# Synthesis of Shape Amphiphiles Based on POSS Tethered with Two Symmetric/Asymmetric Polymer Tails via Sequential "Grafting-from" and Thiol−Ene "Click" Chemistry

Yiwen Li,[†] Xue-Hui Dong,[†] Kai Guo,[†] Zhao Wang,[†] Ziran Chen,[†] Chrys Wesdemiotis,[†,‡] Roderic P. Quirk,*,[†] Wen-Bin Zhang,*,[†] and Stephen Z. D. Cheng*,[†]

[†]Department of Polymer Science, College of Polymer Science and Polymer Engineering, [‡]Department of Chemistry, The University of Akron, Akron, Ohio 44325-3909, United States

Ⓢ *Supporting Information*

ABSTRACT: A series of shape amphiphiles based on functionalized polyhedral oligomeric silsesquioxane (POSS) head tethered with two polymeric tails of symmetric or asymmetric compositions was designed and synthesized using sequential "grafting-from" and "click" surface functionalization. The monofunctionalization of octavinylPOSS was performed using thiol−ene chemistry to afford a dihydroxyl-function-

alized POSS that was further derived into precisely defined homo- and heterobifunctional macroinitiators. Polymer tails, such as polycaprolactone and polystyrene, could then be grown from these POSS-based macroinitiators with controlled molecular weight via ring-opening polymerization and atom transfer radical polymerization (ATRP). The vinyl groups on POSS were found to be compatible with ATRP conditions. These macromolecular precursors were further modified by thiol−ene chemistry to install surface functionalities onto the POSS cage. The polymer chain composition and POSS surface chemistry can thus be tuned separately in a modular and efficient way.
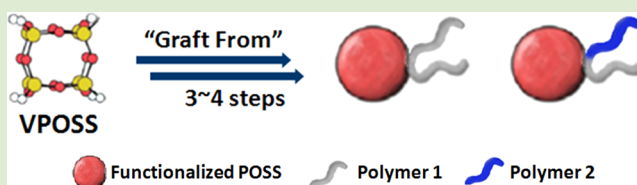
The emergence of shape amphiphiles as important building blocks for "bottom-up" nanofabrication of functional materials has sparked substantial interest because conformation rigidity and shape anisotropy provide additional factors in directing self-assembly into various hierarchical structures.[1−4] Polymer-tethered nanoparticles, a typical class of shape amphiphile, usually have a nanometer-sized polar or macroionic headgroup and one or several hydrophobic polymer chains as tails at various locations.[2,5] Generally, the large polar or macroionic heads could provide several important intrinsic features, leading to rich phase behavior and diverse structures.[6] In recent years, various nanobuilding blocks have been employed as the heads of different giant amphiphiles, ranging from enzyme/protein,[7−10] dendrimers,[11,12] buckyball,[13,14] polyoxometalate clusters,[15,16] cyclodextrin,[17] to polyhedral oligomeric silsesquioxanes (POSS).[6,18] Specifically, due to their precisely defined molecular structures and readily modifiable surface chemistry, POSS have been developed and established as one of the most versatile candidates for shape amphiphiles.[6,18−20]

POSS are regarded arguably as the smallest shape-persistent silicon nanoparticles with a cage diameter around 1.0 nm.[20−24] Diverse surface functionalities have been installed onto POSS cage including hydrophilic[6,18,19,25] and fluorophilic functionalities[26,27] and electro-active[28,29] and bioactive moieties.[6,30,31] Many novel macromolecular architectures have been achieved, such as POSS-based dendrimers,[32,33] molecular Janus particles,[19] and giant surfactants.[6,18] Enabled by thiol−ene "click" chemistry, the vinyl-functionalized POSS (VPOSS) can be

viewed as the precursor to a large variety of functionalized POSS (XPOSS), as demonstrated by our previous work.[6,18] Although the "grafting-onto" approach provides better control over the molecular parameters of the tethered polymer tail, the "grafting-from" strategy circumvents the need for fractionation to remove unreacted polymer and higher adducts that are usually present in the products of the "grafting-onto" approach. Provided that the polymerization conditions are compatible with VPOSS, the latter offers a simple, versatile, and efficient way to prepare POSS-based shape amphiphiles with various architectures.

In this letter, we strive to expand the scope of shape amphiphiles to XPOSS tethered with two polymeric tails of symmetric/asymmetric compositions using the "grafting-from" approach and "click" surface functionalization for a modular, robust, and efficient synthesis (Scheme 1). The method provides a versatile platform for the synthesis and study of shape amphiphiles with novel architectures and compositions.

