PRECISE SYNTHESIZE AND PHASE BEHAVIORS OF POSS BASED
SYMMETRIC GIANT “BOLAFORM-LIKE” SURFACTANTS

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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May, 2016
PRECISE SYNTHESIZE AND PHASE BEHAVIORS OF POSS BASED
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Thesis

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ABSTRACT

Self-assembly has been a long lasting research topic studied in many fields. With the aid of two critical roles, symmetry breaking of geometries and interactions, diverse self-assembly structures with different properties have been designed and created, making this field rather intriguing. Recently “giant surfactants” are attracting very special attentions, since the conjugation of polymer linker and “nano-atom” heads can achieve both symmetry breaking of geometries and interactions, facilitating creating hierarchical structures in sub-10 nm level.

In this project, we will focus on a kind of multi-heads “giant surfactants”. Specifically, we have synthesized two kinds of this giant surfactants, one contains one hydrophilic functionalized polyhedral oligomeric silsesquioxane (DPOSS) cages at both ends linked with a strip of hydrophobic polystyrene (PS), the other contains three hydrophilic DPOSS cages at both ends. The PS was polymerized by atom transfer radical polymerization (ATRP) to ensure the well-defined molecular weights and polydispersity. Sequential click reactions including thiol-ene reaction and copper catalyzed “3+2” cycloaddition reaction were used to synthesize these giant surfactants, which were characterized by NMR, FT-IR, and GPC. The whole self-assembly process in the bulk will be thoroughly studied by many different characterization tools, including small angle x-ray scattering (SAXS) and transmission electron microscopy (TEM). By changing the molecular weight of PS, there are two kinds of phase behavior we can observe, lamellar and hexagonal cylinder phase.
ACKNOWLEDGMENTS

There are so many people I would like to say thanks for helping me finish my master degree. The first person is my advisor, Dr. Stephen, Z. D. Cheng, for offering me a great chance to do the research in his research group, and for his wonderful guidance on not only in academic area but also how to be a good person.

I would also say thanks to Dr. Mingjun Huang, who help me a lot through the whole experiments. Especially the first time I went to the lab, his patience and instruction make me more confident in research. Without his help, I couldn’t finish this project so easily and wonderful.

Then I want to say thanks to all the group members in Dr. Cheng’s group. Their kindly help make me feel living in a big house full of harmony. With their help I had a wonderful experience in America.

Last but not least, special thanks are sent to my family members. Their love and support is the most important back up to me.
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3.1 Self-assembly behavior of all the molecules studied in this project

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CHAPTER I

INTRODUCTION

1.1 Self-assembly and close packing

Self-assembly has been a long lasting research topic studied in many fields and is still playing an important role in the area of developing and creating new materials. The macroscopic structures and properties of the materials are closely related to the microscopic assembly of the units. Yet, predicting the superstructure from the shape and interactions of specific building blocks still remains a problem for human beings. As John Maddox announced about two decades ago “One of the continuing scandals in the physical science is that it remains impossible to predict the structure of even the simplest crystalline solids from a knowledge of their composition.” Thus, this area has attracted both theorists as well as experimentalists, trying to find out the relationship between the microscopic structure and the macroscopic assembly.

Self-assembly is the process in which disordered components spontaneously form ordered structures. It covers a wide range including molecular crystals, colloids, lipid bilayers, phase separated polymers, polypeptide folding into proteins and so on. The structures formed in self-assembly are usually in thermodynamic equilibrium state.

Here, we would limit our discussion about the assembly within hard particles such as atoms, small molecules, hard colloidal particles etc., with a certain shape and surface
interaction. In this case, we can discuss the thermodynamic of the assembly process. For particles with weak interactions and with relative big size (especially for colloidal particles), the thermodynamic behavior of hard particle assembly can be understood through entropy maximization, as discussed by Daan Frenkel. The system tend to minimize its free energy in the ordering process. Conflicting to our intuitive idea that an ordering process is energy driven (or enthalpy driven) with a decrease in entropy compensated by the decrease of internal energy, Frenkel suggested that the ordering process is entropy driven by maximizing the entropy of the system.

With this theory, it is necessary for us to pay more attention to the entropy change in the assembly process. In nature, one way to form ordered structure is close packing of the units. Close packing is a dense arrangement of units into an ordered structure with least free space. To simplify, we may regard the units as spheres and the spheres would close pack into FCC (face centered cubic) or HCP (hexagonal close packing) structure, which can be represented by copper metal and magnesium metal respectively. Both structures are close packed and arestable.

Figure 1.1 Face center cubic (left) and hexagonal close packing (right)
1.2 Intermolecular Interaction and Crystal Engineering

After the processing of self-assembly, many macromolecules can form different phase behavior in bulk or solution. There are three key parameters in determining the self-assemble behavior: Degree of Polymerization (N), Volume Fraction ($f_A$), and Flory-Huggins Interaction Parameter ($\chi$).

Figure 1.2 Phase diagram
Although it is a simple theory, how to control the self-assembly behavior by bottom-up method still is a challenge. Because there are some complex factors that will affect the self-assembly behavior lie among molecules. To be more specific, there are two vital important factors (enthalpy and entropy) that play a key role in self-assembly behavior. Since the molecular self-assembly reduces free energy to get a thermodynamic equilibrium state. The intermolecular interaction which is related to the enthalpy definitely is an important issue in studying the self-assembly behavior of many molecules.

