Design of Hybrid Conjugated Polymer Materials: 1) Novel Inorganic/Organic Hybrid Semiconductors and 2) Surface Modification Via Grafting Approaches

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DESIGN OF HYBRID CONJUGATED POLYMER MATERIALS:
1) NOVEL INORGANIC/ORGANIC HYBRID SEMICONDUCTORS AND
2) SURFACE MODIFICATION VIA GRAFTING APPROACHES

A Dissertation Presented
by
JOSEPH J. PETERSON

Submitted to the Graduate School of the
University of Massachusetts-Amherst in partial fulfillment
of the requirements for the degree of

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Polymer Science and Engineering Department
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David A. Hoagland, Head
Polymer Science and Engineering
For my loving wife and Family
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I am grateful to the many people who encouraged, helped, and enabled me on this journey in my life. First, I would like to express sincere thanks and appreciation to my advisor and friend, Prof. Kenneth R. Carter. From the moment I joined his research group Ken has been a constant mentor and a guide. We have shared some amazing experiences together, both in the trials and triumphs of our research pursuits and in life’s journey with the births of our children, who have practically become siblings. I am truly grateful to him for his passion for science, and his patient guidance, which enabled my work. I feel very humbled by the freedom he gave me to pursue my own projects and research ideas. This is perhaps the most important and difficult role for a research advisor, knowing how much freedom to give a student and when to step in with guidance.

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lovingly supported me, moving here with me for my studies, and moving her career around to support me. She is my inspiration, my partner in life, and my soul mate; her love gives me the strength to accomplish anything.
ABSTRACT

DESIGN OF HYBRID CONJUGATED POLYMER MATERIALS:
1) NOVEL INORGANIC/ORGANIC HYBRID SEMICONDUCTORS AND
2) SURFACE MODIFICATION VIA GRAFTING APPROACHES

FEBRUARY 2012

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The research presented in this dissertation focuses on the design and synthesis of novel hybrid conjugated polymer materials using two different approaches: 1) inorganic/organic hybrid semiconductors through the incorporation of carboranes into the polymer structure and 2) the modification of surfaces with conjugated polymers via grafting approaches. Hybrid conjugated polymeric materials, which are materials or systems in which conjugated polymers are chemically integrated with non-traditional structures or surfaces, have the potential to harness useful properties from both components of the material to help overcome hurdles in their practical realization in polymer-based devices. This work is centered around the synthetic challenges of creating new hybrid conjugated systems and their potential for advancing the field of polymer-based electronics through both greater understanding of the behavior of hybrid systems, and access to improved performance and new applications. Chapter 1 highlights the
potential applications and advantages for these hybrid systems, and provides some historical perspective, along with relevant background materials, to illustrate the rationale behind this work.

Chapter 2 explores the synthesis of poly(fluorene)s with pendant carborane cages. The Ni(0) dehalogenative polymerization of a dibromofluorene with pendant carborane cages tethered to the bridging 9-position produced hybrid polymers produced polymers which combined the useful emissive characteristics of poly(fluorene) with the thermal and chemical stability of carborane cages. The materials were found to display increased glass transition temperatures and showed improved emission color stability after annealing at high temperatures relative to the non-hybrid polymer.

The design and synthesis of a poly(fluorene)-based hybrid material with carborane cages in the backbone, rather than as pendant groups, begins in chapter 3. Poly(fluorene) with $p$-carborane in the backbone is synthesized and characterized, and the material is found to be a high MW, soluble blue emitter which shows a higher glass transition temperature and greater stability than a non-hybrid polymer. UV absorbance and fluorescence spectroscopy indicated some electronic interaction between the conjugated polymer and the cages, but they did not appear to be fully conjugated in the traditional sense.

Chapter 4 describes the design, synthesis, and characterization of poly(fluorene) with $o$-carborane in the backbone. Profound changes in the behavior of the polymer, from its polymerization behavior to its emission characteristics, were observed and their origins are discussed. Experiments to explore the nature of the cage/polymer interactions
were performed and possible applications which take advantage of the unique nature of the $o$-carborane hybrid polymer are explored and discussed.

Hybrid conjugated polymer materials via grafting approaches to surfaces and surface modification are discussed starting in chapter 5. The synthesis of a dibromofluorene-based silane coupling agent for the surface functionalization of oxide surfaces is presented, and the surface directed Ni(0) dehalogenative polymerization of poly(dihexylfluorene) is explored.

Chapter 6 focuses on the exploration of conjugated polymer/cellulose hybrid materials. Surface modification of cellulose materials with monomer-like anchor points is discussed. Grafting of the modified cellulose with conjugated polymers was explored and the grafting of three different repeat structures based on fluorene-, fluorenevinylene-, and fluoreneethynylene motifs were optimized to provide a general route to cellulose/conjugated polymer hybrid materials. Characterization and possible applications of such hybrid materials are discussed.

Finally, chapter 7 is devoted to the simultaneous surface patterning and functionalization of poly(2-hydroxyethylmethacrylate) thin films using a silane infusion-based wrinkling technique. While not a conjugated polymer system, the spontaneous patterning and functionalization methods explored in this chapter produce hybrid organic/inorganic polymer thin films which have applications that range from optics, to adhesion, to polymer-based electronics, and the research compliments the other chapters. The spontaneous generation of complex patterns, of a small scale approaching 100nm feature size, over a large area with simultaneous control over surface chemistry is explored. Examples of complex, hierarchically patterned films which integrate
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<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>AIE</td>
<td>Aggregation Induced Emission</td>
</tr>
<tr>
<td>BNCT</td>
<td>Boron Neutron Capture Therapy</td>
</tr>
<tr>
<td>BrPh-TCS</td>
<td>Bromophenyltrichlorosilane</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>Chloroform</td>
</tr>
<tr>
<td>COD</td>
<td>1,5-Cyclooctadiene</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DBDHF</td>
<td>Dibromodihexylfluorene</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DMAP</td>
<td>Dimethylaminopyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>¹PrOH</td>
<td>Isopropanol</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl Group</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>MTS</td>
<td>Methyltrichlorosilane</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance Spectroscopy</td>
</tr>
<tr>
<td>PA</td>
<td>Poly(acetylene)</td>
</tr>
<tr>
<td>PANI</td>
<td>Poly(aniline)</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PDHF</td>
<td>Poly(dihexylfluorene)</td>
</tr>
<tr>
<td>PEG-TCS</td>
<td>Polyethylene glycol (6-9)trichlorosilane</td>
</tr>
<tr>
<td>PF</td>
<td>Poly(fluorene)</td>
</tr>
<tr>
<td>PHEMA</td>
<td>Poly(2-hydroxyethylmethacrylate)</td>
</tr>
<tr>
<td>PLED</td>
<td>Polymer Light Emitting Diode</td>
</tr>
<tr>
<td>PPE</td>
<td>Poly(p-phenyleneethynylene)</td>
</tr>
<tr>
<td>PPP</td>
<td>Poly(p-phenylene)</td>
</tr>
<tr>
<td>PPV</td>
<td>Poly(phenylenevinylene)</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>R</td>
<td>Undefined Substituent</td>
</tr>
<tr>
<td>RFID</td>
<td>Radio Frequency Identification</td>
</tr>
<tr>
<td>TBDMS</td>
<td>Tertbutyldimethylsilane</td>
</tr>
<tr>
<td>TCS</td>
<td>Trichlorosilane</td>
</tr>
<tr>
<td>TFT</td>
<td>Thin Film Transistor</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilane group</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethylsilane</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VTCS</td>
<td>Vinyltrichlorosilane</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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CHAPTER 1
INTRODUCTION

The overarching theme of this work is to enable future technologies of polymer-based electronics and devices through the discovery, development, and understanding of new conjugated polymer systems. This is an inherently interdisciplinary and collaborative pursuit. True progress will require all areas of materials science; polymer chemistry, physics, and engineering are necessary to design and harness new polymer systems for devices simultaneously from the molecule up and the top level device structures down, to seamlessly integrate a molecular engineering project into a practical, functioning, physical device. This work focuses on the molecular engineering level and the design of structures from the molecule upwards, and is more broadly based on the exploration of synthetic polymer chemistry as it relates to new conjugated polymer structures.

This introduction presents brief overviews of the several topics that are necessary to understand the background and motivations for the research presented in this dissertation. A more specific, project oriented introduction is contained within each of the respective chapters to give more focused background and the state of the art in each very specialized topic area. The introductory chapter contains a brief introduction to conjugated polymers as a segway to the main bulk of this work in which conjugated polymer hybrid materials are explored. The hybrid materials explored in this work focus on 1) inorganic/organic conjugated polymer structures containing carborane cages and 2) hybrid structures via a grafting approach, or tethering conjugated polymers to surfaces.
Therefore brief introductions to boron and carborane cages as well as surface grafted polymers and polymer brushes are presented to prepare for the more detailed introductions contained in later chapters. The final topic of the dissertation, patterning via wrinkling, requires a short overview of the field of wrinkling and its use as a spontaneous patterning technique. The introduction chapter, combined with the specific introductions of each following chapter as a guide to the approaches and experiments detailed in the dissertation.

1.1 Introduction to Conjugated Polymers

The dream of polymer-based electronic devices has driven intense research into conjugated polymers for over four decades. The idea that organic molecules, especially polymers because of their facile processing, could replace their traditional inorganic semiconductor analogs has sparked syntheses of materials for completely new designs of electronic devices. While it’s not certain when the first conjugated polymer was synthesized, the first detailed reports are likely from the 19th century, though their true polymer nature wouldn’t be widely accepted until well into the next century.(1) A report from 1862 describes the electropolymerization and observations of chemical doping of poly(aniline). Spurred by a rash of fatal nitrobenzol poisonings, H. Letheby, a professor of chemistry in the College of the London Hospital, was in search of a sensitive test for the compound. After finding that it was converted into aniline in the stomach, his research on the salts of aniline led him to the discovery that the electrolysis of sulphate of aniline produced deep blue/green insoluble powders on his electrodes, poly(aniline), though he did not realize the significance of his experiment.(2) Mentioned occasionally in the scientific literature through the first half of the 20th century, the field of organic
electronics began to gain momentum with work on organic charge transfer complexes in the 1950s, conducting poly(pyrrole) in the 1960s, and even an organic switch based on the amorphous organic semiconductor melanin in 1974.(3, 4) (Figure 1.1) These appear largely forgotten, however, and the birth of the modern field of conjugated polymers, however, can be traced to the late ‘70s, when Heeger, MacDiarmid, Shirakawa and others reported high conductivity upon doping poly(acetylene)s with halogens.(5, 6) The tantalizing promise of all-plastic electronics has been a driving factor for sustained interest and growth in this field of research since. Work has continually focused on increasing the performance, stability, and cost-effectiveness of conducting polymers for applications ranging from flexible displays to plastic solar cells to wearable or disposable electronics.

Figure 1.1: An active organic polymer switch based on melamine, arguably one of the first conjugated polymer device. (3)

Compared to traditional inorganic based semiconducting systems, many of the details of the amazing behavior of these materials remain poorly understood. As a result, many of the early dreams and promises of polymer-based electronics have yet to be realized. Efforts to overcome the shortfalls of conjugated polymers have strived to
explore an ever-expanding variety of repeat structures, gain control over morphology and crystallization, and better understand their electronic behavior.

Conjugated polymers are, at their very basic level, polymeric materials which have delocalized electron density along their backbone repeat structure. Most often this arises from structures containing alternating C-C $\sigma$- and $\pi$-bonds. Other polymers with very useful and interesting electronic behavior, redox polymers such as poly(vinylcarbazole) or ferrocene-based polymers, do not have aromatic or conjugated backbone structures and are not considered here. The classical example is poly(acetylene), though variations on aromatic ring structures, such as poly(phenylene)s, are perhaps the most currently studied and useful materials for organic polymer devices. (Figure 1.2) The electron density can be thought of as delocalized over a certain distance of the polymer repeat unit; these materials are semiconductors.

![Idealized structures of cis-poly(acetylene) and poly(p-phenylene).](image)

Like their well known inorganic counterpart, silicon, doping conjugated polymers can dramatically increase conductivity. It was discovered very early on that doping, the introduction of charge carriers, could have a dramatic influence on the electrical properties of the polymer, in many cases transforming essentially insulating polymers into materials approaching metal-like conductivities. (1, 6) (Figures 1.3 and 1.4)
Figure 1.3: Relative conductivities of conjugated polymers and other common materials for reference. Reprinted with permission from Ref. (8). Copyright 2004 Society of Chemical Industry.

Figure 1.4: A representation of a segment of poly(\(p\)-phenylene) in its quinoid form after a doping event. Reprinted with permission from Ref. (8). Copyright 2004 Society of Chemical Industry.
The properties of these polymer systems depend on their repeat structure, \textit{i.e.} the atomistic arrangement of the monomer units within the chain, and the morphology of the chains, \textit{i.e.} how they are arranged and packed together. Suitable materials for each potential application (light emitting diodes, solar cells, etc) can only be obtained then by controlling both the chemical repeat structure and the morphology of the polymers. Research efforts focus on designing molecular structures to optimize properties such as band-gap, mobility, and processability, as well as controlling the morphology of the chains for each specific application of conducting or conjugated polymers.

Efforts have, of course, been attempted to apply conjugated polymers for nearly every device structure or function in analogy to their inorganic counterparts. The differences in their behavior and operation, driven from their organic nature and structures, have led to efforts to understand and control their properties in order to enable these analogous devices. The main advantages of polymeric conjugated materials arises from their polymeric nature; they can be solution processed, driving much lower costs in production and manufacture, enabling new applications such as flexible or wearable structures, and they are nearly infinitely tunable through synthetic chemistry for specific applications and optimization. This polymeric and organic nature also gives rise to their biggest drawbacks for practical use, \textit{i.e.} stability, lifetime, and synthetic challenges in producing polymer structures with appropriate properties, along with a lack of knowledge in the understanding of their behavior as compare to the well understood and established inorganic semiconductors. Conjugated polymers are at a critical crossroads: their practical use in real-world devices has just begun to be realized in applications such as polymer light-emitting diodes (PLEDs), photovoltaic (PV) cells, thin film transistors
(TFTs), and sensors, but they must compete with the robust and established traditional inorganic semiconductors whose infrastructure is well established. The success or failures of a sustained push towards better understanding and harnessing these conjugated polymeric systems will be the ultimate deciding factor as to whether they will ultimately have the wherewithal to supplant current materials in our everyday lives.

1.1.1 Polymer Light-Emitting Diodes

Polymer light-emitting diodes, or PLEDs, are one application where conjugated polymers are pushing towards practical applications in real world devices. These applications include large-panel, solid-state lighting systems, cell-phone and television displays, and flexible, perhaps even disposable, printable paper-like displays. The basic structure of a PLED is shown in Figure 1.5. As electrons are injected from the cathode and holes from the anode, polaron (p⁻ and p⁺, respectively) are generated in the active polymer layer and move towards the opposite electrode. Their recombination forms an exciton in the active material, which can decay through the emission of photons, yielding light emission.

![Figure 1.5: Structure of a typical PLED device showing multiple layers including electron injection, active emission, and hole injection layers between the electrodes. Reprinted with permission from Ref. (8). Copyright 2004 Society of Chemical Industry.](image-url)
The behavior and performance of these systems depends strongly on several factors including the interfaces of the materials in the device, and the nature of the polymer itself (morphology, optoelectronic properties, etc).\(^7\) The interfaces control charge injection, or how efficiently holes or electrons can enter the active material, while the material’s inherent electrical properties control mobility for holes and electrons and quantum efficiency. Generally, interfaces are controlled by choosing materials that have favorable work functions to efficiently interact with the polymer’s energy levels; multilayer devices are commonly employed to enhance electron and hole injection.\(^8,\) \(^9\) (Figure 1.5) Control over the polymer’s properties is generally achieved through synthetic design (intrinsic color, stability, etc.) and processing conditions such as film thickness, annealing, or other treatments (efficiency, brightness, etc.). PLEDs have been commercially demonstrated for color video displays and flexible devices, among other applications, but significant research opportunities exist for advancements in understanding the polymer physics, lifetime and stability, and efficiency improvements.

1.1.2 Photovoltaic Devices

Polymer photovoltaic devices, or PVs, are in some senses the opposite of PLEDs. Incident photons on the device create charges, which are harvest for electrical work. The photovoltaic effect has been known for polymer systems for some time, but efficiently harnessing this behavior to compete with other systems such as inorganic semiconductor solar cells has been the main challenge.\(^10\) The main challenge in the operation of an organic polymer-based PV, as opposed to an inorganic semiconductor PV, is that conjugated polymers generally have lower dielectric constants and higher exciton binding...
energy than inorganic semiconductors. Excitons formed from the absorption of photons in inorganic semiconductors can be dissociated into electrons and holes using the available thermal energy in the semiconductor.\(^{8}\) The relatively high mobility of inorganic systems for both holes and electrons means that the separated charges are quickly carried away before recombination. Polymers, on the other hand require more energy to dissociate the charges, and most conjugated polymers generally are poor electron conductors. Most polymer PV systems require two semiconductors, a p-type and an n-type.\(^{10}\) p-Type polymers are the most common, while the n-type material can be specially synthesized polymers or, more often, inorganic materials or fullerene derivatives.\(^{11, 12}\) (Figure 1.6) The basic principle, then, is to absorb photons using the polymer, transfer the electron to the electron transporting material quickly, and separate the charges to the cathode and anode to harvest electricity.

![Diagram of a bulk heterojunction solar cell structure using a conjugated polymer as the donor and C60 and the acceptor.](image)

**Figure 1.6: Example of a bulk heterojunction solar cell structure using a conjugated polymer as the donor and C60 and the acceptor.** Reprinted with permission from Ref. \((8)\). Copyright 2004 Society of Chemical Industry.

Some of the challenges associate with producing efficient polymer PVs (some of the best examples report up to 9% efficiency for highly optimized and complex to
synthesize systems, compared to > 25% for inorganic systems) include designing and synthesizing efficient p-type and n-type materials, creating productive, intimate interfaces to maximize charge separation, and optimizing fabrication techniques for cost-effective production. Of importance to this work, especially, are the efforts to create efficient junctions between the p-type polymers and the n-type polymers or other materials, and the morphology of the polymer. As discussed later, polymer brushes or surface tethered chains are one possible approach to fabricating, and studying, unique architectures which allow control over the patterning and orientation of the polymer brushes at an interface.

1.1.3 Polymer Thin Film Transistors

Polymer Thin Film Transistors (TFTs) are another application of conjugated polymers that has been demonstrated commercially. (Figure 1.7) The draw to these systems is that they can be processed like any other polymer system: printed, painted, laminated, etc. Roll-to-roll printing of plastic circuits is already being used for applications such as RFID tags, plastic logic, and other applications.(13) Most polymer transistors are field effect transistors (FETs), in which an electric field induces changes in charge mobility or current flowing through the material.

![Figure 1.7: Basic structure of a top-gate, bottom contact polymer thin film transistor.](image)
The field applied by the gate voltage controls whether or not, and how much, current can flow between the source and drain. The challenges with polymeric materials are often due to 1) the poor electron transporting ability and 2) the morphology of the chains because the electrical properties are strongly dependent on the orientation and alignment of the chains or lack thereof.

Figure 1.8: Integrated polymer transistor driven PLED structure (A) and in operation (B). Reprinted with permission from Ref. (14). Copyright 1998 American Association for the Advancement of Science.

Polymeric transistors have been successfully produced in operational devices and large area, flexible applications. (Figure 1.8) The current opportunities for research are to improve polymer stability and lifetime, processing and morphology control, and improving mobility and operational efficiencies. Hybrid organic/inorganic systems are one promising avenue of research towards more useful polymer-based transistor devices. (15)
1.2 Boron- and Carborane Containing Polymer Systems

1.2.1 Introduction to Boron

Boron, a group 13 element with atomic number 5, is one of the simplest elements with a formal ground state electron shell configuration \([\text{He}]2s^22p^1\). It’s mainly found as one of several borate ores such as ulexite (NaCaB$_5$O$_9$.8H$_2$O), borax (Na$_2$B$_4$O$_5$(OH)$_4$.8H$_2$O), colemanite (Ca$_2$B$_6$O$_{11}$.5H$_2$O) and kernite (Na$_2$B$_4$O$_6$(OH)$_4$.2H$_2$O). These are the ancient evaporative remains from the aqueous capture of volcanic emissions of boric acid. (16) Boron goes mostly unnoticed in everyday life; borax laundry aids, such as the famous 20 Mule Team®, are possibly the only product that may be familiar to people outside of scientific and industrial professions. However, boron touches almost every aspect of our lives in some way. Advanced steel alloys in our cars, Pyrex borosilicate glassware in the kitchen and laboratory, insecticides, eye drops, and moderators and shielding for nuclear reactors are just some of the practical uses which employ boron. Boron generally exists in a trivalent state, formally +3, and possesses rich possibilities for bonding nearly as infinite as its better known neighbor carbon. Boron is also used as a dopant in inorganic semiconductors such as crystalline silicon. Trivalent boron impurities present during the formation of the Hope Diamond give the stone its famous blue color. The boron atoms (<1ppb) in the carbon lattice leave positive “holes”, making the rare diamond a p-type semiconductor. The blue color is largely a result of the absorbance of light corresponding to the electronic transitions from the valence band to the conduction band within the stone. (17, 18)
1.2.2 Boron Clusters and Carboranes

As its neighbor carbon can, Boron can self-catenate and can form complex molecular architectures with itself. (Figure 1.9) And, similar to carbon and the alkanes, compounds composed of boron and hydrogen are termed *boranes*. The similarities of carbon and boron bonding and the molecular structures of alkanes and boranes however, ends there.

![Diborane(6) and Tetraborane(10)](image1)

![Pentaborane(9) and Pentaborane(11)](image2)

![Hexaborane(10) and Decaborane(14)](image3)

Figure 1.9: The six borane compounds proposed by Stock. Reprinted with permission from Ref. (19). Copyright 2001 American Chemical Society.

Consider diborane, with formula B₂H₆. Though diborane has an analogous empirical formula to ethane, C₂H₆, it has two fewer bonding electrons. This illustrates the nature of the difference in alkane and borane bonding. While standard bonding would be thought
of as 2-center, 2-electron bonding, with an electron pair forming a bond between two atoms, boranes also display 3-center, 2-electron (3c, 2e') bonds. In the case of diborane, this yields a structure in which the boron atoms are linked by two bridging hydrogens, forming two B-H-B 3c, 2e' bonds, with the remaining hydrogens being bonded in 2c, 2e' bonds to the boron atoms.\textsuperscript{(19, 20)} (Figure 1.10)

![Diagram of 2-center and 3-center, 2-electron bonds](image)

Figure 1.10: 2-Center and 3-center, 2-electron bonds. Reprinted with permission from Ref. (19). Copyright 2001 American Chemical Society.

This bonding scheme, which is a field of study unto itself, gives boron a rich chemistry and the ability to form cluster compounds. Based on the bonding scheme and number of atoms, the clusters can take on closed, 3-D geometric shapes, and can be reasonably well predicted using polyhedral skeletal electron pair theory (Wade-Mingo’s rule). The shapes for boranes, and carboranes, can often be predicted using the “4n” rules, which accounts for roughly 4 electrons per vertice. \textsuperscript{(21)} (Table 1.1)

Table 1.1: Number of Polyhedral Skeletal Atoms, Electron Pairs, and Edges for Closo-, Nido-, and Arachno- Boron Clusters. Adapted from Ref. (21)

<table>
<thead>
<tr>
<th>Polyhedron</th>
<th>Skeletal Electron Pairs</th>
<th>Closo</th>
<th>Nido</th>
<th>Arachno</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trigonal bipyramid</td>
<td>6</td>
<td>5</td>
<td>9</td>
<td>5,6,8,3</td>
</tr>
<tr>
<td>Octahedron</td>
<td>7</td>
<td>6</td>
<td>12</td>
<td>8,4,5</td>
</tr>
<tr>
<td>Pentagonal bipyramid</td>
<td>8</td>
<td>7</td>
<td>15</td>
<td>10,11,5</td>
</tr>
<tr>
<td>D\textsubscript{2d} (trigonal) dodecahedron</td>
<td>9</td>
<td>8</td>
<td>18</td>
<td>13-14,8-11</td>
</tr>
<tr>
<td>Tricapped trigonal prism</td>
<td>10</td>
<td>9</td>
<td>21</td>
<td>16,17,11</td>
</tr>
<tr>
<td>Bicapped square antiprism</td>
<td>11</td>
<td>10</td>
<td>24</td>
<td>19,20,14-16</td>
</tr>
<tr>
<td>Octadecahedron</td>
<td>12</td>
<td>11</td>
<td>27</td>
<td>19-21,16-19</td>
</tr>
<tr>
<td>Icosahedron</td>
<td>13</td>
<td>12</td>
<td>30</td>
<td>25,20,21</td>
</tr>
</tbody>
</table>
A continuum exists for these deltahedral clusters from the closed structures \((\text{closo}-)\) with skeletal electron pairs as \(n + 1\) pairs, open cages \((\text{nido}-)\) with electron pairs \(n + 2\) pairs, and open clusters \((\text{arachno}-)\) with electron pairs \(n + 3\) pairs, where \(n\) is the number of skeletal atoms.\(^{(21)}\) (Figure 1.11)

![Arachno, Nido, Closo clusters](image)

**Figure 1.11:** Deltahydral shapes of closo-, nido-, and arachno-clusters.

Polyhedral carboranes are analogues of boron clusters in which one or more boron atoms have been replaced with carbon. Of specific interest to this work are derivatives of \(\text{closo}\)-dicarbodecaboranes, \(\text{C}_2\text{B}_{10}\text{H}_{12}\), which will be referred to hereafter simply as carboranes. They are the neutral isoelectronic analogues of the \(\text{B}_{12}\text{H}_{12}^2^-\) anions.\(^{(19, 21)}\) Their development began during research in the 1960’s when boranes were being heavily researched during Cold War for jet fuels and rocket propellants.

\[
\text{B}_{10}\text{H}_{12}\text{L}_2 + \text{HC≡CH} \rightarrow \text{C}_2\text{C} + \text{L}_2 + \text{H}_2
\]

**Scheme 1.1:** Formation of 1,2-dicarbo-closo-decaborane or \(\text{o-carborane}\) through the closing of an open cage decaborane lewis-base adduct with acetylene.

