alder healing system to achieve its goal it must be healable in the same location as the initial damage and thus we took the DA film and cut it again with a razor blade across the original cut that was healed. The film was once again placed in a vacuum oven preheated at 120 °C and allowed to heal for 1 h. After thermal treatment the film was once again analyzed using an optical microscope (Figure 3-12).

![Optical Microscope Image](image)

**Figure 3-12.** DAHePAES film second scratch with a razor blade before heating (left) and after heating at 120 °C for 1 h (right). Healing is evident once again due to crack closure.

The film once again displayed an inherent ability to heal the damage; however, complete crack closure was not fully realized. The reason for this is not fully clear; however, it may be due to the amount of reversible linkages present at the site of damage. Comparing our micrographs to those that have been published elsewhere\textsuperscript{15} suggests that our approach is quite promising.

In order to test recovery of mechanical properties, dogbones were cut from a sample of DAHePEEK film (the only film fully robust enough to do mechanical testing). Dogbones were also cut from a high molecular weight HePEEK standard film to serve as a control. Three sets of samples were then prepared (two sets for the control), one set with no razer blade damage, one set cut through once and healed, and one set cut through, healed and then cut through and healed at the same place. Heal cycles were conducted by treating the samples in an oven for 1.5 h at 120 °C
and then treating them for 24 h at 80°C to ensure complete rebonding of the DA linkages. Mechanical recovery was calculated using the maximum tensile strength at breaking for each sample.

**Figure 3-13.** Stress-strain data for Diels-Alder HexylPEEK samples. The top curve (orange, no damage) displays a breaking tensile strength of 30 MPa, the middle curve (gray, damaged with a razor blade and then healed) displays a breaking tensile strength of 26 MPa, and the bottom curve (blue, damaged with a razor blade, healed, then damaged with a razor blade and healed again) displays a breaking tensile strength of 12 MPa.

The healing efficiency of the first healing cycle was calculated to be ~87% and the second healing cycle was calculated to be ~40% for the DA polymer (Figure 3-13). In comparison the HexylPEEK control (Figure 3-14) displayed only 50% recovery of mechanical properties after a healing cycle. This result agrees with the results obtained from the optical microscopic analysis; the polymers containing DA linkages are effectively recombining to heal damage and restore properties.
Figure 3-14. Stress-strain data for HexylPEEK control samples. The top curve (blue, no damage) displays a breaking tensile strength of 18 MPa. The bottom curve (gray, damaged with a razor blade then healed 50 °C above the T_g) displays a breaking tensile strength of 9 MPa. These data show that only modest tensile-strength recovery can be realized through bulk flow.

These results are quite promising, especially when considering the CPD-based Diels-Alder healing systems reported by Murphy and co-workers, wherein only 49% recovery of breaking tensile strength on the 1st healing cycle and 19% recovery of breaking tensile strength on the 2nd healing cycle were found. Du and coworkers were able to obtain somewhat better mechanical recovery on further healing cycles with a maximum of 66% recovery of breaking tensile strength on the second healing cycle, using maleimide-furan linked segmented polyurethanes. However, their mechanical recovery percentages – especially over several cycles – likely gained the advantage of significant bulk flow as their T_g values are far below their healing temperatures.

3.4 Conclusion

We have demonstrated the synthesis and characterization of n-alkylated, HQ-terminated PAES and PEEK derivatives, their smooth conversion to CPD-end-capped telechelics, and their chain extension using Diels-Alder reactions with a bis-maleimide. These DA-linked segmented
polymers formed creaseable films, which demonstrated self-healing during scratch testing and recovery of mechanical properties up to 87% after one healing cycle.

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Chapter 4. Rapid, Selective Introduction of Electrophilic Side-Groups in Poly(aryl ether sulfone)s.

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Foreward. With the exception of supporting information relegated to the end of the dissertation, this chapter represents a stand-alone manuscript in preparation for submission to the journal Macromolecules. I performed all of the work reported in this chapter except as follows: Anastasia Volokhova performed preliminary synthetic experiments under my supervision, Mehdi Ashraf-Khorassani performed MS analyses, and Prof. Paul A. Deck supervised my work.

Graphical Abstract

Abstract

This article describes a method to introduce reactive, electrophilic \( \omega \)-bromopentyl side-groups into well-defined aromatic polymers after polymerization. \( \omega \)-Phenoxypentyl-substituted hydroquinones are incorporated into poly(aryl ether sulfone)s (PAESs), and then the \( \omega \)-phenoxy group is cleaved cleanly using boron tribromide, converting the pendant \( \omega \)-phenoxypentyl groups to \( \omega \)-bromopentyl groups. This approach avoids drawbacks such as chain cleavage, incomplete conversion, or the need for large excesses of reagents. These functionalized PAESs react smoothly with nucleophilic reagents (such as triethylamine) because the reactive group is extended from the
backbone. This strategy has potential in the synthesis of new polymers for anion-exchange fuel cell membranes.

**Keywords**

Poly(aryl ether sulfone), boron tribromide, hydroquinone. polycondensation
4.1 Introduction

Poly(aryl ether sulfone)s (PAESs) are aromatic polymers that belong to a class of high-performance thermoplastics typically used for engineering applications and membranes due to their excellent mechanical, thermal, and chemical stability.\textsuperscript{54,66} Divergent applications require both wide and fine tuning of polymer properties, which in turn requires synthetic access to new polymer chemistries and architectures. Because of the intrinsic stability of the PAES backbone, post-polymerization synthetic modification presents excellent opportunities for the modification of polymer structure and properties.\textsuperscript{67-68}

As an example of the importance of functionality in high-performance applications, PAESs have shown promise for use in films and membranes that transport water and water-dissolved species, especially ions.\textsuperscript{69-72} In particular, fuels cells require membranes that can transport ions while serving as barriers to dissolved gases. Fuel cells are important, alternative energy-conversion solutions to fixed-capacity batteries, because fuel can be continuously resupplied and converted to electrical energy.\textsuperscript{73} Of the two main types of ion-exchange membranes,\textsuperscript{74} anion-exchange membranes (AEM) have recently received more attention due to their enhanced properties over proton-exchange membranes (PEM). PEM fuel cells suffer from a sluggish oxygen-reduction reaction (ORR) and the corrosiveness of the acidic media toward many cell components.\textsuperscript{75-76} Currently, the most promising anion-exchange membranes have arylene backbones bearing pendant quaternary ammonium cations (QACs).

Because of the intrinsic basicity of PAES polycondensation synthesis, the most general approach to installing QACs in PAES systems is through post-polymerization oxidation of alkyl side-chains attached to the hydroquinone backbone moiety. This approach has notable drawbacks.\textsuperscript{75} For example, bromination of a methyl substituent (eq 1) followed by substitution
with trimethylamine affords a QAC-functionalized PAES. However, the bromination is difficult, requiring forcing reaction conditions (high temperatures, excess NBS) and also resulting in incomplete substitution. In some cases, decreases in the molecular weight of the polymer are found, suggesting chain-cleavage side-reactions.\textsuperscript{77} For high-performance applications, complete control over the polymer chemistry is strongly desired. It should be noted that there are polymeric systems other than PAES that have been functionalized by QACs for AEM applications,\textsuperscript{78-79} but the work described herein focuses on PAES chemistry.

\begin{equation}
\begin{array}{c}
\text{O} \quad \text{O} \quad \text{O} \\
\text{S} \quad \text{O} \quad \text{O} \\
\text{H} \quad \text{O} \\
\text{C} \quad \text{H}_3 \\
\end{array}
\xrightarrow{1. \text{NBS} \quad 2. \text{NMe}_3}
\begin{array}{c}
\text{O} \quad \text{O} \quad \text{O} \\
\text{S} \quad \text{O} \quad \text{O} \\
\text{Br} \quad \text{Me}_2\text{N} \\
\text{C} \quad \text{H}_3 \\
\end{array}
\end{equation}

In earlier work, we devised a general synthetic approach to various 2-substituted hydroquinones.\textsuperscript{65} As part of that work, we envisioned a substituent that would survive the conditions of PAES polycondensation but that could also be converted to a reactive, electrophilic group post-polymerization. Obviously, diaryl ethers are stable toward polycondensation conditions, but aryl alkyl ethers can be cleaved selectively using strong Lewis acids, especially boron tribromide.\textsuperscript{80-82} BBr\textsubscript{3} is an especially attractive reagent because reaction conditions for aryl alkyl ether cleavage are mild and workup conditions are simple. In any post-polymerization chemistry, mild reaction conditions and procedural simplicity are of paramount importance. We therefore envisioned developing a PAES bearing a pendant phenoxy group that we could cleave to form a reactive bromoalkyl group, averting the negative aspects of NBS chemistry. From the bromoalkyl substituent, we envisioned not only attachment of QACs for AEM applications, but a broader range of chemistries that might lead to applications of PAESs, including self-healing materials. An exhaustive review of self-healing polymeric systems would not be appropriate here,
but we envisioned systems that involved combinations of furan and maleimide functionalities, which have been reviewed elsewhere.$^{5,7,10}$

