SOFT FULLERENE MATERIALS: CLICK CHEMISTRY AND
SUPRAMOLECULAR ASSEMBLIES

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SUPRAMOLECULAR ASSEMBLIES

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Dissertation

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ABSTRACT

Fullerenes are fascinating carbon nanostructures with outstanding structural and functional properties, which critically rely on their spatial arrangements. However, their strong aggregation makes them difficult to pack into ordered structures in different dimensions and across multiple length scales. The purpose of this research is to develop “soft fullerene materials,” in particular, using self-assemblies of polymers as templates to manipulate their order and symmetry. Synthesis of fullerene polymers with high purity and well-defined structure has been difficult due to the reactive nature of fullerene towards various reaction intermediates and the often unavoidable multiple additions. To address this, a “click chemistry” approach has been developed, as demonstrated by the model reaction between azide-functionalized polystyrene (PS-N$_3$) and highly reactive alkyne-functionalized fullerene (Fulleryne01). Fullerynes with different structures and reactivities have been designed and synthesized. Combined with living/controlled polymerization techniques, the method has been successfully extended to fullerene polymers based on poly(ethylene oxide) (PEO) and poly(ethylene oxide)-block-polystyrene (PEO-b-PS) with controlled molecular weight and narrow polydispersity. The C$_{60}$ was placed at the chain-end [PEO-C$_{60}$ and PEO-b-PS-C$_{60}$], or at the junction point between two blocks [PEO-(C$_{60}$)-PS], or randomly tethered along one block [PEO-b-PS/C$_{60}$]. The self-assembly of these polymers, such as crystallization from dilute solution,
micellization in selective solvents, and phase separation in the bulk or thin films, have been studied. Preliminary results have shown that they could template the spatial arrangements of $C_{60}$. For example, the single crystals of PEO-$C_{60}$ have been grown to generate PEO single crystal lamellae with $C_{60}$ tethered to the surface, forming a 2D $C_{60}$ molecular sheet. The alternating, epitaxial growth of PEO and PEO-$C_{60}$ single crystals might lead to near-1D ring patterns of $C_{60}$. The diblock copolymers, PEO-(C$_{60}$)-PS and PEO-$b$-PS-$C_{60}$, were found to form micelles in DMS/water mixed solvent, in which $C_{60}$ was either confined to the interface between the core and corona, or inside the core. The bulk self-assembly of PEO-(C$_{60}$)-PS has shown an unusual decrease in d-spacing, as compared to its parent polymer PEO-(N$_3$)-PS; whereas both PEO-$b$-PS-$C_{60}$ and PEO-$b$-PS/$C_{60}$ showed increase in d-spacing. This drastic difference was due to the location of $C_{60}$ in the final structure. This study has demonstrated the concept and the promising future of “soft fullerene materials.” In addition, during the development of these materials, a “retro-functional analysis” approach has been proposed as the molecular design principle for advanced materials. It enables efficient and modular development of functional molecular materials with engineered hierarchical structure across different length scales to exhibit a specific macroscopic property. Being function-oriented rather than synthesis-oriented, it fuels innovation in molecular design and provides future targets for material research.
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CHAPTER I
INTRODUCTION

Fullerenes, being the third carbon allotrope, possess fascinating nanostructures constructed via sole carbon atoms with outstanding structural and functional properties.\textsuperscript{1-3} Following the discovery of [60]fullerene (C\textsubscript{60}) in 1985 by R. F. Curl, H. W. Kroto, and R. E. Smalley,\textsuperscript{4} the procedure for the multigram-scale preparation of C\textsubscript{60} developed and reported by Krästchmer, Huffman et al.\textsuperscript{5} significantly stimulated research in this field. It opened a whole range of new possibilities in the chemical modification of this perfectly spherical molecule and physical manipulation of novel fullerene derivatives to explore their practical applications at will. The intense research in fullerenes perhaps gave rise to the birth of the burgeoning field of nanoscience and nanotechnology.\textsuperscript{6} The excitement and achievements in fullerenes have been recognized by the award of Nobel Prize to the three discoverers in 1996, just ten years after their discovery.

Nowadays, the principles of fullerene chemistry have been understood for the most part.\textsuperscript{2} Fullerene-based materials are continuously being developed and applied in a broad range of areas from ferromagnets, solar cells, superconductors, optical limits, to photosensitizers, medicine, cosmetics, and molecular electronics.\textsuperscript{1,7} One of the most popular applications is perhaps in microelectronics, such as organic photovoltaics. Fullerenes can serve as electron acceptors, semiconductors, conductors, and even
superconductors, depending on the hierachical structures from the molecular level (the chemical structure, the energetics, etc.) to the physical state (doping effect, packing order and symmetry in condensed state, etc.). However, being a molecular carbon allotrope, fullerenes are very hydrophobic and exhibit a strong aggregation tendency and low solubility in most solvents. Hence, they are difficult to form ordered structures in different dimensions and across multiple length scales. Traditionally, fullerenes have been considered as a “hard” matter. To fully explore their potential application, it is necessary to find ways to manipulate them into different ordered structures, such as 1-dimensional (1D) wires, 2-dimensional (2D) sheets, and 3-dimensional (3D) networks (Figure 1.1).

Figure 1.1. Manipulating C_{60} into different ordered structures (1D wire, 2D sheet, and 3D network).

Soft matter has been proposed by Prof. de Gennes to describe the fourth state of condensed matter. The common feature about soft matters is that they are able to self-assemble into different ordered heterogeneous structures in multiple length scales with entropy being the major driving force. They exhibit non-Newtonian flow behavior and give a strong response to a weak command signal (small foreign stimuli). Phenomenologically, soft matter includes polymers, liquid crystals, amphiphiles, colloidal, biomolecules, etc. “Soft fullerene materials” refers to their corresponding fullerene derivatives. It is anticipated that the self-assembly of soft matters, such as
polymers and liquid crystals, can serve as templates to direct fullerene’s ordered packing so as to utilize its excellent electronic properties. The unique combination of fullerene material and highly versatile soft matter creates a new class of functional materials -- “soft fullerene materials.”

To date, work in this new interdisciplinary field has mostly focused on relatively conventional subjects such as synthesis, mechanical strength, processing, and micellization. Meanwhile, exciting examples of novel fullerene-based, self-assembled structures are emerging. In this dissertation, our group’s current effort in this field will be described. First, in order to avoid the complexity in doing chemistry with pristine fullerene, an efficient “click” chemistry approach has been successfully developed to synthesize fullerene materials of high purity and structure fidelity. Alkyne-functionalized fullerenes, named “fullerynes”, were made readily available in gram quantities. They possess high reactivity in the “click” coupling reaction with functional polymers. This method has been applied to the synthesis of fullerene polymers with different compositions and architectures (homopolymers and block copolymers). The effect of $C_{60}$ on the self-assembly of polymers (crystallization, micellization, bulk self-assembly) has been studied. Fullerene structures of different orders could be achieved in this approach. This work provides an opportunity to use polymer self-assembly as a template to direct $C_{60}$’s ordered packing. The concept and method can be extended to other soft matters such as liquid crystals and amphiphiles, all of which demonstrate the promising field of “soft fullerene materials.”

In this dissertation, Chapter II provides a historical background that summarizes the current understanding of fullerene chemistry and the reactions available to
functionalize them. The click chemistry concept and philosophy will also be introduced and detailed “click” reactions will be discussed with respect to their structure-property relationships. This Chapter also provides an overview of “soft fullerene materials,” from fullerene amphiphiles, to liquid crystals, liquids/gels, and further to polymers, with focus and critical comments on ordered structure formation in these materials. Chapter III describes the experimental details for the material syntheses and self-assembly manipulation. Chapter IV is the central part of this dissertation that proposes a new scheme of “retro-functional analysis” for the design of advanced materials. The concept is proposed in an effort to create a modular approach in the design of materials with consideration from both molecular functions and the hierarchical structures of the materials that can transfer and amplify molecular functions to macroscopic properties. Chapter V presents a model “click” reaction between PS-N$_3$ and Fulleryne01. Chapter VI summarizes results on the synthesis of various fullerynes, the processes, yields, and their reactivity. Chapter VII reports the synthesis of fullerene polymers with various architectures and precisely controlled C$_{60}$ functionality placement along the chain. Chapter VIII describes preliminary results on the supramolecular assemblies of these fullerene polymers, from solution crystallization to micellar aggregates and bulk phase separation. Finally, Chapter IX is a summary of the research in this dissertation and includes a personal perspective on future directions in this field.
CHAPTER II
BACKGROUND

When one looks back reviewing the development of human history, he or she would probably agree that it is a history driven by economy, which relies critically on the development of materials. The trend is so apparent that each era could be defined or characterized by the materials of its choice, naming a few examples, the Stone Age, the Bronze Age, and the Steel Age.\(^\text{15}\) In this sense, our age could be *arguably* classified as the Polymer Age. Nowadays, polymers, in particular synthetic polymers, are almost everywhere, from everyday commodities such as polyethylene milk bottles, polyisoprene tires, polyester shirts, polypropylene carpets, and polystyrene furniture, to “high-tech” chemical sensors and solar cells. It represents one of the most spectacular achievements of human-kind that strongly influence practical technological applications and boost the advancements of society. Research and development of new materials has now become an intense systematic human endeavor aiming at understanding the properties with respect to their applications in various fields and at creating new materials with rationally designed and tailored properties rather than exploring haphazardly in the hope of serendipity. This highly interdisciplinary field is a central theme in today’s research activities. The creation of materials in the future, from my personal perspective, can be a combination of four levels. The first level is the construction of molecules from *atoms*
via covalent bonds by means of chemistry. The second level is the manipulation of intermolecular/secondary interactions to assemble molecules into supramolecular assemblies with different structures possessing various properties based on the understanding of physical principles. The third level is tuning the responsive and dynamic interactions of these supramolecular assemblies within a specific but systematic complex environment, similar to what happens in biological systems. The fourth level is an organic connection of these phases to construct an object system with specific functions. These four levels constitute an integrated approach to functional materials with molecular precision and relating to its macroscopic properties. This philosophy will be applied to the development of soft fullerene materials in the form of a retro-functional analysis approach with the concept of functional synthon and structural synthon, as described later in Chapter IV.

The versatility and moderate strength of the carbon-carbon bonds are the foundation of organic compounds. Combined with other types of bonds, chemicals possessing diverse molecular architectures can be designed with the only limitation being one’s imagination. Among them, molecules of high symmetry and unique composition are especially appealing, not only owing to their aesthetic value but also because of their huge potential in practical applications. With the thriving and climaxing of organic chemistry, more and more target molecules, from those with high symmetry and unique composition to those of extreme complexity, have been conquered and surrendered to the hands of materials scientists. The structures of two successful examples are shown in Figure 2.1.
Figure 2.1. Examples of molecules with high symmetry and unique composition: fullerene C\textsubscript{60} (a); polyhedral oligomeric silsesquioxane (b). Black: carbon; red: oxygen; white, hydrogen; blue: silica.

Molecule (a) is the molecular carbon allotrope called fullerene C\textsubscript{60}. It is composed of 60 carbon atoms organized in a perfect spherical cage formed by 12 pentagons and 20 hexagons with an $I_h$ symmetry. Because the structure is very reminiscent of a geodesic dome designed by the American architect Richard Buckminster Fuller (1895-1983),\textsuperscript{19} it has been named after him as “fullerene.” It is an organic, nanosized, perfectly spherical particle with a diameter of ~ 1.0 nm.\textsuperscript{2} In contrast, the main framework of molecule (b), polyhedral oligomeric silsesquioxane T8 (POSS), is an inorganic, cubic-shaped, silicate cage with eight modifiable organic side groups.\textsuperscript{20} Molecule (b) can be viewed as the smallest inorganic silica nanoparticle with the center cage diameter around 1.0 nm and tunable overall molecular size depending on the size of the side groups. While their chemical compositions are as different as day and night, both share certain common features, such as a rigid conformation and incompressibility. Being advanced functional materials, they have received extensive and intensive research attention and hold broad practical applications.\textsuperscript{3,7,21,22} Both molecules can be regarded as
the counterpart of each other, and can serve as molecular scaffolds to build nano-architectures via a “bottom-up” approach.\textsuperscript{23,24} Although there are significant efforts ongoing in our group to combine these two materials in this direction, the discussion in this dissertation will mainly focus on molecule (a), fullerene C\textsubscript{60}, and its extension to soft materials within the scope of polymers. In this Chapter, fullerene and its chemical principles will be first introduced, followed by a brief summary of the “click” chemistry concept and then, an overview of the state-of-the-art in the area of “soft fullerene materials” with focus on the formation of various ordered fullerene structures via self-assembly.

2.1 Fullerene

\textit{“Call me Trimtab.”}

---- R. Buckminster Fuller

2.1.1 General Aspects\textsuperscript{2}

In contrast to graphite and diamond with extended solid state structures, fullerenes represent a molecular carbon allotrope with well-defined size and molecular shape. They are a large family of compounds built up of fused pentagons and hexagons. The existence of pentagons introduces curvature to fullerenes, making them unique three-dimensional molecular systems. While there are unlimited possibilities for such structures with different carbon atom numbers (C\textsubscript{28}, C\textsubscript{60}, C\textsubscript{70}, etc.), different symmetries (C\textsubscript{60}-I\textsubscript{h}, C\textsubscript{70}-D\textsubscript{5h}, etc.), and different architectures (onion-like fullerenes, carbon nanotubes, etc.), the most abundant, the most studied, and the smallest stable fullerene is C\textsubscript{60}-I\textsubscript{h}. C\textsubscript{60}
is also known as a “buckyball” because it has the shape of a soccer ball. Nowadays, C_{60} is being produced annually on the scale of tons and the largest manufacturer is the Frontier Carbon Corporation in Japan. Its availability allows for extensive and intensive research into its chemistry and applications. The molecular nature of C_{60} imparts this carbon allotrope with certain solubility in organic solvents, which, though quite limited, is a prerequisite for chemical manipulations and physical characterization.

Macroscopic quantities of C_{60} were first synthesized by resistive heating of graphite to produce soot that contains a mixture of fullerenes followed by purification via extraction and chromatography. Other methods include the arc vaporization, solar furnace generation, inductive heating, and pyrolysis in combustion. The rational total synthesis approach to C_{60} was also developed based on different substrates, which holds potential to yield specific fullerene derivatives such as endohedral fullerenes and heterofullerene through modified procedures using similar methods. Two decades after C_{60}’s discovery, its preparation in large scale has become routine by burning toluene into fullerenes. The price of C_{60} in the market has dropped from thousands of dollars per gram in 1989 to thirty dollars per gram in 2009. The current challenge is basically directed at the synthesis of higher fullerenes and various endofullerenes, which possess unprecedented properties not found in pristine C_{60}.

The basic physical properties including solubility in different solvents of C_{60} are listed in Table 2.1. In the solid state, as expected for a perfect spherical molecule, C_{60} forms a face-centered-cubic structure at room temperature with a density of 1.72 g/cm\(^3\) (as compared to theoretical density of 1.68 g/cm\(^3\) from four molecules in a unit cell with a = 1.417 nm). The crystals undergo a melting process to enter a mesophase at -17 °C,
and this mesophase has been known as a classic example of a “plastic crystal” where the molecules have positional order but no orientational order – they rotate freely above the melting temperature. The heat-of-formation of C\textsubscript{60} has been determined by calorimetry and confirmed by theoretical calculation to be 38.0 kJ/(mol per C-atom). It reveals that C\textsubscript{60} is less thermodynamically stable than graphite (0 kJ/mol per C-atom) and diamond (1.67 kJ/mol per C-atom). Therefore, the binding energy per C-atom is smaller than that of graphite. It should be noted that the electron affinity of C\textsubscript{60} (\(E_A\)) is quite high, indicating that it can easily accept electrons. In fact, cyclic voltammetry has shown that one C\textsubscript{60} molecule can accept up to 6 electrons. Understanding these physical properties is very useful for the design of fullerene materials.

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Value</th>
<th>Solvent</th>
<th>Solubility (mg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume per C\textsubscript{60}</td>
<td>5.2×10\textsuperscript{-22} cm\textsuperscript{3}</td>
<td>Density</td>
<td>1.72 g/cm\textsuperscript{3}</td>
</tr>
<tr>
<td>Boiling point</td>
<td>Sublimes at 800 K</td>
<td>Carbon disulfide</td>
<td>7.9</td>
</tr>
<tr>
<td>C\textsubscript{60} mean ball diameter</td>
<td>6.83 Å</td>
<td>n-Hexane</td>
<td>0.043</td>
</tr>
<tr>
<td>C\textsubscript{60} outer diameter</td>
<td>10.18 Å</td>
<td>Cyclohexane</td>
<td>0.036</td>
</tr>
<tr>
<td>C\textsubscript{60} inner diameter</td>
<td>3.48 Å</td>
<td>Toluene</td>
<td>2.8</td>
</tr>
<tr>
<td>Compressibility</td>
<td>6.9×10\textsuperscript{-12} cm\textsuperscript{3}·dyne\textsuperscript{-1}</td>
<td>Chlorobenzene</td>
<td>7.0</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.2 (600 nm)</td>
<td>(o)-Dichlorobenzene</td>
<td>27</td>
</tr>
<tr>
<td>Band gap</td>
<td>1.7 eV</td>
<td>1-Chloronaphthalene</td>
<td>51</td>
</tr>
<tr>
<td>Electron Affinity</td>
<td>2.65 eV</td>
<td>Tetrahydrofuran</td>
<td>0</td>
</tr>
<tr>
<td>Ionization Potential</td>
<td>7.58 eV (1st)</td>
<td>Methanol</td>
<td>0</td>
</tr>
<tr>
<td>[5, 6] Bond length</td>
<td>1.45 Å</td>
<td>Methylene Chloride</td>
<td>0.26</td>
</tr>
<tr>
<td>[6, 6] Bond length</td>
<td>1.38 Å</td>
<td>Chloroform</td>
<td>0.16</td>
</tr>
</tbody>
</table>

The C\textsubscript{60}’s solubility has also been systematically studied. The rule-of-thumb, “like likes like,” still applies. Polar and H-bonding solvents, such as tetrahydrofuran and methanol, essentially do not dissolve C\textsubscript{60}, while nonpolar, aromatic solvents, such as
carbon disulfide, dichlorobenzene, toluene, chlorobenzene, and bromobenzene, exhibit relatively good solubility for C$_{60}$. However, it should be noted that even in those “good” solvents, the solubility is still very low in terms of molar fraction (typically $10^{-4}$ M), as compared to other organic molecules.

C$_{60}$ also exhibits a variety of remarkable photophysical properties. For example, C$_{60}$ can be readily excited to its singlet state, which decays very efficiently via intersystem crossing to the energetically lower-lying triplet excited state with high quantum yields (~100%). Several deactivation processes can happen as shown in Scheme 2.1. Among these, queching by oxygen to generate $^{1}O_2$ is worth noting. It is the foundation for its application in phototherapy. Also, owing to the exceptionally low reorganization energy in the rigid fullerene core, C$_{60}$ can accelerate photoinduced energy- and/or electron-transfer processes, such as charge separations, while retarding charge recombination in the dark to achieve long-lived, charge-separated states. This property leads to significant applications in solar cells.

Scheme 2.1. Photophysical processes for C$_{60}$.²
Because of all of these outstanding properties, C\textsubscript{60} has received enormous interests and research attention. It has already been applied to various fields in material science. However, practical applications of C\textsubscript{60} are quite limited by its low solubility in solvents and difficulty associated with processing. Chemical modification of C\textsubscript{60} greatly expands the scope of fullerene materials. To do so, an understanding of the principles of fullerene chemistry is essential.

2.1.2 Principles of Fullerene Chemistry

There are basically two approaches to manipulate fullerene: physical methods and chemical methods. In the former process, no chemical bond is broken or formed. Typical methods include sublimation onto surfaces\textsuperscript{33} or controlled crystallization at interfaces,\textsuperscript{34} both being tricky processes to conduct. In contrast, the chemical method seems much more versatile. C\textsubscript{60} can be chemically modified with various functional moieties to extend its capability or improve its processibility. The advantage in this approach is that it significantly expands the scope of fullerene-based materials, while the downside is that properties, such as electronic properties, might be compromised depending on the structural modification. Nevertheless, if careful balance in the molecular design is achieved, the material’s properties could be tuned to match a specific application, which makes the chemical modification a viable and versatile method today.

In general, fullerenes have a unique “three-dimensional” (3D) structure with fused pentagons and hexagons. All the C atoms of fullerene are quaternary and contain no hydrogen. This determines the unique features of fullerene chemistry: (1) they have both endo- and exo-hedral reactivities and (2) the main reactions are addition and redox
reactions. The curved surface in fullerenes leads to the pyramidalization of the C-atom and thus, large strain energy. Therefore, the main driving force for fullerene reactivity is the relief of strain in the fullerene cage. From this point of view, it can be envisioned that the endohedral reactivity will be very low because it does not relieve the strain. As a matter of fact, a highly reactive single atom, such as hydrogen, nitrogen and fluorine, can be trapped and kept inside the C₆₀ cage over a long period of time without reaction. In contrast, a large variety of reaction intermediates can attack the C₆₀ cage from the outside, as shown in Scheme 2.2.

Scheme 2.2. Examples of C₆₀ addition reactions.

The C-C bonds on C₆₀ can be distinguished into two types: the bonds at the junctions between two hexagons ([6,6] bonds) or between a hexagon and a pentagon ([5,6] bonds). It has been found that the bond length of [6,6] bonds (1.38 Å) is significantly
shorter than that of [5,6] bonds (1.45 Å), which means that [6,6] bonds have significantly more double bond character than [5,6] bonds, and the electrons on the surface of C_{60} are mostly localized in the [6,6] bonds rather than delocalized onto the whole spherical surface. The reactivity of the bonds on fullerene has been found to be similar to that of an electron-deficient olefin.^{2} Therefore, it is subject to olefin reactions, such as nucleophilic additions, radical additions, cycloadditions, hydrogenation, halogenation, and redox processes (Scheme 2.2). A few well-known reactions that were used in this dissertation study are summarized as follows.

(1) Diels-Alder reaction (Scheme 2.2a). The well-establish Diels-Alder reaction has been successfully applied to fullerene using many functional dienes (e.g., Danishefsky diene^{36}) with addition occurring mainly at [6, 6] bonds, as reported by Rubin et al.^{37,38} The reaction conditions required for D-A reaction vary, depending on diene reactivity.^{33} It creates very stable cyclohexene structures that can be converted to other functionalities. For example, ketone-functionalized C_{60} (1) can be obtained in good yields (54%) after hydrolysis of the uncharacterized intermediate silyl enol ether under chromatographic conditions and reduced by DIBAL-H to give hydroxyl-functionalized C_{60} (2) in excellent yield (93%) (Scheme 2.3).^{37} It should be noted that unfunctionalized C_{60} and higher addition products such as regioisomeric dimers (3, 4, respectively for ketone- and hydroxyl-functionalized C_{60}) are inevitable, but they can be chromatographically separated from the monoadduct in the case of small molecules.^{39} The di-adducts were obtained as a mixture of regioisomers. Bulkier dienes, such as dimethylanthracene, can undergo reversible D-A reaction and be used to control the regiochemistry in higher addition products.^{40}
(2) Azide addition (Scheme 2.2b). This chemistry was first discovered by Wudl et al.\textsuperscript{41,42} Two mechanisms are possible: (1) a sequential \([3+2]\) cycloaddition reaction, followed by thermal extrusion of nitrogen;\textsuperscript{43} and (2) nitrene addition.\textsuperscript{44} While the former yields a [6,6] triazoline intermediate that is further converted mainly to [5,6]-open azafulleroids, the latter almost exclusively attacks the [6,6] bond to afford [6,6]-closed aziridines (Scheme 2.4). Depending on the structure and stability of the azide, the reaction conditions mainly determine the reaction pattern (i.e., if the temperature is high enough to induce the loss of nitrogen to generate nitrene prior to cycloaddition).\textsuperscript{44}

The reaction was later embraced in fullerene polymer chemistry due to the ease of preparation of azides by nucleophilic substitution and the generally sufficient yields. This was first demonstrated by Hawker et al.\textsuperscript{45,46} in the synthesis of C\textsubscript{60} functionalized dendrimer and polystyrene and then, by many others in the synthesis of PEO-C\textsubscript{60}\textsuperscript{47} and PtBA-C\textsubscript{60}\textsuperscript{48}. However, one fact often neglected in most of these studies is that [5,6]-open
product was found to be susceptible to oxidation by singlet oxygen generated via photosensitization of oxygen in air upon illumination on $C_{60}$. While this does not cleave the $C_{60}$-polymer linkage, it does change the polarity and could possibly affect other physical properties as well. Moreover, although the amount of multiple-addition products can be minimized by controlling the stoichiometry, the unreacted homopolymers are hard to remove, and the functionalized structures are not well-defined.

Scheme 2.4. Reaction of azide with $C_{60}$ by 1,3-dipolar cycloaddition mechanism and nitrene addition mechanism.

(3) Bingel-Hirsch cyclopropanation (Scheme 2.2c). First developed by Bingel as reaction with bromomalonate in the presence of NaH and later improved by Hirsch to allow direct reaction with malonate in the presence of CBr$_4$ (or I$_2$) and diazabicyclo[5.4.0]undec-7-ene, this reaction has been considered as one of the most versatile and efficient methodologies for the functionalization of $C_{60}$ because of its high tolerance to functional groups, synthetic facility of malonates, and mild reaction conditions required. It cleanly affords a simple and stable methanofullerene product in
moderate to good yields. The reaction proceeds via an addition-elimination mechanism as shown below (Scheme 2.5). \(^{50}\)

![Scheme 2.5. Reaction mechanism for Bingel-Hirsch cyclopropanation.](image)

The chemistry for multiple additions, which truly exemplifies the 3D nature of fullerene chemistry, is an active area of research with significant achievements as well as grand challenges.\(^2\) The isomer number for higher adducts increases dramatically with the number of adducts. Regioselectivity can be achieved by electronic effects,\(^{43,52}\) template mediation,\(^{40}\) tether-directed remote functionalization,\(^{53}\) and topochemically controlled solid state reactions.\(^{54}\) An interesting recent work is the finding that excess CBr\(_4\) in Bingel-Hirsch cyclopropanation yields the symmetric hexa-adduct in high yield in the absence of a template,\(^{55,56}\) the mechanism of which has yet to be clarified.

As described above, doing chemistry with fullerene usually has issues associated with the low yields, large amount of toxic solvents required for reaction and purification, instability of the product to the singlet oxygen, and the lack of regio- and chemo-selectivity in higher adducts. It works fine for small fullerene derivatives, since they can be purified relatively easily using chromatography. When it comes to polymers, separation of unreacted C\(_{60}\), homopolymers, mono-functionalized polymers, and higher
adducts is often difficult, if at all possible. Thus, a highly efficient, mild, and modular method is desired to attach fullerene to polymers. This is particularly important for the study of structure-property relationships requiring well-defined, homogeneous samples with narrow polydispersity.

2.2 Click Chemistry

“In order to be acceptable, the solution to a scientific problem must satisfy exacting criteria and demands. These constrains, however, do not eliminate creativity. They provoke it.”

----- I. Prigogine

2.2.1 The Concept

Ever since the birth of organic chemistry, people have been trying to find “perfect chemical reactions.” Although a perfect chemical reaction might be different for different people with different expectations, basic features of this type of reactions must include easy set-up, high yields, minimum work-up and side reactions, precise chemical connections, etc. It was not clear until 2001 when the Nobel Laureate, Professor K. B. Sharpless, proposed the concept of “click” chemistry to describe this type of reactions.\(^5^8\) The concept was soon accepted by the chemical community and thrived into an active research area with enormous impact on many interdisciplinary areas where chemistry plays a role.\(^5^9-6^7\)

“Click” chemistry is a chemical philosophy that describes the stringent criteria defining an ideally perfect chemical reaction.\(^5^8\) To qualify as “click” chemistry, the reaction itself must be modular, wide in scope, tolerant to other functional groups, giving very high yields and only inoffensive by-products that can be easily removed, and be
stereospecific, preferably giving only one product. Furthermore, from a process chemistry viewpoint, the reaction should be simple to set-up and insensitive to the environment such as solvents, oxygen, and moisture; the starting materials and chemical reagents should be readily available; the reaction condition should be benign, and use of no solvent is preferred; purification of products, if ever required, must be via non-chromatographic methods and the product needs to be stable under physiological conditions. Usually, such reactions have a very high thermodynamic driving force (> 80 kJ/mol) and can be viewed as being “spring-loaded” for a single trajectory to a single final product with high atom economy. Therefore, “click” chemistry is not a specific chemical reaction; it is rather a chemical concept or a framework that comprises different reactions with common features.

With the concept proposed and defined, chemists have developed or re-discovered many chemical reactions that share certain criteria of “click” chemistry under certain conditions, such as Cu(I)-catalyzed azide-alkyne cycloaddition and thiol-ene reaction. Because of their high selectivity, almost-perfect reliability, excellent yields, and exceptional tolerance towards functional groups and reaction conditions, they have been successfully applied to many different subjects, from polymer synthesis to modifications of surfaces and nano- and meso-scale structures, to viruses, and to in vivo labeling in biological environments. Libraries of complex molecular structures could be constructed in a few steps from simple and small components via heteroatom joints, just as Nature does in the construction of diverse primary metabolites with distinct functions from less than 40 chemical monomers. The concept of “click” chemistry has had an enormous impact on the field of materials science and brought significant advances in areas such as
polymer chemistry, medicinal chemistry, bio-conjugated materials, and others. This concept has thus expanded the tools of material scientists to such an extent that they can start to focus on function of materials rather than paying meticulous attention to detailed synthesis and chemical structure of the materials.

2.2.2 Typical “Click” Reactions

Two hundred years after the birth of organic chemistry, chemists still have to admit that there is simply no such reaction to be qualified as “perfect.” An ideal chemical reaction that fits every stringent requirement may only be available to the hands of God, the Higher Power. However, in reality, there are reactions that fit more or less into this category. Under certain conditions, they might be deemed “perfect” enough or close to perfect for certain applications. These reactions have thus been categorized under the name of “click chemistry”, even though they are not “click” by the most stringent definition. Nowadays, the use of the name “click” chemistry seems to represent a fashion of doing chemistry, rather than implying a controlled reaction that really satisfies every exacting criterion and demand. Nevertheless, by keeping those constraints and goals in mind, it provokes creativity and incentive in the development or re-discovery of reactions that have more “click” features than others. It should be also noted that by naming a reaction “click”, it recognizes the essential features of a good chemistry in this reaction, as well as the people who have contributed to the development of this chemistry. In this section, the typical “click” reactions that have been reported in the literature are summarized as follows.
(1) Cu-catalyzed acetylene azide [3+2] cycloaddition (CuAAC, Scheme 2.6).\textsuperscript{59,68,69} The 1,3-dipolar cycloaddition reaction was first known as the Huisgen reaction,\textsuperscript{68,69} a thermally promoted reaction that usually gives a mixture of 1,4- and 1,5-regioisomers. In 2002, the reaction was re-discovered independently by two groups to be highly robust and efficient under the catalysis of Cu(I) to give only the 1,4-regioisomer.\textsuperscript{70,71} It was thus recognized as the first “click” chemistry and soon gained its popularity. Using different catalysts, such as ruthenium complexes, it can also afford exclusively the 1,5-regioisomer through a different mechanism.\textsuperscript{72,73} The pros of CuAAC are its high reliability and ease of operation; the cons are, in certain cases, the generation of a bulky, polar triazole linkage between functional groups, which sacrifices elegance in molecular design and adds complication and modification to molecular properties. The mechanism and scope will be discussed in more detail in a later section.

![Scheme 2.6. 1,3-Dipolar cycloaddition reaction between azide and acetylene.](image)

(2) Thiol-ene coupling reaction (TEC, Scheme 2.7). Although this reaction has been developed and widely used in polymer chemistry for thio-ene polymers and curable coatings, its potential was not fully appreciated until recently.\textsuperscript{74} The reaction mechanism involves the abstraction of a hydrogen atom from thiol by a radical initiator to generate a thiol radical that can rapidly add to a double bond to create another carbon radical, which
then abstract a hydrogen atom from another thiol to continue the chain reaction. Although it is a radical reaction, it is not significantly affected by the presence of moisture and oxygen. The reaction can be initiated either photochemically (using low-energy light at 365 nm) or thermally, solvent-free in the bulk or at high concentrations. Since many functional thiols are commercially available, and the reaction is highly tolerant towards various functional groups, it is a very useful “click” process. The pros in this approach include its simple procedure, mild conditions, minimum work-up, and high reactivity. The cons are associated (1) with the instability of the thiols and the thiol-ether linkages because they are sensitive towards oxidation and radical attack and (2) with the reduced coupling efficiency in the case of macromolecular thiols, leading to significant amounts of dimer as side products.

![Scheme 2.7. Thiol-ene coupling reaction.](image)

(3) Diels-Alder [4+2] cycloaddition and others (Scheme 2.8). Being considered as the “Mona Lisa” of reactions in organic chemistry, this historical chemistry is still very useful and important, especially when coupled with advanced catalysts. It is known to have a high thermodynamic driving force and the addition is highly stereo- and regiospecific. The pros are high reliability and regio-/stereo-selectivity, and the cons are the less availability of functional dienes.
Other typical click reactions include nucleophilic substitution and ring-opening reactions of strained heterocycles, amidation reactions, thiol-yne reactions, thio-bromo click, and oxime-bond formation (Scheme 2.8). The nucleophilic substitution, especially for reactive benzyl halides, acetyl halides, primary halides, is highly efficient and affords only one single product in most cases. The ring-opening of strained cyclics, such as epoxy groups, possesses spring-loaded reactivity. These reactions and their reaction conditions were common at early days of organic chemistry when purification techniques were so limited that processes with high reliability in giving only one isolable product were highly appreciated. Thiol-yne and oxime bond formations have emerged recently as “click” reactions and hold particular promise for biological applications, since no metal catalyst is required and no by-product are formed.

Of course, there are other reactions that might be viewed to possess features of “click” chemistry under certain conditions, such as acyl chloride-amine amidation, olefin
metathesis, isocyanate-amine reactions, etc. Due to limited space, they cannot be discussed further herein. Despite the many reactions described above, it should be always kept in mind that no reaction so far is ideally perfect and “click” reactivity is only conditional. In other words, it does not “click” all the time. It is necessary to know the limitations and when these reactions do exhibit “click” reactivity, instead of using these reactions indiscriminately. Since the 1,3-dipolar azide-alkyne dipolar cycloaddition is the most popular “click” chemistry so far, the structure-property relationships will be briefly discussed and summarized for this reaction in this section.59,84

Generally speaking, the more electron-deficient the alkyne is, the more activated it is due to the lowered energy level of the alkynes’ lowest unoccupied molecular orbital (LUMO).84 Therefore, the presence of an electron-withdrawing group (such as carbonyl, fluorine, and hydroxyl) near the alkyne functionality can significantly activate the alkyne (Figure 2.2). Despite the high reactivity, carbonyl groups are not always preferred, since they could sometimes compromise the reaction’s orthogonality. For example, being a π-withdrawing group, the carbonyl substitution generates a Michael acceptor, that might be subject to Michael addition under certain conditions. In contrast, being a σ electron-withdrawing group, fluorine is effective in activating the alkyne yet stable and inert, “invisible” in most reactions.

![Figure 2.2. Reactivity of substituted terminal alkynes.](image)
Ring strain is an alternative method to activate the alkyne. Back in 1961, the reaction of cyclooctyne and phenylazide was found to "proceed like an explosion to give a single product."\textsuperscript{85} This was employed by Bertozzi et al.\textsuperscript{62,86,87} in the development of copper-free, \textit{in vivo} biomolecule-labeling reagents. Figure 2.3 shows the structures of the four generations of such alkynes and their relative second-order rate constants. When modified with fluorine to alter the electronics of the alkyne, the cyclooctyne derivatives can have reactivity that is comparable to that of the Cu-catalyzed reactions.\textsuperscript{85} The more fluorine atoms that are adjacent to the alkyne, the more reactive the cyclooctyne is. In the design of the 4\textsuperscript{th} generation, the incorporation of one more sp\textsuperscript{2}-like amide center to dibenzocyclooctynes further increases strain energy and enhances the reaction rate significantly, yet the compound remains stable for benchtop handling.\textsuperscript{88}

![Figure 2.3. Structures of the four generations of cyclooctyne reagents for Cu-free [3+2] cycloaddition with azides. The numbers in parentheses are relative second-order rate constants (M\textsuperscript{-1}·s\textsuperscript{-1}) determined in model reactions with benzyl azide in CD\textsubscript{3}CN.\textsuperscript{62,88}](image)

Specifically, in the CuAAC reaction, the structure-reactivity relationships still follow that of the Huisgen reaction with certain peculiarities, which can be best understood based on the mechanism as shown in Scheme 2.9. From the mechanism, the terminal coordination of the two reactants to Cu(I) is unhindered and independent of substitutions. Therefore, the most significant influence lies in the electronic effects,
Scheme 2.9. Possible mechanism for the CuAAC reaction.\(^{59}\)

which influence the formation of the Cu(I) acetylates and the establishment of the transition state of the reaction. This is the reason why it still follows the structure-reactivity relationships found for Huisgen reactions. However, there are indeed steric and proximity effects in the reaction. When several azide groups are held together in the same molecular scaffold (such as dendrimers, polymers, and calixarenes), significant rate enhancements can be observed; yet it does not always work the other way around (Figure 2.4).\(^{89}\) The reason, from a mechanistic point of view, can be attributed to the environment that the catalytic Cu(I) complex leaving a completed cycle of triazole formation is exposed to.\(^{90}\) A locally high density of azide facilitates the catalyst to participate in the reaction again while a high density of alkyne might saturate the Cu(I) complex by coordination, leading to homocoupling as a significant reaction path. Efforts
to inhibit such side reactions by reducing reaction temperatures are complicated by the reduced “click” reactivity as well.

