Synthesis, Reactions, and Applications of Bis-ortho-diyynyl Arene (BODA) Monomers, Polymers, and Derivatives

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SYNTHESIS, REACTIONS, AND APPLICATIONS OF BIS-ORTHO-DIYNYL ARENE (BODA) MONOMERS, POLYMERS, AND DERIVATIVES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Mark Wilson Perpall
May 2007

Accepted by:
Dr. Dennis W. Smith, Jr., Committee Chair
Dr. Stephen E. Creager
Dr. Dev P. Arya
Dr. Jason McNeill
This work focuses on the expansion of the scope of processability, reactivity, and synthesis of bis-ortho-diynyl arenes (BODA) monomers. This unique class of monomers consists of molecules that contain two arenediyne functional groups linked together through a variable spacer group X. There is also variable functionality at the alkyne terminal group, R. These arenediyne moieties undergo thermal Bergman reactions to cycloaromatize and form naphthyl diradical species. The inclusion of two of these arenediyne functionalities allows the polymer to grow without losing processability and solubility as most aromatic polymer do. The second functionality acts as a solubilizing group until all functionalities are consumed in the fully cured network polymer.

BODA polymers were initially developed as processable high-yield carbon precursors. When heated above 800 °C, the polymer converts to a glassy carbon material. This work has been extended with the fabrication of nano-scale features in a carbon inverse opal photonic crystal. The carbon inverse opal structure consists of 3-dimensionally alternating carbon and voids. The wavelength excluded depends on both the fixed scale of the periodicity and the dielectric contrast between the carbon and the voids. This has been demonstrated by using the carbon inverse opal as a sensitive detector element by filling the voids with solvents to detect concentrations, the liquid crystal 5CB to detect the phase change, and hemoglobin in buffered solutions.

Disordered porous foam has also been developed for use as an electrode material in H₂ fuel cell MEAs. The pore size and surface area are examined as a function of
BODA monomer functionality. Bimodal carbon foams that consist of nanoporous foam coating the interior surfaces of a macroporous foam are also demonstrated. Compatibility between the carbon electrode and fluorinated proton exchange membrane has been addressed by the development of a new carbon surface fluorination technique involving a trifluorovinyl ether containing diazonium salt.

BODA produced radicals have been demonstrated to be capable of direct surface addition reactions to functionalize and solubilize fullerene materials. This is demonstrated with both C\textsubscript{60}, and the newer carbon nano-onion materials. The copolymers thus produced are examined by TEM, Raman, TGA, MALDI-TOF MS, GPC, MALLS, and solubility tests. This is one of the first additions of a conjugated polymer to a C\textsubscript{60}, and of any polymer to CNOs. The copolymers may have applications in photovoltaic materials.

BODA chemistry has been extended with the complementary technology of mono-ortho-diynyl arene (MODA) monomers. These monomers consist of one enediyne group and a functional group on the ring. Six MODA monomers have been synthesized and their utility has been demonstrated as a way to increase the chain length between crosslinks in a BODA network, a way to endcap a functional oligomer to produce a BODA macromonomer as demonstrated with the endcapping of a poly(aromatic ether sulfone) , and as a route to new previously unattainable BODA monomers, as demonstrated with a fluorescent monomer.
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I sincerely thank all of the people who have enabled me to pursue this goal.

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CHAPTER 1

INTRODUCTION

Polyarylenes

This work focuses on advances and application of bis-ortho-diynyl arene (BODA) monomers and the high-performance polyarylenes and copolymers derived therewith. Polyarylenes are a broad class of polymers with aromatic moieties in the repeat unit. Broadly, they are considered very valuable materials due to their unique combination of high-performance properties. Polyarylenes have been utilized for applications ranging from engineering materials, due to their mechanical strength and high thermal and environmental stability; to optoelectronic materials due to their electro- and photoluminescence and potential for conductivity as organic electronics; to ceramic carbon precursors, due to their dimensional stability, and high thermal stability. The most common polyarylene backbones are poly(para-phenylene)s (PPP), polythiophenes (PT), polyfluorenes, polybenzoxazoles, polybenzimidazoles, phenolic resins, and nitrogen heterocycle containing polymers including polyaramides and poly(2,7-carbazoles), Scheme 1-1.

A wide variety of methods exist to synthesize polyarylenes. Many polyarylenes are produced using coupling reactions. PTs are produced from the Lewis acid (FeCl₃ or AlCl₃) enabled oxidative coupling of 3-alkylthiophenes, producing soluble high-molecular-weight polymers. Polyfluorenes are synthesized via the reductive Ni(0)
catalyzed coupling of 9,9-dialkyl-2,7-dibromofluorenes. Many other polymers are formed from cross-coupling reactions of either AB or AA to BB type monomers. Suzuki condensations have been used to produce PPP from both the homocondensation of 4-bromo-2,6-dialkylphenyl-boronic acid, and the cross-condensation of 1,4-dibromo-2,5-dialkylbenzenes with 2,5-dialkylphenyl-1,4-diboronic acids, yielding soluble

\[
\begin{align*}
\text{poly(paraphenylenne)} & \quad \text{poly(3-alkylthiophene)} & \quad \text{poly(2,7-fluorene)} \\
\text{polybenzoxazole} & \quad \text{poly(2,7-carbazole)} & \\
\text{polybenzimidazole} & \quad \text{polypyrrole}
\end{align*}
\]

**Scheme 1-1.** Examples of common polyarylenes structures.

stereoregular polymers. Stereoregular 3-alkyl PTs have also been synthesized using Kumada couplings of 2-magnesium bromide-5-bromo-3-alkyl thiophenes with a Ni(II)
catalyst\textsuperscript{15} or Negishi coupling of 2-zinc bromide-5-bromo-3-alkyl thiophenes with another Ni(II) catalyst.\textsuperscript{16} Metal catalyzed coupling is hindered however by high cost and difficulty associated with catalyst removal.

Polyphenylene has also been synthesized from benzene using a unique precursor method involving oxidation to 1,2-dihydrocatechol, conversion of the alcohols to acetates, and radical polymerization of the internal diene to yield poly(3,6-(1,2-diacyetyl-4-cyclohexene).\textsuperscript{17} This soluble polymer may then be processed into a film and baked at 310 °C under vacuum to eliminate two equivalents of acetic acid and yield insoluble PPP.

Condensation polymerizations also make use of this type of precursor route for polyarylene synthesis, especially poly(phenylene oxadiazole).\textsuperscript{18} First the precursor polymer is formed from the condensation polymerization of 1,4-di-(2,5-dialkoxyphenyl)acetyl chloride with 1,4-di-(2,5-dialkoxyphenyl)hydrazide, then dehydrated with phosphoryl chloride to yield the poly(phenylene oxadiazole).

Polyimides are formed from the reaction of dianhydrides with diamines,\textsuperscript{19} where the amine functionality first ring-opens the anhydride to form the precursor polyamide. Dehydration of the carboxylic acid and the secondary amide linkages yields the aromatic polyimide. Polybenzimidazole (PBI) is formed from the condensation of an aromatic tetramine with an aromatic dicarboxylic acid or the synthon of an aromatic diester.\textsuperscript{20} Here the initial condensation leads to an aromatic amine-amide, which then cyclizes through a nucleophilic addition and removal of the water or alcohol to form the final polymer product. Other condensation polymers are formed in one step including polybenzoxazoles and polybenzthiazoles, formed from the reactions of an aromatic
dicarboxylic acid with either a difunctional \( o \)-aminophenol or a difunctional \( o \)-aminothiol as appropriate.\(^{21}\)

Still other polyarylenes, such as PT, polyaniline (PAN), polycarbazole, and polypyrrole are formed by electrochemical polymerization.\(^{22}\) This involves the oxidation of a monomer (for example pyrrole) at the anode of an electrochemical cell to form a radical cation, which then couples with another radical cation to form a dimeric dication which is then reduced at the cathode to the neutral species. The polymer thus grows in a stepwise fashion. For most of these polymers, carbon-carbon bonds are formed between the monomers, but PAN grows through the amine coupling with the arene to include the amine in the backbone of the polymer. The electrically conductive doped polymers formed from electrochemical polymerization usually precipitate out of solution and coat the surface of the anode.

Enediynes

Enediynes, or more formally \( cis \)-enediynes, undergo a thermal rearrangement reaction first postulated by Robert Bergman in 1972,\(^{23}\) to form a reactive intermediate 1,4-didehydrobenzene. The Bergman reaction, as it is now known, is reversible and thus may lead to two different enediyne product via the reverse reaction (Scheme 1-2). The Bergman reaction has been shown to be a unimolecular reaction.\(^{23}\) The 1,4-diradical aromatic intermediate was confirmed with trapping of the radical intermediate formed from \( cis \)-3-hexene-1,5-diyne with the hydrogen radical source 2,6,10,14-tetramethylpentadecane to yield benzene, with \( CCl_4 \) to yield 1,4-dichlorobenzene, and with methanol to yield anisole.\(^{23}\) The reactivity of the diradical intermediate is related to
the inability of the radicals to homocondense to form an intramolecular sigma bond, and to their orthogonality to the plane of the aromatic species.\textsuperscript{24}

\begin{center}
\includegraphics[scale=0.5]{scheme1.png}
\end{center}

\textbf{Scheme 1-2.} Bergman cyclization of enediynes is a reversible concerted radical cycloaromatization to 1,4-didehydroaromatic. The interalkyne distance $d$ is shown.

Bergman cyclization of enediynes has shown up in the mechanism of several naturally occurring anti-tumor agents,\textsuperscript{25} reportedly due to DNA intercalation and hydrogen abstraction by the radical intermediate, hindering DNA’s role in cell reproduction, and thus weakening tumors. Many enediyne-containing synthetic targets have been investigated to study this property and develop more selective antitumor compounds.\textsuperscript{26}

The 6-membered Bergman cyclization product is the thermodynamically preferred pathway for the thermal rearrangement of an enediyne, as well as for the aromatic analogue, an arenediyne. There do exist, however, other kinetic reaction pathways that play roles of varying importance based on the reactive conditions, such as the presence of metal catalysts, nucleophilic, or electrophilic reagents. The five-membered ring closure product is a benzofulvene,\textsuperscript{27,28,29,30} and the 4-membered ring closure product is a benzocyclobutane (\textbf{Scheme 1-3}).\textsuperscript{31} The favorability of these cyclizations are described by the Baldwin rules,\textsuperscript{32} which define ring closures based on 1)
the size of the ring being formed, 2) the geometry of the electrophilic atom (tet for sp\(_3\), trig for sp\(_2\), and dig for sp hybridizations), and 3) the location of the displaced electrons on the product (endo for in the formed ring, or exo for out of the formed ring). Therefore, according to this nomenclature, the Bergman product is a 6-endo-dig product, the benzofulvene is a 5-exo-dig product, and the benzocyclobutane is a 4-exo-dig product. The Baldwin rules indicate that the 6-endo-dig and the 5-exo-dig products are favored, but the 4-exo-dig product is disfavored.

Among the many factors affecting the Bergman reaction, the substituents on the enediyne have the largest effect on both the kinetics of the reaction, and the resultant product. The trans-alkyne distance, \(d\), (Scheme 1-2) is defined as the distance between the terminal carbons of the alkynes, and has been shown to have a major effect on the reaction kinetics.\(^{33}\) The trans-alkyne distance is in turn affected by the steric size of the terminal substituents, and the presence of coordinating metals.\(^{34,35}\)
Enediyne Polymers

Several polymer systems have been designed with the enediyne functional group as a reactive handle towards polyarylenes (Scheme 1-4). Keller et al. first reported in 1993 on their studies on the synthesis and cure chemistry of multiple phenylethynyl-containing benzene compounds (Scheme 1-4 A). The resins obtained from these monomers showed good thermal stability and high carbon yields. The substitution pattern of the phenylethynyl groups on the benzene core was correlated to the thermal oxidative stability of the carbons. The order of stability was 1,2,4,5-substituted > 1,2,4-substituted > 1,3,5-substituted benzene, indicating that ortho-substitution leads to a denser carbon. Grubbs et al. also reported in 1993, on acetylenic conjugated polymers synthesized from 1,2-diethynylaryl precursors. Swager et al. then reported on ladder polymers and macrocycles (Scheme 1-4 B, synthesized from diacetylene containing precursors formed from the oxidative coupling of 1,2-diethynyl benzene derivatives). These precursor polymers were very reactive, and indicated a chain-addition polymerization mechanism. The tetraradical product from the cyclization of the macrocyclic dimer (n=1) was trapped with I₂, and indicated the benzofulvene structure was forced by the strained geometry.

Then Tour et al. began experimenting with producing linear polyarylenes from enediynes (Scheme 1-4 C) and arenediynes (Scheme 1-4 D) to produce substituted PPPs and poly(1,4-napthalenes) respectively. Trapped radical species confirmed the structure of the cyclized species. Kinetic studies indicated that the polymerization occurred by a step-growth mechanism, where each monomer is cyclized to form the diradical, then radical couples to form a higher molecular weight diradical. This is in
Scheme 1-4. Enediyne Derived monomers and polymers.
contrast to the other possible mechanism whereby a small fraction of monomers thermally cyclize and initiate a radical chain-growth polymerization, by reacting with other uncyclized enediyne monomers. These two mechanisms are distinguished by following the growth of the polymer molecular weight relative to monomer consumption. In the step-growth mechanism, the molecular weight grows slowly, until nearly all of the monomer has been consumed, then rapidly grows as larger oligomeric species couple. In chain growth, the molecular weight grows rapidly at high monomer concentrations then slows as the monomer reserves are depleted.

Tolbert et al. reported in 2001, on the synthesis of an enediyne containing prepolymer produced from the radical initiated vinyl polymerization of 3,4-bis(phenylethynyl)styrene (Scheme 1-4 E). This polymer was designed and tested as a plasma etch resistant material and was shown to be superior to conventional organic reactive ion etching (RIE) materials.

Thorough structural comparisons of arenediyne polymerizations indicate that the products are not simply polynaphthalenes but rather more complex copolymers of naphthalenyl as well as the five-membered benzofulvenyl structures and possibly even polyacetylenyl repeat units.

All of these polymers, however, were limited in their usefulness due to the inability to produce soluble, high molecular weight polymers. Many of these polymers required the addition of solubilizing alkyl side-chains, or were only characterized as soluble oligomers. The inherent insolubility and infusibility is largely associated with the chain rigidity limits the applicability of what are otherwise high-performance materials.
BODA polymers characterization.

In 1998, Smith et al. first reported the synthesis and characterization of a new class of bis-enediyne containing monomers that extended the concept of Bergman polymerizations and eliminated many of the drawbacks. Bis-ortho-diynyl arene (BODA) monomers are similar tetrafunctional and structurally similar to two of the monomers prepared by Tour et al. connected by a bridging group.

**Scheme 1-5.** Thermally initiated cycloaromatization and radical polymerization of BODA monomer to intermediate branched and fully cured polymer network. Further eating in an inert atmosphere leads to high yield glassy carbon.

Complete reaction of the enediyne functionalities of BODA monomers leads to crosslinked network versions of these polymers (Scheme 1-5 illustrates the idealized polynaphthalenyl structure for clarity of the branching scheme, though the actual backbones are probably more akin to the poly-(naphthalene-co-benzofulvene) structure illustrated in Scheme 1-6). The intrinsically branched architecture resulting from the
Scheme 1-6. Structure of poly(naphthalene-co-benzofulvene) likely produced from radical polymerization of arenediynes, including BODA monomers.

tetra-functionality of BODA monomers lead to oligomers with excellent melt and solution processability which can be utilized in molding and coating applications prior to final cure.\textsuperscript{46} The cured BODA network polymers also serve as excellent precursors to glassy carbonaceous material.

Scheme 1-7. BODA monomer synthesis from bisphenols (X(PhOH)\textsubscript{2}), via bromination, triflation, and Sonagashira coupling of terminal acetylenes (HCCR).

BODA monomers are prepared from commercially available bisphenols in three high-yielding steps: selective ortho bromination, trifluoromethyl sulfonato esterification (triflation), and finally Sonagashira coupling of terminal alkynes as shown in Scheme 1-
7. Polymerization grade monomers (99+\% pure) are purified by either recrystallization from acetone/ water mixture or by flash chromatography over silica or neutral alumina. The monomers may be easily varied in both the bridging group, X, by changing the starting bisphenols, and at the alkyne terminal position, R, by changing the alkyne used in the coupling reaction. The crystal structures of two polymorphs of monomer 1-1 have been solved (Figure 1-1). Monomer 1-3 also exhibits polymorphism as shown in Figure 1-1.47-48

Figure 1-1. Single crystal x-ray diffraction structures of the three concomitant crystalline polymorphs of Monomer 1-1 (X = C(CF3)2, R = Ph)49

BODA-derived branched polymers and crosslinked polyarylene networks are able to overcome the processability-performance trade-off issues common to linear polyarylenes. As with other cyclopolymerizations of enediynes, polymerization of BODA monomers requires no catalysts or initiators and produces no condensates.40 Unlike the linear polyarylenes, however, the branched oligomer and polymer structures resulting from the inherent tetra-functionality of BODA monomers greatly improves both
their melt and solution processability making them suitable for molding and coating applications.

![Differential scanning calorimetry scans of α and β crystalline polymorphs of monomer 1-1, showing the two distinct melting endotherms, and the large polymerization exotherms.](image)

**Figure 1-2.** Differential scanning calorimetry scans of α and β crystalline polymorphs of monomer 1-1, showing the two distinct melting endotherms, and the large polymerization exotherms.\(^{49}\)

Phenyl substitution at the R position in BODA monomers provides large melt processing windows ranging from 4-5 hours at 210 °C between monomer melt, and polymer network gellation, as measured by dynamic mechanical spectroscopy. The polymerization exotherm of BODA monomers in the melt are detected by differential scanning calorimetry (DSC, 10 °C/min) with onset at 200-210°C. The resulting thermal reaction profiles are consistent with known phenyl substituted arenediynes (**Figure 1-2**).

Several BODA monomers exhibit polymorphism as revealed by DSC measurements. For example, two crystalline forms of 1-1 have been observed and isolated. DSC measured polymerization profiles of both polymorphs were almost
identical as shown in Figure 1-2, showing the melting of the α phase melts at 166 °C and immediately recrystallizes to the more stable β form, which melts at 192 °C. Then a stable melt window opens before the onset of polymerization near 210 °C then a peak exotherm at 310 °C and a return to baseline near 380 °C.

![Graph](image)

**Figure 1-3.** Monomer consumption during polymerization indicates first-order polymerization kinetics for both melt and solution polymerization.\(^4^9\)

Early studies of BODA polymerization kinetics by isothermal and dynamic DSC techniques revealed that the polymerization follows first-order kinetics with activation energies of 129.7-142.3 kJ mol\(^{-1}\). These values are consistent with the values reported by Keller\(^3^7\) for tetrakis(phenylethynyl)benzene. The first-order kinetics indicate a chain addition polymerization mechanism where each diradical cyclized monomer produced is surrounded by an essentially infinite concentration of uncyclized enediyne monomer with which it reacts. This is supported by a rigorous kinetic study of alkyl substituted 1,2-diethynylbenzenes that also found first-order reaction kinetics with \(E_A = 105.0 \pm 3.3\) kJ/mol for the 1,2-diethynyl benzene, and \(E_A = 142.3 \pm 1.3\) kJ/mol for the more sterically substituted 1,2-bis-(methyl, hept-2-ene-6-yneate).\(^4^9\) Plots of monomer conversion (by
GPC) versus time also show first-order rates for both neat and solution (1.2 M in tri-*iso*-propylbenzene) polymerization as shown in Figure 1-3. The observed rate constant for neat polymerization $k_{obs} = 6 \times 10^{-5} \text{ s}^{-1}$ from Figure 1-3 agrees with the value predicted from DSC of $k = 4 \times 10^{-5} \text{ s}^{-1}$ at 210 °C. The thermal properties of monomers 1-1—1-5, including monomer melting points, heats of polymerization, activation energies and approximate gel time at 210 °C, are compared in Table 1-1. The polymerization of BODA monomers proceeds faster in solvents without abstractable hydrogen atoms. Polymerization in tri-*iso*-propylbenzene significantly retards the rate of polymerization, when compared to other solvents such as diphenyl ether, due to the abstractable aliphatic protons.

Table 1-1. Thermal Properties of BODA monomers 1-1—1-5.\(^{49}\)

<table>
<thead>
<tr>
<th>BODA monomer</th>
<th>$T_m$ (°C)[a]</th>
<th>Exotherm -ΔH, (kJ mol(^{-1}) alkyne)[a]</th>
<th>$E_a$ (kJ mol(^{-1}))[b]</th>
<th>Gel Time at 210 °C (h)[c]</th>
<th>Wt. Loss at 450 °C (%/h) [d]</th>
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<tr>
<td>1-1</td>
<td>$\alpha = 163$</td>
<td>110.9</td>
<td>130.1</td>
<td>3.5</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>$\beta = 190$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-2</td>
<td>$\alpha = 108$</td>
<td>103.7</td>
<td>131.0</td>
<td>3.2</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 144$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-3</td>
<td>$\beta = 173$</td>
<td>112.3</td>
<td>139.3</td>
<td>2.9</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 182$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-4</td>
<td>$\alpha = 114$</td>
<td>104.6</td>
<td>136.8</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>1-5</td>
<td>$\alpha = 147$</td>
<td>107.5</td>
<td>142.3</td>
<td>&gt; 4</td>
<td>3.0</td>
</tr>
</tbody>
</table>

[a] DSC (5 °C / min) in nitrogen. [b] DSC nth order kinetics. [c] Gel point to vitrification by dynamic mechanical spectroscopy (parallel plate). [d] TGA at 450 °C for 10 h in N\(_2\).

Variation of the X spacer group did not have a measurable effect on the rate of polymerization for monomers 1-1—1-4, as measured by DSC, but the polymerization onset of monomer 1-5 was found to be significantly higher (271 °C) than the other
BODA monomers including the hexafluorine containing structural analog 1-1 (210 °C). This difference in reactivity has not been explained, but single crystal x-ray structures of monomers 1-1 and 1-5 suggest that they have nearly identical trans-alkyne distances. It has been suggested that the overall slow polymerization rate stems from the abstraction of hydrogen from the isopropyl spacer group by the aggressive phenyl radicals formed from monomer 1-5.

![Figure 1-4. Gel permeation chromatograms (GPC) of BODA polymerization at different reaction times inset in extracted UV-Vis spectra of separated oligomers as a function of GPC retention times.](image)

Reactive oligomeric mixtures of controlled molecular weight were obtained through melt polymerization of monomers 1-1—1-5 at 210 °C (Figure 1-4). Molecular weights of 3000-24,000 M₆ and polydispersities (M₆/M₈) of 3-11 were obtained by GPC vs. polystyrene. The UV-Vis spectra of oligomer fractions of increasing molecular weight of poly1 (210 °C for 12 h), extracted from the photodiode array detector of the
GPC, shows a bathochromic spectral shift with increasing molecular weight indicative of the evolving extended conjugation and electronic band structure in these materials. GPC molecular weight distributions are also illustrated in Figure 1-4 (inset).

