NOVEL APPROACH TO POLYHEDRAL OLIGOMERIC SILSESQUIOXANE-BASED GIANT SURFACTANTS BASED ON THIOL-MICHAEL ADDITION “CLICK” REACTION

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NOVEL APPROACH TO POLYHEDRAL OLIGOMERIC
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ABSTRACT

Nowadays, giant molecules have been focused by a series of researches for the different sizes-structural engineering to design materials. Based on composition, shape and structure, they can be classified into giant surfactants, giant shape amphiphilics and giant polyhedral. Taking advantages of these giant molecules will overcome defects existing in traditional route of creation materials from atoms. Among them, with a polar and shape-persistent molecular nanoparticles tethered by flexible polymers, giant surfactants is the common element for molecular fabrication. Unlike absence of sharp micro-phase separation in small surfactants and short of tiny segregation pattern in block copolymers, giant surfactant can keep precisely defined shape, structure and functionalities to bridge the gap by capturing the structural features from small molecules but at the large size. Several self-assembly behavior morphologies in solution, bulk and thin film have been developed in our group. Since their valuable hierarchical structures which can be extended, we have developed the precise and efficient “sequential click strategy” to achieve a certain giant molecule structure. This method makes use of the common click reactions like CuAAC and thiol-ene reaction. However, only using these two methods will limit the development of new generations of giant surfactants. In this thesis, another click
reaction—thiol-Michael addition reaction—is introduced into our system. The synthesis of a precisely defined giant surfactant consisting of one polar polyhedral oligomeric silsesquioxanes (POSS) tethered with one, two and four polystyrene (PS) tails in one site is reported. The final product is fully characterized by $^1$H NMR, $^{13}$C NMR, MALDI-TOF mass spectrum. And then, thermogravimetry (TGA) and differential scanning calorimetry (DSC) are employed for the thermal analysis. Finally, the morphology of self-assembly behavior of these giant surfactants will be characterized by TEM and X-ray experiments in the future.
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CHAPTER I

INTRODUCTION

Originally, engineering of structures is a specific concept in civil engineering field. It refers to the engineering field of analyzing and designing structures to achieve specific functionalities. As the development of studies on molecular self-assembly behaviors, this concept has been introduced into researches in molecular scope due to its features fitting that of formation of materials with desired properties. To chemists, it refers to restrosynthesis of macromolecules starting from units. When it comes to materials scientists, it indicates a novel method to easily and modularly construct materials with diversity and desired properties. Nowadays, creating materials with desired properties and functions possesses more and more reliance on molecular building blocks assembling into specific structures in areas of materials science and engineering.¹ These building blocks are arrange into a specific sequence will bring designable properties and functions into materials. In the past years, a lot of complex ordered structures based on this assembly of nano building blocks have provide us plentiful revolutions in various areas such as electronics, therapeutics and so forth.²⁻⁵

With different from the common but old method, which constructs materials from atoms to molecules then to assemblies, in our group, to achieve desired structure
over various length scales, we use the “bottom-up” method to enable rigorous control and perfect fabrication of interactions between nano particles for achieve the design of materials. Relying on this method, we can achieve our precisely defined giant molecules from “nanoatoms” via “bottom-up” route and then take advantages of collective secondary interactions to enables materials achieved with a hierarchical structure and desired properties.

Through this route, we are planning to build a molecular system to precisely design materials and devices from smallest units via synthesis of giant molecules. In this process, the intermediate, giant molecules, is the key of the whole route. In accord with Staudinger’s concepts, common giant molecules studied by chemists are polymers or polymer-like molecules. Herein, giant molecule refers to those molecules smaller than traditional macromolecules but larger than small molecules in size. In our group, we hope to take advantages of uniform and regular giant molecule self-assemblies to precisely design materials.

To enable this goal, we need two prerequisites. First and foremost, we need essential building blocks to develop a series of giant molecules, which possess precisely defined shape, volume, structure, and properties. Various molecular particles in nano size extend the range of giant molecules in our group. These building blocks with 1nm size, rigid cage and modifiable surface includes Polyhedral Oligomeric Silsesquioxane (POSS), [60]Fullerene (C_{60}), and Polyoxometalates (POMs). In this thesis, my work will make use of POSS. Since Dr. Scott discovered the Polyhedral Oligomeric Silsesquioxane (POSS) in 1946, this nano-structure was developed its
scientific utilization rapidly.\textsuperscript{13} It greatly extends the range of nanoscience and kept the importance in chemical modification and physical manipulation with other compounds such as block copolymers or nanoparticles. Due to its nano-sized, compact structure and easily functionalized surface, POSS had been applied into biomedical, electric, mechanical and other areas.\textsuperscript{14} Therefore, as a common and useful unit in the self-assembly system, we made use of this rigid and precisely defined symmetry cage to extend the range of our molecule system.

Secondly, to achieve these molecules, we need a tool that can precisely and efficiently control the synthesis of giant molecules. This tool, called “click chemistry” coined by Sharpless \textsuperscript{15} in 2001, refers to those reactions with advantages of modular, wide in scope, very high yields, only easily-removed inoffensive byproducts, stereospecificity, simple conditions, and readily available starting reagents. By this method, a series of molecules can be created through precise chemical connection between different “building blocks”. Thus, it becomes an available and efficient way to achieve our precisely well-defined giant molecules. Herein, we use narrow distributed polymers and “nanoatoms” as building block to achieve those precisely well-defined giant molecules through click chemistry. Since the difference in yields and difficulty of separation of products and byproducts depends on the sequence of various reactions, a lot of previous work in our group has focused on how to optimize the synthesis route. The consequence of this exploration has been concluded into specific concept--“sequential click chemistry”, which is a highly efficient way to optimize the synthesis route.\textsuperscript{16-18}
In this thesis, we focus on the synthesis of a specific giant surfactant, which is a typical class of giant molecules. With the sequential click chemistry, giant surfactant, consisting of compact and polar molecular nanoparticles and flexible polymer tails of various composition and architecture at specific sites, can be easily and precisely achieved. However, the common click reactions used in sequential click chemistry method are CuAAC and thiol-ene reaction. Herein, we are planning to extend the click reaction types in this method through introducing thiol-Michael addition click reaction into the synthesis route. Same with thiol-ene click reaction, thiol-Michael addition, as a nucleophilic addition, is an efficient and precise reaction of click chemistry. Nevertheless, unlike the necessary of UV light in thiol-ene reactions, thiol-Michael only needs the catalyst of base to initiate the reaction. Therefore, it will be more efficient, more precise, and simpler reaction conditions. In accord with these, the Chapter Two will summarize some concepts of giant molecules, nanoatoms, sequential click chemistry and thiol-Michael addition reaction. Then, Chapter Three will primarily provide the experimental details of synthesis work and characterization work of self-assemblies. Chapter Four will focus on the discus of advantages through introducing this new click reaction. Finally, Chapter Five will present several conclusions which support the advantage of this thiol-Michael addition compared with the synthesis route of traditional sequential click chemistry.
CHAPTER II

BACKGROUND

2.1 Nanoatoms

Molecular nanoparticles (MNPs) refers to those nano-objects with persistent shape and volume with precisely-defined structure and desired symmetry.\textsuperscript{19} Although MNPs are used to indicate nanoparticle aggregates formed by small molecules via noncovalent interactions, herein, the nanoatom is not exactly fit this explanation of MNPs.

