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To Karen and Ed, my parents:

All that I am was made by your love, support, and teaching.
   You made me a trail through the forest
   And while everyone didn’t make it to see the end of the path
   the journey belongs to all of us.

And to Brittany, my wife:

Not too long ago we were passing secret notes in ochem lectures,
   And now I am writing about you in the dedication of my PhD thesis.
   You are the brightest star in my sky.
DESIGN AND SYNTHESIS OF FUNCTIONAL GRAPHENIC AND TRIPTYCENE POLY(ARYLETHIER) MATERIALS

BY

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ABSTRACT

This thesis describes the design and development of new methods to functionalize graphitic materials as well as the synthesis and properties of a new triptycene poly(arylether), triptycene-PEEK (Trp-PEEK) and its derivatives. In chapters 1-3, the development of new methods to functionalize graphitic materials with both small molecule functional groups and polymers and their implementation as functional materials is described. Chapter 4 explores the synthesis, post-polymerization functionalization, and applications of a new poly(arylether), Trp-PEEK.

Chapter 1: In this chapter, I describe an attempt to covalently functionalize graphene oxide with ketone derivatives via the Carroll rearrangement, a [3,3]-sigmatropic reaction. Graphene oxide was reacted with 5-acyl derivatives of Meldrum’s acid to produce β-ketoester functionalized graphene, and these materials were submitted to multiple reaction conditions to induce the Carroll rearrangement. A $^{13}$C labeling study under the explored reaction conditions revealed that Carroll product is not predominant. However, it was found that the 20% of the installed functionality was not removed by exposure to strong base, suggesting some rearranged product may have been produced. 5-acyl derivatives of Meldrum’s acid were ultimately found to be versatile reagents for the functionalization of graphene oxide with various functional groups, allowing for the synthesis of graphenes with controlled intergallery spacings.

Chapter 2: Using a modified version of the Arbuzov reaction, graphene oxide is covalently functionalized with phosphonate functionalities. Due to the oxidizing nature of graphene oxide, the reaction produces a large amount of phosphate salts which organize around the covalently installed phosphonate anchor sites. This results in a graphene material which can be extensively decorated with a controllable amount of phosphate material. The ligand properties of this material
were explored by synthesizing a number of metal composites. Graphene phosphate was ultimately found to possess outstanding compressive strength properties, which could be tuned according to the reaction conditions. Portions of this chapter contain work which was assisted by Prof. Stefanie A. Sydlik, who aided in the compression strength testing of graphene phosphate and associated analysis. Additionally, Dr. Joseph Walish fabricated the iron molds used to create the graphene phosphate pellets.

**Chapter 3:** The synthesis of a brine-stable graphene is reported. Using AIBN initiated radical polymerization, random co-polymers containing both aniline and imidazole species were synthesized. These polymers were then covalently attached to the graphene basal plane using diazonium chemistry and converted into imidazolium betaine structures. The resulting composite shows indefinite stability in high-temperature brine solutions, which are particularly relevant for the imaging of oil reservoirs. The work reported in this chapter was performed with equal contributions from both John B. Goods and Dr. Carlos Zuniga. Dr. Jason Cox also provided valuable discussions.

**Chapter 4:** A new poly(aryl ether), triptycene poly(ether ether ketone) (Trp-PEEK) was synthesized and its properties investigated. Incorporation of a triptycene into the PEEK backbone results in a significantly elevated glass transition temperature, and its increased solubility allows for high molecular weight polymer to be synthesized without the use of specialty solvents and high temperatures typically required for PEEK. This polymer is derivatized by both sulfonation and nitration. The sulfonated S-Trp-PEEK can be cast into robust transparent membranes, and shows exceptional performance as a proton conductor in this form. It can also stabilize solutions of single-walled carbon nanotubes in polar solvents, such as water and methanol. From these solutions, conductive films and foams can be cast. The NO2-Trp-PEEK derivative can be reduced into its amine form and then reacted with isocyanates to form urea and thiourea derivatives of Trp-PEEK. Thio-Trp-PEEK can be used as a selector in the gas-phase sensing of acetone. Its hydrogen bonding properties can also be exploited to form self-healing viscoelastic materials when blended with poly(THF). The work contained in this chapter regarding sulfonated Trp-PEEK and proton conductivity of those polymers was performed with equal contributions from John B. Goods and Lionel Moh. Lionel Moh also assisted with the characterization of the other polymers covered in this chapter.

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TABLE OF CONTENTS

Title Page ........................................................................................................................................ 1
Signature Page...................................................................................................................................... 2
Dedication........................................................................................................................................... 3
Abstract............................................................................................................................................. 4
Table of Contents............................................................................................................................. 6
List of Figures.................................................................................................................................... 8
List of Schemes .................................................................................................................................. 11
List of Tables..................................................................................................................................... 14
List of Equations............................................................................................................................... 15
List of Abbreviations ......................................................................................................................... 16

Chapter 1: Functionalization of Graphene with 5-acyl Derivatives of Meldrum’s Acid
1.1 Abstract....................................................................................................................................... 18
1.2 Introduction................................................................................................................................... 19
1.3 Results and Discussion .................................................................................................................. 32
   1.3.1 Synthesis ................................................................................................................................ 32
   1.3.2 Characterization ....................................................................................................................... 36
   1.3.3 Sorption Experiment ................................................................................................................. 41
   1.3.4 $^{13}$C labeling Experiment ....................................................................................................... 42
1.4 Conclusions................................................................................................................................... 47
1.5 Experimental................................................................................................................................ 48
1.6 References...................................................................................................................................... 52

Chapter 2: Graphene Phosphate
2.1 Abstract....................................................................................................................................... 52
2.2 Introduction................................................................................................................................... 56
2.3 Results and Discussion.................................................................................................................... 60
   2.3.1 Synthesis ................................................................................................................................ 60
   2.3.2 Characterization ....................................................................................................................... 61
   2.3.3 Origin of Phosphate .................................................................................................................. 62
   2.3.4 Role of Phosphite/Mechanism of Monolith Formation ............................................................ 63
   2.3.5 Hydrolysis/Thermolysis of Graphene Phosphate ..................................................................... 65
   2.3.6 Alternative Synthesis of Phosphonate Graphene ................................................................... 67
   2.3.7 Iron/Lithium Graphene Phosphate Composites .................................................................... 70
   2.3.8 Cu/Ce Graphene Phosphate Composites ................................................................................ 73
   2.3.9 High-Strength Properties ........................................................................................................ 78
2.4 Conclusions................................................................................................................................... 81
2.5 Experimental................................................................................................................................ 82
2.6 References...................................................................................................................................... 86
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Oxidation of graphite into graphene oxide</td>
<td>22</td>
</tr>
<tr>
<td>1.2</td>
<td>XPS spectra of A PhBrGraphene and B TrisClGraphene</td>
<td>35</td>
</tr>
<tr>
<td>1.3</td>
<td>TGA traces of PhBrGraphene, AdamGraphene, TrisClGraphene run under nitrogen</td>
<td>37</td>
</tr>
<tr>
<td>1.4</td>
<td>FT-IR spectra of functionalized graphenes, PhBrGraphene, AdamGraphene, TrisClGraphene</td>
<td>38</td>
</tr>
<tr>
<td>1.5</td>
<td>Powder X-ray diffractograms for AdamGraphene and TrisClGraphene</td>
<td>39</td>
</tr>
<tr>
<td>1.6</td>
<td>Solubility of functionalized graphenes in DMF</td>
<td>40</td>
</tr>
<tr>
<td>1.7</td>
<td>Results of the sorption experiment</td>
<td>42</td>
</tr>
<tr>
<td>1.8</td>
<td>$^{13}$C SSNMR of $^{13}$C labeled Carroll graphene when reacted at 150 °C</td>
<td>44</td>
</tr>
<tr>
<td>1.9</td>
<td>$^{13}$C SSNMR of $^{13}$C labeled Carroll graphene when the reaction temperature was increased to 180 °C and when treated with two equivalents of LiHMDS</td>
<td>45</td>
</tr>
<tr>
<td>1.10</td>
<td>TGA curves graphene oxide reacted with a 5-acyl Meldrum's acid derivative and corresponding acid chloride</td>
<td>46</td>
</tr>
<tr>
<td>2.1</td>
<td>Possible mechanisms of nucleophilic attack on graphene oxide</td>
<td>58</td>
</tr>
<tr>
<td>2.2</td>
<td>Graphene phosphate monolith</td>
<td>60</td>
</tr>
<tr>
<td>2.3</td>
<td>$^{31}$P SSNMR of graphene monolith. The majority of the monolith is comprised of phosphate and phosphonate moieties</td>
<td>61</td>
</tr>
<tr>
<td>2.4</td>
<td>SEM Micrographs of graphene phosphate and associated EDX analysis</td>
<td>65</td>
</tr>
<tr>
<td>2.5</td>
<td>Powder X-ray diffractogram of graphene phosphate (black) and hydrolyzed graphene phosphate (blue)</td>
<td>66</td>
</tr>
<tr>
<td>2.6</td>
<td>$^{31}$P SSNMR of hydrolyzed graphene phosphate</td>
<td>67</td>
</tr>
<tr>
<td>2.7</td>
<td>SEM Micrographs of a cross-section of a typical graphene phosphate pellet, thermogravimetric analysis and linear dependence of the mass of the produced graphene phosphate monolith on initial LiBr loading</td>
<td>68</td>
</tr>
<tr>
<td>2.8</td>
<td>SEM Micrographs of graphene phosphate</td>
<td>70</td>
</tr>
</tbody>
</table>
Figure 2.9. SEM image of CePhosGraphene ............................................. 75
Figure 2.10. PXRD diffractogram and SEM image of CuCeOGraphene ........... 76
Figure 2.11. TEM images of bare CuO/CeO2 nanoparticles, CuO/CeO2 nanoparticles loaded onto unfunctionalized graphene oxide, and CuO/CeO2 nanoparticles loaded onto hydrolyzed graphene phosphate ................................................ 77
Figure 2.12. CO oxidation performance of HGP CuO/CeO2 nanoparticle composite .... 78
Figure 2.13. Summary of ultimate compressive strength of all compositions .......... 80
Figure 3.1. Generalized schematic of the use of nano-reporters for oil reservoir imaging .......... 91
Figure 3.2. Tyndall effect on graphene solution ............................................ 92
Figure 3.3. The above figure provides a simplified summary of depletion interactions in colloids ................................................................. 95
Figure 3.4. Polymers in the literature which have reported brine stability .................. 98
Figure 3.5. Unstable mixtures of GO in Arab D and API brines at initial preparation and after 24 h at 90 °C .......................................................... 100
Figure 3.6. ZG1 in Arab-D brine at room temperature ........................................ 101
Figure 3.7. Chitosan functionalized graphene CGI destabilized at 90 °C .................... 103
Figure 3.8. Synthesis and dispersibility of ZCG1 in Arab-D brine after 24 h at 90 °C .... 104
Figure 3.9. PVPy-SB is ineffective at stabilizing GO in Arab-D brine ...................... 106
Figure 3.10. PVI-SB is effective at stabilizing GO in Arab-D brine ......................... 107
Figure 3.11. Photographs of aliquots of stable composite dispersions in Arab D and API brines at initial preparation and after 1, 10, 20, 30, and 140 days at 90 °C .............. 110
Figure 3.12. UV-Vis spectra and DLS data of PVIM-co-PVPy solutions at 1 day, 10 days, 20 days, 30 days, and 140 days at 90 °C .................................................... 111
Figure 4.1. Representative structures of the most common class of PAE’s ................. 125
Figure 4.2. General schematic of a proton exchange membrane fuel cell .................. 131
Figure 4.3. Digital images of S-Trp-PEEK hydrogel and as-produced S-Trp-PEEK ........ 137
Figure 4.4. Representative TGA curve of S-Trp-PEEK.................................141
Figure 4.5. S-Trp-PEEK membrane cast from a 7% wt/v DMAc solution........142
Figure 4.6. Nyquist plots of the S-Trp-PEEK polymers synthesized at 45, 65, and 85 °C.....147
Figure 4.7. Nyquist plot of Nafion film.............................................................148
Figure 4.8. Digital image of a dispersion of [6,5]SWCNTs in water-based solution of S-Trp-PEEK.................................................................149
Figure 4.9. Digital images of S-Trp-PEEK/SWCNT foam and paper...................151
Figure 4.10. SEM images of the S-Trp-PEEK/SWCNT composite.............................152
Figure 4.11. SEM image of S-Trp-PEEK/SWCNT/Pd(II) composite.........................153
Figure 4.12. IR spectra of NO₂-Trp-PEEK, NH₂-Trp-PEEK, Urea-Trp-PEEK,
Thiourea-Trp-PEEK.....................................................................................158
Figure 4.13. Response values for Thiourea-Trp-PEEK/SWCNT composite in the chemiresistive gas-phase sensing of acetone.................................161
Figure 4.14. Structure of poly(THF)................................................................163
Figure 4.15. Digital images of Thiourea-trp-PEEK/poly(THF) composite..............165
Figure 4.16. Self-healing properties of Thiourea-Trp-PEEK/poly(THF) composite........166
List of Schemes

Scheme 1.1 Synthesis of graphene oxide via modified Hummer’s Method..........................21
Scheme 1.2 Proposed mechanism for the origin of graphene oxide’s acidity in water........21
Scheme 1.3 Functionalization of graphene oxide with aryl diazonium salts................24
Scheme 1.4 Eschenmoser-Claisen and Johnson-Claisen reactions on graphene oxide.......26
Scheme 1.5 Mechanism of the Carroll Rearrangement on graphene oxide..................27
Scheme 1.6 Treatment of allylic β-ketoesters with two equivalents of LDA can promote a room temperature Carroll Rearrangement.........................................................28
Scheme 1.7 Substituent effects on [3,3]-sigmatropic rearrangements........................29
Scheme 1.8 Proposed mechanism of the Pd-catalyzed Carroll Rearrangement..............30
Scheme 1.9 Some common methods of synthesizing β-ketoesters..........................31
Scheme 1.10 General route to β-ketoesters via 5-acyl Meldrum’s acid derivatives........31
Scheme 1.11 Synthesis of acylated Meldrum’s acid derivatives..........................33
Scheme 1.12 Reaction of graphene oxide with acylated Meldrum’s acids 1-3..........34
Scheme 1.13 Synthesis of sorption experiment control ketone...............................41
Scheme 1.14 Synthesis of $^{13}$C labeled acylated Meldrum’s acid and its reaction with graphene oxide..................................................................................................................43
Scheme 2.1 Mechanism of the Arbuzov reaction..................................................56
Scheme 2.2 Atypical Arbuzov reactions................................................................57
Scheme 2.3 Triethyl phosphite does not react with LiBr even at high temperatures.....62
Scheme 2.4 Proposed mechanism of graphene phosphate formation........................64
Scheme 2.5 Synthesis of phosphonate graphene PG1..................................71
Scheme 2.6 Synthesis of iron/graphene monolith FeG1..................................72
Scheme 2.7 Conditions for the synthesis of a graphene monolith LiFeG1..................72
Scheme 2.8  Conditions for the synthesis of Li/Fe/graphene phosphate composites FeG2, FeG3, and LiFeG2.................................................................73

Scheme 2.9  General synthetic approach toward constructing a CuO/CeO2 graphene phosphate composite.................................................................74

Scheme 2.10  Synthesis of hydrolyzed graphene phosphate nanoparticle composite..............76

Scheme 3.1  Treatment of graphene oxide with triethylorthoacetate functionalizes the basal plane of graphene with esters.........................................................100

Scheme 3.2  Synthesis of zwitterion graphene ZG1.........................................................101

Scheme 3.3  Synthesis of zwitterion graphene ZG2.........................................................102

Scheme 3.4  Synthesis of chitosan/graphene composite CG1........................................103

Scheme 3.5  Synthesis of polymers PVPy-SB and PVI-SB.............................................107

Scheme 3.6  Synthesis of polymer PVIM-co-PVPy and functionalization of partially reduced graphene oxide.................................................................108

Scheme 4.1  Bonner’s synthesis of poly(ether ketone)..................................................126

Scheme 4.2  Johnson and Farnham’s synthesis of PEEK...............................................126

Scheme 4.3  Rose and Staniland’s synthesis of high molecular weight PEEK.............127

Scheme 4.4  Hydrolysis of the difluoro monomer results in chain-termination of the polymer, lowering molecular weight..................................................129

Scheme 4.5  Potassium carbonate decomposes into CO2 and water when protonated at high temperatures.................................................................129

Scheme 4.6  Synthesis of PEEK-WC.........................................................................130

Scheme 4.7  DuPont synthesis of Naftion.................................................................133

Scheme 4.8  Synthesis triptycene diol 1......................................................................134

Scheme 4.9  Synthesis of Trp-PEEK..........................................................................135

Scheme 4.10  Use of industry PEEK synthesis conditions to synthesize Trp-PEEK........136
Scheme 4.11  Mechanism of polymer degradation by ipso electrophilic aromatic substitution reactions........................................................................................................140

Scheme 4.12  Nitration of Trp-PEEK at elevated temperatures results in significant reduction of the molecular weight............................................................................................154

Scheme 4.13  Synthesis of Trp-PEEK-NMP .................................................................................................................................................................................155

Scheme 4.14  Reduction of NO₂-Trp-PEEK to NH₂-Trp-PEEK..............................................................................................................................157

Scheme 4.15  Synthesis of Thiourea-Trp-PEEK and Urea-Trp-PEEK..........................................................................................................................159

Scheme 4.16  Synthesis and structure of Lycra and Kevlar..............................................................................................................................................162

Scheme 4.17  Summary of composites containing thiourea-Trp-PEEK and poly(THF).................164

Scheme 4.18  The Newman-Kwart rearrangement.........................................................................................167

Scheme 4.19  Synthesis of triptycene T2 and its use as a monomer in in the synthesis of Trp-S-PEEK.............................................................................................................................................168
List of Tables

Table 2.1. Atomic composition of graphene phosphate before and after hydrolysis.............66
Table 3.1. Composition of Arab-D and API brines.............................................................97
Table 4.1. Molecular weights of Trp-PEEK and its sulfonated derivatives............................138
Table 4.2. Summary of the dispersive properties of S-Trp-PEEK when mixed with SWCNT's in water........................................................................................................150
Table 4.3. Degrees of nitration on Trp-PEEK-NMP.............................................................156
List of Equations

**Equation 4.1.** Number average molecular weight (Mn) and weight average molecular weight (Mw).................................................................127

**Equation 4.2.** Determination of the degree of sulfonation by TGA.........................................................142
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AcOH</td>
<td>Acetic acid</td>
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<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DMAc</td>
<td>Dimethylacetamide</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DS</td>
<td>Degree of sulfonation</td>
</tr>
<tr>
<td>DSM</td>
<td>Dynamic structural model</td>
</tr>
<tr>
<td>EAS</td>
<td>Electrophilic aromatic substitution</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
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<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>ICDD</td>
<td>International centre for diffraction data</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>IS</td>
<td>Impedance spectroscopy</td>
</tr>
<tr>
<td>NKR</td>
<td>Newman-Kwart Rearrangement</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methylpyrrolidinone</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PAE</td>
<td>Poly(aryl ether)</td>
</tr>
<tr>
<td>PEEK</td>
<td>Poly(ether ether ketone)</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton exchange membrane</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>prGO</td>
<td>Partially reduced graphene oxide</td>
</tr>
<tr>
<td>PTTK</td>
<td>Poly(thioether thioether) ketone</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder X-ray diffraction</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>SSNMR</td>
<td>Solid state nuclear magnetic resonance</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-walled carbon nanotube</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>UCS</td>
<td>Ultimate compressive strength</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1: Functionalization of Graphene with 5-acyl Derivatives of Meldrum's Acid
1.1 Abstract

In this chapter, I describe an attempt to covalently functionalize graphene oxide with ketone derivatives via the Carroll rearrangement, a [3,3]-sigmatropic reaction. Graphene oxide was reacted with 5-acyl derivatives of Meldrum's acid to produce β-ketoester functionalized graphene, and these materials were submitted to multiple reaction conditions to induce the Carroll rearrangement. A $^{13}$C labeling study under the explored reaction conditions revealed that Carroll product is not predominant. However, it was found that the 20% of the installed functionality was not removed by exposure to strong base, suggesting some rearranged product may have been produced. 5-acyl derivatives of Meldrum's acid were ultimately found to be versatile reagents for the functionalization of graphene oxide with various functional groups, allowing for the synthesis of graphenes with controlled intergallery spacings.
1.2 Introduction

Since the experimental confirmation of its exceptional electronic properties by Novoselov and Geim in 2004, graphene has dominated materials research.\(^1\) Investigations have suggested that in addition to its ballistic charge transport properties, this single atom thick lattice of sp\(^2\) hybridized carbon atoms is the world’s strongest and stiffest material.\(^2\) However, one the challenges preventing graphene from achieving widespread implementation in commercial materials is its poor processibility and lack of scalable production.\(^3\) Early work on graphene was limited to micromechanical exfoliation of graphite with scotch tape, which could produce miniscule amounts of graphene after laborious mechanical manipulation. Advances in chemical vapor deposition have facilitated the production of pristine graphene for use in electronics which require minimal defects in the lattice; however, for production of graphene for other applications, graphene oxide (GO) represents one of the most promising pathways toward mass production.

Graphene oxide is produced by the exposure of graphite to extremely harsh oxidation conditions which introduces defects into the basal plane and functionalizes the surface with numerous oxygen containing functional groups. Although the exact composition of these functional groups depends on the reaction conditions, the most commonly found moieties include hydroxyl groups, epoxides, carboxylic acids, lactones, and enones.\(^4\)

Graphene oxide chemistry is over 150 years old - the first synthesis was reported by Oxford chemist Benjamin Brodie in 1855 when he exposed graphite to a mixture of potassium chlorate and fuming nitric acid.\(^5\) The most important synthetic development was reported in 1958, when Hummers used KMnO\(_4\) with NaNO\(_3\) in concentrated sulfuric acid to produce the material.\(^6\) Modern improvements to graphene oxide synthesis have for the most part been slight modifications to the
original Hummers procedure, and include the varying of reagent ratios, exclusion of NaNO₃ to prevent NOₓ outgassing, and use of a H₃PO₄/H₂SO₄ mixture as solvent.⁷,⁸

Scheme 1.1 Synthesis of graphene oxide via modified Hummer's Method. A single sheet of graphene is shown as a starting material for simplicity. In actuality, the graphite starting material is composed of tightly stacked sheets of graphene ~3.3 Å apart which are exfoliated via oxidation. The graphene oxide is represented within the Lerf-Klinowski model, which posits that it is defined by both extended sp² aromatic domains and heavily oxidized sp³ carbon regions.

The structural model of graphene oxide has been revised several times. As a non-stoichiometric material with a significant degree of variance dependent the source of its synthesis, its precise composition has been a source of much debate. Scheme 1.1 shows a simplified structure of graphene oxide which is based on the Lerf-Klinowski model. This model explains graphene oxide as being comprised of two randomly distributed domains: one composed of sp² hybridized,
pure' graphene, and the other as heavily oxidized sp³ carbon. This model is currently the most widely accepted and is supported by both ¹³C labeling solid state nuclear magnetic resonance (SSNMR) experiments and high resolution transmission electron microscopy. A newer model has been suggested by Tour which has been dubbed the “Dynamic Structural Model” (DSM). Proposed to explain the acidity of graphene oxide solutions in water, this model proposes that the structure of graphene oxide is constantly changing. Although it has been long accepted that graphene oxide possesses a large number of carboxylic acids, its pKa in water is around 3.93-3.96, making it a stronger acid than similar carboxylic functional groups (benzoic acid pKa in water = 4.20). The DSM suggests that this acidity arises out of a slow degradation in water which generates acidic functional groups. Scheme 1.2 summarizes the proposed mechanism by which graphene oxide degrades in water and generates acid.

![Scheme 1.2 Proposed mechanism for the origin of graphene oxide’s acidity in water.](image)

The implications of this model are significant. If correct, the structure of graphene oxide is not static, and the oxygen functionality which decorates its surface can rearrange itself depending on its environment. Accordingly, the effect of this dynamic character on GO’s reactivity and should be considered when designing functionalization methods for the material.

While the structural model of GO continues to be refined, it is clear that by submitting graphite to Hummer’s type conditions the material becomes extensively oxidized, resulting in
expansion of the interlayer distance (Figure 1.1) This is turn permits penetration of solvent molecules between graphene layers. Indeed, in contrast to both graphite and graphene sheets, graphene oxide is highly dispersible in water and moderately dispersible in a number of organic solvents. The most common organic solvents for graphene oxide are polar aprotic amides, and include dimethylformamide (DMF), dimethylacetamide (DMAc), and N-methylpyrrolidone (NMP). Ethers, while less effective at dispersing GO, are also commonly used, the most frequent of which include THF and glymes such diethylene glycol dimethylether (diglyme). In conjunction the impartation of dispersibility, the large amount of oxygen containing functional groups allow for improved synthetic manipulation.

