ACS Macro Letters

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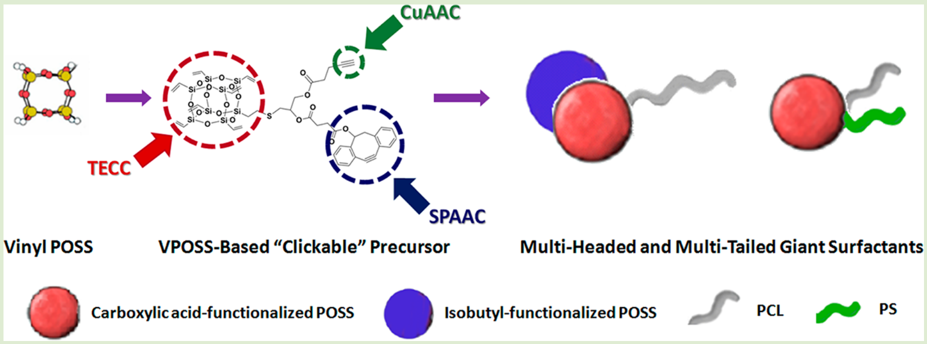
Sequential Triple "Click" Approach toward Polyhedral Oligomeric Silsesquioxane-Based Multiheaded and Multitailed Giant Surfactants

Hao Su,[†] Jukuan Zheng,[†] Zhao Wang,[†] Fei Lin,[†] Xueyan Feng,[†] Xue-Hui Dong,[†] Matthew L. Becker,[†,‡] Stephen Z. D. Cheng,*[,†] Wen-Bin Zhang,*[,†] and Yiwen Li*[,†]

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

[‡]Center for Biomaterials in Medicine, Austen BioInnovation Institute in Akron, Akron, Ohio 44308, United States

Supporting Information



ABSTRACT: This letter reports a sequential triple "click" chemistry method for the precise synthesis of functional polyhedral oligomeric silsesquioxane (POSS)-based multiheaded and multitailed giant surfactants. A vinyl POSS-based heterobifunctional building block possessing two alkyne groups of distinct reactivity was used as a robust and powerful "clickable" precursor for ready access to a variety of POSS-based shape amphiphiles with complex architectures. The synthetic approach involves sequentially performed strain-promoted azide−alkyne cycloaddition (SPAAC), copper-catalyzed azide−alkyne cycloaddition (CuAAC), and thiol−ene "click" coupling (TECC). Specifically, the first SPAAC reaction was found to be highly selective with no complications from the vinyl groups and terminal alkynes in the precursor. The method expands the toolbox of sequential "click" approaches and broadens the scope of synthetically available giant surfactants for further study on structure−property relationships.

The "bottom-up" fabrication via self-assembly has been widely used to develop different nanomaterials and nanopatterns.[1−3] One of the key targets is to create nanostructures of high complexity which would otherwise be difficult to achieve by the "top-down" approach.[1−3] Typical self-assembling materials used in the "bottom-up" approach include small-molecule surfactants and lipids,[4,5] Janus dendrimers,[6,7] block copolymers,[8−10] and, more recently, shape amphiphiles.[11−15] Among them, shape amphiphiles refer to molecules possessing segments of incommensurate features including distinct surface interactions and anisotropic shapes.[16−19]