4.2 Experimental Section

**General:** Pinacolborane (Alfa-Aesar), Wilkinson’s catalyst (Strem), borane dimethyl sulfide (Oakwood), potassium persulfate (Oakwood), and silver nitrate (Sargent Welch) were used as received. Bis(4-fluorophenyl) sulfone (Oakwood) was recrystallized from toluene. BBr$_3$ (1 M in dichloromethane) was used as received from Sigma-Aldrich. NMP (Fisher) was dried and distilled from calcium hydride (80 °C at 10 mmHg). Toluene (Fisher) was used as received. Potassium carbonate (Oakwood) was dried in a vacuum oven at 100 °C for 2 d. Furfuryl alcohol (Oakwood) was used as received. Allyl phenyl ether (1a) was used as received from Oakwood. 2-(3-Phenoxypropyl)-1,4-hydroquinone (3a) was prepared as previously reported by us (“Method C”).$^{65}$ NMR spectra were collected using Agilent (Varian) U4-DD2 and Agilent (Varian) MR4 spectrometers ($^1$H at 400 MHz and $^{13}$C at 101 MHz). A line broadening window function (0.5 Hz) was applied to the FIDs prior to Fourier transformation, and Whittaker baseline corrections were applied to frequency-domain spectra. High-resolution mass spectra were collected using an Agilent 6220 with electrospray ionization (ESI) and time-of-flight (TOF) mass analysis; samples were introduced by direct infusion of a methanol solution containing 1% formic acid. Thermogravimetric analyses (TGA) were conducted on all of the polymer samples with a TA-Q50 under a stream of nitrogen (40 mL/min for the balance and 60 mL/min for the sample) from RT to 600 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was conducted on all of the polymer samples with a TA Instruments Q-2000 DSC under a stream of nitrogen. DSC thermograms were analyzed from the second heating cycle which was conducted from 0 °C to 250 °C at a heating rate of 5 °C/min. Molecular weights and dispersities were obtained using SEC run
with THF as a solvent at RT on two Agilent PLgel 10 µm MIXED-B columns connected in series with a Wyatt Dawn Helios 2 light scattering detector and a Wyatt Optilab Rex refractive index detector. Molecular weights were calculated by using dn/dc values obtained from the peak assuming 100% mass elution from the columns. Microscopic images were obtained using an AmScope M150C-E5 with 40x magnification. Polymer films of approximately 30 µm thick were placed on a glass slide and a glass cover was placed on top of the site of interest. Images were taken of a cross-section and cropped to show the relevant area of interest.

4.2.1 Previously reported compounds.

4.2.1.1. 4-Phenoxy-1-butene (1b). A literature procedure was adapted. A flame dried 500-mL round bottom flask was charged with 20.9 g (0.222 mol) of phenol, 25.0 g (0.185 mol) of 4-bromo-1-butene, 34.5 g (0.250 mol) of potassium carbonate, and 150 mL of acetonitrile. The mixture was stirred at 90 °C for 12 h. After cooling, the solvent was removed by rotary evaporation. The residue was extracted with dichloromethane (150 mL), washed with 10% aqueous potassium hydroxide (3 x 100 mL) and water (3 x 150 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was then vacuum distilled (90 °C at 15 mmHg, lit. bp 209 °C) to yield the desired alkene (6.92 g, 27%).

4.2.1.2. 5-Phenoxy-1-pentene (1c). A literature procedure was adapted. A flame dried 500-mL round bottom flask was charged with 19.0 g (0.202 mol) of phenol, 25.0 g (0.168 mol) of 5-bromo-1-pentene, 31.8 g (0.230 mol) of potassium carbonate, and 200 mL of acetonitrile. The mixture was stirred at 90 °C for 12 h. After cooling, the solvent was removed by rotary evaporation. The residue was dissolved in 200 mL of ether, washed with 10% aqueous potassium hydroxide (3 x 100 mL) and water (3 x 150 mL), dried over anhydrous magnesium sulfate, filtered, and
evaporated. The crude product was then vacuum distilled (60 °C at 0.2 mmHg, lit. bp 109 °C at 13 Torr) to give the desired alkene (23.0 g, 85 %).

4.2.2. *Previously unreported compounds.*

4.2.2.1. 2-(4-Phenoxybutyl)-1,4-hydroquinone (3b) was prepared according to “Method C” described by Kaurich et al., on a small scale (0.125 g of 1,4-benzoquinone). A 53% yield was obtained (0.150 g, mp 67.3-69.4 °C). $^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.53 (s, 1H, OH), 8.49 (s, 1H, OH), 7.32-7.20 (m, 2H), 6.94-6.88 (m, 3H), 6.58 (d, $^3$J = 9 Hz, 1H, CH), 6.50 (d, $^4$J = 3 Hz, 1H, CH), 6.40 (dd, $^3$J = 9 Hz, $^4$J = 3 Hz, 1H, CH), 3.96 (t, $^3$J = 6 Hz, 2H, CH$_2$), 2.53-2.46 (m, 2H, CH$_2$), 1.78-1.58 (m, 4H, CH$_2$). $^{13}$C($^1$H) NMR (101 MHz, DMSO-d$_6$) δ 149.6 (aromatic C), 147.5 (aromatic C), 129.5 (aromatic C), 128.8 (aromatic CH), 120.3 (aromatic CH), 116.4 (aromatic CH), 115.4 (aromatic CH), 114.4 (aromatic CH), 67.2 (OCH$_2$), 28.5 (CH$_2$), 25.9 (CH$_2$). HRMS ESI (+) Calc for C$_{16}$H$_{18}$O$_3$ (M*+) 258.1250; Found 258.1240. $R_f$ (Silica gel, 30% EtOAc/Hexanes) = 0.23.

4.2.2.2. 2-(5-Phenoxypentyl)-1,4-hydroquinone (3c) was prepared initially using “Method C” described by Kaurich et al., on a small scale (0.125 g of 1,4-benzoquinone). A 56% yield was obtained (0.176 g). This procedure, unfortunately, did not scale up well. For a larger scale we modified “Method A” from the same paper as follows. A flame-dried three-neck 500-mL round-bottomed flask was charged with 0.050 mol of BH$_3$(SMe$_2$) and 50 mL of ether. A nitrogen inlet and condenser were fitted. Liquid 5-phenoxy-1-pentene (0.150 mol) was added dropwise with magnetic stirring. Once all of the alkene was added and reflux had subsided, the solvent was distilled from the mixture using a steam bath. A solution of 1,4-benzoquinone (4.32 g, 0.040 mol) in ether (100 mL) was added to the solution using an addition funnel. Upon complete addition of
the 1,4-benzoquinone, the ether was distilled from the mixture using a steam bath. To the residue was added 40 mL of ethanol, 0.700 g iodine, and 20 mL of 30% aqueous hydrogen peroxide. The solution was stirred for 2 h at 45 °C. The resulting yellow precipitate (confirmed by NMR spectrometry as 2-(5-phenoxy)-1,4-benzoquinone) was collected on a filter, washed with ethanol (3 x 20 mL), and dried. Immediately after drying, the yellow intermediate was dissolved in 40 mL of THF and 40 mL of water. After the solid completely dissolved, 13.1 g (0.200 mol) of granular zinc and 8.56 g (0.160 mol) of ammonium chloride were added. The solution was allowed to stir rapidly until the transient yellow color completely disappeared. The solution was then extracted with ether, washed with water (3 x 20 mL), dried over MgSO₄, and evaporated. The brownish oil was dissolved in hot toluene/hexanes (50/50) and cooled in a freezer overnight to give the desired hydroquinone as a brown solid. The crystalline compound was collected on a filter, washed with hexane, and dried using a vacuum pump. (7.62 g, 70%. mp 79.1-81.5 °C. ¹H NMR (400 MHz, DMSO-d₆) δ 8.51 (s, 1H, OH), 8.45 (s, 1H, OH), 7.31-7.22 (m, 2H, aromatic CH), 6.95-6.83 (m, 3H, aromatic CH), 6.56 (d, ³J = 9 Hz, 1H, aromatic CH), 6.47 (d, ⁴J = 3 Hz 1H, aromatic CH), 6.38 (dd, ³J = 9, ⁴J = 3 Hz, 1H, aromatic CH), 3.93 (t, ³J = 7 Hz, 2H, CH₂), 2.45 (t, ³J = 7 Hz, 2H, CH₂), 1.79-1.66 (m, 2H, CH₂), 1.60-1.49 (m, 2H, CH₂), 1.48-1.37 (m, 2H, CH₂).¹³C{¹H}NMR (101 MHz, DMSO-d₆) δ 158.7 (aromatic C), 149.6 (aromatic C), 147.5 (aromatic C), 129.5 (aromatic C), 129.0 (aromatic CH), 120.3 (aromatic CH), 116.4 (aromatic CH), 115.4 (aromatic CH), 114.4 (aromatic CH), 112.8 (aromatic CH), 67.3 (CH₂), 29.7 (CH₂), 29.3 (CH₂), 28.7 (CH₂), 25.5 (CH₂). HRMS ESI (+) Calc for C₁₇H₂₀O₃ (M⁺) 272.1407; Found 272.1412. Rf (Silica gel, 30% EtOAc/Hexanes) = 0.25