POSS-based homo- and hetero-bifunctional initiators: To apply the "grafting-from" approach, POSS-based homo- and heterobifunctional initiators should be synthesized. This is achieved by monofunctionalization of octavinyl POSS with a bifunctional thiol derivative, 1-thioglycerol, using thiol−ene chemistry followed by esterification. The method keeps as

Scheme 1. General Synthetic Approach Using a Combination of "Grafting-from" Strategy and Thiol−Ene "Click" Chemistry[a]
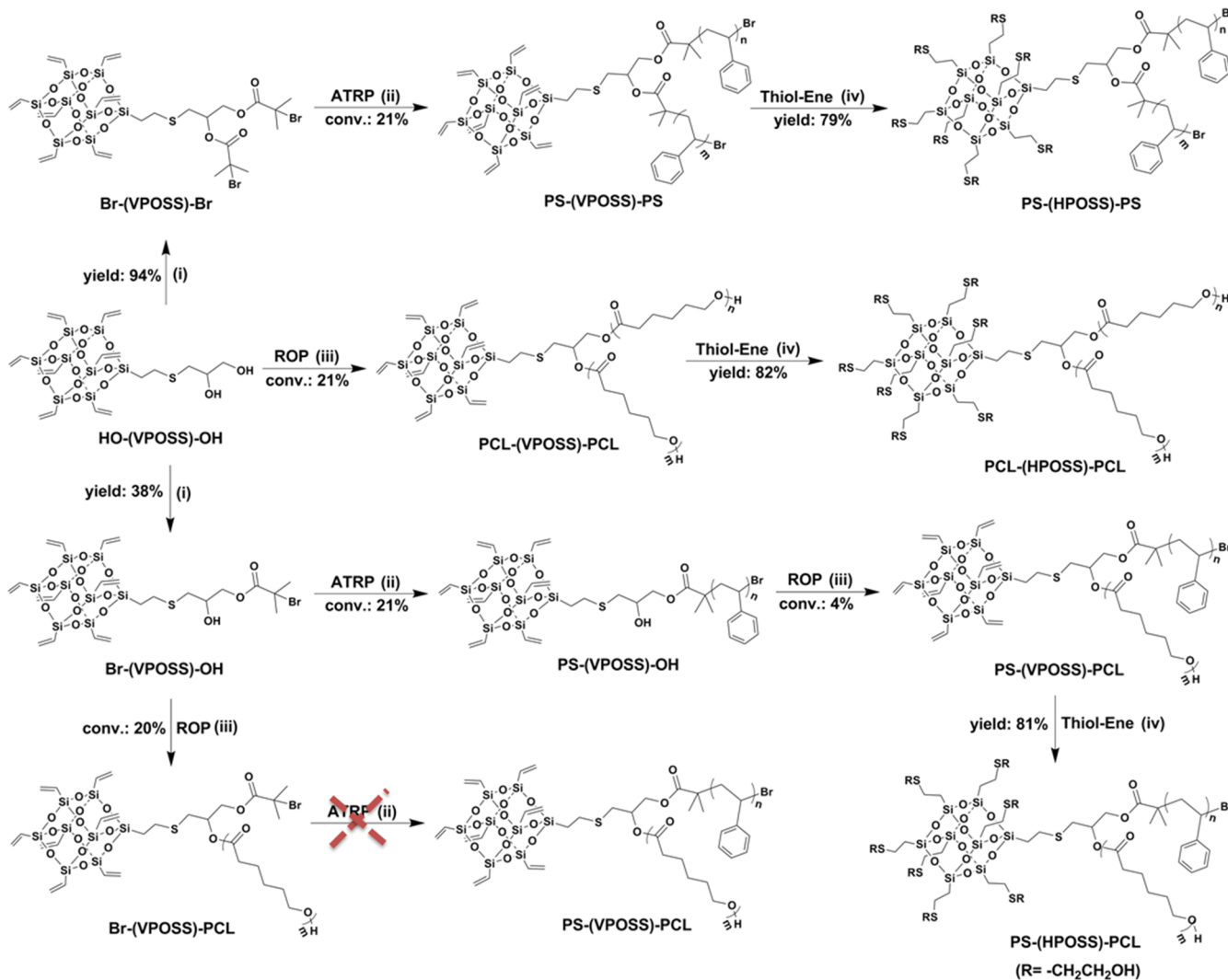
[a]Reagents and conditions: (i) 2-bromoisobutyryl bromide, Et₃N, CH₂Cl₂, r.t.; (ii) styrene, CuBr, PMDETA, toluene, 110 °C; (iii) ε-caprolactone, Sn(Oct)₂, toluene, 90 °C; (iv) HOCH₂CH₂SH, DMPA, THF, r.t., 15 min.

many as seven vinyl groups intact for final surface chemistry diversification. The preferential monofunctionalization was achieved by control of stoichiometry (1:1). Although higher addition products were also observed, the monoadduct, HO-(VPOSS)−OH, could be easily isolated by chromatography in ~30% yield. Considering that ~50% of the VPOSS was recovered after reaction, the yield based on conversion is ~60%. While the yield is comparable, the process is much simpler and faster than other methods for monofunctionalization of VPOSS.[6,19] It is also anticipated that the yield of the monoadduct may be further optimized by decreasing the concentration of VPOSS and adjusting the stoichiometry of the reactants. The versatile hydroxyl groups on HO-(VPOSS)-OH can be used to directly initiate the ring-opening polymerization[6] or further converted into other functional groups, such as 2-bromoisobutyryl, a well-known ATRP initiator.[34−36] In this work, a homobifunctional ATRP initiator, Br-(VPOSS)-Br, and a heterobifunctional initiator, Br-(VPOSS)-OH, were synthesized by esterification with 2-bromoisobutyryl bromide in the presence of triethylamine in CH₂Cl₂. In the former case, the esterification was performed with excess 2-bromoisobutyryl bromide to ensure a complete reaction (~94% yield, Figure 1a