Crystal engineering, which makes up relative large-scale solid-state crystal structures by relative small molecules, inspires us to find the role of molecular interaction in the self-assembly of molecules. Crystal can be considered as a special self-assembly result. The non-covalent bonding in crystal engineering is a significant tool, because the engineers take advantage of the intermolecular interactions to build their designed structures. These non-covalent bonds are much weaker than the covalent bonds linking atoms, however this weak interactions can form solid-state supermolecule structures through arranging molecules in a proper manner. Hydrogen bonding, metal-ligand coordination, Van Der Walls force, hydrogen bonding, halogen bonding, π-π stacking, ion-ion force, hydrophilic/hydrophobic interaction and dipole-dipole interaction can all be regarded as the non-covalent bonding. Among these non-covalent interactions, crystal engineers mostly utilize metal-ligand and coordination hydrogen bonding for their relatively high directionality and strength. Strong bonds leads to a stable structure. Directionality make sure the location and orientation of a single small molecule to be available for order pattern construction.
Crystal engineering scientists had already designed different kinds of crystal structures ranging from 0-dimensional to 3-dimensional. Among these crystal structures 1-D and 2-D are relatively easy to understand, however, 3-D and 0-D are still under fast development in recent years. The schematic illustration of some architectures are shown in Figure 1.3.

Figure 1.3 Simple network architecture from 1-D to 3-D.6 (a)1D Zigzag Chain (b)1D Ladder (c)2D Honeycomb (d)2D Square Grid Diamondroid (e)3D Octahedral (f)3D Hexagonal

1.2.1 One dimensional structure

A lot of works had been done by smartly using non-covalent bonding such as metal-ligand coordination bonds and hydrogen bonding to get large-scale crystal structures from zero to three dimension. Two or three dimension structures are more related to the crystals, however, zero and one dimension structure are the basic factors that scientists can count on to regulate the ultimate crystal architecture in a precise way. As for 0D architecture, it is actually not a continuous solids with critical geometry. Thus, the
molecules shipment in this system will have a big influence in the self-assembly behavior. For 1D structures, helical and zig-zag chains are reported in hydrogen bonding and metal-ligand system. Guo et al. had showed a chain of AgCN·2AgClO4·2H2O in zig-zag manner with cyanide units bonding to four silver atoms unsymmetrically. The chain’s kink is likely generating from diagonal pull on the C and N by disparate silver atoms. One interesting section of these chains is they are linked with hydrogen bonds and produced elongated hexagonal channels. 3D networks were discovered due to the channel packing closely. Another type of 1D structure is molecular ladder which needs T-shape building blocks. Losier et al. published a paper about a molecular ladder of [Co(NO3)2(4,4’-bpy)1.5]. In this structure, three 4,4’-bpy ligands coordinate to the Co(II) and these T-shape molecules could self-assemble into a ladder formation. The ligands, in this case, play a significant role of side rails.

1.2.2 Two dimensional structure

Typically, 2D structure is square grid and can be networks constitute of ligand and metal (2:1). The ligands are usually bifunctional and linear. Fujita et al. had reported by using bipy as spacer ligands an open framework of square grids can be formed. Many transition metals, including Co(II), Cd(II), Zn(II) and Ni(II) can be the used as nodes in the square. Also, some scientists had reported two spacer ligands with different length in a same grid and the square turned to rectangle. “Herringbone”9 and "brick wall"10 are another two 2D structures. The common features of them are that the shipment of the nodes is T-shape and also have three coordination sites. We can see these three structures
from Figure 1.4 In fact, if we can obtain suitable molecules, these structures can also be formed by hydrogen bonding.

Different from the metal-ligand bonds, hydrogen bonding leads molecules into unique 2D structures and one simple situation is shown in Figure 1.5.
The solid line in Figure 1.5 is made on behalf of a molecule with three symmetry groups. The dot line in this diagram represents the hydrogen bonding formed between two groups. The 1,3,5-benzenetricarboxylic acid is a good example.\textsuperscript{11,12,13}

1.2.3 Three dimensional structure

3D structure is definitely the most complicated one to study, since the orientation and location of one molecule are much more flexible compare to 1D or 2D network. In an ideal case, when a 3D molecule has symmetrical intermolecular interactions, it is possible to form a good 3D structure. As a matter of fact, researchers had proved this prediction. Ermer\textsuperscript{14} reported that the adamantane-1,3,5,7-tetracarboxylic acid with four carboxylic acid groups in a tetrahedrally position is able to build diamond-shape lattice. For the fake of filling the empty cavities, one network need to accommodate other networks.\textsuperscript{15} Therefore, a 5-fold structure is formed when five independent networks intercross into each other. Following this result, different intercross have been gotten depending on the size of the cavities. Just like hydrogen bonds, metal-ligand coordination bonds also appear potential to generate diamond-shape networks. Cd(CN)\textsubscript{2} is a good example.

1.3 Giant Surfactants

The appearing of the concept of giant surfactant is on the strength of the fact that lots of marvelous breakthroughs in synthesizing of nanobuilding blocks in recent decades and their potential future applications based on their self-assembly behavior in bulk and solution.\textsuperscript{16}
1.3.1 Definition

With the developing of nano science, the application of nanotechnology is more and more important to areas such as photonics and electronics, chemical and biological sensors, energy storage, and catalysis system. All of these areas require the manipulation of these nano-objects to apply them into functional materials and devices.

