Synthesis of Shape Amphiphiles Based on Functional Polyhedral Oligomeric Silsesquioxane End-Capped Poly(L-lactide) with Diverse Head Surface Chemistry

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Supporting Information

ABSTRACT: This paper reports a facile, modular, and efficient approach to the synthesis of shape amphiphiles with a hydrophobic polymer chain as the tail and a polar, compact, functional polyhedral oligomeric silsesquioxane (POSS) nanoparticle as the headgroup. A poly(L-lactide) (PLLA) chain was grown from monohydroxyl-functionalized heptavinyl POSS (VPOSS–OH) with controlled molecular weight and narrow polydispersity by stannous octoate-mediated ring-opening polymerization of L-lactide. To impart tunable polarity and functionality to the headgroup, various functional groups, such as carboxylic acids, hydroxy groups, and sugars, were attached to the POSS cage in high efficiency by thiol–ene “click” chemistry, which provides a straightforward and effective approach to synthesize shape amphiphiles with diverse head surface chemistry. The polymers have been fully characterized by 1H NMR, 13C NMR, FT-IR spectroscopy, MALDI-TOF mass spectrometry, and size exclusion chromatography. These functional POSS can serve as versatile nanobuilding blocks in the “bottom-up” construction of nanoscale structures and assemblies that may exhibit rich self-assembling behavior and potentially useful physical properties.

INTRODUCTION

In the “bottom up” construction of nanoscale structures and assemblies, self-assembly of nanohybrids from a library of nanobuilding blocks plays a central role.1,2 The past 2 decades have witnessed the development of a large variety of nanobuilding blocks with different composition (organic, inorganic, biological, etc.),3,4 and geometry/symmetry (nanospheres, cubes, discs, rods, etc.).5–7 In comparison to typical inorganic metal clusters and nanocrystals, polymers,8 dendrimers,9 and other molecular clusters (e.g., carborane,10 C6011) have also been recognized as versatile nanobuilding blocks, and they present a significant advantage as molecular nanomaterials in their well-defined molecular structures and the possibility to precisely control the molecular variables such as compositions, overall size/shape, and location of surface/interior functionalities. To date, the bottom-up approach has attracted enormous research interest both in the development of these fine-tuned nanobuilding blocks and the use of their hybrids to assemble into diverse nanostructures with desired properties.

Shape amphiphiles usually refer to molecules possessing amphiphilic features based on differences in the shape of the molecular segments.12 Typical shape amphiphiles are composed of a functional nanobuilding block tethered with polymer chains at precise locations.13–16 Two factors are important in the self-assembly of these shape amphiphiles: (1) shape effects of the 3D rigid and compact nanobuilding blocks that might pose different packing constraints and lead to various hierarchical structures (which can be counted as entropic contributions) and (2) important interaction effects that dominate the enthalpy contributions in the self-assembly process. Similar to small-molecule surfactants and block copolymers, they are expected to undergo microphase separation and self-assemble into a variety of nanoscale morphologies in solution.13–15 Computer simulation has predicted asymmetric phase behaviors with far richer, interesting, hierarchical phase structures in these nanoparticle-tethered shape amphiphiles.7,17,18 Experimentally, there are already a few reported examples, including polymers tethered with C6019 quantum dots,20 and gold nanoparticles.21 But there are relatively few reports on their ordered assembly in bulk or in solution, probably due to the unbalanced interactions and incommensurate shapes between the tethered head and the polymer tail that result in random aggregation. We recently reported the synthesis and self-assembly of carboxylic acid-functionalized polyhedral oligomeric silsesquioxane end-capped polystyrenes as a typical “shape amphiphile” and called it a “giant surfactant” with emphasis on its similarity to small-molecule surfactants.14 They were found to self-assemble into various well-defined morphologies, such as spheres, cylinders, and vesicles, in selective solvents with surprisingly...
highly stretched polymer chains in these assemblies, a behavior similar to small-molecule surfactants but unlike amphiphilic block copolymers. It is thus important to control the surface chemistry of the polar head of shape amphiphiles to tune these multivalent interactions between the head and the tail and the resulting self-assembly behavior. Polyvalent interactions have been recognized as a ubiquitous strategy used by Nature for the creation of a wide variety of functions not achievable with monovalent interactions. Therefore, if the head of a shape amphiphile could be readily modified with multiple functional groups, it could lead to simultaneous, collective, and cooperative polyvalent interactions in a well-defined configuration. Moreover, it is also possible to impart functions to the assemblies by modifying the polar head with, for example, signal molecules for sensory or target application. Therefore, a facile and efficient method for the synthesis of these shape amphiphiles with readily tunable head surface chemistry is highly desired.