for ¹H NMR). In the latter case, Br-(VPOSS)-OH was obtained by stoichiometry-controlled, selective esterification of the primary hydroxyl, which is known to be more reactive due to less steric hindrance. The selectivity is evidenced by the ¹H NMR spectrum of the crude product, which consists of >85% of Br-(VPOSS)-OH. After chromatographic separation, the desired Br-(VPOSS)-OH was obtained in good yield (~40%). The structure was unambiguously confirmed by NMR (Figure 2a), FT-IR, and MALDI-TOF mass spectrometry.

HPOSS with two symmetric tails: The compatibility of VPOSS cage with polymerization mechanism is critical in determining the feasibility of this "grafting-from" strategy. Recently, we have shown that ring-opening polymerization of lactides and ε-caprolactone is compatible with the vinyl groups on POSS.[6] The synthesis of PCL-(VPOSS)-PCL was thus similarly performed with success, as shown by NMR (Figures S1 and S2), SEC (Figure S3), and MALDI-TOF mass spectrometry (Figure 3b and Table 1). To emphasize the variation in tethered chain composition, the surface functionalization of POSS was performed with 2-mercaptoethanol through this work to make hydroxyl-functionalized POSS (HPOSS) so as to introduce amphiphacity. The simultaneous,
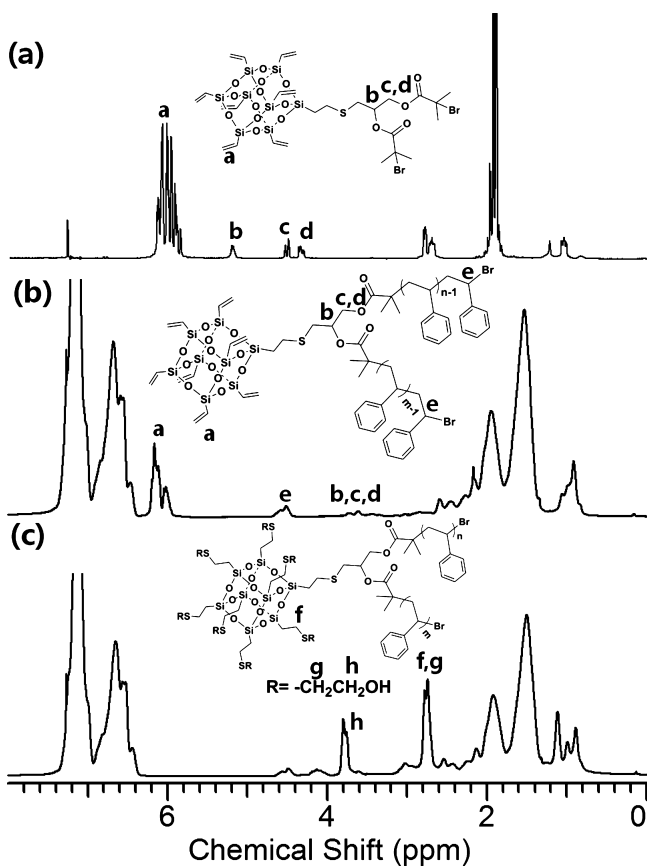
Figure 1. ^{1}H NMR spectra of (a) Br-(VPOSS)-Br, (b) PS-(VPOSS)-PS, and (c) PS-(HPOSS)-PS.

Figure 2. ^{1}H NMR spectra of (a) Br-(VPOSS)-OH, (b) PS-(VPOSS)-OH, (c) PS-(VPOSS)-PCL, and (d) PS-(HPOSS)-PCL.

multiple-site functionalization of POSS cage using thiol−ene chemistry was completed within 15 min, as revealed by the disappearance of the vinyl proton in the resonance range of δ 5.78−6.08 ppm and the new characteristic thiol ether proton resonances at δ 2.80−2.61 ppm in the ^{1}H NMR spectrum (Figure S1c). The MALDI-TOF mass spectrum of PCL-(HPOSS)-PCL (Figure 3a) further shows a single, narrow molecular weight distribution with peak mass shift of m/z = 546.88 (Figures S4) relative to its precursor PCL-(VPOSS)-PCL, which corresponds to the precise addition of seven 2-mercapoethanol molecules (Table 1). Therefore, ROP is fully compatible with VPOSS and, when combined with thiol−ene chemistry, allows the facile synthesis of PCL-(HPOSS)-PCL as designed.