The closo-dicarbodecaborane cage can exist in three isomers, \(\text{ortho-}\), \(\text{meta-}\), and \(\text{para-}\), depending on the position of the carbon atoms. (Figure 1.12) Synthesis of \(\text{o-}\)
carborane is accomplished by reacting bis(ligand) derivatives of decaborane with acetylene to yield the closed cage (the carbons of the acetylene are the carbons of the cage), free ligand, and hydrogen. (Scheme 1.1) The other isomers are made through high temperature isomerization of \( o \)-carborane (~500 °C for \( m \)-carborane, ~700 °C for \( o \)-carborane). Not surprisingly, the cages are very thermally and oxidatively stable.(20)

![Diagram of carborane isomers](image)

**Figure 1.12:** The isomers of \( C_2B_{10} \) carboranes. The hydrogen on each vertex has been omitted for clarity.

The stability of these cages is a manifestation of the unique bonding of boranes, and carboranes. The smaller borane species are generally very energetic and unstable (hence the research during the Cold War), but these systems, because of their 3c, 2e\(^-\) bonding, have aspects of σ-aromaticity, lending stabilization to the system much as the aromaticity does for benzene. They are 3-dimensionally aromatic, or super-aromatic.(19, 21) For instance, carboranes can undergo electrophilic substitutions as other, traditionally aromatic, systems can. The electron withdrawing nature of the boron cluster also makes the hydrogens of the carbon vertices relatively acidic (pK\(_a\) values are approximately 22, 25.6, and 26.8 for \( o \), \( m \), and \( p \)-carborane, respectively).(20) Functionalization schemes for the carbon vertices, then, generally center around deprotonation or metalation approaches.(20) \( o \)-Carborane can be functionalized at the carbon vertices by way of a functionalized acetylene during cage formation, but few
functional groups survive isomerization to the other isomers and these must be functionalized in their final isomeric form.

1.2.3 Boron and Carboranes in Polymer Systems

Boron has been widely explored for use in polymeric systems for applications including but not limited to preceramics, polymeric catalysts, high performance materials, medicine, luminescent materials, and organic electronics. (22, 23) Boron nitride and other boron containing ceramics for high strength and high thermal stability materials and coatings have been explored with respect to boron-based polymer precursors which can be processed easily and thermally converted into ceramics. Boronic acid derivatives have been researched as catalyst species and coupling partners, as well as delivery vehicles for BNCT. Boron-containing fluorescent species show great promise as dyes, emissive layers, and sensors for various applications. (24)

Several families of polymer structures based-on or containing carboranes have been explored for various potential applications. The only examples to be produced commercially, Olin’s Dексsil family and Union Carbide’s UCARSIL products, were poly(m-carboranesiloxane) based specialty polymers. (20) They were low volume polymers used in high performance applications such as jet engine parts, missile nose cone seals, gaskets, etc. were the extreme stability gained from the carborane cages overcame the difficulty and cost of production. While many carborane polymers have been described in the research literature over the past five decades or so, the synthesis of new carborane polymers has undergone a small renaissance lately as research interest has grown in several areas of boron chemistry. The pursuit of new delivery vehicles for BNCT has driven new synthetic efforts, (24) and the expanding field of organic
electronics has begun to take interest in these materials. This topic is of particular interest for the work contained here and will be discussed in some detail in chapters 2-4. The thermal and oxidative stability of carboranes makes them attractive candidates for incorporation into conjugated polymers. Further, the unique structure of carboranes opens the door to possible interactions between the 3-D aromatic cages and extended π-conjugated polymer systems. Conjugated polymers can play a unique role in exploring this area, as they can serve as a means to explore the nature of the interactions through observing the cages effect of the polymer behavior. The introduction of carborane into conjugated polymer systems has the potential to yield completely new hybrid materials for organic electronics, especially in the areas light emission, sensors and detectors.

1.2.4 Nuclear Chemistry of Boron

A short discussion of boron’s nuclear chemistry is warranted here, because of its unique properties and the several nuclear applications of boron compounds. Boron is found naturally as a mixture of two stable isotopes, $^{10}\text{B}$ and $^{11}\text{B}$, with $^{10}\text{B}$ comprising about 19.9% of the natural abundance (thus boron’s atomic mass is 10.811). Boron 10 is extremely useful for its large neutron capture cross-section.(16) Unlike other types of radiation such as alpha particles, gamma rays, or x-rays, a material’s interactions with neutrons do not depend straightforwardly on atomic mass, i.e. while lead may be a common shielding material for x-rays, it is ineffective against neutron radiation. The neutron cross-section of hydrogen is nearly twice that of lead, for example, even though lead’s atomic mass is ~207 times greater than that of hydrogen.(25) Neutrons, being uncharged particles, pass through most materials relatively freely, interacting only with atomic nuclei. They can interact with matter only through diffraction, scattering,
nuclear reactions. Materials commonly used for neutron moderation and shielding include high hydrogen content materials such as water, paraffin, or polyethylene, lithium-containing materials, and boron compounds.\(^{(25)}\)

Neutron cross sections (\(\sigma\)) are measured in units of Barns \(10^{-24}\ \text{cm}^2\). Examples of elements with high neutron cross sections include gadolinium, lithium 6, and boron 10. Upon capturing a neutron, boron10 undergoes spontaneous fission to produce an alpha particle, lithium 7, and gamma radiation. (Figure 1.13) These events have total energies on the order of 2.5 MeV. This has led not only to the use of boron for shielding and detectors, but also the research for the development of new medicine in the fight against cancer, boron neutron capture therapy (BNCT).\(^{(26, 27)}\)

![Figure 1.13: Illustration of the boron neutron capture event.](image)

Relatively non-toxic (compared to some cancer treatments) boron compounds can be delivered to the cancerous area, and treatment with neutron radiation leads to capture events, releasing high energy particles into the cancer cells. Because these particles have
a path-length on the order of microns in human tissue, the destruction is very localized and surrounding healthy tissue is spared. While this is an active area of research, especially for the development of new, perhaps polymeric, delivery systems, it sheds some light on possible applications of boron-containing conjugated polymers. If the capture events take place within a conjugated polymer, the high energy events will produce detectable signals that can be picked up via the polymer electronic device. This opens pathways to cheap, larger area, all-polymer detectors and dosimeters for use in nuclear safety, medicine, and national security.

1.3 Surface Tethered Conjugated Polymers

1.3.1 Polymer Brushes and Applications to Conjugated Polymer Devices

Polymer brushes occur when polymer chains are anchored at a surface or interface such that the distance between anchor points is smaller than the radius of the chain in solution, forcing an elongation of the polymer coil away from the surface. These systems have been well studied in the case of more traditional chain-growth polymers such as polystyrene, etc.; the brush structures and their effects on the polymer/surface properties are fairly well understood.
Figure 1.14: Illustration of a polymer chain in various configurations, showing an isolated chain, tethered chains below brush density, above brush density, and an ideal high density brush configuration (from left to right, respectively).

In the case of conjugated polymers, however, surface tethered chains and brush systems are not clearly understood. Significant questions remain about the synthesis and behavior of conjugated polymers tethered to surfaces or interfaces that can be broken down into two main categories. 1) Practical synthetic considerations: How can conjugated polymers be grown efficiently from surfaces? How does the surface polymer compare to solution grown polymer? 2) Consideration of brush-driven molecular architecture: Does a brush configuration change optical and/or electronic properties? How do brush polymers compare to traditional polymer layers in polymer devices?

Figure 1.15: Typical PLED structure (left) and an example of chain packing in idealized poly(p-phenylene) segments.

Electronic devices based on polymeric active materials are generally fabricated through traditional layer-forming techniques (e.g. spin-coating, drop-casting, etc.).
Polymer layers lend themselves to facile processing and are a major advantage for polymer-based devices. Device layers are deposited through spin-coating, layer-by-layer deposition, printing, etc. with much of the resulting device properties and performance depending on the behavior and stability of these deposited layers. (Figure 1.15)

![Diagram of polymer layers](image)

**Figure 1.15**: Example PLED devices showing a tethered active layer with control over the oxide interface and some degree of morphological control (left) and a traditional spin-coated device structure with unorganized chain structure.

The degree of pi-stacking or crystallinity, the interactions with other layers or heterojunction materials, and the stability of the chains during device operation are all factors which need to be controlled for efficient device operation. A conjugated brush structure should have a large effect on and possibly allow relative control of chain orientation, charge mobility, and stability, while at the same time providing a platform for studying the polymer structures through the devices themselves. (Figure 1.16) Practical synthetic schemes to attach conjugated polymers to relevant surfaces are the first steps towards conjugated brush devices.
1.3.2 Synthetic Routes to Conjugated Polymers

The vast majority of conjugated polymers require the efficient coupling of sp$^2$-hybridized carbons to form poly(arylene), poly(arylene-vinylene), and poly(arylene-ethynylene) type repeat structures.\(^{(32)}\) For poly(arylene)s, polymerizations are generally accomplished through the use of one of many well known organometallic coupling reactions such as Kumada, Suzuki, Sonogashira, and Stille couplings.\(^{(33)}\) In each of these coupling reactions, one coupling partner is an aryl halide (Cl, Br, I) or pseudo-halide (tosylate, etc.) which allows the catalyst to undergo oxidative addition and insert itself into the aryl-halide bond. The other coupling partner is generally an aryl metal species (aryl-boron species in the case of Suzuki couplings) that readily undergoes transmetallization with the transition metal catalyst to give a diaryl intermediate. Reductive elimination of the diaryl-species gives the desired C-C bond formation and prepares the catalyst for re-insertion into another aryl halide species.

Another important coupling reaction for poly(arylene) polymers is the Ni(0) Yamamoto-type polycondensation reaction of aryl halides.\(^{(34, 35)}\) This reaction is used for the synthesis of polyaryls and is not catalytic in nickel. It can be used to synthesize many backbone structures, and is often used for the synthesis of polyfluorene-based conjugated polymers. In this reaction scheme, the monomers are self-condensing with only an aryl-halide species being necessary. After oxidative addition, two Ni(II)-aryl species disproportionate to give a diaryl-nickel species and a nickel (II) halogen salt. Reductive elimination of the diaryl-species gives the bond formation.

There are many routes to arylene-vinylene and arylene-ethynylene backbones: two of the more widely used transition metal catalyzed reactions are Heck and Sonogashira couplings, respectively.\(^{(33)}\) The Sonogashira coupling links aryl halides
with terminal acetylenes catalyzed by Pd and Cu, with Cu being used to generate the metal-acetylene species for transmetallation. Amine bases commonly are employed help deprotonate the acetylene units and form the copper species. The Heck coupling generates aryl-vinylene bonds and is generally a Pd-catalyzed reaction between an aryl-halide species and a vinyl group. It differs from the other couplings in that the vinyl functionality forms a π-complex with the Pd followed by a σ-bond intermediate structure, forming the desired new C-C bond via a beta-hydride elimination. Reductive elimination of H-X from the Pd is nessecary to recover the Pd(0) species.

Regardless of backbone structure, the characteristic shared by these C-C bond forming coupling reactions is the need for an aryl-halide species as a coupling partner. One approach to conjugated polymer brushes, then, is to create surfaces with aryl halide or monomer-like functionality so that polymers can be either grown from or tethered to the surfaces. A small number of examples of these systems have been reported for poly(thiophenes) and poly(phenylenes) grown from surface bound initiator formed in-situ from a transition metal inserted into a tethered aryl halide.(36-38)

There has been little work reported on using other coupling chemistries to attach conjugated polymers to surfaces. The use of more traditional solution polymerization reaction conditions which are widely used and easily performed remains relatively unexplored for tethering conjugated polymers to surfaces. Some previous results from the Carter research group have shown that conjugated polymers can be tethered to reactive polymer surfaces and that poly(fluorene) could be grafted onto the substrates using Ni(0) Yamamoto-type reactions.(39) For more direct investigation of conjugated brushes, especially in the context of devices, suitable initiating layers must be formed on
substrates which are amenable to characterization and relevant to device preparation. These surfaces could be conducting surfaces for diodes, such as indium tin oxide or doped silicon. The surfaces could also be insulators such as silica or non-conducting polymer layers for transistor-based devices or even flexible substrates for conjugated polymer-based batteries and solar cells.

For oxide surfaces such as ITO or silica, surface functionalization is a mature research area and many precedents exist for modifying the surfaces of these materials. One well known method of attachment to surfaces, especially silica, is through the use of silanes or siloxanes. Monolayers of silanes can be created on many oxide surfaces and could serve as the initiating or tethering layer for conjugated brushes.

Other surfaces can also be functionalized for polymer growth and attachment. Cellulose and similar bio-materials are of great interest for use in new technologies as films, fibers, and substrates that can be sourced from biological materials and are environmentally friendly. Modifications of materials such as cellulose or other hydroxyl-containing polymers or fibers could also be accomplished via silane chemistry, but the stability of the alkoxy-silane linkage would be a significant disadvantage. Another classic route to functionalize alcohol groups is to use an acid halide to form an ester linkage. Acid halides with appropriate functionality for attaching conjugated polymers are widely available from commercial sources. The functionalization of cellulose with conjugated polymers is of interest for several applications including batteries and flexible electronics.
1.4 Spontaneous Surface Patterning Via Wrinkling

1.4.1 Non-Traditional and Spontaneous Patterning Techniques

Photolithographic patterning techniques are the underlying technologies that have enabled the growth and advancement of the microelectronics revolution. Every feature of every device on every chip has been meticulously patterned using a repetitive series of steps involving the photo-patterning of a resist material to define structures, followed by the necessary sequence of etching, metallization, lift-off and other steps to produce a single layer of the device. This process has been all but perfected and its limits continually pushed in terms of feature size, resolution, and processing parameters. The cost of such photolithographic processes has generally moved in an exponentially larger direction as the critical feature size of microchips has been reduced. This trend, along with the need for non-traditional surface patterns that are difficult to access via traditional lithography has spurred research into other routes for patterning surfaces and films. New lithography techniques, such as nano-imprint lithography, have shown promise for lower cost access to small features, but remain in their infancy compared to photolithography. Patterning via non-traditional methods, especially spontaneous phenomenon, which can be performed over large areas very simply, and at low cost, have been a field of growing interest and show great promise for access to new surface structures which are difficult or entirely impossible to develop using current patterning technology.(45)

Various patterning techniques have been explored using several different spontaneous thin film or surface events which can drive surface patterns or topology. One of the best known and widely studied examples is the phase separation of block copolymers.(46) The synthesis and control over block copolymer repeat structure has allowed researchers to take advantage of the polymers’ ability to phase separate and self-
assemble into nano-sized domains of segregated polymer blocks. These can be well ordered on a surface and have very small dimensions. They show promise for applications in which dense arrays might be needed, such as components of data storage systems.

Other processes have been explored as well, including breath figures, colloidal crystals, Langmuir-Blodget films, layer-by-layer electrostatic deposition, and bio-based self assembly, among other techniques. The draw to these techniques is more than just possible access to small features. These techniques can offer other advantages such as facile processing over large or flexible areas and access to unusual shapes and patterns that would be hard to produce with a traditional top-down photolithographic approach. Wrinkling, along with buckling and creasing, is another family of spontaneous events that can occur in thin film systems and be harnessed to produce ordered structures and surface patterns, as well as for metrology and probing mechanical properties of thin films.

1.4.2 Wrinkling and Applications as a Patterning Technique

The primary definition of the word “wrinkle” in the Merriam-Webster dictionary is listed as “a small ridge or furrow especially when formed on a surface by the shrinking or contraction of a smooth substance”. This is a familiar phenomenon which is observed daily in the natural world in everything from the surface of raisins to our own skin. For much of the history of patterning and fabrication of features on a small scale, wrinkling and related events have been an unfortunate circumstance to be avoided. Traditional patterning, which often requires various layers and depositions can be severely hampered if wrinkle structures develop during patterning. However, a secondary definition can also mean “a change in a customary procedure or method”, which is especially
appropriate to consider in the context of this work, in which wrinkling processes are being harness to produce surface patterns.

Many systems which undergo wrinkling, for the purposes of this work, can be thought of as bi-layer systems in which one material layer or “skin” is strongly adhered onto a bottom layer, and they have different mechanical properties.\textsuperscript{(52, 53)} If the system is placed under some critical compressive force, the layers can buckle or wrinkle. (Figure 1.17) This compressive strain could be driven by mechanical compression, thermal compression, film swelling, or other means.

![Figure 1.17: Generic schematic of a system showing wrinkling behavior. Reprinted from Ref. (49). Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.](image)

The period and amplitude of the wrinkles, assuming the bottom layer is infinitely thick relative to the top skin, depends on the elastic modulus of the skin and bottom layer ($E_s$ and $E_b$, respectively), the Poisson ratios ($\nu_s$ and $\nu_b$), and the thickness and width of the skin ($h$ and $w$, respectively).\textsuperscript{(53)} The force during compression can be described using the equation shown below, where $\lambda$ is a sinusoidal disturbance in the skin layer:

\begin{equation}
F = E_s \left[ \frac{\pi}{\lambda} \left\{ \frac{wh^3}{3(1-\nu_s^2)} + \frac{\lambda}{\pi} \frac{E_s w}{4(1-\nu_s^2) E} \right\} \right]
\end{equation}

Equation 1.1: Compressive Force in the Skin Layer
Equation 1.2: Critical Wavelength

\[ \lambda_c = 2\pi h \left[ \frac{(1-\nu_i^2)E_s}{3(1-\nu_i^2)E_f} \right]^{1/3} \]

When the force exceeds some critical values the system can wrinkle. The critical wavelength depends again on thickness, modulus, and Poisson ratio of the layers.\(^{(53)}\) (Equation 1.2) Already, it becomes clear that the wavelength and amplitude of thin films in bilayers can be controlled simply by adjusting their relative modulus and thicknesses, and that very small features should be possible.

This spontaneous wrinkling has been exploited to produce patterns in a variety of systems including metals on polymers, oxides on polymers, and polymer bilayers with size scales ranging from nanometers to centimeters.\(^{(54-57)}\) Such patterned surfaces have applications ranging from optics, to adhesion, to controlling biological interactions with the surfaces. (Figure 1.18)

Figure 1.18: Examples of wrinkling used for the fabrications of metal lines (a, top) and complex surface patterns (b, bottom). Reprinted with permission from Refs: \((50)\) and \((58)\), respectively. Copyright 2010 and 2008, American Chemical Society.
In addition to control over the wavelength and amplitude of the winkle patterns, wrinkling systems have also shown the ability to self-organize into hierarchical structures within defined boundaries or at edges. (Figure 1.19) This yields control over surface patterns over multiple length scales and the ability to simply fabricate extremely complex designs over large areas. Elegant examples of this phenomenon have been demonstrated in which one patterning technique, such as focused ion beam, masked plasma etching, photocuring reactions, etc., have been used to create one relatively large pattern design, while the inducement of wrinkling creates self-organized hierarchical patterns spontaneously within the desired regions. (59-63)

![Figure 1.19: Examples of systems which might show spontaneous formation and ordering of wrinkle patterns.](image)

While several possible applications of these techniques have been demonstrated for optics and other uses, there are significant opportunities for research within this area. Many of the wrinkling techniques are based on systems in which the bottom layer is very thick relative to the very thin films normally used for traditional wafer patterning and photolithography, which means that the wrinkling approaches to patterning would be difficult to integrate into traditional patterning processes. Additionally, the formation of patterns may not be sufficient catalyst to drive rapid progress in surface science. The ability to control both morphology and surface chemistry or functionality simultaneously
would be strong leverage for enabling new applications. Many wrinkling systems described in the literature are variations based either on the oxidation of PDMS or the deposition of thin metal or polymer films on compliant substrates.\textsuperscript{(53, 57, 61, 64, 65)} These would appear to offer very little in the way of control over surface chemistry. A system in which thin films compatible for integration into current patterning technology can be induce to undergo spontaneous wrinkling, with simultaneous control over the surface chemistry would then be a great advantage. This work focuses on exploring and controlling the wrinkling based patterning and functionalization of poly(2-hydroxyethylmethacrylate) (PHEMA) films using a reactive silane infusion and crosslinking strategy.

1.5 Outline of the Dissertation

This introduction discussed background material nessecary to understand the rationale and approach for the research described in this dissertation, which is focused broadly on the design and synthesis of conjugated polymer hybrid materials. That is, conjugated polymers in marriage with non-traditional materials to create new hybrid structures, specifically 1) the incorporation of non-traditional inorganic repeat segments and 2) surface modification with covalently attached conjugated polymers. The basic structure of conjugated polymers were discussed, followed by introductions to boron and carboranes, and their potential applications as non-traditional structural segments in conjugated polymer hybrid materials. Surface grafted polymers and polymer brushes were discussed to provide an introduction to surface modification with conjugated polymers, and how such structures might provide access to new hybrid materials with unique properties. Chapters 2-4 describe the design, synthesis, and characterization of
poly(fluorene)s with carborane cages as pendant groups and the poly(fluorene)s with \( p \)- and \( o \)-carborane in the backbone, respectively. Chapter 5 details the synthesis of poly(fluorene) layers for the surface modification of oxide surfaces, while chapter 6 explores hybrid conjugated polymer/cellulose materials through a covalent grafting approach.

Finally, an introduction to spontaneous surface patterning and wrinkling was discussed. Chapter 7 of this work focuses on the exploration and control over a new method of spontaneous surface patterning based on a silane infusion and crosslinking of PHEMA thin films.

1.6 References


CHAPTER 2

POLY(FLUORENE) WITH PENDANT CARBORANES

2.1 Introduction

Chemists have achieved great synthetic control over the chemical repeat structures of conjugated polymers, producing and controlling their properties for device applications. Monomer structures containing hetero-atoms such as oxygen, nitrogen, or sulfur are routinely designed and synthesized to engineer a polymer’s band gap, mobility, or optoelectronic properties for some particular desired application. However, structures containing boron are much less common, and conjugated polymer systems containing carboranes even less so.

Boron is an attractive and interesting atom for incorporation in to the structure of conjugated systems for several reasons. First, as discussed in the introduction, it is electron deficient which means that it will produce electron withdrawing portions of the repeat structure. Second, it has a rich bonding chemistry that allows it to take on many diverse molecular architectures, much as carbon can. Perhaps most importantly for electronic materials, boron atoms may be able to interact with conjugated system by extending electron delocalization into their empty p-orbital or participating in 3c, 2e bonding in clusters which are themselves aromatic. These attributes have given boron the ability to participate in donor-acceptor situations, emissive materials, sensors and other new directions in conjugated polymer behavior. (Figure 2.1)
Figure 2.1: Examples of conjugated polymers containing boron atoms in their repeat structure including poly(fluorene) (A), poly(thiophene) (B), and poly(phenylene) (C) based structures.(1-3)

The use of carboranes in polymeric systems is not a new one, but the investigation of their influences on conjugated polymers has only recently been undertaken by a few research groups. A handful of examples have been reported and their properties are not well understood. The unique bonding and electronic structure of the C$_2$B$_{10}$ carboranes make them ideal candidates for investigating boron cage systems in conjugated polymers and there has been much chemistry developed for carboranes in the context of small molecules. The easiest initial target route for covalently attaching carborane cages to the repeat structure of a conjugated polymer is the hang the cages as pendant groups along the chain. The first reported example of a conjugated polymer, by Vicente and co-workers, was an electropolymerized poly(pyrrole) system with pendant cages.(4) (Figure 2.2) The monomer was found to homopolymerize, and some minor effects due to the electron deficient cage and the steric congestion were noted during polymerization. The electropolymerized homopolymer films were found to be conductive when doped,
although the cages reduced the overall conductivity of the films by several orders of magnitude relative to poly(pyrrole) without carborane functionality.

The electropolymerization motif was then extended to thiophenes and to structures containing the cages within the main chain repeat structures.\(^5, 6\) The materials were shown to have excellent oxidative stability resulting from the incorporation of the very stable carborane cage systems.

\[\text{Figure 2.2: Structures of poly(pyrrole) with pendant o-carborane cages (left) and a thiophene-based polymer with o-carborane in the backbone.}\(^4, 6\)\]

The promising results contained in these papers, limited as they were by the nature of the insoluble polymer films formed via electropolymerization, inspired this work to further explore the idea of covalently attached carborane cages in the context of other conjugated polymer systems which may greatly benefit from carborane incorporation, particularly those that would be fully soluble and emissive, in order to obtain a more complete picture of the effects the cages might have on the nature of the polymer chain and its optoelectronic behavior. The additional stability derived from the carboranes, plus the possible aspects of electronic interactions between the 3-D cages, make conjugated polymer/carborane hybrid materials extremely promising for device applications and merits more detailed investigation.
Poly(fluorene)s, a widely investigated family of polymer structures for their emissive properties, was chosen as the basic backbone repeat structure.\(^{(7)}\) (Figure 2.3) The large amount of research on this structure provides an excellent window through which to view any influences the carborane cages may have on the polymer properties, and opens the door to potential applications. The stable cage structures may lend themselves to enhanced device performance, especially in light emitting diode applications where considerable attention has been paid to poly(fluorene)s as blue emitters.

![Figure 2.3: Repeat structure of poly(fluorene).](image)

While the bridged ring structure, with easily varied substituents on the 9-position, bridging carbon, lends stability and processability to the polymer chain, as a blue emitter poly(fluorene)s are plagued by several problems that lower energy emitters often avoid. Poly(fluorene)s often lose color stability over time, especially during exposure to elevated temperatures, oxidizing environments, or under device operation conditions. Often the films will develop green impurities resulting from several possible sources, the two most likely of which are ketone defects from oxidation of fluorene to fluorenone and aggregation based emissions from an excited state formed between well packed (π-stacked) chains, often referred to as excimers. (Figure 2.4) \(^{(7-12)}\)
These two types of defect sites are both lower in energy than the native blue emission and undergo very efficient downward energy transfer from the excited fluorene backbone to emit in the green. The excellent thermal stability, oxidative stability, and steric bulk of a carborane cage should impart enhanced properties to a poly(fluorene)-based conjugated system.

