HIERARCHICAL SUPRAMOLECULAR STRUCTURES BASED ON MOLECULAR NANOPARTICLES FROM BULK TO THIN FILM STATE

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HIERARCHICAL SUPRAMOLECULAR STRUCTURES BASED ON MOLECULAR NANOPARTICLES FROM BULK TO THIN FILM STATE

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Dissertation

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ABSTRACT

Molecular nanoparticles (MNPs), such as [60]fullerene (C_{60}), polyhedral oligomeric silsesquioxane (POSS), and polyoxometalate (POM), are nano-objects possessing shape- and volume-persistency and precisely defined molecular structure with specific symmetry. Because of their inherent physical properties and the feasible functionalization, MNPs have been considered as a unique class of building blocks for nanomaterials to bridge the molecular functionalities and material properties across different length scales through supramolecular hierarchical structures. The well-developed “click chemistry” in our group facilitates a diverse molecular design of “giant molecules” consisted of MNPs as building blocks, such as giant shape amphiphiles, giant polyhedron, and giant surfactants. The purpose of this research is to study the formation of hierarchical structures and transition behaviors of giant molecules in bulk and thin film states to reveal the structure formation mechanisms and to further build up the understanding of dependencies of the molecular architectures, topologies, and volume fraction of building blocks on the self-assembled supramolecular structures. The supramolecular hierarchical structures and phase behaviors of two giant shape amphiphiles, C_{60}-C_{8}-C_{12} and BPOSS-LIND, in bulk were studied and both of them were found to form layered structures because of their commensurate building blocks in size. In addition, the first study on the supramolecular structure of a giant polyhedron, C-tetra-BPOSS, was conducted and found it forms a cylinder-like supramolecular structure induced by the molecular architecture and the crystallization of BPOSS cages. Finally,
the self-assembled morphologies of 3-component AC$_{60}$-based and FPOSS-based giant surfactants in thin films were studied, especially the morphological transition with volume fractions change and the topological effect on the morphologies. Because of the affinities of the building blocks, AC$_{60}$-based giant surfactants are analogues of ABA-type terpolymers and form 2-component morphologies while FPOSS-based ones are analogues of ABC-type terpolymers and form 3-component morphologies. In general, the self-assembled structures of these giant molecules are profoundly affected by the physical interactions among MNPs. The molecular architectures and the selection and proportion of counter parts in a molecule have been proved able to fine tune the supramolecular structures. These understanding of self-assembly of giant molecules allow us to modularly develop novel nanomaterials with desired supramolecular structures consist of specific MNPs of targeting properties.
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CHAPTER I
INTRODUCTION

The objective of this research is to demonstrate an efficient and modular design of functional nanomaterials through the transfer and accumulation of molecular functionalities from the primary molecular entities to material properties through hierarchical supramolecular structures across different length scales. The recently developed molecular design has become supramolecular structure- and material property-orientated instead of synthesis-orientated, benefited from the well-developed “click chemistry” for feasible combining building blocks through covalent bonds. The central idea of constructing hierarchical structures to bridge the molecular designs and material properties relies on incorporating molecular nanoparticles to aliphatic chains, dendrimers, polymers, etc. to form a well-defined “giant molecules”. Moreover, giant molecules can be built mainly upon molecular nanoparticle in diverse molecular geometries. The micro-phase separation between counter parts of giant molecules could serves as frameworks to guide the nano-phase separation of molecular nanoparticles to form hierarchical supramolecular structures.

According to the molecular designs, giant molecules can be classified in three different categories: giant shape amphiphiles, giant polyhedra, and giant surfactants. Giant shape amphiphiles are consisted of molecular segments of distinct shapes and
competing interactions. The specific shapes and sizes of the molecular segments in certain symmetries would tend to pack in their own unique way to minimize the free energy, providing an additional parameter for us to engineer the desire supramolecular structures. Giant polyhedra are consisted of molecular nanoparticles linked in a specific polyhedral geometry. In this case, geometries of the giant molecules and physical interactions between building blocks would both contribute to the self-assembly behavior. Giant surfactants are the size-amplification of small-molecule surfactants in a form of molecular nanoparticles / polymers hybrid materials. Incorporating the compact and incompressible molecular nanoparticles to polymers generates a new class of polymeric materials, which exhibit copolymer-surfactant duality: self-assembly in bulk and thin film state are similar to block copolymer, while their behaviors in solution are similar to small-molecule surfactants.

In this dissertation, I am going to discuss the supramolecular structures and phase behaviors in bulk of two examples of giant shape amphiphiles and an example of giant polyhedra. To demonstrate the self-assembly of giant molecules, the morphological transitions of two sets of giant surfactants and four series of topological isomers in thin film state will be also discussed. Through these examples, we will realize that in the case of developing functional materials, the primary molecular entities are not the only controlling factor. The molecular geometries and architectures also play a crucial part in determining the final hierarchical supramolecular structures, which are highly related to the material properties.

In the first part of Chapter II, the research backgrounds are introduced that include the discussion of definitions for states of matters and mesophases, an introduction of
supramolecular structures, molecular nanoparticles, and examples of supramolecular structures consisted of molecular nanoparticles. The central part of this chapter focuses on the molecular designing of giant molecules based on molecular nanoparticles with three rational approaches: giant shape amphiphiles, giant polyhedra, and giant surfactants. The last part of this chapter introduces the concept of grazing incidence X-ray scattering technique, which is powerful in analysis of nano- and micro-structures in thin films. Several examples of copolymer thin films analyzed by the technique are provided here to illustrate the practicability in thin film structural determinations.

In Chapter III, the detailed sample preparation, experimental conditions, and instruments are presented in four sections: the first three sections are the three major steps to analyze supramolecular structure and phase behavior in bulk, and the last section is mainly focused on the morphological identification in thin films. The first section focuses on techniques for phase identification and morphology observation including DSC, TGA, bright field TEM. The second section describes the crystallographic unit cell determination utilizing 1D and 2D WAXD, SAXS, SAED. The third section describes the molecular packing determination by packing model construction, ED pattern simulation, and density measurement. The fourth section delineates the characterizations of thin films including GISAXS and GIWAXD, reflectivity, bright field TEM in plan-view and cross-sectional view.

In Chapter IV, the hierarchical structure and phase behavior of C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12} are carefully studied. The physical properties of ordered crystal I phase and less-ordered crystal II phase are discussed. Based on experimental diffraction data, the simulation of superlattice contain detailed C\textsubscript{60} packing are presented.
In Chapter V, the supramolecular structure and phase behavior of BPOSS-LIND dyad are studied. The driving force of forming the unique 2D layered structure is recognized as the crystallization of BPOSS cages, and the Lindqvist-type POMs are accommodated in the 2D molecular arrangement created by BPOSS cages.

In Chapter VI, the supramolecular structure of a giant polyhedra with tetrahedral geometry, C-\textit{tetra}-BPOSS, is presented. The 3D molecular architecture of C-\textit{tetra}-BPOSS induces a complex yet interesting supramolecular structure with cylinder-like sub-structures. This case manifests the importance of molecular architecture and primary building block on the self-assembled structures. The tetrahedral symmetry is recognized as the crucial driving force of forming cylindrical supramolecular sub-structures, and the crystallization of BPOSS cages is recognized to control the lateral packing of these supramolecular cylinders.

In Chapter VII, the study of morphology behavior of \textit{AC}_{60}-based and FPOSS-based giant surfactants with various volume fractions of building blocks and different molecular topologies are presented. The incorporation of molecular nanoparticles with PS-\textit{b}-PEO diblock copolymers generates two sets of linear giant surfactants and 4 series of topological isomers. The morphological change of giant surfactants upon changing volume fraction of the major block, PS, and different morphologies in thin films from bulk were observed. The topological effect of giant surfactants on the self-assembled structure is also described.
2.1 Definition of State of Matters, Phases and Mesophases

To qualitatively describe the state of matters and phases, the concept of order and symmetry has to be introduced. Not intuitively, order is actually an opposite concept to symmetry, i.e. the higher order a phase possesses, the lower symmetry the phase is, and vice versa. There are perfect crystals, which possess the highest order and lowest symmetry, and liquids / gas, which possess the lowest order and highest symmetry. The phases with order and symmetry lie in between these two extreme cases are classified as mesophases.

2.1.1 Description of Phases and States

The states of matter and the transition between one another phases not only are of scientifically interesting but also provide a fundamental understanding of materials science and engineering. Macroscopically, solids, liquids, and gases are the three basic states of matter, and these phases can be identified utilizing the thermodynamic properties based on classical thermodynamic.\textsuperscript{1} To categorize and define the phases microscopically, a set of arbitrary symmetry operations of translation, rotation and reflection was introduced. The whole group of arbitrary symmetry operations was known as the Euclidean group. Liquids can be viewed as the condensed state of gases. Since
both of the two states are statistically invariant under all of the operations, liquids and gases possess the highest symmetry. As the result, liquids and gases cannot be distinguished by symmetry. On the other hand, an ordered structure is only invariant under certain symmetry group (subgroup of Euclidean group)\(^2\), possessing a lower symmetry than that of liquids and gases. The reciprocal relation between “order” and “symmetry” indicates that liquids and gases are the least ordered phases while possess the highest symmetry.

The order of a microscopic structure can be classified by the positional, bond orientational, and molecular orientational order. In the Dr. Stephen Cheng’s published book in 2008, these three orders were clearly described. Positional order represents the periodic arrays of motifs (atoms, group of atoms, or molecules). Bond orientational order represents the alignment of directional vectors which used for determining lattice axes. Finally, the molecular orientational order describes the alignment of motifs with respect to particular directional vectors.\(^3\) Moreover, the aforementioned three orders can be long range, quasi-long range, or short range order, which referred to how spatial and orientational correlation decay as a function with distance. As illustrated in Figure 2.1, in the case of long range order, the correlation function decay with respect to distance as a step function; in the case of quasi-long range order, the correlation function decay with respect to distance as a power function; while in the case of short range order, the correlation function decay with respect to distance as an exponential function. Consequently, the corresponded diffraction patterns are sharp peaks, broaden peaks, and broaden halos for long range, quasi-long range, and short range order, respectively.
Figure 2.2 illustrates 2D lattices in real space with different combinations of degree of range in positional, bond orientational, and molecular orientational orders. In terms of symmetry and order, the condensed phases are general categorized into three classical phases: melt phase (liquid), the crystal phase, and the glass (solid). In addition to these three classical phases, there are six more mesophases existed with certain orders in quasi-long range or short range.
<table>
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**Long-Range Order**

- $D(r)$: Decaying correlation function
- $/Q(r)$: Decreasing diffraction pattern

**Quasi-Long-Range Order**

- $D(r)$: Oscillating correlation function
- $/Q(r)$: High peak at $2\pi/a$ and decreasing pattern

**Short-Range Order**

- $D(r)$: Exponential decay $\exp(-r/\xi)$
- $/Q(r)$: Smooth pattern

Figure 2.1 Illustration of the decay of correlation functions and corresponding diffraction patterns for long range, quasi-long range, and short range order.³
Figure 2.2 Illustration of the decay of positional, bond orientational, and molecular orientational order. $a$ and $b$ indicate lattice translational vectors of the plane lattice. $\gamma$ is interaxial lattice angle between $a$ and $b$. The molecular orientation is set to be perpendicular to the 2D lattice.

2.1.2 Description of Mesophases

Based on the definition of orders, a crystalline phase possesses all three positional, bond orientational, molecular orientational long range orders, while an isotropic phases, melt solid or glass solid, possess all three orders in short range. Between a 3D long range ordered crystalline phase and a short range ordered isotropic phase, there are phases exhibit long range decay in certain orders and only quasi-long or short range decay in the rest orders. The classical phases and mesophases are listed in Figure 2.3. In between the crystalline solid and melt liquid, there are three mesophases including condis crystal (CD), plastic crystal (PC), and liquid crystal (LC). CD phase has conformational disorder in the ordered structure. They usually show long range positional and orientational order but with partially or fully conformationally mobile. LC phase is a mesophase that
possesses long range molecular orientational order but short range positional order. In opposite, PC phase is a mesophase possesses long range positional order but short range molecular orientational order. A list of characteristic properties of these three mesophases is given in Figure 2.4. As the temperature decreased to be lower than the glass temperature \((T_g)\), the three mesophases would be verified into their glassy states counterparts: LC glass, PC glass, and CD glass. Because the transition from one mesophase to its glassy counterpart does not alter the order of microscopic structures, the transition would not involve enthalpy or entropy change.\(^1\)
Figure 2.3 List of three classical phases (white character on black background) and six mesophases (black character on white background).³
Generally speaking, the structural order is promoted by the interactions between motifs. However, in the case of mesophases, the shapes of motifs also play crucial role to determine the final phase. For instance, the motifs of LC phase generally possess rod-like or disc-like geometries, as known as mesogens. The motifs of PC phases usually possess spherical geometry, such as [60]fullerene (C_{60}), and that of DC phases often have chain-like geometries, such as polytetrafluoroethylene (PTFE). Thus we know a delicate design of molecular interactions and shapes would able to fine-tune and generate system with ordered structures of interest. In this dissertation, a number of molecular building blocks with various shapes and interactions will be introduced and discussed. The spherical-shape, cubic-shape, and chain-like molecular building blocks are included in
the molecular design. Furthermore, it was took one more step to study the effect of molecular shape on the formation of ordered phases in molecular design by assembling building blocks into different topographies, such as lipid-like, dumbbell-like, tetrahedral, linear and star topographies. The formation of ordered phases of these target molecules are majorly driven by the affinity or crystallization of building blocks and the incompatibility of dissimilar building blocks.

2.2 Introduction of Supramolecular Structure

As there is a field of molecular chemistry, a chemistry of covalent bonds, there is a field of supramolecular chemistry focused on assembles of subunits held by non-covalent intermolecular interactions. The subunits could be a single molecule or a group of molecules. To illustrate the concept of supramolecular chemistry, Lehn used an analogy to clearly expound the relationship between supermolecules (supramolecular entities) and molecules, “supermolecules are to molecules and the intermolecular bond what molecules are to atoms and the covalent bond.” Because supramolecular chemistry is the chemistry of intermolecular bond, it is also known as chemistry beyond the molecules. The intermolecular interactions used to self-organize and construct structures are usually physical bonds, such as hydrogen bonding, electrostatic interactions, $\pi-\pi$ interactions and Van der Waals force, which are weaker than chemical bonds such as covalent bond.

The most studied fields in supramolecular chemistry include the molecular recognition and molecular self-organization. Molecular recognition is often referred as host-guest system. The complementary host and guest motifs are able to recognize each
other through non-covalent to form host-quest complexes. This kind of molecular recognition can be applied to molecular sensors and catalysts.

Molecular self-organization involves the molecular design with programmed molecular functionalities/interactions in the molecular chemistry level and the consequent self-assembly in the supramolecular chemistry level. The motifs could follow the guidance of implanted non-covalent interactions to develop self-assembled supramolecular structure. Because of the weak secondary interactions used in supramolecular chemistry, both thermodynamics and kinetics of the resulted supramolecular systems are usually sensitive to temperature. A high temperature would tend to dissociate the supramolecular assemble due to the low intermolecular bond energy. On the other hand, a low temperature would slow down the dynamics in the supramolecular system. It is thus important to design proper supramolecular system based on the understanding of building subunits in order to reach supramolecular architecture with desired functions.

As there are various levels of structures in the self-assembled supramolecular structures throughout different length scales, the hierarchical architectures would be promising to transfer and amplify the motifs’ functionalities in the microscopic level to material properties in the macroscopic level. This dissertation will mainly focus on the supramolecular hierarchical structures constructed by self-assembly of motifs with specific shapes and functionalities.
2.3 Supramolecular Structure based on Molecular Nanoparticles

The main trend of supramolecular chemistry was focused on the small molecules, while this concept can be extended to macromolecules which also possess secondary interaction to hold and guide themselves to self-assemble into ordered structures. DNA and proteins, in nature, are great macromolecular examples to illustrate the concept. To perform specific biological functions, proteins fold into various special conformations in different length scales, driven by the collective non-covalent bonds, such as hydrogen bonds among amino acids. The sequence of amino acids forms the primary structure of polypeptide chains. The further folding of polypeptide chains forms secondary, tertiary, or even quaternary structures throughout distinct length scales to arrange atoms in the three-dimensional (3D) space. Such a hierarchical structure needs precisely defined hierarchy of forces to stabilize. Today, although various living/controlled polymerizations have been developed to produce macromolecules with high homogeneity in terms of polydispersity, tacticity, molecular weight, etc, there is still plenty of room for precisely arranging repeating motifs in a desired sequence or topology left for improvement to truly mimic the complex hierarchical structures in nature.

To construct such precise and complex structures, most of the synthetic macromolecules encounter the problem in controlling precise arrangements of motifs in such a large size with a large number of functional groups and problem in purification process. One possible way to overcome the difficulty and make predictable supramolecular structures is to build macromolecules based on precise molecular building blocks. For clear differentiation, the term “giant molecule” discussed henceforth in this dissertation refers precisely-defined macromolecules constructed by
MNPs as building blocks and their conjugates with other building blocks, such as flexible olefin chains, polymers, and dendrimers. The concept of giant molecules is beyond the general meaning of macromolecules in terms of not only possessing huge molecular weight but also emphasizing the precise molecular structures. The major key importance of giant molecules is reflected in the relationship among molecular primary structures, hierarchical structures, and material properties.

Among existing macromolecules, dendrimers\textsuperscript{9-11} are unique because they possess, theoretically, precise molecular topography and monodispersed molecular weights. The exterior functionalities, generation of branches, and core compositions can be precisely controlled to be used as building blocks to construct desired giant molecules. However, the spatial shapes of dendrimers are affected by the environment. For instance, dendrimers usually adopt a spherical shape in the solution state while adopt a pancake-like shape in the solid state.\textsuperscript{12} The flexible nature of dendrimers makes themselves lack of volume- and shape-persistency in a 3D space.

To consider both rigidity and functionality, a new candidate for the building block, molecular nanoparticles (MNPs), will be exclusively discussed in this dissertation. MNPs are defined as shape- and volume-persistent nano-motifs with precisely-defined molecular structure and specific symmetry.\textsuperscript{13} The most typical MNPs are cage-like compounds, such as polyhedral oligomeric silsesquioxane (POSS), [60]fullerene (C\textsubscript{60}), and polyoxometalate (POM). These cage-like chemical structures are incompressible and impenetrable, and the periphery of MNPs can be precisely functionalized with target molecular function or interactions. Furthermore, the specific symmetry, size, and shape of each MNP provide packing constrain during self-assembly and usually result in unique
The self-assembled structure of MNP-based giant molecules can thus be predicted from the pristine MNPs’ structures. This kind of predictable structures based on MNPs suggests a platform of constructing proper hierarchical structures to express target material properties from molecular design to transfer and amplify molecular functionalities into macroscopic scales. Crystal structures of aforementioned MNPs and their derivatives will be introduced in the next section to have basic understanding how will these MNPs direct MNP-based giant molecules to form supramolecular hierarchical structures.

2.4 Crystal Structure of Molecular Nanoparticles

Three most representative MNPs, [60]fullerene (C₆₀), polyhedral oligomeric silsesquioxane (POSS), and polyoxometalate (POM) will be introduced in this section in terms of chemical structures, molecular symmetries, and crystal structures. These MNPs have different shapes, intermolecular interactions, and functionalization which are summarized in Figure 2.5. By attaching or functionalizing the MNPs to break their original molecular symmetries, the asymmetric shape and interactions would result in incommensurate packing of MNPs. Some of the crystal structures of MNP derivatives will also be introduced in this section.
2.4.1 Crystal Structure of C$_{60}$ and Ordered Phases of Its Derivatives

[60]fullerene, C$_{60}$, is the smallest and abundant stable fullerene. It is a spherical cage-like molecule with diameter of 7.1 Å consisted of only sp$^2$ hybrid carbon atoms. The 60 carbon atoms arranged in 12 pentagons and 20 hexagons to form a truncated icosahedron with $I_h$ symmetry. Because of the unique shape of C$_{60}$ is identical to the geodesic dome structure, C$_{60}$ is also known as buckminsterfullerene, which is named after Buckminster Fuller, the inventor of geodesic domes. C$_{60}$ was first synthesized by Kroto and co-workers in 1985.$^{18}$ The Nobel Prize in Chemistry was awarded to Kroto, Curl, and Smally for their contribution in discovery of buckminsterfullerene and related molecules in 1996. The crystal structure of C$_{60}$ at room temperature is a face-centered-cubic (fcc) structure with lattice parameter of $a = 14.17$ Å.$^{19,20}$ In the fcc structure, each C$_{60}$ has 12 closest neighboring C$_{60}$s, and the shortest distance between C$_{60}$s is 10.0 Å. The C$_{60}$ molecules in the lattice are freely rotated at the fixed molecular positions. Thus, this is a plastic crystal (PC) phase with long-range positional and bond orientational orders but short-range or quasi-long range molecular orientational order. The space group of the PC
phase is \( Fm-3m \). Upon cooling, \( C_{60} \) will undergo a first-order phase transition from the \( fcc \) structure to a simple-cubic (sc) structure with lattice parameter of \( a = 14.04 \text{ Å} \) at \(-24^\circ C\). There are 4 molecules in both \( fcc \) and sc structure; however, in the sc structure, the \( C_{60} \) molecules are rotated in the lattice points. The sc crystal phase thus possesses all the long-range orders in the 3D space. The space group of the sc phase is Pa-3. This phase transition can be detected by DSC (9.3 kJ/mol) or X-ray / neutron power-diffraction measurements. Thermodynamically, an exothermic peak contributed to the configurationally entropy change and volume change can be observed during cooling. In the diffraction pattern of sc structure, because of the symmetry, new peaks can be observed with mixed odd and even indices, which are forbidden \( fcc \) reflections.

The structural change of \( C_{60} \) in the phase transition can also be analysis by the TEM electron diffraction (ED) technique. For the \( fcc \) structure of \( C_{60} \), three most characteristic zones for ED patterns are [001], [110], and [111] (Figure 2.6). For clear illustrating the packing of \( C_{60} \)s in the lattice, the corresponding simulated molecular packing and ED pattern utilizing Cerius\(^2\) package in these three zones are shown in Figure 2.7. In the projection along the [001] direction as shown in Figure 2.7a, \( C_{60} \)s are packed in an orthogonal manner. This packing thus generate an orthogonal reciprocal \( a^* \)- and \( b^* \)-axes in the [001] zone of ED pattern (Figure 2.7d). The \( C_{60} \)s in the projection along the [110] direction as shown in Figure 2.7b are packing in a zig-zag manner and thus generates the rhombus-like 2D reciprocal lattice in the corresponding ED pattern as shown in Figure 2.7e. A \( fcc \) structure can also be described as stacking of closest packed layers of spheres along the spatial diagonal direction, and the layers are packed in the ABC sequence. The projection along [111] direction of the \( fcc \) structure reveals the
hexagonally close-packed \( \text{C}_{60} \) (Figure 2.7c), and the corresponding ED pattern shows a hexagonal reciprocal 2D lattice (Figure 2.7f). The ED pattern of [001] and [110] zones are mutually perpendicular in the reciprocal space as well as in the real space for their corresponding projections. While the ED pattern of [111] zone can be obtained by tilting the pattern of [001] zone along its [110] direction by 55°.29
Figure 2.6 Electron diffraction patterns of fcc structure of C$_{60}$ in (a) [001] zone, (b) [110] zone, and (c) [111] zone.$^{27}$

Figure 2.7 Simulated molecular packing of C$_{60}$s in the fcc lattice on (a) $ab$-plane projected along the [001] direction, (b) projection along the [110] direction, and (c) projection along [111] direction. The corresponding simulated ED patterns in the (d) [001] zone, (e) [110] zone, and (f) [111] zone. The simulated data was generated via Cerius$^{2}$ package with cubic lattice dimension of $a = 14.17 \text{ Å}$. The different colors of C$_{60}$s are used to indicate the different height of C$_{60}$s along c-axis.
One of the most famous $C_{60}$-derivative is [6,6]-phenyl-$C_{61}$-butyric acid methyl ester (PCBM)\textsuperscript{30} because of its outstanding performance as an electron acceptor material in photovoltaics.\textsuperscript{31} Due to the mono-substituent on the $C_{60}$, the crystal of PCBM grow from 1,2-dichlorobenzene (ODCB) solution shows a layered structure. The side group breaks the icosahedral symmetry of $C_{60}$ and result in steric hindrance for intermolecular $\pi$-$\pi$ interactions, forcing the PCBM adopts a lower structural symmetry than that of $fcc$ structure. The resulted layered structure is shown in Figure 2.8a. The crystal structure of PCBM with solvent inclusion can be altered by the used solvent. For instance, the crystal of PCBM grow from chlorobenzene possess a 3D network structure as shown in Figure 2.8b. In the case of layered structure grow from ODCB, the center-to-center distance between $C_{60}$s is in the range of 10.00Å to 10.22Å; while in the case of 3D network structure grow from chlorobenzene, the center-to-center distance between $C_{60}$s is in the range of 9.85 Å to 10.13Å.
Figure 2.8 Crystal structure of PCBM (a) grow from ODCB viewing along [-10-1] zone, and (b) grow from chlorobenzene viewing along [001] zone. Both projections are shown in 2 x 2 x 2 unit cells.\textsuperscript{32}

Nakanishi \textit{et al.} have vastly studied the self-organization of mono-functionalized C\textsubscript{60}s.\textsuperscript{33} By attaching alkyl chains on the surface of C\textsubscript{60}s, the relative balance between two hydrophobic interactions, namely, intermolecular $\pi-\pi$ interactions of C\textsubscript{60}s, and van der Waals interactions among alkyl chains can direct and induce the formation of supramolecular structures. The C\textsubscript{60}-derivative functionalized with a 3,4,5-tri(hexadecyloxy)phenyl group (Figure 2.9a) shows clearly layered structure with diffraction peaks in 1D X-ray diffraction pattern of $q/q^*$ ratio of 1 : 2 : 3 : 4 : 5 : 6 (Figure 2.9b). By comparing the long-period $d$-spacing of the layered structure and the molecular length, the layered structure was proposed as shown in Figure 2.9c with interdigitated alkyl tails. Although this model suggests a head-to-head double-layered structure of C\textsubscript{60}s, there is no diffraction peak attributed from the close packing of C\textsubscript{60}s in the 1D X-ray
diffraction pattern, indicating the C₆₀S remain in a disorder state in the layered structure and have average intermolecular distance correlated to the halo at 2θ ≈ 9.5° (d-spacing of 9.3 Å).

Figure 2.9 (a) Chemical structure of mono-functionalized C₆₀ and (b) its corresponding 1D X-ray powder pattern. (c) Illustration of the proposed interdigitated double-layer structure.34

By integrating UV-curable functional groups on the alkyl tails (Figure 2.10a), the layered structure can be fixed by cross-linking the diacetylene groups (Figure 2.10b).35 The 1D X-ray diffraction pattern displays reflections of (001) to (009) planes with corresponding d-spacing of 6 Å. The two halos at 10.3° and 19.4° could be attributed to the in-plane average intermolecular distance of C₆₀S and the average distance between molten alkyl chains, respectively.
In Chapter IV, the self-assembly behavior of a similar C_{60}-derivative to these alkyl-tethered C_{60} will be discussed. The major difference is the newly designed C_{60}-derivative contains an alkyl spacer linked between the C_{60} moiety and alkyl tails. The result shows that the C_{60}-derivative with alkyl spacers can construct an ordered C_{60} domain in the layered structure, which is a supramolecular hierarchical structure.

2.4.2 Crystal Structure of POSS with Variety Substituents

Polyhedral oligomersilsequioxane (POSS) is a family of hybrid inorganic-organic nanoparticles with variety of sizes and symmetries, among which the cubic T\textsubscript{8} cage is the most common one for utilizing as a nanobuilding block (Figure 2.11). POSS are composed of inner inorganic framework made up of silicone and oxygen (SiO\textsubscript{1.5})\textsubscript{x}
covered by external organic substituents. This set of molecular nanoparticles and its derivatives have attracted a lot of interesting during the past decade because of their thermal stability, etching selectivity, and feasible functionalization. POSS nanoparticles have sizes ranged from 1 to 3 nm in diameter, which can be viewed as the smallest silica. Unlike conventional silica or silicones, POSS cages can be precisely functionalized with organic substituents on the outer surface, and that make POSS compatible with polymers, biological systems, or surfaces.36

Figure 2.11 Structure of Polyhedral oligomeric silsequioxane (SiO1.5)x, x = 8 for T8, x =10 for T10, and x = 12 for T12.

The substituents of POSS ranged from totally hydrocarbon to versatile polar structures or functional groups. The POSS cage basically provide molecular framework with specific symmetry and initial size, and the outer functional groups determine the explicit molecular functionalities. The nature and sizes of the POSS nanoparticle can thus be changed and controlled to allow generating to enormous number of POSS-based nanobuilding block for constructing supramolecular structure. For a more comprehensive understand of the functional groups alter the packing of POSS nanoparticles, the crystal structures and packing schemes of POSS are introduced here. Larsson37-39 studied the
crystal structures via X-ray extensively for the functionalized T₈ POSS nanoparticles. A systematic summary of the crystal structures of POSS with various aliphatic and aromatic substituents is shown in Table 2.1 and Table 2.2. From the information of tables, one can find that most aliphatic functionalized POSS adopt hexagonal structures, which should be attributed to the cage-like molecular shape; while, as the aliphatic substituents getting longer or changed to aromatic substituents, the crystal structure will tend to adopt a triclinic lattice by minimizing the conformational energy of the substituents and maximizing the molecular packing efficiency.

Table 2.1 Crystallographic data for T₈ POSS with aliphatic substituents (RSiO₁.₅)₈.

<table>
<thead>
<tr>
<th>Octa-(alkyl)silsequioxane</th>
<th>Form I of (n-C₄H₈SiO₁.₅)₈</th>
<th>Form II of (n-C₄H₈SiO₁.₅)₈</th>
<th>(i-C₃H₇SiO₁.₅)₈</th>
<th>(n-C₆H₄SiO)₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystals grown from</td>
<td>tetralin</td>
<td>acetone</td>
<td>acetone</td>
<td>ether</td>
</tr>
<tr>
<td>Crystal system</td>
<td>hexagonal</td>
<td>hexagonal</td>
<td>hexagonal</td>
<td>hexagonal</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.498 ± 0.010</td>
<td>14.04 ± 0.02</td>
<td>15.33 ± 0.03</td>
<td>10.0</td>
</tr>
<tr>
<td>b (Å)</td>
<td>12.498 ± 0.010</td>
<td>15.33 ± 0.03</td>
<td>15.40 ± 0.02</td>
<td>13.0</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.087 ± 0.015</td>
<td>14.54 ± 0.03</td>
<td>16.44 ± 0.04</td>
<td>10.3</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>92</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>90</td>
<td>90</td>
<td>92</td>
<td>94</td>
</tr>
<tr>
<td>γ (°)</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>98</td>
</tr>
<tr>
<td>Z (molecules/cell)</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Density measured (g.cm⁻³)</td>
<td>1.49</td>
<td>1.31</td>
<td>1.08</td>
<td>1.18</td>
</tr>
<tr>
<td>Density calculated (g.cm⁻³)</td>
<td>1.51</td>
<td>1.30</td>
<td>1.09</td>
<td>1.20</td>
</tr>
<tr>
<td>Possible space groups</td>
<td>R ³</td>
<td>R ³</td>
<td>R ³</td>
<td>P 1 or P 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R ³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P 1 or</td>
</tr>
</tbody>
</table>
Table 2.2 Crystallographic data for T₈ POSS with aromatic substituents (ArSiO₁.₅)₈.