**Figure 1.1** Oxidation of graphite into graphene oxide expands the interlayer spacing from 3.3 Å to 6-12 Å.

These properties make graphene oxide a promising material for the cost-effective, scalable production of graphene. In contrast to other methods, such as chemical vapor deposition, micromechanical exfoliation, and dispersive sonication of graphite, graphene oxide has been suggested to be the first viable path toward the ton scale production of chemically modified graphenes.¹¹ It should be stressed, however, that graphene oxide is not graphene. The same oxidative treatment which provides GO with its valuable and unique properties also results
significant disruption of the sp² carbon network; accordingly, GO has low electrical conductivity. However, its oxygen functionalities can be easily removed via reduction, restoring the conjugated \( \pi \)-network and the conductivity it affords. The term reduction in this case does not precisely conform to the classical chemistry definition, however, wherein electrons are added to a system. The term reduction as it is applied to GO is most accurately characterized as a deoxygenation event.

Reduction of GO, which is characterized by loss of the oxygen containing functional groups and restoration of the sp² carbon lattice, can be carried out via a number of methods, most commonly exposure to hydrazine or ascorbic acid. Heating graphene oxide both in neat form and in dispersion to temperatures above 50 °C will also initiate deoxygenation, but at a significantly slower rate than what is obtained with chemical methods.

It should be noted that due to the defects imparted during the synthetic process, it has yet to be demonstrated that reduction can restore graphene oxide to the level of pristine graphene’s charge transport properties. Accordingly, graphene obtained by the reduction of graphene oxide is typically referred to as reduced graphene oxide (rGO) to emphasize its dissimilarity to pristine graphene sheets. As suggested by the drawings shown earlier, rGO likely has many chemical defects.

In spite of these limitations, graphene oxide represents a rich opportunity for the synthetic manipulation of graphitic materials. By exploiting its solubility and functional group rich composition, chemists have developed many different methods for both the covalent and non-covalent functionalization of GO. Among the earliest reported methods for covalent functionalization is the treatment of GO with thionyl chloride, which converts the numerous carboxylic acids found on the edges of the basal plane to acid chlorides. Subsequent exposure to
an amine of choice results allows for the covalent attachment of amides bearing many different functional groups. However, this method is limited as its imparted functionality is restricted to the edges of the graphene sheet, precluding the resulting graphene from use in applications in which control over the intersheet gallery is necessary. Other covalent functionalizations include the use of highly reactive intermediates, such as aryl radicals (via diazonium salts),\cite{14} and nitrenes (via azides),\cite{15} which react with the π-system of the basal plane. Tour's method for graphene basal plane functionalization via aryl diazonium BF₄ salts is particularly effective.\cite{14} Similar to the mechanism of a Meerwein arylation, when graphene oxide is treated with an aryl diazonium salt, electron transfer occurs between the basal plane and reagent, resulting in the formation of an aryl radical which then reacts with the π-system of graphene oxide. As a significant portion of the reactive species is generated in close proximity to the basal plane, this method is highly effective for the covalent functionalization of graphene. This method is most effective when the graphene oxide is slightly reduced prior to the addition of the diazonium species in order to maximize the amount of accessible π-bonds on the basal plane.

\begin{center}
\includegraphics[width=\textwidth]{functionalization_scheme.png}
\end{center}

**Scheme 1.3** Functionalization of graphene oxide with aryl diazonium salts. Reduced graphene oxide is represented as a fragment for clarity.

GO hosts a diverse number of hydroxyl environments, and due to the ubiquity of π-bonds in its structure it is likely that many of these are allylic in nature. As allylic alcohols are known
participants in a number of sigmatropic reactions, by reacting graphene oxide with the appropriate reagent, a [3,3]-sigmatropic rearrangement can be induced on the surface of GO, resulting in the decoration of its surface with carboxylic derivatives. This approach was first demonstrated by the Swager group in 2010 by using an Eschenmoser-Claisen rearrangement to install amide groups on the basal plane (Scheme 1.4). The presence of nitrogen in the functionalized graphene allowed for confirmation of the method by X-ray photoelectron spectroscopy (XPS).

XPS is among the most important analytical techniques for graphene functionalization and a brief explanation will be provided here. XPS is a surface characterization technique that provides information regarding the elemental composition of a sample. A sample is mounted within an ultra-high vacuum chamber (P < 10^{-9} mbar) and irradiated with a beam of focused, monochromatic X-rays. These X-rays are of such an energy as to expel electrons from the inner shells of the elements which compose the sample (a manifestation of the photoelectric effect). These electrons are collected and their kinetic energy is correlated to a given element and core shell (i.e. C 1s). An XPS spectrum is represented as electron energy vs electron count; in this way, the relative amounts of a given element for a given sample can be obtained. Electrons are typically expelled from only top 10 nm of the material, if depth profiling is required, it is possible to etch the sample using an ion gun.

While not as sensitive as SSNMR, XPS is a useful tool for the analysis of solids. It is more easily obtained than SSNMR spectra and can quantify any element except for H and He. In addition to quantitation of elements, it can give information regarding the local chemical environment of that element, as the energy of expelled electrons is dependent on oxidation state. It is possible to use this property to gain some information about carbon environments, however in graphene oxide.
samples, the diversity of carbon environments already present in the starting material can obfuscate the analysis of synthetic methods which introduce new carbon identities. It is therefore advantageous to use elemental tags in any functionalization study, as it can offer clear evidence for or against the success of a given transformation.

**Scheme 1.4** Eschenmoser-Claisen and Johnson-Claisen reactions on graphene oxide.

Having demonstrated that using [3,3]-sigmatropic rearrangements to functionalize graphene were a viable method for installing functionality to its surface, the Swager group expanded upon this method by using the Johnson-Claisen rearrangement to attach esters to the basal plane.\(^1\) This method was an improvement over the previous, as the relatively inexpensive triethylorthoacetate reagent could be used as both solvent and reagent. Additionally, the ester moieties produced via the Johnson-Claisen could be more easily hydrolyzed than their amide counterparts, allowing for a more facile route to carboxylic acid derivatives.

Chapter 1 of this thesis records efforts undertaken to expand this methodology to an even more modular approach. While both the Eschenmoser-Claisen and Johnson-Claisen methods offered paths to carboxylic acid functionalized graphene, further derivatizing these materials required subsequent reactions, which typically involved conversion of the carboxylic acids to acid
chloride and condensation with amines. The resulting amides are susceptible to hydrolysis, limiting applications of the resulting materials. To address these issues, we identified the Carroll rearrangement as a possible solution.

Discovered in 1940, the Carroll Rearrangement is a [3,3]-sigmatropic rearrangement which involves the reaction of an allylic β-ketoester under high temperature.\(^{20}\) By developing a method to install β-ketoesters on the surface of graphene oxide, we hypothesized that we would be able to install ketones bearing a diverse number of functional groups to graphene (Scheme 1.5).

![Scheme 1.5 Mechanism of the Carroll Rearrangement on graphene oxide.](image)

As in any [3,3]-sigmatropic rearrangement, the Carroll proceeds by thermodynamic control, primarily driven by the exchange of a C-C π-bond for a C-O π-bond.\(^{16}\) In the case of the Carroll, the reaction is further driven to completion by the release of CO\(_2\) by the product, preventing the retro-rearrangement and eliminating the equilibrium between reactant and product. However, the Carroll is considered to be among the least utilized [3,3]-sigmatropic rearrangements.
due to the high temperatures (160-220 °C) required to effect it. There is little evidence to directly explain why this is the case. Numerous reports have reported that base can accelerate the reaction. This suggests that the sluggishness of the Carroll may be due to a low population of the required enol form. Indeed, when allylic β-keto esters are treated with two equivalents of LDA, locking in the required confirmation, the reaction can proceed at room temperature. Interestingly, when the reactants are treated with only one equivalent of LDA, this effect is not observed. The authors of this study suggest by adding 2 eq. of strong base, the electron density at the reacting enolate carbon is greatly increased, thereby accelerating the reaction.

![Scheme 1.6](image)

**Scheme 1.6** Treatment of allylic β-ketoesters with two equivalents of LDA can promote a room temperature Carroll Rearrangement. At these temperatures, decarboxylation does not occur, allowing for isolation of the β-ketoacid products. Treatment with one equivalent of LDA does not promote the reaction under these conditions.

Much work has been performed to study the influence on substituents on the rate of [3,3]-sigmatropic rearrangements. Lowering the activation energy of the reaction via substituent effects has been explained by stabilization of the transition state through both electronic induction and radical stabilization. Because the exact nature of the transition state for the many types of [3,3]-
sigmaotropic rearrangements are still debated, the precise nature of the stabilization is difficult to state definitively. Evidence for stabilization via inductive effects and radical delocalization has been reported, and it has been suggested that the transition state adopts the features which afford it the lowest energy state based on the substituents attached to it.23

Scheme 1.7 While the substituent effects on [3,3]-sigmatropic rearrangements are myriad, in general, these reactions can be accelerated (in comparison to a hydrogen atom) by both electron-donating and electron-withdrawing groups at the 1, 2, and 4 positions. Rate acceleration is also observed with acceptor groups at position 5 and donor groups at position 6, while rate deceleration is observed when acceptor and donor groups are swapped at these positions.

As shown in Scheme 1.7, electron-donating groups in the 6 position can accelerate [3,3]-sigmatropic rearrangements; in the case of the Carroll, the C-6 position bears an decelerating electron withdrawing ketone, which may offer another explanation for the high temperatures required to effect this reaction. Another important effect on the rate of the Carroll is the type of allylic alcohol found in the starting material. Primary alcohols react slowest, while tertiary alcohols react most rapidly.21

Another effective method for accelerating the Carroll rearrangement was developed by Tsuji in 1980, wherein he reported the use of Pd to catalyze the reaction.24 The suggested mechanism for this reaction is highlighted in Scheme 1.8. This method was used to great effect in the first asymmetric Carroll rearrangement;25 however, transition metal catalyzed reactions are difficult to perform on graphene oxide, as the numerous functional groups found on its surface can
alter reactivity such that reactions which normally proceed on small molecules will fail. Additionally, it is difficult to remove transition metals from the surface of graphene oxide once introduced.

![Diagram of proposed mechanism of the Pd-catalyzed Carroll Rearrangement.]

**Scheme 1.8** Proposed mechanism of the Pd-catalyzed Carroll Rearrangement.

Access to β-ketoesters from the corresponding alcohols can be achieved in a number of ways. Claisen condensations provide a well-known synthetic path toward these functional groups but would be challenging to perform on the surface of graphene: one would first have to install the requisite ester on the surface of GO, then perform a second reaction to form the β-ketoester. Complicating this synthesis is the use of strong base in the Claisen condensation, as it would effect significant reduction on the GO surface and likely remove the installed functionality. Another method is the use of diketene (Scheme 1.9). While diketene could possibly provide a simple one-step procedure for the formation of β-ketoesters on the graphene oxide basal plane, it is difficult to synthesize a wide variety of diketene derivatives, limiting the scope of the reaction.
We eventually determined that the most facile method to generate β-ketoesters on the surface of graphene oxide was through 5-acyl Meldrum's acid. Upon heating to 80-100 °C, these species generate acyl ketenes, providing a facile route toward β-ketoesters upon reaction with alcohols. These derivatives are easily accessible from the reaction between Meldrum's acid and acid chlorides (Scheme 1.10). For substrates in which acid chlorides are not viable, peptide coupling reagents, such as N,N'-dicyclohexylcarbodiimide or diethyl cyanophosphate are effective in synthesizing the desired substrates. Acid chlorides which can be difficult to couple to Meldrum's acid include those with a phenyl ring or bulky substituents alpha to the carbonyl, i.e. benzoyl chloride or pivaloyl chloride.

Scheme 1.10 General route to β-ketoesters via 5-acyl Meldrum's acid derivatives.
1.3 Results and Discussion

1.3.1 Synthesis. Graphene oxide was synthesized via a modified Hummer’s reaction which excluded NaNO$_3$.\textsuperscript{6} In order to explore the effect of functionalization on the intergallery spacing of graphene as well as demonstrate the scope of the reaction, three different Meldrum’s acid derivatives were prepared. When possible, derivatives were designed to incorporate elements which do not naturally occur in graphene oxide as it facilitates the characterization of the materials via surface analysis by X-ray photoelectron spectroscopy (XPS). Scheme 1.11 summarizes the synthesis of these derivatives from carboxylic acid starting materials. It was found that the most efficient means of synthesizing the 5-acyl Meldrum’s acids was to convert carboxylic acids into the acid chloride intermediate and use this intermediate without purification. Benzylic carboxylic acids and those bearing bulky substituents did not react with Meldrum’s acid under these conditions. Other incompatible starting materials were those with containing electrophilic sites which could react with the Meldrum’s acid anion, such as primary alkyl halides.
Scheme 1.11 Synthesis of acylated Meldrum's acid derivatives.

Scheme 1.12 summarizes the general reaction method used for reacting acylated Meldrum's acid derivatives with graphene oxide. As graphene oxide is a non-stoichiometric material, oxygen content was determined by X-ray photoelectron spectroscopy (XPS) and used as a basis for stoichiometry.

The reason for the two stage heating process in the synthesis derives from graphene oxide's facile reduction at temperatures in excess of 50°C. 5-acyl Meldrum's acid has been shown to produce β-keto allyl esters at temperatures as low as 65°C, so in order to keep oxygen content...
high and maximize the probability that the acyl ketene generated would react with an allylic alcohol, a temperature of 80° C was maintained for four hours to produce the desired moiety before attempting the rearrangement.

Scheme 1.12 Reaction of graphene oxide with acylated Meldrum's acids 1-3.

The second stage of the functionalization, the Carroll rearrangement, requires relatively high temperatures to proceed, so the reaction was heated to 150° C for 21 h.

It is important to remove any non-covalently adsorbed material from the graphene sheets prior to analysis, so work-up of functionalized graphene material consists primarily of extensive
sonication and washing of isolated product. In this case, work-up consisted of extensive washings, which involved dispersing the graphene in 40 ml of solvent, sonicating for 10 minutes, then centrifuging and discarding the supernatant. The solvents used are as follows: methylene chloride (4x), acetone (2x), water (3x), acetone (2x).

Figure 1.2 XPS spectra of A PhBrGraphene and B TrisClGraphene. Adamgraphene is not shown because it does not possess any elemental tags which allow for characterization by XPS.
1.3.2 Characterization. The resulting black powders were characterized using standard methods for graphene characterization. X-ray photoelectron spectroscopy revealed the presence of bromine and chlorine in the PhBrGraphene and TrisClGraphene respectively, suggesting that some degree of covalent functionalization had occurred (Figure 1.2). As the AdamGraphene material did not have a relevant marker for XPS, its spectrum was not obtained. To confirm the presence of covalent functionalization in the AdamGraphene sample, thermogravimetric analysis (TGA) was performed (Figure 1.3). TGA is an analytic technique commonly used in graphene functionalization work where samples are heated and their mass loss is precisely recorded. By knowing at what temperature covalently attached moieties typically thermolyze, functionalized samples can be compared to bare graphitic materials to determine if a method adds mass to GO materials.

As a control for this TGA experiment, graphene oxide was treated identically within the functionalization reaction conditions but not exposed to the 5-acyl Meldrum’s acid reagent. As can be seen in Figure 1.3, the mass loss of AdamGraphene is between graphene oxide and the reduced graphene oxide (rGO) control, suggesting presence of the acyl Meldrum’s acid attaches some mass to the GO samples.
Figure 1.3 TGA traces of PhBrGraphene A, AdamGraphene B, TrisClGraphene C run under nitrogen. The blue trace represents the rGO control, the green trace the functionalized graphene, and the red trace graphene oxide.
Figure 1.4 FT-IR spectra of functionalized graphenes, PhBrGraphene, AdamGraphene, TrisClGraphene. Characteristic stretches of functionalized rGO are highlighted. As with the TGA analysis, a reduced GO control was used as a comparison.
While it is clear from the TGA that treatment of graphene oxide with acylated Meldrum's acid results in the attachment of some mass to the graphene sheet, it is necessary to determine that that mass is attributable to the desired functionality. To help confirm this, FT-IR analysis was performed on each graphene sample (Figure 1.4). These spectra indicate that the functionality imparted is likely attributable to the expected functional groups. Diagnostic peaks that are observed include the aromatic C-Br stretch at \( \sim 740 \text{ cm}^{-1} \) in the PhBrGraphene sample, and the C-H stretch at \( \sim 2850 \text{ cm}^{-1} \) in the AdamGraphene sample.

![Figure 1.5](image)

**Figure 1.5** Powder X-ray diffractograms for AdamGraphene and TrisClGraphene. The x-axis represents the angle of diffraction, which in the case of graphene samples correlates to intergallery spacing. For an unknown reason, PhBrGraphene did not display any characteristic diffractions.
In order to determine whether a synthetic method results in functionalization of the basal plane, powder X-ray diffraction can be used. In graphitic samples, the diffraction angle of incident X-rays can be directly correlated to the intergallery spacing between graphene sheets. Graphite typically displays a single sharp signal which corresponds to a gallery spacing of 3.3 Å, while graphene oxide displays a broad signal between 6-12 Å. As can be seen in Figure 1.5, both the AdamGraphene and TrisClGraphene samples display characteristic peaks which can be attributed to gallery spacing caused reaction with 5-acyl Meldrum’s acid reagent. This suggests that not only is the method effective at chemically altering the basal plane, by altering the functional group we can obtain control over the intergallery spacing between graphene sheets.

Figure 1.6 Solubility of functionalized graphenes in DMF. All samples were sonicated for 5 min, then centrifuged at 3200 RPM for 15 min.
Finally, the solubility of the functionalized graphenes were compared a reduced graphene oxide control. As solubility represents one of the most common desired properties to functionalized graphenes, determining whether a given functionalization method can produce soluble rGO is important. As expected, the rGO control did not display solubility and all functionalized samples were found to be soluble in DMF, with solubilities of .85, .89, .91 mg/mL for PhBr, Adam, and TrisCl graphenes respectively.

Scheme 1.13 Synthesis of sorption experiment control ketone.

1.3.3 Sorption experiment. Due to reduced graphene oxide’s high surface area, it is important to establish that any properties observed are the result of covalent functionalization and not merely from the sorption of organic material to the graphene surface. As any of the previously summarized characterization methods could also be explained by byproduct adsorption to the graphene surface, an experiment was performed to confirm the presence of covalent bonds linking introduce functional groups to the graphene surface. In the presence of water, acylated Meldrum’s acids will form the β-ketoacid, which when heated will release CO₂ to form a ketone (Scheme 1.13). By mixing an equivalent amount of this ketone with graphene oxide and submitting it to identical reaction conditions, a graphene material which approximates that which would be created by byproduct adsorption is created. This material could not be dispersed in organic solvents, which suggests that the action of the acylated Meldrum’s acid is critical to the observed properties.
Figure 1.7 Results of the sorption experiment. Only the graphene treated with acylated Meldrum’s acid displayed solubility in dichloromethane. All solutions were sonicated 30 seconds prior to photograph being taken.

1.3.4 $^{13}$C labeling experiment. Having ruled out adsorption of reaction byproducts as the source of the functionalized graphenes’ properties, it is reasonable to claim that treating graphene oxide with acylated Meldrum’s acid at elevated temperatures results in the covalent modification of GO’s basal plane. However, these data do now present compelling evidence for the Carroll rearrangement occurring. In order to determine whether or not the rearrangement was proceeding under the reaction conditions, a $^{13}$C labeling experiment was employed.

Under normal circumstances, $^{13}$C SSNMR is not a valuable technique for determining the efficacy of graphene functionalization, as most methods introduce relatively small amounts of carbon functionality which are obscured within the many carbon identities inherent in the graphene oxide structure. However these limitations can be overcome by employing $^{13}$C enriched reagents which greatly enhance their NMR signal. We therefore synthesized an acetic acid derivative of
Meldrum's acid and reacted it with graphene oxide under the standard reaction conditions (Scheme 1.14).

Scheme 1.14 Synthesis of $^{13}$C labeled acylated Meldrum's acid and its reaction with graphene oxide.

The $^{13}$C SSNMR analysis found no evidence of the rearrangement, with the only apparent carbonyl signal occurring at ~167 ppm (Figure 1.8). If the rearrangement did occur, a more characteristic ketone signal at approximately 200 ppm would be expected. A 167 ppm $^{13}$C shift is consistent with the enol form of the $\beta$ carbonyl in a $\beta$-ketoester. It is possible that the diagnostic ketone signal is obscured within the spinning sidebands of the peak at 167 ppm. However, even if this is the case, it is apparent that the Carroll rearrangement species is not the major product under these reaction conditions.
Figure 1.8. $^{13}$C SSNMR of $^{13}$C labeled Carroll graphene when reacted at 150 °C. The only two observable peaks occur at 133 ppm and 167 ppm. These correspond to the aromatic carbon of the graphene sheet and the enol form of a β-keto ester respectively. Spinning sidebands were identified by increasing rotor speed. Peaks which change chemical shift with changes in rotor speed can be considered spinning sidebands.

When the temperature of the reaction is increased in 180 °C, no effect on the outcome was observed; similarly, treating the reaction with LiHMDS only resulted in reduction of the GO and removal the $^{13}$C label entirely (Figure 1.9).
Figure 1.9. $^{13}$C SSNMR of $^{13}$C labeled Carroll graphene when the A) reaction temperature was increased to 180 °C and B) when treated with two equivalents of LiHMDS. The only two observable peaks in A occur at 133 ppm and 167 ppm. When treated with LiHMDS, the $^{13}$C Label is removed entirely, and the only observable peak is the aromatic graphene signal. Spinning sidebands were identified by increasing rotor speed.
Some evidence for the rearrangement was obtained using thermogravimetric analysis (Figure 1.10). One of the primary motivations for developing this functionalization method was to covalently attach functionality to the graphene surface via stable C-C bonds. When graphene oxide is reduced, modifications which are attached through oxygen functionality can be lost. Therefore, if the Carroll rearrangement was indeed occurring, TGA curves should reveal the presence of more stable C-C bonds to the surface. To probe this, graphene oxide was reacted under identical thermal conditions with both a 5-acyl Meldrum’s acid derivatives and an acid chloride bearing an identical functional group.

**Figure 1.10.** TGA curves graphene oxide reacted with a 5-acyl Meldrum’s acid derivative and corresponding acid chloride. The curves at the top of the figure correspond to the y-axis on the left, the weight (%) as temperature is increased. The curves at the bottom of the figure correspond to the right y-axis, and represent the 1st derivative of the top curves: d(weight%)/d(temperature). At approximately 430 °C, there exists a mass loss which is not observed in the acid chloride control.
Figure 1.10 reveals some interesting results. It appears that treatment of graphene oxide with a 5-acyl Meldrum's acid derivative introduces some functionality which differs in its degradation properties from that which is introduced from an acid chloride alone. However, whether or not this mass can be attributed to the Carroll rearrangement product cannot be determined by TGA alone. The presence of a small degree of Carroll product is also supported by the fact that when the bromine labeled functionalized graphene is refluxed in 11 M KOH for 24 h, 20% of the bromide label remains when analyzed by XPS. As any esters would likely be hydrolyzed under these conditions, it is possible some of the rearrangement product exists.

1.4 Conclusions

Covalently functionalized graphenes were synthesized via reaction with 5-acyl derivatives of Meldrum's acid. Characterization by XPS, TGA, FT-IR, and XRD confirmed the presence of covalent functionalization to the graphene basal plane using this method. A $^{13}$C labeling experiment and SSNMR analysis suggested that major material produced is not the expected Carroll Rearrangement product. Subsequent alteration of the reaction conditions by both increasing the reaction temperature and use of LiHMDS had no positive effect on the reaction. However, by using thermogravimetric analysis, it was found that the reaction of 5-acyl Meldrum's acid with GO produces a material which is unique from what is obtained by simply treating graphene oxide with an acid chloride. Furthermore, it was found by XPS analysis that the functionalization introduced non-hydrolyzable moieties, which further supports the presence of some Carroll product. It is possible that by further altering the reaction conditions either through higher reaction temperatures or with the addition of a catalyst it may be possible to more efficiently
effect the Carroll rearrangement on the surface of GO, opening a potential pathway to many
different types of functionalized graphenes.

1.5 Experimental

General. All chemicals were reagent grade and used as received from Sigma-Aldrich. Diethylene
glycol dimethyl ether (diglyme) was purchased from Sigma-Aldrich and dried over 4Å molecular
sieves prior to use. Reactions were performed under standard Schlenk techniques under inert
atmosphere unless otherwise noted. All glassware was flame-dried prior to use.

Instrumentation. Thermogravimetric analysis (TGA) was performed with a TA Instruments Q50
under nitrogen at a scan rate of 10 °C/min from 50 °C to 800 °C. Fourier transform infrared
spectroscopy (FTIR) spectra were acquired using a Thermo Scientific Nicolet 6700 FT-IR with a
Ge crystal for ATR and subjected to the ‘atmospheric suppression’ correction in OMNIC™ Specta
software. XPS spectra were recorded on a Kratos AXIS Ultra X-ray Photoelectron Spectrometer.
XPS samples were prepared by drop-casting solutions onto silicon wafers. X-ray data was
collected using an Inel CPS 120 position sensitive detector using an XRG 2000 S2 generator (Cu
Ka) and a Minco CT 137 temperature controller. XRD samples were prepared by dropcasting
concentrated solutions of the graphene derivative onto silicon wafers.