In contrast to alkynes, the electronic effects do not notably affect the reactivity of azides; they are generally very reactive. Organic azides are more reactive than azide anions. But depending on their structure, they might be susceptible to certain side reactions, such as hydrolysis for acylazides and sulfonylazides, and 1,3-sigmatropic rearrangements for substituted allylic azides.\textsuperscript{59} It should be noted that at elevated temperature, significant amounts of azides will undergo thermal nitrogen extrusion to become nitrenes.\textsuperscript{44} In particular, the molecules with high azide content tend to detonate.
upon heating or mechanical shocks. Special caution should be taken when handling these azides.

Steric effects are also important in determining azide reactivity. Matyjaszewski and coworkers\textsuperscript{92} studied the substituent effects based on structures similar to the end-groups typically present in polymers obtained by ATRP. The fastest reactions were found for those with electron-withdrawing substituents but with less steric hindrance (Figure 2.5).

![Figure 2.5. Reactivity of substituted azides.\textsuperscript{92}](image)

2.2.3 Robustness, Efficiency, and Orthogonality

The most important features about click chemistry can be described as \textit{robust, efficient, and orthogonal}.\textsuperscript{76} This is extremely beneficial to \textit{accelerate} the construction and discovery of new materials to meet the demand of sophisticated functional materials today. Robustness refers to high fidelity of the reaction, which ensures a well-defined product structure under different reaction conditions (solvent, temperature, moisture, oxygen, etc.). Efficiency refers to high atom-economy, which means most, if not all, of the atoms in the starting raw material can be converted into the final desired product.\textsuperscript{93} Orthogonality refers to environment and reactive group independence, leading to protection-group-free, step-economy synthesis.\textsuperscript{94,95} The importance of robustness and efficiency can be understood in terms of reliability and convenience. The significance of
orthogonality of click reactions is attracting more and more attention in the material science community as it can greatly accelerate the synthesis of complex and multifunctional materials, possibly even in a one-pot, multistep fashion.\textsuperscript{96}

\textit{Robustness and Efficiency:} The “click’ chemistry is particularly useful when universal ligation and high efficiency are desired, such as in the synthesis of dendrimers and functional polymers, functionalization of heterogeneous systems, biological molecules, etc.

In 2004, the application of click chemistry in material science made its debut for the synthesis of dendrimers.\textsuperscript{97} Due to the iterative nature of dendrimer synthesis and its sensitivity to defects, it is an ideal vehicle to test the efficiency of ligation. Different click chemistries, such as CuAAC,\textsuperscript{97} thiol-ene,\textsuperscript{76} thiol-yne,\textsuperscript{98} and thio-bromo,\textsuperscript{82} were successfully applied to the synthesis of dendrimers using both divergent and convergent strategies.

Similarly, functional groups on polymers are known for their reduced reactivity due to this intrinsic dilution. Therefore, it is natural for click chemistry to flourish in macromolecular engineering to facilitate access to functional polymers of different architecture, some of which are not possible to construct via traditional methods (Figure 2.6). For example, cyclic polymers are traditionally very difficult to synthesize.\textsuperscript{99} Grayson et al.\textsuperscript{100} has shown that “click” chemistry enables efficient cyclization of $\alpha,\omega$-telechelic polymers at an infinitesimally low concentration created by a slow, continuous addition technique via a syringe pump. Liu et al.\textsuperscript{101} used micellar assembly as a template to direct a selective click reaction to synthesize macrocyclic diblock copolymers in high efficiency. Click chemistry can also be used in polymerization and crosslinking. While
thiol-ene polymers were already well-known, triazole polymers by CuAAC were a more recent finding.\textsuperscript{102} Other examples include the synthesis of macromonomers, multiblock copolymers, etc.\textsuperscript{103} Polymer functionalization can be readily made in this case (for example, with glycols,\textsuperscript{104} peptides,\textsuperscript{105} proteins,\textsuperscript{106} DNA,\textsuperscript{107} and fullerene derivatives\textsuperscript{14}). High functionality can also be assured. This is particularly important in macromolecular science, since separating macromolecules based solely on the difference of one or two functional groups (functionalized vs. unfunctionalized) is often difficult, if not impossible.

![Figure 2.6](image.png)

Figure 2.6. Various functional polymer architectures synthesized from combination of ATRP and CuAAC “click” chemistry.\textsuperscript{66} Reprinted with permission from ref. 66. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

The “unstoppable” universal ligation power of click chemistry is best demonstrated by its ability to link two distinct functional moieties together, regardless of how different they are chemically and physically (Figure 2.7). For example, it has been used to modify or pattern various surfaces, from silica gel,\textsuperscript{108} nanoparticles,\textsuperscript{109} to electrodes\textsuperscript{110} and silicon surfaces.\textsuperscript{111} Hydrogels with different functionalities can be
Figure 2.7. Different functional materials can be conjugated by click chemistry to give multifunctional hybrid materials.

Figure 2.8. Using highly efficient click chemistry to lock in the supramolecular structure. Adapted with permission from ref. 117. Copyright American Chemical Society.
formed by this universal method\textsuperscript{112} and sequentially patterned if orthogonal click reactions are used.\textsuperscript{113} Due to high bio-orthogonality, labeling of biologically-relevant objects, such as cells\textsuperscript{114} and viruses,\textsuperscript{115} has also been demonstrated.

Moreover, it can be also used to functionalize supramolecular assemblies and fix their hierarchal structures at different length scales (Figure 2.8). For example, Stoddart et al.\textsuperscript{116} used CuAAC to fix the rotaxane structures after complexation and achieved high efficiency in the template synthesis of rotaxanes. This concept is particularly useful in the discovery of drug leads. When the precursor components bind to active sites via a preferred organization, they are coupled by click chemistry to create an enzyme inhibitor exhibiting very high affinity to the host.\textsuperscript{65}

\textbf{Orthogonality:}\textsuperscript{117} In chemistry, it remains a grand challenge to precisely control the reactivity of each individual functional group towards a specific reaction within a complex molecule. Traditionally, protective groups and “orthogonal coupling strategy” were developed to address this problem by masking the unwanted reactive sites.\textsuperscript{118} Their intrinsic, strategic drawbacks include increased reaction steps and waste production. These have led to a recent trend to avoid them completely in total synthesis.\textsuperscript{95} The new approach can be carried out by developing reactions with high chemoselectivity and orthogonality. The advent of click chemistry presents a tool box of reactions that are highly specific and orthogonal. These reactions thus allow simultaneous, parallel or cascade reactions occurring in one-pot with little or no cross-functionalization and interference (Figure 2.9). Complex (macro)molecular architectures and diverse functions can be created in such a way that fewer reaction and purification steps are involved, possibly without the use of protective groups.\textsuperscript{96}
Figure 2.9. Orthogonal click reactions allow construction of complex molecular architectures in fewer steps by cascade or simultaneous reactions without the use of protective groups. Reprinted with permission from ref. 67. Copyright American Chemical Society.

For example, Hawker and coworkers have reported an extensive study on the orthogonal approach to multifunctional polymers. The combination of CuAAC with other orthogonal reactions (esterification, amidation, etc.) allows the highly efficient and modular simultaneous/cascade functionalization strategies. A large variety of functional groups have been successfully introduced. Using the orthogonal approach, a triblock copolymer can be created in one-pot from a trifunctional initiator using simultaneous nitroxide-mediated polymerization, ring-opening polymerization, and CuAAC. Similarly, double-click reactions of CuAAC and Diels-Alder afforded a triblock copolymer in a one-pot process. This sequential orthogonal click strategy can also facilitate the synthesis and patterning of three-dimensional cell microenvironments. First, the CuAAC reaction was used to trap cells by the formation of a hydrogel and then, thiol-ene coupling was used to pattern the hydrogel three-dimensionally. The orthogonality between the reactions and between functional groups is very important in making these new materials possible. Furthermore, the bio-orthogonality of these
reactions is critical in dealing with biological systems where a large variety of functional molecules are present (proteins, peptides, DNA, etc.). The recognition and use of orthogonal click chemistry have been expanded to a broad range of applications, and its successful implementation greatly facilitates the development of novel advanced materials and biomaterials.

2.3. Soft Fullerene Materials

“The soft overcomes the hard; and the weak the strong. The softest thing in the world dashes against and overcomes the hardest.”

--- Laozi

2.3.1 Soft Matter

The early days of materials in human history were overwhelmingly occupied by hard materials, from readily available stone and woods, to iron and steel, to resin, and the latest inorganic semiconductors. While our understanding of these “hard” materials is reasonably well advanced, we are only at the early stage of the learning curve of “soft” materials. The concept of soft materials was proposed by Professor P.-G. de Gennes in 1992 to describe the molecular systems giving a large response to small foreign stimuli. The term “soft” originates from macroscopic mechanical properties usually exhibited by these systems. Such systems typically include colloidal particles, amphiphiles, liquid crystals, and polymers. The concept was actually inspired by Nature. In biological systems, the components are able to self-organize into soft assemblies to perform specific functions with high precision and ultra-sensitivity. Their major difference from hard
materials is their ability to self-assemble into functional complexes, as directed by non-
covalent interactions. In addition to these phenomenological descriptions of soft matter, a
clear scientific definition of soft matter must be derived from its structure and dynamics.
Below, Table 2.2 summarizes these scientific descriptions of soft matter. Comparisons
with liquids and solids have also been included.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure</th>
<th>Interaction Energy</th>
<th>Flow</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>Atoms and molecules</td>
<td>Isotropic amorphous</td>
<td>$E \sim k_B T^*$</td>
<td>Newtonian</td>
</tr>
<tr>
<td>Soft Matter</td>
<td>Non-uniform self-assembly</td>
<td>Clusters in multiscales</td>
<td>$E \geq k_B T$</td>
<td>Non-Newtonian</td>
</tr>
<tr>
<td>Solid</td>
<td>Atoms and molecules</td>
<td>Crystals, glasses</td>
<td>$E \gg k_B T (H &gt; S)$</td>
<td>None</td>
</tr>
</tbody>
</table>

$k_B$: Boltzmann constant; $k_B T$: thermal energy at temperature T.

The physical structure and dynamic of soft matter can be understood from their
interaction energy, which is comparable to thermal energy at room temperature and in
between that of liquids and solids. Therefore, there are few perfect long-range positional
and bond/molecular orientational orders as found in a crystalline solid, but they always
exhibit certain combination of long-range and short-range orders in structure. In this
sense, they are fundamentally different from the liquid which possesses a Newtonian
flow behavior. It should be noted that long-range order or short-range order can not be
distinguished based on their size but rather the way their order decays. The biggest
challenge in many technological applications today is to acquire ordered structures with
periodicity on a length scale of 2 - 100 nm. Materials with periodicity on this length
scale often exhibit interesting, unusual physical phenomena; however, they can neither be
constructed by atomic crystals nor formed by crystal engineering via metal and/or ligand complexation. The self-assembled structures from soft materials usually possess periodicities in multidimensions and across many length scales – they are hierarchically ordered structures. For example, phase structures with a 1D translational order are found in lamellar assemblies. Phase structures with a 2D translational order are commonly observed in thermotropic (columnar phases) and lyotropic (hexagonal phases) liquid crystals. Phase structures with a 3D translational order include micellar cubic phases, and bicontinuous cubic phases in block copolymers and colloids. While they are similar to crystalline solids built from atoms and molecules, the building blocks here are supramolecular aggregates held together via physical bonds. The molecules inside these aggregates could be short-range ordered.

The advantages of soft materials are thus evident. First, they facilitate processing to generate material structures with specifically designed long-range and short-range order. The nature of self-assembly provides opportunities to generate materials that are self-healable, viable, and durable. Second, versatile structures with specifically desired order and symmetry possess different “soft” properties, such as modulus, reflectivity, conductivity, etc., and may be suitable for various applications. Third, the phase transitions in these ordered structures can be triggered relatively easily by small foreign stimuli, since these transitions are mostly entropy-driven. This is the basis for today’s modern devices and sensory technologies. It can be imagined that, if functional materials, such as fullerenes, are incorporated into soft materials to capture these advantages, the scope of fullerene functional materials can be greatly extended, while their properties can be tuned and optimized for target applications. So far, although the concept of “soft
“fullerene materials” has not been clearly elucidated, there have already been numerous research activities in the conjugation of fullerene with conventional soft materials, both chemically and physically, to improve the properties of fullerene materials. Yet there have been relatively few studies on how ordered structures can be formed from these fullerene-soft material hybrids. Herein, a brief and critical summary will be provided on the state-of-the-art in this field with focus on “soft fullerene materials” that are able to self-assemble into different ordered structures.

2.3.2 Fullerene Amphiphiles

Amphiphiles refer to molecules with two distinct parts. The most common type of amphiphiles is a surfactant with both hydrophilic and hydrophobic parts; however, it is not the only combination. Other pairs, such as fluorophobic and fluorophilic, can also be regarded as amphiphiles in a broad sense. They can be small molecules as well as polymers, or even nanoparticles. They can be charged (ionic) as well as neutral. The key point is their “Janus” nature -- there is something that unambiguously distinguishes two parts of the molecule which are covalently bonded. The propensity for them to stay away from each other is the driving force for their self-assembly. In this section, the discussion shall be limited to two types of fullerene amphiphiles: (1) fullerene as hydrophobic part and a chemical addend as hydrophilic part; (2) fullerene-lipid conjugates because they have different interactions with solvents.

Fullerenes are known to be very hydrophobic and entirely insoluble in water; however, their solubility in water is very important for their biomedical applications, such as in phototherapy using their high reactivity against toxic, reactive oxygen species and in
gene delivery as a vector.\textsuperscript{126} To explore their bio-applications, fullerenes have been chemically modified with hydrophilic groups (both ionic and nonionic) to make fullerene amphiphiles, and their molecular assembly behavior in water has been studied. The first well-defined, water-soluble organo-functionalized C\textsubscript{60} (compound 5 in Figure 2.10) was reported in 1993.\textsuperscript{127} Numerous water-soluble fullerenes have been synthesized since then. Meanwhile, fullerene lipid conjugates have also been developed as a class of fullerene amphiphile to explore their structure formation and interaction with lipids. Figure 2.10 provides a snapshot of typical fullerene amphiphile structures.

Despite the huge number of water-soluble fullerene derivatives synthesized, the true nature of solubilization of C\textsubscript{60} derivatives in water has remained a question for many years – “are they truly molecularly dissolved?” It was later found that most of them actually form supramolecular aggregates of various morphologies and structures of different order and symmetry, including nanoparticles, fibrous rods (nanowires), bilayer-based membranes or disks, vesicles, and globules, some of which were not found in conventional surfactants and lipids. Figure 2.11 shows a cartoon of various structures from these supramolecular aggregates.

Ever since the discovery of fullerene, the molecular layers of such spherical molecules have been of great interest; yet in the early attempts, the strong aggregation force among themselves led to unsatisfactory results (e.g., multilayer formation and the instability of the formed films). Amphiphiles are characterized by their ability to assemble at interfaces to form ordered structures and thus are very promising in the fabrication of fullerene monolayers. Amphiphile 5 (Figure 2.10) was found to form uniform L-B films at the air-water interface, which contained much fewer defects.
Figure 2.10. Chemical structures of typical fullerene amphiphiles. See text for references.
Figure 2.11. Cartoons of typical arrangements of fullerene amphiphiles in different supramolecular assemblies. (a) Reprinted with permission from ref. 128. Copyright American Chemical Society; (b) Reprinted with permission from ref. 129. Copyright the American Association for the Advancement of Science; (c) Adapted from ref. 125; (d) Reprinted with permission from ref. 134. Copyright Wiley-VCH Verlag GmBH & Co. KGaA; (e) Reprinted with permission from ref. 132. Copyright Wiley-VCH Verlag GmBH & Co. KGaA; (f) Adapted from ref. 125.

compared to those obtained from unmodified \( C_{60} \).\(^{128}\) The structure of the membranes has been proposed, as shown in Figure 2.11a. Similarly, 7 (Figure 2.10) can also form an L-B film. The symmetry of six carboxylates in all-equatorial arrangements promotes a
well-ordered hexagonal pattern of fullerenes, which further assembles into rods within the monolayer.125

Surprisingly, as an organic potassium salt, amphiphile 6 (Figure 2.10) can dissolve in water while retaining its ionic feature (in other words, not protonated). Even at very low concentration, it forms (or dissolves as) uniform spherical aggregates with definite size of ~ 34 nm as shown in Figure 2.11b, a rigid morphology entirely unconventional in vesicles.129

When dispersed in water, fullerene amphiphiles form either spherical aggregates (nanoparticles) if short ionic group are linked (e.g., 8 as shown in Figures 2.10 and 2.11f); or nanofibers/nanorods and disk-like morphologies if a longer ionic group is present (e.g., 9 as shown in Figures 2.10 and 2.11c).125 When the linkage is too short, the solubility in water is quite limited, and it exhibits complex aggregation behavior. For example, amphiphile 10 (Figure 2.10) forms nanorods in DMSO/H2O/benzene mixed solvent and vesicles in water after sonication.130

Being a conjugate of lipid and fullerene, lipofullerene 11 (Figure 2.10) can be regarded as an amphiphile in terms of their different intermolecular interactions. It was found to form multibilayer membrane films that possess main and subphase transitions with regulated electronic properties.131 Another lipofullerene 12 (Figure 2.10) can be incorporated into lipid bilayers and serve as a membrane anchor to load bio-functionalities, such as biotin, to the lipid membrane (Figure 2.11e).132

Amphiphile 13 (Figure 2.10), a Newkome-type-G2-dendron-modified C60, is known to have the highest water-solubility (254 mg/mL at pH = 10) reported to date for fullerene derivatives.126 It was further modified to give an artificial lipid (e.g., 14 in
Figure 2.10), which possesses a more balanced structure with the hydrophobic part and the hydrophilic part occupying similar spaces. This structure is in sharp contrast to the conical overall shape of fullerene derivatives, such as amphiphile 13. In this case, lipofullerene 14 readily forms bilayered liposomes (“buckysomes”) of dimensions between 50 and 400 nm.133

Due to their steric hindrance and conformational rigidity, some fullerene amphiphiles show distinct internal structures, which is completely different from the conventional dynamic, loose, and uneven micellar aggregates. They are thus referred to as “shape-persistent micelles.”126 An example is the [3:3]-hexakis adduct 15 (Figure 2.10) that forms uniform spherical objects with a diameter of about 5 nm during aggregation. Without cryo-fixation, the morphology can be clearly seen and the 3D reconstruction revealed a well-defined, spherical, compact, six-molecule aggregate with an unambiguous structure (Figure 2.11d).134

It should be pointed out that although the cartoons can be easily drawn as shown in Figure 2.11, few studies have provided solid evidence to prove the structures. Most of the studies were only morphological investigations, which was insufficient to relate the properties with the molecular packing in solid state. The study of “shape-persistent micelles” is an exception with clearly elucidated structure and truly exemplifies the uniqueness of the 3D nature of C_{60} building blocks.126 Although a significant amount of work has been done in the area, there is still room left for future investigation. A few points of particular interest will be: (1) how to truly take advantage of the unique 3D structure of C_{60} as a structural scaffold; and (2) how to truly utilize the unusual C_{60}
properties by manipulating amphiphilic interactions to afford well-defined, organized structures with desired properties.

2.3.3 Fullerene Liquid Crystals\textsuperscript{135,136}

As the fourth state of matter, liquid crystals are known to be a phase with a degree of order between the molecular short-range order of a liquid and the regular structure of long-range order in a crystal. All of liquid crystals have long-range molecular orientational order, which requires anisotropy in their molecular structures. Such structures are called mesogens, since they will lead to mesomorphic behavior. Typical mesogens are rod-like, disc-like, and banana-shaped molecules. The shape of C\textsubscript{60} is spherical and thus, it is isotropic. To introduce molecular anisotropy (either structurally or conformationally) and create fullerene liquid crystals, there are mainly two approaches: (1) by coupling fullerene to the mesogens and (2) by making fullerene part of the mesogens.

In the first approach, liquid crystalline mesophases could only be generated if a delicate balance between the mesogen-mesogen, mesogen-C\textsubscript{60}, and C\textsubscript{60}-C\textsubscript{60} interactions can be achieved. Mesogen-mesogen interactions are \(\sim 5\text{-}40\text{ kJ/mol}\),\textsuperscript{137} which is comparable to or smaller than C\textsubscript{60}-C\textsubscript{60} interactions of \(\sim 30\text{ kJ/mol}\).\textsuperscript{138} The first reported thermotropic fullerene liquid crystal was obtained by conjugating two cholesterol mesogens to C\textsubscript{60},\textsuperscript{139} it exhibited a smectic A phase. The stability of the mesophase is significantly reduced by the introduction of C\textsubscript{60} as compared to its precursor compound. It could be attributed to the strong C\textsubscript{60}-C\textsubscript{60} interaction that disturbs the mesogen-mesogen interaction. In addition, the special spherical feature of C\textsubscript{60} is incommensurate within the
bulk liquid crystal. Thus, although a thermotropic liquid crystalline behavior was observed, no ordered supramolecular fullerene organization was found. To ensure the formation and stabilization of mesophases, mesogen-mesogen interaction should be able to override the $C_{60}$-$C_{60}$ interaction. This can be achieved either by increasing the number of mesogens in the designed molecules or using mesomorphic mesogens with stronger interactions.

It was soon proposed to utilize dendrimers as a scaffold to counterbalance the influence of the spherical shape of $C_{60}$ and to allow more strongly mesomorphic mesogens to be attached.\textsuperscript{135} This approach keeps the integrity of the conjugated system on $C_{60}$ and thus keeps most of its electronic properties intact. The effect was found to be profound. The results have been well reviewed recently by Deschenaux et al.\textsuperscript{136} Examples of compounds and some unique supramolecular organizations from them are shown in Figure 2.12. Both columnar and smectic phases have been obtained from these materials. Ordered arrangements of fullerenes in these supramolecular organizations have also been proposed. Moreover, it also allows the incorporation of functional moieties, such as ferrocene, oligo($p$-phenylvinylene), and tetrathiafulvalene units, to prepare multifunctional liquid crystalline materials for diverse applications.\textsuperscript{136} It is thus a versatile platform for fullerene liquid crystals.

Another approach to introduce many mesogens to $C_{60}$ is by multiple-addition to the $C_{60}$ core. In this way, the electronic properties of fullerene might be sacrificed and $C_{60}$ might only serve as a structural scaffold. Interestingly, this can create materials with structures that are isotropic at first glance but also lead to mesophase behavior, such as in the case of 21 (Figure 2.13).\textsuperscript{140} The supramolecular organization has been proposed to
Figure 2.12. Typical molecular structures and supramolecular organizations of liquid crystalline fullerodendrimers and fullero(codendrimers). Adapted and reprinted from ref. 136. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reprinted with permission.
result from the packing of stretched, cylinder-like structures rather than spherical structures, as the molecule seems to be. It provides an opportunity to construct strong liquid crystals from relatively weak-interacting mesogens, or even non-mesomorphic units. Indeed, when a benzoate derivative 22 (Figure 2.13), itself not mesomorphic, is used instead of cyanobiphenol in 21, the hexa-adduct 23 gives an unusual nematic phase for a fullerene liquid crystal. The supramolecular organization is also shown in Figure 2.13, indicating an additional ordering within the nematic phase.
The use of strongly interacting mesogens to induce a fullerene liquid crystal phase behavior can be exemplified by the formation of a columnar phase from a mixture of 24 and 25 in Figure 2.14.\textsuperscript{11} The columnar mesophases formed from the complexation between triphenylene and dipyrazino[2,3-f:2′3′-h]quinoxalene are known to be robust and stable. As a result, they are able to accommodate bulky side-chain substituents within the alkyl chain continuum between the columns. In the case, 24 is a triphenylene derivative modified with C\textsubscript{60} at the side chain via a long flexible spacer to decouple the triphenylene and C\textsubscript{60}. The complexation between 24 and 25 dominates the mesophase formation to give rise to a hexagonal columnar phase with C\textsubscript{60} attached and wrapped around the columns to form a 2D superlattice. The overall order is a combined result of the C\textsubscript{60}-C\textsubscript{60} interaction, the columnar packing, and the spacer between C\textsubscript{60} and the discotic mesogens.

Figure 2.14. The complexation between 24 and 25 forms a columnar phase with alternating stacking structure wrapped by C\textsubscript{60}. The C\textsubscript{60}s tethered to and wrapped around the column form a 2D superlattice templated by the hexagonal lattice of the columnar structure.\textsuperscript{11} Adapted from ref. 11. Reprinted by permission of The Royal Society of Chemistry.

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In addition to the mesogen-mesogen interactions, hydrophobic and hydrophilic effects can also be utilized to aid in the mesophase formation. Recently, Aida et al.\textsuperscript{12} reported a rational strategy in the design of fullerene liquid crystals with tailored bicontinuous electron donor and acceptor arrays for use in organic photovoltaics (Figure 2.15). The oligothiophene segment serves as the main mesogen and light-harvesting moiety. C\textsubscript{60} is attached in a relatively rigid way onto one end of the rod-like mesogen. The two sides are then connected with long alkyl chains and oligo(ethylene glycol)\textsubscript{s}, respectively, which induces the phase separation to form a bilayered smectic A phase over a wide temperature range. The C\textsubscript{60}s were found to form channels located at the interface of two different phases. Such structure not only prohibits donar-acceptor interactions leading to the trapping of charge carriers but also guarantees a long-range continuous conducting pathway in the material. Indeed, it has been found to significantly enhance the photovoltaic effect. Yet the authors did not address how the C\textsubscript{60}s arrange themselves at the interface. This is an interesting question since the spherical C\textsubscript{60} unit is usually incommensurate with other components in the molecule.

Figure 2.15. An amphiphilic fullerene liquid crystal that leads to bicontinuous electron donor and acceptor arrays (I), as compared to its nonamphiphilic reference molecule (II).\textsuperscript{12} Reprinted from ref. 12 by permission of the American Chemical Society.
Non-covalent, complexation-induced fullerene liquid crystals can be viewed as a special class of using strong interacting mesogens to induce fullerene mesophase formation. Although the binding between the mesogens and C$_{60}$ is relatively weak physical interactions, their complementary shape and chemistry could enable efficient molecular recognition and strong binding events. To the best of our knowledge, there is only one report so far using host-guest recognition to incorporate C$_{60}$ into the liquid crystal.$^{142}$ The authors used a room temperature nematic cyclotrimeratrylene derivative to complex with C$_{60}$ in 2:1 stoichiometry to form 26, as shown in Figure 2.16. The C$_{60}$ is now shielded completely from the environment. As a result, the C$_{60}$-C$_{60}$ interactions are reduced to a minimum, while the electronic properties of a single C$_{60}$ molecule are fully retained. The complex 26 shows a room temperature nematic phase. Above 70 °C, it transforms into a cubic phase of $I4_132$ symmetry. Although the complex’s thermal stability is limited, the non-covalent binding represents an interesting approach in fullerene liquid crystals.

![Figure 2.16. Structure of a fullerene-containing supramolecular complex exhibiting a nematic mesophase.$^{142}$](image)
The second approach (i.e., to induce mesophase formation by making fullerene part of the mesogens) is more delicate and not so obvious at first. Since it takes advantage of the $\text{C}_{60}\text{-C}_{60}$ interaction to form liquid crystals, rather than counter-balancing it with other mesogenic interactions, this approach does provide an easier access to fullerene liquid crystals and can give enhanced supramolecular organizations than those from the first approach. From the literature, it seems that a rigid linkage between $\text{C}_{60}$ and mesogen is effective in making $\text{C}_{60}$ mesogenic to direct the mesophase formation.

The very first example is conical shuttlecock molecules with a fullerene apex obtained from a highly efficient five-fold addition reaction (Figure 2.17) reported by Nakamura et al.\textsuperscript{143} Such molecules have very high molecular anisotropy. When there is a small substituent in the shuttle-cock, such as hydrogen, and the molecular shape fits, the molecules can stack together in a line to maximize the $\text{C}_{60}\text{-C}_{60}$ interaction to form a polar columnar phase with the $\text{C}_{60}$ units lined up in a column. A slight modification in the structure changes the phase structure completely. The introduction of a methyl group instead of hydrogen prevents the $\text{C}_{60}\text{-C}_{60}$ interaction in this direction. As a result, they can not stack to form a column but form smectic liquid crystals with an ordered fullerene bilayer structure.\textsuperscript{144}

A simple and elegant example was presented by Nakanishi et al.\textsuperscript{145,146} in the development of a series of compounds possessing a rigid phenylene linkage between $\text{C}_{60}$ and long aliphatic chains. Using this class of compounds, the authors have successfully achieved hierarchical organizations of $\text{C}_{60}$s for the first time (Figure 2.18). Changing solvent polarity induced the formation of a variety of hierarchical supramolecular nano-objects, from discs, fibers, tapes, discs, and vesicles, to membranes, windmills, conical-
Figure 2.17. Shuttlecock-like molecules with C$_{60}$ as the apex leading to polar columnar structures or lamellar structures.$^{143,144}$ Adapted from ref. 143 and 144. Reprinted by permission of the Nature Publishing Group and the American Chemical Society, respectively.

Figure 2.18. The fullerene liquid crystal developed by Nakanashi et al.$^{145,146}$ and the self-assembled hierarchical structures from lamellar disc to flower-shape object. Reprinted with permission from ref. 145. Copyright Wiley-VCH Verlag GmBH & Co. KGaA.
and flower-shaped objects. Moreover, it has been found that these compounds can self-assemble into perfectly straight nanowires via epitaxial assembly of the alkyl chains on graphite. When the length and position of alkyl groups are tuned, it can also give a long-range-ordered lamellar structure of C_{60}s.

From the discussion above, one can see that liquid crystals possessing fullerene are very versatile in creating various ordered structures. The interactions need to be carefully balanced in order to achieve mesophases with ordered fullerene arrangements. Strong interactions can possibly template the formation of ordered C_{60} structures. On the other hand, making fullerene mesogens is an effective way to achieve ordered fullerene arrangements in mesophases, yet only a few examples in this direction have been reported. Future development in the area could be focused on multifunctional fullerene liquid crystals with desired hierarchical structures to exhibit specific macroscopic function. A relationship between the hierarchical structures and the macroscopic properties should be the focal point in this research.

2.3.4 Bucky Liquids and Gels

Fullerenes, such as C_{60} and carbon nanotubes, are very useful electronic materials. But they are difficult to process due to their low solubility in most solvents and low vapor pressures for vapor deposition manipulation. To reduce the cost of device fabrication, it would be ideal to make them soft. One of the options is to make bucky liquids and bucky gels. This have been achieved by both physical and chemical means. The first room temperature fullerene liquid was obtained by modifying C_{60} chemically with twelve long alkyl chains. Nakanishi and coworkers has shown that 30 (Figure
2.19) exhibits a fluid phase at room temperature and studied the rheological, electrochemical, and charge carrier transport properties of these liquid fullerenes. Aida et al.\textsuperscript{152} have demonstrated an elegant “mix and grind” method to create highly electroconductive “buckyl gels” from carbon nanotubes and ionic liquids (Figure 2.19). It was speculated that the ionic liquid intercalated in between the carbon nanotube bundles and efficiently dispersed them in a physical way.\textsuperscript{153} The bucky gel, thus obtained, could be readily processed into devices, such as actuators. Although the main idea is simply to break the strong intermolecular $\pi-\pi$ interactions, the literature results are, so far, scarce. Therefore, there is plenty of room left for development in this direction.

![Figure 2.19: Structures and formation of liquid fullerenes.\textsuperscript{150,151,152,153} Adapted from ref. 150, 151, 152, and 153. Reprinted with permission by Wiley-VCH Verlag GmBH & Co. KGaA and the American Chemical Society.](image-url)
2.3.5 Fullerene Polymers\textsuperscript{10,136}

With the ubiquitous nature of polymers in our age, it is not surprising that the first paper combining C\textsubscript{60} with a polymer came out as early as a few months after fullerene’s mass availability.\textsuperscript{154} The development of fullerene polymers has thrived over the past two decades, and there is a monograph published very recently with a comprehensive summary of the state-of-the-art in this field.\textsuperscript{136} Fullerene polymers are not only useful, but also aesthetically beautiful. It is an art of nano-jewelry. People have synthesized numerous fullerene polymers with almost as many structures as one could image. An overview is given in Figure 2.20. It includes all-C\textsubscript{60} polymers, organometallic polymers, C\textsubscript{60}-end-capped polymers, dendrimers, star-shaped polymers, main-chain or side-chain C\textsubscript{60}-containing polymers, double-cable polymers, and supramolecular polymers. Among all these structures, fullerene polymers that lead to an ordered arrangement of C\textsubscript{60} after self-assembly will be the focus of our discussion.

In the literature, there are basically three ways to create ordered structures of C\textsubscript{60} via the self-assembly of polymers: (1) through the secondary structure of a polymer, such as attaching C\textsubscript{60} to helical polymers to form a helical array of C\textsubscript{60}; (2) via phase separation in the bulk or thin film to control spatial location of C\textsubscript{60}; and (3) using micellization in selective solvents to obtain micelles of various morphologies. Despite of the large number of polymers synthesized, there are relatively few reports on utilizing them to template the ordered arrangements of C\textsubscript{60}. The reason is probably two-fold: (1) polymers are intrinsically more difficult to form ordered structures, especially when the system is further complicated by the strong interactions and the bulkiness of C\textsubscript{60}; and (2) it is relatively difficult to solve and elucidate the structure in polymers. Moreover, the
situation is further complicated by the lack of pure, well-defined fullerene polymers. Nevertheless, the current work in this direction does reveal some exciting results along this research direction.

By attaching fullerene to a helical polymer (covalently or non-covalently), the helical chain conformation can lead to the formation of fullerene helical arrays. Figure 2.21 shows three types of helical fullerene polymers, one with pendant covalently linked fullerene, one with pendant non-covalently linked fullerene, and one with encapsulated fullerene. Typical chemical structures (31, 32, 33) are also shown. Hierarchical structures can be assembled from these helical fullerene polymers. For example, 31 was found to form small particles with an average diameter of about 15-30 nm. These particles then aggregate into larger particles with an average diameter of about 100-200 nm (Figure 2.22).
Figure 2.21. Helical polymers with (a) pendant, covalently linked C_{60}s, (b) pendant, non-
covalently linked C_{60}s, and (c) encapsulated C_{60}s.\textsuperscript{136} Adapted and reprinted from ref. 136.
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Figure 2.22. Hierarchical aggregation observed for 31.\textsuperscript{136,155} Adapted and reprinted from ref. 136. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reprinted with permission.
Diblock copolymers are known to form a variety of ordered structures, such as spheres, cylinders, as well as bicontinuous and lamellar structures.\textsuperscript{158} If C\textsubscript{60} is confined to one of the blocks, either chemically or physically, and assuming phase separation of the two blocks still dominates, it should give self-assembled structures with C\textsubscript{60} content richer in one phase. In this way, the 3D spatial arrangement of C\textsubscript{60} can be controlled. For example, polystyrene-\textit{b}-polyisoprene diblock copolymers were grafted onto the C\textsubscript{60} core to form a well-defined, six-arm copolymer star.\textsuperscript{159} The star polymers can self-assemble in the bulk to form the phase-separated structures as described in the literature.\textsuperscript{144} Since C\textsubscript{60}s are located at the center of each star with the environment predominantly being polystyrene, it stays in the polystyrene phase as a central “thread,” as shown in Figure 2.23. Although the spatial arrangement of fullerene can be controlled in this case, the loading of C\textsubscript{60} is low and the electronic properties of C\textsubscript{60} are sacrificed, since multi-addition has taken place on fullerene. The resulting ordered structure hardly possesses any functional properties characteristic of C\textsubscript{60}.

Figure 2.23. The organization of fullerene cores of block copolymer star (a) in the final assembled morphologies: (b) lamellar, (c) cylindrical, and (d) bicontinuous morphologies.\textsuperscript{159} Adapted and reprinted from ref. 159 by permission of Elsevier.
Micellization represents another interesting scheme to achieve ordered structures. Owing to their different interaction with solvents, amphiphilic block copolymers can self-assemble into various micellar morphologies. In fullerene polymers, C\textsubscript{60}-end-capped polymers (such as acrylates and methacrylates) have been widely studied in this respect. The results have been comprehensively documented in a recent review. From the viewpoint of using polymers as the structural templates to control C\textsubscript{60} arrangements in the formation of micelles, two literature results are well worth discussion here.