<table>
<thead>
<tr>
<th>Octa-(aryl)silsesquioxane</th>
<th>Form I of ( (C₆H₄SiO₁₅)₈ )</th>
<th>Form II of ( (C₆H₄SiO₁₅)₈ )</th>
<th>( (C₆H₄C₆H₄SiO₁₅)₈ )</th>
<th>C₁₂H₈SiO₁₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aryl group</td>
<td>pyridine</td>
<td>pyridine</td>
<td>ethyl acetate</td>
<td>benzene</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
<td>monoclinic</td>
<td>orthorhombic</td>
<td>triclinic</td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>12.6</td>
<td>13.6</td>
<td>14.8</td>
<td>15.0</td>
</tr>
<tr>
<td>( b ) (Å)</td>
<td>10.8</td>
<td>12.8</td>
<td>16.8</td>
<td>16.2</td>
</tr>
<tr>
<td>( c ) (Å)</td>
<td>10.7</td>
<td>20.4</td>
<td>24.0</td>
<td>15.9</td>
</tr>
<tr>
<td>( \alpha ) (°)</td>
<td>70</td>
<td>90</td>
<td>90</td>
<td>80</td>
</tr>
<tr>
<td>( \beta ) (°)</td>
<td>76</td>
<td>131</td>
<td>90</td>
<td>80</td>
</tr>
<tr>
<td>( \gamma ) (°)</td>
<td>79</td>
<td>90</td>
<td>90</td>
<td>87</td>
</tr>
<tr>
<td>( Z ) (molecules/cell)</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Density measured (g.cm⁻³)</td>
<td>1.34</td>
<td>1.30</td>
<td>1.25</td>
<td>1.24</td>
</tr>
<tr>
<td>Density calculated (g.cm⁻³)</td>
<td>1.29</td>
<td>1.27</td>
<td>1.27</td>
<td>1.24</td>
</tr>
<tr>
<td>Possible space groups</td>
<td>( P \bar{1} ) or ( P \bar{1} )</td>
<td>( P \bar{2} \bar{1} \text{ or } P \bar{2} \text{ } \bar{m} )</td>
<td>( P \bar{2} \text{ } \bar{1} \text{ } m )</td>
<td>( P \text{ } \bar{2} \text{ } \bar{1} \text{ } n )</td>
</tr>
</tbody>
</table>

In the later works, Waddon and Coughlin⁴⁰ studied the alkyl functionalized POSS using X-ray diffraction and electron microscopy, and they made similar conclusion about the effect of functional group on the packing scheme of POSS nanoparticles. The alkyl attachments on the corners are accommodated to make the whole POSS molecule can be treated as a sphere to pack hexagonally in ABCA sequence (Figure 2.12).

Another commonly used POSS nanoparticle is the octa-tert-butyl POSS (OBPOSS) because of its accessibility and adequate intermolecular distance (~ 1 nm). Bassindale and coworkers⁴¹ have determined the crystal unit cell as well as the atomic
positions of BPOSS. Because the tert-butyl groups cannot sufficient round the whole OBPOSS as a sphere, OBPOSS adopts a triclinic unit cell rather than a hexagonal packing. The triclinic unit cell parameters are $a = 9.988$ Å, $b = 10.818$ Å, $c = 10.954$, $\alpha = 96.54^\circ$, $\beta = 91.27^\circ$, and $\gamma = 99.44^\circ$.\textsuperscript{41} Based on the unit cell parameters and atomic positions, the molecular crystal model and electron diffraction patterns can be simulated via Cerius$^2$ package as shown in Figure 2.13. These crystallographic information are able give us a guideline to design novel molecular architectures with precisely defined MNPs. Also, it could help us to understand the ordered and disordered states observed in nano-composite systems such as the conjugated nanoparticle materials discussed in Chapter V and VI and the POSS-polymer hybrid system discussed in Chapter VII.
Figure 2.13 Simulated molecular packing of OBPOSS in the triclinic lattice on (a) projected $ab$-plane, (b) projected $ac$-plane, and (c) projected $bc$-plane. The corresponding simulated ED patterns of (d) [001] zone, (e) [010] zone, and (f) [100] zone. The simulated data was generated via Cerius$^2$ package with triclinic lattice dimension of $a = 9.988$ Å, $b = 10.818$ Å, $c = 10.954$ Å, $\alpha = 96.54^\circ$, $\beta = 91.27^\circ$, and $\gamma = 99.44^\circ$.

2.4.3 Crystal Structure of POM and Its Derivatives

Polyoxometalates (POMs) are an unique class of ionic MNPs with frameworks from by early-transition metals (usually molybdenum, tungsten and vanadium) linked with oxygen atoms and other hetero atoms. The transition metal oxyanions linked by shared oxygen atoms to form closed 3D framework with a variety of sizes, structures, symmetries, and compositions. The common POMs (Figure 2.14) include Lindqvist $[M_6O_{19}]^{n-}$ composed of only transition metal and oxygen atoms (isopolyoxometalate), and Anderson $[H_xXM_{6}O_{24}]^{n-}$, Dawson $[X_2M_{18}O_{62}]^{n-}$, and Anderson $[H_xXM_{6}O_{24}]^{n-}$ with hetero atoms (heteropolyoxometalates). Because POM nanoparticles are charged, in additional
to functionalized of POMs’ surface, the counter-ions also play an important role to determine the self-assembly behaviors.

Figure 2.14 Schematic illustrations of representative POMs.\textsuperscript{44}

Most of POMs can be crystallized with their counter-ions, and the crystal structure of Lidqvist type POM (LIND) with tetrabutylammonium counter-ions is introduced here. LIND forms a monoclinic unit cell with space group of $C_2/c$ and lattice parameters of $a = 16.280$ Å, $b = 17.204$ Å, $c = 17.738$ Å, $\alpha = 90^\circ$, $\beta = 101.42^\circ$, and $\gamma = 90^\circ$.\textsuperscript{45} There are 4 LIND nanoparticles and 8 counter-ions in a unit cell. Figure 2.15 shows the projected $ab$-, $ac$-, and $bc$-planes and the corresponding simulated ED patterns of [001], [010], and [100] zones, respectively. From the packing scheme of molecular model in real space, LINDs indeed retain their shape and volume in the crystalline state, making LIND a great candidate as a MNP to construct supramolecular structures in newly designed giant molecules.
Figure 2.15 Simulated molecular packing of LIND in the monoclinic lattice on (a) projected $ab$-plane, (b) projected $ac$-plane, and (c) projected $bc$-plane. The corresponding simulated ED patterns of (d) [001] zone, (e) [010] zone, and (f) [100] zone. The simulated data was generated via Cerius$^2$ package with triclinic lattice dimension of $a = 16.280$ Å, $b = 17.204$ Å, $c = 17.738$ Å, $\alpha = 90^\circ$, $\beta = 101.42^\circ$, and $\gamma = 90^\circ$ and space group $C2/c$ ($Z = 4$). The counter-ions are omitted for clarity.

Based on the specific symmetries of POMs and their composition, there are usually specific sites for each type of POMs. The approach to modify the surface of POMs through covalently bonds has been well developed. The functionalization can be either mono- or multi-functionalization to not only fine tune the molecular properties but also bring novel synergistic effects with other hybrid, and organic nanoparticles or organic substituents. The functional group can also affect the molecular packing in during self-assembly. Herein, the crystal structure of an iodo-functionalized LIND (LIND-Iodide) is introduced to compare the molecular packing with its counterpart with no functional groups. LIND-Iodide forms a triclinic lattice with space group of $P-1$ and
lattice parameters of \( a = 12.435 \, \text{Å}, b = 19.065 \, \text{Å}, c = 25.492 \, \text{Å}, \alpha = 103.72^\circ, \beta = 92.31^\circ, \) and \( \gamma = 99.78^\circ. \)^{46} There are total 4 LIND-Iodide molecules and 8 tetrabutylammonium counter-ions within a unit cell. Figure 2.16 shows projected \( ab-, ac-, \) and \( bc- \) planes and the corresponding simulated ED patterns of \([001], [010], \) and \([100] \) zones, respectively. The molecular model shows that the functional group can alter the molecular packing of the MNPs by breaking the symmetry of LIND MNPs. This result confirms the idea that we can use the POMs as nanobuilding block to construct desire supramolecular structures by fine tuning the collective interactions between nanoparticles and between substituents.
LIND-Iodide is a widely used precursor to react and bond with organic building blocks to form organic/inorganic hybrid materials. In Chapter V, the nanoparticle dyad, BPOSS-LIND, was synthesized via covalently bonding BPOSS and LIND-Iodide. Thus, both the crystal structures of LIND and LIND-Iodide would be helpful to understand the self-assembly behavior of the new hybrid material, BPOSS-LIND.

2.5 From Molecular Nanoparticles to Giant Molecules

Have a variety of candidates for MNPs in hand as mentioned in the last section, the following step will be how to design the giant molecules constructed based on the
MNPs. Figure 2.17 illustrates the most representative giant molecules in cartoons. The library of giant molecules includes three major categories: giant shape amphiphiles, giant polyhedra, and giant surfactants. Different colors of the MNPs are used to distinguish from one another by their surface functionalities and/or amphiphilicities. The cubic MNPs in cartoons could be realized by POSS cages and the octahedral ones could be POM cages. The spherical MNPs could be $C_{60}$s or even properly functionalized POSS cages. While, the flat MNPs could be porphyrin or fused benzene ring compounds, such as perylene dimide (PDI) and hexabenzocoronene (HBC) that are square, rectangular, and hexagonal plats in shape, respectively. The boundaries between these three categories of giant molecules cannot be clearly drawn because these molecular designs are not entirely parallel and independent but somehow orthogonal to each other. However, such a categorization captures the essential philosophy of molecular features and provides a guideline for future molecular design.
2.5.1 Giant Shape Amphiphiles

The first type of giant molecules is the giant shape amphiphiles, which is consisted of MNPs with distinct molecular shapes and competing interactions (Figure 2.17a). The concept of investigating the shape of amphiphiles and corresponding self-
assembly behavior can be traced back to the studies on bimolecular films. The term of “shape amphiphiles” was proposed for discotic-rod liquid crystalline molecules and later extended for nanoparticle conjugates with specific 3D shapes by Glotzer et al.16,51 There are numerous ways to build giant shape amphiphiles by linking MNPs, such as sphere-cube, sphere-disc, sphere-rod, sphere-plate, cube-plate-cube and cube-disk conjugates. The packing scheme of giant shape amphiphiles is highly affected by their specific geometries, symmetry, and competing interactions. For instance, as the enthalpic interaction between discs (usually π-π interactions) dominates the disc-contained shape amphiphile systems, it usually forms cylindrical supramolecular structures with the counterparts of MNPs surrounding the cylinders stacked from the disc-like MNPs.

One of the examples would be the sphere-disc giant shape amphiphile, prophyrin-C$_{60}$, reported by Wang et al.53 (Figure 2.18). The sphere-disc molecule was synthesized by attaching a C$_{60}$ MNP to one side of the prophyrin and attaching alkyl chains to the rest three sides of the prophyrin disc (Figure 2.18a). The resulted supramolecular structure was examined by 1D WAXD powder pattern and the reflections shows 1 : $\sqrt{3}$ : 2 of $q/q^*$ ratio, the characteristic reflections for hexagonally close-packed cylinders. In addition, the discs are stacked and twisted to each other to form 129 helical columnar structures, which is evidenced by the split arcs along column axial direction observed in the SAED pattern (Figure 2.18b). The driving force of forming such a helical structure is a delicate balance among the intermolecular interactions of porphyrins, C$_{60}$s and the steric hindrances of spherical C$_{60}$s. In this system, the π-π interactions of porphyrins dominate the energy of packing to form columns by stacking prophyrins. However, the C$_{60}$s on the
periphery of porphyrins also tend to contact to each other due the van der Waals force between the 6- and/or 5-member rings of C₆₀s. The distance between porphyrins (3.2 Å) is not sufficient to hold C₆₀s packed in line, thus each porphyrins twist 123° to each other to accommodate the steric hindrances caused by C₆₀ packing. Figure 3c shows the final molecular packing model of side-view and top-view of a single helical column (left and middle image), and the top-view of supramolecular hexagonal packing of the helical columns (right image).
Previously, a sphere-cube type giant shape amphiphile, C$_{60}$-BPOSS, was also investigated by Sun et al. in our group (Figure 2.19).$^{52}$ C$_{60}$-BPOSS was synthesized through covalently connect the two distinct MNPs via a short linkage (Figure 2.19a). Since the two MNP components are chemically immiscible with each other, a nano-phase segregation would occur to form C$_{60}$-to-C$_{60}$ and BPOSS-to-BPOSS alternating double-layered structure. According to the affinities of the substrates used to grow crystals, two different morphologies and molecular packing schemes can be obtained (Figure 2.19b).
On a glass substrate, the C60-BPOSS forms a crystal structure with orthorhombic lattice, and it is believed that because the BPOSS cages and glass share more chemical features in common and BPOSS would interact with glass surface to form a first layer. Due to the cubic shape of BPOSS cages, they arrange in an orthogonal 2D lattice in the first layer of MNPs to have better contact with the substrate. The following double layered structure of MNPs have to adopt the molecular packing scheme built in the first layer and then forms a orthorhombic hierarchical structure.

On the other hand, when the substrate changed to carbon-coated mica, the C60s would tend to form the first layer with a hexagonal close packing scheme due to their spherical shape. The top layers of MNPs, again, need to adopt the packing scheme built in the first layer and then form a hexagonal hierarchical structure. The molecular packing models are shown in Figure 2.19c.

In the case of C60-BPOSS, double layered structure is determined by the comparable size and incommensurate chemical natures of the two MNP components. However, the detail packing of MNP could be fine-tuned by the substrate used, indicating the energy difference between these orthorhombic and hexagonal packing scheme are not prominent.
Figure 2.19 Sphere-cube type giant shape amphiphile, C₆₀-BPOSS. (a) The schematic illustration and chemical structure. (b) The bright field images of crystal grown from glass substrate (top image) and carbon-coated mica (bottom image). (c) Molecular packing models of orthorhombic lattice (images in the top row) and hexagonal lattice (images in the bottom row).\textsuperscript{52}

Recently, Li and co-workers\textsuperscript{62} reported a POSS-POSS giant shape amphiphile with distinct chemical functionalities on the two POSS cages via click reactions. One representative case is a POSS cage functionalized with hydrophobic isobutyl groups (BPOSS) linked with another POSS cage functionalized with hydrophilic carboxylic groups (APOSS) as shown in Figure 2.20a. The symmetry breaking in the chemical sense (Janus type) makes the giant shape amphiphile self-assembled into a double layered
structure with alternating BPOSS-to-BPOSS and APOSS-to-APOSS layers in the crystalline state (Figure 2.20b). The driving force of the structure is the crystallization of BPOSS. Because the APOSS is an amorphous material, it is believed that the APOSS cages are dragged into the 3D crystal lattice dominated by BPOSS (Figure 2.20c). Interestingly, above the melting temperature of BPOSS crystals, the X-ray data shows it remain the layered feature but lose the long range positional order of MNPs, indicating the BPOSS-APOSS forms a supramolecular liquid crystal at high temperature region.
Figure 2.20 Janus type cube-cube giant shape amphiphile. (a) The chemical structure. (b) The SAED pattern and bright field image (inset) of the double layered structure. (c) The projected $ac$-plane of the molecular packing model to show the BPOSS-to-BPOSS and APOSS-to-APOSS alternating layers packing along the $c$-axis.\textsuperscript{62}

These cases of giant shape amphiphile have shown the ability to construct lower dimensional supramolecular structures, such as 1D columns and 2D layered structures. These lower dimensional structures would benefit the transformation and amplification of molecular functions to material properties anisotropically. In Chapter V, the supramolecular structure and phase behavior of a giant shape amphiphile built up by a $C_{60}$ and flexible alkyl tails will be discussed. In Chapter VI, the crystal structure of a dumbbell-like giant shape amphiphile of BPOSS-POM will also be discussed.
2.5.2 Giant Polyhedra

Unlike the category of giant shape amphiphile focused on the shapes and competing interactions of MNPs, the giant polyhedra concern about the topology and geometry of giant molecules by properly arranging MNPs and linked with each other to exhibit specific giant-molecular symmetries. The approach is to position MNPs on the apexes of polyhedra to have the resulted giant polyhedra adopt the symmetry of the polyhedral frameworks. The representative cartoons of giant polyhedra are shown in Figure 2.21.

![Figure 2.21 Schematic cartoon illustrations of explanatory giant polyhedra.](image)

The geometry of the linkers is one of the features in designing giant polyhedra. The linkers could be linear in 1D, planar in 2D, or polyhedral in 3D. Linking MNPs by linear linkers coincides the concept of giant shape amphiphiles. As mentioned before, these three categories of giant molecules overlap in some point but consider in different aspects in the giant molecular design. Connecting MNPs with 2D linkers could generate triangular, tetragonal, or even pentagonal giant molecules. Because pentagonal symmetry is forbidden in the crystallography, the packing scheme of pentagonal giant
molecules will be an intriguing research topic. The 3D polyhedral giant molecules will be even interesting because the geometries can mimic the valence-shell electron-pair repulsion (VSEPR) models of small molecules including tetrahedral, trigonal bipyramidal, and octahedral geometries.

The linkers of giant polyhedra should be able to hold the specific geometries, while the detail chemical entities can be still designed as rigid or relatively mobile. Take the giant tetrahedron as example, the four MNPs can be connected to an adamantane core to have a rigid linker or connected to a $sp^3$ hybridized carbon to have a relatively soft linker (Figure 2.22). The subtle difference of linkers is believed to have certain effect on the packing of giant molecules due to the steric hindrance, resulting in diverse supramolecular structures. Interestingly, if we choose MNPs with distinct surface functional groups to form giant polyhedra, the chirality in the level of giant molecules can be introduced. Consequently, complex supramolecular structures and material properties can be expected. All of these possible molecular designs clearly demonstrate the potential of this class of materials in the future development of material science.

![Figure 2.22 Explanatory tetrahedral linkers for constructing giant tetrahedral with $sp^3$ hybridized carbon and adamantane cores.](image)

Because this is a quite new research field, so far, there are only few works reported on this kind of materials. However, the computer simulation has predicted this
class of materials can form diverse interesting structures, including liquid crystals, plastic crystals, quasi-crystals, and crystals. In Chapter VI, the supramolecular hierarchical structure of giant tetrahedron composed of four BPOSSs will be discussed. The result shows that even the amphiphilicity is absent in the giant tetrahedron, an unique columnar structure can be induced by its 3D molecular geometry.

2.5.3 Giant Surfactants

The third category of giant molecules, giant surfactants, considers the combination of MNPs and polymers (Figure 2.23). The most straightforward geometry of a giant molecule is to attaching a MNP on the end of a polymer chain, which is reminiscent of the small-molecular surfactants yet have a comparable size of a conventional block copolymer. However, the compact and incompressible MNP head of a giant surfactant makes the phase behavior of itself differ from that of block copolymer in terms of conformational entropy. In addition, the cross-sectional area ratio of MNP head and polymeric tails is another key factor to determine the self-assembly behavior. The cross-sectional area can be easily tuned by changing the number / chemical entities of the MNP head or polymeric tails. Therefore, giant surfactants can be considered as a new class of materials which bridge the gap between small-molecular surfactants and block copolymers. Thus, theoretical descriptions of this system must not simply obey the mean-field or self-consistent field theories which are widely used in diblock copolymers. In this aspect, new theoretical study on this system is necessary for further understanding these new materials.
Although the unavoidable polydispersity of polymer tails in molecular weights violate the strict definition of giant molecules, the cooperation of polymers and well-defined MNPs has dramatically decreased the possible polydispersities in molecular weights and molecular architectures. Through controlled / living polymerizations, the, so far, best approximation of giant surfactants can be synthesized, and the preliminary results have shown that giant surfactants possess a duality of small-molecular surfactants and block copolymers in phase behavior.\textsuperscript{64} The phase behavior of giant surfactants in solution was found to be similar to block copolymers yet have stretched polymer chains, which is similar to small-molecular surfactants. In bulk state, giant surfactants shows a wide compositional window to form lamellar structure because the domain of bulky MNPs is unfavorable in energy terms to be bent. This unique behavior makes giant surfactants able to form highly asymmetric lamellar structures which are unlikely to be observed in conventional block copolymers. Figure 2.24a shows the explanatory giant surfactant of XPOSS-PS with diverse surface functional groups on the POSS cage including \textit{di}-hydroxyl groups (DPOSS), carboxyl acid groups (APOSS) and fluorinated
chains (FPOSS). The SAXS and TEM investigations on DPOSS-PS reveal a variety of ordered phases (Figure 2.24b). As increasing the volume fraction of PS ($V_{PS}$), DPOSS-PS exhibits the lamellar structure, the double-gyroid $bi$-continuous structure, the hexagonally packed cylinders, and then the body-centered cubic packed spheres with feature sizes ranged from $sub$-10 nm to 11 nm. It should be noticed that the upper boundary of $V_{PS}$ for lamellar structure is up to 0.76, which is a highly asymmetric ordered phase.$^{13}$

The cooperation of MNPs with polymer tails makes giant surfactants capable of forming uniform thin film with large area of ordered structures through solvent processes. Figure 2.25 shows the self-assembled structures of DPOSS-PS$_{35}$ ($N = 35$) and APOSS-PS$_{80}$ ($N = 80$) via solvent annealing examined by grazing-incidence small-angle X-ray (GISAXS) and TEM experiments.$^{13}$ The well-defined MNPs with size about 1nm are great candidates to construct ordered features below 5 nm. Besides, the silicon oxide-based POSS cages could provide additional etching contrast in the lithography. All of these observations for giant surfactants suggest it is a potential material for nanopatterning in the field of microelectronics.
Figure 2.24 Illustration of self-assembled structure of giant surfactants. (a) The chemical structure of giant surfactants including DPOSS-PS, APOSS-PS, and FPOSS-PS. (b) Phase diagram of DPOSS-PS determined by SAXS patterns and bright field TEM images of microtomed samples.\textsuperscript{13}
Another interesting research topic on giant surfactants relies on the feasible chemistry to synthesize giant surfactants with multiple MNP heads or polymeric tails. This development gives us a chance to study the effect of molecular topologies on self-assembled structures under the condition of exactly the same volume fractions of each parts but different molecular architectures. In other words, through rational designs, giant surfactants could provide “topological isomers” which possess the identical composition but distinct head and tail topologies to reveal the relationship between the primary chemical structures and the self-assembled structures.

Figure 2.26 shows the self-assembled structure resulted from two pairs of topological isomers. The constituent parts for each pair of topological isomers is formed by attaching a single MNP to either one polymer chain or two polymer chains at a single junction point, and the overall composition remained identical. The 1D SAXS data shows that the AC$_{60}$-PS$_{44}$ forms lamellar structure with feature size of 9.4 nm, while AC$_{60}$-2PS$_{23}$
forms hexagonally packed cylinders with feature size of 7.6 nm (Figure 2.26a). In the case of other pair of topological isomers, DPOSS-PS_{35} forms double-gyroid bi-continuous structure with feature size of 8.4 nm, while DPOSS-2PS_{17} forms lamellar structure with feature size of 6.9 nm (Figure 2.26b). The different self-assembled structures for topological isomers indicate that the volume fraction is not sufficient to describe the phase behavior of giant surfactants. Another order parameter associate with the geometric shapse of MNPs and molecular architectures of giant surfactants should be introduced to further understand the relationship between primary structure and self-assembled structures. So far, we speculate the cross-sectional area ratio between MNP head and polymeric tails is one of the order parameters to affect the self-assembly.

In Chapter VII, the study three-component giant surfactant systems in thin film state will be discussed. The MNPs of the giant surfactants are composed of either AC_{60} or FPOSS, and the polymer tails are composed of PEO with a fixed molecular weight and PS with varied molecular weights. The topological effect will also be discussed for the linear giant surfactants and the star-like ones with identical compositions.
2.6 Thin Film Analysis by X-ray Scattering

In order to study the ordered structure of giant surfactants in thin film state, in addition to the TEM technique, an X-ray technique exceptional for thin films is necessary. Due to the fact that the intensity of thin film in transmission mode of X-ray experiments is very low, the reflection mode of X-ray with small incident angles is adopted for thin film samples. In this section, a brief background of the X-ray analysis for thin films and some works on the block copolymer system will be introduced.
The transmission of x-rays is inversely proportional to exponential of beam path as shown in the following equation.

\[ \frac{I_t}{I_0} = \exp(-2\mu_{\text{eff}}l) \]  

(2.1)

where \( I_0 \) and \( I_t \) are intensities of the incident and transmitted beams, \( \mu_{\text{eff}} \) is effective linear absorption coefficient (mm\(^{-1}\)), and \( l \) is beam path (mm\(^{-1}\)) through the sample.\(^{65}\) The beam path is related to the sample thickness as \( l = \frac{t}{\sin\theta} \), where \( t \) is sample thickness and \( \theta \) is incident angle. In the case of thin film specimens with thickness in the nanometer size, the film is substantially transparent for x-ray beam in the transmission geometry, resulting in the difficulty of investigating thin film structure in the transmission geometry. It is also difficult to study thin film structure in the regular reflection (Bragg-Brentano) geometry of x-ray due to the fact that the beam path is too short to generate sufficient peak-to-noise ratio in the typical Bragg incident angle. Consequently, the structural information of thin films cannot be extracted in the conventional diffractometry.

To analyze the structure of thin films, x-ray diffraction techniques have been developed in a configuration with a primary beam entering the sample at very small angles of incidence. This configuration is called grazing incidence x-ray diffraction (GIXRD).\(^{66}\) According to Equation 2.1, very small incident angles cause the path traveled by the x-ray beam to increase significantly and the structural information can be obtained in the configuration of GIXRD. Also, if the beam impinges the thin film sample in an incident angle \( \alpha_i \), the penetration depth, i.e. the depth where the intensity of radiation falls to 1/e of its original value, is \( \frac{1}{\mu_{\text{eff}}}\sin\alpha_i \). Consequently, the smaller the incidence angle is, the larger the surface sensitivity can be achieved.
2.6.1 Grazing Incidence X-ray Diffraction (GIXRD)

Depending on the angle of incidence, the GIXRD technique can be subcategorized into grazing incidence small angle x-ray scattering (GISAXS) and grazing incidence wide angle diffraction (GIWAXD). Small angles of incidence probe large domain spacing (nanometer to micrometer length), and wide angles of incidence provides structural information in small domain spacing in atomic level (few to tens of Ångström). There are several advantages of using GIXRD to study the morphology and structure of polymeric thin films: (1) this technique is non-destructive because of the small interaction of hard X-rays with sample; (2) the measurement is averaged over several square millimeters of sample surface, providing statistical information in macroscopic level; (3) by varying the angle of incidence, the probed depth can be adjusted to accommodate the study of interest from only few Å to hundreds of nm below the sample surface. (4) the technique can be applied in various types of environment from ultra-high vacuum, solvent annealing chamber, to rotating stage; (5) by combining the GISAXS and GIWAXD, the morphological and structural information ranged from length scales in angstroms to micrometers can be detected.
Figure 2.27 Grazing incidence X-ray scattering geometry.

Figure 2.27 shows a schematic illustration of measurements in grazing incident scattering geometry. The incident beam, of wave vector $k_i$, impinges the sample surface in an angle of $\alpha_i$, which is generally small and close to the angle of total external reflection $\alpha_c$ of the sample. The scattered beam, of wave vector $k_f$, makes the scattering angle $\alpha_f$ and $2\theta_f$ with respect to the sample surface and transmitted beam, respectively, describing the out-of-plane and in-plane angels between the incident and scattered wave vectors. The scattering vector is defined as $q = k_f - k_i$, which can be decomposed into three components according to the $x$, $y$, and $z$ axes:

$$q_x = k_0 [\cos(2\theta_f) \cos(\alpha_f) - \cos(\alpha_i)]$$

$$q_y = k_0 [\sin(2\theta_f) \cos(\alpha_f)]$$

$$q_z = k_0 [\sin(\alpha_f) + \sin(\alpha_i)]$$

where $k_0 = |k_i| = |k_f| = 2\pi/\lambda$, and $\lambda$ is the X-ray wavelength. While in the case of GISAXS and GIWAXD with very small incident angle (usually between 0.1° to 0.5°), the
curvature of the Ewald’s sphere can be considered as negligible, and the components of scattering parallel with and perpendicular to the surface can be simplified as following:

\[ q_x \approx 0 \quad (2.5) \]
\[ q_y \approx k_0 \left[ \sin(2\theta_f) \right] \approx k_0 2\theta_f \quad (2.6) \]
\[ q_z \approx k_0 \alpha_f \quad (2.7) \]

Because the incident angle is small, it is necessary to consider the effects of refraction at the surface. The Born approximation, used in SAXS, which treat the incident waves are plane waves is insufficient for calculating scattering factor from surfaces. To treat scattering from buried structures as perturbations of the incident, reflected and refracted waves as shown in Figure 2.28, a Distorted Wave Born Approximation (DWBA) has to be considered. In the DWBA, four terms of \( q_z \) is considered to describe the scattering from surfaces:

\[ q_{z,1} = k_{f,z} - k_{i,z} \quad (2.8) \]
\[ q_{z,2} = -k_{f,z} - k_{i,z} \quad (2.9) \]
\[ q_{z,3} = k_{f,z} + k_{i,z} \quad (2.10) \]
\[ q_{z,4} = -k_{f,z} + k_{i,z} \quad (2.11) \]
Besides the fact that the reflected beam has to be considered in four different refraction-reflection contributions, another important consideration in GIXD analysis, especially in GISAXS, is that the overall pattern is composed of two different sets of patterns generated by reflected and transmitted beams (Figure 2.29). These two sets of pattern have a translational difference in position along \( q_z \) direction of \( 2\alpha_i \) as shown in Figure 2.29. In the case of that diffraction spots are symmetric over the equatorial plane, the patterns along the \( q_z \) and \(-q_z\) are identical. Consequently, the four terms of scattering vectors have their own positive and negative counterparts. The \( q_{z,1} \) and \( q_{z,4} \) has same lengths but opposite direction, which are overlapped. This situation is the same for \( q_{z,2} \) and \( q_{z,3} \) pair. Thus, the diffraction spots from the first and last terms overlapped, and the
second and third terms overlapped. In the case of $k_{f,z} = k_{i,z}$, the value of $q_{z,1}$ and $q_{z,4}$ are zeros, and in the case of $k_{f,z} = -k_{i,z}$, the values of $q_{z,2}$ and $q_{z,3}$ are zeros, which means that the four scattering terms can be considered as only two terms: the scattering around the transmitted beam ($k_{f,z} = k_{i,z}$) and the scattering around the reflected beam ($k_{f,z} = -k_{i,z}$). In other words, the GISAXS pattern can be interpreted as the overlap of scatterings centered on the transmitted beam position and those centered on the reflected beam position.\textsuperscript{67}

Figure 2.29 A schematic illustration of transmitted and reflected beams contributed on a GISAXS pattern. The blue arrow in the right side indicates the $q_z$ vector along the film normal direction on the 2D detector.
2.6.2 Block Copolymer Thin Film Analysis by GIXD

After the DWBA theory developed to describe the complicated reflection and refraction effects, the technique of GIXD has widely used in the ordered phase determination in the thin films.\textsuperscript{67,69-73} Besides, the sufficiently long path length of the X-ray source through the film and no unfavorable scattering from the substrate give the additional advantages to apply GIXD on thin film studies. Furthermore, GIXD is a feasible tool to examine the nanostructure in the active layer of bulk heterojunction (BHJ) photovoltaics\textsuperscript{74,75} or in organic semiconductors.\textsuperscript{76,77} The basic concept of GIXD has been introduced in the last section, and some of the works regard applying GIXD technique on polymeric thin films will be introduced in this section.

