SYNTHESIS OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANE(POSS)-BASED
SHAPE AMPHIPHILES WITH TWO POLYMERIC TAILS OF SYMMETRIC OR
ASYMMETRIC COMPOSITIONS

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SYNTHESIS OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANE(POSS)-BASED SHAPE AMPHIPHILES WITH TWO POLYMERIC TAILS OF SYMMETRIC OR ASYMMETRIC COMPOSITIONS

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ABSTRACT

The investigation in the design and synthesis of a new class of well-defined functionalized polyhedral oligomeric silsesquioxane (POSS)-based shape amphiphiles with two polymeric tails of symmetric or asymmetric compositions raised intensive attention recently. Polyhedral oligomeric silsesquioxanes (POSS), regarded arguably as the smallest silicon nanoparticles with cage diameter around 1.0 nm, are promising nanoscopic building blocks for the development of functional materials with hierarchical structures due to their conformational rigidity, shape persistence and diverse peripheral functionalities. The sequential “grafting-from” approach and thiol-ene “click” surface functionalization were employed in the synthesis, which involved thiol-ene monofunctionalization of octavinylPOSS, ring-opening polymerization, atom transfer radical polymerization for “grafting” polymer tails from the POSS-based macro-initiators with controlled molecular weight and low polydispersity, and subsequent thiol–ene “click” surface functionalization. Surprisingly, the vinyl groups on POSS cages were compatible with atom transfer radical polymerization (ATRP) conditions. Thiol-ene “click” chemistry then was applied to give versatile surface functionalizations onto POSS cage. In this way, the polymer chain composition as well as POSS surface chemistry can be tuned separately and efficiently. All the products have been thoroughly characterized by $^1$H NMR, $^{13}$C NMR, FT-IR, size exclusion chromatography and MALDI-TOF mass
spectrometry to establish their chemical structures and purities. These POSS-based shape amphiphiles with novel architecture could serve as important model systems in the study of their self-assembling behaviors in bulk, solution, and thin-film states.
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CHAPTER I

INTRODUCTION

The synthesis, assembly and applications of shape amphiphiles have significantly intensified over the past two decades. The unique structures assembled by Janus particles make this class of materials very attractive as promising candidates in diverse areas\textsuperscript{1-5} ranging from biomedical applications\textsuperscript{2} to electronic devices.\textsuperscript{3} My graduate thesis focus on the synthesis of functional polyhedral oligomeric silsesquioxane (POSS)-based shape amphiphiles with two polymeric tails of symmetric or asymmetric compositions using the “grafting-from” approach and “click” chemistry (Scheme 1). Precisely-defined macro-initiators were simply prepared by mono-functionalization of 1-thioglycerol onto VPOSS cage via stoichiometry-controlled thiol-ene “click” chemistry\textsuperscript{6-9} and further esterification, from which polymer chains, including polycaprolactone (PCL) and polystyrene (PS), were grown by ring opening polymerization (ROP) and atom transfer radical polymerization (ATRP), respectively. Surprisingly, the vinyl groups on POSS were found to be compatible with atom transfer radical polymerization (ATRP) conditions. All the targeted molecules have been thoroughly characterized by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, MALDI-TOF mass spectrometry, self-assembly behavior. The method provides a
versatile platform for the synthesis and study of shape amphiphiles with novel architectures and composition.

Scheme 1 General Synthetic Approach using a Combination of “Grafting-from” Strategy and Thiol-Ene “Click” Chemistry. (i) 2-bromoisobutyryl bromide, Et$_3$N, CH$_2$Cl$_2$, r. t.; (ii) styrene, CuBr, PMDETA, toluene, 110 °C; (iii) ε-caprolactone, Sn(Oct)$_2$, toluene, 90 °C; (iv) HOCH$_2$CH$_2$SH, DMPA, THF, r. t., 15 min
CHAPTER II

BACKGROUND

2.1 A Brief Review of Shape Amphiphiles

The concept, shape amphiphiles, (see Figure 1) usually refers to a kind of molecules with difference in the shape of molecular segments. Recently, a new class of shape amphiphiles with both of shape and interaction incommensuration has been designed and synthesized by the use of nanoparticles-tethered polymers. Two important factors greatly effect the self-assembly of this new class of shape amphiphiles: entropic contributions and enthalpy contributions. The shape-persistent nanoparticles may contribute a new packing parameter which is a factor to measure the shape commensuration and this can be regarded as entropic contributions, while the important interaction effects like amphiphilic interaction, specific interaction between DNAs, can be countered as enthalpy contributions. In block polymer systems, the enthalpy contributions dominate the self-assembly either in solution or in bulk, but in
shape-persistent system, like Polyhedral Oligomeric Silsesquioxane (POSS)-Based Janus Particles, the entropic contributions play an important role.\textsuperscript{13} Giant surfactant, like giant lipid, is a typical kind of new shape amphiphiles, which has a nanometer-sized polar or macroionic head group and one or two hydrophobic polymer chains as tails.\textsuperscript{14} Generally the large polar or macroionic rigid heads could provide several intrinsic effects, such as shape effect or multivalent interactions, to balance the entropy and enthalpy contributions in the self-assembly behavior of the whole macromolecule. Computer simulation and experiments shown that these giant surfactants could not only self-assemble into diverse hierarchical supramolecular structures, but also exhibit different self-assembly behavior by tuning the shape and symmetry of the macroionic heads as well as the geometry and topology of the tethered polymer tails.\textsuperscript{15-16} A variety of nano-building blocks, like enzyme/protein,\textsuperscript{17-20} dendrimers,\textsuperscript{21-22} buckyball,\textsuperscript{23} polyoxometalate clusters,\textsuperscript{24-25} cyclodextrin,\textsuperscript{26} and functionalized polyhedral oligomeric silsesquioxane (POSS) nanocages\textsuperscript{27-28} have been investigated as the head groups of series of shape amphiphiles, tethered with tails of different chemical component ranging from short length alkyl chain to long length polymers. Among these nano-building blocks, POSSs have become a widely used class of candidate for shape amphiphiles because of their precise-defined molecular structures and tunable surface chemistry.\textsuperscript{27-29}