2.1.1 Definition

Nanoatom is a new concept, which refers to those shape- and volume-persistent molecular nanoparticles with precisely defined chemical structures, symmetry and surface functionalities.\textsuperscript{20}

These nanoparticles are the subclass of predictable and robust nanocompounds prepared by “quantized nanoelements” which indicate dendrimers or other molecular motifs with a well-defined 3D structure.\textsuperscript{21} Besides their rigid cage and well symmetry, nanoatoms should have the most important features which is its size around 1nm. And
appropriate size and easily-functionalized surface provide nanoatoms the potential to be elemental building blocks for the following synthesis of giant molecules by “bottom up” method. Following are several typical types of nanoatoms commonly used in our group.

2.1.2 Introduction of Common Types

(a)   (b)   (c)   (d)

Figure 1. Examples of typical nanoatoms: (a) C\(_{60}\); (b) POSS; (c) POM; (d) folded globular proteins.\(^{20}\)

The most important features of molecular nanoparticles (MNPs) are their precisely-defined molecular structure and the capability to enable precise modification. Furthermore, during reaction, it will not occur to MNPs for changing the overall profile and symmetry, and for eliminating the symmetry and well-defined sequence of functional groups.

Therefore, such MNPs can serve as nano building blocks for constructing giant molecules. The inherent properties of site-selective monofunctionalization, regio-selective multifunctionalization and simultaneous multisite functionalization enable the diverse surface chemistry from common precursor, and enable efficient and
stoichiometric combination between different building blocks. Molecules shown in Figure 1 are several types of MNPs, which are common used in our group researches.

MNP (a) consists of full of carbon atoms. It is [60]Fullerene, or \( C_{60} \). \( C_{60} \) is one member of fullerenes family which is a series of common materials serving as nano building blocks. \( C_{60} \) is the most accessible type among all fullerenes which possess closed-cage shape. However, carbon atoms on \( C_{60} \) surface are entirely stay in sp\(^2\)-hybridized state. Owing to lacking carbon-carbon double bonds in pentagonal rings, fullerene molecules present poor delocalization of electrons and no aromatic molecules. But the reactivity of \( C_{60} \) is greater than that of other carbon components with different chemical structures due to a symmetry structure of \( C_{60} \). Without hydrogen atoms, \( C_{60} \) cannot undergo substitution reactions unless derivatives have been synthesized. Therefore, all the reactions that are carried out on \( C_{60} \) molecules are associate with poorly-conjugated and electron-deficient alkenes. A lot of reactive groups, which can afford materials with useful properties and improve tractability, have successfully functionalized \( C_{60} \) surface. Although \( C_{60} \) is inert, the derivatives of \( C_{60} \) appear a high reactivity. However, this advantage also will bring opposite influence to application of \( C_{60} \). It leads to the synthetic process of \( C_{60} \) incorporated with ligands more vital, because control of polydispersity of products under such an accessible reaction condition has to be paid more attention. Whatever, stable nanometer structure of \( C_{60} \) makes it an ideal nano-colloid which is able to be widely used in preparation of colloidal nanoparticles. Recently, a living polymerization from \( C_{60} \) under catalyst of rutenium has been developed relying on ring-opening metathesis.
polymerization (ROMP) strategy. This ROMP process leads to modification of C$_{60}$ easier. Therefore, it broadens the applications of C$_{60}$.

MNP (b) primarily consisting of silicon atoms and oxygen atoms is Polyhedral Oligomeric Silsesquioxanes (POSS). POSS refers to a type of compound with all structures being the empirical formula of RSiO$_{3/2}$, where Si is the element silicon, O is oxygen and R can be hydrogen, alkyl group, aryl group, chloroethane group and so forth.

MNP (c) is a cluster carrying negative charges formed by early transition metals and oxygen atoms. This is polyoxometalate (POM) which can be regarded as metal cations formed oligomeric aggregates connected with oxide anions through a self-assembly process. After Berzelius first describing the yellow (NH$_4$)$_3$PMo$_{12}$O$_{40}$ (shown on Figure 2) in 1826 and Marignac’s discovery to definitely analyze the composition of hetero-polyacids in 1862, plentiful reports focus on types and structure definitions of POMs appear since their good molecular diversity relying on shape, charge and polarity enable POM possess good applications in catalysis chemistry, science of materials, and medicine.

Ninety years later, the precise structure of [Mo$_7$O$_{24}$]$^{28-}$ reported by Lindqvist, currently is used in the molecular system in our group. With unique topological and electronic versatility, this compound possesses precisely defined symmetry, shape and volume, and can be easily functionalized.

There are two common kinds of POMs: one containing only one class of metal cations and accompanied oxide anions, [MmO$_y$]$^{p-}$, is called isopoly compounds; the
other one containing more than one heteroatoms, $[XxMmOy]^{q^-}$, is defined as heteropoly compounds.\textsuperscript{24, 25}

Heteroatoms in POMs are located in buried when solventless, or on the surface when solvent accessible. Due to the readily modified structure and good electronic properties, POMs also can serve as desired nanoatoms to couple with other building blocks.

Molecular model shown above is the most commonly useful type in group. It is easy to demonstrate the structures of assemblages of POMs polyhedral linked by shared corners, edges and faces\textsuperscript{30} owing to the structure controlled by electrostatic and radius-ratio principles.
MNP (d) is 3D folded protein domains. The overall shape and the three dimensional conformation are held by strong secondary interactions between different residues of polypeptide chain. Therefore, this protein also presents the persistent cage-like shape, specific symmetry, and other properties.

2.1.3 Polyhedral Oligomeric Silsesquioxanes (POSS)

While the first oligomeric organosilsesquioxanes was classified by Scott in 1946, the desired cage structure (show as Figure 4) is synthesized in the past few years.

![Figure 4. Molecular model of POSS cage structures](image)

POSS particle has been frequently applied in many fields such as photoresist coatings for electronics and optical devices. The reason for its ubiquitous use is that its original structure has been successfully extended into a variety of synthetic new forms. POSS compound contains an inner inorganic framework consisting of silicon and oxygen. Corners on its surface can be externally modified by organic substituents. These substituents can be either hydrocarbon or a range of polar functional groups. It makes silsesquioxane surface-modifiable. Based on a variety of
functional groups, POSS can incorporate with polymer tails via being graft, blended and copolymerized with monomers. Owing to good solubility in monomers, POSS molecules can possess a true molecular dispersion in mixture. What’s more, this good solubility makes POSS monomers no dramatic changes during this process, and no phase separation in mixture. In addition, POSS is a chemical with a three dimensional highly symmetric structure which present a diameter from one to three nanometers. Although POSS molecules consist of silicon and oxygen elements which are similar to the components in silica or silicones, modification of POSS molecules surface by organic substitutes is easier than that of silica and silicones. With appropriate functionalities on its surface, POSS particle presents a perfect compatibility with polymers, biological systems or hydrophobic environment. Thus, such a modifiable nanoparticle is a useful nano building block for nanocomposites.