In 2006, Yashima et al. reported an aggregation-fractionation method to prepare well-defined, C\textsubscript{60}-end-capped stereoregular polymers with high purity, namely, \textit{it}-PMMA-C\textsubscript{60} and \textit{st}-PMMA-C\textsubscript{60}. These well-defined polymers were used for subsequent physical studies. It was found that uniform spherical micelles were formed when the two polymers were mixed simultaneously in H\textsubscript{2}O/CH\textsubscript{3}CN (9:1, v/v), in which the stereocomplexation took place at once (Figure 2.24). When the two polymers were used first separately in H\textsubscript{2}O/CH\textsubscript{3}CN (1/9, v/v) to form aggregates with core-shell structures and then mixed for further aggregation, nano-networks were obtained.

Shinkai and coworkers mixed the diblock copolymer \textbf{34} and the C\textsubscript{60} carboxylic acid \textbf{35} to prepare a supramolecular diblock copolymer, since \textbf{35} can bind to pyridine moieties of \textbf{34} via hydrogen bonding (Figure 2.25). The binding event makes the pyridine block rigid and become rod-like with low solubility, while the PS blocks remain highly soluble. This drives the phase separation and self-assembly to form globular aggregates with diameters of \textasciitilde 20-25 nm.

An interesting class of fullerene polymers is the double-cable polymers where the main chain of the polymer consists of \textit{p}-type organic conjugated polymers and the side
Figure 2.24. The formation of core-shell nanospheres and nanonetworks based on \textit{it}- and \textit{st}-PMMA-C\textsubscript{60} through their stereocomplex formation and interaction with the terminal C\textsubscript{60}.\textsuperscript{162} Adapted from ref. 163 and reprinted by permission of the American Chemical Society.

Figure 2.25. Supramolecular binding of fullerene derivative 35 to the poly(vinylpyridine) block of 34 and the resultant micellar formation in solution.\textsuperscript{163} Adapted from ref. 163. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reprinted with permission.

Chains consist of \textit{n}-type organic semiconductors, such as C\textsubscript{60} (Figure 2.26).\textsuperscript{136} It was initially proposed for application in solar cells. In bulk hetero-junction organic photovoltaics, the active layer contains conjugated materials (donor) with delocalized electron systems, which can absorb sunlight and donate electron to an acceptor to create photoinduced charge carriers. The charges can then be transported to the electrode to
generate current. Fullerenes and their derivatives have been widely used as acceptors due to their very high electron affinity and ability to effectively transport charge. It was anticipated that the use of double-cable polymers could improve the solubility and processibility of fullerenes, while the polymers could undergo nano-phase separation into bicontinuous structures with large donor-acceptor interfaces for efficient charge generation and transportation in separated channels.\textsuperscript{164} However, although numerous double-cable polymers have been prepared and enhanced photo-induced charge separation has been indeed reported, their performance in devices did not live up to the expectations.\textsuperscript{165} The problem probably lies in the lack of control in their synthesis and the packing structures in the solid state, which leaves room for future improvement. A double-cable polymer that is able to self-assemble into a bicontinuous phase is highly desired.

![Figure 2.26. A double cable polymer and its working mechanism. A bicontinuous phase of fullerene is desired for electron transport.\textsuperscript{164} Reprinted from ref. 164 by permission of the Nature Publishing group.](image-url)
2.3.6 Perspectives

The work in combining soft materials with fullerene has progressed significantly over the past two decades. It is an integrated, versatile approach to achieve various ordered arrangements of fullerenes using both chemical and physical methods. In designing these soft fullerene materials, certain special features about fullerenes (C\textsubscript{60} in particular) need to be taken into consideration: (1) fullerenes are highly hydrophobic; (2) fullerenes have unique impenetrable 3D structures with C\textsubscript{60} being spherical and isotropic; (3) fullerenes are prone to irregular self-aggregation; and (4) fullerenes are conformationally very different from other molecular moieties, such as alkyl chains, and thus incompatible and incommensurate with most functional materials. These aspects have to be considered and balanced delicately for a successful design of soft fullerene materials with desired properties.

While there has been significant amount of work on fullerene amphiphiles and liquid crystals, there is much less work on using polymer self-assembly to achieve ordered structure of fullerene. The fact that fullerene polymer research revealed less ordered structures is, in my personal view, due to lack of control in synthesizing pure, homogeneous polymers with well-defined structures. Despite the diverse routes to functionalize fullerenes, only a few of them are highly efficient and specific.\textsuperscript{166,167} Most of the functionalization reactions will give a mixture of C\textsubscript{60}, monoadduct, and multiadducts. The situation is further complicated in polymers where purification based on a difference of functional group is usually difficult. Moreover, the reduced chain end reactivity in polymers might sometimes require drastic reaction conditions (high temperature, long time, etc.), which could lead to potential polymer degradation.\textsuperscript{168} In
addition, some derivatives are unstable either by themselves (e.g., retro D-A reaction) or with singlet oxygen generated by [60]fullerene (e.g., azafulleroid). All of these, and numerous other issues, can complicate the study of the physics of fullerene polymers. Therefore, in order to manipulate fullerenes into ordered structures using polymer self-assembly, a reliable and efficient strategy to create stable, well-defined fullerene polymers under very mild reaction conditions will be necessary.

Supramolecular engineering is then the next step to physically manipulate the self-assembly of fullerene polymers. Based on the strength and operating distance of the physical interactions, the supramolecular structures at multiple dimensions and across different length scales can be controlled and tailored. In this way, our understanding on supramolecular chemistry can be integrated with fullerene to create advanced, intelligent, responsive, and durable fullerene materials to accomplish certain functions, such as mimicking the photosynthetic processes in biological systems. Although fullerenes have been well-recognized as a unique 3D building block in chemistry with applications in many different fields, it is still far from satisfying the expectations for their outstanding properties based on their initial discovery. Supramolecular “soft engineering” of fullerenes into soft fullerene materials represents an important direction in the development of fullerene-based advanced materials.
CHAPTER III
EXPERIMENTAL

The development of materials is highly interdisciplinary. To achieve a better understanding of structure-property relationships, precise control over the molecular structure is essential. As will be described in the following chapters, a “click” chemistry approach has been developed for the synthesis of soft fullerene materials, in particular, fullerene polymers. In this Chapter, the synthetic procedures for the preparation of these compounds and the methods for self-assembling them into supramolecular aggregates are presented.

3.1 Inert Atmosphere Techniques

To meet the stringent requirements involved in organic synthesis, especially in the handling of highly reactive organometallic compounds and other air- and moisture-sensitive materials, three inert atmosphere techniques were used in our laboratory: the high vacuum line, the Schlenk line, and the glove box.

3.1.1 High Vacuum Line Techniques\textsuperscript{169,170}

The high vacuum line was originally developed to meet the extremely stringent requirements to exclude traces of oxygen and moisture from the system to allow safe-
handling of highly reactive organolithiums and to achieve precise control in anionic polymerization. A typical set-up for a high vacuum line is shown in Figure 3.1.

![Diagram of a high vacuum line](image)

**Figure 3.1.** Typical set-up of a high vacuum line for anionic polymerization. Image courtesy of Ms. Camilla Garces.

It was built from Pyrex® glass tubing with Teflon Rotoflo® stopcocks. With the aid of an oil diffusion pump, a vacuum as low as $\sim 10^{-3}$ torr could be achieved. The quality of the vacuum was be tested by a Tesla coil. If vacuum was lower than $\sim 10^{-3}$ torr, the Tesla coil would be quiet when placed close to the line surface. Otherwise, it would create purple-colored electrical discharges with noise. When manipulating chemicals on the line, they were cooled to -78 °C and pumped to remove trace amounts of air. The solvents were transferred under vacuum into ampoules, which are subsequently flame-sealed off the line using a hand torch. The ampoules were then connected to reactors by glass-blowing techniques. The addition of chemicals under vacuum was achieved by
breaking the break-seal in the ampoule with magnetic hammer. High purity, extra dry nitrogen gas was used and connected to the system through an oil bubbler.

3.1.2 Schlenk Line Techniques

Without the need for glass-blowing, Schlenk techniques are commonly used for handling air/moisture sensitive compounds under conditions less stringent than anionic polymerization. A typical Schlenk line (Figure 3.2) was built from Pyrex® glass and consisted of a glass manifold containing two-way taps (one for vacuum and one for inert gases). A catalyst tower (Alumina and Deoxo® catalysts) was installed between the line and the argon cylinder to remove adventitious water and oxygen. At the end of the line, a pressure release, oil bubbler was attached to monitor the pressure in the inert gas line. The chemicals were usually handled with gas-tight syringes and with degassed solvents.

Figure 3.2. Typical construction of a Schlenk line.
3.1.3 Dry-box Techniques

An inert atmosphere glove box, or “dry box” (Vacuum Atmospheres Co., HE-43-2 Dri-Lab Model in our laboratory), is ideal for the manipulation of air/water-sensitive materials. With an optimal oxygen level of less than 5 ppm, it is very convenient for operations such as recrystallization, titration of initiators, filtration, etc., since this is a completely enclosed, spacious, inert chamber. The dry box was equipped with a continuous recirculation system consisting of three sequential glass catalyst columns to remove water and solvent residue as well as oxygen. To ensure a desired low level of moisture and oxygen, the atmosphere was tested with sodium and a liquid indicator solution [bis(cyclopentadienyl)titanium dichloride with excess zinc dust in benzene], respectively. In the presence of moisture, the shiny surface of sodium would dim. In the presence of oxygen, the indicator color changed from green through yellow to orange. During experiments, all of the air-sensitive compounds were weighed, mixed, or placed in an ampoule in the glove box with an argon gas atmosphere. All the glassware and chemicals were pre-dried completely in an oven before being taken into the dry box.

3.2 Chemicals and Solvents

Most of the chemicals were purchased with high purity and used as received. When necessary, reagents were purified to eliminate or reduce potential side reactions. The requirements for purification depended on the tolerance of the reaction.
3.2.1 Chemicals Used as Received

The following chemicals are used as received: [60] Fullerene (C₆₀, MTR Ltd., 99.5%), ethyl 2-bromo-isobutyrate (EBiB, Aldrich, 98%), \(N,N',N'',N''\prime\)-pentamethyldiethylentriamine (PMDETA, Aldrich, 99%), propiolic acid (Alfa Aesar, 98%), ethynylmagnesium chloride solution (Aldrich, 0.5 M in THF), \(N,N'\)-dicyclohexyldicarbodiimide (DCC, Aldrich, 99%), \(N,N'\)-diisopropylcarbodiimide (DIPC, Aldrich, 99%), 4-(dimethylamino)pyridine (DMAP, Aldrich, ReagentPlus®, 99%), potassium tert-butoxide (\(\text{tBuOK, Aldrich, sublimed grade, 99.99\% trace metals basis}\)), \(\alpha\)-bromo-isobutyryl bromide (Aldrich, 98%), bis(2-methoxyethyl)aminosulfur trifluoride (Aldrich, Deoxo-Fluor®), malonyl dichloride (Acros, 97%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Acros, 98%), carbon disulfide (CS₂, Aldrich, ACS reagent, > 99.9%), tetrabromomethane (CBr₄, Aldrich, ReagentPlus®, 99%), 4-pentynoic acid (Aldrich, 95%), propargyl alcohol (Aldrich, 99%), \(p\)-toluenesulfonic acid monohydrate (\(p\text{TsOH, Aldrich, ACS reagent, > 98.5\%}\)), sodium azide (\(\text{NaN}_3, \text{Aldrich, ReagentPlus®, > 99.5\%}\)), epichlorohydrin (Acros, 99%), bromoacetyl bromide (Aldrich, 98%), \(N,N'\)-dimethylformamide (DMF, Aldrich 99.9%), methanol (MeOH, Fisher Scientific, reagent grade), CDCl₃ (Aldrich 99.8 atom % D), dibutylmagnesium (FMC Lithium Division, 17 wt% in heptane), monomethyl monopotassium malonate (Acros, 98%), propargyl bromide solution (Aldrich, 80% in toluene), chlorotrimethylsilane (Acros, 98%).
3.2.2 Purification\textsuperscript{169,170,174}

Most purification was associated with removing oxygen or moisture or other additives/impurities. The purification methods mainly include recrystallization, sublimation, and distillation. In the case of anionic polymerizations, it was crucial to remove all moisture and oxygen from the reaction system.

3.2.2.1 Cuprous Bromide (CuBr, Aldrich, 98%)

It was freshly purified by stirring in acetic acid overnight, washed with acetone, and dried in vacuum.

3.2.2.2 Ethylene Oxide (EO, Aldrich, > 99.5%)

Ethylene oxide was transferred through the high vacuum line to an evacuated flask cooled to -78 °C and containing freshly-ground calcium hydride (Acros Organics, 93%, 0-20 mm grain size). It was stirred and degassed periodically over a period of 4 h. It was then transferred through the vacuum line to another flask containing neat dibutylmagnesium and a small amount of 1,10-phenanthroline (Aldrich, > 99%) as the indicator. The mixture became purple if the oxygen and moisture have been completely excluded. It was further stirred for 30 min at -78 °C before being transferred into a calibrated ampoule, diluted with an equal amount of THF, and flame-sealed off from the vacuum line.
3.2.2.3 Triethylamine (TEA, Aldrich, 99%)

Triethylamine was purified by redistillation under nitrogen after being stirred with freshly ground calcium hydride for 12 h. It was then stored over activated 4 Å molecular sieves under argon.

3.2.2.4 Styrene (Aldrich, 99%)

For ATRP and RAFT, styrene was purified by stirring over freshly-ground calcium hydride for 12 h and redistilled under vacuum before use.

3.2.2.5 Toluene (EMD, ACS grade)

Toluene was first stirred over freshly-ground calcium hydride in a flask on the vacuum line with intermittent degassing by cooling to -78 °C in an isopropyl alcohol (IPA)/dry ice bath, pumping, and warming up to 25 °C to remove air and hydrogen gas generated during the drying process. This should be sufficient for most purposes after re-distillation. For further drying, toluene was vacuum transferred into a second flask containing sodium dispersion (Hodgson Chemicals Inc., 40% sodium dispersion in paraffin). The toluene was again subjected to several freeze-pump-thaw cycles before final distillation into flasks containing poly(styryl)lithium and equipped with Rotaflo® stopcocks. The orange color of the poly(styryl)lithium was used as an indication of purity. Toluene was distilled directly from these flasks, as needed, through the high vacuum line.
3.2.2.6 Methanol (MeOH, Fisher Scientific, reagent grade)

For general purposes such as precipitation, methanol was used as received. When used as a quenching agent or reactant, it was purified by degassing intermittently on high vacuum line using repeated freeze-pump-thaw cycles with liquid nitrogen cooling and transferred to pre-calibrated ampoules.

3.2.2.7 Tetrahydrofuran (THF, EMD, ACS grade)

Tetrahydrofuran was stirred over freshly-ground calcium hydride for 24 h with frequent degassing on the high vacuum line using a dry ice/isopropyl alcohol bath for cooling. It was vacuum transferred onto a sodium mirror in a 2-L flask equipped with a Rotaflo® stopcock. This step was repeated until the sodium mirror maintained its integrity. The purified THF was distilled directly from the sodium mirror into ampoules and reactors, as needed.

3.2.2.8 1-Chloronaphthalene (Acros, technical grade)

1-Chloronaphthalene was purified by stirring over freshly-ground calcium hydride for 24 h with frequent degassing on the high vacuum line. It was then distilled on the high vacuum line into a flask that was subsequently sealed from the line. The flask was opened in the dry box and the solvent was transferred to a crimp bottle and stored over activated 4Å molecular sieves under argon.
3.2.2.9 Dichloromethane (EMD, ACS grade)

Dichloromethane was purified by distillation under nitrogen after stirring with freshly ground calcium hydride for 12 h. It was then stored over activated 4Å molecular sieves under argon.

3.2.2.10 Silica Gel (VWR, 230-400 mesh)

Generally, the silica gel was used as received. When necessary (e.g., for higher chromatographic resolution), silica gel was activated by heating at 140 °C for 12 h.

3.2.2.11 4-Vinylbenzyl Chloride (VBC, Aldrich, 90%)

This compound was purified by stirring over freshly-ground calcium hydride for 12 h and distilled under high vacuum before use. It was stored under argon at -30 °C for about a month without significant effects on controlled free radical polymerization.

3.2.2.12 Methyl Vinyl Ketone (Acros, c.a. 95%, stabilized)

Just before use, the compound was stirred with calcium hydride for 3 h and freshly distilled at a slightly reduced pressure.

3.3 Molecular Characterizations

All $^1$H and $^{13}$C NMR spectra were acquired in CDCl$_3$ (Aldrich, 99.8% D) or a mixture of CDCl$_3$ and CS$_2$ for some fullerene derivatives using a Varian Mercury 300 or Varian 500 NMR spectrometer. The $^1$H NMR spectra were referenced to the residual
proton impurities in the CDCl$_3$ at $\delta$ 7.27 ppm. The $^{13}$C NMR spectra were referenced to $^{13}$CDCl$_3$ at $\delta$ 77.00 ppm.

Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting polymer films onto KBr plates from polymer solutions or by making a KBr pellet from a mixture with the sample. The data were processed using Win-IR software. UV-vis spectra were recorded on a HP 8453 UV-vis Spectrometer System.

Size-exclusion chromatographic analyses (SEC) were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/103/104 Å), mixed bed (103/104/106 Å)] and a double detector system with THF as eluent at a flow rate of 1.0 mL/min at 30 °C; the detector system consisted of a differential refractometer (Waters 410) and a laser light scattering detector (Wyatt Technology, DAWN EOS, $\lambda = 670$ nm). Regular SEC calibrations were conducted with polystyrene standards (Polymer Laboratories). Some fullerene polymers were tested on an SEC instrument with a triple detector: UV detector (at 330 nm), light scattering detector, and refractive index detector.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Reflex-III TOF mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with an LSI model VSL-337ND pulsed 337 nm nitrogen laser (3 nm pulse width), a single-stage pulsed ion extraction source, and a two-stage gridless reflector. The matrix used is usually DCTB {Aldrich, trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile, $\geq 99\%$} for fullerene derivatives and dithranol (Alfa Aesar, 1,8,9-anthracenetiol, 97+%) for polymers.
Solutions of matrix (20 mg/mL), sample (10 mg/mL), and a cationizing agent [silver trifluoroacetate (10 mg/mL) (Aldrich, 98%), or sodium iodide (10 mg/mL) (Aldrich, 98%)] were prepared in THF (Aldrich, 99.9%). These solutions were mixed in the ratio of matrix/sample (5:1) for fullerene derivatives and matrix/cationizing salt/sample (10:1:2) for polymers. Then, 0.5 μL of the final mixture was applied to the MALDI sample target and allowed to dry. To minimize undesirable fragmentation and achieve optimal intensity, the intensity of nitrogen laser pulses was frequently attenuated and adjusted. Mass spectra were measured in the reflection mode.

3.4 Synthetic Procedures

Compounds 1,37,38 2,37,38 methyl prop-2-ynyl malonate (36),175 diprop-2-ynyl malonate (37),176 Raft-CTA 38,177 and Raft-CTA acyl chloride 39178 were prepared according to literature. Representative procedures for the preparation of new compounds as well as repeating/improving the literature synthesis are described below.

3.4.1 Preparation of Known Compounds

2-(Trimethylsilyloxy)-1,3-butadiene. An oven-dried, 250-mL, three-necked, round-bottomed flask was fitted with two oven-dried addition funnels, one reflux condenser, and a magnetic stirrer, and placed in an 80–90 °C oil bath. Under an inert atmosphere, methyl vinyl ketone (10.0 g., 0.143 mol) in 20 mL of DMF and chlorotrimethylsilane (17.4 g., 0.160 mol) in 20 mL of DMF were added over 30 minutes to a magnetically stirred solution of triethylamine (16.2 g., 0.160 mol) in 80 mL of DMF. The reaction gradually darkens from colorless to yellow or dark brown, and supported a white precipitate. After
14 hours, the reaction was cooled to room temperature, filtered, and transferred to a 2-L separatory funnel containing 120 ml. of pentane. To this solution was added 400 ml of cold 5% sodium hydrogen carbonate solution to facilitate the separation of phases and remove the DMF. The pentane layer is separated, and the aqueous layer extracted twice with 120 mL portions of pentane. The pentane extracts were combined, washed with 200 ml. of cold distilled water, dried over powdered anhydrous sodium sulfate, and filtered into a 1-L, round-bottomed flask. The pentane and other volatiles were removed by fractional distillation, using a 5-cm. long vigorox column and heating the pot in a 70° oil bath. A water aspirator vacuum is applied, and 5.0 g (23%) of the diene was distilled as colorless liquid, b.p. 61–65° (50 mm). \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm, \(\delta\)): 6.24 (dd, 1H), 5.48 (dd, 1H), 5.10 (m, 1H), 4.36 (m, 2H), 0.25 (s, 9H).

**Compound 1 (Scheme 2.3).** 473.4 mg (3.34 mmol) of freshly redistilled 2-(trimethylsilyloxy)-1,3-butadiene was carefully dissolved in 20 mL of dry toluene. The solution was slowly added over 1 hour by pressure-equilibrating addition funnel to a refluxing solution of 2.00 g (2.78 mmol) of C\(_{60}\) in 700 mL of dry toluene under argon. After complete addition, reflux was continued for 24 h and the reaction mixture was then cooled to room temperature. The solvent was evaporated under reduced pressure and the crude product was redissolved in minimum amount of CS\(_2\). This solution was loaded on top of a column packed with silica gel (flash) in hexanes and eluted with CS\(_2\) first and then toluene to give 1120 mg (yield: 51%) of 1 as a shiny black crystalline material. \(^1\)H NMR (CS\(_2\):CDCl\(_3\) = 1:2, 500 MHz, ppm, \(\delta\)): 4.40 (s, 2H), 3.90 (m, 2H), 3.60 (m, 2H).

**Compound 2 (Scheme 2.3).** 700 mg (0.886 mmol) of ketone 1 was dissolved in 150 mL of dry toluene and the solution was added dropwise 2.2 mL of a 1.0 M solution
of diisobutylaluminum hydride (DIBAL-H) in hexane at 25 °C. The reaction mixture was stirred overnight at 25 °C and then treated with 50 mL of saturated NH₄Cl aqueous solution for 30 min. The organic layer was separated and the aqueous layer was extracted with toluene twice. The combined organic phases were dried over Na₂SO₄ followed by evaporation of the solvent. Flash chromatography on silica gel with toluene afforded 600 mg (86%) of final compound as a shiny black crystalline solid. ¹H NMR (CS₂:CDCl₃ = 1:2, 500 MHz, ppm, δ): 5.21 (dddd, J = 9.4, 9.1, 5.3, 4.0Hz, 1H), 3.78 (ddd, J = 13.6, 11.7, 4.2 Hz, 1H), 3.68 (dd, J = 13.4, 9.1 Hz, 1H), 3.55 (dd, J = 13.4, 5.3 Hz, 1H), 3.35 (ddddd, J = 15.4, 11.7, 9.4, 4.0 Hz, 1H), 3.26 (ddd, J = 13.6, 5.6, 4.0 Hz, 1H), 2.68 (ddddd, J = 15.4, 5.6, 4.2, 4.0 Hz, 1H), 1.99 (br s, 1H, OH).

*Methyl prop-2-ynyl malonate 36.* At room temperature, monomethyl monopotassium malonate (8.0 g, 0.05 mol) in 50 mL of DMF was placed in 100 mL round-bottom flask fitted with a pressure-equilibrating addition funnel containing 8.4 mL of propargyl bromide solution in toluene and 10 mL of DMF. The solution was slowly added. The yellow color of the propargyl bromide solution persisted in the flask. The mixture was then stirred overnight. Gradually, the solution turned white with salt precipitations. After filtration to remove the salt, the filtrate was diluted with 200 mL of water and extracted with ether (100 mL × 3 times). The combined colorless organic phase was washed with sodium bicarbonate aqueous solution (10%, 150 mL) and brine (150 mL) and dried over anhydrous Na₂SO₄. After removal of solvent, chromatography on silica gel (eluent: toluene, Rₜ = 0.25) gave the product as light yellow oil (7.6 g, 78%). ¹H NMR (CDCl₃, 500 MHz, ppm, δ): 4.76 (d, 2H), 3.77 (s, 3H), 2.51 (t, 1H).
**Diprop-2-ynyl malonate 37.** A solution of malonyl dichloride (5.7 g, 0.04 mol) in 15 mL of THF was added dropwise to a solution of propargyl alcohol (5.0 g, 0.09 mol) and triethylamine (12.0 g, 0.12 mol) in 100 mL of THF at 0 °C. White solids precipitated out of the solution quickly and the mixture turned yellow to orange. It was an exothermic reaction. After stirring overnight, water was added to quench the reaction. The mixture was then extracted with ethyl acetate three times and the combined organic phase was washed with brine and water, and dried over anhydrous Na₂SO₄. After removal of solvent, it was purified by chromatography on silica gel (eluent: toluene, \( R_f = 0.25 \)) to give a light yellow oil (4.6 g, 72 %). ^1H NMR (CDCl₃, 500 MHz, ppm, \( \delta \)): 4.76 (d, 2H), 2.52 (t, 1H).

**Raft-CTA 38.** 1-Dodecanethiol (80.76 g, 0.40 mol), acetone (192.4 g, 3.31 mol), and tricaprylylmethylammonium chloride (6.49 g, 0.016 mol) were mixed in a jacketed reactor which is cooled to 10 °C under a nitrogen atmosphere. And then sodium hydroxide solution (50%) (33.54 g, 0.42 mol) was slowly added for about 30 min. The reaction was stirred for an additional 15 min before carbon disulfide (30.42 g, 0.40 mol) in acetone (40.36 g, 0.69 mol) solution was added over 20 min, during which time the color turned red. Ten minutes later, about 100 g chloroform was added in one portion, followed by dropwise addition of 50% sodium hydroxide solution (160 g, 2 mol) over 30 min. The reaction was stirred overnight. 600 mL of water was added, followed by 100 mL of concentrated HCl to acidify the aqueous solution. Then Nitrogen was purged through the reactor with vigorous stirring to help evaporate off acetone. The solid was collected with a Buchner funnel and then stirred in 1 L of 2-propanol. The undissolved solid was filtered off and the 2-propanol solution was concentrated to dryness under reduced
pressure, and the resulting solid was recrystallized from hexanes to afford yellow crystalline solid (yield: 70%). $^1$H NMR (CDCl$_3$, 500 MHz, ppm, δ): 13.05 (s, 1H), 3.42 (t, 2H), 1.75 (s, 6H), 1.37-1.47 (m, 20H), 0.99 (t, 3H).

Raft-CTA acyl chloride 39 (Scheme 7.5). Compound 38 (2.18 g, 0.006 mol) was dissolved in 5 mL of anhydrous CH$_2$Cl$_2$ in a 25 mL round-bottom flask and oxalyl chloride in CH$_2$Cl$_2$ (4.5 mL, 0.009 mol) was syringed into the solution. The system was stirred for 4 h at room temperature. The volatiles were removed by vacuum to give the acyl chloride as yellow oil that was used for esterification without further purification.

3.4.2 Fullerene Derivatives

Fulleryne01 (Scheme 5.2, by Steglich esterfication). A 500 mL, round-bottom flask was charged with a degassed solution of 2 (260 mg, 0.328 mmol) in 300 mL of toluene. After sonicating, a dark brown clear solution was obtained. To this stirred solution, propiolic acid (230 mg, 3.28 mmol), and DMAP (40 mg, 0.328 mmol) were added, followed by DCC (677mg, 3.28 mmol) at room temperature. The solution immediately turned cloudy. After stirring at 25 °C overnight, the mixture was filtered and the solid was washed with toluene (2×30 mL). The combined solutions were evaporated to dryness and then re-dissolved in a minimum of CS$_2$, applied to the top of the column (diameter 3 cm × length 15 cm, silica gel). The sample was then eluted with cyclohexane/toluene (v:v = 1:1). The first band was collected and evaporated to give Fulleryne01, as a dark solid (47 mg, 17%). $^1$H NMR (CS$_2$:CDCl$_3$ = 1:2, 500 MHz, ppm, δ): 6.21 (dddd, $J$ = 9.5, 9.3, 5.4, 3.4 Hz, 1H), 3.87 (dd, $J$ = 13.4, 9.5 Hz, 1H), 3.86 (ddd, $J$ = 13.4, 12.0, 3.9 Hz, 1H), 3.72 (dd, $J$ = 13.4, 5.4 Hz, 1H), 3.49 (dddd, $J$ = 15.6, 12.0, 9.5, 3.4 Hz, 1H), 3.42 (t, 2H), 1.75 (s, 6H), 1.37-1.47 (m, 20H), 0.99 (t, 3H).
3.9 Hz, 1H), 3.35 (ddd, J = 13.7, 5.4, 3.7 Hz, 1H), 2.99 (s, 1H), 2.83 (ddddd, J = 15.6, 5.4, 3.9, 3.4 Hz, 1H). $^{13}$C NMR (CS$_2$:CDCl$_3$ = 2:1, 125 MHz, ppm, δ): 29.31, 29.79, 34.66, 39.95, 61.49 (C$_{60}$, sp$^3$-C), 63.30 (C$_{60}$, sp$^3$-C), 71.85 (C≡C-H), 74.57 (C≡C-H), 134.83, 134.95, 135.40, 140.19, 140.25, 140.27, 141.49, 141.54, 141.55, 141.56, 141.76, 141.80, 141.81, 141.92, 141.93, 141.94, 141.95, 142.44, 142.48, 142.51, 143.08, 144.49, 144.53, 144.56, 144.60, 144.96, 145.09, 145.17, 145.29, 145.32, 145.34, 145.37, 145.49, 145.62, 146.13, 146.15, 146.16, 146.30, 146.32, 146.35, 146.36, 147.55, 151.54, 155.27, 155.46, 155.82, 163.50 (C=O). FT-IR (KBr) ν (cm$^{-1}$): 3283 (C-H), 2118 (C≡C), 1710 (C=O), 1227 (C-O), 527 (C-C in C$_{60}$). UV-vis (CH$_2$Cl$_2$) (λ$_{max}$ (nm): 255, 307, 433. MS (MALDI-TOF): Calcd for C$_{67}$H$_8$O$_2$ 844.05, Found: 844.13 (100 %) (M$^+$).

Fulleryne03 (Scheme 6.2). To a degassed solution of 1 (100 mg, 0.126 mmol) in 100 mL of toluene, an ethynylmagnesium chloride solution in THF (0.5 mL, 0.25 mmol) was added dropwise via syringe at 25 °C. The clear dark brown solution immediately turned turbid. After 30 minutes, 1 mL of saturated aqueous ammonium chloride solution was added to quench the reaction. The solution turned clear and dark brown again with stirring. The solution was then washed with water twice and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent, the product was purified chromatographically on silica gel (toluene, $R_f$ = 0.35) to give Fulleryne03, as a brown solid (94 mg, 92%). $^1$H NMR (CS$_2$:CDCl$_3$ = 1:2, 500 MHz, ppm, δ): 4.00 (m, 1H), 3.85 (m, 1H), 3.50 (m, 3H), 3.19 (m, 1H), 2.82 (s, 1H), 2.58 (s, 1H). $^{13}$C NMR (CS$_2$:CDCl$_3$ = 2:1, 125 MHz, ppm, δ): 29.83, 34.76, 38.94, 50.22, 61.30 (C$_{60}$, sp$^3$-C), 63.56 (C$_{60}$, sp$^3$-C), 73.06 (C≡C-H), 88.58 (C≡C-H), 135.22, 141.37, 141.84, 142.36, 145.19, 145.23, 146.00, 146.22, 147.43,
155.76, 156.06, 156.91. FT-IR (KBr) \( v \) (cm\(^{-1}\)): 3300 (≡C-H), 2800 (C-H), 1510, 527 (C-C in C\(_{60}\)). MS (MALDI-TOF): Calcd for C\(_{66}\)H\(_8\)O 816.06, Found: 816.18 (100 %) (M\(^+\)).

*Fulleryne04* (Scheme 6.3). To a degassed solution of Fulleryne03 (158 mg, 0.194 mmol) in 100 mL of toluene cooled to 0 °C was added dropwise bis(2-methoxyethyl)aminosulfur trifluoride (88 mg, 0.40 mmol) via syringe. After 1 h, thin layer chromatography (TLC) showed that the reaction was complete and it was then quenched by the addition of 5% aqueous NaHCO\(_3\) solution. The solution was then washed with water twice and dried over anhydrous Na\(_2\)SO\(_4\). After removal of the solvent, the product was purified chromatographically on silica gel (cyclohexane:toluene = 1:1 volume ratio, \( R_f = 0.8 \)) to give Fulleryne04, as a brown solid (120 mg, 76%). \(^1\)H NMR (CS\(_2\):CDCl\(_3\)=1:2, 500 MHz, ppm, \( \delta \)): (given in Figure 6.9). \(^{13}\)C NMR (CS\(_2\):CDCl\(_3\) = 2:1, 125 MHz, ppm, \( \delta \)): (given in Figure 6.9). FT-IR (KBr) \( v \) (cm\(^{-1}\)): 3300 (≡C-H), 2800 (C-H), 1510, 527 (C-C in C\(_{60}\)). MS (MALDI-TOF): Calcd for C\(_{66}\)H\(_7\)F 818.05, Found: 818.02 (100 %) (M\(^+\)).

*Fulleryne05* (Scheme 6.4). To a degassed solution of 1 (100 mg, 0.126 mmol) in 100 mL of toluene, an ethynylmagnesium chloride solution in THF (0.5 mL, 0.25 mmol) was added dropwise via syringe at 25 °C. The clear dark brown solution immediately turned turbid. After 30 minutes, bromoacetyl bromide (0.58 g, 0.25 mL, 2.87 mmol) was added to quench the reaction. The solution gradually turned clear and then dark brown again after overnight stirring. The solution was then washed with water twice and dried over anhydrous Na\(_2\)SO\(_4\). After removal of the solvent, the product was purified chromatographically on silica gel (cyclohexane:toluene = 1:1 volume ratio, \( R_f = 0.7 \)) to give Fulleryne05, as a brown solid (81 mg, 68 %). Further eluting with toluene yielded
Fulleren 03 (21 mg, 19%). $^1$H NMR (CS$_2$:CDCl$_3$=1:2, 500 MHz, ppm, δ): 4.30 (d, 1H), 4.11 (d, 1H), 3.92 (s, 2H), 3.65 (m, 2H), 3.45 (m, 2H), 2.95 (s, 1H). $^{13}$C NMR (CS$_2$:CDCl$_3$ = 2:1, 125 MHz, ppm, δ): 26.04, 29.82, 34.40, 36.89, 47.07 (C-O), 60.92 (C$_{60}$, sp$^3$-C), 63.39 (C$_{60}$, sp$^3$-C), 75.57 (C≡C), 83.68 (C≡CH), 134.95, 135.67, 141.49, 141.55, 142.45, 145.34, 145.37, 145.63, 146.28, 155.05, 155.38, 155.48, 156.17, 164.74 (C=O). FT-IR (KBr) v (cm$^{-1}$): 3294 (≡C-H), 1745 (C=O), 527 (C-C in C$_{60}$). MS (MALDI-TOF): Calcd for C$_{68}$H$_9$BrO$_2$ 935.98, Found: 935.99 (100 %) (M$^+$).

Fulleridyne 06 (Scheme 6.5). A 500 mL, round-bottom flask was charged with C$_{60}$ (200 mg, 0.28 mmol), CBr$_4$ (85 mg, 0.33 mmol), and malonate 36 (65 mg, 0.42 mmol) dissolved in 150 mL of toluene. The solution was then degassed and back-filled with argon. DBU (51 mg, 0.33 mmol) was then added dropwise via syringe at 25 °C. The purple-colored solution gradually turned wine-red with stirring. After overnight reaction, the solution was evaporated to dryness and directly transferred to a column of silica gel. Elution with cyclohexane:toluene (v/v) = 1:1 ($R_f$ = 0.8) gave Fulleridyne 06 as a brown solid (100 mg, 41 %). Further eluting with toluene yielded diaddition products that are a mixture of regioisomers. $^1$H NMR (CS$_2$:CDCl$_3$=1:2, 500 MHz, ppm, δ): 5.09 (d, 2H), 4.12 (s, 3H), 2.62 (t, 1H). $^{13}$C NMR (CS$_2$:CDCl$_3$ = 2:1, 125 MHz, ppm, δ): 29.81, 53.56, 54.00, 70.90, 76.09, 128.04, 138.77, 140.76, 141.59, 141.98, 142.79, 144.66, 145.04, 162.11, 162.91 (C=O). FT-IR (KBr) v (cm$^{-1}$): 3300 (≡C-H), 1745 (C=O), 527 (C-C in C$_{60}$). MS (MALDI-TOF): Calcd for C$_{67}$H$_6$O$_4$ 874.03, Found: 873.74 (100 %) (M$^+$).