\textbf{“Grafting-Onto” Approach}

\textbf{“Graft-From” Approach}

Figure 2. Illustration of “grafting-from” and “graft-onto” approach to obtain the nanoparticle-polymer conjugates
2.2 Methods for Syntheses of Nanoparticles-Polymers Conjugates

Polyhedral oligomeric silsesquioxanes (POSS), regarded arguably as the smallest silicon nanoparticles with cage diameter around 1.0 nm, are promising nanoscopic building blocks for the development of functional materials with hierarchical structures due to their conformational rigidity, shape persistence and diverse peripheral functionalities.\textsuperscript{30-35} As has mentioned above, the self-assembly behaviors of this shape-persistent nanoparticles are absolutely different from those of di-block copolymers, making POSS a nice candidate as a build block to develop functional materials with distinct properties. A variety of well-defined POSS cages with distinct nature of functionalities, such as hydrophilic,\textsuperscript{24, 36} fluorinated \textsuperscript{37-38} or biomolecules-modified,\textsuperscript{39-40} have been prepared by simultaneous multiple-site functionalizations including hydrolytic condensation of trifunctional organosilicons,\textsuperscript{38} Cu(0)-catalyzed Huisgen [3+2] cycloaddition reaction,\textsuperscript{39} and thiol-ene reaction.\textsuperscript{24, 36-37, 40} Both of “grafting-from” (growing polymer chain from a well-defined nano-initiator) and “grafting-onto” (coupling a pre-formed polymer chain to the nanoobject strategies) (see Figure 2) have been successfully employed to explore the well-defined POSS-based shape amphiphiles with various architectures, such as POSS end-capped one polymer chain\textsuperscript{36, 41-42} and POSS tethered two polymer tails.\textsuperscript{12, 41} Compared with “graft-from” approach of growing a polymer chain from an octa-functionalized POSS macroinitiator, the “graft-onto” strategy exists several disadvantages in the synthesis of functionalized POSS-based giant amphiphiles. For example, high polarity adducts like unreacted polymers are difficult to remove. It is thus desired to construct novel amphiphilic nanoparticles-polymers conjugates by combining these versatile POSS building blocks together with polymers for the creation of novel supramolecular
structures which may possess advanced materials’ properties. Our group reported a giant surfactant consisting of carboxylic acid-functionalized POSS end-capped polystyrene (PS) (APOSS-PS). The efficient hydrosilylation reaction was applied to obtain PS with controlled molecular weight and low polydispersity. Subsequent thiol–ene reaction gave precise surface functionalization meaning that all seven vinyl groups on one POSS cage surface were fully reacted. It was found that the APOSS-PS could self-assembled into different micellar morphologies, from spheres to cylinders and further to vesicles with increasing the ionization of carboxylic acid groups in selective solvents.\textsuperscript{36} Interestingly, the polystyrene tail is highly stretched, a feature like small molecule surfactant,\textsuperscript{36-43} compared with block polymer micelles, of which is coil in the core.\textsuperscript{44-45}

Nanoparticles–polymer conjugates syntheses are now receiving increasing attention as applications become more widely known.\textsuperscript{42} Established synthetic approaches (such as attachment of polymers to preformed nanoparticles via non-covalent and covalent interactions) have recently been supplemented by approaches based on living radical polymerization techniques combined with orthogonal conjugation chemistries. The new synthetic methods have opened up new opportunities to create nanoparticle-polymer conjugates with improved control over the number, conjugation-site and orientation of conjugated nanoparticles, together with the molecular architecture. This enhanced design control is important in optimizing the performance of nanoparticle-polymer conjugates in many applications such as nanoreactors, advanced drug delivery, imaging and biosensor systems and the development of smart purification strategies for biotechnological processes. Further new opportunities can be envisaged by combining multiple nanoparticles within one unit structure (using the polymer not
just as a binder, but also to imbue favorable properties such as increased stability, modified bioactivity, tailored self-assembly and phase-transition behavior).
3.1 Materials

Styrene (99%, Aldrich) and e-caprolactone (97%, Aldrich) were purified by distillation from calcium hydride under reduced pressure prior to use. Tetrahydrofuran (THF, Certified ACS, EM Science), methanol (Fisher Scientific, reagent grade), toluene (Certified ACS), dichloromethane (Certified ACS), chloroform (Certified ACS), and hexanes (Certified ACS) were used after distillation. Cuprous bromide (CuBr, Aldrich, 98%) was freshly purified by stirring in acetic acid overnight, washed with acetone, and dried in vacuum. Tin(II) 2-ethylhexanoate [Sn(Oct)$_2$, Aldrich, > 95%] was fractionally distilled and diluted with anhydrous degassed toluene to make a 1 M solution before use. Octavinyl POSS (VPOSS, Hybrid Plastics, >97%), N,N,N’,N’’,N’’-pentamethyldiethylene-triamine (PMDETA, Aldrich, 99%), triethylamine (TEA, Aldrich, 99%), 2-bromoisobutyryl bromide (Aldrich, 98%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Acros Organics, 99%), 1-thioglycerol (Sigma, >99%), 2-mercapoethanol (Aldrich, 99 %) were used as received. Silica gel (VWR, 230-400 mesh) was activated by heating to 140 °C for 12 h.
3.2 Characterization.

Size exclusion chromatographic analyses (SEC) for the synthesized polymers were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/103/104 Å), mixed bed (103, 104, 106 Å)], and a triple detector system. The three detectors included a differential refractometer (Waters 410), a differential viscometer (Viscotek 100), and a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm). THF was used as eluent with a flow rate of 1.0 mL/min at 30 °C.

All $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were acquired in CDCl$_3$ (Aldrich, 99.8% D) using a Varian Mercury 300 NMR and 500 NMR spectrometer. The $^1$H NMR spectra were referenced to the residual proton signals in the CDCl$_3$ at δ 7.27 ppm. The $^{13}$C NMR spectra were referenced to $^{13}$CDCl$_3$ at δ 77.00 ppm.

Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting material films on KBr plates from polymer solutions with subsequent drying at 40 - 50 °C. The data were processed using Win-IR software.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). All spectra were measured in positive reflection or linear mode. The instrument was calibrated prior to each measurement with external PMMA or PS standards at the molecular weight under consideration. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Santa Cruz Biotechnology, Inc., >99%) served as matrix and was prepared in CHCl$_3$ at a concentration of 20 mg/mL. Sodium
trifluoroacetate or silver trifluoroacetate served as cationizing agent and was prepared
in MeOH/CHCl₃ (v/v = 1/3) at a concentration of 5 mg/mL or 10 mg/mL. All the
samples were dissolved in CHCl₃. The matrix and salt were mixed in a ratio of 10/1
(v/v). 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 (the 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 undesired polymer fragmentation and to
maximize the sensitivity.

Thin-layer chromatographic analyses of the functionalized polymers were carried
out on by spotting samples on flexible silica gel plates (Selecto Scientific, Silica Gel
60, F-254 with fluorescent indicator) and developing using toluene or its mixture with
other polar solvents as eluents.

3.3 Preparation Method

HO-(VPOSS)-OH. Octavinyl POSS (2 g, 3.159 mmol), 1-thioglycerol (341 mg,
3.159 mmol), and DMPA (5 mg, 0.013 mmol) were dissolved in 60 mL of THF.
After irradiation under a 365 nm UV lamp at room temperature for 30 minutes, the
solution was concentrated and then precipitated in deionized water. The white solid
was collected after filtration and dried under vacuum overnight. Then crude sample
was further purified by flash column chromatography (silica gel, with THF as the
eluent) to afford the final product (677 mg, 29 %). ¹H NMR (300 MHz, CDCl₃, ppm,
δ): 6.21-5.82 (m, 21H, CH=CH₂), 3.77 (m, 2H, CHOCH₂OH), 3.54 (m, 1H,
CHOHCH₂OH), 2.78-2.64 (m, 4H, CH₂SCH₂CHOH), 1.09 (t, 2H, SiCH₂). ¹³C NMR
(75 MHz, CDCl₃, ppm, δ): 137.44, 128.62, 69.84, 65.38, 35.53, 26.38, 13.89. FT-IR (KBr) v (cm⁻¹): 3400 (O-H), 1108 (O-Si-O). MS (MALDI-TOF): Calcd. for C₁₉H₃₂O₁₄Na₈Si₈ 762.96, Found: 762.20 (M·Na)⁺.

Br-(VPOSS)-Br. HO-(VPOSS)-OH (300 mg, 0.405 mmol) and 25 mL of anhydrous CH₂Cl₂ were added into a 50 mL round-bottom flask equipped with a magnetic stirrer. After complete dissolution, TEA (0.376 g, 3.75 mmol) was added. The solution was cooled to 0 °C in an ice bath and 2-bromoisobutyryl bromide (0.467 g, 2.03 mmol) in 5 mL of anhydrous CH₂Cl₂ was added dropwise within 20 mins. The solution was stirred at room temperature for 24 h. The mixture was then diluted with 200 mL CH₂Cl₂ and washed three times with water. The organic layer was dried over anhydrous Na₂SO₄ overnight and evaporated under vacuum after filtration. The residue was purified by flash column chromatography on silica gel with hexanes/CH₂Cl₂ (v/v = 1/1) as eluent to afford the targeted product (396 mg, 94%).

¹H NMR (300 MHz, CDCl₃, ppm, δ): 6.21-5.82 (m, 21H, CH=CH₂), 5.23 (m, 1H, CH₂CH(OCO)CH₂), 4.56 (m, 1H, CH₂CH(OCO)CH₂OCO), 4.37 (m, 1H, CH₂CH(OCO)CH₂OCO), 2.85-2.72 (m, 4H, CH₂SCH₂CH), 2.00 [s, 6H, OCOCBr(CH₃)₂], 1.10 (t, 2H, SiCH₂). ¹³C NMR (75 MHz, CDCl₃, ppm, δ): 176.81, 171.17, 137.08, 128.63, 72.16, 64.70, 55.42, 55.28, 31.64, 30.73, 30.54, 30.03, 27.05, 13.07. FT-IR (KBr) v (cm⁻¹): 1740 (C=O), 1112 (O-Si-O). MS (MALDI-TOF): Calcd. for C₂₇H₄₂Br₂NaO₁₆Si₈ 1058.86, Found: 1058.99 (M·Na)⁺.

Br-(VPOSS)-OH. The procedure is similar to that of Br-(VPOSS)-Br except a more diluted solution [HO-(VPOSS)-OH (300 mg, 0.405 mmol) in 60 mL anhydrous CH₂Cl₂] and a stoichiometric amount of 2-bromoisobutyryl bromide (0.093 g, 0.405 mmol) in 20 mL of anhydrous CH₂Cl₂ were used. After purification by flash column chromatography on silica gel with hexanes/CH₂Cl₂ (v/v = 1/2) as the eluent, the
product was obtained as a white powder (172 mg, 38%). $^1$H NMR (300 MHz, CDCl$_3$, ppm, δ): 6.21-5.82 (m, 21H, CH=CH$_2$), 4.28 (m, 2H, CH$_2$CHOHCH$_2$OCO), 3.98 (m, 1H, CH$_2$CHOHCH$_2$OCO), 2.83-2.62 (m, 4H, CH$_2$SCH$_2$CH), 1.97 [s, 6H, OCOCBr(CH$_3$)$_2$], 1.10 (t, 2H, SiCH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm, δ): 171.55, 137.11, 128.57, 68.34, 67.72, 55.57, 35.64, 30.73, 29.71, 26.54, 13.11. FT-IR (KBr) v (cm$^{-1}$): 1738 (C=O), 1112 (O-Si-O). MS (MALDI-TOF): Calcd. for C$_{23}$H$_{37}$BrNaO$_{15}$SSi$_8$: 910.91, Found: 911.02 (M∙Na)$^+$.

PCL-(VPOSS)-PCL. HO-(VPOSS)-OH (42 mg, 0.057 mmol) was added into a Schlenk flask equipped with a magnetic stirrer, and dried under vacuum for 3 hours at 25 °C. ε-Caprolactone (2.0 mL), Sn(Oct)$_2$ (30 mg, 0.075 mmol), anhydrous toluene (20 mL) were introduced into the flask under nitrogen protection by syringe. The mixture was degassed by three freeze-pump-thaw cycles, and then immersed into a 90 °C oil bath. After 5 hours, the flask was quenched by immerging into liquid nitrogen. The solution was precipitated into a large excess of cold methanol three times. After filtration, the sample PCL-(VPOSS)-PCL was collected and dried under vacuum overnight to give a white powder (300 mg; Conversion: 21%). SEC: Mn = 8.5 kg/mol, PDI = 1.08.