![IR spectra of BODA monomer and polymer](image)

**Figure 1-5.** IR spectra of BODA monomer 1-1 (X = C(CF₃)₂, R = Ph, solid lines) and polymer (dashed lines) for (a) alkyne region and (b) substituted naphthalene region.⁴⁹

BODA monomer polymerization has been followed by *in-situ* infrared spectroscopy (IR, **Figure 1-5**)⁴⁹ The IR spectra of monomer 1-1 shows an alkyne stretch at 2214 cm⁻¹ that gradually disappears upon heating to the fully cured thermoset. The mono-substituted phenyl bending mode observed at 688 cm⁻¹ in the monomer shifts to 701 cm⁻¹ in fully cured polymer. The phenyl wagging at 754 cm⁻¹ lessens in intensity. Otherwise, only subtle shifts and peak broadening in the mono- and tri-substituted phenyl absorbances are observed, **Table 1-2**. The IR data assignments are supported by the model compounds shown in **Table 1-3**:⁵¹ the phenyl bend of BODA monomers (685- 688
cm$^{-1}$) is modeled by diphenylacetylene (688 cm$^{-1}$) and the phenyl bend fully Bergman cyclized BODA networks (698-700 cm$^{-1}$) is modeled by 1,2-diphenyl benzene (694 cm$^{-1}$). The phenyl wag mode (750-756 cm$^{-1}$) is independent of the monomer substitution. The existence of benzofulvenes is assumed in the polymer as well, as they are very difficult to distinguish from the naphthalene absorbance bands, and are seen in similar polymers. No bands indicative of aliphatic or olefinic linkages are observed in the IR spectra for any BODA derived polymer networks, though they are seen in similar polymers derived from thermal polymerization of 1,2-ethynyl benzenes.

Table 1-2. IR peaks for BODA monomer 1-1 (X = C(CF$_3$)$_2$, R = Ph) and polymer.$^{49}$

<table>
<thead>
<tr>
<th>Vibrational Mode</th>
<th>IR Frequencies (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH stretch</td>
<td>3059, 3026</td>
</tr>
<tr>
<td></td>
<td>3060, 3027</td>
</tr>
<tr>
<td>CC Ring Stretch</td>
<td>1599,† 1500,† 1442†</td>
</tr>
<tr>
<td></td>
<td>1599, 1494, 1442</td>
</tr>
<tr>
<td>In-plane CH bend</td>
<td>1210, 1185,† 1137</td>
</tr>
<tr>
<td></td>
<td>1203, 1136</td>
</tr>
<tr>
<td>Out-of-plane CH bend</td>
<td>966,† 914, 719, 688†, 754</td>
</tr>
<tr>
<td></td>
<td>964, 825, 725, 694, 754</td>
</tr>
<tr>
<td>CF Stretch</td>
<td>1253</td>
</tr>
<tr>
<td></td>
<td>1252</td>
</tr>
<tr>
<td>Alkyne Stretch</td>
<td>2215</td>
</tr>
<tr>
<td></td>
<td>none</td>
</tr>
</tbody>
</table>

† Contributions from terminal phenyl group.

Solution $^{13}$C NMR of monomer 1-1 shows a decrease in the alkyne signals at 87.3, 87.5, 94.6, and 95.6 ppm upon polymerization.$^{49}$ Pendant and branched terminal arenediyne groups (not observed in the IR due to symmetric stretching) formed during polymerization are seen as new $sp$ carbon peaks (Scheme 1-5). Multiple broad carbon signals from 124-134 ppm around the aromatic methyne and $ipso$ monomer signals indicate that naphthalene and benzofulvenes structures are both formed during polymerization.
Table 1-3. IR bands of BODA monomers 1-1—1-5 their polymers compared to model compounds.\textsuperscript{49}

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Phenyl Bend</th>
<th>Phenyl Wag</th>
<th>Polymer</th>
<th>Phenyl Bend</th>
<th>Phenyl Wag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenyl model*</td>
<td>689 *</td>
<td>750 *</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>polymer model**</td>
<td>699**</td>
<td>750**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BODA 1-1</td>
<td>687</td>
<td>752</td>
<td>700</td>
<td>756</td>
<td></td>
</tr>
<tr>
<td>BODA 1-2</td>
<td>685</td>
<td>750</td>
<td>698</td>
<td>754</td>
<td></td>
</tr>
<tr>
<td>BODA 1-3</td>
<td>688</td>
<td>752</td>
<td>698</td>
<td>754</td>
<td></td>
</tr>
<tr>
<td>BODA 1-4</td>
<td>688</td>
<td>754</td>
<td>698</td>
<td>741</td>
<td></td>
</tr>
<tr>
<td>BODA 1-5</td>
<td>689</td>
<td>755</td>
<td>700</td>
<td>756</td>
<td></td>
</tr>
</tbody>
</table>

all IR frequencies in cm\textsuperscript{-1}.

Solid state \textsuperscript{13}C CP-MAS NMR for the cured polymer from monomer 1-1\textsuperscript{49} showed broad signals at 115-150 ppm which correspond to both the aromatic carbons and the benzofulvene structures produced in the polymer (Figure 1-6). A quaternary signal at 65 ppm is attributed to an intact C(CF\textsubscript{3})\textsubscript{2} of the X group. Another quaternary signal at 55 ppm may be attributed to radical addition side reactions. Alkyne signals are not observed in the fully cured (450 °C) polymer network.

Glass transition temperatures (T\textsubscript{g}) are not observed for the fully cured polymer networks, by either DSC or thermomechanical analysis (TMA) below 400 °C.\textsuperscript{49}

Parallel plate capacitance measurements showed dielectric constants ranging from 2.5-2.7 for cured films of network BODA polymers.\textsuperscript{49}
BODA derived oligomers and polymers exhibit visible luminescent properties, characteristic of many $\pi$-conjugated organic polymers. Solid state absorbance spectra of BODA oligomers and fully cured networks of monomer 1-1 (Figure 1-7) lack a well defined $\pi-\pi^*$ band gap and vibronic features commonly observed in linear polyarylenes and polyarylene vinylenes. This has been attributed to branching which leads to a broad distribution of conjugation lengths and therefore of $\pi-\pi^*$ transitions, and to the presence of both naphthalene and benzofulvene structures in the backbone.

Superposition of the various absorptions from the branches should lead to a broad emission spectrum, but instead the emission profile from processable oligomers show a red-orange peak at about 615 nm, and the fully cured networks red-shift 100 nm to a deep-red emission, because the emission occurs from the states with the lowest $\pi-\pi^*$ energies. This intense coloring characteristic of polymers derived from cyclized arenediynes supports the distinction of these polymers from strict polynaphthalene which has a pale ivory color due to nonplanarity of the monomer units.
BODA-derived polymers have been determined to be among the most thermally stable organic polymers known by both isothermal and dynamic thermogravimetric analyses (TGA) in nitrogen and air. Monomers were isothermally heated at 3 °C/min to 325 °C followed by 2 h isothermal cure and continued heating at 3 °C/min to 450 °C. The equilibrium isothermal weight loss rates at 450 °C were found to be 0.7 %/hour for monomer 1-1 and between 0.5-1.5 %/hour for other BODA monomers (Table 1-1).

BODA polymer networks cured at 450 °C were heated to 1600 °C in nitrogen and air to measure densification of the networks and glassy carbon yields. A rapid weight loss of about 20% starting at ~500 °C is observed during the carbonization process for samples heated in N₂. With further heating, a gradual weight loss is observed between

Figure 1-7 Thin film absorbance and emission spectra of processable oligomer and fully cured network from monomer 1-1 (X = C(CF₃)₂, R = Ph, normalized).
Figure 1-8. Thermal gravimetric analyses (TGA) of monomer 1-1 in both N₂ and air.¹⁹

1100-1600 °C attribute to further carbonization or graphitization. Samples heated in air completely degrade between 500 and 700 °C, but is stable at 494 °C in air indicating very high thermal stability of cured networks in oxidative atmosphere (Figure 1-8).¹⁹ Equilibrium carbon yields at 900 °C for other monomers range from 80-90 %. Pyrolysis of BODA polymers yields electrically conductive monolithic glassy solids. BODA derived carbon properties will be discussed in chapter 3.

Figure 1-9. MALDI-TOF MS of BODA polymerization relative to reaction time.
BODA polymerizations have been followed by matrix assisted laser desorption ionization-time-of flight mass spectrometry (MALDI-TOF MS, Figure 1-9). Different length oligomers were observed with the m/z of the long-lived diradical species up to the dodecamer. The hydrogen end-capped species were not observed. The distribution of molecular weights observed were indicative of a step-growth mechanism.

![Figure 1-10.](image.png)

**Figure 1-10.** Electron Paramagnetic Resonance (EPR) intensity of long-live radical species in polymerization of BODA monomer 1-1 (X = C(CF3)2, R = Ph) relative to time.59

Electron paramagnetic resonance spectroscopy (EPR) has been used to study BODA polymerizations and unpaired spins have been observed for both in situ heated BODA polymerizations and sampled BODA polymerizations (Figure 1-10).60 First-order kinetics was observed. The X bridging group again showed little effect on the kinetics of the polymerization, but heterocycles in the R position did show an increased rate of polymerization when compared to phenyl substituted monomers. The radicals were proved to be very long-lived species, detectable after three weeks even when stored at room temperature and under normal atmosphere.
The BODA strategy uses Bergman cyclization in a novel way to prepare high-performance, thermally-stable, polymer networks from commodity phenolic materials without sacrificing processability. Thermal polymerization can be performed either neat or in solution to yield soluble branched oligoarylenes with reactive pendant and terminal arenediyne functionality. Fully processable oligomers can be solution or melt coated or molded and thermally cured without the formation of volatile products. Only minimal weight loss was measured from the cured BODA network at 450 °C in nitrogen. The processability combined with the high-performance thermal resistance of BODA derived polymer networks have potential applications in integrated circuits, carbon matrix composites, and emerging π-conjugated optoelectronic and optical devices.
CHAPTER 2
EXPERIMENTAL

Materials

Chemicals

All chemicals were purchased and used as supplied without further purification unless stated otherwise.

BODA Monomer Synthesis

2,2-Bis(3-bromo-4-hydroxyphenyl)-1,1,3,3,3-hexafluoropropane To a 250 mL 4-neck flask equipped with condenser, N₂ purging tube, thermocouple, and a magnetic stirring bar, 10.00 g (0.0297 mol) of 2,2-bis(4-hydroxyphenyl)-1,1,3,3,3-hexafluoropropane and 0.35 g (0.0059 mol) of iron powder was dissolved/ suspended in 100 mL of CCl₄ and 16.64 mL of glacial acetic acid (HOAc). The solution was maintained at room temperature while 19.5 g (0.122 mol) bromine was added dropwise over 150 min. The reaction mixture was stirred for 3 hrs and the organic layer was washed with satd. aq. NaHCO₃, then twice with water, and dried over MgSO₄, filtered and evaporated providing 13.14 g (0.026 mol) yellow powder (90 % yield). mp 95-96 °C. FTIR (KBr
disk): (cm$^{-1}$) 1046, 1136, 1175, 1208, 1256, 1499, 157, 1605, 3506 HRMS for
C$_{15}$H$_8$Br$_2$O$_2$F$_6$ calcd. (found): 491.8795 (491.8744).

2,2-Bis(3-bromo-4-trifluoromethanesulfonatophenyl)-1,1,1,3,3,3-hexafluoropropane
To a 250 mL three neck flask equipped with N$_2$ inlet and thermocouple was added 34 mL
CH$_2$Cl$_2$, 5 mL N(CH$_2$CH$_3$)$_3$, and 6.0 g (0.012 mol) 2,2-Bis(3-bromo-4-hydroxyphenyl)-
1,1,1,3,3,3-hexafluoropropane at 25 °C. The solution was cooled to 10 °C and 3.56 g
(0.0256 mol) CF$_3$SO$_2$Cl was added and the mixture was stirred for 3 h, then quenched
with 200 mL water, and washed with satd. aq. NaHCO$_3$, dried over MgSO$_4$, filtered and
evaporated to provide 8.38 g (91 %) white crystals. Mp 86-88 °C FTIR (KBr disk): (cm$^{-1}$)
737,882,1137,1213, 1429, 1479  $^1$H NMR (400 MHz, CDCl$_3$ $\delta$: 7.4 (4H, m), 7.74 (2H, s), $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 64.00 (hept, C(CF$_3$)$_2$, J = 30 Hz, 116.57, 116.98,
122.97, 130.94, 133.71, 135.81, 147.83. $^{19}$F (376 MHz, CDCl$_3$) $\delta$: -63.84 (6F, s) HRMS
for C$_{17}$H$_6$Br$_2$F$_{12}$S$_2$ calcd. (found): 755.7779 (755.7780).

2,2-bis(3,4-di(phenylethynyl)phenyl)-1,1,1,3,3,3-hexafluoropropane (1-1) To a 250 mL
4-neck flask equipped with a thermocouple, N$_2$ purging tube, dropping funnel and a
magnetic stirred was added 10.00 g (0.01323 mol) of 2,2-Bis(3-bromo-4-trifluoromethanesulfonatophenyl)-1,1,1,3,3,3-hexafluoropropane, 50 mL
dimethylformamide and 50 mL N(CH$_2$CH$_3$)$_3$. The solution was deoxygenated by
sparging with dry N$_2$. Then 0.687 g (9.79 x 10-4 mol) PdCl$_2$(P(Ph)$_3$)$_2$ was added at 65 °C
and the solution was heated to 90 °C. Then, 6.59 g (0.0647 mol) phenyl acetylene was
added dropwise over about 15 minutes. The solution was heated to 90 °C and heated
overnight. The reaction mixture was worked up by diluting with 100 mL CH₂Cl₂, and washed with 10 % HCl, and twice with water, dried over MgSO₄ and evaporated to give a dark brown crude oil. This was purified by flash chromatography, (silica/ hexane) to yield a yellow solid (81 %), mp 189-191 °C. FTIR (KBr): (cm⁻¹) 686, 752, 825, 877, 912, 966, 991, 1068, 1097, 1135, 1182, 1207, 1251, 1321, 1413, 1442, 1500, 1598, 2213, 3020, 3058. ¹H NMR (400 MHz, CDCl₃) δ: 7.30 – 7.40 (13H, m) ¹³C NMR (100 MHz, CDCl₃) δ: 64.00 (hept, C(CF₃)₂, J = 30 Hz), 87.23, 87.48, 94.51, 95.38, 122.77, 126.16, 126.93, 128.36, 128.40, 128.71, 128.78, 129.40. 131.63, 11.72, 132.51, 133.11. ¹⁹F NMR (376 MHz, CDCl₃) δ: -63.84 HRMS for C₄₇H₂₆F₆ calcd. (found): 704.1939 (704.1926)

2,2-Bis(3,4-di(2-methyl-3-butyn-2-ol)phenyl)-1,1,1,3,3,3-hexafluoropropane (1-6) To a dried 100 mL flask equipped with a condenser, N₂ purging tube, an inlet septum and a magnetic stirrer was added 2.00 g (2.646 x 10⁻³ mol) of 2,2-Bis(3-bromo-4-trifluoromethanesulphonatophenyl)-1,1,3,3,3-hexafluoropropane, 16 mL dimethylformamide and 16 mL N(CH₂CH₃)₃. The solution was deoxygenated by sparging with dry N₂. Then 0.1372 g (9.79 x 10⁻⁴ mol) PdCl₂(P(Ph)₃)₂ and 0.0375 g (1.96 x 10⁻⁴ mol) was added at room temperature. The solution was purged with N₂, and heated to 50 °C with stirring. Then, 1.29 mL (0.0133 mol) 2-methyl-3butyn-2ol was added dropwise over about 15 minutes. The solution was heated to 90 °C for 2 hours. The reaction mixture was worked up by diluting with 100 mL CH₂Cl₂, and washed with 10 % HCl, and twice with water, dried over MgSO₄ and evaporated to give a dark brown crude oil. This was purified by flash chromatography, (silica/ 1:10 ethyl acetate:hexane) to yield a yellow solid (81 %), mp 90-91 °C. FTIR (KBr): (cm⁻¹) 544, 655, 735, 827, 913,
MODA Monomer Synthesis

1,2-bis(phenylethynyl)benzene\textsuperscript{61} (5-1) To a clean dry 100 mL 3-neck flask equipped with a N\textsubscript{2} inlet, condenser, rubber septum, and a magnetic stirrer, 1.0 mL (8.48 x 10\textsuperscript{-3} mol), 0.6612 g (9.42 x 10\textsuperscript{-4} mol) PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}, and 0.3599 g (1.88 x 10\textsuperscript{-3} mol) CuI were added along with 50 mL N(CH\textsubscript{2}CH\textsubscript{3})\textsubscript{3}. The solution was purged with 2 freeze pump thaw cycles. After warming back up to 90 °C in an oil bath, 2.0 mL (1.87 x 10\textsuperscript{-2} mol) phenyl acetylene was added dropwise. The solution was refluxed overnight. The brown crude oil was dissolved in CH\textsubscript{2}Cl\textsubscript{2}, washed with satd. NH\textsubscript{4}Cl, and water, then vacuum evaporated. The product was purified with flash chromatography (silica/ hexane) to yield 1.68 g (72 %) yellow solid product \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \textit{δ}: 7.41 (m), 7.45 (m), 7.74 (m). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \textit{δ}: 88.79, 94.04, 123.59, 126.14, 128.36, 128.79, 129.05, 131.97, 132,10, 133.91, 134.16, 137.45, 137.59.

t-Butyl-3,4-dihydroxybenzoate In a clean dry round bottomed flask, 4.9954 g (3.24 x10\textsuperscript{-2} mol) 3,4-dihydroxybenzoic acid was dissolved in 125 mL t-butanol. Then 3.9623g (3.24 x 10\textsuperscript{-2} mol) DMAP, and 6.6902 g (3.24 x10\textsuperscript{-2} mol) DCC was added to produce a slurry,
which was stirred at room temperature overnight. The reaction mixture was filtered and washed with water, 1M HCl, then vacuum evaporated and purified by flash chromatography (silica, Hexane:EtOAc) to yield 1.49 g (22 %) white crystalline product.  

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 1.52 (9H, s), 6.83 (1H, d), 7.36 (1H, d), 7.44 (2H, s), 8.36 (2H, broad s). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 28.7, 79.59, 114.75, 116.28, 122.31, 123.93, 144.60, 149.50, 165.09. GC-MS for C$_{11}$H$_{14}$O$_4$ calcd. (found): 210.09 (210).

t-Butyl-3,4-bis(trifluoromethanesulfonato)benzoate  In a flame dried flask, 1.4204 g (6.76 x 10$^{-3}$ mol) t-Butyl-3,4-dihydroxybenzoate was suspended in 50 mL CH$_2$Cl$_2$, and 1.6 mL pyridine and cooled in an ice bath. Then, 3.8124 g (1.35 x 10$^{-4}$ mol) triflic anhydride (CF$_3$SO$_2$)$_2$O was added dropwise and allowed to stir for 30 min, then warmed to room temperature and reacted for 5 hrs. The reaction mixture was washed twice with water and dried over MgSO$_4$, then dried under vacuum to yield 1.8996 g (59 %) solid product.  

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 1.55 (9H, s), 7.50 (1H, d), 8.05 (1H, s), 8.08 (1H, d). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 27.63, 82.97, 116.48, 120.72, 123.43, 124.68, 130.59, 133.85, 140.26, 143.22, 162.25.

t-Butyl-3,4-bis(phenylethynyl)benzoate  In a clean dry flask, 1.8996 g ( 4.00 x10$^{-3}$ mol) t-Butyl-3,4-bis(trifluoromethanesulfonato)benzoate was dissolved in 3 mL N(CH$_2$CH$_3$)$_3$ and 15 mL DMF. The solution was purged with bubbling N$_2$. Then, 0.2291 g (3.24 x 10$^{-4}$ mol) PdCl$_2$(PPh$_3$)$_2$ and 1.1 mL (9.39 x 10$^{-3}$ mol) Phenylacetylene were added and the solution was heated to 80 $^\circ$C for two hrs. The reaction was allowed to cool to room temperature and then diluted in CH$_2$Cl$_2$, washed with satd. NH$_4$Cl, and vacuum
evaporated. The crude product was purified with flash chromatography (silica, 1:10 CH₂Cl₂:hexane) to yield 1.2 g (80%) yellow solid product. ¹H NMR (300 MHz, CDCl₃) δ: 1.61 (9H, s), 7.39 (6H, m), 7.61 (4H, m), 7.66 (1H, d), 7.90 (1H, s), 7.95 (1H, d). ¹³C NMR (75 MHz, CDCl₃) δ: 29.82, 82.39, 99.20, 120.92, 122.50, 128.62, 128.96, 131.95, 133.45, 163.45.

3,4-bis(phenylethynyl)benzoic acid (5-2) In a clean dry 25 mL flask, 0.1261 g (3.34 x 10⁻⁴ mol) t-Butyl-3,4-bis(phenylethynyl)benzoate and 4 mL 5M HCl/Et₂O solution was added and allowed to react at room temperature with stirring overnight. The solution was vacuum evaporated at room temperature, redissolved in Et₂O, separated, and recrystallized in acetonitrile to yield a yellow solid product. ¹H NMR (300 MHz, DMSO-d₆) δ: 3.34 (1H, broad s), 7.43 (6H, s), 7.57 (4H, s), 7.74 (1H, d), 7.92 (1H, d), 8.10 (1H, s). ¹³C NMR (75 MHz, DMSO-d₆) δ: 87.72, 88.05, 94.69, 96.62, 122.0, 125.5, 129.07, 129.49, 129.80, 129.88, 130.10, 132.03, 132.69, 132.88, 166.60. LC-MS for C₂₃H₁₄O₂ calcd (found) 322.1 (320.7).

N-(p-chlorophenyl)-3,4-bis(phenylethynyl)benzamide To a clean dry 25 mL round bottomed flask equipped with a rubber septum and a magnetic stirrer, 0.0516 g (1.55 x 10⁻⁴ mol) 3,4-bis(phenylethynyl)benzoic acid, 0.0505 g (2.32 x 10⁻⁴ mol) DCC, and 0.0330 g (2.32 x 10⁻⁴ mol) DMAP were added and dissolved in 5 mL anhydrous CH₂Cl₂. Then 0.0358 g (2.32 x 10⁻⁴ mol) 4-chloroaniline was added. The solution was flushed with N₂ and allowed to stir at room temperature overnight. The crude reaction mixture was dried under vacuum and separated with flash chromatography (silica, EtOAc:hexane) to yield
0.0794 g product (118%)  

$^1$H NMR (300 MHz, CDCl3) $\delta$: 7.26 (8H, m), 7.58, (7H, m), 7.78 (1H, m), 8.01 (1H, s), 8.10 (1H, s).  

$^{13}$C NMR (75 MHz, DMSO-d6) $\delta$: 87.47, 87.71, 94.89, 96.48, 121.65, 122.8, 126.0, 126.5, 126.9, 128.59, 128.97, 129.26, 130.23, 131.85, 132.2, 133.8, 135.4, 154.05.  

LC-MS for C$_{29}$H$_{18}$ClNO calcd. (found) 431.11 (430.0).

3,4-bis(trifluoromethanesulfonato)benzaldehyde  

To a clean dry 100 mL round bottomed flask equipped with a rubber septum and a magnetic stirbar, 1.0105 g (7.24 x10$^{-3}$ mol) 3,4-dihydroxybenzaldehyde was added and dissolved in 40 mL CH$_2$Cl$_2$ and 1.2 mL pyridine. The solution was cooled to 0 °C in an ice bath. Then, 2.5 mL (1.44 x 10$^{-2}$ mol) (CF$_3$SO$_2$)$_2$O was added dropwise and allowed to react at 0 °C for 30 minutes, then warmed to room temperature and allowed to react for 5 h. The reaction mixture was washed twice with water and dried over MgSO$_4$, then dried under vacuum to yield 1.6807 g (20 %) solid product.