POSS (polyhedral oligomeric silsequioxane), arguably the smallest silica nanoparticle with diameter around 1.0 nm, is the subject of intense research, from the synthesis and modification to conjugation with other functional materials. Owing to the ease in its modification both on the cage structures (e.g., \( T_8 \), \( T_{12} \)) and the periphery functionality (mono-, multi-, homo- or heterofunctionalized), POSS is very promising as a versatile nanobuilding block for the construction of various nanohybrids that exhibit novel self-assembled structures and physical properties.

### EXPERIMENTAL SECTION

**Chemicals and Solvents.** Trifluoromethanesulfonic acid (Aldrich, ReagentPlus, >99%), octavinyl POSS (OVPOSS, Hybrid Organics, >99%), mercaptoacetic acid (Acros Organics, 99%), tin(II) 2-ethylhexanoate (Aldrich, ReagentPlus, >99%), and 1-thioglycerol (Fluka, >98.0%), and 1-thio-β-D-glucose tetracetate (sugar—SH, Alfa Aesar, 99%) were used as received. VPOSS—OH was prepared from OVPOSS according to the literature procedure. 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. L-Lactide (Purac Biomaterials, >99.5%) was used after recrystallization from anhydrous toluene twice. Silica gel (VWR, 230–400 mesh) was activated by heating to 140 °C for 12 h. Dichloromethane (CH$_2$Cl$_2$, EMD, ACS grade) was purified by distillation from CaH$_2$. Toluene

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**Scheme 1. Synthesis of XPOSS—PLLA via Ring-Opening Polymerization and Thiol—Ene Click Chemistry**

![Scheme 1](image-url)
(EMD, ACS grade) was purified by distillation from CaH₂ and then sodium, before it was stored over poly(1-1-1-1yl)thium. Chloroform (EMD, ACS grade), tetrahydrofuran (THF, EMD, ACS grade), methanol (Fisher Scientific, reagent grade), and hexane (EMD, ACS grade) were used as received.

Characterizations. Size exclusion chromatographic analyses (SEC) for the synthesized polymers were performed using a Waters Tres system with three Styragel columns at 35 °C and a refractive index detector. Samples were run at a flow rate of 0.5 mL/min with THF as the mobile phase. The molecular weight vs elution time was calibrated using narrow polydispersity polystyrene standards.

All ¹H and ³¹C nuclear magnetic resonance (NMR) spectra were acquired in CDCl₃ (Aldrich, 99.9% D) as solvent using a Varian Mercury 300 NMR spectrometer. The ¹H NMR spectra were referenced to the residual proton impurities in the CDCl₃ at δ 7.27 ppm. ³¹C NMR spectra were referenced to ¹³CDCl₃ at δ 77.00 ppm.

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

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Ultra flex III TOF/TOF mass spectrometer (Bruker Daltonics, Billerica, MA), equipped with a Nd:YAG laser emitting at a wavelength of 355 nm. trans-2-[(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Aldrich) and a matrix and salt mixture on top of each sample on a spot of dry matrix and salt mixture on top of the peaks at δ 3.98 (2OH), 2.68 (m, 28H, −CH₂(OH)−), 1.06 (m, 26H, −CH₂−), 1.67 (m, 12H, −CH₂−), 1.16 (m, 26H, −CH₂−). FT-IR (KBr) (cm⁻¹): 3290.7 (br, O−H), 2925.4, 2971.5, 2601.0, 1759.1 (C=O), 1453.4, 1360.4, 1211.3, 1185.7, 1132.3, 1095.7 (Si−O−), 1045.3, 917.8, 871.7, 756.1, 692.4, 545.9. MS (MALDI-TOF): calcd monoisotopic mass for 38-mer, C₁₄₅H₂₉₀NaO₁₀₁S-Si₂ = 4053.7 Da, found m/z 4053.7 (100) (M−Na⁺). Mₙ/NM = 5000 g/mol. SEC: Mₙ/Mₚ = 1.12.