Synthesis

Synthesis of Graphene Oxide (GO). Graphene oxide was synthesized from natural source graphite
(300-mesh) via a modified Hummer’s method in which NaNO₃ was excluded.¹⁰ g graphite
(natural flake, Alfa Aesar, 2-15 um) was dispersed in 200 mL conc. H₂SO₄ and stirred at 0 °C.
g KMnO₄ was added portionwise over a 2 h period so not to allow the temperature to exceed 20 °C. The mixture was allowed to return to room temperature and stirred overnight, then 500 mL of ice-water was added slowly. Following this, 20 mL of 30% H₂O₂ was added. 500 mL ice-water was then poured into the reaction and stirred for 3 h. The resulting solids were then collected via ultracentrifugation and redispersed in 10% aq. HCl, and subsequently washed with copious amounts of DI water. The solids were then dialyzed against DI water until the water reached a pH of approximately 4. The resulting material was then lyophilized until dry.

**General synthesis of acylated Meldrum’s acid precursors.** 0.0218 mol carboxylic acid is dissolved in 50 mL dry methylene chloride and the resulting solution is stirred brought to 0 °C with an ice-bath and 0.1 mL DMF added. 2.19 mL (3.19 g, 0.0251 mol, 1.15 eq) freshly distilled oxalyl chloride is added by syringe over 10 min, and the ice-bath removed. The reaction vessel is sealed and vented through an oil bubbler to monitor the reaction progress. After 4 hrs, or when the reaction is no longer evolving gas, the solution is degassed with argon for 10 min to promote removal of residual HCl. While this reaction is degassing, 3.61 g Meldrum’s acid (0.0251 mol, 1.15 eq) is dissolved in 10 mL dry methylene chloride in a two-necked round bottom flask. The clear solution is stirred brought to 0 °C with an ice-bath and 4.41 mL (4.31 g, 0.0545 mol, 2.5 eq) dry pyridine is added by syringe over 5 min. To this solution, the solution containing 2 is added dropwise by cannula over 30 min. Upon addition the clear solution becomes an orange dispersion. After addition, the reaction is stirred at 0 °C for 1 hr. Following this, the ice-bath is removed and the reaction stirred at room temperature for an hour. The now deep red dispersion is poured into a 50 mL solution of 2 M HCl containing ice. This mixture is then poured into a separatory funnel and the organic layer isolated. The organic layer is washed with 2x 50 mL 2 M HCl and 1x 50 mL brine, dried over
MgSO₄ and filtered. The deep red solution is adsorbed onto 5 g silica gel and purified by column chromatography (eluent = 9:1 hexanes:ethyl acetate, with 1% AcOH added).

**Synthesis of 5-(3-(2-bromophenyl)-1-hydroxypropylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (Acylated Meldrum’s acid 1).** 1 was obtained using the general procedure outlined previously, using 3-(2-Bromophenyl)propionic acid as starting material. (5.0 g, 0.0218 mol) as the starting material (6.51 g, 84% yield). ¹H NMR (500 MHz CDCl₃) 15.35 (s, 1H), 7.55 (m, 1H), 7.26 (m, 1H), 7.22 (m, 1H), 7.10 (m, 1H), 3.40 (t, 2H), 3.12 (t, 2H), 1.68 (s, 6H).

**Synthesis of 5-(2-adamantan-1-yl)-1-hydroxyethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (Acylated Meldrum’s acid 2).** 2 was obtained using the general procedure outlined previously, using 1-adamantane acetic acid as the starting material. (3.2 g, 0.0165 mol) as the starting material (3.96 g, 75% yield). ¹H NMR (500 MHz CDCl₃) 15.35 (s, 1H), 3.01 (s, 2H), 1.74 (s, 6H), 1.67 (m, 18H).

**Synthesis of 2,2-dimethyl-5-(3,3,3-tris(4-chlorophenyl)-1-hydroxypropylidene)-1,3-dioxane-4,6-dione (Acylated Meldrum’s acid 3).** 3 was obtained using the general procedure outlined previously, using 3,3,3-Tris(4-chlorophenyl)propionic acid as the starting material. (15.04 g, 0.037 mol) as the starting material (15.5 g, 79% yield). ¹H NMR (500 MHz CDCl₃) 15.50 (s, 1H), 7.22 (m, 12H), 2.09 (s, 2H), 1.54 (s, 6H).

**Synthesis of 5-(1-hydroxyethylidene-1⁻¹³C)-2,2-dimethyl-1,3-dioxane-4,6-dione (¹³C labeled acylated Meldrum’s acid).** 1.87 g Meldrum’s acid (0.0126 mol, 1.15 eq) is dissolved in 10 mL dry methylene chloride in a two-necked round bottom flask. The clear solution is stirred brought to 0 °C with an ice-bath and 2.4 mL (2.33 g, 0.0295 mol, 2.5 eq) dry pyridine is added by syringe over
5 min. To this solution, a solution of 1.0 g acetyl chloride (1.13C) in 10 mL DCM is added dropwise over 10 min. After addition, the reaction is stirred at 0 °C for 1 hr. Following this, the ice-bath is removed and the reaction stirred at room temperature for an hour. The now deep red dispersion is poured into a 50 mL solution of 2 M HCl containing ice. This mixture is then poured into a separatory funnel and the organic layer isolated. The organic layer is washed with 2x 50 mL 2 M HCl and 1x 50 mL brine, dried over MgSO4 and filtered. The deep red solution is adsorbed onto 5 g silica gel and purified by column chromatography (eluent = 9:1 hexanes:ethyl acetate, with 1% AcOH added) (2.18 g, 93%) 1H NMR (500 MHz CDCl3) 15.13 (s, 1H), 2.69 (d, 3H), 1.74 (s, 6H). 13C NMR (125 MHz CDCl3) 194.9.

General procedure for the reaction of acylated Meldrum's with graphene oxide. 20 mg graphite oxide is dispersed in 100 mL dry diglyme (diethylene glycol dimethyl ether). The dispersion is sonicated for 30 min and then 0.005 mol (5 eq. to oxygen content of graphite oxide) acylated Meldrum's acid is added. This dispersion is stirred for 1 hr at room temperature then immersed in a 100 °C oil bath. After approximately 10 min the previously brown dispersion has become black. After 4 hr the oil bath temperature is increased to 130° C, and the reaction stirred for 21 hr. The black dispersion is filtered through a Millipore 0.4 µm PTFE membrane. The resulting filter cake is washed with a copious amount of acetone and then the black material is redispersed in 20 mL CH2Cl2. The dispersion is vortexed for 10 seconds then centrifuged at 11000 rpm for 10 min and the supernatant discarded. This procedure is repeated 3x with 20 mL CH2Cl2, followed by 2x 20 mL acetone, 3x 20 mL water, 2x 20 mL acetone. The resulting black slurry is then dried in a vacuum oven overnight at 50° C to produce a fine black powder.
1.6 References

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52


Chapter 2: Graphene Phosphate

2.1 Abstract

Using a modified version of the Arbuzov reaction, graphene oxide is covalently functionalized with phosphonate functionalities. Due to the oxidizing nature of graphene oxide, the reaction produces a large amount of phosphate salts which organize around the covalently installed phosphonate anchor sites. This results in a graphene material which can be extensively decorated with a controllable amount of phosphate material. The ligand properties of this material were explored by synthesizing a number of metal composites. Graphene phosphate was ultimately found to possess outstanding compressive strength properties, which could be tuned according to the reaction conditions. Portions of this chapter contain work which was assisted by Prof. Stefanie A. Sydlik, who aided in the compression strength testing of graphene phosphate and associated analysis. Additionally, Dr. Joseph Walish fabricated the iron molds used to create the graphene phosphate pellets.
2.2 Introduction

Graphene is a unique scaffold from which to create functional nanomaterials\textsuperscript{1,2,3} with high surface area,\textsuperscript{4} electrical conductivity,\textsuperscript{5,6} and mechanical strength.\textsuperscript{7} In Chapter 1, the synthesis and properties of graphene oxide (GO), were explored in detail. As a brief review, GO is produced by the exposure of graphite to extremely harsh oxidizing conditions and possesses chemical functionalities that can be used to produce modified graphene derivatives.\textsuperscript{8,9} Dispersible in both water and a number of organic solvents, it is a chemically dynamic, non-stoichiometric material.\textsuperscript{10} The primary functional groups of GO are alcohols, epoxides, and a variety of carbonyl containing moieties including ketones, esters, and carboxylic acids.\textsuperscript{11}

Most covalent functionalizations of graphene utilize highly energetic reactive intermediates, which attack the $\pi$-system of the basal plane.\textsuperscript{12,13,14} Substitution reactions that exchange the reactive C-O bonds for other functionality are attractive and these methods have been extended to carbon nucleophiles, resulting in the synthesis of a covalently functionalized graphene with excellent solubility in both aqueous and organic solvents.\textsuperscript{15} Early work by Lerf and Klinowski demonstrated that GO was functionalized by primary amines.\textsuperscript{11} Envisioning that this established electrophilicity of graphene oxide could be extended to phosphorus based nucleophiles, we have employed a variant of the Arbuzov reaction. In this classic organic transformation, a trialkyl phosphite reacts with a carbon electrophile under high temperature, resulting in the formation of a phosphonate (Scheme 2.1).\textsuperscript{16}

\begin{equation*}
\text{(RO)₃P:} \quad \begin{array}{c}
\text{R'} X \\
\text{100-150° C}
\end{array} \quad \begin{array}{c}
\text{R'O} \quad \text{R'O} \\
\text{RX}
\end{array}
\end{equation*}

Scheme 2.1. Generalized mechanism of the Arbuzov reaction.
The Arbuzov reaction is thermodynamically driven by the formation of a P=O bond which provides a 32-65 kcal/mol net energetic gain.\textsuperscript{16} The allowed electrophilic substrates for this reaction follow the general rules of $\text{SN}_2$ chemistry: primary alkyl halides are facile substrates while most secondary and all tertiary alkyl halides will not react. Similarly vinyl and aryl halides are inert under normal conditions. However, the Arbuzov is not limited to primary alkyl halide substrates. There are numerous examples in the literature of Arbuzov reaction on non-alkyl halide substrates, including enones,\textsuperscript{17} epoxides,\textsuperscript{18} and lactones\textsuperscript{19} (Scheme 2.2).

**Scheme 2.2. Atypical Arbuzov reactions**

Although it is not difficult to envision how the numerous epoxide and enone functional groups native to graphene oxide could act as electrophilic sites for this reaction (Figure 2.1), the last step of the Arbuzov, a nucleophilic back-attack on the phosphonium species, is unlikely occur between phosphite and GO alone. With this in mind, we predicted that if we supplemented the reaction between GO and phosphite with an anion ion capable of this step, we would be able to perform the Arbuzov reaction on graphene oxide, producing a graphene derivative covalently functionalized with phosphonates.
Our motivation for pursuing the covalent functionalization of graphene with phosphonate groups is derived from the unique properties of graphene/metal nanoparticle composites. Graphene's high surface area makes it a particularly attractive substrate upon which metal nanoparticles can be immobilized. As a precursor to graphene, graphene oxide represents a synthetically manipulatable high surface area material which can be readily combined with any number of metal nanoparticle precursors.

Often the valuable properties of metal nanoparticles are directly correlated with their size. In transition metals, this is known as the quantum size effect, and is a result of the large reduction in free electrons available in the valence band. Accordingly, it is advantageous to develop methods which can affix nanoparticles to a surface and prevent Ostwald ripening and agglomeration. By keeping nanoparticles dispersed, the active surface area of the metal is enhanced and mass transport to and from this surface is aided.

**Figure 2.1.** Possible mechanisms of nucleophilic attack on graphene oxide.
What sets graphene apart from other high surface area materials such as activated carbon is a well-defined conjugated aromatic chemical structure. This $\pi$-bond network forms valence and conduction bands which can contribute to the electronic character of the metal nanoparticles which are affixed the basal plane. In applications which involve electrochemical processes, graphene can provide a 'well' of electrons from which affixed metals can draw from and deposit electrons.\textsuperscript{22} In this way, graphene oxide represents a means toward constructing solid electrodes which can be customized with any number of metal nanoparticle materials. For example, when Co(OH)\textsubscript{2} nanoparticles were generated on the surface of GO, they gained superparamagnetic behavior while Co(OH)\textsubscript{2} nanoparticles not loaded onto graphene remained paramagnetic.\textsuperscript{23} The authors attribute this magnetic enhancement to a charge transfer mechanism between Co and the graphene sheet. In another report, Pt nanoparticles displayed enhanced electrocatalytic activity in the oxidation of methanol and ethanol into CO\textsubscript{2} as opposed to those loaded on carbon black.\textsuperscript{24}

Metal oxides are of particular interest for combination with graphene oxide, as the oxidizing properties of GO can be harnessed for in situ generation of the metal oxide product. \textsuperscript{25} TiO\textsubscript{2}, \textsuperscript{26} ZnO, \textsuperscript{26} SnO\textsubscript{2}, \textsuperscript{27} Cu\textsubscript{2}O, \textsuperscript{28} MnO\textsubscript{2}, \textsuperscript{29} NiO, \textsuperscript{30} and SiO\textsubscript{2}, \textsuperscript{31} represent just some of the examples in which metal oxide nanoparticles have been affixed to the graphene surface.

Graphene/metal nanoparticle composites are particularly promising in the area of energy storage. When combined with RuO\textsubscript{2} or MnO\textsubscript{2},\textsuperscript{32,33} reduced graphene oxide has been showed to have exceptional performance as a supercapacitor material. Cyclic performance and lithium storage were enhanced when SnO\textsubscript{2} nanoparticles were combined with reduced graphene oxide sheets.\textsuperscript{34} This effect was attributed to the large surface area of graphene accommodating lithium metal and thereby limiting the volume expansion inherent in lithium battery cycling.
As can be seen by the numerous examples in the literature, graphene/metal composites represent an extremely promising area for materials research. With this in mind, we believed developing a method to covalently functional graphene with a ligand-type functional group would provide a material with broad utility. To this end, phosphonates were identified as attractive targets. Carboxylates, which can be considered the native ligand structures in graphene oxide, form weaker bonds with metals than phosphonates. Furthermore, phosphonates have three oxygen atoms per functional group which can bind metals, allowing for multiple modes of coordination. Therefore, we believed if we could covalently functionalize graphene with phosphonates we could produce a valuable material for the creation of graphene metal composites.

2.3 Results and Discussion

2.3.1 Synthesis. Graphene oxide was ultrasonically dispersed in triethyl phosphite (1 mg/mL) with excess LiBr and stirred at 150°C for 36 h under flowing nitrogen. Filtration of the reaction mixture unexpectedly yielded a structurally durable monolith (Figure 2.2) with a mass far greater than the graphene (600 mg GO yielded 13 g monolith). After pulverizing the monolith into a fine powder and washing it several times in organic solvents (see experimental for detailed washing procedure) the resulting material was chemically characterized.

![Figure 2.2. Graphene phosphate monolith (shape is a result of filtration apparatus).](image)

60
2.3.2 Characterization. Though we initially believed the majority of the mass of the monolith was a result of LiBr salt incorporation, analysis of the monolith by X-ray photoelectron spectroscopy (XPS) reveals no detectable bromine present in the material. The monolith is composed of 18% phosphorus, 17% lithium, 34% oxygen, and 31% carbon. $^{31}$P MAS SSNMR was used to further classify the phosphorus material, and identifies several signals at 0-10 ppm characteristic of complex phosphate oligomers as the most prevalent constituents of the phosphorus content (Figure 2.3). There are several smaller peaks, which we attribute to phosphonate groups, between 20-30 ppm.

![Phosphonate Region](Phosphate Region)

$^{31}$P SSNMR of graphene monolith. The majority of the monolith is comprised of phosphate and phosphonate moieties. Spinning sidebands were determined by increasing rotor speed and identifying those peaks which changed in chemical shift.

Figure 2.3. $^{31}$P SSNMR of graphene monolith. The majority of the monolith is comprised of phosphate and phosphonate moieties. Spinning sidebands were determined by increasing rotor speed and identifying those peaks which changed in chemical shift.
2.3.3 Origin of Phosphate. The large amount of phosphate observed in the material is produced as a result of the oxidation of phosphite by graphene oxide.\textsuperscript{11} To elucidate the extent of phosphite oxidation within our system, a 1 mg/mL dispersion of graphene oxide in triethyl phosphite was sonicated for 1 h, then the dispersion was filtered (in air) and analysed by $^1$H NMR. This analysis revealed that the resulting solution was comprised of $\sim$20% triethyl phosphate, with the remaining portion comprised of triethyl phosphite.

The extensive oxidation achieved can be explained by both the facile nature of phosphite oxidation as well as the previously reported role of ambient $O_2$ as a terminal oxidant in graphene oxide facilitated oxidations.\textsuperscript{36} When triethyl phosphite is converted to phosphate in the presence of LiBr, the increased positive character on the central phosphorus atom renders the ethyl groups sufficiently electrophilic to react in a nucleophilic substitution reaction with free Br\textsuperscript{-}, resulting in the formation of both ethyl bromide and a lithium phosphate salt.

![Scheme 2.3](image.png)

**Scheme 2.3.** Triethyl phosphite does not react with LiBr even at high temperatures. However, it is oxidized in the presence of GO to triethyl phosphate,\textsuperscript{11} which then can react with LiBr.

To confirm the activity of LiBr in this regard, the headspace of the reaction was captured and analyzed by $^1$H NMR. This analysis revealed that the primary constituent of the volatile components of this reaction was indeed ethyl bromide. The origin of ethyl bromide appears to be exclusive to either phosphonate formation on the graphene basal plane and/or phosphate produced.
the activation of the triethyl phosphite by graphene oxide, as when a control reaction between triethyl phosphite and LiBr were submitted to identical conditions in the absence of graphene oxide, no reaction was observed (Scheme 2.3).

2.3.4 Role of Phosphite/Mechanism of Monolith Formation. It is unlikely that the formation of the graphene phosphate monolith is a result of an interaction between phosphate and graphene oxide alone, as when triethyl phosphite was excluded from the reaction and triethyl phosphate substituted in its place, filtration of the reaction mixture did not yield a cohesive solid material (i.e. a monolith). When the black powder obtained in this control experiment was washed in an identical manner as the original monolith and analyzed by XPS, no phosphorus was observed, suggesting that phosphite is a necessary component for the strong binding of the phosphorus functionality to the graphene oxide.

The critical role of phosphite in the reaction can be explained by a seed-growth mechanism wherein phosphonate anchors are produced on the graphene basal plane via the original proposed Arbuzov-like mechanism. These phosphonate seed sites then facilitate the agglomeration of the generated lithium phosphate salts around them, either through ionic associations, van der Waals interactions, and/or by the formation of covalent bonds via phospho-transesterification (Scheme 2.4).
Scheme 2.4. Proposed mechanism of graphene phosphate formation (graphene represented as fragment for simplicity).

Scanning electron microscopy reveals flower-like phosphate features on the graphene surface, which would appear to support the proposed seed-then-growth mechanism (Figure 2.4). Additionally, as seen in the higher magnification images of Figure 2.4 and associated EDX analysis, the basal plane of the graphene sheet is not smooth as would be expected for a bare graphene sheet, but appears to be extensively decorated with phosphorus based material.
2.3.5 Hydrolysis/Thermolysis of Graphene Phosphate. Powder X-ray diffraction (PXRD) shows the monolith's phosphate content to lack crystallinity (Figure 2.5). The single major well-defined peak of the PXRD spectrum likely corresponds to the gallery spacing between graphene sheets, $\sim$13 Å. As a result, it appears that the graphene sheets are separated by an amorphous polyphosphate network.
Figure 2.5. Powder X-ray diffractogram of graphene phosphate (black) and hydrolyzed graphene phosphate (blue).

The graphene phosphate material can be washed and sonicated in any number of organic solvents with no apparent change in composition; however, when the material is suspended and agitated in water, it loses the majority of its mass due to hydrolysis of the polymers and the dissolution of water-soluble phosphate salts. PXRD reveals that the hydrolysis coincides with the collapse of the gallery spacing between graphene sheets from 12.8 Å to at 8.1 Å (Figure 2.5). The 8.1 Å peak is broad and diffuse in nature, indicating a loss in uniformity of the inter-graphene spacing.

Table 2.1. Atomic composition of graphene phosphate before and after hydrolysis (by XPS).

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon (% atomic composition, by XPS)</th>
<th>Oxygen (% atomic composition, by XPS)</th>
<th>Phosphorus (% Atomic Composition, by XPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene Phosphate</td>
<td>52</td>
<td>30</td>
<td>18</td>
</tr>
<tr>
<td>Hydrolyzed Graphene Phosphate</td>
<td>92</td>
<td>7</td>
<td>2</td>
</tr>
</tbody>
</table>

66
XPS analysis reveals that the hydrolyzed material retains 2% phosphorus content after 3x washing and sonication in THF, DMF, DCM, water, and acetone (Table 2.1). Hence, in addition to the formation of the hydrolyzable phosphate networks, there appears to be some irreversible covalent modification of the graphene sheet in this functionalization scheme.

![Phosphate Region](Phosphonate Region)

*Spinning Sideband

**Figure 2.6.** $^{31}$P SSNMR of hydrolyzed graphene phosphate. While the majority of the material’s mass is lost after extensive washing in water, some phosphorus based material remains, suggesting covalent attachment to the graphene surface.

A $^{31}$P SSNMR of the hydrolyzed material supports this assertion (Figure 2.6). The $^{31}$P SSNMR spectrum shows the presence of two major phosphorus environments: a smaller broad peak in the phosphonate region (~36 ppm), and a larger broad peak in the phosphate region (~3 ppm). From this, it appears likely that the nature of the phosphorous bound to the graphene is indeed phosphonate, which forms anchor sites for the formation of lithium phosphate oligomeric
structures via phospho-transesterification as summarized in Scheme 2.4. Based on the PXRD data, it is reasonable to assume that this functionalization occurs on the basal plane of the graphene sheet, as simple reductive deoxygenation of graphene oxide produces materials wherein the graphene sheets display inter-sheet spacings of around 4 Å.
Figure 2.7. SEM Micrographs of a cross-section of a typical graphene phosphate pellet A. before annealing and B. after annealing. C. Chart displaying the linear dependence of the mass of the produced graphene phosphate monolith on initial LiBr loading. D. The dependence of the monolith phosphate content on LiBr loading. The amount of phosphate was determined by holding the graphene oxide mass constant over several reactions while varying LiBr loading and subtracting the mass of reduced graphene oxide from each monolith. The remaining mass was attributed to phosphate. E. Thermogravimetric analysis of i. graphene phosphate ii. hydrolyzed graphene phosphate, iii. reduced graphene oxide.
The amount of phosphate in the final product can be precisely controlled, as the mass of the monolith is proportionally related to the LiBr loading in the initial reaction (Figure 2.7). This correlation is demonstrated in the SEM micrographs of the material, as the graphene sheet becomes progressively more covered in phosphate material as the relative loading of LiBr is raised (Figure 2.8).

![Figure 2.8. SEM Micrographs of graphene phosphate produced from a LiBr loading of A. 2.5:1 B. 5:1 C. 7.5:1 LiBr mass loading relative to graphene oxide. D. From left to right, graphene phosphate monoliths produced from 2.5:1, 5:1, 7.5:1 LiBr mass loadings relative to graphene oxide. The SEM images directly above each monolith correspond to that monolith.](image)

2.3.6 **Alternative Synthesis of Phosphonate Graphene.** Interestingly, it is possible to functionalize graphene with phosphonate groups without the formation of a monolith and lithium phosphate salts. Utilizing the Michaelis-Becker reaction, diethyl phosphite is treated with sodium hydride,
then reacted with graphene oxide. By XPS, the resulting material is virtually indistinguishable from the hydrolyzed graphene phosphate (Table 2.1).

Scheme 2.5. Proposed mechanism of formation and synthesis of phosphonate graphene PG1.

2.3.7 Iron/Lithium Graphene Phosphate Composites. Having characterized the composition of the graphene phosphate monolith, we then explored the effect of incorporating metals into its composition. Our first attempts involved substituting iron bromide salts in place of LiBr. We were particularly interested in iron because of the widespread use of LiFePO₄ as a cathode material for in Li-ion batteries. LiFePO₄ is less commonly used than LiCoO₂ in consumer electronics as a result of its slightly lower energy density. However, because of its lower toxicity, longer lifetimes, and better power density, LiFePO₄ is a common component of batteries in electric and hybrid vehicles and medium to large scale grid storage.

When FeBr₂ is substituted for LiBr, a monolith similar to what is obtained under normal conditions is obtained (Scheme 2.6). XPS was used to confirm that the monolith was comprised of both phosphorus and iron material. PXRD of this material displayed only one diffraction peak, which likely corresponded to the gallery spacing of the graphene sheets. While it is possible that this monolith was comprised of FePO₄, its amorphous nature prevented characterization via PXRD.
Scheme 2.6. Synthesis of iron/graphene monolith FeG1. FeBr\textsubscript{2} displayed similar activity to LiBr as a source of bromide ion in the synthesis of a graphene monolith.