3,4-bis(phenylethynyl)benzaldehyde (5-4)  

To a clean dry 3-necked flask with a condenser, two rubber septa and a magnetic stirrer, 1.6807 g (4.17 x10$^{-3}$ mol) 3,4-bis(trifluoromethanesulfonato)benzaldehyde was added and dissolved in 4 mL DMF and 4 mL N(CH$_2$CH$_3$)$_3$. The solution was bubbled with N$_2$ gas, then eated to 65 °C. 0.1177 g (1.67 x 10$^{-4}$ moles) PdCl$_2$(PPh$_3$)$_2$, and 0.0208 g (8.36 x 10$^{-5}$ mol) CuI were added. Then, 1.15 mL (1.04 x 10$^{-2}$ mol) phenylacetylene was added dropwise. The solution was heated to 90 °C for 2.5 h. The crude product was cooled, diluted with CH$_2$Cl$_2$, washed with 1M HCl, and water, then separated and dried under vacuum. The crude oil was separated by flash chromatography, (silica, 1:9 CH2Cl2: hexane) to yield 0.6520 g (51
% yellow solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.36 (6H, s), 7.59 (4H, m) 7.72, (1H, s), 7.75 (1H, s), 7.99 (1H, s) 9.93 (1H, s). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 87.43, 88.14, 95.16, 97.75, 122.74, 122.8, 127.6, 128.23, 128.68, 129.04, 129.31, 131.49, 131.91, 132.03, 132.45, 133.34, 135.34, 190.84. GC-MS for C$_{23}$H$_{14}$O calcd (found): 306.10, (306).

3,4-dihydroxybenzamide$^{62}$ To a clean dry 25 mL round bottomed flask equipped with a stirbar, 0.6783 g (5 x 10$^{-3}$ mol) 3,4-dihydroxybenzonitrile was added along with 15 mL 12M HCl, and heated at 40 °C for 3 hrs. The solution was then cooled to room temperature, poured into ice water, washed with ethyl acetate. The aqueous fraction was then reduced under vacuum to yield 0.74 g (96%) off white crystalline product. $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$: 6.17 (3H, broad s), 6.91 (1H, d), 7.37 (1H, d), 7.48 (1H, s). $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$: 115.20, 116.5, 121.26, 122.78, 144.72, 149.94, 210.39.

3,4-bis(trifluoromethanesulfonato)benzamide To a clean dry 100 mL round bottomed flask equipped with a stirbar and a rubber septum, 0.4634 g (3.03 x 10$^{-3}$ mol) 3,4-dihydroxybenzamide was added and dissolved in 20 mL anhydrous CH$_2$Cl$_2$, and 1.5 mL anhydrous pyridine. The solution was cooled to 0 °C in an ice bath, while stirring. Then 1.04 mL (6.36 x 10$^{-3}$ moles) triflic anhydride, (CF$_3$SO$_2$)$_2$O was added dropwise and allowed to react for 2.5 hrs. The reaction was warmed to room temperature and reacted overnight. The crude reaction mixture was quenched with water, dissolved in CH$_2$Cl$_2$, and separated. The organic layer was vacuum evaporated and purified by flash chromatography (silica, EtOAc: Hexane) to yield 0.1633 g (13%) yellow product. $^1$H
NMR (300 MHz, acetone-d6) \( \delta \): 7.19 (2H, broad s), 7.89 (1H, d), 8.24 (2H, m). \(^{13}\)C NMR (75 MHz, acetone-d6) \( \delta \): 116.54, 120.77, 123.37, 124.19, 129.54, 136.77, 140.18, 142.17, 164.96.

3,4-bis(phenylethynyl)benzamide (5-5) To a clean, dry 100 mL round bottomed flask equipped with a condenser, 2 rubber septa, and a magnetic stirbar, 0.2900 g (6.95 x10^{-4} mol) 3,4-bis(trifluoromethanesulfonato)benzamide was added and dissolved in 15 mL DMF and 15 mL N(CH2CH3)3 and purged with N2. Then 0.0481 (5.56 x 10^{-5} mol) PdCl2(PPh3)2 was added to the solution. Then 0.17 mL (1.53 x 10^{-3} mol) phenylacetylene was added dropwise. The solution was heated to 90 °C and allowed to react for 4.5 hrs. The crude mixture was cooled, diluted in CH2Cl2, washed with 1M HCl, then water, separated and dried under vacuum. The product then precipitated out to yield 0.0827 g (37 %) yellow solid. \(^1\)H NMR (300 MHz, DMSO-d6) \( \delta \): 3.37 (2H, broad s), 7.43 (6H, d), 7.56 (4H, s), 7.69 (1H, d), 7.89 (1H, d), 8.12 (1H, d). \(^{13}\)C NMR (75 MHz, DMSO-d6) \( \delta \): 88.11, 88.14, 94.40, 95.86, 122.32, 125.21, 127.69, 128.40, 129.50, 129.86, 131.21, 131.90, 132.39, 134.66, 166.92. LC-MS for C23H15NO calcd (found): 321.12 (320.0).

3,4-bis(phenylethynyl)aniline (5-6) 30.2 g NaOH was dissolved in 120 mL DI water, and cooled to 0 °C in an ice bath. Then 8.4 mL (26.2 g) Br2 was added and cooled to 0 °C again to yield 132 mL of NaOBr. Then, 0.0134 g (4.17 x10^{-5} mol) 3,4-bis(phenylethynyl)benzamide was added to a clean dry vial, and 0.2 mL (NaOBr solution added to cover solid. The reaction was then stirred at room temperature overnight. The
solution was extracted with CH$_2$Cl$_2$ to remove the product as a yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 3.66 (2H, broad s), 7.37-7.62 (13H, m).

3,4-dibromoanisole  To a clean dry 250 mL round bottomed flask, 4.0515 g (0.021 mol) 3-bromoanisole was added to 42 mL acetone, 3.806 g (0.021 mol) N-bromosuccinimide was added. Then, 0.2 mL 1M HCl was added. The solution was stirred for 30 min, then 105 mL Hexane was added and the solution was cooled in an ice bath. The succinimide was filtered out, and the solution was evaporated to yield a yellow solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 3.59 (3H, s), 6.56 (1H, dd), 6.97 (1H, d), 7.26 (1H, d). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 56.3, 115.0, 118.9, 124.6, 133.7, 159.2, 206.5.

3,4-dibromophenol  In a flame dried round bottom flask, 2.514 g dibromoanisole was dissolved in 30 mL CH$_2$Cl$_2$, and purged with N$_2$. The solution was cooled in a N$_2$ (l)/acetone bath. A 1M solution of BBr$_3$ (10.7 mL BBr$_3$ in 111 mL CH$_2$Cl$_2$) was added dropwise. The solution was reacted in cold bath for 30 minutes, then warmed to room temperature and stirred overnight. Then, 250 mL ice water added. Solution was washed with 1M NaOH, then extracted with ethyl acetate, washed with NaHCO$_3$, and brine, then dried over MgSO$_4$. Crude product was purified by flash chromatography (silica/ 2:1 hexane: CH$_2$Cl$_2$) to yield 0.96 g (40%) off-white crystals. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 5.69 (1H, broad s), 6.66 (1H, dd), 7.13 (1H, d), 7.41 (1H, d). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 115.68, 116.41, 128.87, 125.13, 134.19, 155.05  GC-MS calcd (found): 249.86 (250), 251.86 (252), 253.86 (254).
3,4-bis(phenylethynyl)phenol (5-7) To a clean dry 3-neck flask fit with a condenser, two rubber septa, and a magnetic stirrer, 0.6591 g (2.61 x 10^{-3} mol) 3,4-dibromophenol was dissolved in 15 mL DMF and degassed with bubbling N\textsubscript{2}. Then 5 mL N(CH\textsubscript{2}CH\textsubscript{3})\textsubscript{3}, 0.0684 g (9.68 x 10^{-5} mol) PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} and 0.0105 g (0.0094 mol) CuI were added. The solution was heated to 65 °C. Then 0.75 mL (6.5 x 10^{-3} moles) phenylacetylene were added dropwise, and the solution was heated to 90 C and allowed to react overnight. The crude oil was diluted in CH\textsubscript{2}Cl\textsubscript{2}, and washed with 10 % HCl, and water, then vacuum evaporated. The product was found to be primarily starting material however, and was not isolated.

4-(4-(3,4-bis(phenylethynyl)styryl)-2,5-bis(octyloxy)styryl)-1,2-bis(phenylethynyl)benzene To a clean dry 3-neck 100 mL flask, 0.1644 g (5.37 x 10^{-4} mol) 3,4-bis(phenylethynyl)benzaldehyde was added, and dissolved in 20 mL ethanol. Then 0.1732 g (2.68 x 10^{-4} mol) 1,6-bis(diethylmethylphosphonate)-2,5-bis-octyloxybenzene was added to the solution. The solution was cooled to 0 °C in and ice bath. The flask was evacuated and flushed with nitrogen in three cycles. Then, 0.52 mL (5.2 x 10^{-4} mol) 1M KOTBu in THF was added in four parts at 15 minute intervals. The solution was allowed to warm to room temperature and react for 24 h. The product was isolated by flash chromatography (silica, 1:5 CH\textsubscript{2}Cl\textsubscript{2}: hexane) to yield 0.2041 g (81 %) bright yellow green solid. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ: 0.85 (6H, m), 1.24 (20H, m), 1.72 (4H, m), 3.63 (4H, qt), 6.87 (4H, s), 7.30 (16H, m), 7.52 (6H, m), 7.54-7.8 (4H, dd), 7.96 (2H, s). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) δ: 6.53, 6.61, 14.17, 16.39, 18.41, 22.73, 26.20, 29.34, 29.47, 29.53, 31.89, 57.97, 61.54, 61.62, 62.01, 69.01, 87.19, 87.91, 95.03,
**N-ethyl-1-(3,4-bis(phenylethynyl)benzene-2,3-[60]fullereno-pyrrolidine** To a clean dry 25 mL flask fitted with a condenser, 0.0328 g (1.07 x 10^{-4} mol) 3,4-bis(phenylethynyl)benzaldehyde and 0.0259 g (0.32 x 10^{-4} mol) C\(\text{C}_{60}\) was added and dissolved in 3 mL DMF. Then, 0.0129 g (1.07 x 10^{-4} mol) N-ethyl glycine was added to the solution. The reaction was heated to 130 °C for 5 days, cooled to room temperature and analyzed without purification. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 0.83 (3H, m), 1.25 (2H, m), 1.58 (H, s), 2.17 (H, s), 3.95 (2H, qt), 7.38, (6H, m), 7.45 (2H, d), 7.58 (1H, m), 7.65 (1H, d), 7.72 (1H, s), 8.96 (s, leftover aldehyde). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 13.38, 14.23, 22.80, 29.80, 36.21, 86.93, 87.35, 95.49, 96.87, 122.66, 127.0, 127.99, 128.60, 129.08, 129.21, 131.87, 131.94, 132.06, 132.32, 132.85, 143.19, 163.79, 171.12. MALDI-TOF-MS (1:2:1, analyte:dithranol:AgTFA) calcd. (found) 1067.17 (1067.038).

**Instrumentation**

**Nuclear Magnetic Resonance (NMR)**

\(^1\)H NMR 500 MHz, proton decoupled \(^{13}\)C NMR 125 MHz, \(^1\)H NMR 400 MHz, proton decoupled \(^{13}\)C NMR 100 MHz, \(^1\)H NMR 300 MHz, proton decoupled \(^{13}\)C NMR 75 MHz, and \(^{19}\)F NMR 188 MHz spectra were obtained with JEOL Eclipse + 500,Varian Unity Plus, Bruker AF-300, and Bruker AF-200 spectrometer systems, respectively. Chloroform-d was used as the solvent unless otherwise noted, and all chemical shifts
were calculated relative to tetramethylsilane (TMS, 0 ppm), and CDCl$_3$ ($^{13}$C, 77 ppm) internal standards.

**Liquid Chromatography/ Mass Spectrometry (LC/MS)**

Liquid chromatography/ mass spectrometry data was obtained using in the R. K. Marcus laboratory with an EI-MS detector.

**Gel Permeation Chromatography (GPC)**

Gel Permeation Chromatography was performed on a Waters 2695 Separations Module with Waters 996 Photodiode array and 2410 Refractive index detectors and Polymer Laboratories PLGel 5 µm Mixed Bed D and Mixed Bed-E analytical columns and a PL guard column were maintained at 35 °C to obtain the separation. Polymer Laboratories narrow polystyrene standards ($M_p = 377400-580$) were used to calibrate the columns. The mobile phase was CHCl$_3$, at 1 mL/min. The sample concentration was 1 mg/ml and the injection volume was 100 µL.

**Multi-Angle Light Scattering (MALS)**

A Wyatt Technologies MiniDawn 3-angle light scattering module was used in conjunction with the GPC system above to obtain the MALLS data. The Waters 996 Photodiode array detector was used as the concentration detector.
Thermogravimetric Analysis (TGA)

TGA experiments were conducted using a Mettler Toledo SDTA851e TGA with a N\textsubscript{2} flow rate of 40-50 mL/min, and an alumina pan.

Electron Microscopy

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) experiments were performed using a Hitachi S4700 Field Emission SEM and an Hitachi S4800 Field Emission SEM. Hitachi Model NANO H9500 transmission electron microscope for high resolution images (HRTEM, 300 kV) and a Hitachi Model 7600 transmission electron microscope for low resolution images (LRTEM, 120 kV) respectively.

Energy Dispersive X-Ray Spectroscopy (EDX)

Energy dispersive x-ray spectroscopy was performed with an Oxford INCA Energy 200 EDS module equipped on the Hitachi S4800 Field Emission SEM.

Raman Spectroscopy

The Raman spectra were recorded using a Renishaw 1000 Raman spectrometer with the 785 nm emission line of a near infrared laser as the excitation source.

Reflectance Spectroscopy

Reflectance measurements were obtained with an Ocean Optics PC2000 fiber optics spectrometer routed through an optical stereomicroscope.
Dilatometry

A vertical Linseis dilatometer L75 with single push rod at the Air Force
Research Labs (Edwards Air Force Base, CA) was used for carbonization and CTE
measurements.

High-Resolution Mass Spectrometry (HRMS)

High-resolution mass spectrometry was obtained from the FAB micromass 70-
SE-4FE and micromass 70VSE (chemical ionization) instruments at the University of
Illinois.

Elemental Analysis

Powdered monomer samples were analyzed for C, H, O by Atlantic Microlab,
Inc., Norcross, GA with a detection limit of 0.3 %.

Contact Angle Goniometry

Contact angles were obtained using a simple manual contact angle goniometer.

Infrared Spectroscopy

IR spectra were recorded on a Perkin-Elmer model 2000 instruments (liquid
film, KBr disks).
Electron Paramagnetic Spectroscopy (EPR)

EPR experiments were performed using a Bruker EMX spectrometer and temperature controller. Radical formation during the in situ polymerization was monitored with continuous EPR measurements at varying microwave power.

Surface Area Measurement

BET (Brunauer, Emmett and Teller method) Surface area measurements were performed using a Micromeritics ASAP 2010 N₂ gas adsorption analyzer in S.E Creager’s laboratory.

Thermomechanical Analysis (TMA)

Thermomechanical analysis was performed using a Seiko Instruments Inc. TMass 350C Thermal Mechanical analyzer with a flat circular probe of diameter 3.5 mm in K. Ivey’s laboratory.

Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS)

Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry recorded with an Omni Flex MALDI-TOF mass spectrometer.
Experimental Procedures

Fabrication of Carbon Inverse Opal.

Monodisperse SiO$_2$ nanospheres were made by a modified Stober-Fink-Bohn method,$^{30-31}$ and permitted to self-assemble by sedimentation into the close packed opal structure.$^{19}$ Tetraethyl orthosilicate used in the sol-gel colloid synthesis was distilled prior to use.

This structure was then sintered between 900-1000 °C in a quartz tube in order to create necks between the spheres. The particle necks are important as they will later be used to facilitate the complete removal of the SiO$_2$. The opal was washed with saturated aqueous NaHCO$_3$ and dried. Monomer 1 was melted above 90 ºC slowly into the pores between the SiO$_2$ spheres, cured at about 240 °C for 10 minutes and, then further heated to about 900 °C for 10 minutes under N$_2$ to complete the pyrolysis step and take the polymer to a glassy carbon state. Initial attempts with monomer 2 followed the same procedure with the exception of melting temperatures above 190 ºC and curing above 210 ºC. Carbon yields by TGA have been shown to be 77-78 % carbon from the initial mass of monomer used. The glassy carbon impregnated opal was then treated with HF (48% aq.) for 2 hours to remove the SiO$_2$ template, washed well with water and allowed to dry.

Carbon Inverse Opal sensing

The reflectance data were obtained at either 100x or 200x magnification. The solvent sensing attenuation experiments were performed by placing a drop of each mixed
solvent solution on the opal surface and measuring the reflectance while wet and then again after the solvent has evaporated, to avoid movement of the inverse carbon opal.

The 5CB liquid crystal switching experiment was performed by placing the inverse carbon opal on a thermoelectric plate, with a thermocouple. The pores in the ICO were filled with 4-pentyl-4’cyanobiphenyl. Then a reflectance spectrum was obtained on the spectrometer. The plate was then heated to above the transition temperature, to 51.1 °C, and another reflectance spectrum was obtained. The plate was then allowed to return to room temperature, below the liquid crystal phase transition temperature, and a third reflectance spectrum was taken.

The hemoglobin sensing experiment was performed by dissolving 1/16 g lyophilized hemoglobin in 1 mL of borate buffers. The borate buffers were made by dissolving 3.875 g H₃BO₃ in 1000 mL DI H₂O to produce a 0.0627 M solution with a pH = 6.62. The remaining four solutions were titrated to their proper pHs (7.0, 7.5, 8.0, 8.5) with a 0.0997 M solution of Na₂B₄O₇ (38 g Na₂B₄O₇ in 1000 mL DI H₂O, pH = 9.31). The ICO was examined for a reliably reproducible reflectance. Then the ICO was filled with each solution and a reflectance spectra was taken. After each spectra, the ICO was washed with the clean buffer for the following solution.

**Disordered Porous Carbon.**

The disordered carbon foam was produced in the same manner as the inverse carbon opal. This colloidal silica template was not perfectly monomodal or not self-assembled. A monolith of this template was gently heated on a piece of PTFE plastic on top of a hot plate at about 100 °C. Solutions of BODA monomer were then allowed to
soak into the silica monolith, where the solvent evaporated. This was repeated until the silica no longer absorbed the solution. The silica was then heated in a tube furnace to 1000 °C to carbonize the polymer. The monolith was removed and carefully treated with aq. HF to remove the silica template. Crushing the monolith before treatment with the HF increases the rate of etching. The carbon was then washed with water and dried.

BET surface area experiments were performed in Dr. Creager’s lab with a powdered sample.

**Dimodal Carbon Foam**

Dimodal carbon foams were fabricated using colloidal silica as above. Specifically, 92 mL ethanol, 3.2 mL NH4OH (aq), and 38.4 mL DI water, were mixed and 10.2 mL tetraethyl orthosilicate was added dropwise to a clean Erlenmeyer flask while stirring. The solution was allowed to stir for 3 hours to produce the silica spheres of ~200 nm diameter. This solution was diluted with an equal portion of DI water. A small cube of macroporous carbon (produced from mesophase pitch, as provided by Oak Ridge National Laboratories, pore size ~1 mm) was treated with an aqueous solution of lauryltrimethyl ammonium chloride, while suspended by a string. The treated carbon macrofoam was then saturated with the diluted silica suspension, and allowed to dry. The silica infiltrated carbon macrofoam, was heated under N2 flow in tube furnace to 1000 °C to sinter the silica. The sintered silica infiltrated carbon macrofoam was then treated with a solution of BODA monomer (X = C(CF3)2, R = C(CH3)2OH) in CH2Cl2, dried and again heated to 1000 °C under N2 in a tube furnace. The carbonized foam was treated with HF (aq) to remove the silica.
**Carbon Fluorination**

A carbon pellet was generated by heating BODA monomer to 1000 °C under N2 in an alumina TGA pan. The resulting carbon pellet was embedded near the surface of an epoxy casing (Caroplastic). The epoxy encased carbon was then sanded with a water cooled sanding table until the surface of the carbon was completely exposed and flat. The contact angle of both water and mineral oil were determined by averaging 3 measurements each. The pellet was cleaned and dried between each measurement. An EDX spectrum was taken to determine the elemental composition of the carbon pellet.

The pellet was then treated with 13.8 mL solution of 4-(4-trifluorovinyloxyphenyl)-1-phenyl-diazonium tetrafluoroborate at 90 °C for 1 hr. This solution was prepared from 0.0785 g (2.96 x 10-4) moles 4-(4-trifluorovinyloxyphenyl)-aniline dissolved in 0.5 mL diethyl ether, treated with a mixture of 8 mL BF3·Et2O and 3 mL HF (48%) (1:1 BF3:HF mole ratio), cooled to 0 °C, and treated with 2.6 mL isoamyl nitrite at 0 °C for 1 hr. The pellet was removed from the reaction mixture and washed thoroughly with acetone, water, and chloroform. The carbon pellet was then again tested for contact angle with water and mineral oil as above. An EDX spectrum was again taken to determine the elemental composition of the fluorinated carbon pellet.

**Carbon nanotubules**

A Whatman Anodisc alumina filter with 0.2 µm pore sizes was coated in a solution of BODA monomer (X = C(CF3)2, R = C(CH3)2OH) in CH2Cl2, and allowed to dry. The coated filter was then heated to 1000 °C under N2 in a tube furnace. The
carbonized sample was then treated with saturated KOH to etch the alumina, washed with water, and dried, then analyzed under SEM.

**BODA-co-C$_{60}$**

BODA (X = C(CF$_3$)$_2$, R = Ph) homopolymerization and copolymerization were carried out under identical conditions. In a copolymerization experiment, 32.1 mg BODA monomer 1 and 14.0 mg C$_{60}$ were added to a clean dry schlenk tube, and dissolved in 4 mL 1-methyl pyrrolidinone (NMP), flushed with dry nitrogen and sealed. The reaction was then heated in oil bath at reflux with magnetic stirring for 24 h. NMP was removed by heating at 80 °C under vacuum to give BODA-co-C$_{60}$ as a black powder.

**BODA-co-Carbon Nano-onions**

Typically, a suspension of 20.0 mg purified (annealed 1 hour at 400 °C; refluxed for 48 hrs. in 3M HNO$_3$ 48h, annealed 1 hour at 400 °C and supercritical water dried) sample of carbon nano-onions (CNOs) with 40.0 mg BODA monomer (X = C(CF$_3$)$_2$, R = Ph) in 1 mL 1-methyl-pyrrolidinone (NMP) was ultrasonicated for 30 min, followed by refluxing for 4 days in a sand bath at 240 °C. After cooling to room temperature, the black-green suspension was separated by five cycles of centrifugation for 18 hrs., decanting, adding 3 mL clean NMP, and sonicating for 5 minutes until the supernatant NMP solution remained colorless. The remaining solid was then washed twice with 3 mL diethyl ether to remove the remnant NMP and dried at 200 °C in the vacuum oven until a constant weight was obtained. The NMP solutions were evaporated to dryness under high vacuum at 100 °C, washed with 2 mL ether, sonicated, and centrifuged until
the supernatant remained colorless to remove the unreacted BODA fraction (as
determined by TEM. The dried NMP soluble fractions were then washed with 4 cycles
of sonication in 2 mL volumes of CHCl₃, and centrifugation to remove a deep red
solutions. These were collected filtered with a Whatman 0.45 µm PP filter and
evaporated to dryness. This fraction was then washed 5 mL of ether, sonicated for 30
min, centrifuged, decanted and at 150 ºC under high vacuum for 48 hrs. to yield the
highly BODA-functionalized CNOs as determined by TGA. The fraction of NMP
soluble fraction that remained insoluble in CHCl₃ was determined by TGA to remain
soluble in NMP and to be a BODA-functionalized CNOs fraction with a lower portion of
BODA polymer.