Fulleridyne 01 (Scheme 6.6). A 500 mL, round-bottom flask was charged with C$_{60}$ (200 mg, 0.28 mmol), CBr$_4$ (85 mg, 0.33 mmol), and malonate 37 (70 mg, 0.39 mmol) dissolved in 150 mL of toluene. The solution was then degassed and back-filled with 80
argon. DBU (51 mg, 0.33 mmol) was then added dropwise via syringe at 25 °C. The purple-colored solution gradually turned wine-red with stirring. After overnight reaction, the solution was evaporated to dryness and directly transferred to a column of silica gel. Elution with cyclohexane:toluene (v/v) = 1:1 (Rf = 0.8) gave Fullerdiyne01 as a brown solid (54 mg, 21 %). 1H NMR (CS2:CDCl3=1:2, 500 MHz, ppm, δ): 5.07 (d, 4H), 2.61 (t, 2H). 13C NMR (CS2:CDCl3 = 2:1, 125 MHz, ppm, δ): 29.81, 54.02, 55.32, 70.70, 76.17, 128.02, 128.78, 138.90, 139.04, 139.05, 140.74, 141.97, 142.76, 143.63, 144.47, 145.04, 161.64 (C=O). FT-IR (KBr) ν (cm⁻¹): 3300 (≡C-H), 1750 (C=O), 527 (C-C in C₆₀). MS (MALDI-TOF): Calcd for C₆₇H₈O₂ 898.03, Found: 898.04 (100 %) (M⁺). Further eluting with toluene yielded diaddition products that are a mixture of regioisomers.

Fulleryne01 (Scheme 6.1, by Fisher esterification). The glassware as shown in Figure 3.3 was first completely dried by being connected to high vacuum line and flame-dried three times. After cooling, flask A was charged with 2 (0.50 g, 0.63 mmol), p-toluenesulfonic acid (20 mg, 0.11 mmol), and 1-chloronaphthalene (16 mL) while flask B was charged with activated 4Å molecular sieves. The whole system was further dried under vacuum for a day. Then, propiolic acid (1.0 mL, 1.138 g, 16.3 mmol) was added to flask A and the system was degassed. Toluene (20 mL) was distilled into the reactor by vacuum transfer into flask A. After purging with argon, both flask A and B were put into an oil bath of 120 °C to allow a circulation of toluene going on from A to B to C and back to A. After 12 h, the reactor was cooled down to room temperature and the materials in flask A were transferred out by syringe and concentrated in vacuo. The residue was directly applied to the top of silica gel for chromatography. It was eluted with hexane first to remove the 1-chloronaphthalene and then with cyclohexane/toluene (v:v = 1:1) to
give the product Fulleryne01 (yield: 35 % ~ 92 %). Further elution with toluene recovered unreacted 2 (2 % ~ 56 %).

3.4.3 Azide-Functionalized Polymers

The azide-functionalized polymers were obtained by a combination of anionic polymerization,\textsuperscript{179} atom-transfer radical polymerization (ATRP),\textsuperscript{180} and nucleophilic substitution. PEO was synthesized using anionic polymerization techniques with controlled molecular weight and narrow polydispersity using potassium tert-butoxide as the initiator.\textsuperscript{181}

\textit{PS-Br}. Ethyl 2-bromoisobutyrate (1.21 g, 6.2 mmol), CuBr (0.32 g, 2.2 mmol), PMDETA (0.87 mL, 4.5 mmol), styrene (30 mL, 0.26 mole), and toluene (40 mL) were combined in a Schlenk flask. The flask was subjected to 3 freeze–pump–thaw cycles and polymerization was performed under inert atmosphere at 110 °C for 5.5 h. The polymerization was stopped by quenching the flask in ice water. The polymer solution was passed through an alumina column three times to remove any trace of copper. The purified solution was precipitated into cold methanol to afford the polymer (PS-Br). By adjusting the ratio of initiator to copper salt to monomer and controlling the time for polymerization, polystyrenes with different molecular weights were obtained. PS-Br (2k): \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz, ppm, δ): 6.12-7.42 (br m, 100 H), 4.40-4.65 (br m, 1 H), 3.40-3.77 (br m, 2 H), 1.25-2.60 (br m, 57 H), 0.80-1.11 (m, 9 H). Calcd. \(M_n = 2280\); SEC: \(M_n = 2270\), PDI = 1.04.

\textit{PS-N\textsubscript{3}} (Scheme 5.2). PS-Br (10 g, 4.5 mmol) was dissolved in anhydrous DMF (50 ml) and then sodium azide (1.5 g, 23 mmol) was added. The mixture was stirred at
25 °C under argon for 24 h. The solution was precipitated into cold methanol. The white precipitate was collected and dried under vacuum. The PS-N₃ was obtained as a white powder. PS-N₃ (2k): ^1^H NMR (CDCl₃, 300 MHz, ppm, δ): 6.15-7.42 (br m, 103 H,), 3.82-4.10 (br m, 1 H), 3.38-3.77 (br m, 2 H), 1.25-2.60 (br m, 62 H), 0.80-1.11 (m, 9 H).

Calcd. $M_n = 2330$; SEC: $M_n = 2440$, PDI = 1.04. FT-IR (cm⁻¹): 3061, 3027, 2924, 2851, 2095 (strong, azide), 1945, 1871, 1759, 1726 (C=O), 1602, 1493, 1450, 1184, 1131, 1091, 1029, 907, 758, 699, 541.

**PEO-OH** (Scheme 7.1, Figure 3.3). The reactor as shown in Figure 3.4 was equipped with an ampoule of ethylene oxide in THF, an ampoule of t-BuOK in THF, and a methanol ampoule. After connecting to the high vacuum line, the reactor was thoroughly dried by using a soft yellow flame. Anhydrous THF was transferred into the reactor by using a dry ice/isopropanol bath of – 78 °C. The reactor was sealed off the line under vacuum using a hand torch. The initiator was added by breaking the initiator ampoule. The cooled EO ampoule was then broken by a magnetic hammer to add the monomer into the reactor. The reaction mixture was left to stir for 12-24 h. A sample was taken at this time by sealing off the ampoule and it could be functionalized with different functional groups by using various quenching reagents. When quenched by the addition of excess methanol, it gave hydroxyl-end functionalized PEO (PEO-OH). After concentration, the material was precipitated into cold ethyl ether to give PEO-OH as a white powder (or wax depending on molecular weight).

**PEO-Br** (Scheme 7.3). PEO-OH (2.2 g, 0.25 mmol) and 25 ml anhydrous CH₂Cl₂ were added into a 50ml, round-bottle flask equipped with a magnetic stirrer. After dissolving completely, TEA (0.375 g, 3.75 mmol) was added. The solution was cooled to
0 °C in an ice bath and 2-bromoisobutyryl bromide (0.85 g, 3.75 mmol, diluted with 5 ml anhydrous dichloromethane) was added dropwise within 20 min. The solution was stirred at 25 °C for 24 h. The mixture was diluted with 200 ml CH₂Cl₂ and washed with water three times to remove salt. The organic layer was dried over anhydrous Na₂SO₄ overnight. After concentration, the polymer was precipitated into excess cold ether ethyl and collected by filtration. The resultant white powder was dried in vacuo for 24 h to give PEO-Br (1.93 g, 88 %).

**PEO-b-PS-Br** (Scheme 7.3). PEO-Br (0.5 g, 0.06 mmol), styrene (3 ml), CuBr (7 mg, 0.06 mmol) and 5 ml anhydrous toluene were added into a reaction flask equipped with a magnetic stirrer. The mixture was degassed by three freeze-vacuum-thaw cycles. PMDETA (11 mg, 0.06 mmol) was introduced into the mixture under nitrogen protection and the mixture became light green. After three extra freeze-vacuum-thaw cycles, the
flask was immersed into a 90 °C oil bath. After the reaction was carried out for a definite time, the flask was quenched by liquid nitrogen. The resultant solution was passed through a short column of neutral alumina for removal of the metal salt. By adding the polymer solution into an excess of cold ethyl ether, the PEO-b-PS-Br was precipitated and collected by vacuum filtration. The block copolymer was obtained in 38 % yield (1.24 g) after drying in vacuo for 24 h.

PEO-b-PS-N3 (Scheme 7.3). PEO-b-PS-Br (0.8 g, 0.045 mmol), sodium azide (29 mg, 0.45 mmol) and anhydrous DMF (10 ml) were added into a 50 ml, round-bottom flask. The mixture was stirred at 25 °C for 24 h. The resultant mixture was diluted with 200 ml of chloroform and washed with water three times to remove unreacted sodium azide. After removal of the majority of the solvent, the polymer was precipitated into excess ethyl ether and a white solid was collected by filtration. The PEO-b-PS-N3 was obtained in 87 % yield (0.69 g) after drying under vacuum for 24 h.

PEO-Epoxy (Scheme 7.2). PEO-OH (3.5 g, 0.40 mmol), epichlorohydrin (15 ml), and NaOH (5 g, 125 mmol) were added into a 50 ml round bottle flask equipped with a magnetic stirrer. After stirring for 36 h at 25 °C, the resultant mixture was filtered to remove undissolved solid. By precipitating the filtrate into excess cold ethyl ether, the product was collected in 75 % yield (2.62 g).

PEO-(N3)-OH (Scheme 7.2). PEO-Epoxy (2.2 g, 0.25 mmol) was dissolved in 15 ml of DMF. NaN3 (0.33 g, 5 mmol) and ammonium chloride (0.27 g, 5 mmol) were then added. After stirring at 50 °C for 24 h, the mixture were dissolved in 200 ml of dichloromethane and washed with water for 3 times to remove unreacted inorganic salts. The organic layer was collected and dried over anhydrous Na2SO4 overnight. After
concentration by rotatory evaporation, the product was obtained as a white powder by precipitation into excess cold diethyl ether with a yield of 76% (1.67 g).

**PEO-(N3)-Br (Scheme 7.4).** PEO-(N3)-OH (1.5 g, 0.17 mmol) and TEA (0.17 g, 1.7 mmol) were dissolved in 25 ml of anhydrous CH2Cl2. After cooling to 0 °C, 2-bromobutyryl bromide (0.39 g, 1.7 mmol, diluted with 5 ml of anhydrous CH2Cl2) was added dropwise within 20 min. The solution was stirred at 25 °C for 24 h. The resultant mixture was diluted with 200 ml of CH2Cl2 and washed with water three times to remove salt. The organic layer was collected and dried over anhydrous Na2SO4 overnight. After concentration by rotatory evaporation, the macro-initiator was obtained by precipitating into excess cold diethyl ether. The product was dried in vacuo for 24 h (1.3 g, 87%).

**PEO-(N3)-PS (Scheme 7.4).** PEO-(N3)-Br (0.5 g, 0.06 mmol), styrene (3 ml), CuBr (7 mg, 0.06 mmol) and 4 ml of anhydrous toluene were added into a reaction flask equipped with a magnetic stirrer. The mixture was degassed by three freeze-vacuum-thaw cycles. PMDETA (11 mg, 0.06 mmol) was introduced into the mixture under nitrogen protection and the mixture became light green. After three extra freeze-vacuum-thaw cycles, the flask was immersed into a 42 °C oil bath. After the reaction was carried out for a definite time, the flask was quenched by immersing into liquid nitrogen. The resultant solution was passed through a short column of neutral alumina for removal of the metal salt. By adding the polymer solution into an excess of cold diethyl ether, the PEO-(N3)-PS was precipitated and collected by vacuum filtration.

**PEO-Raft (Scheme 7.5).** The macro-RAFT agent was synthesized by reacting PEO-OH with Raft-CTA 38. PEO-OH (2.6 g, 0.30 mmol), TEA (0.3 g, 3.0 mmol) and 25 ml of anhydrous CH2Cl2 were added into a 50 ml, round-bottom flask with a stirrer.
After the solution was cooled to 0 °C, Raft-CTA acyl chloride 39 (prepared from 38 by reacting with SOCl₂, 1.2 g, 3.0 mmol, diluted with 5 ml of anhydrous CH₂Cl₂) was added dropwise within 20 min. The solution was stirred at 25 °C for 24 h. The resultant solution was diluted with 200 ml of CH₂Cl₂ and washed with water three times to remove salt. The organic layer was dried over anhydrous Na₂SO₄ overnight. The solvent was removed by rotatory evaporation and polymer was obtained by precipitation into excess cold diethyl ether. The product was dried in vacuo for 24 h (2.2 g, 85 %).

*PEO*-b*-PS/Cl* (Scheme 7.5). PEO-Raft (0.5 g, 0.06 mmol), AIBN (0.9 mg, 0.006 mmol), styrene (2.0 ml), and VBC (0.07 ml) and 2 ml of anhydrous toluene were added into a reaction flask with a stirrer. After three freeze-pump-thaw cycles, the flask was immersed into a 110 °C oil bath. After the reaction was carried out for a definite time, the flask was quenched by liquid nitrogen. The polymer was obtained by precipitating into excess cold ethyl ether.

*PEO*-b*-PS/N₃* (Scheme 7.5). PEO-PS/PVBC (0.8 g, 0.040 mmol), sodium azide (26 mg, 0.40 mmol) and 10 ml anhydrous DMF were added into a 50 ml round bottle flask. The mixture was stirred at 25 °C for 24 h. The resultant mixture was diluted with 200 ml of chloroform and washed with water three times to remove unreacted sodium azide. After concentrated by rotatory evaporation, the polymer was precipitated into excess diethyl ether and white solid was collected by filtration. The PEO-PS/N₃ was obtained in 85 % yield (0.68 g) after dried in vacuo for 24 h.
3.4.4 The “Click” CuAAC Reactions

Fullerene polymers with controlled fullerene placement along the chain can be obtained by “click” reaction between the fullerenes and azide-functionalized polymers following the typical procedure as described below.

Model “click” reaction between PS-N₃ and Fulleryne01 (Scheme 5.2). To a mixture of the PS-N₃ ($M_w = 2,000$, 220 mg, 0.1 mmol) and Fulleryne01 (51 mg, 0.06 mmol) in degassed toluene (60 mL, $c \sim 10^{-3}$ mol/L) was added one drop of PMDETA (~10 mg, 0.057 mmol) and then CuBr (1 mg, 7 μmol). The wine-red clear solution was then stirred at 25 °C for 24 h. The reaction mixture was concentrated, applied to the top of a short column of silica gel. The column was eluted with toluene first to remove the excess starting material PS-N₃ (78 mg was recovered). It was then further eluted with toluene/ethyl acetate (v:v = 95:5) to give a colored fraction, which was collected, concentrated, and precipitated into cold methanol to give PS-C₆₀ as a brown powder (144 mg, 75%). For PS-N₃ (6k) and (10k), excess Fulleryne01 was used and the column was directly eluted with toluene/ethyl acetate (v:v = 95:5) to give the colored fraction, which was then concentrated and precipitated into methanol. The yield was 91% for PS-N₃ ($M_n = 6,000$) and 95% for PS-N₃ ($M_n = 10,000$).

PEO-C₆₀ (Scheme 7.2). PEO-(N₃)-OH (0.2 g, 0.024 mmol), Fulleryne01 (23 mg, 0.027 mmol), CuBr (3 mg, 0.022 mol) and anhydrous toluene (30 ml) were added into a reaction flask with a magnetic stirrer. After three freeze-pump-thaw cycles, PMDETA (4 mg, 0.022 mmol) was introduced into the mixture under nitrogen protection. The flask was degassed for three extra freeze-vacuum-thaw cycles, and stirred at 25 °C for 24 h. The reaction mixture was concentrated and applied to the top of a short column of silica
gel. The column was eluted with toluene first to remove the excess Fulleryne01. Further elution with chloroform/methanol (v:v = 90:10) gave a colored fraction, which was collected, concentrated, and recrystallized in amyl acetate. PEO-C₆₀ was obtained as brown powder after drying in vacuo for 24 h (158 mg, 72 %).

**PEO-b-PS-C₆₀** (Scheme 7.3). The fullerene was introduced into the block copolymer by click chemistry. A typical procedure was as follows. PEO-b-PS-N₃ (0.4 g, 22 μmol), Fulleryne01 (23 mg, 27 μmol), CuBr (3 mg, 22 μmol) and anhydrous toluene (30 ml) were added into a reaction flask with a magnetic stirrer. The mixture was degassed by three freeze-vacuum-thaw cycles. PMDETA (4 mg, 22 μmol) was introduced into the mixture under nitrogen protection. After three extra freeze-pump-thaw cycles, the flask was stirred at 25 °C for 24 h. The reaction mixture was concentrated and applied to the top of a short column of silica gel. The column was eluted with toluene first to remove the excess Fulleryne01. It was then further eluted with chloroform/methanol (v:v = 90:10) to give a colored fraction, which was collected, concentrated, and recrystallized in amyl acetate to give PEO-b-PS-C₆₀ as a brown powder (310 mg, 77 %).

**PEO-(C₆₀)-PS** (Scheme 7.4). PEO-(N₃)-PS (0.4 g, 22 μmol), Fulleryne01 (23 mg, 27 μmol), CuBr (3 mg, 22 μmol) and anhydrous toluene (30 ml) were added into a reaction flask with a magnetic stirrer. The mixture was degassed by three freeze-vacuum-thaw cycles. PMDETA (4 mg, 22 μmol) was introduced into the mixture under nitrogen protection. After three extra freeze-vacuum-thaw cycles, the flask was stirred at 25 °C for 24 h. The reaction mixture was concentrated and applied to the top of a short column of silica gel. The column was eluted with toluene first to remove the excess Fulleryne01. It
was then further eluted with chloroform/methanol (v:v = 90:10) to give a colored fraction, which was collected, concentrated, and recrystallized in amyl acetate to give PEO-(C$_{60}$)-PS, as a brown powder (280 mg, 71 %).

$\text{PEO-b-PS/C}_{60}$ (Scheme 7.5). PEO-PS/N$_3$ (0.3 g, 15 μmol), Fulleryne01 (65 mg, 76 μmol), CuBr (9 mg, 76 μmol) and anhydrous toluene (30 ml) were added into a reaction flask with a magnetic stirrer. The mixture was degassed by three freeze-vacuum-thaw cycles. PMDETA (13 mg, 76 mmol) was introduced into the mixture under nitrogen protection. After three extra freeze-vacuum-thaw cycles, the flask was stirred at 25 °C for 24 h. The reaction mixture was concentrated and applied to the top of a short column of silica gel. The column was eluted with toluene first to remove the excess Fulleryne01. It was then further eluted with chloroform/methanol (v:v = 80:20) to give a colored fraction, which was collected, concentrated, and recrystallized in amyl acetate to give PEO-b-PS/C$_{60}$ as a brown powder (255 mg).

3.5 Self-Assembling Techniques

Self-assembly is not a formalized subject and involves numerous processes ranging from non-covalent association of organic molecules to the crystal growth of a polymer. Crystallization has been recognized as one of the strongest self-assembly process in polymers. Micellization and nano-phase-separation are spontaneous self-organization process and their formation and transition are mostly reversible. In this section, the experimental procedures for polymer self-assembly are presented.
3.5.1 Self-seeding Techniques for Single Crystal Growth

The self-seeding techniques were first introduced by Lotz et al.\textsuperscript{183} as a way of growing uniformly-sized polymer single crystals. The basic outline of the procedure is shown in Figure 3.5.

![Figure 3.4. Self-seeding techniques for polymer single crystal growth.](image)

The semicrystalline polymer and the solvent were first mixed in a clean test tube at room temperature at very dilute solution conditions (~ 0.005 wt%). The solvent quality should be theta-to-poor for the polymer so that dissolution is only possible at higher temperature. The test tube was then placed at an oil bath of the dissolution temperature ($T_d$) and kept there for a predetermined amount of time, $t_d$. It was then either directly quenched to room temperature or slowly cooled down to 25 °C ($T_q$) overnight to crystallize the polymers with the same thermal history. Then, the test tube was again placed in an oil bath at the self-seeding temperature, $T_s$, for a time $t_s$. At this temperature, more than 99 % of the crystals would dissolve leaving only small nuclei with high crystallinity to nucleate crystal growth. Finally, it was quickly transferred into an oil bath
of a set isothermal crystallization temperature, \( T_x \), and allowed to sit there for \( t_x \) until complete crystallization. Both the \( T_d \) and \( T_s \) were strongly dependent on sample, solvent, and concentration. Generally, \( t_d \) was 10 minutes and \( t_s \) was 20 minutes. A typical TEM morphology of the PEO single crystal obtained is shown in Figure 3.6.

![Figure 3.5](image)

Figure 3.5. A typical TEM morphology of the PEO single crystal obtained via the self-seeding techniques.\textsuperscript{184} The inset shows the electron diffraction from the single crystal. Reprinted from ref. 184 by permission of the American Chemical Society.

3.5.2 Alternating Single Crystal Growth

An interesting scheme to create nanopatterns from polymer single crystals is by alternating homo- and functionalized-polymer single crystal growth. One example is the lateral epitaxial growth of homopolymers and diblock copolymers.\textsuperscript{185} The single crystals are grown under certain conditions and then used as the seeds for further growth of another polymer. The crystalline block and homopolymer should be identical so that epitaxial growth can occur along the lateral surface of the original single crystal. When repeated with a controlled crystallization time, the procedure creates nanostructures of channel-wire arrays of different composition and height across the 2D single crystal surface (Figure 3.7).
Specifically, the inner-most crystal is first grown using the self-seeding procedure. After the complete crystallization of the homopolymer crystals, a mixture of the diblock sample in the same solvent is dissolved at $T_d$. This sample is then placed in the isothermal bath at the same temperature ($T_x$) as the homopolymer seeds. The solution is allowed to come to thermal equilibrium for 10 minutes to prevent dissolution of the homopolymer seeds. Then, a few drops of the homopolymer solution are transferred into the diblock solution before the diblock crystals can grow. Finally, the crystalline block grows epitaxially on the seed at the same isothermal $T_x$. This procedure can also be conducted with the opposite structure where the diblock crystals are grown as the seeds and added to the dissolved homopolymer. Then, the homopolymer grows epitaxially on the diblock single crystal. The width of each “layer” is determined by the mass of material in the solution and the $T_s$.

Figure 3.6. TEM image of alternating growth of homopolymer and diblock copolymer of PEO and PS-$b$-PEO to form the step-profile surface. Reprinted from ref. 185 by permission of the American Chemical Society.
3.5.3 Micellization in Selective Solvents\textsuperscript{160,186,187}

To prepare the micelle morphologies, water was chosen as the selective solvent for the PEO blocks. In brief, for the DMF/water system, 10 mL of a stock solution (0.1 wt\%) was placed in a vial each time. Deionized water was added dropwise to reach a predetermined DMF and water ratio at a rate of 20 \( \mu \text{L}/10 \text{ min} \). The contents of the vial were stirred continuously to allow rapid mixing of DMF and water. Each drop added was 0.1 wt\% water with respect to the total solution weight, and at least a 30-min gap was kept between the additions of consecutive drops. After the predetermined DMF/water ratio was reached, the solutions were sealed and left to equilibrate for 6 h to several days with mild stirring. After the solutions were equilibrated, they were left standing without stirring for at least 30 min before samples were taken for micelle morphological observations. To prepare samples for morphology observation, 0.1 mL of solution was first dropped into 2 mL of cold water to quench the morphology. A drop of quenched solution was put on the copper grid. After several minutes, the excess water was removed with filter paper. The remaining solvent was evaporated and then submitted for TEM observations.

3.5.4 Bulk Self-Assembly

The sample was prepared by melting the powder sample on Kapton\textsuperscript{®} polyimide film, annealing at 95 °C for 48 h and then crystallization at 25 °C for 24 h. Nitrogen protection during annealing was not necessary at this temperature.
3.6 Physical Characterization Techniques

The characterization methods for the single crystals included the size and morphology (PLM and PCM), the determination of morphology and thickness using atomic force microscopy (AFM), morphology and crystal structure using transmission electron microscopy (TEM) and electron diffraction (ED), and crystallization of the tethers by TEM ED and differential scanning calorimetry (DSC). The characterization methods for the micelles included the study of micelle size and distribution in solution by light scattering and the morphology observation by TEM and SEM.

3.6.1 Differential Scanning Calorimetry (DSC)

The thermal characteristics of the bulk and crystal mat samples were obtained using a Perkin-Elmer PYRIS Diamond DSC coupled with an Intracooler 2P apparatus. A typical sample weight was 1.0 mg for bulk samples and 0.3 mg for crystal mat samples. The difference in pan weights between the reference and sample was kept less than 0.005 mg. The heating and cooling rates were varied depending on the sample.

3.6.2 Atomic Force Microscopy (AFM)

A few drops of single crystal solution were transferred onto glass cover slides, and the solvent was allowed to evaporate. They were then placed in a vacuum oven for several hours to ensure the complete removal of the solvent. A Digital Instruments Nanoscope IIIA AFM was used in the tapping mode to determine the overall thickness of the sandwiched single crystal. The tapping mode with a carefully chosen cantilever tip-to-sample force was best for limiting damage to the single crystal. The scanner was
calibrated in both the lateral and vertical directions using the standard grid. The typical measurement conditions were a scan size of 20 μm x 20 μm at a scan rate of 1 Hz with operation and resonance frequencies around 300 kHz. The resolution of the captured image was 512 × 512.

3.6.3 Transmission Electron Microscopy (TEM)

A few drops of the crystal solution were deposited onto a carbon-coated copper TEM grid with a mesh size of 400 μm. A similar solvent removal technique to the AFM sample preparation was used. A Philips Tecnai 12 microscope was used to obtain bright field (BF) and electron diffraction (ED) images. The accelerating voltage was 120 kV. The ED spacing was calibrated with a TiCl sample with specific d-spacing values and several higher-order diffractions.

3.6.4 Light Scattering Techniques

To determine the polydispersity of the micelle, static light scattering experiments were conducted using a Brookhaven Instrument coupled with a BI-200SM goniometer, BI-9000AT correlator, and an EMI-9863 photomultiplier tube for photon counting. A Meller Griot 35 mW He-Ne laser was used as light source (632.8 nm). A cylindrical glass scattering cell with a diameter of 12 mm was placed at the center of a thermostated bath (± 0.01 °C) with decahydronaphthalene used for refractive index matching. The measurements were carried out at 90° scattering angle at 25 °C. The glass scattering cells were extensively cleaned by ultrasonication in THF and ethanol to eliminate any dust and
impurity. The micelle solutions were filtered into the scattering cells through filters of 0.45 μm pore size.

3.6.5 Small Angle X-ray Scattering

SAXS data were collected with a Rigaku MicroMax-002+ sealed tube X-ray generator coupled with multiwire position sensitive X-ray detector. Calibration was performed using silver behenate. Background scattering was subtracted from the sample patterns. A hot stage with temperature control of ±0.5 degree was used to obtain scattering patterns at elevated temperatures. The exposure time for each SAXS pattern was 10 min.
CHAPTER IV
RETRO-FUNCTIONAL ANALYSIS AS THE
MOLECULAR DESIGN PRINCIPLE

In the design of advanced molecular materials, a “trial-and-error” approach is frequently used to establish structure-property relationships and perform property optimization by tuning chemical structures. The molecular design is more or less an empirical experience, based on current knowledge of synthetic methodology with some common guidelines on the understanding of molecular function and interactions. However, the performances of functional materials do not depend only on their chemical structures, but also how these molecular entities organize at different length scales. This has been recognized in the materials research community and led to the rapidly growing area of “crystal engineering.” The term was defined by Desiraju as “the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties.” This is a highly interdisciplinary area that is target oriented and property directed. The concept of “supramolecular synthon” was also proposed to describe the modularity of the approach and the general units used in the design and synthesis of molecular crystals. It is great in that the importance of structure in determining material properties was fully appreciated and the modularity of these interactions in the
molecular design and synthetic methods was acknowledged. This has advanced the field of material research tremondously.

Besides molecular crystalline solids, there are also many other materials that are of significant technological and practical importance, yet they are not considered or included in this category. In particular, soft matters with degree of order somewhere between crystalline solids and liquids should be our next focus. In soft matters, the hierarchical structures are often critically important in determining material properties and functions. In other words, they are a combined outcome of the molecular entities at the atomic level (the primary structure), their aggregates in specific conformations to form building blocks on a higher level (the secondary structure), and the micro-structure built upon these building blocks (the tertiary structure), and finally, the phase structures self-assembled to form an even larger, macroscopic object (the quaternary structure). The so-called primary, secondary, tertiary, and quaternary structures are used in an analogy to that in structural biology to describe the hierarchy in Nature, but they differ in their detailed structure and length scale. Therefore, it is not only important to design the molecular chemical structures held by strong chemical bonds, but it is also essential to engineer the intermolecular physical interaction to induce these molecules to form self-assembled objects and construct macroscopic structures in a reversible and versatile way. Experience suggests that the desired performance that exists at the molecular level is not automatically and necessarily transferred and amplified to structures of higher hierarchy across the length scale to provide the desired macroscopic property. A successful molecular design that achieves predicted properties requires a highly integrated and intelligent approach. In an effort to rationally deduce
this complex process, a “RETRO-FUNCTIONAL ANALYSIS” approach is proposed and described in this Chapter. This approach has guided us and helped develop novel functional hybrid materials possessing exceptional properties.

Retro-functional analysis in advanced material design is defined as the function-oriented molecular design principle that combines molecular function and structure engineering across many length scales. The basic philosophy underlying the retro-functional analysis approach is that (1) the development of materials should be function-oriented; (2) the construction of materials should be modular and efficient; (3) the components of building blocks should be well-understood in terms of their mutual interaction and molecular functions; and (4) using the physical interaction principle, the building blocks will be assembled into proper hierarchical structures so that the molecular function are transferred and amplified into desired macroscopic properties. This philosophy should be able to guide future innovations to provide molecular designs that are otherwise not obvious or apparent from a conventional point of view.

The strategy for retro-functional analysis is outlined in Scheme 4.1. The molecular design starts from the analysis of a desired function with specific macroscopic properties. To achieve that property, a specific macroscopic phase structure is usually highly desired, while certain molecular functions are necessary. In an analogy to the “retro-synthetic analysis” in total synthesis, the concept of synths is used to represent the building blocks of functional materials, which can be categorized into two types depending on their role in the final molecular design: (1) functional synths that possess certain specific molecular functions, such as redox activity, π-conductivity, etc.; and (2) structural synths that possess well-defined physical interactions for supramolecular

engineering into specific macroscopic phase structures with desired orders. The size scale of synthons is hierarchical in nature. It can be an atom, certain parts of a molecule, a specific molecule, or even supermolecules, such as several molecules held together via physical interactions. A library, or tool box, of such synthons can be established with well-characterized state-of-the-art understanding and knowledge. Selected synthons can then be put together to create a molecular scaffold that is expected to provide an ordered arrangement of functional synthons with the aid of (or in the template of) structural synthons. The detailed chemical structures will then be deduced based on the scaffold by selecting the desired structural and functional synthons, which provide a class of detailed structures with similar properties. This strategy has been successfully applied to the development of soft fullerene materials in this research (Figure 4.1).

The emergence of “click” chemistry\(^{58}\) is a natural integrated component in this retro-functional analysis, since it offers a modular approach to link these synthons in an ordered, predetermined manner and greatly simplifies the material synthesis. With the
enormous knowledge accumulated on the understanding of structure-property relationships and the various types of “click” chemistry reactions available, this retro-functional analysis approach allows us to focus on the function of the final materials in the molecular design with proper phase structures to exhibit the optimal functional properties on the macroscopic scale, rather than the synthesis and chemical structures of the materials.

4.1 Physical Principles

The formation of hierarchical structures in different length scales critically relies on non-covalent interactions, which are physical bonds. A deep understanding of such non-covalent interactions is necessary for the molecular design and supramolecular engineering of functional materials. The general aspects of non-covalent interactions are summarized and briefly compared in Table 4.1.
<table>
<thead>
<tr>
<th>Name</th>
<th>Energy</th>
<th>Directionality</th>
<th>Origin</th>
<th>Length Scale</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals Force</td>
<td>&lt; 5 kJ/mol</td>
<td>No</td>
<td>Electron cloud polarization-induced; weak electrostatic attraction</td>
<td>Several Å</td>
<td>Ubiquitous; decays rapidly with distance</td>
</tr>
<tr>
<td>Hydrogen Bonding (D-H···A)</td>
<td>~ 4 - 120 kJ/mol</td>
<td>Yes</td>
<td>Weakly electrostatic</td>
<td>5 Å</td>
<td>Masterkey in supramolecular chemistry</td>
</tr>
<tr>
<td>Halogen Bonding (D-X···A)</td>
<td>~ 5 - 180 kJ/mol</td>
<td>Yes</td>
<td>The tendency of halogen atoms to interact with atoms possessing lone electron pair</td>
<td>~2-5 Å</td>
<td>Effective and reliable, similar to hydrogen bonding</td>
</tr>
<tr>
<td>Ion-dipole Interactions</td>
<td>~ 50 - 200 kJ/mol</td>
<td>Yes</td>
<td>Electrostatic attraction between an ion and a neutral molecule that has a dipole</td>
<td>~0.1-10 nm</td>
<td>Medium range interactions (~1/r²), important in solvation processes</td>
</tr>
<tr>
<td>Ion-Ion Interactions</td>
<td>~ 100 - 350 kJ/mol</td>
<td>No</td>
<td>Electrostatic attraction/repulsion</td>
<td>~0.1-10 nm</td>
<td>Basis for the formation of ionic structures and colloids</td>
</tr>
</tbody>
</table>
Table 4.1. Comparison between different non-covalent interactions (continued).

<table>
<thead>
<tr>
<th>Name</th>
<th>Energy</th>
<th>Directionality</th>
<th>Origin</th>
<th>Length Scale</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole-dipole Interactions</td>
<td>~ $5 - 50$ kJ/mol</td>
<td>Yes</td>
<td>Attractive interactions from either a single pair of poles on adjacent molecules (type I) or opposing alignment of one dipole with the other (type II)</td>
<td>~ $0.1 - 10$ nm</td>
<td>Significant in solid state; relatively weak in solution</td>
</tr>
<tr>
<td>Cation- π Interactions</td>
<td>~ $5 - 80$ kJ/mol</td>
<td>Yes</td>
<td>The face of an electron-rich π system with an adjacent cation</td>
<td>&lt; 1 nm</td>
<td>Strong in transition metals; weak in alkaline and alkaline earth metal cations</td>
</tr>
<tr>
<td>π - π Interactions</td>
<td>~ $0 - 50$ kJ/mol</td>
<td>Yes</td>
<td>Electrostatic intermolecular overlapping of p-orbitals in π-conjugated systems</td>
<td>~ 3-5 Å</td>
<td>Important in understanding organic electronic materials</td>
</tr>
<tr>
<td>Metal-ligand Coordinations</td>
<td>Varies with metal, ligand, and coordination number</td>
<td>Yes</td>
<td>Lone electron pair occupying the empty orbitals</td>
<td>Several Å</td>
<td>Important in crystal engineering and supramolecular self-assembly</td>
</tr>
<tr>
<td>Hydrophobic effect</td>
<td>&lt; $40$ kJ/mol</td>
<td>No</td>
<td>Nonpolar molecules that tend to minimize unfavorable interaction with solvent</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
The physical interactions, though distinctly different from strong chemical bonds, dictate the formation of hierarchical orders and the phase structure of a material, which in turn determines the transfer and amplification of the microscopic functions to macroscopic properties of materials. These interactions can be classified by their nature, origin, strength, and operating length scale. Manipulating these interactions at different length scales can help tune the hierarchical structure of the materials. In this section, a brief discussion on these interactions will be given.