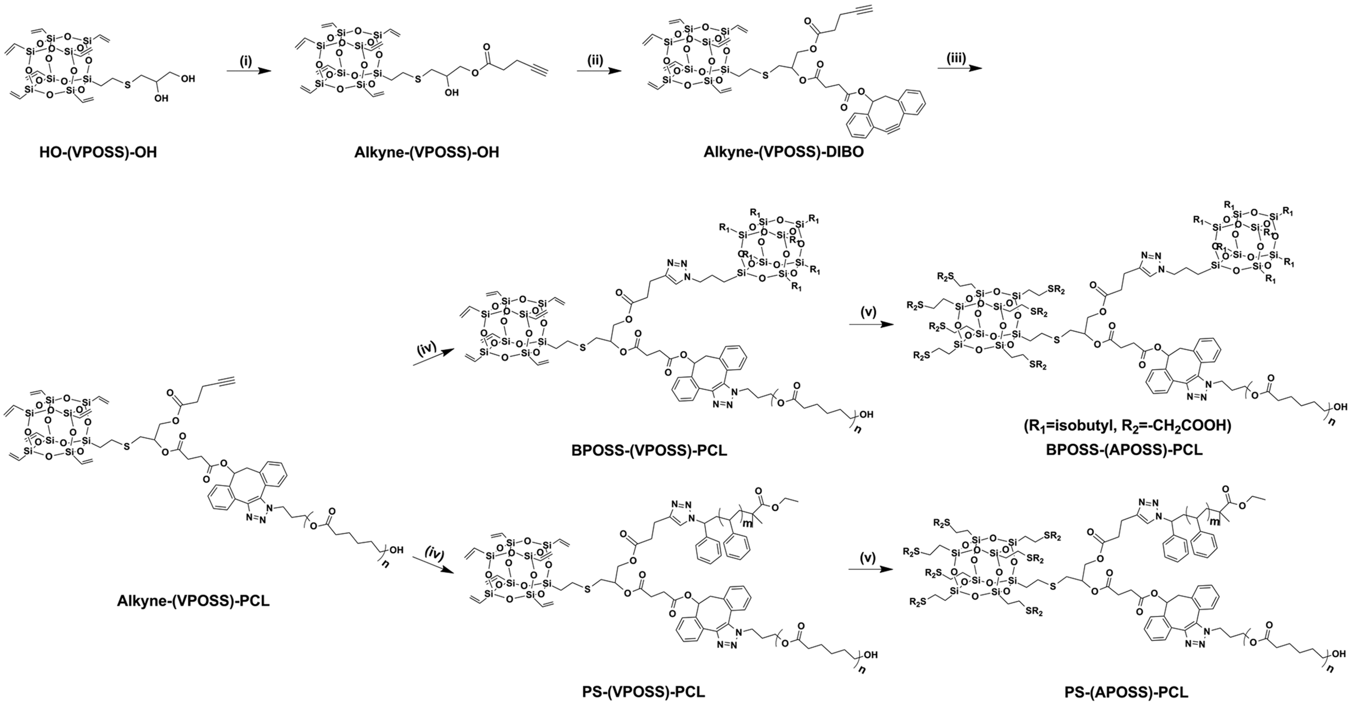
Polyhedral oligomeric silsesquioxane (POSS)-based shape amphiphiles have attracted considerable research interests in recent years, both as model compounds for supramolecular structure engineering[14−16,20,21] and as hybrid materials for potential technological and industrial applications.[20,21] The precisely defined molecular structures and readily modifiable surface chemistry on POSS[21−27] provide ideal scenarios in establishing a library of shape amphiphiles with virtually unlimited possibilities for structural variation. Among them, polymer-tethered POSS is of particular interest as a new class of shape amphiphiles—the "giant surfactants"[15,16,28]—since it captures the essential structural feature of small-molecule surfactants but has a size of several nanometers. Our recent results have demonstrated that giant surfactants possess a duality of small-molecule surfactants and block copolymers, providing a versatile platform to engineer nanostructures with sub-10 nm feature sizes.[15,20] In analogy to their small-molecule counterparts, a family of giant surfactants with diverse architectures can be constructed, including giant lipids,[29] giant gemini surfactants,[14,30] giant bolaform surfactants,[30] multiheaded and multitailed giant surfactants (MHGS and MTGS), and others.

Multiheaded/multitailed surfactants are an interesting class of small-molecule surfactants with unique properties in their aggregates states.[31,32] For example, the micellar sizes and aggregation numbers of multiheaded surfactants in solution would decrease with the increase of the number of head groups

Received: May 31, 2013
Accepted: July 10, 2013
Published: July 15, 2013

dx.doi.org/10.1021/mz4002723 | *ACS Macro Lett.* 2013, 2, 645−650

Scheme 1. Synthetic Route Using Sequential Triple "Click" Chemistry[a]



[a](i) 4-Pentynoic acid, DPTS, DIPC, dry CH_2Cl_2, 0 °C, 50%; (ii) DIBO−COOH, DPTS, DIPC, dry DMF, 0 °C, 92%; (iii) PCL−N_3, $CHCl_3$, 25 °C, 89%; (iv) PS-N_3 or BPOSS−N_3, CuBr, PMDETA, toluene, 25 °C, 81% for BPOSS−(VPOSS−PCL, and 90% for PS−(VPOSS)−PCL; (v) 2-mercaptoacetic acid, DMPA, THF, 25 °C, 15 min, 79% for BPOSS−(APOSS)−PCL, and 85% for PS−(APOSS)−PCL.