Different from the system which only contain one nanobuilding blocks, i.e. nanorods, nanocubes, nanospheres, or nanoplates, hybrid nanobuilding blocks are composed of those nano-atoms and linked by covalent bonds, forming different geometric shapes and they also have different chemical compositions. Some of those hybrid nanobuilding blocks are named as “giant surfactants”. Thus giant surfactants are usually composed of two different parts, hydrophilic part and hydrophobic part. They are also regarded as promising building blocks for studying crystal structures by self-assembly process. This system doesn’t exist macrophase4 separation just like oil and water, although every part of the giant surfactants do not like each other and have a trend to get together with their own kind for the sake of minimizing the free energy. It is because they are collected together by covalent bonds, just the same with block copolymers. Because of the similar physics controlling those two systems, it is more easily to observe well ordered microphase in the self-assembly behavior of giant surfactants. Generally speaking, block copolymers can be regarded as one kind of giant surfactants. Some cartoons of typical giant surfactants are listed in Figure 1.6.
1.3.2 Selective Simulation Results

Many researchers have used computer simulation to predict intriguing and various phase behaviors and hierarchical structures based on these giant surfactants. Also they have successfully predicted the effects of solvent compositions, molecular concentrations and anisotropy in both interaction and shape on their self-assembly behaviors. The following images show the selective simulation results of various kinds of giant surfactants from previous papers.\textsuperscript{17, 18}
Solvent selectivity effect on self-assemble behavior of tethered nanospheres: Figure 1.7 (a) displays a lamellar structure generated in a relatively poor solvent for nanospheres and relatively good solvents for tethers. The nanospheres form a compact 3D clusters due to the effort to reduce contacts with solvent, if there were no tethers. On the contrary, the nanospheres pack into 2D hexagonal array and form double layers to increase contact and fits excluded volume interactions among tethers in Figure 1.7 (b). Figure 1.7 (c) and (d) display changing the solvent selectivity to be poor for tethers and good for nanospheres induces the generation of spherical micelles, where tethers cluster to avoid touch with the solvent, leading the nanospheres to form spherical shells instead of double layers.
Effect of relative concentration of each part on assembled structures: Equilibrium lamellar structures can be observed in Figure 1.7 e and f, because tethered nanorods are in natural solvent. The rods pack in layers, oriented with a tilt angle, with respect to the normal direction of the lamellar surface. Here, by increasing the tether length from five to six monomers the tilt angle increases from 16° to 33° (i.e., increasing tether’s relative volume fraction). The tilt angle increases for entropic reasons, because the tethers’ excluded volume interactions, and its reliance on the block length has been found in rod-coil block copolymers where the “rod” block is liquid crystal or rodlike polymer chain.

1.3.3 Relevant Work in Our Group

Although there are lots of simulation researches have studied and analyzed self-assembly of giant surfactants, experimental research are relatively preliminary in literature. Actually, in this field, our research group has made eminent contribution to the synthesis of various giant surfactants and also the studying of their self-assembly behavior and morphological transitions.20

In 2012, Kan Yue et al. utilized a highly efficient and modular sequential “click” approach to syntheses of giant surfactants based on polymer-tethered polyhedral oligomeric silsesquioxane (POSS).21 This approach is composed of both “post-functionalization” and “grafting-to” strategies (shown in Figure 1.8).
Figure 1.8 Sequential “Click” Approach to Synthesize XPOSS-PS and HexPOSS-PEO.\textsuperscript{21}

It contains the copper-catalyzed Huisgen [3+2] cycloaddition (CuAAC) to synthesize POSS–polymer ligation and subsequent thiol–ene reaction to get POSS cage functionalized. Beginning with a simply available POSS precursor bearing seven vinyl groups and one alkyne group (VPOSS–alkyne), the CuAAC reaction is effective in making sure the stoichiometric bonding between azide-functionalized polymers and POSS cages, with no need for fractionation in purification process. After that the thiol–ene reaction was applied to transform all the seven vinyl groups on the POSS cage into various functional groups, including carboxylic acids, hydroxyls, and alkyls, thereby introducing hydrophilic and hydrophobic interaction to drive self-assembly. Such giant surfactants are brand new model systems for studying their self-assembly behaviors, hierarchical structure formation, and functional properties in both bulk and solution states.
1.4 Molecular Design Based on Polyhedral Oligomeric Silsesquioxane (POSS)

It is worthy to mention self-assembly based on nano-particles or giant molecules is an important and easy way to form different crystal phases. The reason is simple. Molecular self-assembly is a minimizing free energy process, thus both enthalpy and entropy are equally important. Small molecules which have a neglected geometry effect self-assemble mainly via enthalpy change (intermolecular interaction). While the nano-particles with certain shapes were driven into order structures by entropy change. Although this type of system is good for self-assembly and forms ordered structures, there are still two essential problems remaining unsolved. Firstly, it is still a challenge to synthesize particles with mono-dispersed size and shape. So it will turn much more difficult for the particles to self-assemble, if we can’t get well-defined structures of building blocks. Highly ordered crystal phases will become difficult to appear since a fluctuation in shape or size may cause defects in the final structure. Another weakness of these nano-particles is their relatively large size. Larger size actually means more energy is needed to provide the driving force for assembly. Thermal fluctuation alone is not enough to drive the system into order structures. Thus, external force such as mechanical force or magnetic force should be used.

For the first problem, which is preparing mono-disperse and precisely defined giant molecules in size and shape, it can be solved by connecting suitable nano-building blocks through high efficient and selective reactions. In the synthetic route part, we will discuss this problems in details. To solve the second problem, our group has already provided an excellent solution. By combing different shaped and functionalized nano-building blocks utilizing covalent bond, we can create a bank of giant molecules with size in 3 nm to 10
nm range. This exactly fills the size gap between traditional small molecules and colloidal particles. Surprisingly, such a simple geometry could provide a rather complicated self-assemble behavior. By changing the molecular weight of polystyrene (PS), different phase structures could appear. Here, it is worth mentioning the similar work by Balagurusamy. He and his coworkers synthesized monodendron with tapered fan shape or cone shape. They proved that these monodendrons could form cylinder and sphere respectively and further generate a superlattice order structure. The cylinder in fact could further self-assembly into columnar hexagonal structures and the sphere could pack together, generating cubic supramolecular assemblies such as A15 phase.