Moonhor Ree and coworkers reported the first work of utilizing GISAXS technique to study in block copolymer thin films (Figure 2.30).\textsuperscript{67} The PS-\textit{b}-PI with weight fraction of 18/82, 37/63, and 65/35 in thin films show hexagonally packed cylinder (HEX), hexagonally perforated layer (HPL), and gyroid (GYR) structures, respectively, after thermal annealing at 120°C-160°C for 1-3 days. They also analyzed the effect of film thickness on the HEX morphology: thinner film usually generate shape diffraction peaks instead of Debye-Scherrer rings of reflections. For instance, the GISAXS pattern of a 400 nm thick PS-\textit{b}-PI film (Figure 2.31a) shows stronger intensity of diffraction spots and weaker ring reflections than that of a 800 nm thick film (Figure 2.30a). These two patterns have been determined as HEX phase with its \{10\} planes parallel to the film surface (see inset of Figure 2.31c). However, when the film thickness increased to 1600 nm, the GISAXS pattern only shows ring diffractions which means randomly orientated cylinders at the film plane (Figure 2.31b), indicating the preferred
orientation of cylinders in the interfaces cannot be passed through the whole film thickness (see the inset of Figure 2.31d). The GISAXS patterns of these two different ordered HEX morphologies can be simulated as shown in Figure 2.31c, and d. In the following works, the order-order phase transition from HPL to GYR of PS-\textit{b}-PI was also investigated via GISAXS. The authors cooperated the experimental data and the DWBA-based computer-simulated patterns to reveal the ABC packing scheme of HPL phase and the epitaxially converting the HPL \{121\} plane to the GYR \{121\} planes which is parallel to the substrate surface during the phase transition.\textsuperscript{70}
Figure 2.30 GISAXS patterns obtained at incident angle of 0.21° of (a) hexagonally packed cylinders (HEX) of a 800 nm thick PS-b-PI (18/82, Mw = 68 kDa) film, (b) hexagonally perforated layered (HPL) structure of a 450 nm thick PS-b-PI (37/63, Mw = 34 kDa) film, and (c) gyroid structure of a 650 nm thick PS-b-PI (65/35, Mw = 23.5 kDa) film. All the polymer films were deposited on silicon substrates with native oxide layers and annealed at 120°C-160°C for 1-3 days.67

Figure 2.31 GISAXS patterns obtained at incident angle of 0.21° of (a) 400 nm thick and (b) 1600 nm thick PS-b-PI film. Simulated GISAXS pattern of HEX morphology (c) with its {10} planes parallel to the film surface or (d) randomly orientated along the cylinder long axis in the film plane (see the model in the inset).
In the later work, Du Yeol Ryu and coworkers\textsuperscript{78} investigated a more comprehensive order-order transition behavior of PS-\textit{b}-PI thin films utilizing \textit{in situ} GISAXS experiments. Compared with the phase transitions observed in bulk state: lamella (LAM) to HPL to GYR to HEX and finally to disordered state during heating from 90 °C to 250 °C, the thin films only show phase transition from LAM to HPL to GYR and then to disordered state (Figure 2.32). The missing HEX phase in thin film may attribute to the suppressed compositional fluctuation resulted from the interactions between PI block with the substrate and air. Also, they found an increased order-disorder temperature which is likely a consequence of interfacial interactions.\textsuperscript{78}

These works on polymeric thin films have demonstrated the GIXD technique is a very powerful tool for deterring the nanostructures and morphologies of thin films. The phase behavior and nanostructures of a series of giant surfactant in thin film state will be discussed in Chapter VII based on investigations of GISAXS, GIWAXD, and TEM techniques.
Figure 2.32 Order-order phase transition of PS-b-PI ($V_{PS} = 0.33$, Mw = 42 kDa). (a) 1D SAXS patterns of the bulk sample measured. (b) *in situ* 2D GISAXS patterns obtained at incident angle of 0.18° of a 962 nm thick PS-b-PI film on silicon substrate. All patterns are recorded during heating from temperature from 90 °C to 250 °C at a heating rate of 0.9 °C/min.78
3.1 Phase Identification and Morphology Observation in the Bulk State

Thermal analyses were conducted on samples to understand the thermal stability and the phase transition behavior by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA), respectively. The morphology of single crystals and phase-separated structure was visualized through bright field Transmission Electron Microscopy (TEM).

3.1.1 Thermogravimetric Analysis (TGA)

A TA TGA Q500 instrument was utilized to study the thermal stability and degradation temperature of samples. Typical procedure was conducting 1 to 3 mg of samples which subject to 10 °C/min heating rate from room temperature to 500 °C under nitrogen atmosphere. Every sample was conducted TGA prior to DSC measurement to understand the temperature window for study the phase transition without degrading samples in the DSC chamber.

3.1.2 Differential Scanning Calorimetry (DSC)

DSC experiments were conducted on a Perkin-Elmer PYRIS Diamond differential scanning calorimetry with an Intracooler 2P cooling system. Calibration was performed
by using zinc and indium as the standards on the temperature and heat flow scale from -50 to 300 °C at various heating and cooling rates (2.5 – 40 °C/min). Typical sample mass was 2 to 5 mg sealed in standard aluminum pans (Perkin-Elmer). Two reference pans (empty) were run prior to the sample with exactly same thermal history to produce a baseline. The weight differences between the two reference pans and between the sample pan and another reference pan were controlled within 0.005 mg. All heat flow data for samples were analyzed after subtraction of the heat flow from the baseline collected before the measurement. Phase transition temperatures were determined according to the onset temperatures which were defined as the cross-point of the peak slope and the baseline in the thermal diagrams. The onset temperature was determined at the low-temperature side during heating and at the high-temperature side during cooling. The heat of fusion was calculated based on the area beneath the transition peak, the sample weight, and the molecular weight of sample. The first heating curve was recorded to study the phases induced by solvent evaporation. The first cooling and second heating curves were obtained at the same scan rate to avoid hysteresis and used to study the phase transition in the bulk state.

3.1.3 Transmission Electron Microscopy (TEM)

TEM bright field images were obtained with a JEOL (1200 EX II) and a Philips (Tecnai 12) TEM both at an accelerating voltage of 120 kV. Single crystals grown from solution evaporation was prepared from casting a drop of dilute solution (0.02 wt%) on carbon coated mica and kept in the solvent atmosphere for slow evaporation. Single crystals grown from thermal annealing was prepared from casting a drop of dilute solution (0.02 wt%) on carbon coated mica and conducted the thermal treatments in a
Mettler hot stage (FP-90). The sample along with the carbon film on the mica was floated upon distilled water surface and then transferred to clean copper grids for TEM observations.

3.2 Crystallographic Unit Cell Characterization

Based on the information of phase transition obtained from thermal analysis and morphology investigation, the pathway to reach each phase of interest can be identified. The structure of the ordered phase (i.e., crystalline, liquid crystal, plastic crystal phases) were study by several diffraction techniques such as 1D and 2D wide angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS), and selective area electron diffraction (SAED). By combining all the information obtained from these diffraction techniques, the crystal system and lattice parameters can be determined. The structure of a crystal can be described by periodically repeating the unit cell in three dimensions, and the unit cell is identified by \( a, b, c, \alpha, \beta, \) and \( \gamma \) parameters.

3.2.1 Wide Angle X-ray Diffraction (1D and 2D WAXD)

1D WAXD measurements were carried out on a Rigaku Multiflex 2 kW Automated Diffractometer equipped with Cu K\( _\alpha \) radiation source \( (\lambda = 0.1542 \text{ nm}) \). A temperature controller calibrated with a deviation within \( \pm 0.5 \) °C is coupled with the diffractometer for phase transition study at various temperatures. The angular scanning rate was set at 1 °/min within the 2\( \theta \) range of 1.8° - 4°. The sample chamber was vacuumed before recording the spectrum to reduce the scattering from air. 2D WAXD experiments were performed on a Rigaku 18 kW rotating anode X-ray source attached to an R-AXIS-IV image plate system with 3000 x 3000 pixels. The X-ray beam were
monochromatized by graphite crystals. The 2θ diffraction angles below 15° were calibrated by silver behenate, and the diffraction angles higher than 15° were calibrated by the silicon crystal powder. The deviation of the measured diffraction angle was ±0.05°.

3.2.2 Small Angle X-ray Scattering (SAXS)

SAXS experiments were performed on a Rigaku MicroMax 002+ instrument equipped with a 2D multiwire area detector and a sealed copper tube. The working voltage and current for the X-Ray tube are 45 kV and 0.88 mA, respectively. The wavelength of the X-Ray is 0.154 nm. The scattering vector (q) was calibrated using silver behenate with the primary reflection peak at (q = 1.067 nm⁻¹). The SAXS diffraction patterns covering the q range between 0.2 and 2.0 nm⁻¹ were recorded. The recording time for each data was 5 to 10 min, depending on the scattering intensity. The background scattering was subtracted and further analyzed with the Rigaku software SAXSgui.

3.2.3 Selective Area Electron Diffraction (SAED)

The SAED experiments were performed on both JEOL (1200 EX II) and Philips (Tecnai 12) Transmission Electron Microscopy under 120 kV accelerating voltage. The tilting experiments were specifically conducted on the Philips TEM equipped with double-tilting stage to provide the ED pattern of different crystallographic zones. The tilting axis is almost parallel to the beam stop and can be easily identified from an ED pattern. The samples were carefully brought to eucentric height prior to tilting experiments to ensure the correct tilting angle and illumination area. The camera length was set in a range between 0.8 m to 4.2 m depending on the dimension of interest. The $d$-
spacings of crystallographic faces were calibrated by evaporated thallous chloride (TlCl) standard, which has its largest $d$-spacing of 0.384 nm. The thickness of samples for SAED experiments were kept under 100 nm for good quality of diffraction patterns.

3.3 Molecular Packing Determination in Unit Cell

After the unit cell been determined by the diffraction experiments, the final step for a structure determination was to reveal how the motifs or molecules arranged themselves in the unit cell. Density measurements were firstly conducted to confirm the number of molecules exist in one unit cell. The measured density was also compared with the calculated one based on the experimental determined unit cell parameters. The molecular packing was performed by computer simulation to generate the conformation and arrangement of molecules in the unit cell with minimized overall energy. Simulated ED patterns from the constructed packing models were also generated to compare with experimental patterns to confirm the agreement between the constructed crystal model and the actual crystal structure.

3.3.1 Construction of Packing Model and Simulation of Electron Diffraction Pattern

Molecular packing modeling and crystallographic simulation was performed using the Accelrys Cerius$^2$ simulation package (Version 4.6) with COMPASS force field. The global equilibrium conformation with lowest energy at 0 K was chosen as the initial molecular conformation. Based on the unit cell parameters deduced from diffraction experiments, the space group analyzed from ED pattern, and the number of molecules calculated from density measurement, the initial crystal unit cell can be constructed in the Cerius$^2$ software. Simulated ED and 2D WAXD fiber patterns were calculated according
to the energy-minimized packing model. The molecular packing model refinement was performed by adjustment of atomic positions based on the comparison between experimental and simulated ED and 2d WAXD fiber patterns.

3.3.2 Density Measurement

A small amount of crystals, ca. 0.5 mg, was collected and placed in a vial filled with water followed by ultrasonication to remove the residual air bubbles on the crystal surface. In the usual case, crystal of organic materials possess a density greater than water (1 g/cm³) and potassium iodide (KI) was gradually added into the aqueous solution to match the densities of solution and crystals; on the contrary, if the density of crystal is lower than that of water, methanol can be added to the aqueous solution to match the densities of solution and crystals. After the sample suspended stably (suspension for hours) in the middle of the solution, the density of the sample is equivalent to that of the solution. The density of the crystal can be accessed by measuring the weight of the aqueous solution in a volumetric flask.

3.4 Characterization of Phase Separation Morphology in the Thin Film State

Thin film samples were prepared by spin coating (Specialty Coating Systems, INC Spincoater Model P6700) on silicon wafers with a 3 nm-thick natural silicon oxide layer. The silicon wafer substrates were cleaned by treating with piranha solution (concentrated H₂SO₄/ 30%H₂O₂ =3/1 (v/v)) at 80 °C for 30 minutes to form a clean silicon oxide surface, followed by extensively rinsed with deionized water and then dried under nitrogen flow. The film thickness was controlled by solution concentration and spin coating rate. The solution concentration used was 1 wt% and the spin rate was 6000
rpm. The thin films were further annealed at 120 °C under vacuum for various periods. The thin films were used for GISAXS and GIWAXS experiments without further treatment. The same set of thin film samples were prepared for TEM experiments with a multi-step procedure.

3.4.1 Grazing Incidence Small Angle Scattering (GISAXS) and Grazing Incidence Wide Angle Scattering (GIWAXS)

GISAXS and GIWAXS data was collected at the X-ray Operations and Research beamline 8-ID-E at the Advanced Photon Source, Argonne National Laboratory (ANL). The schematic illustration of equipment set-up in beamline 8-ID-E is shown in Figure 3.1. A transmission diamond monochromator provided intense radiation of wavelength of 0.1686 nm that was focused to a beam size of 100 mm in width and 50 mm in height. The beam impinged upon samples at three different incident angles: 0.15°, 0.20°, and 0.22°. The lowest incident angle (i.e., 0.15°) was set below the critical angle of polymeric thin film in order to extract structural information in the film surface. The mediate and high incident angles (i.e., 0.20° and 0.22°) were set between the critical angles of polymeric thin films and the silicon wafer substrate to extract the structural information throughout the thin film thickness. The scattered intensity was recorded by a Pilatus 1M-F area detector (7 ms/frame, 169 mm by 179 mm).
Figure 3.1 Schematic illustration of set-up in X-ray scattering beamline 8-ID-E of the Advanced Photon Source at Argonne National Lab.

3.4.2 Reflectivity

Reflectivity measurements were conduct prior to GISAXS measurements with the same setup. All the reflectivity data was analysis after subtracting baselines and correcting the footprint effects.

3.4.3 Transmission Electron Microscopy Observation for Thin Films

After the structural information was collected from GISAXS and GIWAXS in reciprocal space, the TEM investigation in both transmitted and cross sectional modes were conduct to confirm the phase-separated structure in real space. AC$_{60}$-PS-PEO samples were stained by OsO$_4$ for 16 hours, and FPOSS-PS-PEO samples were stained by RuO$_4$ for 10 minutes for better contrast under TEM bright field experiments.

3.4.3.1 Cross Sectional Images of Thin Film Samples

The thin films on silicon wafer substrates were first subjected to deposit a thin layer of carbon (around 20 nm). One drop of poly(acrylic acid) 25% aqueous solution was cast on the carbon coated thin film sample. After the solidification of the poly(acrylic acid) drop, the carbon coated thin films were peeled off the silicon wafer substrates by a
razor blade. By placing the carbon coated thin films on the distilled water surface with the poly(acrylic acid) drop faced the water surface, the poly(acrylic acid) dissolved in water in 20 minutes and left the carbon coated thin films floated on the water surface. The carbon coated thin films were picked up by a small piece of polyimide sheet (125 µm thick), and then subjected to stain by either RuO4 or OsO4. The stained samples were deposited another layer of carbon to make the thin film sample sandwiched by two layers of carbon. The samples on the polyimide sheets were further embedded in the epoxy and subjected to microtome (PowerTome PC/CR-X cryosectioning system, RMC) into 80 nm thick slices for TEM observation.

3.4.3.2 Transmission Images of Thin Film Samples

By using same technique to detach the thin films from substrate as mentioned above, the thin films along with one layer on carbon were floated on the water surface and then were picked up by carbon coated copper grid with 300 meshes. The thin films on copper grids were stained before TEM observation.
CHAPTER IV

HIERARCHICAL SUPRAMOLECULAR STRUCTURE DETERMINATION OF

\[ \text{C}_{60}\text{-BASED SHAPE AMPHIPHILE (C}_{60}\text{-C}_8\text{-C}_{12}) \]

In this chapter, the solid state hierarchical structure and phase behavior of a [60]Fullerene derivative (C\(_{60}\)-C\(_8\)-C\(_{12}\)) were determined. The packing scheme of C\(_{60}\) MNPs within the hierarchical structure was also investigated through various experimental techniques as well as computer simulations.

4.1 Introduction

In this Chapter, the design, phase behavior, and the hierarchical structure of a sphere-spacer-tail shape amphiphile based on C\(_{60}\)-C\(_8\)-C\(_{12}\) were reported. The C\(_{60}\)-C\(_8\)-C\(_{12}\) compound possesses a C\(_{60}\) MNP tethered by an alkyl spacer consisted of 8 carbons followed by three alkyl tails and each tail consists of 12 carbons. Although C\(_{60}\)S and alkyl tails are both hydrophobic, this shape amphiphile was expected to form separated phases and further construct hierarchical structure due to the distinct molecular interaction and affinities as well as geometric shapes between C\(_{60}\)S and alkyl tails. Major phase transitions and its origins in C\(_{60}\)-C\(_8\)-C\(_{12}\) were studied via differential scanning calorimetry (DSC), small angle X-ray scattering (SAXS), one dimensional (1D) wide angle X-ray diffraction (WAXD), and solid state nuclear magnetic resonance (SSNMR) techniques. Its hierarchical supramolecular structure was further identified through combined
techniques of 2D WAXD on oriented sample s and selective area electron diffraction (SAED) in transmission electron microscopy. Results based on computer simulations confirmed the structure determination. It was found that C_{60}-C_{8}-C_{12} possesses two ordered phases below its isotropic temperature: a less-ordered crystal I phase and a ordered crystal II phase. The crystal II phase, at the lowest temperature region, exhibited ordered 2D C_{60} layers separated by crystalline alkyl tails. The crystal I phase, on the other hand, showed the C_{60}s formed sheets separated by amorphous alkyl tails due to the nanophase separation of C60s and flexible tails. The two-dimensional C_{60} sheets was determined to be composed of three layers C_{60}s arranged in a fcc packing, and this three-layer structure is constructed by the assistance of the designed alkyl spacer. This supramolecular hierarchical structure can be described as three molecules in an orthorhombic unit cell with lattice parameters of $a = b = 1.41$ nm, $c = 5.43$ nm, $\alpha = \beta = \gamma = 90^\circ$. Because the domain of alkyl tails is amorphous, there is no crystallographic correlation between different C_{60} layers. Because the fcc-packed C_{60}s possess long-range positional, bond orientational, and molecular orientational order in only two dimensions, the C_{60} sheets in the hierarchical structure can be view as a pseudo-2D crystal. This highly ordered liquid crystal structure is hierarchical in nature and promising for a variety of application because of the conductive C_{60} 2D sheets.

4.2 Molecular Design and Synthetic Route

The concept of molecular design and sample preparations in experimental procedures will be described in this section. The chemical structure and the molecular model constructed by Cerius² 4.6 package is shown in Scheme 4.1, where the geometric shape and dimension of each part of the C_{60}-C_{8}-C_{12} shape amphiphile is shown in the...
extended conformation. The shape amphiphile contains three parts: a C\textsubscript{60} MNP designed to carry targeted molecular functionalities, an alkyl spacer consisted of 8 carbon atoms tethered on a C\textsubscript{60} to provide the mobility for MNP packing and decouple the other two parts,	extsuperscript{79,80} and three alkyl tails each has 12 carbon atoms located on the other end of alkyl spacer to increase the mobility of the whole molecule. The dissimilarity between C\textsubscript{60} and alkyl tails in terms of geometrical shape, physical interaction, and chemical nature would drive the C\textsubscript{60} and alkyl tails separated in different domain; however, these two parts are covalently connected by a spacer, which only allow a micro-phase separation at a nano-scale in the supramolecular structure formation.

Scheme 4.1 Chemical structure and molecular model of C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12}. Molecular model was constructed by Cerius\textsuperscript{2} 4.6 software package.

Compound C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12} was synthesized by sequential Steglich esterification reactions and the synthetic route in summarized in Scheme 4.2. Firstly, 3,4,5-tris(dodecyloxy)benzoic acid (2) was reacted with excess 1,8-octanediol (1) using
Steglich esterification reaction to give the alkyl compound 3. The compound 3 further underwent esterification reaction with the carboxylic acid derivative of methanofullerene (4), which was synthesized through the hydrolysis of tert-butyl [60]fullerenoacetate,\textsuperscript{81} to give the final product of C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12} (5).

Scheme 4.2 Synthetic route of C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12} (5)

4.3 Sample Preparation

For DSC experiments, C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12} was weighted \(\sim 4.0\) mg and sealed in a aluminum pan. The sample and reference pan weights were kept in constant with a precision of \(\pm 0.001\) mg. The sample pan was firstly heat up to 120 °C (above the isotropic temperature) to erase any previous thermal history, and then recorded in the following cooling and heating scan in various rates (2, 5, 10, and 20 °C/min) in the temperature window between -20 °C and 120 °C.

For the 1D WAXD, around 40 mg of sample was melt on an aluminum plate by a thermal treatment of heating up to 120 °C followed by subsequent cooling to 30 °C at a rate of 1 °C/min under N\textsubscript{2} atmosphere. The phase transitions and the corresponding
structural transformations were monitored by 1D WAXD experiments in thermal processes of heating followed by cooling at temperatures according to the transition temperatures observed in DSC thermal diagrams. First, the 1D WAXD was conducted at 30 °C, 55 °C, 75 °C, and 100 °C during heating, and at 70 °C, 55 °C, and 30 °C at subsequent cooling. The heating and cooling rate of 1D WAXD was kept in 5 °C/min, and measurement was conducted after 5 minutes of reaching set temperatures to ensure the thermal equilibrium. The same procedure of sample preparation and recorded temperatures were also used in SAXS measurements. The 1D WAXD pattern of pristine C$_{60}$ was conducted on [60]fullerene (MTR ltd., 99.5%) at 30 °C as purchased without further treatment.

The samples for 2D WAXD measurements were prepared via mechanically shearing. The tool for mechanically shearing was described in the reference of Sun et. al. Around 2 mg of sample was placed in the shearing tool and then extruded at 60 °C. The extruded sample is in a cylindrical shape, and the diffraction patterns were recorded with the X-ray beam aligned perpendicular to the long axis of the cylinder. The measurements were first conducted at 80 °C after 30 minutes at 80°C, and then conducted at several set temperatures during subsequent cooling and heating in the temperature range between -80 °C and 80 °C.

To prepare the TEM samples for SAED experiments and morphological investigation, a dilute solution of C$_{60}$-C$_8$-C$_{12}$ was prepared in CH$_2$Cl$_2$ (0.02% w/v). The solution was drop casted onto carbon coated mica and subject to thermal treatment identical to the sample prepared in 1D WAXD experiments. After thermal treatments, the sample on the carbon film was transferred to a copper gird for observation in TEM of
flat-on lamellar morphology and corresponded SAED patterns. To study the edge-on lamellae and the corresponded SAED pattern, the sample was soft-epitaxial crystalized onto benzoic acid. This technique was widely used in aligning polymer single crystals.\textsuperscript{83} In a short description of this method, 1 mg of sample was first mixed with around 100 mg of benzoic acid and placed on a carbon-coated mica, and then heated up to 140 °C (above melting temperature of benzoic acid as well as the disordering temperature of \textit{C}_{60}-\textit{C}_{8}-\textit{C}_{12}) on a thermal control stage. After the benzoic acid melting and dissolving samples, the mica was moved to have its half area positioned outside the surface of thermal control stage to create a thermal gradient. The thermal gradient could induce oriented crystals of benzoic acid. After cooling back to the room temperature, the specimen was transfer to a thermal stage and heated up to 80 °C (below both the melting temperature of benzoic acid and disordering temperature of \textit{C}_{60}-\textit{C}_{8}-\textit{C}_{12}) and then cooled to 30 °C at a rate of 1 °C/min under N\textsubscript{2} atmosphere. The excess benzoic acid was then remove by rinsed of warm methanol (30 ~ 50 °C). The residual samples on the carbon-coated mica were then transfer to TEM grid for observation. Another method to observe the edge-on lamellae under TEM was cryo-micromotmed sample at -40 °C. Other preparation methods and instrument details are described in Chapter 3.

4.4 Phase Behavior Investigation

The \textit{C}_{60}-\textit{C}_{8}-\textit{C}_{12} was first examined by DSC to reveal the phase transitions and thermodynamic parameters, and then utilized SSNMR to identify the origin of the phase transition. Finally, the temperature-variable X-ray diffraction patterns were conducted to realize the structural change during the phase transitions.
4.4.1 Differential Scanning Calorimetry

The phase behavior of C$_{60}$-C$_8$-C$_{12}$ was first investigated utilizing DSC. Figure 4.1a shows the DSC thermal diagrams of both cooling from the melt and subsequent heating at various rates of 2, 5, 10, and 20 °C/min. Upon cooling from 120 °C, two exothermic transitions were observed at around 40 ~ 60 °C (8.04 kJ/mol) and -8 °C (18.50 kJ/mol), respectively. During the subsequent heating, two corresponding endothermic transitions occurred, indicating an enantiotropic phase transition behavior. The phase behavior can be understood as three successively appeared phases: ordered crystal II, less-ordered crystal I, and isotropic disordered phases. Each phase possesses its own thermodynamic free energy, and within each particular temperature region, one phase has the lowest free energy, making it the most stable phase. Although the phase behavior is very similar to the enantiotropic phase transition behavior is shown in Figure 4.1b, after realizing the phase transition are actually originated from decoupled alkyl domains and C$_{60}$ domains instead of from a single system in the following sections, the plot of Gibbs free energy versus temperature for the C$_{60}$-C$_8$-C$_{12}$ should be more complicated than Figure 4.1b. As shown in Figure 4.1a, the melting temperature of ordered crystal II phase is -8 °C, and the disordering temperature of less-ordered crystal I phase is around 84 °C. In addition, the huge scan rate-depended supercooling in the formation of crystal I phase during cooling, indicating a huge free energy barrier in the phase transition from disordered phase to the crystal I phase. The phase transition occurred at -8 °C and 84 °C were expected to be resulted from crystallization of alkyl chains and C$_{60}$ packing, respectively. The origins of these two phase transitions were then be analyzed and confirmed via SSNMR and variable-temperature WAXD measurements.
Figure 4.1 (a) DSC thermal diagrams of cooling and subsequent heating scans at 2, 5, 10, and 20 °C/min. The top four lines are heating scans, and the bottom four lines are corresponding cooling scans. Different phase regions were indicated by black dashed line according to the heating scan data. (b) Illustration of the free energy versus temperature at constant pressure for enantiotropic phase transition behavior. The disordering temperature is denoted as $T_d$ and the melting temperature as $T_m$.

4.4.2 Solid-State Nuclear Magnetic Resonance

Solid-state $^{13}$C NMR experiment was conducted to understand the origin of the phase transition at -8 °C and the result is shown in Figure 4.2. The chemical shift at 33.5 ppm in the Bloch decay $^{13}$C solid-state NMR spectra of C$_{60}$-C$_8$-C$_{12}$ represents the methylene carbon atoms in the long trans zigzag segments (tt) of the alkyl tails, while the chemical shift at 30.5 ppm corresponds to the carbon atoms in the disordered, statistically distributed trans and gauche conformations (tg).$^{84,85}$ The relative intensities of tg were dramatically decreased upon cooling in the temperature region between -5 °C and -10 °C; while the relative intensities of tt were increased upon cooling, indicating the alkyl chains
of C60-C8-C12 crystallized at -8 °C to exhibit the high percentage of trans conformation of methyl groups.

4.4.3 X-ray Diffraction

After the identification of the first phase transition from crystal II to crystal I phase belonged to the crystallization of alkyl chains, the second phase transition from crystal I to disordered phase was then identified utilizing variable-temperature X-ray diffraction techniques. Samples for 1D SAXS and 1D WAXD were first thermal annealed as described in section 4.3. Figure 4.3 shows a set of 1D SAXS and 1D WAXD powder patterns collected by stepwise heating at each of the indicated temperatures after
the sample was first cooled from 120 °C to 30 °C at a rate of 1 °C/min. In the SAXS patterns, single diffraction peak can be observed at the first three temperatures, 30 °C, 55 °C, and 75 °C during heating. This peak vanished during further heating at 100 °C and then emerged again in the subsequent cooling at 70 °C, 55 °C, and 30 °C. There are much more diffraction peaks in the WAXD patterns, however, these peaks followed the same rule that appeared at the first three temperatures and disappeared at 100 °C during heating, and then re-appeared in the following cooling steps. This structural transition observed in X-ray diffraction coincides with the phase transition observed in DSC measurements at 84 °C.

Based on preliminary analysis of these diffraction peaks, two sets of peaks can be distinguished. The first set of peaks has a $q$ ratio of $1 : 2 : 3 : 4 : 5 : 6 : 7$ (marked by black arrows) with its first-order peak at small angle region, indicating a layered structure in a nanometer size; the second set of peaks has a $q$ ratio of $1 : \sqrt{2} : 2$ (marked by red arrows) with its first-order peak of around 1 nm in $d$-spacing, indicating a ordered structure of C$_{60}$ MNPs. Because the alkyl chains of crystal I phase had been confirmed to be disordered by SSNMR experiments, the coexistence of layered and ordered C$_{60}$ structures indicates the crystal I phase possesses molecularly ordered C$_{60}$ layers separated by disordered alkyl chains. As long as the temperature above 84 °C, the dissociation of C$_{60}$ packing causes the phase transition from crystal I to disordered state. Therefore, the crystal II phase can be determined as molecularly ordered C$_{60}$ layers separated by crystalline alkyl chains. The structural determination of crystal I phase will be discussed in details in the following sections.
Figure 4.3 (a) 1D SAXS and (b) 1D WAXD powder patterns of C₆₀-C₈-C₁₂ collected at indicated temperatures during heating and subsequent cooling. The sample was first cooled from 120 °C to 30 °C at 1 °C/min.