4.2.2.3. General synthesis of Substituted Poly(aryl ether sulfone) (PAES-OPh). A flame-dried 100-mL Schlenk flask was charged with 4.90 g (0.018 mol) of 3c, 2.902 g (0.021 mol) potassium
carbonate, and 4.58 g (0.018 mol) bis(4-fluorophenylsulfone), followed by 80 mL of NMP and 80 mL of toluene. A Dean-Stark trap with a condenser and nitrogen inlet was fitted to the flask and the mixture was stirred at 160 °C for 4 h. Following the complete (apparent) removal of toluene, the temperature was raised to 180 °C and the mixture was allowed to stir for an additional 12 h. The solution was cooled to RT and added to rapidly stirred water (300 mL) to precipitate the polymer. In some cases a small amount of brine (30 mL) was added to obtain better precipitation. The polymer was collected on a filter, dissolved in chloroform (20 mL), and reprecipitated in methanol (300 mL). The resulting brown solid was collected in a fritted glass funnel, washed with methanol 3 x 30 mL, and dried in a vacuum oven for 24 h at 100 °C to give the desired polymer as a tan solid (7.32 g, 82% yield). 

\[
{^1}H \text{ NMR (400 MHz, CDCl}_3) \delta 7.90-7.81 (m \ 4H), 7.26-7.20 (m, 2H), 7.10-6.79 (m, 10H), 3.88 (t, J = 6 Hz 2H), 2.52 (t, J = 8 Hz, 2H), 1.76-1.66 (m, 2H), 1.64-1.54 (m, 2H), 1.49-1.37 (m, 2H).
\]

\[
{^{13}}C \text{ NMR (101 MHz, CDCl}_3) \delta 162.2 \text{ (aromatic C), 162.0 (aromatic C), 159.1 (aromatic C), 152.0 (aromatic C), 149.5 (aromatic C), 137.2 (aromatic C), 135.8 (aromatic C), 135.5 (aromatic C), 130.0 (aromatic CH), 129.6 (aromatic CH), 120.7 (aromatic CH), 119.4 (aromatic CH), 117.7 (aromatic CH), 117.0 (aromatic CH), 114.5 (aromatic CH), 67.6 (CH}_2, 30.1 (CH}_2, 29.6 (CH}_2, 29.1 (CH}_2, 25.9 (CH}_2).
\]

4.2.2.4. General Cleavage of Phenyl Ether Side Chain (BrPAES). A flame-dried 100-mL Schlenk flask was charged with 4.00 g (8.20 mmol) of PAES-OPh and 10 mL of dry dichloromethane. The solution was cooled to 0 °C using an ice bath, and BBr\textsubscript{3} (10 mL, 1.0 M in dichloromethane) was added dropwise using a syringe fitted with a 6” steel needle. The mixture was stirred overnight at RT. The reaction was then cautiously quenched by dropwise addition of methanol (10 mL). Once the fuming completely subsided the remaining solution was poured into methanol (300 mL). The resulting brown solid was filtered, washed with methanol (3 x 30 mL), and dried under vacuum.
for 24 h at 100 °C to give the desired product (3.82 g, 96% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96-7.82 (m, 4H), 7.12-6.85 (m, 7 H), 3.31 (t, $^3$J = 7 Hz, 2H), 2.51 (t, $^3$J = 8 Hz, 2H), 1.84-1.69 (m, 2H), 1.64-1.48 (m, 2H), 1.45-1.33 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.2 (aromatic C), 162.0 (aromatic C), 152.1 (aromatic C), 149.4 (aromatic C), 137.0 (aromatic C), 135.7 (aromatic C), 135.5 (aromatic C), 130.0 (aromatic C), 130.0 (aromatic CH), 122.6 (aromatic CH), 119.5 (aromatic CH), 117.7 (aromatic CH), 116.9 (aromatic CH), 33.8 (CH$_2$), 32.4 (CH$_2$), 29.9 (CH$_2$), 29.0 (CH$_2$), 27.8 (CH$_2$).

4.2.2.5. **Synthesis of PAES Bearing Pendant Furfuryl Group.** A flame-dried 100-mL Schlenk flask was charged with 0.200 g (0.40 mmol) of BrPAES, 3 mL of THF, 0.118 g (1.20 mmol) of furfuryl alcohol, and 0.036 g (1.5 mmol) of sodium hydride. The mixture was allowed to stir at 60 °C for 18 h under nitrogen. The mixture was cooled to RT and poured into rapidly stirring methanol (50 mL). The precipitated crude polymer was collected on a filter, washed with methanol (3 x 20 mL), and dried under vacuum to give the desired product (0.155 g, 75% yield). The $^1$H NMR spectrum (CDCl$_3$, 400 MHz) showed new signals that we assigned to the furfuryl ether, notably 7.36, 6.30, 6.26, 4.38, and 3.39 ppm (the furan CH’s and CH$_2$’s on either side of the ether). Additional signals (5.69, 4.90, and 2.00 ppm) indicated that some elimination of the bromoalkyl group had occurred.

4.2.2.6. **Synthesis of Crosslinked Furfuryl Alcohol PAES.** A 3-dram vial was charged with 0.1000 g of furfuryl alcohol PAES (0.200 mmol) and 0.003 g (0.010 mmol) of 1,6-hexane-bis-N-maleimide. The mixture was dissolved in 1 mL of chloroform, filtered, and cast onto a glass plate. The solvent was allowed to evaporate for 15 h, and the plate was placed in an oven at 120 °C for 15 h to cure. The resulting film was then soaked in water for 30 min, lifted off the glass plate using a razor blade, and dried under vacuum for 24 h, to afford a transparent orange, creaseable film that was entirely insoluble in chloroform.
4.3 Results and Discussion

As part of a broader effort to explore functionalization of aromatic polymers generally, we wanted to develop a practical synthesis of well-defined aromatic polymers (especially PAESs) bearing electrophilic groups pendant to the backbone, which would serve as reactive sites for further functionalization, including cross-linking and grafting. Whereas methods exist to achieve bromomethylation of hydroquinone moieties, these are beset by various problems such as inefficiency and undesirable side-reactions. Moreover, bromomethyl groups may be somewhat unreactive owing to their proximity to the polymer backbone. Our alternative approach uses a pendant phenyl alkyl ether that can be cleaved to a bromoalkyl group using boron tribromide.

Scheme 4-1 describes the synthesis of the three phenoxyalkyl-substituted hydroquinones (3) that were used for this study. The preparation of the phenyl ethers (1) is generally unremarkable, except that the homoallylic ether 1b was formed in low yield (27%) owing to competing elimination to form 1,3-butadiene. The remaining steps were reported previously by us for 3a and were extended to the homologues 3b and 3c in straight-forward fashion. All three congeners (3a, 3b, and 3c) are colorless to pale gray microcrystalline solids that were stable and fully characterized. In a subsequent section, an alternative synthesis of the phenoxypentyl derivative 3c will be described.
We started our study of polycondensation with the least expensive of the three hydroquinones, the phenoxypropyl derivative 3a (Scheme 4-2). However, we immediately noticed that molecular weights, whether determined by SEC or NMR, were surprisingly low. NMR spectrometric analysis also revealed additional unexplained signals, which did not decrease in intensity despite subjecting the polymer to multiple reprecipitation and drying cycles. The spacer length between the hydroquinone and phenoxy group (3 CH₂ groups) enables a six-membered cyclic ether to form by displacement of phenoxide at the end group of the growing polymer chain (Scheme 4-2). In the NMR spectrum (Figure 4-1), we assign the triplet at 4.2 ppm to the OCH₂ group of the cyclic ether and the triplet at 3.9 ppm to the OCH₂ of the desired uncyclized phenoxypropyl group. In addition, there is evidence in the spectrum (small triplet at 7.4 ppm) that the released phenoxide reacted, at least partially, with the 4-fluorophenyl chain ends to form diphenyl ether end groups. We were able to confirm this assignment while also testing the cleavage of the phenoxy substituent by treating this polymer with BBr₃. Both the cyclic and acyclic ethers are cleaved to afford the same 3-bromopropyl substituent, characterized by the three signals between 3.5 and 2.0 ppm in Figure 4-2b.
Scheme 4-2. Side reaction cyclization mechanism competing with polymerization of 3a that limits obtaining high molecular weights.

Figure 4-1. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of polymeric product obtained in the reaction shown in Scheme 4-2 showing signals at 7.4 ppm and 4.2 ppm resulting from the competing cyclization side reaction.
The small triplet at 7.4 ppm assigned to the phenoxy end group is unchanged because BBr$_3$ does not cleave diaryl ethers. We tentatively assign the additional small signals between 3.5 and 2.0 ppm in the NMR spectrum of the BBr$_3$-treated polymer (Figure 4-2b) to end groups.