![Figure 1.9 model of molecule in this project](image)

After proposing an ideal molecule model we should then to find a suitable nano-size building block. Up to now, some nano-particles have been considered and among them the polyhedral oligomeric silsesquioxane (POSS) is chosed for Its stability, size and well defined functionality. To understand the attraction of POSS, we should have a look at its chemical structure at first. POSS is a compound consists of RSiO3/2 unit (called T) where R is an organic group. Different structure of POSS can be obtained, among them a
widely used and understand is so called T8. The structure of (RSiO3/2)8 is shown in Figure 1.10.

![Figure 1.10 The structure of T8 POSS. Left: ball and stick model, Si (yellow), O (red), R (grey). Right: chemical formula of POSS](image)

This figure shows clearly that the T8 POSS has a cubic shaped cage. In the cage, O is on the edge and Si is at the vertex. Each Si atom is connected with an organic R. The organic R group determine the size of POSS. For example, if R= (CH3), then the size will be 1 nm. Another important property of POSS cage is that it is stable, except for the small size. Thermal gravimetric analysis (TGA) shows a good thermal stability. And the chemical stability can be proved by IR spectrum. The characteristic peak of Si-O-Si is around 1100 cm-1.51 By comparing this peak from the spectrum before and after reactions, we can see whether the cage has been destroyed or not. Nowadays, chemists can synthesize POSS with large number kinds of R group such as –H, -CH3, -Ph, -CH=CH2, -(CH2)3NH2, and so on. Besides, the asymmetric modification of POSS into T8R7R' and even T8R(8-n)R'n have been successfully synthesized and purified.
Therefore, a nano-particle with well defined shape and relatively small size can be created by using this POSS cage.

1.5 Huisgen 1,3-dipolar cycloaddition “click” Reaction

Huisgen 1,3-dipolar cycloadditions are fusion processes that combine two unsaturated chemical reactants and make fast access to an great variety of fivemembered heterocycles. The cycloaddition of azides and alkynes to give triazoles is possibly one of the most value member of this family.

1.5.1 Basic concepts

This reaction was discovered not until 1960s, far beyond the time when Dr. Sharpless introduced the concept of “click chemistry” to the scientific world by. Though, the original Huisgen 1,3-dipolar cycloaddition between alkynes and azides are processed under elevated temperature, the triazoles forming cycloaddition always results a mixture of 1,4 and 1,5 regioisomers.

![Figure 1.11 The regiochemistry of Huisgen 1,3-dipolar cycloaddition](image)

In 2002, Sharpless et al. discovered that copper(I) – catalyzed reaction sequence was able to regiospecifically unite azides and terminal acetylenes to form only
1,4—disubstituted 1,2,3-triazoles. This reaction can now be regarded as a family member of “click reaction”, which all have high productivity and little or even no byproducts under temperate reaction condition. The reason why azides is unique for “click chemistry” purposes is because their eminent stability toward H2O, O2, and most of organic synthesis conditions.

![Figure 1.12 Reagents and conditions of CuAAC reaction](image)

They also found that the catalyst is much better prepared in situ by reducing CuII salts, such as CuSO4•5H2O, which are much less costly and purer than CuI salts. As the reductant, sodium ascorbate and ascorbic acid proved to be perfect, since they enable preparation of a broad spectrum of 1,4-triazole products in a high productivity and purity at 0.25-2 mol% catalyst loading. Copper (I) salts, for example, CuI and CuOTf•C6H6, can also be utilized in the absence of a reducing agent. In order to prevent CuI system from producing undesired by-products, oxygen must be evacuated from the system and also the nitrogen base need to be chosen carefully.

The following picture shows the mechanism of catalytic cycle proposed by Sharpless and coworkers. The cycle starts with formation of copper(I) acetylide. However, the concerted [3+2] cycloaddition is strongly disfavored by the density
functional theory calculation. In fact, the results of the calculation points to a stepwise, annealing sequence, which proceeds via the intriguing six-membered copper-containing intermediate.

Figure 1.13 Proposed catalytic cycle for the CuI-catalyzed ligation

1.5.2 Recent utilization in designing of soft matter

With the increase of demand in a widerange of industrial and research settings, it is necessary to build up soft matter materials with precise control over domain size, architecture, functionality, polarity, solubility, and reactivity. Besides these materials and structural requirements, scientists have also wanted to prepare these systems via high yielding, simple covalent chemistry. One of the most famous reaction which fulfills the above-mentioned requirement and have already been utilized in last 10 years is the Cu-
catalyzed azide/alkyne cycloaddition (CuAAC) reaction. There are some examples below to show its importance in synthesizing soft materials.