4.5 Unit Cell Parameters of Superlattice and Sub-Unit Cell

Based on phase behavior investigation and preliminary analysis of X-ray diffraction patterns, the crystal I and crystal II phases of C₆₀-C₈-C₁₂ have been identified to possess ordered C₆₀ layer structures. The ordered phases can be described in a superlattice composed of molecularly ordered C₆₀ domain and crystalline or amorphous alkyl domain. Because the only difference between crystal I and crystal II phases is the degree of order in the alkyl chain domain, their overall superlattices are extremely similar. The morphology of crystal I phase was also investigated via cryo-microtomed, thermal annealed, and aligned samples under TEM bright field mode. In addition, the unit cell parameters determination of crystal I superlattice was chosen to understand the molecular
packing of C_{60}-C_8-C_{12} shape amphiphile utilizing 1D SAXS, 1D & 2D WAXD, and SAED techniques.

4.5.1 Morphology Investigation and Corresponding Electron Diffraction

To further understand the morphology and the C_{60}s’ packing in the layer structure, TEM bright field and electron diffraction experiments were firstly conducted. Figure 4.4 shows the TEM bright field image and its corresponding SAED pattern of C_{60}-C_8-C_{12} crystal I phase. The sample of crystal I phase was prepared by heated up to 120 °C and then cooled back to 30 °C at a rate of 1 °C/min. The bright field image clearly shows the layered structure stacked along the film normal direction (Figure 4.4a). The SAED pattern with [001] zone obtained from the selected circular area marked in the bright field image shows well-resolved diffraction spots (Figure 4.4b) with an orthogonal equivalent $a^*$- and $b^*$-axes, indicating a 2D tetragonal reciprocal lattice in the $a^*b^*$-plane. Moreover, the $(h00)$ with odd $h$, $(0k0)$ with odd $k$, and $(hk0)$ with odd $(h+k)$ diffractions are extinct. The dimensions of the 2D tetragonal lattice are thus determined to be $a = b = 1.41$ nm, and $\gamma = 90^\circ$. This lattice is a reminiscent of fcc structure of C_{60} with cubic lattice of $a = b = c = 1.41$ nm. However, because of the high symmetry of face-centered-cubic structure (space group Fm-3m$^{20,21,24}$ of C_{60} at room temperature, it possesses a more restrict extinction rule: reflections with mixed odd, even $h$, $k$, $l$ absent. The difference of extinction between the crystal I phase of C_{60}-C_8-C_{12} and fcc structure of C_{60} should be due to the fact that C_{60} MNPs in crystal I phase is only a 2D structure with few nanometer thick, which is lack of long-ranged order in the third dimension, resulting in some forbidden reflections in the fcc C_{60} structure could appear in crystal I phase of C_{60}-
C\textsubscript{8}-C\textsubscript{12}. A more detailed comparison between these two structures will be discussed in the following sections by X-ray diffraction patterns and computer simulated data.

One thing worth to be noticed is that the single zone SAED pattern was obtained from single layer of the structure as indicated in the Figure 4.4a. If the selective area was selected in a region of multiple layers, the corresponding SAED pattern shown a superposition of multiple [001] patterns, indicating that there is no crystallographic correlation between C\textsubscript{60}'s packing in different layers separated by alkyl chains. Moreover, the amorphous ring (\textit{d}-spacing = 4.47 Å) in Figure 4.4b represents the average inter-chain distance of alkyl chains, confirming the alkyl chains are disordered in the \textit{crystal I} phase. The disordered alkyl domain cannot transfer the ordering from one to the other layer of C\textsubscript{60}s, allowing the lattice of C\textsubscript{60}s freely shifted or rotated in \textit{ab}-plane with respect to its adjacent C\textsubscript{60} layers.
Figure 4.4 (a) TEM bright field image of C_{60}-C_{8}-C_{12} crystal I phase in flat-on morphology, and (b) the corresponding [001] zone of SAED pattern from the selected circular area marked in (a). Sample of flat-on crystal I phase was prepared by heated up to 120 °C and then cooled back to 30 °C at a rate of 1 °C/min.

By simply thermal annealing drop-cast sample, the layered structure can only exhibit flat-on lamellae as shown in Figure 4.4a. In order to study the packing scheme of C_{60}s in the layered structure, samples of edge-on lamellae of crystal I phase has to be prepared. It can be prepared via benzoic acid alignment and the bright field image and corresponding SAED pattern are shown in Figure 4.5. The detail procedure of benzoic acid alignment was described previously in the section 4.3. The bright field image of edge-on lamellae of crystal I phase shows parallel orientated strips with a periodicity of 5.4 nm (Figure 4.5a). The dark and white regions in the bright field image correspond to C_{60}s and alkyl chains, respectively, because of the higher electron density of C_{60}s than that of alkyl region. The corresponded SAED pattern (Figure 4.5b) shows distinct diffraction spots along the c*-axis, which represent the layered structure, and it also shows two strong streaks on the direction perpendicular to the c*-axis, which represent the packing of C_{60}s in the layers. By matching the d-spacings of diffractions with that in
the [001] zone SAED pattern, the (110) of 9.99 Å and (220) of 4.99 Å can be indexed accordingly. This SAED pattern can then be determined as [110] zone because the simultaneously observed ($hk0$) with $h = k$, and (00$l$) diffractions. In the [110] zone SAED pattern, the electron beam is parallel to the $ab$-plane of the 2D $C_{60}$ layers and shoot at the peripheral edges. The observation of the diffraction streaks is because the 2D ordered structure of $C_{60}$s without repetition of unit cells along the layer normal direction generates elongated reciprocal ellipsoids in the reciprocal space.29

The superlattice has been determined as $a = b = 14.14$ Å, and $\gamma = 90^\circ$ from the [001] zone SAED pattern (Figure 4.4a). The other two angles can also be determined as $\alpha = \beta = 90^\circ$ from the [110] zone SAED pattern (Figure 4.5b) because the angle between $c^*$-axis and 110 direction is 90°. Thus, the superlattice was then confirmed as a tetragonal lattice. However, because of the noticeable deviation for calculating $d$-spacings of diffraction spots close to main beam (low angle region) in an ED pattern, the dimension of $c$-axis need to be further determined from X-ray measurements for better precision. Also, in order to fully index the [110] zone SAED pattern, a sub-unit cell for solely $C_{60}$s has to be introduced in the superlattice, and it will be discussed in the next section of X-ray diffractions.
Figure 4.5 (a) TEM bright field image of $C_{60}$-C$_8$-C$_{12}$ crystal I phase in edge-on morphology by benzoic acid alignment, and (b) the corresponding [110] zone of SAED pattern. Sample of edge-on crystal I phase was prepared by soft-epitaxial growth from benzoic acid and then heated up to 100 °C and cooled back to 30 °C at a rate of 1 °C/min.

4.5.2 Superlattice and Sub-Unit Cell Determination via X-Ray Diffraction

Figure 4.6 shows the comparison of 2D WAXD patterns of $C_{60}$-C$_8$-C$_{12}$ and pristine $C_{60}$ collected at 30 °C. Form the single peak in the SAXS pattern of $C_{60}$-C$_8$-C$_{12}$ at 30 °C (Figure 4.3a) and its higher order peaks in the WAXD indexed as (002), (003), (004), (005), (006), and (007) in the Figure 4.6, the dimension of $c$-axis of the tetragonal superlattice can be determined as 54.30 Å. Besides the set of (00l) diffraction peaks in the WAXD pattern of $C_{60}$-C$_8$-C$_{12}$, there are several other peaks belong to the structure of $C_{60}$ itself. It has long been know that pristine $C_{60}$ forms face-centered-cubic plastic crystal at room temperature$^{20}$, and the characteristic diffractions of pristine $C_{60}$ in the Figure 4.6 can be indexed accordingly based on the $fcc$ unit cell with $a = b = c = 14.14$ Å, and $\alpha = \beta = \gamma = 90^\circ$. By comparing the WAXD patterns of $C_{60}$-C$_8$-C$_{12}$ and pristine $C_{60}$, the scattering angles of (220) and (420) were found unchanged from the $fcc$ lattice of pristine $C_{60}$ to the tetragonal superlattice of $C_{60}$-C$_8$-C$_{12}$. However, those (hkl) diffractions of
pristine C\textsubscript{60} cannot be found in the pattern of C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12}, indicating the C\textsubscript{60} MNPs of C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12} adopt the same \textit{fcc} packing scheme and dimensions of the pristine C\textsubscript{60} in \textit{ab}-plane but possess a different dimension of \textit{c}-axis.

Figure 4.6 1D WAXD patterns of C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12} (black) and pristine C\textsubscript{60} (red) collected at 30 \textdegree C (\textit{crystal I} phase for C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12} and \textit{fcc} plastic crystal structure for pristine C\textsubscript{60}). For C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12}, the (\textit{hkl}) indices represent crystal planes of the tetragonal superlattice, and the (\textit{hkl'}) indices represent crystal planes of the tetragonal sub-unit cell.

To properly describe the packing of C\textsubscript{60} MNPs of C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12} in its superlattice, a sub-unit cell of solely C\textsubscript{60} MNPs has to be introduced with a same tetragonal lattice in two dimensions (\textit{ab}-plane) but a different third dimension (\textit{c'}-axis). The illustration of the tetragonal superlattice and the sub-unit cell is shown in Figure 4.7. The top views of both lattices are identical. Tetragonal superlattice is characterized by \textit{a}-, \textit{b}-, and \textit{c}-axes, and tetragonal sub-unit cell is characterized by \textit{a}-, \textit{b}-, and \textit{c'}-axes. Different colors of spheres are represented for C\textsubscript{60} MNPs in different layers in the unit cell. After introducing the sub-unit cell, the (\textit{hkl}) and (\textit{hkl'}) reflections will be used to index crystal planes of the
superlattice and the sub-unit cell, respectively. Because the diffraction peaks other than the (00l) should corresponds to the packing of C_{60} MNPs, which can be described by the sub-unit cell. By fitting the diffraction peaks, it was found out that the c’-axis of the sub-unit cell is 17.20 Å, which is larger than the c-axis of fcc structure of pristine C_{60} of 14.14 Å. Those characteristic diffraction peak of fcc structure of pristine C_{60} can be found a corresponding diffraction peaks for the tetragonal sub-unit cell as (111’), (311’), (222’), (331’), and (422’) indexed in Figure 4.6. A comparison of calculated scattering angles and d-spacings of the fcc structure of C_{60} and tetragonal sub-unit cell for C_{60} MNPs are summarized in Table 4.1. Moreover, the two-dimensional geometry of C_{60} MNPs crystal structure and its different c’-axis lead to a different crystallographic symmetry from that of a normal fcc structure, resulting some forbidden reflections of fcc structure of pristine C_{60}, such as (110), (112’), and (310) in Figure 4.6. The calculated and observed (WAXD) crystallographic planes of the superlattice are summarized in Table 4.2.
Figure 4.7 Illustration of tetragonal superlattice in top view (a) and perspective view (c), and tetragonal sub-unit cell in top view (b) and perspective view (d). Tetragonal superlattice is characterized by $a$, $b$, and $c$-axes, and tetragonal sub-unit cell is characterized by $a'$, $b'$, and $c'$-axes. The top views of both lattices are identical, and different colors of spheres are represented for $C_{60}$ MNPs in different layers in the unit cell. The empty space of the superlattice is filled by the alkyl spacers and tails, which are not shown here for clarity.
Table 4.1 Comparison of calculated scattering angles and \(d\)-spacings of a face-centered-cubic lattice of pristine C\(_{60}\)S and the tetragonal sub-unit cell of C\(_{60}\) MNPs.

<table>
<thead>
<tr>
<th>No.</th>
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<th>(d)-spacing (Å)</th>
</tr>
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<td></td>
<td></td>
<td>(fecc^a)</td>
<td>(tetragonal^b)</td>
</tr>
<tr>
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<td>10.22</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>6</td>
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<td>28.19</td>
</tr>
<tr>
<td>7</td>
<td>(422)</td>
<td>30.94</td>
<td>30.07</td>
</tr>
</tbody>
</table>

\(^a\) face-centered-cubic unit cell with \(a = b = c = 14.14\) Å, and \(\alpha = \beta = \gamma = 90^\circ\).  
\(^b\) tetragonal unit cell with \(a = b = 14.14\) Å, \(c = 17.20\) Å, and \(\alpha = \beta = \gamma = 90^\circ\).

Table 4.2 Crystallographic parameters of C\(_{60}\)-C\(_{8}\)-C\(_{12}\) crystal I phase. \(^a\)Experimental values observed in SAXS, WAXD, and TEM. \(^b\)Calculated based on the tetragonal superlattice unit cell of \(a = b = 14.14\) Å, \(c = 54.3\) Å, and \(\alpha = \beta = \gamma = 90^\circ\).

<table>
<thead>
<tr>
<th>No.</th>
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<th>(d)-spacing (Å)</th>
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<th>No.</th>
<th>((hkl))</th>
<th>(2\theta (^\circ))</th>
<th>(d)-spacing (Å)</th>
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<td>8.68</td>
<td>17</td>
<td>(422')</td>
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<td>30.05</td>
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<tr>
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<td>(007)</td>
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<td>7.71</td>
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\(^a\) Experimental values observed in SAXS, WAXD and TEM. \(^b\) Calculated based on the orthorhombic unit cell of \(a = 14.14\) Å, \(b = 14.14\) Å, \(c = 54.30\) Å, \(c' = 17.20\) Å, and \(\alpha = \beta = \gamma = 90^\circ\).
The combination of SAXS, 1D WAXD, and TEM results at room temperature discussed above provides the structural information of crystal I phase of C_{60}-C_{8}-C_{12}. To gain more insight of the structure evolution during the phase transition, variable-temperature SAXS and 1D WAXD had been conducted to show the structural change from crystal I phase to the disordered phase. The set of 1D WAXD patterns in Figure 4.3 shows that C_{60}-C_{8}-C_{12} exhibit crystal I phase in the temperature from 30 °C to 75 °C during heating. With subsequent further heating to 100 °C, the 1D WAXD pattern show only two amorphous halos centered at 8.9° and 19.5° (d-spacing of 9.9 Å and 4.5 Å, respectively), corresponding to the average intermolecular distance between C_{60} MNPs and average interchain distance of disordered alkyl chains in the disordered state. It should be noticed that the amorphous halo centered at 19.5° remained unchanged from the first heating to the disordered state to the subsequent cooling, indicating the alkyl chains are disordered throughout the crystal I phase and disordered phase. In addition, an obviously shift of the first order peak of the layered structure (Figure 4.3a) in q-value indicated the dimension of layered structure also changed with respect to the temperature. The q-value of diffraction peak at SAXS pattern gradually increased as temperature increased from 30 °C to 75 °C in the heating process and gradually decreased as temperature decreased from 75 °C to 30 °C in the cooling process. In other words, the layered structure possessed smaller periodicity at high temperatures than that at low temperature in the crystal I phase. Because this trend of structural change contradicts to the common thermal expansion and contraction phenomenon, there must be another factor affect the dimension of the layered structure.
The $d$-spacing change can be observed more clearly in the whole temperature from 80 °C to -80 °C from the variable-temperature 2D WAXD fiber patterns (Figure 4.8). Because the fiber axis of the sheared sample was aligned vertically in the patterns, the reflections on the equator represent the layer structures, which shows very similar pattern as the [110] zone of SAED pattern (Figure 4.5b). The arcs in the widest angle region shown in Figure 4.8 represent the average inter chain distance of alkyl chains (4.5 Å). During the cooling process, the transition from crystal I phase transfer to crystal II phase can also be recognized by observing the abruptly increased intensity of the alkyl chain arcs at temperature under 0°C. Furthermore, the fiber pattern can be indexed by both the tetragonal superlattice and sub-unit cell described previously in the section accordingly (Figure 4.9a). Also, the reflections on the quadrant of [110] zone of SAED pattern can be indexed by the tetragonal sub-unit cell as (111’) and (112’) (see Figure 4.5b). The difference between a [110] single zone and the fiber pattern is that the (002) reflection can be observed in the fiber pattern but not in the [110] single zone.
Figure 4.8 Variable-temperature 2D WAXD fiber patterns of C_{60}-C_{8}-C_{12}. The fiber patterns were collected during a cooling process from 80 °C to -80 °C with the fiber axis aligned vertically in the patterns.

Figure 4.9 (a) 2D WAXD fiber pattern of C_{60}-C_{8}-C_{12} collected at 20 °C during cooling, and (b) the computer simulated 2D WAXD fiber pattern by Cerius² package.

By integrating the 2D WAXD pattern into a 1D WAXD pattern and focused on the small angle region, the $d$-spacing of layered structure can be determined from the (003) reflections in the Figure 4.10a. The change of $d$-spacing of layered structure with respect to the temperature during cooling process from 80 °C to -80 °C was plotted in
Figure 4.11a. It is clear to see that the $d$-spacing increased during the cooling from 80 °C (53.7 Å) to 0 °C (54.8 Å), and suddenly dropped to 53.7 Å at -20 °C, and then almost unchanged during further cooling to -80 °C. The sudden change at between 0 °C and -20 °C can be explained by the phase transition from crystal I to crystal II phases induced by the crystallization of alkyl chains. The crystallization caused the density of alkyl domain increased, leading to a contraction of layered $d$-spacings in $c$-axis because the dimension of $ab$-plane was fixed. To explain the expansion of layered structure in the crystal I phase during cooling, we need to consider the dimensional change of $ab$-plane during cooling. The dimension of $ab$-plane is determined by the inter-distance between C$_{60}$ MNPs, which can be deduced from the (220) reflections, i.e. the inter-distance between C$_{60}$ MNPs is twice of the $d$-spacing of (220) plane. The integrated 1D WAXD pattern at various temperatures from 80 °C to -80 °C was redrawn in the wide angle region as shown in Figure 4.10b, and its corresponded plot of inter-distance of C$_{60}$ MNPs versus temperatures is shown in Figure 4.11b. The inter-distance of C$_{60}$ MNPs indeed didn’t show much change at temperature lower than -20 °C, which confirm the previous assumption that the dimension of $ab$-plane was fixed at crystal II phase. On the other hand, the inter-distance of C$_{60}$ MNPs decreased much more profoundly during cooling from 80 °C to 0 °C in the crystal I phase, indicating that in the cooling process, the expanded layered structure in $c$-axis could be resulted from the shrink of inter-distance of C$_{60}$ MNPs in the $ab$-plane.
Figure 4.10 Integrated 1D WAXD patterns from the variable-temperature 2D WAXD fiber patterns in the (a) small angle region ($2^\circ \sim 6^\circ$) and (b) wide angle region ($15^\circ \sim 21^\circ$).

Figure 4.11 Plots of (a) $d$-spacing of the layered structure calculated from the (003) reflections and (b) inter-distance between C$_{60}$ MNPs calculated from the (220) reflections in the variable-temperature 2D WAXD patterns with respect to temperatures.
4.5.3 Sub-Unit Cell Identification via SAED Tilting Experiments

The c-axis of the tetragonal sub-unit cell (17.20 Å) of C₆₀ MNPs has been determined from the 1D WAXD pattern to be different from that of a common fcc lattice of pristine C₆₀s (14.14 Å). This dramatic change of dimension in lattices can be further verified by a set of SAED tiling experiments in TEM. Figure 4.12 shows a set of tilting SAED patterns from [001] zone at the tilting angle of 0° to [111] zone at the tilting angle of 50°. The first row of illustrated images in the Figure 4.12 show the tetragonal sub-unit cell with C₆₀ MNPs in real space at assigned tilting angle. The a-, and b-axes of the sub-unit cell are marked in the first row image of Figure 4.12a. The second row images show the SAED patterns tilted at assigned angle along the -110 direction. Some characteristic diffractions and the a*- and b*-axes were indicated in the second row image of Figure 4.12a. The third row images show the [110] zone of SAED patterns with black dashed lines to indicate the projection line of observed tilted SAED on the [110] pattern. Characteristic diffractions and directions of 110 and c*-axis were also depicted on the third row image of Figure 4.12a.

Because the [001] zone and the [110] zone of diffraction pattern are actually perpendicular to a tetragonal lattice in the reciprocal space. The observed a*b* reciprocal plane of [001] zone SAED pattern at titling angle of 0° can be found as a projected line on the [110] zone SAED pattern as indicated by black dashed line in Figure 4.12a. In the [110] zone of SAED pattern, the black dashed line intersected streak of (110) and (220) reflections to show the (110) and (220) on the meridional direction of [001] zone of SAED pattern at tilting angle of 0° in the Figure 4.12a. As the [001] zone of SAED pattern started to be tilted to 5°, the pattern shows almost identical pattern as at 0°
because the observed SAED pattern still intersected the (110) and (220) streaks as indicated by the black dashed line in the Figure 4.12b. When the tilting angle increased to 20°, the reflection of (220) disappeared while the (110) remained with slightly different \( d \)-spacing because now the projected black dashed line only intersected the streak located on the (110) but not (220) (see Figure 4.12c). When the tilting angle further increased to 30°, the \( C_{60} \) MNPs in the sub-unit cell aligned horizontally in real space to give the (111’) and (222’) reflections in the tilted SAED pattern, and it can be confirmed by the intersection of the black dashed line and (111’) and (222’) reflections in the [110] zone of SAED (see Figure 4.12d). Finally, when the tilting angle increased to 50°, the \( C_{60} \) MNPs in the sub-unit cell show a hexagonally packed scheme in real space, and the tilted SAED pattern also show the hexagonally arranged diffraction peaks, which can be indexed as (2-20), (202’), (022’), (-220), (-202’), and (0-22’), respectively. This pattern can then be determined as the [111’] zone of the SAED pattern. There are no reflection on the tilted pattern in the meridional direction because the black dashed line didn’t intersect any strong reflection in the [110] zone of SAED pattern at tilting angle of 50° (see Figure 4.12e).
Figure 4.12 A set of SAED patterns tilted along the -110 direction from 0° to 50°. The first row of images show the illustration of the tetragonal sub-unit cell with C_{60} MNPs in real space; the second row of images show the result of tilted SAED patterns; the third row of images show the [110] zone of SAED pattern with the black dashed line to indicate the projected line of tilted patterns observed in the second row at assigned tilting angles at (a) 0°, (b) 5°, (c) 20°, (d) 30°, and (e) 50°.
It is known that to observed a [111] zone pattern tilted from a [001] zone pattern for a \( fcc \) structure, it has to be tilted along \( 110 \) direction for 55°. The different tilting angles for tetragonal sub-unit cell and \( fcc \) structure to reach [111] zone from [001] zone indicates these two lattices possessing different dimensions of the \( c \)-axis (\( c' \)-axis). The dimension of \( c \)-axis of a \( fcc \) C\(_{60}\) unit cell is already know as 14.14 Å, while the dimension of \( c' \)-axis of the tetragonal sub-unit cell of C\(_{60}\) MNPs determined as 17.20 Å can be confirmed by the angle between [001] and [111'] zones as illustrated in the Figure 4.13. Figure 4.13a shows an illustration of [001] zone of SAED pattern which represents the same pattern as the middle image of Figure 4.12a. The (200) reflection is pointed out and the relative position with respect to the \(-110\) axis is depicted by a red dashed line. The reciprocal dimension of this red dashed line is then deduced as \((2/14.14)\cos45° \ (Å^{-1})\). Figure 4.13b illustrates the SAED pattern viewed along the \(-110\) direction, which is a perpendicular view with respect to Figure 4.13a. The red dashed line in Figure 4.13b indicates the identical reciprocal dimension of that in the Figure 4.13a. Because (202') can be observed in a [111'] zone of SAED patter, the included angle, \( \theta \), indicated in Figure 4.13b represents the angle need to be tilted from [001] zone to observe the [111'] zone. Since the projection of reciprocal dimension of (202') on the \( c'^* \)-axis is 2/17.20 (Å\(^{-1}\)), the angle, \( \theta \), can be calculated as following equation.

\[
\theta = \tan^{-1}\left(\frac{2}{17.2\ \text{Å}} \cdot \cos45°\right) = 49.2°
\]

(4.1)

The calculated tilting angle (49.2°) matches the experimental one (50°) very well, confirming the dimension of \( c' \)-axis is 17.20 Å.
4.6 Molecular Packing Model Construction and Simulation

The molecular packing scheme was realized and constructed in three major steps. Firstly, the number of molecules in a unit cell has to be extracted from density measurements. Second, the molecular packing model in a 3D crystal lattice is generated by the determined space group based on experimental observations. Third, the simulated ED pattern has to quantitatively and qualitatively match the experimental one in terms of diffraction positions and intensities to ensure the molecular model catches the major features in the crystal structure.

4.6.1 Density Measurement

After the unit cell parameters being determined by X-ray diffraction and TEM SAED experiments, the number of molecules in a unit cell has to be calculated from the density. According to the procedure to measure density described in section 3.3, the measured density of crystal I phase of C$_{60}$-C$_8$-C$_{12}$ is 1.22 g/cm$^3$. Based on the molecular weight of C$_{60}$-C$_8$-C$_{12}$, i.e. 1562 g/mol, and the fcc-like packing of C$_{60}$ MNPs in the
projection on $ab$-plane, if there are two layers of C$_{60}$ MNPs in the sub-unit cell (four molecules in a superlattice), the calculated density can be calculated as

$$\frac{(4*1562)}{(6.02*10^{-23}*14.14*14.14*54.3*10^{-24})} = 0.95 \text{ g/cm}^3,$$

while if there are three layers of C$_{60}$ MNPs in the sub-unit cell (six molecules in a superlattice), the calculated density can be calculated as

$$\frac{(6*1562)}{(6.02*10^{-23}*14.14*14.14*54.3*10^{-24})} = 1.43 \text{ g/cm}^3.$$

Because the measured density is much higher than the one calculated from 2-layer model, the possibility of C$_{60}$-C$_8$-C$_{12}$ forms merely double layers is eliminated. The structure is then determined as triple layer of C$_{60}$ MNPs. The smaller value of measured density compared to the theoretical value should be due to defects of crystal lattice and the amorphous parts.

4.6.2 Computer Simulation

Based on the previously determined unit cell parameters and the result of density measurement, the detailed molecular packing scheme can then be constructed via Accelrys Cerius$^2$ package. Figure 4.14 shows the superlattice in different views without alkyl spacers and tails for clearly illustrating the packing of C$_{60}$ MNPs. The different color of C$_{60}$ MNPs was used to indicate different positions in the triple layer of C$_{60}$s. White C$_{60}$ MNPs is the external layers of the triple layer, which sandwiched the middle layer C$_{60}$ MNPs (denote as blue). Based on the model, the ED pattern of [001] zone and [110] zone can be simulated (Figure 4.15), and these two patterns agrees with the experimental SAED patterns (Figure 4.4b and Figure 4.5b) very well in terms of positions and relative intensities of diffraction spots, indicating the molecular
arrangement depicted in Figure 4.14 represents an accurate description of the symmetry and molecular packing of C₆₀ MNPs in the tetragonal superlattice.

Figure 4.16 shows six whole molecules in a superlattice to form the triple layer model. It should be noticed that, in order to form a triple layer structure, the spacer of the middle layer of C₆₀ MNPs have to penetrate the external C₆₀ MNPs layers. The possibility for the spacers of middle layer of C₆₀ MNPs to penetrate top or bottom layers of external C₆₀ MNPs should be the same. The model merely shows the average condition with half number of spacers in the middle layer toward up and the other half toward down. The conformation of the molecules was simulated by fixing the position of C₆₀ MNPs and relaxing fully stretched alkyl spacers and tails by the energy-minimize process under COMPASS force field. Based on the model, an X-ray fiber pattern can be simulated (see Figure 4.9b), and it shows weak (005) and strong (006) diffractions, which matches the experimental data well (Figure 4.9a). The high intensity of (006) diffraction should be due to the d-spacing (8.6 Å) of the (002’) plane with high electron density in the sub-unit cell coincide with the d-spacing of (006) plane in the superlattice.

Figure 4.17 shows two superlattices stacked in c-axis in different views to illustrate the interpenetration of alkyl spacers and tails to form the top and the bottom of a superlattice to form the alkyl domain. This illustration also shows terminal methyl group in the alkyl tails is in the vicinity of the C₆₀ MNPs. This specific closed distance of CH₃ group and C₆₀ can be further determined by SSNMR experiments and the detail will be discussed in the next section.
Figure 4.14 Projections of triple layer of C$_{60}$ MNPs packing in the tetragonal superlattice along the (a) [001] direction on the $ab$-plane, (b) [100] direction on the $bc$-plane, and (c) [110] direction. The tetragonal superlattice viewed in a perspective view. The white and blue C$_{60}$S represent the MNPs on the external and middle layers of the triple layer, respectively.
Figure 4.15 The computer simulated ED patterns along the (a) [001] zone, and (b) [110] zone.

Figure 4.16 The overall tetragonal superlattice with four C₆₀-C₈-C₁₂ molecules in a single unit cell of views along (a) [100] direction, (b) [110] direction, and (c) the perspective view. The kind of atoms was differentiated by colors as indicated. The conformation of alkyl spacers and tails are determined through energy-minimization process via Cerius² package with COMPASS force field.
Figure 4.17 Three different views of 1x1x2 simulated tetragonal superlattices (a) along [100] direction, (b) along (110) direction, and (c) in the perspective view.
4.6.3 Confirmation of Triple Layer Model

To form a triple layer structure, the alkyl spacers belong to the C₆₀ MNPs in middle layer have to penetrate the gaps between C₆₀ MNPs in the external layer. The alkyl spacers could be the key component to form and stabilize this kind of 2D ordered structure of C₆₀s. This triple layer structure of C₆₀s containing alkyl spacers are reminiscent of the C₆₀-n-pentane clathrate structure.¹⁸ This kind of clathrate structure is a co-crystal structure of C₆₀s and small molecules, and it confirms the ability for aliphatic chain to fill in the caps of the crystal structure of C₆₀s. In the previous sections, the triple layer structure has been confirmed by crystallographic methods, such as density measurement and simulated diffraction patterns; nevertheless, this unexpected structure could always be further confirmed by techniques other than crystallographics. In the sense of chemistry, if the spacers have to penetrate a layer of C₆₀s, the length of the spacers must be longer than the diameter of a C₆₀. To approach this point of view, a different set of sample was synthesized by Prof. Tu in Soochow University. The set of samples was designed in the same way of C₆₀ MNP-spacer-tail, and the alkyl spacer was synthesized in different length from 8 CH₂ to 6 CH₂, and then to only 2CH₂. The alkyl tails were synthesized in the length of 14 CH₂. The C₆₀-C₈-C₁₄ showed identical tetragonal superlattice as that of C₆₀-C₈-C₁₂ with slightly larger dimension in c-axis. Figure 4.18 shows the 1D WAXD patterns of the set of samples after thermal treatments as same as for C₆₀-C₈-C₁₂. The patterns clearly show that if the alkyl spacers are longer enough (C₈- and C₆-spacer), the shape amphiphiles can form ordered tetragonal superlattice; however, if the alkyl spacer is too short (C₂-spacer), the shape amphiphile cannot form ordered phase. The diameter of a C₆₀ is about 7 Å, and the length of 8, 6, and
2 carbon-carbon single bonds at the zig-zag conformation is 9.1 Å, 6.8 Å, and 2.3 Å, respectively. By adding the length of 2 ester bonds on the two ends of the spacers, the length of C\textsubscript{8}- and C\textsubscript{6}-spacers are capable to penetrate the external C\textsubscript{60} layers, but the length C\textsubscript{2}-spacer is insufficient to do so. This result support the triple layer model that the spacers of the middle layer molecules need to penetrate out of the external layer of C\textsubscript{60} MNPs.