Additionally, as noted in the introduction, the large neutron capture cross-section of boron makes these polymers attractive candidates for neutron detection as the high energy capture events are transduced through the cages interactions with the polymer and displayed as a change in optoelectronic or electronic behavior. The first obstacle to hybrid conjugated polymer/carborane materials, however, is the design of a suitable monomer, its polymerization, and its initial characterization.
2.2 Experimental

2.2.1 Materials and Instrumentation

All organic reactants and reagents were purchased from Aldrich Chemical Co. and used as received unless specified otherwise. The pendant carborane monomer was obtained from Dr. Yoan Simon (formerly of the Coughlin research group) with whom the work in this chapter was a collaborative effort. Its detailed synthesis is described in the literature. (15)

Gel permeation chromatography (GPC) measurements for the polymers were performed in tetrahydrofuran (THF) at 1.0 mL/min using a Knauer K-501 pump with a K-2301 refractive index detector and a K-2600 UV detector and a column bank consisting of two Polymer Laboratories PLGel Mixed D columns at 40 °C. All other measurements were performed using a similar system with a column banks consisting of three Polymer Laboratories PLGel Mixed D columns at 40 °C. Molecular weights are reported relative to polystyrene standards. $^1$H, $^{11}$B, and $^{13}$C NMR were recorded at 300, 128, and 100 MHz, respectively, on a Bruker NMR spectrometer at room temperature in deuterated chloroform. The individual NMR spectral assignments do not list the carborane B–H resonances. Because of the quadrupolar nature of boron, the resonances for the 10 B–H are observed as broad multiplets ($\delta = 3.20−1.01$ ppm). The integration of these multiplets accounts for 10 H. Differential scanning calorimetry was performed on a TA Q2000 DSC with refrigerated cooling system using a heat–cool–heat program at 10 °C/min. $T_g$ was taken to be the onset $T_g$ during the second heating cycle. Fluorescence emission spectra of thin films on quartz slides were recorded on a Perkin-Elmer LS-50B using an excitation wavelength of 365 nm.
2.2.2 Synthetic Procedures

*Microwave-Assisted Homo- and Copolymerization of M2 into P2 and P2.1.* In a microwave tube equipped with a stir bar, the monomer M2 (1 equiv) was added along with bipyridine (2.2 equiv). The tube was then pumped into a glovebox, and Ni(COD)2 (2.3 equiv) was added. The tube was sealed and taken out of the glovebox. Additional COD (2.7 equiv) was added, and the reagents were dissolved in 4 mL of a toluene:DMF (4:1) mixture. The tube was quickly degassed and filled with nitrogen twice. The tube was then introduced in a microwave apparatus, and the solution was allowed to react for 20 min at 130 °C. The solution was then filtered using a syringe mounted with filter paper as well as a 0.45 μm PTFE filter and precipitated in 20 mL of a solution of acidified methanol (0.5 M HCl). A yellowish solid was recovered and identified as the desired polymer. The yield of homopolymer was 49% (56% for the co-polymer); the synthesis of poly(dihexylfluorene) was achieved in 71% by using a similar coupling protocol.

*Preparation of Thin Films.* Solutions of the homopolymer, co-polymer, and poly(dihexylfluorene) were prepared by dissolving 2.0 mg/mL of polymer in a 2:1 mixture of toluene/THF. Quartz slides were cleaned in a solution of concentrated H$_2$SO$_4$ and 30% hydrogen peroxide (5:1 by volume) at 100 °C for 30 min, rinsed with DI water and ethanol, and dried under a stream of N$_2$. The polymer solutions were spun onto the slides at 2000 rpm for 30 s and dried in a vacuum oven for 1 h at room temperature.

*Annealing Study.* Fluorescence emission of the thin films was taken after drying and the slides were placed on a temperature-controlled aluminum plate heated to 160 °C and covered with a Petri dish under air for 3 h. The slides were then cooled to room temperature, and fluorescence emission was retaken.
2.3 Results and Discussion

The polymerization of the pendant carborane monomer, M2, was accomplished using Ni(0) dehalogenative polymerization, or Yamamoto-type polymerization, of the arylbromides.\(^{(16)}\) This is one of two main routes to poly(fluorene)s, the other being a Suzuki-type polymerization between arylhalides and arylboronic acids/esters.\(^{(7)}\) The Ni(0) route was chosen for several reasons. These polymerizations have been shown to reliably produce polymer for many monomer structures and are homopolymerizations, avoiding the need for the synthesis of a co-monomer or accidental stoichiometric imbalances which might hinder the study of this new monomer. Additionally, the Suzuki routes are based on a transmetallation step with the arylboronic acid/ester, and any interactions with the typically used palladium catalysts and the B-H bonds of the carborane cages would be detrimental to the polymerization.

Scheme 2.1: Polymerization of P2 via Ni(0) dehalogenative coupling polymerization.
The polymerization of the monomer M2 into poly(fluorene) with pendant carborane cages, P2, was accomplished using the Yamamoto-type Ni(0) dehalogenative polymerization. (Scheme 2.1) The polymerization was found to be limited to an upper number average molecular weight, $M_n$, of about 7.3 kg/mol. (Figure 2.5) This is in contrast to the polymerization of poly(dihexylfluorene), PDHF, which often attain $M_n$ of 50 - 100 kg/mol or more. Efforts at prolonged reaction times and elevated reaction temperatures had little effect on the ultimate molecular weight. Microwave heating, which has been very successfully applied to many organometallic couplings including the polymerization of poly(fluorene) via the Yamamoto route, was used in an attempt to increase the molecular weight. (16, 17) It was found that, although the polymerization proceeded exponentially faster (20 min vs 24 + hrs), the ultimate molecular weight was relatively unaffected.

It is possible that the carborane cages, with their 3-dimensional volume and bulky silyl protecting groups, cause a large degree of steric hinderance and lead to relatively low degrees of polymerization. If this is the case and the cages are created situations in
which the polymer is self-limited its polymerization because of steric hinderance and conformational changes, the addition of a co-monomer should increase the molecular weight. Indeed, the co-polymerization of M2 with 2,7-dibromo-9,9-dihexylfluorene (Scheme 2.2) led to an increased $M_n$ of 13 kg/mol when polymerized in a 1:1 monomer feed ratio. (Figure 2.5)

![Figure 2.5: GPC trace of P2 (right, blue) and P2.1 (left, green). (THF vs poly(styrene)).](image)

The polymers were investigated using UV/vis and fluorescence spectroscopy to observed any effects the cages imposed on the optoelectronic properties of the polymer. The results were compared with PDHF ($M_n \sim 50$ kg/mol) as a reference. Much work has been devoted to the photophysical characterization of poly(fluorene)s in the literature, and provides an excellent background for gauging the effects of pendant groups on the polymer behavior. PDHF will typically have a peak UV absorption near 390 nm and a fluorescence emission peak near 425nm when excited optically. In comparison, P2 shows a signifigantly blue-shifted absorption near 375 nm, while the co-polymer P2.1 shows an absorption very near that of PDHF. The fluorescence emission of the pendant polymers shows a similar shift, with the homopolymer being blue-shifted with respect to
the co-polymer, which emits near 420 nm, in a very similar fashion to PDHF. (Figure 2.6)

![Absorbance and Fluorescence Spectra](image)

**Figure 2.6: UV-vis absorbance and fluorescence spectra for P2 and P2.1.**

It has been shown that high molecular weight poly(dialkylfluorene) has an effective conjugation length, i.e. the observed number repeat units participating in any given segment of conjugation regardless of ultimate chain length, of about 12-15 units. This is a result of loss of conjugation not due to serious structural defects which de-aromatize the system, but rather because of out of plane twisting and chain conformations that remove fluorene segments from effectively participating in the delocalized π-system. If the effective conjugated length falls below this number, either by conformational changes or low degree of polymerization, a blue shift will be observed in the UV absorption and emission spectra. The blue-shifted absorption and emission of the homopolymer may be further evidence that the degree pendant carboranes are influencing the polymer by lowering the degree of polymerization and potentially causing a large degree of twisting due to the bulky pendant groups and steric effects.
The bulky carborane cages, which were initially used in polymeric systems for their extreme thermal properties, should stabilize the poly(fluorene) by increasing the glass transition temperature ($T_g$) and limiting chain mobility, and by helping to prevent efficient chain packing and aggregation-based emissions. The $T_g$ of PDHF synthesized in an analogous manner to the pendant polymers was found to be 102 °C, while the homopolymer P2 and co-polymer P2.1 were found to be 181 °C and 132 °C respectively.

The effects of increased $T_g$ and the bulky pendant groups can be observed through an annealing study. Films the pendant polymers P2, P2.1, and PDHF as a control were formed through spin coating and them annealed at elevated temperatures in air. Fluorescece emission spectra were taken before and after annealing to observe the effects of the pendant cages. While the films appear very similar before annealing, the cages have a clear effect on the suppression of the green emissions that plague poly(fluorene)s as blue emitters. The pendant polymers showed increased color stability compared to the PDHF control, in which the green emission near 535 nm became nearly as intense as the primary blue emission after heating only half the time the pendant polymers were exposed to. (Figure 2.7) This stability is very attractive for light emitting applications where color-fastness and lifetimes of blue emitters are the primary limiting factor to their wider adoption.
Figure 2.7: Fluorescence emission of PDHF and pendant polymers before and after annealing illustrates improved emission stability through reduction in the green emission near 535 nm.

2.4 Conclusions

The incorporation of carborane cages as pendant groups along the backbone of poly(fluorene) imparts enhanced thermal stability to the chains as evidenced by significant increases in the glass transition temperature. The homopolymerization of M2 was found to limit the attainable $M_n$ to $\sim 7.5$ kg/mol, whilst the addition of a comonomer improved the molecular weight. The combination of the increased $T_g$ and the influence of the bulky, oxidation resistant pendant groups serves to increase the color stability of the fluorescence emissions by helping to prevent oxidation and prevent efficient chain packing, which discourages the formation of aggregates from which excimer-based emissions can arise. The improved stability of these materials makes them attractive candidates for active materials for light emitting diodes.

Future work should focus on determining whether the stability observed for photoexcited emissions translates to electroluminescence under device conditions and improves device color purity and lifetime. Future work should also explore their uses as
materials for neutron detection. Several initial attempts were made at fabricating crude systems for neutron detection. While it was observed that the homopolymer and copolymer were absorption neutrons, as evidenced by observing their shielding effect against a scintillating screen, little in the way of a detectable change in the behavior of the poly(fluorene) was observed. This is likely due to the fact that the cages are isolated from the main chain and would necessarily rely on chance encounters with secondary capture products to produce any change in the polymer. The observation of an already low capture rate is lowered further and likely will not be detectable in this case. A detector scheme based on electrical changes in the material will likely be more sensitive, while placing the cages in direct conjugation with the polymer should produce optimal sensitivity.

2.5 References


3.1 Introduction

The incorporation of boron into conjugated polymer systems is a promising approach to improving, and tuning, materials for organic electronics and carborane cages present an alternate route to incorporate boron into polymeric systems. p-Carborane, a C$_2$B$_{10}$H$_{12}$ icosahedron with carbons at opposite vertices,(1) represents an electron deficient boron cage unit that can be incorporated into conjugated polymers without disrupting their linear rigid rod behavior. While there have been many reports on carboranes in polymeric systems, there have been relatively few examples of conjugated polymers with covalently attached carboranes in the backbone. (2-5) Excellent thermal and chemical stability along with their electron deficient σ-aromatic bonding scheme make carboranes an attractive structural unit for use in conjugated polymers. (6)

One of the early examples of a p-carborane/conjugated polymer, an analog of poly(phenylene) which was likely only obtained as low MW oligomers, was conceived as an off-shoot to the predominant polymeric applications of carboranes, high temperature performance materials.(5) The introduction of p-carborane into the already thermally robust poly(phenylene) by Colquhoun et al did in fact produce very stable material, but the lack of solubilizing side groups and the choice of coupling reaction through aryl-chlorides (a dehalogenative polymerization technique using arylchlorides and Zn/Ni) likely prevented any high MW products from being formed.
Figure 3.1: Example of a poly(p-phenylene) based cage system. Reprinted with permission from Ref. (5). Copyright 1998 American Chemical Society.

Perhaps more importantly, though, the authors of this study did not mention or investigate the electronic effects of the caborane cages with respect to any interactions with the delocalized electron system of the poly(phenylene) structure. Theoretical studies have predicted the 3-D aromaticity of caborane cages, and have debated the possibility of electronic communication across the cage between the carbon vertices. (7) There are several papers that suggest there is some electronic communication through the p-carborane cage when placed as a spacer between organometallic centers, (8) while other papers have found little evidence of electronic communication. (9)
Figure 3.2: Examples of carborane based small molecules in which the cage acts as the spacer between organometallic species. Little electronic communication was reported for A, while communication between the ferrocenyl species was postulated for B. (8, 9)

The benefits for incorporating carboranes into polymer systems has clearly been established for cases where the polymer can benefit from the thermal and oxidative stability of the cages, however the suggestion of electronic interactions with the cages raises an arguably more important question: can carboranes participate, or at least directly influence in a significant way, with conjugated polymer systems if bonded directly into the backbone structure?

Research on small molecules constitutes the bulk of the available data on the topic, but seminal work along the polymer front, again by Vicente and co-workers, has explored the possibilities of incorporating \( p \)-carborane into electronically active polymer systems. (10) Their work focuses on electropolymerized thiophene systems, which allows them to easily polymerize thin films of polymer on a conducting substrate, such as ITO. Their results showed that films containing \( p \)-carborane in the backbone of a thiophene polymer were electrically active and could be conductive, although the other isomers appeared more conductive (this topic will be discussed in more detail in chapter 4).
Still, there remain questions about the cages’ influence on conjugated polymers that cannot easily be deduced from the limited data collected for the electropolymerized films. How do the cages effect polymerization of a soluble, processable polymer? How will \( p \)-carborane effect the optoelectronic properties of fluorescent polymers or in an operating device? Further study is warranted to clarify the true nature of the influence of carborane cages on extended \( \pi \)-conjugated systems. Therefore, a new monomer was desired to allow for the incorporation of \( p \)-carborane into the backbone repeat structure of a fully soluble and easily characterized polymer. Poly(fluorene) is a logical choice because the results of this experimental work can be related to the previous work on pendant carborane-based fluorene polymers and to the greater volume of data on poly(fluorene)s in the literature.

3.2 Experimental

3.2.1 Materials and Instrumentation

All reactants, reagents, and solvents were purchased from Aldrich Chemical Co and used as received unless specified otherwise. All reactions were performed under N2 atmosphere unless otherwise noted. Anhydrous 1,2-Dimethoxyethane was stored over calcium hydride under N2 atmosphere and freshly distilled before each use. \( p \)-carborane was supplied by KatChem. Ni(COD)2 was purchased from Strem Chemicals and used as
received. Copper chloride, potassium iodate, iodine, N-bromosuccinimide, 1-bromohexane, sodium hydroxide, anhydrous pyridine, and bipyridine were purchased from Acros Organics and used as received except for copper chloride, which was purified using methods described in literature.\(^{11}\)

Thin layer chromatography (TLC) was performed on Analtech GF silica gel with gypsum binder on glass backing. In addition to using the fluorescent indicator under 254nm handheld lamp, TLC’s of carborane containing compounds were developed by dipping the plates quickly into solution of PdCl₂ in dilute HClaq, which upon heating produces Pd black where boron is present. Silica gel used for column chromatography was purchased from EMD (Silica gel 60).

Gel permeation chromatography (GPC) measurements for the polymers were performed in tetrahydrofuran (THF) at 1.0 mL/min using a Knauer K-501 Pump with a K-2301 refractive index detector and a K-2600 UV detector, and a column bank consisting of two Polymer Labs PLGel Mixed D columns at 40°C. Molecular weights are reported relative to polystyrene standards.

\(^{1}\)H NMR, and \(^{13}\)C NMR were recorded at 400 MHz, and 100 MHz respectively on a Bruker NMR spectrometer at room temperature in deuterated chloroform. The individual NMR spectral assignments do not list the individual shifts of the carborane B-H resonances. Due to the quadrupolar nature of boron, the resonances for the 10 B-H are observed as broad multiplets (δ = ~4.1-1.4 ppm). The integration of these multiplets accounts for 10 H.

Mass spectral data were obtained at the University of Massachusetts Spectrometry Facility which is supported, in part, by the National Science Foundation.
Melting points were measured with a Thomas Hoover Uni-Melt capillary melting point apparatus. Differential scanning calorimetry was performed on a Thermal Analysis (TA) Q-2000 in aluminum pans using a heat-cool-heat cycle at 10°C/min. Tg was taken as the onset glass transition of the second heating cycle using TA Universal Analysis software.

Fluorescence measurements were taken on a Perkin-Elmer LS-50B using either quartz slides (25x25x1mm, Chemglass) or quartz cuvets with a 1cm path-length. UV-vis spectra were recorded on a Hitachi U-3010 spectrometer in 1cm path-length quartz cuvets. Infrared spectroscopy of polymer films were performed on a Nicolet 6700 FT-IR spectrometer equipped with a Harrick grazing angle ATR accessory (GATR).

3.2.2 Synthetic Procedures

2-bromo-9H-fluorene (3.1). Fluorene (30 g, 180 mmol, 1 equiv.) was placed into a 500 mL two neck round bottom flask and flushed with nitrogen. Propylene carbonate (250 mL) was added and the solution was heated to 60°C. N-bromosuccinimide (32.1 g, 180 mmol, 1 equiv.) was added quickly in one portion during a slight nitrogen overpressure. The oil bath was turned off and the reaction mixture was stirred as it cooled slowly to RT over the course of ~2hrs. The cooled reaction was precipitated into ~2L of water yielding an off-white solid, which was stirred as a slurry overnight. The solid was filtered, dissolved in 500mL toluene, and extracted with water (3x 100mL). The organic phase was then dried over Na₂SO₄, filter, and concentrated by rotary evaporator to give a white solid. The product was recrystallized from a minimum amount of refluxing ethanol/water (6/1) to yield off-white crystals (30.8g, 71%). m.p: 104-107 °C.
2-bromo-7-iodo-9H-fluorene (3.2). 2-bromo-9H-fluorene 1 (25 g, 102 mmol, 1 equiv.), iodine (10.85 g, 43 mmol, 0.42 equiv.), and potassium iodate (5.45 g, 25 mmol, 0.24 equiv.) were placed into a 1 L round-bottom flask. Water (20 mL), glacial acetic acid (425 mL) and concentrated sulfuric acid (10 mL) were added and the flask was heated in a 90° C oil bath under nitrogen. After 2 hours of stirring, the reaction was cooled to RT, at which point a light yellow precipitate formed. After filtration, the precipitate was washed with acetic acid and water and recrystallized from dichloromethane/methanol to yield white, wispy crystals (29.5 g, 78%) m.p.: 178-180 °C.(12)

2-bromo-9,9-dihexyl-7-iodo-9H-fluorene (3.3). In a 500 mL two-neck round-bottom flask fitted with a mechanical stirrer, 2-bromo-7-iodo-9H-fluorene 2 (25 g, 67.4 mmol, 1 equiv.) was added to 250 mL of dimethylsulfoxide under nitrogen atmosphere. 50% aq. NaOH (26 mL) was introduced drop-wise giving a bright red solution, darkening quickly with time to a maroon. The solution was stirred vigorously as 1-bromohexane (23.8 mL, 168.5 mmol, 2.5 equiv.) was added and the solution turned purple. After 1 day of stirring at room temperature, the reaction was poured into 500 mL ethyl acetate, precipitating the salts. The solids were filtered off and the organic phase was washed (250mL portions) with 1x diluted NaOH, 1x brine, and 3x water with the red color fading to light yellow after the water washes. The organic phase was dried over MgSO₄, filtered, and concentrated by rotary evaporation to yield a viscous yellow oil. The oil was dissolved in a minimum amount of gently warmed isopropanol and allowed to cool slowly, yielding flaky amber crystals. (29.4g, 81%). ¹H NMR (CDCl₃): δ (ppm) = 7.67 (d, 1H, J = 7.5 Hz) , 7.66 (s, 1H), , 7.54 (d, 1H, J = 8.4 Hz) , 7.47 (d, 1H, J = 7.5 Hz) ,
7.45 (s, 1H), 7.43 (d, 1H, J = 8.4 Hz), 1.92 (m, 4H), 1.10 (m, 12H), 0.80 (t, 6H, J = 7.0 Hz), 0.59 (m, 4H) 13C NMR (CDCl₃): δ (ppm) = 152.7, 152.4, 139.7, 139.1, 136.0, 132.1, 130.1, 126.1, 121.6, 121.5, 121.2, 93.0, 55.6, 40.2, 31.5, 29.6, 23.6, 22.6, 14.0; HRMS (FAB+): m/z calcd 538.073, found 538.070; m.p.: 55-56 °C.

1,12-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)-closo-dicarbodecaborane (M3):

p-Carborane (0.30g, 2.08 mmol, 1 eq.) was added to a 25 mL three-neck round-bottom flask fitted with condenser and a Merlic-type solid addition adapter (“tip-tube”) containing copper chloride (0.45g, 4.58 mmol, 2.2 eq.). A stir bar was added and the flask and condenser were carefully purged with N₂ so as not to disturb the powdered reactants for 10 minutes and then sealed with a rubber septum. 1,2-dimethoxyethane (8.5 mL) was injected via syringe and the mixture was stirred. The reaction flask was cooled to 0° C for 30 minutes using an ice bath and n-butyllithium (2.6M in hexane, 1.64mL, 4.26 mmol, 2.05 eq.) was injected drop-wise via syringe. The reaction was stirred for 5 minutes and then pyridine (1.25mL) was injected drop-wise via syringe. The copper chloride was added in one portion by rotating the “tip-tube” towards the reaction flask and the reaction, slightly cloudy after the addition of the pyridine, immediately produced a brown ppt. The reaction was heated to reflux forming a dark purple, almost black solution. After 30 minutes, 2-bromo-9,9-dihexyl-7-iodo-9H-fluorene 3 (2.3g, 4.26 mmol, 2.05 equiv.) dissolved in 2 mL 1,2-dimethoxyethane was injected in one portion and the reaction was continued under reflux. After 96 hrs, the reaction was cooled to room temperature and ~100mL diethylether was added. The reaction was washed with water (3x 100mL), dilute HCl solution (1x 100mL), and again with water and the organic phase was dried over MgSO₄, filtered, and concentrated by rotary evaporator to a brown oil.
The oil was loaded onto a silica column and eluted with methylene chloride/hexanes (1:1), giving a clear viscous oil after rotary evaporation. The product was recrystallized twice from ethanol/acetone (9:1) to give fine colorless crystals. (205mg, 10%)  

*Note*: Alkyllithiums, which are extremely reactive and pyrophoric, should be used under inert atmosphere and with extreme caution!

1H NMR (CDCl₃): δ (ppm) = 7.53-7.44 (m, 6H), 7.27-7.21 (m, 6H), 3.8-1.75 + 1.90 (bm + m, 18H), 1.10 (m, 24H), 0.82 (t, 12H, J = 7.3 Hz), 0.58 (bm, 8H), 13C NMR (CDCl₃): δ (ppm) = 153.39, 150.25, 140.29, 139.00, 135.61, 130.08, 126.24, 121.82, 121.53, 121.30, 119.21, 119.16, 83.21, 55.47, 39.85, 31.31, 29.43, 23.54, 22.48, 14.02. MS (FAB+): m/z calcd 966.5163, found 966.5043; m.p. = 187-188°C.

*Polymerization of M3 Poly(fluorene-p-carborane) (P3)*. In a reaction tube equipped with a stir bar, the monomer (100 mg, 0.10 mmol, 1 eq) was introduced along with bipyridine (40mg, 0.25 mmol, 2.5 eq). The tube was then pumped into an argon filled glove box and Ni(COD)₂ (71 mg, 0.25 mmol, 2.5 eq) was added. The tube was sealed with a crimp-on aluminum cap with a PTFE coated septum seal and taken out of the glove box. Additional 1,5 COD (32 μL, 0.25 mmol), 2.5 eq) was added via syringe and the reagents were dissolved in 4 mL of an anhydrous toluene:DMF (4:1) mixture. The tube was quickly degassed and filled with nitrogen three times. The tube was placed in an oil bath heated to 80°C and stirred for 24 hrs. The still warm solution was then filtered using a syringe mounted with filter paper as well as a 0.45 μm PTFE syringe filter and precipitated into 100 mL of slightly acidified methanol (0.1M HCl). The p-carborane polymer P3 was recovered as a white solid (72 mg, 85%). P1: 1H NMR (CDCl₃): δ
(ppm) = 7.35 (m, 10H), 7.13 (m, 2H), 3.9 - 1.5 + 1.78 (bm + m, 18H), 0.97 (m, 24H), 0.85 (m, 12H), 0.30 (m, 8H).

Synthetic References Cited:


3.2 Results and Discussion

Scheme 3.1: Synthetic route to poly(fluorene) with p-carborane in the backbone (P3).

The monomer, 1,12-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)-closo-1,12-dicarbodecaborane (M3), was synthesized as shown in Scheme 3.1. Fluorene was brominated, iodinated, and alkylated in three steps to give 2-bromo-9,9-dihexyl-7-iodo-9H-fluorene 3 in 45% yield. The effort to create an aryl iodide bromide rather than a
dibromo- species was necessary to promote the attachment of the carborane cage at the iodo-position and preserve the less active bromides for subsequent polymerization. Aryliodides have been shown to be reactive in couplings with a copper-carborane species, in what amounts to essentially an Ullmann-type coupling.\(^{(13)}\) Aryl bromides, on the other hand, have been shown to be much less active in these couplings, and examples of selective coupling of carborane at the iodo-position of 1,4-bromoiodobenzene have been demonstrated.\(^{(7, 14)}\) With this concept in mind, a fluorene-based monomer was designed and synthesized to contain a \(p\)-carborane cage in the backbone, sandwiched between fluorene segments. \(p\)-Carborane was deprotonated using 2 equiv. of \(n\)-butyllithium to yield \(\text{Li}_2[\text{C}_2\text{B}_{10}\text{H}_{10}]\).\(^{(1, 13)}\) Lithium carbanions are very reactive, and this species was not isolated but was subsequently reacted with \(\text{CuCl}\) to give \(\text{Cu}_2[\text{C}_2\text{B}_{10}\text{H}_{10}]\), stabilized in situ with pyridine, and reacted with two equivalents of 3.3 in an Ullmann-type coupling to give the monomer M1 in 10% yield.\(^{[13]}\) The structure was confirmed by \(^1\)H NMR, where the characteristic broad carborane B-H signals were observed from \(\delta 1.4\)–4.1 ppm, and by \(^{13}\)C NMR where the carbons residing at the 1,12 cage positions give a single resonance at \(\delta 83.21\) ppm. High resolution mass spectrometry gave final structure confirmation. The yield in the final step may be a consequence of the poor solubility of the copper species and the hindered nature of the fluorene/carborane coupling partners.

Polymerization of M1 was accomplished using a Yamamoto-type Ni(0) dehalogenative polymerization as shown in scheme 3.1.\(^{(15)}\) The polymerization was carried out in a mixture of toluene/DMF (4:1) under an inert atmosphere for 24 h. \(^1\)H NMR of the polymer matched the expected structure and FT-IR showed B-H stretches at
~2600 cm⁻¹ in addition to the aromatic and aliphatic C-H signals. The polymer product was soluble in chloroform, THF, and toluene. The molecular weight was found to be 50k g/mol with a PDI of 2.3 by GPC (THF vs PS standards), typical of step growth Ni(0) polymerizations of aryl bromides. Differential scanning calorimetry showed a glass transition temperature (T_g) of 137 °C compared to 102 °C for poly(dihexylfluorene) of similar MW (by GPC) and synthesized under analogous conditions. In addition to a T_g, an exotherm was noted on the first heating cycle at 215°C, possibly as a result of the formation of a new crystalline state.