2.2 Giant Molecules

Giant molecules built upon nanoatoms introduced above through “bottom up” method possess monodispersity, precisely defined chemical structure with desired sequence, composition, and topology and the capability to form those precisely-defined 3D supramolecular structures. With the development of precisely synthesized macromolecules via coupling building blocks, it is possible to enable desired properties that not exist or is beyond the corresponding products in nature. With developing of MNPs and precisely synthesis through combining various
building blocks, three typical giant molecular formulations formed. In these giant molecules, MNPs and well-defined polymers are the nanoelements. Through them, giant molecules can achieve structure-property relationships.

2.2.1 Giant Surfactants

Figure 5. Typical model of giant surfactant: one or more than one compact and polar heads tethered with one or more than one polymer tails.20

Giant Surfactants possess structural features similar to small surfactants but are close to block copolymers in size.

2.2.1.1 Definition

Size amplification of those small-molecule surfactants develops a new type of materials with an intriguing approach.19 It is constructed by different building blocks which possess distinct shape and size, and enables plentiful ordered structures which can be driven by chemical incompatibility and geometric incommensurateness.34-37 The typical structure of giant surfactants consists of shape-persistent and modifiable 3D rigid cage in nano size which usually takes advantages of MNPs
commonly used in our group, and polymer chains served as tails with various molecular weight and diverse number of polymer chains precisely “grafted onto” \(^{38-39}\), \(^{16}\) or “grafted from” \(^{39-40}\) one or more reactive sites on the cage. For instance, in our group, there is one giant surfactant constructed by polystyrene (PS) endcapped by carboxylic acid-functionalized POSS synthesized via hydrosilylation and efficient functionalization reaction of thiol-ene reaction. \(^{38}\)

This type of molecules of giant surfactants captures those essential features of structures of surfactants consisting of small molecules, but possess larger sizes around 10 nanometers, which is comparable to the scale of block copolymers.

In accord with different tails and MNPs, there are several subcategories of giant surfactants, including giant bola-form surfactants, giant Gemini surfactants, giant multi-headed, and giant multi-tailed surfactants. And some important parameters, including the identity, number, and position of surface functional groups on MNPs, the polydispersity, composition, MW, sequence, and topology of the tethered tails. \(^{20}\)

2.2.1.2 Typical Sturture

With the precisely defined nanobuliding blocks and well established chemical reactions, a group of giant surfactant has been studied in our group.

Since the structure with rigid modifiable and rigid cage tethered with flexible polymer chains, the variations for this molecule include the type of MNPs, the functionalization of cages, number of heads, length of polymer chains, number of
polymer chains, and type of polymer chains. Following are some instances in our group. For example, as following figure shown, it was the first time that Wenbin Zhang, et al. ⁴⁰ synthesizes giant surfactant in our group.

![Image]

Figure 6. Giant surfactant consisting of rigid POSS head functionalized by various motifs on this surface and flexible polymer tails. ⁴⁰

Through stepwise process and precisely controlled reactions, there are three types of giant surfactants developed with various functionalizations.

![Image]

Figure 7. Schematic illustrations of various types of shape amphiphiles: (a) giant surfactants; (b) giant lipids; (c) multi-tailed giant surfactants; (d) giant bolaform surfactants; (e) giant gemini surfactants; and (f) multi-headed giant surfactants. ⁴¹

Molecules shown on Figure 6 are giant surfactant with six categories through variation of number and symmetry of heads and tails. ⁴¹ Through precisely controlled
reactions, such as copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction$^{15}$,  
and the thiol–ene reaction,$^{43-45}$ we can enable precisely and efficiently synthesize 
stoichiometric polymer–MNP ligation, and achieve the goal of efficient functionalization of multi-site on MNPs surface simultaneous.$^{38-39, 16, 40, 46}$ Among 
these molecules, there are two types of polymers, polystyrene (PS) and poly(ethylene oxide) (PEO), are commonly used in this molecule system in our group. Herein, Kan Yue,$^{41}$ takes advantage of nano-particle, POSS, multi-site functionalized by hydroxyl groups, as the rigid and polar nano “head”.

In accord with the concept of traditional giant surfactant composed of one head tethered on tail, there is a new name, which is “giant lipid”, proposed for molecule (b), that is hydroxyl groups-functionalized POSS (DPOSS) cage coupled with two PS tails on the same reactive site on surface of cages, and for molecule (c), that is DPOSS cage tethered with three PS tails with one conjunction point. This concept belongs to the category of giant surfactants. Finally there are three novel types of giant molecules belonging to sub categories of giant surfactants. They are molecule (d), that is PS tail tethered with hydroxyl groups-functionalized POSS (DPOSS) cage at both ends of the chain, molecule (e), that is Gemini surfactant consisting of two DPOSS particles and two PS chains with one junction site, and molecule (f), that is multi-head surfactant containing three DPOSS heads coupled at one end of one PS chain, shown on Figure 7.

Zhao Wang,$^{11}$ developed these two molecules shown on Figure 8 (a), (b) and (c), both of which are giant surfactants constructed by carboxylic acid-functionalized
POSS end-capped polystyrene (PS) (APOSS–PS), and by two APOSS cage coupled with two PS chains at one conjunction point. To these molecule structures, when molecules in solvent self-organizing into micelles, the PS tail reside in the core of micelles and is highly stretched as the feature respect to small-molecule surfactants.\textsuperscript{38,47}

![Figure 8](image_url)

Figure 8. Illustration by cartoon picture of (a) giant surfactant and (b) giant gemini surfactant; (c) depiction of molecular structures of giant gemini surfactant.\textsuperscript{11}

Molecule (b) or (c) is Gemini surfactant, which displays distinguish physical properties compared with surfactants with single chain, including higher surface activity and distinct morphologies within interfacial regions in solution.\textsuperscript{48-51}

Molecules above are carboxylic acid-functionalized C\textsubscript{60} (AC\textsubscript{60}) coupled with one or two PS chains at single reaction site, PSn–AC\textsubscript{60} and 2PSn–AC\textsubscript{60}. We use hydrophilic fullerene cage served as the rigid and polar head, which is comparable to hydrophilic POSS particle, and is also different from common amphiphilic fullerene-constructed blocks.\textsuperscript{53, 54} Fullerene, with persistent volume and shape of
particle, varies the identity of the “head”, in this molecular system. Although it would eliminate the electronic property of C$_{60}$ after reacted into amphiphiles, the surface functionalization gives rise to diverse morphologies due to the distinct amphiphilic property in molecules.$^{52}$

However, it is also possible that we can recover the electronic properties of C$_{60}$ through controlled potential electrolysis including formation of self-assembled morphologies, and remove of all the malonates.$^{55}$

![Figure 9](image)

Figure 9. Cartoon Illustration of the two types of Giant Surfactants with C$_{60}$ served as rigid and modifiable head. (a) Carboxylic acid-functionalized POSS (APOSS) coupled by one PS tail. (b) Two PS tails tether with on APOSS particle.$^{52}$

The reaction of the Huisgen 1,3-dipolar cycloaddition “click” reaction will enable the connection between functionalized C$_{60}$ with PS chains.