DPOSS−PLLA. 1-Thioglycolic acid (27 mg, 0.29 mmol, 10 equiv per polymer or 1.4 equiv per vinyl) and THF (2 mL) were used. After reaction, the mixture was precipitated into deionized water twice and then into cold hexane, to give a white solid (83 mg). Yield: 71%. ¹H NMR (CDCl₃, 500 Hz, ppm, δ): 5.18 (q, 52H, −CH(CH₃)O−), 4.37 (q, 4H, −CH₂(CH₃)OH), 4.27 (m, 2H, −SiCH₂CH₂O−), 3.31 (m, 14H, −CH₂CH₂O−), 2.70 (m, 14H, −CH₂−), 1.59 (d, 187H, −CH₂(CH₃)O−), 1.21 (m, 2H, −SiCH₂CH₂O−), 1.06 (m, 14H, −SiCH₂−). ¹³C NMR (CDCl₃, 125 Hz, ppm, δ): 175.07 (−CH₂CO₂H), 169.53 (−C=O), 69.16, 68.71 (−CH₂CH₂O−), 33.16 (−CH₂−), 26.35 (−CH₂−), 16.72, 16.43, 16.14 (−CH₂(CH₃)O−), 11.90 (−CH₂−). FT-IR (KBr) (cm⁻¹): 3054.0 (br, O−H), 2995.4, 2947.1, 2650.1, 1759.1 (C=O), 1453.4, 1360.4, 1288.4, 1211.3, 1185.5, 1132.3, 1095.7 (Si−O−), 1045.3, 872.3, 754.2, 696.3, 533.6. MS (MALDI-TOF): calcd monoisotopic mass for 38-mer, C₁₄₅H₂₉₀NaO₁₀₁S-Si₂ = 4053.7 Da, found m/z 4053.7 (100) (M−Na⁺). Mₙ/NM = 5000 g/mol. SEC: Mₙ/Mₚ = 1.12.

General Procedure for the Polymerization. In a drybox, VPOSS−OH (0.15 g, 0.23 mmol), t-lactide (1.25 g), and 25 mL of toluene were added into a flame-dried Schlenk flask followed by the addition of Sn(Oct)₂ (1 M in toluene, 0.23 mL, 0.23 mmol). The reaction mixture was precipitated into deionized water twice and then into cold hexane, to give a white solid (100 mg). Yield: 82%. ¹H NMR (CDCl₃, 500 Hz, ppm, δ): 5.18 (q, 49H, −CH₂(CH₃)O−), 4.39−4.17 (m, 3H), 3.87−3.47 (m, 21H, −COOHCH₂OH), 2.68 (m, 28H, −CH₂−), 1.59 (d, 176H, −CH₂(CH₃)O−), 1.06 (m, 26H, −SiCH₂−). ¹³C NMR (CDCl₃, 125 Hz, ppm, δ): 169.59 (−C=O), 69.20, 68.76 (−CH₂CH₂O−), 16.78 (−CH₂−), 16.49 (−CH₂(CH₃)O−). FT-IR (KBr) (cm⁻¹): 3383.8 (br, O−H), 2995.7, 2945.8, 2878.6, 1758.8 (C=O), 1453.4, 1384.6, 1360.1, 1271.1, 1211.3, 1184.7, 1130.3, 1093.2 (Si−O−), 1045.3, 917.7, 871.7, 756.1, 692.4, 545.9. MS (MALDI-TOF): calcd monoisotopic mass for 38-mer, C₁₄₅H₂₉₀NaO₁₀₁S-Si₂ = 4166.9 Da, found m/z 4166.0 (100) (M−Na⁺). Mₙ/NM = 4900 g/mol. SEC: Mₙ/Mₚ = 1.15.

SPOSS−PLLA. 1-Thio-β-glucose tetraacetate (sugar−SH, 222 mg, 0.61 mmol, 21 equiv per polymer or 3 equiv per vinyl) and CHCl₃ (1 mL) were used. After reaction, the mixture was diluted with 10 mL of methanol and put in a refrigerator at −35 °C. The polymer precipitated out of solution in 6 h. It was collected by filtration, redissolved in minimum THF, and precipitated again into cold methanol. The final product weighed 155 mg. Yield: 89%. ¹H NMR (CDCl₃, 500 Hz, ppm, δ): 5.25−4.97 (m, 66H), 4.56 (m, 7H), 4.25 (m, 7H), 4.13 (m, 7H), 3.76 (m, 7H), 2.76 (d, 14H), 2.02 (m, 84H), 1.59 (d, 153H), 1.05 (m, 14H). ¹³C NMR (CDCl₃, 125 Hz, ppm, δ): 170.44, 170.04, 169.53, 169.24, 83.53, 73.60, 70.02, 69.16, 68.70, 67.89, 61.97, 24.02, 21.34, 20.75, 20.51, 16.72, 16.43, 16.15, 12.80. FT-IR (KBr) (cm⁻¹): 2995.8, 2945.6, 2258.6, 2099.3, 1752.5 (C=O), 1454.2, 1368.9, 1223.1, 1186.5, 1130.7, 1094.3 (Si−O−), 1037.6, 915.0, 868.0, 734.0, 648.7. MS (MALDI-TOF): calcd monoisotopic mass for 38-mer, C₁₃₂H₂₈₃NaO₁₀₁S-Si₂ = 5958.3 Da, found m/z 5958.0 (100) (M−Na⁺). Mₙ/NM = 6300 g/mol. SEC: Mₙ/Mₚ = 1.16.