![GPC Trace of poly(fluorene-p-carborane)](image)

Mn ~ 50kg/mol, PDI ~ 2.3, (THF vs PS)

**Figure 3.4: Gel permeation chromatography trace for P3.** (16)

Previous reports on p-carboranes suggest that there may be some electronic communication between the carbon centers in p-carborane, though data suggests that it is not truly conjugated in the traditional sense. To help investigate the behavior of P3, small molecule analogs of the fluorene units were used. To represent the fluorene units on either side of the carborane cage in the monomer M3, we chose dibromodihexylfluorene. For the polymer, which has a repeat structure of a carborane
cage followed by two fluorene units, we synthesized a discrete dimer of dihexylfluorene to represent the two fluorene units between each carborane cage along the backbone.

**P3** was photoluminescent under UV light, giving a bright blue emission. Fluorescence spectroscopy in chloroform revealed a peak emission at 400 nm, a 15 nm bathochromic shift compared to the fluorene dimer. (Figure 3.5) A 20 nm bathochromic shift was observed in the UV absorption of the polymer **P3** compared to the fluorene dimer, while the monomer **M3** and a single fluorene unit display strikingly similar absorbances. (Figure 3.5) The UV and fluorescence peaks would be expected to red-shift with an increase in the effective conjugation length in polyfluorene systems. (17) The observed shifts in the UV absorption and fluorescence emission indicate that the p-carborane cages are extending the conjugation length of each fluorene dimer unit of the polymer backbone. Recent work on conjugated polymers containing m-carborane in the backbone suggests that, while the carborane cages extended the conjugation length of the aromatic units between the cages, there was little conjugation between the aromatic segments through the cages. (18) The shifts observed for **P3** could be due to the electron deficient nature of carboranes and some extension of the aromatic conjugation into the cages, but the similarity of **M3** to a single fluorene unit in their UV spectra suggests that the carborane cages limit effective conjugation between the fluorene segments.
Figure 3.5: UV-vis (top) and fluorescence emission (bottom) spectra of P3 and fluorene dimer or monomer.\textsuperscript{(16)}

Nevertheless, the excellent thermal properties of the carborane cages impart stability to the polyfluorene structure. In chapter 2 it was shown that pendant carborane cages improve the thermal stability of polyfluorene, increasing $T_g$ and spectral integrity during annealing. \textsuperscript{(19)} Annealing studies on films of P3 showed a minimal rise in green emission after heating to 180°C in air for 2 hrs. This is in marked contrast to
poly(dihexylfluorene) which shows a pronounced green emission after heating to 150°C for only an hour. (Figure 3.6) The carborane cages act to effectively suppress the green emission that commonly plagues blue emitting polyfluorene systems, due in part to aggregation based excimer formation. Color stable blue emitters are crucial for polymer LED’s as performance and lifetime could limit their wide adoption compared to traditional display materials.

![Annealing of Polyfluorene Films](image)

Figure 3.6: Fluorescence emission before (black) and after (red) annealing above $T_g$ for P3 samples and PDHF for comparison.(16)

### 3.4 Conclusions

In summary, we have synthesized a new carborane containing fluorene monomer and successfully polymerized it to provide a poly(fluorene) based polymer with $p$-carborane directly in the conjugated backbone. The $p$-carborane cage acts to increase $T_g$
and thermal properties while still being solution processable, creating a stable blue emitter that has potential applications for light emitting devices and sensors.

3.5 References


CHAPTER 4
POLY(FLUORENE) WITH \textit{o}-CARBORANE IN THE BACKBONE

4.1 Introduction

As discussed in some detail already in the previous chapters, carboranes have been widely investigated for their thermal stability, chemical resistance, unique geometry, and the high neutron capture cross-section of boron 10.\textsuperscript{(1, 2)} While they have been widely incorporated into small molecules, metal complexes, and polymer systems,\textsuperscript{(3,4-6)} relatively little work exists relating their unique properties to systems with extended conjugation. Incorporation of \textit{o}-carborane cages into the conjugated backbone of semi-conducting polymers may provide insight into the behavior of these boron cages, and the properties they impart may lead to new classes of hybrid organic-inorganic conjugated systems for polymer-based electronics. The icosahedral carborane cages of 10 boron atoms and two carbon atoms (C\textsubscript{2}B\textsubscript{10}H\textsubscript{12}) are not only quite stable (both thermally and chemically), but they also have somewhat unusual bonding structures, with 3-center 2-electron bonds.\textsuperscript{(1)} This creates extremely electron deficient cage systems which possess aspects of $\sigma$-aromaticity, making them attractive targets for incorporation into conjugated systems.

The C-C bond of \textit{o}-carborane is of particular interest, in that it presents itself as an unusual bond displaying both $\sigma$- and $\pi$-characteristics. Carboranes can be thought of in some respects as 3-dimensional analogs of benzene. They displace a similar 3-D volume to a rotating phenyl-ring, and the C-C bond can undergo some of the same reactions as
can the bonds in benzene, carborane forming carboryne vs. benzene to benzyne, for example.

![Chemical structures](image)

**Figure 4.1: Example reactions forming carboryne and benzyne structures illustrate similarities between the C-C bond of carborane and those in benzene.**

The bond has also been observed to be sensitive to the electronic environment of the substituents bonded to the carbon vertices. (7) The C-C bond of o-carborane has been shown to have a variable length, depending on its substituents. This fluctuation in bond lengths has been found to occur to a greater extent than would be expected simply by making predictions based on steric repulsion and space filling. A significant bond lengthening, observed for phenyl substituents among other things, has been attributed to back-donation of electron density to the antibonding orbital of the C-C o-carborane bond. The bond length for 1,2-diphenyl-o-carborane has been determined to be 1.73 Å, which would equate to a bond order of approximately 1/2, if making an analogy to standard C-C bonds.(7) This is particularly curious when considering the evidence that this C-C displays some aspects of both σ- and π-bonding characteristics, which traditionally have bond lengths significantly shorter than this. This is evidence that there may be some inherent electronic interactions between the C-C bond of the cage and its substituents, which would be very interesting to observe through its effects on a conjugated polymer. This line of investigation would not only yield insight into the nature of the electronic
communication of the cages with the $\pi$-system, but also give access to a new class of materials which can take advantage of not only the stability of the cages, but the unique geometry and electronic structure of $o$-carborane.

Small molecule investigations make up the vast majority of the previous work studying possible interactions of $o$-carborane and conjugated systems. Examples of luminescent small molecules and dyes in which the cages participate with the conjugated systems and even enhance emissions have been described.\cite{8} There have even been examples of dendrimers and polymer systems containing $o$-carborane in which there is no formal conjugation that have been observed to display luminescent properties.\cite{4, 9}

![Figure 4.2: Examples of $o$-carborane in conjugated (left) and non-conjugated luminescent systems.\cite{8, 9}](image)

A small number of previous reports have discussed the incorporation of $o$-carboranes into conjugated polymers including thiophenes\cite{10, 11} and polyfluorenes,\cite{12} while more recent work by Chujo and co-workers (much of which appears to have been carried out simultaneously to this work and was published during the experimental portions of the research) described the introduction of $o$- and $m$-carborane into the backbone of phenylene-ethynylene based polymers.\cite{13-15}
The electropolymerized thiophene structure was found to display the highest conductivity of the three carborane isomers, although there is some question as to whether the polymerization may be bridging the thiophene units adjacent the cage and bypassing many of the cages altogether. More compelling evidence for unusual activity, however, is found in the results of Kokado et al’s work on phenylene-ethynylene based o-carborane systems.(13, 15) Their polymers, though they are arguably relatively low molecular weight oligomers by GPC, display unusual photoluminescence both due to the bent geometry of the cages (aggregation induced emission, AIE) and the electronic structure of the cage via the C-C bond (quenching of the polymer emissions by the variable C-C bond).

The evidence for the interaction and modulation of emission modes by o-carborane in conjugated systems points towards possible applications. Besides the obvious applications as materials for dyes or active layers for light emitting diodes, the unique molecular structures can also be thought of in terms of their applications to sensors or responsive systems.
Figure 4.4: Examples of conjugated polymers containing boron for sensing fluoride (A) and amines (B). (16, 17)

Conjugated organic systems containing boron are interesting as emissive materials and active materials for sensors and devices. (3) Boron containing conjugated and fluorescent systems show excellent potential for enabling the tuning of the behavior of the materials. (18-22) Incorporation of boron atoms has also been shown to be effective in modulating the emissive behavior of conjugated polymers based on their response to chemical species. Chemosensitive behavior has been described previously for several boron containing conjugated polymers: poly(fluorene) has been combined with boron to show sensitivity to fluoride ions, (16) and a thiophene-based, boron-containing polymer has recently been shown to be sensitive to the vapors of certain amines. (17) (Figure 4.4)

\[ \text{o-Carboranes are another approach towards boron-containing conjugated polymers which can display responsive behavior, and literature shows a surge in current research activity on these materials. (15, 23-26) The C}_2\text{B}_{10} \text{ cages provide interesting} \]
building units for conjugated systems, due to their unique electronic structure and geometry. Besides the work in this dissertation, a few research groups are exploring the possibilities for carborane-based functional groups. Chujo’s group at Kyoto University, in Japan, is perhaps the most active at present. From their initial report on phenylene-ethynylene-base carborane polymers has come several following reports describing, among other things, responsive and tunable emission behavior. (Figure 4.5) This has been centered around the concept that the cage geometry promotes AIE, while the electronic environment of the polymer structure can influence emission behavior as well. These materials are of interest especially for chemo-responsive systems where interactions of small molecules, ions, or other polymers can induce changes in the optoelectronic behavior of the material for detection or quantification.

Figure 4.5: Examples of responsive o-carborane systems (top), and tunable emission from caborane-based emissive systems (bottom). Reprinted with permission from Refs. (27) and (14). Copyright 2010 and 2011 American Chemical Society
As noted in Chapter 1, boron 10’s high thermal neutron capture cross-section has generated interest in using boron-containing materials as neutron moderators and shielding, neutron capture cancer therapy (BNCT), dosimetry, and neutron detection. This last potential application is particularly attractive for conjugated polymer systems containing boron. Polymer-based neutron detectors are not a new idea and they have been fabricated successfully for several applications, mostly scintillators. (28, 29) Several smaller, more recent approaches have begun to explore the idea of using semiconducting polymer systems as neutron detectors, the research occurring mostly at the national labs and directed towards the detection of illicit nuclear materials.

The general concept is to replace the traditional semiconductors in a detection device, such as silicon, with a conjugated polymer, thereby gaining advantages in cost, production speed, and detector geometries, i.e. the semiconducting materials could theoretically use solution based processing or printing and could cover large, flexible areas in a cost effective manner. The difficulty with this approach is that the atomistic compositions of semiconducting polymers, in general, display relatively small neutron capture cross-sections which requires a high cross section component (such as isotopes of boron, lithium, etc) be added to (or placed near) the polymer. The basic principle, then, is for the high cross-section material to interact with the incident neutrons, converting the interaction into an event, such as producing ionizing radiation or charged particles, that can be transduced through the semiconducting polymer and recorded either as an electrical or optical signal change. This is essentially the detection of secondary species.
The few efforts to harness conjugated polymers for neutron detection have relied mostly on known or commercially available conjugated polymers. Early work studied poly(acetylene)s and poly(pyrrole)s and their ability to become doped by irradiation.\(^{(30, 31)}\) In a later example, a poly(phenylenevinylene) derivative, MEH-PPV, was used in a diode configuration. It relied on the cross-section of hydrogen for neutron interaction, and thus required fairly thick films for operation, causing very poor mobility of the signal through the material. Another example used a poly(thiophene)/PCBM blend (essentially the well studied “bulk-heterojunction” organic photovoltaic cell) as a signal transducer for the charged particles exiting a slab of boron carbide placed in close proximity to the device during exposure to neutrons.\(^{(32)}\) Blending approaches have also been studied.\(^{(33)}\) Only one described conjugated polymer containing boron directly bonded into the structure has been mentioned with respect to neutron detection, as a scintillator, a poly(pyrazabole) derivative. (Figure 4.7)
The advantage to a semiconducting polymer designed to contain chemically bonded boron is multi-faceted. First, simply by the nature of the basic design, the boron loadings could be very high, especially with carborane cages, relative to the simple blends or mixtures commonly described for loaded plastic scintillators. Second, the polymers could, in theory, take advantage of multiple pathways for detection. The conjugated polymer segments would interact with the high energy particles and gamma rays produce by boron neutron capture events in the same way the schemes above detected the secondary species. Additionally, however, the sites which undergo capture presumable leave a vacant position or hole, causing a direct change in the bonding and electronic structure of the polymer itself. In other words, it may be possible to directly detect a neutron capture event using this approach.

Based on the available data contained in previous reports, it seems clear that direct incorporation of o-carborane into the conjugated backbone of semi-conducting polymers may give rise to new structures and properties for applications in organic electronics and emissive materials. This body of accumulated knowledge in the literature, and the previous results in this work on poly(fluorene), again provide an excellent vantage point from which to observe new conjugated o-carborane structures based on the poly(fluorene) backbone. In this chapter, the synthesis of a new monomer and polyfluorene-based polymer with o-carborane in the conjugated backbone is
described, and the effects of the carborane cage on the polymers optoelectronic behavior is explored.

4.1 Experimental

4.1.1 Instruments and Materials

All reactants, reagents, and solvents were purchased from Aldrich Chemical Co and used as received unless specified otherwise. All reactions were performed under N2 atmosphere unless otherwise noted. Pd(PPh3)2Cl2 was purchased from Alfa Aesar and used as received. Ni(COD)2 was purchased from Strem Chemicals and used as received. Potassium iodate, iodine, N-bromosuccinimide, 1-bromohexane, trimethylsilylacetylene, triethylamine, potassium hydroxide, sodium hydroxide, anhydrous pyridine, and bipyridine were purchased from Acros Organics and used as received.

Thin layer chromatography (TLC) was performed on Analtech GF silica gel with gypsum binder on glass backing. In addition to using the fluorescent indicator under 254nm handheld lamp, TLC’s of carborane containing compounds were developed by dipping the plates quickly into solution of PdCl2 in dilute HClaq which upon heating produces Pd black where boron is present. Silica gel used for column chromatography was purchased from EMD (Silica gel 60).

Gel permeation chromatography (GPC) measurements for the polymers were performed in tetrahydrofuran (THF) at 1.0 mL/min using a Knauer K-501 Pump with a K-2301 refractive index detector and a K-2600 UV detector, and a column bank consisting of two Polymer Labs PLGel Mixed D columns at 40°C. All other measurements were performed using a similar system with a column banks consisiting of
three Polymer Labs PLGel Mixed D columns at 40°C. Molecular weights are reported relative to polystyrene standards.

$^1$H NMR, and $^{13}$C NMR were recorded at 400 MHz, and 100 MHz respectively on a Bruker NMR spectrometer at room temperature in deuterated chloroform. The individual NMR spectral assignments do not list the individual shifts of the carborane B-H resonances. Due to the quadrupolar nature of boron, the resonances for the 10 B-H are observed as broad multiplets ($\delta = 3.20-1.01$ ppm). The integration of these multiplets accounts for 10 H. Mass spectral data was obtained at the University of Massachusetts Spectrometry Facility which is supported, in part, by the National Science Foundation. Melting points were measured with a Thomas Hoover Uni-Melt capillary melting point apparatus. Differential scanning calorimetry was performed on a Thermal Analysis (TA) Q-2000 in aluminum pans using a heat-cool-heat cycle at 10°C/min. Tg was taken as the onset glass transition of the second heating cycle using TA Universal Analysis software. Fluorescence measurements were taken on a Perkin-Elmer LS-50B using either quartz slides (Chemglass) or quartz cuvets with a 1cm path-length. UV-vis spectra were recorded on a Hitachi U-3010 spectrometer in 1cm path-length quartz cuvets. Infrared spectroscopy of polymer films were performed on a Nicolet 6700 FT-IR spectrometer equipped with a Harrick grazing angle ATR accessory (GATR).

Microwave heating was performed using a Personal Chemistry Smith Creator bench-top microwave in 2-5mL microwave vials. Solid reactants and reagents were added to the tube and sealed in an argon filled glovebox with crimp-on aluminum septum caps. Liquid materials were injected via syringe through the septum cap.
For investigations of the polymer optical properties in response to organic vapors and amines, the polymer was reprecipitated from THF into methanol three times and dried under vacuum for 24hrs. For solid sample vapor exposure, a $2 \times 2$ cm square of a composite laboratory wipe (thermally bonded polypropylene and cellulose, ITW Texwipe Betawipes TX 2009) was dipped in a 0.5 mg/mL methylene chloride solution of the polymer and dried under a stream of nitrogen to yield a polymer impregnated sample that fluoresced green under UV light. The sample was then placed in a Petri dish on an angled microscope slide so that the sample was not in contact with the bottom of the dish. One mL of the organic solvent or amine was then placed in the bottom, and the dish was covered with a lid. After 5 min, the sample was irradiated with UV light from a hand-held lamp while an optical picture or fluorescence spectrum was taken through the Petri dish lid.

For fluorescence spectra, samples were irradiated with 365 nm UV light from an Entela UVGL-25 and the emission was recorded with an Ocean Optics USB4000 UV–vis spectrometer. Optical images were taken under using an Olympus E-420 digital camera.

Neutron exposure experiments were performed at the research reactor at the University of Massachusetts-Lowell Radiation Radiation Laboratory. The polymer samples were spin-coated onto quartz slides and placed into “rabbit” tubes, which were pneumatically shuttled near the core for specified amounts of time, which control total dose. The samples were then dissolved from the slides, diluted in chloroform and compared to control samples using fluorescence spectroscopy.
4.1.2 Synthetic Procedures

2-bromo-9H-fluorene. Fluorene (30 g, 180 mmol, 1 equiv.) was placed into a 500 mL two neck round bottom flask and flushed with nitrogen. Propylene carbonate (250 mL) was added and the solution was heated to 60°C. N-bromosuccinimide (32.1 g, 180 mmol, 1 equiv.) was added quickly in one portion during a slight nitrogen overpressure. The oil bath was turned off and the reaction mixture was stirred as it cooled slowly to RT over the course of ~2hrs. The cooled reaction was precipitated into ~2L of water yielding an off-white solid, which was stirred as a slurry overnight. The solid was filtered, dissolved in 500mL toluene, and extracted with water (3x. 100mL). The organic phase was then dried over Na₂SO₄, filter, and concentrated by rotary evaporator to give a white solid. The product was recrystallized from a minimum amount of refluxing ethanol/water (6/1) to yield off-white crystals (30.8g, 71). m.p: 104-107 °C.

2-bromo-7-iodo-9H-fluorene. 2-bromo-9H-fluorene 1 (25 g, 102 mmol, 1 equiv.), iodine ( 10.85 g, 43 mmol, 0.42 equiv.), and potassium iodate (5.45 g, 25 mmol, 0.24 equiv.) were placed into a 1 L round-bottom flask. Water (20 mL), glacial acetic acid (425 mL) and concentrated sulfuric acid (10 mL) were added and the flask was heated in a 90°C oil bath under nitrogen. After 2 hours of stirring, the reaction was cooled to RT, at which point a light yellow precipitate formed. After filtration, the precipitate was washed with acetic acid and water and recrystallized from dichloromethane/methanol to yield white, wispy crystals (29.5 g, 78%). m.p.: 178-180 °C.

2-bromo-9,9-dihexyl-7-iodo-9H-fluorene (4.1). In a 500 mL two-neck round-bottom flask fitted with a mechanical stirrer, 2-bromo-7-iodo-9H-fluorene 2 (25 g, 67.4 mmol, 1 equiv.) was added to 250 mL of dimethylsulfoxide under nitrogen atmosphere. 50% aq. NaOH (26 mL ) was introduced drop-wise with giving a bright red solution,
darkening quickly with time to a maroon. The solution was stirred vigorously as 1-bromohexane (23.8 mL, 168.5 mmol, 2.5 equiv.) was added and the solution turned purple. After 1 day of stirring at room temperature, the reaction was poured into 500 mL ethyl acetate, precipitating the salts. The solids were filtered off and the organic phase was washed (250mL portions) with 1x diluted NaOH, 1x brine, and 3x water with the red color fading to light yellow after the water washes. The organic phase was dried over MgSO₄, filtered, and concentrated by rotary evaporation to yield a viscous yellow oil. The oil was dissolved in a minimum amount of gently warmed isopropanol and allowed to cool slowly, yielding flaky amber crystals. (29.4g, 81%).  

\(^1\)H NMR (CDCl₃): \(\delta\) (ppm) 
- 7.67 (d, 1H, \(J = 7.5\) Hz), 7.66 (s, 1H), 7.54 (d, 1H, \(J = 8.4\) Hz), 7.47 (d, 1H, \(J = 7.5\) Hz), 7.45 (s, 1H), 7.43 (d, 1H, \(J = 8.4\) Hz), 1.92 (m, 4H), 1.10 (m, 12H), 0.80 (t, 6H, \(J = 7.0\) Hz), 0.59 (m, 4H)

\(^{13}\)C NMR (CDCl₃): \(\delta\) (ppm) = 152.7, 152.4, 139.7, 139.1, 136, 132.1, 130.1, 126.1, 121.6, 121.5, 121.2, 93.0, 55.6, 40.2, 31.5, 29.6, 23.6, 22.6, 14.0 ; HRMS (FAB+): m/z calcd 538.073, found 538.070; m.p.: 55-56 °C.

\(((7\text{-bromo-9,9-dihexyl-9H-fluoren-2-yl})\text{ethynyl})\text{trimethylsilane (4.2)}\) 2-bromo-9,9-dihexyl-7-iodo-9H-fluorene 3 (5.0g, 9.27 mmol, 1 eq.), copper iodide (71 mg, 0.37 mmol, 0.04 eq.), and Pd[PPh₃]Cl₂ (133 mg, 0.19 mmol, 0.02 eq.) were placed in a 100 mL round bottom flask with a stir bar and sealed with a rubber septum under N₂. THF (66mL) and triethylamine (10mL) were injected via syringe and the light yellow solution was sparged with N₂ for 30 minutes. Trimethylsilylacylene (1.28mL, 9.27 mmol, 1 eq.) was injected via syringe and the solution began darkening to a brown/black, returned to yellow after ~ 3 min., and finally darkened to brown with a light ppt forming after about 5 minutes. The reaction was stirred at room temperature for 3 hrs, filtered through a
celite pad, concentrated by rotary evaporator, and purified via column chromatography (silica gel, hexanes eluent) to yield a clear viscous oil. (3.6 g, 76% yield). $^1$H NMR (CDCl$_3$): $\delta$ (ppm) = 7.6 (d, 1H, J = 7.8 Hz), 7.55 (d, 1H, J = 8.5 Hz), 7.46 (m, 4H), 1.93 (m, 4H), 1.06 (m, 12H), 0.80 (t, 6H, J = 7.0 Hz), 0.57 (m, 4H), 0.31 (s, 9H), $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) = 153.3, 150.2, 140.5, 139.4, 131.3, 130.1, 126.2, 126.2, 121.7, 121.6, 121.4, 119.6, 106.0, 94.3, 55.5, 40.3, 31.5, 29.7, 23.6, 22.7, 14.1, 0.1; MS (FAB+): m/z calcd 508.22, found 508.2.

2-bromo-7-ethynyl-9,9-dihexyl-9H-fluorene (4.3). ((7-bromo-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)trimethylsilane 4 (3.0g, 5.9 mmol) was placed in a 250mL round bottom flask. Potassium hydroxide (6.0 g, 150 mmol), THF (80 mL), methanol (40mL), and water (20mL) were added and the solution was stirred under N2 at room temperature for until the starting material was completely used up as followed by thin layer chromatography, ~ 4hrs. Dichloromethane (250mL) was added, and the reaction was extracted water (3x, 100mL), diluted HCl$_{aq}$ (1x, 100mL), and again with water (1x, 100mL). The organic phase was dried over MgSO$_4$, filtered, and concentrated by rotary evaporator to yield a clear viscous oil which crystallized very slowly upon standing after residual solvent was removed with high vacuum. (2.53 g, 98% yield). $^1$H NMR (CDCl$_3$): $\delta$ (ppm) = 7.54 (d, 1H, J = 7.6 Hz), 7.47 (d, 1H, J = 8.5 Hz), 7.39 (m, 4H), 3.08 (s, 1H), 1.85 (m, 4H), 1.00 (m, 12H), 0.70 (t, 6H, J = 6.8 Hz), 0.49 (m, 4H); $^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) = 150.26, 150.34, 140.82, 139.28, 131.30, 130.15, 126.54, 126.21, 121.71, 121.45, 120.66, 119.71, 84.52, 68.03, 40.29, 31.53, 29.68, 25.65, 23.67, 22.65, 14.08; MS (FAB+): m/z calcd 436.18, found 436.2.
2-bromo-ethynyl-9,9-dihexyl-9H-fluorene 5 (2.21 g, 5.05 mmol, 1 eq.) and 2-bromo-9,9-dihexyl-7-iodo-9H-fluorene (2.86, 5.30 mmol, 1.05 eq.) were placed into a 250mL two-neck round bottom flask fitted with a Merlic-type solid addition adapter "tip-tube" containing copper iodide (38 mg, 0.20 mmol, 0.04 eq.), and Pd[PPh₃]Cl₂ (71 mg, 0.10 mmol, 0.02 eq.). THF (60mL) and triethylamine (8mL) were injected via syringe and the solution was sparged with N₂ for 20 minutes. The tip-tube was rotated to release the Pd and copper into the reaction, which turned brown/black, lightened to an amber color, and then darkened to brown with light ppt formation. The reaction was stirred at room temperature for 3 hrs until no starting 5 remained by TLC. The reaction was concentrated to dryness with rotary evaporation, dissolved in 250mL hexanes/ethyl acetate (1:1) and washed with water (3x, 100mL), dried over MgSO₄, filtered, and concentrated by rotary evaporator. The reddish brown solids were recrystallized from a minimum amount of isopropanol/ethyl acetate (6:1) to yield very fine tan needles. The hindered nature of our acetylene species may have contributed to increasing the energy barrier for cage closing. Although the reaction generally consumed all or most of the acetylene as monitored by TLC, a significant amount of material was stationary on silica under the conditions needed to elute the product, a similar behavior observed for the decaborane-sulfide adduct. This may imply that the final cage closing is the limiting step and an intermediate open-cage species may account for the lost yield. (3.45 g, 81%) ¹H NMR (CDCl₃): δ (ppm) = 7.64 (d, 2H, J = 8.0 Hz), 7.54 (dd, 4H, J = 8.4 Hz), 7.51 (s, 2H), 7.46 (m, 4H), 1.95 (m, 8H), 1.07 (bm, 24H), 0.77 (t, 8H, J = 6.6 Hz), 0.59 (s, 8H), ¹³C NMR (CDCl₃): δ (ppm) = 153.25, 150.47, 140.17, 139.48, 130.68, 130.14, 125.80,
121.92, 121.52, 121.25, 119.73, 90.53, 55.40, 40.40, 31.54, 29.60, 23.62, 22.53, 13.92; MS (FAB+: m/z calcd 848.335, found 848.340; m.p. = 105-106 °C.

\[ B_{10}H_{14} \cdot 2[S(CH_3)_2]. \] Using a modified literature procedure, Decaborane (0.5 g, 4.09 mmol, 1 eq.) and dimethylsulfide (3.13 mL, 42.6 mmol, 10 eq.) were added to a 10mL round bottom flask fitted with a condensor under nitrogen. The resulting solution was refluxed for 4 ½ hrs, cooled to room temperature, and allowed to sit under nitrogen for 24 hrs, after which time white crystals had grown. The crystals were collected by filtration, washed with heptane (3x, ~30mL), and dried. (0.97g, 96%) No further purification or characterization was performed. *Note*: Toxic! Stench! Decaborane and dimethylsulfide both have potent, unpleasant aromas and the product \( B_{10}H_{12} \cdot 2[S(CH_3)_2] \) was even more noxious.


\[ 1,2\text{-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)}\text{-closo-dicarbodecaborane} \quad (M4). \] 1,2-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)ethyne (0.5g, 0.59 mmol, 1 eq.) and \( B_{10}H_{12} \cdot 2[S(CH_3)_2] \) (0.174g, 0.707mmol, 1.2 eq.) were added to two-neck 10mL round bottom flask fitted with a condensor under nitrogen. 5mL of dry toluene was injected via syringe to give an orangish-tan mixture. The reaction was heated to reflux for 48 hrs, yielding a yellow solution with solids. The reaction was cooled to room temperature, concentrated by rotary evaporation, and purified by column chromatography (hexanes, silica). The product fluoresced yellow/orange against the green TLC indicator under 254nm handheld lamp, with an Rf ~ 0.6. The columned product was recrystallized from isopropanol, and again from acetone giving clear flaky crystals. (0.256g, 45%). ¹H
NMR (CDCl$_3$): $\delta$ (ppm) = 7.47-7.34 (12H), 4.41-1.45 (br, 10H), 1.81 (t, 8H, 7.8 Hz), 1.09 (m, 8H), 0.94 (m, 16H), 0.78 (t, 12H, J = 7.2 Hz), 0.39 (m, 4H), 0.29 (m, 4H)

$^{13}$C NMR (CDCl$_3$): $\delta$ (ppm) = 153.40, 150.37, 141.98, 138.26, 130.18, 129.94, 129.74, 126.21, 125.15, 122.22, 121.60, 119.09, 86.23, 55.39, 39.82, 31.32, 29.46, 23.47, 22.54, 13.99; MS (FAB+): m/z calcd 966.515, found 966.534; m.p. = 157-158 °C.