![Figure 10](image)

Figure 10. Cartoon Illustration of the two types of Giant Surfactants: left one is two heads composed of APOSS and isobutyl-functionalized POSS (BPOSS) tethered with
one polycaprolactone (PCL) tail; right one is single APOSS coupled by one PS tail and one PCL tail on single junction point.\textsuperscript{18}

Hao Su, et al.\textsuperscript{18} reported a general, useful and powerful precursor for synthesizing giant surfactants with a capability to change its structure by tune various variations. And taking advantages of the stepwise reaction method to precisely synthesize functional surfactants will enable different types of amphiphiles starting from this precursor. And the two polymer tails can be either symmetric one or asymmetric one. Successful synthesis, through precisely controlled reactions, of this molecule achieves the goal that POSS-based precursor with multiheaded and multi reactive site, is a robust and powerful model for readily accessing to giant amphiphiles with complicated architectures.

2.2.1.3 Intriguing Physics Phenomenon

According to both experimental data and results of computer simulation, it is found that giant surfactants can self-assemble into hierarchical structures in bulk states, and to self-organize into various micellar morphologies in specific solvents. There self-assembly behaviors can occur only under tiny differences between MNPs heads in shape and symmetry, and between the tethered polymer tails in the geometry and topology.\textsuperscript{52,56} To enable precisely control the materials with desired properties and functions, the tethered polymer tail should keep monodispersity, which is a
challenge in polymer chemistry. Until now, only limited number polymers, such as monodisperse long n-alkanes,\textsuperscript{57} oligo(\varepsilon\text{-caprolactones}),\textsuperscript{58} and oligo(L-lactic acids)\textsuperscript{59} can achieve this goal. Alternatively, the polymers with narrow dispersion sever as an approximating method to replace the monodisperse polymers, and can be prepared in a large amount by various techniques of living or controlled polymerization. Although we can extend the length of polymer tails, the tail used in studying self-assembly behavior is usually short, so that it is sensitive to the quantity of MW and MW siribution. In our group, there are some researches related with self-assembly behaviors reported. These examples occur in all of the bulk, solution, and thin film state, with molecules possessing less polydispersity. Furthermore, self-assembly research of these giant surfactants fill the gap between conventional small-molecule self-assembling materials and amphiphiles composed of block copolymers in a length scale greater than 10 nm.

In bulk state, two types of giant surfactants: DPOSS cage tethered with PS chain, and AC\textsubscript{60} tethered with PS chain were investigated.\textsuperscript{60} Giant surfactants possess rapid self-assembly dynamics with a time hours to achieve thermodynamical stability, due to the high diffusion mobility of their MNPs heads and fail to form entanglement for their tails.\textsuperscript{60} In Figure 11 (a), it shows a set of images of one-dimensional (1D) small-angle X-ray scattering (SAXS) profiles in reciprocal space and transmission electron microcopy (TEM) bright-field mass-thickness-contrast images, recorded from samples DPOSS-PSn, with the length of PS chain increasing from left to right.\textsuperscript{60} With the increment of the length of PS tail, which is equal to the volume fraction of
PS, it is found that according to SAXS profiles, the self-assembled structures vary from lamellae (Lam), to double gyroids (DG), to hexagonally packed cylinders (Hex), and further to body-centered cubic spheres (BCC). This result fits the phenomenon recorded by TEM.

Figure 11. One-dimensional SAXS profiles and TEM bright-field mass-thickness contrast images of the giant surfactant samples.

In these patterns, the strong contrast in TEM without external assistance indicates molecules possess high electron density contrast. This result demonstrates that with changing the volume fraction of hydrophilic part or hydrophobic part, the corresponding structure in bulk will be changed.
On the other hand, giant surfactant coupled by multiheads at short length of polymer tails, shown on Figure 11 B, indicates a structure change from Lam to Hex. Furthermore, topological isomers which consist of identical volume fraction of PS, but different polymer topologies are observed, shown on Figure 11 B that is \( \text{AC}_{60}\text{-PS}_{44} \) with a Lam structure and \( \text{AC}_{60}\text{-2PS}_{23} \) with a Hex structure. Therefore, besides the quantity of heads and the length of tail, the geometric cross-sectional area ratio is also a parameter during determining the phase structure. This phenomenon of sensitive to structure, which is lacking in block polymer system, is similar to that of small molecules.

In solution state, two types of giant surfactants: APOSS cage tethered with PS chain, and \( \text{AC}_{60} \) tethered with PS chain were investigated by Xinfei Yu. \(^{38}\)

Figure 12. (a-c) TEM and (d-f) cryo-TEM images of PS-APOSS micelles in solution with an initial concentration of 0.8 wt % and a final water content of 50 wt % for the following common solvents: (a, d) 1,4-dioxane; (b, e) DMF; (c, f) DMF/NaOH. Scale bars represent 80 nm. \(^{38}\)

Self-assembly morphologies in selective solvents of giant surfactant, APOSS-PS, are shown on Figure 12. Similar to small-molecule surfactants,
APOSS-PS molecule form the micelle morphology, and enable be varied through tuning the water content in solvent mixture. These morphologies recorded by normal TEM and cryo-TEM are exactly identical in these cases. Water will provide more ionization of carboxylic acid groups on the surface of POSS cage. With the increment the ionization of carboxylic acid (COOH) groups from left to right, morphologies are varied from vesicle to branched worm-like cylinders, and finally to spherical micelles. During this process, both the average diameter in TEM, and the polymer core radius proven by cryo-TEM are corresponding increasing. This variation of morphologies is a result of APOSS-APOSS interactions, which is created by the degree of ionization of COOH groups.

Figure 13. DLS results and TEM images (inset) of the self-organized morphologies of (a) PS$_{44}$-AC$_{60}$ and (b) 2PS$_{23}$-AC$_{60}$ in solution with a mixture of 1,4-dioxane and DMF (w/w = 1/1) as the common solvent and water as the selective solvent.

Similar to the structure variation in bulk state, changing the topologies of tails, with maintaining the PS volume fraction, will vary the morphologies in solution,
shown on Figure 13. Herein, APOSS serves as a well-defined hydrophilic head coupled with hydrophobic PS tail via thiol-ene reaction. Left molecule and right one are a pair of topological isomers. Left on is PS$_{44}$–AC$_{60}$ which self-assembled into spherical micelles with a hydrodynamic radius around 7.0 nm via analysis of DLS, which is less than that, about 100nm of 2PS$_{23}$–AC$_{60}$ that self-assembled into bilayered vesicles.