In order to test the hypothesis of ring-closure (Scheme 4-2), we studied the self-reactions of the phenoxyalkyl-substituted hydroquinones on their own by subjecting them to the conditions of polymerization (0.125 g, 0.50 mmol, 3a, 0.083 g, 0.60 mmol, potassium carbonate, 1 mL NMP, 180 °C, 16 h) but without the sulfone monomer present (Scheme 4-3). We did not isolate and fully characterize the cyclic product from 3a, but the NMR spectrum of the mixture (Figure 4-3c) clearly contains a signal (triplet at 4.14 ppm) that corresponds neatly to the cyclic end group assigned in Figure 4-1b.

**Scheme 4-3.** Model study of 3a under polymerization conditions to observe the competing cyclization side reaction.
Figure 4-2. $^1$H-NMR spectra (CDCl$_3$, 400 MHz) comparison of 3a-PAES before (a) and after (b) treatment with BBr$_3$. The signal at 4.2 ppm is noticeably gone after treatment with BBr$_3$ whereas the signal at 7.4 ppm still remains due to the inability of BBr$_3$ to cleave diaryl ethers.

Figure 4-3. $^1$H-NMR spectra (CDCl$_3$, 400 MHz). (a) Monomer 3a, (b) 3a-PAES with undesired end-group cyclization chemistry, and (c) Monomer 3a after treatment with K$_2$CO$_3$ (NMR, 180 °C, 18 h) showing cyclization. The signal at 4.2 ppm in spectrum (b) matches the large signal present at 4.2 ppm in spectrum (c).
In fact, as we were developing this chemistry, it was the observation of the cyclization side-reaction shown in Scheme 4-2 that led us to synthesize the homologues 3b and 3c. Rings larger than six-membered form less quickly,\(^\text{87-88}\) and we reasoned that adding one or two CH\(_2\) groups between the hydroquinone and the phenoxy group would limit the cyclization side reaction or prevent it entirely. We found that subjecting either homologue 3b or 3c to the same reaction conditions as 3a (Scheme 4-3) returned only the starting hydroquinones (Figure 4-4). Noting also that the synthesis of 3b was much less efficient than 3c (Scheme 4-1), we continued our study using only the monomer with the (CH\(_2\)\(_5\)) spacer (3c).

**Figure 4-4.** \(^1\)H-NMR spectra (DMSO-d\(_6\), 400 MHz) showing absence of cyclization upon treatment of (a) monomer 3c and (b) 3b monomer with K\(_2\)CO\(_3\) in NMP at 180 °C for 18 h. The expected pseudotriplet at 4.2 ppm based on the cyclization of 3a is not observed.

The polymerization of 3c proceeded smoothly to give the corresponding PAES-OPh derivative (Scheme 4-4). All signals were assignable in the \(^1\)H-NMR and treatment with BBr\(_3\) gave complete conversion to BrPAES with overall yield of the polymer being 96% (Figure 4-5).
Scheme 4-4. Step-growth polymerization of 3c to a poly(arylene ether) sulfone and subsequent side-group cleave with BBr₃ to yield a pendant alkyl bromide.

Figure 4-5. ¹H-NMR spectrum comparison of PAES-OPh (a) and BrPAES (b). The complete disappearance of the signal at 3.9 ppm and the appearance of the signal at 3.3 ppm indicates complete conversion of the phenyl ether group into an alkyl bromide.

Because these results were very promising we optimized the synthetic chemistry to improve the efficiency of the monomer synthesis (3c). In particular we wanted to avoid the need for a costly rhodium catalyst, and we especially wanted to obviate liquid chromatography. We decided to revisit the synthesis of alkylated hydroquinones using BH₃-SMe₂. The main limiting factors for this method are the loss of the alkene (only one of the three alkyl groups of a trialkylborane are
transferred to benzoquinone) and also difficulty in removing the borinic acid byproduct. We speculated that the phenoxy-pentyl-1,4-benzoquinone derivative might be more easily isolated than the corresponding hydroquinone. Ultimately, we optimized a scalable procedure that is quite efficient despite the counter-intuitive step of oxidizing the crude hydroquinone (with I₂/H₂O₂), isolating it by crystallization, and reducing it using dissolving zinc (Scheme 4-5). The key to this strategy was the use of ethanol, which is not only an effective solvent for the oxidation reaction, but a poor solvent for the benzoquinone product.

**Scheme 4-5.** Modified synthesis of 3c for larger scale without needing expensive Rh catalyst.

4.3.1 Thermal Analysis

Thermo-gravimetric analysis (TGA) was performed on the synthesized polymers. A comparison of TGA curves between **PAES-OPh** and **BrPAES** is shown in Figure 4-6. **PAES-OPh** displayed 10% weight loss around 417 °C whereas **BrPAES** displayed 10% weight loss at a much lower temperature of 340 °C. It is noteworthy that the first feature in the thermogram of the **BrPAES** corresponds roughly to the loss of HBr (ca 17%). The remaining decomposition seems to occur at about the same temperature as the phenoxy-pentyl derivative.
Figure 4-6. TGA Comparison of PAES-OPh and BrPAES. The prominent difference in weight loss can be attributed to the loss of HBr for BrPAES.

Differential scanning calorimetry (DSC) was performed on the synthesized polymers to determine their glass transition temperatures ($T_g$). PAES-OPh displays a $T_g$ around 85 °C and BrPAES displays a $T_g$ around 113 °C. This trend is likely due to the more compact and rigid nature of the alkyl bromide, which would serve to increase the $T_g$ compared to the phenyl ether group.

4.3.2 Molecular Weight Determination

Size exclusion chromatography (SEC) was performed on the synthesized polymers to determine their molecular weights. A comparison of PAES-OPh and BrPAES is shown in Figure 4-7. As can be seen from the chromatogram no major change in molecular weight is seen, indicating that the cleavage reaction with BBr$_3$ does not induce chain scission commonly seen in the NBS route to brominated poly(aryl ether sulfone). Analysis of the molecular weight values...
obtained also reveals no major decreases or unexpected changes: **PAES-OPh** $M_n = 20.0 \text{ kDa}$ $M_w = 27.0 \text{ kDa}$ PDI = 1.4. **BrPAES** $M_n = 18.0 \text{ kDa}$ $M_w = 26.0 \text{ kDa}$ PDI = 1.4.

![Figure 4-7](image)

**Figure 4-7.** SEC data (light scattering) of **PAES-OPh** (blue) and **BrPAES** (orange). No indication of a significant change in molecular weight can be seen, nor any formation of crosslinks.

Our next step was to functionalize the polymer further by substitution of the bromide with other groups, especially trialkylammonio substituents. Adapting the homogeneous amination procedure of Hickner and co-workers, the 5-bromopentyl-substituted **PAES** was treated with trimethylamine in DMAC at 25 °C for 2 d, and the resulting solution was cast onto a glass plate and dried in a vacuum oven (60 °C). Note here that Hickner’s procedure was intended for the conversion of a bromomethyl-substituted **PAES** (thus, a benzylic bromide), and his reagent was excess aqueous trimethylamine. We obtained a transparent film, and a sample was dissolved in DMSO-$d_6$ for NMR spectroscopic analysis. The NMR spectrum showed only partial conversion to the triethylammoniopentyl-substituted polymer (along with residual DMAC). The signal at 3.17 ppm is characteristic of the $\text{NCH}_2\text{CH}_3$ of the triethylammonio group; however, the presence of the
CH$_2$Br signal at 3.36 ppm still indicated that the reaction was incomplete and required optimization (Figure 4-8).

![NMR spectra](image)

**Figure 4-8.** $^1$H-NMR spectra (CDCl$_3$, 400 MHz). (a) Initial BrPAES; (b) BrPAES after treatment with Et$_3$N (DMAC, 25 °C, 2 d). While characteristic triethylammonio signals can be seen at 1.1 ppm and 3.17 ppm the presence of the signal at 3.36 ppm indicates the reaction was incomplete.

Based on this result we decided to conduct an NMR tube study using 0.015 g of BrPAES and 0.032 g (tenfold excess) of triethylamine dissolved in 0.6 mL of DMSO-$d_6$ (Figure 4-9). NMR spectra of BrPAES and BrPAES + triethylamine (at t=0) are shown for comparison. The sample was heated at 80 °C and analyzed at intervals. After 6 h approximately 60% conversion to the triethylammonium bromide was evidenced by the shift of the CH$_2$Br at 3.36 ppm to 3.01 ppm (CH$_2$NCH$_2$CH$_3$). After 18 h complete conversion was noted.
Figure 4-9. $^1$H-NMR spectra (DMSO-$d_6$, 400 MHz). (a) BrPAES; (b) BrPAES and Et$_3$N after ca. 15 min at 25 °C; (c) BrPAES and Et$_3$N after 6 h at 80 °C; (d) BrPAES and Et$_3$N after 18 h at 80 °C. Approximately 60% conversion to the triethylammonium bromide is realized after 6 h of heating at 80 °C and complete conversion is seen after heating for 18 h at 80 °C.