*Polymerization of M1 to Poly(fluorene-o-carborane) (P4).* In a microwave tube equipped with a stir bar, the monomer (100 mg, 0.10 mmol, 1 eq) was introduced along with bipyridine (40 mg, 0.25 mmol, 2.5 eq). The tube was then pumped into an argon filled glove box and Ni(COD)$_2$ (71 mg, 0.25 mmol, 2.5 eq) was added. The tube was sealed with a crimp-on aluminum cap with a PTFE coated septum seal and taken out of the glove box. Additional 1,5 COD (32 μL, 0.25 mmol), 2.5 eq was added via syringe and the reagents were dissolved in 4 mL of an anhydrous toluene:DMF (4:1) mixture. The tube was quickly degassed and filled with nitrogen three times. For conventional heating, the tube was placed in an oil bath heated to 80°C for 24 hrs. Or, for microwave assisted heating, the tube was introduced in a microwave apparatus and the solution was allowed to react for 20 min at 130 °C. The solution was then filtered using a syringe mounted with filter paper as well as a 0.45 μm PTFE syringe filter and precipitated into 100 mL of slightly acidified methanol (0.1M HCl). The o-carborane polymer P4 was recovered as grayish solid. (72 mg, 85%) P1: $^1$H NMR (CDCl$_3$): $\delta$ (ppm) = 7.73 (m, 2H), 7.56 (m, 6H), 7.28 (m, 4H), 4.10-1.65 + 1.98 (bm + m, 18H), 1.09 (m, 24H), 0.80 (m, 12H), 0.65 (m, 8H). P4 shows a characteristic B-H FT-IR absorption ~2560 cm$^{-1}$.

*Synthesis of o-carborane dimer (D4).* Using the procedure described for 2, 2-iododfluorene was synthesized and subsequently hexylated using the procedure described
for 3 to give 2-iodo-9,9-dihexylfluorene which was coupled to 5 using the Sonogashira coupling as described. The carborane formation protocol was the same as that for the synthesis of M4. Using the Ni(0) coupling from the polymerization above (adjusted for stoichiometry) the dimer was synthesized and purified with column chromatography (hexanes:THF, 20:1) to yield a white powder. (75%) \[ ^1\text{H NMR (CDCl}_3\rceil \]: \( \delta \) (ppm) = 7.58-7.36 (m, 20H), 7.25 (m, 6H), 3.8-1.75 + 1.90 (bm, 20H + m, 16H), 1.07 (m, 16H), 0.95 (m, 30H), 0.75 (t, 24H, J = 7.2 Hz), 0.37 (bm, 18H), \[^{13}\text{C NMR (CDCl}_3\rceil \]: \( \delta \) (ppm) = 152.02, 151.23, 150.94, 150.71, 143.08, 142.61, 141.19, 139.29, 138.65, 129.85, 129.76, 129.35, 129.28, 127.99, 126.89, 126.25, 125.26, 125.17, 122.85, 121.41, 120.54, 120.29, 119.01, 118.95, 86.67, 86.58, 55.18, 55.07, 39.96, 39.86, 31.37, 31.29, 23.51, 22.56, 22.50, 14.00, 13.99, ; MS (FAB+): m/z calc 1616.37, found 1616.1

**Synthesis of 9,9-dihexylfluorene dimer.** 2-bromo-9,9-dihexylfluorene was synthesized straightforwardly using previously described synthesis techiques. Ni(0) coupling as described above gave the desired compound. \[^1\text{H NMR (CDCl}_3\rceil \]: \( \delta \) (ppm) = 7.84 (d, 2H, J = 7.9Hz ), 7.80 (d, 2H, J = 7.4 Hz ), 7.71 (d, 2H, J = 7.9 Hz), 7.69 (s, 2H), 7.71 (m, 6H), 2.10 (m, 8H), 1.15 (m, 24H), 0.83 (m, 20H), MS (FAB+): m/z calc 666.5165, found 666.5146.

**Degradation of D4 to form Nido-cages.** 10mg of D4 was placed in a microwave vial along with KOH (0.1-8 eq.) and 3mL of a 3:1 mixture of ethanol/THF. The tube was sealed under N2 and reacted under microwave heating at 80°C for 20 minutes, cooled, and pipetted into a cuvet for fluorescence.
4.3 Results and Discussion

4.3.1 Synthesis and Polymer Characterization

The logical monomer for the preparation of an \( o \)-carborane based poly(fluorene) analogous to the previous \( p \)-carborane version is a 1,2-bisbromofluorene-\( o \)-carborane species. The brute force, head-on coupling approach used for M1 in the previous chapter, however, will not apply to \( o \)-carborane. The 1,2 orientation of the carbon vertices to be functionalized cannot, in general, be difunctionalized with aryl groups because of steric considerations and, likely, electronic aspects of the bond.\(^{(34)}\) Therefore a new approach was needed which can form the cages \textit{in-situ}.

The basic reaction used to produce \( o \)-carborane provides a template on which to build a synthetic route to the desired polymer; the cage closing reaction of decaborane onto functionalized acetylene species in solution has been well studied since its initial discovery in the 1960’s. Much of the early work, occurring during the Cold War, both in Russia and the United States, came out of research towards high energy fuels and propellants for rockets motors and jet engines. Many boranes and borane cage species are highly energetic (researchers were apparently quite surprised to find the carborane family to be extremely thermally and chemically stable). As discussed in chapter 1, the formation of \( o \)-carborane can be accomplished through \textit{in situ} closing of the cage by reacting a lewis base adduct of decaborane with acetylenes. The synthesis of 1,2-bis(7-bromo-9,9-dihexylfluorene) intermediate species, then, could lead to the formation of the desired monomer for dehalogenative polymerization upon cage closing with decaborane.
Scheme 4.1: Synthetic route to monomer M4 and polymer P4. (35)

The synthesis of the o-carborane fluorene monomer M4 began with the synthesis of 2-bromo-7-iodo-9,9-dihexylfluorene, 4.1, as in chapter 3 for the p-carborane-based synthetic route. This convenient intermediate, which allowed for selective coupling of p-carborane in the previous section, also permits selective reaction at the iodo-position for many other organometallic couplings. In order to obtain the necessary acetylene species for cage formation, a Sonogashira reaction can be performed on the iodo-position with excellent selectivity. As in chapter 3, Fluorene was first brominated with 1 eq. of N-bromosuccinimide to give 2-bromofluorene, 1, which was subsequently iodinated using iodine and potassium iodate in acidic media to yield 2-bromo-7-iodofluorene, 2. The
alkylation of 2 with 1-bromohexane was accomplished through deprotonation with sodium hydroxide in DMSO, aided by a phase-transfer catalyst to give 2-bromo-7-iodo-9,9-dihexylfluorene, 4.1. A Sonogashira coupling of 4.1 with trimethylsilylacetylene gave a TMS-protected ethynylfluorene, 4.2. A facile deprotection of the acetylene with potassium hydroxide in methanol/THF gave 4.3 in nearly quantitative yield, which was then coupled with a second equivalent of 3, again using a Sonogashira coupling to obtain 1,2-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)ethyne, 4.4. Following literature precedents,19 we used an adduct of decaborane and dimethylsulfide to form the o-carborane in situ by closing the cage with 4.4 to obtain our o-carborane monomer M4 in modest yields of about 45%. The synthesis of M4 was carried out on a multi-gram scale with little difficulty.
Polymerization of \textbf{M4} was performed following the widely used Ni(0) dehalogenative Yamamoto-type polymerization. Using bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$), bipyridine, and 1,5-cyclooctadiene (1,5-COD) in a mixture of toluene and dimethylformamide (4:1), \textbf{M4} was polymerized to the o-carborane polymer \textbf{P4}. (Kokado and Chujo’s recent work on o-carborane systems described difficulty in forming high molecular weight polymers, possibly due the bent conformation of o-carborane monomers. Similarly, polymerization of \textbf{M4} did not display typical fluorene polymerization behavior and tended to give lower molecular weight (MW) product, Mn $\sim$2.4-10 kg/mol, with multi-modal gel permeation chromatography (GPC) results.)
Thermal analysis of the polymerization product showed a \( T_g \) of 128 °C by differential scanning calorimetry.

Interestingly, a sharp, intense, low MW peak was observed in the GPC at the same elution volume for several different sets of conditions. To investigate the nature of the polymerization, a short study was initiated to observe the effects of heating conditions and concentration. It was found that reaction temperature had little effect on the polymerization as monitored by GPC. Microwave heating, previously shown to improve some Yamamoto polymerizations,(36) also appeared to have little effect on the reaction. It was hypothesized that the low MW species might be the result of intra-molecular effects due to the kinked, hindered conformation of the o-carborane monomer.

![Heating Effects on GPC](image1)

![Concentration Effects on GPC](image2)

**Figure 4.9:** GPC traces of polymerizations of M4 at various temperatures and heating methods (left) and at different concentrations and a copolymer (right).(35)

To test this, we ran the polymerization at various concentrations. The GPC traces showed a decreased intensity of the low MW peak and a significant increase in higher MW fractions with increasing concentration, though the complete elimination of the low MW peak was not achieved. (Figure 4.9) The addition of a co-monomer (2,7-dibromo-
9,9-dihexylfluorene) had a very similar effect. (Figure 4.9) These results appear to indicate that the polymerization of M4 is somehow intra-molecularly limiting. We synthesized a discreet dimer, D4, to compare to an enriched fraction (careful repeated column chromatography of dilute polymerizations) of the unknown low MW species. (Scheme 4.2) The unknown species displaced a larger hydrodynamic volume than both the monomer M4 and the dimer D4 according to GPC. (Figure 4.10)

Scheme 4.2: Synthesis of a discreet dimer, D4.(35)

Figure 4.10: GPC traces for the monomer M4, dimer D4, and an enriched fraction of the low MW peak from dilute polymerizations.(35)
It is noteworthy that both our p-carborane polyfluorene and the reported phenylene-ethynylene m-carborane polymer display well behaved polymerization characteristics, but the analogous o-carborane systems do not; considering the different polymerization chemistries of Chujo and co-workers and this work, the bent structure induced by the o-carborane likely limits efficient polymerization. (13, 15, 37) It may be possible that o-carborane promotes cyclization into macrocycles, as these have been reported for both fluorene and carborane based systems. (38-40) For this work, however, the polymer and the discrete dimer are sufficient to observe any large effects the o-carborane may have on the photoluminescent behavior of the material.

The wide interest in polyfluorenes as a luminescent material provides direction towards a path for investigating the influence of the carborane cages; there exists a large body of previous work on the fluorescence and UV-vis spectroscopy of fluorenes with which to compare our materials. It was observed that the incorporation of o-carborane caused a 30 nm bathochromic shift in the fluorescence emission and a 14 nm shift in the UV absorption relative to a discrete dihexylfluorene dimer, the repeat structure between the cage units. (Figure 4.11) As described in chapter 3, synthesis of poly(fluorene) with p-carborane in the backbone resulted in similar red-shifting behavior. 13 This suggests that the incorporation of carborane is extending the conjugation length of the fluorene segments between the cages. A red-shift upon incorporation of carborane into a conjugated system is consistent with the recent reports on o- and m-carborane in phenylene-ethynylene systems. (13, 15)
Figure 4.11: UV absorption of M4 and P4, with a single unit of fluorene and a fluorene dimer for comparison.(35)

Perhaps more interesting, incorporation of o-carborane into both the dimer D1 and the polymer P1 gave rise to a new lower energy emission in the solution fluorescence spectrum in the region of 565 nm in addition to the blue emission from the fluorene units, resulting in a solution that appeared yellow/orange under UV light. (Figure 4.12) This behavior was not observed in the analogous p-carborane polymer from chapter 3. The emission characteristics of D4 and P4 are similar to those reported for other polyfluorene structures containing conjugated, electron withdrawing groups such as benzothiadiazoles, in which energy absorbed by the fluorene units is transferred to the electron withdrawing groups and emitted at a lower energy. However, the lower energy emission is also in the same spectral region where green emissions are commonly observed for annealed polyfluorene films that are thought to be due, at least in part, to excimer formation due to aggregation. The recent report of aggregation-induced emission (AIE) of conjugated
polymers based on o-carborane backbone structures lends support for aggregation-induced phenomenon. In the reported o-carborane polymers, direct π-π stacking in the solid state was not necessary to observe AIE. (13) It is possible that, in the present system, we observe some combination of energy transfer and aggregation-based phenomena overlapping in the same spectral region. The absence of the low energy emission in p-carborane polyfluorene is evidence that the structure of the o-carborane repeat unit is responsible for this additional fluorescence emission peak, either through aggregation (induced by the bent conformation of the monomer) or through the unusual electronics of the C-C bond of o-carborane. Solution fluorescence excitation experiments revealed that the 565 nm emission of the o-carborane polymer has a peak excitation wavelength of 380 nm, while the peak excitation for the emission at 415 nm occurs at 390 nm, with significant overlap of the two. Additionally, the monomer M4 showed no lower energy fluorescence emission. This suggests that the o-carborane segments are likely being excited through an energy transfer process rather than being directly excited, or excited by the 415 nm emission of the fluorenyl units. Further study is necessary to define the exact nature of the emitting species, but the solution spectrum of the o-carborane polymer in good solvents suggests that o-carborane is conjugated with the backbone, or at least strongly affects its behavior.
Figure 4.12: Solution fluorescence of a fluorene dimer and P4 in CHCl₃. (35)

The solid state spectra of the P4 displays a single well defined green emission centered around 520 nm. (Figure 4.13) The solid state green emission was also found to be thermally stable; after annealing in air at 180°C for two hours the films showed no shift in the emission wavelength and actually increased in intensity, probably as a result of increased aggregation from rearrangements above T_g. Spectral stability and lifetime are important for light emitting applications and incorporation of carborane is one approach towards spectrally stable active materials.
The cages clearly have a strong influence on the overall emission properties of the polymer, but more intuition on their behavior might be observed if the affects of cage degradation on the conjugated system are investigated. If the cages are directly participating with the conjugation of the polymer backbone, changes in the cage bonding structure should directly affect the properties of the polymer system. While carboranes are generally chemically and thermally stable species, o-carborane is susceptible to nucleophilic bases, fluorides, and certain amines which open the cage to the anionic nido-species through deboronation.\textit{(1, 41, 42)} With this in mind, the o-carborane dimer, D4, was subjected to hydroxide ions in an ethanol/THF mixture and changes in fluorescence emission were observed. (Scheme 4.3)
Scheme 4.3: Cage opening on the dime D4 with ethanolic KOH.

Figure 4.14: Fluorescence changes with increasing amounts of base during cage deboronation.

The dimer, rather than the polymer was chosen because it is monodisperse; it allowed for an accurate molar ratio of base to cages to be calculated for each degradation reaction. A decreasing intensity of the peak near 570 nm and a simultaneous large increase in intensity near 430 nm with increasing concentrations of hydroxide ions was observed, visibly changing the fluorescence from orange to bright blue. (Figure 4.14) The formation of nido-cage species can be observed in NMR by the proton bridging the
borons on the open face of the cage, giving rise to a low, broad signal at $\delta = -1.5$ ppm relative to TMS. (18)

![NMR spectrum](image)

**Figure 4.15:** $^1$H NMR of the crude deboronated dimer showing a signal from the bridging proton of the *nido*-cage at -1.5 ppm relative to TMS.

It has been shown that the introduction of ionic species to the structure of polyfluorene can alter color and properties, (43) but it was observed that even after neutralization of the anion, the fluorescence spectra of the *nido*-species remained virtually unchanged. This would suggest that the observed intensity changes are due to the changing bonding structure of the cage and not simply the introduction of charged species to the system. Interestingly, when the nido-species solutions were drop cast into
films, the characteristic solid state green emission remained when placed under UV illumination. This may be further evidence that multiple influences on fluorescence are at work; while the conjugation with the cage appears to influence the solution fluorescence, enhanced aggregation due to the bent structure of the backbone may remain dominant in the solid state even after cage opening begins to disrupt the emission resulting from energy transfer to the electron deficient cage units. While others have reported small wavelength shifts upon cage opening in luminescent species,(18) the dramatic changes observed with our conjugated system may open up new avenues of research towards conducting polymer sensors and detectors and work is currently underway to explore these possibilities.

Table 4.1: Cyclic voltametry data for D4 and P4.

<table>
<thead>
<tr>
<th>Material</th>
<th>Epa</th>
<th>[Eonset]ox</th>
<th>λonset (nm)</th>
<th>HOMO/LUMO</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-carb-polymer</td>
<td>1.414V</td>
<td>1.143V</td>
<td>384</td>
<td>5.5/2.27</td>
<td>3.23</td>
</tr>
<tr>
<td>(P4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-carb-dimer</td>
<td>1.33 V</td>
<td>1.16 V</td>
<td>384</td>
<td>5.52/2.29</td>
<td>3.23</td>
</tr>
<tr>
<td>(D4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorene dimer</td>
<td>1.34 V</td>
<td>1.14 V</td>
<td>363</td>
<td>5.5/2.08</td>
<td>3.42</td>
</tr>
</tbody>
</table>

The polymer was also investigated using cyclic voltametry (CV), to determine what effect if any the cages may have on the band gap of the polymer. Based on the results, it appears that the introduction of the cages causes a lowering of the band gap, through a change in the LUMO level, compared to a fluorene dimer without cages. (Table 4.1) It doesn’t appear to depend on molecular weight as the values for the dimer D4 and polymer P4 are virtually identical. This supports the idea that conjugation may be extended into the cages, but not officially through the cages. The band gaps for the cage
containing polymers were found to be 3.23 eV, compared to the 3.0 eV expected for PDHF.

4.3.2 **Modulation of Photoemission and Applications for Sensing and Detecting**

Incorporation of o-carborane into poly(fluorene) clearly imparts new emissive behavior. Based on the results presented so far, it is clear that the unique behavior of the o-carborane polymer system could be harnessed as a sensor or detector. The o-carborane system provides a unique system in which several possible routes towards sensing are available in a single material. Three potential emissive modes were observed to be possible with the o-carborane conjugated polymer P4. (Figure 4.16) Under UV excitation of dilute polymer solutions in chloroform, typical blue emission were observed from the fluorene segments near 420 nm, a green emission from aggregation-induced phenomena between fluorene segments was observed near 525 nm, and a lower energy orange/red emission was observed near 570 nm. Modulation of these emissions using small molecules provides a new route towards conjugated polymer sensors.
As discussed in the introduction to this chapter, o-Caborane units can promote aggregation induced emission (AIE) in conjugated polymer systems. This has been recently described in work by Kokado et al., which focused on polymers based on an arylene-ethynlene backbone synthesized via Sonohashira couplings.\cite{14, 25, 27} The poly(fluorene)-based o-carborane polymer synthesized in this work was found to display AIE behavior as well, displaying green photoluminescence in the solid state resulting from the AIE of the fluorene segments adjacent to the carborane cages.\cite{44, 45} This phenomenon is dependent on the proximity and packing of the fluorene segments in the polymer. In solution, where solvent molecules generally help to partially suppress chain aggregation, the o-carborane units in our polymer can also give rise to lower energy
orange/red emissions, likely a result of energy transfer from the excited fluorene units to
the electron deficient cages.\textit{(14)} A Mataga-Lippert plot of the stokes shift vs solvent
polarity parameter, $\Delta f$, shows an increasing bathochromic shift with more polar
environments. (Figure 4.17) The roughly linear behavior can be an indication of energy
transfer to the electron deficient cages as has been noted in phenylene ethynylene-based
carborane species.\textit{(14)}

\begin{center}
\textbf{Emission Energy vs $\Delta f$}
\end{center}

![Figure 4.17: Mataga-Lippert plot of the solvent polarity parameter vs Stoke’s shift. $\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (\eta^2 - 1)/(2\eta^2 + 1)$, where $\varepsilon$ is the dielectric constant of the solvent and $\eta$ is the refractive index.}

The emissions were also investigated using time-resolved fluorescence
spectroscopy, courtesy of help from Prof. Barnes group in the chemistry department at
UMass-Amherst. The results showed that when excited by a laser ($\lambda_{ex}$ 405nm), two
detectable emissions were observed: a blue emission (460 nm) that is likely one of the
primary emissions from the fluorene segments and a lower energy emission, depending on the solvent (560 nm in toluene or 600 nm in THF). (Figure 4.18) The blue emissions show a shorter lifetime (~ ½ ns) than did the longer wavelength emissions (~1 ½ ns), which provides further evidence for aggregation based emissions and energy transfer. (Figure 4.19)

Figure 4.18: Emissions observed from 405 nm laser excitation during fluorescence lifetime experiments.

Figure 4.19: Decay plots of emission intensity in toluene and THF at various wavelengths showing longer lifetimes for the lower energy emissions.
In the solid state, a green AIE appears to be dominant, suppressing other emissions. This opens the door to sensor behavior. If the emissions can be moderated through interactions of small molecules with the polymer in the solid state, then the lower energy emissions may become competitive with the green AIE and lead to a color change. Indeed, the \( o \)-carborane poly(fluorene) in the solid state was found to undergo a shift in its emission wavelength upon exposure to organic solvent liquid or vapors, changing from bright green to shades of yellow, orange or red under UV light depending on the vapors. The shift appears to correlate most closely to the polarity of the solvent, with more polar solvents producing greater red-shifts, similar to solvochromatic shifts observed for fluorescent molecules in the solution phase.\(^{(14, 46)}\) Exposure to the vapors also appeared to decrease emission intensity and is likely related to the fact that the AIE of \( o \)-carborane systems can be quenched to a large extent in solution.\(^{(13, 14)}\) To illustrate this phenomenon, we fabricated a simple test “sensor” by coating the polymer onto small squares of laboratory wipes by dip coating. Coated onto the substrate, the polymer fluoresced at 550 nm under a handheld UV longwave lamp. The solid state samples of the polymer were then exposed to a number of solvent vapors. (Figure 4.20, Figure 4.21) The various solvents affected a range of color changes on the emission of the polymer, which was monitored using a portable spectrometer.
Figure 4.20: Optical images under UV light of the pristine polymer (1) and in the presence of tetrahydrofuran, ethyl acetate, methylene chloride, acetone, methanol, toluene, and hexanes vapors (2-8, respectively). (The polymer is coated onto squares of laboratory wipes, ~2 cm x 2 cm)

Figure 4.21: Photoluminescence spectra of the pristine polymer and after exposure to various vapors.
Upon exposure to ambient air, the samples regained their previous green emission as the vapors dissipated and could be used repeatedly with different solvents without any apparent negative effects. As an example, a plot of the intensity ratio of the photoemissions at 585 nm vs 550 nm as a sample is exposed to dichloromethane illustrates the time scale at which these changes are occurring. (Figure 4.22) Color changes can be observed with the naked eye after several seconds and saturate after several minutes. Upon removal of the sample from solvent vapor exposure the color returns quickly to its original green emission in ~1-2s.

![Emission During Solvent Exposure Cycles](image)

**Figure 4.22:** Ratio of the intensity of the photoemissions at 585 nm vs. 550 nm over time as the sample is exposed to CH\(_2\)Cl\(_2\) then removed from exposure.

The unique electronic nature of the carborane cage structure might also be utilized for sensing behavior through its influence on the conjugated polymer backbone. Carboranes possess aspects of σ-aromaticity and can interact with π-conjugated systems. \(o\)-Carborane cages can be opened to the \textit{nido}-species through deboronation by
nucleophilic bases, commonly ethanolic hydroxide solutions, amine bases, and fluoride ions. (1, 47) As previously shown, opening of the cages by deboronation disrupts the 3-D aromaticity and directly affects the photoluminescent properties of the polymer system. In our previous studies we observed that this disruption of the 3D cage structures led to an orange to blue color change in solution. (45) This was attributed to the disruption of the energy transfer from the fluorene segments to the carborane cages; with the cage effects moderated and solvent molecules helping to suppress aggregation, the fluorene segments were then able to emit in the blue.