In accord with Figure 14, a fixed head but different numbers of hydrophobic tails will present various self-assemblies which exhibit micellar morphologies with distinctly different size in solvent. Molecules with different molecular weight of PS chains will self-assemble into spheres, cylinders and vesicles corresponding to increasing molecular weight.
2.2.2 Giant Shape Amphiphilies

Giant shape amphiphile are constructed by molecular segments which possess competing interactions and characteristics-persistent shapes. Nano building blocks served as parts of giant shape amphiphiles keep desired 3D shape with persistent geometry, symmetry, and preferred packing scheme, all of which are parameters for engineering of constructing hierarchical materials.  

![Figure 15. Typical model of giant shape amphiphiles: two heads with different shape and hydrophilic ability.](image)

In accord with shape amphiphiles, giant shape amphiphiles built upon MNPs, will have the similar amphiphilic properties to that of small molecules. Giant surfactant can be considered as one type of giant shape amphiphiles due to hydrophobic property of polymer tail relying on its shape. In our group, there are several examples studied. Based on “Janus” particle structure, an amphiphilic molecule is precisely designed with POSS-based molecules reported by Yiwen Li.  

Two POSS particles which keep distinct surface are connected via a short chain to create Janus feature. The overall molecular shape changes from spherical to dumbbell-or snowman-like. Two POSS cage particles are functionalized by different groups, one of which is modified by isobutyl groups and the other is separately covered by carboxylic acid, hydroxyl alkyl and fluorinated alkyl. Under simultaneous
control of size, shape and surface chemistry through “click” chemistry to offer a series of precisely defined particles, the difference in surface chemistry predominantly affects the driving force for self-assemblies. Isobutyl POSS (BPOSS) linked with carboxylic POSS (APOSS) self-assemble into a bilayered structure with heat-to-head, tail-to-tail arrangement of on the each others, which will further organized into a three-dimensional orthorhombic lattice.

2.2.3 Giant Polyhedra

![Figure 16. Typical model of giant polyhedral: various nanoatoms with different or similar polarity of surface stay together.](image)

There are two typical types. First is faceted MNP itself, and another is built upon multiple smaller MNP units. With size increased, shape and the shape persistency affect the structure formation more deeply.

2.3 Click Chemistry

Although reaction to form carbon-carbon bond is the most important way to construct materials with building blocks in carbonyl chemistry, gradually it goes far away from the organic chemistry goal of providing useful properties due to its more
and more complex reaction strategies which are justified only if they enables desirable properties efficiently. With summarizing a lot of works on organic synthetic strategies especially in drug discovery, development and manufacture, Dr. Sharpless, et al. proposed a powerful and selective carbon-heteroatom connections that can be used to assemble various building blocks (from small to large scale) into macromolecules. This is “click chemistry”, with following features: reactions are modular, high yields, wide in scope, with only inoffensive byproducts, easy purification by nonchromatographic methods, stereospecific; process should be insensitive to water or oxygen, facile starting materials and reagents, no solvent or benign solvent, and easily handling products; reactions possess high thermodynamic driving force, always larger than 20 kcal/mol; reactions are not only proceed rapidly to completion but also highly selective to a specific product. To enable the goal of efficient, precise, easily-process and highly-yielding preparation of our well-defined molecular structures, it is important to take advantages of “click chemistry” as a precise and efficient way for combining different building blocks into macromolecules with a desirable sequence of units. And during the formation of carbon-heteroatom bonds, carbon-carbon bonds are always made to accompany the combination process. There are many appropriate methods which can provide choices to design a desired nanobuilding block particle. For instance, Cycloaddition reactions, such as the 1,3-dipolar family, and also including hetero-Diels-Alder reactions; Nucleophilic ring-opening reactions, especially those strained heterocyclic electrophiles, like epoxides and aziridines; Carbonyl chemistry without aldol
formation such as making oxime ethers and aromatic heterocycles; Addition reactions onto carbon–carbon multiple bonds especially oxidation reactions like epoxidation,\textsuperscript{67} and aziridination,\textsuperscript{68} also including reactions related with Michael addition. These precisely controllable reactions provide us a lot of methods to construct molecules.

2.3.1 Copper-catalyst Azide Alkyne Cycloaddition

Azide alkyne Huisgen cycloaddition provides a fast access to efficiently make two unsaturated reagents combined with each other into a five-membered heterocycles (scheme is shown as Scheme 2.1). The 1,3-dipola cycloaddition reaction, designed by Huisgen in the 1960s, gains a focus when the concept of “click chemistry” developed.\textsuperscript{69} This special reaction occurs between acetylenes and azides, which has readily achieved reaction conditions. Furthermore, the stereospecific products also present high yield. All of these characters prove azide alkyne cycloaddition being an efficient access to producing new useful compounds.

\[
\begin{align*}
\text{R}_1\text{N}_3 + \equiv \equiv \text{R}_2 & \xrightarrow{\Delta} \begin{array}{c}
\text{R}_1\text{N} = \text{N} = \text{N} = \text{N} = \text{R}_2 \\
\end{array} + \begin{array}{c}
\text{R}_1\text{N}_3 = \equiv \equiv \text{R}_2 \\
\end{array}
\end{align*}
\]

Scheme 2.1. Scheme of generating 1,4 and 1,5 regioisomer \textsuperscript{70}

At first, the classical Huisgen 1,3-dipolar cycloaddition cannot match the above definition, due to producing a mixture of 1,4- and 1,5- regioisomers at room temperature within a very short reaction time.\textsuperscript{71} However, the discovery of copper(I) salts makes it possible. Under harsh conditions, copper(I) salts such as cuprous bromide are able to catalyze the reaction to a regioselective one which can achieve highly pure generation of 1,4-regioisomer, compared to Ru-based catalysis yields the
1,5-regioisomer (shown as Scheme 2.2).\textsuperscript{72} However, it is more favorable to choose copper salts because of its small band gap energy. In addition, another advantage of this reaction is that copper(II) salts present many good properties such as non-toxicity, environmental protection, high stability, and available recyclability.

![Scheme 2.2. 1,3-Dipolar cycloaddition between azides and alkynes.\textsuperscript{72}](image)

These supplying special advantages also support that azide alkyne cycloaddition is a good choice which can be used to precisely control the combination between various molecules.

2.3.2 Thiol-Ene Addition

The term “thiol-ene reaction” refers to the addition reaction of a thiol to an ene bond. The system of thiol-involved couplings, such as thiol-ene, thiol-bromo, and para-thiol, is a valuable tool for precise control the process of chemical reaction.\textsuperscript{44} Generally, it includes two types of reactions: the radical addition of thiols to enes; and the pathway takes advantages of base to enable nucleophile-mediated thiol additions with activated substrates.\textsuperscript{43} The thiol-ene reaction, with a scheme shown below, has
been developed about 100 years, with widely employed for preparing perfect networks or films.

Scheme 2.3. Typical thiol-ene reaction model. 44

As a type of click chemistry reaction, thiol-ene reaction has appealed to a lot of researchers.