To further explore the general synthetic utility of the bromopentyl-substituted PAES, we speculated that the pendant alkyl bromides should be susceptible to nucleophilic displacement with furfuryl alcohol under appropriate conditions. The furfuryl group was chosen because it could when serve as a Diels-Alder diene for reversible cross-linking and other “self-healing” chemistries – which are presently under investigation in our laboratories and will be reported elsewhere. Conditions were first optimized using a soluble model, 1-bromododecane (1BD), and reactions were evaluated using $^1$H NMR spectroscopy (Figure 4-10). Combining 1BD with furfuryl alcohol and sodium hydride in THF (reflux, 18 h) resulted in about 90% conversion of the starting bromide. The characteristic signals of unreacted 1BD (Figure 4-10a) are found at 3.4 ppm (triplet, CH$_2$Br)
and 1.8 ppm (pentet, CH\textsubscript{2}CHBr). The product spectrum (Figure 4-10c) reveals a small amount of unreacted furfuryl alcohol (furyl-CH\textsubscript{2}O at 4.56 ppm), as well as the desired substitution product (furyl-CH\textsubscript{2}O at 4.43 ppm), and the starting bromide at an approximately 10% level. There was a minor side-product (about 7%) that we assigned to elimination (multiplets at 5.81, 4.97, 4.93 for the terminal CH=CH\textsubscript{2} and a pseudo-quartet at 2.0 ppm for the allylic CH\textsubscript{2}).

![Figure 4-10. ¹H-NMR spectra (CDCl\textsubscript{3}, 400 MHz). (a) 1BD standard; (b) furfuryl alcohol standard, (c) Product of reaction of 1BD and furfuryl alcohol (NaH, THF, 65 °C, 18 h, then aqueous workup). (d) inset showing minor elimination product after expansion of the baseline in spectrum (c); (e) Product of reaction of 1BD and furfuryl alcohol (K\textsubscript{2}CO\textsubscript{3}, DMF, 90 °C, 18 h, then aqueous workup). The reaction with NaH/THF gives the desired dodecyl furfuryl ether whereas reaction with K\textsubscript{2}CO\textsubscript{3}/DMF gives a complex mixture of unidentifiable products.]

Due to the undesirable presence of an elimination side-reaction, we tried the same model substitution but using potassium carbonate as the base and DMF as the solvent (18 h at 90 °C). We reasoned that the more polar solvent and weaker base should favor substitution over
elimination. However, aside from unreacted furfuryl alcohol and residual DMF (8.0, 2.94, and 2.85 ppm), we were unable to assign the NMR spectrum of the product (Figure 4-10e). The conversion of the starting bromide is complete, but we cannot identify the product. Notably, additional signals appeared in the downfield (furan) region, suggesting decomposition of the furan which is documented in the literature.\textsuperscript{89}

Based on our model chemistry, we converted the bromopentyl-substituted PAES using furfuryl alcohol and sodium hydride in THF (reflux, 18 h). Using our model spectra to assign the spectrum of the polymer (Figure 4-11) we determined that conversion of the pendant alkyl bromide was complete, but elimination was more competitive than the model reaction predicted. About 30% of the pendant bromides were converted to terminal alkenes.

![Figure 4-11. ¹H-NMR spectra (CDCl₃, 400 MHz). (a) BrPAES; (b) BrPAES after treatment with furfuryl alcohol and NaH (THF, 65 °C, 18 h). Substitution of the alkyl bromide is quantitative; however, the elimination side product is slightly favorable (signals at 5.67 ppm, 4.90 ppm, and 2.0 ppm) giving 30% of the side with alkene functionality.](image-url)
Next we attempted to use the furfuryl alcohol substituted polymer (**FA-PAES**) in a preliminary study of self-healing chemistry. While having pendant alkenes also present in the polymer is undesirable, they should not interfere with Diels-Alder chemistry. We reasoned that a reaction of **FA-PAES** with 1,6-hexane-bis-N-maleimide in solution would result in a cross-linked polymer (a gel) that would be difficult to isolate and purify. Accordingly we carried out crosslinking in the bulk by co-dissolving **FA-PAES** and 1,6-hexane-bis-N-maleimide (furfuryl:maleimide ratio of 8:1 to minimize the formation of dangling maleimides) and casting a film. Subsequent heating at 120 °C after the solvent evaporated afforded a crosslinked film. Placing a sample of this polymer in chloroform showed minimal swelling and no dissolution after 1 d.

We next attempted to demonstrate the reversibility of the crosslinked **FA-PAES** by performing scratch-healing tests. A small film of the polymer was scratched on the surface with a razor blade and then placed in an oven preheated at 120 °C. The sample was analyzed after 1 h (Figure 4-12). A large reduction in the size of the cut was seen and can likely be attributed to the Retro Diels-Alder reaction, allowing for chains to flow and reconnect to help close the crack.

*Figure 4-12.* Preliminary scratch healing tests on **FA-PAES** crosslinked network. Left (before heating), middle (after heating for 1 h at 120 °C), and right (after heating for 1 h at 190 °C). Partial crack closure can be noted after the initial healing treatment; however, further heating for longer times or even higher temperatures (>120 °C) yielded no additional crack closure.
However, despite additional heating at 120 °C for 1 h and even 24 h no further crack closure can be noticed. Increasing the temperature to 190 °C for 1 h also did not help the crack completely close. This phenomenon may be due to the number of reversible linkages generated in the polymer network, making complete healing of the fractured surface not possible. It would be fair to describe these findings as inconclusive but promising.

4.5 Conclusion

In summary we have developed a method to generate poly(aryl ether sulfone)s bearing pendant alkyl bromide groups without any of the drawbacks of the currently employed literature methods. Preliminary findings show that this system should serve as a synthetic platform for ionomers and other post-functionalized aromatic polymers.

Acknowledgments

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Chapter 5  Overall Conclusions and Future Work

This dissertation described the synthesis of alkylated hydroquinones, their incorporation in poly(arylene ether)s, self-healing in polymers, and post-polymerization modification of phenyl ether poly(arylene ether)s. Chapter 1 explored the current research effort behind self-healing materials and what has been studied in the literature. Chapter 2 explored the use of several boron reagents to create n-alkylated hydroquinones necessary to control the $T_g$ of poly(arylene ether)s. Chapter 3 explored the properties of n-alkylated poly(arylene ether)s and their subsequent end-capping and chain extension with Diels-Alder chemistry. The incorporation of Diels-Alder linkages in the backbone enables self-healing in the bulk. Chapter 4 explored a novel use of a special hydroquinone to enable post-polymerization modification of poly(arylene ether)s that has not been explored in the literature. The use of BBr$_3$ to generate a pendant alkyl bromide on the polymer backbone opens up many pathways to substitution reactions with differing species and also ion-containing polymers.

The main hypothesis of this dissertation was borne out: That bringing the $T_g$ of the polymer below the RDA temperature would enable self-healing in the bulk.

A system of ongoing interest in our group is the case of poly(aryl ether sulfone)s containing bromopentyl side chains (Scheme 5-1). This dissertation generated “proof of concept” that may allow this research to proceed with agency funding.

**Scheme 5-1.** Conversion of bromopentyl-functionalized PAES into a linear ionomer.
Appendix A  Supporting information for Chapter 2. Synthesis of 2-substituted hydroquinone derivatives from 1,4-benzoquinone and allyl ethers