**RESULTS AND DISCUSSIONS**

Synthesis of VPOSS-PLLA. The synthetic approach outlined in Scheme 1 is very straightforward. The synthetic route was designed in an effort to fulfill the click philosophy: to construct...
materials with complex structure and diverse function from a set of simple reactions and readily available building blocks. From the commercially available octavinyl-POSS, the monofunctionalized VPOSS−OH was readily prepared in gram quantities with all of the characterizations consistent with the literature.42 The hydroxyl group is capable of initiating ring-opening polymerization of various monomers under different conditions. It can also be further converted to other functional initiators, such as tosylate for cationic polymerization and halide for atom transfer radical polymerization, or chain transfer agents for controlled radical polymerization. Considering the compatibility of the vinylsilsesquioxanes with different polymerization mechanisms, ring-opening polymerization of l-lactide was first chosen as the model system.43,47 The method should be equally applicable to other functional lactone monomers, such as ε-caprolactone and modified lactides.46

The ring-opening polymerization of l-lactide under the catalysis of Sn(Oct)\(_2\) has been known to proceed in a controlled fashion, giving PLLA with narrow polydispersity and controlled molecular weight.43,47 Combined with unique and complex molecular scaffolds (such as POSS, fullerene, and dendrimers), it allows rapid and effective construction of functional materials of diverse molecular architectures in just a few steps.44 In our case, in order to tune the nature of the POSS head groups and their interaction parameter with the PLLA backbone, a variety of functional groups has been successfully introduced to the POSS head. The model functionalizations were performed to introduce carboxylic acid and hydroxyl groups. The syntheses were rapid and straightforward from commercially available starting materials and the functional polymers were fully characterized by various techniques.

Hawker and co-workers\(^{42,53}\) have demonstrated that the reaction between periphery vinyl groups and mercaptoaetic acid is a convenient way to modify dendrimer surfaces with carboxylic acids. Our previous work has also proved the high efficiency of radical addition of mercaptoaetic acid to vinylsilsesquioxanes in the synthesis of the polystyrene analogue, APOS−PS.14 The first trial in POSS−PLLA was also based on this reaction. The successful ligation was proven by the complete disappearance of POSS vinyl proton resonances at δ 5.88−6.15 ppm and the appearance of the two thio-ether methylene linkages at δ 3.31 and 2.70 ppm in the \(^1\)H NMR spectrum (Figure 1b). The chemical shifts agree well with that of the reported analogue

Figure 1. \(^1\)H NMR spectra of (a) VPOSS−PLLA, (b) APOSS−PLLA, (c) DPOSS−PLLA, and (d) SPOSS−PLLA. The complete disappearance of the vinyl protons at 5.88−6.15 ppm and the emergence of new characteristic resonances indicate complete functionalization.
(AOPSS—PS). Similarly, in the $^{13}$C NMR spectrum (Supporting Information, Figure S1b), no vinyl sp$^2$ carbons could be observed while four new peaks appeared at $\delta$ 11.90, 26.35, 33.16, and 175.07 ppm, consistent with the formation of $-\text{SiCH}_3\text{CH}_2\text{SCH}_2\text{CO}_2\text{H}$ on POSS. Due to the small size of the functional group, the SEC trace of AOPSS—PLLA (Figure 3) only shows a slight shift to lower retention volume; however, the peak remains narrow and symmetric, basically the same as the starting material VPOSS—PLLA. The corresponding mass spectrum (Figure 2c,d) shows a AOPSS—PLLA distribution centered at $\sim$4500 Da, which confirms the formation of this product by the matching of the observed monoisotopic mass to the calculated ones (e.g., $m/z$ 4053.9 observed vs 4053.7 Da calculated for 38-mer; see also Table 1). Meanwhile, several minor distributions of low intensity (Figure 2d) and a low-mass distribution of PLLA, $\text{HO-(CH(CH}_3\text{COO)}_n-H}$ (Na$^+$ adducts, data not shown) were observed, which could probably be due to the fragmentation upon MALDI.