Scheme 2.4. illustration of reaction (left) and the mechanism for the hydrothiolation of C=C bond under photoinitiator and ultraviolet. 43

With a lot of advantages, such as reactions can performed under plentiful conditions including processed by radical pathway 73 or mediated by nucleophiles or bases 74 with the existence of catalyst; starting materials of enes possessing a huge range of choices; strength of S-H bond desired; reaction performed rapidly and
insensitive to oxygen or moisture.\textsuperscript{43} Under the conditions of photoinitiator and irradiation of ultraviolet, scheme 2.4 demonstrates the initiation, propagation and termination steps of thiol-ene reaction by a radical pathway.\textsuperscript{43} Propagation includes two steps that are directly adding thyl radicals across $C=\text{C}$ bond forming carbon-centred radicals, and transferring chain to a second thiol to give the thiol-ene addition product, with anti-Markovnikov orientation and generation of new radicals.\textsuperscript{43}

2.3.3 Thiol-Michael Addition Click Reactions

![Scheme 2.5. Illustration of reaction (left) bearing an electron-withdrawing substituent and the mechanism for the hydrothiolation of $C=\text{C}$ bond under base-catalysis.\textsuperscript{43}](image)

All of base/nucleophile-mediated additions with activated enes can be described as conjugate additions or thiol-Michael addition click reactions.\textsuperscript{75} Unlike traditional thiol-ene reaction, this reaction occurs between a thiol and an electron-deficient ene.
Thiol-Michael reaction is performed under conditions of catalysis such strong base, mild base, Lewis acids, metals or organometallics. This reaction also can occur directly in solvent with high polarity, like DMF. Due to C=C need being activated by catalyst, this type of thiol-ene reaction is slightly less versatile than the radical-mediated thiol-ene reactio. However, a lot of commercially available enes possess a wide range of application through this type of reaction since there are suitable activated substrates.

There are several reactions belonging to Thiol-Michael Addition, such as thiol-Michael, sulfa-Michael and thiol-maleimide click. Thiol-Michael addition can be considered as base/nucleophile-mediated thiols added onto activated C=C bonds. Among plentiful examples of Michael reactions, it is always enough to catalyze the whole process to utilize weak base catalysts, such as NEt3, shown on Scheme 2.5. Net3 will react with thiol to create triethylammonium cation. Then, the powerful nucleophile will attack he electrophilic b-carbon of activated C=C bonds to form an intermediate of carbon-centered anion. Besides this, this type reaction also can be performed easily under the catalysis of simple primary/secondary amines or certain phosphines. Introduction of this reaction into our group to build up molecules system can simplify the functionalization of POSS head and connection between compact head with larger ligands or polymer tails.
2.3.4 Application Example

There are a lot of applications which combine both advantages of thiol-ene reaction and of thiol-Michael addition.

For example, 10-undecenoic acid (UDA) and a dithiol are “clicked” to prepare alkene-functionalized linear polymers by thiol-ene click step growth polymerization. Then, a modification of end groups by 2-Mercaptoethanol and 3-mercaptopropionic acid improves ability of functionalization of double bond via replacing it with hydroxyl and carboxylic acid to become biobased telechelic diols and diacids. This
methodology provides a fast, highly efficient and green approach used in precise synthesis.

2.4 Sequential Click Chemistry

Scheme 2.7. General sequential click strategy to functional materials.  

This is a type of “bottom up” methods to connect various molecular building blocks. It possesses highly efficiency, higher yields and simple execute. Starting from a readily available POSS precursor consisting of one alkyne and seven vinyl groups, CuAAC reaction efficiently bonds POSS and azide-functionalized polymers. Then, specific functionalities are connected to POSS head surface. In accord with the philosophy of “click”, this approach described here is robust and efficient for rapid construction of functional shape amphiphilies with complex structures and diverse molecular architectures.
CHAPTER III

MATERIALS AND INSTRUMENTS

3.1 Operation of Remove of Moisture and Oxygen

The Schlenk line consisting of a set of enclosed glass tubes and a vacuum pump provided a way to remove oxygen and moisture in the atmosphere. It was employed to the reaction of synthesis of sulphydryl polystyrene since there were a large quantity of intermediates sensitive to air and water.

![Figure 17. Typical construction of a Schlenk line](image)

Shown in the figure above, this Schlenk technique was usually employed on dealing with moisture or oxygen sensitive compounds with conditions less stringent.
than anionic polymerization. Figure showed a typical line, built from Pyrex®
glass. This line included a kind of two-way taps. One of them was used to vacuum,
and the other one, in contrast, was aerated insert gases. Oil bubbler and release for
pressure attached onto the end of this line were used to control the gas flows. There
were many applications for this Schlenk line used, such as removing hybrid gas,
drying samples, or providing protection of an inert atmosphere.

3.2 Chemicals Purchased for Use in Reaction.

There were many chemicals used in a set of experiments. Some were
chemicals and solvents certified by ACS that could be directly utilized as received.
However, others needed to be purified before inputted into reactions for prevent
side reactions from occurring. Following chemicals are used as received:
Tetrahydrofuran (THF, Certified ACS, EM Science), methanol (MeOH, Fisher
Scientific, reagent grade), ethyl acetate (EtOAc, Fisher Scientific), toluene (Certified
ACS), dichloromethane (Certified ACS), chloroform (Certified ACS), hexanes
(Certified ACS), Octavanyl POSS (VPOSS, Hybrid Plastics, >97%),
2,2-dimethoxy-2-phenylacetophenone (DMPA, Acros Organics, 99%), N,
N'-diisopropylcarbodiimide (DIPC, Acros Organics, 99%), Sodium Chloride (NaCl,
EMD, 99%), Hydrochloric Acid (HCl, Sigma, 37%), Mercaptoethanol (SH-OH,
Sigma, ≥99%), Triethylamine (EtN₃, ACROS, 99%), 4-(Dimethylamino)pyridine
(DMAP, Sigma, ≥99%), 3-Mercaptopropane-1,2-diol (SH-2OH, Apollp Scientific,
97%), Chloroform-D (CDCl$_3$, Cambridge Isotope Lab, Inc. 99.8%). On the other hand, purification via distillation for eliminating side reactions was necessary to following chemicals before reaction: Styrene (Aldrich, 99%), Propiolic acid (Sigma, 95%).

In this experiment, the molecule as building blocks, 1-ethyl isobutyrate-sulfhydryl styrene (PS-SH), was synthesized through RAFT polymerization according to the process on literature. The RAFT process would take advantages of the Schlenk line.

3.3 Instruments Used for Characterization of Products.

There were two techniques employed to characterize the products. And these techniques are commonly used to determine the chemical structure of molecules.