However for sensor applications it is probably not desirable, or necessary, to completely open the cages via deboronation using such harsh conditions. Other reported sensor systems utilize boron in conjugated polymers, (48) under the principle that the Lewis acidic boron atoms influence the conjugated polymer, and can in turn be influenced by Lewis basic molecules interactions with the empty p-orbital. While the o-carborane cages cannot interact via empty p-orbitals, amines are known to react with the cages during deboronation reactions. (1) This is thought to occur via the amine attacking the boron adjacent to the C-C bond, which is the most electron deficient. There has been some postulating on whether or not some initial amine adduct is formed during these reactions, which might influence the polymer system. (49-52) When solid films of the o-carborane based poly(fluorene) were exposed to vapors of amines, the fluorescence emissions were red-shifted, reduced in intensity, or largely quenched, in the case of triethylamine and piperidine, which have been reported to deboronate o-carborane in solution reactions. (1) (Figure 4.23, Figure 4.24) The amines appear to be able to
influence the AIE, much as the solvent molecules do, and have the added possibility of further quenching the emissions.

Figure 4.23: Emission under UV light of the pristine polymer (1) and in the presence of triethylamine, diisopropylamine, n-butylamine, pyridine, DBU, aniline, and piperidine (2-8, respectively). (The blue color is the observed color of the composite wipe under UV light, not an emission from the fluorene segments.)

![Emission under UV light](image)

Figure 4.24: Photoluminescence emission of the polymer and during exposure to amine vapors.
It is interesting to note that the blue emission from the fluorene units appears to remain largely quenched. In our previous studies we found that chemically opening the cages in solution restored the characteristic blue emission from the fluorene segments. The amine sensing behavior is also quickly reversible upon removal from the vapors. It may be that the cages remain intact during the short, room temperature exposure to amine during the experiment in which the amines only loosely interact with the cages, or there may be quenching via another mechanism. Future work may be able to better understand these results.

Finally, some initial proof-of-concept experiments for neutron detection were performed. Based on the results which showed large changes in fluorescence emission upon cage degradation by base, some response should be expected if the cage structures are disrupted by neutron capture events. In this experiment, samples of P4 were coated onto quartz slides and sent near the UMass-Lowell research reactor core for set periods of time and reactor power to control total dose. After exposure, the samples were re-dissolved into dilute solutions and investigated with fluorescence spectroscopy. The spectra showed a slight decrease in lower energy emissions and a rise in the blue emissions, relative to a control sample with no exposure. These results are very similar to, albeit much lower in magnitude, the cage opening experiments with base. This suggests that the boron capture events are disrupting the cage structures and causing similar changes in the photoluminescence behavior. This is very promising evidence for future applications of these hybrid carborane/conjugated polymer materials for neutron detection. Introduction of these materials as the active layers in electronic devices,
especially diodes or transistors would allow much more sensitive detection as both cage disruption and secondary particles and doping events could be detected.

**Figure 4.25**: Fluorescence spectra of P4 samples after exposure to neutron flux. The numbers listed indicate total neutron flux through the sample area during exposure (control = zero flux).

### 4.4 Conclusions

In conclusion, we have synthesized a new o-carborane-containing fluorene monomer and polymerized it to create a conjugated hybrid carborane-fluorene polymer. The nature of the polymerization of the o-carborane fluorene monomer was investigated and found to be self-limiting, most likely due to its bent conformational structure. The incorporation of o-carborane was found to contribute to the conjugation of the system and gave rise to a new lower energy emission in the solution state. In the solid state, the o-carborane materials are stable pure green emitters. The degradation of the o-carborane
cages was found to significantly influence the solution fluorescence spectra leading to the conclusion that the bonding structure of the cage can directly influence the behavior of the conjugated polymer system. The incorporation of carborane into the backbone of conjugated polymers may provide an important route to new materials for sensors and light emitting devices while at the same time serving as a platform for further study of the nature of carborane cages.

O-Carborane based conjugated polymers are a new and promising class of materials for sensor applications. Poly(fluorene-o-carborane) was shown to act as a reversible colorimetric sensor for volatile nitrogen containing molecules based on their moderation of one or more of the material’s possible photoluminescence emission pathways. Exposure to common laboratory solvent vapors led to a color change in the film’s emission under UV light via a disruption of the green aggregation based emission, shifting the observed color towards the red. Exposure to certain amines quenched emission completely by both disrupting the AIE and interacting with the Lewis acidic boron cages. As has been shown for other conjugated polymer sensors, the structure of the conjugated segments between the carborane cages could be tuned to promote specific interactions with analyte molecules. The polymers are also sensitive to neutron radiation and have shown promising results for neutron detection or dosimetry. These materials have potential applications for sensors for detecting explosives, fissile materials, or perhaps even biological species and work towards these applications is currently underway in our laboratories.
4.5 References


5.1 Introduction

Surface grafted conjugated polymers, ideally polymer brushes, have been the target of synthetic polymer chemists for some time now. Their synthesis has both the potential to answer specific questions about the nature of conjugated polymer device behavior and to make possible practical access to polymer surface structures that are difficult or unattainable via traditional patterning techniques. In principle, grafting reactions can combine control over polymer layer deposition, patterning, and morphology, among other things, in perhaps a few simple steps. However, the nature of the coupling reactions generally used for solution polymerizations is much less understood in terms of their performances near surfaces and in hindered spaces, and they often underperform in surface reactions. The first step towards the study and use of surface grafted conjugated polymer systems is to design and explore suitable synthetic strategies. This work will explore the surface grafting oxide surfaces with poly(fluorene) using silane-based functionalization and the Ni(0) dehalogenative coupling polymerization method.

Relative to the broader field of polymer brushes, dominated by living and controlled polymerizations of non-conjugated polymers, the synthesis of conjugated polymer brushes is a new and growing field, populated by comparatively few active research groups. This chapter focuses on the step-growth Ni(0) dehalogenative polymerization of 2,7-dibromo-9,9-dihexylfluorene (PF) from oxide surfaces. PF grafting using this chemistry has been shown for other surfaces, namely photopolymer
(2P) resins containing a monomer-like anchor group. The first example of this chemistry used a methacrylate-based photopolymer network containing 4-bromostyrene as the anchoring group.\textsuperscript{(1, 2)} This work was later extended to 2P resins containing a dibromofluorene moiety to better mimic the reactivity of the solution monomer in hopes of increasing grafting efficiency.\textsuperscript{(3)} (Figure 5.1)

Figure 5.1: Photopatterned resin with embedded functionality to anchor grafted chains (a), \textit{Ni}(0) dehalogenative polymerization of PDHF from embedded bromophenyl-groups, and \textit{Ni}(0) dehalogenative polymerization of PDHF from embedded dibromofluorene-groups. Reprinted with permission from Refs. (1-3). Copyright 2006 American Chemical Society (a, b). Copyright 2008 Wiley-VCH Verlag GmbH & Co.
The grafting strategies from 2P have the advantage that they can be easily combined with patterning techniques, such as nanoimprint lithography, to yield patterned surface with embedded functionality. This allows facile patterning of the active grafting areas and, after polymerization, patterned polymer grafts. The disadvantages, however, include the fact that the methacrylate-based 2P networks are inherently insulators and prevent active devices from being fabricated from these grafts. Characterization is also an issue, in that being polymer networks the 2P is prone to swelling during polymerization and may expose functionality within the resin. This would lead to grafting reactions beginning inside the 2P films, creating an almost interpenetrating network (IPN) structure.(3) This may not ultimately be a bad situation for devices, but it does make characterization of the grafted layers quite difficult. How much of the the height increase before and after grafting is due to swelling or polymer attachment? How long is the average grafted chain? These are just a few questions that are difficult to determine with a grafting approach based on 2P networks. A synthetic approach using hard, non-reactive surfaces might be able to circumvent some of these difficulties.

Silicon oxide and quartz surfaces are ideal rigid substrates for studying grafting reactions. Their functionalization chemistry is well known, and characterization of brush layers from surfaces such as silicon wafers, glass, and quartz slides have been thoroughly explored for other polymer brush growth mechanisms such as living radical polymerizations.(4) Such oxide surfaces can be functionalized using silanes, taking advantage of the surface hydroxyl-groups present. A wide variety of functional silanes can be purchased or synthesized easily to produce a functionalization layer with monomer-like anchor points to participate in polymerization reactions. This well known
technique has been used before for non-conjugated polymer brush synthesis via ATRP, RAFT, etc, (4) and has been effectively harnessed for conjugated polymer grafting reactions in a few instances.(5, 6)

Figure 5.2: Grafting of poly(acetylene) to oxide surfaces using a silane-based anchor layer. Reprinted with permission from Ref. (5). Copyright 2007 American Chemical Society.

Figure 5.3: Example of grafting poly(phenylene) brushes from an oxide surface functionalized with a silane-based anchor/initiator. Reprinted with permission from Ref. (6, 6). Copyright 2010 American Chemical Society.

This chapter will focus on grafting poly(fluorene) to oxide surfaces using monomer-like anchor points, synthesized as dibromofluorene-based silane agents for the
functionalization of the surfaces, and proceeding via the Ni(0) dehalogenative polymerization route. Polymerizations in the solution are then able to participate, tethering chains to the surface during the progress of the reaction. This technique, studied on silicon oxide and quartz, should be readily expanded to conducting oxides such as indium tin oxide (ITO) and could be fabricated into devices, with the grafted polymer acting as the active material to give insight into structure property relationships and new device architectures.

5.2 Experimental

5.2.1 Materials and Instrumentation

Unless specified, all reagents were used without further purification. Karstedt catalyst (platinum-divinyl tetramethylsiloxane complex in xylene, 2.1-2.4% Pt) was purchased from Gelest, Inc. 2,7-Dibromofluorene (97%), bis(1,5-cyclooctadiene)nickel(0), [Ni(COD)₂], 1,5-cyclooctadiene (COD, 99+% ) and 2,7-dibromo-9,9-dihexylfluorene (DBDHF; 97%) were purchased from Sigma-Aldrich Company. Trichlorosilane (98%) and quartz microscope slides (Chemglass Inc. 25mm X 25mm) were purchased from Fisher Scientific. Silicon substrates (orientation 1-1-1, thickness 600-650 μm) were purchased from Wacker Siltronic Corp. All reactions were run under dry N₂ unless otherwise noted.

The film thicknesses were measured using a F20 Filmetrics spectrometry system. A refractive index of 1.6 was used for all the thickness measurements with the Filmetrics spectrometer. Water contact angle measurements were observed using a VCA Optima video contact angle goniometer equipped with a Hamilton syringe having a flat-tipped
needle. Deionized water was used as the probe fluid after filtering numerous times through a 20 nm syringe filter. The drop size was 0.50 µL. All reported values are the average of five static contact angle measurements of water drops on different areas of the sample surface. The modified surfaces exhibited homogeneous coating as evidenced by a tight distribution of measured contact angles; measured values were typically within ±1° of the average. Atomic force microscopy (AFM) images were collected on a Digital Instruments Nanoscope III in intermittent contact mode under ambient conditions using silicon cantilevers (spring constant 0.58 N/m) and a scan rate of 2 µm/s. RMS roughness was calculated with the AFM manufacturer’s provided software on images of 1µm x 1µm scan size. A Perkin Elmer LS50B luminescence spectrometer was used to measure the fluorescence emission. Gel permeation chromatography (GPC) was performed in tetrahydrofuran (THF) at room temperature with 1.0 mL/min elution rate. A Waters R403 differential refractometer and three PLgel columns (105, 104, and 103 Å) calibrated with narrow molecular weight polystyrene standards were used. For high resolution mass spectroscopy (HRMS) samples were analyzed by the University of Massachusetts Amherst Mass Spectrometry Core Facility. Analysis was performed on a JMS-700 double focusing sector mass spectrometer (JEOL Inc., Peabody MA) in electron ionization mode (70 eV, 300 µA ionizing current). Narrow scan range high resolution measurements were performed in electric field scan mode with a resolution setting of 5000, using perfluorokerosene for internal calibration.
5.2.2 Synthetic Procedures

*Synthesis of 9,9-diallyl-2,7-dibromo-9H-fluorene (5.1).* 2,7-Dibromofluorene (2.0 g, 6.17 mmol) was added to a test-tube filled with 10 mL of DMSO and equipped with a stir-bar and a rubber septum. The test tube was charged with sodium hydroxide (0.62 g, 15.43 mmol) and heated at 70°C for 12 hours. The solution slowly turned from colorless to orange to dark red/brown, indicative of the formation of the fluorene anion. Allyl bromide (2.24 g, 18.51 mmol) was added dropwise via a syringe. The reaction mixture was allowed to stir for another 12 hours and was continuously monitored via TLC (with hexanes as mobile phase) until complete disappearance of both the starting material as well as the mono-allylfluorene intermediate and appearance of the diallyl product was observed. The solution was poured into 150 mL water and 50 mL of brine was added to break the resulting emulsion. The solid precipitate was filtered and washed with water (10 mL) and methanol (3 times with 10 mL) and dried under vacuum to obtain 9,9-diallyl-2,7-dibromo-9H-fluorene 1 (1.27 g, 51%) as a light yellow solid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.53-7.46 (m, 6H, aromatic), 5.22 (m, 2H, vinyl CH), 4.87 (m, 4H, vinyl CH$_2$), 2.68 (d, 4H, aliphatic CH$_2$). 13C NMR (300 MHz, CDCl$_3$) δ 151.13, 138.72, 132.57, 130.52, 126.98, 121.30, 121.25, 118.53, 54.72, 43.19. HRMS (EI+) for C$_{19}$H$_{16}$Br$_2$ calcd. 403.9598, found 403.9599.

*Synthesis of (3,3’-(2,7-dibromo-9H-fluorene-9,9-diyl)bis(propane-3,1-diyl))bis(trichlorosilane) (5.2).* 9,9-Diallyl-2,7-dibromo-9H-fluorene, 1 (50 mg, 0.123 mmol), was dissolved in toluene (2 mL) and added to a test-tube fit with a rubber septum. Karstedt catalyst solution (0.01 mL) was added to the solution followed by dropwise addition of trichlorosilane (50 mg, 0.369 mmol). The reaction was heated at 70°C for 2 hours then excess trichlorosilane was removed from the reaction by blowing a stream of
dry nitrogen over the product for 30 minutes. The concentrated dark brown reaction mixture consisted mainly of the desired bistrichlorosilane derivative 5.2, as observed from NMR and high resolution mass spectrometry with traces of catalyst and solvent present. No residual trichlorosilane or unreacted allyl groups were detected. Attempts to further purify 2 by distillation, chromatography, or recrystallization were unsuccessful due to the high reactivity of the trichlorosilyl groups. \textit{NOTE: Trichlorosilane and its derivatives must be handled with care as exposure to vapors can cause serious eye injury and blindness.} \[1^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta 7.60-7.48 (\text{m, 6H, aromatic}), 2.11 (\text{m, 4H, CH}_2\text{-CH}_2\text{-C}), 1.22 (\text{m, 4H, CH}_2\text{-CH}_2\text{-CH}_2\text{-C}), 0.92 (\text{m, 4H, Si-CH}_2\text{-CH}_2\text{-C}). \] 13C NMR (300 MHz, CDCl\textit{\textsubscript{3}}) \[\delta 150.50, 139.02, 130.96, 126.10, 121.87, 121.60, 55.32, 41.77, 24.19, 16.96. \] HRMS (EI+) for C\textsubscript{19}H\textsubscript{18}Br\textsubscript{2}Cl\textsubscript{6}Si\textsubscript{2} calcd. 673.7395, found 673.7396.

\textit{Surface attachment of (3,3\textsuperscript{\prime}-(2,7-dibromo-9H-fluorene-9,9-diyl)bis(propane-3,1-diyl))bis-(trichlorosilane).} The silicon and quartz substrates were cleaned in a piranha bath (5:1 conc. H\textsubscript{2}SO\textsubscript{4} / 30\% H\textsubscript{2}O\textsubscript{2}) at 100 C for 30 min, washed with water and isopropanol, and dried prior to use. They were then treated with oxygen plasma for 5 min. In a reaction tube, 2 (80 mg) was diluted with 5 mL of toluene and a piece of substrate was introduced into the tube, immersed in the solution and the tube sealed and heated at 100\textdegree C. After 12 hours the tube was cooled to room temperature and the wafer was removed, washed excessively with toluene and dried under a stream of dry nitrogen.

\textit{PF Surface Grafting.} General procedure for the surface polymerization of DBDHF is described below. Substrate and catalyst manipulations prior to heating were performed in an inert atmosphere glove box. DBDHF (49 mg, 0.10 mmol), 2,2\textsuperscript{\prime}-dipyridyl (38 mg, 0.243 mmol) and the functionalized wafer were added to a reaction
tube along with a stir bar. Ni(COD)$_2$ (62 mg, 0.23 mmol) was added to the tube and the reaction tube was sealed. COD (33 μL, 0.27 mmol) and 3mL dry toluene/DMF (4:1 v/v) were injected and the reaction tube was degassed and backfilled with nitrogen. The reaction tube was heated at 80°C for 16 hours. The reaction was cooled to room temperature and the wafer was removed from solution. The wafer was rinsed twice with toluene, THF, and dichloromethane to remove any free polymer and salts. The wafer was then placed sequentially in 15 mL of dichloromethane, THF, and dil. HCl (1%) for 15 minutes each before rinsing excessively with water and isopropanol. The wafer was dried and stored prior to further characterization. The thick polymer solution from the reaction tube was collected, filtered through a syringe filter (0.45 μm) and precipitated by adding dropwise into methanol. The resulting white powder was filtered and dried to obtain polymer (32 mg, 95%). GPC was carried out on the THF soluble fraction of the isolated polymer. GPC (THF): $M_n = 49,144$, PDI = 2.08.

5.3 Results and Discussion

Surface functionalization of the oxide surfaces began with the design and synthesis of a suitable grafting agent. 4-bromostyrene had previously been incorporated into 2P resins for grafting, but the apparent grafting efficiency was quite low as evidence by small film thickness changes.(2) Later improvements designed a monomer-like dibromofluorene component in order for the resist to better participate with the solution polymerization.(3) With this in mind, the surface grafting agent was chosen to be a mimic for the monomer, a dibromofluorene-based silane species.

Functionalization of the 9-position bridging carbon is the best route for modifying fluorenes without disrupting the active polymerization sites at the 2,7-positions.(7, 8)
The 9-position has a relatively low pKa, and can be easily deprotonated using common bases such as sodium hydroxide or potassium tert-butoxide. It can then be functionalized via nucleophilic attack on the desired R-group, often an alkyl halide for solubilizing side chains for polymer synthesis. Silanes are easily synthesized via hydrosilylation of alkenes with platinum catalysts; nucleophilic attack of allylbromide with dibromofluorene provided a bis-allyl functionalized monomer unit. The allyl groups were then reacted with trichlorosilane and Karstedt’s catalyst (a divinylsiloxane platinum complex) to yield a monomer-like unit functionalized with trichlorosilanes.

Scheme 5.1: Synthesis of a bis(trichlorosilane)-dibromofluorene for surface functionalization of an oxide surface and subsequent participation in grafting of PDHF.

Trichlorosilanes react readily with oxide surfaces, creating Si-O-Si bonds between the surface hydroxyl groups and the silane, and often their neighboring silane groups to form a thin silica-like network of surface functionality. Trichlorosilanes often form multilayer structures, especially with any residual water present in the system. In this case, especially due to the fact that the anchor species is a bis-trichlorosilane species, it is
expected that multilayers of silane groups will be formed. This will ensure coverage of the surface with monomer-like anchor groups. While not isolated, the near quantitative conversion of the allyl groups to reactive trichlorosilanes was confirmed by $^1$H NMR of a sample of the hydrosilylation reaction which has had the solvent removed and been redissolved in deuterated chloroform under inert atmosphere. The vinylic CH and CH$_2$ peaks observed at 5.22 ppm and 4.87 ppm, respectively, were replaced by a –CH$_2$- peak at 1.92 ppm and a –CH$_2$-Si- at 0.92 ppm.

The concentrated residue from the hydrosilylation reaction was diluted with toluene, and used directly to functionalize cleaned oxide surfaces. The oxide surfaces, silicon wafers or quartz slides, were cleaned thorough using a variety of solvent washes to remove crude organic contaminants that may be residuals from production or processing. They were then subjected to a treatment of concentrated sulfuric acid and 30% hydrogen peroxide (5:1) at 100 °C to oxidize any remaining trace organics on the surface. The substrates were then subjected to an oxygen plasma treatment to ensure the oxide surfaces were activated for efficient surface functionalization. The wafers were placed in the reaction solution for a set period of time, usually 12 hrs. They were then removed, rinsed, and analyzed.
Fresh oxide surfaces has very low water contact angles (<10°), and this serves as a qualitative measure of surface functionalization. After functionalization with the silanes, the contact angles rose to around 95° and 100° for silicon and quartz, respectively. This shows that the normally hydrophilic oxide surfaces had been converted to hydrophobic, organically functionalized surfaces. Because of the multifunctional nature of the silane species, and multilayer was likely formed. The thickness of the silane anchor layer was measure to be ~29 nm. AFM analysis confirmed that the silane treated surfaces had an RMS roughness of 3 nm.

Polymerization of PDHF in the presence of the treated surfaces was performed using the Yamamoto-type Ni(0) dehalogenative polymerization of 2,7-dibromo-9,9-dihexylfluorene. (Scheme 5.1) The polymerization was performed under benchtop heating conditions at 80 °C for 16hrs. Although microwave heating has been shown to be very effective at increasing the rate of the polymerization, it was not found to be effective for the surface grafting reactions. It is possible that the microwave irradiation is

Figure 5.4: AFM height images of the oxide surfaces before (silicon (a) and quartz (b)) and after grafting of PDHF (silicon (c) and quartz (d)).
negatively effecting the surface functionality. Contact angles of the surfaces post-microwave dropped substantially and may indicate some damage to, or loss of, the monomer-like layers. Nevertheless, benchtop heating generally produces effective polymerizations and substrates placed in reaction solutions appeared to be grafted with polymer. After exhaustive rinses and extractions to ensure that no physically adsorbed polymer was present, the surfaces were characterized.

![Image](image_url)

**Figure 5.5:** Optical images of silane functionalized (left) and grafted (right) quartz wafers under ambient room lighting (top) and under a handheld UV lamp (bottom) showing typical blue emission from PDHF from the grafted sample.

The total thicknesses of the grafted layer was found to be around 98 nm. Assuming the silane layer accounts for approximately 30nm of this thickness, the grafted polymer layer thickness should be some 68nm. AFM analysis shows this thickness to unevenly distributed, with an RMS roughness of 20 nm. Contact angles were found to be 82° and 65° for silicon and quartz surfaces, respectively. RMS roughness of a spin-coated layer of PDHF was found to be 1.8nm, with a contact angle of 98°, for comparison. This difference could be due to several factors, including the initial anchor layer thickness variations, the step-growth nature of the polymerization, and possible side
reactions in which the polymer grows across the surface, rather than from it, using up possible anchor sites for further grafting. (Figure 5.4)

As in previous chapters, poly(fluorene)s can be investigated using fluorescence spectroscopy. The previous results from grafting PF onto 2P resins showed blue-shifted fluorescence spectra, which are an indication of shortened effective conjugated length. This is a possible warning sign of low molecular weight of the grafted material. The fluorescence spectra of the oxide-grafted PF from this study showed a peak emission at 425 nm, which corresponds nicely to high MW PDHF from solution polymerizations using the same chemistry. (Figure 5.6) This indicates that the surface chains are at least attaining the maximum effective conjugated length for PF, approximately 10-15 units. This would make them sufficiently long for device applications in future work.

![Fluorescence spectra of the grafted samples on silicon wafer at various excitation wavelengths display the typical emission expected for PDHF, with a peak emission near 425 nm.](image-url)

Figure 5.6: Fluorescence spectra of the grafted samples on silicon wafer at various excitation wavelengths display the typical emission expected for PDHF, with a peak emission near 425 nm.
5.4 Conclusions

The surface-directed grafting of poly(dihexylfluorene) layers onto oxide surfaces was successfully carried out through the synthesis of a new silane-based anchor unit, which mimics the monomer during polymerization reactions. Silicon wafers and quartz slides were functionalized using this new anchor species and placing the substrates in the presence of a Ni(0) dehalogenative polymerization produce surface grafted polymer. The polymer layers were found to have thicknesses on the order of 68 nm, but the roughness was found to increase significantly during polymerization as compared to the silane treated layers. Fluorescence spectroscopy showed that the grafted layers emitted at 425 nm and were characteristic of high MW PDHF from solution polymerizations. Future work should extend this approach to conducting oxides for the fabrication of devices, especially light emitting diodes where PF could be directly bonded to one of the active electrodes, indium tin oxide.

5.5 References


CHAPTER 6

FLUORENE-BASED CONJUGATED POLYMER/CELLULOSE HYBRID MATERIALS VIA GRAFTING

6.1 Introduction

Cellulose, the structural component of the primary cell wall of green plants, is the most abundant organic material on the planet and because of its useful materials properties it is one of the most widely used substances. Cellulose comprises a large fraction of wood, papers, and fibers and chemically modified cellulose yields materials such as plastics, photographic films, and rayon. Cellulose derivatives also find wide application as adhesives, explosives, food additives, and coatings. Interestingly, cellulose products have had minimal impact upon the information technology evolution which has given rise to everything from fast, complex computer processing to color displays to high density data storage. If anything, there has been a drive to replace paper as an information storage/display medium with the advent of “paper-like” displays that strive to mimic the advantageous properties of printed paper while adding advanced properties such as video and changing display patterns. However, cellulose-based materials have great potential as materials for organic electronics if they can be effectively coupled to semiconducting polymers. Renewable and able to be processed with mature technologies, cellulose-based materials are attractive for use in devices as flexible substrates, high surface area and nano-structured materials, and molecular scaffolds. Flexible electronics applications have required the merging of complex advanced electronics with suitable flexible substrates, typically polyester or polyimide-based films. Now, there is a small renaissance underway for cellulose and paper materials in
electronics,(2-4) not only because they are a green and renewable resource but also because the structure of cellulose can play important roles as a substrate, high surface area scaffold material, and nano-structured functional material.