Figure 4.18 1D WAXD pattern of C\textsubscript{60}-C\textsubscript{m}-C\textsubscript{14} with m = 8, 6, and 4 recorded at 30 °C after thermal annealing.

On the other hand, the thickness of the C\textsubscript{60} MNPs domain in the triple layer model can be estimated from the tetragonal sub-unit cell as the dimension of c'-axis plus the diameter of a C\textsubscript{60} (17.20 + 7 = 24.2 Å). The thickness of the C\textsubscript{60} layer can be analyzed from the experimental SAXS patterns by the one-dimensional correlation function. Figure 4.19 shows the SAXS pattern of \textit{crystal I} phase of C\textsubscript{60}-C\textsubscript{8}-C\textsubscript{12} conducted at 35 °C and the plot of corresponded 1D correlation function. From the (001) and (002)
reflections in the SAXS pattern (Figure 4.19a), the long periodicity of the superlattice has been determined as 54.3 Å. The red curve shown in Figure 4.19b is the result of calculated 1D correlation function, and the two black lines represent the tangents of the first slope and first minimum of the red curve. The intersection of these two black lines gives a $x$ value of 22.0 Å in the plot of correlation function, indicating the thickness of $C_{60}$ layer is 22.0 Å at 35 °C. This experimental thickness matches the one estimated from the tetragonal sub-unit cell with triple layer of $C_{60}$ MNPs.

![Figure 4.19](image)

Figure 4.19 (a) SAXS pattern of crystal I phase of $C_{60}$-$C_8$-$C_{12}$ recorded at 35 °C, and (b) the plot of corresponded 1D-correlation function.

The contact between alkyl spacers and $C_{60}$ MNPs as well as the contact between terminal methyl groups of alkyl tails and $C_{60}$ MNPs observed in the simulated model (see Figure 4.16 and Figure 4.17) can be confirmed by SSNMR experiments. Figure 4.20 is the 2D heteronuclear correlation (HETCOR) spectrum of $C_{60}$-$C_8$-$C_{12}$ in CDCl3 solution with chemical shift in $^{13}$C NMR on the $x$-axis and $^1$H NMR on the $y$-axis. The HETCOR spectrum was conducted with a Cross-Polarization (CP) time of 2 ms at 25 °C. The $^1$H chemical shift is externally referred to tetramethylsilane (TMS) at 0 ppm at ambient temperature. The signals in the HETCOR represent the polarization transfers from $^1$H to
the $^{13}\text{C}$ in the vicinity. There are strong correlation signals between C$_{60}$ carbons and aliphatic (~1 ppm) and alkoxy proton (~4 ppm). According to the chemical structure of C$_{60}$-C$_8$-C$_{12}$, the aliphatic protons and C$_{60}$ carbons are separated by 5 sigma bonds (~6 Å), and such a long distance is too far to be detected as correlation signals. Thereby, the polarization transfers from aliphatic protons and C$_{60}$ carbons could be only resulted from intermolecular correlations but not intramolecular correlations.

Figure 4.20 Two dimensional Heteronuclear correlation spectrum of C$_{60}$-C$_8$-C$_{12}$ with 2ms CP contact time. $V_r = 12$kHz

Figure 4.21 shows the local magnifies of HETCOR spectrum to observe the correlation between aliphatic protons and C60 carbons (Figure 4.21a) and between aliphatic protons and aliphatic carbons (Figure 4.21b). The red dotted lines indicate the protons of terminal CH$_3$ ($^1\text{H}$, 0.7 ppm) and inner CH$_2$ ($^1\text{H}$, 1.4 ppm), and the black dashed lines indicate the carbon of C$_{60}$ ($^{13}\text{C}$, 145.1 and 142.8 ppm), inner CH$_2$ ($^{13}\text{C}$, 30.7 ppm),
and terminal CH$_3$ ($^{13}$C, 14.8 ppm). The line-cut of cross peaks at 145.1 ppm, 142.8 ppm, 14.8 ppm and 30.7 ppm of $^{13}$C spectrum were plotted against to $^1$H spectrum (Figure 4.22) to show the line shape of each cross peaks. C60 matched with the signal of both terminal CH$_3$ and inner CH$_2$. The $^1$H chemical shifts of C$_{60}$ are well consistent with those of CH$_3$ and CH$_2$ protons, indicating the terminal CH$_3$ and inner aliphatic CH$_2$ are both spatially close to the C$_{60}$ MNPs (<4 Å). This result again substantiates the observation from the simulated tetragonal superlattice with triple layer of C$_{60}$ MNPs in the sub-unit cell.
Figure 4.21 Locally magnified spectra for polarization transfer (a) between aliphatic protons and C$_{60}$ carbons and (b) between aliphatic protons and aliphatic carbons.

Figure 4.22 Line-cuts of characteristic cross peaks in the HECTOR spectrum. The intensity of inner CH$_2$ is reduced to one fourth of its original intensity due to the high intensity.
4.7 Summary

In summary, the design, phase behavior, and crystal structure of a sphere-tail shape amphiphile composed of a C\textsubscript{60} MNP and alkyl spacers and tails has been reported in this Chapter. The MNP and tails are both hydrophobic, however, the different molecular shapes and affinities among these two components can still induce microphase separated phase. Enantiotropic phase transition behavior has been identified by thermal analysis. Under cooling from disordered state at high temperature, the C\textsubscript{60} MNPs can crystallize into 2D ordered structure stabilized by the alkyl spacers to form the pseudo-2D crystals. The existence of a 2D ordered structure of C\textsubscript{60} MNPs has been confirmed by TEM technique in both bright field and diffraction mode. At the temperature region between 88 °C and -4 °C, the pseudo-2D crystals of C\textsubscript{60} MNPs are separated by amorphous alkyl regions (\textit{crystal I} phase), while at temperature lower than -4 °C, the pseudo-2D crystals are separated by crystalline alkyl regions (\textit{crystal II} phase). The crystallization of alkyl tails was confirmed by SSNMR and variable-temperature 2D WAXD techniques. Both \textit{crystal I} and \textit{crystal II} phases exhibit the nature of structure within structure as hierarchical structures. Based on the data from 1D WAXD, 2D WAXD, SAXS and SAED, the supramolecular hierarchical structure of C\textsubscript{60} MNPs and all the alkyl parts can be described by a tetragonal superlattice, and the pseudo-2D crystal structure of C\textsubscript{60} MNPs was further determined by a tetragonal sub-unit cell. The packing of three layers of C\textsubscript{60} MNPs in the sub-unit cell was realized by the penetrating of alkyl spacers and the pseudo-2D crystals. It was also found the length of spacer is a crucial part to enable the shape amphiphile form such highly ordered structure. Using such a well-defined MNP in shape and chemistry as the model system, the work has more
implications in understanding the physical principles underling the self-assembly of shape amphiphiles constructed using different nanobuilding blocks. Moreover, the self-assembly of 2D ordered structure of nanobuilding blocks bearing intrinsic electronic properties gives a promising platform to build materials with conductivity in two dimensions.
CHAPTER V
HIERARCHICAL SUPRAMOLECULAR STRUCTURE DETERMINATION OF BPOSS-POM CONJUGATED HYBRID DYAD (BPOSS-LIND)

In the previous chapters, the phase behavior and solid state crystal structure of a giant shape amphiphile ($C_{60}$-$C_{8}$-$C_{12}$) composed of a MNP head and flexible alkyl tails were studied. The symmetry was broken by simply the geometry and rigidity of building blocks to form a unique triple-layered supramolecular structure. To further explore the influence of chemical identities of the building blocks on the properties of the self-assembly behavior, the first study in our group regarding POM as building blocks of giant shape amphiphiles was conducted. In this chapter, the supramolecular structure of a dumbbell-like giant shape amphiphile (BPOSS-LIND) consisted of a BPOSS and a Lindqvist type POM will be discussed. The symmetry breaking in both chemical composition and geometric shape of BPOSS-LIND leads to the formation of bilayered molecular packing scheme in a triclinic lattice driven by the crystallization of BPOSS cages.

5.1 Introduction

Dimensionality is one of the most important parameters for functional materials. The ability to reduce the dimensionality of bulk materials promotes the development of novel materials in many fields of nanotechnology. Two-dimensional (2D) crystalline
materials exhibit unique dimension-dependent properties\textsuperscript{90} in mechanical, electric, and optical\textsuperscript{91-94} which are potentially applied to controlling surface properties,\textsuperscript{95} structurally reinforced composites\textsuperscript{96,97}, electronics,\textsuperscript{89,98} and energy storage.\textsuperscript{99} The work in the previous chapter and other works\textsuperscript{52,62} have demonstrated the ability of giant shape amphiphiles to form layered structure with highly ordered in-plane MNP packing. However, the layered structures are stacked 2D crystalline sheets bonded by physical interactions, and are usually difficult to be exfoliated to obtain individual 2D sheets.

Because POM cages are a unique class of ionic clusters, the surface can be tuned by the counter ions or solvent with diverse polarities. By integrating POMs in giant shape amphiphiles, the crystalline MNP sheets of POMs could be dissociated from one to another by controlling the polarity of solvents. Prior to the study of individual 2D sheets, the structure of the supramolecular layered structure has to be determined to understand the packing scheme of MNPs and the mechanism of forming 2D sheets. This chapter will mainly focus on the structure determination of the crystal structure at room temperature and the supramolecular liquid crystal structure at 190 °C of BPOSS-LIND.

5.2 Molecular Design of BPOSS-POM

POMs are a large family of metal-oxygen anionic clusters composed of early transition metals (most commonly molybdenum, vanadium and tungsten) in their high oxidation states, and other heteroatoms (such as silicon and phosphorous) and thus, provide extensive structural building blocks with tunable sizes, varied symmetries, selective chemical modification capabilities, and interesting physical properties. As our first attempt, a POSS-POM conjugate (BPOSS-LIND, see Scheme 5.1) is constructed as a novel shape amphiphile. Lindqvist-type POM hexamolybdate [Mo\textsubscript{6}O\textsubscript{19}]\textsuperscript{2-} is used due to
its well-developed functionalization chemistry with aromatic amine species\textsuperscript{46} and the comparable size with common POSS derivatives (~1 nm).

Scheme 5.1 outlines the chemical structure, synthetic route, and molecular dimension of the BPOSS-LIND shape amphiphile. The synthesis applied the well-established palladium-catalyzed Sonogashira reaction\textsuperscript{100} to couple an alkyne-bearing POSS derivative (BPOSS-Alkyne) and an iodo-functionalized Lindqvist precursor (LIND-Iodide) to give the dumbbell-shaped hybrid molecule (BPOSS-LIND) in a good yield (~ 80%). The amphiphilic nature of BPOSS-LIND originates from the chemical integration of the nonpolar isobutyl-POSS cage and the highly polar, ionic Lindqvist-type POM moiety, triggering its unique self-assembly behaviors.
Scheme 5.1 (a) Synthesis of the POSS-POM hybrid shape amphiphile BPOSS-LIND. Reaction condition: (i) Pd(PPh$_3$)$_4$, CuI, NEt$_3$, room temperature, 0.5 h, 80%. (b) A molecular model generated by Cerius$^2$ showing the fully extended length of the BPOSS-LIND to be ca. 3.2 nm (excluding the counter ions). The left part is the BPOSS building block while the right part is the Lindqvist POM moiety.

5.3 Supramolecular Structure Determination of BPOSS-LIND

The supramolecular structure of BPOSS-LIND was determined by SAXS, WAXD, and SAED techniques with complementary of the density measurement and computer simulation of crystal model. Furthermore, the drive force of forming the supramolecular structure at room temperature and the supramolecular structure at elevated temperature are discussed.

5.3.1 Lattice Parameters Determination

Structural investigation of BPOSS-LIND was firstly conducted by X-ray diffraction on the powder samples obtained by evaporation from a semi-dilute acetone
solution (3.0 mg/mL). In the small-angle X-ray scattering (SAXS) \( q \) region (Figure 5.1a), only one diffraction peak is detected at scattering vector \( q = 1.14 \text{ nm}^{-1} \). The corresponding \( d \)-spacing is 5.48 nm, about twice the length of a fully extended BPOSS-LIND molecule (Scheme 5.1c). Wide-angle X-ray diffraction (WAXD) pattern (Figure 5.1b) shows multiple sharp diffraction peaks with \( d \)-spacing ranging from nanometer to sub-nanometer scales. Indexing of these diffractions requires information of the crystal unit cell lattice and symmetry group that can be obtained by selected area electron diffraction (SAED) technique under transition electron microscopy (TEM).

Figure 5.1 (a) 1D SAXS and (b) 1D WAXD powder patterns recorded at room temperature of the BPOSS-LIND grown from acetone solution. Crystallographic planes are indexed based on the triclinic unit cell with lattice parameters of \( a = 1.05 \text{ nm}, b = 0.92 \text{ nm}, c = 5.48 \text{ nm}, \alpha = 95.6^\circ, \beta = 98.1^\circ, \) and \( \gamma = 96.9^\circ \).

Single crystals of BPOSS-LIND are grown via slow evaporation of a 0.1 mg/mL BPOSS-LIND acetone solution deposited on carbon-coated mica substrate and are
subsequently examined by TEM. The SAED pattern in Figure 5.2a represents a pattern obtained from the circled area of the flat crystal in the inset. There is no systematic absence of diffractions can be observed, the most relevant $d$-spacings of 1.03 nm and 0.91 nm can thus be indexed as (100) and (010), respectively, which should be related to the inter-distance between MNPs because of the comparable dimensions. The reciprocal angle $\gamma^*$ between $a^*$- and $b^*$-axes of $82^\circ$ can also be measured from the SEAD pattern. Because the $d$-spacing (5.48 nm) of the single diffraction observed in the SAXS is much larger than that of (100) and (010), the peak in SAXS pattern should be attributed to the correlation along the third dimension, $c^*$-axis, and can be indexed as (001). By comparing the $d$-spacing of diffraction peaks in WAXD and SEAD patterns, the strongest peak in the WAXD pattern at $2\theta = 8.55^\circ$ can be assigned as (100) and the peak of (010) is located in the high angle shoulder of (100) diffraction.
Through the least-square refinement of all the peaks in diffraction patterns, the SAXS and WAXD patterns could be indexed (Figure 5.1) with a triclinic unit cell of $a = 1.05$ nm, $b = 0.92$ nm, $c = 5.48$ nm, $\alpha = 95.6^\circ$, $\beta = 98.1^\circ$, and $\gamma = 96.9^\circ$ (see Figure 5.1b).

The comparison of the calculated crystallographic data with the experimentally observed values from WAXD results is listed in Table 5.1. The good agreement for all twenty major Miller-indexed diffractions appearing in SAXS and WAXD patterns confirms the determined crystallographic parameters of the BPOSS-LIND crystals. One thing noticeable in the indexed WAXD pattern is that several diffractions with mixed $h$, $k$, and $l$ Miller index indicate there are crystallographic correlations between layers of molecules. Therefore, it is a 3D supramolecular hierarchical structure with the ordered MNP packing of feature size $\sim 1$ nm within the layered structure with long period $\sim 5$ nm.

After acquiring the lattice parameters, the crystal density was then conducted to know the number of molecules in the lattice. The experimentally measured density is
1.47 g/cm$^3$, which is in good agreement with the calculated crystal density of 1.48 g/cm$^3$ with two BPOSS-LIND molecules and four counter ions in one unit cell. Based on the experimental observation of no systematic absence of diffractions, the crystal unit cell was determined as one unit cell houses one motif consisting of two BPOSS-LIND molecules and four counter ions ($Z = 2$) linked by an inversion center (space group $P\overline{1}$).
Table 5.1 Crystallographic parameters of crystal structure of BPOSS-POM. *Experimental values observed in both WAXD and TEM data. **Calculated based on the triclinic unit cell of \( a = 1.05 \) nm, \( b = 0.92 \) nm, \( c = 5.48 \) nm, \( \alpha = 95.6^\circ \), \( \beta = 98.1^\circ \), and \( \gamma = 96.9^\circ \).

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5.3.2 Molecular Modeling of Crystal Structure of BPOSS-LIND

Molecular modeling and crystal packing analysis utilizing the Accelrys Cerius$^2$ software package reveals the essential features of the structure. The molecular conformation was determined by energy minimization process under COMPASS force field with space group $P\overline{1}$ in the fixed triclinic lattice. Projections of the triclinic unit cell along the [001], [100], and [010] directions are shown in Figure 5.3. In the molecular model, the BPOSS cages are shown in brown (yellow indicates iso-butyl groups), the Lindqvist cages are shown in blue, and the spacers are shown in gray. Counter ions are omitted for clarity. From the model, it can be observed that BPOSS-LIND underwent nano-phase separation and adopt the head-to-head and tail-to-tail arrangements of the molecules to form a double-layered supramolecular structure. Moreover, each layer of the molecules displace to one another within the $ab$-plane along the layer normal direction, resulting in the triclinic unit cell. Also, it is worth noting that the counter ions must be localized around the anionic Lindqvist clusters to reach charge balance, which are omitted in Figure 5.3 for clarity.

The simulated ED pattern along the [001] zone based on the molecular model is shown in Figure 5.4a. The both qualitative and quantitative matches in terms of relative intensities and positions in the reciprocal lattice for the diffractions between simulated and experimental SAED patterns (Figure 5.4b) indicate the model captures the molecular packing features of BPOSS-LIND in this triclinic lattice. Figure 5.4c depicts the characteristic crystallographic planes in the ED pattern: (100), (010), (120), and (210) in real space to illustrate the planes with high electron occupancy.
Figure 5.3 Simulated molecular packing model in the triclinic crystal lattice of BPOSS-LIND projected on (a) $ab$-plane along [001] direction, (b) $bc$-plane along [100] direction, and (c) $ac$-plane along [010] direction with $4 \times 4 \times 2$ repeated unit cells. The BPOSS cages are shown in brown (yellow indicates iso-butyl groups), the Lindqvist cages are shown in blue, and the spacers are shown in gray. Counter ions are omitted for clarity. (d) The perspective view of $10 \times 10 \times 2$ repeated unit cells for clearly illustrating the 2D layered structure.
Figure 5.4 (a) Simulated electron diffraction patterns and (b) experimental SAED pattern of the [001] zone of the BPOSS-LIND triclinic crystal lattice. (c) Schematic illustration of the corresponding ab-plane of 2×2 repeated unit cells.

5.3.3 Driving Force of Forming Layered Structure

The molecular model has demonstrated that the close packing of MNPs in the ab-plane the triclinic lattice. Moreover, the [001] zone SEAD pattern is reminiscent of the ED patterns of OBPOSS (Figure 2.13). After closely examining the [001], [010], and [100] zone of simulated ED patterns of OBPOSS, the [001] zone SAED pattern of BPOSS-LIND shares the most features with the simulated [001] zone ED pattern of OBPOSS (Figure 2.13d). The experimental SAED pattern of OBPOSS in [001] zone (Figure 5.2b) was also conducted to ensure the similarity of ED patterns between BPOSS-LIND and OBPOSS. The almost identical SAED patterns in [001] zone of BPOSS-LIND and OBPOSS in dimensions and relative intensities suggest that the formation of the supramolecular structure is driven by the crystallization of BPOSS MNPs, and the crystal structure of BPOSS-LIND expands the c-axis of OBPOSS’s unit cell (Figure 2.13) to accommodate the linkers and POM.

To further understand the origin of the double-layered structure, the SAED pattern of one of the precursor, BPOSS-Alkyne, was conducted and it shows additional
diffractions along $b^*$-axis, indicating a doubled dimension of $b$-axis (Figure 5.5). This observation clearly shows that the BPOSS cages of BPOSS-Alkyn are packed in the same manner as that in OBPOSS crystals in the $ab$-plane. However, the attached linkers of BPOSS-Alkyn are inclined with respect to the $ab$-plane and aligned in an ABABA arrangement along $b$-axis to generate doubled dimension of $b$-axis compared to that of OBPOSS. Interestingly, while after long exposure to electron beam, the additional diffraction peaks along $b^*$-axis disappeared and the SAED pattern return back to simply the [001] zone ED pattern of OBPOSS (Figure 5.6). This disappearance of diffraction peaks is attributed to that the arrangement of the linkers (ABABA) is disturbed by the energy of electron beam and it no longer possesses long-ranged order after long exposure time. Therefore, the SEAD pattern of BPOSS-Alkyn after long exposure (Figure 5.6b) only exhibits the order of BPOSS cages, which is identical to the packing of OBPOSS in $ab$-plane.

The inclined arrangement of the linkers of BPOSS-Alkyn is very similar to that of BPOSS-LIND. Nevertheless, based on the observation of the SAED pattern of BPOSS-LIND, the linkers are inclined in a same direction within a layer. This means the tethering of LIND MNPs to BPOSS-Alkyn break the packing symmetry of linkers and the molecules can only adopt a packing scheme with a lower symmetry. Besides, the similarity of the SAED pattern between OBPOSS, BPOSS-Alkyn, and BPOSS-LIND again confirm the crystallization of BPOSS cages dominate the molecular packing of BPOSS-LIND.
Figure 5.5 SAED pattern of the [001] zone of BPOSS-Alkyne crystals obtained from the circled region shown in the insert.

Figure 5.6 SAED pattern of the [001] zone of BPOSS-Alkyne crystals (a) with short exposure time (~10s) and (b) with long exposure time (~30s).

On the other hand, the dissimilarity of the ED patterns of LIND (Figure 2.15) or LIND-Iodide (Figure 2.16) with that of BPOSS-LIND indicates the packing of LIND
cages of BPOSS-LIND do not follow their own packing scheme but adopt the one of BPOSS cages. In the crystal structure of LIND (Figure 2.15), the closest intermolecular distance is 1.08 nm and the second closest intermolecular distance is 1.15 nm, which are larger than the dimension of $a$- and $b$-axis (1.05 and 0.92 nm, respectively) of BPOSS-LIND. It shows that at room temperature although the packing of LIND MNPs in a smaller area would increase overall internal energy of the BPOSS-LIND crystal structure, the energy penalty is overwhelmed by the crystallization of BPOSS cages. However, this crystallographic strain frozen in the double layer of LIND may be released by thermal energy at elevated temperature. To test this thought, the study on the structure of BPOSS-LIND at elevated temperature was conducted and will be discussed in the next section.

5.3.4 Ordered Structure of BPOSS-POM at Elevated Temperature

Thermal properties of the BPOSS-LIND and its two precursor molecules BPOSS-Alkyne and LIND-Iodide were studied by DSC. As shown in Figure 5.7 the DSC thermograms of these three molecules in the second heating cycle at heating rate of 10 $^\circ$C/min. It is clear that only one endothermic peak can be observed for each of the two precursors, which is attributed to the melting of their crystals. However, two endothermic peaks can be observed at 173 $^\circ$C and 214 $^\circ$C, respectively, for BPOSS-LIND crystals during heating, indicating that BPOSS-LIND crystals lose order in a stepwise manner.

The first transition temperature of BPOSS-LIND is almost identical to the $T_m$ of BPOSS-Alkyne (172 $^\circ$C), and the heat of fusion (11 J/g) is about 1/3 of that of pure BPOSS-Alkyne. Note that BPOSS cages possess around 35% of overall molecular mass of BPOSS-LIND, which indicates that BPOSS cages in BPOSS-LIND crystals are almost
fully crystallized. However, the second transition temperature of BPOSS-LIND is 12 °C lower than the $T_m$ of Lind-Iodide (226 °C) and the heat of fusion (0.7 J/g) is much less than 2/3 of that of pure Lind-Iodide crystals (2.1 J/g), which suggests that in BPOSS-LIND crystals, the POM moieties possess a much less ordered structure compared to pure Lind-Iodide crystals. These thermodynamic properties again indicate that the interaction between BPOSS cages must dominate the molecular packing in the crystalline phase.

Figure 5.7 DSC heating diagrams at 10 °C/min of Lind-Iodide (black curve), BPOSS-Alkyne (blue curve), and BPOSS-LIND (red curve). The peak temperature and the corresponding integrated heat of fusion value of each compound are also shown.

The SAXS and WAXD experiments of the high temperature phase of BPOSS-Lind at 190 °C (Figure 5.8) were conducted to investigate the structure after BPOSS crystals melting. At 190 °C where BPOSS groups fully melt, a diffraction peak in the small-angle region and several diffraction peaks associated with the double layered LIND groups in the wide-angle region are still observed (Figure 5.8b). The SAXS data shows that melt BPOSS part increases the distance between POM layers with increasing the $d$-
spacing of (001) plane to 6.28 nm, and the first diffraction peak (1.01 nm) in WAXD indicates that the distance between POM groups remain almost unchanged during the first transition. The indices can thus be assigned accordingly by assuming the overall symmetry remains the same during the first transition with extended dimension of c-axis. The triclinic unit cell of BPOSS-LIND at high temperature can thus be determined as $a = 1.05$ nm, $b = 0.92$ nm, $c = 6.39$ nm, $\alpha = 95.6^\circ$, $\beta = 98.1^\circ$, and $\gamma = 96.9^\circ$ with two molecules in one unit cell. The result structure precisely shows that after melting the BPOSS crystals, the molecular packing of LIND does not changed or relaxed but still keeps the arrangement in the BPOSS lattice at room temperature.

The only first order peak of (00$l$) plane indicates the ordered structure at 190 °C only possess either short-ranged or quasi-long-ranged order along the layer normal direction. In addition, the only few diffractions in the WAXD pattern manifest that the layers of LINDs are no longer crystallographic correlated after melting BPOSS crystals. This high temperature phase of BPOSS-LIND can thus be viewed as a supramolecular liquid crystalline phase.
Figure 5.8 (a) 1D SAXS and (b) 1D WAXD powder patterns recorded at 190 °C of the BPOSS-LIND grown from acetone solution. Crystallographic planes are indexed based on the triclinic unit cell with lattice parameters of $a = 1.05$ nm, $b = 0.92$ nm, $c = 6.38$ nm, $\alpha = 95.6^\circ$, $\beta = 98.1^\circ$, and $\gamma = 96.9^\circ$.

5.4 Summary

The BPOSS-LIND hybrid molecule reported here represents the first model compound in a library of unexploited shape amphiphiles based on POSS and POM building blocks. The unique self-assembly behaviors lead to a phase transition from 3D double-layered crystals at low temperature to supramolecular liquid crystals with 2D sheets of POM separated by amorphous BPOSSs at high temperature. The formation of 3D double-layered crystals with head-to-head / tail-to-tail molecular conformation is dominated by the crystallization of BPOSS cages and the LIND cages are dragged into the crystal lattice created by BPOSSs. After melting of BPOSS crystals at 190°C, the double-layered LIND sheet keep the in-plane arrangement at low temperature but lose the long-ranged order along the layer normal direction.
CHAPTER VI
HIERARCHICAL SUPRAMOLECULAR STRUCTURE DETERMINATION OF
GIANT POLYHEDRON (C-tetra-BPOSS)

6.1 Introduction

The assembly of building blocks with specific shape and symmetry in 3D is a long-lasting topic in scientific research. Integrating polyhedron as frameworks into molecular design is one of the most promising strategies to have self-assembled 3D ordered structures because of its well-defined symmetries and the chemically feasibility. The most recognized polyhedra are the Platonic solids consist of one type of regular polygon (equal angles and edge lengths) meeting at identical vertices: tetrahedron, hexahedron, octahedron, dodecahedron and icosahedron (see the first row of Figure 6.1). Another class of polyhedra distinct from Platonic solids is Archimedean solids consisted of two or more types of regular polygons that meet at identical vertices, including truncated tetrahedron, cuboctahedron, truncated cube, truncated octahedron, rhombicuboctahedron, snub cube, icosidodecahedron, truncated cuboctahedron, truncated dodecahedron, truncated icosahedron, rhombicosidodecahedron, snub dodecahedron, and truncated icosidodecahedron (see second to fourth rows of Figure 6.1).

With the aid of the coordination between transition metals and ligands, several clusters or networks possess the geometry or symmetry of these polyhedron have been achieved in the field of metal-organic framework (MOF). Yaghi et al. and Fujita et
have reported MOF based on tetrahedron. For the Platonic polyhedra, Thomas et al.\textsuperscript{103-105}, Eddaoudi et al.\textsuperscript{106} and Chan et al.\textsuperscript{107} have studied on the cluster with the hexahedra (cube) geometry. An octahedron of metal-organic cluster was also reported by Eddaoudi et al.\textsuperscript{109} For the Archimedean polyhedra, Stang et al. reported a series of truncated tetrahedral\textsuperscript{110,111}, and Yaghi et al. reported an example of truncated octahedra.\textsuperscript{112}

Figure 6.1 Illustrations of Platonic and Archimedean solids. First row (left to right): tetrahedron, hexahedron (cube), octahedron, dodecahedron, and icosahedron. Second row: truncated tetrahedron, cuboctahedron, truncated cube, truncated octahedron, and rhombicubotahedron. Thrid row: truncated cuboctahedron, snub cube, icosidodecahedron, and truncated dodecahedron. Fourth row: truncated icosahedron, rhombicosidodecahedron, truncated icosidodecahedron, and snub dodecahedron.

Without transition metals to form coordination complex, Atwood and MacGillivray also found an organic, hydrogen bonded version of an Archimedean snub
The molecular network is composed of capsules built by 8 molecules through 60 hydrogen bonds. Other examples of organic polyhedra are mostly focused on tetrahedron, because among the diverse geometries and symmetries of the polyhedron, it is the simplest one in architecture and the most abundant one in organic chemistry, e.g. sp$^3$ hybridized carbon.

Due to the tetrahedral geometry, organic tetrahedron usually forms a diamondoid (diamond-like) structure. For example, a hypothetical tetrahedral compound with specific interaction sites, e.g. hydrogen bond donors or acceptors, on the four ends should be guided by its tetrahedral geometry and interaction sites to form the cubic diamondoid network (Figure 6.2) or related hexagonal lonsdaleite structure (Figure 6.3). Although the cubic (diamond) and hexagonal (lonsdaleite) structures are both theoretical possible, based on the published works and structures in nature, i.e. carbon, the tetrahedron usually adopt diamondoid rather than lonsdaleite structure. Figure 6.4 shows the diamond structure of carbon atoms in the perspective view and the view along $a$-axis of the cubic structure. Similar networks formed by organic molecules often have less symmetry than the ideal diamond structure and sometimes have compressed or elongated axes, thus this kind of structure called diamondoid structure.