On the other hand, due to the susceptibility of vinyl silsesquioxanes to radical addition, the compatibility of VPOSS with free radical polymerization was yet to be demonstrated. Vinyl siloxanes are known to be a simple vinyl monomer and have been copolymerized with other vinyl monomers, such as styrene, acrylonitrile, vinyl chloride, and so on.[37,38] In particular, octavinyl-POSS has been widely used as a free-radical cross-linker in the preparation of gels and nano-composites.[24,39,40] The polymerization was, thus, carried out in a large excess of styrene and the conversion was purposely limited as a precaution to avoid possible radical addition to vinyl silsesquioxane groups. While the result is similar to that of selective radical addition to conjugated vinyls,[41] the strategy is conceptually reminiscent of the previous work reported by Li et al. in the preparation of C$_{60}$-end-capped polystyrene using ATRP due to the increased reactivity of vinyl siloxanes.[42]
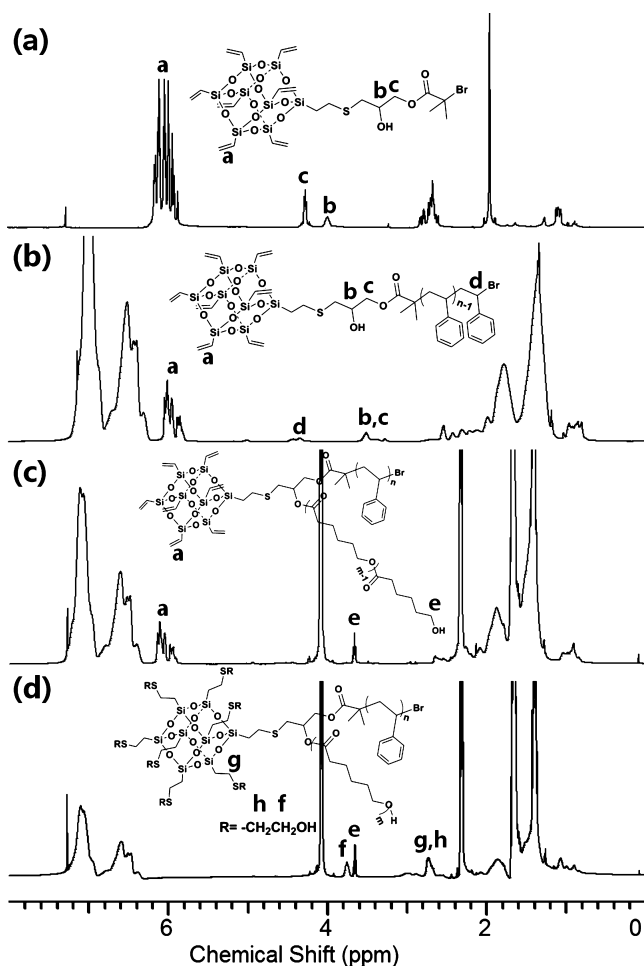
Indeed, by controlling conversion ($\sim$ 20%), no side reaction was observed, as revealed by the monomodal elution profile with low polydispersity in SEC (Figure 4). The well-defined structure of PS-(VPOSS)-PS was further proved by NMR, SEC, and MALDI-TOF mass spectrometry. The intact VPOSS unit is confirmed by the resonance signals at δ 6.11−5.78 ppm in the ^{1}H NMR spectrum (Figure 1b). In addition, the resonances assigned to the protons (a−c) near the ester bonds (Figure 1a) in Br-(VPOSS)-Br have shifted to new positions at δ 3.62−3.16 ppm in PS-(VPOSS)-PS, indicating a complete initiation. New resonances at δ 4.67−4.40 ppm correspond to the chain end protons (−CH$_2$CHPhBr) in PS and have an integration ratio of 2.00/3.05 when compared to that at δ 3.76−3.08 ppm (−CHOHCH_2O−), confirming the "grafting" of two PS chains "grafts" on the VPOSS. Furthermore, in the MALDI-TOF mass spectrum (Figure 3d), a single narrow molecular weight distribution can be clearly seen. A representative peak m/z value of 5041.64 corresponds to a 39-mer of PS-(VPOSS)-PS losing two HBr molecules (Table 1). Such a loss of chain-end HBr by fragmentation is common under the MALDI-TOF conditions for ATRP polymers with silver ion as cationizing agent.[43] Overall, the results suggest that the vinyl groups on the POSS cage do not interfere with ATRP and a precisely defined macromolecule, PS-(VPOSS)-PS, has been successfully synthesized. Subsequent surface functionalization was performed in a similar way to that of PCL-(VPOSS)-PCL. While similar evidence was also obtained in NMR, FT-IR, and SEC, the
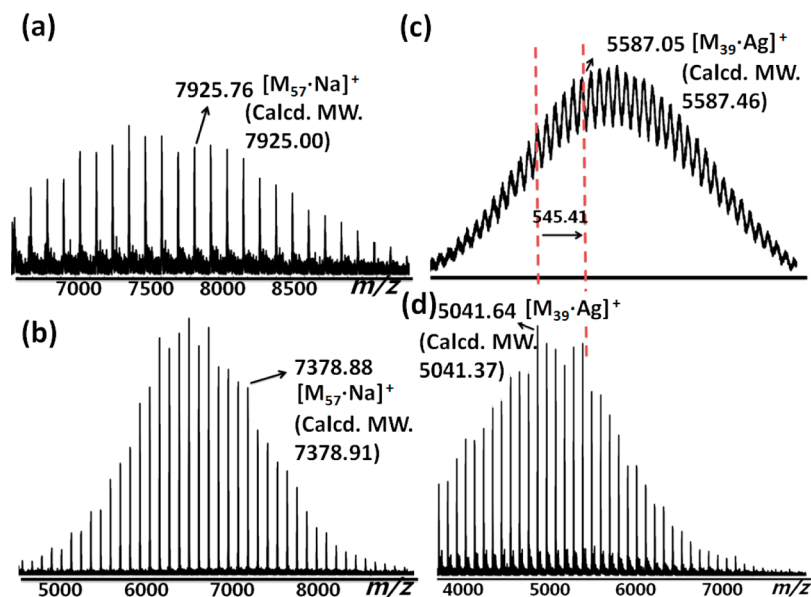
Figure 3. MALDI-TOF mass spectra of (a) PCL-(HPOSS)-PCL, (b) PCL-(VPOSS)-PCL, (c) PS-(HPOSS)-PS, and (d) PS-(VPOSS)-PS.