After washing with water and annealing at 350 °C for 2 h under inert atmosphere, the iron/graphene monolith FeG1 was resubmitted for PXRD analysis. In contrast to the un-annealed FeG1, this material did display crystalline features. Attempts to match the PXRD diffractogram with the International Centre for Diffraction Data (ICDD) Powder Diffraction File database yielded no results.

We also synthesized a graphene phosphate material using a mixture of LiBr and Fe(II) and Fe(III) bromide salts (Scheme 2.7). After annealing the resulting material at 350 °C for two hours under inert atmosphere, we characterized the fine black powder by XPS and PXRD.

\[
\begin{align*}
\text{LiBr} & \quad \text{FeBr}_2 & \quad \text{FeBr}_3 \\
(1 \text{ eq.}) & \quad (1 \text{ eq.}) & \quad (2 \text{ eq.})
\end{align*}
\]

\[
\text{Graphene Oxide} \xrightarrow{\text{P(OEt)}_3 \quad 150^\circ C \quad 24 \text{ h}} \quad \text{LiFeG1}
\]

Scheme 2.7. Conditions for the synthesis of a graphene monolith LiFeG1.

Again, attempts to match the PXRD diffractogram with the ICDD Powder Diffraction File database yielded no results.
We also examined the effect of combining the as-produced monoliths with iron or lithium salts after their formation and then annealing the obtained composite. Scheme 2.8 summarizes these attempts. With the exception of FeG2, crystalline materials were again obtained and compared to the ICDD Powder Diffraction File database. Unfortunately no match could be found. While these results do not preclude the possibility that some form of lithium iron phosphate/graphene composite was formed under these conditions, due to the difficulty in determining the precise composition of the composites, we believed our efforts would be better served pursuing other metal compositions and applications.

Scheme 2.8. Conditions for the synthesis of Li/Fe/graphene phosphate composites, FeG2, FeG3, and LiFeG2.
2.3.8 Cu/Ce Graphene Phosphate Composites. CuO/CeO$_2$ is a well-studied material which is commonly used for heterogeneous gas-phase oxidation of CO into CO$_2$. Such materials are attractive for the detoxification of cigarette smoke and other aerosol pollutants; however, fouling of the catalyst surface is a significant problem in implementation of these materials. We believed that by providing a support a CO oxidation catalysts we could both enhance the surface area of the active catalyst surface and shield the catalysts from fouling. Scheme 2.9 summarizes our approach to develop a CuO/CeO$_2$ graphene phosphate composite for CO oxidation.

![Scheme 2.9. General synthetic approach toward constructing a CuO/CeO$_2$ graphene phosphate composite. The structures shown represent idealized representations of the material compositions.](image)

When the material which was produced under these conditions was annealed under inert atmosphere, PXRD analysis reveals that a CePO$_4$/graphene composite (CePhosGraphene) was obtained. Figure 2.9 shows an SEM image of this material. While the desired metal oxide material was not produced under these conditions, calcination under inert atmosphere creates an extremely well dispersed (~10-100 nm in diameter) CePO$_4$ nanoparticle/graphene composite.
When graphene phosphate is combined with cerium and copper in an identical manner but annealed under air, PXRD confirms that the desired CuO/CeO$_2$ nanoparticle composition (CuCeOGraphene) is obtained (Figure 2.10). The broad peaks in the PXRD confirm that the metal oxide is in nanoparticle form. An SEM image of this material reveals that these nanoparticles are organized into two domains, agglomerated spherical structures 100-300 nm in diameter and smaller 5-50 nm groups.
Figure 2.10. PXRD diffractogram and SEM image of CuCeOGraphene. The PXRD peak match what is expected for a CuO/CeO$_2$ nanoparticle composition. The SEM image reveals extensive decoration of the graphene sheet by two separate nanoparticle domains, one composed of spherical structures 100-500 nm in diameter, and the other of smaller 5-50 nm structures.

It was also found that the hydrolyzed graphene phosphate was effective as dispersing CuO/CeO$_2$ nanoparticles. When this material was combined nanoparticle precursors and annealed under oxygen (Scheme 2.10), the resulting material was more effective at dispersing nanoparticles than unfunctionalized graphene (Figure 2.11).

Scheme 2.10. Synthesis of hydrolyzed graphene phosphate/Cu$_2$O/CeO$_2$ nanoparticle composite.
Figure 2.11. TEM images of A bare Cu$_2$O/CeO$_2$ nanoparticles, B Cu$_2$O/CeO$_2$ nanoparticles loaded onto unfunctionalized graphene oxide, and C Cu$_2$O/CeO$_2$ nanoparticles loaded onto hydrolyzed graphene phosphate. As can be seen in the above images, in contrast to A and B, the hydrolyzed graphene phosphate material is highly effective at dispersing the nanoparticles across the sheet.

This material’s performance in CO oxidation was analyzed by Joseph Elias of the Shao-Horn group at MIT. When compared the bare Cu$_2$O/CeO$_2$ nanoparticles, the composite performed slightly better (Figure 2.12). Interestingly, the materials show very different rate dependence on CO and O$_2$ concentrations. In the graphene composite, a slight dependence on CO concentration is shown, while there is little dependence on O$_2$ concentration. In the bare nanoparticles, rate is adversely affected by increasing CO concentration, and strongly enhanced by increasing oxygen concentration.
Figure 2.12. CO oxidation performance of HGP Cu$_2$O/CeO$_2$ nanoparticle composite. A shows that the rate of CO oxidation is slightly higher in the composite than in the nanoparticles alone. Interestingly, B and C show how the materials show very different rate dependence on CO and O$_2$ concentrations, respectively. The CO oxidation experiment and associated analysis were performed by Joseph Elias.

It ultimately discovered that residual phosphate can have an adverse effect on the heterogeneous gas-phase oxidation of CO, ultimately limiting the utility of this material for this application. However, based on these data, graphene phosphate appears to be highly effective in serving as a template for forming dispersed metal phosphate nanoparticle composites.

2.3.9 High-Strength Properties. Graphene is known to have extraordinary mechanical strength as a result of its two-dimensional lattice of strong C-C bonds. Based on graphene's known mechanical strength, we investigated the performance of graphene phosphate in compression. Graphene
phosphate can be compressed into robust, free-standing pellets using a steel mold and a mechanical press (Figure 2.10). The compressive strength of the material is dependent on the initial mass loading of the halide salt in the reaction and the resulting composition of phosphate in the product. Additionally, sample preparation plays a key role in the resulting composite properties. We found that loading a cylindrical mold (diameter of 10.2 mm) with 300-350 mg of graphene phosphate and applying a pressure of 10000 psi for 1 minute to give the most reproducible and mechanically robust samples (thickness of 4 ± 1 mm).

Samples were synthesized at varying ratios of salt to graphene oxide and the properties of the resulting composites were compared. In addition to LiBr, graphene phosphate was synthesized using CaCl₂ as a halide source in order to explore the impact of a divalent cation in the material’s mechanical properties. Of the CaCl₂ samples, a ratio of 3.125 g CaCl₂ to 1 g GO (highest graphene content) produced the material with the highest modulus, with an ultimate compressive strength of 60 MPa. Materials produced with 6.25 and 10 g CaCl₂ (lower graphene content) produced weaker materials. A slightly different trend and behavior was observed for the graphene phosphate prepared with LiBr. At the highest graphene content (2.5 g LiBr to 1 g GO), the material shows a modest ultimate compressive strength (UCS) of 35 MPa. When the phosphate polymer content is increased raising the LiBr:GO ratio to 5 g:1 g, a tough material results. This material shows a classical polymer behavior with a yield stress at 53 MPa followed by a long plastic deformation region, with the phosphate graphene ultimately failing at a UCS of nearly 100 MPa. This was the only composition that exhibited polymeric-type behavior, so we assume that this is a result of a composition that allows an ideal synergy between the stiff graphene sheets and the ductile polyphosphate matrix. Like the phosphate graphene prepared with CaCl₂, samples prepared with higher ratios of LiBr (7.5 and 10 g LiBr to 1 g GO) resulted in decreased mechanical properties.
Annealing did not dramatically impact the properties of the tougher samples, only the weaker materials (i.e. 7.5:1 and 10:1 LiBr and 10:1 CaCl₂) were marginally stiffened by the annealing process.

![Figure 2.13. A. Summary of ultimate compressive strength of all compositions; B. Typical stress-strain curves for the compositions; C. 2.5 kg steel weight on a typical graphene phosphate monolith; D. 300 mg graphene phosphate and pellet produced from compression in a steel press at 10000 psi](image)

It is likely that the phosphate salts promote adhesion between graphene sheets to create a ductile, yet high strength composite material. This is congruent with the recent results of Ruoff et al. that demonstrate a reduction in the interstitial space between adjacent graphene sheets enhances the compressive strength. A crossectional SEM confirmed the ability of our material to form just such a contiguous non-porous structure (Figure 2.7). However, upon annealing, the graphene phosphate pellets lose ~50% of their mass and become highly porous. Interestingly, even after
annealing at 850 °C, the material remains 10-12% phosphorus by XPS. Due to the characteristic phosphate stretches in the IR spectrum of this annealed material, the remaining phosphorus is likely high-melting lithium phosphate salts, which as a result of the high temperatures involved, are unlikely to be covalently attached to the graphene sheet. The increased porosity of the annealed pellets has the predictable effect of lowering the materials elastic modulus relative to the unannealed graphene phosphate. Additionally, unlike the as-produced graphene phosphate, the annealed material does not hydrolyze upon immersion in water.

2.4 Conclusions
We have developed a synthesis of a graphene phosphate composition. This material is generated from the reaction of graphene oxide, a highly oxidizing electrophile, with triethyl phosphite, a nucleophilic reductant, in the presence of lithium bromide. The graphene sheet’s basal plane is covalently functionalized with phosphonate groups and sheets are separated by lithium phosphate networks. The resulting material shows remarkable compressive strength that can be tailored by altering the identity and amount of metal halide salt in the original reaction to produce materials of differing strength and elasticity. Although the as-produced material hydrolyzes easily in water, the close association between water-soluble lithium phosphate salts and the covalently functionalized phosphonate-graphene provides a thermolytic template by which the creation of porous, hydrophobic graphene phosphate structures can be achieved upon annealing. The annealed graphene phosphate retains 10-12% phosphate by XPS, and possesses elastic strength properties as well as exceptional ultimate compressive strength. Ongoing investigations are seeking to create related metal-phosphate/graphene nanocomposites for energy storage applications.
2.5 Experimental

Materials and Instrumentation. All reagents and solvents were purchased from Sigma-Aldrich and used as received unless otherwise noted. Thermogravimetric analysis (TGA) was performed with a TA Instruments Q50 under nitrogen at a scan rate of 10 °C/min from 50 °C to 800 °C. Fourier transform infrared spectroscopy (FTIR) spectra were acquired using a Thermo Scientific Nicolet 6700 FT-IR with a Ge crystal for ATR and subjected to the ‘atmospheric suppression’ correction in OMNIC™ Spectra software. XPS spectra were recorded on a Kratos AXIS Ultra X-ray Photoelectron Spectrometer. XPS samples were prepared by drop-casting solutions onto silicon wafers. Powder X-ray diffraction patterns were recorded on a Bruker Advance D8 diffractometer using Nickel-filtered Cu-Kα radiation (λ = 1.5418 Å), with accelerating voltage and current of 40 kV and 40 mA, respectively.

Synthesis of graphene oxide (GO) Graphene oxide was synthesized from natural source graphite (300-mesh) via a modified Hummer’s method in which NaNO₃ was excluded.⁴²

Synthesis of graphene phosphate. In a typical reaction, 250 mg graphene oxide was dispersed in 250 mL triethyl phosphite and sonicated for 1 h. LiBr was added and the reaction mixture was further sonicated for 30 min. The resulting dispersion was maintained at 150° C under magnetic stirring and flowing N₂ for 36 h. Upon completion, the reaction was filtered and the resulting monolith was dried at 125° C under vacuum for 24 h. The monolith was pulverized in a mortar and pestle and dispersed in THF. After ultrasonication for 10 min, the dispersion was centrifuged and the supernatant discarded. This washing was repeated 5x in THF, 5x in DMF, 5x in methylene chloride. To hydrolyze the graphene phosphate to the phosphonate graphene, a 5x sonication and
washing in water step was inserted in between in the THF and DMF. To anneal graphene phosphate, a pellet was placed inside of a quartz tube in a tube furnace and allowed to sit under flowing N\textsubscript{2} for 30 min. The material was then brought to 850° C at a heating rate of 20° C/min then allowed to return to room temperature naturally.

*Synthesis of phosphonate graphene PG1.* 10 mL (10.72 g, 0.0776 mol) diethyl phosphite was dissolved in 100 mL dry THF and cooled in an ice-bath. 3.2 g NaH (60% in mineral oil) was added slowly so as not to allow the mixture to boil. Meanwhile, 100 mg graphene oxide was sonciatively dispersed in 100 mL dry THF. The diethyl phosphite mixture was added via cannula to the graphene oxide dispersion over 10 min. The mixture was then brought to reflux for 24 h. The reaction filtered and the resulting solids were washed and sonicated in 50 mL DMF (3x), 50 mL H\textsubscript{2}O (5x), 50 mL acetone (2x), and 50 mL dichloromethane (4x).

*Synthesis of FeG1.* FeG1 was synthesized in an identical fashion as graphene phosphate, with the exception that 4.2 g FeBr\textsubscript{2} was substituted for LiBr. Upon addition of FeBr\textsubscript{2} the reaction immediately gelled. After sonication, the reaction de-gelled, and the reaction maintained at 150 °C for 24 h. Filtration of the reaction mixture yielded a 2.94 g monolith.

*Synthesis of LiFeG1.* 1.0 g LiBr, 1.5 g FeBr\textsubscript{2}, and 0.8 g FeBr\textsubscript{3} were mixed in 10 mL dry THF. The THF was evaporated yielded a brown paste. Meanwhile, 150 mg graphene oxide was ultrasonically dispersed in 150 mL triethyl phosphite for 1 h. This mixture was stirred and the salt paste added. The resulting mixture was sonicated for 30 min then brought to 150 °C for 24 h under flowing N\textsubscript{2}. Filtration of the reaction mixture yielded a 2.52 g monolith.

83
Synthesis of FeG2. 100 mg graphene phosphate was mixed with 100 mg Fe(acac)$_3$ in 10 mL DI water. The mixture was lyophilized and the resulting solids were placed into a tube furnace and heated to 350 °C under flowing N$_2$ for 2 h.

Synthesis of FeG3. 100 mg mmol Fe(NO$_3$)$_2$ · 9 H$_2$O was dissolved in 10 mL THF and 3Å molecular sieves were added. The solution was allowed to sit overnight under inert atmosphere, the molecular sieves removed by filtration and then 100 mg graphene phosphate was added. The mixture was stir for 1 h and then the solvent removed in vacuo. The resulting solids were placed into a tube furnace and heated to 350 °C under flowing N$_2$ for 2 h.

Synthesis of LiFeG2. 100 mg FeG1 was mixed with 50 mg Li$_2$CO$_3$ in 10 mL DI water. The mixture was stirred for 1 h then was lyophilized. The resulting solids were placed into a tube furnace and heated to 515 °C under flowing N$_2$ for 2 h.

Synthesis of CePhosGraphene and CuCeOGraphene. 0.255 g Ce(NO$_3$)$_3$ · 6 H$_2$O and 0.0283 g Cu(NO$_3$)$_3$ · 3 H$_2$O were mixed in 10 mL THF and 3Å molecular sieves were added. After standing under N2 overnight, the molecular sieves were removed by filtration. To this solution, 100 mg graphene phosphate was added. The mixture was stirred for 1 h, and the solvent removed in vacuo. The resulting solids were pressed in a circular steel mold at 12500 lbs/in2 for 90 seconds. The resulting pellet was then heated to 350 °C under either flowing N$_2$ or flowing air for 2 h.

Mechanical Testing. Ultimate compressive strength was measured using a Zwick/ Roell mechanical tester, model BTC-EXMACRO.001, using a 10 kN force cell. Data was analyzed using
testXpert II software package. Samples were prepared in a mold specifically machined for these purposes with an inner diameter of 10.2 mm (0.40") and a 45 mm (2.54") chamber depth. The cavity was filled with 300-350 mg sample and a pellet was pressed using a fitted ballast to apply 10,000 psi for 1 minute. In this way, small cylindrical samples with a thickness of 4 ± 1 mm (0.16"), and a diameter of 10.2 mm (0.40") were prepared. The test specimens were placed between the compression platens on the universal testing machine the sample was crushed at a rate of 10 mm/ min (0.39"/ min) until failure occurred.
2.5 References


Chapter 3: Brine Stable Graphene
3.1 Abstract

The synthesis of a brine-stable graphene is reported. Using AIBN initiated radical polymerization, random co-polymers containing both aniline and imidazole species were synthesized. These polymers were then covalently attached to the graphene basal plane using diazonium chemistry and converted into imidazolium betaine structures. The resulting composite shows indefinite stability in high-temperature brine solutions, which are particularly relevant for the imaging of oil reservoirs. The work reported in this chapter was performed with equal contributions from both John B. Goods and Dr. Carlos Zuniga. Dr. Jason Cox also provided valuable discussions.
3.2 Introduction

The stabilization of nano-sized materials in aqueous environments with high salinities (high ionic strength) has become an important area of research due to the relevance of these materials for the petroleum industry. The delivery of nanoscale materials deep into oil reservoirs are of particular interest, as these materials can act as imaging enhancers and/or reporter probes, providing useful information on the state of the reservoir, which is essential to the improvement of recovery yields (Figure 3.1). Designing effective reservoir imaging materials is challenging as a result of the fact that the internal environment of oil reservoirs contains high salinity and high temperature brines which can readily destabilize nano-materials injected into them.

Figure 3.1. Generalized schematic of the use of nano-reporters for oil reservoir imaging. Material is injected suspended in a brine which matches that which is found within the reservoir. The injected materials are collected downstream for analysis. Changes in the material, such as fluorescence, magnetic properties, or the presence or absence of chemical ‘cargo’ can provide information on the amount of oil in the reservoir, harmful contaminants, porosity of the rock, and other properties.
Reduced graphene oxide is a particularly attractive platform for delivery of nano-reporters into reservoirs. Its high surface area allows it to carry large amounts of chemical cargo while simultaneously shielding that cargo from the harsh environment of the reservoir. This is particularly important when the physical state of the reporter material is critical to the analytical technique, i.e. paramagnetic nanoparticles. Furthermore, graphene oxide contains synthetically addressable functional groups which allow for controlled functionalization, allowing for wide compatibility with many types of chemical cargo as well as chemical modification which can improve its stability within the reservoir. Finally, due to electronic interaction its valence and conduction bands, metal nanoparticles are known to possess enhanced properties when loaded onto graphene.²,³

While reduced graphene oxide is insoluble in nearly all solvents including water, it is possible to covalently functionalize graphene to provide dispersibility in organic and aqueous solvents.⁴ It is inaccurate to classify graphene dispersions as true solutions, however, as they do not possess many of the necessary attributes of a homogenous mixture of one phase. For example, graphene dispersions display the Tyndall effect and scatter incident light (Figure 3.2).

**Figure 3.2.** When laser light is shown through a graphene dispersion, the light is scattered by the suspended particles. This is known as the Tyndall effect, and can be used to demonstrate the presence of graphene in a liquid medium.
Graphene dispersions can also be separated by filtration and are multi-phasic (liquid solvent and solid graphene). Accordingly, graphene dispersions are best understood as colloids. A colloidal system is most commonly composed of a solid phase distributed within a liquid medium, with particles sizes 1 to 1000 nm in diameter.  

At temperatures above freezing, the normal course of Brownian motion will cause dispersed colloid particles to collide with one another constantly. The outcome of these collisions is what defines the stability of a given colloid. In each collision event, two outcomes are possible: either the two particles will coalesce to form a larger particle or repulse and remain separate. The outcome of each event is determined by the contributions from the attractive and repulsive forces that exist between the two particles. When over time, attractive forces contribute more strongly to these collisions the dispersion can become unstable.

Interactions within colloids are best understood through van der Waals interactions. Van der Waals interactions can be defined as the attractive and repulsive forces between molecules that are not due to electron sharing or electrostatic interactions. These can be further subdivided into forces between two permanent dipoles (Keesom), forces between a permanent dipole and an induced dipole (Debye), and a force between two induced dipoles (London dispersion forces). In brines, the large amount of charges in solution result in ionic screening between permanent dipoles; accordingly, in these systems London dispersion forces are the most important interactions to consider.

As colloid dispersions are composed of similar, if not identical particles, the attractive forces between them are significant. To overcome these forces the particles must similarly possess long-range repulsive properties. There are typically three methods to induce long-range repulsion between colloids: electrostatic stabilization, depletion stabilization, and steric stabilization.
Electrostatic stabilization requires the decoration of colloid particles with ionic functionality. This results in the particle being surrounded by a charged surface 5-10 nm diameter which experiences Coulombic repulsion when another particle with like charges is encountered. Electrostatic stabilization can be a highly effective means for maintaining stable colloids in low ionic strength solutions; however, in brine solutions with high ionic strength, the charged surface surrounding particles shrinks in diameter, and long-range attractive London dispersion forces overcome this barrier, resulting in cohesion between particles. Therefore, in designing a functionalization strategy for brine stability, electrostatic repulsion is not an effective design principle.

Depletion stabilization is best understood as a product of osmotic pressure and entropic effects. Its original description involves the addition of a polymer solute into a colloid to promote stability (Figure 3.3). As two particles approach one another, the concentration of polymer additive between these particles becomes depleted, resulting in an osmotic pressure gradient across the area between two particles and the surrounding solution. In a good solvent, the two particles cannot approach any farther, as further depletion of the solute concentration becomes energetically unfavorable. However, if two particles are allowed to become so closely associated as to deplete solute concentration between them to nearly zero, the dominant osmotic gradient shifts, and the now nearly pure solvent between them will mix with the surrounding solution. Without solvent between the two particles, they coalesce, resulting in depletion flocculation. Depletion stabilization is a viable strategy for producing brine stable colloids because it does not rely upon electrostatic interactions to produce stability. However, in the case of introducing functionalized material into oil reservoirs, utilizing such a strategy becomes more difficult, as the stability of the colloid is dependent upon a species which is not bound that the colloid. In other words, depletion
stabilization is highly dependent on concentration. When the previously stable solution is introduced into the massive volume of the reservoir, the concentration of the stabilizing polymer solute will approach zero, and the colloid will collapse.

![Diagram showing depletion, flocculation, and stabilization](image)

**Figure 3.3.** The above figure provides a simplified summary of depletion interactions in colloids. As two graphene fragments approach one another, if they become close enough that solute concentration between approaches zero (left box), an osmotic gradient will cause the pure solvent between them to mix with the surrounding solution, forcing the graphene sheets to flocculate. In the right box, the graphene sheets do not become close enough to exclude polymer solute from the area between them. This creates an osmotic gradient which causes polymer solute to enter the space between the particles, keeping them separated and stable.

A third method for creating stable colloids is through steric stabilization. Steric stabilization is similar to depletion stabilization; however, in this case, the polymer which imparts stability is attached, either covalently or through adsorption, to the colloid particle. When two polymer chains from different particles approach one another, there exists an entropic cost to confining the chains between the particles. As the polymer chains lose degrees of freedom in their movement, an osmotic gradient develops and solvent molecules swell the chains and prevent aggregation. This steric repulsion between polymer chains prevents the colloid particles from reaching proximities which could result in flocculation. Steric stabilization is an attractive means for developing brine stable materials for oil reservoir imaging as it is not dependent on ionic
interactions and the functionality is covalently linked to the colloid surface, meaning stable materials can be introduced into the large volume of the reservoir without dilution effects inducing flocculation.

Steric stabilization is dependent upon a favorable interaction between the polymer chains which project from the colloid into the dispersion medium. One important reason for this is because long-range repulsion is most effective when the polymer chains extend deeply into the solvent. The more effective the liquid medium swells the polymer, the larger the steric radius of the colloid, and therefore the lower the probability that two particles will reach a distance which can result in flocculation. Zwitterionic polymers are known to be particularly compatible with brine solutions, due to the anti-polyelectrolyte effect. The ionic screening inherent in such solutions is typically considered a destabilizing effect for ionic compositions, however in the case of zwitterionic polymers, it actually promotes dissolution. In pure water, zwitterionic polymers are often insoluble, as the ionic associations within the polymer itself are stronger than interactions with the polar solvent. However, when salt is added to the water, the ionic attractions between functional groups within the polymer are effectively screened, and osmotic and entropic effects become dominant, promoting dissolution of the poly-zwitterion. Such materials have been used in applications as seawater antifouling coatings but have also been suggested for potential use in enhanced oil recovery.

Two of the most important brine compositions for oil reservoir applications are American Petroleum Institute (API) brine and Arab-D brine. Arab-D brine can be found in the largest oil well in the world known as the Ghawar field found in Saudi Arabia. Table 1 provides the relative weight percentages and salt compositions of these high salinity brines. As compared to the standard
API brine, the Arab-D brine possesses a more complex salt mixture and a significantly higher content of divalent ion species like calcium chloride and magnesium chloride.

Table 3.1. Composition of Arab-D and API brines.