End-functional polymers are one of the part of the simplest functional macromolecular architectures, having only one functionalized group at the end of a single polymer chain. Despite this simplicity, end-functional polymers are still an important starting point for synthesizing a wide diversity of functional materials. One of the most popular initiator based approaches to obtain end-functional polymers includes the combination of functional initiators with ATRP (Atom Transfer Radical Polymerization). Narumi et al. reported the potential power of attaching small molecules to the chain end of a well-defined polymer. In their study, an ATRP initiator with azide group was used to grow poly(N-isopropylacrylamide) (P(NIPAM)), which precisely has an relatively lower critical solution temperature (LCST) around 32°C. The authors could modify the LCST of the polymer over a temperature range of 10°C by attaching small molecules with varying polarities to the end of the P(NIPAM) via copper-catalyzed alkyne-azide cycloaddition (CuAAC) reactions, which is given the high molecular weight of the polymer chain. The high efficiency of the CuAAC modification was determined by NMR spectroscopy and matrixassisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectroscopy.
Figure 1.14 Modifications of the chain terminus of Poly(NIPAM) polymers

Block copolymers are of great significance for their unique physical properties. Those block copolymers are usually synthesized by living polymerization. However, through an efficient coupling step, (Figure 1.15) CuAAC we can also synthesize AB diblock copolymers with great success. Van Hest et al. used alkyne-bearing ATRP initiators as well as azide displacement to create a series of complementary CuAAC functional PMMA, PS and PEG homopolymers, which was able to be coupled to give diblock copolymers in high productivity.²⁹
Star polymers are usually grown by one of three different strategies: the “core first” approach, the “arm first” technique, and the “coupling to” method. As for the “coupling to” method, the diversity of the star polymers that can be synthesized is confined by the selectivity and efficiency of the reactions utilized in the conjugation step. Therefore, choosing a robust and efficient coupling reaction is very important. As expected, there are a lot of examples that utilize the CuAAC reaction between an alkyne and an azide to conjugate linear polymer chains onto multifunctional cores to get well-defined star polymers. A seminal example of this strategy involved the synthesis of three- and four-arm stars using ATRP and click cycloadditions. (Figure 1.16) Matyjaszewski et al. utilized ethyl 2-bromo isobutyrate as the initiator and CuBr/PMDETA as the catalyst system to synthesize polystyrene by ATRP. The resulting bromine chain ends were transformed into azide groups by nucleophilic substitution with sodium azide. Subsequently, the azido-functionalized PS was reacted with trialkyne- and tetraalkyne-containing coupling agents to produce three- and four-arm PS star polymer, respectively.
In this work, it was found that when the molar ratio of alkynyl groups to azido groups was 1:1, triazoles formation was very efficient and resulted in a 90% yield and 83% yield of three- and four-arm star polymers, respectively.

![Diagrams of star polymers](image)

Figure 1.16 Examples of three- and four-arm star polymers
2.1 Preface

At the end of the introduction, the chemical structures of the giant surfactants in this project were briefly proposed. In this project, two kinds of giant surfactants are successfully synthesized and both of the two giant surfactants have two parts: functionalized hydrophilic POSS cage acted as the “head” of the molecule at both end and polystyrene (PS) acted as the “tail” of the molecule. The first kind of molecules are composed of one hydrophilic DPOSS at both ends of a PS tail. The second kind of molecules are composed of three hydrophilic DPOSS at both ends of a PS tail. Synthesizing the first kind of molecules is a relatively easy job. However, in order to synthesize the second kind of molecules we need a linkage molecule to combine three “head” and one “tail” together. In this project we follow esterification and use 3-Bromo-2,2-bis(bromomethyl)-1-propanol reacts with 4-Pentynoic acid following esterification to form our linkage molecule. The nano atoms in this work are POSS with 7 di-hydroxy groups on the R position and we call it DPOSS. The two parts will be combined through Azide-Alkyne Huisgen Cycloaddition. It is a kind of click reaction with a high efficiency and can form 5-member ring between azide and alkyne group catalyzed by Copper (I). In conclusion, the strategy to prepare these molecules can be divided into three parts. Firstly, azide groups have to been introduced to polystyrene. Then, linking PS with core molecule by click reaction. After that, giving the core molecule azide group. Next, the
core molecule can react with an alkyne-POSS cage by click reaction. Finally, we use thiol-ene reaction to functionalize the POSS cage to make it become a hydrophilic DPOSS. The following pictures show the synthetic routine of two kinds of molecules.

Figure 2.1 Scheme of synthesis of DPOSS-PSn-DPOSS
Figure 2.2 Synthetic route of 3DPOSS-PSn-3DPOSS
2.2 Chemical and solvent

OctavinyloPOSS (VPOSS, 99%, Hybrid Plastics), 4-Pentynoic acid (99%, Aldrich), Bromo-2,2-bis(bromomethyl)-1-propanol (Aldrich, 99%), 2-Mercaptoethanol (Aldrich, 99%), 3-Mercapto-1,2-propanediol (Aldrich, 99%), Tetrahydrofuran (THF, 99%, Aldrich), Dichloromethane (CH2Cl2, Fisher), Silica gel (VWR, 230-400 mesh), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, Aldrich), 4-Dimethylaminopyridine (DMAP, Aldrich), Sodium azide (NaN3 Aldrich), Dimethyl Formamide (DMF, Fisher), N,N'-Diisopropylcarbodiimide (DIPC, Aldrich), CDC13 (Aldrich, 99.8% atom D), Toluene (Aldrich, 99.5%), Methanol (Aldrich, 99%), Hexane (Aldrich, 99%), Deionized water, Cuprous bromide (CuBr, Aldrich, 98%) was purified by stirring in acetic acid, washed with methanol, repeated for three times, and dried in vacuum.

2.3 Instrumentations

All 1H and 13C nuclear magnetic resonance (NMR) spectra were acquired in CDC13 using a Varian Mercury 300 or Varian 500 NMR spectrometer. The 1H NMR spectra were referenced to the residual proton impurities in the CDC13 at δ 7.27 ppm. 13C NMR spectra were referenced to 13CDC13 at δ 77.00 ppm.

Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by compressing the powder mixture of KBr and sample into a thin plate. The data were processed using Win-IR software.
Size-exclusion chromatography (SEC) analyses were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns and a double detector system. The detector system consisted of a differential refractometer and a laser light scattering detector. THF was used as eluent with a flow rate of 1.0 mL/min at 30 °C. Regular SEC calibrations were conducted with polystyrene standards.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a BrukerUltraflex-III TOF/TOF mass spectrometer (BrukerDaltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (335 nm). All spectra were measured in positive reflector or linear mode. The instrument was calibrated prior to each measurement with external PMMA or PS standard at the molecular weight under consideration. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Aldrich, >99%) served as matrix and was prepared in CHCl3 at concentration of 20 mg/mL. Silver trifluoroacetate served as cationizing agent and was prepared in MeOH/CHCl3 (1/3, Vol/Vol) at concentrations of 5 mg/mL. All the thiol-ene functionalized materials were dissolved in CHCl3 for future MALDI-TOF mass evaluations. The matrix and AgTFA were mixed with the ratio of 10/1 (Vol/Vol). The sample preparation involved depositing 0.5 μL of matrix and salt mixture on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μL of each sample on a spot of dry matrix, and adding another 0.5 μL of matrix and salt mixture on top of the dry sample (sandwich method). After evaporation of the solvent, the plate was inserted into the MALDI source. The attenuation of the Nd:YAG laser was adjusted to minimize unwanted polymer fragmentation and to maximize the sensitivity.
Small angle X-ray scattering (SAXS) was conducted on a Rigaku MicroMax 002+ instrument equipped with a CCD detector and a high-intensity anode tube Cu X-ray generator with a wavelength of 0.154 nm. The working voltage and current for the X-ray source are 50 kV and 0.6 mA, respectively. A small piece of sample was immobilized with Kapton tape on the sample holder. The collection time for each data was 5 to 10 min, depending on the scattering intensity. The instrument was calibrated using silver behenate with the primary reflection peak (1.067 nm-1). Data is analyzed with the Rigaku software SAXSgui.

TEM experiments were carried out with a Philips Tecnai 12 using an accelerating voltage of 120 kV. Selected area electron diffraction (SAED) patterns with different crystal orientations are obtained using a tilting stage to determine the crystal structure parameters. The d-spacings are calibrated using a TiCl standard. The tilting angle is defined as positive if the tilting direction is clockwise and negative for counter-clockwise.

2.4 Synthetic routine of 3DPOSS-PS-3DPOSS

The following texts show how the samples of 3DPOSS-PS-3DPOSS are synthesized and purified.

2.4.1 Polystyrene with azide group at both ends

Atom transfer radical polymerized (ATRP) PS with Br group (Molecular weight is 8000, 2g, 1.23mmol) and sodium azide (1604mg, 24.33mmol) are dissolved by 10 mL DMF. The solution is stirred for 24h under 358K temperature. Solvent is evaporated
under reduced pressure, the residue is extracted with CH2Cl2. The product is obtained after removing the solvent. 1H NMR (300 MHz, CDCl3) δ 7.22 – 6.13 (m, 80H).

2.4.2 HeptavinylPOSS with one hydroxyl group

The synthesis of HeptavinylPOSS with one hydroxyl group is based on OctavinylPOSS (10 g, 15.79 mmol) and 2-Mercaptoethanol (1.23 g, 15.79 mmol) are added into THF (50 mL) and mixed with photoinitiator then reacting under UV light (365 nm) for ten minutes. After remove the solvent, the residue is purified by column chromatography on a silica gel column, eluting with hexane and CH2Cl2. 1H NMR (300 MHz, CDCl3) δ 6.19 – 5.76 (m, 21H), 3.71 (q, J = 6.0 Hz, 2H), 2.80 – 2.58 (m, 2H), 2.09 (t, J = 6.2 Hz, 2H), 1.29 – 1.23 (m, 1H)

2.4.3 HeptavinylPOSS with one alkyne group

To get HeptavinylPOSS with one alkyne group we need to do an esterification. HeptavinylPOSS with one hydroxyl group (1g, 1.40 mmol), DMAP (17.08 mg, 0.14 mmol) and 4-Pentynoic acid (164.64 mg, 1.68 mmol) are all added into purified CH2Cl2 solvent, and the solution stay in the ice water for 30 minutes. Then use needle to inject the DIPC (529 mg, 4.2 mmol) in the solution. Finally, let the reaction stay at room temperature for an overnight. The product is purified by column chromatography on a silica gel column, eluting with hexane and CHCl2. 1H NMR (300 MHz, CDCl3) δ 6.24 – 5.71 (m, 21H), 4.23 (t, 2H), 2.42-2.58 (s, J = 2.5 Hz, 4H), 2.47 (s, H), 1.14 – 1.26 (t, 2H).
2.4.4 3Br-alkyne molecule

4-Pentynoic acid (443.6mg, 4.57mmol), Bromo-2,2-bis(bromomethyl)-1-propanol (250mg, 4.47mmol) and DMAP(138.1mg, 1.14mmol) are all added into purified CH2Cl2 solvent, and the solution stay in the ice water for 30 minutes. Then use needle to inject the DIPC (951.1mg, 7.62mmol) in the solution. Finally, let the reaction stay at room temperature for an overnight. The product is purified by column chromatography on a silica gel column, eluting with hexane and CHCl2. 1H NMR (300 MHz, CDCl3) δ 4.20 (s, 6H), 3.51 (s, 6H), 2.67 – 2.38 (m, 6H), 2.00 (dt, J = 2.5, 1.2 Hz, 3H), 1.25 (s, 2H).