Table 1. Summary of Molecular Weight Characterizations[a]

sample	molecular formula	M (calcd; Da)	m/z (obsd)	$M_{n,NMR}$ (g/mol)	$M_{n,SEC}$ (g/mol)	PDI
PCL-(VPOSS)-PCL	$C_{367}H_{612}NaO_{130}SSi_8$	7378.91	7378.88	6.9k	8.5k	1.08
PCL-(HPOSS)-PCL	$C_{381}H_{654}NaO_{137}S_8Si_8$	7925.00	7925.76	7.4k	8.6k	1.06
PS-(VPOSS)-PS	$C_{339}H_{354}AgBr_2O_{16}SSi_8$-2HBr	5041.37	5041.64	5.7k	6.4k	1.03
PS-(HPOSS)-PS	$C_{353}H_{396}AgBr_2O_{23}S_8Si_8$-2HBr	5587.46	5587.05	5.9k	6.7k	1.02
PS-(VPOSS)-OH	$C_{215}H_{229}BrNaO_{15}SSi_8$−HBr	3328.49	3328.98	4.5k	4.8k	1.08
PCL-(VPOSS)-PCL				8.2k	8.8k	1.08
PS-(HPOSS)-PCL				8.7k	9.1k	1.12

[a]The adjusted molecular formula (molecular formula), the calculated monoisotopic molecular weights (M(calcd)), and the experimentally observed m/z (m/z (obsd)) are based on the observed molecular species in MALDI-TOF mass spectrometry with the corresponding cation, respectively: PCL-(VPOSS)-PCL (57-mer with Na⁺), PCL-(HPOSS)-PCL (57-mer with Na⁺), PS-(VPOSS)-PS (39-mer with Ag⁺), PS-(HPOSS)-PS (39-mer with Ag⁺), and PS-(VPOSS)-OH (24-mer with Na⁺).
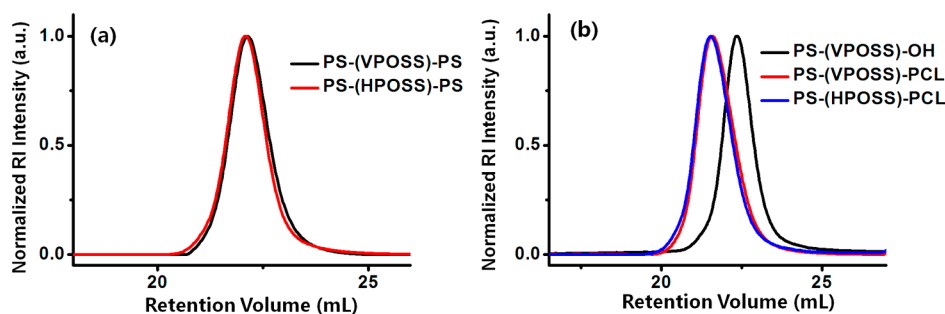

Figure 4. SEC diagrams for polymers: (a) PS-(VPOSS)-PS and PS-(HPOSS)-PS and (b) PS-(VPOSS)-OH, PS-(VPOSS)-PCL, and PS-(HPOSS)-PCL.

MALDI-TOF mass spectrum of PS-(HPOSS)-PS (Figure 3c) is worth discussion. Although the molecular homogeneity was demonstrated under the linear mode, where one single molecular weight distribution was observed, the monoisotopic resolution was only possible under reflection mode, yet with significant fragmentation (data not shown). The shift of 545.41 in m/z values (Table 1) suggests a complete reaction and a well-defined structure as designed. The PS-(HPOSS)-PS is an important model analogue of the previously reported "giant surfactant", the carboxylic acid-functionalized POSS-end-capped polystyrenes (APOSS-PS),[18] and is expected to exhibit

diverse self-assembly behaviors. The compatibility of VPOSS with free radical polymerization promises to greatly expand the scope of shape amphiphiles by facilitating the attachment of polymer tails of diverse composition and topology.