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\[
\begin{align*}
\text{ Allyl ether } & \rightarrow \text{ 2-substituted hydroquinone derivative } \\
O & \quad O
\end{align*}
\]
**Figure A1.** $^1$H-NMR spectrum (DMSO-$d_6$, 400 MHz) of 2-hexylhydroquinone. Water is present at 3.3 ppm. The spectrum is referenced to the solvent residual isotopomer at 2.50 ppm.
Figure A2. $^1H^{13}C$-NMR spectrum (DMSO-d$_6$, 101 MHz) of 2-hexylhydroquinone. The spectrum is referenced to the solvent at 39.5 ppm.
Figure A3. $^1$H-NMR spectrum (DMSO-d$_6$, 400 MHz) of 2-octylhydroquinone. H$_2$O is present at 3.3 ppm. The spectrum is referenced to the solvent residual isotopomer at 2.50 ppm.
Figure A4. $^1$H$^{13}$C-NMR spectrum (DMSO-d$_6$, 101 MHz) of 2-octylhydroquinone. The spectrum is referenced to the solvent at 39.5 ppm.
Figure A5. $^1$H-NMR spectrum (DMSO-d$_6$, 400 MHz) of 2-cyclooctylhydroquinone. Water is present at 3.3 ppm (broad signal). The spectrum is referenced to the solvent residual isotopomer at 2.50 ppm.
Figure A6. $^{13}$C-NMR spectrum (DMSO-d$_6$, 101 MHz) of 2-cyclooctylhydroquinone. The spectrum is referenced to the solvent at 39.5 ppm.
Figure A7. $^1$H-NMR spectrum (DMSO-d$_6$, 400 MHz) of 2-(3-ethoxypropyl)-1,4-hydroquinone. Water is present at 3.3 ppm. The spectrum is referenced to the solvent residual isotopomer at 2.50 ppm.
Figure A8. $[^1\text{H}]^{13}\text{C-NMR}$ spectrum (DMSO-d$_6$, 101 MHz) of 2-(3-ethoxypropyl)-1,4-hydroquinone. The spectrum is referenced to the solvent at 39.5 ppm.
Figure A9. $^1$H-NMR spectrum (DMSO-<tex>d_6</tex>, 400 MHz) of 2-(3-(2,2,2-trifluoroethoxy)propyl)-1,4-hydroquinone. Water is present at 3.3 ppm. The spectrum is referenced to the solvent residual isotopomer at 2.50 ppm.
Figure A10. $^1$H$^{13}$C-NMR spectrum (DMSO-d$_6$, 101 MHz) of 2-(3-(2,2,2-trifluoroethoxy)propyl)-1,4-hydroquinone. The spectrum is referenced to the solvent at 39.5 ppm.
Figure A11. $^{19}$F$^{13}$C-NMR (DMSO-d$_6$, 101 MHz) of 2-(3-(2,2,2-trifluoroethoxy)propyl)-1,4-hydroquinone showing CF$_3$ group at ca. 125 ppm. The spectrum is referenced to the solvent at 39.5 ppm (not shown in this expansion).
Figure A12. $^{19}$F-NMR spectrum (DMSO-d$_6$, 376 MHz) of 2-(3,2,2-trifluoroethoxy)propyl)-1,4-hydroquinone.
Figure A13. $^1$H-NMR spectrum (DMSO-d$_6$, 400 MHz) of 2-(3-(2,2,3,3,3-pentafluoropropoxy)propyl)-1,4-hydroquinone. Water is present at 3.3 ppm. The spectrum is referenced to the solvent residual isotopomer at 2.50 ppm.
Figure A14. $^1$H$^{13}$C-NMR spectrum (DMSO-d$_6$, 101 MHz) of 2-(3-(2,2,3,3,3-pentafluoropropyloxy)propyl)-1,4-hydroquinone. The spectrum is referenced to the solvent at 39.5 ppm.
Figure A15. $^{19}\text{F}^{13}\text{C}-\text{NMR}$ (DMSO-$d_6$, 101 MHz) of 2-(3-(2,2,3,3,3-pentafluoropropoxy)propyl)-1,4-hydroquinone showing CF$_2$ at 114 ppm and CF$_3$ at 119 ppm. The spectrum is referenced to the solvent at 39.5 ppm.
Figure A16. $^{19}$F-NMR spectrum (DMSO-$d_6$, 376 MHz) of 2-(3-(2,2,3,3,3-pentafluoropropoxy)propyl)-1,4-hydroquinone.
Figure A17. $^1$H-NMR spectrum (DMSO-d$_6$, 400 MHz) of 2-(3-phenoxypropyl)-1,4-hydroquinonone. H$_2$O is present at 3.3 ppm. The spectrum is referenced to the solvent residual isotopomer at 2.50 ppm.
Figure A18. $^1$H$^{13}$C-NMR spectrum (DMSO-d$_6$, 101 MHz) of 2-(3-phenoxypropyl)-1,4-hydroquinonone. The spectrum is referenced to the solvent at 39.5 ppm.
**Figure A19.** $^1$H-NMR spectrum (DMSO-d$_6$, 400 MHz) of a mixture of 2-(3-(4-bromophenoxy)propyl)-1,4-hydroquinone (ca. 70%) and 2-(3-phenoxypropyl)-1,4-hydroquinone (ca. 30%). H$_2$O is present at 3.3 ppm. The spectrum is referenced to the solvent residual isotopomer at 2.50 ppm. The pendant 4-bromophenyl group is assigned to the two pseudo-doublets at 7.43 and 6.90 ppm.
Figure A20. $^{1}H^{13}$C-NMR spectrum (DMSO-d$_6$, 101 MHz) of a mixture of 2-(3-(4-bromophenoxy)propyl)-1,4-hydroquinone (ca. 70%) and 2-(3-phenoxypropyl)-1,4-hydroquinone (ca. 30%). The spectrum is referenced to the solvent at 39.5 ppm.
Figure A21. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of 2-(3-phenoxypropyl)-1,4-benzoquinone. H$_2$O is present at 1.6 ppm. TMS is present at 0.0 ppm. Signals at ca. 1.3 ppm are assigned to unidentified impurities. The spectrum is referenced to the solvent residual isotopomer at 7.26 ppm.
Figure A22. $^1$H$^{13}$C-NMR spectrum (CDCl$_3$, 101 MHz) of 2-(3-phenoxypropyl)-1,4-benzoquinone. The spectrum is referenced to the solvent at 77.0 ppm.
Figure A23. $^1$H-NMR spectrum (DMSO-d$_6$, 400 MHz) of 2-(3-(4-bromophenoxy)propyl)-1,4-hydroquinone. Water is present at 3.3 ppm. The spectrum is referenced to the solvent residual isotopomer at 2.50 ppm.
Figure A24. $^1\text{H}^\text{13}$C-NMR spectrum (DMSO-$d_6$, 101 MHz) 2-((3-(4-bromophenoxy)propyl)-1,4-hydroquinone. The spectrum is referenced to the solvent at 39.5 ppm.
Figure A25. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of 2-(3-(4-bromophenoxy)propyl)-1,4-benzoquinone. The spectrum is referenced to the solvent residual isotopomer at 7.26 ppm.
Figure A26. \(^{1}H\)\(^{13}\)C-NMR spectrum (CDCl\(_3\), 101 MHz) of 2-(3-(4-bromophenoxy)propyl)-1,4-benzoquinone. The spectrum is referenced to the solvent at 77.0 ppm.
Appendix B Supporting information for Chapter 3. Synthesis and Characterization of Linear Segmented Aromatic Polymers Containing Thermally Reversible Linkages