MALDI-TOF-MS

BODA-co-C₆₀ MALDI data was obtained by grinding 2 mg BODA-co-C₆₀ (1.8
wt% C₆₀) with 27 mg sulfur (S₈) in a mortar and pestle. Mass Spectrometry recorded
with an Omni Flex MALDI-TOF mass spectrometer (70-80 % laser power, reflectron
positive mode.)

Electron Paramagnetic Resonance (EPR)

BODA monomer (X = C(CF₃)₂, R = Ph) and fullerene C₆₀ (50.6 wt% C₆₀) were
placed in a 1:1 molar ratio in a degassed and flame-sealed quartz tube, and heated in situ
at 210º C for the duration of the experiment. Radical formation during the
polymerization was continuously monitored at varying microwave power (0.2 – 200 mW).
Transmission Electron Microscopy (TEM)

The size and morphology of the polymers of the BODA-co-C_{60} (2:1 molar ratio) and BODA-co CNOs were prepared from solution by placing a drop onto a Cu grid bought from SPI Supplies® (300 mesh Cu grid, lacey carbon coated), dried at 100 °C under high vacuum, observed using a Hitachi Model NANO H9500 HRTEM and the Hitachi Model 7600 LRTEM

Thermal Gravimetric Analysis

TGA of the fullerene copolymer samples were typically performed using ~10 mg copolymer sample heated under N\textsubscript{2} flow at 40-50 mL/min to the ceiling temperature at 3 °C/min. The BODA-co-C_{60} copolymer (30.4 wt% C\textsubscript{60}) was heated to 1000 °C, and the BODA-co-CNOs samples were heated to 1100 °C.

Raman Spectroscopy

The Raman spectra were recorded using a Renishaw 1000 Raman spectrometer with 785 nm emission line from a NIR laser excitation source. The solid analyte compound was placed onto a glass slide underneath the laser, and the spectra were recorded with 50x objective lens, high detector gain, with laser power 25, for 3 accumulations of 30 s each. The BODA-co-C_{60} copolymer was the 30.4 wt% C\textsubscript{60}.

Diodes

BODA-co-C_{60} (15:5 molar ratio, 10 mg/mL) prepolymerms were spin-cast (1000 rpm, 180 sec, 2 cycles) on to plain glass slides, ITO glass slides, and aluminum coated
glass slides. Half of the prepolymer films were then cured by gently heating to ~200 °C for 2 hrs on a hot plate. Aluminum dots were then vacuum evaporated onto the films and the I-V characteristics of each film were determined in collaboration with Dr. Harrell’s laboratory using a four point probe semiconductor parameter analyzer between -7 — 7 V.

**Multi-Angle Light Scattering (MALS)**

Multi-Angle Light scattering was performed on identically polymerized samples of BODA (x = C(CF₃)₂, R = Ph) homopolymer, C₆₀ copolymer, and CNOs copolymer. Each polymer was dissolved in a 1 mg/mL solution of HPLC grade CHCl₃, and filtered through a 0.45 µm PVDF or PP filter. Each was run through the GPC-MALLS system described above. A graph of the cumulative hydrodynamic radius (rₐ) of each compound shows the step nature of the two fullerene containing copolymers, in opposition to the gradual growth of the homopolymer (Figure 2). The C₆₀ containing polymer has a sharp increase in polymer fraction at rₐ = 6-8 nm. The multilayered CNOs containing polymer has a similar increase at rₐ = 8-9 nm, and smaller steps at rₐ = 11 and 15 nm.

**Thermomechanical Analysis (TMA)**

A glass microscope slide cut into equal ~1 cm² pieces. A film of each of 5 different molar ratios of MODA (X = H), and BODA (X = C(CF₃)₂, R = C(CH₃)₂OH) (1:0, 1:2, 1:10, 1:20, and 0:1 BODA:MODA, each in NMP solutions heated at 202 °C for 5 hrs) were cast onto these slides, and cured on a hotplate at ~200 °C for 2 hrs. The pieces were then tested in collaboration with Dr. Luzonov’s laboratory on the TMA with a load of 5 mN, and a probe diameter of 3.5 mm, for a duration of 20 minutes.
Amine endcapped Poly(aromatic ether sulfone) was polymerized by first deprotonating 0.1000 g (4.38 x 10^{-4} mol) bisphenol-A \( (\text{C}(\text{CH}_3)\text{2}(\text{C}_6\text{H}_5\text{OH})_2 \) with 0.1438 g (1.05 x 10^{-3} mol) in a clean dry 50 mL round bottomed flask with 5.0 mL anhydrous toluene and 20 mL DMAc. The reaction was heated to 120 °C with stirring. The water was azeotroped with the toluene and caught with a Dean-Stark trap. After about 3 hrs, the Dean-Stark trap was removed, and 0.1007 g (3.50 x 10^{-4} mol) 4,4’-dichlorodiphenylsulfone, and 0.0224 g (1.75 x 10^{-4} moles) 4-chloroaniline were added. A clean dry condenser was attached to the flask, and the reaction was heated to 175 °C overnight, cooled and precipitated in methanol to yield the amine endcapped poly(arylene ether sulfone) of average degree of polymerization = 11 (2 NH2-Ph endcaps around a core of 5 bisphenol-A and 4 –diphenylsulfone residues) \(^1\text{H} \) NMR (300 MHz, CDCl\(_3\)) \( \delta \): 1.25 (56H, singlet), 4.40 (1H, broad s), 6.91-7.01 (41H, dd), 7.22 (33H, d), 7.82 (16H, d).

This polymer was then endcapped with the MODA-carboxylic acid (5-1). To a clean dry 25 mL round-bottomed flask, 0.0111 g (5.09 x 10^{-6} mol) of the functional prepolymer was added, followed by 0.0046 g (1.12 x 10^{-5} mol) MODA-carboxylic acid and 0.0035 (1.52 x 10^{-5} mol) DCC and dissolved in 1 mL DMF, 0.5 mL N(CH\(_2\text{CH}_3\))\(_3\). The solution was purged with N\(_2\), connected to a condenser, heated to 50 °C with magnetic stirring overnight. The solution was cooled and precipitated in methanol. \(^1\text{H} \) NMR (300 MHz, CDCl\(_3\)) \( \delta \): 0.83 (H, m), 1.25 (H, m), 4.2 (broad s), 6.91-7.01 (dd), 7.22 (s), 7.36 (t), 7.57 (m), 7.7 (m), 7.8 (d), 7.9 (s). \(^1\text{C} \) NMR (75 MHz, CDCl\(_3\)) \( \delta \): 29.81, 49.49, 84.19, 87.77, 99.99, 117.75, 119.90, 122, 126, 128.55 130, 131.87, 162.07, 165.02.
CHAPTER 3
BODA PROCESSING AND CARBON DERIVATION

Polymeric Carbons

Carbon may be produced through the incomplete oxidation of many organic polymeric materials. The carbon thus produced may be of several different forms and varying yields depending highly upon the nature of the original polymeric material. Heating in an inert atmosphere initiates one of several different reactions: degradation into evolvable gasses, chain collapse into a liquid crystalline mesophase followed by softening into graphitic carbon, or chain coalescence into a hard isotropic char. The latter two mechanisms both lead to residual carbon, though of different types. 63

There are three distinct crystalline forms of elemental carbon. The two ancient forms of diamond and graphite have proved useful for centuries, exhibiting somewhat opposing properties. Diamond, whose carbons are all in the tetrahedral sp³ hybridization bonding state, is optically clear and the defining compound for the highest measurable hardness on the Mohs hardness scale. Graphite, on the other hand, is formed of stacked planar sheets of sp² hybridized carbon in extended hexagonal structures. This anisotropic structure leads to a highly absorbing black crystal, which is very stiff in the plane of the layers, but with relatively weak van der Waals bonds between the planes leading to easy shearing, thus providing graphite’s good lubricating properties. The third crystalline structure is not an extended structure like the first two, but crystal stacking of the
molecular carbon allotrope, C₆₀, known as Buckminsterfullerene, or fullerene[60]. Here again the carbons are in the sp² hybridization state, but instead of forming extended two dimensional arrays of 6-membered rings, fullerenes are formed of both 5- and 6-membered rings. The five-membered rings lend a curvature to the structure that permits it to close back upon itself and form the spherical molecule that has caught both the scientific and the popular imagination. At temperatures above 1800 °C, diamond converts to graphite, indicating that the sp² hybridization is more stable than the sp³ state at these temperatures.

Scheme 3-1. Carbon in sp³ “diamond” structure converts to sp² “graphite” structure above 1800 °C.

There also exist in addition to these crystalline carbon forms, several non-crystalline structures. The most common of these is that known as vitreous or glassy carbon. Structural studies of glassy carbon indicate that it is composed of stacked layers or aromatic ribbons that are tangled randomly together. The layers themselves have been compared to the layers found in the graphite structure, though severely limited in both the size of the crystallite in the directions parallel to the plane of the layers (Lₐ) and in the
thickness of the crystallites in the plane perpendicular to the layers (Lc).\textsuperscript{65} X-ray
diffraction studies correlate these two distances to the (110) and (002) lines respectively
(as defined by the crystal structure of graphite) in the diffraction patterns of the glassy
carbons.\textsuperscript{66} The presence of the (002) peak indicative of the interlayer spacing in graphite
in the diffraction patterns of glassy carbons support the layered structure model. Glassy
carbons are, however, different from graphite in both hardness and anisotropy. The
sheets of glassy carbon are in distinct bundles which are tangled up together, and
randomly oriented relative to each other, preventing the shear induced slipping seen in
graphite.

Pyrolyzed carbon, formed from the heating of organic materials in an inert
atmosphere, forms either a coke from materials that are liquid directly prior to
carbonization, or a char from solid-state carbonizations. Chars largely maintain the
morphological shape of the original material, such as charcoal formed from wood, while
cokes tend to take the shape of the container in which they are held. Carbon precursor
polymers are also often compared using the quantitative measures of carbon yield,
defined as the percent of carbon residue that is maintained from an initial polymer sample

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image}
\caption{Scheme 3-2. Polyacrylonitrile and proposed intermediate ladder and ribbon structures
during carbonization.}
\end{figure}
that has been thermally carbonized, and the conversion efficiency, defined as the percent of carbon maintained compared to the weight of the carbon in the initial polymer.

The most common synthetic polymeric carbon precursors are polyacrylonitrile (PAN) and phenol-formaldehyde resins. PAN \((\text{CH}_2=\text{CH-CN})_n\) is used in the commercial production of carbon fibers; phenolic resins are commonly used in the production of glassy carbon objects. These polymers, whose structures are given in \textbf{Schemes 3-2} and \textbf{3-3}, respectively, each form a cyclic structure in the backbone prior to pyrolysis. This ability to cyclize, undergo ring fusion or chain coalescence is the general feature of good carbon precursor polymers. The phenolic resins, of course, have the phenyl groups of the phenol, linked together through the one-carbon linkages from the

![Scheme 3-3. Phenol-formaldehyde resins.](image)

formaldehyde monomers. Phenol and formaldehyde initially react to form various methylolphenols, which then undergo condensations of either water or methanol to yield ether or methylene bridges between the aromatic rings. Shown are the two methylolphenol monomers, and the seven possible dimer structures from homocondensation of each and cross-condensation of the two monomers.

The cyclic structure of the polyacrylonitrile (PAN) on the other hand, is less obvious. PAN, like other vinyl polymers, requires a preoxidation step prior to carbonization to give high-yield carbon. In PAN this leads to the heterocyclic ladder polymer shown in

\textbf{Scheme 3-2}. The cyclic backbone structures of the polymers can more easily coalesce
into the carbon ribbon layers that form the layers of a graphitic or glassy carbon structure. There is an empirical limit of one carbon atom between aromatic rings to still maintain a high carbon yield.\textsuperscript{68} Greater alkyl linkages lead to chain scission and volatilization.

Other common carbon precursor polymers include poly(vinyl chloride), (PVC)\textsuperscript{69}; poly(vinylidene chloride), (PVDC)\textsuperscript{70}; cellulose\textsuperscript{71}; and tar pitch.\textsuperscript{72} PVC (CH\textsubscript{2}=CHCl)\textsubscript{n}, and PVDC (CH\textsubscript{2}=CCl\textsubscript{2})\textsubscript{n} are both linear polymers consisting of methylene carbons alternating with chlorine bound carbons. When heated under an inert atmosphere, each polymer evolves gaseous HCl, due to elimination to form a polyene. The polyene then coalesces to form the carbon material. Cellulose (C\textsubscript{6}H\textsubscript{10}O\textsubscript{5})\textsubscript{n} undergoes many dehydration steps to eventually yield a very highly graphitic carbon.\textsuperscript{1} Tar pitch has a high carbon yield relative to cost, and has also been used to produce carbon fibers.\textsuperscript{1}

**BODA-Derived Carbon**

Bis-ortho-diynyl arene (BODA) monomers and polymers hold a unique place in the world of carbon precursor polymers, combining the most desirable properties for a processable carbon precursor.\textsuperscript{73} The BODA monomers thermally cyclize, as previously described, to form either the cycloaromatized naphthalene linkage or the alternative benzofulvene linkage through a radical mechanism.\textsuperscript{74} (\textbf{Scheme 3-4}) Due to the fact that the population of radically cyclized monomers is much smaller than the population of the uncyclized monomers, the polymerization propagates using these in situ generated radicals as initiators. Therefore, the tetrafunctional monomers initially form intermediate linear or branched oligomers. Meanwhile, the unreacted enediyne functionalities serve as solubilizers for these oligomers, allowing them to stay soluble and pliable after the linear
oligomers formed from comparable difunctional monomers would have precipitated out of solution. The solubilizing pendant motif is a common approach used to make insoluble polymers behave as required for their applications and has been previously used to solubilize polyarylenes.75,76,77

The advantage of the BODA strategy for carbon precursor applications lies in the fact that the solubilizing pendants are not lost weight during pyrolysis. An unfunctional solubilizer is subject to the same structural restrictions as the main chain of the polymer during pyrolysis. Therefore any solubilizer that is not fit for carbonization, especially any alkyl chains larger than one carbon long will be broken, volatilized, and will count against the converted masses in both the carbon yield and carbon conversion efficiency calculations. But, in the case of the BODA oligomers, the enediyne solubilizers do eventually become integrated into the overall BODA network. This network is essentially a highly crosslinked network of polynaphthalenes bound together by the linker groups (X), which are invariably 0 or 1-atom spacers. This unique ‘double duty’ function of the enediynes, allows for a very high carbon yield for BODA polymers without compromising the solubility and processability properties normally sacrificed in polyarylenes.11,78
BODA monomers react in an additive or non-condensation mechanism. This means that the empirical formula for the monomer is the same as that for the polymer. There are no condensates formed during the polymerization. We can compare this with the two counter examples discussed above, polyacrylonitrile and phenolic resins. If we begin with the phenolic resins, we can immediately see that for each new linkage formed in the polymerization, there is a condensate formed: either H₂O or CH₃OH, dependant on whether an ether or a methylene bridge is formed, respectively. In the case of the PAN, the initial polymerization itself is an addition type mechanism, yielding no condensates similar to the BODA polymerization, but the PAN itself is a rather middling carbon precursor polymer, as seen in Table 3-1.

PAN has a carbon yield of 44%, when heated to 1000 °C under inert conditions.² The PAN that is used in the manufacture of carbon fibers is a preoxidized polymer,
Scheme 3-2, that has been preheated in air at 220 °C, to yield the oxidized ladder polymer shown. This oxidized prepolymer has an improved carbon yield of 62%, but then has the added condensates of H₂O, and CO₂ during the carbonization process. The preoxidized PAN also suffers from a drop in solubility relative to the virgin PAN. Practically, this requires the PAN to be processed prior to the oxidation step, limiting the dimensions of the carbon object ultimately to be produced.

Table 3-1. Carbon Yields of Polymers Pyrolyzed at 1000 °C in Inert Atmosphere.

<table>
<thead>
<tr>
<th>Carbon Precursor</th>
<th>Carbon Yield (wt %)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>Ramie</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>Rayon (cellulose)</td>
<td>13</td>
<td>1</td>
</tr>
<tr>
<td>Saran (PVDC)</td>
<td>25</td>
<td>1</td>
</tr>
<tr>
<td>Polyacrylonitrile</td>
<td>44</td>
<td>1</td>
</tr>
<tr>
<td>Phenol Benzaldehyde</td>
<td>37</td>
<td>1</td>
</tr>
<tr>
<td>Poly(Vinyl Chloride)</td>
<td>42</td>
<td>1</td>
</tr>
<tr>
<td>Phenol-Formaldehyde</td>
<td>52</td>
<td>1</td>
</tr>
<tr>
<td>Polyacrylonitrile (preoxidized)</td>
<td>54</td>
<td>1</td>
</tr>
<tr>
<td>BODA monomer 1-1 (X = C(CF₃)₂, R = Ph)</td>
<td>75</td>
<td>16</td>
</tr>
<tr>
<td>BODA monomer 1-2 (X = C(CF₃)₂, R = C(CH₃)₂OH)</td>
<td>52</td>
<td>18</td>
</tr>
<tr>
<td>BODA monomer 1-3 (X = -, R = Ph)</td>
<td>79</td>
<td>16</td>
</tr>
</tbody>
</table>
This example illustrates several other advantages of the BODA carbon precursor route. BODA polymers do not require any preliminary oxidation steps, produce no condensates during polymerization, have a very large processability window, and still maintain a very high carbon yield.

**BODA-derived Carbon Properties**

BODA carbon has been characterized in a few important publications.\textsuperscript{11,16,79,80,81} The carbon yield of polymers is determined using thermo-gravimetric analysis (TGA), a technique that combines an atmosphere controlled furnace with a sensitive microbalance. A sample may thus be heated according to a precise temperature program, and the change in mass continually monitored and correlated to temperature. This method also provides a quantitative way to compare carbon precursor polymers, by heating under standard conditions of heating rate, final temperature and atmosphere. BODA polymers heated under these standard conditions (10 °C/min to 1000 °C under N\textsubscript{2}(g)) yields carbons at 52-79%, depending on monomer (Figure 3-1). These data are compared to the industry standards in Table 3-1.
Figure 3-1. Thermal Gravimetric analysis of Carbon yield of BODA Monomer 1-1 (X = C(CF₃)₂, R = Ph), and corresponding cure pyrolysis temperature program (H. Shah).¹²

The carbon derived from a BODA polymer is a glassy polymer, as described above. This is determined using wide angle x-ray diffractometry (WAXD) on ground powder samples of the carbon produced at different temperatures (neat polymer, 900, and 1600 °C, Figure 3-2.)¹¹-¹² The diffraction pattern of a glassy carbon sample expresses the (002) and (110) signals from the diffraction pattern of graphite. These two peaks get sharper and more distinct as the carbonization temperature of the polymer is increased. This indicates an overall increase in the graphitic crystalline phase size throughout the carbon.
Figure 3-2. Wide Angle X-ray Diffraction of BODA polymer and derived carbon as a function of cure temperature. The glassy carbon (110) and (200) peaks become sharper as crystalline regions grow. (H. Shah)\textsuperscript{12}

The electrical evolution of BODA polymer on its way to becoming BODA-derived carbon has been analyzed electrically in a clever experiment, wherein a BODA polymer rod was fashioned into an electrode with Pt lead wires.\textsuperscript{11,82} The resistivity of the polymer was then continually monitored using a multimeter while the polymer was carbonized in a tube furnace (Figure 3-3). Above 528 °C, the resistivity dropped within the measurable range of the multimeter. From there the resistivity drops quickly over the next 200 °C and approaches a plateau value just above zero by about 800 °C, where it is posited that further carbonization has no appreciable effect on the conductivity, due to the presence of a fully conductive network by this temperature.
Figure 3-3. The evolution of the resistivity of BODA polymer during pyrolysis to 1000 °C in N₂ atmosphere. (X. Wu)²⁰

Figure 3-4. Cyclic Voltammetry of $1 \times 10^3$ M Fe(CN)$_6^{3/-4-}$ in 1 M KCl with BODA-derived Carbon electrode in comparison with commercially available GC10 glassy carbon electrode. (X. Wu)²⁰

This carbon also behaves similarly to commercial glassy carbon for use as carbon electrodes. A carbon electrode produced from BODA polymer was compared to a commercial glassy carbon electrode in a series of cyclic voltammetry (CV) experiments,¹¹²⁰ wherein the electrodes were used to perform reactions on a series of redox systems, including ascorbic acid, Fe$^{2+/3+}$, and Fe(CN)$_6^{3/-4-}$ (Figure 3-4). In each of
these cases the two electrodes behaved qualitatively the same. The amplitude difference is due to differences in effective working areas of the two electrodes. The one difference between the two electrodes as observed in an acidic medium, where the BODA-derived carbon electrode showed a current at negative potentials that was unobserved in the commercial electrode. This evidently indicates sites in the BODA carbon that support the reduction of the acidic protons to H₂ gas.

Figure 3-5. Dilatometry of BODA polymer rod showing the onset of carbonization (solid line), and corresponding cure temperature program (dashed line). (S. Iacono)¹⁹

The onset of carbonization has also been observed using dilatometry to measure the coefficient of thermal expansion of BODA polymer rods during the carbonization process, and on the resultant carbon rods after the carbonization process.¹⁹ The onset of carbonization is seen as a change in the slope of the thermal expansion graph, where the rod begins to shorten rather than lengthen, reflecting the chemical changes within the
polymer samples. For a 1:4 ratio of monomer 1-1 \((X = C(CF_3)_2, R = Ph)\) to monomer 1-4 \((X = O, R = Ph)\), this temperature was seen to occur at 550 °C (Figure 3-5). The onset temperature varied between 535 and 575 °C for all monomers measured. Coefficient of thermal expansion (CTE) values were observed to be between 2.85 x10^{-6} and 6.92 x10^{-6} K^{-1} for all samples, depending on both monomer composition and carbonization temperature. Samples carbonized to 1500 °C had smaller CTE values than those only cured to 1000 °C, due to greater graphitization at the higher temperatures as observed with scanning tunnelling microscopy (STM, Figure 3-6). The crystalline graphitic regions are denser and have stronger \(\pi-\pi\) interactions, and are therefore less prone to

![Figure 3-6. Scanning Tunneling Micrograph of BODA-derived carbon cured to 1500 °C under N_2, indicating regions of graphitization.](image)
movement and rearrangement when heated than the largely amorphous glassy carbon regions.

**BODA-Derived Carbon Applications**

The utility of BODA polymers as a carbon precursor has been demonstrated through progressively more intricate processing methods. The micromolding in capillaries (MIMIC) technique developed by Whitesides et al. provided a nice demonstration of this. MIMIC processing involves the vacuum-assisted filling of capillary patterns in silicone rubber molds with a polymer resin. When this is performed with a carbon-precursor polymer, it provides a route for producing microstructured carbon, that have potential applications in micro-electro-mechanical systems (MEMS). BODA polymers’ high carbon yield, good solubility, and lack of condensates made it a perfect candidate for this application.