On the molecular scale, van der Waals forces, dipolar interaction, and hydrogen bonding, are the major non-covalent interactions. The common feature of these interactions is that their strength depends critically on distance, typically at a fraction of a nanometer. Though they are weak, they are very important in self-assembling the molecules into the secondary and tertiary structures, and the macroscopic properties are determined by the structures on all of these different hierarchical scales. The influence of van der Waals interactions is profound in the chemistry and physics world. For example, van der Waals forces have been found to be responsible for the Gecko’s power to defy gravity. Such a small force, when used and aligned collectively, can create huge adhesion forces while its weak nature makes it easy to peel off under certain conditions. Hydrogen bonding has been recognized as the master key in supramolecular chemistry, simply because it is so versatile. For example, though weak by itself, when being engineered to give multiple complementary electron donor-acceptor (D-A) structures, hydrogen bonding can generate dynamic linkages as strong as a covalent bond, yet still readily susceptible to break under certain conditions, such as addition of a hydrogen-bonding solvent or increasing temperature. It is also evidenced by its significance in
maintaining the DNA double helix and the secondary/tertiary structures (α-helix, β-sheet, etc.) of proteins and by the success in synthesis of supramolecular polymers, as demonstrated by Lehn and Meijer et al.\textsuperscript{203} Halogen bonding is not new, but the recognition of its importance is relatively recent.\textsuperscript{197} It is similar to hydrogen bonding but the electron acceptor (Lewis acid) in this case is a halogen atom. Its existence may be easily overlooked, but in fact it is essential in certain cases such as enzyme active sites. Dipole-dipole interactions are very useful and relatively strong. The antiparallel packing of cyanobiphenyl derivatives due to strong quadruple dipole-dipole interactions is responsible for the formation of liquid crystalline phases in its alkyl derivatives. Metal-ligand coordination can be either weak and reversible or strong and irreversible, depending on the type of metal and ligand used. With the presence of a metal (and also the possibility to put different metal atoms in the different positions of the molecule) as building block, it represents an interesting and useful tool to create self-assembled structures, especially when they are pre-organized to do so. Well-known examples include Stang’s work on the formation of cyclics from a simply pre-organized, rigid ligand,\textsuperscript{204} Fujita’s work on the formation of large cage entities from a 3D self-assembling monomer,\textsuperscript{205} and Newkome’s work on hexamer formation from the \textit{bis}-terpyridine compounds.\textsuperscript{206} The ion-ion interactions are less explored in supramolecular chemistry because the interaction is non-directional, strong, and difficult to handle, particularly in polyelectrolyte systems. Nevertheless, molecules designed to possess both positive and negative charges in the same molecule, but being strategically put in a spatially-controlled way are of great interest. It shall provide insights into the importance of ionic interactions in the formation of higher structure as in proteins. The ion-dipole
interactions are prevalent in supramolecular science. It was the discovery of crown ethers and cavitands that selectively bind to certain types of cations that initiated this active and fast-growing research field.\textsuperscript{194} The $\pi$-$\pi$ interaction may have interaction energy from almost zero to 50 kJ/mol, depending on the way two $\pi$-conjugated systems interact with each other (e.g., face to edge or face to face) and the size and electronic structure of the $\pi$-conjugated systems.\textsuperscript{200} This large, anisotropic interaction leads to their preferred face-to-face continuous stacking, key to the formation of discotic liquid crystals. This tendency is more evident in large $\pi$-conjugated systems. The interactions of electronic structures can be elucidated by the example of complexation between electron-rich benzene ring and electron-deficient hexafluorobenzene ring with energy around 3.7–4.7 kJ/mol.\textsuperscript{207} In comparison to the melting point of 5.5 °C for benzene and 3.7 °C for hexafluorobenzenes, the complex has a melting point as high as 23.7 °C. A combination of two factors can substantially increase the interaction energy, as seen in the case of perylenediimide derivatives. The center perylene moiety is relatively electron-rich while the side imide moieties are relatively electron-deficient. The face-to-face interaction with a slight offset generates the maximum interaction energy. The high asymmetry of interactions leads to the preferential growth of single crystals along one direction, giving rise to so-called “low-dimensional organic semiconductor materials.”\textsuperscript{208}

When considering the interactions on a larger length scale from a few nanometers to micrometers, other types of interactions have proven to be effective. For example, the hydrophobic effect, close packing of molecules of specific shapes, and microphase separations come into play on this length scale. These interactions can be viewed as a result of collective interactions on a smaller length scale, such as van der Waals,
hydrogen bonding, and others. Hydrophobic effects are generally related to the exclusion from polar solvents, particularly water, of the weakly solvated entities. It is crucial in the formation of ordered structures from surfactants and lipid molecules as well as in the binding of organic guests by cyclodextrins and cyclophanes in water.\textsuperscript{194} This interaction has two origins: enthalpic and entropic. The enthalpic origin involves the stabilization of water molecules to be excluded from the surface of the hydrophobic part, since they do not like each other. The entropic origin arises from the fact that such a release of water from the hydrophobic part causes an entropic gain and is thus a favorable process. By maximizing favorable isotropic van der Waals interactions, close packing is a significant driving force for self-assembly in order to construct solid state structures, such as in the process of crystallization. As a result, crystal structures always have minimum free volumes. The overall geometric shape of molecules plays an important role in this case. This is particularly important when the molecules are shape-persistent and of high conformational rigidity.\textsuperscript{209}

In the case of macromolecules, nanoscopic and microscopic phase separations in block copolymers and polymer blends possess technological importance in practical applications. Similar to the hydrophobic effect, both enthalpic and entropic effects contribute to their physical behavior to reduce the unfavorable mutual interactions. The enthalpic interaction term can be simplified using the Flory-Huggins factor ($\chi$) in polymers. The larger the $\chi$ is, the more they repel each other. The entropic side is critically related to the degree-of-polymerization, $N$. When $N$ increases, they are more prone to be phase separated. At small $N$, strong $\chi$ is required to facilitate the nanophase separation. The key feature that distinguishes a polymer from small molecules is that
they are long-chain molecules. The *physical non-covalent interactions* of the monomer units on the polymer chain, as well as their *properties*, can act *cumulatively*, *cooperatively*, and *complementarily* to exhibit a *collective* behavior. This is evidenced by Swager’s development of chemical sensors based on a conjugated polymer structure for their amplified response towards foreign stimuli.\textsuperscript{210,211}

The development of supramolecular chemistry in the past decades has tremendously advanced our understanding of non-covalent interactions -- their origin, what they can do, and how they are related to the detailed chemical structures. The current challenge is to use the understanding of these interactions to engineer both at the molecular and supramolecular level across hierarchical length scales to tune the phase and structures of the materials and eventually to control the macroscopic properties and functions of materials.

4.2 Building Blocks: Functional Synthon and Structural Synthon

The essence of the the retro-functional analysis approach is that it is a function-oriented, modular approach taking into consideration the desired self-assembled structures from the primary to quaternary structures. Basically, the building blocks in functional materials can be divided into two classes: functional synthon and structural synthon. *Functional synthons* are molecular entities that possess certain specific active functions and *structural synthons* are molecular entities that possess well-defined physical interactions for supramolecular engineering to achieve specific phase and object structures with desired orders.
Functional synthons refer to function only, which does not discriminate on the basis of molecular size. The smallest functional synthons are those functional groups such as carboxylic acids, amines, thiols, possessing specific reactivity and physical properties. Functional synthons can also be part of the molecule or a particular arrangement of functional groups responsible for the desired property, such as the active sites in an enzyme, conjugated π-segments capable of absorbing light, peptide sequences that can be recognized by cells, and groups showing high fluorescence. The functional synthons also include individual molecular entities, such as C₆₀, carbon nanotubes, a protein within a larger complex. Ever larger functional synthons are supramolecular assemblies, such as protein complexes, gold nanoparticles, quantum dots, and micelles. The future materials will not be limited to molecular entities but will also include supramolecular entities as building blocks.

This is exactly what Nature does. For example, the organization of an intelligent species like a human being starts from the smallest molecules, such as lipids and amino acids, which self-assemble into bilayered membranes and protein complexes, respectively, each performing a certain function (compartmentation, enzyme activity, etc.). These constitute the cells that can perform specific functions (red blood cell, osteoblast, T-cell, etc.). The cells form tissues to perform a complex function at a larger scale as a whole, such as parenchyma to assimilate and store reserve food materials and chlorenchyma to conduct photosynthesis. Then, organs are a collection of tissues joined in a structural unit to serve a common, even more complex function, such as the circulatory system and the endocrine system in animals. Only the cooperative workings of organs can lead to a living species, and intelligent species will then be possible.
The functional synthons can be categorized by the functions they serve or possess. However, the categorization will be by no means comprehensive because both the functions that one expects from molecules and that the molecules possess change with time and new synthons continue to emerge. Meanwhile, materials are often multifunctional, meaning that they can be simultaneously classified in different categories. Nevertheless, such a classification is essential and helpful. It will provide a clear idea on what kinds of materials are available for specific functions and what kinds of macroscopic properties they possess. In addition, they can be related to specific molecular entities with detailed chemical structures in each category, facilitating future modular construction of functionalities.

With the non-covalent interactions well-understood and related to molecular structures, one is able to tune, or even design interactions by modifying chemical structures. Molecular moieties that lead to specific phase and object structures via defined interactions are named “structural synthons.” For example, mesogens in liquid crystals are a typical class of structural synthons. Similar to functional synthon, structural synthon refers to their structure-forming ability only.

Since structure is hierarchical, structural synthons also have different sizes, each governing the structure at a specific length scale. At the sub-molecular level, these can be categorized by interactions as hydrogen bonding synthon, halogen bonding synthon, \( \pi-\pi \) stacking synthon, and dipolar synthon. At the molecular level, van der Waals forces and close packing reign, which critically depend on their complementary shape and chemistry. The overall molecular shape plays a critical role here, so there could be a class called “shape synthons” at this level. They are important in dictating the 3D
packing of molecules to form phases and structures. At the supermolecular level, on the other hand, interactions such as hydrophobic, hydrophilic, fluorophobic, fluorophilic, crystalline close-packing, phase separation, and micellization come into play. Synthons can thus be categorized as such.

It should be recognized that functional synthons and structural synthons are not distinctly separate. They are characterized by their role in the final designed materials. Certainly, any synthons placed on the molecules or supramolecular assemblies contribute more or less to the final structural formation and phase behavior. In other words, a functional synthon can also play the role of a structural synthon while a structural synthon may or may not be a functional synthon. The question arises then, why do we need to distinguish them? The rationale lies in simplicity. A clear distinction between the two will rationalize and aid in the modular design of materials. The categorization will provide a readily available toolbox with well-understood properties. What is more important is that it can drive future innovation to both add new synthons to the toolbox and afford novel hybrid material architectures that are otherwise not apparent (examples will be given and discussed in the next section). This is in a sharp contrast to our current “trial-and-error” methodology and the effort to fit molecular design into our current synthetic scheme and knowledge, where incentives and guidelines for innovation are somewhat vague and disconnected from the final function.

4.3 Retro-Functional Analysis

When designing materials, one should always keep the desired function in mind and think hierarchically and dynamically to consider a three-dimensional atomic
organization, overall molecular shape, and mutual interactions, as well as the macroscopic self-assembled structure on different length scales. Both chemical and physical approaches must be integrated to achieve the goal. To illustrate the advantage of this approach, an example is given below (Scheme 4.2).

In this example, memory materials that would require a high dipole moment were the target. Molecularly, dipole moments result from the displacement of the center of positive charges and the center of negative charges. Structure-wise, the displacement should be large and permanent and should be spatially aligned in order to exhibit a macroscopic property. This can be achieved from long-range ordered structures, such as lamellar assemblies. The structural synthon that would lead to lamellar assemblies on this scale are mainly the phase separation synthons. This includes, for example, block copolymer synthons, amphiphilic synthons, and shape synthons. Block copolymers are known to be able to self-assemble into lamellar structures in the bulk or in thin film. However, their conformations are too flexible. The factors such as chain entanglements and the dipole interactions will make it difficult to align and maintain an ordered structure. In contrast, shape synthons contain moieties of well-defined, incompressible shapes. For example, linking two particles of similar size together could lead to lamellar assembly. If the positive charges and negative charges are separately located on two particles, a molecule with a huge dipole moment can be created. The designed molecular functional synthons in this case are positively charged groups, such as quaternary-amine groups, pyridium salt derivatives, etc. on one particle, and negatively charged groups such as carboxylates on the other particle. Combining the two, a basic molecular scaffold is generated. With a choice of each synthon from each category, the final structure can
Scheme 4.2. Example for retro-functional analysis in the molecular design of new materials. It should be noted that it is actually a library of compounds exhibiting similar properties. Only two of them, one based on POSS, the other based on C$_{60}$, are shown in Scheme 4.2 as an example. The former can be readily synthesized by sequential “click” reactions, but the latter has a novel structure not readily accessible and not apparent from a conventional design approach, which fuels the innovation to develop...
new chemistry as well as to set novel molecular architectures in challenging the synthetic chemists.

When applying this principle to the development of “soft fullerene materials,” the role of fullerene as both a functional synthon and a structural synthon should be first elucidated. As a functional synthon, C₆₀ is very versatile. The electronic applications require C₆₀ to maintain its 60 π-electrons conjugation as much as possible. But to serve as a structural synthon, multifunctionalization is always required, and the electronic properties might be sacrificed in this case. Pristine fullerenes, or fullerenes with minimum chemical modification, have a very strong tendency to aggregate and this special interaction should not be overlooked in the molecular design. One special feature about C₆₀ as a structural synthon is its perfectly spherical shape and conformational rigidity. C₆₀ is impenetrable, incompressible nanoparticle with a curved surface and possessing a defined molecular shape and size, which does affect the self-assembly process since they are so different from the random coil conformations in polymers. In summary, fullerenes are (1) highly hydrophobic; (2) of unique rigid three-dimensional structures; and (3) prone to irregular self-aggregation and phase separation from other components. To make them become integrated parts of the materials, the following strategies can be taken: (1) take advantage of the strong aggregation of fullerenes to interplay with other interactions, not counter each other in the formation of ordered structures; (2) introduce a conformationally rigid, incompressible, impenetrable counterpart in shape for fullerene to assist their packing into supramolecular assemblies; and (3) use chemical modification and covalent attachment to prevent macroscopic phase
separation. Examples for the design of “soft fullerene materials” using the retro-functional analysis are given in Schemes 4.3 and 4.4.

In our laboratory, it is of our great interest to create nano-capacitors which require separated nanolayers of conductors and insulators. The functional synthon in this case should possess electric conductivity and suitable synthons for this purpose includes fullerenes, carbon nanotubes, or $\pi$-conjugated molecules. The structural synthon should lead to a lamellar structure, which includes single crystal lamellae synthons and phase-separation synthons. It is known that semi-crystalline polymers can grow single crystal lamellae from dilute solution. The single crystal lamellae have a thickness of $\sim 10$ nm and lateral dimensions of several micrometers. In this case, if a semicrystalline polymer, say PEO, is chosen as the structural synthon, the molecular scaffold can be constructed as the end-capped PEO (PEO-$C_{60}$), as shown in Scheme 4.3. Crystallization should yield PEO single crystal lamellae with both top and bottom covered by $C_{60}$ conducting sheets. Many other structural synthons could also lead to phase separation into lamellar structure, such as block copolymer synthons, amphiphilic synthons, and shape synthons. In the case of block copolymers, when the functional synthon is connected to the junction point, after self-assembly it should be confined to the interface of two blocks and take the shape of the assembled structure, such as in the case of PS-$(C_{60})$-PEO. In the case of shape synthons, where $C_{60}$ is chosen as the conductor synthon, POSS can be introduced as the insulator synthon as well as a structural synthon in order to match $C_{60}$’s unique three-dimensional structure and assist its packing in the solid state. A detailed chemical structure based on this scaffold is shown in Scheme 4.3 with the side chains being non-interacting isobutyl groups and the linkage being a simple ester. This exemplifies the
Scheme 4.3. Retro-functional analysis for the design of fullerene materials possessing layered C$_{60}$ structure for application as super- or nano-capacitors.

modular nature and versatile features of this approach in the design of novel molecular architectures with desired structure and function.

In order to create an efficient photovoltaic material, a bicontinuous nano-phase-separated structure of donor and acceptor is highly desired. The functional synthons in this case are donor synthons and acceptor synthons, each containing a class of chemical structures. The types of phase-separation synthons that would lead to a bicontinuous nano-phase-separation includes block copolymer synthons, amphiphilic
Scheme 4.4. Retro-functional analysis for the design of molecular materials for efficient organic solar cell performance.

donors, acceptors, and shape synthons. Following an analysis similar to the last paragraph, three main molecular scaffolds are derived. Examples of two detailed chemical structures are shown (Scheme 4.4). The first one consists of a block copolymer with one block being poly(p-phenylene vinylene) modified with hydrophilic groups to ensure phase separation and the other block being C₆₀-tethered polystyrene. With proper composition, it should be possible to self-assemble into a bicontinuous structure with one phase rich in PPV, the
donor, and the other rich in C$_{60}$, the acceptor. The separated location of donor and acceptor in the hydrophobic phase and hydrophilic phase, respectively, would significantly avoid recombination. If porphyrin is chosen as the donor synthon and perylenediimide, as the acceptor synthon, their roles as structural synthons are recognized as a $\pi$-$\pi$ interaction synthon on the molecular level and as a discotic liquid crystal synthon on the mesoscopic level. Therefore, a dyad can be designed to form columnar liquid crystalline phase with separated, continuous porphyrin packing and perylene diimide packing.

The retro-functional analysis approach provides a rational and modular approach for the development of functional materials from a set of building blocks called functional synthons and structural synthons. The synthons include a library of entities (molecules and supramolecular aggregates) that possess certain functions (functional synthon) or lead to the formation of a specific structure and phase. It allows us to focus on function rather than the synthesis and detailed chemical structure in the design of materials by taking molecular function and self-assembled structure across different length scales into consideration in an integrated and balanced way. In this way, the supramolecular interactions are carefully engineered to achieve specific organization/arrangements of functional moieties to achieve designed functions. The emergence of click chemistry provides a simplified access to these compounds. Sometimes novel architectures and designs can be created that are otherwise not obvious from conventional design and not readily available from current synthetic techniques. In this case, it provides guidelines and targets to drive innovation in chemistry and material science in this particular direction. This is in sharp contrast to the current “trial-and-error”
approach to fit in our current knowledge of molecular design. Moreover, well-documented libraries of synths of all categories should facilitate the molecular design and even allow material design by computer in the future. This is user-friendly, and is especially useful for newcomers in the field. In addition, it should also facilitate interdisciplinary research in advanced materials. Using this approach, many molecular scaffolds have been designed as shown in Figure 4.1. There are essentially unlimited possibilities for molecular design. While there are many related projects on-going in our laboratory, the focus of molecular design and discussion will be limited within the scope of polymers in this dissertation (Chapters V, VII, and VIII).
CHAPTER V
MODEL “CLICK” REACTION WITH FULLERYNE01

The popularity of the “click” CuAAC chemistry did not reach fullerene derivatives for quite some time, probably due to the complications from the thermal [3+2] cycloaddition reaction with azide and the low solubility of fullerene derivatives in polar solvents commonly used for the “click” reaction. The first example in doing “click” chemistry with fullerene was probably reported by Adronov et al.\textsuperscript{213} to functionalize single-walled carbon nanotubes with well-defined PS-N\textsubscript{3}. But the system was not well-defined and it was not clear if the azide also react with carbon nanotubes directly at the reaction condition (60 °C for 24 h). In this dissertation, to address this issue, a model reaction between PS-N\textsubscript{3} and an alkyne-functionalized fullerene (Fulleryne01) was performed at room temperature. It has been shown that there was no cycloaddition reaction occurring at room temperature and the reaction was efficient, giving well-defined C\textsubscript{60}-end-capped polystyrenes. The results were published in 2008.\textsuperscript{14} Since then, many studies were reported in this area on the synthesis of fullerene-functionalized small molecules,\textsuperscript{214-218} star molecules,\textsuperscript{219-221} dendrimers,\textsuperscript{222} viral nanoparticles,\textsuperscript{223} and polymers.\textsuperscript{221,224} The method is very versatile in preparing fullerene hybrid materials and could be viewed as a general functionalization scheme for introducing fullerene into a functional material (Scheme 5.1). This Chapter is mainly adapted from our published

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Scheme 5.1. A general functionalization methodology for fullerene based on “click” chemistry.

paper on the model reaction between PS-N<sub>3</sub> and Fulleryne01 to show the efficiency of the reaction.<sup>14</sup>

5.1 Molecular Design and Synthesis of Fulleryne01

In order to apply CuAAC “click” chemistry to fullerene derivatives, alkyne-, or azide-functionalized fullerene had to be prepared. Since azide was known to react with C<sub>60</sub> at elevated temperatures,<sup>41</sup> alkyne-functionalized fullerenes were preferred to avoid this possible complication. Moreover, it also allowed the design of the alkyne structure to tune the reactivity of the alkyne in “click” reaction. For the sake of simplicity, the monoalkyne-functionalized fullerenes were named “fulleryne”. There will be numerous kinds of fullerynes, depending on the chemistry to functionalize fullerene and the distinct structures that can be created. The fullerynes can also be tailored to possess diverse functions, either photo-(in)active or electro-(in)active, for future incorporation into multifunctional materials. Moreover, incorporation of a higher number of alkyne functional groups was also possible and would be useful in the preparation of fullerene polymers and fullerene gels. The dialkyne-functionalized fullerenes were named “fullerdiyne” and the trialkyne-functionalized fullerenes were named “fullertriyne”,

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respectively. The synthetic steps towards the synthesis of fullerynes should be equally applicable to that of fullerdiynes and fullertriynes. The detailed investigation on the synthesis and structure of various fullerynes and fullerdiynes with diverse structures will be discussed in the next Chapter.

Both the mechanistic studies and experiments on the Huisgen cycloaddition reaction of an alkyne and an azide revealed that electron-deficient alkynes enhanced the rate of triazole formation under very mild reaction conditions. Therefore, the terminal alkynes with an adjacent carbonyl group, such as fullerene propiolates, were chosen as a prototype of the fullerynes. The structure and synthetic route to Fulleryne01 is outlined in Scheme 5.2. Rubin et al. have demonstrated that several stable ketone- and hydroxyl-functionalized fullerene derivatives serve as versatile synthons. The ketone-functionalized fullerene 1 was obtained in 59% yield from C₆₀, which was pretty good yield in comparison to most functionalization reactions on the C₆₀ core. The ketone functionality could undergo many reactions, such as reduction and nucleophilic addition; so it could serve as a versatile starting material for the preparation of other fullerene materials. For example, it was successfully reduced to an alcohol 2 in high yield (93%) using diisobutylaluminum hydride (DIBAL-H), which was reported not to interfere with the C₆₀ core. The fullerol 2 had a cyclohexane ring in the molecule, which made it stable towards the singlet oxygen generated by C₆₀ (Scheme 2.1). In this research, the fullerol 2 was further converted to Fulleryne01 using Steglich esterification with propiolic acid in a low yield of 17% (Scheme 5.2). Fulleryne01 was obtained as a brown powder that features high stability to moisture and air as well as enhanced solubility in common organic solvents, as compared to C₆₀.
Scheme 5.2. Model “click” reaction between Fulleryne01 and PS-N₃ prepared via ATRP. Reaction conditions: (i) 2-trimethylsiloxy-1,3-butadiene, toluene, reflux, 59%; (ii) DIBAL-H, r.t., 93%; (iii) propiolic acid, DCC, DMAP, r.t., 17%; (iv) NaN₃, DMF, r.t., >99%; (v) Fulleryne01, CuBr, PMDETA, toluene, r.t., 95%.

Fulleryne01 has been fully characterized by ¹H NMR, ¹³C NMR, FT-IR, UV-vis, and MALDI-TOF mass spectrometry. A comparison of the ¹H NMR spectra of 1, 2, and Fulleryne01 is listed in Figure 5.1, showing the progression of the reaction. Only three peaks were observed for 1, which is in good agreement with literature results.³⁷ After reduction, 2 was actually a racemate, showing complex coupling between hydrogen atoms. The peak at 5.35 ppm was assigned to the proton near the hydroxyl group (proton d in 2) and the proton at the hydroxyl group showed up at around 2.0 ppm (proton c in 2). The shift of the proton d to 6.20 ppm and the disappearance of proton c after esterification indicated successful reaction. The characteristic acetylene hydrogen atom was also clearly seen at 3.0 ppm.²²⁶ The ¹³C NMR spectrum of Fulleryne01 is shown in Figure 5.2. The existence of carbonyl carbon (163.50 ppm), sp² carbon on C₆₀ (134.83 – 156.30 ppm), sp³ carbon on C₆₀ (61.49 and 63.30 ppm), and alkyne sp³ carbon (71.85 and 74.57 ppm) are evident. The FT-IR spectrum (Figure 5.3) also confirmed the presence
Figure 5.1. $^1$H NMR spectra of 1 (a), 2 (b), and Fulleryne01 (c).

Figure 5.2. $^{13}$C NMR spectrum of Fulleryne01.
Figure 5.3. FT-IR spectrum of Fulleryne01.

Figure 5.4. UV-vis spectra of Fulleryne01 and PS-C$_{60}$ (2k). The inset shows the enlarged spectrum between 400 nm and 550 nm. Please refer to Section 5.2 for information on PS-C$_{60}$ (2k).
of carbonyl group (1710 cm$^{-1}$), alkyne group (2118 cm$^{-1}$), and C$_{60}$ (527 cm$^{-1}$). In MALDI-TOF mass spectrum, the monoisotopic molecular weight was observed at 844.13 Da, using DCTB as a matrix. This is in good agreement with the calculated molecular weight of 844.05 for the formula of C$_{67}$H$_8$O$_2$. The brown (in dilute solution), or wine-red (at higher concentration) color of its solution could be understood from its UV-vis absorption spectrum, which showed a small absorption peak at 433 nm in the visible light region (Figure 5.4). All of this characterization data unambiguously established the chemical structure of Fulleryne01.

The synthesis of Fulleryne01 using Steglich esterification was straightforward, but the yield of 17% was too low for a satisfactory overall process. The result was consistent with the literature on the DCC/DMAP mediated esterification of propiolic acid with phenolic derivatives, which gave the yields of 20~40%.

It could be attributed to the conjugated system of carbonyl and acetylene, making it susceptible to side reactions, such as Michael addition. Many methods were also tried to improve the yield. The acyl chloride route resulted in immediate formation of a resinous precipitate upon the addition of propynoyl chloride, and no product could be detected. The attempts using the mixed anhydride route were plagued by difficulty in purifying fullerene carbonochloridate and its re-dissolution in THF for reaction with sodium prop-2-ynoate. The low solubility of C$_{60}$-derivatives in terms of molar concentration made Fisher esterification in toluene very inefficient. However, using a special solvent and designed reactor, the yields of Fisher esterication were successfully improved from trace amounts to somewhere between 35% and 92%. The results will be further discussed in detailed in Chapter VI.
5.2 Model “Click” Reaction

The synthesis of azide-functionalized materials, ranging from small molecules to macromolecules, nanoparticles, and to various surfaces, is well-established.\textsuperscript{63,230} As a straightforward example to demonstrate the concept, an azide-functionalized polystyrene, prepared via ATRP and subsequent nucleophilic substitution, was chosen in the model reaction (Scheme 5.2). Since polymers are known for their decreased end-group reactivity, the result should also serve as a criterion for evaluating the efficiency of the reaction.

The synthesis of polystyrene using a commercially available ATRP initiator (ethyl 2-bromoisobutyrate, EBiB) was performed successfully with controlled molecular weight and narrow polydispersity ($M_w/M_n = 1.04$) by a reported procedure.\textsuperscript{231} A representative $^1$H NMR spectrum of the prepared well-defined PS-Br is shown in Figure 5.5. The peak at around 4.60 ppm could be assigned to the hydrogen atom on the methane group attached to bromo at one chain-end and the peak at around 3.70 ppm could be assigned to the methylene hydrogens at the other chain-end ester. The hydrogen atoms on the phenyl groups showed up at around 7 ppm. Their intergration ratio was used to determine the molecular weights of the polymers. It was in good agreement with the molecular weight determined from SEC. For example, for the target molecular weight at 2k, the molecular weight ($M_n$) was determined to be 2300 g/mol both by $^1$H NMR and SEC. The molecular weight control was achieved by controlling the conversion and polymerization time. Polystyrenes with three molecular weights were successfully prepared ($M_n = 2.3, 6.1, 10$ kg/mol) and they were denoted as PS (2k), PS (6k), and PS (10k).
Figure 5.5. $^1$H NMR spectrum of PS-Br (2k).

Conversion of the chain-end bromine group to an azide by nucleophilic substitution with sodium azide in DMF was effected in high yield. Purification was readily performed by precipitation into methanol several times. A representative $^1$H NMR spectrum of the PS-N$_3$ is shown in Figure 5.6. Compared to PS-Br, the chemical shift of the methine hydrogen bonded to the terminal benzyl carbon and to bromine shifted completely from 4.60 ppm to 4.00 ppm. The characteristic absorbance of the azide functionality in FT-IR spectrum could be clearly seen at around 2095 cm$^{-1}$ (Figure 5.7).

The click reaction was first performed at room temperature in toluene with CuBr/PMDETA as the catalyst (Scheme 5.2). For PS (2k), excess of PS-N$_3$ was used to in order to determine if there was any side reaction between azide and C$_{60}$ core. It was found that there was no [3+2] cycloaddition reaction between the PS-N$_3$ and the fullerene.
Figure 5.6. $^1$H NMR spectra of Fulleryne01, PS-N$_3$(2k), and PS-C$_{60}$(2k).

Figure 5.7. FT-IR spectra of the PS-N$_3$ (2k) and the PS-C$_{60}$ (2k), verifying the loss of the azide (2095 cm$^{-1}$) and the addition of C$_{60}$ (528 cm$^{-1}$) functionality.
core, even with excess of PS-N₃, as evidenced by TLC (eluent: toluene; PS-N₃, Rᶠ = 0.90; PS-C₆₀, Rᶠ = 0.05) and other characterization techniques. The excess PS-N₃ was isolated by chromatography using toluene and the characterization results (¹H NMR, SEC, FT-IR) were exactly the same as the starting material. Further elution using toluene:ethyl acetate (v:v = 95:5) gave the desired PS-C₆₀ in 75% yield. When excess Fulleryne01 (1.1 eq) was used, the purification was readily performed by passing the products through a short silica gel column to remove the catalyst and excess starting material, followed by precipitation into methanol. The triazole product was obtained as a brown powder, readily soluble in common organic solvents such as THF, CH₂Cl₂, etc. The brown-colored solution indicated the covalent linkage of C₆₀ with PS (see Figure 5.4 for UV-vis). The click reaction was successfully carried out on PS-N₃ with three different molecular weights (Mₙ = 2.3, 6.1, 10 kg/mol). When excess Fulleryne01 was used, the yield of the final product was generally over 90%. Representative characterization results are presented below in the case of PS-C₆₀ (2k) (note: 2k refers to the molecular weight of the PS block alone).

The success of the cycloaddition was supported by evidence from ¹H NMR, ¹³C NMR, FT-IR, and MALDI-TOF mass spectrometry. The product exhibited characteristic resonances of protons both in benzylic 1,2,3-triazole (5.1-5.3 ppm for –CH(Ph)-triazole-, and 7.6-7.8 ppm for H at the triazole ring) and near the terminal C₆₀ unit (2.8-3.0, 3.3-4.0 ppm as compared to that of Fulleryne01) in ¹H NMR spectra (Figure 5.6).²²⁶ It also showed the sp³ carbons (60.2 and 64.0 ppm) as well as sp² carbons of the terminal C₆₀ unit (135-155 ppm overlapping with aromatic carbons) in ¹³C NMR spectrum (Figure 5.8).²²⁶ The FT-IR spectrum showed the complete disappearance of the azide (2095 cm⁻¹)
and the appearance of a sharp peak at 528 cm$^{-1}$, which is characteristic for fullerene C$_{60}$ (Figure 5.7). The most convincing evidence was from the MALDI-TOF mass spectrum, which showed a monomodal, very narrow distribution with molecular weight in accordance with the proposed structure (Figure 5.9). The Gaussian distribution of the molecular weights was due to the different chain lengths of the polymers obtained during the polymerization. The difference in molecular weight between the two neighboring peaks was 104.1, exactly that of a styrenic repeating unit. Despite the distribution, the chemical structure of the material was very homogeneous and uniform. In other words, all the polymers in the sample possessed the same chemical structure with the only difference being the chain length, i.e., the number of styrene repeating units. For example, the 15mer with silver ion has a formula of C$_{193}$H$_{139}$AgN$_3$O$_4$ with the calculated molecular weight of 2669.0. A monoisotopic peak was observed at $m/z$ 2668.9, as shown in Figure 5.9. This good agreement again confirms the cleanliness of the reaction and the stability of the resulting fullerene polymers upon storage and ionization (Figure 5.9).

Considering the fact that MALDI-TOF mass spectrometry can detect impurities as low as 1% and that the starting materials (homopolystyrene and Fulleryne01) have much lower molecular weight and thus should be much easier to ionize, these results provide proof that the samples were free of homopolymer. These results thus unambiguously established the structure, uniformity, and purity of the polymer obtained.

The PS-C$_{60}$ was quite stable towards singlet oxygen. It could be handled without special precautions to exclude oxygen. The ease of reaction and purification, along with the high efficiency in the final coupling step (> 90% for CuAAC, Scheme 5.2) made it a viable and general method to incorporate fullerene into functional materials. This
Figure 5.8. $^{13}$C NMR spectra of PS-N$_3$(2k) and PS-C$_{60}$(2k).

Figure 5.9. MALDI-TOF mass spectra for PS-C$_{60}$(2k).
method is particularly useful when the materials to be functionalized are unstable under more drastic reaction conditions (e.g., biological molecules), or when the products are very difficult to separate (e.g., polymers), or when the materials are heterogeneous (e.g., surfaces, nanoparticles, etc.).

5.3 Unusual SEC Observations

To illustrate the basic physics of fullerene polymers, model compounds with 100% fullerene functionality, well-defined structure, and narrow polydispersity are highly desired. The fullerene polymers obtained in this research serve as excellent model compounds. Sometimes, well-defined fullerene polymers can show significantly different behavior than those contaminated by impurities such as homopolymers or multiadducts. Indeed, unusual, interesting phenomena were observed in SEC. As expected, the samples gave monomodal, symmetric peaks with narrower polydispersity (1.02 for 2k and 1.01 for 6k and 10k) than the corresponding PS-N3 (1.04 for 2k and 1.03 for 6k and 10k) (Figure 5.10). Contrary to literature reports that the retention volumes of C_{60}-end capped polystyrenes corresponded well with that estimated from the parent polystyrenes, a difference is significant for $M_w$ 2k but less so for $M_w$ 6k; there is no difference for $M_w$ 10k. Normally, when the molecular weight of a polymer increases, the hydrodynamic volume would increase while the retention volume would decrease. The unusual results indicated (1) no aggregation of PS-C_{60} in THF occurred and (2) there seemed to be a very small, even negative impact of the C_{60} unit to the overall hydrodynamic volume of the polymer. There were two possible reasons: (1) since THF
was a non-solvent for C\textsubscript{60} but a good solvent for polystyrene, the polystyrene chain may have tended to wrap around the buckyball in dilute solution due to $\pi$-$\pi$ interactions to keep solvent molecules away from C\textsubscript{60}, resulting in decreased hydrodynamic volume; at low $M_\text{w}$, it resulted in decreased hydrodynamic volume while at high $M_\text{w}$, the influence of end-groups became insignificant; (2) the C\textsubscript{60} unit might possess specific interaction with the SEC columns which delayed the polymers’elution. Due to the small size of the polymers with low molecular weight, it was difficult to use light scattering techniques to characterize the system to verify the first rationale. As will be discussed in Chapter VII,
C\textsubscript{60} indeed shows little influence on the overall hydrodynamic volume (and thus retention volume) of the polymer in most fullerene polymers, although it indeed induces aggregation in certain cases if the polymers are immiscible with C\textsubscript{60}. The results indicated that high purity polymers are a prerequisite in physical studies to elucidate the underlying basic physical principles.

5.4 Summary

As a model system to demonstrate the idea of applying “click” chemistry to fullerene materials, Fulleryne01 was designed, synthesized, and reacted with PS-N\textsubscript{3} to afford a C\textsubscript{60}-end-capped polystyrene. The carbonyl group near the alkyne in Fulleryne01 significantly enhanced the alkyne’s reactivity and enabled the efficient cycloaddition reaction at room temperature with yields up to 95%. There was no [3+2] cycloaddition reaction between azide and double bonds on C\textsubscript{60} core under these conditions. No fractionation was necessary in the purification. The PS-C\textsubscript{60} obtained possessed 100% fullerene functionality and well-defined structure, free of homopolymers and higher addition products, as demonstrated by SEC and MALDI-TOF mass spectrometry. The pure PS-C\textsubscript{60} exhibited unusual SEC results: their retention volume increased as compared to their parent polymer PS-N\textsubscript{3}, although their molecular weights were much higher. The method represents an efficient, mild, and modular approach to incorporate fullerene into other functional materials and might be particularly useful in materials whose structural or functional properties might be compromised by degradation under drastic reaction conditions.
CHAPTER VI
FINDING FULLERYNES

In the model reaction discussed in Chapter V, Fulleryne01 was shown to be a very useful fullerene derivative with high reactivity in “click” reaction. It “clicked” to azide-functionalized polymers in high efficiency (over 90% yields in the final coupling step) and gave well-defined product with 100% fullerene functionality. In this way, no complicated purification procedures, such as fractionation, were necessary. It has many advantages for a variety of applications. However, its practical application was first hindered by its availability. The 17% yield in the Steglich esterification was a bottleneck in the overall process. The solutions to this problem were based on two different approaches. First, alternative synthetic methods were explored for more efficient preparation of Fulleryne01. This has been successfully achieved by a special reactor design to remove the trace amounts of water from the system and drive the equilibrium of Fisher esterification far to the product side. The yield was significantly improved up to 92%. Second, fullerenes with different structures were designed and synthesized with better synthetic facility and high chemical reactivity in the CuAAC reaction. In addition, multialkyne-functionalized fullerenes (e.g., fullerdiynes and fullertriynes) were also designed and some of them have been successfully synthesized. The details of both approaches are presented in this Chapter.
6.1 Improved Synthesis of Fulleryne01 by Fischer Esterification

Previous work in our group has demonstrated the power of “click chemistry” in the incorporation of fullerene into functional materials, using Fulleryne01;\textsuperscript{14} however, the synthesis of Fulleryne01 was plagued by the low yield (~17%) in the esterification step. Many methods have been tried, but most of them were in vain because the carbonyl group also activates the alkyne towards side reactions, such as Michael addition.\textsuperscript{228}

The Fisher esterification is a classic reaction and has been used to synthesize propiolates, generally in high yield. It is known to be an equilibrium reaction between an alcohol and an acid to give the desired ester and water under the catalysis of acidic species (Scheme 6.1).\textsuperscript{234} The higher concentration of the starting materials, the more products it will form when reaching equilibrium. A common method to improve the efficiency is by continuously removing the water generated from the system and thus shifting the equilibrium far to the right. Fisher esterification works well with large scale preparations where significant amount of water are generated and removed. The Dean-Stark apparatus is often used in the laboratory to remove water by azeotropic distillation from toluene or benzene. In general, the laboratory scale for reaction involves grams of sample.