2.4.5 Three azide group linked at the both ends of PS tail

Corel molecule (60.97mg, 0.693mmol), PS with azide group (500mg, 0.308mmol) and CuBr (5mg, 0.034mmol) are all put in a click reaction glassware. After the glassware becomes vacuum atmosphere, drop 3-4 drops of PMEDTA into the reaction. Let the reaction stay for an overnight. Then the product is purified by column chromatography on a silica gel column, eluting with hexane and CHCl2. After getting the product, mix it with some sodium azide under 358K temperature for a day. Solvent is evaporated under reduced pressure, the residue is extracted with CH2Cl2. The final product is obtained after removing the solvent. 1H NMR (300 MHz, CDCl3) δ 7.22 – 6.13 (m, 1235H).
2.4.6 Three VPOSS cages linked at the both ends of PS tail

PS linked with three azide groups at both ends (120mg, 0.024mmol), Heptaviny1POSS with one alkyne group (27.11mg, 0.185mmol) and CuBr (5mg, 0.034mmol) are all put in a click reaction glassware. After the glassware becomes vacuum atmosphere, drop 3-4 drops of PMEDTA into the reaction. Let the reaction stay for an overnight. Finally the product is purified by column chromatography on a silica gel column, eluting with hexane and CHCl2. 1H NMR (300 MHz, CDCl3) δ 7.22 – 6.13 (m, 1235H), 6.24 – 5.71 (m, 126H).

2.4.7 Three DPOSS cages linked at both ends of PS tail

PS linked with three VPOSS cages at both ends (50mg, 0.0083mmol), 3-Mercapto-1,2-propanediol (37.76mg, 1.74mmol) and photoinitiator (10mg, 0.044mmol) are all added into test tube and solved by 5ml THF. Put the test tube under UV light (365nm) to react for 10 minutes. Then evaporate the THF and sediment the product in mixture solution (methanol and deionized water, ratio 1:1). After centrifuging the final product is gotten. 1H NMR (300 MHz, CDCl3) δ 7.22 – 6.13 (m, 1235H).

2.5 Synthetic routine of DPOSS-PS-DPOSS

The following texts show how the samples of DPOSS-PS-DPOSS are synthesized and purified.
2.5.1 Polystyrene with azide group at both ends

Atom transfer radical polymerized (ATRP) PS with Br group (Molecular weight is 8000, 2g, 1.23mmol) and sodium azide (1604mg, 24.33mmol) are dissolved by 10 mL DMF. The solution is stirred for 24h under 358K temperature. Solvent is evaporated under reduced pressure, the residue is extracted with CH2Cl2. The product is obtained after removing the solvent. 1H NMR (300 MHz, CDCl3) δ 7.22 – 6.13 (m, 80H).

2.5.2 HeptavinylPOSS with one hydroxyl group

The synthesis of HeptavinylPOSS with one hydroxyl group is based on OctavinylPOSS (10 g, 15.79 mmol) and 2-Mercaptoethanol (1.23g, 15.79mmol) are added into THF (50 mL) and mixed with photoinitiator then reacting under UV light (365nm) for ten minutes. After remove the solvent, the residue is purified by column chromatography on a silica gel column, eluting with hexane and CH2Cl2. 1H NMR (300 MHz, CDCl3) δ 6.19 – 5.76 (m, 21H), 3.71 (q, J = 6.0 Hz, 2H), 2.80 – 2.58 (m, 2H), 2.09 (t, J = 6.2 Hz, 2H), 1.29 – 1.23 (m, 1H)

2.5.3 HeptavinylPOSS with one alkyne group

To get HeptavinylPOSS with one alkyne group we need to do an esterification. HeptavinylPOSS with one hydroxyl group (1g, 1.40mmol), DMAP (17.08mg, 0.14mmol) and 4-Pentynoic acid (164.64mg, 1.68mmol) are all added into purified CH2Cl2 solvent,
and the solution stay in the ice water for 30 minutes. Then use needle to inject the DIPC (529mg, 4.2mmol) in the solution. Finally, let the reaction stay at room temperature for an overnight. The product is purified by column chromatography on a silica gel column, eluting with hexane and CHCl2. 1H NMR (300 MHz, CDCl3) δ 6.24 – 5.71 (m, 21H), 4.23 (t, 2H), 2.42-2.58(s, J = 2.5 Hz, 4H), 2.47 (s, H), 1.14 – 1.26 (t, 2H).

2.5.4 One VPOSS cage linked at the both ends of PS tail

PS linked with one azide groups at both ends (120mg, 0.092mmol), Heptaviny1POSS with one alkyne group (27.11mg, 0.185mmol) and CuBr (5mg, 0.034mmol) are all put in a click reaction glassware. After the glassware becomes vacuum atmosphere, drop 3-4 drops of PMEDTA into the reaction. Let the reaction stay for an overnight. Finally the product is purified by column chromatography on a silica gel column, eluting with hexane and CHCl2. 1H NMR (300 MHz, CDCl3) δ 7.22 – 6.13 (m, 1235H), 6.24 – 5.71 (m, 42H).

2.5.5 One DPOSS cages linked at both ends of PS tail

PS linked with one VPOSS cages at both ends (50mg, 0.0083mmol), 3-Mercapto-1,2-propanediol (42.34mg, 0.58mmol) and photoinitiator (10mg, 0.044mmol) are all added into test tube and solved by 5ml THF. Put the test tube under UV light (365nm) to react for 10 minutes. Then evaporate the THF and sediment the product in mixture
solution (methanol and deionized water, ratio 1:1). After centrifuging the final product is gotten. 1H NMR (300 MHz, CDCl$_3$) $\delta$ 7.22 – 6.13 (m, 1235H).
CHAPTER III

RESULTS AND DISCUSSION

3.1 Chemical Structure Characterization

All the chemical structures of the molecules were determined by 1H NMR and 13C. Herein, only the final giant molecule's structures are discussed.