PCL-(HPOSS)-PCL. PCL-(VPOSS)-PCL (Mn = 8.5 kg/mol, 100 mg, 0.012 mmol), 2-mercapoethanol (10 mg, 0.12 mmol), and DMPA (2 mg, 0.005 mmol) were dissolved in 5 mL of THF, followed by irradiation with UV 365 nm for 15 minutes. The solution was then precipitated into cold methanol solution three times. The sample PCL-(HPOSS)-PCL was collected and dried under vacuum overnight to afford a white powder (88 mg; Yield: 82%). SEC: Mn = 8.6 kg/mol, PDI = 1.06.

PS-(VPOSS)-PS. Br-VPOSS-Br (150 mg, 0.14 mmol), styrene (4.0 mL), CuBr (16 mg, 0.14 mmol) and 5 mL of anhydrous toluene were added into a reaction flask
equipped with a magnetic stirrer. The mixture was degassed by three freeze-pump-thaw cycles. PMDETA (25 mg, 0.14 mmol) was introduced into the mixture under nitrogen protection and the mixture became light green. After three extra freeze-pump-thaw cycles, the flask was immersed into a 110 °C oil bath. After 1.5 hours, the flask was quenched by immersing into liquid nitrogen. The solution was passed through a short column of silica gel and precipitated into an excess of cold methanol three times. After filtration, the sample PS-(VPOSS)-PS was collected and dried under vacuum overnight to give white powder (650 mg; Conversion: 21%). SEC: Mn = 6.4 kg/mol, PDI = 1.03.

PS-(HPOSS)-PS. The procedure is identical to that of PCL-(HPOSS)-PCL using PS-(VPOSS)-PS (Mn = 6.4 kg/mol, 100 mg, 0.016 mmol), 2-mercapoethanol (13 mg, 0.16 mmol), and DMPA (2 mg, 5 μmol). The sample PS-(HPOSS)-PS was obtained as a white powder (86 mg; Yield: 79%). SEC: Mn = 6.7 kg/mol, PDI = 1.02.

PS-(VPOSS)-OH. The procedure is identical to that of PS-(VPOSS)-PS except that Br-(VPOSS)-OH (150 mg, 0.17 mmol) was used as the initiator and that the polymerization was allowed to proceed for 3 hrs. The sample PS-(VPOSS)-OH was obtained as a white powder (713 mg; Conversion: 21%). SEC: Mn = 4.8 kg/mol, PDI = 1.08.

PS-(VPOSS)-PCL. The procedure is identical to that of PS-(VPOSS)-PS except that PS-(VPOSS)-OH (Mn = 4.8 kg/mol, 150 mg, 0.03 mmol) was used as the initiator and that the polymerization was allowed to proceed for 3 hrs. The sample was obtained as a white powder [PS-(VPOSS)-PCL, 200 mg; Conversion: 4%). SEC: Mn = 8.8 kg/mol, PDI = 1.08.

PS-(HPOSS)-PCL. The procedure is identical to that of PCL-(HPOSS)-PCL using PS-(VPOSS)-PCL (Mn = 8.8 kg/mol, 100 mg, 0.0114 mmol), 2-mercapoethanol (9
mg, 0.114 mmol), and DMPA (2 mg, 0.005 mmol). The sample PS-(HPOSS)-PCL was obtained as a white powder (86 mg; Yield: 81%). SEC: Mn = 9.1 kg/mol, PDI = 1.1
CHAPTER IV

RESULTS AND DISCUSSION

4.1 POSS-Based Homo- and Hetero-Bifunctional Initiators

To apply the “grafting-from” approach to the synthesis of functionalized POSS tethered with two symmetric/asymmetric polymer tails, homo- and hetero-bifunctional initiators need to be synthesized. A bifunctional thiol derivative (1-thioglycerol) was used to synthesize the mono-functionalized octavinyl POSS using thiol-ene chemistry and subsequent esterification reactions. 1-Thioglycerol, a AB2 monomer, has already been widely used as a versatile ligand in the construction of many different polymeric architectures, such as dendrimers\textsuperscript{46-48} and “V”-shaped copolymers.\textsuperscript{49} In our system, its use minimized the modification of the POSS cage by keeping the initiation sites at only one of the POSS peripheral groups and leaves the rest intact for final surface chemistry diversification. By control of stoichiometry, a high yield of mono-functionalized octavinyl POSS compared with multi-functionalized octavinyl POSS was successfully achieved. The experiment was performed at a stoichiometric ratio (1:1). Although the reaction did yield higher addition products, the mono-adduct, HO-(VPOSS)-OH, could be easily isolated by chromatographic method. The yield (~30%) is essentially on the same scale as those reported previously for the monofunctionalization of VPOSS from our group,\textsuperscript{28,50} but
the process is simpler, cheaper, and faster. It should be noted that after the thiol-ene reaction, ~50% unreacted VPOSS could be recovered for further modifications and thus, the actual yield based on conversion can be as high as ~60%. Higher adducts including di-adduct and tri-adduct were obtained as a mixture of regio-isomers in much lower yields that could not be further purified. Nevertheless, they also serve as intriguing and potentially useful building blocks for further functionalization. Considering the rapid and highly efficient nature of thiol-ene reaction, it is anticipated that the yield of mono-adducts may be optimized by further decreasing the concentration of VPOSS and adjusting the stoichiometry of the ligand.