HPOSS with two asymmetric tails: The combination of various living/controlled polymerization methods has become a valuable and practical approach to polymers with asymmetric composition and complex architecture.[44,45] Whereas shape amphiphiles possessing two different polymer tails have been synthesized by "grafting-onto" strategy via conjugation of block copolymers and nanoparticles,[14,46−50] the heterobifunctional

initiator, Br-(VPOSS)-OH, offers a versatile alternative by the "grafting-from" approach due to the high compatibility of VPOSS with different polymerization conditions. Nevertheless, the sequence of polymerization could affect the result. In the trial with the sequence of ROP and ATRP, although Br-(VPOSS)-PCL was successfully synthesized with a well-defined structure (Figure S6), subsequent ATRP failed to give a homogeneous product, as shown by the bimodal SEC diagram (Figure S7) despite many efforts to optimize the condition by changing temperature, conversion, initiator/monomer ratio, and so on. In this case, the steric effect of a tethered polymer chain and the chemical composition of the tethered polymer chain do not seem to be responsible for the inefficient initiation because the polymerization sequence swap gives satisfactory result (vide infra and see also ref 51.) and ATRP is known to be compatible with both PCL and PS.[51,52] The complication should thus arise from the side reactions between the initiation/propagation species and the vinyl groups on POSS during ATRP, yielding addition products that hardly reinitiate again. It was speculated that, not only the initiation efficiency of bromoisobutyryl group is significantly reduced when buried in between VPOSS and PCL, the possibility for radical addition of the active center to the vinyl groups in the vicinity also increases. Due to the higher compatibility of ROP with VPOSS than ATRP, the sequence swap gave successful results. The PS block was first synthesized similar to that of PS-(VPOSS)-PS. The disappearance of the resonances at δ 4.28 and 3.98 ppm and the appearance of new resonances at δ 4.58−4.31 and 3.82−3.30 ppm in the ^{1}H NMR spectrum of PS-(VPOSS)-OH suggest the efficient initiation and successful growth of a PS chain (Figure 2b). The well-defined structure is also evidenced by the MALDI-TOF mass spectrum (Figure S8). The ROP of ε-caprolactone was then performed using PS-(VPOSS)-OH as the macroinitiator. The second block formation is clearly shown in the SEC diagram of PS-(VPOSS)-PCL (Figure 4b) where a monomodal, symmetric peak with low polydispersity (M_n = 8.8 kg/mol, PDI = 1.08) was observed at much lower retention volume compared to PS-(VPOSS)-OH (M_n = 4.8 kg/mol, PDI = 1.08). The newly formed PCL block was characterized by the resonances at δ 4.08, 2.33, 1.67, and 1.40 ppm in the ^{1}H NMR spectrum (Figure 2c) and at δ 173.47, 64.11, 34.10, 28.33, 25.51, and 24.56 ppm in the ^{13}C NMR spectrum (Figure S9a). In addition, the integration ratio between the resonance at δ 3.66 ppm ($-CH_2OH$ at the PCL chain end) and at δ 5.78−6.11 ppm ($CH_2=CH-$) is 2.0:21.5, which suggests the precisely defined structure with one POSS per PCL tail and PS tail. Although it was difficult to get MALDI-TOF mass spectrum for PS-(VPOSS)-PCL, the above evidence suggests a successful sequential growth of two polymer chains. This is again followed by thiol−ene "click" functionalization of VPOSS. The high efficiency is proved by the disappearance of the vinyl proton resonances at δ 5.78−6.11 ppm after 15 min of reaction, which indicates the heterogeneous tethered-chain composition does not affect the reaction. The SEC diagram of PS-(HPOSS)-PCL (Figure 4c) shows a monomodal symmetric peak at slightly lower retention volume than that of PS-(VPOSS)-PCL. Therefore, shape amphiphile with two polymer tails of asymmetric composition was synthesized by sequential ATRP, ROP, and thiol−ene "click" chemistry. It is noteworthy that, because ATRP and ROP are both controlled polymerization techniques, the molecular weights and the monomer composition of each block may be separately controlled,

providing a modular approach to a class of shape amphiphiles for a systematic study.