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Figure B1. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of 5KHexylPEEK. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. Integrals shown are skewed due to unresolved end-group signals, as such the following analysis attempts to integrate and account for only what should be backbone signals. δ 7.86-7.78 (m, 4H), 7.10-6.93 (m, 7H), 2.63-2.53 (m, 2H), 1.64-1.49 (m, 2H), 1.34-1.18 (m, 6H), 0.90-0.79 (m, 3H).
Figure B2. $^1$H$^{13}$C-NMR spectrum (CDCl$_3$, 101 MHz) of 5KHexylPeek. $^1$H$^{13}$C-NMR didn’t prove as useful a diagnostic tool as $^1$H-NMR and $^{19}$F-NMR and as such only this example is shown; however, an important observation can be noted. Due to the random distribution of hexyl groups in the ortho and meta position of the hydroquinone monomer the quaternary carbons adjacent to the hydroquinone moiety (see below) all experience a different chemical environment causing a slight split in these carbons. This is seen for the carbons at 162 ppm and also at 132 ppm. Aside from this phenomenon all other carbons are regularly assignable. $\delta$ 194.4 (C=O, 162.1 (aromatic C), 162.1 (aromatic C), 161.7 (aromatic C), 161.6 (aromatic C), 152.4 (aromatic C), 149.5 (aromatic C), 137.5 (aromatic C), 132.4 (aromatic C), 122.5 (aromatic C), 122.4 (aromatic C), 119.0 (aromatic C), 117.1 (aromatic C), 116.1 (aromatic C), 31.6 (CH$_2$), 30.2 (CH$_2$), 30.0 (CH$_2$), 29.1 (CH$_2$), 22.6 (CH$_2$), 14.2 (CH$_3$).
Figure B3. Quaternary carbons adjacent to the hydroquinone moiety (162 ppm) that display the “splitting” in the $^{1}\text{H}^{13}\text{C}$-NMR spectrum due to the carbons all experiencing a different chemical environment. This is due to the random orientation of the hydroquinone moiety when it polymerizes (meta versus ortho). As mentioned above the quaternary carbons adjacent to the carbonyl also experience this effect and the signals at 132 ppm are “split”. For a similar documentation of this effect with MethylPEEK see Wang, F.; Roovers, J.; Toporowski, P. M. Macromolecules 1993, 26, 3826.
Figure B4. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of 24KHexylPEEK. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. $\delta$ 7.90-7.72 (m, 4H), 7.11-6.90 (m, 7 H), 2.56 (t, $J$ = 8 Hz, 2H), 1.64-1.50 (m, 2H), 1.38-1.17 (m, 6H), 0.84 (t, $J$ = 7 Hz, 3H).
Figure B5. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of 5KHexylPAES. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. Integrals shown are skewed due to unresolved end-group signals, as such the following analysis attempts to integrate and account for only what should be backbone signals. $\delta$ 7.93-7.85 (m, 4H), 7.07-6.89 (m, 7H), 2.52-2.43 (m, 2H), 1.56-1.44 (m, 2H), 1.27-1.14 (m, 6H), 0.85-0.76 (m, 3H).
Figure B6. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of 5KOctylPEEK. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. Integrals shown are skewed due to unresolved end-group signals, as such the following analysis attempts to integrate and account for only what should be backbone signals. $\delta$ 7.87-7.78 (m, 4H), 7.11-6.93 (m, 7H), 2.64-2.52 (m, 2H), 1.64-1.49 (m, 2H), 1.41-1.09 (m, 12H), 0.90-0.78 (m, 3H).
Figure B7. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of 5KOctylPAES. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. Integrals shown are skewed due to unresolved end-group signals, as such the following analysis attempts to integrate and account for only what should be backbone signals. δ 7.92-7.85 (m, 4H), 7.07-6.90 (m, 7H), 2.52-2.43 (m, 2H), 1.57-1.44 (m, 2H), 1.33-1.12 (m, 12H), 0.90-0.79 (m, 3H).
Figure B8. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of CPDHexylPEEK. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. $\delta$ 7.87-7.74 (m, 4H), 7.10-6.90 (m, 7H), 3.57 (CPD CH$_2$, s, 0.23 H) 2.56 (t, J = 8 Hz, 2H), 1.63-1.50 (m, 2H), 1.36-1.16 (m, 8H, alkyl CH$_2$ and CPD tert-butyl end groups), 0.84 (t, J = 7 Hz, 3H).
Figure B9. $^{19}$F-NMR spectrum (CDCl$_3$, 376 MHz) of CPDHexylPEEK. The multiplet at -138 ppm correspond to the fluorines ortho to cyclopentadiene, the multiplet at -140 ppm corresponds to the meta fluorines, the multiplet at -153 ppm corresponds to the fluorines ortho to the hydroquinone end group.
Figure B10. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of CPDHexylPAES. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. δ 7.94-7.82 (m, 4H), 7.07-6.84 (m, 7H), 3.57 (CPD CH$_2$, s, 0.33 H) 2.47 (t, J = 8 Hz, 2H), 1.57-1.44 (m, 2H), 1.30-1.13 (m, 8H, alkyl CH$_2$ and CPD tert-butyl end groups), 0.81 (t, J = 7 Hz, 3H).
Figure B11. $^{19}$F-NMR spectrum (CDCl$_3$, 376 MHz) of CPDHexylPAES. The multiplet at -138 ppm correspond to the fluorines ortho to cyclopentadiene, the multiplet at -140 ppm corresponds to the meta fluorines, the multiplet at -153 ppm corresponds to the fluorines ortho to the hydroquinone end group.
Figure B12. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of CPDOctylPEEK. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. δ 7.87-7.74 (m, 4H), 7.10-6.92 (m, 7H), 3.57 (CPD CH$_2$, s, 0.30 H) 2.55 (t, J = 8 Hz, 2H), 1.64-1.49 (m, 2H), 1.37-1.12 (m, 13H, alkyl CH$_2$ and CPD tert-butyl end groups), 0.84 (t, J = 7 Hz, 3H).
**Figure B13.** $^{19}$F-NMR spectrum (CDCl$_3$, 376 MHz) of CPDOctylPEEK. The multiplet at -138 ppm correspond to the fluorines ortho to cyclopentadiene, the multiplet at -140 ppm corresponds to the meta fluorines, the multiplet at -153 ppm corresponds to the fluorines ortho to the hydroquinone end group.
Figure B14. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of CPDOctylPAES. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. $\delta$ 7.95-7.80 (m, 4H), 7.08-6.84 (m, 7H), 3.57 (CPD CH$_2$, s, 0.28 H) 2.48 (t, $J = 8$ Hz, 2H), 1.57-1.42 (m, 2H), 1.33-1.08 (m, 13H, alkyl CH$_2$ and CPD tert-butyl end groups), 0.84 (t, $J = 7$ Hz, 3H).
Figure B15. $^{19}$F-NMR spectrum (CDCl$_3$, 376 MHz) of CPDOctylPAES. The multiplet at -138 ppm correspond to the fluorines ortho to cyclopentadiene, the multiplet at -140 ppm corresponds to the meta fluorines, the multiplet at -153 ppm corresponds to the fluorines ortho to the hydroquinone end group.
Figure B16. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of Diel-Alder chain extended HexylPEEK. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. δ 7.87-7.74 (m, 4H), 7.10-6.91 (m, 7H), 2.56 (t, J = 8 Hz 2H), 1.63-1.51 (m, 2H), 1.35-1.15 (m, 8H), 0.84 (t, J = 7 Hz, 3H).
Figure B17. $^{19}$F-NMR spectrum (CDCl$_3$, 376 MHz) of Diel-Alder chain extended HexylPEEK. The signals at -138 and -153 ppm correspond to the fluorinated aromatics. A mixture of 5 isomers. Integration is not 6:2 due to a large amount of line broadening (5 Hz) used to see the signals (signals are very diluted).
**Figure B18.** $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of Diel-Alder chain extended HexylPAES. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. $\delta$ 7.92-7.83 (m, 4H), 7.06-6.85 (m, 7H), 2.47 (t, $J = 8$ Hz 2H), 1.55-1.44 (m, 2H), 1.37-1.05 (m, 8H), 0.81 (t, $J = 7$ Hz, 3H).
**Figure B19.** $^{19}$F-NMR spectrum (CDCl$_3$, 376 MHz) of Diele-Alder chain extended HexylPAES. The signals at -138 and -153 ppm correspond to the fluorinated aromatics, a mixture of 5 isomers.
Figure B20. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of Diel-Alder chain extended OctylPEEK. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. $\delta$ 7.87-7.74 (m, 4H), 7.10-6.91 (m, 7H), 2.55 (t, J = 8 Hz 2H), 1.62-1.52 (m, 2H), 1.44-1.07 (m, 13H), 0.84 (t, J = 7 Hz, 3H).
Figure B21. $^{19}$F-NMR spectrum (CDCl$_3$, 376 MHz) of Diel-Alder chain extended OctylPEEK. The signals at -138 and -153 ppm correspond to the fluorinated aromatics, a mixture of 5 isomers. Integration is not 6:2 due to a large amount of line broadening (5 Hz) used to see the signals.
Figure B22. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of Diel-Alder chain extended OctylPAES. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. $\delta$ 7.93-7.83 (m, 4H), 7.06-6.84 (m, 7H), 2.47 (t, $J = 8$ Hz 2H), 1.57-1.44 (m, 2H), 1.36-1.06 (m, 14H), 0.84 (t, $J = 7$ Hz, 3H).
Figure B23. $^{19}$F-NMR spectrum (CDCl$_3$, 376 MHz) of Diel-Alder chain extended OctylPAES. The signals at -138 and -153 ppm correspond to the fluorinated aromatics, a mixture of 5 isomers.
Figure B24. TGA curve for 5HexylPEEK displaying a 10% mass loss at 410 °C. Scan rate: 10 °C/min (nitrogen).
Figure B25. TGA curve for 24kHexylPEEK displaying a 10% mass loss at 444 °C. Scan rate: 10 °C/min (nitrogen).
Figure B26. TGA curve for 5KOctylPEEK displaying a 10% mass loss at 398 °C. Scan rate: 10 °C/min (nitrogen).
Figure B27. TGA curve for 5KHexylPAES displaying a 10% mass loss at 377 °C. Scan rate: 10 °C/min (nitrogen). Slight abnormalities in the curve are due to the sample pan touching the sides of the furnace.
Figure B28. TGA curve for 5KOctylPAES displaying a 10% mass loss at 363 °C. Scan rate: 10 °C/min (nitrogen).
Figure B29. TGA curve for CPDHexylPEEK displaying a 10% mass loss at 406°C. Scan rate: 10 °C/min (nitrogen).
Figure B30. TGA curve for CPDOctylPEEK displaying a 10% mass loss at 405 °C. Scan rate: 10 °C/min (nitrogen).
Figure B31. TGA Curve for CPDHexylPAES displaying a 10% mass loss at 399 °C. Scan rate: 10 °C/min (nitrogen).
Figure B32. TGA curve for CPDOctylPAES displaying a 10% mass loss at 401 °C. Scan rate: 10 °C/min (nitrogen).
Figure B33. TGA curve for Diels-Alder chain extended HexylPEEK displaying a 10% mass loss at 411 °C. Scan rate: 10 °C/min (nitrogen).
**Figure B34.** TGA curve for Diels-Alder chain extended OctylPEEK displaying a 10% mass loss at 399 °C. Scan rate: 10 °C/min (nitrogen).
**Figure B35.** TGA curve for Diels-Alder chain extended HexylPAES displaying a 10% mass loss at 396 °C. Scan rate: 10 °C/min (nitrogen).
Figure B36. TGA curve for Diels-Alder chain extended OctylPAES displaying a 10% mass loss at 393 °C. Scan rate: 10 °C/min (nitrogen).
**Figure B37.** DSC curve (2\textsuperscript{nd} heating cycle) for 5KHexylPEEK. The $T_g$ was taken as the value in the middle of the endotherm (70 °C). Scan rate: 5 °C/min (nitrogen).
Figure B38. DSC curve (2nd heating cycle) for 24kHexylPEEK. The $T_g$ was taken as the value in the middle of the endotherm (76 °C). Scan rate: 5 °C/min (nitrogen).
Figure B39. DSC curve (2nd heating cycle) for 5KOctylPEEK. The \( T_g \) was taken as the value in the middle of the endotherm (55 °C). Scan rate: 5 °C/min (nitrogen).
Figure B40. DSC curve (2nd heating cycle) for 5KHexylPAES. The $T_g$ was taken as the value in the middle of the endotherm (93 °C). Scan rate: 5 °C/min (nitrogen).
Figure B41. DSC curve (2nd heating cycle) for 5KOctylPAES. The $T_g$ was taken as the value in the middle of the endotherm (74 °C). Scan rate: 5 °C/min (nitrogen).
Figure B42. DSC curve (2\textsuperscript{nd} heating cycle) for CPDHexylPEEK. The $T_g$ was taken as the value in the middle of the endotherm (80 °C). Scan rate: 5 °C/min (nitrogen).
**Figure B43.** DSC curve (2\textsuperscript{nd} heating cycle) for CPDHexylPAES. The $T_g$ was taken as the value in the middle of the endotherm (103 °C). Scan rate: 5 °C/min (nitrogen).
Figure B44. DSC curve (2\textsuperscript{nd} heating cycle) for CPDOctylPEEK. The $T_g$ was taken as the value in the middle of the endotherm (61 °C). Scan rate: 5 °C/min (nitrogen).
Figure B45. DSC curve (2nd heating cycle) for CPDOctylPAES. The $T_g$ was taken as the value in the middle of the endotherm (83 °C). Scan rate: 5 °C/min (nitrogen).
Figure B46. DSC curve (2\textsuperscript{nd} heating cycle) for Diels-Alder chain extended HexylPEEK. The T\textsubscript{g} was taken as the value in the middle of the endotherm (88 °C). Scan rate: 5 °C/min (nitrogen).
Figure B47. DSC curve (2nd heating cycle) for Diels-Alder chain extended HexylPAES. The $T_g$ was taken as the value in the middle of the endotherm (113 °C). Scan rate: 5 °C/min (nitrogen).
**Figure B48.** DSC curve (2\textsuperscript{nd} heating cycle) for Diels-Alder chain extended OctylPEEK. The T\textsubscript{g} was taken as the value in the middle of the endotherm (69 °C). Scan rate: 5 °C/min (nitrogen).
Figure B49. DSC curve (2nd heating cycle) for Diels-Alder chain extended OctylPAES. The $T_g$ was taken as the value in the middle of the endotherm (100 °C). Scan rate: 5 °C/min (nitrogen).
Figure B50. DSC curve (2nd heating cycle) for Hexyl-Methyl PAES copolymer (0:100). The $T_g$ was taken as the value in the middle of the endotherm (191 °C). Scan rate: 5 °C/min (nitrogen).
Figure B51. DSC curve (2nd heating cycle) for Hexyl-Methyl PAES copolymer (60:40). The $T_g$ was taken as the value in the middle of the endotherm (137 °C). Scan rate: 5 °C/min (nitrogen).
Figure B52. DSC curve (2\textsuperscript{nd} heating cycle) for Hexyl-Methyl PAES copolymer (80:20). The T\textsubscript{g} was taken as the value in the middle of the endotherm (123 °C). Scan rate: 5 °C/min (nitrogen).
Figure B53. DSC curve (2\textsuperscript{nd} heating cycle) for Hexyl-Methyl PAES copolymer (40:60). The T\textsubscript{g} was taken as the value in the middle of the endotherm (161 °C). Scan rate: 5 °C/min (nitrogen).
Figure B54. DSC curve (2\textsuperscript{nd} heating cycle) for Hexyl-Methyl PAES copolymer (15:85). The $T_g$ was taken as the value in the middle of the endotherm (187 °C). Scan rate: 5 °C/min (nitrogen).
Figure B55. SEC Refractive Index trace for 5KHexylPEEK.