The two hydroxyl groups on HO-(VPOSS)-OH are quite versatile. They can be used to directly initiate the ring opening polymerization and they can also be further converted into other functional groups, for example, a widely-used- ATRP initiator called 2-bromoisobutyryl. Herein, 2-bromoisobutyryl bromide was applied to react with HO-(VPOSS)-OH in the presence of triethylamine in CH$_2$Cl$_2$ to synthesize the homo-bifunctional ATRP initiator, Br-(VPOSS)-Br, and the hetero-bifunctional initiator, Br-(VPOSS)-OH. To synthesize Br-(VPOSS)-Br, excess 2-bromoisobutyryl bromide was used to ensure a complete reaction, which is evidenced by the disappearance of the resonances at δ 3.77 and 3.54 ppm and the appearance of the new resonances at δ 5.23, 4.56 and 4.34 ppm in the $^1$H NMR spectra of Br-(VPOSS)-Br. The product was indeed obtained in excellent yield (94%). On the other hand, Br-(VPOSS)-OH was prepared by stoichiometry-controlled, selective esterification of the primary hydroxyl. Although there are two hydroxyl groups, the primary hydroxyl group is known to be more reactive due to less steric hindrance. This could be confirmed by $^1$H NMR spectrum of the crude sample, which showed the targeted product was dominant in the reaction mixture of isomers (> 85%). In addition, their
difference in location also leads to a slight difference in the polarity of final products, which enables chromatographic purification of these isomers. As a result, the desired Br-(VPOSS)-OH functionalized with 2-bromobutyryl group at the primary hydroxyl was obtained in good yield (~40%). This is confirmed by \(^1\)H NMR spectrometry (Figure 7a). In the \(^1\)H NMR spectrum, the peaks at around \(\delta 4.28\) and \(3.98\) ppm, the characteristic resonances for the protons near the ester bond and hydroxyl group, respectively, have the integration ratio of 2:1 and there are no peaks appearing at \(\delta 5.06\) and \(3.87\) ppm that could be attributed to the isomer, confirming the well-defined structure and the high purity. The POSS-based macro-initiators were then thoroughly characterized by \(^1\)H NMR, \(^{13}\)C NMR, FT-IR, and MALDI-TOF mass spectrometry to establish their identity and uniformity of the molecular structures.

4.2 Shape Amphiphiles Based on POSS Tethered with Two Symmetric Tails.

Using homo-bifunctional POSS-based macro-initiators, two symmetric polymer chains can be simultaneously grown from POSS. The feasibility of “grafting-from” approach is based on the compatibility of VPOSS cage with polymerization. Recently, Zhang et al., have demonstrated that ROP of lactides and \(\varepsilon\)-caprolactone is compatible with the vinyl groups on POSS. It was thus tried as of the first example.\(^{28}\) The successful synthesis of PCL-(VPOSS)-PCL via ROP was confirmed by NMR, SEC, and MALDI-TOF mass spectrometry. Compared with macro-initiator HO-(VPOSS)-OH, the new peaks at \(\delta 5.19, 4.40,\) and \(4.18\) ppm can be assigned to the newly formed protons at the ester linkage of \(-\text{SCH}_2\text{CH(OOC-)}\text{CH}_2\text{OCO-},\) respectively, suggesting that both hydroxyl groups on the VPOSS cage have fully initiated (Figure 3b). The characteristic protons on PCL backbones at \(\delta 4.06, 3.75, 2.30, 1.65\) and \(1.39\) ppm can be clearly assigned in Figure 3b. The integrity of VPOSS
cage after ROP is demonstrated by the observations of characteristic vinyl protons at δ 6.21-5.82 ppm in \(^1\)H NMR spectrum (Figure 3b) as well as sp\(^2\) carbons of vinyl groups at δ 137.11 and 128.65 ppm in the \(^{13}\)C NMR (Figure 9), which is in good agreement with our pervious results.\(^{28}\) The SEC chromagram shows a narrow peak (PDI = 1.08) with molecular weight (Mn = 8.5 kg/mol) close to that obtained from \(^1\)H NMR spectrum (Mn,NMR = 6.9 kg/mol). Moreover, the MALDI-TOF mass spectrum in Figure 4b shows only one single narrow distribution with molecular weights in accordance to the proposed structure. For example, a representative monoisotopic mass peak at m/z 7378.88 for PCL-(VPOSS)-PCL (Na\(^+\) adduct) is in perfect match with the calculated molecular mass of 7378.91 Da for 57-mer of [C\(_{367}\)H\(_{612}\)NaO\(_{130}\)Si\(_8\)]\(^+\) (Figure 10 & Table 1). These results unambiguously confirm the molecular structure and uniformity of the product.

Previously, thiol-ene “click” chemistry has been demonstrated as an efficient, robust and modular tool for simultaneous multiple-site functionalization of the VPOSS cage, leading to a class of functional POSS cage with diverse surface chemistry.\(^{27-28, 50, 54}\) In this work, to emphasize the change in tethered chain composition and for the sake of comparison, only 2-mercaptoethanol was chosen to react with these VPOSS derivatives to install seven hydroxyl groups onto POSS to impart hydrophilicity and construct model shape amphiphiles. Meanwhile, the hydroxyl groups are amenable to further functionalizations. Our previous study has already shown the high efficiency of radical addition of 2-mercaptoethanol onto VPOSS cage in the preparation of molecular Janus nanoparticles.\(^{50}\) The functionalization was conveniently performed by mixing PCL-(VPOSS)-PCL with commercially available thiol ligand and photoinitiator in a common solvent followed by 15 minutes of irradiation under UV 365 nm. All of the major impurities, including excess thiol, the initiator residue, and
disulfide by-products, were removed simply by repeated precipitation into methanol. The complete functionalization is revealed by the complete disappearance of the vinyl proton peaks at $\delta$ 5.78-6.08 ppm in the $^1$H NMR spectrum (Figure 3c) and sp2 carbon signals at $\delta$ 137.11 and 128.65 ppm (Figure 9) in the $^{13}$C NMR spectrum of PCL-(HPOSS)-PCL. This is in good agreement with the new characteristic resonance peaks emerging at $\delta$ 2.80-2.61 ppm in the $^1$H NMR spectra that are attributed to the formation of thiol ether bonds. Compared with PCL-(VPOSS)-PCL, there appears a strong absorbance peak at around at 3440 cm⁻¹ in FTIR spectra (Figure 11), which also provide direct evidence for the hydroxyl hydrogen bonding formation. In addition, the comparison of the MALDI-TOF mass spectra of PCL-(VPOSS)-PCL and PCL-(HPOSS)-PCL is shown in Figure 4, indicating a single narrow distribution of peaks for the two macromolecules. The peaks shifts of [PCL-(HPOSS)-PCL·Na]^+ relative to [PCL-(VPOSS)-PCL·Na]^+ with the same repeating units clearly showed an increase of m/z = 546.88 (Figure 10a and Figure 10b), corresponding to the precise additions of seven 2-mercapoethanol molecules onto one VPOSS cage after thiol-ene reaction ($7 \times 78.13 = 546.91$). Their observed representative monoisotopic masses both agree well with that of the calculated ones (Figure 10 & Table 1), confirming their high purity and precisely-defined structure. Moreover, the SEC overlay of PCL-(HPOSS)-PCL with PCL-(VPOSS)-PCL (Figure 3a) still shows single symmetric peak but shifted to a slightly lower retention volume due to a small increase in molecular weight (Mn = 8.6 kg/mol, PDI = 1.06) (Table 1). Therefore, it is concluded that the shape amphiphile based on POSS tethered with two semicrystalline PCL chains possessing were readily synthesized by ROP and thiol-ene “click” chemistry with precisely defined structures as proposed.
Figure 3 $^1$H NMR spectra of (a) HO-(VPOSS)-OH, (b) PCL-(VPOSS)-PCL, and (c) PCL-(HPOSS)-PCL.
Figure 4 MALDI-TOF mass spectra of (a) PCL-(HPOSS)-PCL, (b) PCL(VPOSS)-
PCL, (c) PS-(HPOSS)-PS, and (d) PS-(VPOSS)-PS.
Figure 5 Overlay of SEC traces for all polymers: (a) PCL-(VPOSS)-PCL and PCL-(HPOSS)-PCL; (b) PS-(VPOSS)-PS and PS-(HPOSS)-PS; and (c) PS-(VPOSS)-OH, PS-(VPOSS)-PCL and PS-(HPOSS)-PCL.
### Table 1 Summary of molecular weight characterizations.