Hydroxyl groups are basically neutral and hydrophilic. Molecules possessing multiple hydroxyl groups usually play interesting roles in biological systems, and prime examples are the carbohydrates. Further transformation of hydroxyl groups also allows construction of more complex structures, such as dendrimers. In self-assembly, the strong hydrogen-bond-forming ability of hydroxyls leads to intriguing and stable morphologies that, unlike carboxylic acids, are not easily influenced by the pH of the solution. Reacting VPOSS—PLLA with 1-thioglycerol should install 14 hydroxyl groups into the POSS head at one time. Following an identical procedure as for AOPSS—PLLA, the DPOSS—PLLA was prepared by the thiol—ene reaction with 10 equiv of 1-thioglycerol. In the $^1$H NMR spectrum, the new resonance at $\delta$ 2.68 ppm is characteristic of the protons on the two...
methylene groups adjacent to sulfur atom, and the resonance at δ 3.47–3.87 ppm can be assigned to the protons on the carbons bonded to the oxygens (−CH(OH)CH$_2$OH). There is no alkene proton signal in the range of δ 6.15–5.88 ppm, suggesting complete functionalization. The MALDI-TOF mass spectrum also provides evidence for complete functionalization and a well-defined structure (Figure 2f). Similar to that of the starting material, two apparent distributions could be seen in Figure 2c for DPOSS–PLLA as well, which are actually assignable to the same chemical structure. The molecular formula and molecular monoisotopic mass are based on 38-mer with a sodium ion (M$^+$Na$^+$).

Table 1. Summary of Characterizations for POSS–PLLA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular Formula</th>
<th>M (calc)</th>
<th>m/z (obs)</th>
<th>M$_{n,\text{NMR}}$ (g/mol)</th>
<th>M$_{n,\text{SEC}}$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPOSS–PLLA</td>
<td>C$<em>{133}$H$</em>{218}$NaO$_{152}$S$_7$Si$_8$</td>
<td>3409.8</td>
<td>3409.5</td>
<td>3.4K</td>
<td>5.9K</td>
<td>1.13</td>
</tr>
<tr>
<td>APOSS–PLLA</td>
<td>C$<em>{144}$H$</em>{250}$NaO$_{155}$S$_7$Si$_8$</td>
<td>4053.7</td>
<td>4053.9</td>
<td>5.0K</td>
<td>6.3K</td>
<td>1.12</td>
</tr>
<tr>
<td>DPOSS–PLLA</td>
<td>C$<em>{151}$H$</em>{248}$NaO$_{155}$S$_7$Si$_8$</td>
<td>4165.9</td>
<td>4166.0</td>
<td>4.9K</td>
<td>6.0K</td>
<td>1.15</td>
</tr>
<tr>
<td>SPOSS–PLLA</td>
<td>C$<em>{222}$H$</em>{334}$NaO$_{152}$S$_7$Si$_8$</td>
<td>5958.3</td>
<td>5958.0</td>
<td>6.3K</td>
<td>8.0K</td>
<td>1.16</td>
</tr>
</tbody>
</table>

The successful preparation of SPOSS–PLLA was proved by $^1$H NMR, $^{13}$C NMR, FT-IR, and MALDI-TOF mass spectrometry. The proton at −SH in sugar–SH at δ 2.32 ppm and the alkene glyoclusters has been achieved both by standard amidation$^{56}$ and thiol–ene reaction.$^{40}$ The resulting conjugate exhibited ~200 times stronger inhibition effects in lectin binding study than that from free lactose. Similar glyoclusters have also been achieved on the basis of the C$_{60}$ structural scaffold using the Cu(0)-catalyzed Huisgen 1,3-dipolar cycloaddition of azides and alkynes.$^{57}$ It was thus of great interest to use these glyoclusters as the polar head in shape amphiphiles. It was anticipated that these sugar-ball-headed shape amphiphiles with polylactide tails would be promising candidates as potential target drug delivery vehicles in biomedical engineering.