<table>
<thead>
<tr>
<th>Salt Species</th>
<th>Arab D</th>
<th>API</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>7.5%</td>
<td>8.0%</td>
</tr>
<tr>
<td>CaCl(_2\cdot2)H(_2)O</td>
<td>5.0%</td>
<td>2.0%</td>
</tr>
<tr>
<td>MgCl(_2\cdot6)H(_2)O</td>
<td>1.3%</td>
<td>-</td>
</tr>
<tr>
<td>BaCl(_2)</td>
<td>0.001%</td>
<td>-</td>
</tr>
<tr>
<td>Na(_2)SO(_4)</td>
<td>0.006%</td>
<td>-</td>
</tr>
<tr>
<td>NaHCO(_3)</td>
<td>0.005%</td>
<td>-</td>
</tr>
</tbody>
</table>

Work by Bagaria et al in 2013\(^1\) showed that iron oxide nanoparticles wrapped with poly(AMPS-co-AA) could effectively stabilize the nanoparticles in American Petroleum Institute (API) brine (aqueous 8 wt% sodium chloride and 2 wt% calcium chloride) at 90 °C for up to one month (Figure 3.4). The polymer successfully imparted electrosteric stabilization and repulsion required to stabilize the nanoparticles against agglomeration in the brine.

Another example using an ionic polymer was shown to stabilize carbon nanoparticles in API brine as reported by Hwang et al in 2012.\(^2\) Polyvinyl alcohol was grafted onto the surface of the nanoparticles and could be sulfated with a chlorosulfonic acid treatment. It was shown that the lightly sulfated nanoparticles could be stably dispersed in API brine at 100 °C while the unsulfated nanoparticles were not dispersible in the brine. The highly sulfated nanoparticles were not as stable as the lightly sulfated variant forming a suspension of small particulates upon heating. The long-term stability of the stable dispersion over time was not examined; however, the nanoparticles were shown to act effectively as carriers for a reporter molecule when injected into a simulated reservoir environment. Other work has shown that a polyimidazole betaine was dispersible in 22.6
wt% NaCl solutions (Figure 3.4). Again, long term stability was not reported or the effect of temperatures was not reported.

Figure 3.4. Polymers in the literature which have reported brine stability.

To meet the demanding conditions for solubility and stability in brine at elevated temperatures, we have focused on the functionalization of nano-sized graphene sheets (<1 μm). As mentioned previously, an advantage of this approach is the large surface area and chemical reactivity of the graphene oxide basal plane, which facilitated functionalization as well as the potential ability to encapsulate nanomaterials deemed of interest. As a result, success with this system could find utility for stabilizing and transporting different payloads (molecules or nanoparticles).

3.3 Results and Discussion

3.3.1 Graphene oxide synthesis. Highly oxidized graphene oxide (made with a 5:1 permanganate ratio versus the typical 3:1) forms stable dispersions in aqueous concentrated sodium chloride solutions up to 5 wt%, as reported by Johnston and coworkers. The stability of the GO sheets in the brine was ascribed to the presence of a large number of negatively charged groups on the sheet edges that provide sufficient electrostatic repulsion even in a high ionic strength environment. This
GO could be used to stabilize oil/water emulsions, but was not examined under harsher conditions including higher ionic strength brine and/or elevated temperatures. The graphene oxide used in this chapter is similarly synthesized with an increased amount of potassium permanganate. Additionally, prior to submitting graphite to oxidation, it was ball-milled for 30 min at 30 Hz. By ball-milling graphite, the obtained graphene oxide was of a smaller platelet size than GO synthesized under normal Hummer's conditions.

The motivation for ball-milling graphite to obtain smaller graphene platlets was to more easily create dispersable graphene materials. It was hypothesized that by producing smaller graphene sheets, there would be a smaller entropic cost for solvent ordering around those sheets and therefore a more stable graphene dispersion could be obtained. Platelet size was estimated by dynamic light scattering (DLS).

Preliminary stability testing was performed on mixtures of water dispersed sub-micron sized graphene oxide (GO; average DLS determined sheet diameter of 338.2 ± 27.9 nm) with either the Arab-D or API brines. These studies reveal that the GO was highly unstable in both brines immediately upon mixing and after 24 h at 90 °C, as shown in the Figure 3.5.

XPS of the black flocculated materials after thorough washing revealed only the presence of calcium in addition to the rGO's carbon and oxygen signals. This suggested that the primary cause of destabilization was probably the result of ionic crosslinking of the negatively charged GO sheets by the divalent calcium cations.
At preparation: After 24 hours at 90°C:

Arab D API Arab D API

Figure 3.5. Unstable mixtures of GO in Arab D and API brines at initial preparation and after 24 h at 90°C.

3.3.2 Functionalized Claisen Graphene. Our first attempt to functionalize graphene with brine stabilizing groups focused upon utilizing the Claisen rearrangement chemistry developed in our lab. Highlighted in Chapter 1, this functionalization is shown again in Scheme 3.1.

Scheme 3.1. Treatment of graphene oxide with triethylorthoacetate functionalizes the basal plane of graphene with esters, which can then be hydrolyzed and transformed into acid chloride groups. This acid chloride graphene can then be reacted with a number of nucleophiles.
With the acid chloride Claisen graphene, we could functionalize the basal plane with numerous nucleophiles. Our first attempt was the decorate graphene with a simple zwitterion (ZG1, Scheme 3.2).

Scheme 3.2. Synthesis of zwitterion graphene ZG1.

XPS confirmed the presence of both nitrogen and sulfur in this graphene, suggesting that the functionalization was successful. When mixed with Arab-D brine, this material showed stability at room temperature (Figure 3.6). However, when the dispersion was heated to 90 °C, it immediately destabilized.

Figure 3.6. ZG1 in Arab-D brine at room temperature. After heating is 90 C, the dispersion quickly destabilized.
We also explored the use of diazonium chemistry to functionalize the graphene sheet with imidazolium-based zwitterions structures (Scheme 3.3). As covered in previous chapters, aryl diazonium salts react with graphene oxide to form aryl radicals, which are highly effective in covalently functionalizing the basal plane of graphene with phenyl rings. Like ZG1, ZG2 was stable in Arab D brine at room temperature but quickly flocculated at 90 °C.

Scheme 3.3. Synthesis of zwitterion graphene ZG2 and an image of a dispersion of ZG2 in Arab-D brine at room temperature. This dispersion destabilized at 90 °C.

It was hypothesized that functionalizing graphene with small molecules did not impart enough functional group density to overcome the attractive forces at high temperatures. Methods to attach polymers to the basal plane were therefore investigated. In general, polysaccharides show exceptional stability in brine solutions, and therefore represented an attractive target for graphene functionalization. In particular, chitosan was identified as a potential polysaccharide because of the primary amines in its backbone which can react with the acid chloride Claisen graphene.

Scheme 3.4 shows the synthesis of the graphene chitosan composite CG1. XPS was used to confirm the functionalization. However, nitrogen content by XPS was estimated at 4%, which is lower than what would be expected for a polymer functionalization of graphene. This is likely attributable to chitosan’s low solubility in organic solvents. Like the other materials, CG1 was stable in Arab-D brine at room temperature but destabilized at 90 °C (Figure 3.7).

Figure 3.7. Like ZG1, and ZG2, chitosan functionalized graphene CG1 destabilized at 90 °C.

We then sought to enhance chitosan’s dispersant qualities by introducing zwitterionic elements into its structure. By reacting CG1 with propane sultone, a material was obtained which displayed solubility in Arab-D brine for over 24 h at 90 °C (Figure 3.8). However, further exposure at this
temperature led to flocculation. While the chitosan based composites were unable to remain stable for extended periods of time, this experiment provided valuable information, as it was apparent that treatment with propane sultone improved the colloid stability.

Figure 3.8. Synthesis and dispersibility of ZCG1 in Arab-D brine after 24 h at 90 C. The scattering of light (Tyndall effect) through this dispersion indicates the presence of graphene.

3.3.3 Other Polymer Compositions. Other polymers were screened for stability in graphene oxide brine dispersions. Poly(vinyl imidazole) (PVI), and poly(vinyl pyridine) (PVPy) were selected. Sulfobetaine structures were obtained via reaction with propane sultone (Scheme 3.5). These polymers were then combined with graphene oxide and dispersed in Arab-D brine to determine
which, in any, were suitable targets for developing graphene based covalent functionalization chemistries. In Figure 3.9 it can be seen that PYPy-SB was ineffective in stabilizing graphene oxide in Arab-D brine at room temperature. Accordingly, this polymer was eliminated as a possible target.

Figure 3.10 shows dispersions of graphene oxide and PVI-SB in Arab-D brine both at room temperature and after exposure to 90 °C for various lengths of time. From these images, it is clear that PVI-SB is capable of stabilizing graphene oxide platelets in the brine only when sufficient polymer is added. At a 4:1 polymer:graphene weight ratio, some degree of what is likely depletion
stabilization is achieved; however, after four weeks at 90 °C flocculation occurs. At a 6:1 polymer to graphene w/w ratio, five weeks at 90 °C was not sufficient to fully destabilize the graphene dispersion; however, it is clear that over time the dispersion was losing stability.

\[ \text{Graphene} + \text{Polymer} \rightarrow \text{Stabilized Dispersion} \]

**Figure 3.9.** PVPy-SB is ineffective at stabilizing GO in Arab-D brine. Varying the ratio of GO to polymer did not affect this observation.

The slow destabilization is likely due to a slowly manifesting depletion flocculation mechanism. As graphene oxide is exposed to high temperatures, it slowly reduces and becomes less polar, lowering its adsorptive association with the more polar stabilizing polymer. As this association becomes weaker, the diameter of the protective barrier around graphene sheets shrinks, and more collision events can reach the critical distance for flocculation. With this in mind, it was hypothesized that by covalently linking PVI-SB to the graphene sheet, permanent stabilization could be achieved.
Time zero at room temperature

24 hours of heating at 90 °C

One week at 90 °C

Two weeks at 90 °C

Four weeks at 90 °C

Five weeks at 90 °C

Figure 3.10. PVI-SB and graphene oxide mixtures in Arab-D brine. The ratios on each vial indicate the mass ratio between polymer to GO. While PVI-SB was found to be effective at stabilizing GO in Arab-D brine, this stability was dependent upon concentration, and decreased over time, suggesting a depletion based mechanism.

3.3.4 Development of ‘Grafting-to’ Covalent Graphene/Polymer Functionalization. To covalently attach a PVI-SB type polymer to graphene, 1-vinylimidazole and 4-aminostyrene with a molar feed ratio of 9:1 were reacted via by radical polymerization initiated by AIBN in DMSO at 60 °C for four days (Scheme 3.6). The aminostyrene groups permitted the use of diazonium chemistry\textsuperscript{17,18,19,20} for producing covalent attachment of the polymer chain directly to the graphene basal plane. Although the use of diazonium species to covalently decorate the basal plane of
graphene is well-established, the use of a diazonium containing polymer in a 'grafting-to' approach is unreported, and represents a particularly advantageous method to covalently functionalizing graphene with polymers.

Covalent functionalization of the graphene sheets was carried out as shown in Scheme 3.6 by first preforming the diazonium salt of the aminostyrene groups present in polymer PVIM-co-PVPy under typical conditions with tetrafluoroboric acid and sodium nitrite in methanol. Separately, a partial reduction of GO was carried out by reaction with l-ascorbic acid at a low 1:1 weight ratio of GO:acid to increase the graphitic domains available for reaction with the diazonium species. The partially reduced GO (prGO) which remained dispersed in water was rapidly chilled and subsequently added to the diazonium containing PVIM-co-PVPy solution as shown in reaction scheme. An excess of polymer PVIM-co-PVPy versus GO was used to ensure complete functionalization of the sheets.

The resulting polymer-prGO composite was isolated by precipitation, washed and subsequently reacted with l-propanesultone in methanol to achieve a post-reaction functionalization of the imidazole groups to form the target imidazole-sulfobetaine groups and impart zwitterionic character on the prGO attached polymer chains. The resulting black dispersion was found to be highly stable and resisted isolation by centrifugation (even at 10000 rpm for 10 min). Therefore, it was decided to isolate the fraction of the composite remained as a stable black aqueous dispersion in water after centrifugation by removal of the methanol solvent in vacuo. The solids isolated by centrifugation and may represent less functionalized materials and/or crosslinked aggregates composed of multiple sheets. The composite may owe some its stability as a dispersion in brine as a result of residual surface charges present. Although a purely zwitterionic polymer would be expected to have no net charge overall, the composite likely has negatively charged groups present from the prGO sheets helping to stabilize the material in water. This behaviour is unusual in zwitterionic materials, which typically are only stable in brine solutions and not pure water. XPS analysis of the solids confirmed the presence of C, N, O and S in the composite sample.
3.3.5 Characterization of functionalized graphene dispersions. The zwitterionic polymer-prGO composite material discussed in this chapter was shown to be stable in both standard API brine, as well as a higher ionic strength Arab-D brine, with excellent long-term stability upon standing at 90 °C (>140 days to-date). The dispersion stability was monitored both visually and spectroscopically and dynamic light scattering (DLS) measurements was used to monitor changes in average particle size over time.

100 mL dispersions were prepared by adding 10 mL of the aqueous composite dispersion to 90 mL of the respective brines and sonication of the mixtures for 5 min to achieve homogeneous dispersions that were free of aggregates by visual inspection. After the initial preparation, a small aliquot of each dispersion was removed for spectroscopic (%T) and dynamic light scattering (DLS) characterization. The remainder of the dispersions in the Arab-D and API brines were allowed to stand undisturbed in an oven set at 90 °C. After 24h (day 1) and on days 10, 20, 30, and 140 small aliquots were removed for characterization purposes as described.

Figure 3.11. Photographs of aliquots of stable composite dispersions in Arab-D (above) and API (below) brines at initial preparation and after 1, 10, 20, 30, and 140 days at 90 °C.
Photographs of the aliquots taken showed no noticeable evidence of instability, flocculation or settling of the dispersed composite in either the Arab D or API brines after one month at 90 °C as shown in Figure 3.11. In order to monitor the dispersion stability quantitatively, we examined the percent transmittance of the dispersions as shown in Figure 3.12.

![Graphs showing percent transmittance](image)

**Figure 3.12** UV-Vis (top) spectra and DLS data of PV1M-co-PVPy solutions at 1 day, 10 days, 20 days, 30 days, and 140 days at 90 °C. Particle size remained largely the same over time, while only day 140 showed significant deviance in absorbance. This is likely due an increased concentration of graphene in day 140 dispersion. While the containers holding these dispersion were tightly sealed, it is likely that 140 days at 90 °C resulted in some evaporation of water.

It was observed that the initial and day one data were essentially superimposable for the initial and day one curves in Arab D and with only subtle differences were detected in the API brine. Lower transmittance was also observed in the ranges of 300 – 350 nm that was not present in the day 10, 20 and 30 curves. GO possesses absorption bands in this region and their disappearance after 10
days is likely an indication of on-going thermal reduction process at the elevated brine temperatures. The most notable changes in the transmittance data were in the range of 500 – 600 nm. Examination of the %T values at the arbitrarily chosen wavelength of 550 nm revealed that the transmittance changed most between the initial and first day and then remained essentially stable over the month long test period until day 140, where absorbance over the entire UV-Vis spectrum increased. This is likely due to both a reduction of the graphene sheets as well as an increase in the concentration of graphene in the day 140 dispersion.

Both by visual inspection and from the spectroscopic data, the conclusion that the polymer wrapped sheets were stable in the brines was supported. Furthermore, the lack of observable precipitates/flocculants and the negligible changes in the monitored transmittance (as a function of time) suggested that polymer desorption was not occurring appreciably as a result of the covalent attachment between the polymer and the basal plane.

Further corroboration of composite in brine stability was obtained from dynamic light scattering (DLS) data recorded on the dispersions in order to examine changes in the hydrodynamic diameter of the composite over time when heated at 90 °C. Based on DLS, the average hydrodynamic diameter of the graphene oxide sheets in water was found to be 338.2 ± 27.9 nm. The data for the initially prepared composite dispersed in Arab-D brine demonstrated particles with a mean diameter of 770 ± 92 nm and in API brine a diameter of 1077 ± 218 nm. It was assumed that the composite dispersed in brine was formed of pseudospherical nanoparticles comprised of partially reduced GO (prGO) nanosheets wrapped by attached zwitterionic polymer chain(s). In the high ionic strength environment of the brines, the electrolyte ions present can effectively screen the interactions of the zwitterionic sulfobetaine ionic groups and the chains can expand providing sufficient steric repulsion effect to solubilize and prevent...
aggregation/flocculation of the composite particles. The DLS measured diameters of the composite dispersion in Arab-D brine showed excellent stability over 140 days with stable mean diameters of ca. 750 nm. In the case of the API brine dispersed composite, the initial data points indicated particles of ca. one micron size in diameter that stabilized over time to a mean diameter of ca. 750 nm (based on the day 10, 20, 30, and 140 data points).

The excellent stability of the composite in the complex and higher ionic strength Arab-D brine (containing a higher content of divalent ion species, such as calcium (II) and magnesium (II)) was particularly promising. It is further noted that the relative stability of the composite particles was for 140 days with no appreciable destabilization having occurred up to that point. Based on the data at hand, is likely that composite dispersions should have prolonged stability at elevated temperatures in brine.

3.4 Conclusions

Partially reduced graphene covalently functionalized with a polyzwitterionic polymer was synthesized and shown to display highly stable solutions in the high salinity brines known as Arab-D and API at elevated temperatures for 140 days. These findings were well supported by the noted stability of the dispersions by visual inspection, spectroscopic monitoring and the relative stability of the particle sizes as determined by DLS. Creating brine stable graphene-based systems has been a challenge and it is our view the functionalization of graphene basal plane, as reported herein, represents an attractive and useful platform. One could envision use or these functional composites both as a carrier for delivery molecules or as a protective “wrapper” of nanomaterials. Furthermore, the polymer developed may be applicable in imparting brine stability other types of particles or materials. The application of our polyzwitterion-graphene system is of use in the petroleum
industry for reservoir mapping and/or improving oil recovery. In addition, the functionalization of the prGO nanosheets achieved through diazonium chemistry for covalent attachment of polymer chains to the basal plane of graphene will likely find utility in the development of other graphene-polymer composites for various types of applications.

3.5 Experimental

General Materials and Methods: All chemicals were purchased from Sigma-Aldrich and used as received unless stated otherwise. X-ray photoelectron spectroscopy (XPS) analyses were performed on a Versaprobe II X-ray photoelectron spectrometer from Physical Electronics with a monochromated Al Kα X-ray source (1486.6 eV) and operated at a base pressure of $1 \times 10^{-9}$ Torr with 45.7 Watts of power, a 200 μm spot beam size and a take-off angle of 45°. The XPS spectra were analyzed and atomic peaks were integrated using the CasaXPS software to determine the relative atomic percentages of the element species present in the samples. Thermogravimetric analyses were performed on a TA Instruments Discovery TGA in the range of 50 – 800 °C at a constant ramp rate of 20 °C min⁻¹ under nitrogen atmosphere. Percent transmittance (%T) spectra of composite in brine samples were taken on a Varian Cary 6000i instrument using a zero/background correction in quartz cuvettes. Dynamic light scattering (DLS; Brookhaven Instruments BI-200SM) of the brine dispersed composites was performed by adding a small amount of the tested dispersions into filtered brine. The data was collected in triplicate at a 90° scattering angle for 3 min at room temperature and fitted using the CONTIN algorithm.

Graphene Oxide Preparation Procedure: 10 g graphite (natural flake, Alfa Aesar, 2-15 μm) was ball-milled at 30 Hz for 30 min, then dispersed in 200 mL conc. H₂SO₄ and stirred at 0 °C. 30 g
KMnO₄ was added portionwise over a 2 h period so not to allow the temperature to exceed 20°C. The mixture was allowed to return to room temperature and stirred overnight, then 500 mL of ice-water was added slowly. Following this, 20 mL of 30% H₂O₂ was added. 500 mL ice-water was then poured into the reaction and stirred for 3 h. The resulting solids were then collected via ultracentrifugation and redispersed in 10% aq. HCl, and subsequently washed with copious amounts of DI water. The solids were then dialyzed against DI water until the water reached a pH of approximately 4.

Synthesis of Claisen Graphene (CG): A flame-dried 500 mL round bottom flask was charged with GO and triethyl orthoacetate (98%, 250 mL). The GO was dispersed via 10 min of bath sonication. Catalytic para-toluene sulfonic acid (> 97%) was added in one shot. The reaction vessel was placed in an oil bath and outfitted with a condenser column. The reaction was allowed to proceed at reflux (130 °C) for 36 h. To favor the formation of carboxylic acid functional groups, at this point, 50 mL of 1 M sodium hydroxide was added. The reaction was allowed to cool to room temperature, while continuing to stir vigorously for an additional 3 h. The reaction mixture was then centrifuged (10 min at 11 000 rpm) and the supernatant was discarded. The residue was resuspended in deionized water using a vortex mixer and then centrifuged (10 min at 11 000 rpm) and the supernatant discarded. This was repeated three times with water and twice with acetone. The remaining residue was dried under high vacuum to yield CG2.

Synthesis of Acid Chloride Graphene (ACG): A flame-dried 100 mL round bottomed flask was charged with CG2, 50 mL dioxane, and 5 drops dimethyl formamide. The reaction mixture was sonicated for 10 min to ensure good dispersion and 0.7 mL oxalyl chloride (99%) was added.
dropwise over 5 min. The bubbling started immediately and the reaction vessel was allowed to react overnight at room temperature. After 12 h, the reaction mixture was centrifuged (10 min at 11000 rpm). The supernatant was discarded and the residue was redispersed in dichloromethane via vortex mixer and then centrifuged (10 min at 11000 rpm). This process was repeated twice more with dichloromethane and and three more times with acetone. The product was dried under vacuum overnight.

**Synthesis of zwitterion graphene ZG1.** To neat acid chloride graphene (ACG) was added 2 mL N,N-dimethylpropane-1,3-diamine, resulting in fuming vapor. The mixture was then sonicated for 30 min and allowed to stand overnight. The solids were isolated by centrifugation and washed with acetone and THF then allowed to dry under vacuum. The resulting solid was redispersed in THF via sonication for 30 min and 200 mg propane sultone was added. The mixture was refluxed overnight. Solids were isolated by centrifugation and washed with acetone (2x), methanol (2x), water (2x), then lyophilized.

**Synthesis of zwitterion graphene ZG2.** 1.3 g 4-(1H-imidazol-1-yl)aniline was dispersed in 25 mL water and chilled with an ice-water bath. 5 mL HBF$_4$ (48 %) was added to the mixture. Separately, 620 mg NaNO$_2$ was dissolved in 10 mL DI water and cooled with an ice-water bath. The NaNO$_2$ solution was added to the aniline mixture and stirred for 15 min. This solution was then added to 100 mg reduced graphene oxide and heated to 60 C. The reaction was stirred at 60 °C overnight and the solids were isolated by centrifugation, washed with 2x DI water, 3x acetone, 3x MeOH, and 2x water. The slurry was the lyophilized. The resulting black solids were sonicatedally
dispersed in anyhydrous THF for 30 min. 250 mg of propane sultone was added and the mixture refluxed overnight. The reaction was purified in an identical manner to ZG1.

*Synthesis of chitosan graphene composite CG1.* 100 mg acid chloride graphene was sonicatively dispersed in 100 mL dry DMF. To this was added 500 mg chitosan. Then, 1 mL triethyl amine was added slowly to the reaction mixture. The reaction was heated to 130 °C and stirred overnight. The dispersion was allowed to stir 100 °C for 24 h. The solids were isolated by centrifugation and then washed with 3x DMF, 3x water and 3x acetone. The resulting black solid was dried overnight under vacuum.

*Synthesis of chitosan zwitterion graphene composite CZGt.* CG1 was sonically dispersed in 100 mL dry DMF and 250 mg propane sultone was added to the reaction mixture. The reaction was heated to 130 °C and stirred overnight. The solids were isolated by centrifugation and then washed with 3x DMF, 3x water and 3x acetone. The resulting black solid was dried overnight under vacuum.

*Synthesis of polymer PVPy-SB.* 300 mg poly(4-vinylpyridine) (Mw = 60,000, Aldrich) was dissolved in 20 mL anhydrous MeOH. 350 mg propane sultone was added and the mixture was heated to reflux for 3 h. The solvent was removed in vacuo and the sticky solid was used without further purification.

*Synthesis of polymer PVI-SB.* 1.5 g 1-vinylimidazole and 0.0151 g AIBN were dissolved in 5 mL DI water. The mixture was submitted to three free-pump-thaw cycles and then heated at 60 °C for
12 h under N$_2$. The resulting thick gel is diluted with methanol and then precipitated into acetone twice, affording a gummy cream colored materials. The materials is redissolved into methanol and precipitated into cold ethyl acetate. After drying the resulting solid, 1.165 g material was obtained. 0.25 g of this material was dissolved in anhydrous methanol (20 mL) while stirring under N$_2$. 0.326 g propane sultone was added to the reaction and the mixture refluxed overnight. The reaction mixture is filtered and washed with methanol. The resulting solid was dried in vacuo.