<table>
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<tr>
<th>Sample</th>
<th>Molecular Formula</th>
<th>M (calcd.) (Da)</th>
<th>m/z (obs.)</th>
<th>M&lt;sub&gt;n, NMR&lt;/sub&gt; (g/mol)</th>
<th>M&lt;sub&gt;n, SEC&lt;/sub&gt; (g/mol)</th>
<th>PDI</th>
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<td>PCL-(VPOSS)-PCL</td>
<td>C_{50}H_{12}NaO_{3.9}SSi₈</td>
<td>7378.91</td>
<td>7378.88</td>
<td>6.9k</td>
<td>8.5k</td>
<td>1.08</td>
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<tr>
<td>PCL-(HPOSS)-PCL</td>
<td>C_{33.2}H_{61.2}NaO_{5.7}Si_{8}</td>
<td>7925.00</td>
<td>7925.76</td>
<td>7.4k</td>
<td>8.6k</td>
<td>1.06</td>
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<tr>
<td>PS-(VPOSS)-PS</td>
<td>C_{21}H_{43}AgBrO_{2.3}SSi₈-2HBr</td>
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<td>5041.64</td>
<td>5.7k</td>
<td>6.4k</td>
<td>1.03</td>
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<td>PS-(HPOSS)-PS</td>
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<td>5587.46</td>
<td>5587.05</td>
<td>5.9k</td>
<td>6.7k</td>
<td>1.02</td>
</tr>
<tr>
<td>PS-(VPOSS)-OH</td>
<td>C_{21}H_{42}BrNaO_{2.3}SSi₈-HBr</td>
<td>3328.49</td>
<td>3328.98</td>
<td>4.5k</td>
<td>4.8k</td>
<td>1.08</td>
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<tr>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>8.2k</td>
<td>8.8k</td>
<td>1.08</td>
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<td>--</td>
<td>8.7k</td>
<td>9.1k</td>
<td>1.12</td>
</tr>
</tbody>
</table>

*(a): The molecular formula adjusted based on the observed molecular species in MALDI-TOF mass spectrometry with corresponding counternions; (b) the calculated monoisotopic molecular weight of PCL-(VPOSS)-PCL, PCL-(HPOSS)-PCL, PS-(VPOSS)-PS, PS-(HPOSS)-PS, PS-(VPOSS)-OH; and (c) experimentally observed m/z are based on 57-mers of PCL-(VPOSS)-PCL, PCL-(HPOSS)-PCL with a sodium ion (M·Na⁺); 39-mers of PS-(VPOSS)-PS, PS-(HPOSS)-PS with a silver ion (M·Ag⁺); and 24-mers of PS-(VPOSS)-OH with a sodium ion (M·Na⁺), respectively.

Due to the susceptibility of vinyl silsesquioxanes to radical addition, the compatibility of radical polymerization conditions, such as ATRP and reversible addition-fragmentation group transfer radical polymerization (RAFT), were not clear at first. Nevertheless, the reaction was tried with the hope that the presence of a large excess of styrene would make such additions quite unlikely, particularly at low conversions. Indeed, by controlling the conversion (~ 20%), no side reaction could be observed. This strategy is similar to the synthesis of C₆₀-end capped polystyrene by ATRP, as reported by Li et al. The well-defined structure of PS-(VPOSS)-PS is proved by ¹H NMR, ¹³C NMR, SEC, and MALDI-TOF mass spectrometry. Not only does the SEC chromagram show only one symmetric peak, the intact of the VPOSS unit is also demonstrated by the peaks at around δ 6.11- 5.78 ppm in the ¹H NMR spectrum (Figure 6b) and at δ 137.29, 128.35 ppm in the ¹³C NMR spectrum (Figure 12a). After polymerization, it was found that the peaks assignable to protons (a, b, c) near the ester bonds (Figure 6a) completely shifted to new position at δ 3.62- 3.16
ppm, which indicates complete ATRP initiation of Br-(VPOSS)-Br (Figure 6b). The occurrence of new peaks at δ 4.67- 4.40 ppm corresponding to two polymer chain end protons (-CH₂CH₂PhBr) also confirms two PS chains “grafting” on the VPOSS. The integration ratio between peaks at δ 3.76- 3.08 ppm and that at δ 4.67- 4.40 ppm is about 3.05:2.00 as expected. In addition, in the MALDI-TOF mass spectrum (Figure 6d), a single narrow distribution can be clearly seen with the m/z value of 5041.64, which corresponds to a 39-mer of PS-(VPOSS)-PS losing two HBr molecules (Mcalcd. = 5041.37 Da, see also Table 1). Such a loss of chain-end HBr by fragmentation is common under the MALDI-TOF working conditions for ATRP polymers when silver ion was used as the cationizing agent. Overall, the results have unambiguously shown that the vinyl group on the POSS cage does not interfere with the ATRP reaction and a precisely-defined macromolecule processing one VPOSS cage with two PS chains was achieved.