The 1-thio-$β$-d-glucose tetraacetate (sugar–SH) is commercially available and was used as the model glyco-thiol to prepare SPOSS–PLLA. At first, when only 10 equiv of sugar–SH was used, a strong shoulder peak could be observed in SEC of the product (Supporting Information, Figure S4), suggesting the formation of higher molecular weight fractions that are most likely polymeric dimers from the radical coupling of the intermediates. This is common for polymers of higher molecular weight and for thiol compounds of large size.$^{53}$ In this case, the thiol in sugar–SH is linked directly to a glucose ring without a spacer and thus imposes considerable steric hindrance, both for the higher additions of sugar–SH and for the abstraction of hydrogen from −SH by a polymeric radical. The situation is worse in the absence of a large excess of sugar–SH. Indeed, when sugar–SH was used in 21 equiv at high concentration, the formation of high molecular weight fractions could be suppressed to a minimum (Supporting Information, Figure S4). In contrast, the use of 10 equiv of thiol is already sufficient for complete functionalization without formation of trace high molecular weight fractions in APOSS–PLLA and DPOSS–PLLA. Although a large excess of sugar–SH is required, it was found that most of the excess could be recovered after reaction. It is also anticipated that the situation could be alleviated with the use of less sterically hindered, primary thiols (available in one step from amino-terminated glycosides.$^{40}$

The successful preparation of SPOSS–PLLA was proved by $^1$H NMR, $^{13}$C NMR, FT-IR, and MALDI-TOF mass spectrometry. The proton at −SH in sugar–SH at δ 2.32 ppm and the alkene...
protons at VPOSS—PLLA at $\delta$ 5.88—6.15 ppm disappeared in the $^1$H NMR spectrum (Figure 1d). The newly formed thiol ether bond is evidenced by its methylene proton resonance at $\delta$ 2.76 ppm. The C1 glucose proton adjacent to the thio-ether bond could not be clearly distinguished because its chemical shift (~5.25 ppm) overlaps with that of the backbone methine proton (5.18 ppm). The resonances assigned to the other protons of the glucose ring remain at the same chemical shifts but lose resolution and broaden. The carbon atoms on the glucose scaffold were also observed by $^{13}$C NMR spectroscopy (Supporting Information, Figure S1d), including those around $\delta$ 170 ppm for acetyl carbonyls and $\delta$ 83 ppm for the C1 carbon bonded to sulfur. In the corresponding SEC chromatogram (Figure 3), the peak completely shifts to a lower elution volume due to the large increase in molecular weight. A small shoulder peak is present, as discussed previously. As a result, the polydispersity index slightly increased to 1.16. Despite the existence of trace amounts of higher molecular weight fractions, the MALDI-TOF mass spectrum shows unequivocally the distribution of molecular weights in accordance with the proposed structure (Figure 2gh and Table 1). No high molecular weight product was actually observed, because they are usually more difficult to ionize than low molecular weight fractions. Owing to the large differences in molecular weight (~12 vs ~6 kDa) and relative contents (high molecular weight fraction ~10% from SEC by peak deconvolution), the laser might selectively ionize the low molecular weight fractions. Nevertheless, the spectrum clearly shows the homogeneity and well-defined structure of SPOSS—PLLA at that molecular weight range.

**CONCLUSIONS**

In summary, we have demonstrated a facile approach to prepare shape amphiphiles (XPOSS—PLLA) with diverse head surface chemistry via the combination of ring-opening polymerization and thiol—ene click chemistry. The polymers comprise a poly(l-lactide) chain tethered with a carboxylic-acid-functionalized POSS head (APOSS—PLLA), with a 14-hydroxyl-functionalized POSS head (DPOSS—PLLA), or with a glycolucrose head (SPOSS—PLLA). The synthesis fulfills a click philosophy in material construction, namely, to build diverse and complex structures/functions from a simple set of highly efficient chemical transformations. The method should be easily extended to other polymers (e.g., PCL) and other functional groups (e.g., charged, or flocculent functional groups) for fine-tuning of the interaction parameters in shape amphiphiles. The shape amphiphiles reported in this study serve as model compounds to demonstrate the versatility of the method and to explore their self-assembly behaviors. Notably, these functional POSS heads can be used as versatile nanobuilding blocks to be incorporated into other molecular structures for bottom-up construction of mesoscopic nanomaterials via self-assembly. The relevant work on the synthesis, self-assembly, and application of various shape amphiphiles based on POSS is currently under intense investigation in our laboratory.

**ASSOCIATED CONTENT**

Supporting Information. Detailed characterization data, including $^{13}$C NMR spectra, FT-IR spectra, and SEC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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