3.2 Synthesis of 3DPOSS-PS-3DPOSS

In order to get good phase diagrams of lamellar and hexagonal cylinder phase and find phase transformation, we need to design an amphiphilic molecule: the head is hydrophilic and the tail is hydrophobic. According to our group’s previously research, if the volume fraction of hydrophobic PS to hydrophilic DPOSS around 1:1 it will be more likely to form lamellar phase. When the volume of PS is higher than DPOSS cage to some extent, the phase will change from lamellar to hexagonal cylinder. However, when the volume of DPOSS cage is higher than PS to some extent, we could also find another form of hexagonal cylinder phase and we call this phase inversed hexagonal cylinder phase. Thus, a series of molecular weight of PS with low PDI is needed. In order to get such PS, we need to atom transfer radical polymerization to synthesize PS.

The synthesis of 3N3-PS-3N3 is relatively easy. NaN3 was added in excess to make sure all the Br group could be substituted. In order to link the DPOSS cage with PS effectively, “click” reaction was chosen. “Click” reaction refers to a group of reactions
that have high yield, fast reactive rate and high selectivity. They include reactions such as Diels-Alder reactions, thiol-ene reaction etc. Here, we employ the [3+2] Cu(I) catalyzed Azide-Alkyne Huisgen cycloaddition. This reaction is between an azide and a terminal or internal alkyne to give a 1,2,3-triazole. In this work, alkyne group was introduced to VPOSS and azide group was introduced to PS. The following figure shows the NMR diagram of VPOSS with one alkyne group.

![Figure 3.1 1H NMR of VPOSS with one alkyne group](image)

Also we can see from Figure 3.2, after utilizing click reaction to combine VPOSS cage with 3N3-PS-3N3, there will be a no more very sharp peak at the location of 2100.
Figure 3.2 FTIR of 3N3-PS-3N3 and 3VPOSS-PS-3VPOSS

Usually Br group transforms to azide group need less energy, but in this project transforming 3Br-PS-3Br to 3N3-PS-3N3 needs more energy, cause the atom Br in 3Br-PS-3Br is not active, therefore this reaction is acted under 358K temperature atmosphere. The 1H NMR of 3DPOSS-PS-3DPOSS is shown in Figure 3.3. From the figure, we can see the multiple peaks during 6.24 – 5.71 ppm have disappeared, which represents the vinyl groups in VPOSS have vanished, indicating that thiol-ene reaction have completely finished.
We have successfully synthesized a series of molecular weight of DPOSS-3PSn. According to the GPC Figure 3.4, it shows clearly that different molecular weight is in accord with different retention time. The molecule with higher molecular weight has bigger volume and will pass relatively short range of the GPC machine, so the retention time will be shorter. In the same way, lower molecular weight means longer retention time.
3.3 Self-assembly Structure Analysis

The 3DPOSS-PS-3DPOSS and DPOSS-PS-DPOSS shown distinct self-assembly results. For these molecules, highly ordered phase structures had been successfully prepared for X-ray and TEM diffraction experiment after thermal annealing at 463K temperature for twelve hours. And the result from small angle X-ray and TEM shows lamellar and hexgonal cylinder phase.
The following table shows all of the experiment results. We can see from the table, for DPOSS-PSn-DPOSS series, with the increasing of molecular weight of PS the phase was changed from lamellar to hexagonal cylinder. For 3DPOSS-PSn-3DPOSS series, with the increasing of molecular weight of PS the phase was changed from inversed hexagonal cylinder phase to lamellar phase. All of this phenomenon can be explained by the changing of volume fraction.

Figure 3.5 Phase diagram of 3DPOSS-PS-3DPOSS and DPOSS-PS-DPOSS
Table 3.1 Self-assembly behavior of all the molecules studied in this project

<table>
<thead>
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<th>Samples</th>
<th>Morphology</th>
<th>d-spacing (nm)</th>
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<tbody>
<tr>
<td>DPOSS-PS-DPOSS(3.5k)</td>
<td>Lamella</td>
<td>3.52</td>
</tr>
<tr>
<td>DPOSS-PS-DPOSS(6.4k)</td>
<td>Hex Cylinder</td>
<td>3.94</td>
</tr>
<tr>
<td>DPOSS-PS-DPOSS(8.4k)</td>
<td>Hex Cylinder</td>
<td>4.72</td>
</tr>
<tr>
<td>DPOSS-PS-DPOSS(16k)</td>
<td>Poorly Ordered</td>
<td>5.79</td>
</tr>
<tr>
<td>3DPOSS-PS-3DPOSS(3.5k)</td>
<td>Inversed Hex Cylinder</td>
<td>8.05</td>
</tr>
<tr>
<td>3DPOSS-PS-3DPOSS(5.5k)</td>
<td>Inversed Hex Cylinder</td>
<td>10.64</td>
</tr>
<tr>
<td>3DPOSS-PS-3DPOSS(8.4k)</td>
<td>Lamella</td>
<td>10.82</td>
</tr>
<tr>
<td>3DPOSS-PS-3DPOSS(16k)</td>
<td>Lamella</td>
<td>13.95</td>
</tr>
</tbody>
</table>
CHAPTER IV

SUMMARY

The assembly of particles with different shapes and sizes are always of great interest. In this work, we synthesized a series of molecular weight of DPOSS-PS-DPOSS and 3DPOSS-PS-3DPOSS based on POSS nano building block and ATRP polymerized PS. The products were characterized by 1H NMR, GPC, FTIR, MALDI-TOF and proved to be correct and pure. Crystal formation was by a thermal heating machine under 465K temperature. The crystal phases lamellar, hexagonal cylinder, inverted cylinder phase were observed from SAXS and TEM.
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