Scheme 6.1. Synthesis of Fulleryne01 by Fisher esterification.
At first, it does not seem to work for fullerene derivatives since they usually have low solubility in toluene, benzene, etc. in terms of molar concentration. For example, the solubility of $C_{60}$ is only $2.1 \times 10^{-4}$ mol/L (1.7 mg/mL) in benzene and $4.0 \times 10^{-4}$ mol/L (2.8 mg/mL) in toluene (Table 2.1, P10). Furthermore, fullerene derivatives are not usually readily available in gram quantities. If the reaction is run at several hundreds of milligrams scale, considering the high molecular weight of fullerene derivatives (e.g., 792 Da for 2), the water generated in this case is only at the milligram scale, which is almost impossible to phase separate from toluene and be removed. For example, the water generated from the reaction between 0.2 g of 2 and propiolic acid will be 4.5 mg, assuming 100% yield. If the solubility of 2 is similar to $C_{60}$ in toluene (2.8 mg/mL), the saturated toluene solution will have a volume of 71 mL, corresponding to a weight of 61.4 g (density of toluene is 0.86 g/mL). The concentration of water in toluene will be 0.0073 wt%, far below the solubility limit of water in toluene (0.033 wt%). As a result, the reaction will be extremely sensitive to any residual moisture in the system. It was thus not practically viable. Indeed, in a trial run of the reaction in toluene using a Dean-Stark apparatus overnight, there is only trace amount of product formation observed, even after activated 4 Å molecular sieves were used in the Dean-Stark apparatus to remove the water. Therefore, due to all of these difficulties, there has not been any report on the application of Fisher esterification to the synthesis of fullerene derivatives.

Despite all of the above-mentioned difficulties, there was still possibility to modify the reaction conditions to completely excluding moisture from the system so as to drive the reaction to product formation. With training in anionic polymerization where the most stringent reaction conditions are required to exclude oxygen and moisture, it was
possible to do so with glass-blowing and high vacuum line techniques. The basic idea is that if water can be completely removed from the system (down to ppm level), the reaction should still work. After all, it is an equilibrium reaction. To address this, two strategies were used: (1) a special reactor (Figure 6.1) was designed based on our understanding of the reaction mechanism and made by glass blowing techniques; (2) a relatively good solvent for $C_{60}$, 1-chloronaphthalene, was used. The solubility of fullerene is generally low in terms of molar concentration. The highest solubility reported so far is 51 mg/mL ($97 \times 10^{-4}$ mol/L) in 1-chloronaphthalene, which is a chlorinated aromatic solvent with a very high boiling point ($236^\circ$C) and inert under most of conditions. It was thus chosen as the reaction medium. Toluene was still used, mainly for azeotropic distillation to remove water from the system. The method proved to be effective to drive the reaction equilibrium far to the product side, increasing the yield from only a trace under conventional conditions to 92% under the above conditions.

Figure 6.1 shows the schematic drawing of this reactor and Figure 6.2 shows a real working reactor. It is composed of three flasks. Flask A is the reaction flask; flask B is the water-removal flask; flask C is the toluene reservoir flask. The three flasks form a circulating system where toluene can go from A to B to C and then back to A. All the reactants and solvents were carefully purified and thoroughly dried before reaction. The reactor was attached to vacuum line and flame dried several times to exclude any moisture residue trapped in glass. The reactants were placed in flask A and the dried, activated 4 Å molecular sieves were placed in flask B. The toluene was transferred in by vacuum distillation. The system was placed under slight vacuum to facilitate toluene
Figure 6.1. Schematic drawing of the reactor setup for Fisher esterification to prepare Fulleryne01.

Figure 6.2. The actual glass reactor used for the Fisher esterification to prepare Fulleryne01.
circulation. After flame-sealing off from the line, the reaction was then carried out in flask A while the removal of water by activated 4 Å molecular sieves was conducted in flask B. The toluene distilled to flask C, condensed, and flowed back to the flask A where reaction takes place. This cycle continuously removes trace amounts of water out of flask A and the reaction was pushed to completion.

The reaction required high temperature to achieve reasonable rates. The reaction was thus carried out under a slightly reduced pressure to maintain reflux conditions at around 90~100 °C. Different drying agents were tried in flask B. Phosphorous pentoxide seemed to generate side reactions because after reaction, the acetylene proton could not be observed in the product. It was speculated that some volatiles might have been generated and distilled back to flask A to cause undesired reactions. Calcium hydride easily reacted with the propiolic acid that could be distilled to flask B little by little. Molecular sieves were inert and efficient, fitting this purpose very well.

An additional advantage is that after reaction, the reaction mixture can be directly applied to the top of a silica gel column and eluted with hexanes first to recover the chlorinated solvent while the product can be obtained by further elution by toluene/cyclohexane = 1:1 (volume ratio). The unreacted starting material 2, can be recovered by eluting with toluene and subject to further reaction to increase the overall yield.

The reaction has been carried out on a scale from 200 mg to 500 mg. It was found that it required special attention and skillful practice to exclude moisture as much as possible from the system in order to achieve good results because the water generated was only at the milligram scale. The yield was sensitive to how careful one was during
the experiment. The best yield was 92% in a single run; while the worst yield was around 35%, which was still much better than that by Steglich esterification since the starting materials could be recovered. It shows that based on an understanding of reaction mechanism, careful manipulation of experimental conditions can lead to significant improvements in processes.

6.2 Molecular Design of Fullerynes

Through improvement using Fisher esterification, Fulleryne01 could now be prepared in gram quantities. However, the stringent requirement in reaction conditions made it difficult for people without expertise to repeat this reaction with high yield and the use of a toxic, halogenated solvent was not desired for both safety and environmental considerations. It was our hope to find fullerynes that are readily available from C₆₀ (synthetic facility), very reactive (chemical reactivity), and can be multifunctional (material functionality). To this end, a variety of different fullerynes were designed and synthesized with the chemical structures as shown in Figure 6.3.

The design of fullerynes followed these criteria: (1) the electronic properties of C₆₀ should be influenced to the least level; (2) minimum chemical functionalization, i.e., fewest step and highest yield, is desired; (3) the linkage between fullerene core with alkyne should be as simple as possible; (4) if possible, it should allow multifunctionalization with high and orthogonal reactivity; and (5) multi-alkyne-functionalized C₆₀ as interesting targets could be prepared accordingly.

The reason that the esterification of Fulleryne01 was plagued with low efficiency in Steglich reaction was that the carbonyl group adjacent to acetylene group activated the
alkyne, making it a reactive substrate for other side reactions, such as Michael addition. To avoid it, spacers such as methylene groups can be added between the carbonyl group and the alkyne group (Fulleryne02), yet the reactivity might be compromised. To maintain a high reactivity, it is more preferable to use σ-electron-withdrawing groups, such as hydroxyl group (Fulleryne03), fluorine (Fulleryne04), etc. The existence of a hydroxyl group also allows the installment of other functionalities onto fullerene, such as a bromine group (Fulleryne05). Fulleryne05 was designed with a highly reactive bromoacetyl ester group, which could be readily transformed into other functionalities by highly efficient nucleophilic substitution.\textsuperscript{37} Due to the banana-type bonding in cyclopropane rings,\textsuperscript{237} methanofullerenes with a cyclopropane linkage maintained the π-conjugated system much better and thus preserved the electronic properties much better. Fullerynes with such a linkage are also of great interest (Fulleryne06).

The design and synthesis of multi-alkyne-functionalized fullerenes, such as fullerdiynes and fullertriynes, should follow the same design principles and preparation
procedures described for other fullerenes. The chemical structures of some fullerdiynes are shown in Figure 6.4. They can be either well-defined molecule (Fullerdiyne01) or a mixture of regio-isomers (Fullerdiyne02 and Fullerdiyne03), depending on the chemistry to synthesize them.

Figure 6.4. Chemical structure of fullerdiynes.

The reactivity of double bonds on C₆₀ is known to be similar to that of an electron-deficient olefin. Alkynes and olefins both contain unsaturated carbon-carbon bonds and are susceptible to similar reactions. When chemically modifying C₆₀ to attach an acetylene group, it is necessary to avoid any side reactions associated with the alkyne group. Therefore, one can either use a protection-deprotection scheme or use a post-functionalization method to attach alkyne functionalities, both of which increase the reaction steps and decrease the overall yield and efficiency. It is highly desirable to find reagents and reactions that differentiate the reactivities of the acetylene groups and the C₆₀ double bonds to facilitate the synthesis. To this end, two chemistries were found to be effective: the addition of 1-ethynylmagnesium chloride to a ketone and the cyclopropanation by malonate esters. The synthesis and characterization of selected fullerenes will be presented in the following sections.
6.3 Fulleryne03

1-Ethynylcyclohexanol derivatives are known to possess high reactivity towards the CuAAC reaction\(^7\) however, the synthesis of its fullerene derivative seemed difficult at first, since any reaction intermediate that reacts with C\(_{60}\) might react with the acetylene group as well. Fulleryne03 is an ethynylcyclohexanol derivative that is expected to exhibit high click reactivity. Fortunately, with the reduced nucleophilicity and higher stability of 1-ethynylmagnesium chloride,\(^{238}\) it was synthesized in just one-step from the reaction of 1 with 1-ethynylmagnesium chloride in high yield without protection of the acetylene group (Scheme 6.2). The \(sp\) hybridization of the carbon on the acetylene group increased its stability as an anion and reduced its nucleophilicity tremendously. In contrast to ethynyllithium compounds, such as [(trimethylsilyl)ethynyl]lithium, that would add to C\(_{60}\) rapidly with multiple-addition in an uncontrolled manner,\(^2\) 1-ethynylmagnesium chloride was reported not to react with C\(_{60}\) at room temperature, even after prolonged reaction time.\(^{238}\) As a result, 1-ethynylmagnesium chloride could only add to the carbonyl group on 1 to form the magnesium salt. This was evidenced by immediate formation of a turbid solution after the addition of the Grignard reagent. The reaction was very fast, essentially complete within just a few minutes (judged by TLC). Quenching the solution with aqueous NH\(_4\)Cl solution generated the hydroxyl functionality and the solution was then clear again. After chromatographic purification on silica gel using toluene as an eluent, the product was obtained as a dark solid in high yield (92%). No protection of acetylene group was necessary in this case and it should be noted that one-pot functionalization is possible by quenching the addition product with various chemicals, such as acyl chlorides (e.g., Fulleryne05).
Scheme 6.2. Synthesis of Fulleryne03.

The chemical identity of Fulleryne03 has been established by \(^1\)H NMR, \(^{13}\)C NMR, FT-IR and MALDI-TOF mass spectrometry. The \(^1\)H NMR spectrum and the assignment of the peaks are shown in Figure 6.5. The coupling between hydrogen atoms could be clearly seen, from which the assignment was achieved in comparison to that of Fulleryne01. The hydrogen atoms (a) at the methylene group near the tertiary carbon on the cyclohexanol ring were observed at 4.00 and 3.85 ppm. The hydrogen atoms at the methylene group d and e exhibited complex coupling behavior, while the hydrogen atoms at the acetylene (c) and hydroxyl group (b) showed up as singlets at 2.82 and 2.58 ppm, respectively. Compared to that in Fulleryne01 (2.99 ppm), the chemical shift of alkyne C-H in Fulleryne03 was significantly shifted upfield (2.82 ppm). This is due to the lack of a conjugated, electron-withdrawing carbonyl structure in Fulleryne03.\(^{226}\) The \(^{13}\)C NMR spectrum is shown in Figure 6.6. The peaks in the spectrum could be assigned accordingly. The carbons on the ethynyl group showed up at 88.58 ppm and 73.06 ppm, respectively. The peaks between 135.22 and 156.91 ppm could be assigned to the sp\(^2\) carbons on the C\(_{60}\), while the peaks at 63.56 and 61.30 ppm were due to the sp\(^3\) carbon on the C\(_{60}\) (e, f). The other four sp\(^3\) carbons at the cyclohexanol ring were clearly observed at 50.22, 38.94, 34.76, and 29.83 ppm, respectively.
Figure 6.5. $^1$H NMR spectrum of Fulleryne03.

Figure 6.6. $^{13}$C NMR spectrum of Fulleryne03.
Figure 6.7. MALDI-TOF mass spectrum of Fulleryne03.

Figure 6.8. FT-IR spectrum of Fulleryne03.
The structure of Fulleryne03 was further proved by MALDI-TOF mass spectrometry (Figure 6.7). The peak at $m/z = 816.18$ corresponded to the monoisotopic molecular ion (M+) of Fulleryne03, which agreed well with the calculated molecular weight of 816.06 Da ($C_{66}H_{8}O$) for Fulleryne03. The characteristic peak of the alkyne group (3300 cm$^{-1}$ for $≡C-H$ stretching) and $C_{60}$ (527 cm$^{-1}$) were also evident in the FT-IR spectrum (Figure 6.8). The structure and identity of Fulleryne03 were thus established.

6.4 Fulleryne04

An intriguing feature of Fulleryne03 is the presence of a hydroxyl group that can be facilely converted to other functional groups, such as a fluorine atom (Scheme 6.3). The conversion was performed using Deoxo-Fluor® [bis(2-methoxyethyl)aminosulfur trifluoride]. Being a milder fluorinating agent than (diethylamino)sulfur trifluoride (DAST), it was expected to reduce the amount of side reactions. A detailed review can be found in literature and the fluorinating reaction is orthogonal to acetylene groups. The reaction was conducted in toluene at 0 °C through dropwise addition of Deoxo-Fluor®. TLC was used to monitor the reaction (eluent: toluene; Fulleryne03, $R_f = 0.35$; Fulleryne04, $R_f = 0.85$) and it was found that the reaction was essentially complete within one hour. The isolated yield of 76% was quite good, considering the ease of reaction.

Scheme 6.3. Synthesis of Fulleryne04 from Fulleryne03 and the model reaction between Fulleryne04 and PS-N$_3$ (2k).
Figure 6.9. $^1$H NMR and $^{13}$C NMR spectra of Fulleryne04. The inset in (b) shows the zoom-in view in the region between 75 and 80 ppm.

Figure 6.10. FT-IR spectrum of Fulleryne04.
The $^1$H NMR and $^{13}$C NMR spectra of Fulleryne04 are shown in Figure 6.9. Due to the existence of a fluorine atom and $C_{60}$ unit, the spectrum was very complicated from the cross-coupling between fluorine and hydrogen and it was difficult to make assignments. Nevertheless, the existence of the alkyne proton was evident at a chemical shift of 3.00 ppm in $^1$H NMR spectrum. In the $^{13}$C NMR spectrum, the chemical shifts at 76.1, 79.2, and 76.0 ppm might be assigned to the carbons of $C_1$$\equiv$$C_2$$-$$C_3$$-$$F$, respectively. The chemical shifts for the $sp^2$ carbons on $C_{60}$ at $\sim$ 140 ppm were also evident. In the FT-IR spectrum, the characteristic $≡$$C$$-$$H$ stretching peak at 3300 cm$^{-1}$ was observed (Figure 6.10). In addition, the MALDI-TOF mass spectrum (Figure 6.11) shows the desired molecular peak at $m/z$ 818.02, as expected for the formula $C_{66}H_7F$ ($M_{calc.} = 818.05$). There was a significant peak at a higher molecular weight of $m/z$ 890.10(Figure 6.11). This was probably due to the complexation between Fulleryne04 and the THF used in the MALDI-TOF experiment. The complex of Fulleryne04·THF would have a formula of $C_{66}H_7F$$\cdot$$C_4H_8O$ (or $C_{70}H_{15}FO$) with calculated monoisotopic molecular weight at 890.11, which was in good agreement with the experimentally observed $m/z$ (890.10). Such cluster formation is normal in MALDI-TOF mass spectrometry.\textsuperscript{232}

To further verify the structure of Fulleryne04, a model click reaction with PS-N$_3$(2k) was performed (Scheme 6.3). The product was obtained in 93% when 1.10 eq. of Fulleryne04 was used, again confirming the high reactivity of Fulleryne04. The product was then analyzed by MALDI-TOF mass spectroscopy. The result is shown in Figure 6.12. The inset is the overview of the spectrum, where one major distribution with two minor distributions were observed. The Figure 6.12 shows the zoom-in spectrum. For a
Figure 6.11. MALDI-TOF spectrum of Fulleryne04. M$^+$ at 818.02, M·THF$^+$ at 890.10.

Figure 6.12. MALDI-TOF mass spectrum of the PS-C$_{60}$ obtained from Fulleryne04. For 15mer, M·Ag$^+$ at 2643.32, M·H$_2$O·Ag$^+$ at 2661.32, M·CH$_3$OH·Ag$^+$ at 2675.31. The inset is the overview of the spectrum.
15mer with silver ion, the molecular formula is $C_{192}H_{138}AgFN_3O_2$ with calculated molecular weight at 2642.98. This is in good agreement with the observed $m/z$ of 2643.32. The other two minor distributions have a molecular weight difference of 18 and 32, respectively. This corresponds to the cluster formation with water (H$_2$O) and methanol (CH$_3$OH), respectively.\textsuperscript{232}

6.5 Fulleryne05

An intriguing feature of Fulleryne03 is the ability to undergo further functionalization on the hydroxyl group to prepare multi-functional fullerenes. This can be achieved either by post-reaction functionalization (from isolated, purified Fulleryne03) or a “living” functionalization scheme (from the intermediate addition product - the magnesium salt). The former involves reactions such as esterification and is quite straightforward, but it requires separation and purification of Fulleryne03 and adds to the overall synthetic steps. The latter involves \textit{in situ} generation of the addition intermediate and one-pot functionalization, which should be much more efficient than the former, although the scope of the chemistry and functionality to be introduced are relatively limited. For example, methyl iodide was chosen to reacte with the magnesium salt, but no methyl ether was obtained and the product was solely Fulleryne03 after quenching the reaction after 24 hours. It was found that acyl halides were effective in the one-pot functionalization of this intermediate. For example, after the addition of the Grignard reagent to 1, the solution turn turbid due to the formation of the magnesium salt that was then quenched by the addition of bromoacetyl bromide (Scheme 6.4). The reaction was slow. It took hours for the solution to gradually become clear, indicating that the
esterification reaction was in progress. After separation, Fulleryne05 was obtained in 68% yield, in addition to ~19% of Fulleryne03 due to incomplete reaction even after 12 hours. Efforts are being directed to improve the yields and process by lengthening the reaction time or by additives such as triethyl amine and DMAP to promote the reaction.

Scheme 6.4. Synthesis of Fulleryne05.

The $^1$H NMR and $^{13}$C NMR spectra were clean and are shown in Figures 6.13 and 6.14, respectively. This was compared to that of Fulleryne03 (Figures 6.5 and 6.6). In $^1$H NMR spectrum, the chemical shifts of hydrogen atoms near the hydroxyl group shifted significantly to lower field (a: 4.30, 4.11 ppm compared to 4.00, 3.85 ppm; d: 3.45 ppm compared to 3.19 and 2.58 ppm), due to the esterification of the hydroxyl group. A new peak assignable to the newly introduce methylene group was observed at 3.92 ppm. In $^{13}$C NMR spectrum, the carbon atom at the ester group was observed at 164.74 ppm and the new methylene group at 26.04 ppm. Meanwhile, the acetylene carbon (g) shifted upfield (83.68 ppm, as compared to 88.58 ppm), while the other carbon (h) shifted downfield (75.57 ppm, as compared to 73.06 ppm). The tertiary carbon next to oxygen atom was observed at 47.07 ppm, while that of Fulleryne03 was at 50.22 ppm.
Figure 6.13. $^1$H NMR spectrum of Fulleryne05.

Figure 6.14. $^{13}$C NMR spectrum of Fulleryne05.
The successful introduction of bromoacetyl group was also supported by the FT-IR spectrum (Figure 6.15) and the MALDI-TOF mass spectrum (Figure 6.16). The characteristic absorbances of C=O at 1745 cm$^{-1}$, \( \equiv \text{C-H} \) at 3294 cm$^{-1}$, and C-C on C$_{60}$ at 527 cm$^{-1}$ are evident in the FT-IR spectrum. In the MALDI-TOF spectrum, the monoisotopic molecular weight was observed at 935.99, which was in very good agreement with the calculated monoisotopic molecular weight of 935.98 for C$_{68}$H$_9$BrO$_2$. Moreover, the pattern of the molecular weight (i.e. peaks of almost equal intensity at 935.99 and 937.99) was a signature of the presence of one bromine atom in the molecule.\textsuperscript{226} All of these characterizations unambiguously established the identity of Fulleryne05.

The bromine atom in Fulleryne05 is a very reactive functional group towards nucleophilic substitution. For example, it could be transformed into azide and further functionalized by “click” chemistry to install other functional materials. The method is also being extended to other functional acyl halides, such as ferrocene-, or tetrathiafulvalene-acyl halides. This “living” functionalization method thus represents a facile method to introduce functionality to fullerenes in a one-pot process.

6.6 Fulleryne06

All of the fullerenes discussed above required more than one step to synthesize them from C$_{60}$. It was highly desired to have fullerenes that could be readily synthesized in just one step from C$_{60}$, yet possessing high “click” reactivity of the alkyne. The key was to differentiate the reactivity of alkyne and double bonds on C$_{60}$ to avoid the side reactions. The Bingel-Hirsch reaction is very efficient and requires only mild reaction
Figure 6.15. FT-IR spectrum of Fulleryne05.

Figure 6.16. MALDI-TOF spectrum of Fulleryne05. The inset is the whole spectrum.
conditions. It has been used to prepare fullerenes in the literature using DBU and I₂, as reported by Nierengarten et al.²¹⁵ But it has also been found that side reactions, such as iodination of the hydrogen atom on the acetylene group, occurred to a certain extent. The authors then used a protection-deprotection scheme to solve the problem. Trimethylsilyl (TMS) groups were used to protect the alkyne group and later cleaved by TBAF, which also allowed the preparation of functionalized [5:1]-hexaadducts of C₆₀.²²⁰ Our approach was to tune the reaction conditions and choose reagents to minimize the side reactions. If iodination was the main side reaction, CBr₄ can be used instead, since CBr₄ is a milder halogenation reagent than I₂ and would not add to the unsaturated bonds, such as alkynes. Strict stoichiometry control was necessary. It was anticipated that if alkyne is in an excess compared to CBr₄, most of CBr₄ would prefer to react with the methylene group on the malonate, rather than reacting with alkyne. Indeed, when 1.2 equivalent of CBr₄ and 1.5 equivalent of malonate relative to C₆₀ were used, the reaction proceeded with very few side reactions to afford Fulleryne06 (Scheme 6.5), as evidenced by the ¹H NMR spectrum and the MALDI-TOF mass spectrum (vide infra). The reaction was allowed to proceed overnight and then worked up promptly. The product was obtained in 41% yield.

Scheme 6.5. Synthesis of Fulleryne06 by Bingel-Hirsch cyclopropanation.
The $^1$H NMR and $^{13}$C NMR spectra are shown in Figures 6.17 and 6.18, respectively. In the $^1$H NMR spectrum, the chemical shifts for hydrogen atoms on the methyl and methylene groups were observed at 4.12 and 5.09 ppm as a singlet and doublet, respectively. The triplet peak at 2.62 ppm was attributed to the hydrogen atom at the alkyne. The integration ratio between them was 3:2:1, as expected. In the $^{13}$C NMR spectrum, the alkyne carbons were observed at 76.09 and 70.90 ppm. The carbonyl carbons showed up at 162.91 and 162.11 ppm. The peaks at 128.04 ppm could be attributed to cyclopropane carbons on C$_6$O and the peak at 54.00 ppm was assigned to be the carbon between the two carbonyls. These functional groups were also evident in FT-IR spectrum (Figure 6.19). For example, the strong sp C-H stretching band was observed at 3296 cm$^{-1}$ and the C=O stretching band at 1743 cm$^{-1}$. In MALDI-TOF mass spectrum (Figure 6.20), the peak was observed with monoisotopic molecular weight of $m/z$ 873.74, which was in good agreement with the calculated molecular weight of 874.03 for C$_{67}$H$_6$O$_4$. There were few higher molecular weight impurities observed, indicating very little halogenation of the alkyne proton during the reaction. Although the reactivity of the alkyne group might be compromised in this case, it has the advantages of ease in synthetic facility and better electronic properties.

6.7 Fullerdiyne01

Using malonate 37 under the same reaction conditions as for Fulleryne06, Fullerdiyne01 were prepared (Scheme 6.6). However, the yields in this case (~ 21%) were much lower than that for Fulleryne06 (~ 41%). The $^1$H NMR spectrum of Fullerdiyne01 is shown in Figure 6.21. Due to the highly symmetric structure, only two
Figure 6.17. $^1$H NMR spectrum of Fulleryne06.

Figure 6.18. $^{13}$C NMR spectrum of Fulleryne06.
Figure 6.19. FT-IR spectrum of Fulleryne06.

Figure 6.20. MALDI-TOF mass spectrum of Fulleryne06.
peaks were observed: the one at 5.07 ppm could be assigned to the methylene group and the one at 2.61 ppm could be assigned to the hydrogen atom at the alkyne group. The $^{13}$C NMR spectrum (Figure 6.22) was very similar to that of Fulleryne06. The carbons on alkyne were observed at 76.17 and 70.10 ppm. The carbonyl carbons showed up at 161.64 ppm. The peaks at 128.02 ppm could be attributed to cyclopropane carbons on C$_{60}$ and the peak at 54.00 ppm was assigned to be the carbon between two carbonyls. In the FT-IR spectrum (Figure 6.23), all the expected characteristic absorbance bands were present. The structure was further confirmed by MALDI-TOF mass spectrometry (Figure 6.24). The monoisotopic ion was observed at $m/z$ 898.04, compared to the calculated molecular weight of 898.03 Da for C$_{69}$H$_6$O$_4$. There were several higher molecular weight ions of lower intensity, assignable to the sodium complex [M·Na$^+$ at $m/z$ 921.03 (calc. 921.02 Da for C$_{69}$H$_6$O$_4$Na)]. Fullerdiyne01 has a well-defined structure. Furthermore, the schemes and methods used for the synthesis of Fulleryne03-06 (Schemes 6.2 – 6.5) could be applied to synthesize fullerdiynes using the same process (see Figure 6.4 for representative structures) by using a different stoichiometry (2 equivalents of reactant relative to C$_{60}$). These multialkyne-functionalized fullerenes are useful compounds in the synthesis of fullerene polymers or bucky gels.

![Scheme 6.6. Synthesis of Fullerdiyne01 by Bingel-Hirsch cyclopropanation.](image)

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Figure 6.21. $^1$H NMR spectrum of Fullerdiyne01.

Figure 6.22. $^{13}$C NMR spectrum of Fullerdiyne01.
Figure 6.23. MALDI-TOF mass spectrum of Fullerdiyne01.

Figure 6.24. FT-IR spectrum of Fullerdiyne01.
6.8 Summary

Several fullerynes possessing different structures and reactivities were successfully developed. Some of the processes in their synthesis have been optimized. The results are summarized in Table 6.1. Some fullerynes were indeed synthesized with great ease and would maintain their high reactivity. Multifunctional fullerynes can also be prepared by derivatization from the hydroxyl and bromo functionalities on Fulleryne03 and 05. Moreover, the same process can be readily applied to the synthesis of fullerdiynes and fullertriynes (fullerenes with more than one alkyne functionality for click reaction) for use in the synthesis of polymers and bucky gels. The application of “click chemistry” to fullerene and the ready availability of highly reactive and multifunctional fullerynes offer a ready access to new fullerene materials with desired properties and potential applications.

<table>
<thead>
<tr>
<th>Fulleryne</th>
<th>Process</th>
<th>Yield</th>
<th>Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fulleryne01</td>
<td>3</td>
<td>~24%</td>
<td>Good</td>
</tr>
<tr>
<td>Fulleryne03</td>
<td>2</td>
<td>~54%</td>
<td>Good</td>
</tr>
<tr>
<td>Fulleryne04</td>
<td>3</td>
<td>~41%</td>
<td>Good</td>
</tr>
<tr>
<td>Fulleryne05</td>
<td>2</td>
<td>~40%</td>
<td>Good</td>
</tr>
<tr>
<td>Fulleryne06</td>
<td>1</td>
<td>~41%</td>
<td>OK</td>
</tr>
<tr>
<td>Fullerdiyne01</td>
<td>1</td>
<td>~21%</td>
<td>OK</td>
</tr>
</tbody>
</table>

(a): Processes are counted as the number of steps from $C_{60}$; (b): Overall yield from $C_{60}$; (c) Reactivity based on the relationship discussed in the Chapter II: those with electron-withdrawing and less bulky substituents are expected to be more reactive.
CHAPTER VII
SYNTHESIS OF FULLERENE POLYMERS

For physical studies, high material purity is a prerequisite. Living anionic polymerization offers unprecedented control over molecular weight, polydispersity, composition, functionalization, etc.\textsuperscript{179} In combination with other controlled polymerization techniques, such as atom-transfer radical polymerization (ATRP)\textsuperscript{180} and reversible-addition-fragmentation group transfer radical polymerization (RAFT),\textsuperscript{240,241} it can give rise to a large number of polymeric architectures with controlled functional group placement. In this Chapter, the design and synthesis of fullerene polymers with controlled architecture and C\textsubscript{60} functionalization using the click chemistry approach will be discussed.

7.1 Molecular Design and General Aspects for Polymer Synthesis

To use the self-assembly of a polymer as a template to arrange C\textsubscript{60}s into an ordered structure, it is necessary to introduce C\textsubscript{60} to a pre-determined position on the chain in a well-defined way and the self-assembly of the polymer template should be well-understood. In our laboratory, a tremendous amount of work has been done on poly(ethylene oxide) (PEO) and poly(ethylene oxide)-\textit{b}-polystyrene (PEO-\textit{b}-PS).\textsuperscript{160,184-186,242} Therefore, the molecular design of fullerene polymers was mainly
based on these two polymers. There are many ways to functionalize a block copolymer with C₆₀. C₆₀ can be either attached to one end, at the junction point, randomly along one block, or even at both ends of the blocks and at the junction point and the ends. Each will lead to distinctly different self-assembly behaviors. The fullerene polymer architectures of interest are thus shown in Figure 7.1. The maturing of the modern polymerization techniques allows the facile construction of such architectures.

To preserve C₆₀’s electronic properties, minimum chemical modification on C₆₀ is desired. With click chemistry and the fullerynes described in Chapters V and VI, it is possible to convert azide-functionalized polymers into fullerene polymers with high efficiency and eliminate the need to remove unfunctionalized polymers. Using different fullerynes, it is also possible to introduce additional functionalities to the system. In this section, the polymers that were synthesized using Fulleryne01 are the focus of research for simplicity and consistency.

Syntheses of azide-functionalized polymers have been prevalent in the literature, since the CuAAC reaction gained its popularity as the prototype “click” chemistry. Generally speaking, there are two ways to prepare azide-functionalized polymers: (1) post-polymerization functionalization; and (2) using an azide-functionalized initiator. In the post-polymerization functionalization method, azidation is usually achieved by nucleophilic substitution or by a ring-opening reaction, both types of reactions known to
possess “click” reactivity. In combination with ATRP, this technique has become a very powerful tool in synthesizing functional polymers, since ATRP readily yields well-defined polymers with halogen end groups. In order to introduce multiple azide functionalities into the system, multihalogen atoms have to be introduced into various positions of the polymer chain. The ATRP method might not serve this purpose very well. It is then necessary to use other stable free radical polymerization techniques, such as reversible-addition-fragmentation group transfer (RAFT) polymerization, that are compatible with halogen atoms. In the case of using an azide-functionalized initiator, care should be taken to avoid side reactions due to the azide functionality. It is known that azide will loss nitrogen to become a reactive nitrene at higher temperature, which might cause side reactions with monomers. Recently, Perrier and coworkers reported that the azide undergoes 1,3-dipolar cycloaddition with the double bonds of the monomer, N-isopropylacrylamide (NIPAM) at 60 °C in the absence of catalysts over long reaction times. To avoid this, Liu et al. conducted the ATRP at room temperature. When the polymerization is performed using an azide-functionalized initiator, it should be always kept in mind that potential loss of azide functionality during the polymerization might take place.

Synthesis of the PEO block from ring-opening polymerization of ethylene oxide via an anionic mechanism has been known to possess many features similar to that of a living polymerization. In THF, it can be initiated by a variety of initiators, such as RO−K+, or RO−Na+ under high pressure, or RO−Li+ in the presence of t-P4 base. In our experiments, commercially available potassium tert-butoxide of sublimed grade (> 99.9%) was used as the initiator. Before reaction, it was weighed, dissolved, and ampouliized
using anhydrous THF in a dry-box. The polymer molecular weight was controlled by the monomer/initiator ratio and the conversion. The molecular weight distribution of the prepared PEO was narrow. Moreover, using different quenching agents, it was possible to do various chain-end “living” functionalizations.\textsuperscript{181} For example, quenching with solutions of methanol, propargyl bromide, and allyl bromide gave chain-end hydroxyl-, alkene-, or alkyne-functionalized polymers, respectively (Scheme 7.1). The hydroxyl group is very versatile and can be transformed into different functionalities for click reaction or to facilitate the synthesis of a second block by different polymerization mechanisms. For example, an epoxy functionality could be installed and then transformed into azide and hydroxyl functionality,\textsuperscript{182} an ATRP initiator, $\alpha$-bromoisobutyrate, could be synthesized after esterification using $\alpha$-bromoisobutyryl bromide; a RAFT-CTA could be attached to prepare a macro-RAFT-chain-transferring-agent.\textsuperscript{178} These chain-end-transformations have been reported in the literature and are well-established for their high reactivity and high reliability.

Scheme 7.1. Living anionic polymerization of ethylene oxide and subsequent living chain-end-functionalization.
In current work, anionic polymerization of ethylene oxide in THF, controlled free radical polymerization, and “click” chemistry were combined to synthesize functionalized PEO and PEO-b-PS with controlled molecular weight, narrow polydispersity, definite functional group positions, and high degree of functionalization.

7.2 Synthesis of PEO-C_{60}

The anionic polymerization of ethylene oxide was performed in THF using the high vacuum techniques. The polymerization was usually allowed to proceed for 24 hours to ensure a high conversion (~80%) for targeted molecular weight. The hydroxyl-functionalized PEO was then obtained by quenching the living PEO-K\(^+\) polymer with methanol (Scheme 7.1) and precipitation into cold ethyl ether. After drying in vacuo for 24 hour, the PEO was characterized by \(^1\)H NMR spectroscopy and SEC to determine the molecular weight and polydispersity. Since THF is not a good solvent for PEO, PEO would adopt a more compact conformation in THF and thus the molecular weights obtained from SEC by standard calibration curve were not reliable. More accurate molecular weight measurement was obtained by \(^1\)H NMR analysis. A representative \(^1\)H NMR spectrum is shown in Figure 7.2. The singlet peak at 1.20 ppm (integration area = \(S_A\)) was assigned to the nine hydrogens at the initiating chain-end [–C(CH\(_3\))\(_3\)] and the peaks at 3.65 ppm (integration area = \(S_B\)) were assigned to the methylene protons (-OCH\(_2\)CH\(_2\)-) on the PEO backbone (\(4 \times n; n = \) degree of polymerization). The integration ratio between these peaks (\(S_B/S_A\)) was then used to calculate the number average molecular weight by the following equation (Eq. 7.1).
\[ M_a = \frac{9 \times S_B \times 44}{4 \times S_A} \quad \text{(Eq. 7.1)} \]

The hydroxyl-functionalized PEO (PEO-OH) were obtained with several different molecular weights, ranging from \( M_n = 5,100 \) to 11,000 g/mol. The characterizations of these PEOs are summarized in Table 7.1. Representative SEC traces are shown in Figure 7.3, indicating that they exhibited monomodal, symmetric distributions with narrow polydispersities.

<table>
<thead>
<tr>
<th>Label</th>
<th>( M_{n,\text{target}} ) (kg/mol)</th>
<th>( M_{n,\text{SEC}} ) (kg/mol)</th>
<th>( M_{n,\text{NMR}} ) (kg/mol)</th>
<th>PDIa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO1-OH</td>
<td>5.0</td>
<td>6.2</td>
<td>5.1</td>
<td>1.10</td>
</tr>
<tr>
<td>PEO2-OH</td>
<td>10.0</td>
<td>13.5</td>
<td>11.0</td>
<td>1.07</td>
</tr>
<tr>
<td>PEO3-OH</td>
<td>10.0</td>
<td>12.8</td>
<td>9.0</td>
<td>1.10</td>
</tr>
<tr>
<td>PEO4-OH</td>
<td>10.0</td>
<td>12.0</td>
<td>8.4</td>
<td>1.10</td>
</tr>
</tbody>
</table>

(a) polydispersity were measured using SEC.

The synthesis of functionalized PEO and PEO-b-PS polymers began with these hydroxyl-functionalized PEOs. The synthetic route for PEO-C\(_{60}\) is outlined in Scheme 7.2. The hydroxyl chain-end was first converted to epoxy functionality (PEO-Epoxy), followed by nucleophilic ring-opening to introduce an azide and a hydroxyl group to the chain end [PEO-(N\(_3\))-OH]. The “click” reaction between PEO-(N\(_3\))-OH and Fulleryne01 afforded the desired PEO-C\(_{60}\). The chain-end multifunctionalized PEO [PEO-(N\(_3\))-OH] is also useful in the construction of in-chain-functionalized diblock copolymers, which will be further discussed in the synthesis of PEO-(C\(_{60}\))-PS.
Figure 7.2. Representative $^1$H NMR spectrum of PEO-OH.