_Synthesis of poly(vinylimidazole)-co-poly(aminostyrene) (PVIM-co-PYPy):_ 1-vinylimidazole, 4-aminostyrene and DMSO were distilled prior to use. 1-vinylimidazole (2.51 g, 26.7 mmol) and 4-aminostyrene (0.32 g, 2.7 mmol) and DMSO (5 mL) were combined in a Schlenk tube with a stir bar. The mixture was degassed by freeze-pump-thaw (3 ×) and sealed under static inert atmosphere and stirred at 60 °C for four days. The resulting lightly yellow viscous solution was cooled and diluted by the addition of methanol. The mixture was precipitated into acetone (2 ×) and then dried overnight to produce a clear hard yellowish solid.

_Synthesis of PVIM-co-PYPy – partially reduced graphene oxide (prGO) Composite:_ First, 15 mL of graphene oxide dispersed in deionized water (1 mg mL$^{-1}$) was diluted up to a total volume of 30 mL with deionized water. l-Ascorbic acid (15.1 mg) was added and the mixture was stirred at 60 °C for one hour and then rapidly chilled to <5 °C and set aside for immediate use. Separately, polymer I (150.5 mg) was dissolved in methanol (50 mL) under mild sonication (5 min) and stirring. 48% aq. tetrafluoroboric acid (25.8 mg) was dissolved in deionized water (10 mL) and added to the methanol mixture. The solution was subsequently chilled to <5 °C. In separate vial, sodium nitrite (9.8 mg) was dissolved in deionized water (2 mL) and likewise chilled. The sodium
nitrite solution was added to the solution of polymer I with stirring and after 15 min the chilled partially reduced graphene oxide (prGO) dispersion was added slowly and stirred for 30 min. Afterward, the mixture was sonicated for 30 min and then stirred at 60 °C overnight. The cooled solution was concentrated in vacuo and then sufficient acetone was added to induce flocculation and the solids were collected by centrifugation (5k rpm; 15 min). The solids were air dried and used directly in the next step.

**Synthesis of PVIM-co-PYPy – prGO Composite Dispersion:** The above composite solids were sonicatively dispersed in methanol (100 mL) and then 1,3-propane sultone (350.2 mg) was added. The mixture was refluxed under inert atmosphere overnight and then 30 mL of deionized water was added. Afterward the cooled solution was centrifuged (2.5k rpm, 15 min) and the supernatant was decanted. The remaining solids were washed with methanol and deionized water and after centrifugation the supernatant was combined with the previously collected solution. The methanol was removed from the supernatant in vacuo to afford the zwitterionic Polymer I – prGO composite as a dispersion in water (~45 mL) and stored in a sealed container. The remaining solids isolated from centrifugation were lyophilized.

**Preparation of Low Salinity Arab-D Brine:** Sodium chloride (37.3 g), calcium chloride dihydrate (24.9 g), magnesium chloride hexahydrate (6.6 g), barium chloride (5 mg), sodium sulfate (0.3 g) and sodium bicarbonate (0.26 g) were dissolved to a total volume of 500 mL in high purity distilled water.
Preparation of American Petroleum Institute (API) Brine: Sodium chloride (20.0 g) and calcium chloride dihydrate (5.0 g) were dissolved in high purity distilled water (225 mL).

Brine Stability Testing of PVIM-co-PYPy – prGO Composite at 90 °C: To two separate capped bottles with seals labeled Arab-D and API brine were added 90 mL of each respective brine solution. Then 10 mL of the composite in water were added to each to afford a 9:1 volume ratio. The bottles were sonicated for 5 min and then allowed to stand undisturbed in an oven set at 90 °C. Aliquots (3 mL) for characterization were taken immediately after preparation (before heating), after 24 hours (day 1) and again on days 10, 20 and 30, and 140. Pictures were taken on those days in smaller scintillation vials and those solutions were promptly returned to the larger bottles.
3.5 References

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Ma, Q. Qu, Y. Zhao, Z. Luo, Y. Zhao, K. W. Ng, Y. Zhao, J. Mat. Chem. B. 2013, 1, 6495.; K. T. Nguyen, Y. Zhao, Nanoscale 2014, 6, 6245.


Chapter 4: Triptycene Poly(ether ether ketone)
4.1 Abstract

A new poly(aryl ether), triptycene poly(ether ether ketone) (Trp-PEEK) was synthesized and its properties investigated. Incorporation of a triptycene into the PEEK backbone results in a significantly elevated glass transition temperature, and its increased solubility allows for high molecular weight polymer to be synthesized without the use of specialty solvents and high temperatures typically required for PEEK. This polymer is derivatized by both sulfonation and nitration. The sulfonated S-Trp-PEEK can be cast into robust transparent membranes, and shows exceptional performance as a proton conductor in this form. It can also stabilize solutions of single-walled carbon nanotubes in polar solvents, such as water and methanol. From these solutions, conductive films and foams can be cast. The NO₂-Trp-PEEK derivative can be reduced into its amine form and then reacted with isocyanates to form urea and thiourea derivatives of Trp-PEEK. Thio-Trp-PEEK can be used as a selector in the gas-phase sensing of acetone. Its hydrogen bonding properties can also be exploited to form self-healing viscoelastic materials when blended with poly(THF). The work contained in this chapter regarding sulfonated Trp-PEEK and proton conductivity of those polymers was performed with equal contributions from John B. Goods and Lionel Moh. Lionel Moh also assisted with the characterization of the other polymers covered in this chapter.
4.2 Introduction

Poly(arylethers) (PAEs) are polymers that have found widespread commercial use. As a member of the ‘engineering thermoplastic’ family, this class of polymers is known for its high chemical resistance, low cost, high thermal stability, and excellent mechanical properties.\(^1\) As a result of these properties, its main applications are found in ‘high-performance’ materials, which demand mechanical integrity in harsh environments, such as in aircraft or automobiles.\(^2\) The origin of this stability and performance can be traced to the aromatic ether linkages which form the backbone of the polymer.\(^3\) There are numerous subcategories of poly(aryl ethers), the most notable of which are polyarylethersulfones, polyaryletherketones, polyetherimides, and polyphenylene ethers.

![Figure 4.1. Representative structures of the most common class of PAE’s. From top, polyarylethersulfones, polyaryletherketones, polyetherimides, and polyphenylene ethers.](image)

One of the first syntheses of this class of polymer can be traced to DuPont, where in 1962 Bonner reported the synthesis of poly(ether ketone) (PEK) by Friedel-Crafts polymerization of terephthaloyl chloride with diphenyl ether.\(^4\)
Much of the work immediately following Bonner’s synthesis focused upon modifying the Friedel-Crafts polymerization method, with chemists attempting to enhance yield and performance by altering monomer ratios, reaction temperatures, solvent choice, and catalyst. However, the most significant advancement in PAE synthesis occurred in 1967 when Johnson and Farnham reported the synthesis of poly(ether ether ketone) (PEEK) by nucleophilic aromatic substitution.

While thermal processing of PAE’s is famously straightforward, they are similarly renowned for their insolubility of nearly all solvents. The early syntheses listed here were restricted to low molecular weights, as the polymer would precipitate before it could polymerize to completion. Rose and Staniland developed the first commercially viable process for the synthesis of high-molecular weight PAE’s when they used K$_2$CO$_3$ as a base and diphenylsulfone as a solvent (Scheme 4.3). For the first time, chemists were able to produce high molecular weight PAE’s in large-scale.
Molecular weight is one of the most important attributes of polymers, as it influences many of its physical properties. In particular, molecular weight is important for high-strength applications, as it generally correlates with tensile strength due to the increased entanglement inherent in extended polymer chains. It should also be noted that when the molecular weight of polymers is discussed it is implied that this number represents a statistical distribution of molecular weights. The size of polymers is most commonly represented by both $M_n$ and $M_w$. $M_n$ is the number average molecular weight, or the statistical average weight of a polymer. $M_w$ is the weight average molecular weight, and emphasizes the contributions of the larger chains to the weight distribution. $M_w$ is an important property to consider because it is often the case that larger polymer chains contribute more significantly to a material’s properties. The ratio of these two numbers is the polydispersity index, or PDI, for a polymer. PDI provides information regarding the distribution of molecular weights for a given polymer, where 1 represents unity, or a polymer with no variance in its mass, such as proteins synthesized within living organisms. PDI’s for synthetic polymers are much more variant and are highly dependent on reaction conditions.

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \quad M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

**Equation 4.1.** Number average molecular weight ($M_n$) and weight average molecular weight ($M_w$). While $M_n$ represents statistical average weight of a polymer mixture, the square of the mass value in the $M_w$ numerator results in an emphasis of the higher molecular weight polymer.
Molecular weight of polymers is typically determined by gel permeation chromatography (GPC). GPC is a type of size exclusion chromatography used to determine the molecular weight of polymer solutions. These solutions are injected into the instrument and then passed through a porous column. Polymers with a larger hydrodynamic radius have decreased retention as they do not fit into the small pores of the column. The solution that exits the column is monitored by spectroscopically, usually by UV-Vis, fluorescence, or dynamic light scattering, allowing for quantitation of polymer which exits the column at a particular time. By calibrating the instrument to a known standard, retention times can then be correlated to molecular weight.

Since Rose and Staniland's synthesis of high molecular weight PEEK, nucleophilic aromatic substitution has since become the standard method to produce high molecular weight PAE's. However, this method requires the use of a sufficiently activated dihalogen in order to react with the hydroquinone nucleophile. As a step-growth polymerization, the yield of the reaction must exceed 99% in order to obtain high molecular weights. As can be expected, among the halogens, the most effective electrophilic monomers are difluorides. In certain cases, dichloro compounds can be substituted, while dibromo and diiodo monomers are typically not sufficiently activating to yield polymer. Nitro displacement has also been demonstrated to be an effective means for PAE synthesis.9

It is also necessary that the electrophilic monomer possesses an activating group ortho or para to the halogen. These groups are more commonly para to the halogen, and include sulfones, ketones, and diazo groups, with sulfones being the most activating, and diazo groups the least. Electron deficient heterocycles such as oxadiazole can similarly activate the electrophilic monomer.10
It is important to exclude water from the reaction, as the most prevalent chain terminating side reaction involving hydrolysis of the fluorinated monomer (Scheme 4.4). This disrupts the stoichiometry of the reaction, and as step-growth polymerizations require yields approaching 100%, the molecular weight of the polymer suffers significantly.

\[
\text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{KOH}
\]

Scheme 4.4. Hydrolysis of the difluoro monomer results in chain-termination of the polymer, lowering molecular weight.

Although K\textsubscript{2}CO\textsubscript{3} has found widespread utility in S\textsubscript{NAr} polymerization, it has one important limitation, which is at the temperature required for the reaction, upon protonation it can decompose liberating CO\textsubscript{2} and water (Scheme 4.5). To combat this, it is advisable to use a Dean-Stark apparatus and toluene to azeotropically distill off water from the reaction as it is created.

\[
\text{K}_2\text{CO}_3 + \text{HB} \rightarrow \text{KHCO}_3 + \text{B}^- \\
\text{KHCO}_3 \xrightarrow{\Delta} \text{CO}_2 + \text{H}_2\text{O} + \text{K}_2\text{CO}_3
\]

Scheme 4.5. Potassium carbonate decomposes into CO\textsubscript{2} and water when protonated at high temperatures.

Because PAE's owe much of their utility to the stability of their aryl ether backbone, it is possible to obtain a wide variety of high performance materials with numerous different properties
by modifying the polymer with different chemical functionalities. Whether this involves simply altering the activating group found in the dihalo monomer or multi-step post-polymerization chemistry, a wide variety of PAE materials with many different properties have been synthesized.

Of these, poly(ether ether ketone) (PEEK) is one of the most important. Even within the high performing class of PAE’s PEEK remains among the most chemically resistant and mechanically tough polymers. Victrex®, a UK based company which is the primary manufacturer of PEEK based materials, is expected to produce 7,000 metric tons/year in 2015, with the majority of polymer being used in aerospace applications. However, due to its insolubility, chemical modification of PEEK can be difficult. Pre-polymerization modification of monomers is one way to combat this problem. A popular method to alter the thermal properties of PEEK is to install alkyl groups to the hydroquinone monomer. In another example, one of the more prevalent modern analogs of PEEK, known as PEEK-WC, substitutes phenolphthalein for hydroquinone, resulting in a polymer which preserves much of the thermal stability and mechanical properties of PEEK in addition to being soluble in many organic solvents (Scheme 4.6).

![Scheme 4.6. Synthesis of PEEK-WC.](image)

Of the many reported modified PEEK materials, sulfonated PEEK has drawn particular attention for its performance in proton exchanging membranes (PEM’s). PEM’s are a critical
component of proton exchange membrane fuel cells (PEMFC’s). As its most basic definition, a fuel cell is a device which generates electrical work from chemical energy without combustion. In these devices, fuels such as hydrogen gas, methanol, and ethanol are oxidized, generating water, electrical energy, and heat. Figure 4.2 shows a general schematic of how a hydrogen fuel cell operates. Hydrogen is oxidized at the anode, generating electrons and protons. The electrons flow from the anode to the cathode through a circuit and generate electrical work, and as a consequence protons must be shuttled across an electrically insulating membrane to the cathode, where they combine with molecular oxygen and electrons to form water.

Figure 4.2. General schematic of a proton exchange membrane fuel cell. Electrical work is generated from the oxidation of hydrogen and reduction of oxygen. In order to link these reactions within a circuit, a proton exchange membrane is required to shuttle protons from the anode where they are generated to the cathode, where they are required for the reduction of oxygen into water.
Fuel cells have high power conversion efficiencies and do not emit environmentally harmful gases associated with combustion; as such, they have attracted considerable attention as a means to cheaply and cleanly generate large amounts of electricity.\textsuperscript{16} However, while the fuels which are required to power fuel cells, such as H\textsubscript{2} and O\textsubscript{2}, are abundant, widespread commercialization is hindered by three factors 1) fuel crossover (i.e. fuel leaking from the anode to the cathode); 2) anodic catalyst poisoning by CO; and 3) high cost of the proton exchange membrane. Although both cost and fuel crossover are readily apparent membrane issues, even catalyst poisoning can be addressed through membrane engineering. In general, the higher the operating temperature of a fuel cell, the less catalyst poisoning occurs.\textsuperscript{16} As the membrane is the component which limits operation temperature, by creating new membrane materials which can perform at higher temperatures catalyst poisoning can be minimized.

The current industry standard material for PEM's is Nafion. Nafion is a sulfonated tetrafluoroethylene based fluoropolymer which was first synthesized by Walther Grot at DuPont in the late 1960's (Scheme 4.7).\textsuperscript{17} DuPont first demonstrated Nafion's has exceptional cation transport properties for membrane applications a decade later, and this material has remained the most popular choice for cation conduction ever since.

In addition to Nafion's relatively high cost to manufacture, it also possesses some drawbacks in performance. While Nafion is thermally stable to temperatures up to 200-250 °C, its optimal operating temperature ranges from 80-100 °C, and quickly loses performance at temperatures exceeding 100 °C. As mentioned previously, a high operating temperature is critical to prevent catalyst poisoning, so fuels cells which incorporate Nafion have limited catalyst lifetimes.
Scheme 4.7. DuPont synthesis of Nafion. While Nafion is currently considered the industrial standard for PEM's, its expensive synthesis has fueled research into alternatives.

S-PEEK has drawn attention as an alternative to Nafion because of its relatively lower cost and comparable proton conductivity.\(^{18}\) It is also more thermally stable, can perform at a wider range of temperatures, and has lower fuel crossover.\(^{19,20}\) By incorporating triptycene into the PEEK backbone and synthesizing its sulfonated derivative, it was hypothesized that the enhanced porosity of the material would aid proton conduction. Furthermore, it is likely proton conductivity would also be increased by simply having more sulfonate groups per repeat unit as afforded by the three aryl rings of triptycene versus the one of hydroquinone.

Previous work in the Swager group has shown that incorporating triptycene into polymers can impart desirable properties such as enhanced porosity, increased glass transition temperatures, and improved solubility.\(^{21}\) It was also shown that by incorporating triptycene into the main chain
of poly(arylene ethers), the rigid triptycene structure to and resulting porous matrix allows for the production well-dispersed metal nanoparticle embedded thin-films.\textsuperscript{22}

In this chapter, the synthesis of a new polymer, triptycene PEEK (Trp-PEEK) will be detailed. In particular, the post-polymerization functionalization of this polymer by both sulfonation and nitration will be covered, with a focus on how these modifications can facilitate the use of these materials in a wide range of applications, including proton-conducting membranes, carbon nanotube composites, gas-phase sensing, and elastomeric materials.

4.3 Results and Discussion

4.3.1 Synthesis of Trp-PEEK. Triptycene diol 1 can be easily synthesized in large scale via the Diels-Alder reaction between benzoquinone and anthracene (Scheme 4.8). Treatment of the resulting adduct with cat. HBr in acetic acid yields 1 in good yields.

\begin{center}
\begin{tikzpicture}
\node at (0,0) (a) {\includegraphics[width=\textwidth]{Scheme_4.8}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 4.8.} Synthesis triptycene diol 1.

As mentioned in the introduction to this chapter, S\textsubscript{N}Ar polymerization requires highly accurate stoichiometry so it is essential to obtain pure monomer. It is therefore important to recrystallize the Diels-Alder adduct prior to tautomerization into the hydroquinone. Further purification of 1 can be achieved by recrystallization in acetone. After extensive purification,
Triptycene diol 1 was used as a monomer in an SNAr polymerization with 4,4'-difluorobenzophenone to produce Trp-Peek (Scheme 4.9).

\[
\begin{align*}
\text{Triptycene diol} & \quad + \quad \text{4,4'-difluorobenzophenone} \\
\text{K}_2\text{CO}_3 & \quad \text{in} \quad \text{DMAc, tol} \\
\text{Dean-Stark} & \quad 150-165 \degree C \\
& \quad 18 \text{ h}
\end{align*}
\]

**Scheme 4.9.** Synthesis of Trp-PEEK.

4.3.2. **Characterization of Trp-PEEK.** Trp-PEEK displays slight solubility in THF, DMF, and DMAc, and complete solubility in hot NMP. The molecular weight of the polymer was determined by GPC. Interestingly, when conditions identical to those used to synthesize commercial PEEK were used to synthesize Trp-PEEK, lower molecular weights were obtained (Scheme 4.10). This was attributed to the lack of solubility of triptycene diol in diphenylsulfone, even at high temperatures. It is likely that under the industrial conditions, the hydroquinone monomer melts, aiding its mixture with the difluorobenzophenone co-monomer. Triptycene diol melts at around 330 °C, which is close to its decomposition temperature.

Even when accounting for the increased mass of the triptycene, the synthesis of Trp-PEEK results in polymer of greater chain lengths than commercial PEEK. Commercial PEEK is reported at possessing molecular weights of around 30,000 Da, which would give a chain length of around 100 repeat units. In the case of Trp-PEEK, chain length is estimated at around 210 repeat units.
Scheme 4.10. Use of industry PEEK synthesis conditions to synthesize Trp-PEEK.

By thermogravimetric analysis (TGA), the polymer shows excellent thermal stability, decomposing at 550 °C under an atmosphere of N₂. In line with previous work, incorporating triptycene into the backbone of PEEK raises the glass transition temperature significantly, from 143 °C to 257 °C. Glass transition is the temperature at which the material transforms from a hard and brittle state into a materials that can flow without stress. It is an important attribute in polymers as it provides information both about processing conditions as well as about the temperature at which a polymer will lose its mechanical integrity. Materials with high glass transition temperatures are important because they allow for implementation of these materials in mechanical applications which require high temperatures.

4.3.3 Sulfonation of Trp-PEEK. As mentioned previously, sulfonation of PEEK materials is a common method of covalently modifying PEEK post-polymerization. Sulfuric acid represents one of the only solvents which is capable of producing PEEK solutions. Others include related acids, such as methane sulfonic acid and chlorosulfonic acid. While sulfonation of PEEK at room temperature is slow, when these solutions are heated, electrophilic aromatic substitution rapidly occurs. The kinetics of this reaction are well studied, and the degree of sulfonation can be precisely controlled by both reaction time and temperature.²³ However, when heated, the molecular weight
of the polymer suffers. In order to obtain a high degree of sulfonation without lowering the molecular weight of the polymer, long reaction times at room temperature are required. As expected, sulfonation occurs first at the electron rich hydroquinone; in order to sulfonate the more electron poor aryl rings of the benzophenone, extended reaction times and higher temperatures are required.

Sulfonated triptycene PEEK (S-Trp-PEEK) was synthesized by dissolution of Trp-PEEK in concentrated sulfuric acid and heating for 1 h at various temperatures. S-Trp-PEEK by visual inspection is a brittle yellow polymer foam, which differs significantly from the white powder of Trp-PEEK. It is soluble in MeOH, DMSO, DMF, and DMAc. When mixed with water, a hydrogel results (Figure 4.3); however, it is possible to obtain S-Trp-PEEK which is soluble in water by extending the reaction time of the sulfonation reaction to 12 h.

![Figure 4.3. Digital images of S-Trp-PEEK hydrogel (left) and as-produced S-Trp-PEEK (right).](image-url)
Table 4.1 shows the molecular weights of the starting Trp-PEEK material and S-Trp-PEEK's synthesized at various temperatures. While it is clear that these conditions lower the molecular weight of the Trp-PEEK starting material, the effect is not drastic. Unexpectedly, the lowest temperature conditions unexpectedly produces the smallest polymer. This is likely attributable to solubility differences in the polymers. As DS decreases, so does solubility in polar organic solvents like the DMF used for GPC analysis. It is likely that the higher molecular weight fraction of S-Trp-PEEK45 is not solubilized by DMF. This assertion is supported by the fact that a visual inspection of S-Trp-PEEK DMF solutions reveals that of the three sulfonated derivatives, only S-Trp-PEEK45 forms a cloudy solution.

Table 4.1. Molecular weights of Trp-PEEK and its sulfonated derivatives. The number in each sulfonated polymer refers to the temperature used in its synthesis. The lower molecular weight of the polymer synthesized at 45 °C is likely due to its low solubility in DMF, the solvent used for GPC analysis.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PDI</th>
<th>Degree of Sulfonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trp-PEEK</td>
<td>43000</td>
<td>99000</td>
<td>2.28</td>
<td>0</td>
</tr>
<tr>
<td>S-Trp-PEEK-45</td>
<td>22400</td>
<td>37000</td>
<td>1.66</td>
<td>1.46</td>
</tr>
<tr>
<td>S-Trp-PEEK-65</td>
<td>32000</td>
<td>59000</td>
<td>1.83</td>
<td>1.53</td>
</tr>
<tr>
<td>S-Trp-PEEK-85</td>
<td>32000</td>
<td>55000</td>
<td>1.71</td>
<td>1.67</td>
</tr>
</tbody>
</table>

The most likely mechanism of polymer degradation when PEEK type polymers undergo electrophilic aromatic substitution (EAS) are ipso reactions (Scheme 4.11). In considering these reactions, it is worthwhile to examine the substituent effects within Trp-PEEK which are relevant to this discussion.

As the two non-hydroquinone benzene rings of the triptycene are not a part of the polymer backbone and are unlikely to cause chain fragmentation, they will not be considered in this
discussion. Within the backbone is contained both hydroquinone and benzophenone units. As mentioned previously, EAS is strongly favored on the hydroquinone ring because the electron donation of the ether oxygens can stabilize the Wheland intermediate during EAS. Similarly, the benzophenone unit is deactivated toward EAS because the electron withdrawing ketone makes the formation of the positively charged Wheland intermediate higher in energy. Both of these effects are strongest at the ortho and para positions.

Scheme 4.11 summarizes the three possible mechanisms of chain fragmentation via ipso substitution. The top two mechanisms in this scheme possess resonance stabilization of their respective Wheland intermediates; however, they also form high energy products, an aryl carbocation or acylium ion. The bottom reaction’s Wheland intermediate is not stabilized through resonance, but its fragmentation products are considerably lower in energy than the top two reactions. With this in mind, it is difficult to definitively state the degree to which each of these possible mechanisms dominate, but it is likely the high-energy aryl carbocation produced in the top reaction makes it unfavored relative to the other two mechanisms.

It should also be noted that in the case of sulfonation and nitration, if a non-ipso substitution occurs, the strong electron withdrawing ability of these groups lowers the probability of a subsequent substitution on that ring.
Degrees of sulfonation (DS) in the sulfonated materials were determined by TGA. DS represents the average number of sulfonate groups per repeat unit of the polymer. Previous studies have shown that TGA data provides accurate measurements of sulfonation in PEEK type polymers.\textsuperscript{24} The TGA curve shown in Figure 4.4 shows a typical S-Trp-PEEK decomposition. The curve is characterized by two distinct decomposition events. The first, at \( \sim 300 \, ^\circ C \), can be attributed to the thermolysis of SO\textsubscript{3} groups. The second decomposition event at \( \sim 550 \, ^\circ C \) is assigned the thermolysis of the polymer backbone. By knowing the percent weight loss which can be attributed to the sulfonic acid groups in the polymer, the degree of sulfonation can be determined by Eq. 4.2.
Figure 4.4. Representative TGA curve of S-Trp-PEEK. The weight loss from 300 to 450 °C is attributed to thermolysis of SO3H groups, and weight loss from 550 to 650 °C is assigned to thermolysis of the main chain of the polymer.