Interestingly, because of diamondoid structure left plenty room in the 3D space, the unoccupied space can be filled by either solvent molecules or additional sets of diamondoid networks. The illustration of the interpenetrated diamondoid is shown in Figure 6.4e with 4 different colors to represent 4 interlocked networks (4-fold interpenetrating diamondoid in this case). The interpenetrated diamondoid networks are stacked along the 4$\bar{4}$ axis of the tetrahedrons (Figure 6.4e), and the interpenetrated
networks thus still possess the 4-fold symmetry in the view along c-axis of the cubic structure (or tetragonal for same distorted diamondoid structure) (Figure 6.4c,d). One thing need to be noticed is that although the interpenetration of networks fill the 3D space and result in a much higher density than that of single-fold diamondoid structure, the interpenetrated diamondoid still left empty channels along the stacking direction. The empty channels can be clearly seen in Figure 6.5a from the top view of interpenetrated diamondoid structure and the blue cylinder depicted in Figure 6.5b.
Figure 6.2 Formation of Diamondoid network from hypothetical tetrahedral molecules with specific interaction sites (●). Broken lines represent directional intermolecular interactions.\textsuperscript{122}

Figure 6.3 The illustration of (a) diamond structure and (b) lonsdaleite (hexagonal diamond). The outlined cages in red are the natural units for these structures.\textsuperscript{123}
Figure 6.4 Illustrations of cubic diamond structure in the perspective view of (a) ball and stick model and (b) stick model, and the view along $a$-axis of (c) ball and stick model and (d) stick model. (e) The illustration of 4-fold interlocked diamondoid structure with $1 \times 1 \times 3$ array of lattice with different networks in different colors.

Figure 6.5 (a) Top view of the interpenetrated diamondoid structure formed by 2-AS-TPMA TMB. (b) Illustration of the 3-fold interpenetrated diamondoid structure with the empty channel remarked as a blue cylinder.\textsuperscript{116}
Hydrogen bonding interaction is the most widely used physical interaction to form the diamondoid structure in organic systems. Figure 6.6a shows two examples of hydrogen bonding pairs for the interaction sites of organic tetrahedrons with hydrogen bond donors in red and acceptors in blue. The corresponding illustration of diamondoid structure is shown in Figure 6.6b. Three exemplary organic tetrahedrons which can form diamondoid structure are shown in Figure 6.6c. The compound 1 and 2 form a 5-fold and a 3-fold interpenetrated diamondoid structure, respectively. Figure 6.7 displays the diamondoid structure formed by compound 3 in the perspective and top views, and the empty channels occupied by butyric acid molecules can be clearly observed in the top view.

These complex and 3D-ordered structures built by the tetrahedron intrigue us to study the supramolecular structure constructed by giant tetrahedron based on MNPs. In this chapter, the self-assembled structure of the first giant tetrahedron synthesized in our research group based on four BPOSS cages will be discussed.
Figure 6.6 (a) A schematic representation of dimeric motifs of hydrogen bonding to form (b) a diamondoid structure. Red circles represent hydrogen bond donors and the blue ones represent hydrogen bond acceptors. (c) Chemical structures of exemplary organic tetrahedrons with hydrogen bonding interaction on the four corners.\textsuperscript{114}

Figure 6.7 The Diamondoid structure of compound 3 in the Figure 6.6 (a) in the perspective view and its corresponding illustration of diamondoid unit, and (b) in the view along the $b$-axis showing the channels containing butyric acid molecules.
6.2 Molecular Design of C-tetra-BPOSS

The C-tetra-BPOSS was synthesized via click reaction\textsuperscript{124} to connect four BPOSS MNPs on the corners of a tetrahedral core,\textsuperscript{125} and the synthetic route is show in Scheme 6.1. POSS precursor bearing one alkyne and seven butyl groups (BPOSS-Alkyne) underwent the copper-catalyzed azide-alkyne [3 + 2] cycloaddition (CuAAC) reaction\textsuperscript{126,127} to bond with azide-functionalized tetrahedral core in a stoichiometric ratio of 4 to 1. The final product, C-tetra-BPOSS, consists a sp\textsuperscript{3} hybridized carbon as the center to introduce the $T_d$ symmetry, four rigid arms to extend the tetrahedral geometry, four aliphatic C3 spacers to couple the tetrahedral core and MNPs, and finally four BPOSS MNPs to form the giant tetrahedron. The arms with six- and five-membered ring after the click reaction are rigid enough to retain the overall tetrahedral geometry generated by the central carbon, and the aliphatic linkers are flexible, which can provide efficient mobility for BPOSS MNPs during self-assembly.

The molecular model of C-tetra-BPOSS is illustrated in Figure 6.8, and the tetragonal geometry is outlined by orange dashed line. The butyl groups, oxygen atoms, and silicon atoms on the BPOSS cages appear in yellow, brown, and orange colors, respectively. For the spacers and the tetrahedral core, carbon atoms appear in grey, oxygen atoms in red, and nitrogen atoms in blue. In the perspective view (Figure 6.8a), the end-to-end distance of adjacent BPOSS cages in a fully stretched molecular conformation is c.a. 3.6 nm, and this distance determines the dimension of the giant tetrahedron. The projected distance in the view along the $\bar{4}$ axis (Figure 6.8b) is c.a. 2.5 nm, correspond s to $3.6 / \sqrt{2}$ nm.
Scheme 6.1 Synthesis route of the giant tetrahedron, C-tetra-BPOSS. Reaction condition: CuBr, \(N,N,N',N',N''\)-pentamethyldiethylenetriamine (PMDETA), 70 °C, 24 h, yield > 90%.

The molecular design is very similar to the compound 3 in Figure 6.6c; however, the interaction used to construct supramolecular structure is different. Compound 3 used 4 pairs of hydrogen bonding donors and acceptors to build a diamondoid network based on its tetrahedral geometry, while the interaction programed in C-tetra-BPOSS is the van der Waals interaction between BPOSS MNPs. Because hydrogen bonding is a directional secondary interaction but van der Waals interaction is not, and the impenetrability and incompressibility of the MNPs should attribute steric hindrance for molecules to pack in self-assembly, it is intriguing to understand the effect of replacement of hydrogen bonding pair by MNPs on the resulted supramolecular structure.
Figure 6.8 Illustrations of molecular structure of C-tetra-BPOSS (a) in the perspective view and (b) in the view along the \( \overline{4} \) axis of the tetrahedral core. The end-to-end distance of C-tetra-BPOSS is around 3.6 nm. Butyl groups appear in yellow, silicon atoms in orange, and oxygen atoms in brown of the BPOSS cage; the carbon atoms appear in grey, nitrogen atoms in blue, and the oxygen atoms in red of the tetrahedral core and linkers.

6.3 Supramolecular Structure of C-tetra-BPOSS

Ordered structure of C-tetra-BPOSS was first examined by thermal analysis including TGA and DSC to understand the thermal stability and phase behavior. The structure was then determined based on WAXD and SEAD patterns with complementary of the density measurement and computer simulation. The morphology and major features of the ordered structure was visualized by bright field TEM image to confirm the determined supramolecular structure.

6.3.1 Thermal analysis

The phase behavior of C-tetra-BPOSS was first examined on DSC. Based on the TGA result of 5% weight loss at 290 °C (Figure 6.9a), the highest temperature for DSC measurements were set as 220 °C to avoid degradation inside the DSC chamber.
However, neither exotherm nor endotherm can be observed for crude samples under various heating and cooling rate from 2.5 °C/min to 40 °C/min. On the other hand, the crystal of C-tetra-BPOSS can be grown from slow evaporating dilute CHCl₃ solution and the melting temperature at 130 °C can be detected in the first heating. Nevertheless, neither crystallization nor crystal melting can be detected for the crystalline samples during the subsequent cooling and heating on DSC. These results indicate that the kinetic of the crystallization of C-tetra-BPOSS is slow under thermal treatment, which means the thermal energy is insufficient to induce the ordering of C-tetra-BPOSS molecules, while the solvent molecules can provide sufficient mobility for C-tetra-BPOSS molecules in this case. It is probably due to the giant molecular structure, which needs tremendous high temperature to drift the molecules by thermal energy.
6.3.2 Determination of unit cell parameters based on diffraction data

The C-tetra-BPOSS crystals grown from dilute CHCl₃ solution was further examined on TEM. The bright field TEM image of C-tetra-BPOSS crystal shows the morphology of flat crystals (Figure 6.10a). The SAED pattern of the single crystal (inset) reveals two sets of strongest diffraction spot with \( d \)-spacing of 1.04 and 1.11 nm on the longitudinal and transverse direction, respectively, belong to two different reciprocal axes. These two diffractions are also shown in WAXD powder pattern as the strongest peaks at \( 2\theta = 7.9^\circ \) and \( 8.5^\circ \) (Figure 6.12). Because the \( d \)-spacings of these two strong diffractions are about 1 nm, which is in the length scale of intermolecular distance of BPOSS cages, the major structural feature of C-tetra-BPOSS should be dominated by the crystallization of BPOSS MNPs. Moreover, at low angle region of the SEAD pattern, there are two additional diffractions along the transverse direction, indicating a crystalline plane of
3.33 nm (3*1.11 nm). This large $d$-spacing also suggests $C$-tetra-BPOSS forms a superlattice consisted of crystalline BPOSS as sub-units.

Besides the single zone of SEAD pattern (Figure 6.10b) obtained from crystals grown on carbon-coated mica, $C$-tetra-BPOSS crystals were also grown on polytetrafluoroethylene (PTFE)-sheared glass slide, and the corresponding SEAD pattern is shown in Figure 6.11. The SEAD pattern was obtained from the cycled region in the inset image, and it displays a fiber pattern with diffractions with $d$-spacing of 1.04 nm (yellow arrows) around the fiber axis and diffractions with $d$-spacing of 1.11 nm (white arrow) and 0.92 nm (red arrow) on the axis perpendicular to the fiber axis. The diffractions in the fiber pattern with $d$-spacings of 1.04 nm and 1.11 nm are coincident to the strongest two diffractions in the single zone ED pattern, while the diffraction with $d$-spacing of 0.92 nm was not observed in the single zone ED pattern, indicating the third diffraction are related to the third dimension and it can provide structural information for the further determination of superlattice parameters.
Figure 6.10 (a) Bright field TEM image and (b) [010] zone of SAED pattern of C-tetra- BPOSS grown from slow evaporating of dilute dichloroethene solution. The SAED pattern is obtained by the circular area marked in the inset.
Figure 6.11 The SEAD pattern of PTFE-aligned C-tetra-BPOSS sample. The pattern was obtained from the cycled region in the inset image. It displays a fiber pattern with $c$-axis as the rotational axis.
Figure 6.12 1D WAXD powder pattern of C-tetra-BPOSS grown from slow evaporating of dilute dichloroethene solution (0.02 wt%). Crystallographic planes are indexed based on the triclinic unit cell with lattice parameters of $a = 3.72$ nm, $b = 3.56$ nm, $c = 1.05$ nm, $\alpha = 97.8^\circ$, $\beta = 90.3^\circ$, and $\gamma = 71.7^\circ$.

By assuming the single zone SEAD pattern (Figure 6.10b) is [100] zone and indexing the transverse and longitudinal directions as $b^*$- and $c^*$-axes, all the diffractions on the pattern can be indexed accordingly. Moreover, the reciprocal angle $\alpha^*$ between $b^*$- and $c^*$-axes can be measured as $82^\circ$. This angle reveals that this crystal structure possesses either triclinic or monoclinic lattice. The SEAD fiber pattern (Figure 6.11) can be indexed as $c^*$-axis around the fiber axis, and the $a^*$- and $b^*$-axes perpendicular to the fiber axis. In this way, (001) and (030) diffractions were indexed for the fiber pattern, and the third diffraction should be $(hk0)$ diffraction.

To acquire information of third dimension and the other two angles of the unit cell parameters, a mutual interpretation between WAXD and SAED patterns is necessary. As
analyzed by dimensions on WAXD pattern, the multiple peaks centered at $2\theta \approx 8^\circ$ should be attributed to the structure of BPOSS cages. Because the peaks located at the low angle region from $2\theta = 2^\circ$ to $7^\circ$ refer to larger $d$-spacing than that of intermolecular distance between BPOSS cages, those peaks should be attributed to the crystal planes of the superlattice. The peak at the lowest scattering angle of $2\theta = 2.5^\circ$ ($d$-spacing = 3.55 nm) was deduced as (100) to represent the third dimension of the superlattice. Based on the known reciprocal parameters of $a^*$, $b^*$, $c^*$, and $\alpha^*$, the superlattice parameters was determined by least-square refinement on the first twelve diffractions of WAXD pattern to be $a = 3.72$ nm, $b = 3.56$ nm, $c = 1.05$ nm, $\alpha = 97.8^\circ$, $\beta = 90.3^\circ$, and $\gamma = 71.7^\circ$. The comparison between measured and calculated scattering angles as well as $d$-spacings based on the determined superlattice parameters are listed in Table 6.1.
Table 6.1 Crystallographic parameters of C-\textit{tetra}-BPOSS superlattice. \textsuperscript{a} Experimental values observed in WAXD and TEM. \textsuperscript{b} Calculated based on the triclinic unit cell of $a = 3.72$ nm, $b = 3.56$ nm, $c = 1.05$ nm, $\alpha = 97.8^\circ$, $\beta = 90.3^\circ$, and $\gamma = 71.7^\circ$.

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After determination of superlattice parameters, the SAED fiber pattern (Figure 6.11) can then be realized as the fiber pattern with its $c$-axis as the fiber axis, and the $(hk0)$ diffraction was determined as $(410)$. The relationship between $c$-, $c^*$-, $a^*$- and $b^*$-axes in space is illustrated in the lower left of Figure 6.11. The fiber pattern should be attributed to the soft-epitaxial grow of $C$-$tetra$-BPOSS on aligned PTFE crystals with $c$-axis of the superlattice along the chain-axis of PTFE.

6.3.3 Computer simulation of molecular packing model

To realize the molecular packing of $C$-$tetra$-BPOSS in the triclinic unit cell, in addition to the analysis of SEAD and WAXD patterns in terms of relative intensities and symmetries of diffraction patterns, computer simulation is essential especially for this complex molecule with a 3D molecular geometry. First of all, it is not intuitive to imagine how two molecules with dimensions of 3.6 nm (Figure 6.8) packed in a lattice with a dimension ($c$-axis) of 1.05 nm. This mismatch in scale between molecular and lattice dimensions suggest an interpenetrated structure, which the periodicity is not determined by the molecular dimensions but by the interpenetration scheme.

The interpenetrated structure is reminiscent of interpenetrated diamondoid structure as shown in Figure 6.4e and Figure 6.5. Therefore, the first model was built by arranging $C$-$tetra$-BPOSS molecules into interpenetrated diamondoid structure. However, the empty channels of interpenetrated diamondoid structure (see Figure 6.5) would cause a lower calculated density than the measured one, and the structure was failed to interpret the observed SEAD pattern. Although $C$-$tetra$-BPOSS and the compound 3 (Figure 6.6c) share a similar tetrahedral core, the compound 3 forms a diamondoid structure and $C$-$tetra$-BPOSS doesn’t. The difference in structures should be attributed to their different
end groups responsible for the intermolecular interactions. The hydrogen bonding for compound 3 is directional, and the structure would tend to maximize the amount of hydrogen bonding to lower the internal energy and result in a network; however, the van der Waals interactions among BPOSS cages are relatively isotropic, and the BPOSS cages would tend to maximize the amount of neighbors to form the crystal structure of BPOSS cages.

Despite the supramolecular structure of C-tetra-BPOSS is not exactly a diamondoid structure, after repetitively building molecular models, the final determined structure shows that it still share some features with interpenetrated diamondoid structure. In an interpenetrated diamondoid structure, the tetrahedral molecules stacked along their \( \bar{4} \) axes (Figure 6.4d and e), which can be illustrated in stacked sp\(^3\) hybridized carbons as shown in Figure 6.13a. In analogous to the carbons, the tetrahedral cores of C-tetra-BPOSS adopt a similar stacking to form geometrically locked columns in molecular level (Figure 6.13c). Each motif of the supramolecular structure consists of two C-tetra-BPOSS molecules and the BPOSS cages of distinct molecules are dislocated instead of directly on top of each other. This molecular packing can be clearly seen in the view along the column axis (top view). The top view of the column (Figure 6.13b) shows that the BPOSS cages spread out due to the steric hindrance by rotated cores in certain degrees and mainly by the flexible C3 aliphatic spacers. In this way, the BPOSS cages belong to the two molecules in a motif are located at a similar height, and those belong to every other molecule sit on top of each other along the column axis. The side view of a C-tetra-BPOSS column is shown in Figure 6.13d, and it can be considered as a column composed of stacked tetrahedral cores surrounded by a shell of BPOSS cages.
Figure 6.13 (a) The illustration of three sp$^3$ hybridized carbons stacked along their $\bar{4}$ axes. (b) The top view of a column consisted of C-tetra-BPOSS molecules. (c) The side view of a column consisted of tetrahedral cores with the periodicity of 1.06 nm between every other core. (d) The side view of a column consisted of C-tetra-BPOSS molecules.
With the main feature of the supramolecular structure – columns in mind, the molecules packing in the unit cell is shown in Figure 6.14. Because of the complexity of the molecular structure and the fact that the aliphatic spacers could decouple the packing of tetrahedral core form that of BPOSS cages, the simulation was done in neglecting the spacers and replacing the BPOSS cages of C-tetra-BPOSS molecules by OBPOSSs. The simulated molecular packing model in the triclinic crystal lattice is shown in projected $ab$-plane along [001] direction, $bc$-plane along [100] direction, and $ac$-plane along [010] direction with $2\times2\times2$ repeated unit cells. Importantly, the tetrahedral cores are stacked along the $c$-axis, the shortest dimension, at four edges of the $ab$-plane and eight OBPOSSs are scattered inside the unit cell, where the position were determined by energy minimization under COMPSS forcefield in the Cerius$^2$ package (Figure 6.14a). The projected $ab$-plane can thus be considered as the cross section of the supramolecular columns by taking each projected core linked with the eight surrounding OBPOSSs as a slice of a column.

The included angle between $a$- and $b$-axes is 71.7°, which is close to but deviated from 60°, the angle for hexagonally packed columns. This observation suggests that the crystallization of BPOSS cages, within and between columns, distorts the hexagonally packing of columns, resulting in a triclinic superlattice with a low symmetry. Moreover, one thing needs to be noticed that the OBPOSSs in the unit cell are not corresponded to the tetrahedral core in the unit cell because of the molecular geometry of C-tetra-BPOSS. In Figure 6.13d, the side view of the column clearly shows the BPOSS cages of a C-tetra-BPOSS molecule are stretched out and located at different heights from that of the tetrahedral core. Therefore, the eight OBPOSSs in the unit cell are actually come from
the molecules with the cores located above and below the unit cell. Besides, the molecular packing in real space shown in Figure 6.14b is corresponded to the experimental observed [100] zone of SEAD pattern.

Figure 6.14 Simulated molecular packing model in the triclinic crystal lattice of C-tetra-BPOSS projected on (a) ab-plane along [001] direction, (b) bc-plane along [100] direction, and (c) ac-plane along [010] direction with 2×2×2 repeated unit cells. The OBPOSS cages are shown in brown (yellow indicates iso-butyl groups), and the tetrahedral core are shown in blue and grey. The BPOSS cages of C-tetra-BPOSS are replaced by OBPOSSs and the aliphatic spacers are neglected in the simulation.
Based on the determined unit cell parameters and the arrangement of motifs in the unit cell, the simulated [100] zone of ED pattern can be generated to compare with the experimental one. The simulated [100] zone ED pattern (Figure 6.15a) qualitatively and quantitatively agrees with the experimental pattern (Figure 6.15b) in terms of relative intensities and positions of diffractions in the reciprocal lattice, suggesting the simulated molecular model capture the major features of arrangement of C-tetra-BPOSSs in the triclinic unit cell. The result supports the concept to break complex giant molecules into separated building blocks in computer simulation, and it will benefit for future works of simulation on other complex giant molecules.

Figure 6.15 Comparison of (a) simulated and (b) experimental [100] zone SAED pattern.
6.3.4 Confirm the supramolecular structure by observation in real space

In the previous section, the molecular packing and unit cell parameters were determined based on information in reciprocal space. To confirm the supramolecular structure, the structural information in real space was also acquired on bright field TEM images with large magnification. Figure 6.16a shows the bright field TEM image of flat crystal. It displays stripes with periodicity of c.a. 3 nm determined by the inset fast Fourier transformation (FFT) image, which corresponds to the (110) plane of the supramolecular structure. The result indicates the stripes are corresponded to the $c$-axis of the supramolecular structure, i.e. column axis (Figure 6.16c). On the other hand, the cross sectional sample of the crystals were obtained by microtome, and the bright field image is shown in Figure 6.16b. It displays a honeycomb-like structure with BPOSS cages as dark regions and tetrahedral cores as light regions. This observation matches the determined structure very well in both real and reciprocal space as illustrated in the Figure 6.16d and the upper right inset of Figure 6.16b. The lower right inset of Figure 6.16b is the zoom-in image, and the outline of $4 \times 4 \times 1$ repeated unit cells are indicated to compare with molecular model in Figure 6.16d.
Figure 6.16 (a) Bright field TEM image of a flat crystal with inset of corresponding FFT image. (b) Bright field TEM image of the cross section of crystals with upper right inset of the corresponding FFT image and lower right inset of zoom-in image. The illustrations of molecular packing in real space corresponded to (c) flat crystals of side view on columns and corresponded to (d) cross section of columns with \(4 \times 4 \times 1\) unit cells.
6.4 Summary

The first giant polyhedron in our group was studied in its phase behavior and crystalline supramolecular structure. The giant polyhedron, C-tetra-BPOSS, consists of a sp\(^3\) carbon as the core and four BPOSS cages as the end building blocks linked by C3 aliphatic spacers. The ordered structure of C-tetra-BPOSS can only be accessed by slow evaporating from solution but not from thermal annealing based on the observation on DSC experiments. The slow kinetic of C-tetra-BPOSSs in crystallization process during thermal treatments should be attributed to the huge molecular weight and the 3D molecular geometry.

The supramolecular structure was determined based on structural information in both reciprocal and real space. Diffraction techniques such as 1D WAXD powder and SEAD were used to determine the unit cell parameters, and the molecular packing was determined with the aid of computer simulation, and finally the supramolecular structure was confirmed by bright field TEM images. The ordered phase of C-tetra-BPOSS had been determined as a column-like structure dominated by the crystallization of BPOSS cages. Stacked tetrahedral cores served as the center of columns and BPOSS cages form shells to cover the columns. Due to the crystallization of BPOSS cages, the packing scheme of the columns is distorted and deviated from hexagonally close-packed columns, generating a triclinic superlattice with parameters of \(a = 3.72\) nm, \(b = 3.56\) nm, \(c = 1.05\) nm, \(α = 97.8°\), \(β = 90.3°\), and \(γ = 71.7°\).

The supramolecular structure can be viewed as a hierarchical structure because the columns construct the ordered structure in c.a. 3 nm scale, meanwhile, the BPOSS cages form ordered structure as the subunit in between the columns in the 1 nm scale.
Besides, the packing scheme of the tetrahedral core is similar to the interpenetrated diamondoid structure, indicating the interactions and steric hindrance of the bulky MNPs and the tetrahedral molecular geometry induce the complex structure, which is different from that solely induced from tetrahedral small molecules with hydrogen bonding as the physical interactions. The crystallization of the incorporated BPOSS MNP plays a crucial part in this unique supramolecular structure.
7.1 Introduction

It is known that diblock copolymers exhibit variety of self-assembled stable phases in the condensed state ranging from lamellae (LAM), double gyroid (DG), hexagonally ordered cylinders (HEX), to body-centered cubic (BCC) spheres\textsuperscript{128-130}. Directed self-assembly of block copolymers has been attracting attention as a technology to extend photoresist-based lithography to smaller dimensions\textsuperscript{131}. It has been demonstrated that the directed self-assembly of block copolymer offers a new route to perfect nanolithographic patterning at sub-50 nm length scale with molecular scale precision. For application in electronic media, it requires large-area, long-range ordered structures, which is both a kinetic and thermodynamic problem and requires subtle balance of various parameters and processing conditions. So far, block copolymer thin films have already achieved certain success, mainly with higher molecular weights and a feature size of c.a. 30 nm. Several challenges remain: (a) the generation of long-range ordered structure with smaller feature sizes (< 22 nm), (b) obtaining sharp interface with high lithographic contrast, particularly for smaller feature sizes, and (c) etch selectivity and resistance between two phases in the nanostructure.
To address these challenges, our research group has designed and synthesized a family of giant surfactants by integrating functionalized MNPs to polymers via a newly developed precision and efficient “sequential click” chemistry\textsuperscript{124,132} combined with well-controlled polymerization methods such as ionic polymerization or atom transfer radical polymerization. The amphiphilicities of MNPs and polymer chains can be tuned independently to optimize the structure-property relationship of giant surfactants. For instance, hydrophilic, macroionic or omniphobic MNPs can be achieved by carboxyl acids-functionalized C\textsubscript{60}s, POMs, and fluoro-functionalized POSS cages, respectively. The functionalization on MNPs is precise in terms of chemical identity, quantity, and geometrical site. On the other hand, hydrophobic and hydrophilic polymers can be commonly achieved by polystyrene (PS) and poly(ethylene oxide) (PEO), respectively. In addition to the chemical entities, these polymer chains are synthesized to possess controlled molecular weights with narrow distributions and various tail topologies.

The extraordinary electronic properties of C\textsubscript{60} and the high etching selectivity between POSS and PS provide diverse advantages over nano-patterning on semiconductors. In the condensed and thin film states, the molecular parameters such as tail lengths and topological isomers also significantly affect the self-assembled morphology. It has been found that triblock copolymers able to self-assemble in more complex structures that that of diblock copolymers.\textsuperscript{133-135} In this chapter, instead of three flexible blocks in a tirblock copolymer system, giant surfactants possess one functional MNP and two polymeric blocks were adopted. By analogy with triblock copolymers, the three-component giant surfactants intrigue a scientific research because of the volume- and shape-persistency of MNP could affect the self-assembly to generate different
structures from that of triblock copolymers. This chapter is mainly focused on self-assembly of giant surfactants in the thin film state.

7.2 Materials and Sample Preparation

The MNP-tethered PS-$b$-PEO giant surfactants were synthesized via precise and efficient “sequential click” chemistry combined with well-controlled polymerization method.$^{124,132,136,137}$ Based on two types of MNPs and two different tethering positions, there are four different sets of MNP/PS-$b$-PEO systems used in this chapter. The first type of MNP is AC$_{60}$, which has 10 carboxylic acid groups on the [60]fullerene surface to make this MNP hydrophilic$^{138}$. The second type of MNP is FPOSS, which has 7 fluorinated chains on the corners of a POSS cage$^{137}$. The detail molecular structures of MNPs are shown in Figure 7.1. By either tethering the MNP to the end of PS or attaching the MNP to the junction point of PS-$b$-PEO, linear and star giant surfactants can be generated, respectively. The detail molecular structures of giant surfactants are shown in Figure 7.2. The synthetic routes of linear FPOSS-PS-PEO and star PS-FPOSS-PEO giant surfactants are shown in Scheme 7.1. The linear AC$_{60}$-PS-PEO and star PS-AC$_{60}$-PEO giant surfactants are synthesized via similar approach of “clicking” the tert-butyl protected C$_{60}$-alkyne with PEO-PS-N$_3$ or PEO-N$_3$-PS. Final AC$_{60}$-based giant surfactants were obtained via deprotection of tert-butyl esters$^{138}$ to generate the carboxylic acid groups on AC$_{60}$ nanoparticles.
Figure 7.1 Chemical structure and schematic illustration of (a) AC$_{60}$ and (b) FPOSS molecular nanoparticles.