Functionalization of surfaces and materials with polymers via grafting or brush growth has been the subject of intense research in recent years.(5, 6) Separately, the modification of cellulose with polymers(7-9) and conjugated polymer nanocomposite/hybrid materials(10, 11) have been attracting increasing amounts of interest. A small but growing number of cellulose/conjugated polymer hybrid materials, however, have been reported for use in several types of electronic devices. The synthesis of conductive cellulose composite materials with poly(pyrole) (PPy),(12-14) poly(aniline) (PANI),(15, 16) and poly(ethylenedioxythiophene) (PEDOT)(17) have been described in the literature(18) and are generally synthesized by in situ adsorption and chemical or electrochemical oxidative polymerization. These hybrid materials show great promise for polymer batteries,(12) polymer actuators,(19) and sensors.(20) Not surprisingly, there are fewer examples of cellulose composites with other conjugated polymer repeat structures that lend themselves less readily to adsorption onto cellulose. Photoluminescent paper and cellulose fibers have been prepared through variations of adsorbing or printing suspensions of fluorescent conjugated polymer nanoparticles onto substrates.(21) Alternatively, layer-by-layer electrostatic deposition has been used to fabricate polymer coated cellulose to create fluorescent and conducting materials.(22-24) Direct chemical grafting has been much less explored and may hold some advantages over other deposition techniques for certain applications; grafted layers could be non-ionic, stable to subsequent processing, and synthesized using essentially any monomers.
normally used for solution polymerizations of conjugated polymers. A covalently attached polymer can’t diffuse away from a phase boundary. Herein, we report a versatile new approach for the grafting of conjugated polymer onto paper substrates. Cellulose samples were modified via esterification with bromophenyl- or acetylene-based anchor points, which can participate with many of the organometallic coupling reactions commonly used to produce conjugated polymers. Using Suzuki, Heck, and Sonogashira polymerizations, this work demonstrates effective example grafting chemistries that could be used to synthesize virtually any poly(arylene), poly(arylenevinylene), or poly(arylene-ethynylene).

6.2 Experimental Section

6.2.1 Materials and Instrumentation

Filter paper used as cellulose substrate: Whatman 1 (listed minimum alpha cellulose content of 98%). All chemicals were purchased from commercial sources and used as received unless otherwise specified. 4-oxo-4-(prop-2-ynyloxy)butanoic acid and 2-bromo-7-iodo-9,9-dihexylfluorene were prepared following published procedures.(8, 25) Diiodobenzene was recrystallized twice from ethanol and dried in vacuo, and stored in the dark before use. Microwave reactions were performed in a Smith Creator Personal Chemistry microwave synthesizer. 1H and 13C NMR measurements were performed on a Bruker DPX300 NMR instrument in CDCl3. GPC measurements were made in CHCl3 on an Agilent 1200 series with 2 Jordi mixed bed columns at 40° C with flow rate of 1ml/min. Water contact angle measurements were obtained using a VCA Optima surface analysis system with a drop size of 0.5 μl. Contact angles were taken 5 seconds after droplet deposition on the surface, and averaged over three drops in various locations on
the sample. Dispersive Raman Spectroscopy: A Jobin-Yvon Horiba LabRam HR800
dispersive Raman spectrometer (HeNe gas laser, \( \lambda = 632.8 \) nm) was used to acquire the
Raman spectra. Spectral resolution was maintained at 4 cm\(^{-1}\) near the lasing line. A total
of 30 scans were co-added to attain the final spectra in the 100-4000 cm\(^{-1}\) range.
Fluorescence spectra were measured on a Perkin Elmer LS50B. Optical microscope
images were obtained performed on an Olympus BX51 microscope having an Olympus
model U-LH100HG mercury lamp and captured with a Sony ExWaveHAD CCD camera.

6.2.1 Synthetic Procedures

*Synthesis of prop-2-ynyl 4-chloro-4-oxobutanoate.* Oxalyl chloride (1.05 mol, 3
eq) was added drop wise to a solution of 4-oxo-4-(prop-2-ynyloxy)butanoic acid (32
mmol, 1 eq) in 200mL dichloromethane (DCM) containing 6 drops of
dimethylformamide. The reaction was allowed to proceed for 4 hrs at RT. The reaction
solution was then concentrated by rotary evaporation, diluted with an excessive amount
of DCM, and the solvent was again removed by rotary evaporation to remove excess
oxalyl chloride. This was repeated 4 times before the concentrated product was placed
under vacuum overnight. Yield 67% \(^1\)H NMR (CDCl\(_3\)): \( \delta 2.52 \) (t, 1H, -CH), \( 2.75 \) (t, 2H,
-CH\(_2\)-), \( 3.26 \) (t, 2H, -CH\(_2\)-COCl), \( 4.73 \) (d, 2H, J = 2 Hz, -C-CH\(_2\)-O-)

*Synthesis of alkyne modified cellulose.* Filter paper (~2 cm\(^2\)) was put into a vial
and DCM (10 ml), triethyl amine (TEA, 101 \( \mu \)l), and prop-2-ynyl 4-chloro-4-
oxobutanoate (0.12 g, 0.67 mmol) were added. A catalytic amount of 4-
(dimethylamino)pyridine (DMAP) was added. The vial was placed on a shaking table and
the reaction proceeded overnight. After the reaction was completed, the modified filter
paper was rinsed thoroughly 2 times each with tetrahydrofuran (THF), DCM, ethanol (EtOH) and again with THF. The sample was sonicated for 2 minutes between the last two washings with THF and dried in vacuo at 50°C overnight.

Synthesis of arylbromide-modified cellulose. Filter paper was put in a vial with a stir bar. DCM, TEA and a catalytic amount of DMAP was added and the mixture was stirred at RT overnight. 4-bromo-benzoylchloride (0.671 mmol) was added and allowed to react overnight. After reaction, the filter paper was rinsed thoroughly 2 times each with THF, DCM, EtOH, and THF. The sample was sonicated for 2 minutes between the last two washings with THF and dried in vacuo at 50°C overnight.

\[
\begin{align*}
\text{Br} & \quad \rightarrow \quad \text{Br} \\
\text{Br} & \quad \rightarrow \quad \text{Br}
\end{align*}
\]

Scheme 6.1: Synthetic route to 2-bromo-7-vinyle-9,9-dihexylfluorene. i) I\_2, KIO\_3, AcOH, H\_2SO\_4 ii) Br-hexane, NaOH, DMSO, PTC iii) tri-n-butylvinyltin, Pd[PPh\_3]\_4, DMF.

Synthesis of 2-bromo-7-vinyl-9,9-dihexylfluorene. 2-bromo-7-iodo-9,9-dihexylfluorene (0.507g, 0.94mmol, 1eq.) was placed into a small test tube with Pd[PPh\_3]\_4 (54mg, 47μmol, 0.05eq) and capped under N\_2. 4mL of anhydrous DMF was injected via syringe, followed by an injection of tri-n-butylvinyltin (0.28mL, 0.94mmol, 1eq.). The reaction was then placed in an 80°C oil bath for 30 min. The reaction was then poured into 50mL of water and extracted into 100mL ethyl acetate, which was washed 3x with water, dried over MgSO\_4, and concentrated by rotary evaporation to give a brown oil. Purification by column chromatography on silica with hexanes gave a clear,
viscous oil after rotary evaporation, which formed white crystals upon storage overnight at -20°C. Yield: 0.386g (93%). $^1$H NMR (300 MHz, CDCl$_3$): δ 0.59 (m, 4H, -CH$_2$-), 0.76 (t, 6H, -CH$_3$), 1.04 (m, 12H, -CH$_2$-), 1.92 (m, 4H, C-CH$_2$-), 5.27 (d, 1H, J = 10.9 Hz, -CH=CH$_2$ - ), 5.80 (d, 1H, J = 17.6 Hz, -C=CH$_2$-), 6.79 (q, 1H, -CH=CH$_2$-), 7.39 (m, 6H, ArH), 7.52 (d, 1H, J = 8.36 Hz, ArH), 7.60 (d, 1H, J = 8.07 Hz, ArH)

![Scheme 6.2: Synthetic route to diethynylfluorene.](image)

**Synthesis of 9,9-dihexyl-2,7-di(2-methyl-3-butyn-2-ol)-fluorene (26)** 9,9-dihexyl-2,7-dibromofluorene (2.46g, 5 mmol, 1 eq) and 2-methyl-3-butyn-2-ol (1.26g,15 mmol, 3 eq) were dissolved in 40mL TEA in a flask fitted with a Merlic-type solid addition adapter (“tip-tube”) containing Pd(Ph$_3$)$_2$Cl$_2$ (70mg, 0.10 mmol, 0.02 eq) and CuI (48mg, 0.25 mmol, 0.05 eq). After the reaction was sparged with N$_2$ gas for 30 minutes, the catalysts were then and the mixture was refluxed at 95°C under N$_2$ for 24 hours. The mixture was cooled to RT and filtered to remove bromide salts, which were washed with diethyl ether. After concentrating by rotary evaporation, the product was purified by flash chromatography on silica gel using ether/ethyl acetate (90/10). Yield: 2.35g (63%). $^1$H NMR (300 MHz, CDCl$_3$): δ 0.54 (m, 4H, -CH$_2$-CH$_2$-), 0.78 (t, 6H, -CH$_2$-CH$_3$), 1.03 (m, 12H, -CH$_2$-), 1.68 (s, 12 H, -C-CH$_3$) 1.92 (m, 4H, H$_3$C-CH$_2$-), 2.29 (s, 2H, -OH ), 7.39 (m, 4H, ArH), 7.59 (m, 2H, ArH)

**Synthesis of 9,9-dihexyl-2,7-diethynylfluorene (26)** 9,9-dihexyl-2,7-di(2-methyl-3-butyn-2-ol)-fluorene (2.35 g, 4 mmol, 1 eq) and pulverized KOH (1.4g, 25 mmol, 6,25
eq) pellets were dissolved in 1-Butanol (50 ml). The mixture was refluxed at 120°C under N₂ for 2 hours. The mixture was then dissolved in ether and transferred to a separation funnel. About 50 ml water was added and the mixture was extracted 3x with diethyl ether. The organic layers were combined and dried over MgSO₄, filtered, and concentrated by rotary evaporation. The product was purified by flash chromatography on silica gel using hexanes. Yield: 1.04g (44%).

¹H NMR (300 MHz, CDCl₃): δ 0.58 (m, 4H, -C-CH₂-CH₂-), 0.79 (t, 6H, -CH₃), 1.06 (m, 12H, -CH₂-), 1.96 (m, 4H, H₃C-CH₂-), 3.18 (s, 2H, -C≡C-H), 7.50 (d, 4H, J = 9.3 Hz, ArH), 7.65 (d, 2H, J = 7.6 Hz, ArH)

_Grafting of poly(fluorene) (P6.1) on arylbromide-modified filter paper_ 9,9-Dihexyl-2,7-dibromofluorene (0.142 mmol, 1 eq), 2,7-bis(trimethyleneborate)-9,9-dioctylfluorene (0.142 mmol, 1 eq), Pd(PPh₃)₄ (0.0042 mmol, 0.03 eq), and a 1x2cm piece of modified filter paper were added to a 5mL microwave reaction tube containing a small stir bar and hollow glass pipe inside a glove box and capped with a crimped aluminum cap with septum. The cellulose filter paper was placed to sit atop the hollow glass tube. After removing from the glove box, nitrogen sparged aqueous K₂CO₃ solution (1 ml, 2M) and toluene (3 ml) were injected and the reaction was sparged with N₂ for 30 minutes. A small amount of phase transfer catalyst (Aliquat 336, 0.01 g) was then injected into the tube and the reaction degassed using 3 freeze/pump/thaw cycles in liquid nitrogen and an N₂ backfill. The reaction was then performed at 90°C for 30 minutes using microwave heating. After cooling to RT, the filter paper was rinsed 2 times each with THF, DCM, EtOH, and THF. The sample was then sonicated in THF for 2 minutes, rinsed, and soxhlet extracted for 12 hours in THF before being dried in vacuo. The polymerization solution was diluted with DCM and washed 3 times with brine. The
organic phase was then dried with Na$_2$SO$_4$, filtered and concentrated by rotary evaporation. It was then dissolved in a small amount of DCM, and precipitated in MeOH to give polymer fiber.

Synthesis of poly(fluorene–vinylene) (P6.2) on arylbromide-modified filter paper

An arylbromide modified filter paper and 2-bromo-7-vinyl-9,9-dihexylfluorene (0.125 mmol, 1 eq), monomer were placed in a test tube. Pd(OAc)$_2$ (0.0062 mmol, 0.05 eq), tri-o-tolylphosphine (0.025 mmol, 0.2 eq), and a stir bar were added. The tube was capped under N$_2$. Solvent (2.5 ml DMF, 1 ml TEA) was injected and the reaction was sparged with N$_2$ for 20 minutes, and then placed under vacuum and backfilled 3 times with N$_2$. The mixture was reacted overnight in a 100°C oil bath. After cooling to RT, the filter paper was removed and washed 2 times each with THF, DCM, EtOH, and THF. The sample was sonicated for 2 minutes between the last two washings in THF and then Soxhlet extracted for 12 hours. The solution polymer was diluted in a small amount of DCM, precipitated in MeOH, and filtered.

Synthesis of poly(fluorene–ethynylene–phenylene) (P6.3) on ethynylene-modified filter paper

9,9-dihexyl-2,7-diethynylfluorene (0.23 mmol, 1 eq), diiodobenzene (0.23 mmol, 1 eq), Pd(OAc)$_2$ (0.0114 mmol, 0.05 eq), PPh$_3$ (0.0171 mmol, 0.075 eq), CuI (0.0114 mmol, 0.05 eq) and a stir bar were placed into a test tube with modified paper and sealed under N$_2$. The solvent, a mixture of THF and diisopropylamine (5:1) was injected into the tube. The solution was reacted overnight at 45°C. The reaction produced a bright orange solution after about 30 minutes. Solution polymer was dissolved in THF and precipitated in methanol (MeOH), filtered and dried. After reaction, the filter paper was washed 2 times each with THF, DCM, EtOH, and THF. The sample was sonicated
for 2 minutes between the last two washings with THF and then soxhlet extracted for 12 hours in THF. Solution polymer and precipitated material were dissolved in THF and precipitated in methanol (MeOH), filtered and dried.

6.3 Results and Discussion

Some of the hydroxyl-groups on the repeat structure of cellulose are accessible on the surface of fibers for chemical reactions and esterification with acid halides is a well known method for functionalizing cellulose, paper, and other natural fibers. Many transition-metal catalyzed coupling reactions used for the synthesis of poly(arylenes) and poly(arylenevinylenes) employ an aryl-halide as one coupling partner. To investigate grafting with these types of polymerization reactions, cellulose filter paper was chosen as a convenient, readily available substrate and was chemically modified with bromo-phenyl groups via esterification, by reacting with a solution of 4-bromobenzoyl chloride in dichloromethane (DCM), triethylamine (TEA), and a catalytic amount of 4-(dimethylamino)pyridine (DMAP).

Scheme 6.3: Esterification of cellulose with acid chlorides.
In the case of poly(arylene-ethynylene)s (PAE), which have gained recent attention for organic electronics,\(^{(29)}\) an acetylene functionality tethered to the fiber surfaces was desired. Poly(arylene-ethynylene)s are polymerized using the Pd/Cu catalyzed Sonogashira-type couplings of acetylenes with aryl halides, commonly employing the more efficient aryl iodides. To avoid any disparity in the efficiency of surface vs. solution couplings during grafting reactions, the substrates were functionalized using an acetylene-based acid chloride rather than 4-bromobenzoyl chloride. Accordingly, using conditions similar to the bromophenyl esterification, a solution of prop-2-ynyl-4-chloro-4-oxobutanoate was used to functionalize paper samples for Sonogashira-type polymerizations. (Scheme 6.3)

Several representative polymerization chemistries were then explored. Three different repeat structures were chosen for grafting including poly(fluorene) \( \text{P6.1} \), poly(fluorenevinylene) \( \text{P6.2} \), and a poly(fluorene-ethynylene) \( \text{P6.3} \), (Figure 6.1) whose grafting chemistries are expected to be readily expanded with the use of different monomers to provide a vast array of possible polymer structures.

![Figure 6.1: Repeat structures of poly(fluorene), poly(fluorenevinylene), and poly(fluorene-ethynylene-phenylene). \( R = \text{n-Hexyl} \)](image)

Our laboratory has extensively studied the Yamamoto-type Ni(0) dehalogenative polymerizations of arylbromides\(^{(30)}\) and it was tested here as a first approach to grafting poly(fluorene) \( \text{P6.1} \) with our substrates. (Scheme 6.4) Polymerizations were performed
in 4:1 toluene/DMF solvent mixture using Ni(COD)$_2$ (2.2 eq. with respect to fluorene), 1,5-cyclooctadiene, and bipyridine as a cis-directing ligand to promote reductive elimination. Grafting reactions were performed both on the bench (100° C for 24hrs) and in the microwave (MW, 100° C for 20min), as we have previously found MW heating to be very effective for this coupling reaction. In all cases free polymer was recovered after precipitating the filtered reaction solution into methanol, and the molecular weight and fluorescence emission of the poly(fluorene) appeared very similar to that obtained in the absence of functionalized cellulose (MW ~ 50kg/mol, max. $\lambda_{em} = 425$ nm).

Scheme 6.4: Surface grafting via Ni(0) dehalogenative polymerization.

However, while the Ni(0) methods are generally robust and produce polymer reliably, they are not catalytic and a stoichiometric excess of metal is required. These reactions produced cellulose substrates saturated with residual metal and salts; samples appeared almost completely black after grafting polymerization and could not be easily cleaned or characterized. Excessive washing, sonicating, and Soxhlet extraction with multiple solvents failed to produce clean samples. Some polymer was likely grafted during the process, as observed by faint blue fluorescence under a UV lamp, but for most practical applications the large amount of metal impurities impregnated into the paper renders this approach essentially useless. A more suitable catalytic polymerization was
required for grafting poly(arylenes). Many other organometallic coupling reactions are available for the polymerization of conjugated polymers that enable the use of catalytic amounts of metal.

Suzuki-coupling based polymerizations are widely used to produce a variety of poly(arylenes), including poly(fluorene), and these polymerizations should also participate in grafting reactions with surfaces bearing the arylbromide functionality. Grafting of poly(fluorene) was performed via a typical Suzuki polymerization of 9,9-dihexyl-2,7-dibromofluorene and 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester using Pd(PPh$_3$)$_4$ and K$_2$CO$_3$ in toluene/water with a catalytic amount of a phase transfer catalyst (PTC, Aliquat 336). (Scheme 6.5) In the initial experiments, modified paper samples were immersed in the biphasic reaction media with monomer and catalyst and heated to typical reaction temperatures (80-100° C for 24-48 hrs).

Heating of the Br-phenyl-modified cellulose substrates in the hot, high pH aqueous phase led to disintegration of the paper samples into pulp during the reaction. A simple method was devised to circumvent this problem by suspending the paper sample above the aqueous layer in the toluene phase and by employing microwave heating to greatly reduce the time of the reaction (30min @ 90° C vs ≥24 hrs @ 90° C). A small
section of glass tubing, just small enough in diameter to slide inside the microwave reactions vial, was cut to be slightly taller than the depth of the aqueous phase when placed in to a microwave reaction tube. When placed into the reaction tube, the cellulose samples could be rested on the top of the inner glass tube in the toluene phase while a small stir bar was still free to spin within the aqueous phase in the bottom of the tube during heating. (Figure 6.2) This setup allowed Suzuki polymerization/grafting of poly(fluorene) P6.1 to cellulose samples without damage. Additionally, by utilizing MW heating at 90° C for just 30 minutes, the exposure time to the reaction solution was minimized and poly(fluorene) was able to be effectively grafted with the modified paper samples without damage to the substrate while still maintaining high efficiency in the polymerization reaction.(34)

![Diagram of microwave setup](image)

**Figure 6.2: Microwave setup for Suzuki grafting with damage to the cellulose sample.**

After the grafting reaction was complete, the free solution polymer P6.1 was precipitated and analyzed, and was found to be very similar to polymer synthesized in the absence of paper substrates. The molecular weight was analyzed by gel permeation chromatography (GPC, CHCl₃ vs linear polystyrene standards) and found to have a Mₙ~
14.5 kg/mol. (Figure 6.3) While this measurement may not directly represent the degree of polymerization of the grafted polymer, it gives some insight into the efficiency of the reactions and whether or not the presence of the paper samples negatively affect the polymerizations. The $M_n$ values observed are consistent with reported values for solution polymerizations and with control polymerizations without cellulose samples, although the free polymer produced during the grafting reactions generally was more polydisperse compared to commonly observed values for traditional solution polymerizations (PDI ~ 7 vs 2-4, typically).

![Figure 6.3: GPC traces for P6.1, P6.2, and P6.3.](image)

The grafted paper was rinsed extensively with various solvents to remove adsorbed polymer and residual catalyst, then sonicated in THF followed by Soxhlet extraction with THF. After drying in vacuo, static water contact angle measurements were used as a fast, qualitative test to visualize whether or not successful grafting had occurred. The ungrafted cellulose samples show no contact angle before grafting; the pristine paper and the functionalized paper absorbed water droplets almost immediately.
After grafting, the samples were found to be relatively hydrophobic, showing a static contact angle of ~100°. (Figure 6.4) Control polymerizations over pristine paper produced solution polymer, but no polymer was observed on the paper sample after washing with solvent and the paper samples showed no contact angle. The grafted sample was light tan in color by eye and optical microscopy showed no visible difference in the gross morphology of the fibers from the pristine, functionalized, or grafted paper, although a small amount of residue from the polymerizations was noticed, likely colloidal palladium. (Figure 6.5)

Figure 6.4: Static water contact angles for P6.1, P6.2, and P6.3, left to right, respectively.

The polymer modified cellulose samples were also investigated by FT-IR and Raman spectroscopy. Due to the weak absorbance of the conjugated polymers relative to
the cellulose matrix, and perhaps the irregular fibrous structure, no appreciable differences in the infrared spectra were observed between unmodified cellulose paper, modified paper, and the polymer grafted samples. Raman spectroscopy of the grafted samples, however, revealed a new signal at 1613 cm\(^{-1}\) not found in either the unmodified cellulose paper or the Br-phenyl-modified cellulose. (Figure 6.6) This signal has been attributed to a ring stretching mode of the fluorene rings from the conjugated polymer P6.1.\(^{(35, 36)}\)

**Figure 6.6: Raman spectra of grafted samples, modified cellulose, and cellulose.**

In addition to contact angle measurements and Raman, the samples were also investigated using fluorescence spectroscopy. Poly(dihexylfluorene), **P6.1**, has a characteristic blue emission with \(\lambda_{\text{max}}\) near 425 nm when excited by UV light (365 nm). It has been shown that poly(fluorenes) have a maximum effective conjugation length of
approximately 10-15 units, above which its emission properties level off for higher molecular weights.\textsuperscript{(37)} For chains shorter than this size, the emission shifts progressively to shorter wavelengths with decreasing number of repeat units. This gives a quick measure of the conjugation length based on emission wavelength. By comparing the fluorescence of the grafted samples to films of the solution polymer, some insight into the conjugation length of the grafted chains might be gained. For P1, the grafted samples show an emission near 421 nm compared to 427 for a film of the free polymer. (Figure 6.7) This would indicate that the effective conjugation length of the grafted polymer is slightly lower than the solution polymer, which may be a result of either shorter chains or disruption of the conjugated through some conformational twisting of the surface structures.

![Fluorescence Emission](image)

**Figure 6.7:** Fluorescence emission spectra of grafted paper samples and free polymer in solid state. $\lambda_{\text{ex}} = 365\text{nm}$. 

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Paper samples modified to display arylbromide functionality can also participate in other grafting chemistries. The Heck reaction, which couples arylhalides to vinyl groups, was chosen as a possible route to grafted poly(arylenevinylene)s. An A-B polymerization scheme was pursued, requiring the synthesis of a new monomer. A-B type polymerizations are valuable for step-growth reactions, especially on surfaces where absolute control over stoichiometry might not be possible. Starting from 2-bromofluorene, the 7 position was iodinated using I\textsubscript{2} and KIO\textsubscript{3} in acidic media, followed by alkylation at the 9-position with hexyl chains for solubility. The 7-position was then selectively vinylated using tri(n-butyl)vinyl tin, taking advantage of the greater reactivity of the aryliodide vs arylbromide under Stille conditions.

Under typical Heck coupling conditions, we grafted poly(fluorenevinylene) using Pd(OAc)\textsubscript{2} and tri-o-tolylphosphine in dimethylformamide/triethylamine. Microwave heating was not observed to affect an exponential decrease in the time necessary to reach high MW in this particular case. The cellulose samples appeared to survive intact during benchtop heating conditions at 100 °C overnight and the grafting of poly(fluorenevinylene) P\textsubscript{6.2} was accomplished under normal reaction conditions without microwave heating.

After grafting, work-up followed the procedure described for P\textsubscript{6.1}. The solution polymer from the reaction was analyzed by GPC and found to have M\textsubscript{n} ~ 11.8 kg/mol. The PDI of the free polymer was ~ 2, approaching the ideal step growth behavior, and is a result of the A-B polymerization scheme which eliminated the need for exact stoichiometric additions of two separate monomers. Additionally, this A-B scheme may be important for future applications; the end functionality of each chain should be
the bromine group, which may be available for subsequent reactions. Water contact angle again increased from 0° for the bromophenyl-functionalized paper to a relatively hydrophobic 114° after grafting, indicating successful attachment of polymer chains. (Figure 6.4) Optical microscopy showed no visible difference in the gross morphology of the fiber structure. (Figure 6.5) A peak in the Raman spectra was observed at 1615 cm⁻¹ resulting from the fluorene segments of the polymer. (Figure 6.6) Comparison of the fluorescence emissions of the grafted paper and a film of the free polymer showed similar spectra, emitting in the green which is consistent with reported values for poly(fluorenevinylene), although the grafted sample was slightly blue shifted compared to the solution polymer. (Figure 6.7)

Scheme 6.6: Grafting poly(fluorenevinylene) via Heck polymerization.

Poly(arylene-ethynylene)s have attracted attention for use in sensors and other devices which may benefit from the high surface area and nanostructured nature of certain cellulose materials.(23, 39) A poly(fluorene-ethynylene-phenylene) based
polymer, P6.3, was chosen for grafting experiments on the acetylene-functionalized cellulose. Using literature procedures, 2,7-diethynyl-9,9-dihexylfluorene was synthesized from the Sonogashira coupling of 9,9-dihexyl-2,7-dibromofluorene and 2-methyl-3-butyn-2-ol, followed by deprotection under basic conditions. (26) Polymerization and grafting were accomplished under Sonogashira-type conditions with 2,7-diethynyl-9,9-dihexylfluorene and 1,4-diiodobenzene using Pd(OAc)$_2$, PPh$_3$, and CuI in THF/diisopropylamine. (Scheme 6.7) No microwave heating was necessary as the polymerization proceeded at low temperatures (≤ 45° C), producing grafted paper samples under mild conditions.

Scheme 6.7: Synthetic route to poly(fluorene-ethynylene)-based graft via Sonogashira-type polymerization.