Similar to PEEK, increase in temperature was observed to correlate with the degree of sulfonation in Trp-PEEK. Table 4.1 shows these data. As hypothesized, incorporating a triptycene into the backbone allows for the installation of a larger number of sulfonate groups per repeat unit. For PEEK, fractional sulfonation per repeat unit only approaches 1 at either very long reaction times (over 50 h at 35 °C), or at high temperatures (6 h at 75 °C). Here, we can see that 1.4 sulfonic acid groups per repeat unit can easily be achieved after reaction for 1 h at 45 °C. This is likely attributable to the two aryl rings on the triptycene unit, as sulfonation of the deactivated benzophenone aryl groups is unfavored.
Equation 4.2. Determination of the degree of sulfonation by TGA. 5.81 represents the molecular weight ratio between the Trp-PEEK repeat unit (464.5 g/mol) and SO\(_3\) (80.01 g/mol). \(\Delta\text{wt}\%_{\text{sulfonate}}\) represents the change in weight percent attributable to SO\(_3\) decomposition, and \(\text{wt}\%_{i}\) refers to the initial weight percent of the material after the initial water loss event at -100 °C.

4.3.4 S-Trp-PEEK as Proton Exchange Membrane Material.

S-Trp-PEEK can be cast into robust transparent membranes from DMAc, DMF, and MeOH (and also water if the DS is high enough) (Figure 4.5). As mentioned in the introduction to this chapter, sulfonated PEEK materials have drawn interest as low cost alternative to Nafion for proton exchange membranes. We therefore sought to explore the ion conduction properties of S-Trp-PEEK.

Figure 4.5. S-Trp-PEEK membrane cast from a 7% wt/v DMAc solution.
7% w/v DMF solutions of each S-Trp-PEEK polymer (45, 65, and 85) were made. These solutions were cast into Teflon wells and dried overnight at 70 °C under vacuum. The resulting films were removed by adding a small amount of DI water to the wells and peeling off the film. After soaking the films in DI water for 2 h, the proton conductivity of the hydrated films were obtained using impedance spectroscopy.

Impedance spectroscopy (IS), also known as dielectric or electrochemical impedance spectroscopy, is a technique to obtain information about a material by analyzing how it responds to changes in the both the frequency and magnitude of a voltage applied across it.\textsuperscript{25} With the exception of superconductors, all materials have some amount of impedance, which is defined as the delay in the movement of electrons when a voltage is applied. Impedance is closely related to resistance -- where resistance is represented by only magnitude, impedance is both a magnitude and a phase. This phase represents the temporal aspects of the delay in electron movement previously mentioned. This means that probing the impedance of a material tells us more than just the extent to which a material resists the flow of charges, it also tells us about how the material resists that flow.

Consider an insulating material. If we apply direct current (DC) voltage across this material, we are creating a unidirectional potential from one electrode to the other. Because of this potential difference, charged species will flow in one direction at a certain rate. By measuring this rate we can determine the current of the circuit at a particular voltage, and therefore its resistance. However, if we apply an alternating current (AC) voltage across the material, we introduce a frequency factor along with the magnitude of the potential difference. Instead of a unidirectional force, charge carriers will feel forces alternating in direction as the potential changes polarity at a certain frequency. In other words, instead of pulling charges in one direction and their reluctance
to flow (DC), we are now pulling charges back and forth between the electrodes at a defined frequency and measuring their resistance to movement as well as the rate of this process.

By introducing a temporal element to the measurement, we can obtain much more complex information about the system. Physically, this information is gained by analyzing the frequency dissipation of the applied voltage. As the direction of potential is constantly changing from one electrode to the other, charge carriers do not respond in perfect resonance. There is always a phase shift, or time delay between the applied potential and the response of charge carriers. If the frequency of the applied field is too high, the charges are essentially feeling no forces at all, because their movement through space is slower than the changes in the field. The phase shift is then zero, and we do not gain any information about the system. If the frequency is too low, the charges can sufficiently counter the applied potential before the field can reverse; now, from the perspective of the charge, it is within a DC field, and again the phase shift is zero. However, when the frequency of the voltage is such that a charge carrier can respond to the applied field but cannot cancel it, the material is in resonance with the AC voltage. Simply determining this frequency provides valuable information about the species of study. But furthermore, as mentioned previously, the charge will not respond immediately to the applied field: its response will be delayed. This time delay or phase shift is called dissipation, and it is recorded by the instrument. Dissipation is heavily dependent upon the local environment of a charge species, and therefore by determining this value, we can gain information about the nature of the charged species and its surrounding environment.

Like traditional electromagnetic-based spectroscopy, in IS the frequency of the applied field has a reciprocal relationship with the characteristic time of the process with which it resonates. In other words, the higher the frequency of the applied field, the lower the effective
mass of the charged species of study. At applied AC voltages of $10^{13}$ Hz, the only charges which can respond to the applied field are the electron clouds around nuclei. At slightly lower frequencies, around $10^{12}$ Hz, it is the reorientation of nuclei themselves which is analyzed. At approximately $10^9$ Hz the applied field resonates with permanent and induced dipoles -- here dissipation correlates with the speed at which the dipoles can reorient themselves within the medium, and can therefore be correlated with the viscosity of the material. Finally, at below $10^6$ Hz, the frequency of the applied field is slow enough that ions can move within the material in response. At these frequencies, IS becomes a technique for determining ionic conductivity.\(^{27}\)

When trying to determine the ionic conductivity of a material, in its simplest terms we are trying to determine how quickly an ion will move along a defined vector when a potential difference is applied. While the magnitude of resistance can be easily understood as simply the distance this ion travels along the defined vector, the phase shift of this movement relative to the frequency of the applied voltage represents more complex attributes. A byproduct of a rapidly alternating electric field is the separation of charges across space, or in other words, the creation of localized capacitive elements within the material. These capacitors store the energy of the potential difference applied as non-productive electrical work. In designing a high-performance ionic conductor, we want a particular ion to move from one point in space to another as efficiently as possible. It is therefore desirable that an applied field use 100% of its work on moving ions along the preferred vector.

However, all known ionic conductors are inefficient, and when voltages are applied to these materials what results is work lost to the creation of localized capacitors. This is known as capacitive energy loss. When we use IS to measure the dissipation of the frequency of the applied
field, we are essentially measuring the energy lost to non-productive pathways within the material. This is one of the major advantages of IS as an ionic conductivity characterization technique.

Ionic conductivity data obtained by IS is typically represented by a Nyquist plot. A Nyquist plot is composed of an x-y plot with points whose locations are defined by a vector. The magnitude of this vector is determined by the magnitude of resistance, and the angle of the vector is determined by the phase shift. In this way, the contribution from both the resistive and dissipative elements of the material can be represented on a simple x-y plot. The y-axis is called the imaginary resistance or reactance, and is attributed to the capacitive energy loss mechanisms discussed previously. The x-axis is the real resistance, or the pure magnitude of electrical resistance between the electrodes. When the plot crosses the x-axis, there is zero contribution from the imaginary resistance; therefore, at this point, we can determine the true resistance, and therefore the conductivity of a particular material with respect to this ion of study.
Figure 4.6. Nyquist plots of the S-Trp-PEEK polymers synthesized at 45, 65, and 85 °C. The point at which each curve crosses the x-axis the second time (from left) corresponds to the proton resistivity of the material. S-Trp-PEEK45 = 20 Ω; S-Trp-PEEK65 = 14 Ω; S-Trp-PEEK85 = 17 Ω.

Figure 4.6 shows Nyquist plots of the three S-Trp-PEEK materials. Of the three, the S-Trp-PEEK65 showed the greatest proton conductivity. This is unexpected, as degree of sulfonation typically correlates with conductivity. To compare the performance of these materials to the current industry standard, we then tested Nafion within our experimental setup. As mentioned previously, Nafion is currently the most widely used material for PEM's in commercial fuel cells. Figure 4.7 shows that under testing conditions identical to those used on S-Trp-PEEK, Nafion has a resistivity of 99 Ω, placing it well below S-Trp-PEEK in proton conduction performance. While proton conduction is one of the most important attributes for a fuel cell PEM, other factors should be considered, including longevity, methanol permeability (for direct methanol fuel cells), fuel
crossover, and the effect of elevated temperatures (80-130 °C) on performance. Further study is warranted to determine the quality of S-Trp-PEEK within these metrics.

![Nyquist plot of Nafion film.](image)

**Figure 4.7.** Nyquist plot of Nafion film. The resistivity (99 Ω) of the Nafion film in our system was significantly higher than S-Trp-PEEK.

4.3.5 *Single Walled Carbon Nanotube Composites.* Interestingly, the S-Trp-PEEK can form a robust composite with single walled carbon nanotubes (SWCNTs). Since their discovery in 1991 by Ijima, CNT’s have received an extremely high amount of attention in the scientific community.\(^{28}\) While the production and cost of SWCNT’s remains an important hurdle in their commercial implementation, their exceptional mechanical and electronic properties make them an extremely promising material. CNT’s can be thought of as a single sheet of pristine graphene rolled up into a cylinder; based on the orientation of the hexagonal carbon lattice which results, CNT’s can have differing electronic properties. Accordingly, CNT’s can be either semi-conducting or
metallic in regards to electrical conductivity. CNT's are also extremely strong; the highest recorded strength of a carbon nanotube material was 63 GPa, which is an order of magnitude stronger than the highest strength carbon fiber wires.\textsuperscript{29}

CNT's are notoriously insoluble in all solvents, and are only moderately dispersible in a few solvents with the aid of surfactants. Most of these dispersions suffer from a lack of thermodynamic stability, and often destabilize slowly over time. It was found that when S-Trp-PEEK was mixed with [6,5]SWCNTs in both water and methanol, a stable dispersion resulted (Figure 4.8).

\textbf{Figure 4.8.} Digital image of a dispersion of [6,5]SWCNTs in water-based solution of S-Trp-PEEK. This photograph was taken 1 week after initial mixing.

Interestingly, S-Trp-PEEK did not form stable dispersions with all types of carbon nanotubes. Currently, there is no universal standard for SWCNT synthesis and purification; as such, the composition of carbon nanotubes can vary between commercial suppliers. It is difficult to determine the precise differences between suppliers and it is not uncommon to CNT
compositions to be sold with as much as 25% non-CNT material. Common contaminants include amorphous carbon and metal catalysts such as iron oxides.

It was found that the best dispersions were achieved with [6,5] enriched SWCNT’s as supplied by Sigma-Aldrich. Table 4.2 summarizes the dispersive properties of S-Trp-PEEK when mixed with various types of SWCNT’s in water.

Table 4.2. Summary of the dispersive properties of S-Trp-PEEK when mixed with SWCNT’s in water. Nano-C SWCNT’s are 2/3 semiconducting and 1/3 metallic.

<table>
<thead>
<tr>
<th>SWCNT Type</th>
<th>Stable Dispersion?</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6,5) Carbon &gt;90%, 77%</td>
<td>Yes</td>
</tr>
<tr>
<td>Carbon as SWCNT (Aldrich)</td>
<td></td>
</tr>
<tr>
<td>(7,6) Carbon &gt;90%, 77%</td>
<td>No</td>
</tr>
<tr>
<td>Carbon as SWCNT (Aldrich)</td>
<td></td>
</tr>
<tr>
<td>Nano-C® Purified</td>
<td>No</td>
</tr>
<tr>
<td>Nano-C® As Produced</td>
<td>Partial</td>
</tr>
<tr>
<td>Carbon Nanotechnologies Inc.</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Water based dispersion of SWCNTs are important, as they can allow for improved processing and manipulation of carbon nanotubes in a wide variety of applications. It was found that when the S-Trp-PEEK/SWCNT water dispersions were lyophilized, a black conductive foam ($R = \sim 100 \, k\Omega$) resulted (Figure 4.9). This foam can be cast into any number of shapes, as it adopts the shape of its container when lyophilized. It is also moderately elastic due to its porous structure. When the dispersion was cast into a film and dried, a conductive paper was obtained.
Figure 4.9. Digital images of S-Trp-PEEK/SWCNT foam (left), paper (top right), and conductivity measurement (bottom right). The shape of the conductive foam is dependent upon the container in which it was lyophilized, and thus can be cast into a number of shapes.

Figure 4.10 shows representative SEM images of an S-Trp-PEEK/SWCNT composite. SEM analysis revealed that the material was composed of contiguous smooth domains, which when broken, revealed the presence of SWCNT's within the structure.
**Figure 4.10.** SEM images of the S-Trp-PEEK/SWCNT composite. The above images highlight a cracked region of the surface in which multiple CNT fibers embedded within the material can be clearly seen.
Because it allows for the creation of aqueous dispersion of SWCNTs, S-Trp-PEEK provides a facile route toward creating metal/CNT composites. Furthermore, the native sulfonate groups should provide a ligand structure which further facilitates dispersions of metal nanoparticles within the composite. Sulfonic acids such as the ones found in S-Trp-PEEK have a pKa of approximately -2.8 in water, therefore when the polymer is mixed with metal acetate salts, ligand exchange can occur with the formation of acetic acid. Figure 4.8 shows an SEM image of a and S-Trp-PEEK/SWCNT/Pd(II) composite.

Figure 4.11. SEM image of S-Trp-PEEK/SWCNT/Pd(II) composite. The lighter colored Pd structures 100-1000 nm in diameter can be seem embedded within the film.
4.3.6 Post-polymerization Nitration of Trp-PEEK. Nitration of PEEK based materials is another common method to functionalize these polymers post-polymerization.\textsuperscript{30} Nitration is typically carried out under standard electrophilic aromatic substitution conditions: PEEK is dissolved in conc. sulfuric acid and nitric acid is added. While these reports claim that no sulfonation occurs under these conditions, we found that when Trp-PEEK was used, sulfonation was unavoidable. Conceicao et al. reported the ability to nitrate PEEK in a suspension of sulfuric and nitric acids at elevated temperatures, however they make no mention of the molecular weight of their polymers.\textsuperscript{31} When these conditions were implemented in our lab on Trp-PEEK, it was found that they resulted in significant reduction of the molecular weight of the starting material (Scheme 4.12).

\textbf{Scheme 4.12.} Nitration of Trp-PEEK at elevated temperatures results in significant reduction of the molecular weight.

Like sulfonation, nitration of PEEK materials can be estimated by TGA. By TGA it was determined that the conditions shown in Scheme 4.11 results in 2.85 nitro groups per repeat unit. It is likely that nitration occurs first on the electron rich hydroquinone, and then on the other two aryl rings of the triptycene. Nitration of the benzophenone is possible, but less likely, due to deactivation by the carbonyl.
Scheme 4.13. Synthesis of Trp-PEEK-NMP. The resulting polymer was insoluble in all tested solvents, suggesting an increased molecular weight relative to polymer synthesized in DMAc.

If the lowering of molecular weight is inherent in the nitration procedure, by supplying high molecular weight Trp-PEEK as starting material, the resulting nitrated polymer will be of a similar high molecular weight. Therefore, in an attempt to produce nitrated materials of higher molecular weights, a new synthesis of Trp-PEEK was attempted. To achieve this, NMP was substituted for DMAc as a solvent due to its similar solvation qualities and higher boiling point. The temperature of the reaction can then be raised from 163 °C to 190 °C, which should not only accelerate the kinetics of the S_NAr polymerization, but more effectively solvate higher-molecular weight polymer and allow for the formation of longer polymer chains.

By visual inspection, unlike when the polymerization is carried out in DMAc, the polymer was fully solvated at the end of the reaction. The resulting white polymeric material was found to be completely insoluble in THF and DMF, the two solvents used of GPC characterization. Therefore, it is not possible to obtain a molecular weight in the normal manner. However, based on the qualitative properties of this reaction when compared to the Trp-PEEK synthesized in DMAc it is likely that a molecular weight in excess of 100,000 Da was achieved.
Table 4.3. Degrees of nitration on Trp-PEEK-NMP when dispersed and stirred in 4:1 v/v conc. HNO₃: conc. H₂SO₄ for 1 h at various temperatures and the solubilities of the resulting polymers.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Degree of Nitration</th>
<th>Soluble in THF/DMF?</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 °C</td>
<td>0</td>
<td>No</td>
</tr>
<tr>
<td>25 °C</td>
<td>0</td>
<td>No</td>
</tr>
<tr>
<td>25 °C (3h)</td>
<td>0</td>
<td>No</td>
</tr>
<tr>
<td>25 °C (6h)</td>
<td>0</td>
<td>No</td>
</tr>
<tr>
<td>35 °C</td>
<td>0.13</td>
<td>No</td>
</tr>
<tr>
<td>45 °C</td>
<td>0.33</td>
<td>No</td>
</tr>
<tr>
<td>55 °C</td>
<td>0.68</td>
<td>No</td>
</tr>
<tr>
<td>75 °C</td>
<td>1.10</td>
<td>No</td>
</tr>
</tbody>
</table>

When Trp-PEEK-NMP was submitted to nitration conditions at various temperatures for 1 h, it was found that nitration did not occur until 45 °C and the degree of nitration steadily increased as the temperature of the reaction was raised. However, even the most nitrated polymer was not soluble in the GPC solvents, THF and DMF, which prevented the determination of molecular weight. The marked contrast in reactivity between this high molecular weight polymer and the previous Trp-PEEK is likely due to solubility differences. The nitration reaction is carried out in dispersion, and it is likely the tightly wrapped chains of the high molecular weight Trp-PEEK-NMP only provide a limited number of reactive sites on the outside of the colloid particle. Further investigations are necessary to fully determine the reactivity of this polymer under these nitration conditions.

Reduction of the low molecular weight NO₂-Trp-PEEK into NH₂-Trp-PEEK can be carried out by treatment with H₂ and Pd/C, ammonium formate and Pd/C, or with sodium dithionite
(Scheme 4.14). Complete reduction of the nitro groups is suggested by the disappearance of the NO$_2$ stretch by IR (Figure 4.12). As NH$_2$-Trp-PEEK is decorated with nucleophilic amine groups, further functionalization by treatment with appropriate electrophiles can lead to a wide variety of materials.

Scheme 4.14. Reduction of NO$_2$-Trp-PEEK to NH$_2$-Trp-PEEK. Alternate successful conditions include the use of ammonium formate in place of hydrogen gas, and sodium dithionite.

Scheme 4.15 summarizes how NH$_2$-Trp-PEEK was reacted with 3,5-trifluoromethyl phenylisocyanate or 3,5-trifluoromethylphenylthioisocyanate to give the corresponding urea and thiourea structures. This reaction is most effective when the reduced NH$_2$-Trp-PEEK is used without isolation. Because the urea protons occur within strongly downfield (6-7 ppm) by NMR, it is difficult to use $^1$H NMR to determine the extent of functionalization. However, IR reveals the expected carbonyl and thiocarbonyl stretches in these materials (Figure 4.12).
Figure 4.12. IR spectra of A) NO₂-Trp-PEEK, B) NH₂-Trp-PEEK, C) Urea-Trp-PEEK, D) Thiourea-Trp-PEEK. Diagnostic stretches are highlighted. After reduction, the NO₂ stretches in NO₂-Trp-PEEK disappear and N-H stretches in the resulting polymer can be seen.
Scheme 4.15. Synthesis of Thiourea-Trp-PEEK and Urea-Trp-PEEK. Because it is difficult to determine the precise degree of functionalization, the above structures should be considered speculative. However, IR confirms the presence of the expected urea and thiourea moieties within these polymers.

4.3.7 Urea/Thiourea Trp-PEEK as a Selector for Chemiresistive Sensing of Acetone. Seminal work by Etter and co-workers in the early 1990s first laid the groundwork for the molecular recognition properties of urea compounds.32 Through extensive crystallization studies, Etter found that diaryl ureas bearing electron withdrawing groups were potent hydrogen-bond donors, and could bind carbonyl compounds through this interaction. This property has been exploited to great effect in the field of organocatalysis, where Jacobsen and co-workers pioneered the use of both thiourea and urea derivatives as catalysts in the asymmetric synthesis of numerous substrates.33,34 Jacobsen
demonstrated that it was through the hydrogen bond donation ability of these compounds by which they could effect catalysis.\textsuperscript{35}

In the Swager group, electron-deficient diaryl ureas and thioureas have been used as selectors for both the fluorescence-based\textsuperscript{36} and chemiresistive\textsuperscript{37} sensing of cyclohexanone, an important marker for the energetic material RDX. Interestingly, the case of the squaraine-based urea fluorescent sensor, acetone did not induce a response. This was attributed to steric effects, wherein the relatively smaller acetone molecule did not swell the polymer enough to disrupt energy transfer.

Acetone is important bio-marker for diabetes, as diabetic patients will exhale higher concentrations of acetone in their breath than individuals without diabetes.\textsuperscript{38} Breath analysis can therefore offer an unobtrusive diagnosis of this disease. In contrast to GC-MS, chemiresistive carbon nanotube based gas-sensors are a low cost, portable alternative which can be easily used by non-experts. This type of sensor operates by applying a voltage across a carbon nanotube film which links two conductive electrodes. When the film is exposed to an appropriate analyte, the current across it is altered. This change can be attributed to either doping effects and/or swelling/contraction of the nanotube network. By monitoring these changes, exposure to various analytes can be quantified. A critical component of these sensors is a selector. Selectors are chemical additives which are mixed with the nanotubes and impart unique responses to various analytes. Selectors can either enhance or decrease the nanotubes’ response to a particular analyte, or can create a response where one did not previously exist.

Urea-Trp-PEEK or Thiourea-Trp-PEEK was mixed with [6.5]SWCNT’s at various weight ratios in DMF and briefly sonicated. This resulting dispersions were dropcast onto gold electrodes and allowed to dry under vacuum. When these films were exposed to acetone vapor, they showed
a greatly increased response relative to pristine SWCNT's. While both urea and thiourea polymers elicited a response, the best performer was the Thiorea-Trp-PEEK mixed with SWCNT's at a 6:1 w/w ratio. The performance of this material is shown in Figure 4.13. More work is required for the optimization of this sensor, but these data show that Thiourea-Trp-PEEK is a promising material for the gas-phase sensing of acetone.

Figure 4.13. Response values for Thiourea-Trp-PEEK/SWCNT composite in the chemiresistive gas-phase sensing of acetone.

4.3.8 Mechanical Properties of Urea/Thiourea Trp-PEEK Poly(THF) Composites. The bulk properties of polymers rely heavily upon the forces which exist between polymer chains. In many cases, the most significant contribution to these interactions arise from hydrogen bonding. Lycra, the primary component of spandex, has two major domains which produce its strength and elasticity. While the polyglycol provides the degrees of freedom necessary to impart elastic behavior, it is the urea domain which gives the material its strength. Similarly, it is the amide
linkages in Kevlar, which can act as both hydrogen bond acceptors and donors, which form a rigid structure that allow for its widespread implementation in ballistic body armor (Scheme 4.16).

Scheme 4.16. Synthesis and structure of Lycra (top) and Kevlar (bottom). Hydrogen bonding between polymer chains provides both of these materials with much of their tensile strength.
We sought to explore the ability the Urea/Thiourea-Trp-PEEK polymers to form hydrogen bonding networks in polymer blends with poly(THF). Poly(THF), or Tetrathane, is a polyether derived from the acid-catalyzed polymerization of tetrahydofuran. Most commonly used as a macromonomer is the synthesis of elastic fibers like Lycra and other polyurethanes, it is commercially available at narrow molecular weights between 500 and 2900 daltons, and is terminated by hydroxyl groups (Figure 4.14).

![Image](image)

**Figure 4.14.** Structure of poly(THF). Sold under the tradename Tetrathane, it is a waxy, low-melting solid which commercially available in various molecular weights from 500-2900 daltons.

At room temperature, it is an inelastic waxy solid which melts at 28-35 °C. We expected that when mixed with the urea and thiourea derivatives of Trp-PEEK, that hydrogen bonding between the ether linkages of poly(THF) and the urea protons would impart unique mechanical properties.
After mixing these polymers in various ratios, it was found that where the Thiourea-Trp-PEEK was previously a rigid solid, when mixed with poly(THF) in equal mass proportions in a THF solution, the resulting solution could be cast into a robust film with viscoelastic properties (Scheme 4.17, Figure 4.15). Mass ratios near 1:1 were required to obtain such a material. When excessive amounts of Thiourea-Trp-PEEK are added, its mechanical properties dominate and viscoelasticity is lost. Similarly, when the composite is comprised of mostly poly(THF), a viscous sticky material is obtained.

Scheme 4.17. Summary of the physical properties of composites containing thiourea-Trp-PEEK and poly(THF) (Mw=1000 Da) at various ratios.
Figure 4.15. Digital images of the material which is obtained when Thiourea-Trp-PEEK and poly(THF) are mixed in solution at a 1:1 mass ratio and cast into a film. The top image shows the original film and the material obtained when this film is removed and shaped by hand into a cylinder. The bottom two images show viscoelastic deformation of this cylinder.