The polydimethylsiloxane (PDMS) rubber template was filled with an oligomeric BODA prepolymer, under vacuum, then cured at 250 °C, cooled for mold removal, and finally carbonized at 1000 °C to yield a microstructured carbon structure with minimal dimensional change (16%) from the original template, and high fidelity to the pattern shape (**Figure 3-7**). The carbon structure was thereafter shown, with the use of a 4-point probe to be semiconductive.
Figure 3-7. Micromolding in capillaries (MIMIC) processed BODA polymer network, cured at 250 °C, left, BODA derived carbon pyrolyzed at 1000 °C, right. Minimal dimensional change and high fidelity to the original PDMS template is observed.17

The excellent processability and space-filling capability of BODA polymers was further demonstrated through the replication with a BODA prepolymer of a photolithographically-defined optical grating using a technique called sub-micron microtransfer molding.11-12,83 The scope of utility was broadened by an order of magnitude. The silicon optical grating consisted of 0.5 µm lines. The BODA replicate (Figure 3-8) maintained the optical properties and gave clear visible diffraction as a function of angle.

Macroscale carbon is also possible using the BODA polymer approach, as demonstrated with the fabrication of carbon tubes of about 600 µm outer diameter using glass capillaries as templates (Figure 3-9).11,21-84 The capillaries were filled with BODA prepolymer both neat and in a solution with THF and cured vertically in a vacuum oven prior to carbonization at 1000 °C in the TGA. The neat polymer yielded a high-quality solid carbon rod, while the polymer solution yielded a hollow carbon tube due to migration and coating of the capillary walls by the polymer during evaporation of the
solvent. The solid carbon rod showed a 38.8% decrease in diameter size from the cured rod to the carbon rod stages. The hollow fiber showed only a 9.1-9.5% change in all dimensions (inner diameter, outer diameter, and wall thickness) from the cured stage to the carbonized stage. This indicates that the solvent evaporation may have also helped with the removal of the weight loss during the curing stage, thereby minimizing the shrinkage during the carbonization process.
Figure 3-9. Scanning electron micrographs of BODA-derived carbon rod (d = 604.6 µm and hollow tube (O.D. = 612.5 µm, I.D. = 375 µm) carbonized at 1000 °C. (H. Zengin)\textsuperscript{22}

BODA carbon has also shown function as a component in organic/inorganic hybrid materials. This class of materials combines the advantages of inorganic and organic materials, by combining them in composites. Often, the physical improvements in the composites depend on the interfacial area between the two components which in turn depends on the component domain sizes. BODA monomer 1-2 (X = Ph, R = C(CH\textsubscript{3})\textsubscript{2}OH) was designed to provide alcohol functionality that could be condensed with a silica precursor monomer, tetramethyl orthosilicate (TMOS, Si(OCH\textsubscript{3})\textsubscript{4}) to form a composite sol-gel glass, which was then thermally cured.\textsuperscript{85} The molecular level of the composite in “BODA-Glass” composite led to BODA polymer domain sizes of 25 nm diameter as measured by transmission electron microscopy-energy dispersive x-ray spectroscopy (TEM-EDX). Carbonization of the polymer by heating to 1000 °C under an inert N\textsubscript{2} atmosphere led to a carbon-glass composite, or heating under air produced nanoporous silica glass by oxidative removal of the organic phase.
BODA-Derived Carbon Photonic Crystals

Photonic crystals are the optical analogy of a traditional crystal. While the traditional crystal is formed from a periodic array of atoms or molecules that exhibit Bragg-type diffraction of electrons dependent on both the geometry of the crystal and the lattice potential of the crystalline components, a photonic crystal is formed from a periodic array of alternating dielectric constants that exhibit Bragg-type diffraction of photons dependent on the geometry of the crystal, including the spacing of the periodicity,
and the dielectric constant difference of the crystalline components. If the dielectric constant difference is great enough, a photonic bandgap is formed where a wavelength of light is excluded from propagation through the medium. The photonic bandgap concept is scalable to many different wavelengths from microwaves to infrared. The simplest photonic crystal is 1-dimensionally periodic: essentially a layered structured. There also exist 2-dimensional and 3-dimensional photonic crystals. (Scheme 3-5) With a 3-dimensional photonic crystal, a complete bandgap is possible, wherein a photon of the excluded wavelength will be excluded at any incident angle. Photonic crystals may be used as optical devices either through reflection at the surface, a dielectric mirror, or through defects in the photonic crystal that act as waveguides.

Figure 3-11. Scanning electron micrograph of sintered silica opaline template

The fabrication of photonic bandgap materials, alternately known as photonic or electromagnetic crystals, is very interesting due to potential applications in optical communication and sensor technologies. Visible photonic crystals are materials that
possess periodicities in their dielectric structure on the same order of magnitude as the visible wavelengths. The extent of the bandgap at this wavelength is dictated by the degree of dielectric contrast. Silicon infiltrated silica templates have already been used to create a photonic crystal with a complete three-dimensional bandgap near the 1550 nm optical communications wavelength. Many reports of inorganic inverse opals exist with much focus on TiO₂ due to its high refractive index.

Scheme 3-5. Photonic crystals are composed of periodically alternating dielectric materials on the scale of the wavelength of the electromagnetic radiation to be excluded from propagation. The periodicity can be either 1-, 2- or 3-dimensional as illustrated.

Silica opals are three-dimensional close-packed arrays of silica spheres whose diameters are on the scale of wavelengths of light (Figure 3-11). Silica opals produced artificially via self-assembly of sol-gel prepared particles have been utilized to produce a photonic bandgap. Self-assembled systems are used instead of nano-lithographic methods to produce the ordered periodicities, in general, because of potential cost and rapid production advantages. An inverted opal structure is a photonic crystal architecture with the same symmetry as an opaline structure, but with inverted dielectric contrast. For example a silica opal has silica spheres surrounded by air in the interstitial spaces. An inverse opal would consist of a close packed array of spheres defined by a
higher dielectric constant material in the remaining space. In order to achieve an inverted opal structure or to further modify the refractive index contrast, the opals can be infiltrated with a dielectric material and the template phase removed chemically. Fabrication of an inverted opaline structure takes advantage of the bi-continuous nature of the opaline geometry, wherein each of the two phases are continuous with themselves throughout the whole of the structure, allowing for infiltration of the dielectric material and removal of the template material without disturbing the photonic crystalline structure. The opaline crystal can be produced either from silica spheres as described or with sol-gel synthesized polymer spheres that can be removed thermally.96,97

Although amorphous carbon is not an optical material of much value given its high absorption, the high refractive index (~ 2.1) has led to interest in their use in photonic structures where surface chemistry and reflection are the operative phenomena. Carbon structures, including photonic crystals, suffer from the limited availability of suitable, easily fabricated organic precursors. Zakhidov, Baughman, et al.,31 have demonstrated the use of phenolic resins and hydrocarbon CVD to prepare inverse carbon opals. However as previously mentioned, these methods are limited due to poor carbon yield. BODA polymers make very good carbon precursors for producing inverse carbon opal (ICO) via the alcohol terminated acetylenic precursor monomer (1-2, X = C(CF3)2, R = C(CH3)2OH). This method allows the fabrication of inverse carbon opals with relative ease compared to CVD methods and with more fidelity to the template and less shrinkage than previous polymeric routes.31

Initial attempts at impregnation of the interstitial spaces with the phenyl terminated monomer 1-1 resulted in hydrophobic beading of the monomer and oligomers
on the surface of the opal. However, the alcohol functional monomer 1-2 (Scheme 3-6) in particular has shown compatibility with silica sol-gel precursors in the production of the BODA-glass composites\(^3\) and was an obvious choice for coating and infiltrating silicate structures (Figure 3-11). The sol-gel process produces silica spheres which are monodisperse and, given adequate time, naturally self assemble in the close packed structure

![Diagram of alcohol terminated BODA monomer 1-2](image)

**Scheme 3-6.** Alcohol terminated BODA monomer 1-2 (X = C(CF\(_3\))\(_2\), R = C(CH\(_3\))\(_2\)OH)

**Scheme 3-7** illustrates the process for fabricating the inverse carbon opal in addition to optical images of the surface at different stages.\(^1\) Silica opals were prepared from tetraethyl orthosilicate (TEOS, Si(OCH\(_2\)CH\(_3\))\(_4\)) by a previously reported sol-gel route\(^9\) and allowed to self-assemble either with centrifugation or gradual settling. BODA monomer was melted in contact with the washed silica opal, and allowed to soak into the opal as a liquid, followed by cure and pyrolysis to glassy carbon in a TGA. The excellent space-filling capability of the monomer and oligomers make the polymer very suitable for nano-scale molding and templating. The silica template was then etched with hydrofluoric acid (HF), rinsed with deionized water, and dried to yield the dry ICO with air voids in place of the silica template.
Scheme 3-7. Fabrication of BODA-derived carbon inverse opal, with optical micrographs of A) the silica opal, B) the carbon impregnated silica opal composite, and C) the etched BODA-derived carbon inverse opal.

The reflectance spectra of the silica opal template is compared to the inverse carbon opal in Figure 3-12 to show the difference in the bandgaps of the two structures with the same periodic distances, and different dielectric material components. The bandgap at the L-point of the opaline structure can be predicted from formula 3-1,

$$\lambda_{\text{max}} = 2 \sqrt{\frac{2}{3}} d n_{\text{average}}$$  \hspace{1cm} (3-1)$$

where d is the periodic distance (center-to-center of two adjoining spheres) in the opal structure, and $n_{\text{average}}$ is the average refractive index as calculated by equation 3-2. Since the scale of the composite is on the scale of the wavelength of light, the composite is seen to have one composite refractive index, $n_{\text{average}}$ as described by effective medium theory.

$$n_{\text{average}}^2 = \sum n_i^2 V_i$$  \hspace{1cm} (3-2)
This makes a convenient type of analysis for close-packed opaline and inverse opaline structures because both $\lambda_{\text{max}}$ and $d$ are measurable, from reflectance measurements (Figure 3-12) and scanning electron micrographs (Figure 3-13), respectively. The volume fractions of the two components, carbon and voids, are calculable from the geometry of the face-centered cubic structure. Assuming that the inverse opal volume fraction = 0.26, and the void fraction = 0.74, $d = 233$ nm (Figure 3-13), $\lambda_{\text{max}} = 535$ nm (Figure 3-12), and the refractive index of air = 1.00, then the refractive index of the glassy carbon is calculated to be 2.18. This analysis assumes complete filling of the matrix with polymer/glassy carbon and a perfect close packed crystalline structure. The carbon refractive index is typically difficult to measure by classical optical techniques.

**Figure 3-12.** Reflectance spectra of Silica opal template and air filled BODA derived Carbon Inverse Opal, normalized.
Figure 3-13. Scanning electron micrographs of carbon inverse opals. The close packed array of voids in the carbon is visible, in both the top layer and the second layer visible through the holes left by the connective contacts between the original silica spheres.

because of the high optical loss, but reported values of refractive index for graphite as calculated from the measured optical dielectric constant, are between 2.04 (± 0.04) and 2.15 (± 0.04) for the basal plane.\textsuperscript{101} The index of refraction of glassy carbon is less fixed than that of graphite due to structural variety based on the amount of aromaticity (i.e. polarizability) of the carbon. The calculated index of refraction for our opal carbon is reasonably within this range.

Carbon Inverse Opal-Based Sensor Elements

The dependence of the ICO bandgap wavelength on the indices of refraction of both the carbon and the void material may be exploited by filling the open voids with
varying refractive index materials to produce optical sensor elements\textsuperscript{102,103,104,105,106,107,108}.

(Scheme 3-8)

Scheme 3-8. ICO sensor concept. The bandgap of the ICO is monitored with a fiber optic spectrometer attached to a microscope. When the analyte fills the voids of the ICO, the photonic bandgap shifts, and is recorded by the spectrometer.

A simple demonstration of this phenomenon was accomplished by filling the voids with a series of solutions of miscible solvents, acetonitrile (n = 1.341 \text{ @ } 20 \degree C) and water (n = 1.330 \text{ @ } 20 \degree C), and observing the change in excluded wavelength with the change in refractive index (Figure 3-14). The change in refractive index between 100\% acetonitrile and 100\% water is only 0.011 r.i.u., but shows a reproducible and gradual shift of 13 nm over this refractive index change\textsuperscript{11,18}.
The sensor concept was further elaborated by filling the spaces with the electroactive liquid crystal, 4-pentyl-4'-cyanobiphenyl (5CB) to form kind of optical switching device. In addition to the electrically-activated liquid crystalline response that is often used in liquid crystalline displays (LCDs), 5CB undergoes its nematic to isotropic liquid phase transition thermotropically at 35 °C. This phase transition was detectable in the 5CB/ICO composite as a change in the excluded wavelength (Figure 3-15). There is a shift of ~20 nm from 612 nm at 23.5 °C, in the nematic phase, to 632 nm, at 51.1 °C in the isotropic phase. The wavelength excluded remains at 632 nm at 60.6 indicating that the change is not due to a first order transition in the liquid, such as thermal expansion, but is instead a second order transition such as that expected for the phase transition.
Figure 3-15. Switching of bandgap $\lambda_{\text{max}}$ with liquid crystalline order/disorder phase change of 5CB at 35 °C. The ICO-5CB reflects light at 632 nm in the nematic phase, and 612 nm at both temperatures in the liquid phase.

Since the nematic phase is rather tightly defined temperature-wise, between the melting point at 22.5 °C and this transition at 35 °C, there was not another data point taken in the nematic phase. The optical switch described could be either a thermo-optical switch as demonstrated, or an electro-optical switch, by taking advantage of the electrical conductivity of the glassy carbon material used to form the photonic crystal as an electrode.

Biodetectors are also possible using the BODA-ICO technology framework. This was demonstrated by using the blood protein hemoglobin. Hemoglobin (Hb) is a beautifully intricate tetrameric complex of protein subunits with iron containing porphyrin rings located in the center of each protein. The porphyrin, or heme group, binds $O_2$ and $CO_2$ on the Fe atom, for cellular respiration transport. The binding of these gasses is regulated within the body using several mechanisms. The saturation of these
Figure 3-16. Reflectance spectra of ICO filled with solutions of Hemoglobin in borate buffers of pH = 6.62 (blue), 7.0 (green), 7.5 (yellow), 8.0 (orange) and 8.5 (red). The ICO was washed with clean buffer between each measurement.

sites depends on several factors including the partial pressures of O$_2$ and CO$_2$, temperature, the concentration of cofactors such as δ-2,3-bisphosphoglycerate (BPG), and the pH of the solution. The binding of an O$_2$ molecule to the Fe in one of the heme groups causes a conformation change within the protein tetramer that cooperatively promotes the binding of oxygen molecules at the additional three heme sites. This process also reverses itself upon dissociation. An increase in temperature or in acid, CO$_2$, or BPG levels all decrease the affinity of the heme group for O$_2$ binding.
Figure 3-17. The reflectance bandgap $\lambda_{\text{max}}$ vs. buffer pH of hemoglobin solutions. The physiological pH of 7.4 seems to correspond to an inflection point in the photonic crystal response.

The simplest control in this list is acid content, which can be controlled with buffer solutions. All other factors being the same, the oxygen content is inversely related to the acid content in the solutions. Borate buffer solutions between the pH 6.62 and 8.50 were used to make solutions of hemoglobin to fill ICO spaces. The rejected wavelength was shifted with the different pH solutions over the range of 471 to 502 nm. (Figure 3-16) A plot of the rejected $\lambda_{\text{max}}$ of the Hb-ICO vs. the pH of the borate buffer solutions, shows what appears to be an inflection point between pH = 7.0 and 7.5, (Figure 3-17) the natural biological pH range under which Hb usually operates, where the photonic response would be even more sensitive to changes in the solution pH, correspondent to the cooperative conformational changes in the protein quaternary structure.

It is not immediately obvious why there should be a change in the refractive index of the solutions with different O$_2$ contents. The possibilities include the concentrations of the borate buffer components, the concentrations of O$_2$ in the hemoglobin, the
conformation changes that occur upon binding, and the chromatic change that occurs in the hemoglobin upon complexation of the iron. A control experiment using the borate buffers themselves to fill the spaces in the ICO, showed a shift of the excluded wavelength from 500 to 516 nm, a smaller shift than that seen with the Hb solutions, and not following a definite pattern relative to pH, so while that may account for some of the signal shift, it cannot account for all of it. The color of the Hb changes due to the change in the binding order of the Fe atom from 5 to 6 coordinate upon oxygenation. Deoxyhemoglobin appears purplish-blue, and has a visible $\lambda_{\text{max}} = \sim 550$ nm, and oxyhemoglobin appears red, and has visible $\lambda_{\text{max}} = 540$ and 575 nm.\textsuperscript{47} These are all out of the range of the observed photonic response. The concentration of bound oxygen and the induced conformation changes in the protein are difficult to separate from each other, except to say that the conformation changes that occur within the protein upon the binding of the O$_2$, from the unoxygenated ‘T’ form to the oxygenated ‘R’ form, is the opposite of the conformational change that occurs upon the uptake of the protons by basic protein residues, from the R to T state. Therefore the photonic signal change acts as a measure of the bound oxygen, through what appears to be a conformation induced change in solution refractive index.

### Disordered Carbon Foams

The demonstration of the ability to form nanostructured porous carbons with BODA polymer precursors for photonics applications, inspired a new application in electronics. Hydrogen fuel cells are a much talked about development in alternative
power sources. Fuel cell technology provides a fascinating example of a collection of problems which must all be addressed to produce a functional, feasible system.

**Figure 3-18.** The hydrogen fuel cell membrane electrode assembly, showing the flow of gaseous reactants in and products out from the reactive sites in the MEA. The electrochemical reaction equations are also shown.

A hydrogen fuel cell (Figure 3-18) operates through the controlled electrochemical oxidation of hydrogen gas at a catalytic site on an anode on one side of a cell. The protons then transport through a proton exchange membrane (PEM), while the electrons flow through a circuit, producing usable electricity along the circuit. The protons and electrons meet again on the other side of the cell at another catalytic site on the cathode where they reduce an oxygen atom to form water.111

The heart of the fuel cell is the membrane electrode assembly (MEA): a complex system encompassing three primary components (1) the PEM, often a fluoropolymer electrolyte to transport protons between the anode and the cathode, and separated the reactive gasses; (2) the catalyst, usually nanoparticles of platinum or an alloy to facilitate the electrochemical redox reactions; and (3) the carbon electrodes, to which conduct the electrons from the oxidation site, through the working circuit, and back to the reduction site.
Self-supporting nanoporous carbon materials provide alternatives to carbon black as support electrodes in proton exchange membrane fuel cells (PEM-FCs). The nanoporous nature of these carbons should allow for rapid mass transfer of fuel, oxygen, and water within the continuous electrically and ionically conductive electrode while retaining the high catalyst and electrolyte loading required for high activity.

The important issues in the electrode are varied, and include the electrical conductivity, the surface area, the surface functionality and surface energy, the microscopic structure including pore size and distribution, the particle size, mechanical properties, chemical and thermal stability, catalyst loading and distribution, and layer thickness. Many of these issues are addressable with a materials approach.

Porous carbon electrode architecture can be introduced using templating, molding, or porogen inclusion. The latter is the most common method involving the formation of a carbon aerogel via sol-gel synthesis of a carbon precursor network, followed by drying and pyrolysis. An example using resorcinol-formaldehyde resins produced carbons with a BHJ pore size of 0.3-20 nm and BET surface areas of 500-600 m²/g.

The templating technique developed for the ICOs was used to create disordered porous carbons from silica templates for potential use as an electrode for MEAs. The BET specific surface area of the carbons produced varies (from 51-275 m²/g) depending upon the monomer functionalities (R, X, see Table 3-2).
Figure 3-19. Disordered carbon foams templated from colloidal silica, using different carbon precursors: A) BODA monomer 1-1, B) BODA monomer 1-1, C) (Ph-CC-Ph)\textsubscript{2}O, (5) and D) 80 % BODA 1-1, 20 % 1-5.

Table 3-2. BET specific surface area of disordered carbon foams templated from BODA and related carbon precursors.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>BET SSA (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BODA 1-1</td>
<td>135</td>
</tr>
<tr>
<td>BODA 1-2</td>
<td>275</td>
</tr>
<tr>
<td>Monomer 1-5</td>
<td>95</td>
</tr>
<tr>
<td>80% BODA 1-1, 20 % monomer 1-5</td>
<td>51</td>
</tr>
</tbody>
</table>

This carbon foam may not have enough free space to enable the improved mass transport of the reactants and products to and away from the reactive sites near the PEM. Bimodal carbon foams, which have foams of two different size domains may be better suited for this application. (Scheme 3-9) The BODA templating method was once again
utilized to produce a layer of nano-scale pores on the inner surfaces of a mesophase pitch with micropores of ~1 mm diameter. (Figure 3-20) This microporous carbon foam is synthesized and was donated by Oak Ridge National Laboratories.\textsuperscript{10}


Figure 3-20. Scanning electron micrographs of A) mesoporous carbon foam (ORNL), and B) 15k x C) 3.5k x magnifications of dimodal carbon foams derived from BODA nanoporous foam fabrication in pores of dimodal foam.
Silica colloid was used to coat the pores the microfoam by first coating the microfoam with a sodium lauryl trimethylammonium surfactant, then adding the aqueous silica colloid, by dropping onto a suspended piece of foam, and carefully drying the template, first at room temperature, then in a tube furnace. The template was then sintered at 1000 °C under N2 to anneal the silica template, and cooled. A solution of BODA monomer 1-2 (X = C(CF3)2, R = C(CH3)2OH) was then used to backfill the dry silica template, then polymerized and pyrolyzed by again heating to 1000 °C in N2. The silica template was removed by HF etch. The resultant hierarchical dimodal carbon structure is shown in Figure 3-20.

**Carbon Surface Fluorine Decoration**

The interface between the carbon electrodes and the fluoropolymer PEM is a source of performance loss in the PEM-FC due to the highly energetic contacts between the two incompatible materials. One method of producing materials that can promote intimate mixing between the electrically conductive carbon and ionically conductive electrolyte portions of the electrode is by covalently grafting the fluorinated compatibilizers onto the surface of carbon supports.120 This intimate integration is essential for high activity and long life in the PEM electrode.