Subsequent surface functionalization of PS-(VPOSS)-PS with hydroxyls were performed in a similar way to that of PCL-(VPOSS)-PCL. While similar characterization results were obtained for PS-(HPOSS)-PS as PCL-(HPOSS)-PCL concerning the POSS cage functionalization, the MALDI-TOF mass spectrum is worth further discussion here (Figure 4). Due to the relatively high molecular weight of the final product and the significant difference in chemical composition between the hydrophilic POSS head and hydrophobic PS tail, it was difficult to get a decent MALDI-TOF mass spectrum for PS-(HPOSS)-PS. The laser intensity was optimized to minimize fragmentation while still keep a reasonable signal intensity. The overview of the spectrum shown in Figure 4c exhibits one single distribution of peaks under the linear modal condition. Similarly to that of PS-(VPOSS)-PS, the observed molecular weight corresponds to the one with silver cation and losing two HBr
molecules (Table 1). In addition, a molecular weight increase of \( m/z = 545.41 \) can be observed when comparing \([\text{PS-}(\text{HPOSS})-\text{PS·Ag-2HBr}]^+\) (m/z value could be obtained under reflecting modal condition (data not shown)) to \([\text{PS-}(\text{VPOSS})-\text{PS·Ag-2HBr}]^+\) with the same number of repeating units, suggesting the completely thiol-ene modification of VPOSS cage. In the SEC spectrum (Figure 5b), the elution profile of \( \text{PS-}(\text{HPOSS})-\text{PS} \) is at slightly lower retention volume than that of \( \text{PS-}(\text{VPOSS})-\text{PS} \), but the difference is much smaller than that for \( \text{PCL-}(\text{VPOSS})-\text{PCL} \) and \( \text{PCL-}(\text{HPOSS})-\text{PCL} \). It suggests that the addition of seven mercaptoethanol groups has very little impact to the overall hydrodynamic volume of the shape amphiphile. All of the evidence supports the successful formation of \( \text{PS-}(\text{HPOSS})-\text{PS} \) as proposed. The giant surfactants based on functional POSS (XPOSS) and polystyrene are important model shape amphiphiles for the study of their self-assembled structures and phase behaviors. For example, Our group has recently reported an interesting example of carboxylic acid-functionalized POSS-end capped polystyrenes (APROSS-PS) that are capable of self-organizing into different well-defined nano-morphologies ranging from spheres to cylinders, and vesicles in selective solvents.\(^{27}\) The surprising compatibility of VPOSS with radical polymerization mechanisms such as ATRP is expected to greatly expand the scope of such shape amphiphiles by facilitating the attachment of polymer tails of diverse composition and topology.
4.3 Shape Amphiphiles Based on POSS Tethered with Two Asymmetric Tails.

With the advent of various living/controlled polymerization methods, it has become a natural, valuable, and practical approach for the synthesis of block copolymers and/or star polymers of asymmetric compositions via the combination of different polymerization mechanism.\textsuperscript{57-58} POSS-based hetero-bifunctional initiator, Br-
(VPOSS)-OH, offers the opportunity to synthesize shape amphiphiles possessing two polymer tails of different chain compositions tethered to one junction point using two-step polymerizations. This type of macromolecular architecture can also be regarded as a diblock copolymer with a nanoparticle at the junction point. Several methods have already been developed for their synthesis, mostly using the “grafting-onto” strategy by the efficient conjugation between block copolymers and nanoparticles.\textsuperscript{23,25,59-62} Herein, the high compatibility of VPOSS with different polymerization conditions (ROP, ATRP) allows the use of “grafting-from” polymerizations strategy to achieve such an asymmetry in tethered chain compositions. The reaction was successfully performed in the sequence of ATRP, ROP, and thiol-ene modification. The products in each step were fully characterized by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, MALDI-TOF mass spectrum, and SEC chromatography.

As expected and similar to that of PS-(VPOSS)-PS, the disappearance of the resonances at δ 4.28, 3.98 ppm and the appearance of new resonances at around δ 4.58-4.31, 3.82-3.30 ppm in the \textsuperscript{1}H NMR spectrum of PS-(VPOSS)-OH suggest the efficient functionalization of 2-bromoisobutyryl group and successful growth of a PS chain via ATRP (Figure 7b). The integration ratio between peaks at δ 4.58-4.31 ppm and those at δ 3.82-3.30 ppm is about 1 : 3, indicating that the presence of a hydroxyl group does not interfere with the ATRP reaction and no protection/deprotection is necessary. The well-defined structure is best evidenced by the MALDI-TOF mass spectrum (Figure 13). The inset is the overview of the spectrum (Figure 13b), which exhibits only one narrow distribution with molecular weights in accordance to the proposed structure. For example, a representative monoisotopic mass peak at m/z 3328.98 (Table 1 and Figure 13a) agreed well with the calculated monoisotopic molecular weight of 3408.41 Da for the 24-mer of [PS-(VPOSS)-OH·Na]+
(C_{215}H_{229}BrNaO_{15}Si_{8}^{8+}) with the loss of a HBr molecule from the chain end (79.43 Da). Such a fragmentation process is commonly observed under the MALDI-TOF working conditions.\textsuperscript{63-64} The structure of the desired product is thus unambiguously established and serves as the macroinitiator for the ROP of ε-caprolactone monomer.