Figure 7.3. SEC chromatogram of PEO-OH with four different molecular weights (black: PEO1-OH; blue: PEO4-OH; red: PEO3-OH; purple: PEO2-OH, see Table 7.1).
Scheme 7.2. Synthetic route to PEO-C₆₀.

The PEO-Epoxy was synthesized by treating hydroxyl-functionalized PEO with epichlorohydrin under basic conditions as reported in the literature. The product was obtained in 75% yield. In the ¹H NMR spectrum, the signals at 3.15, 2.78, and 2.59 ppm were assigned to the protons of the epoxide end group, in agreement with the expected structure (Figure 7.4b). The degree of chain-end functionality was determined by the integration ratio between the peaks at 3.15, 2.78, 2.59, and 1.20 ppm, which is 0.99:0.91:0.96:9.04, very close to 1:1:1:9 and consistent with a quasi-quantitative conversion. The integration ratio between peaks at 3.65 and 1.20 ppm was very close (725.68:9.04) to that of starting material PEO-OH (763.34:9.00), indicating that no chain degradation occurred during the reaction. The polymer was subsequently transformed into PEO-(N₃)-OH via nucleophilic ring-opening reaction by sodium azide. The success of the reaction was evidenced by the complete disappearance of the signals at around chemical shifts 3.15, 2.78, and 2.59 ppm (Figure 7.4c) in the ¹H NMR spectrum of PEO-(N₃)-OH and a strong band near 2110 cm⁻¹ characteristic of the azide in the FT-IR spectrum (Figure 7.5). Since the new signals from methylene near azide and hydroxyl
group have very similar chemical shifts to the methylene hydrogens on the PEO backbone,\textsuperscript{182} no new peaks could be observed. The SEC overlay of these polymers shows that their elution volumes and polydispersities were essentially unchanaged (Figure 7.6), since the small chain-end functional groups exerted very little influence on the overall hydrodynamic radius of the polymer. The polydispersity of PEO-Epoxy and PEO-(N$_3$)-OH remained narrow at 1.10.

Figure 7.4. $^1$H NMR spectra of (a) PEO-OH; (b) PEO-Epoxy; (c) PEO-(N$_3$)-OH; and (d) PEO-C$_{60}$. The samples were based on PEO4-OH with PEO molecular weight of 8.4 kg/mol.
Figure 7.5. FT-IR spectra of PEO-(N$_3$)-OH (red line) and PEO-C$_{60}$ (blue line). The samples were based on PEO4-OH with PEO molecular weight of 8.4 kg/mol.

Figure 7.6. SEC chromatogram of PEO-OH (black); PEO-(N$_3$)-OH (red); and PEO-C$_{60}$ (blue). The samples were based on PEO4-OH with PEO molecular weight of 8.4 kg/mol.
The “click” reaction at room temperature between PEO-(N₃)-OH (1 equivalent) and excess Fulleryne01 (1.2 equivalents) yielded the desired C₆₀-end-capped PEO (Scheme 7.2). After removal of excess Fulleryne01 chromatographically followed by precipitation and recrystallization, PEO-C₆₀ was obtained as a brown powder in 72% yield.

The successful covalent linkage was first evidenced by the FT-IR spectrum (Figure 7.7). The characteristic azide absorption band near 2110 cm⁻¹ completely disappeared, which suggested a complete reaction since side reactions such as nitrene formation and thermo-promoted cycloaddition to C₆₀ had been shown to be absent under these reaction conditions (Chapter V). It was also supported by the ¹H NMR spectrum where the characteristic peaks owing to Fulleryne01 (6.45, 4.66, 4.54 and 2.90 ppm) and the triazole formation (8.50 and 4.55 ppm) were observed (Figure 7.5d). The integration ratio between the peaks at 6.45 (hydrogen of –CH₂O on Fulleryne01), 4.66, 4.54, 2.90 ppm (–CH- on Fulleryne01) and the one at 1.20 ppm [hydrogen of –OC(CH₃)₃] were 0.69:1.02:0.83:1:38:9.00, very close to 1:1:1:1:9 as expected for the structure within the range of measurement errors, confirming high degree of functionality.

A quantitative estimation of fullerene functionality was achieved using Beer-Lambert law. Since Fulleryne01 has strong absorbance at 330 nm in the UV-vis spectrum (Figure 5.4) and the unfuncitonalized PEO-b-PS is essentially transparent at this wavelength (absorbance ~ 10⁻⁴), the absorbance at this wavelength could be used to determine the degree of C₆₀-functionality of these polymers quantitatively. A calibration curve was then obtained using Fulleryne01 dilute solution in toluene (Figure A.1 in Appendix). The linear relationship was fitted to the following equation:
where $A$ is the absorbance of the UV light at 330 nm, $c$ is the molar concentration of the $C_{60}$ derivative, $k$ is the slope, and $b$ is the intercept. The slope $k$ was determined to be $3.5376 \times 10^4 \text{ M}^{-1}$, and the intercept $b$ was determined to be $2.14 \times 10^{-2}$. The square of correlation coefficient ($r^2$) was 0.999, indicating very good linearity. There was no attempt to force the fitting line back through the origin ($b = 0$), although if it works perfectly, it would pass through the origin. Depending on samples and concentrations for testing, some deviation might occur in experiments. Fullerene polymer solutions in toluene with a series of concentrations were prepared and their absorbances were measured at 330 nm. A standard curve was obtained for the fullerene polymer and fitted to Eq. 7.2. For PEO-$C_{60}$ with PEO molecular weight of 8.4 kg/mol, the slope $k$ was determined to be $3.96827 \times 10^4 \text{ M}^{-1}$, and the intercept $b$ was determined to be $-1.285 \times 10^{-2}$ (Figure A.2 in Appendix). The similar slope value of PEO-$C_{60}$ to that of Fulleryne01 indicated that same chromaphore was responsible for absorbance in both samples. At a specific absorbance, the ratio between the corresponding $c_{\text{Fulleryne01}}$ and $c_{\text{polymer}}$ determines the functionality $C_{60}\%$ (Eq. 7.3).

$$C_{60}\% = \frac{c_{\text{Fulleryne01}}}{c_{\text{polymer}}} \times 100\% \quad (\text{Eq. 7.3})$$

For the measurement to be reliable, the absorbance should be kept in a reliable range of spectrometer scale, preferably between 0.2 and 0.8. At $A = 0.30$, this corresponds to $c_{\text{Fulleryne01}} = 7.8753 \times 10^{-6} \text{ M}$ and $c_{\text{polymer}} = 7.8838 \times 10^{-6} \text{ M}$; hence $C_{60}\% = 99.9\%$. Therefore, the $C_{60}\%$ functionality was determined to be quantitative within the range of measurement errors. The power of “click” chemistry has indeed provided a solid ground for optimal results, as expected with the high efficiency as demonstrated in
the model reactions. In this way, both the molecular weight and molecular weight
distribution of the PEO segment would remain the same after functionalization. Based on
this, the C$_{60}$ content in the polymer (C$_{60}$ wt%) could be estimated using the following
equation (Eq. 7.4):

$$C_{60\text{ wt} \%} = \frac{M_{C_{60}} \times n}{M_{\text{polymer}} + M_{\text{Fullerene01}} \times n} \times 100\% \quad \text{(Eq. 7.4)}$$

where $n$ is the number of C$_{60}$ per chain, $M_{C_{60}}$, $M_{\text{polymer}}$, $M_{\text{Fullerene01}}$ are the molecular
weights of C$_{60}$, the azide polymer, and Fullerene01, respectively. The characterization
results were summarized in Table 7.2.

<table>
<thead>
<tr>
<th>Label</th>
<th>$M_n,\text{PEO}$</th>
<th>$M_{C_{60}}$</th>
<th>PDI$^a$</th>
<th>C$_{60}$ wt$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO1-C$_{60}$</td>
<td>5100</td>
<td>720</td>
<td>1.10</td>
<td>12%</td>
</tr>
<tr>
<td>PEO4-C$_{60}$</td>
<td>8400</td>
<td>720</td>
<td>1.10</td>
<td>7.8%</td>
</tr>
</tbody>
</table>

(a) $M_n,\text{PEO}$ and polydispersity were based on that of the precursor PEO-(N$_3$)-OH (see
discussion below for SEC results of PEO-C$_{60}$); (b) the C$_{60}$ wt% was estimated using Eq.
7.4.

The SEC chromatogram of PEO-C$_{60}$ is shown in Figure 7.6. The retention volume for
PEO-C$_{60}$ remained essentially the same as the precursor PEO-(N$_3$)-OH, but a shoulder
peak was also observed for PEO-C$_{60}$. Since higher additions have been proven to not
occur under these reaction conditions, these high molecular weight peaks were unlikely
due to the formation of multi-addition products. Considering the fact that THF is a
nonsolvent for C$_{60}$ and a theta solvent for PEO and that PEO is not miscible with C$_{60}$, the
shoulder peaks were probably due to aggregation of PEO-C$_{60}$ in THF. Similar
observations were also reported for C$_{60}$ end-capped PEO stars. Many methods were
attempted to prove this. It was speculated that if it was indeed from aggregation, the
aggregation would show up differently on different SEC columns and at different concentrations. Indeed, with decreasing or increasing concentration, changes in the profile of the shoulder peaks did occur. However, due to the strong aggregation between C$_{60}$s, the shoulder peaks was always present, even at concentrations down to less than 0.5 mg/mL. It was also characterized by a different SEC instrument equipped with triple detectors [UV detector (330 nm), light scattering, and refractive index]. The result is shown in Figure 7.7. The shoulder peaks became multimodal, probably due to the high resolution of the aggregated species of the instrument. Since UV absorbance at 330 nm only reveals materials with C$_{60}$, it can help us to determine how homogeneous the sample is. All three detectors show consistent results, indicating that the polymer chains were uniformly functionalized with C$_{60}$.

![SEC chromatogram of PEO-C$_{60}$ using three different detectors. Red: light scattering detector; blue: refractive index detector; green: UV detector at 330 nm. The sample has a molecular weight of 8.4 kg/mol for PEO segment.](image)

Figure 7.7. SEC chromatogram of PEO-C$_{60}$ using three different detectors. Red: light scattering detector; blue: refractive index detector; green: UV detector at 330 nm. The sample has a molecular weight of 8.4 kg/mol for PEO segment.
7.3 Synthesis of PEO-$b$-PS-C$_{60}$

The synthetic route for chain-end-C$_{60}$-functionalized PEO-$b$-PS is outlined in Scheme 7.3, which was similar to the model reaction discussed in Chapter V (Scheme 5.2). The macroinitiator for ATRP, PEO-Br, was synthesized by esterification with $\alpha$-bromoisoobutyryl bromide and obtained as a white powder in 88% yield. After esterification, new peaks appeared at 1.92 and 4.30 ppm, which were assigned to hydrogen atoms on $-\text{C(CH}_3\text{)}_2\text{Br}$ and adjacent to ester linkage [-(C=O)OCH$_2$], respectively (Figure 7.8a). The degree of functionalization for PEO-Br could be determined by the integration ratio between the peaks at 4.30, 1.92, and 1.20 ppm. It was 1.78:6.34:9.00, close to the expected 2:6:9, indicating that the terminal hydroxyl group had been transformed into the $\alpha$-bromoisoobutyrate group with high efficiency.

Scheme 7.3. Synthetic route to PEO-$b$-PS-C$_{60}$. 

![Scheme 7.3. Synthetic route to PEO-$b$-PS-C$_{60}$.](image-url)
Figure 7.8. $^1$H NMR spectra of (a) PEO-Br; (b) PEO-$b$-PS-Br; (c) PEO-$b$-PS-N$_3$; and (d) PEO-$b$-PS-C$_{60}$. The sample has a PEO molecular weight of 8.4 kg/mol and a PS molecular weight of 10 kg/mol.

With this macroinitiator, ATRP was performed at 90 °C to prepare the diblock copolymer. The conversion was controlled by polymerization time at < 50% conversion so as to control the molecular weight of the PS block and keep a narrow polydispersity. The polymer was obtained as a white powder. The molecular weight was then determined by both $^1$H NMR and SEC. In the $^1$H NMR spectrum (Figure 7.8b), the peaks at around 7.10 and 6.50 ppm were assigned to the hydrogens on the phenyl rings on PS block and their integration area was $S_B$. The peaks at around 3.65 ppm can be
Figure 7.9. SEC overlay of PEO-Br (black), PEO-\textit{b}-PS-Br (red), and PEO-\textit{b}-PS-C_{60} (blue) chromatograms. The samples were based on PEO molecular weight of 8.4 kg/mol and PS molecular weight of 10 kg/mol.

assigned to the hydrogens on the methylene groups on PEO block and their integration area was $S_A$. The integration ratio between $S_B$ and $S_A$ could be used to calculate the number average molecular weight of the PS block based on that of the PEO block using the following equation (Eq. 7.5):

$$M_{n,PS} = M_{n,PEO} \times \left( \frac{S_B}{S_A} \right) \times \left( \frac{104 \times 4}{44 \times 5} \right) \quad \text{(Eq. 7.5)}$$

where $M_{n,PS}$ is the number average molecular weight of the PS block, $M_{n,PEO}$ is the number average molecular weight of the PEO block. The SEC overlay of the macroinitiator PEO-Br, the block copolymer PEO-\textit{b}-PS-Br, and the PEO-\textit{b}-PS-C_{60} chromatograms is shown in Figure 7.9. It clearly indicates the block copolymer formation, since the block copolymer eluted at a significantly lower elution volume. The baseline resolution between PEO-Br and PEO-\textit{b}-PS-Br suggested very little
macroinitiator residue in the sample and confirmed again the high degree of functionalization in the macroinitiator.

The success of the “click” reaction was supported by $^1$H NMR, FT-IR spectroscopy, SEC, and quantitative UV analysis. In the $^1$H NMR spectrum, the signals, though weak, could be seen for the Fulleryne01 component (2.9 ppm), hydrogen atom near the triazole (5.2 ppm), and the triazole part (7.8 ppm), as the arrow indicated in Figure 7.8d. Due to the high molecular weight of the diblock copolymer, it was difficult to measure their integration ratio quantitatively and accurately. In SEC chromatogram, after C$_{60}$ functionalization, the retention volume essentially remained the same but a high molecular weight shoulder peak appeared (Figure 7.9). The SEC chromatogram using on a different instrument using three detectors [UV detector (330 nm), light scattering, and refractive index] is shown in Figure 7.10. The shoulder peaks was separated in this case due to the high resolution of the instrument. It was also speculated to be a result of aggregation, similar to that of PEO-C$_{60}$ (Figures 7.6 and 7.7). Since all three detectors show consistent results, the results indicate that the polymer chains were uniformly functionalized with C$_{60}$. The FT-IR spectrum of the PEO-$b$-PS-C$_{60}$ showed the complete disappearance of azide peaks found in PEO-$b$-PS-N$_3$, suggesting complete reaction (Figure 7.11). To further verify the fullerene functionality, the absorbance-concentration plot was obtained for PEO4-$b$-PS6-C$_{60}$ with $M_{n,PEO} = 8.4$ kg/mol and $M_{n,PS} = 9.0$ kg/mol and is shown in Figure A.3. It also exhibited a linear relationship. This was fitted to Eq. 7.2. The slope $k$ was determined to be $3.7416 \times 10^4$ M$^{-1}$, which was close to that of Fulleryne01 at $3.5376 \times 10^4$ M$^{-1}$, confirming same chromaphore as in Fulleryne01. The intercept $b$ was determined to be $6.66 \times 10^{-3}$. The C$_{60}$ functionality was then determined as
Figure 7.10. SEC chromatogram of PEO-$b$-PS-C$_{60}$ using three different detectors. Red: light scattering detector; blue: refractive index detector; green: UV detector at 330 nm. The sample has a molecular weight of 8.4 kg/mol for PEO segment and 10 kg/mol for PS segment.

Figure 7.11. FT-IR spectra of PEO-$b$-PS-N$_3$ (red) and PEO-$b$-PS-C$_{60}$ (blue). The samples were based on PEO molecular weight of 8.4 kg/mol and PS molecular weight of 10 kg/mol.
described for PEO-C\(_{60}\). At \(A = 0.30\), this corresponds to \(c_{\text{Fullerene01}} = 7.8753 \times 10^{-6} \text{ M}\) and \(c_{\text{polymer}} = 7.8400 \times 10^{-5} \text{ M}\); hence \(C_{60}\% = 100.4\%\). The results clearly indicate that the PEO4-\(b\)-PS6-C\(_{60}\) has quantitative functionality within the range of measurement errors. The \(C_{60}\) wt\% can then be estimated using Eq. 7.4. The main characterization results are summarized in Table 7.3.

Table 7.3. Characterization of PEO-\(b\)-PS-C\(_{60}\).

<table>
<thead>
<tr>
<th>Label</th>
<th>(M_n,\text{PEO}) (^a) (kg/mol)</th>
<th>(M_n,\text{PS}) (^a) (kg/mol)</th>
<th>PDI(^b)</th>
<th>(C_{60}) wt%(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO2-(b)-PS7-Br</td>
<td>11.0</td>
<td>13.0</td>
<td>1.20</td>
<td>--</td>
</tr>
<tr>
<td>PEO2-(b)-PS7-N(_3)</td>
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<td>13.0</td>
<td>1.17</td>
<td>--</td>
</tr>
<tr>
<td>PEO2-(b)-PS7-C(_{60})</td>
<td>11.0</td>
<td>13.0</td>
<td>--</td>
<td>2.9%</td>
</tr>
<tr>
<td>PEO4-(b)-PS5-Br</td>
<td>8.4</td>
<td>10.0</td>
<td>1.07</td>
<td>--</td>
</tr>
<tr>
<td>PEO4-(b)-PS5-N(_3)</td>
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<td>10.0</td>
<td>1.10</td>
<td>--</td>
</tr>
<tr>
<td>PEO4-(b)-PS5-C(_{60})</td>
<td>8.4</td>
<td>10.0</td>
<td>--</td>
<td>3.7%</td>
</tr>
<tr>
<td>PEO4-(b)-PS6-Br</td>
<td>8.4</td>
<td>9.2</td>
<td>1.05</td>
<td>--</td>
</tr>
<tr>
<td>PEO4-(b)-PS6-N(_3)</td>
<td>8.4</td>
<td>9.2</td>
<td>1.03</td>
<td>--</td>
</tr>
<tr>
<td>PEO4-(b)-PS6-C(_{60})</td>
<td>8.4</td>
<td>9.2</td>
<td>--</td>
<td>3.9%</td>
</tr>
</tbody>
</table>

(a) \(M_n\) was determined by \(^1\text{H NMR}\); (b) polydispersity was determined by SEC; (c) \(C_{60}\) wt\% was calculated using Eq. 7.4.

7.4 Synthesis of PEO-(C\(_{60}\))-PS

The method was then extended to the synthesis of in-chain-functionalized fullerene polymers from a multi-functionalized PEO, PEO-(N\(_3\))-OH (Scheme 7.4). First, the ATRP macrorinitiator, PEO-(N\(_3\))-Br, was synthesized by esterification with \(\alpha\)-bromoisobutyryl bromide in a way similar to PEO-Br. After recrystallization, the sample was obtained as a white powder and characterized by \(^1\text{H NMR spectroscopy}\). In the \(^1\text{H NMR spectrum}\) (Figure 7.12a), new peaks appeared around 1.92 and 5.15 ppm, which were assigned to hydrogen atoms on \(-C(CH_3)_2Br\) and those adjacent to ester linkage \([-\text{(C=O)OCH}_2\text{-}\], respectively. The integration ratio between the peaks at 5.15, 1.92, and
1.20 ppm was 0.10:0.77:1.05, close to the expected 1:6:9, indicating a high degree of chain-end functionality and well-defined structure.

Scheme 7.4. Synthetic route to in-chain-functionalized PEO-(C₆₀)-PS.

The in-chain-functionalized block copolymer was then synthesized from this azide-functionalized macroinitiator by ATRP. The reaction was carried out at a lower temperature of 42 °C to avoid side reactions. This low reaction temperature was reported to proceed without degradation of the azide functionality.²²⁴ Due to the low temperature, it took up to several days to polymerize. After polymerization, the FT-IR spectrum of PEO-(N₃)-PS showed a strong absorption band around 2110 cm⁻¹, characteristic of azide functionality (Figure 7.13). Therefore, the azide functionalities should be intact during the polymerization, but the degree of azide functionality was very difficult to determine.
Figure 7.12. $^1$H NMR spectra of (a) PEO-(N$_3$)-Br; (b) PEO-(N$_3$)-PS; and (c) PEO-(C$_{60}$)-PS. The samples were based on PEO molecular weight of 9.0 kg/mol and PS molecular weight of 9.2 kg/mol.

Figure 7.13. FT-IR spectra of PEO-(N$_3$)-PS (red) and PEO-(C$_{60}$)-PS (blue).
due to the low signal intensity of chain-end groups in the $^1$H NMR spectrum (Figure 7.12b). Nevertheless, after $C_{60}$ was attached, the degree of $C_{60}$ functionality could be measured by UV-absorbance, as described previously, which would provide an insight on the degree of azide functionality on the precursor polymer. In the $^1$H NMR spectrum, the peaks at around 7.00 ppm that are attributed to the protons on phenyl groups of polystyrene could be clearly seen. The molecular weights of the block copolymers could be calculated in a similar way to that for PEO-$b$-PS-Br using Eq. 7.5. The SEC overlay signifies a block copolymer formation by an apparent shift of the peak towards lower retention volume (Figure 7.14). There was no baseline resolution between the two polymers in this case and they overlapped to a certain degree, so it was hard to tell if there was any homopolymer residue. The polydispersity of the block copolymer was narrow (1.10), indicating a minimum amount of side reaction influence on polymerization.

The “click” functionalization was then performed in a similar way to the preparation of PEO-$b$-PS-$C_{60}$. After reaction, the azide absorbance band completely disappeared in the FT-IR spectrum (Figure 7.13). The product was obtained as a brown powder in 77% yield. The brown color indicated the successful covalent linkage of $C_{60}$ to the polymer. No significant change was observed in the $^1$H NMR spectrum (Figure 7.12c), due to the low intensity of the chain-end group. Nevertheless, in the $^{13}$C NMR spectrum (Figure 7.15), the peaks at around 142 ppm were observed, assignable to the $sp^2$ carbons on $C_{60}$. The SEC overlay (Figures 7.14 and 7.16) showed that the retention volume was essentially unchanged after functionalization with $C_{60}$, but there appeared high molecular weight shoulder peaks, as in the case for PEO-$C_{60}$ and PEO-$b$-PS-$C_{60}$. 
Figure 7.14. SEC overlay of the macrorinitiator PEO-(N$_3$)-Br (black), the block copolymer PEO-(N$_3$)-PS (red), and the PEO-(C$_{60}$)-PS (blue) chromatograms. The samples were based on PEO molecular weight of 9.0 kg/mol and PS molecular weight of 9.2 kg/mol.

Figure 7.15. $^{13}$C NMR spectrum of PEO-(C$_{60}$)-PS. The sample has a PEO molecular weight of 9.0 kg/mol and PS molecular weight of 9.2 kg/mol.
Figure 7.16. SEC chromatogram of PEO-(C$_{60}$)-PS using three different detectors. Red: light scattering detector; blue: refractive index detector; green: UV detector at 330 nm. The sample has a molecular weight of 9.0 kg/mol for PEO segment and 9.2 kg/mol for PS segment.

The concentration-dependent UV-absorbance was again used to determine the chain-end C$_{60}$ functionality. The absorbance-concentration plot was obtained for PEO-(C$_{60}$)-PS with $M_{n,\text{PEO}} = 9.0 \text{ kg/mol}$ and $M_{n,\text{PS}} = 9.2 \text{ kg/mol}$ and is shown in Figure A.4 in Appendix. The linear relationship was fitted to Eq. 7.2. The slope $k$ was determined to be $3.8088 \times 10^4 \text{ M}^{-1}$, which was close to that of Fulleryne01 at $3.5376 \times 10^4 \text{ M}^{-1}$, confirming same chromaphore as in Fulleryne01. The intercept $b$ was determined to be $9.57 \times 10^{-4}$. At $A = 0.30$, this corresponds to $c_{\text{Fulleryne01}} = 7.8753 \times 10^{-5} \text{ M}$ and $c_{\text{polymer}} = 7.8514 \times 10^{-5} \text{ M}$; hence $C_{60}\% = 100.3\%$. The results clearly indicate that the PEO-(C$_{60}$)-PS has quantitative functionality within the range of measurement errors. Therefore, the azide functionality in the precursor should have survived the polymerization condition and remain intact after prolonged reaction time. The C$_{60}$ wt% can then be estimated using Eq. 7.4. The characterization results are summarized in Table 7.4.
Table 7.4. Characterization of PEO-(C\textsubscript{60})-PS.

<table>
<thead>
<tr>
<th>Label</th>
<th>(M_{n,\text{PEO}})\textsuperscript{a} (kg/mol)</th>
<th>(M_{n,\text{PS}})\textsuperscript{a} (kg/mol)</th>
<th>PDI\textsuperscript{b}</th>
<th>C\textsubscript{60} wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO4-(N\textsubscript{3})-PS\textsubscript{3}</td>
<td>8.4</td>
<td>11</td>
<td>1.10</td>
<td>--</td>
</tr>
<tr>
<td>PEO4-(C\textsubscript{60})-PS\textsubscript{3}</td>
<td>8.4</td>
<td>11</td>
<td>--</td>
<td>3.6%</td>
</tr>
<tr>
<td>PEO3-(N\textsubscript{3})-PS\textsubscript{6}</td>
<td>9.0</td>
<td>9.2</td>
<td>1.09</td>
<td>--</td>
</tr>
<tr>
<td>PEO3-(C\textsubscript{60})-PS\textsubscript{6}</td>
<td>9.0</td>
<td>9.2</td>
<td>--</td>
<td>3.8%</td>
</tr>
</tbody>
</table>

(a) \(M_n\) was determined by \(^1\text{H} \text{NMR}\); (b) polydispersity was determined by SEC; (c) C\textsubscript{60} wt\% was determined by Eq. 7.4.

7.5 Synthesis of PEO-\(b\)-PS/C\textsubscript{60}

An interesting class of fullerene polymers is the side-chain fullerene polymers with C\textsubscript{60} randomly or regularly attached to one of the blocks. When the main chain is a conjugated polymer, they are known as “double cable” polymers. Such polymers hold great promise in improving organic solar cell’s performance by forming two separate channels to transport holes and electrons, respectively. However, most of the double cable polymers developed so far failed expectations, showing only low efficiency in the devices. Attaching many fullerenes to one block will surely affect the phase behavior and self-assembling results tremendously, since not only does it add significant amounts of C\textsubscript{60}-C\textsubscript{60} interaction into the system, but also it changes the volume fraction dramatically. To gain insight into such systems, PEO-\(b\)-PS/C\textsubscript{60} was chosen as a model system to study their self-assembling behaviors, in the hope of elucidating the basic underlying physics using well-defined samples of high purity prepared by click chemistry.

To prepare block copolymers with multi-functionalities on the PS block, it is not suitable to use ATRP since benzyl chloride is also a good initiator for ATRP. Instead, RAFT-mediated polymerization has better functional group tolerance\textsuperscript{241} and was chosen as the method to prepare PEO-\(b\)-PS/Cl (Scheme 7.5).
The RAFT chain transfer agent (CTA) 38 was synthesized according to the literature in quantities of tens of grams. After recrystallization, long, yellow, needle-like crystals were obtained. The $^1$H NMR spectroscopy characterization was consistent with literature reports (see Chapter III). The corresponding acyl chloride was prepared by reacting 38 with thionyl chloride in dichloromethane for 4 hours. After removal of the excess thionyl chloride, the acyl chloride 39 was directly reacted with PEO-OH ($M_n = 9.0$ kg/mol) in the presence of DMAP and triethylamine without further purification. The macroCTA PEO-Raft was obtained as a light yellow solid in 85% yield. The success was evidenced by the appearance of several new peaks in the $^1$H NMR spectrum ranging from 1.20 to 1.70 ppm which are derived from the alkyl chain on the Raft-CTA and at 4.30 ppm assignable to the methylene group adjacent to ester linkage (Figure 7.17a). The degree of functionalization of PEO could not be accurately determined in this case, due to
Figure 7.17. $^1$H NMR spectra of (a) PEO-Raft; (b) PEO-$b$-PS/Cl; (c) PEO-$b$-PS/N$_3$; and (d) PEO-$b$-PS/C$_{60}$. The samples were based on PEO molecular weight of 9.0 kg/mol and PS molecular weight of 10 kg/mol.

The overlapping of the $-C(CH_3)_3$ peak (1.20 ppm) with those from Raft-CTA alkyl chains. However, it should be identical to the precursor PEO-OH, since the change was only associated with a small chain-end functional group. This was supported by the SEC chromatogram that showed little change of retention volume and polydispersity, as compared to the starting materials (Figure 7.18).
The polymerization was performed using 5% AIBN as the initiator at 110 °C in toluene. The molecular weight was controlled by the monomer/(initiator+CTA) ratio and conversion (< 50%). The degree of functionalization was roughly controlled by the feed ratio of polystyrene and 4-vinylbenzyl chloride. Due to the presence of the RAFT-CTA agent in the molecule, the polymers were obtained as a slightly yellow or white solid depending on the molecular weight. In the $^1$H NMR spectrum, the methylene groups of benzyl chloride were clearly seen at 4.50 ppm (Figure 7.17b). The integration ratio between the peaks at around 7.00 ppm and 4.50 ppm was used to determine the average degree of functionalization of chloride monomers in the polymers based on Eq. 7.6:

$$Cl\% = \frac{n_{cl}}{n_s} \times 100\% = \left( \frac{S_A}{S_B} \right) \times \left( \frac{5}{2} \right) \times 100\% \quad (Eq. 7.6)$$
where $\text{Cl}\%$ is the molar percent of the 4-vinylbenzyl chloride monomer in the polystyrene block, $n_{\text{Cl}}$ is the number of 4-vinylbenzyl chloride monomer units incorporated into the chain, $n_s$ is the total number of polystyrene repeating units, $S_A$ is the integration of the peak at 4.50 ppm, and $S_B$ is the integration of the peaks at 6.50 and 7.10 ppm. The degree of functionalization was found to be 2.6%. This corresponded to 2 or 3 chlorides per 100 repeating units. For a molecular weight of 10k for the PS block, this corresponded to 2 or 3 C$_{60}$s per chain in the final fullerene polymer, assuming 100% conversion. The SEC trace of PEO-$b$-PS/Cl showed a monomodal distribution, which indicated that there were few side reactions (Figure 7.18). Because of the lack of baseline resolution, the existence of homopolymer residues could not be fully excluded.

Reaction with sodium azide in DMF facilely transformed the chloride into azide in high efficiency, as evidenced by the complete shift of the peak assignable to the methylene groups near chloride from 4.50 ppm upfield to 4.20 ppm (Figure 7.17). The integration ratio of this peak with that at 6.50 and 7.10 ppm was consistent with that of the starting material, suggesting that the reaction proceeded quantitatively without side reactions. The strong, characteristic azide absorbance band in FT-IR spectrum was clearly visible (Figure 7.19).

The “click” reaction between PEO-$b$-PS/N$_3$ and excess Fulleryne01 went smoothly at room temperature. The purification was achieved by passing the product through the silica gel column to remove unreacted fullerenes, followed by precipitation and recrystallization. The product was obtained as a brown powder. It has been reported that such C$_{60}$-grafted polymers are susceptible to crosslinking during preparation and storage.$^{248}$ As a result, after precipitation to form a solid, they tended not to dissolve.
Figure 7.19. FT-IR spectra of PEO-b-PS/N₃ (red) and PEO-b-PS/C₆₀ (blue). The samples were based on PEO molecular weight of 9.0 kg/mol and PS molecular weight of 10.0 kg/mol.

Figure 7.20. $^{13}$C NMR spectrum of PEO-b-PS/C₆₀. The sample has a PEO molecular weight of 9.0 kg/mol and a PS molecular weight of 10 kg/mol.
again. Thus, they were stored in solution in dark after reaction without further purification.\textsuperscript{248} Surprisingly, the PEO-\textit{b}-PS/C\textsubscript{60} synthesized by this method exhibited high solubility and could reversible dissolve and precipitate, which suggests that no crosslinking occurred during the “click” reaction and subsequent storage. This confirmed again that no multi-addition occurred under these conditions and that only the cycloaddition between azide and alkyne took place. This advantage is very important in the preparation of “double cable” polymers, for which processibility and high C\textsubscript{60} loading are critical.

The polymer was then characterized by $^1$H NMR, $^{13}$C NMR, FT-IR spectrometry and SEC. In the $^1$H NMR spectrum (Figure 7.17), the chemical shift for methylene group near azide (-CH\textsubscript{2}N\textsubscript{3}) completely shifted downfield from 4.20 to 5.40 ppm. The characteristic peak of triazole formation (hydrogen on the triazole ring) appeared at 7.60 ppm. The integration ratio of the benzyl methylene protons ($\delta = 5.45$ ppm) with the phenyl protons ($\delta = 6.50$ and 7.00 ppm) were smaller than that observed in the azide precursor. The reason was probably due to the shielding effect of the conjugated system of C\textsubscript{60}, which lowered the integration area for hydrogens adjacent to it. In the $^{13}$C NMR spectrum (Figure 7.20), the $sp^2$ carbons on C\textsubscript{60} could be observed near 142 ppm. The SEC overlay of the graft polymer showed a strong shoulder peak while its retention volume remained unchanged, as compared to its azide precursor (Figure 7.20). Finally, the strong absorbance band at 2100 cm\textsuperscript{-1} characteristic of azide completely disappeared after the reaction and the new peak at 527 cm\textsuperscript{-1} characteristic of a fullerene moiety could be observed (Figure 7.19). These confirmed the successful coupling of the C\textsubscript{60}s to random positions of the polystyrene block without crosslinking. Since the method
excluded the degradation or side reaction of azide functionality, the complete disappearance of azide signals in both $^1$H NMR and FT-IR spectra suggested complete reaction. The fullerene content was estimated according to the azide precursor to be 2 to 3 $C_{60}$s per chain with an average of 2.6 per chain. The characterization results are summarized in Table 7.5.

<table>
<thead>
<tr>
<th>Label</th>
<th>$M_n^{\text{PEO}}$ (kg/mol)</th>
<th>$M_n^{\text{PS}}$ (kg/mol)</th>
<th>PDI$^b$</th>
<th>$C_{60}$ wt%$^c$</th>
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<tbody>
<tr>
<td>PEO3-$b$-PS3/Cl</td>
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<td>PEO3-$b$-PS3/N$_3$</td>
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<td>PEO3-$b$-PS3/C$_{60}$</td>
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<td>8.8%</td>
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(a) $M_n$ was determined by $^1$H NMR; (b) polydispersity was determined by SEC; (c) $C_{60}$ wt% was determined using Eq. 7.4 for $n = 2.6$.

7.6 Summary

Using the combined techniques of anionic polymerization, ATRP, RAFT-mediated polymerization, and fullerene “click” chemistry, a series of fullerene polymers with controlled architecture and definite $C_{60}$ functionalization positions were successfully synthesized. The polymers have been characterized by $^1$H NMR, $^{13}$C NMR, FT-IR, and SEC. The syntheses of azide-functionalized PEOs and PS-$b$-PEOs were relatively well established and straightforward. Good molecular weight control and narrow polydispersity were obtained using combined polymerization techniques of anionic polymerization, ATRP and RAFT polymerization. For the fullerene polymers thus prepared, due to the presence of PEO in the polymer that does not favor interactions with $C_{60}$, evidence for association/aggregation of $C_{60}$s in solution was observed, which complicated the material characterization. Nevertheless, the model reaction has
unambiguously demonstrated the power of “click” chemistry in efficient incorporation of fullerene into polymers without side reactions. This was expected to work in this case to give well-defined fullerene polymers with 100% functionality, since the reactivity of azide was not significantly affected by substrate structure. The success in the synthesis of multi-C$_{60}$-grafted PEO-\(b\)-PS/C$_{60}$ without crosslinking further demonstrates the usefulness of this method in the controlled synthesis of fullerene materials. In this way, the position of C$_{60}$ functionalization could be exactly controlled in the block copolymer, as determined by the azide precursor. With these well-defined fullerene polymers, the studies of the physics of their supramolecular assemblies are underway. The basic information of fullerene polymers to be used for physical study (Chapter VIII) is summarized in Table 7.6.
Table 7.6. Basic information of fullerene polymer samples.