![Chemical Structures](image)

**Scheme 3-10.** Two mechanisms for the dediazoniation of an aryl diazonium salt. The heterolytic mechanism occurs spontaneously with heating. The homolytic mechanism requires an initial electron transfer.
This interface was addressed by the synthesis and covalent attachment of fluorine containing groups to the carbon surface via aromatic diazonium compounds. Previously, this technique has been used to attach aromatic groups onto carbon electrodes.\textsuperscript{121}

\textbf{(Scheme 3-10)} Aryl diazonium moieties undergo dedazioniation reactions either through electroreduction or thermolysis to form highly nucleophilic aromatic cation or radical species capable of forming robust, covalent bonds to carbon surfaces.\textsuperscript{122} In the cationic mechanism, the de-diazonation reaction consists of the reversible dissociation of N\textsubscript{2} from the aromatic radical. The reversibility of this reaction implies that the aromatic cation is so nucleophilic as to react with the paradigm of inertness, elemental N\textsubscript{2}.\textsuperscript{123} The diazonium approach is also one of only a handful of reactions available for the direct functionalization of carbon surfaces, without recourse to linkages such as esters and amides, which would be labile in the superacidic conditions of the fuel cell. Precedence exists for the decoration of many carbon substrates including fuel cell-grade carbon black for both the reductive and thermolytic mechanisms.\textsuperscript{124}

\begin{center}
\begin{align*}
\text{Ar} & \text{-O} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{Ar} \\
\text{Ar} & \text{-O} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{Ar}
\end{align*}
\end{center}

\begin{center}
\begin{align*}
\text{Ar} & \text{-O} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{Ar} \\
\text{Ar} & \text{-O} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{Ar}
\end{align*}
\end{center}

\begin{center}
\begin{align*}
\text{CF}_2 & \text{FC} & \text{O} & \text{-X} & \text{-} & \text{Ar} & \text{CF}_2 & \text{FC} & \text{O} & \text{-X} & \text{-} & \text{Ar}
\end{align*}
\end{center}

\begin{center}
\begin{align*}
\text{F}_2\text{C} & \text{FC}_2 & \text{O} & \text{-X} & \text{-} & \text{Ar} & \text{CF}_2 & \text{FC} & \text{O} & \text{-X} & \text{-} & \text{Ar} \\
\text{F}_2\text{C} & \text{FC}_2 & \text{O} & \text{-X} & \text{-} & \text{Ar} & \text{CF}_2 & \text{FC} & \text{O} & \text{-X} & \text{-} & \text{Ar}
\end{align*}
\end{center}

\textbf{Scheme 3-11.} Thermal cycloaddition reaction of trifluorovinyl ether (TVE) groups to form perfluorocyclobutyl (PFCB) group. This mechanism is used to form PFCB polymers with good tolerance for a wide range of functional spacers, X.
Scheme 3-12. Synthesis of aniline containing TVE monomer via Suzuki coupling, conversion to diazonium salt, and thermal dediazonium in the presence of carbon to yield TVE decorated carbon surface.

The fluorine-containing aryl diazonium compound 7 is an aryl trifluorovinyl ether (TVE) designed to be suitable for co-reaction with any other TVE containing monomer. This class of polymers polymerizes in a condensate free [2+2] cycloaddition reaction to form the thermally stable perfluorocyclobutyl (PFCB) linkage, and is extremely tolerant of functional groups within the monomers (Scheme 3-11). There exist several TVE containing monomers that contain acidic functionalities which would further add to the compatibility of the anchored polymer with the acidic fluoropolymer of the PEM.

The TVE-containing aryl diazonium salt (7) was synthesized through the Suzuki coupling of boronic acid-TVE with 4-bromoaniline (Scheme 3-12), followed by diazoniation of the aromatic amine using BF₃·Et₂O/HF and isoamyl nitrite. The diazonium was not stable enough to isolate from the reactive solution, so this reaction was performed in the presence of the carbon to be decorated with the aromatic TVE.
Figure 3-21. Scanning electron micrograph (SEM) of roughening of A) polished BODA-derived carbon surface, and B) commercial Vulcan carbon black, during carbon fluorination procedure with Compound 7. The energy dispersive x-ray spectrum of the fluorinated Vulcan surface after thorough wash showing surface elemental composition.

There was an observable roughening of the carbon surface on the scale of 10s of nanometers indicating an apparent instability of the carbon in these strong reactive conditions. There was however good evidence from the EDX that the functionalization of the carbon with the fluorine containing TVE group was successful. The fluorophilicity of the carbon surface could also be seen in the concomitant increase in both the hydrophilicity and the oleophilicity of the carbon.
surface, as measured by contact angle goniometry. (Figure 3-22) Subsequent addition of the difunctional TVE containing monomer, 4,4’-bis(trifluorovinyl ether)-biphenyl (BPVE)\textsuperscript{131} via polymerization of the BPVE monomer in

![Contact angle goniometry images]

**Figure 3-22.** Contact angle goniometry of polished BODA-derived carbon surface with A) water (45.0° ± 4.9°), and B) mineral oil (18.0° ±1.9°), and the same carbon surface after TVE addition with C) water (66.2° ±4.2°), and D) mineral oil (23.9° ±2.9°).

the presence of the decorated carbon by heating a melt of 4-4’-bis(trifluorovinyl ether) biphenyl on the surface of the functionalized carbon at 160°C for 2 h in a tube furnace, (Scheme 3-13) however did not lead to an increase in the surface fluorine content, as measured by EDX. This observation is either due to a coincidental matching of the fluorine content in the decorated carbon surface to the maximum fluorine content of the poly(BPVE), or due to a deactivation of the TVE functionality during the diazoniation or carbon functionalization steps. The first possibility is supported by comparison of the carbon-TVE fluorine content as measured by EDX with that of the biphenyl TVE anchor
(after addition to carbon) and the poly(BPVE) homopolymer from their. The C-TVE has an EDX surface fluorine content of 17.82 ± 6.66 wt%, the biphenyl TVE anchor has a calculated fluorine content of 22.79 wt% and poly(BPVE) has a calculated fluorine content of 32.92 wt%. Subsequently, it

![Diagram](image)

**Scheme 3-13.** Perfluorocyclobutyl polymer growth from TVE anchored carbon surface. The variable aromatic functionality is in this case, 4,4'-biphenyl, but may also be other groups such as sulfonated aromatic groups.

has been revealed that this deactivation probably occurs during the diazoniation reaction. The TVE functionality is unreactive under most conditions, but BF$_3$ catalyzed electrophilic addition of HF across the double bond of the TVE produces the –OCHFCF$_3$ group which is incapable of undergoing cycopolymerization.$^{132}$ Therefore it appears that the TVE functionality is destroyed before additional molecular weight may be added to the anchor points.

**Carbon Nanotubules**

Carbon nanotubules have also been templated using anodic aluminum oxide disks, sold commercially as Anodiscs (Whatman), as the template.$^{133}$ Anodiscs, are alumina
membranes that have arrays of parallel nanopores running through them. As the name suggests, the pores are formed through the anodic oxidation of aluminum. The pores were filled with a solution of BODA oligomer, \((X = C(CF_3)_2, R = C(CH_3)_2OH)\), then dried in an oven, and pyolyzed in a tube furnace. The alumina template was then etched away with NaOH, yielding nanotubules of templated Carbon. The carbon nanotubules remained in bundles where the \(Al_2O_3\) was not fully removed, but freestanding tubes and tube meshes are also obtained. (Figure 3-23) From the micrographs the diameters of the nanotubules are measured to be \(~260\) nm.

Figure 3-23. Scanning electron micrographs of BODA 1-2 templated carbon nanotubules.

The applications in this chapter has been meant to demonstrate versatility which has been achieved using BODA derived polymers as high-yield precursors for carbon structures. It has been demonstrated that BODA-derived carbon is higher yielding than
any other carbon precursor polymer while still maintaining an impressive degree of processability. This unique combination ensures that research in this area is always continuing and will continue to find new interesting applications.
CHAPTER 4

FULLERENE REACTIONS WITH BODA MONOMERS

Fullerenes

Since the confirmation of the existence and remarkable stability of clusters of sixty carbon atoms by Kroto, Smalley et al. in 1985,\textsuperscript{134} the new three-dimensional, soccer ball-shaped, molecular carbon allotrope has captured the thoughts and efforts of scientists around the world. This was, after all, the first carbon allotrope to be discovered since the advent of science. C\textsubscript{60}, was popularly termed Buckminsterfullerene, and the class of compounds stemming from this seed, fullerenes. Once the molecule was discovered and publicized, methods of generation and purification were developed using a variety of methods, mainly through different methods of heating graphite\textsuperscript{135,136,137} or pyrolysis of aromatics.\textsuperscript{138,139} Total synthesis of C\textsubscript{60} has also been performed,\textsuperscript{140,141,142} opening the way for the rational synthesis of substituted heterofullerenes,\textsuperscript{9} and endofullerenes.\textsuperscript{143}

C\textsubscript{60} consists of an icosahedral arrangement of 12 pentagons and 20 hexagons comprised of sp\textsubscript{2} carbons. Each of the pentagons is surrounded by 5 hexagons, and therefore isolated from each other. Each carbon is equivalent, but the arrangement leads to two distinct C-C bonds, that at a hexagon-hexagon edge, and that of a hexagon-pentagon edge. The hexagon-hexagon edge bond is 1.38 Å long, compared to the slightly longer 1.45 Å bond at a hexagon-pentagon edge.\textsuperscript{144} This difference leads to a difference in the reactivity of these two non-degenerate bonds.\textsuperscript{145} The lowest energy structure of
C₆₀ puts each of the double bonds at a hexagon-hexagon edge, and not at the hexagon-
pentagon edges. The spherical shape of the arrangement keeps the p-orbitals of the
carbons from being completely overlapped as they would be in an aromatic six-
membered ring, but the strain is distributed as evenly as possible throughout the molecule.
Each six-membered ring therefore behaves like a cyclohexatriene.¹⁴⁶

Since all of the curvature arises from the presence of the 12 hexagons, the
presence of higher (and lower) fullerenes can be predicted according to the formula
C₂(10+M). The lowest theoretically predicted fullerene structure then is the B₂₀ structural
analogue, C₂₀. Practically however, C₆₀ is the lowest stable fullerene, the stability arising
from the structural isolation of the pentagons. Higher fullerenes that conform to both of
these rules are numerous, including C₇₀, C₇₆, C₇₈, C₈₄, have been isolated and
characterized.¹⁴⁷ The number of possible isomers increases for each of the higher
fullerenes.

The existence of higher fullerenes also suggests the possibility of layered
fullerenes which are fullerenes of a high enough order to contain a lower order fullerene
within its cavity. Multilayered fullerenes, popularly referred to as carbon nano-onions
(CNOs), that contain 20-50 such layers have been produced and are just now beginning
to be isolated and utilized.¹⁴⁸,¹⁴⁹,¹⁵⁰

Cyclic voltammetric (CV) measurements of solutions of C₆₀ have proved it to be a
very electronegative molecule, reversibly reducible up to a hexa-anion in a stepwise
fashion with essentially equal jumps in reduction potential for each one-electron
reduction step.¹⁵¹ The reduction potentials of C₆₀ are shown in Table 4-1. Similar
behavior is observed for $C_{70}$. This electron accepting ability has made fullerenes interesting as components in photovoltaic materials.

**Table 4-1.** Reduction potentials of $C_{60}$ in toluene/ acetonitrile

<table>
<thead>
<tr>
<th>$C_{60}$</th>
<th>$C_{60}^1$</th>
<th>$C_{60}^2$</th>
<th>$C_{60}^3$</th>
<th>$C_{60}^4$</th>
<th>$C_{60}^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{60}^{0/-1}$</td>
<td>-980</td>
<td>-1370</td>
<td>-1870</td>
<td>-2350</td>
<td>-2850</td>
</tr>
<tr>
<td>$C_{60}^{1/-2}$</td>
<td>-1870</td>
<td>-2350</td>
<td>-2850</td>
<td>-3260</td>
<td></td>
</tr>
</tbody>
</table>

\[ a \text{ mV vs } Fc/Fc^+ \]

**Photovoltaic Materials**

Photovoltaic processes convert light energy directly into electrical energy, by first striking a photovoltaic material and exciting an electron, thereby creating an electron-hole pair, or exciton, in the material. The key step in making an efficient photovoltaic material, is to separate these charges and maintain that separation. If the electron merely relaxes back into the hole (or a degenerate hole) the energy will be lost as radiation or heat. If the charges can be separated towards electrodes, however, the energy will be converted into useful electricity. Charge separation is most often accomplished by incorporating two different materials in the photovoltaic cell, an electron donor (D), and an electron acceptor (A). Light energy is absorbed by the donor phase, D, and forms the exciton, D*. The donor exciton, D*, complexes with the acceptor phase, A, to form an excited complex, (A-D)*. Charge transfer occurs between the two phases, (A$^\delta$-D$^{\delta+}$). Electron transfer forms a radical ion pair, (A$^-$$D^{+}$), and finally the two phases separate as their radical ions, A$^-$ and D$^+$, completing the charge separation. These charges must then migrate towards their respective electrodes.

Traditionally, photovoltaic materials have been inorganic, particularly crystalline silicon, which was found to be a good semiconductor with photovoltaic properties.
Eventually boron doped, or p-doped silicon was used as the acceptor phase, and phosphorus doped, or n-doped silicon was used as the donor phase.$^{20}$

Organic photovoltaic materials, on the other hand, is a much newer field. While organics offer certain advantages$^{156}$ over inorganic materials in the field of photovoltaics, such as low fabrication cost, the possibility of large area coverage, mechanical flexibility (especially over curved surfaces), and low specific weight, the fundamental science of conductive organic materials lagged behind until just a few decades ago, when electrically conductive polymers were discovered.$^{157-158}$

Shortly after this discovery, the concept of using p-type semiconducting polymers with fullerenes, themselves a sort of n-type semiconductor for photoinduced charge separation was devised.$^{159,160,161,162}$ The electron transfer was subsequently shown to be very fast, under a picosecond, and produced a highly delocalized radical cation in the conjugated polymer.

Scheme 4-1. A photovoltaic cell consists of a p-type and an n-type semiconductor sandwiched between an optically clear ITO anode and a metal cathode.

It is somewhat appropriate that the molecule named after R. Buckminster Fuller plays such a vital role in the development of modern organic photovoltaic materials, as
the concept of an efficient, sustainable clean energy source fits quite well with his systemic worldview, which integrated geometry with energy and material efficiency.

The geometry of the bulk heterojunction between the donor and acceptor phases also has a large effect on the overall efficiency of the photovoltaic cell. A bilayer structure of the donor and acceptor phase is the simplest morphology, but offers the smallest interface at which charge separation may occur. Other morphologies including interdigitated layers, blends, interpenetrating networks, and copolymers seek to maximize this interfacial area, but require functionalization of the fullerene phase to increase the solubility/compatibility of the two phases.

**Fullerene Functionalization**

As previously mentioned, the hexagons of a fullerenes behave more like a cyclohexatriene than an aromatic ring, due to the curvature of the ring and departure from coplanarity of the carbon p-orbitals. Addition reactions to these double bonds are therefore quite possible as has been demonstrated with nucleophiles to form the intermediate, $\text{C}_{60}\text{Nu}_{n}^{n-}$, which then adds an electrophile such as an abstracted proton to yield the final product, $\text{C}_{60}\text{Nu}_{n}\text{E}_{n}$.\textsuperscript{163} Nucleophilic addition usually occur in the 1,2 mode due again to the poor overlap of p-orbitals.\textsuperscript{12} This mechanism has been utilized to add alkyl, aryl, and acetilidyl carbon nucleophiles;\textsuperscript{164} amine\textsuperscript{31} nitrogen nucleophiles; hydroxide\textsuperscript{165} and alkoxide\textsuperscript{166} oxygen nucleophiles; phosphorus\textsuperscript{167,168} nucleophiles; and silicon\textsuperscript{169} nucleophiles.

Cycloadditions are another class of widely-used reactions for the functionalization of fullerenes with a wide variety of functionality.\textsuperscript{170} Diels-Alder type [4+2] reactions
have been used by the addition of reactive dienes to the dienophilic fullerene hexagon-
hexagon double bonds.\textsuperscript{171}

Otherwise, [3+2] cycloadditions have been utilized for the addition of diazo-
compounds,\textsuperscript{172} azides,\textsuperscript{173} trimethylenemethanes,\textsuperscript{174} or most commonly, azomethine
ylides.\textsuperscript{175} The triazoline intermediate formed from the azide [3+2] addition may also lose
\( \text{N}_2 \) to form a nitrene compound. The nitrene compound has the distinction of being able
to add across the pentagon-hexagon single bond of the fullerene to create a bicyclo[4.3.1]
bridge. The dipolar azomethine ylide [3+2] cycloaddition to fullerenes was first
introduced by Prato and Maggini, and quickly became one of the most widely-used
methods for the functionalization of fullerenes. The popularity stems from the ease of
applicability to many substrates. The reactive azomethine ylide intermediate is
commonly produced \textit{in situ} from the co-reaction of a \( \alpha \)-amino acids with aldehydes or
ketones. This allows for functionality to be introduced at either the amino acid sites or
the aldehyde site. The cycloaddition product is a pyrrolidine with the 3- and 4- carbons
being provided by the fullerene.

Further cyclizations include the [2+2] addition of benzynes,\textsuperscript{176-177} ketenes,\textsuperscript{178}
enones,\textsuperscript{179} and certain electron-rich alkynes;\textsuperscript{180} or the [2+1] addition of carbenes\textsuperscript{181} and
nitrenes.\textsuperscript{182}

Radicals produced either thermally and photochemically have both been added to
fullerenes and followed using electron spin resonance (ESR). Fullerenes have been
characterized as a “radical sponge”\textsuperscript{183} due to their high efficiency in trapping radicals for
use as both radical scavengers and in materials synthesis.

Radical precursors including hydrocarbons, $\text{CCl}_4$, alkyl halides, dialkylmercury compounds, dialkylperoxides, azobisisobutyronitrile (AIBN) and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) nitroxides have been added. The stability of the radical adduct $R\text{-C}_{60}^\cdot$ varies with the steric size of $R$. These additions always occur at the
fullerene hexagon-hexagon edge double bonds. Multiple radical additions to different double bonds may lead to structures with double bond localization at the hexagon-pentagon edge, but evidence using $^{13}$C labeled benzyl radicals indicates that further radical additions continue to occur at other hexagon-hexagon double bonds.

**Radical Addition of Conjugated Polymers to Fullerenes**

A few radical polymerizations of vinyl monomers have been used to add to C$_{60}$, including polystyrene$^{184}$ and PMMA$^{185}$. These materials are soluble fullerene-cored star polymers, with lower yields and molecular weights and narrower distributions than the control reactions, indicating a chain transfer mechanism. The radical reactivity of C$_{60}$ is more frequently utilized in the previously-mentioned nitrene-mediated mechanism reported by Hawker$^{48}$ and the carbene-mediated mechanism reported by Wudl$^{47}$. The nitrene method has been used to add a N-tethered poly(phenylenevinylene) (PPV) to C$_{60}$ in order to incorporate a conjugated polymer in intimate contact with the fullerene core$^{186}$. PPV has also been incorporated through a C-bridge$^{187}$ utilizing the Wudl method. The Prato [3+2] dipolar addition mechanism$^{188}$ is however the most common method for the incorporation of conjugated polymers. It has been used to attach PPV$^{189}$, polythiophene$^{190}$, and poly(thiophenevinylene)$^{191}$. A star shaped poly anilinated C$_{60}$ has also been produced from hexanitro[60]fullerene$^{192}$.

**BODA-co-C$_{60}$**

Soluble BODA polymers have an extremely high absorbance cross-section. The step-growth polymerization kinetics of BODA polymerization$^{193}$ combined with
evidence from the EPR\textsuperscript{194} and MALDI-TOF experiments speak of a very long-lived radical species in the polymer. Though, there have been no previous reports of the direct radical addition of a conjugated polymer to a fullerene, Bergman cycloaromatized naphthalene diradicals from BODA monomers have been used to react with C\textsubscript{60} to produce conjugated polymer-fullerene adduct copolymers that may have interesting donor-acceptor properties useful for photovoltaic applications.\textsuperscript{195,196,197,198}

\begin{center}
\textbf{Scheme 4-3}. BODA monomer cycloaddition and addition to C\textsubscript{60} to form proposed trimeric diradical structure.
\end{center}

A suspension of fullerene C\textsubscript{60} in a N-methyl-2-pyrrolidinone (NMP) solution of a BODA monomer (X = C(CF\textsubscript{3})\textsubscript{2}, R = Ph) was heated for 24h at reflux (206 °C, typically ca. 1 wt\% total solids) to give a copolymer product with C\textsubscript{60} content ranging from 2-30 \%. After removal of the reaction solvent, the remaining solid product was soluble in
common organic solvents. In all cases, the $C_{60}$ had been completely consumed by the end of the reaction time, as measured by gel permeation chromatography (GPC) as shown in Figure 4-1.

A solution of $C_{60}$ starting material (Figure 4-1A) has a GPC retention time of 21.2 minutes, longer than the polystyrene calibration range. Residual $C_{60}$ was not observed in the copolymer reaction mixtures. The chromatogram for the BODA-$co$-$C_{60}$ copolymer (Figure 4-1B) is more broad and of higher weight average molecular weight ($M_w$) than that of the homopolymer (Figure 4-1C) after identical polymerization conditions. These data illustrate the expected increase in average functionality of the monomers by the addition of $C_{60}$ as a monomer.

The photodiode array (PDA) detector of the GPC was also used to extract retention time-dependent UV-Vis spectra from an incomplete polymerization. In this chromatogram, the $C_{60}$ was still observable, as well as a two polymer peaks. One polymer peak has a longer retention time than the monomer, but shorter than the BODA monomer. This peak was taken to be the BODA-$co$-$C_{60}$ oligomer peak. The spectra for the three components show the changing absorbance spectra with incorporation of the $C_{60}$. The $C_{60}$ spectrum ($t_{retention} = 21.2$ min) shows two maxima at 257.3 and 330.9 nm, the BODA homopolymer spectrum ($t_{retention} = 16.66$ minutes) has one maxima at 270.3 nm, and the BODA-$co$-$C_{60}$ product spectrum ($t_{retention} = 20.59$ min) has a shifted BODA-fraction maxima at 253.8 nm and a pronounced shoulder around the 330.9 peak of the $C_{60}$, indicating incorporation of the $C_{60}$ into the polymer structure (Figure 4-2).
Figure 4-1. Gel permeation chromatograms of A.) C<sub>60</sub> starting material, B.) BODA (X = C(CF<sub>3</sub>)<sub>2</sub>, R = Ph) homopolymer, and C.) BODA-co-C<sub>60</sub>.

Figure 4-2. Extracted UV-Vis spectra from partially polymerized BODA-co-C<sub>60</sub> gel permeation chromatogram. The C<sub>60</sub> spectrum, blue, was extracted at t<sub>ret</sub> = 21.20 minutes, the BODA homopolymer, black, at t<sub>ret</sub> = 16.66 minutes, and the BODA-co-C<sub>60</sub>, red, at t<sub>ret</sub> = 20.59 minutes.

The molecular incorporation of the fullerene into the polymer is best seen in the MALDI-TOF spectrum of the copolymer (Figure 4-3). The BODA dimer (m/z = 1408); and 2:1 BODA-co-C<sub>60</sub> trimer (m/z = 2128) are clearly seen in the mass spectrum.
Another major peak at m/z = 696 may be a fragmented BODA monomer. The single monomer-co-C₆₀ adduct (m/z = 1424) is not observed.

Figure 4-3. MALDI-TOF mass spectrum of BODA-co-C₆₀ showing peaks at m/z = 696, 1408, and 2128.

There are two radical routes to produce the dominant hetero-trimer observed at 2128 g/mole. The reactive BODA-derived napthalene diradical must react first with either a double bond of the fullerene, to produce the fullerene radical which subsequently reacts with the second BODA monomer to form the trimer, or a BODA dimer reacts with the fullerene directly. The former approach better explains the lack of the 1:1 BODA-co-C₆₀ dimer, due to a difference in relative reactivities. The C₆₀ would be expected to have the same reactivity towards both the monomeric and dimeric, (and higher order oligomeric) radical species. BODA-derived radicals have been shown to have remarkably long lifetimes by EPR, whereas fullerene radicals are usually very reactive, and have shorter lifetimes.