The precursor shape amphiphile, PS-(VPOSS)-PCL, was obtained by directly precipitation into methanol after ROP of ε-caprolactone. In the \textsuperscript{1}H NMR spectrum shown in Figure 7c, the characteristic resonance peaks for the protons at δ 4.08, 2.33, 1.67, 1.40 ppm suggests that the newly formed PCL block. In addition, the peak at δ 3.66 ppm (Figure 7c) can be assigned to the methylene protons -CH2OH at PCL chain end, with the integration ratio of 2.0: 21.46 to the protons at δ 5.78-6.11 ppm that are assigned to the protons on vinyl groups of the VPOSS cage. Therefore, it is concluded that every POSS cage is grafted with precisely one PCL chain and one PS chain. The \textsuperscript{13}C NMR spectrum of PS-(VPOSS)-PCL further confirmed the successful installation of one PCL chain onto the VPOSS cage surface. In Figure 14b, the characteristic carbons for the PCL backbone can be also clearly observed at δ 173.47, 64.11, 34.10, 28.33, 25.51, 24.56 ppm, respectively. The SEC trace of PS-(VPOSS)-PCL (Figure 5c) showed a monomodal, symmetric peak with a narrow molecular weight distribution (Mn = 8.8 kg/mol, PDI = 1.08). There is a very clear shift in retention volume compared to its macro-initiator, PS-(VPOSS)-OH (Mn = 4.8 kg/mol, PDI = 1.08), consistent with the molecular weight increase due to new block formation.

The subsequent thiol-ene “click” functionalization of VPOSS cage turned out to be fully compatible and efficient. The \textsuperscript{1}H NMR peaks at δ 5.78-6.11 ppm, corresponding to the vinyl group, completely disappeared after 15 minutes of reaction and the new protons at the thiol-ether linkages can be clearly observed at around δ 2.73 ppm (Figure 7d), as discussed before. On the other hand, the resonance peaks at around δ
3.76 ppm in the $^1$H NMR spectrum are assigned to the new formed methylene protons of –CH2OH on the POSS cage head. In addition, the SEC overlay of PS-(HPOSS)-PCL with PS-(VPOSS)-PCL (Figure 5c) now showed a single symmetric peak at slightly lower retention volume, owing to the increase in molecular weight (Mn = 9.1 kg/mol, PDI = 1.12). Therefore, a well-defined shape amphiphile based on POSS tethered with two polymer tails of asymmetric composition was achieved by sequential modification of ATRP, ROP and thiol-ene “click” chemistry. In addition, the sequence of polymerization in the process is worth discussion here. It was also tried by performing ROP first, followed by ATRP for the synthesis of PS-(VPOSS)-PCL. It was found that, although Br-(VPOSS)-PCL could be successfully obtained by ROP and possesses well-defined structure (Figure 15), subsequent ATRP always led to a mixture of the desired block copolymer and the remaining initiator (Figure 16), despite of many efforts to optimize the condition by changing temperature, conversion, and initiator/monomer ratio, etc. Therefore, not only the initiation efficiency of bromoisobutyryl group is reduced significantly when buried in the center between POSS and PCL, the presence of multiple vinyl groups in the vicinity also increased the possibility of the radical addition of the active center to the POSS cage during ATRP, leading to species that could hardly initiate further. The sequence of reactions plays an important role for a successful “grafting-from” synthesis of well-defined shape amphiphile tethered with two polymer tails of asymmetric composition.
Figure 7 $^1$H NMR spectra of (a) Br-(VPOSS)-OH, (b) PS-(VPOSS)-OH, (c) PS-(VPOSS)-PCL, and (d) PS-(HPOSS)-PCL
CHAPTER V

CONCLUSIONS

In conclusion, a new class of well-defined functionalized polyhedral oligomeric silsesquioxane (POSS)-based shape amphiphiles tethered with two polymer tails of symmetric or asymmetric compositions has been successfully synthesized by a combination of “grafting-from” approach and thiol-ene “click” chemistry. It was found that the vinyl groups on VPOSS are compatible with ROP and ATRP conditions, allowing the synthesis of these shape amphiphiles with different chain compositions and precise functionality. In addition, thiol-ene reaction is demonstrated to be a highly robust, convenient, and efficient way to introduce functionalities onto VPOSS. Besides the multiple-site functionalization performed to install diverse functional groups on POSS, we successfully achieved mono-functionalization on VPOSS by controlling stoichiometry. In general, the method discussed in the thesis give a facile method for the synthesis of model shape amphiphiles with precise control over molecular parameters such as surface functionalities, molecular weights, and polydispersity for a systemic study of their self-assembly. The study is now under investigation to reveal the intriguing hierarchical structures and the physical principles underlying their self-assembly in solution, bulk, and thin-film states.
Figure 8 $^1$H NMR spectra of POSS-based macro-initiators: (a) HO-(VPOSS)-OH, (b) Br-(VPOSS)-Br, and (c) Br-(VPOSS)-OH.
Figure 9. $^{13}$C NMR spectra of (a) PCL-(VPOSS)-PCL, and (b) PCL-(HPOSS)-PCL.

Figure 10. Zoom-in view of MALDI-TOF mass spectrum for (a) PCL-(VPOSS)-PCL, and (b) PCL-(HPOSS)-PCL at specific mass range.
Figure 11 FTIR spectra of (a) PCL-(HPOSS)-PCL, and (b) PCL-(VPOSS)-PCL.

Figure 12 $^{13}$C NMR spectra of (a) PS-(VPOSS)-PS, and (b) PS-(HPOSS)-PS.
Figure 13 MALDI-TOF mass spectrum for PS-(VPOSS)-OH, showing only one narrow distribution with molecular weights that agree well with the proposed structure.
Figure 14 $^{13}$C NMR spectra of (a) PS-(VPOSS)-OH, (b) PS-(VPOSS)-PCL, and (c) PS-(HPOSS)-PCL.
Figure 15 MALDI-TOF mass spectrum for Br-(VPOSS)-PCL, showing only one narrow distribution with molecular weights that agree well with the proposed structure. For example, a representative monoisotopic mass peak at m/z 2736.30 agreed well with the calculated monoisotopic molecular weight of 2836.00 Da for the 16-mer of [Br-(VPOSS)-PCL·Na⁺] (C₁₁₉H₁₉₇BrNaO₄₇SSi₈⁺).

Figure 16 Overlay of SEC traces for Br-(VPOSS)-PCL (black line) and the crude product of PCL-(VPOSS)-PS obtained after ATRP of styrene using Br-(VPOSS)-PCL as the macroinitiator (red line).
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