Figure B56. SEC Light Scattering trace for 5KHePEEK.
Figure B57. SEC Refractive Index trace for 5KOctylPEEK.

Figure B58. SEC Light Scattering trace for 5KOctylPEEK.
Figure B59. SEC Refractive Index trace for 5KHexylPAES.

Figure B60. SEC Light Scattering trace for 5KHePAES.
**Figure B61.** SEC Refractive Index trace for 5KOctylPAES.

**Figure B62.** SEC Light Scattering trace for 5KOctylPAES.
**Figure B63.** SEC Refractive Index trace for CPDHEPEEK.

**Figure B64.** SEC Light Scattering trace for CPDHePEEK.
Figure B65. SEC Refractive Index trace for CPDOctylPEEK.

Figure B66. SEC Light Scattering trace for CPDOctylPEEK.
Figure B67. SEC Refractive Index trace for CPDHexylPAES.

Figure B68. SEC Light Scattering trace for CPDHePAES.
Figure B69. SEC Refractive Index trace for CPDOctylPAES.

Figure B70. SEC Light Scattering trace for CPDOctylPAES.
**Figure B71.** SEC Refractive Index trace for Diels-Alder chain extended HexylPEEK.

**Figure B72.** SEC Light Scattering trace for Diels-Alder chain extended HexylPEEK.
Figure B73. SEC Refractive Index trace for Diels-Alder chain extended OctylPEEK.

Figure B74. SEC Light Scattering trace for Diels-Alder chain extended OctylPEEK.
Figure B75. SEC Refractive Index trace for Diels-Alder chain extended HexylPAES.

Figure B76. SEC Light Scattering trace for Diels-Alder chain extended HexylPAES.
Figure B77. SEC Refractive Index trace for Diels-Alder chain extended OctylPAES.

Figure B78. SEC Light Scattering trace for Diels-Alder chain extended OctylPAES.
Figure B79. SEC Refractive Index trace for 24KHexylPEEK.

Figure B80. SEC Light Scattering trace for Diels-Alder chain extended 24KHexylPEEK.
**Figure B81.** SEC Refractive Index trace for FMI end-capped OctylPAES.

**Figure B82.** SEC Light Scattering trace for FMI end-capped OctylPAES.
Appendix C  Supporting information for Chapter 4. Rapid, Selective Introduction of Electrophilic Side-Group in Poly(aryl ether sulfone)

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\[ \begin{align*}
\text{F-} & \quad \text{OH} + \text{K}_2\text{CO}_3 \\
\text{S-} & \quad \text{OH} + \text{Br}_2, \text{CH}_2\text{Cl}_2, \text{RT}, 18 \text{ h}
\end{align*} \]
NMR Spectra

**Figure C1.** $^1$H-NMR spectrum (DMSO-$d_6$, 400 MHz) of 2-(4-phenoxybutyl)-1,4-hydroquinone. Water is present at 3.3 ppm. The spectrum is referenced to the solvent residual iostopomer at 2.50 ppm.
Figure C2. $^1$H$^{13}$C-NMR (DMSO-$d_6$, 101 MHz) of 2-(4-phenoxybutyl)-1,4-hydroquinone. The spectrum is referenced to the solvent at 39.5 ppm.
Figure C3. $^1$H-NMR spectrum (DMSO-d$_6$, 400 MHz) of 2-(5-phenoxypentyl)-1,4-hydroquinone. Water is present at 3.3 ppm. The spectrum is referenced to the solvent residual iostopomer at 2.50 ppm.
Figure C4. $^1{^1}H^13$C-NMR (DMSO-d$_6$, 101 MHz) of 2-(5-phenoxypentyl)-1,4-hydroquinone. The spectrum is referenced to the solvent at 39.5 ppm.
Figure C5. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of the benzoquinone intermediate, 2-(5-phenoxypentyl)-1,4-benzoquinone. The spectrum is referenced to the residual solvent isotopomer at 7.26 ppm. We did not attempt to fully characterize this compound and as such this $^1$H-NMR only serves as a reference to complement our modified procedure.
Figure C6. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of PAES-OPh. The spectrum is referenced to the solvent residual isotopomer at 7.26 ppm.
Figure C7. $^1$H$^{13}$C-NMR (CDCl$_3$, 101 MHz) of PAES-OPh. The spectrum is referenced to the solvent at 77.0 ppm
Figure C8. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of BrPAES. The spectrum is referenced to the solvent residual isotopomer at 7.26 ppm.
Figure C9. $^{1}H^{13}C$-NMR spectrum (CDCl$_3$, 101 MHz) of BrPAES. The spectrum is referenced to the solvent at 77.0 ppm.
Figure C10. $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) for attempted synthesis of Furfuryl Alcohol PAES. The spectrum is referenced to the solvent residual isotopomer at 7.26 ppm.
Figure C11. TGA curve for PAES-OPh displaying a 10% mass loss at 417 °C. Scan rate: 10 °C/min (nitrogen).
Figure C12. TGA Curve for BrPAES displaying a 10% mass loss at 341 °C due to the loss of HBr. Scan rate: 10 °C/min (nitrogen).
Figure C13. DSC curve (2\textsuperscript{nd} heating cycle) for PAES-OPh. The $T_g$ was taken as the value in the middle of the endotherm ($85 \, ^\circ C$). Scan rate: 5 $^\circ C$/min (nitrogen).
Figure C14. DSC curve (2\textsuperscript{nd} heating cycle) for BrPAES. The T\textsubscript{g} was taken as the value in the middle of the endotherm (113 °C). Scan rate: 5 °C/min (nitrogen).
SEC

**Figure C15.** SEC Refractive Index trace for PAES-OPh.

**Figure C16.** SEC Light Scattering trace for PAES-OPh.
Figure C17. SEC Refractive Index trace for BrPAES.

Figure C18. SEC Light Scattering Trace for BrPAES.