Following the feasible functionalization methodology of click chemistry, the giant surfactants were synthesized with fixed molecular weight of PEO at 2k Da for all the samples, and the molecular weights of PS range from 2.8k to 15.1k Da. All the giant surfactants possess precisely defined functionalities and narrow polydispersities below 1.13. The composition information for all samples of MNP-PS-PEO system is listed in Table 7.1.
Scheme 7.1 Synthetic routes of linear FPOSS-PS-PEO and star PS-FPOSS-PEO giant surfactants via copper catalyzed Huisgen [3+2] cycloaddition “click” chemistry.\textsuperscript{137}
Figure 7.2 Chemical structure and schematic illustrations of (a) AC$_{60}$-PS-PEO, (b) FPOSS-PS-PEO linear giant surfactants, and (c) PS-AC$_{60}$-PEO, (d) PS-FPOSS-PEO star giant surfactants.
Table 7.1 Sample information of giant surfactants.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Topology</th>
<th>$M_{w,PS}$</th>
<th>$M_{w,PEO}$</th>
<th>PDI</th>
<th>$f_{MP}$</th>
<th>$f_{PS}$</th>
<th>$f_{PEO}$</th>
<th>$\chi_{PS/PEO}$</th>
<th>Bulk morphology</th>
<th>Thin film morphology</th>
<th>Film thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A1)</td>
<td>AC60-PS28-PEO45</td>
<td>linear</td>
<td>2800</td>
<td>2000</td>
<td>1.10</td>
<td>0.23</td>
<td>0.46</td>
<td>0.31</td>
<td>3.4</td>
<td>LAM</td>
<td>LAM</td>
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<tr>
<td>(A2)</td>
<td>AC60-PS50-PEO45</td>
<td>linear</td>
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<td>2000</td>
<td>1.09</td>
<td>0.17</td>
<td>0.60</td>
<td>0.23</td>
<td>4.5</td>
<td>DG</td>
<td>ML</td>
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<tr>
<td>(A3)</td>
<td>AC60-PS64-PEO45</td>
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<td>6400</td>
<td>2000</td>
<td>1.06</td>
<td>0.14</td>
<td>0.66</td>
<td>0.20</td>
<td>5.1</td>
<td>HEX</td>
<td>HEX</td>
</tr>
<tr>
<td>(A4)</td>
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<td>7800</td>
<td>2000</td>
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<td>0.12</td>
<td>0.71</td>
<td>0.17</td>
<td>5.8</td>
<td>HEX</td>
<td>HEX</td>
</tr>
<tr>
<td>(A5)</td>
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<td>15100</td>
<td>2000</td>
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<td>0.08</td>
<td>0.82</td>
<td>0.10</td>
<td>9.2</td>
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<td>BCC</td>
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<tr>
<td>(A6)</td>
<td>PS52-AC60-PEO45</td>
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<td>0.17</td>
<td>0.60</td>
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<td>LAM</td>
<td>LAM</td>
</tr>
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<td>2000</td>
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<td>0.12</td>
<td>0.71</td>
<td>0.17</td>
<td>5.8</td>
<td>HEX</td>
<td>HEX</td>
</tr>
<tr>
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<td>2000</td>
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<td>CL3 / LAM3</td>
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<td>2000</td>
<td>1.09</td>
<td>0.24</td>
<td>0.55</td>
<td>0.21</td>
<td>4.5</td>
<td>LAM3</td>
<td>LAM3</td>
</tr>
<tr>
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<td>FPOSS-PS64-PEO45</td>
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<td>LAM3</td>
<td>PL3</td>
</tr>
<tr>
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<td>7800</td>
<td>2000</td>
<td>1.11</td>
<td>0.18</td>
<td>0.66</td>
<td>0.16</td>
<td>5.8</td>
<td>HEX3</td>
<td>CPL3</td>
</tr>
<tr>
<td>(F5)</td>
<td>FPOSS-PS151-PEO45</td>
<td>linear</td>
<td>15100</td>
<td>2000</td>
<td>1.13</td>
<td>0.11</td>
<td>0.79</td>
<td>0.10</td>
<td>9.2</td>
<td>HEX3</td>
<td>CPL3</td>
</tr>
<tr>
<td>(F6)</td>
<td>PS78-FPOSS-PEO45</td>
<td>star</td>
<td>5000</td>
<td>2000</td>
<td>1.10</td>
<td>0.24</td>
<td>0.55</td>
<td>0.21</td>
<td>4.5</td>
<td>$\tau_1$</td>
<td>CSC</td>
</tr>
<tr>
<td>(F7)</td>
<td>PS151-FPOSS-PEO45</td>
<td>star</td>
<td>7800</td>
<td>2000</td>
<td>1.09</td>
<td>0.18</td>
<td>0.66</td>
<td>0.16</td>
<td>5.8</td>
<td>$\tau_1$</td>
<td>CSC</td>
</tr>
</tbody>
</table>

$^a$ Sample label, the subscripts represent the degree of polymerization, $N$; $^b$ Molecular weight (g/mol) calculated from $^1$H NMR; $^c$ Polydispersity index measured by SEC; $^d$ volume fraction based on molecular weights and densities ($\rho_{PS} = 1.053$ g/cm$^3$, $\rho_{PEO} = 1.121$ g/cm$^3$, $\rho_{AC60} = 1.6$ g/cm$^3$, $\rho_{FPOSS} = 2.0$ g/cm$^3$), details in SI; $^e$ $\chi$ is the Flory-Huggins interaction parameter at 120 °C estimated by equation $\chi_{PS/PEO} = -7.05 \times 10^{-3} + 21.3/T$; $^f$ Bulk morphology determined by SAXS and TEM at 25 °C; $^g$ Thin film morphology determined by GISAXS and TEM at 25 °C. $^h$ Film thickness determined by reflectivity at 25 °C.
7.3 Result and Discussion

Different physical and chemical properties of the functional groups on the MNPs could result in distinct exterior shapes of MNPs because of their excluded volumes and orientations. For instance, the carboxylic acid groups of AC\textsubscript{60} are amorphous, as the result, the exterior shape of AC\textsubscript{60} is expected to adopt the spherical shape of C\textsubscript{60} covered by a hydrophilic and fuzzy shell; the FPOSS MNP, on the other hand, has crystallized fluorinated chains, which make the FPOSS possess a rectangular exterior shape with orientated fluorinated chains. This rectangular shape is manifested by comparing FPOSS with a similar fluorinated POSS (FDPOSS) as shown in Figure 7.3. Figure 7.3a shows the chemical structure of FDPOSS\textsuperscript{139}, which has a shorter alkyl spacer between POSS cage and fluorinated chains compared to that of FPOSS and it possesses a triclinic unit cell with dimension of $a = 10.35$ Å, $b = 21.98$ Å, $c = 28.65$ Å, $\alpha = 102.08^\circ$, $\beta = 95.70^\circ$, and $\gamma = 90.90^\circ$.\textsuperscript{139} The detail crystal structure of FDPOSS is shown in Figure 7.3b. By viewing along the $b$-axis, the distance between fluorinated chains can be clearly determined as 0.47 nm, and the long axis of FDPOSS is around 3.2 nm. To determine the structure of FPOSS, the wide angle X-ray diffraction pattern (Figure 7.3d) was conducted and it shows a series of diffraction peaks with $q$ ratio of 1:2:3 corresponding to the dimension of the long axis of FPOSS, which was determined as 3.53 nm. In addition, there is strong, sharp Bragg peak at $q = 1.28$ Å\textsuperscript{-1}, which corresponds to 0.49 nm, indicating the distance between fluorinated chains of FPOSS is 0.49 nm. Based on the WAXD data, the geometry of FPOSS can be described as a rectangular shape with 3.53 nm in length and around 1 nm in both width and height (Figure 7.3e).
Figure 7.3 (a) Chemical structure of FDPOSS and the (b) crystal structure of FDPOSS in perspective view and projections along three different axes; (c) chemical structure of FPOSS, and the (d) WAXD fiber pattern (inset) and the integrated 1D pattern. (e) the schematic illustration of FPOSS with dimensions. The functional group, R, is identical to both FDPOSS and FPOSS as shown in (a) and (c).
Because the MNPs and blocks of the copolymer possess different affinities, the immiscibility and incommensurate in terms of chemical and geometrical senses of building blocks in giant surfactants could induce microphase separation into ordered and complex phases. Because AC$_{60}$ and PEO are both hydrophilic, PS is hydrophobic, and FPOSS is omniphobic, the linear AC$_{60}$-PS-PEO exhibits a hydrophilic-hydrophobic-hydrophilic (ABA) type, and the linear FPOSS-PS-PEO exhibits an omniphobic-hydrophobic-hydrophilic (ABC) type giant surfactants. In addition, the linear and star giant surfactants were designed to have identical compositions. Since the only difference between linear and star surfactants is their topologies, these two sets of giant surfactants can be recognized as topological isomers. Two sets of topological isomers are labeled in Table 7.1. The study of topological isomers is of scientific interesting to reveal the effect of the molecular topology on the resulted supramolecular structures because it could serve as an additional factor to fine tune a desired structure.

The morphology of MNP-PS-PEO in bulk state were determined by small-angle X-ray scattering (SAXS) in the previous work and the data is summarized in Table 7.1. Similar to the diblock or triblock copolymer systems, MNP-PS-PEO systems can form microphase-separated morphologies in the bulk state. In the linear giant surfactant system, as the molecular weight of PS increases from 2.8k to 15.1k Da, the morphology of AC$_{60}$-PS-PEO changes from LAM to DG and then to HEX; while, the morphology of FPOSS-PS-PEO changes from LAM to HEX. In the star giant surfactant system, as the molecular weight of PS increases from 5.2k to 7.8k Da, the morphology of PS-AC$_{60}$-PEO changes from LAM to HEX, and that of PS-FPOSS-PEO remains in LAM. The volume fractions
of PS and PEO can be calculated based on the molecular weight and density of each block by

\[
f_{\text{PS}} = \frac{M_{\text{PS}}/\rho_{\text{PS}}}{M_{\text{PS}}/\rho_{\text{PS}} + M_{\text{PEO}}/\rho_{\text{PEO}} + M_{\text{MNP}}/\rho_{\text{MNP}}}
\]

(7.1)

\[
f_{\text{PEO}} = \frac{M_{\text{PEO}}/\rho_{\text{PEO}}}{M_{\text{PS}}/\rho_{\text{PS}} + M_{\text{PEO}}/\rho_{\text{PEO}} + M_{\text{MNP}}/\rho_{\text{MNP}}}
\]

(7.2)

where \(\rho_{\text{PS}} = 1.05 \text{ g/cm}^3\), \(\rho_{\text{PEO}} = 1.09 \text{ g/cm}^3\), \(\rho_{\text{AC60}} = 1.60 \text{ g/cm}^3\), \(\rho_{\text{FPOSS}} = 2.0 \text{ g/cm}^3\), \(M_{\text{AC60}} = 2.1 \text{ kg/mol}\), and \(M_{\text{FPOSS}} = 4.1 \text{ kg/mol}\).

The Flory-Huggins interaction parameter \((\chi)\) between the styrene and ethylene oxide monomers was determined to be \(\chi = -0.00705 + 21.3/T\).\(^{140}\) Therefore, the \(\chi N\) (N is overall degree of polymerization) values for all the compositions at 120 °C (annealing temperature) can be calculated and are listed in Table 7.1. Because of the low degree of polymerization, the \(\chi N\) values for all the compositions of PS-\(b\)-PEO diblock copolymers (without MNP) are estimated to be below 10.5, suggesting that the PS-\(b\)-PEO diblock copolymers are in the weak segregation limit. This result indicates the self-assembly behavior of these giant surfactants is induced by the incorporation of MNPs, and makes giant surfactant a great candidate for engineering small feature sizes with low molecular weight of block copolymers.

Because of the effects of geometrical confinements, preferential blocks on the interfaces, substrate surface modifications, surface fields on self-assembly and the applicable thermal or solvent annealing conditions for thin films, the self-assembly behavior of block copolymers in thin films have been found to be different from that in bulk.\(^{141-144}\) Under this circumstance, the self-assembly of giant surfactants in thin film are expected to exhibit some extraordinary ordered structure in addition to that in bulk state,
and worth to have a systematic study of MNPs and topology on the self-assembled structures of giant surfactant in thin film.

7.3.1 Morphology of Linear AC$_{60}$-PS-PEO in Thin Film

To study the thin film phase behavior of MNP-PS-PEO, films were spun cast from THF solution onto wafer substrates. The thin film thickness was controlled by solution concentration (1 wt%) and spin rate (6000 rpm). Thermal treatment was done by annealing the samples under vacuum at 120 °C for 4 and 2 days for AC$_{60}$-PS-PEO and FPOSS-PS-PEO, respectively. The morphology of MNP-PS-PEO thin film after spin coating was examined by GISAXS, GIWAXS, and TEM in both plan-view and cross-sectional view.

Figure 7.4 and Figure 7.5 are GISAXS and GIWAXS patterns taken at an incident angle of 0.20° for linear AC$_{60}$-PS-PEO. The linear giant surfactant with 2.8k, 5k, 6.4k, 7.8k, and 15.1kDa of PS are labeled as A$_1$, A$_2$, A$_3$, A$_4$, and A$_5$, respectively. For this set of giant surfactants, similar to the phase behavior in the bulk state, the thin film morphology transfers from LAM to HEX then to BCC as PS molecular weight increased. However, there are two discrepancies of morphologies between bulk and thin film states. First, in a narrow compositional window between LAM and HEX phases, the sample A$_2$ with 5k Da of PS exhibits DG morphology in bulk state; nevertheless, it only shows modulated lamella (ML) in thin film evidenced by the GISAXS pattern (Figure 7.4b) due to the geometrical confinement in the dimension of film normal. Second, the transition from HEX to BCC cannot be observed in bulk state; however, the sample A$_5$ with 15.1k Da of PS showed BCC spherical morphology in thin film.
To study the smaller feature size in the ordered morphologies, the GIWAXS experiments were conducted for linear $\text{AC}_{60}$-PS-PEO as shown in Figure 7.5. No reflection can be observed throughout every molecular weight of PS in the wide angle region in these patterns, indicating the $\text{AC}_{60}$ MNPs are amorphous and are randomly distributed in the PEO domain nearby the interface of PS/PEO in the micro-separated phase. The morphologies and dimensions of the GISAXS patterns were further analyzed by the software of GIXSGUI, developed by Argonne National Laboratory based on DWBA theory and shown in Figure 7.6 – 7.8. The open circles and squares in the analyzed patterns indicate the reflections scattered by transmitted and reflected beams, respectively.

For the LAM morphology of $\text{A1}$ (Figure 7.6a), the theoretical calculation was conducted based on a unit cell with characteristic $c$-axis perpendicular to the substrate and dimensions of $a = b = \infty$ (black dashed border in Figure 7.6b). For the HEX morphology of $\text{A3}$ and $\text{A4}$ (Figure 7.7a and c), the theoretical calculation was conducted based on a hexagonal unit cell with dimensions of $a$ equals to $b$, and $c = \infty$ (black dashed border in Figure 7.7b and d). The $[10]$ and $[21]$ directions of the hexagonal lattices are parallel and perpendicular to the substrate, respectively. The dimension of $c$-axis was set to be infinity to calculate only the periodicity in the cross section of hexagonally packed cylinders. The theoretical calculation of BCC spherical morphology of $\text{A5}$ was conducted based on a body-centered cubic unit cell with dimensions of $a = b = c$, and its $[110]$ direction perpendicular to the substrate (black dashed border in Figure 7.8b). The BCC spherical morphology can be also confirmed by the ratio of second-to-first nearest neighbor distance $a_2/a_1$, which can be obtained via GISAXS as shown in
Figure 7.9. For the hexagonal packing, the $a_1/a_2$ ratio equals to 1, and the ratio equals to 1.154 for the (110) plane of spherical BCC packing. In the Figure 7.8a, $a_1$ and $a_2$ can be obtained to be 13.5 nm and 11.7 nm, respectively. The ratio of $a_1/a_2$ equals to 1.154, indicating sample A5 with 15.1k Da of PS forms spherical BCC morphology. Table 7.2 lists the characteristic dimensions based on the theoretical calculation. The characteristic feature size changed from 7.9 nm to 11.7 nm as increasing the molecular weight of PS from 2.8k to 15.1k Da.

Table 7.2 Characteristic dimensions of linear AC$_{60}$-PS-PEO giant surfactants extracted from the GISAXS patterns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_{w,PS}$</th>
<th>$M_{w,PEO}$</th>
<th>PDI</th>
<th>Thin film Morphology ($25^\circ$C)</th>
<th>Characteristic Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A1) AC$<em>{60}$-PS$</em>{28}$-PEO$_{45}$</td>
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<td>2000</td>
<td>1.10</td>
<td>LAM (001): 7.9 nm</td>
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<tr>
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<td>2000</td>
<td>1.09</td>
<td>ML (100): 11.3 nm (010): 17.8 nm</td>
<td></td>
</tr>
<tr>
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<td>2000</td>
<td>1.06</td>
<td>HEX (100): 10.8 nm</td>
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<tr>
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<td>1.11</td>
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<td></td>
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<tr>
<td>(A5) AC$<em>{60}$-PS$</em>{151}$-PEO$_{45}$</td>
<td>15100</td>
<td>2000</td>
<td>1.13</td>
<td>BCC (110): 11.7 nm</td>
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</table>
Figure 7.4 GISAXS patterns at the incident angle of 0.20° of (a) A1, (b) A2, (c) A3, (d) A4, and (e) A5 thin films. The corresponding morphologies are LAM, ML, HEX, HEX, and BCC, respectively.

Figure 7.5 GIWAXD patterns at the incident angle of 0.20° of (a) A1, (b) A2, (c) A3, (d) A4, and (e) A5 thin films.
Figure 7.6 GISAXS patterns at the incident angle of 0.20° with theoretically calculated result of (a) A1 and (c) A2. White squares are simulated diffraction peaks scattered by reflected beam and red circles are simulated diffraction peaks scattered by transmitted beam. Schematic illustrations of corresponded (b) LAM morphology for A1 and (d) ML morphology for A2. Color code: AC$_{60}$ and PEO in blue, and PS in red.
Figure 7.7 GISAXS patterns at the incident angle of 0.20° with theoretically calculated result of (a) A3 and (c) A4. White squares are simulated diffraction peaks scattered by reflected beam and red circles are simulated diffraction peaks scattered by transmitted beam. Schematic illustrations of corresponded HEX morphology for (b) A3 and (d) A4. Color code: AC$_{60}$ and PEO in blue, and PS in red.
Figure 7.8 (a) GISAXS patterns at the incident angle of 0.20° with theoretically calculated result of A5. White squares are simulated diffraction peaks scattered by reflected beam and red circles are simulated diffraction peaks scattered by transmitted beam. (b) Schematic illustration of corresponded BCC morphology for A5. Color code: AC60 and PEO in blue, and PS in red.

Figure 7.9 (a) Illustration of a1/a2 value in hexagonal packing symmetry and BCC (110) plane. (b) Illustration of a1 and a2 planes in GISAXS pattern for BCC sphere with (110) plane parallel to thin film surface.
Besides the GIXS techniques, TEM bright field images of linear AC60-PS-PEO also reveal the morphology transition from LAM to HEX then to BCC packed sphere as increasing the molecular weight of PS. The samples A1 and A2 show featureless in the plan-view TEM (Figure 7.10a and Figure 7.10b), because they form LAM and ML morphologies, respectively, with lamellar normal perpendicular to the substrate. However, the LAM and ML structures can be clearly observed in the cross-sectional TEM images (Figure 7.10c and Figure 7.10d). In the bright field TEM images, the AC60 and PEO domains are selectively stained by OsO4 and appear darker than PS domains. ML morphology was recognized as an intermediate state during the transition from LAM to HEX. Sakurai et al.146 studied the transition from HEX to LAM in the poly(styrene-b-butadiene-b-styrene) system. Based on SAXS and TEM results, the authors suggested that the HEX to LAM transition takes place via lateral coalescence of cylinders, implying a modulated or perforated lamellar intermediate structure. Qi and Wang147 studied the kinetics of LAM to HEX transition in weakly segregated diblock copolymers using a time-dependent Ginzburg-Landau approach. They found that the transition from LAM to HEX goes through a perforated-modulated lamellar (PML) structure, and this structure serves as an intermediate during the transition from LAM to HEX in certain temperature ranges. The sample A2 shows DG morphology in the bulk state; however, due to the fact that bicontinuous gyroid is a three dimensional structure, formation of DG is suppressed and difficult to develop in the geometric confinement of thin films.148 Reported DG morphology in thin film state is usually developed in relatively thick films (c.a. \( \mu \)m-thick).70,78 The GISAXS pattern in Figure 7.4b and the cross-sectional TEM image in Figure 7.10d reveal that A2 exhibits a ML structure, indicating the gyroid morphology is
suppressed in the ~140 nm thick thin film for this specific giant surfactant. As the volume ratio of PS block increased, the sample A3 and A4 self-assemble into HEX morphology with their (10) plane parallel to the substrate surface. The projection of in-plane hexagonally packed cylinders of AC$_{60}$ and PEO domain surrounded by PS matrix can be clearly seen in the plan-view TEM images with AC$_{60}$/PEO domain in dark and PS domain in light grey (Figure 7.11a and b). Because the (10) plane of HEX parallel to the substrate surface (Figure 7.11d), the distance between dark lines (AC$_{60}$/PEO domain) in the plan-view TEM images corresponds to the dimension of (11) plane of the HEX structure, which was characterized by the inset FFT images. The dimensions of (11) planes are 4.82 nm and 5.59 nm for A3 and A4, respectively. As the volume fraction of PS further increased, the sample A5 with highest volume fraction of PS shows spherical BCC morphology. The projection of BCC packing spheres along [110] direction can be observed in the plan-view TEM image (Figure 7.11c), and the corresponded FFT (inset) clearly shows the (110) of 12.36 nm and (200) of 8.16 nm.
Figure 7.10 Plan-view bright field TEM images of (a) A1, and (b) A2. Cross-sectional view bright field TEM image of (c) A1 and (d) A2.
Figure 7.11 Plan-view bright field TEM images of (a) A3, (b) A4, and (c) A5. The upper right insets are the corresponded FFT images, and the upper left inset of (c) is the locally magnified image. (d) The cross-sectional view bright field TEM image of A4.
7.3.2 Morphology of Linear FPOSS-PS-PEO in Thin Film

Another set of linear giant surfactants was introduced by tethering a FPOSS MNP to a PS-\textit{b}-PEO diblock copolymer on the end of PS block. The chemical structure and illustration of molecular geometry of linear FPOSS-PS-PEO are shown in Figure 7.2b. This set of giant surfactants was expected to self-assemble into complex phases with three components because each segment of this giant surfactant possesses distinct affinity: PS is hydrophobic, PEO is hydrophilic, and FPOSS is omniphobic. Moreover, the crystallization of FPOSS makes this giant surfactant promise to form hierarchical structures with domain sizes cover tens of nanometers to few angstroms. The thin film samples were spun-coated from 1 wt\% of THF solution on silicon wafer at a spin rate of 6000 rpm for 1 minute.

This set of giant surfactants were synthesized with fixed molecular weight of PEO block and varied molecular weight of PS block ranged from 2.8 kDa to 15.1 kDa, which have exactly the same PS-\textit{b}-PEO compositions of that of AC\textsubscript{60}-PS-PEO samples. The match of polymeric compositions in two sets of giant surfactants provides us a great opportunity to study the effect of MNP on the self-assembly behavior in the giant surfactant system. The sample details are summarized in Table 7.1. The linear giant surfactant with 2.8k, 5k, 6.4k, 7.8k, and 15.1kDa of PS are labeled as \textbf{F1}, \textbf{F2}, \textbf{F3}, \textbf{F4}, and \textbf{F5}, respectively. The volume fractions of each block can be calculated based on the molecular weights and densities as described in the last section.

The self-assembled phases in thin film state were investigated by GISAXS, GIWAXD, and TEM in both plan-view and cross-sectional view. The combination of structural information from both reciprocal and real space helps us to elucidate the thin
film self-assembly behavior. The GISAXS patterns of a series of FPOSS-PS-PEO giant surfactants are shown in Figure 7.12, and the corresponded GIWAXD patterns are shown in Figure 7.13. The first observation was the in-plane sharp reflection on the $q_y$-axis corresponds to 3.6 nm for $\mathbf{F1}$ and $\mathbf{F2}$ in both GISAXS and GIWAXD patterns. The appearance of high order peaks (Figure 7.13a and b) indicates a long-ranged ordered molecular packing with a periodicity of 3.6 nm along the direction paralleled to the substrate surface. In addition, a halo corresponded to the $d$-spacing of 0.49 nm along $q_z$ direction can be observed on the GIWAXD patterns. The structural information of few nanometer and sub-nanometer scale is reminiscent of crystal structure of FPOSS (Figure 7.3d), and the orientation of FPOSS MNPs in the self-assembled structures of $\mathbf{F1}$ and $\mathbf{F2}$ can be determined to be that their long axis parallel to the substrate surface, i.e. the orientation depicted in Figure 7.3e. No reflection corresponded to the packing of FPOSS MNPs for $\mathbf{F3}$, $\mathbf{F4}$, and $\mathbf{F5}$ was observed, which should be attributed to their low volume fraction of FPOSS, resulting in undetectable intensities.
Figure 7.12 GISAXS patterns at the incident angle of 0.20° of (a) F1, (b) F2, (c) F3, (d) F4, and (e) F5 thin films. The corresponding morphologies are CL3/LAM3, LAM3, PL3, PL3 and PL3, respectively.

Figure 7.13 GIWAXD patterns at the incident angle of 0.20° of (a) F1, (b) F2, (c) F3, (d) F4, and (e) F5 thin films.
The GISAXS pattern of F1 (Figure 7.12a) displays both reflections of both in-plane (along \(q_y\)) and out-of-plane (along \(q_z\)) periodicities. It should be noticed that the periodicity along \(q_z\) direction at \(q_y = 0 \text{ Å}^{-1}\) is different from that at \(q_y = 0.04 \text{ Å}^{-1}\). An analysis of this pattern in detail based on DWBA (Figure 7.14) and the observation of TEM bright field images reveal a coexistence of 3-component cylinder-within-lamellar structure (CL3) and 3-component lamellae (LAM3). By considering the reflections along \(q_z\) at \(q_y = 0.04 \text{ Å}^{-1}\), a 2D centered unit cell of \(a = 16.1 \text{ nm}\) and \(b = 24.0 \text{ nm}\) (Figure 7.14b) was used to represent the ML morphology. Although the ML model matches the peaks at \(q_y = 0.04 \text{ Å}^{-1}\) very well, the reflections along \(q_z\) direction at \(q_y = 0 \text{ Å}^{-1}\) were not because these reflections are superimposed from both CL3 and LAM3. A lamellar model with long period (c-axis) of 14.0 nm can be used to fit the strong reflection at \(q_y = 0 \text{ Å}^{-1}\) (Figure 7.14d). In order to directly observe these two phases, the plan-view TEM image of F1 thin film (Figure 7.17a) and the cross-sectional view TEM image of microtomed F1 sample was conducted (Figure 7.17c). These TEM bright field images were stained by RuO4 for 10 minutes. Since PEO is more reductive than FPOSS and PS,149 PEO domain is more readily to be stained by RuO4 and shows dark region in the TEM images. Also because the electron density of FPOSS is higher than PS, the FPOSS and PS domains show grey and light grey, respectively, in the TEM bright field images. Figure 7.17a reveals the in-plane arranged cylinders of PEO domains, and the corresponded cross-sectional image in Figure 7.17c shows a combination of continuous and discrete dark regions, indicating the PEO domain forms cylinders or lamellae surrounded by PS (white) and sandwiched by FPOSS layers (grey). These two different structures were analyzed in CL3 and LAM3 models as shown in Figure 7.14b and d, respectively, with color codes of
FPOSS in green, PS in red, and PEO in blue. This lateral packing of PEO cylinders in the CL$_3$ morphology attributes to the in-plane ($q_y$ direction) correlation in the GISAXS pattern with a periodicity of 16.1 nm. The coexistence of LAM$_3$ and CL$_3$ morphologies indicates the composition of F$_1$ is close to the boundary of compositional phase transition between LAM$_3$ and CL$_3$.

While increasing the volume fraction of PS, the GISAXS pattern of F$_2$ (Figure 7.15a) shows simply reflections along the $q_z$ direction with periodicity of 17.0 nm, indicating a pure LAM$_3$ phase. Although the plan-view TEM image of LAM$_3$ is featureless (Figure 7.17b), the cross-sectional TEM image (Figure 7.17d) confirms that the composition of F$_2$ has entered the region of LAM$_3$ phase, which shows larger long period than that of F$_1$ because of increased molecular weight of PS block.
Figure 7.14 GISAXS patterns at the incident angle of 0.20° of sample F1 with theoretically calculated result based on the (a) CL_3 model and (c) LAM_3 model. White squares are simulated diffraction peaks scattered by reflected beam and red circles are simulated diffraction peaks scattered by transmitted beam. Schematic illustrations of corresponded (b) CL_3 morphology for F1 and (d) LAM_3 morphology for F1. Color code: FPOSS in green, PS in red, and PEO in blue.
Figure 7.15 GISAXS patterns at the incident angle of 0.20° of (a) sample F2 with theoretically calculated result based on the (b) CL3 model and (b) sample F3 with calculated result base on the (d) PL3 model. In the patterns, white squares are simulated diffraction peaks scattered by reflected beam and red circles are simulated diffraction peaks scattered by transmitted beam. Color codes in the schematic illustration of models: FPOSS in green, PS in red, and PEO in blue.
Figure 7.16 GISAXS patterns at the incident angle of 0.20° of (a) sample F4 with theoretically calculated result based on the (b) CPL3 model and (b) sample F5 with calculated result base on the (d) CPL3 model. In the patterns, white squares are simulated diffraction peaks scattered by reflected beam and red circles are simulated diffraction peaks scattered by transmitted beam. Color codes in the schematic illustration of models: FPOSS in green, PS in red, and PEO in blue.
Figure 7.17 Plan-view bright field TEM images of (a) F1 and (b) F2, and the corresponded cross-sectional TEM images of (c) F1 and (d) F2. TEM samples were stained by RuO4 for 10 minutes, exhibiting the FPOSS in grey, PS in light grey, and PEO in dark.
Figure 7.18 Plan-view bright field TEM images of (a) F3 and (b) F4, and the corresponded cross-sectional TEM images of (c) F3 and (d) F4. TEM samples were stained by RuO4 for 10 minutes, exhibiting the FPOSS in grey, PS in light grey, and PEO in dark.
Figure 7.19 (a) Plan-view bright field TEM image and (b) the corresponded cross-sectional TEM image of F5. TEM samples were stained by RuO4 for 10 minutes, exhibiting the FPOSS in grey, PS in light grey, and PEO in dark.
As further increasing the volume fraction of PS, F3, F4, and F5 show totally different GISAXS patterns (Figure 7.12c - e) from that of F1 or F2, implying another phase transition occurs during the increasing of volume fraction of PS. GISAXS patterns of F3, F4, and F5 share similar in-plane and out-of-plane periodicities, and F4 possesses the highest order among these three samples. The bright field TEM images of F3 shows a net-like pattern in the plan-view image (Figure 7.18a), and dark continuous lines (PEO) accompanied broken grey line (FPOSS) in the corresponded cross-sectional image (Figure 7.18c), indicating a perforated FPOSS layer penetrated by PS domain and sandwiched by lamellar PEO domains. The peripheral order of the perforation in separated FPOSS layers leads to the in-plane and out-of-plane correlations observed in its GISXAS pattern. This self-assembled morphology is coined as 3-component perforated lamella (PL3), and the corresponding model is shown in Figure 7.15d with a 2D lattice with $a = 20.5$ nm and $b = 32$ nm.

As the volume fraction of PS increased to 0.66 of F4, the plan-view TEM image (Figure 7.18b) shows dark in-plane packed cylinders (PEO) superposition to a grey net-like pattern (FPOSS). The corresponded cross-sectional TEM image (Figure 7.18d) reveals that the dark cylinders are packed similar to a hexagonal packing; however, different layers of PEO cylinders are separated by not only PS matrix but also perforated FPOSS layers, resulting in a non-hexagonal packing scheme. This complex morphology is then coined as 3-component cylinder-within-perforated lamella (CPL3), and the overall 2D lattice parallel to the film normal is a centered orthorhombic lattice with $a = 23.0$ nm and $b = 35.0$ nm (Figure 7.16b). As the volume fraction of PS further increased to 0.79 of F5, the GISAXS pattern (Figure 7.16c) shows a similar diffraction pattern as F4 (Figure
7.16b) but has much higher degree of disorder. Thus, the self-assembled morphology of F5 can be deduced as CPL3 with higher degree of disorder due to the sluggish mobility impeded by the large molecular weight of the PS block. The parameters of the 2D lattice can be extracted from the pattern as $a = 21.8$ nm and $b = 34.2$ (Figure 7.16d). Also, the disordered morphology of F5 can be confirmed from both plan-view and cross-sectional view of TEM images (Figure 7.19a and b).

7.3.3 Influence of Molecular Topology on Morphology in Thin Film

Copolymers with the same composition can be built in various architectures, e.g., linear, cyclic, 3-arm star, multi-arm star. The influence of topology on the morphology is well studied in the block copolymer system. Lecommandoux et al.\textsuperscript{150} investigated the morphology of linear PS-\textit{b}-PI and its cyclic counterpart. The morphology of cyclic copolymer exhibited a smaller domain spacing with a typical ratio of 0.707 compared to the linear one. This phenomenon can be explained by the fact that cyclic type copolymers have no chain ends, and they can only adopt a double-loop conformation in the microphase separated phase. Takano et al.\textsuperscript{151} further studied the linear PS-\textit{b}-PI-\textit{b}-PS triblock and its cyclic analogue. The morphological transition of the cyclic block copolymer varies with composition in the same manner as that of the linear triblock copolymer; moreover, the domain spacings of the cyclic one are smaller than those of the triblock linear ones, which can be attributed to the looped chain conformation of the cyclic copolymer and the ability of triblock linear copolymer to adopt either single loops or bridged conformations. A clear illustration of the bridged and looped midblock of a triblock copolymer is shown in Figure 7.20.\textsuperscript{152} In the lamellar structure, the midblock of an ABC triblock copolymer can only have the bridged conformation, while the midblock

\[197\]
of an ABA triblock copolymer can adopt either bridged or looped conformations. This argument is helpful to analysis self-assembly of linear giant surfactants, because AC$_{60}$-PS-PEO and FPOSS-PS-PEO can be viewed as ABA and ABC 3-component systems, respectively, due to the affinity of each block. The chain conformation of the PS block in these two giant surfactants will be discussed in the next section.

Figure 7.20 Schematic comparison of chain conformations of midblock for ABC and ABA triblocks. (a) ABC triblock copolymers only have bridge conformations, while (b) ABA triblock copolymers have bridge and loop conformations.