In summary, a series of well-defined shape amphiphiles based on functionalized POSS tethered with two polymer tails of symmetric/asymmetric compositions has been successfully prepared using a combination of "grafting-from" strategy and thiol−ene "click" chemistry. VPOSS was found to be compatible with both ROP and ATRP, which is expected to greatly expand the scope of shape amphiphiles with various tethered chain compositions. When carried out in sequence of ATRP and then ROP, it affords tethered chains with asymmetric composition, PS-(HPOSS)-PCL. Thiol−ene reaction was demonstrated again as a highly efficient, convenient, and versatile way to functionalize VPOSS. Not only can multiple-site functionalization be performed simultaneously with high efficiency, monofunctionalization can also be effected by stoichiometry control. In general, our methods provide a robust and modular approach for the synthesis of model shape amphiphiles with precise control over molecular parameters for a systemic study. Relevant work is ongoing in our laboratory to reveal the intriguing hierarchical structures and the underlying physical principles of their self-assembly.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, including the synthesis and characterization of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wz8@uakron.edu (W.-B.Z.); scheng@uakron.edu (S.Z.D.C.); rpquirk@uakron.edu (R.P.Q.). Tel: +1 330 990 9801 (W.-B.Z.); +1 330 972 6931 (S.Z.D.C.); +1 330 990 7510 (R.P.Q.). Fax: +1 330 972 8626 (W.-B.Z. and S.Z.D.C.); + 1 330 972 5290 (R.P.Q.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Dirks, A. J.; Nolte, R. J. M.; Cornelissen, J. J. L. M. *Adv. Mater.* **2008**, *20*, 3953−3957.

(2) Reynhout, I. C.; Cornelissen, J. J. L. M.; Nolte, R. J. M. *Acc. Chem. Res.* **2009**, *42*, 681−692.

(3) Zhang, Z.; Horsch, M. A.; Lamm, M. H.; Glotzer, S. C. *Nano Lett.* **2003**, *3*, 1341−1346.

(4) Glotzer, S. C.; Solomon, M. J. *Nat. Mater.* **2007**, *6*, 557−562.

(5) Velonia, K. *Polym. Chem.* **2010**, *1*, 944−952.

(6) Zhang, W.-B.; Li, Y.; Li, X.; Dong, X.; Yu, X.; Wang, C.-L.; Wesdemiotis, C.; Quirk, R. P.; Cheng, S. Z. D. *Macromolecules* **2011**, *44*, 2589−2596.

(7) Velonia, K.; Rowan, A. E.; Nolte, R. J. M. *J. Am. Chem. Soc.* **2002**, *124*, 4224−4225.

(8) Boerakker, M. J.; Hannink, J. M.; Bomans, P. H. H.; Frederik, P. M.; Nolte, R. J. M.; Meijer, E. M.; Sommerdijk, N. A. J. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4239−4241.

(9) Jones, M. W.; Gibson, M. I.; Mantovani, G.; Haddleton, D. M. *Polym. Chem.* **2011**, *2*, 572−574.

(10) Thomas, C. S.; Glassman, M. J.; Olsen, B. D. *ACS Nano* **2011**, *5*, 5697−5707.

(11) Van Hest, J. C. M.; Delnoye, D. A. P.; Baars, M. W. P. L.; Van Genderen, M. H. P.; Meijer, E. W. *Science* **1995**, *268*, 1592−1595.

(12) Román, C.; Fischer, H. R.; Meijer, E. W. *Macromolecules* **1999**, *32*, 5525−5531.

(13) Zhang, W.-B.; Tu, Y.; Ranjan, R.; Van Horn, R. M.; Leng, S.; Wang, J.; Polce, M. J.; Wesdemiotis, C.; Quirk, R. P.; Newkome, G. R.; Cheng, S. Z. D. *Macromolecules* **2008**, *41*, 515−517.

(14) Dong, X.; Zhang, W.-B.; Li, Y.; Huang, M.; Zhang, S.; Quirk, R. P.; Cheng, S. Z. D. *Polym. Chem.* **2012**, *3*, 124−134.

(15) Han, Y.-K.; Zhang, Z.-J.; Wang, Y.-L.; Xia, N.; Liu, B.; Xiao, Y.; Jin, L.-X.; Zheng, P.; Wang, W. *Macromol. Chem. Phys.* **2011**, *212*, 81−87.

(16) Han, Y.; Xiao, Y.; Zhang, Z.; Liu, B.; Zheng, P.; He, S.; Wang, W. *Macromolecules* **2009**, *42*, 6543−6548.

(17) Felici, M.; Marzá-Pérez, M.; Hatzakis, N. S.; Nolte, R. J. M.; Feiters, M. C. *Chem.—Eur. J.* **2008**, *14*, 9914−9920.

(18) Yu, X.; Zhong, S.; Li, X.; Tu, Y.; Yang, S.; Van Horn, R. M.; Ni, C.; Pochan, D. J.; Quirk, R. P.; Wesdemiotis, C.; Zhang, W.-B.; Cheng, S. Z. D. *J. Am. Chem. Soc.* **2010**, *132*, 16741−16744.

(19) Li, Y.; Zhang, W.-B.; Hsieh, I.-F.; Zhang, G.; Cao, Y.; Li, X.; Wesdemiotis, C.; Lotz, B.; Xiong, H.; Cheng, S. Z. D. *J. Am. Chem. Soc.* **2011**, *132*, 10712−10715.

(20) Roll, M. F.; Asuncion, M. Z.; Kampf, J.; Laine, R. M. *ACS Nano* **2008**, *2*, 320−326.

(21) Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* **2010**, *110*, 2081−2173.