3.3.1 $^1$H NMR Spectroscopy

All $^1$H NMR, $^{13}$C NMR spectra were required to utilize a Varian Mercury 300 or Varian NMRS 500-01 spectrometer. Samples for NMR were prepared in solution with a concentration of 10-20 mg/mL in the solvent of CDCl$_3$ or DMSO-$d_6$ for $^1$H NMR or with a conc. of 50-80 mg/mL for $^{13}$C NMR. The reference of $^1$H NMR spectra was referenced to $\delta$ 7.27 ppm in CDCl$_3$ or $\delta$ 2.50 ppm in DMSO-$d_6$, and that of $^{13}$C NMR spectra was referenced to $\delta$ 77.00 ppm in CDCl$_3$ or $\delta$ 39.43 ppm in DMSO-$d_6$. 
3.3.2 Size-exclusion Chromatography (SEC)

Size-exclusion chromatography (SEC) analyses made uses of a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/10^3/10^4 Å), mixed bed (10^3/10^4/10^6 Å)] and a double detector system, which included a differential refractometer (Waters 410) and a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm). THF served as the eluent with a flow rate of 1.0 mL/min at 30 °C and as the solvent to dissolve samples for testing solution preparation with the concentration of ca. 5-10 mg/mL. The sample solutions were filtered through a 0.45 μm Teflon filter prior to injection. Regular SEC calibrations were conducted based on PS standards (Polymer Laboratories).

3.4 Molecular Design.

As discussed in introduction and background section, the subject of this project was to introduce the novel and readily-access thiol-Michael click addition into the giant molecules system in our group. Referred to articles reported from our group, when it comes to a set of molecules built upon “graft-to” method, it was found that the CuAAC cycloaddition was commonly and widely utilized in coupling of two building blocks, such as combining POSS cage with PS tails. And then, conventional thiol-ene reaction was employed to functionalize the surface of MNPs with various motifs. However, no examples that took advantages of thiol-Michael addition existed in this molecule system. Considering thiol-Michael addition as a
more readily-access and more easily post process method, it would be intriguing if this reaction was used. Relying on this addition, it was possible to build a system that molecules totally built upon thiol-ene click reaction, and to compare the efficiency and convenience with conventional thiol-ene reaction and CuAAC click reaction. To achieve this goal, a type of giant surfactant was designed with taking advantages of thiol-Michael addition for coupling of POSS cage and PS tails efficiently, following by making uses of conventional thiol-ene reaction for functionalization of cage surface, and finally characterizing its self-assembly behaviors to find differences and similarities in physical performance between this type of molecules and others synthesized by conventional method.

3.5 Synthesis Process

Scheme 8. Synthesis route for two different giant surfactants.
In accord with the subject of synthesis process proposed in molecule design section, a synthesis route was designed shown below.

3.5.1 Mono-functionalization of POSS Cage

A mixture of Vinyl-POSS (VPOSS) (10.000 g, 15.80 mmol) and 2-Mercapto-ethanol (1.232 g, 15.79 mmol) was dissolved into dichloromethane (150 ml) in a 250 ml beaker. After all of solid dissolved under stirring the solution, DMPA (0.05g 0.20 mmol) was added into beaker slowly. Then this solution was stirred under radiation of ultraviolet at room temperature (25 °C) for 40 minis.

During the reaction, 2-Mercapto-ethanol will react with more than one reactive site on the surface of VPOSS. The portion of various products with different reacted sites fitted statistics distribution.

![Scheme 9. Synthesis route of monofunctionalization of POSS cage.](image)

After 40 minis, the mixture was converted into flask to rotary evaporation for removing the solvent.

With eliminating all solvent, there was a large quantity of white powders left which contained the desired products with one head coupled with one tail. Then, the
product, VPOSS-OH, was purified from the mixture through column chromatography. Since byproducts of this reaction were multifunctionalization of VPOSS, they were easily removed from mixture.

Yield: 32%. $^1$H NMR (300MHz, CDCl$_3$, ppm): $\delta = 6.23$-5.78 (b, 18 H), 3.70 (d, 2H), 2.74(d, 2H), 2.66(d, 2H), 2.10 (s, 1H), 1.08(d, 2H).

5.2 Addition of Olefinic Group onto POSS Head

A mixture of VPOSS-OH (0.500 g, 0.70 mmol), DMAP (0.020 g, 0.16 mmol) and Propynoic acid (0.066 mg, 0.92 mmol) was added into a 100 ml flask with a magnetic stirring bar.

About 30 mL distilled dichloromethane was added into flask. The flask was sealed with rubber stopper and following covered a piece of parafilm. The mixture was stirred until the solution cleaned.

Then the flask was steeped in ice water bath, and the DIPC (1 mL) was dropped into the flask through needle injection at rate of 15 droplets/minis.

![Scheme 10. Addition of olefinic group onto POSS head.](image)

After stirring 24 h at room temp, this reaction was stopped, and the mixture was converted to a Buchner funnel to remove the urea powders created by DIPC reacting with water.
Finally, the product was following filtered to purification via silica gel column which is filled with silica domains in large diameter.

Yield: 90%. $^1$H NMR (300MHz, CDCl$_3$, ppm): $\delta = 6.4$-6.39 (b, 3H), 6.38.-5.80 (b, 18H), 4.31 (d, 24H), 2.80 (d, 2H), 2.71 (d, 2H), 1.10(d, 2H).

3.5.3 Synthesis of Giant Surfactant Consisting of One Head Tethered One Tail

A mixture of precursor, VPOSS-ene (0.200 g, 0.26 mmol), EtN$_3$ (6mL) and prepared PS-SH (1.000 g, 0.33 mmol) was added into a 100 ml flask with a magnetic stirring bar.

Then, it was dissolved in the solvent of dichloromethane (30 mL). After reaction stirred 2 h, the mixture was converted into separating funnel following by a wash of organic phase with prepared solution consisting of saturated NaCl solution mixed with modest HCl for three times to remove EtN$_3$. Then the white solid product was obtained. This product was impure so that a following purification by a column
chromatography was processed. Finally the product, giant surfactant with one rigid head tethered with one polymer tail, VPOSS-PS, was obtained.

Yield: 73%. $^1$H NMR (300 MHz, CDCl$_3$, ppm): δ = 7.37-6.29 (b, 145H), 6.27-5.83 (b, 18H), 4.56 (m, 1H), 4.13 (d, 2H), 3.66 (d, 2H), 2.68 (d, 2H), 2.37 (d, 2H), 2.20-1.12 (b, ), 0.99 (overlap, 87H).

3.5.4 Addition of Double Hydroxyl Groups

A mixture of VPOSS-ene (0.200 g, 0.26 mmol), SH-2OH (0.562 g, 0.52 mmol) and EtN$_3$ (6mL) was added into a 100 ml flask with a magnetic stirring bar following by sealed by a parafilm.

![Scheme 12. Synthesis of addition of double hydroxyl groups.](image)

Then, it was dissolved by the solvent of dichloromethane (30 mL). Stirring this solution mixture until the solution was cleaned. After reaction stirred 2 h, the mixture was converted into separating funnel following by a wash of organic phase with prepared solution consisting of saturated NaCl solution mixed with modest HCl for three times to remove EtN$_3$. Then the white solid product was obtained. This product was impure so that following purification by a column chromatography was
processed. Finally the product, giant surfactant with one rigid head tethered with one polymer tail, VPOSS-2OH, was obtained.