For another kind of topology, i.e. star copolymer, usually experiences a more crowding of segments around the junction point compared to the linear counterpart. The penalty for blocks bending at the interface will be higher, resulting in a shift of the phase boundaries and different domain spacings compared to their linear analogues of the same composition. From the computer simulation based on Self-Consistent Field Theory (SCFT), ABC star copolymers are tent to form stable phase with the junction points located along an interfacial line rather than on an interfacial plane.$^{153,154}$ This tendency
for ABC star copolymers to form 2D tiles has also been confirmed by experiments. Ordered 1D lamellae and 3D substructures (core-shell gyroid, perforated layers, etc.) are also found in the ABC star copolymer system. The star copolymers are found have more stretched chain conformation than their linear analogues, indicating stronger phase segregation. For instance, the symmetric PS$_n$-arm-PIn multi-arm star copolymer shows an increase in the spacing with $n$. This phenomenon indicates an additional chain stretching induced by the spatial confinements nearby the junction point.

The topological isomers are introduced in this work to study the effect of molecular topology on the self-assembly behavior. Topological isomers are molecules composed of identical composition (e.g. entity of polymer / MNP and molecular weight of polymer chains) with different molecular architectures (e.g. linear, star, and cyclic) or the sequence of building blocks. The pairs of giant surfactants of A2/A6, A4/A7, F2/F6, and F4/F7 listed in Table 7.1 are four sets of topological isomers. The star giant surfactant A6 has an identical composition compared to that of linear giant surfactant A2 yet different molecular architecture; likewise, A4/A7, F2/F6, and F4/F7 pairs have the same compositions but different molecular architectures.

7.3.3.1 Morphology of Star PS-AC60-PEO in Thin Film

This section focuses on the self-assembly behavior of PS$_{52}$-A$_{60}$-PEO$_{45}$ (A6) and PS$_{78}$-AC$_{60}$-PEO$_{45}$ (A7) in the thin film state. The chemical structures and molecular architectures of A6 and A7 are depicted in Figure 7.2c. The thin films of star giant surfactants are prepared followed the same procedure for the linear ones.
The morphology determination was conducted by GISXAS, GIWAWD, and TEM to provide structural information in both reciprocal and real space. The GISXAS and GIWAWD patterns of A6 and A7 are shown in the Figure 7.21. The strong reflections exhibited q ratio of 1:2 along the qz direction in GISAXS pattern (Figure 7.21a) and the higher ordered peaks can be observed in the low angle region of GIWAXD (Figure 7.21b), indicating A6 formed a LAM morphology with its normal perpendicular to the substrate surface. The domain spacing of the LAM’s long period can be extracted as 10.8 nm from the GISXAS pattern based on the DWBA theory (Figure 7.22a and b). This micro-phase separation is induced by the incompatibility of hydrophobic PS domain and hydrophilic PEO/AC_{60} domain. Similar to the case of linear AC_{60}-PS-PEO, the hydrophilic AC_{60} MNPs are dispersed in the PEO domain without long-ranged positional order as evidenced by the absence of reflections in the wide angle region (Figure 7.21b). In addition, a Scherrer-Debye ring with intensity concentrated on the qz direction in the Figure 7.21a share the same q value of the first order peak of LAM structure from the transmitted beam, indicating the Scherrer-Debye ring is attributed to the correlation between AC_{60} MNPs in distinct domains of the LAM structure. This observation also confirms the fact that AC_{60} MNPs are dispersed in the PEO domain instead of forming an individual domain with AC_{60}s themselves.
Figure 7.21 GISAXS patterns at incident angle of 0.2° of star giant surfactant (a) A6 and (c) A7. GIWAXD patterns at incident angle of 0.2° of (b) A6 and (d) A7.
Figure 7.22 GISAXS patterns at the incident angle of 0.20° of (a) A6 with theoretically calculated result based on the (b) LAM model, and (b) A7 with calculated result base on the (d) HEX model. In the patterns, white squares are simulated diffraction peaks scattered by reflected beam and red circles are simulated diffraction peaks scattered by transmitted beam. Color codes in the schematic illustration of models: AC$_{60}$/PEO in blue, and PS in red.
Star giant surfactant \textbf{A7} self-assemble into HEX morphology as evidenced by the GISAXS pattern (Figure 7.21c). The dimension of hexagonal lattice can be deduced as $a = b = 14.6$ nm and $\gamma = 120^\circ$ from the (10), (11), and (20) reflections based on DWBA theory (Figure 7.22d). All the reflections in the GISAXS pattern can be indexed accordingly by the hexagonal lattice (Figure 7.22c). Because the majority segment in \textbf{A7} is hydrophobic PS ($f_{PS} = 0.71$, listed in Table 7.1), the HEX morphology is determined as hydrophilic cylinders composed of PEO and AC$_{60}$ packed into hexagonal arrangement in the hydrophobic PS matrix. This morphology is further confirmed by the plan-view TEM image after OsO$_4$ staining for 16 hours (Figure 7.23), and it shows dark strips corresponded to cylindrical PEO domains.

![Figure 7.23 Plan-view bright field TEM image of \textbf{A7}. The TEM sample was stained by OsO$_4$ for 16 hours, exhibiting AC$_{60}$ / PEO domain in dark and PS in light grey.](image)
7.3.3.2 Morphology of Star PS-FPOSS-PEO in Thin Film

This section focuses on the self-assembly behavior of PS\textsubscript{52}-FPOSS-PEO\textsubscript{45} (F6) and PS\textsubscript{78}-FPOSS-PEO\textsubscript{45} (F7) in the thin film state. The chemical structures and molecular architectures of F6 and F7 are depicted in Figure 7.2d. The thin films of star giant surfactants are prepared followed the same procedure for the linear ones.

The morphology determination was conducted by GISXAS, GIWAXD, and TEM to provide structural information in both reciprocal and real space. The GISXAS and GIWAXD patterns of F6 and F7 are shown in the Figure 7.24. The GISAXS pattern of F6 (Figure 7.24a) exhibits a typical diffraction pattern of hexagonally packed cylinders, and an additional diffraction peak at q\textsubscript{y} = 0.17 Å\textsuperscript{-1} (d-spacing of 3.6 nm), which has be recognized as the lateral packing of FPOSS MNPs along their long axes. The higher ordered peak of this lateral packing of FPOSS MNPs can be observed in the GIWAXD pattern (indicated by white arrows in Figure 7.24b). In addition, similar to the patterns of linear FPOSS-PS-PEO samples, the GIWAXD pattern of F6 shows a scattering halo on the q\textsubscript{z} axis with d-spacing of 0.49 nm (indicated by the black arrow in Figure 7.24b), which is attributed to the lateral packing of fluorinated chains on FPOSS MNPs.

On the other hand, the GISAXS pattern of F7 (Figure 7.24c) shows two Scherrer-Debye rings with second ordered reflections along the q\textsubscript{z} direction, indicating a relatively random-oriented morphology. A weak diffraction at the q\textsubscript{y} = 0.17 Å\textsuperscript{-1} (d-spacing of 3.6 nm) in the GISAXS pattern but no higher ordered peaks in GIWAXD pattern (Figure 7.24d) indicates that the arrangement of FPOSS MNPs possess certain order similar to that of crystal structure of FPOSS in only short- or quasi-long range. In this situation, the relatively disorder morphology cannot be determined solely by the GIXS techniques. The
structural information provided by TEM in real space would be helpful to elucidate the morphology of F7.

The bright field TEM images were conducted for both F6 and F7 samples. The TEM samples were stained by RuO4 for 10 minutes to make the FPOSS domains exhibit in grey, PS in light grey, and PEO in dark. Firstly, the plan-view TEM image of F6 (Figure 7.25a) clearly shows in-plane aligned cylinders, and the corresponded cross-sectional TEM image confirms the hexagonally-packed cylindrical packing scheme in the view perpendicular to the long axes of cylinders (Figure 7.25c). Moreover, the side view of the cylinders can also be found in some regions in the microtomed sample, and the TEM image reveals a core-shell cylinders (CSC) with a grey cylindrical core consisted of FPOSS MNPs covered by a shell of dark regions consisted of PEO and the light grey PS matrix (Figure 7.25e). On the other hand, the plan-view TEM image of F7 (Figure 7.25b) also shows the in-plane aligned cylinders, yet, with shorter correlation length, which could be the reason for the diffused and ring-like diffraction peaks observed in the GISXAS pattern. The corresponded cross-sectional TEM image (Figure 7.25d) reveals the laterally hexagonal packing of cylinders, which is similar to that of F6, suggesting F7 also self-assembled in CSC morphology. By comparing the cross-sectional TEM images of F6 and F7, one can observe the larger distance between core-shell cylinders in F7 than that of F6, which is a consequence of increasing the volume fraction of PS block.

After confirming the morphology with the aid of TEM, the GISXAS patterns can be indexed and simulated accordingly as shown in Figure 7.26a and c. In the patterns, white squares are simulated diffraction peaks scattered by reflected beam and red circles are simulated diffraction peaks scattered by transmitted beam based on DWBA.
corresponded schematic illustrations of CSC models are shown in Figure 7.26b and d with dimensions extracted from the GISAXS patterns. The $a$-axes are 14.8 nm and 18.3 nm for the CSC morphology of F6, and F7, respectively, and the increase of distance between core-shell cylinders agrees with the observation in cross-sectional TEM images.
Figure 7.24 GISAXS patterns at incident angle of 0.2° of star giant surfactant (a) F6 and (c) F7. GIWAXD patterns at incident angle of 0.2° of (b) F6 and (d) F7.
Figure 7.25 Plan-view bright field TEM images of (a) F6 and (b) F7. The cross-sectional TEM images of F6 thin film (c) perpendicular and (e) parallel to the long axes of cylinders. (d) The cross-sectional TEM images of F7 thin film perpendicular to the long axes of cylinders. TEM samples were stained by RuO4 for 10 minutes, exhibiting FPOSS in grey, PS in light grey, and PEO in dark.
Figure 7.26 GISAXS patterns at the incident angle of 0.20° of (a) F6 with theoretically calculated result based on the (b) CSC model, and (b) F7 with calculated result base on the (d) CSC model. In the patterns, white squares are simulated diffraction peaks scattered by reflected beam and red circles are simulated diffraction peaks scattered by transmitted beam. Color codes in the schematic illustration of models: FPOSS in green, PS in red, and PEO in blue.
7.4 Discussion

Based on the morphological study on the topological isomer pairs of A2/A6 and A4/A7, the effect of topology of giant surfactant on the self-assembly behavior can be revealed in both aspect of morphology and domain spacings. Linear giant surfactant A2 forms double gyroid bicontinuous structure in the bulk state and forms modulated lamellae (ML) in the thin film state, which is believed to be a frustrated structure under geometrical confinement of thin film. With identical composition of A2, the star giant surfactant A6 forms 2-component lamellae (LAM) with hydrophilic PEO and AC60 as one component and hydrophobic PS as another component for the structure. The 2D cross-sectional images of ML and LAM phases are illustrated in Figure 7.27a and b, respectively. In the illustrations, the blue and red color depict the hydrophilic and hydrophobic portions, respectively, and the lattice dimensions are marked by black dashed contours. To qualitatively analysis the relationship between the domain spacing and degree of stretching of the PS block, the length of $R$ is define as the full length of $c$-axis in LAM, half of the length of $c$-axis in ML, half of the length of $a$-axis in HEX and BCC (Figure 7.27, and the footnote c in Table 7.3). The parameter, $R$, which represents the dimension of a single molecule, is defined as half of the characteristic length for each morphology, and the dimensions for different morphologies are marked by white dashed contours (Figure 7.27). Also, the dimension of the AC60 / PEO domain is depicted by the length of $r$, which is define as half of the averaged thickness of hydrophilic part in LAM and ML, and the radius of the hydrophilic cylinder and sphere in HEX and BCC, respectively. The length of $r$ can be estimated as follow:

$$f_{PS} = 1 - \left(\frac{r}{R}\right) \quad \text{for LAM} \quad (7.3)$$
\[ f_{PS} = 1 - \left(\frac{r}{R}\right)^2 \quad \text{for HEX} \quad (7.4) \]

\[ f_{PS} = 1 - \left(\frac{r}{R}\right)^3 \quad \text{for BCC} \quad (7.5) \]

where \( f_{PS} \) is the volume fraction of PS, which can be calculated based on the molecular weight and density of each block in a giant surfactant, and \( R \) is the characteristic length.

To estimate the degree of stretching in the PS block, the stretching parameter, \( S \), can be characterized by\(^{138} \)

\[ S = L/R_0 \quad (7.6) \]

where \( L \) is the 1D length of the PS portion, which is defined by

\[ L = 2(R - r) \quad (7.7) \]

\( r \) and \( R_0 \) is an average unperturbed (freely jointed) end-to-end distance of the PS chain that can be calculated by\(^{163} \)

\[ R_0 = (N_{PS}/6.92)^{1/2}b \quad (7.8) \]

where \( N_{PS} \) is the degree of polymerization and \( b \) is the Kuhn length (\( b = 1.8 \) nm) for PS.

The measured characteristic length and calculated values of \( R, r, L, R_0, \) and \( S \) are summarized in Table 7.3.
Figure 7.27 Schematic illustrations of linear and star AC\textsubscript{60}-based giant surfactants in (a) ML, (b) LAM, (c) HEX, and (d) BCC morphologies. The blue color represents the hydrophilic AC\textsubscript{60} / PEO domains, and the red color represents the hydrophobic PS domains. The marked length of $R$ depicts the dimension of a whole molecule, and the length of $r$ depicts the dimension of hydrophilic domain.
Table 7.3 Characterization of morphologies of AC_{60}-based giant surfactants in thin film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thin film morphology</th>
<th>Dimension (nm)</th>
<th>Characteristic length of morphology (nm)</th>
<th>R (nm)</th>
<th>r (nm)</th>
<th>L (nm)</th>
<th>R_{0,PS} (nm)</th>
<th>S</th>
</tr>
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<tbody>
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<td>A1</td>
<td>LAM</td>
<td>(001): 7.9</td>
<td>c = 7.9</td>
<td>3.9</td>
<td>2.1</td>
<td>3.6</td>
<td>3.6</td>
<td>1.0</td>
</tr>
<tr>
<td>A2</td>
<td>ML</td>
<td>(001): 11.3</td>
<td>(002) = 8.9</td>
<td>4.4</td>
<td>1.7</td>
<td>5.4</td>
<td>4.8</td>
<td>1.1</td>
</tr>
<tr>
<td>A3</td>
<td>HEX</td>
<td>(001): 10.8</td>
<td>a = 12.5</td>
<td>6.2</td>
<td>3.6</td>
<td>5.2</td>
<td>5.5</td>
<td>0.9</td>
</tr>
<tr>
<td>A4</td>
<td>HEX</td>
<td>(001): 11.7</td>
<td>a = 13.5</td>
<td>6.7</td>
<td>3.6</td>
<td>6.2</td>
<td>6.0</td>
<td>1.0</td>
</tr>
<tr>
<td>A5</td>
<td>BCC</td>
<td>(110): 11.7</td>
<td>a = 16.5</td>
<td>8.2</td>
<td>4.6</td>
<td>7.2</td>
<td>8.4</td>
<td>0.8</td>
</tr>
<tr>
<td>A6</td>
<td>LAM</td>
<td>(001): 10.8</td>
<td>c = 10.8</td>
<td>5.4</td>
<td>2.1</td>
<td>6.5</td>
<td>4.8</td>
<td>1.3</td>
</tr>
<tr>
<td>A7</td>
<td>HEX</td>
<td>(001): 12.6</td>
<td>a = 14.6</td>
<td>7.3</td>
<td>4.0</td>
<td>6.6</td>
<td>6.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

a LAM: lamellae; ML: modulated lamellae; HEX: hexagonally packed cylinders; BCC: body-centered cubic spheres.
b Dimensions are extracted from GISAXS patterns.
c Characteristic lengths are determined for each morphology: c-axis of LAM for A1, half of c-axis of ML for A2, a-axis of HEX for A3 and A4, a-axis of BCC for A5, c-axis of LAM for A6, a-axis of HEX for A7.
d R represents the averaged dimension of a single molecule in the ordered phase, which is half of the characteristic length of each morphology.
e r is the averaged dimension of hydrophilic portion, which can be calculated based on f_{PS} and R (Eq. 7.3 – 7.5).
f L is the 1D length of the PS portion (Eq. 7.7).
g R_{0,PS} is the average unperturbed end-to-end distance of PS(Eq. 7.8).
h S is the stretching parameter, which can be calculated based on L and R_{0} (Eq. 7.6).
For the linear AC$_{60}$-PS-PEO giant surfactants, the calculated stretching parameters, $S$, experience a fluctuation matched with the morphology change with increasing the volume fraction of PS. The stretching parameter slightly increased from 1.0 of A$_1$ to 1.1 of A$_2$, and then dropped to 0.9 of A$_3$ during the morphology change of LAM to ML and then to HEX. A$_3$ and A$_4$ both exhibit HEX morphology, and the increase of volume fraction in the PS block resulted in a slightly increase of stretching parameter from 0.9 to 1.0. With further increased volume fraction of PS, the stretching parameter dropped again to 0.8 for the BCC morphology of A$_5$. This trend indicates the increase of volume fraction of PS would enhance the degree of stretching, while the relaxation of PS block could be a part of the driving force for morphology change.

For the topological isomer pairs, the stretching parameter of the PS block is 1.1 for the ML phase of linear A$_2$ and 1.3 for the LAM phase of star A$_6$, indicating the PS domain spacing of A$_2$ is relatively fit the end-to-end distance of one block of PS chain; however, the PS domain spacing of A$_6$ is too large for one block of PS chain to fill. Because the linear geometry of A$_2$, the midblock of PS can adopt either bridged or looped conformation (Figure 7.28a) to make the PS domain spacing roughly equal to the end-to-end distance of one block of PS chain; while, due to the star geometry of A$_6$, the AC$_{60}$ and PEO blocks of an individual giant surfactant can only stay in the same hydrophilic domain (Figure 7.28b), and the hydrophobic domain is composed of partially overlapped PS blocks belong to different giant surfactants. For the other set of topological isomers, A$_4$ and A$_7$, both of them form HEX morphology, however, with different domain spacings. A$_4$ has a cylinder-to-cylinder distance of 13.5 nm and a stretching parameter of 1.0; while, A$_7$ has a cylinder-to-cylinder larger distance of 14.6
nm and a stretching parameter of 1.1. Again, the PS block of linear A4 can adopt either bridged or looped conformation to make the PS domain spacing roughly equal to the end-to-end distance of single PS block (Figure 7.28c). In contrast, due to the star geometry A7, the AC₆₀ and PEO of a giant surfactant would stay in the same hydrophilic cylinder, and its PS block would partially overlap with other PS blocks to form a hydrophobic domain with spacing slightly larger than a single chain’s end-to-end distance (Figure 7.28d).
Figure 7.28 Schematic illustrations of molecular conformations in the self-assembled morphologies. (a) ML morphology of linear A2 with bridged and looped midblock PS. (b) LAM morphology of star A6. (c) HEX morphology of linear A4 with bridged and looped midblock PS. (d) HEX morphology of star A7.
The another series of giant surfactants, FPOSS-based giant surfactants, show a more plentiful self-assembled structures compared to the AC$_{60}$-based ones because of the entirely distinct affinities for FPOSS, PS, and PEO. Although AC$_{60}$-PS-PEO and PS-AC$_{60}$-PEO giant surfactants consist of three building blocks, the hydrophilic AC$_{60}$ and PEO are usually form a single phase without phase separation. Consequently, AC$_{60}$-based giant surfactant only self-assembled in 2-component ordered phases. In contrary, the crystalline omniphobic FPOSS can phase separated from hydrophobic PS and hydrophilic PEO to make FPOSS-based giant surfactants form 3-component ordered structures.

Because of the complex structures the FPOSS-based formed as introduced in the last section, the degree of chain stretching for the PS blocks can only be qualitatively estimated by the stretching parameter, $S$ (Equation 7.6). The relationships between $R$ and $r$ follow the Equation 7.3 and 7.4 for lamellar and cylindrical phases, respectively (Equation 7.9 and 7.10).

$$f_{PS} = 1 - \left(\frac{r}{R}\right) \quad \text{for } \text{LAM}_3, \text{PL}_3, \text{and } \text{CPL}_3 \quad (7.9)$$

$$f_{PS} = 1 - \left(\frac{r}{R}\right)^2 \quad \text{for } \text{CSC} \quad (7.10)$$

However, the $r$ need to be redefined for the 3-component ordered structures as follow, where $r_1$ and $r_2$ represent the dimensions of FPOSS and PEO domains, respectively.

$$r = r_1 + r_2 \quad \text{for } \text{LAM}_3, \text{PL}_3, \text{and } \text{CPL}_3 \quad (7.11)$$

$$r = r_1 \quad \text{for } \text{CSC} \quad (7.12)$$

The relationships between $r_1$ and $r_2$ are determined by the volume fraction of FPOSS ($f_{\text{FPOSS}}$) and PEO ($f_{\text{PEO}}$) for lamellar or cylindrical structures.

$$\left(\frac{r_1}{r_2}\right) = \left(\frac{f_{\text{FPOSS}}}{f_{\text{PEO}}}\right) \quad \text{for } \text{LAM}_3, \text{PL}_3, \text{and } \text{CPL}_3 \quad (7.13)$$
\[(r_1/r_2) = (f_{\text{FPOSS}}/f_{\text{PEO}})^{1/2} \quad \text{for CSC} \quad (7.14)\]

Because the midblock PS for linear FPOSS-based giant surfactants can only adopt bridged conformation, the 1D length of PS portion, \(L\), is defined as follow:

\[L = R - r \quad \text{for LAM}_3, \text{PL}_3, \text{and CPL}_3 \quad (7.15)\]

while the PS block of star FPOSS-based giant surfactants are not bounded by the other two building blocks, thus the 1D length of PS portion, \(L\), is defined as follow:

\[L = 2(R - r) \quad \text{for CSC} \quad (7.16)\]

All of the characterization parameters are marked on the models of self-assembled phases (Figure 7.29). In the schematic illustration of the models, the color codes are FPOSS in green, PS in red, and PEO in blue, and the 2D lattices are depicted by black dashed contours. The corresponded measured and calculated parameters for each FPOSS-based giant surfactant are summarized in Table 7.4. For the qualitatively estimation of PS chain stretching, the characteristic length of \(\text{F1}\) is only calculated based on the LAM\(_3\) phase without considering its CL\(_3\) phase, and the characteristic lengths for LAM\(_3\), PL\(_3\), CPL\(_3\), and CSC phases are defines as dimensions of \(c\)-axis, half of \(c\)-axis, and \(a\)-axis, respectively (footnote \(c\) in Table 7.4). The parameter \(R\), which represents of the dimension of a single molecule, is defined as half of the characteristic length for each phase and depicted by white dashed contours in Figure 7.29.

In the series of FPOSS-based samples, the most quantitative estimation of the PS chain stretching is the LAM\(_3\) phase of \(\text{F2}\) because of the entirely flat geometry of the lamellar structure without cylindrical or perforated domains. The calculated stretching parameter is 1.0, indicating the midblock PS has the domain size equal to the end-to-end
distance of a equivalent random-coiled PS chian under vacuum. Besides, the stretching parameters for all the linear FPOSS-based giant surfactants (F1, F2, F3, F4, and F5) are all close to unity, which confirm the concept that the midblock of a linear ABC triblock can only adopt the bridged conformation.

For the topological isomer pairs of F2/F6 and F4/F7, the first observation is that although the topological isomers possess identical chemcal compositions, they self-assemble in distinct ordered phases due to the topological effect. The pairs of F2/F6 and F4/F7 form LAM3/CSC and CPL3/CSC morphologies, respectively, and this topological effect on the self-assembled phase is reminiscent to the topological isomers of AC60-based giant surfactants. The molecular conformations of F2, F4, F6, and F7 are depicted in Figure 7.30. As discussed before, the midblock of a linear ABC triblock copolymer can only adopt the bridged conformation, and the midblock PS of F2 and F4 follow the rule to bridge FPOSS and PEO domains. While due to the topology of star giant surfactants, the PS blocks of F6 and F7 do not bridge different domains and form a domain with partially overlapped PS chains, which is supported by the calculated stretching parameter of 1.6 (Table 7.4). It should be noticed that the PS chains of F6 and F7 in the CSC morphology need to penetrate out the shell of PEO, and the portion of PS embedded in the PEO domain is expected to be more stretched than the portion in the PS domain (Figure 7.30b).
Figure 7.29 Schematic illustrations of linear and star FPOSS-based giant surfactants in (a) CL₃, (b) LAM₃, (c) PL₃, (d) CPL₃, and (e) CSC morphologies. The green color represents the omniphobic FPOSS domains, the red color represents the hydrophobic PS domains, and the blue color represents the hydrophilic PEO domains. The marked length of $R$ depicts the dimension of a whole molecule, and the length of $r_1$ and $r_2$ depict the dimension of FPOSS and PEO domains, respectively.
Table 7.4 Characterization of morphologies of FPOSS-based giant surfactants thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thin film morphology</th>
<th>Dimension a ( \text{nm} )</th>
<th>Characteristic length of morphology c ( \text{nm} )</th>
<th>( R^d ) ( \text{nm} )</th>
<th>( r^e ) ( \text{nm} )</th>
<th>( L^f ) ( \text{nm} )</th>
<th>( R_{0,PS}^g ) ( \text{nm} )</th>
<th>( S^h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>CL3 / LAM3 ( (001) ): 24.0 / (001): 14.0</td>
<td>c = 14.0</td>
<td>7.0</td>
<td>4.1</td>
<td>2.9</td>
<td>3.6</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>F2</td>
<td>LAM3 ( (001) ): 17.0</td>
<td>c = 17.0</td>
<td>8.5</td>
<td>3.8</td>
<td>4.7</td>
<td>4.8</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>F3</td>
<td>PL3 ( (100): 20.5, (001): 32.0 )</td>
<td>( 002 ) = 16.0</td>
<td>8.0</td>
<td>3.1</td>
<td>4.9</td>
<td>5.5</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>F4</td>
<td>CPL3 ( (100): 23.0, (001): 35.0 )</td>
<td>( 002 ) = 17.5</td>
<td>8.7</td>
<td>3.0</td>
<td>5.7</td>
<td>6.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>F5</td>
<td>CPL3 ( (100): 21.8, (001): 34.2 )</td>
<td>( 002 ) = 17.1</td>
<td>8.5</td>
<td>1.8</td>
<td>6.7</td>
<td>8.4</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>F6</td>
<td>CSC ( (100): 12.8 )</td>
<td>a = 14.8</td>
<td>7.4</td>
<td>3.6</td>
<td>7.6</td>
<td>4.8</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>F7</td>
<td>CSC ( (100): 15.8 )</td>
<td>a = 18.3</td>
<td>9.1</td>
<td>4.3</td>
<td>9.7</td>
<td>6.0</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) CL3: cylinder-within-lamellae; LAM3: 3-component lamellae; PL3: 3-component perforated lamellae; CPL3: 3-component cylinder-within-perforated lamellae; CSC: core-shell cylinders.

\( ^b \) Dimensions are extracted from GISAXS patterns.

\( ^c \) Characteristic lengths are determined for each morphology: half of \( c \)-axis of LAM3 for \( F1 \), half of \( c \)-axis of LAM3 for \( F2 \), half of \( c \)-axis of PL3 for \( F3 \), half of \( c \)-axis of CPL3 for \( F4 \) and \( F5 \), half of \( a \)-axis of CSC for \( F6 \) and \( F7 \).

\( ^d \) \( R \) represents the averaged dimension of a single molecule in the ordered phase, which is half of the characteristic length of each morphology.

\( ^e \) \( r \) is determined by \( r_1 \) and \( r_2 \) (Eq.7.9 and 7.10), where \( r_1 \) is the averaged dimension of FPOSS portion and \( r_2 \) is the averaged dimension of PEO portion. \( r_1 \) and \( r_2 \) can be calculated based on \( f_{PS}, f_{PEO} \) and \( R \) (Eq. 7.3 – 7.5, 7.11, and 7.12).

\( ^f \) \( L \) is the 1D length of the PS portion (Eq. 7.13 and 7.14).

\( ^g \) \( R_0 \) is the average unperturbed end-to-end distance of PS(Eq. 7.8).

\( ^h \) \( S \) is the stretching parameter, which can be calculated based on \( L \) and \( R_0 \) (Eq. 7.6).
Figure 7.30 Schematic illustrations of molecular conformations in the self-assembled morphologies. (a) CPL$_3$ morphology of linear F2 with only bridged midblock PS. (b) CSC morphology of star F6 and F7. (c) LAM$_3$ morphology of linear F4 with only bridged midblock PS.
7.5 Summary

The overall self-assembly behavior of these AC$_{60}$-based and FPOSS-based giant surfactants can be summarized in a ternary phase diagram based on the calculated volume fraction of each component in Table 7.1. Figure 7.31 depicts the self-assembled morphologies observed in the giant surfactant system with correlation to the compositions. The color code of blue indicates the AC$_{60}$-based giant surfactants, and green indicates the FPOSS-based giant surfactants. Solid and dashed lines indicate linear and star giant surfactants, respectively. Because the molecular weight of PEO is fixed to be 2 kDa in all the samples, which has similar volume to both AC$_{60}$ and FPOSS, all the data points in the ternary phase diagram are close to the composition of $f_{\text{PEO}} = f_{\text{MNP}}$ (black dashed line in Figure 7.31). In this case, the major factor to cause the phase transition is the volume fraction of PS ($f_{\text{PS}}$).

For linear giant surfactants in thin film state, AC$_{60}$-based samples show a morphology transition from LAM to ML to HEX then to BCC, while FPOSS-based samples show a morphology transition from CL$_3$ to LAM$_3$ to PL$_3$ then to CPL$_3$ as increased the volume fraction of PS from 0.41 to 0.79. The morphology transition of AC$_{60}$-based linear giant surfactants is similar to that of diblock copolymer because the AC60-PS-PEO self-assembled in two-phased structures (hydrophilic-hydrophobic). The estimated degree of stretching of PS block raises and falls in the same trend of morphology transition, indicating the stretching and relaxation of PS chains play a crucial part in determine the self-assembled phase. On the other hand, FPOSS-based linear giant surfactants exhibit more diverse morphologies because of the 3-component structures and crystalline FPOSS MNPs. The morphology transition could be due to crystalline FPOSS
domains tend to form layered geometry and the layered structure would be perforated by the majority of PS domain as increased the volume fraction of PS; meanwhile, the PEO domains could form cylindrical or lamellar geometries to approach the lowest total free energy state.

By designing the giant surfactants in linear and star topologies yet in the same chemical compositions, 2 pairs of topologic isomers of AC$_{60}$-based giant surfactants and 2 pairs of FPOSS-based giant surfactants were studied and discussed in this chapter. All the pairs of topologic isomers show distinct self-assembled morphologies in linear giant surfactants from star ones, indicating the topology is a key factor to determine the self-assembled morphology and can serve as an additional factor to fine tune the desired supramolecular structures of giant surfactants.
Figure 7.31 Overall self-assembly of giant surfactants depicted in the ternary phase diagram. The solid lines indicate the linear giant surfactants and dashed lines indicate star giant surfactants. AC$_{60}$-based giant surfactants are indicated in blue, and FPOSS-based giant surfactants are indicated in green. The black dashed line in the ternary phase diagram indicates the composition of $f_{\text{MNP}} = f_{\text{PEO}}$. 
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