(22) Pielichowski, K.; Njuguna, J.; Janowski, B.; Pielichowski, J. *Adv. Polym. Sci.* **2006**, *201*, 225−296.

(23) Tanaka, K.; Chujo, Y. *J. Mater. Chem.* **2012**, *22*, 1733−1746.

(24) Kuo, S.-W.; Chang, F.-C. *Prog. Polym. Sci.* **2011**, *36*, 1649−1696.

(25) Wu, Y.-C.; Kuo, S.-W. *J. Mater. Chem.* **2012**, *22*, 2982−2991.

(26) Xu, J.; Li, X.; Cho, C. M.; Toh, C. L.; Shen, L.; Mya, K. Y.; Lu, X.; He, C. *J. Mater. Chem.* **2009**, *19*, 4740−4745.

(27) Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, B. D. *Angew. Chem., Int. Ed.* **2008**, *47*, 4137−4140.

(28) Lee, J.; Cho, H.-J.; Cho, N. S.; Hwang, D.-H.; Shim, H.-K. *Synth. Met.* **2006**, *156*, 590−596.

(29) Li, K.; Liu, Y.; Pu, K.-Y.; Feng, S.-S.; Zhan, R.; Liu, B. *Adv. Funct. Mater.* **2011**, *21*, 287−294.

(30) Fabritz, S.; Heyl, D.; Bagutski, V.; Empting, M.; Rikowski, E.; Frauendorf, H.; Balog, I.; Fessner, W.-D.; Schneider, J. J.; Avrutina, O.; Kolmar, H. *Org. Biomol. Chem.* **2010**, *8*, 2212−2218.

(31) Gao, Y.; Eguchi, A.; Kakehi, K.; Lee, Y. C. *Org. Lett.* **2004**, *6*, 3457−3460.

(32) Yuan, H.; Luo, K.; Lai, Y.; Pu, Y.; He, B.; Wang, G.; Wu, Y.; Gu, Z. *Mol. Pharm.* **2010**, *7*, 953−962.

(33) Kaneshiro, T. L.; Wang, X.; Lu, Z.-R. *Mol. Pharm.* **2007**, *4*, 759−768.

(34) Xie, M.; Dang, J.; Han, H.; Wang, W.; Liu, J.; He, X.; Zhang, Y. *Macromolecules* **2008**, *41*, 9004−9010.

(35) Li, Z.; Ma, J.; Cheng, C.; Zhang, K.; Wooley, K. L. *Macromolecules* **2010**, *43*, 1182−1184.

(36) Morandi, G.; Montembault, V.; Pascual, S.; Legoupy, S.; Fontaine, L. *Macromolecules* **2006**, *39*, 2732−2735.

(37) Pike, R. M.; Bailey, D. L. *J. Polym. Sci.* **1956**, *22*, 55−64.

(38) Tezuka, Y.; Tanaka, S.; Imai, K. *Polymer* **1986**, *27*, 123−128.

(39) Tan, B. H.; Hussain, H.; He, C. B. *Macromolecules* **2011**, *44*, 622−631.

(40) Yang, B.; Xu, H.; Wang, J.; Gang, S.; Li, C. *J. Appl. Polym. Sci.* **2007**, *106*, 320−326.

(41) Ma, J.; Cheng, C.; Sun, G.; Wooley, K. L. *Macromolecules* **2008**, *41*, 9080−9089.

(42) Zhou, P.; Chen, G.-Q.; Li, C.-Z.; Du, F.-S.; Li, Z.-C.; Li, F.-M. *Chem. Commun.* **2000**, 797−798.

(43) Ladavière, C.; Lacroix-Desmazes, P.; Delolme, F. *Macromolecules* **2009**, *42*, 70−84.

(44) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.

(45) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93−146.

(46) Zhang, W.-B.; Sun, B.; Li, H.; Ren, X.; Janoski, J.; Sahoo, S.; Dabney, D. E.; Wesdemiotis, C.; Quirk, R. P.; Cheng, S. Z. D. *Macromolecules* **2009**, *42*, 7258−7262.

(47) Wang, X.; Zhang, Y.; Zhu, Z.; Liu, S. *Macromol. Rapid Commun.* **2008**, *29*, 340−346.

(48) Li, C.; Hu, J.; Yin, J.; Liu, S. *Macromolecules* **2009**, *42*, 5007−5016.

(49) Zhang, L.; Lu, D.; Tao, K.; Bai, R. *Macromol. Rapid Commun.* **2009**, *30*, 1015−1020.

(50) Gungor, E.; Bilir, C.; Durmaz, H.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5947−5953.

(51) He, J.; Yue, K.; Liu, Y.; Yu, X.; Ni, P.; Cavicchi, K. A.; Quirk, R. P.; Chen, E.-Q.; Cheng, S. Z. D.; Zhang, W. −B. *Polym. Chem.* **2012**, DOI: 10.1039/C2PY20101A.

(52) Du, J.; Chen, Y. *Macromolecules* **2004**, *37*, 3588−3594.