<table>
<thead>
<tr>
<th>Label</th>
<th>Chemical Structure</th>
<th>$M_{n,\text{PEO}}^{a}$ (kg/mol)</th>
<th>$M_{n,\text{PS}}^{a}$ (kg/mol)</th>
<th>$C_{60}$ wt%$^b$</th>
<th>PDI$^c$</th>
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<td>--</td>
<td>12%</td>
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<tr>
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<td><img src="image2" alt="PEO4-C$_{60}$" /></td>
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<td>--</td>
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</tr>
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<td>1.17</td>
</tr>
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<td>10.0</td>
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</tr>
<tr>
<td>PEO4-$b$-PS6-C$_{60}$</td>
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<td>9.2</td>
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<td>1.10</td>
</tr>
<tr>
<td>PEO-$b$-PS/C$_{60}$</td>
<td><img src="image8" alt="PEO-$b$-PS/C$_{60}$" /></td>
<td>9.0</td>
<td>10.0</td>
<td>8.8%</td>
<td>1.20</td>
</tr>
</tbody>
</table>

(a) $M_n$ was determined by $^1$H NMR; (b) $C_{60}$ wt% was determined using Eq. 7.4; (c) polydispersity refers to that of the azide precursor polymer.
As Nobel Laureate, Professor Lehn pointed out in his book, supramolecular chemistry comprises two broad, partially overlapping areas: supermolecules and supramolecular assemblies. The distinction between these two is that the former refers to well-defined, discrete oligomolecular entities assembled from a built-in scheme of molecular recognition; while the latter are extended poly-molecular arrays of less organized microscopic organizations and macroscopic features (films, membranes, vesicles, micelles, microemulsions, gels, mesomorphic phases, etc.). In the past, the building blocks in supramolecular chemistry were predominantly small molecules and monodisperse macromolecules, such as dendrimers, oligopeptides, and DNAs, mainly because of their well-defined structure and interactions. The assembly of polydisperse polymeric materials has gained more and more attention over the past two decades with the development of self-organizing polymers, such as block copolymers and electro-active conjugated polymers. The major shortcoming of using polymers as building blocks is that if the polymers are too heterogenous, they tend to segregate according to their size and composition during the assembly process. However, when the polymers are homogeneous and long enough so that the influence of chain-length is negligible, they will behave uniformly in the self-assembly and lead to
ordered structures. Under these circumstances, polydisperse polymers actually possess an advantage over their monodisperse counterparts in that they are easier to prepare and can sometimes help stabilize metastable states, such as the core-shell gyroid network mesostructure.\textsuperscript{255} With the understanding and knowledge from the supramolecular assemblies of well-defined, monodisperse samples, the incorporation of polydisperse building blocks in supramolecular assemblies is a natural extension and sometimes yields interesting results not found in those from monodisperse building blocks.\textsuperscript{256}

Polymers often form supramolecular assemblies. For example, most of semicrystalline polymers can grow single crystals from dilute solutions using the self-seeding techniques. Amphiphilic block copolymers are known to form various micellar morphologies in selective solvents or to phase-separate into different nanostructures in the bulk or thin films. The self-assembly of polymers may serve as templates to manipulate C\textsubscript{60}s into various ordered structures, if the C\textsubscript{60}s are attached to different locations of these polymers.

With the well-defined fullerene polymer synthesized as described in Chapter VII, physical studies on their self-assembly have been initiated. The basic ideas and preliminary results will be discussed in this Chapter to illustrate the versatility of these hybrid materials. The results have shown that C\textsubscript{60} indeed introduced some interesting behavior to the supramolecular assemblies of these fullerene polymers.

8.1 Fullerene Polymer Single Crystals

The growth of semicrystalline diblock polymer (e.g., PEO-b-PS) single crystals in dilute solution utilizing the self-seeding techniques was discovered almost forty years ago
by Lotz et al.\textsuperscript{183} It was known that these single crystals form “sandwich-like” lamellae with folded crystalline PEO chains in the middle and the amorphous PS chains tethered onto both of the lamellar basal surfaces. Recently, this “old” discovery was re-examined and explored by our group and, in turn, yielded many “new” discoveries. For example, three regimes have been identified based on the different interaction behavior of the tethered chains: the non-interaction, the crossover, and the highly stretched regimes.\textsuperscript{242} The transition between these regimes turned out to be sharp, when the relationship between the reduced surface energy and the reduced tethering density is plotted. Also, channel-wire arrays with chemical and geometrical recognition on a sub-micrometer scale can be constructed by alternating growth of single crystals of the diblock copolymer (e.g., PEO-$b$-PS) and homopolymer (e.g., PEO).\textsuperscript{185} Since the homopolymers and diblock copolymers were usually prepared by anionic polymerization and/or in combination with other controlled polymerization techniques with narrow polydispersity ($< 1.10$), the non-crystallizable chains tethered on the lamellar basal surface could be uniformly distributed.

In this section, preliminary results on using polymer single crystals as templates to obtain the ordered 2D array and near 1D chain of $C_{60}$ on single lamellar surfaces will be discussed. The difference between this study and our previous work lies in the fact that PS chains are interpenetrable; while $C_{60}$ is impenetrable and incompressible.

When an impenetrable nanoparticle, such as $C_{60}$, is connected covalently to a crystalline polymer (e.g., PEO), the single crystal growth of the crystalline polymer will lead to tethered nanoparticles on both of the single crystal basal surfaces, since the $C_{60}$ groups are too bulky to be incorporated into the crystalline lamellae (Figure 8.1). The tethering density, $\sigma$, of these $C_{60}$s can be defined as in Eq. (8.1),
\[ \sigma = \frac{1}{S} \]  

Eq. (8.1)

where \( S \) is the area that a tethered \( C_{60} \) occupies. At a low tethering density, \( C_{60}s \) are more likely to be randomly distributed on the lamellar basal surface; they may be far apart from each other and do not interact with each other. At an intermediate tethering density, they start to interact with each other, yet still far away from two-dimensional hexagonal close packing. At a high tethering density, they probably will be in contact with each other and forced into a close-packed array. This process simulates a 2D phase transition from gas, to liquid and finally, to solid. It should be noted that this is largely an entropy-driven transition rather than of enthalpic origin.

Figure 8.1. Crystallization of \( C_{60}\)-end-capped semicrystalline polymer into polymer single crystal lamellae with tethered \( C_{60}s \) on the surface. Increasing tethering density simulates a 2D phase transition.

At a high tethering density, the \( C_{60}s \) on the crystal basal surface pack closely. Their packing can be either regular or irregular (Figure 8.2), depending on the tethering density of \( C_{60} \), which is indirectly related to the molecular weight, the molecular weight distribution, and the crystallization temperature (\( T_c \)). When the tethering density
Figure 8.2. Comparison between (a) regular close packing and (b) irregular close packing.

Figure 8.3. Crosslinking of C₆₀ on polymer single crystal lamellar surface via multiple [2+2] cycloaddition reactions under UV irradiation.

becomes high enough, the C₆₀s are in close contact with each other. In this case, if UV is utilized to initiate the [2+2] cycloaddition reactions between adjacent C₆₀s, it might possibly generate a crosslinked monolayer or molecular sheet of C₆₀ (Figure 8.3).²⁵⁷ After polymerization, the semicrystalline polymer could possibly be degraded by either chemical or biological means to achieve free-standing C₆₀ monolayer sheets. Such molecular sheets hold great promise in future applications in microelectronics.
Ever since the day $C_{60}$ was discovered, people have been seeking ways to prepare stable monolayers of $C_{60}$, hoping to transfer $C_{60}$’s interesting properties of the bulk onto a surface.\textsuperscript{258} The major problem with its preparation is associated with the high hydrophobicity of the carbon cage compounds and their tendency to aggregate together due to the strong intermolecular interactions. Most Langmuir-Blodgett films obtained are thus unstable for transferring to solid substrates or only form very small domains of ordered structure.\textsuperscript{259} Stable, self-assembled monolayers (SAMs) might be complicated with multilayer formations and head-to-tail assemblies.\textsuperscript{260} So far, only a few successful cases have been reported.\textsuperscript{261} The approach described herein provides a unique way to obtain stable $C_{60}$ monolayers.

When the self-seeding procedure is utilized in the single crystal growth of a crystalline polymer, singles crystals with a uniform lateral size and thickness are usually generated. The thickness is determined by the equilibrium dissolution temperature, $T_d$, and the isothermal crystallization temperature, $T_x$, while the lateral size of the single crystals is mainly by the crystallization time and the concentration of the polymers in dilute solution (i.e., the material supply). If there is only limited amount of material available, the lateral size will be determined by the self-seeding temperature, $T_s$ (i.e., the number of seeds available for crystal growth). The lamellar thickness, $d_{\text{CRYST}}$, is related to the crystallization temperature, $T_x$, as shown in Eq. (8.2):\textsuperscript{184,242}

\[
\frac{1}{d_{\text{CRYST}}} = \frac{\Delta h_f}{2\gamma_c} - \frac{\Delta h_f}{2\gamma_c T_d} T_s 
\]

Eq. (8.2)

where $\Delta h_f$ is the enthalpy of fusion at the dissolution temperature, $\gamma_c$ is the fold surface free energy per area, and $T_d$ is the equilibrium dissolution temperature. Since $\gamma_c$ is
critically related to surface crowdedness, the $d_{\text{CRYST}}$ can serve as an indirect probe of the surface free energy change caused by the surface crowdedness. Therefore, measuring the $d_{\text{CRYST}}$ reveals what happens on the lamellae surfaces due to the change in tethering density.

The PEO-$C_{60}$ single crystals have been successfully grown from amyl acetate using sample PEO1-$C_{60}$ with PEO molecular weight of 5.1 kg/mol (see Table 7.6 for detailed information). The best conditions for single crystal growth were found to be more dilute concentration (~ 0.005 wt%) in amyl acetate and a higher $T_s$ of 42 °C. These conditions minimized the influence of the irregular aggregation of $C_{60}$s. Because $C_{60}$s have strong interactions even at very dilute conditions that could disturb the single crystal growth process, only single crystals with lower population and relatively small lateral sizes were obtained. Figure 8.4 shows a single crystal with a relatively small lateral size (~ 2 μm). The lamellar thickness was measured by AFM scan profile to be 8.06 nm (Figures 8.5).

Since $C_{60}$ has a well-defined, impenetrable size, its tethering density and surface coverage can be readily deduced, based on the information of lamellar thickness, PEO molecular weight, and PEO crystallographic data. The PEO crystal structure has been resolved to be monoclinic with four chains in a unit cell of $a = 0.805$ nm, $b = 1.304$ nm, $c = 1.948$ nm, $\alpha = 90^\circ$, $\beta = 125.4^\circ$, and $\gamma = 90^\circ$ (Figure 8.6b). Therefore, each PEO stem in the crystal occupies $(a \sin \beta \times b / 4) = 0.214$ nm$^2$ on the area of folded basal surface. If both the top and bottom surface of the lamellar single crystals were occupied by $C_{60}$ ($d =$ 1 nm including electron clouds) as Figure 8.6 shows, the PEO lamellar thickness should be $(8.06 - 1.0 \times 2) = 6.06$ nm. The contour length of PEO of molecular weight 5100 could
Figure 8.4. (a) TEM morphology of the PEO-C$_{60}$ single crystal; (b) electron diffraction obtained from the PEO-C$_{60}$ single crystal; (c) AFM phase image of the PEO-C$_{60}$ single crystal; and (d) AFM height image of the PEO-C$_{60}$ single crystal. The single crystals were grown using sample PEO1-C$_{60}$ with PEO molecular weight of 5100 g/mol.

Figure 8.5. The AFM scan profile of the single crystal of PEO-C$_{60}$ (see also, Figure 8.4c) revealed a thickness of 8.06 nm for the single crystal.
be calculated according to literature to be 31.6 nm.\textsuperscript{263} Each chain then contributes at most \([31.6/6.06]\) \approx 5 stems. Since each stem contributes to top and bottom surface areas, the total surfaces created by one chain will be \((5 \times 0.214) \times 2 = 2.14 \text{ nm}^2\). The area that a C\(_{60}\) occupies is \((\pi \times d^2/4) = 0.79 \text{ nm}^2\). Therefore, the tethering density is \((1/2.14) = 0.46 \text{ nm}^{-2}\) and the surface coverage is \((0.79/2.14 \times 100\%) = 37\%\).

The C\(_{60}\)s on the surface were not easy to characterize, since they were so small and only of a molecule thickness. It was also difficult to use scanning tunneling electron microscopy (STEM) to visualize the C\(_{60}\)s on the surface, probably because the PEO crystals were an insulator, and the C\(_{60}\)s were thus shielded from the conducting substrate. High resolution AFM or TEM might be required to resolve the physical topology of the monolayer of C\(_{60}\)s on the lamellar crystal surface, in addition to other spectroscopic methods, such as tip-enhanced Raman scattering techniques.\textsuperscript{264}

![Figure 8.6. Schematic drawing of (a) the side-view of the PEO-C\(_{60}\) single crystal and (b) the crystal structure of PEO.\textsuperscript{262} Adapted from ref. 263 and reprinted by permission of the American Chemical Society.](image)

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An interesting extension of this work would be to use the alternating, epitaxial growth of single crystals of PEO and PEO-C$_{60}$ to prepare near-1D C$_{60}$ nano-wires. Similar work has been done in our group using PEO and PEO-$b$-PS to create channel wire arrays of PS on the surfaces of PEO single crystal lamellae (Figure 8.7). If this can be achieved in a similar way, near-1D nanowires of C$_{60}$ can be grown in a controlled geometry.

Figure 8.7. Near 1-D channel-wire arrays constructed from alternating crystal growth of a diblock copolymer PEO-$b$-PS and a homo-PEO in dilute amyl acetate solutions. Adapted from ref. 185 and reprinted by permission of the American Chemical Society.

8.2 Block Copolymer Micelles in Solution

Block copolymers can form various micellar aggregates in different solvents and their mixtures. For example, PEO-$b$-PS with a PS block molecular weight of 100 k g/mol and a PEO block molecular weight of 10 k g/mol were found to form spheres,
cylinders, and vesicles from DMF/H$_2$O mixed solvent, in which DMF is a common solvent for both PS and PEO and H$_2$O is a selective solvent for PEO (Figure 8.8).$^{160,186,187}$

![Image of micellar aggregates](image)

Figure 8.8. Depending on the water content in DMF, a PEO-$b$-PS block copolymer forms micellar aggregates such as spheres, cylinders, and vesicles. The PEO blocks have a molecular weight of 10 kg/mol and the PS blocks have a molecular weight of 100 kg/mol.$^{160}$ Adapted from ref. 161 and reprinted by permission of the American Chemical Society.

The main driving force for the micelle formation is to reduce the unfavorable interaction between one block with the poor solvent and achieve a free energy minimum. The free energy of the micelle is composed of three terms as shown in the following equation (Eq. 8.3):$^{160,186,187}$

$$F_{\text{micelle}} = F_{\text{core}} + F_{\text{corona}} + F_{\text{interface}} \quad (\text{Eq. 8.3})$$

where $F_{\text{micelle}}$ is the overall free energy of the system, $F_{\text{core}}$ is the free energy of the core, $F_{\text{corona}}$ is the free energy of the corona, and $F_{\text{interface}}$ is the overall free energy at the block interface. It has been found that the main determining term in the micellar formation is attributed to $F_{\text{interface}}$.$^{160}$ As C$_{60}$s are attached to different locations of the block copolymer, an additional interaction (the C$_{60}$-C$_{60}$ interaction) is introduced into the system. In the formation of micelles, this new free energy term may influence the change
in micellar morphologies and their morphological transition kinetics. More importantly, the arrangements and locations of \(\text{C}_6\text{O}_\text{s}\) within these micelles is a very intriguing question. Will they form fine structures and hierarchical orders within these morphologies (Figure 8.9)?

![Anticipated micellar structures formed by PEO-\(b\)-PS block copolymers functionalized with \(\text{C}_6\text{O}_\text{s}\) at different locations in selective solvents. The green color represents the PEO blocks and the pink color represents the PS blocks.](image)

An analysis was made on the micellization of PEO-\(b\)-PS-\(\text{C}_6\text{O}_\text{s}\) and PEO-(\(\text{C}_6\text{O}_\text{s}\))-PS in DMF/water mixed solvent (Figure 8.9). Neither DMF nor water is a good solvent for \(\text{C}_6\text{O}_\text{s}\). Meanwhile, polystyrene can interaction with \(\text{C}_6\text{O}_\text{s}\) with \(\pi-\pi\) interactions. Due to the covalent linkage and confinement of \(\text{C}_6\text{O}_\text{s}\) to definite locations on the chain, such as at the chain-end or at the junction point, \(\text{C}_6\text{O}_\text{s}\) will occupy definite locations in the final aggregate. For example, for PEO-\(b\)-PS-\(\text{C}_6\text{O}_\text{s}\), \(\text{C}_6\text{O}_\text{s}\) is tethered to the chain-end and therefore shall stay in the core with PS. In contrast, for PEO-(\(\text{C}_6\text{O}_\text{s}\))-PS, \(\text{C}_6\text{O}_\text{s}\) is confined at the interface and thus adds a specific interaction to the free energy of the interface in micelles.
The C₆₀s confined at the interface must exhibit certain specific structural features in the micelles, such as forming a hierarchical structure within these supramolecular aggregates. Therefore, it is very interesting to look into the structure and formation mechanism of these interesting micellar aggregates.

The preliminary results are briefly presented here. Two polymer samples were used first to compare their micellar morphological behaviors: PEO-ₜ-PS and PEO₄-ₜ-PS₅-C₆₀ (Table 7.3). Both of the PS and PEO blocks possess identical molecular weights of $M_{w, \text{PEO}} = 8.4$ kg/mol and $M_{w, \text{PS}} = 10.0$ kg/mol. Spherical micelles were observed in both cases, as shown in Figure 8.10. For the PEO-ₜ-PS, the diameter of the spherical micellar aggregates is around 6 nm; for the PEO-ₜ-PS₅-C₆₀, the diameter is around 16 nm. With increasing water concentration up to 23.1 wt%, both samples remain in the spherical micelle region and no morphological transformation has been observed. The results have shown that the fullerene-functionalized diblock copolymer indeed forms micelles.

![Figure 8.10](image)

Figure 8.10. TEM morphologies of spherical micelles obtained from self-assembly of (a) PEO-ₜ-PS and (b) PEO-ₜ-PS₅-C₆₀ from DMF/water mixed solvent. Both copolymers have identical molecular weights of the PS (10k) and PEO (8k) blocks.
Extensive investigations are now ongoing in our laboratory, including increasing the water concentration and/or changing temperature at a fixed water concentration to induce the morphological transformations. Samples with different molecular weights, compositions and locations of $C_{60}$ on the block copolymers are also being prepared to study the morphological phase diagrams of these hybrid polymers and to illustrate the effects of $C_{60}$ on the micellization of these polymers, their structures, and formation mechanism.

8.3 Block Copolymer Self-Assembly in the Bulk

The introduction of $C_{60}$ selectively into certain positions of block copolymers is expected to affect their self-assembly behaviors and phase structures tremendously, due to their strong interactions and rigid 3D conformation with well-defined shape. Block copolymers are known to be able to self-assemble into different ordered nanophase structures as shown in Figure 8.11 with the junction point tethered and confined at the interface.\textsuperscript{158} If $C_{60}$ is selectively introduced to one of the blocks, how will this affect the phase behavior and structure? For example, when $C_{60}$ is bonded at the junction point, after self-assembly, it should be confined and even packed at the interface. These $C_{60}$s will take the shape of the interface (either flat or curved) to become markers of the interfaces. These markers thus form another level of hierarchical structures. If $C_{60}$s are located at the end of the PS blocks, they are mainly associated with the PS phase via the $\pi-\pi$ interactions; the self-assembly process could thus control the 3D spatial arrangements of fullerene. Therefore, it was of great interest to investigate the influence of $C_{60}$ on the self-assembly of block copolymers in the bulk.
Figure 8.11. Self-assembled, nano-phase-separated structures formed by diblock copolymers in the bulk. The junction points of two blocks are tethered to the interface and the polymer chains are stretched away from the interface.

Figure 8.12. Anticipated morphologies formed in the bulk self-assembly of PEO-<i>b</i>-PS with different C<sub>60</sub> locations. The green color represents the PEO blocks and the pink color represents the PS blocks. The dark phase is the PS phase and the white phase is the PEO phase.
Previous study has shown that a polystyrene-\textit{b}-poly(dimethyl siloxane) could dissolve up to \( \sim 1 \) wt\% of \( C_{60} \) in the block copolymer.\textsuperscript{266} Solid-state NMR measurements indicated that the \( C_{60} \)s were completely surrounded by PS chains, even when the \( C_{60} \) loading went above its apparent solubility in PS.\textsuperscript{266} This is mainly due to the \( \pi-\pi \) interaction between PS and \( C_{60} \), making them miscible to a certain extent. Our results on the SEC of PS-\( C_{60} \) also indicated that polystyrene and \( C_{60} \) like each other and do not strongly phase separate.\textsuperscript{14} Therefore, in the PEO-\textit{b}-PS-\( C_{60} \) and PEO-\textit{b}-PS/\( C_{60} \) where \( C_{60} \)s are located at the end of the PS block or randomly attached on the PS block, \( C_{60} \) will mainly stay within the PS phase after self-assembly. In PEO-(\( C_{60} \))-PS where \( C_{60} \) was confined at the interface, it would probably stay at the interface but more on the polystyrene side (Figure 8.12).

To explore the effect of \( C_{60} \) on block copolymer bulk assembly, the SAXS data were collected with a Rigaku MicroMax-002+ sealed tube X-ray generator coupled with multiwire position sensitive X-ray detector using the fullerene polymers synthesized as described in Chapter VII. The preliminary results are briefly discussed here. Figure 8.13 shows a representative SAXS profile for \( C_{60} \)-functionalized block copolymers (PEO-\textit{b}-PS-\( C_{60} \)) at room temperature. Most of the samples under study showed lamellar structures, since the molecular weights of PEO blocks and PS blocks were very close to each other. The \( d \)-spacing \( d \) could be calculated from \( q \) using the following equation:

\[
d = \frac{2\pi}{q} \quad \text{(Eq. 8.4)}
\]

Table 8.1 summarizes the \( d \)-spacings measured for the corresponding polymers using SAXS techniques.
Figure 8.13. Representative SAXS profile of nano-phase-separated structures in the block copolymers under study in this section at room temperature. The data was obtained using PEO-$b$-PS-C$_{60}$ with $M_{n,\text{PEO}} = 8.4$ kg/mol and $M_{n,\text{PS}} = 10$ kg/mol.

Table 8.1. The d-spacings determined for fullerene polymers using SAXS techniques, the corresponding calculated tethering density of junction points at the interface and the interfacial factor $k$ (see detailed discussion in text).

<table>
<thead>
<tr>
<th>Label</th>
<th>$M_{n,\text{PS}}$ (kg/mol)</th>
<th>$M_{n,\text{PEO}}$ (kg/mol)</th>
<th>d-spacing (nm)</th>
<th>Tethering density (nm$^{-2}$)</th>
<th>Interfacial factor $k$</th>
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</thead>
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<tr>
<td>PEO-$b$-PS-Br</td>
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<tr>
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<td>18.3</td>
<td>0.307</td>
<td>--</td>
</tr>
<tr>
<td>PEO-(C$_{60}$)-PS</td>
<td>8.4</td>
<td>11</td>
<td>16.2</td>
<td>0.266</td>
<td>0.323</td>
</tr>
</tbody>
</table>
In the case of PEO-b-PS-C\textsubscript{60} \((M_{n,\text{PEO}} = 8400 \text{ g/mol and } M_{n,\text{PS}} = 10000 \text{ g/mol})\), it showed two scattering peaks at \(q = 0.0343 \text{ Å}^{-1}\) and 0.0681 \text{ Å}^{-1}\, suggesting a lamellar structure and could be assigned to (100) and (200). The corresponding d-spacing was determined to be 18.3 nm. As a control experiment, the d-spacing of the precursor polymer was measured similarly to be 17.6 nm. Therefore, the incorporation of C\textsubscript{60} into the chain-end of polystyrene significantly increased the d-spacing of the nano-phase-separated structure. This effect is more evident in the case of PEO-b-PS/C\textsubscript{60} which has an average of 2.6 C\textsubscript{60} units attached per polymer chain. The lamellar structure was still maintained, due to the relatively small change in volume fraction caused by C\textsubscript{60}. In this case, the d-spacing increased further to 21.2 nm (Figure 8.12), as compared to 17.9 nm for that of the azide precursor polymer, PEO-b-PS/N\textsubscript{3}. This is reasonable since the incorporation of C\textsubscript{60} nanoparticles increases the molecular weight and the overall bulk volume. However, when the C\textsubscript{60} is tethered to junction point of the diblock copolymer in PS-(C\textsubscript{60})-PEO, although the molecular weights of each block were very similar to that of PEO-b-PS-C\textsubscript{60} (8.4k-11k vs. 8.4k-10k), the d-spacing for PS-(C\textsubscript{60})-PEO dropped to 16.2 nm, as compared to 18.3 nm in the azide precursor. This unusual effect has to be associated with the location of C\textsubscript{60} within the self-assembled structure. It is very probable that due to the functionalization position, the C\textsubscript{60} in PS-(C\textsubscript{60})-PEO has to be confined at the interface and take the shape of the interface. Therefore, the change of interface was key to the understanding of this phenomenon.

The lamellar phase assembly of PEO-b-PS with a periodicity of \(d_0\) is first considered as shown in Figure 8.14. In this model, the lamellar phase contains a total of
$N_A$ diblock copolymer molecules ($N_A = \text{Avogadro’s number}$). The cross-section area $S_0$ can thus be calculated as

$$S_0 = \frac{M_0}{(\rho_0 d_0)} \quad \text{(Eq. 8.5)}$$

where $M_0$ is the overall molecular weight of the diblock copolymer, and $\rho_0$ is the average density of PEO-$b$-PS. The average density $\rho_0$ can be calculated using the equation:

$$\rho_0 = \Sigma (f_i \rho_i) \quad \text{(Eq. 8.6)}$$

where $f_i$ is the volume fraction of the block $i$ and $\rho_i$ is the bulk density of the block $i$, based on the assumption that the density of each block in the phase-separated structure is identical to the corresponding homopolymer in the bulk state. For the system considered here, if assuming at 25 °C, $\rho_1 = 1.052 \text{ g/cm}^3$ for amorphous PS; $\rho_2 = 1.124 \text{ g/cm}^3$ for amorphous PEO.$^{184}$ The tethering density of the junction point at the interface can thus be calculated as

$$\sigma_0 = \frac{N_A}{2S_0} = \frac{(N_A \rho_0 d_0)}{(2M_0)} \quad \text{(Eq. 8.7)}$$

The factor 2 is because in such a lamellar structure, the total interfacial area is two times that of the cross-section area $S_0$.

When C$_{60}$ is introduced, a third term of $\rho_3 = 1.72 \text{ g/cm}^3$ for bulk C$_{60}$$^{32}$ along with the number of C$_{60}$s incorporated per chain ($n$) should be considered in the calculation of $\rho$. After self-assembly, the periodicity $d_0$ changes to $d$, the overall molecular weight $M_0$ to $M$, the interfacial cross-section area $S_0$ to $S$. To study and semi-quantitatively describe the effect of C$_{60}$’s net contribution to the interfacial area, as compared to its maximum cross-section area $S_3$, an interfacial factor $k$ is introduced in the following equation:

$$S = S_0 + k(xN_A) \frac{S_3}{2} \quad \text{(Eq. 8.8)}$$
where $S_3$ is the maximum cross-section area of C$_{60}$ and can be calculated as $S_3 = \pi r^2 = 3.14 \times (0.5 \text{ nm})^2 = 0.785 \text{ nm}^2$ including electron clouds. This calculation is possible because C$_{60}$ is a conformationally rigid, incompressible, and impenetrable nanoparticle with well-defined size and shape. Now, if the above analysis for unfunctionalized block copolymer still applies, the following equations can be obtained:

$$\sigma = \frac{N_A \rho d}{2M} \quad \text{(Eq. 8.9)}$$

where $r$ is the radius of the C$_{60}$, including electron clouds leads to $r = 0.5 \text{ nm}$. Then, the interfacial factor $k$ can be calculated as

$$k = \frac{1}{\sigma} \frac{1}{\sigma_0} \frac{1}{\chi N_A S_3} \quad \text{(Eq. 8.10)}$$

Ideally, the unit $k$ means that all of the C$_{60}$s are completely incorporated at the interface with their maximum cross-section area, $S_3$. This might happen when there is no specific interaction between the incorporated nanoparticle (C$_{60}$ in this case) with both blocks and the molecular weights of both blocks are high enough to accommodate C$_{60}$s comfortably...
at the interface. If the value is between 0 and 1, this represents that C_{60}s are present at the interface but they tend to get away from the interface to stay preferentially with one phase. Therefore, the occupation of their cross-section area is smaller than \( S_3 \). If this value is smaller than 0 there are then basically no C_{60} located at the interface. They stay mainly in one phase and forced the chains near or at the interface to stretch further. Based on these analyses, the tethering density \( \sigma \) and the interfacial factor \( k \) can be calculated and listed in Table 8.1.

In this Table, if C_{60} is located at the junction point of each PEO-\( b \)-PS, it is indeed confined to the interface after self-assembly, as shown by its positive contribution to the interfacial area. However, their contribution to the interfaces is only 32\% of the maximum cross-section area \( S_3 \) of C_{60}, which reveals that most of the C_{60}s prefer to stay in the PS block side of the interfaces due to the favorable \( \pi \)-\( \pi \) interaction and they seemed to drift away from the interface. Nevertheless, even this 32\% contribution leads to a significant decrease of the long periodicity (~ 2 nm) observed in SAXS experiments, indicating substantial release of the block polymer chain stretching near and at the interfaces. In comparison, in the other examples, adding C_{60}s to the end of PS blocks (PEO-\( b \)-PS-C_{60}) or within the PS block chains (PEO-\( b \)-PS/C_{60}) does not lead to the allocation of the C_{60}s on to the interfaces, as evidenced by the negative contribution to the interfacial area. All of the C_{60}s are located within the PS phases and thus, cause further stretching of the PS blocks near and at the interfaces. This, in turn, decreases the interfacial area and increases the tethering density at the interface, leading to a significant increase of the long periodicity found in SAXS experiments. These processes are
illustrated in Figure 8.15. The 3D spatial arrangement of C\textsubscript{60} could probably be achieved in this way.

![Diagram](image)

Figure 8.15. The change in d-spacing after incorporation of C\textsubscript{60} into different locations of the diblock copolymer. (I) From PS-\textit{b}-PEO-C\textsubscript{60}; (II) from PS-\textit{b}-PEO; (III) from PS-(C\textsubscript{60})-PEO.

8.4 Summary

Preliminary results in using self-assembly of block copolymers as a template to form various ordered structures of C\textsubscript{60} were presented in this Chapter. The supramolecular assemblies of these fullerene polymers were obtained. The single crystals of PEO-C\textsubscript{60} were grown, resulting in a 2D thin crystalline lamellae covered by C\textsubscript{60} at both top and bottom. The C\textsubscript{60} coverage on the surface might be tuned by changing molecular weight or growth conditions. The extension of this method to alternating epitaxy single crystal growth of PEO-C\textsubscript{60} and PEO could possibly give near-1D channel-wire patterns of C\textsubscript{60}. In mixed solvent system such as DMF/water, the fullerene diblock copolymer formed micelles, just as its parent polymer. It will be interesting to study
where the C$_{60}$s are located and how they affect the phase diagram and formation mechanism. In bulk self-assembly, the C$_{60}$s on the block copolymer mainly stayed in the PS phase, as evidenced by the increase of d-spacing as expected in PEO-$_b$-PS-C$_{60}$ and PEO-$_b$-PS/C$_{60}$. However, an unusual decrease of d-spacing was observed in PS-(C$_{60}$)-PEO. This was rationalized by the consideration of tethering density decrease due to the presence of large, rigid, impenetrable nature of C$_{60}$ cage at the interface, which allowed the chains to relax in the direction parallel to the interface. An interfacial factor $k$ was proposed and calculated from the experimental data to understand the influence of C$_{60}$ to the interfacial area. These results demonstrated that C$_{60}$s could be manipulated and arranged orderly in 3D. Hierarchical structures are also possible in these materials due to the strong aggregation of C$_{60}$s. All of these issues are being studied in detail in our laboratory.
CHAPTER IX
SUMMARY

In this dissertation, the current state-of-the-art in the field of “soft fullerene materials” has been briefly and critically reviewed, including fullerene amphiphiles, bucky liquids and gels, fullerene liquid crystals, and fullerene polymers. In particular, attention was focused on the formation of ordered structures of fullerene from these soft materials. Based on the analysis, fullerene polymers have not been fully explored for their potential in templating fullerene into ordered structures and the problem was mainly due to the lack of pure and well-defined fullerene polymers.

To address this problem, a “click” chemistry approach was developed to attach fullerenes onto polymer chains in an efficient and well-defined way under mild conditions. The copper-catalyzed azide-acetylene cycloaddition was chosen as the chemistry to prepare fullerene materials. The alkyne-functionalized fullerene was named Fulleryne for the sake of simplicity. The model reaction between PS-N\textsubscript{3} and Fulleryne\textsubscript{01} showed that the reaction proceeded in high yield at room temperature and that the excess PS-N\textsubscript{3} did not react with the C\textsubscript{60} core in Fulleryne\textsubscript{01}. PS-C\textsubscript{60} was obtained in over 95% yield with simple purification. The structure has been demonstrated by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, FT-IR, and MALDI-TOF mass spectroscopy. The MALDI-TOF mass spectrum
showed only one distribution of molecular weight matching that of the desired structure. The product was very stable.

The syntheses of fullerynes were then investigated to make them readily accessible. Fulleryne01 was synthesized by an improved Fisher esterification method using 1-chloronaphthalene, as solvent, and using a high vacuum technique to remove trace moisture to improve the yield from trace amounts up to 92%. Other fullerynes with different structures were designed and could be prepared relatively easily. They possess high “click” reactivity as well. An example is Fulleryne03, available from C_{60} in two steps with 54% overall yield. Multifunctional fullerynes are also possible from these designs. Moreover, multialkyne functionalized fullerenes, such as fullerdiynes and fullertriynes, could be designed and synthesized in a similar way. They are expected to be very useful in synthesizing fullerene polymers or gels.

With this “click” chemistry and the readily available fullerynes, fullerene materials can then be designed and synthesized with ease. During the development of fullerene-based soft materials, the importance of structure was recognized in its role to transfer and amplify molecular function across length scales and to determine the macroscopic property and function. The development of supramolecular chemistry and material science has improved our understanding on non-covalent interactions and the molecular structure-property relationships. In an effort to construct an efficient and modular approach for the design of advanced materials, a “Retro-functional Analysis” approach was proposed as the molecular design principle in advanced materials (Figure 9.1).
The basic idea is to simplify and rationalize the molecular design for advanced materials. The emphasis in this approach is that the design of materials should be function-oriented. With the advent of click chemistry and the availability of a synthon toolbox, more focus should be put on the function of the material rather than the synthesis and detailed chemical structure of the materials. The analysis of function reveals the desired molecular moieties exhibiting certain functions, called “functional synthons,” and the desired structure that can be formed via the interactions between molecular moieties, called “structural synthons.” The combination of the two in a preferred configuration gives a molecular scaffold. Filling the scaffold with the choice of detailed synthons as well as the chemistry to link them gives the final structure of the materials.
materials are prepared from such building blocks, they can self-assemble into desired structures to exhibit macroscopic functions. This integrated approach requires a library of synthons with well-documented functions and well-understood interactions. The advantage of this approach is the simple construction of materials from libraries of synthons with engineered supramolecular interactions to give desired hierarchical structure. It facilitates the molecular design and creates libraries of materials for study. Some of the designs might not be apparent from conventional design approaches that always try to fit the design into the current knowledge setting. Instead, it creates goals and targets for guided innovation.

Using this principle, many soft fullerene materials were designed and developed for various applications, such as nano-capacitors, solar cells, etc. While many projects are on-going in our laboratory, fullerene polymers were the focus of this dissertation. “Click” chemistry has been successfully applied to the synthesis of C\textsubscript{60}-functionalized PEO and PEO-b-PS with controlled molecular weight and architecture and defined functionalization position. These fullerene polymers include but are not limited to PEO-C\textsubscript{60}, PEO-(C\textsubscript{60})-PS, and PEO-b-PS-C\textsubscript{60}. The self-assembly processes of these polymers, such as crystallization from dilute solution, micellization in solution, and phase separation in bulk or thin films, have been briefly investigated. Preliminary results have shown that they are able to template the spatial arrangement of C\textsubscript{60}. For example, single crystals of PEO-C\textsubscript{60} have been grown from dilute solution to give rise to PEO single crystal lamellae with C\textsubscript{60} tethered to the surface; the alternating growth of PEO homopolymer single crystal and PEO-C\textsubscript{60} single crystal is expected to provide near one-dimensional ring patterns of C\textsubscript{60}; and the diblock copolymer PEO-(C\textsubscript{60})-b-PS can develop
micelles with different morphology in solution where C$_{60}$ is confined to the interface between core and corona or inside the core, etc. This study has demonstrated the concept and the promising future of “soft fullerene materials.”
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Figure A.1. Calibration curve for Fulleryne01.
Figure A.2. Plots of absorbance vs concentration for PEO-C$_{60}$ ($M_{n,PEO} = 8.4$ kg/mol).
Figure A.3. Plots of absorbance vs concentration for PEO-\textit{b}-PS-C\textsubscript{60} (\(M_{n,\text{PEO}} = 8.4\) kg/mol \(M_{n,\text{PS}} = 9.0\) kg/mol).
Figure A.4. Plots of absorbance vs concentration for PEO-(C₆₀)-PS ($M_{n,PEO} = 9.0$ kg/mol $M_{n,PS} = 9.2$ kg/mol).