The viscoelastic materials obtained at a 1:1 w/w ratio also possess self-healing properties. It can be deformed and reformed any number of times into numerous different shapes and orientations (Figure 4.16). Heating the material increases its ductility significantly, and allows for more precise manipulation. Interestingly, the Urea-Trp-PEEK did not produce a similar material as the Thiourea-Trp-PEEK, instead forming a hard, waxy solid when mixed with poly(THF).
Figure 4.16. Self-healing properties of thiourea-Trp-PEEK/poly(thf) composite. After destroying the film, the fragments are heated, which increases the ductility of the material. After doing so, the material can be reshaped at will.

From these qualitative analyses, it is clear that these types of composites possess interesting mechanical properties which warrant further inquiry. Systematic quantitative mechanical studies on these materials must be performed to better understand them. In particular, it is necessary to determine what effect altering the mass ratios and molecular weights of both polymers has on the mechanical properties of the resulting composites.
4.3.9 Synthesis of Triptycene Poly(thioether thioether ketone) Developed in the 1960s, the Newman-Kwart rearrangement (NKR) is a reaction which converts an O-arylthiocarbamate to an S-arylthiocarbamate allowing for the synthesis of thiophenols from the corresponding phenols (Scheme 4.18).39,40 The NKR generally proceeds in good to high yields, and can provide an effective route to aryl-sulfur linkages. However, the high temperatures required for the rearrangement limit the substrate scope, as molecules which contain functionality which can decompose or undergo undesired reactions at these temperatures limit its use. Recently, a Pd catalyzed NKR was reported, which allowed for the reaction to be carried at temperatures as low as 100 °C.41 Other important synthetic routes to aryl-sulfur linkages include Cu mediated coupling of boronic acids42 (Chan-Lam Coupling), Sandmeyer type reactions, and Pd coupling of aryl halides43 or triflates.44

![Scheme 4.18. The Newman-Kwart rearrangement. The NKR allows for access of thiophenols from the corresponding phenol.](image)

In order to access triptycene-PEEK type polymers with sulfide linkages, the Newman-Kwart rearrangement was used to access the triptycene T2 (Scheme 4.19). It was found that the
use of quinolone as both solvent and base improved the yield of thiocarbamate T1. Double recrystallization of T1 in 2-butanone was necessary to obtain good yields of the rearranged product T2. It was also found that the use of diphenyl ether as a solvent for the rearrangement was superior to heating of the neat precursor T1.

![Diagram](image)

**Scheme 4.19.** Synthesis of triptycene T2, and its use as a monomer in the synthesis of Trp-S-PEEK.

T2 can be used as a monomer directly in the SnAr polymerization with 4,4'-difluorobenzophenone, which is advantageous as it was found that after deprotection of T2, the resulting dithiol was prone to oxidative degradation. It was found that this method could produce the triptycene polymer poly(thioether thioether ketone) (Trp-PTTK) in excellent yields and at high molecular weights. Trp-PTTK was found to have nearly identical thermal properties to Trp-PEEK, with a decomposition temperature of 550 °C and glass transition temperature of 255 °C.
4.4 Conclusions

A new polyarylether, Trp-PEEK, was synthesized and extensively characterized. The incorporation of a triptycene ring into the backbone of PEEK results in high molecular weight polymer with increased glass transition temperature relative to the parent PEEK polymer. Trp-PEEK can be sulfonated to various degrees by dissolution in concentrated sulfuric acid at various reaction temperatures, and this sulfonation results in lowering of its molecular weight by around half. The polymer produced, S-Trp-PEEK is a porous yellow foam which can be cast into mechanically robust transparent membranes. As a membrane, this material shows promise as a high-performance proton conductor for fuel cell applications, outperforming the industry standard, Nafion. Nitration of Trp-PEEK results in a much more significant reduction of its molecular weight. The resulting material NO₂-Trp-PEEK can be reduced to the amine under standard conditions, and this polymer can then be further functionalized with urea or thiourea structures via reaction with isocyanates. The hydrogen bonding abilities of Thiourea-Trp-PEEK make it a highly effective selector for acetone in chemiresistive gas-phase sensing. Furthermore, this polymer can form viscoelastic materials when mixed with a suitable hydrogen-bond acceptor, such as poly(THF). Finally, using the Newman-Kwart rearrangement, a thiocarbamate monomer derived from triptycene diol can be synthesized. This monomer can be reacted with 4,4'-difluorobenzophenone to form poly(thioether thioether ketone) (PTTK) in good yields and high molecular weight. This polymer displayed similar thermal properties to Trp-PEEK.
4.5 Experimental

*General Materials and Methods*: All chemicals were purchased from Sigma-Aldrich and used as received unless stated otherwise. Thermogravimetric analyses were performed on a TA Instruments Discovery TGA in the range of 50 – 800 °C at a constant ramp rate of 20 °C min⁻¹ under nitrogen atmosphere. Differential scanning calorimetry analyses were performed on a TA Instruments Discovery DSC at a scan rate of 10 °C/min. Nuclear magnetic resonance (NMR) data was obtained on a Varian Inova- 500MHz NMR. Polymer molecular weights were determined using an HP series 1100 GPC system in DMF or THF (approx. .5 mg/mL sample concentration) and are relative to polystyrene standards or on Waters GPC in DMF (5 mg/mL sample concentration relative to PMMA standards).

*Ionic conductivity measurements*. Membranes were made by casting from 7 wt% solutions of the polymer in dimethylformamide in a Teflon well and left to dry in the vacuum oven at 70 °C overnight. Membranes were then slightly hydrated with a drop of deionized water and peeled off from the well. The free standing membranes were then soaked in deionized water for at least 2 hours before any measurements. Proton conductivity was measured using a Solartron SI 1287 electrochemical interface coupled with a Solartron SI 1260 impedance/gain-phase analyzer. Films were placed across 4 platinum electrodes spaced 1 cm apart and the measurement was done in galvanostatic mode with an ac current of 0.2 mA over a frequency range of 1 MHz to 0.1 Hz.

Water uptake of the films were obtained gravimetrically using the equation below. Swollen films were first wiped dry and quickly weighed to obtain the swollen mass (W_s). The films were then dried in a vacuum oven at 70 C for over 24 hours and quickly weighed to obtain the dry mass (W_d).

\[ \text{Water uptake} = \frac{W_s - W_d}{W_d} \times 100\% \]
Gas-phase sensing procedure. Gas detection measurements were acquired by placing the sensor array device into a custom-built PTFE enclosure with a small gas inlet and outlet and, with the aid of a 64-pin device test clip (3M) and custom-built PTFE spacer, connecting the gold electrodes of the device to a PalmSens EmStat potentiostat with a MUX16 multiplexer. The potentiostat was used to apply a constant potential of 0.100 V across the electrodes, and the current was recorded using PSTrace software (v. 3.0) as the device was exposed to gaseous analytes. For measuring device response to volatile liquid organic compounds, a KIN-TEK gas generator system calibrated for each compound was used to deliver the gaseous analyte diluted in nitrogen gas (2% relative humidity) as the carrier gas at a fixed flow rate. The sensor array was exposed to each analyte for 60 s with at least 180 s of nitrogen flow in between exposures to analyte.

Synthesis of triptycene diol T2. Prior to synthesis, benzoquinone was purified by dissolving the black and yellow powder in dichloromethane, and running a short silica plug. The obtained yellow solution was rotary evaporated under reduced pressure and the yellow powder dried under vacuum at room temperature overnight. 12.1 g benzophenone (.112 mol) was then mixed with 10.0 g anthracene (.056 mol) in 70 mL xylenes and refluxed under a nitrogen atmosphere for 4 h. The reaction mixture was cooled to room temperature, filtered, and the residue washed twice with 10 mL toluene. The yellow solid was then recrystallized from xylenes and dried at 60 °C in vacuo overnight to give 11.5 g of the Diels-Alder adduct T1 (72% yield). 1H NMR (500 MHz, CDCl3) 7.41 (m, 4H), 7.20 (m, 8H), 7.09 (m, 4H), 6.33 (s, 2H), 4.88 (s, 2H), 3.15 (s, 2H). The crystalline yellow material was then mixed with 150 mL acetic acid and brought to reflux. When the material had completely dissolved, 3 drops 48% hydrobromic acid were added causing the reaction to exotherm considerably. A white precipitate quickly formed and the reaction was refluxed for 1 h.
The reaction was allowed to slowly cool to room temperature, and a white crystalline product continued to precipitate. The reaction mixture was filtered, and the white crystalline solid was dried under vacuum at 80 °C overnight to yield 10.9 g triptycene diol T2 (68% yield). \(^1\)H NMR (500 MHz, CD$_3$OD) 8.83 (s, 2H), 7.37 (m, 4H), 6.95 (m, 4H), 6.29 (s, 2H), 5.79 (s, 2H).

**Synthesis of Trp-PEEK.** Potassium carbonate was pulverized into a fine powder in a mortar and pestle and dried in a vacuum oven at 120 °C for at least 3 days. Dimethyl acetamide (DMAc) was dried over 4A molecular sieves for at least 48 h. Triptycene diol was stored in a vacuum oven at 80 °C prior to use. In a two neck round bottom flask equipped with a N2 inlet, magnetic stir bar, and distillation head, 5.727 g triptycene diol (.0200 mol, 1 eq), 4.364 g 4,4'-difluorobenzophenone (.0200 mol, 1 eq), and 6.35 g K$_2$CO$_3$ (.046 mol, 2.3 eq) was mixed in 100 mL DMAc and 50 mL toluene. The reaction was brought to 150 °C and the toluene distilled under a gentle flow of N$_2$ over 4 h. Then distillation head was removed and replaced with a reflux condenser, and the reaction brought to reflux. Reflux was maintained for 12 h and the hot reaction mixture was poured into stirring water. The water was brought to reflux to remove inorganic salts and then filtered hot. The white polymeric material was then refluxed and filtered alternating between acetone and water at least 3 times each. During this process, it is necessary to grind up the tough polymeric material in a mortar and pestle between wash steps to maximize the surface area available for washing. The resulting white polymeric material was dried in a vacuum oven at 120 °C overnight to yield 8.45 g Trp-PEEK (91% yield) \(^1\)H NMR (500 MHz, DMF-d7) 7.86 (bm, 4H), 7.40 (bm, 4H), 7.08 (bm, 4H), 6.9 (bm, 8H), 5.85 (bm, 2H).
Alternative Synthesis of Trp-PEEK. Diphenylsulfone (DPS) was purified by mixing an acetone solution of DPS with activated carbon and then centrifuging the mixture, and filtering the supernatant. The clear solution was then precipitated into water and the resulting crystalline solid was dried at 120 °C overnight. 25 g DPS was then charged into a two necked flask equipped with a Pyrex coated stir bar and N₂ inlet. Using a K-type thermocouple and heating mantle, the DPS was brought to 180 °C and stirred at this temperature for 30 min to remove dissolved oxygen and water. 12.00 g triptycene diol (.04191 mol) and 9.145 g (.04191 mol) 4,4'-difluorobenzophenone were added to the now liquid DPS and stirred. To this milky white solution was added 5.85 g (.042 mol) K₂CO₃. The reaction temperature was raised to 250 °C and maintained there for 1 h, then raised to 320 °C and maintained there for 1 h. The reaction mixture was allowed to cool and then poured into stirring acetone. The white polymeric material was then refluxed and filtered alternating between acetone and water at least 5 times each. During this process, it is necessary to grind up the tough polymeric material in a mortar and pestle between wash steps to maximize the surface area available for washing. The resulting white polymeric material was dried in a vacuum oven at 120 °C overnight to yield 15.4 g Trp-PEEK (79% yield).

Synthesis of Trp-PEEK-NMP. NMP was dried over 4A molecular sieves for 48 h then distilled under reduced pressure and stored over 4A molecular sieves. Toluene was dried over 4A molecular sieves for 48 h. Potassium carbonate was pulverized into a fine powder in a mortar and pestle and dried in a vacuum oven at 120 °C for at least 3 days. Triptycene diol was stored in a vacuum oven at 80 °C prior to use. In a two neck round bottom flask equipped with a N₂ inlet, magnetic stir bar, and distillation head, 9.445 g triptycene diol (.033 mol, 1 eq), 7.200 g 4,4'-difluorobenzophenone (.0330 mol, 1 eq), and 10.74 g K₂CO₃ (.046 mol, 2.3 eq) was mixed in 100 mL NMP and 25 mL
toluene. The reaction was brought to 160 °C and the toluene distilled under a gentle flow of N₂ over 4 h. Then distillation head was removed and replaced with a reflux condenser, and the reaction brought to 190 °C. This temperature was maintained for 12 h and the hot reaction mixture was poured into stirring acetone. The acetone was brought to reflux and then filtered hot. The white polymeric material was then refluxed and filtered alternating between acetone and water at least 3 times each. The polymer was then purified via Soxhlet extraction with THF. The resulting white polymeric material left in the thimble was dried in a vacuum oven at 120 °C overnight to yield 14.55 g Trp-PEEK-NMP (95% yield).

**Synthesis of S-Trp-PEEK.** 500 mg Trp-PEEK was dissolved in 10 mL concentrated sulfuric acid while stirring. The reaction was placed in an oil bath a pre-determined temperature and maintained that way for 1 h. The reaction was then precipitated in DI water, centrifuged, and the supernatant discarded. The resulting solids were washed with DI water and then centrifuged five more times. The resulting slightly pink gelatinous solid was then dialyzed against DI water for 48 h. The white gelatinous solid was then lyophilized until dry, resulting in a yellow foam. 1H NMR (500 MHz, CD3OD), 7.93 (bm, 4H), 7.82 (bs, 2H), 7.58 (bm, 2H), 7.37 (bm, 2H), 7.07 (bm, 4H), 6.97 (bs, 2H), 5.90 (bm, 2H)

**Synthesis of NO₂-Trp-PEEK.** A stock solution of 4:1 v/v conc. HNO₃:conc. H₂SO₄ was made by combining the two acids in a glass container and allowing them to equilibrate and return to room temperature. 6.25 mL of this acid mixture was added slowly to 500 mg Trp-PEEK and the resulting dispersion was allowed to stir at a defined temperature for 1 h. The reaction was then filtered through a glass frit and the solids collected were washed with DI water 3 times. The solids were
then redispersed in 40 mL DI water and isolated either by filtration or centrifugation. This was repeated with 40 mL methanol and 40 mL acetone and the solids allowed to dry under vacuum at 80 °C. \(^1\)H NMR (500 MHz, DMSO-d6) 8.69 (b, 2H), 8.0 (b, 12H), 7.20 (b, 3H), 6.29 (b, 1H), 6.40 (b, 3H)

**Synthesis of NH\textsubscript{2}-Trp-PEEK.** 500 mg NO\textsubscript{2}-Trp-PEEK was dissolved in 20 mL DMF under stirring and 200 mg 10% Pd/C was added. A hydrogen gas balloon was attached via needle and septa to the reaction and a positive pressure of H\textsubscript{2} gas was maintained during the course of the reaction. After stirring for 24 h at rt, several scoops of Celite were added to the reaction and mixture was filtered. 3.5 mL portions of DMF were used to wash the solids collected and the DMF solution was isolated. This solution was used directly in the synthesis of both Urea-Trp-PEEK and Thiourea-Trp-PEEK. To isolate NH\textsubscript{2}-Trp-PEEK, 10 mL of 1 M HCl was added to precipitate the polymer. The polymer was isolated via centrifugation and washed with DI water and methanol, then dried under vacuum at 80 °C.

**Synthesis of Urea-Trp-PEEK and Thiourea-Trp-PEEK.** Based on the known concentration of NH\textsubscript{2}-Trp-PEEK from its synthesis, 3 eq. 3,5-trifluoromethyl phenylisocyanate or 3,5-trifluoromethylphenylthioisocyanate were added dropwise to a solution of NH\textsubscript{2}-Trp-PEEK in DMF. After stirring at rt under N\textsubscript{2} for 12 h, the solution was poured into water and the polymer was precipitated. The solids were isolated via centrifugation and washed with DI water (3x, 40 mL), and MeOH (3x 40 mL) and the dried under vacuum at 80 °C. **Urea-Trp-PEEK** \(^1\)H NMR (500 MHz, DMSO-d6) 8.57 (bm), 8.50 (bs), 8.25 (bd), 8.15 (bs), 7.95 (bm), 7.60 (bm), 7.25 (bs), 7.10 (bs), 6.90 (bm), 6.40 (bm), 6.20 (bm). **Thiourea-Trp-PEEK** \(^1\)H NMR (500 MHz, DMSO-d6) 8.65
(bm), 8.45 (bs), 8.30 (bs), 8.20 (bs), 8.15 (bs), 7.95 (bs), 7.60 (bm), 7.25 (bs), 7.15 (bs), 7.05 (bs), 6.90 (bm), 6.50 (bs), 6.35 (bs), 6.25 (bs), 6.15 (bm)

**Synthesis of T1.** Glassware was flame-dried prior to use and the reaction was performed under inert atmosphere. Quinoline was distilled under reduced pressure prior to use. In a two necked round-bottom flask equipped with a N₂ inlet, magnetic stirrer, and a thermometer, 28.6 g triptycene diol (.10 mol) and 27.2 g dimethylthiocarbamoyl chloride (.22 mol) were dissolved in 30 mL quinolone. The reaction was heated to 190 °C for 45 min and cooled to room temperature. The resulting brown solid was washed with 20 mL conc. HCl, 20 ml 2 M HCl, 100 ml water, then 30 ml methanol. The brown solid was then recrystallized from CHCl₃/MeOH and the resulting white solid was dried overnight at 60 °C in vacuo, producing 31.72 g T1 (69% yield). ¹H NMR (500 MHz, CDCl₃), 7.36 (dd, 4H), 6.98 (dd, 4H), 6.70 (s, 2H), 3.55 (s, 6H), 3.46 (s, 6H).

**Synthesis of Newman-Kwart Rearranged Monomer T2.** 410 ml diphenyl ether was brought to 245 °C under N₂ and stirred at that temperature for 30 min to remove dissolved oxygen. 18.64 g (.040 mol) T1 was added in several portions and the reaction was maintained at 245 °C for 2 h. The reaction was cooled to just above room temperature and poured into 300 ml hexanes. This resulting dispersion was filtered to yield a brown powder which was washed with hexanes and then dried. This brown powder was then recrystallized twice from 2-butanone to yield 13.08 g T2 (70% yield). ¹H NMR (500 MHz, CDCl₃), 7.37 (dd, 4H), 7.15 (2, 2H), 6.98 (dd, 4H), 5.88 (s, 2H), 3.23 (bs, 6H), 3.08 (bs, 6H). ¹³C (125 MHz), 165.5, 150.5, 144.9, 132.9, 125.8, 125.5, 124.4, 52.6, 37.4.
Synthesis of PTTK. 4.84 g T2 (.0105 mol), 2.29 g 4,4'-difluorobenzophenone (.0105 mol), 3.15 g CaCO$_3$, .35 g CsCO$_3$ and 28 g benzophenone were added to a three neck round-bottom flask equipped with a N$_2$ inlet, magnetic stirrer, and a thermometer. The reaction was brought to 210 °C and maintained there for 6 h. The reaction was allowed to cool to 150 C and poured into ice water. The resulting white polymeric material was boiled in acetone and then filtered. This was repeated with boiling water, room temperature 2 M HCl, boiling water, and boiling acetone. The resulting white powder was dried under vacuum at 80 °C overnight, producing 4.54 g PTTK (87% yield) 1H NMR (500 MHz, THF-d8) 9.60 (m, 2H), 9.49 (m, 4H), 9.12 (m, 4H), 9.01 (m, 4H), 8.96 (m, 4H), 8.68 (m, 4H), 7.85 (m, 2H).
4.6. References


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Appendix
Appendix 1: Functionalization of Graphene with Acylated Derivatives of Meldrum’s Acid
Figure A1.1 $^1$H NMR of acylated Meldrum’s acid 1
Figure A1.2 $^1$H NMR of acylated Meldrum’s acid 2
Figure A1.3 \(^1\)H NMR of acylated Meldrum's acid 3
Figure A1.4 $^1$H NMR of $^{13}$C labeled acylated Meldrum's acid
Figure A1.5 $^{13}$C NMR of $^{13}$C labeled acylated Meldrum's acid
Appendix 2: Graphene Phosphate
Figure A2.1. XPS Spectrum of graphene phosphate monolith

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<td>P</td>
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Figure A2.2. Photograph of filter cake and XPS spectrum of material obtained from triethylphosphate adsorption experiment.

Washed and sonicated:
- 3 X DMF
- 3 X DCM

Filter cake obtained from reaction
Figure A2.3. $^{31}$P NMR of triethylphosphite reaction with LiBr control. The single peak belongs to triethylphosphite.
Figure A2.4. XPS spectrum of graphene phosphate annealed in 800 °C.
Figure A2.5. Dispersibility profile of graphene phosphate
Figure A2.6. XPS spectrum of phosphonate graphene PG1

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Figure A2.7. XPS spectrum of iron graphene phosphate monolith, FeG1.

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Figure A2.8. PXRD spectrum of iron graphene phosphate monolith, FeG1.
Figure A2.9. PXRD spectrum of iron graphene phosphate monolith FeG1 after annealing at 350°C for 2 h under N2 gas.
Figure A2.10. XPS spectrum of lithium/iron phosphate monolith LiFeG1 after annealing at 350 C for 2 h under N2 gas.

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Figure A2.11. PXRD spectrum of lithium/iron phosphate monolith LiFeG1 after annealing at 350°C for 2 h under N2 gas.
Figure A2.12. PXRD spectrum of lithium/iron phosphate composite FeG2 after annealing at 350 C for 2 h under N2 gas.
Figure A2.13. PXRD spectrum of lithium/iron phosphate composite FeG3 after annealing at 350 C for 2 h under N2 gas.
Figure A2.14. PXRD diffractogram of lithium/iron phosphate composite LiFeG2 after annealing at 350 °C for 2 h under N2 gas.
Figure A2.15. PXRD diffractogram of CePhosGraphene.
Appendix 3: Brine Stable Graphene
3A1 XPS of Flocculated graphene oxide in API Brine

C - 72%
O - 26%
Ca - 2%
3.A2 XPS of CG1
3. A3 XPS of ZCG1
3.A4 $^1$H NMR of PVIM-co-PVPy

![NMR Spectrum](image)

ppm (f1)
Appendix 4: Triptycene Poly(ether ether ketone)
Figure A4.1. $^1$H NMR of DA adduct T1.
Figure A4.2. $^1$H NMR of triptycene diol T2.
Figure A4.3. $^1$H NMR triptycene PEEK
Figure A4.4. Thermogravimetric decomposition curve of triptycene PEEK under N₂ atmosphere
Figure A4.5. Differential scanning calorimetry of triptycene PEEK.
Figure A4.6. $^1$H NMR S-Trp-PEEK
Figure A4.7. Gel permeation chromatography elution trace of Trp-PEEK.
Figure A4.8. Gel permeation chromatography elution trace of Trp-PEEK synthesized under industry synthesis conditions.
Figure A4.9. Thermogravimetric decomposition curve of S-Trp-PEEK45 under N₂ atmosphere.
Figure A4.10. Gel permeation chromatography elution trace of S-Trp-PEEK-45.
Figure A4.11. Thermogravimetric decomposition curve of S-Trp-PEEK65 under N₂ atmosphere.
Figure A4.12. Gel permeation chromatography elution trace of S-Trp-PEEK-65.
Figure A4.13. Thermogravimetric decomposition curve of S-Trp-PEEK85 under N₂ atmosphere.
Figure A4.14. Gel permeation chromatography elution trace of S-Trp-PEEK-85.
Figure A4.15. $^1$H NMR of NO$_2$-Trp-PEEK.
Figure A4.16. $^1$H NMR of Urea-Trp-PEEK.
Figure A4.17. $^1$H NMR of Thiourea-Trp-PEEK.
Figure A4.18. $^1$H NMR of Tl.
Figure A4.19. $^1$H NMR of T2.
Figure A4.20. $^{13}\text{C}$ NMR of T2.
Figure A4.21. $^1$H NMR of PTTK.
Figure A4.22. Thermogravimetric decomposition curve of Trp-PTTK under N₂ atmosphere.
Figure A4.23. Differential scanning calorimetry of triptycene PEEK.
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- Designed and synthesized polymers for applications in chemical sensing, energy storage, and nanoparticle composites
- Managed two major grant programs requiring substantial interfacing between academic lab and corporate sponsors Phillip Morris International and Saudi Aramco
- Trained in the fabrication and operation of chemiresistive and fluorescence based sensors for trace chemical detection
- Performed FT-IR analysis on ancient papyrus fragment ‘Gospel of Jesus’s Wife’ which was highlighted by major international media outlets
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- Mentored one visiting undergraduate student in polymer synthesis, purification, and characterization
- Performed as a teaching assistant for two semesters of an OLED synthesis and fabrication course
- Trained in NMR, GC-MS, GPC, FT-IR, XPS, BET, TGA, UV-Vis, DSC and SEM analysis of small molecules, polymers, and materials
Synthesized carbene precursor small molecules for elucidation of novel mechanisms regarding carbene rearrangements

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Tutored multiple students in organic chemistry

Publications


Patents


Conferences


234


Community Service

- MIT Chemistry Outreach Program

Awards

- Outstanding Teaching Award (MIT) 2011
- Bradford P. Mundy Award for Promise in Chemistry (Colby) 2010
- The Evans B. Reid Award in Organic Chemistry (Colby) 2009
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