EPR detects unpaired electrons and can give information about the environment of the unpaired electron, analogous to the way NMR detects the spins of NMR active nuclei. EPR monitoring of an in situ heated 1:1 stoichiometric mixture of BODA
monomer 1 and C60 showed the growth of a singlet signal with a g-value of 2.0018. This is the identical g-value observed with the homopolymer under the same conditions, so this signal has been attributed to the homopolymer species. The presence of another distinct second radical with a similar g-value but greater linewidth not seen in the homopolymer was observed upon increasing microwave power (Figure 4-4). There is no observable hyperfine splitting in either signal, indicating that each radical is located on a carbon center that has no substituents (H or F) capable of splitting the signal. This could indicate either a radical on the cyclized BODA naphthalene ring or on the fullerene shell itself. The similarity of the g-values to that of the free-electron g-value indicate, however, that both radicals are similar in environment. The second observed radical signal does not saturate with increasing microwave power as does the first narrower

![Figure 4-4](image.png)

**Figure 4-4.** Electron paramagnetic resonance spectra of *in situ* heated BODA-co-C60 reveals, under higher microwave powers, a second signal distinct from the lone signal of the BODA homopolymer.
singlet, indicating a more efficient spin-lattice relaxation pathway. Therefore, it seems likely that the second signal originates from a radical centered on a cyclized BODA monomer bound to a fullerene as proposed in Scheme 4-3.

The high-resolution transmission electron microscopy (HR-TEM) images of the copolymer show a texture characteristic of the fullerene, as can be seen by comparison to images of the homopolymer and a sample of neat C_{60}. The intact morphology of the spherical fullerenes is observed in the copolymer (Figure 4-5) and in the unfunctionalized fullerene, but not in the BODA homopolymer. The unfunctionalized fullerene was not observed in the GPC of the copolymer, so the fullerenes in the micrograph are not merely part of a mixture with a homopolymer (Figure 4-1). Distinct fullerenes spheres are observed as circles of in the copolymer micrograph.

![HR-TEM images of BODA-co-C_{60}, left, shows the characteristic pattern of a C_{60} containing sample as seen when compared to neat C_{60}, right. The scale bar in each represents 2 nm.](image)

The $^{13}$C NMR of the copolymer shows a broad peak centered at 145.3 ppm for the C_{60} carbons. Native C_{60} has one carbon peak at 143.2 ppm. The broadness of the peak indicates that the C_{60} carbons have been made non-degenerate by the functionalization
reaction. The BODA polymer carbons also remain in this spectrum between 124 and 134 ppm.

As will be shown in the next section, BODA monomers also react with multilayered carbon nano-onions (CNOs), and these copolymers can be defunctionalized by selectively oxidizing the BODA polymer from the CNOs by heating in air within a small temperature range (~490 °C). This same experiment with the BODA-\textit{co-}C_{60} system revealed a temperature in oxidative TGA heating experiments where the BODA polymer appeared to defunctionalize from the fullerene surface, based on weight loss (Figure 4-6) but Raman analysis of the copolymer after oxidative heating in the TGA, however, did not simply yield recovered C_{60} (Figure 4-7). All that was observed in the spectrum was a glassy carbon structure identical to that formed from the pyrolysis of BODA.

![TGA traces of BODA homopolymer, C_{60}, and the BODA-\textit{co-}C_{60} reveal a window to allow for thermal defunctionalization of BODA from the copolymer to recover C_{60}.](image_url)

**Figure 4-6.** TGA traces of BODA homopolymer, C_{60}, and the BODA-\textit{co-}C_{60} reveal a window to allow for thermal defunctionalization of BODA from the copolymer to recover C_{60}.
homopolymer. None of the characteristic fullerene peaks are seen in the spectrum. This is probably caused by the difficulty associated with spectroscopy through highly absorbing glassy carbon matrix. Whether the fullerene structures are buried in the glassy carbon matrix during or after the oxidation, or whether the fullerene structure itself is destroyed, and therefore contributes to the glassy carbon structure cannot be determined. This last possibility raises the question of whether the outermost functionalized layer of the multi-layer CNOs is similarly destroyed during that defunctionalization process. Given the relative sizes of the monomers to the fullerene and to the CNOs, the CNOs structure would still dominate the Raman spectrum, over any residual glassy carbon. These delaminated CNOs would be indistinguishable from the pre-functionalized CNOs.

**Figure 4-7.** Raman spectrum of $C_{60}$, green, shows its characteristic line structure. The BODA homopolymer spectrum, light blue, is broad and featureless, as is the copolymer spectrum, dark blue. After attempted thermal defunctionalization the spectrum is dominated by glassy carbon peaks, with no observable line structure indicative of $C_{60}$. (in collaboration with A. Rettenbacher)
by Raman, and very difficult to determine by TGA. This mechanism would however make possible the iterative functionalization-defunctionalization of CNOS with the aim of successively removing the outermost layers of the onions to get progressively smaller layered fullerenes, a goal which has proved very difficult by other means.

![I-V plot for a diode with BODA-co-C₆₀ layer between ITO and Ag electrodes.](image)

**Figure 4-8.** The I-V plot for a diode with BODA-co-C₆₀ layer between ITO and Ag electrodes. (In collaboration with R. Harrell’s laboratory)

A film of BODA-co-C₆₀ was fabricated into a simple diode device by spin coating onto an ITO glass slide, and then depositing 1 mm circles of silver onto the surface of the BODA-co-C₆₀ film. In this diode architecture the BODA-co-C₆₀ acts as the semiconducting Schottky barrier layer. The diode showed a linear response on the I-V plot, with a response on the scale of milliamps. **(Figure 4-9)** The average film thickness
was measured by profilometry to be 5.4 µm. This corresponds to a conductivity $\sigma = 3.8 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ which is much less conductive than glassy carbon ($\sigma = 10^{28} \text{ S} \cdot \text{cm}^{-1}$)\textsuperscript{58}, but on the order of doped polythiophene ($\sigma = 10^{-2}–10^{-1} \text{ S} \cdot \text{cm}^{-1}$)\textsuperscript{200}. The copolymer showed a marked difference in semiconductivity as compared to the homopolymers in the same role, which never showed any conductivity. This supports the position that the C\textsubscript{60} component is acting like a p-type dopant for the BODA polymer component, imparting a charge transfer capability to the copolymer. Experiments to determine the effect of light environment on this response are underway.

**BODA-co-Carbon Nano-onions**

Multi-layered fullerenes are referred to as carbon nano-onions (CNOs) and are very much the newcomers in the fullerene arena. While their existence was confirmed in a few papers in the early days of fullerenes, particularly as observed species in TEM studies, their limited quantities, lowered reactivity, and added levels of complexity directed attention away from these more exotic species while many of the fundamental properties and reactivities of the small molecule fullerenes were underway. Recently however, there has been renewed interest in CNOs chemistry as a few reactive strategies have been identified for their solubilization. This opens the doors for such varied applications as optical limiting\textsuperscript{201}, catalysis\textsuperscript{202}, gas storage\textsuperscript{203}, additives for aerospace applications\textsuperscript{204-205}, nickel-based composite coatings\textsuperscript{206}, solar cells and light-emitting devices\textsuperscript{207-208}, and fuel-cell electrodes\textsuperscript{209}.

As in the case of single-walled carbon nanotubes (SWNTs), CNOs are insoluble in both organic and inorganic solvents. Solubilization is therefore necessary to gain access to the fundamental chemical properties of CNOs. Chemical
derivitization is one of the most common methods utilized for the solubilization and study of SWNTs. Recent reports have successfully applied this approach to CNOs, and should lead to many more in the future.210-211 Two successful methods for the exohedral functionalization of CNOs reported included 1) oxidative defect-sites generation and conversion into derivatives such as amides, and PEGylation, and 2) direct chemical functionalization using the 1,3 dipolar cycloaddition of an azomethine ylide. The former a common method for SWNT functionalization, and the latter a common method for both SWNT and C_{60} functionalization.

Another method frequently used with CNTs, is the addition of aryl radicals formed by the reduction of aryl diazonium salts, or the thermolysis of benzoyl peroxide. Attempts to use the reduction of diazonium salt approach, which works very well for CNTs,212,213,214 failed in case of the CNOs.215 The reaction of CNOs with phenyl radicals, generated in situ from aniline and isoamyl nitrite, had no detectable effect on the solubility of the CNOs. The radical addition which works very well for the solubilization of CNTs, fails with the large CNOs. This may be attributed either to a decrease in the

![Scheme 4-4](image)

**Scheme 4-4.** BODA derived radical functionalization of carbon nano-onions (CNOs) and proposed copolymer structure.
Scheme 4-5. Isolation of three different solid products from reaction mixture using differential solubilities and centrifugation.

The chemical reactivity of the CNOs surface as the curvature of the external graphitic sheet decreases with increasing radii, or the increased difficulty of solubilizing the massive CNOs molecules for the small non-polar phenyl functionality. The radicals of the 1,4-didehydronaphthalene formed from the cyclization of BODA monomers do, however, show evidence of addition to CNOs and subsequent solubilization. The high reactivity of the BODA radicals, in combination with the extended branched polymer structure provide one of the first examples of CNOs functionalization and solubilization (Scheme 4-9).

Figure 4-9. High resolution transmission electron micrograph (HR-TEM, 300 keV) of solubilized CNOs in BODA-co-CNOs 2. About 20 concentric rings are countable. The scale bar represents 2 nm. (A. Rettenbacher)
Figure 4-10. Low Resolution TEM (LRTEM, 120 keV) images of BODA-co-CNOs 1 (left), and BODA-co-CNOs 2 (right). The scale bars in each represent 20 nm. (A. Rettenbacher)

BODA monomer 1, \((X = \text{C(CF}_3)_2, R = \text{Ph})\) was used as the polymeric component in the functionalization.

BODA monomer and CNOs were mixed in a 2:1 molar ratio in a suspension of refluxing \(N\)-methyl-2-pyrrolidinone (NMP, bp = 206 °C) for long reaction times, 4 days, to give the best results (Scheme 4-4). This temperature allows for the long reaction times of the BODA polymerization without crosslinking and loss of solubility, while still allowing for a large enough concentration of reactive radical species to minimize the reaction times for the solublization of the CNOs.

The reaction leads to several products of varying BODA:CNOs ratios which are separable based on differences in their solubilities. There remained a fraction of CNOs that showed no solubility in the reaction solvent, NMP, and was removed by several successive cycles of centrifugation, replacement of the solvent phase, and sonication to ensure complete removal of the soluble fraction. The soluble fraction itself was further fractionated by dissolution of the solid remaining after removal of the NMP under rotary vacuum evaporation in second solvent CHCl₃, Scheme 4-5. There are therefore one insoluble (unreacted CNOs) and two soluble fractions (BODA-co-CNOs 1, soluble in
NMP only and **BODA-co-CNOs 2**, soluble in both NMP and CHCl₃). These fractions were all investigated by GPC, TEM, TGA and Raman spectroscopy and compared with a BODA homopolymer control submitted to the same reaction and workup conditions (Scheme 4-4).

The soluble fractions were examined by HR-TEM to verify the incorporation of the CNOs (Figure 4-9). The CNOs starting material is completely insoluble in NMP, whereas both BODA-co-CNOs fractions remained in a stable solution after long centrifugation times. Solutions of the CHCl₃ soluble fraction **BODA-co-CNOs 2** are deep-orange colored; and solutions of the NMP soluble fraction **BODA-co-CNOs 1** are green-black colored. Low resolution TEM images of **BODA-co-CNOs 1** and **BODA-co-CNOs 2** are shown in Figure 4-10. A high resolution TEM image of **BODA-co-CNOs 2**, Figure 4-9, reveals the round layered shape of a BODA functionalized CNO

**Figure 4-11.** GPC of **BODA-co-CNOs 2** bottom compared to BODA homopolymer control reaction. Each sample is 1 mg/mL in CHCl₃, filtered with 0.45 nm filters.
surrounded and partially eclipsed by other CNOs. The layered structure of the CNOs reveals about 20 shells that can be counted for this particular molecule. This shows demonstrably that the reactive BODA-derived radicals are able to add to and solubilize the CNOs. This is the first such example of a radical addition to multi-layer fullerenes.

GPC chromatograms of BODA-co-CNOs and the BODA oligomer control are shown in Figure 4-11. The BODA homo-oligomer control experiment (Figure 4-11, top) has a higher average molecular weight and broader polydispersity than does the copolymer. This is as expected and is attributed to the increased branching in the homopolymer. The BODA-co-CNOs (with 11 wt. % CNO, Table 4-2) on the other hand exhibits limited BODA homopolymerization due to the competing radical addition reaction with the CNOs. The CNOs effectively act as chain transfer agents and thereby lower the polydispersity for the copolymer (Figure 4-11, bottom). Incorporation of the CNOs into the polymer backbone does not have as dramatic effect on the GPC molecular

![Image of Thermal Gravimetric Analysis (TGA)](image)

**Figure 4-12.** Thermal gravimetric analysis (TGA, 3 °C/min, N₂) of BODA-co-CNOs (red line), CNOs (blue line) and BODA homopolymer (yellow line). (A. Rettenbacher)
weight as might be expected due to the actual increase in molecular weight. This is due to the same effect that lengthened the GPC retention time of the C_{60}. The GPC calibration is based on the relationship between the hydrodynamic volume (the effective volume of a polymer molecule in solution, including the integrated solvent molecules) and the known molecular weights of a polymer standard. Smaller polymers chains have smaller hydrodynamic radii, and are therefore more likely to get slowed down by the smaller pores in a gel separation column. The length of the pathway through the column affects the retention times. Therefore the largest polymer chains of a given structure move through the column fastest and are detected first. The smallest polymer chains, oligomers, and monomers, move through the column increasingly slowly and have increasingly longer retention times. This is the theory behind all size exclusion chromatography (SEC), but assumes that the polymers and molecules being compared have the same or similar structures is solution. In this case, the standard polymer used is a linear polystyrene. Therefore any variation from the standard polystyrene structure leads to a secondary variation from the calibrated molecular weights. The effective hydrodynamic volumes of fullerenes, both single and multi-layered, are much lower relative to molecular weight than those of solvated polymers due to their inherently compact structures. This is also the origin of their poor solubilities which increase with molecular weight. Fullerenes therefore exhibit long GPC retention times and lower calculated molecular weights when using the less-compact solvated linear polymers as standards.
Figure 4-13. Raman spectra of BODA-co-CNOs (green) after thermal treatment under N$_2$. The CNOs peaks are not discernible in the glassy carbon matrix remnant from the pyrolyzed BODA component, as seen in the two controls, BODA homopolymer, blue, and CNOs, red. (with A. Rettenbacher)

The previous reports of functionalized CNOs have used a thermal defunctionalization method to confirm the presence of the CNOs in their soluble materials. This technique involves a controlled heating in a thermal gravimetric analyzer (TGA) under inert gas to selectively remove the polymer decorations from the surface of the CNOs, while leaving the more thermally stable CNOs cores intact. This has been successfully utilized for PEG-ylated carbon SWNTs$^{216}$ and CNOs.$^{77}$ Effective use of this technique relies on determination of an appropriate temperature for the removal of the labile solubilizing groups from the CNOs surface that is suitably lower than the decomposition temperature of the CNOs. A TGA scan of the BODA-co-CNOs BODA-co-CNOs 2 under N$_2$ is compared to that of pure CNOs starting material and BODA homopolymer. (Figure 4-12). The BODA homopolymer has a weight loss of $\sim$20% of its original weight starting at 410 °C. Minimal further weight loss is observed on
Figure 4-14. TGA (3 °C/min, air) of BODA-co-CNOs (pink) shows thermal decomposition window available for the defunctionalization of the BODA component from the CNOs marked by vertical line at 490 °C, where the BODA homopolymer (yellow) oxidizes, and the CNOs remains stable (blue). (A. Rettenbacher)

continued heating, as expected due to the carbonization processes that are known to occur under these conditions.\textsuperscript{61} This normally desirable quality of BODA polymers here prohibits an effective defunctionalization process. If the functionalized CNOs are fully defunctionalized under these conditions, the TGA pyrolysis residue is still dominated by the BODA-derived glassy carbon.
Figure 4-15. Raman spectra of BODA-co-CNOs 1, top, before, blue, and after, red, thermal defunctionalization process. The CNOs peaks, visible in the copolymer become sharper in the recovered sample spectra than in the starting material sample, suggesting smaller distribution of sizes. The same experiment for BODA-co-CNOs 2 is shown in the bottom spectra. (A. Rettenbacher)

The Raman spectra of CNOs starting material compared with those of the residues of oligomeric BODA and BODA-functionalized CNOs after TGA controlled heating to 1100 °C in N₂ (Figure 4-13) verify this hypothesis. Glassy carbon dominates the Raman
spectrum of the pyrolyzed BODA-co-CNOs (Figure 4-13, bottom) just as it does with the homopolymer. The D-band is characteristic of graphitic materials and appears at 1580 cm\(^{-1}\) in highly ordered pyrolitic graphite (HOPG). The D-band is seen in graphitic materials with finite domain sizes such as polycrystalline graphite, glassy carbon and carbon nano-onions at about 1310-1320 cm\(^{-1}\).\(^\text{77}\)

A more effective defunctionalization method is possible with the TGA controlled heating in air (Figure 4-14). While the BODA homopolymer does show a remarkably good thermal oxidative stability, there is a weight-loss onset at 390 °C in air, which is sufficiently lower than the onset degradation temperature of the CNOs at 470 °C to effect the thermal defunctionalization process. Isothermal heating within this difference of 80 °C at 490 °C for 1h (see the vertical line and inset in Figure 4-14) allowed recovery of the pure CNOs material from the copolymer network as the oligomeric BODA burns off leaving the CNOs intact. The total weight loss during the oxidative TGA experiment allowed for calculation of the component contributions in the copolymers, Table 4-2. After the stabilization of the mass in the TGA, the remaining mass, obtained as an insoluble black powder, is taken to be the mass of the CNOs fraction in the copolymers. This was 11 % for the CHCl3 soluble fraction BODA-co-CNOs 2 and 79% for the NMP soluble fraction BODA-co-CNOs 1. This is summarized in Table 4-2 where the mass balance for the defunctionalization process is given for each copolymer. The difference in the solubilities of the two copolymers is attributed to this difference in their CNOs component contributions.

The mass balances for both the BODA and CNOs fractions are also given for the polymerization reactions in Table 4-2. In summary, 19.4 mg of the initial 20.0 mg CNOs
starting material was recovered as unreacted CNOs from the polymerization and as
defunctionalized CNOs from BODA-co-CNOs 1 and BODA-co-CNOs 2 and 23.9 mg of
the intial 40.0 mg BODA monomer added to the reactive mixture was incorporated into
the copolymer with the CNOs. The homopolymer was removed from the BODA-co-
CNOs by washing with ether. This indicates that a molar ratio of 2:1 BODA
monomer/CNOs is sufficient to achieve appreciable functionalization.

**Table 4-2.** Mass balance for the each of the two components in the copolymer as
determined by selective thermal oxidation in the TGA at 490 °C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>[mg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BODA monomer (starting material)</td>
<td>40.0</td>
</tr>
<tr>
<td>CNOs (starting material)</td>
<td>20.0</td>
</tr>
<tr>
<td>CNOs in 12.8 mg of insoluble CNOS (100%)</td>
<td>12.8</td>
</tr>
<tr>
<td>CNOs in 4.7 mg of <strong>BODA-co-CNOs 1</strong> (79%)</td>
<td>3.7</td>
</tr>
<tr>
<td>CNOs in 25.8 mg of <strong>BODA-co-CNOs 2</strong> (11%)</td>
<td>2.9</td>
</tr>
<tr>
<td>total sum of CNOs recovered</td>
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</tr>
<tr>
<td>BODA oligomer in 12.8 mg of insoluble CNOS (0%)</td>
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</tr>
<tr>
<td>BODA oligomer in 4.7 mg of <strong>BODA-co-CNOs 1</strong> (21%)</td>
<td>1.0</td>
</tr>
<tr>
<td>BODA oligomer in 25.8 mg of <strong>BODA-co-CNOs 2</strong> (89%)</td>
<td>22.9</td>
</tr>
<tr>
<td>total sum of BODA oligomers</td>
<td>23.9</td>
</tr>
</tbody>
</table>

The accomplishment of both the functionalization and oxidative thermal
defunctionalization processes is further confirmed by the changes evident in the Raman
spectrum of the recovered CNOs from the TGA experiment compared to those of the
CNOs starting material, and the BODA-co-CNOs (**BODA-co-CNOs 2**). The elimination
of the BODA component and recovery of the CNOs is shown in **Figure 4-15**. The
spectrum of BODA-co-CNOs **BODA-co-CNOs 2**, middle, is a broad continuum without
any visible discrete peaks as seen in the unfunctionalized CNOs, bottom, and the
recovered CNOs, top. The difference in relative heights of the two peaks at ~1580 and
1312 cm\(^{-1}\) in the two spectra from the native CNOs and recovered CNOs may support the
idea that the CNOs are being refined based on size during the functionalization-defunctionalization process.

The difference in the two soluble BODA-co-CNOs sample is seen in the Raman spectra of BODA-co-CNOs 1 and BODA-co-CNOs 2 (Figure 4-15). In BODA-co-CNOs 2, the more highly-functionalized BODA-co-CNOs sample, the broad signal of the BODA component dominates the spectrum and obscures all signal from the CNOs component. In BODA-co-CNOs 1, the less-functionalized BODA-co-CNOs sample, however, the component ratios are balanced enough for the weaker Raman bands to be observed within the broader BODA continuum signal.

![Figure 4-16](image)

**Figure 4-16.** Cumulative mass fraction as a function of particle radius of hydration in solutions of CHCl₃ for BODA-co-C₆₀ (red), BODA-co-CNOs (blue), and BODA homopolymer control (green), as measured by multi-angle liner light scattering (MALLS).

The BODA-co-C₆₀ and CHCl₃ soluble BODA-co-CNOs samples were each separated on a GPC column and analyzed with a multiple angle linear light scattering (MALLS) detector. MALLS can determine several different properties of materials, including hydrodynamic radii. Figure 4-16 shows the cumulative weight fractions of
these two BODA-fullerene copolymers and the BODA homopolymer as a function of their hydrodynamic radii, $r_h$. Each sample was fractionated on the GPC column according to the $r_h$ of the substituent fractions. The homopolymer shows a smooth continuum of $r_h$ with normal step-growth polymerization. The BODA-$co$-$C_{60}$ on the other hand shows a large jump in cumulative mass fraction at $r_h = \text{nm}$, indicative of the incorporation of the fullerene species. This is even more evident in the case of the BODA-$co$-CNOs which show several such jumps in cumulative mass fraction at increasing $r_h$ values, indicative of incorporation of several CNOs species with differing numbers of layers.
As mentioned in Chapter 1, poly(enediyne)s were originally developed as linear polymers from mono-enediyne containing monomers. This method worked for the production of linear poly(naphthalene)s and other derivatives, but was limited by the solubility and processability of the resultant polymers. The BODA innovation replaced these difunctional monomers and linear polymers with tetrafunctional monomers and soluble branched polymeric intermediates which perform better in both solubility and processability properties. But BODA polymers themselves suffer from the negative effects of this functionality overcompensation when the reaction is taken farther and the functionalities begin to be fully consumed.

Difunctional monomers produce linear polymers with two reactive chain ends. Each trifunctional monomer adds a branchpoint and another reactive chain end to any polymer chain into which it is incorporated. A polymerization with only trifunctional monomers in the system produces network polymers when the reaction is taken to completion. Network polymers have closed loops where two of the reactive ends of single polymer chain have reacted with each other. This has been quantified by Wallace Carothers in the early days of polymers as a science. He defined functionality $f$ as the number of reactive groups within each monomer that participates in the polymerization.
by linking to another monomer.\textsuperscript{217} It was demonstrated statistically that any polymerization needs to maintain an average functionality $f_{\text{avg}} = 2$ in order to produce sustainable high-molecular weight linear polymers. This can be produced by either a collection of monomers that all have $f = 2$, or through careful balancing of monofunctional monomers ($f = 1$) with trifunctional or higher degree monomers ($f \geq 3$) in addition to any difunctional monomers ($f = 2$).