The free polymer was found to have $M_n$ ~ 13.5 kg/mol with and PDI ~5. (Figure 6.3) The grafted sample displayed a contact angle of 134°, showing the surface had been covered with grafted material. (Figure 6.4) Optical microscopy showed no visual
disruption of the appearance of the fiber structure. (Figure 6.5) A new peak in the Raman spectrum at 1606 cm$^{-1}$ was observed for P3. (Figure 6.6) The fluorescence spectra for the free polymer and the grafted sample were found to be very similar, with a peak emission at 455 nm, indicating that the grafted polymer and solution polymer are very similar. (Figure 6.7).

6.4 Conclusions
In conclusion, a simple and versatile approach to conjugated polymer grafted cellulose hybrid materials has been demonstrated. Poly(fluorene), poly(fluorenevinylene), and a poly(fluorene-ethynylene) were successfully grafted onto cellulose substrates using Suzuki, Heck, and Sonogashira couplings. The effectiveness of the grafting reactions was monitored by water contact angle changes, fluorescence, and by analysis of the free polymer formed in solution. Analogous application of these grafting chemistries with other monomers will allow application specific tune-ability and give access to virtually any poly(arylene), poly(arylenevinylene) or poly(arylene-ethynylene) grafted cellulose/paper materials. Currently we are exploring the synthesis and applications of lower-bandgap conjugated polymer grafted cellulosic-materials. Particularly intriguing are the prospects of combing these grafting approaches with some of the exciting recent reports of cellulose-based materials chemistry in which metal or metal-oxide nanoparticles can be seeded inside the cellulose fibers.
6.5 References


CHAPTER 7

PATTERN FORMATION ON POLYMER THIN FILMS VIA REACTIVE SILANE INFUSION DRIVEN WRINKLING OF POLY(2-HYDROXYETHYL METHACRYLATE)

7.1 Introduction

Patterned surfaces form the foundation of many areas of materials science including microelectronics, optics, adhesion, etc. Interest in more complex patterns with smaller features has inspired research on pattern formation via spontaneous or self assembling processes such as block copolymer phase separation, breath figures, colloidal crystals, and others.\(^{(1-5)}\) The generation of patterns by wrinkling or buckling thin films has also been investigated for applications in several fields, and offers tantalizing possibilities for self ordering and aligned structures over large areas and on a small size scale.

Generally, wrinkling behavior has been viewed as a problematic occurrence within the fields of lithography, nano-patterning, and other fields.\(^{(6)}\) Indeed, any unwanted surface topology can wreak havoc on traditional, top-down patterning techniques. 

(Figure 7.1)
Figure 7.1: Example of uncontrolled wrinkling behavior observed in an AFM image of a patterned, photo-cured resist which would prevent any further processing in a traditional lithographic process.

However, spontaneous generation of patterns through the control of wrinkling has been studied for some time both in theory and in practical applications.\(^7\) Examples of wrinkling systems found in literature are thin layers of metal or polymer atop a compliant under layer,\(^8-10\) gel-based wrinkling systems,\(^11, 12\) or an oxide formed on the surface of an elastomer,\(^13\) commonly poly(dimethylsiloxane) (PDMS).\(^8, 14\) Mechanical manipulation,\(^15\) thermal expansion,\(^16\) or polymer swelling\(^11, 17, 18\) is generally used to generate the strain required to induce wrinkling, with wavelengths ranging from tens of nanometers to millimeters. It has been shown that the wavelength and amplitude of the wrinkling can be controlled by modifying the thickness and modulus of the wrinkling layers.\(^19\) More interestingly, it has also been demonstrated that wrinkling structures can self order or align at interfaces of topographical or modulus mismatch to create more
complex hierarchical patterns. This allows for patterning of features on a relatively gross size scale using traditional methods followed by the creation of more complex and smaller features simply by applying the proper strain profile to the system. Variations on this theme have been elegantly demonstrated by Whitesides, Hutchinson, Mahadevan, and others.

Along with patterning, chemical functionalization of organic thin films is important for a variety of applications in fields such as coatings, sensors, electronics, catalysis, biotechnology, and nanotechnology.

![Figure 7.2: Surface modification of an oxide using chlorosilanes.](image)

Various silane coupling agents have been used to modify the adhesion and release and other physical properties of oxide surfaces. Alkyl and other functionalized trichlorosilanes have been reacted with different structured oxide surfaces such as flat porous alumina membranes, silica nanoparticles and nanowires, indium tin oxide (ITO), and porous nanostructured metal oxide thin films. Trichlorosilanes have also been used to functionalize surfaces of polymers; plasma treated poly(methyl methacrylate) and PDMS surfaces have been shown to be reactive towards trichlorosilanes. A common feature for these examples is that they rely on the presence
of reactive sites on the surface to which the molecule can bind, generally hydroxyl groups in the case of oxides and silanes. (Figure 7.2) In this work, the hydroxyl functionality of films of the polymer poly(hydroxyethylmethacrylate) (PHEMA) are used in reactions with chlorosilanes. (Figure 7.3)

![Figure 7.3: The repeat structure of PHEMA (top), and a visualization of the surface functionalization of a PHEMA film with a chlorosilane.](image)

The bio-compatible and non-toxic nature of PHEMA has made it an attractive polymer for biomedical applications such as soft contact lenses materials,(34) bone implants,(35) and in controlled drug release.(36) There has been a great deal of interest in functionalizing the hydroxyl groups of PHEMA with various chemical functionalities. PHEMA films, membranes and brushes have been reacted with a variety of acyl chlorides,(37, 38) anhydrides and reactive silanes,(39, 40) modifying their surface energy and chemical functionality. Zhou et al. reported that PHEMA brush layers treated with methyl trichlorosilane showed increased water contact angles while at the same time increased the etch resistance of the ultra-thin functionalized PHEMA brush layer to an
aqueous KI/I$_2$ etch.(40) Conveniently, PHEMA can be dissolved in solvents such as ethanol and methanol while the high concentration of polar hydroxyl groups renders PHEMA generally insoluble in non-polar solvents such as toluene, hexane, etc,. This provides an important pathway to direct chemical treatments towards the surface of PHEMA films and structures without dissolving the film or otherwise disrupting the overall structure. Moreover, PHEMA films can be easily patterned using a number of known techniques including nanoimprint lithography (NIL), (41) photolithography, and e-beam lithography (EBL).(42)

![Silicon Wafer
Silicon Wafer
Wrinkled Film
Toluene, 90 C°](image)

**Figure 7.4:** Wrinkling of a PHEMA film on a silicon wafer via a chlorosilane infusion.

In this work, a new approach for producing patterned thin films which have tailored chemical functionality was developed. This has been achieved through a reactive silane infusion of PHEMA which results in thin films which undergo wrinkling to create surface patterns with tunable wavelengths. (Figure 7.4) The chemical functionality can be controlled by judicious choice of trichlorosilane reagent. In combination with traditional patterning techniques, the wrinkled structures undergo self-ordering, resulting in hierarchical surface patterns, giving simultaneous control over surfaces from the molecular to micro- scales.
7.2 Experimental Section

7.2.1 Materials and Instrumentation

Unless specified, all reagents were used without further purification. Methyl trichlorosilane (99%) and 2-hydroxyethyl methacrylate (98%) were purchased from Acros Organics. Bromophenyl trichlorosilane and heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane (HTS) were purchased from Gelest, Inc., 2,2′-azobis(2-methylpropionitrile) (98%), 1-dodecanethiol (98+%), and trichlorovinylsilane (97%) were purchased from Sigma-Aldrich Company. Silicon substrates (orientation 1−0−0, thickness 605-645 μm) were purchased from University Wafer. All reactions were run under dry N₂ unless otherwise noted.

Film thicknesses were measured using a F20 Filmetrics thin film measurement system. The water contact angles were measured using a VCA Optima surface analysis system with a drop size of 0.5 μL. Atomic force microscopy (AFM) images were collected on a Digital Instruments Nanoscope III in tapping mode under ambient conditions using silicon cantilevers (spring constant 0.58 N/m). RMS roughness was calculated with the AFM manufacturer’s provided software on images of 5μm x 5 μm scan size. X-ray photoelectron spectra (XPS) were recorded with a Perkin-Elmer Physical Electronics 5100 with Mg Kα excitation (15 kV, 400 W). Spectra were obtained at a takeoff angle of 45° (between the plane of the surface and the entrance lens of the detector optics). FTIR spectra were recorded using a Nicolet 6700 FT-IR spectrometer equipped with a Harrick grazing angle ATR accessory (GATR). Spectra were recorded under a steady flow of N₂ to minimize absorbance peaks due to moisture and CO₂ and a clean silicon substrate was used as a background. A Phantom III ICP reactive ion etcher (RIE) from Trion Technology, Inc. was used for oxygen plasma cleaning of substrates.
and etching of the polymer films with \( \text{O}_2 \) and CF\(_4\). The \( \text{O}_2 \) flow rate was set at 49 standard cubic centimeters per minute (sccm), the inductive coupled plasma (ICP) power was set at 500 W and the reactive ion etching (RIE) power was set at 25 W. For the CF\(_4\) etching, the CF\(_4\) flow rate was set at 45 sccm, the ICP power was set at 100 W and the RIE power was set at 20 W. The pressure was set at 250 mT.

Imprinting was performed on a Nanonex NX2000 thermal imprinter using the following program: 1 min. of chamber pumping, a pre-print press of 100 PSI at 100°C for 30 seconds, an imprint press of 400 PSI at 150°C for 30 1 min, and then cooling to 55°C before releasing pressure. For direct imprinting into PHEMA, the imprint was made at 85°C at 150 PSI for 30 seconds.

7.2.2 Polymer Synthesis, Film Formation, and Patterning of PHEMA

*Synthesis of Poly(2-hydroxymethyl methacrylate) PHEMA.* Ethanol (7.5 mL) was added to a test-tube and nitrogen was bubbled for 5 minutes. AIBN (0.07 g, 0.43 mmol), HEMA (5.37 g, 5 mL, and 41.31 mmol) and dodecane thiol (0.43 g, 0.5 mL) were added and the solution was heated under N\(_2\) at 60°C for 4 hours. The solution was cooled down and precipitated dropwise in ethyl ether. The polymer was filtered, washed excessively with ethyl ether, and dried in vacuo at 50°C for 48 hrs to obtain PHEMA (4.5 g, 84%) as a white solid. GPC data (in DMF): \( \text{Mn}=32\text{k; PDI } = 1.37 \).

*Infusion and Crosslinking of PHEMA Films.* A general procedure for infusing and crosslinking PHEMA films of various thicknesses with methyl trichlorosilane is described below. A similar procedure for crosslinking was employed to treat the other PHEMA films. Silicon wafers were rinsed with acetone, hexanes, and isopropanol and dried under a stream of N\(_2\). The wafers were then cleaned under oxygen plasma for 5
minutes prior to use or solution cleaned. Solution cleaning of silicon wafers was accomplished by rinsing with increasingly polar solvents (hexanes, THF, acetone, ethanol), immersing the wafers in a mixture of concentrated sulfuric acid and 30% hydrogen peroxide (5:1 v/v) at 100°C for 30 minutes, rinsing excessively with DI water and ethanol and drying under a stream of N₂. Films of PHEMA were spun onto the cleaned silicon substrate at 3000 rpm for 10 seconds from a 4 wt. % solution in methanol (filtered through 0.45μm PTFE syringe filter). The polymer coated wafers were baked at 50°C in vacuo for 30 minutes to remove residual methanol solvent, placed in a glass reactor flask and covered with 20 mL of toluene. Methyl trichlorosilane (1mL, 5% with respect to volume of toluene) was added to the reactor via syringe. Nitrogen was bubbled through the solution for 5 minutes and the reactor was sealed under nitrogen and heated at 90°C for 4 hours, at which time the reactor then cooled to room temperature. The wafer was removed from the reaction solution and washed extensively with toluene and dried under a stream of N₂.

**Patterning and Silane Infusion of PHEMA Structures.** A silicon substrate containing patterned features etched into its surface was used as the original pattern master. These masters were made by known conventional photolithographic procedures. The silicon mold was rinsed with acetone and isopropanol, lightly O₂ plasma cleaned, and heated on a hot-plate at 130°C for 30 minutes in the presence of n-octyldimethylchlorosilane forming a thin hydrophobic film which served as a mold release layer. The treated mold was washed with toluene and dried. The silicon mold was imprinted into the heated PHEMA thin film and the substrate was allowed to cool with the mold in contact. After
removing the mold, the patterned PHEMA film was infused and crosslinked as described above for the flat films.

Polycarbonate molds were prepared by slitting open the sandwich layers of commercial DVD’s, HD-DVD’s and Blu-Ray Discs, and rinsing away the dye with ethanol. The non-metalized side of the disc containing lines and grooves were dried under N₂ stream and used without further treatment.

Imprinting was performed on a Nanonex NX2000 thermal imprinter using the following program: 1 min. of chamber pumping, a pre-print press of 100 PSI at 100 °C for 30 seconds, an imprint press of 400 PSI at 150 °C for 30 1 min, and then cooling to 55 °C before releasing pressure. For direct imprinting into PHEMA, the imprint was made at 85°C at 150 PSI for 30 seconds. Electron beam lithography was performed using standard techniques. The patterned PHEMA films were infused and cross-linked as described above for the flat films.

7.3 Results and Discussion
Smooth, uniform thin films (50-300nm) were created by spin coating poly(2-hydroxyethylmethacrylate) (PHEMA) onto polished silicon wafers from a methanol solution and then dried. The PHEMA was synthesized via free radical polymerization of 2-hydroxyethylmethacrylate in ethanol, using 2,2’-Azobis(isobutyronitrile) (AIBN), using a small amount of a chain transfer agent (1-dodecanethiol) to keep the MW relatively low for fast dissolvability in alchohol solvents.
The films were then infused with a reactive trichlorosilane by immersing and sealing the wafers in a solution of the silane in hot toluene. The infused films are swollen \textit{in situ} and begin cross-linking as the chlorosilanes condense with the hydroxyl groups, producing a siloxane rich surface and a gradient of crosslink density down to the wafer surface. Stress generated upon cooling and drying the wafers can give rise to a wrinkled surface morphology. The primary wrinkling wavelength and amplitude appears to depend on the thickness of the starting film which can be easily changed by varying the solution concentration and the speed during spin coating. A series of films of varying initial thickness were spun and infused to provide un-oriented wrinkle patterns with varying periodicity and complexity. (Figure 7.5) In the thicker samples, multiple wavelengths can give rise to the more complex structure. (Figure 7.5 c,d)

\textbf{Scheme 7.1: Synthesis of PHEMA via free radical polymerization.}

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

white solid. GPC data (in DMF): $M_n=32,350$; PDI = 1.4
Figure 7.5: 5x5 μm top down AFM images of PHEMA films infused with methyltrichlorosilane. Film thickness before infusion was (a) 50nm, (b) 105nm, (c) 230nm, (d) 295nm. Z = 100nm.

Table 7.1: Thickness and wavelength data for PHEMA films.

<table>
<thead>
<tr>
<th>Spin Solution</th>
<th>As-Spun Film Thickness</th>
<th>Thickness After MTS Infusion</th>
<th>Primary Wavelength</th>
<th>Percent Thickness Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2wt%</td>
<td>48</td>
<td>55</td>
<td>150</td>
<td>14</td>
</tr>
<tr>
<td>4wt%</td>
<td>105</td>
<td>100</td>
<td>250</td>
<td>12</td>
</tr>
<tr>
<td>8wt%</td>
<td>230</td>
<td>311</td>
<td>775</td>
<td>23</td>
</tr>
</tbody>
</table>
Figure 7.6: A plot of wavelength vs original film thickness for methyltrichlorosilane infusion PHEMA wrinkles.

Since the wavelength depends on film thickness of the PHEMA, it can be fabricated into complex patterns simply by varying the thickness of the layer, or by depositing it onto a substrate with raised or depressed features. (Figure 7.7) This is a simple approach to complex, non-traditional patterns that would be very difficult to access with top-down lithography alone.
Previous studies on wrinkling systems generally have focused on a rigid layer on a compliant substrate which is very thick relative to the rigid skin. This leads to a wavelength dependence on thickness (of the rigid layer) of approximately $\lambda \sim h^{1/3}$. The PHEMA system, infused with MTS, clearly displays a more linear behavior between the total film thickness and wavelength. Models which include thin films in which the underlayer is of a meaningful thickness relative to the rigid layer are relative few and do not necessarily match with each other in terms of included variables. A better understanding of this system was needed.

To obtain better insight into the trichlorosilane infusion process and the extent of infusion within the polymer films, a careful etch profile study was performed. Both PHEMA and trichlorosiloxane-infused PHEMA films were subjected to $O_2$ and $CF_4$ plasma etch to determine the etch resistance of the films. A 12 wt.% PHEMA solution in
methanol was used to cast a thicker film of PHEMA on silicon wafer. Initial film thickness of the PHEMA film was 364 nm and increased to 425 nm after infusion with methyltrichlorosilane using similar conditions as described above (5 wt.% of silane in toluene, heated at 90°C for 9 hours). The infused films were exposed to reactive ion plasmas (O\textsubscript{2} and CF\textsubscript{4}) and gradually etched down to different thicknesses. (Figure 7.8 and Figure 7.9) For example, the films were placed in an ICP RIE plasma etcher and exposed to an oxygen plasma and thickness was measured as a function of etch time. PHEMA etched at an average rate of 3.9 nm/sec compared to the etch rate of 1.8 nm/sec observed for the trichlorosilane infused film under O\textsubscript{2} plasma. This lower rate (or increased etch resistance) was anticipated due to increased siloxane content – silicon-containing materials resist oxidation by O\textsubscript{2} plasma compared to hydrocarbons.

![CF4 Etch data for Siloxane Infused and Non-infused PHEMA films](image)

Figure 7.8: Etch data for PHEMA and MTS crosslinked PHEMA under CF\textsubscript{4} etching. The etch rate for PHEMA was 0.5nm/s while the MTS treated films etched at a rate of 2nm/s.
A number of etch experiments were performed and the following relative etch rates were observed: PHEMA in O₂ etch >> infused film in O₂ etch > infused film in CF₄ etch > PHEMA in CF₄ etch. Reactive ion etch (RIE) conditions were optimized to maximize removal of material as gaseous products and minimize any material deposition that can occur at high etch rates. XPS analysis was performed on the samples as a function of etch depth to obtain atomic composition profiles through the thickness of the films. The observed atomic compositions from XPS, particularly that of %Si, are extremely instructive as to the extent of infusion of trichlorosilane and give depth profile information regarding the siloxane linkages within the polymer films. A trichlorosilane infused PHEMA film having an initial thickness of 425 nm was exposed to CF₄ plasma for different time intervals, increasing by 40 seconds, up to 200 seconds. The film

Figure 7.9: Comparison of PHEMA and MTS crosslinked PHEMA under O₂ etch. PHEMA etched at a rate of 1.8 nm/s and MTS treated PHEMA etched at a rate of 3.9 nm/s.
thicknesses at each time interval were measured and the etched films were washed with hexanes to remove any residual redeposition residues left due to etching. The films were dried and then analyzed by XPS. The film thickness gradually decreased from 425 nm to 31 nm as a function of etch time. The average etch rate of the infused film exposed to CF$_4$ plasma was 2.08 nm/sec. The measured %C, %O and %Si as a function of etch depth are shown in Table 1. A steep drop in the %Si and %O is observed reaching a constant level at a depth of approximately 100 nm. A concurrent increase in the %C is observed also leveling off at 100 nm. These data suggest that infusion of PHEMA by trichlorosilane is limited to the outer 100 nm of the films and that complete infusion and homogeneous network formation is not achieved. (Figure 7.10) This observation helps explain the observed wrinkling phenomena as the non-infused PHEMA contracts more than the siloxane-crosslinked network skin, resulting in surface buckling upon solvent removal. The thickness changes before and after infusion also support swelling during infusion and the incorporation of a siloxane network. (Table 7.1)
Based on this data, it would be reasonable to suggest that a skin, ~30 nm thick, of more rigid siloxane linked PHEMA forms during MTS infusion. This would then fit known models using thin film systems which have wavelength depend on total film thickness in a roughly linear fashion.

PHEMA films can be patterned using a number of known techniques including thermal nanoimprint lithography (NIL) (41), photolithography, and e-beam lithography.(42) In the case of NIL, two different approaches were explored; first, a NIL mold was used to directly imprint the PHEMA layer prior to siloxane infusion. For thermal imprinting, two techniques were explored. In early experiments, direct imprinting using a silicon mold was used to lightly imprint the surface of the PHEMA.
films before cross-linking to provide topographical boundaries. This was found to require modification of the silicon mold with a release layer, a fluorinated silane treated, to prevent adhesion between the hydrophilic oxide on the silicon and the hydrophilic PHEMA layer. Even with substantial efforts at producing a cleanly imprinting silicon master, only slight imprints were able to be made as adhesion of the PHEMA to the mold was unable to be completely eliminated. (Figure 7.11)

![Example AFM height images of PHEMA imprinted directly with silicon molds.](image)

**Figure 7.11:** Example AFM height images of PHEMA imprinted directly with silicon molds.

Switching from silicon molds to poly(carbonate) (PC) molds, which are relatively hydrophobic compared to PHEMA, sufficiently eliminated mold adhesion and allowed full depth imprinting of a variety of feature sizes from 600 nm down to 120 nm. The PC molds were conveniently fabricated by opening commercially available, blank, re-writable DVD, HD-DVD, and Blu-Ray discs, which are made from PC and come pre-embossed with lines and grooves which could be used for imprinting PHEMA. (Figure 7.12)
Figure 7.12: Schematic for imprinting PHEMA directly with PC molds and infusion (left), and an AFM height image example of the PC molds (right).

Rinsing away the photosensitive dye sandwiched between the disc layers with ethanol provided a ready-made mold that could be used directly. In a secondary NIL patterning technique, a sacrificial layer of polystyrene (PS) was spun onto the PHEMA film, imprinted, and etched to the wafer. The residual PS was removed using toluene, exploiting the solubility mismatch of PS and PHEMA. The PHEMA was then infused in the same manner as the flat films. In both instances wrinkling patterns were found to show alignment within the areas defined through imprint lithography. (Figure 7.13)

For e-beam patterning, a series of lines (~10nm width) were drawn at increasing intervals from 100nm to 1μm to observe the influence of confinement. No development step was performed before wrinkling, leaving the beam damaged areas to act as boundaries. Subsequent wrinkling revealed alignment near line structures and an interesting confinement effect of producing a herringbone pattern when the boundaries were closer.
than ~2 wavelengths (Figure 7.14). These proof-of-concept experiments illustrate an important advantage for thin film systems directly bonded to silicon wafers; the use of conventional lithographic techniques and equipment already in use for processing wafers could lead to wider adoption and lower costs in industrial scale processes.
Figure 7.13: Imprint lithography patterned PS resist on PHEMA film (a) and directly imprinted PHEMA films (b,c) and subsequent wrinkling (a’, b’, c’, respectively). Images are 10x10μm (a) and 5x5μm (b, c).
In addition to pattern generation, silane infusions have the added possible benefit of imparting chemical functionality into the surfaces. Trichlorosilanes are available with a wide range of chemical functionality or can easily be synthesized with tailored functionality in the lab. Based on our results with methyltrichlorosilane, we extended the infusion concept to trichlorosilanes with some representative chemical functionalities including trichlorosilane (TCS), vinyltrichlorosilane (VTCS), bromophenyltrichlorosilane (BrPhTCS), and a polyethyleneglycol-trichlorosilane (PEG-TCS). These infusions provided surfaces which were cross-linked, had wrinkled surface morphologies, and displayed the chemical functionality of the silane. (Figure 7.15) Evidence of surface functionality was observed in the increased water contact angles of the films after infusion. (Figure 7.15) Compared to the un-infused PHEMA films, the wrinkled films showed more hydrophobic character, giving contact angles of 82° (TCS), 91° (VTCS), 84° (BrPhTCS), and 55° (PEG-TCS). The contact of angle for the PEG-silane infused

Figure 7.14: Top down AFM height images of a PHEMA film patterned with EBL and subsequent wrinkling. Images are 5x5 μm, zoomed area is 2x2 μm. Z scales for a, b, & c are 10, 100, and 50nm respectively.
PHEMA closely matches the value previously reported for a PEG-functionalized PHEMA sample.\(^{(43)}\) Surface functionality was also analyzed by grazing-angle attenuated total reflectance FT-IR (GATR-IR). (Figure 7.16) A decrease in the –OH intensity near 3400 cm\(^{-1}\) is consistent with the reaction between the trichlorosilanes and the hydroxyl groups in the PHEMA film. The functional groups can most easily be observed through the rise of new peaks occurring at ~2340 cm\(^{-1}\) (Si-H of TCS), ~1600 cm\(^{-1}\) (C=C of VTCS), ~1540 cm\(^{-1}\) (C-C of BrPhTCS), and ~ 875 cm\(^{-1}\) (C-H of PEG-TCS).

![Figure 7.15: PHEMA films wrinkled with (a) PEG-TCS, (b) Vinyl-TCS, (c) BrPh-TCS, and (d) TCS showing water contact angles (inset) of 55°, 91°, 84°, and 82°, respectively.](image-url)
These experiments illustrate the versatility of wrinkling via silane infusion and show promise for subsequent surface science such as brush growth, responsive surfaces, etc. Si-H surfaces have the potential to be transformed into nearly limitless other functionalities using hydrosilylation chemistries, while the vinyl- and bromophenyl-surfaces may lend themselves to polymer brush attachment or coupling reactions; patterned PEG surfaces may find utility in helping to control biological interactions with surfaces.

Figure 7.16: Grazing angle FT-IR of functional wrinkled films.
7.4 Conclusions
In this work, a new method was developed for creating cross-linked, functional thin films via a reactive silane infusion of PHEMA. Wrinkling morphologies can be induced during the infusion process, which can self-order within lithographically defined boundaries to provide hierarchical structures and complex patterns with tailored surface chemistry. The techniques described in this work allow control over both the morphology and the chemical nature of the surface and could be a powerful tool to expand potential applications wrinkling-based systems. Regardless of ultimate application, however, progress for surface oriented science is certain to become ever-more dependant on systemic control of hierarchical order. Controlling surfaces at the micro-, nano-, and molecular level simultaneously will be crucial for future advancements of surface and material science.

7.5 References


41. "Imprint lithography on poly(2-hydroxyethyl methacrylate), (PHEMA), and epoxydised novolac, (EPN) polymers," *2008*.


BIBLIOGRAPHY


Davidson, G., et al. "Deboronation of Ortho-Carborane by an Iminophosphorane: Crystal Structures of the Novel Carborane Adduct \(Nido\text{-}C_2B_{10}H_{12}\text{HNP}(NMe_2)_3\) and the Borenium Salt \([(Me_2N)_3PNHB(NMe_2)_3]_2O_2^+\text{-}(C_2B_9H_{12})_2\)." Chemical Communications 17 (1999): 1649-50.


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