Yield: 81%. $^1$H NMR (300MHz, CDCl$_3$, ppm): $\delta = 6.14$-$6.35$ (b, 18H), 4.26 (m, H), 4.28(t, 24H), 3.82 (d, 2H), 3.71 (d, 2H), 3.55 (d, 2H), 2.81 (d, 2H), 2.75 (d, 2H), 2.71 (d, 2H), 2.61 (d, 2H), 1.92 (s, 2H), 1.26 (quadruplet, 7H), 0.88 (d, 2H).

3.5.5 Addition of Two Olefinic Groups

A mixture of VPOSS-2OH (0.200 g, 0.23 mmol), DMAP (0.010 g, 0.08 mmol) and Propynoic acid (0.066 g, 0.92 mmol) was added into a 100 ml flask with a magnetic stirring bar.

About 30 mL distilled dichloromethane was added into flask. The flask was sealed with rubber stopper and following covered a piece of parafilm. The mixture was stirred until the solution cleaned. Then the flask was steeped in ice water bath, and the DIPC (1 mL) was dropped into the flask through needle injection at rate of 15
droplets/minis. After stirring 24 h at room temp, this reaction was stopped, and the mixture was converted to a Buchner funnel to remove the urea powders created by DIPC reacting with water. Then, the product was following filtered to purification via silica gel column which is filled with silica domains in large diameter.

Yield: 92%. $^1$H NMR (300MHz, CDCl$_3$, ppm): $\delta = 6.46$-$6.38$ (b, 6H), 6.17-$5.85$ (b, 18H), 5.25 (m, H), 4.45 (d, 2H), 4.36 (d, 2H), 4.23(d, 2H), 2.86 (d, 2H), 2.82 (d, 2H), 2.75 (d, 2H), 2.66 (d, 2H), 1.10 (d, 2H).

3.5.6 Synthesis of Giant Surfactant Composed of One Head with Two Tails

A mixture of VPOSS-2ene (0.100 g, 0.09 mmol), EtN$_3$ (6mL) and prepared PS-SH (1.000 g, 0.33 mmol) was added into a 100 ml flask with a magnetic stirring bar.

Scheme 14. Synthesis of giant surfactant consisting of one head tethered two tails.

Then, it was dissolved in the solvent of dichloromethane (30 mL). After reaction stirred 2 h, the mixture was converted into separating funnel following by a
wash of organic phase with prepared solution consisting of saturated NaCl solution mixed with modest HCl for three times to remove EtN₃. Then the white solid product was obtained. This product was impure so that a following purification by a column chromatography was processed. Finally the product, giant surfactant with one rigid head tethered with one polymer tail, VPOSS-2PS, was obtained.

Yield: 71%. ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.37-6.29 (b, 145H), 6.27-5.83 (b, 18H), 4.56 (m, 1H), 4.13 (d, 2H), 3.66 (d, 2H), 2.68 (d, 2H), 2.37 (d, 2H), 2.20-1.12 (b, 2H), 0.99 (overlap, 87H).
CHAPTER IV

RESULTS AND DISCUSSION

Figure 18. Molecular structure of the product, VPOSS-PS.

This figure above shows the molecular structure of the final product of the giant surfactant, VPOSS-PS. VPOSS particle with a cubic shape served as highly symmetric core with well-defined nanometer size and spherical shape.

Figure 19. $^1$H NMR spectrum of final product, VPOSS-PS
According to this $^1$H NMR spectrum, every peak corresponding to a specific type of hydrogen atoms is correct. It indicates the chemical structure of VPOSS-PS is correct. The ratio of integration value of hydrogen locating benzene to that of value of hydrogen locating on vinyl group is almost 13. This ratio demonstrates that this molecule is one head tethered on tail. Besides the $^1$H NMR spectrum, the $^{13}$C NMR spectrum of final product is characterized to verify the correction of types of carbon atoms in VPOSS-PS molecule. According to this spectrum, it further proves that the chemical structure of VPOSS-PS is correct.

![Figure 20. $^{13}$C NMR spectrum of final product, VPOSS-PS.](image)

This following picture shows the complicated molecular structure of the final product in second reaction route, VPOSS-2PS. VPOSS particle with a cubic shape served as highly symmetric core with well-defined nanometer size and spherical shape. According to this $^1$H NMR spectrum, every peak corresponding to a specific type of hydrogen atoms is correct. It indicates the chemical structure of VPOSS-2PS is
correct. The ratio of integration value of hydrogen locating benzene to that of value of hydrogen locating on vinyl group is almost 18.

Figure 21. Molecular structure of the product, VPOSS-2PS.

Figure 22. $^1$H NMR spectrum of final product, VPOSS-2PS.

This ratio demonstrates that this molecule is one head tethered on tail. This ratio demonstrates that this molecule is one head tethered on tail. Besides the $^1$H NMR spectrum, the $^{13}$C NMR spectrum of final product is characterized to verify the correction of types of carbon atoms in VPOSS-2PS molecule. According to this spectrum, it further proves that the chemical structure of VPOSS-2PS is correct.
To further demonstrate the difference between one tail and two tails molecules, GPC was used to characterize these two molecules respectively.

Figure 23. $^{13}$C NMR spectrum of final product, VPOSS-2PS.

Figure 24. Comparison of GPC curve of VPOSS-PS and VPOSS-2PS. When it comes to compare with two molecules GPC, VPOSS-2PS possess a less retention time than VPOSS-PS, which indicates change the topologies of molecules
without varying the length of polystyrene, the volume will increase with the increment of number of PS tails. Herein, GPC shows a narrow distribution of both products. It indicates that this giant surfactant possesses the essential features of structures.
CHAPTER V

SUMMARY

This project successfully demonstrates that thiol-Michael click addition is a robust and powerful method to synthesize giant surfactant. This successful synthesis indicates that this method can be introduced into our molecule systems. And its readily access, high yields, and rapid react enable it a successful substitution of other precisely controlled click reaction, like CuAAC reaction. In according with this successful attempting to precisely coupling of head particles and tails, we can build up a advanced molecule system which can be precisely controlled and achieved only relying thiol-ene reactions. This project will extend the molecule system in our group.
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APPENDIX

During the process of synthesis of VPOSS-PS, there will be two intermediates created, VPOSS-OH, and following VPOSS-ene. Figure shown below demonstrate the correct chemical structure of these two intermediate molecules.

Figure 25. $^1$H NMR spectrum of VPOSS-OH

In Figure 25, it shows the $^1$H NMR spectrum of monofunctionalized VPOSS.

Figure 26. $^1$H NMR spectrum of VPOSS-ene
According to this NMR profile, it indicates a right structure for monofunctionalized VPOSS. In Figure 26, it shows us the $^1$H NMR spectrum of the precursor for synthesis of VPOSS-PS. According to this NMR profile, it demonstrates the molecular structure of VPOSS-PS precursor is correct.

Before the synthesis of VPOSS-2PS, there will be two intermediates created, VPOSS-2OH, and following VPOSS-2ene. Following profiles are recorded by $^1$H NMR. During the process from Figure 27 to Figure 28, it shows us the correct chemical structure of these two intermediate molecules.

Figure 27. $^1$H NMR spectrum of VPOSS-ene

Figure 28. $^1$H NMR spectrum of VPOSS-ene