The concept of average functionality can be extended beyond this simple consequence and applied to network polymers too. As mentioned earlier, trifunctional monomers yield network polymers. This is true for any polymer system with an average functionality $f_{\text{avg}} > 2$. The average size of the closed loops however varies with exactly what that average functionality is for the system. In the case of BODA monomers $f = 4$, and so $f_{\text{avg}} = 4$. In a system that has consumed all of this functionality, the size of the closed loop is very small, about 4 monomer units. This has consequences for the way the polymer behaves mechanically. Because each of the monomers behaves as a branch point, and is connected to 4 other monomers, there is very little degrees of freedom within the network polymer. This is further complicated by the possibility of entanglement of the closed loops. In a monolithic structure this rigidity imparts strength to the structure, but also imparts brittleness. There are no ways for the polymer to move in order to accommodate an applied stress, and thus the polymer bonds are broken.

This brittleness is especially troublesome when the physical dimensions of the polymer are limited as in a thin film, or a fiber application. In a thin film application, the polymer is cast onto a 2-dimensional substrate, and cured to complete consumption of the reactive functionality. During this process, the closed loops are formed and the degrees
of freedom within the network are diminished. This is accompanied physically by shrinkage of the polymer film. Mismatch within the dimensions of the substrate and the shrinking polymer network film leads to stresses in the network, and eventual breaking of the polymer bonds seen as cracks in the film. For nearly all thin film applications, cracking is disastrous.

The effect can be mollified by increasing the average size of the closed loops, and thereby the degrees of freedom within the polymer network. Practically, this is accomplished by reducing the average functionality back down closer to 2, through the incorporation of difunctional monomers. Separately, the difunctional monomers lack the ability to reach higher molecular weights due to their limited solubilities, and the tetrafunctional BODA monomers incorporate too many stresses at high functionality conversions. But together, it is possible to get the best of both systems in one copolymer system.

**MODA-BODA copolymers**

A mono-ortho-diynyl arene monomer (MODA) is simply a small molecule containing a single enediyne functionality retronymmed to conform with the nomenclature already in place for BODA chemistry. The history of similar chemistry is discussed in Chapter 1 of this work.

MODA monomers were introduced into BODA chemistry initially to deal with the issue of brittleness described above. Thin films of BODA-derived homopolymers were found to be unstable to post-functionalization reactions: reactions which take place after the fully-cured BODA network is formed. This was particularly noticeable during
an attempted sulfonation\textsuperscript{218} of the aromatic rings in the network. The film broke into small pieces and delaminated from the glass slide used as the substrate for the film formation.

\begin{center}
\includegraphics[width=\textwidth]{scheme5-1.png}
\end{center}

**Scheme 5-1.** Copolymerization of BODA monomer 1 and MODA monomer 1. Copolymers can be made in different co-monomer ratios in order to change the poly-MODA chain length between BODA residue crosslinks.

The instability of the thin-films was attributed to the high crosslink density within the polymer network. The same property that imparts the strength to monolithic polymeric structures imparts a brittleness and inflexibility to thin films. Thus, when the films are cured or dried, the shrinkage inherent to the polymer film caused the observed cracking in the films.
In order to test this hypothesis, and simultaneously make an attempt to address the problem, several copolymers were made with the tetrafunctional BODA monomer \textbf{1-1} and a difunctional MODA monomer \textbf{5-1}, \textbf{Scheme 5-1}. The copolymers were made with varying feed ratios of the two monomers. Since it is expected that all of the monomers in the reaction would be incorporated into the fully cured network polymers being synthesized, this feed ratio is also taken to represent the overall co-polymer ratio. Therefore, the monomer feed ratio is directly relatable to the amount of crosslinking in the network polymer, and to all mechanical properties of the film dependent on that crosslinking.

\textbf{Figure 5-1.} A typical Thermal Mechanical Analysis (TMA) trace for the BODA-MODA copolymers thin films. This trace represents the MODA homopolymer.

Thin films were made by curing films of each of the copolymer prepolymers cast on clean glass films. The films thus produced were not freestanding and were therefore not available for any mechanical testing that required it to be. One available mechanical test that is adaptable to both supported thin films, and measures the bulk properties of that
film (as opposed to the surface properties only) is a technique called thermomechanical analysis.\textsuperscript{219} This technique measures the change in mechanical deformation of a sample under a non-oscillating load while undergoing a time resolved temperature program. It may be used to measure glass transition temperatures, softening temperatures and coefficients of thermal expansion.

![Figure 5-2](image_url)

**Figure 5-2.** Moduli of BODA-MODA copolymers films on glass slides as measured by TMA at 30-32 °C, \( F = 5 \) mN, \( D = 3.5 \) mm (ASTM E3207-04). The horizontal line represents the modulus of the glass slide substrate.

The results of the TMA testing of the films showed a trend relative to the crosslink density as affected by the ratio of co-monomer content. The modulus, \( E \), is related to the applied load, \( F \), and the penetration depth, \( d \), of a circular flat probe of diameter \( D \) according to the following equation.\textsuperscript{3}

\[
E = \frac{1}{4} \frac{F}{Dd}
\]

\textbf{Eq. 5-1}
In our experiment a constant load of $F = 5.0$ mN was applied with a circular probe of diameter $D = 3.5 \, \mu m$ until a steady state penetration depth was reached. This usually occurred at within about 20 minutes of load time. The experiment was performed isothermally to compare the five samples and a blank glass slide control. Figure 5-1 shows a typical TMA trace. After the load is applied, the system comes to an equilibrium penetration depth. The modulus can then be calculated with Equation 5-1 and compared to the co-monomer ratios. Figure 5-2 shows the results from this analysis.

Unfortunately, two of the samples did not reach an equilibrium penetration depth within the 20 experiment time frame, and therefore did not give reliable results. The remaining four samples, however, followed the expected trend. Those polymers with higher tetrafunctional BODA crosslinking content showed higher moduli than the copolymers with the higher difunctional MODA content. The 1:10 BODA:MODA comonomer ratio sample has a modulus that is indistinguishable from the MODA homopolymer sample within the limits of the experiment. This result indicates that the average length of about five MODA monomers between BODA crosslinks is sufficient to decrease the modulus of the crosslinked polymer to within the scale of the uncrosslinked MODA homopolymer sample. The BODA homopolymer sample on the other hand displays a higher modulus than the glass slide blank that was used as the substrate on which the polymer slides were cast. The result that the modulus of the glass slide lies between the MODA homopolymer and the BODA homopolymer is also significant. This indicates that the modulus that is being measured is directly related to the polymer film, and is not being overly influenced by the underlying substrate.
MODA-Endcapping

MODA monomers have also been employed in a different strategy that can be used to help remedy the mechanical strains associated with the heavy crosslinking density of BODA derived networks, especially in fully cured thin films. Since MODA monomers have half the functionality of a traditional BODA monomer, they can be thought of as half of a BODA monomer. In order for this paradigm to be useful, however, there must be a way to link the two MODA monomers together to form the new BODA monomer. In order to do this using ordinary organic chemical reactions, the MODA monomers must have a reactive functionality at the 3-position (relative to the enediyne functionality) that can be used as a reactive handle. The coupling reactions and conditions must also be within the tolerance of the enediyne functionality, in order to minimize the side reactions that can occur.

Fortunately, there exists in the literature several molecules which already match the criteria for a functional MODA monomer. These include the monomer shown in Scheme 5-1 and MODA monomer 5-2 shown in Scheme 5-2. MODA monomer 5-2 is a benzoic acid as first synthesized by Kovalenko and Alabugin and reported in Chemical Communications in 2005. From this starting point, the next functional MODA monomer was synthesized, by doing a DCC facilitated amidation of the carboxylic acid group with 4-chloroaniline to form MODA monomer 5-3. The other MODA monomers were then built off of different starting points. The aldehyde monomer, MODA monomer 5-4 was built rather simply from 3,4-dihydroxyaldehyde starting material in two steps by triflation of the alcohols with triflic anhydride followed by Sonagashira coupling of phenylacetylene. Finally the last two MODA monomers were
synthesized from 3,4-dihydroxybenzonitrile by first hydrating the nitrile group to form 3,4-dihydroxybenzamide,\textsuperscript{223} which was then triflated with triflic anhydride and Sonagashira coupled with phenylacetylene to form MODA monomer 5-5. This monomer was then converted to the aniline monomer, MODA monomer 5-6, using the Hofmann rearrangement.\textsuperscript{224}

\begin{center}
\textbf{Scheme 5-2.} Syntheses of MODA monomers, 5-2—5-7.
\end{center}

There were several attempts to form a phenolic monomer, MODA monomer 5-7, by starting with 3,4-dibromoanisole to yield the MODA anisole after Sonagashira coupling with phenylacetylene, and then deprotecting the alcohol which were all ultimately unsuccessful.
While the MODA approach can add several more steps to the synthesis of a monomer, it also allows for much greater variety in the number and type of monomers available for synthesis. This will be demonstrated with several different examples. The inclusion in the list above of a monomer, 5-3, which includes both an amide linkage and an aromatic chloride seems to be an odd choice for this list of functional aromatic monomers, which are for the most part formed of simple functional groups attached to the aromatic ring. The reason for the choice of its inclusion stems from the applicability of the functional monomers.

Scheme 5-3. Application of MODA monomers as endcappers for functional oligomers to form MODA macromonomers and subsequent polymerization to form network polymer with oligomer functionality.

Originally these MODA monomers were chosen to act as endcappers for functional oligomers, or telomers. By attaching the functional MODA monomer to each end of a linear telomer, the oligomer is converted into what is functionally described as a BODA macromonomer, Scheme 5-3. This monomer is structured like the classic model
of a BODA monomer, where the X linkage between the two arendiyynes, has been replaced by an oligomeric spacer group. This approach allows for several innovations, including the inclusion of new functionality in this spacer group, and decreasing the crosslink density, and thereby improving the mechanical properties, of the BODA polymer in an entirely different way than demonstrated above.

The oligomeric system desired for this application is the poly(aromatic ether sulfone), or PAES, that has been developed by James McGrath for the purpose of producing a non-fluorinated membrane polymer proton exchange membrane fuel cells, or PEM-FCs. The PEM-FC versions of the polymers utilize a sulfonated 4,4’-dichlorodiphenyl sulfone in place of the 4,4’dichlorodiphenylsulfone of the base polymer to impart the acidic functionality necessary for the role of the final polymer in the fuel cell. This polymer is then referred to as a sulfonated poly(aromatic ether sulfone), or SPAES. For our purposes however we simplified by using the PAES and manipulating the monomer feed ratio to yield oligo(arylene ether sulfones) with phenolic endgroups, Scheme 5-4a. The MODA acid was then used in a Fischer esterification reaction with these phenolic endgroups to produce the new BODA macromonomer, 5-8. Unfortunately due to the inherent reversibility of the Fischer esterification reaction this approach never gave high enough yields to bother isolating from the complicated reaction mixture. While it is possible to use various experimental techniques to lessen this reverse reaction, it points to a larger problem. The structure given for monomer 5-8 is an impractical solution for the application. If the polymer is to be used in an acidic environment, such as that provided by an SPAES oligomer, instead of the PAES oligomer, the ester linkage
between the MODA endcaps and the oligomer would be cleaved, undoing the previous work.

\[
\begin{align*}
\text{S} & \quad \text{Cl} \\
\text{X} & \quad \text{X} \\
\text{Cl} & \quad \text{OH} \\
\text{HO} & \quad \text{+} \\
\text{O} & \quad \text{O} \\
\text{S} & \quad \text{X} \\
\text{X} & \quad \text{HO} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{X} & = \text{H, SO3Na} \\
\text{X} & = \text{H, SO3Na} \\
n & \\
\text{Na}_2\text{CO}_3, \\
\text{DMAC,} \\
170 \degree \text{C} \\
\end{align*}
\]

**Scheme 5-4a.** Synthesis of functional oligomer and ester endcapping with MODA monomer 5-2 to form functional BODA macromonomer 5-8, and subsequent network formation.

The other available route then is to use the PAES with phenolic endgroups to react not with a carboxylic acid, but with another chloride to form the more acid stable ether functional group as in the rest of the polymer backbone, Scheme 5-4b. This then provided the impetus to develop the chloro-functional MODA monomer.
Scheme 5-4b. Synthesis of functional oligomer and amide endcapping with MODA monomer 5-2 to form functional BODA macromonomer 5-9, and subsequent network formation.

The obvious first choice for this MODA monomer would be the 3,4-bis(phenylethynyl)-chlorobenzene. The synthesis of this monomer, while possible given the relative reactivities of aryl chlorides versus aryl bromides or iodides in the Sonagashira coupling of the phenyl acetylenes, requires starting materials that are neither commercially available nor synthetically trivial. The conversion of the acid functional monomer, 5-2, to the chloride functional monomer 5-3, was much more feasible. The incorporation of an amide functional group is much more desirable for the acidic environment than the ester functionality.
This approach of using the chloride functional MODA, 5-3, has one more distinct advantage over the endcapping with the acidic functional monomer approach. Because monomer 5-3 has the same functionality and reactivity as the 4,4’-dichlorodiphenyl sulfone monomers, the MODA endcapper can be incorporated into the oligomer during the polymerization step by inclusion of the MODA monomer in the reaction mixture with the 4,4’-dichlorodiphenyl sulfone and bisphenol-A. The monomer feed ratio of this system must be adjusted to ensure that the phenolic and aryl chloride functional groups are matched. This is done by using x equivalents of 4,4-dichlorodiphenyl sulfone, x+1 equivalents of bisphenol-A (or bis-A), and 2 equivalents of MODA monomer 5-3. The resulting BODA macromonomer 5-9, will have an average oligomeric spacer group, X = -(bis-A)-(4,4’-dichlorodiphenyl sulfone)x-(bis-A)x-, between two MODA endcappers = -Ph-NH-Ph(CC-Ph)2.

This reaction however, also had its drawbacks. The PAES synthesis includes refluxing in DMAc for long periods of time, over 5 days. The MODA arenediyne functionalities did not prove to be stable enough in this environment for synthetic value. The solution for this problem was to combine the previous two synthetic approaches into one functional approach. The amide linkage is superior to the ester linkage in the final product, but the amide-containing MODA monomer is not thermally stable during the polymerization process. Therefore, the polymerization needs to be performed with the three monomers including x equivalents of 4,4-dichlorodiphenyl sulfone, x+1 equivalents of bis-A, and 2 equivalents of the 4-chloroaniline to yield the amine endcapped oligomer. Then the amidation reaction can be performed between the
carboxylic acid functional MODA and the amine terminated oligomers to yield BODA macromonomer 5-9.

This reaction was followed using gel permeation chromatography. Each of the three monomers as well as the polymer were observable in the chromatograms, so the disappearance of the monomers could be observed as the reaction progressed.

The product of this polymerization is, as mentioned above in essence, a BODA monomer, because of the presence of two of the arenediyne functional groups linked together by the oligomeric species. Therefore, these macromonomers can be further polymerized to yield a BODA derived network polymer with the added functionality of the oligomeric spacer group. A film of this network polymer would be similar in function to a high molecular weight film of the oligomeric spacer group, with a few key differences. First, the molecular weight of the oligomer does not need to be high. The oligomeric content of the final network polymer depends on the feed ratio of the monomers during the oligomerization step. In the current experiments, a 2:2:3 ratio of 4-chloroaniline to 4,4’dichlorodiphenylsulfone to bisphenol-A, yields an polymer with an average degree of polymerization of 7 monomer units, two of which are residues from the 4,4’-dichlorodiphenylsulfone. In an SPAES version, these would be the monomers that contained the acid functionality, an average of 2 per monomer residue or 4 per 7-residue oligomer. After the network formation from the BODA macromonomers, the polymer weight would be essentially infinite. It has been reported by McGrath et al. that the aging of polymers in proton exchange membranes occurs from the endgroups inwards. A network polymer, however, contains no endgroups and therefore should have a considerable advantage in PEM-FCs.
MODA for BODA synthesis

The formation of the BODA macromonomers in the above section introduces the concept of creating new BODA monomers from MODA monomers. This model has been used in an example using MODA monomer 5-4. The aldehyde functionality of this monomer was used in a Wittig synthesis with the bis-phosphine oxide\textsuperscript{227} shown in Scheme 5-5. The resulting monomer is a fluorescent BODA monomer that is not available for synthesis from a commercial bisphenols as BODA monomers are traditionally synthesized.

Scheme 5-5. Fluorescent BODA monomer 5-10, synthesized from MODA monomer, 5-4.
Scheme 5-6. MODA monomer 5-4 in Prato reaction to form 5-membered ring with C_{60}.

The same aldehyde monomer, 5-4, was also used in a Prato reaction\textsuperscript{228} with C_{60} to form a 5-membered ring on the surface of the C_{60}, as described in a previous chapter.
CHAPTER 6

CONCLUSIONS

The scope of BODA chemistry has been expanded in recent years in several different interesting directions. BODA chemistry was initially developed as a low-cost polymer that could be efficiently converted to a carbon material. With this work, and the work of those students that have come before me and have helped me through collaborations, BODA chemistry now has applications far outside this original conception.

The realm of processability and application for BODA-derived carbon has grown considerably due to it’s good space-filling properties, high carbon yield, and versatile processing possibilities. The usefulness of BODA-derived carbon has been demonstrated by its use in templating micro-scale and even down to nano-scale features. BODA-derived inverse carbon opals behave like photonic crystals, by excluding electromagnetic radiation of a narrow wavelength from propagation. These photonic crystals have been demonstrated as successful detector elements in a number of ways. The fact that the carbon is electrically conductive could make these type photonic crystals very useful as chemical detector elements in electronic devices. Disordered carbon foams have applications as electrodes in hydrogen fuel cells. The porosity allows for good mass transport of the reactant and product gasses to and from the reactive sites near the PEM membranes. Demonstrated carbon fluorination techniques, including the new one using a
trifluorovinylether containing diazonium salt should help with the compatibility of the membrane and electrode materials in the MEA.

The surprising discovery that BODA generated naphthalenyl radicals are capable of reacting directly with fullerenes has opened up an entirely new realm of possibilities for the BODA project. The reaction has been demonstrated with C_{60}, and the multilayered carbon nano-onions. This is the first reaction to directly bond absorbing aromatic polymers to a fullerene surface. The simplicity of the reaction for the functionalization of fullerenes is also very attractive. The characterization of these copolymer structures has begun, but the exploration of the application of such materials has the potential of continuing for a long time yet. The BODA-co-C_{60} polymers have been detected in MALDI-TOF MS, Raman spectroscopy, and TEM. Thin films of these polymers have shown promising semiconductor capabilities. The BODA-co-CNOs have been observed under TEM, Raman Spectroscopy and in the TGA. This is one of the first reactions with CNOs materials ever, and one of the only reaction to successfully solubilize these interesting new materials.

The extension of BODA chemistry with the mono-ortho-diynyl arene (MODA) monomers also greatly enhances the possibilities that are open for BODA polymers. Thin films of BODA polymers are made more robust by incorporation of MODA monomers to increase the chain length between crosslinks, thereby decreasing their brittleness. BODA macromonomers are synthesized by the endcapping of functional oligomeric species with appropriate MODA monomers. This both increases the molecular weight of the polymers between crosslinks and allows for incorporation of the added functionality of the oligomeric species into the X spacer group of the new
macromonomer. New BODA monomers may similarly be synthesized from the MODA strategy that were not available when relying on bisphenols as the sole feed stock. This was demonstrated using the Wittig-Horner reaction to create a fluorescent BODA monomer, and by using the Prato mechanism to create a new MODA monomer with a pendant fullerene C₆₀ moiety.

Recommendations for Future Research

Future research in the BODA project has many opportunities.

1) Extension of exploration into the reaction of BODA polymers with fullerenes and their related materials.

2) Synthesis of new BODA monomers to take advantage of the multiple benefits now made possible with the application of MODA strategies.

3) Exploration of other radical initiated reactions that can be initiated or propagated with BODA monomers.

4) Examination of the seeming contradiction between the long-life and the apparent reactivity of the BODA produced radical species.

Work has already begun in exploring the functionalizations of the other great class of fullerene derivatives, the carbon nanotubes (CNTs). This class of molecules comes with their own challenges, but there is hope that the same reactions that functionalized C₆₀ and CNOs should react with CNTs. The functionalization reactions are of course only the initial steps in showing the
worth of the resulting materials. The exploration of these applications will be a very interesting path to follow.

It has been demonstrated that several functional MODA monomers have been synthesized already, including the carboxylic acid, aldehyde, amide, amine, and N-aryl amide. I have demonstrated just a few of the reactions that can be done with these new functional handles. There are many more routes that one could take in this area alone. This number is increased by the number of other functional MODA monomers that could be synthesized. I have mentioned the elusive phenolic monomer already, but an azo-functional monomer, an isocyanate functional monomer, a siloxane-functional monomer, or a vinyl functional monomer would all open up new reactive pathways that could be pursued toward the synthesis of new BODA monomers.

These new monomers, or even one the existing cadre of monomers, can all be enhanced by the application of MODA-BODA copolymers. The post-functionalization of a thin film of a BODA polymer provided the initial motivation for this research, but the poor mechanical properties of BODA monomers when cast as thin films has stood in the way of several different BODA applications in the past. The fluorescent and photo-luminescent polymers that Dr Perera worked on in the past, could almost certainly by enhanced in their thin film form by this strategy.

The reaction of BODA produced radicals with the carbon nano-onions was in hindsight, a reasonable expectation. This is because, it has been known for sometime that phenyl radicals had the capability of reacting with carbon surfaces.
This is the reaction introduced in Chapter 3 during the discussion of diazonium salts for carbon functionalization. The unique reactivity these aromatic radicals remains mysterious. Another reaction that goes through a similar phenyl radical is the thermal dissociation of benzoyl peroxide. This peroxide initially splits homolytically to form two molecules of benzoic radical. This species, however, radically decarboxylates to form a phenyl radical. One of the main applications of these radicals are as initiators for radical polymerizations. The trapping of BODA radicals, has historically been unsuccessful, but if a radical reaction can be initiated from the BODA radicals, much could be learned about the nature of the species that is formed upon BODA monomer cyclization, and an interesting new star-polymer core would be discovered.

Finally, there is an apparent contradiction as to the nature of the BODA produced radical species. The kinetic analysis of BODA monomers indicates that the polymers essentially grow in a step growth mechanism, that two radical species are combined to form the polymer bond. This mechanism would produce a polymer with a poly(naphthalenyl) backbone. Yet, studies have shown that independently grown polynaphthalenes have strikingly different physical characteristics. The radical species can be observed by EPR to be remarkably long-lived, even in an oxygen containing environment. Yet, the radicals have also been shown to be reactive enough to functionalize and solubilize the enormous and unreactive CNOs species. Further exploration into the true nature of the radical species would go along way towards explaining these observations.
$^{13}$C NMR of 5-2
$^{13}$C NMR of 5-3
$^{13}$C NMR of 5-4
$^{13}$C NMR of 5-5
$^{13}$C NMR of 5-9
$^{13}$C NMR of 5-10
MALDI-TOF MS of BODA-co-C₆₀ trimer
MALDI-TOF MS of MODA 5-4 + C₆₀ adduct
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