on the surfactants.[31] It is thus intriguing to study the corresponding MHGS and MTGS and compare their physical behaviors with small-molecule counterparts. If we consider the POSS cages as one block with fixed volume and shape, the POSS-based MHGS and MTGS can also be regarded as miktoarm star polymers.[33−36] The synthesis of MHGS and MTGS presents an immense challenge, particularly when the heads and/or tails are of different compositions. So far, there are only a few reports on MTGS based on a molecular nanoparticle tethered with two distinct polymers, including the synthesis of PS−(APOSS)−PCL,[29] PS−(FPOSS)−PCL,[37] and PS−(BPOSS)−PDMS.[38] In general, the syntheses were achieved by either "grafting-from"[16,29] or "grafting-onto" strategies.[37,38] However, the former lacks good control on the attached polymer chains and has limited scope of applications due to inefficient initiations[29] and/or incompatible polymerization methods.[28] The latter starts either with polymers possessing two different functional groups at one end of the chain[37] or block copolymers possessing one reactive functional group at the junction point.[38] It is more general and precise since the polymers are synthesized before conjugation and are well-defined. To further broaden the scope of the "grafting-to" approach to synthesize POSS-based MHGS/MTGS with even more complex structures, it is necessary to develop a general methodology using a multifunctional POSS precursor.

Sequential "click" chemistry has been demonstrated as a powerful route to synthesize diverse POSS-based shape amphiphiles in a modular fashion.[28,30] Libraries of giant surfactants with precise structures can be readily synthesized in a few steps from common simple precursors using two consecutive "click" reactions in addition to "click" adaptors and/or multifunctional polymer motifs.[20,28,30,39] Although it is possible to apply this method to prepare MHGS/MTGS with hetero head/tail compositions,[38,39] it is nontrivial to synthesize the precursor—a multi-POSS or multiblock polymer precursor with one reactive group at the junction point. Adding additional "clickable" functionalities to the POSS segment seems a feasible alternative. Strain-promoted azide−alkyne cycloaddition (SPAAC) between cyclooctynes and azides has emerged as a bio-orthogonal, metal-free, and highly efficient "click" chemistry.[40−45] The distinctly different chemical reactivity between cyclooctyne and terminal alkyne shall facilitate a selective functionalization of the former in the absence of Cu,[46] which may be utilized to develop a triple "click" POSS precursor.

In this letter, we report a sequential triple "click" chemistry approach and demonstrate its use in the synthesis of model MHGS and MTGS (Scheme 1) with hetero head and tail compositions. The method provides a modular and facile access to POSS-based shape amphiphiles with complex architectures and novel compositions.

Several multifunctional POSS compounds have been developed as precursors for the synthesis of shape amphiphiles with complex architectures.[14,29] In the current work, we introduce an additional "clickable" group, 4-dibenzocyclooctyne motif (DIBO),[47] onto POSS to facilitate the synthesis of MHGS/MTGS consisting of three or more immiscible molecular segments. This was prepared directly by esterification between a reported multifunctional POSS compound, alkyne−(VPOSS)−OH,[14] and DIBO−COOH. The reaction was performed with a stoichiometric mixture of alkyne−(VPOSS)−OH and DIBO−COOH in the presence of 4-(dimethylamino) pyridinium toluene-*p*-sulfonate (DPTS) and *N*,*N*′-diisopropylcarbodiimide (DIPC) in dry DMF. The product was purified by chromatography in a very good yield (92%). The successful incorporation of DIBO was demonstrated by the characteristic resonances of aromatic protons at δ

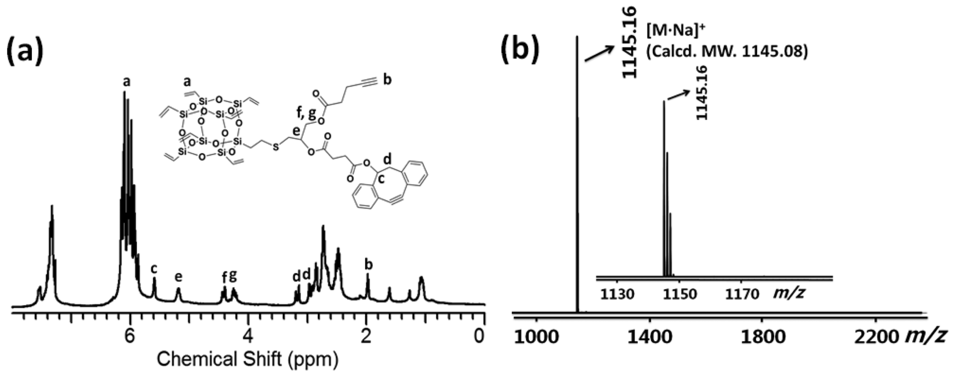


Figure 1. ^{1}H NMR spectrum (a) and MALDI-TOF mass spectrum (b) of alkyne−(VPOSS)−DIBO.

7.54−7.28 ppm in the ^{1}H NMR spectrum (Figure 1a) and related resonances of aromatic carbons at δ 130.14−121.52 ppm in the ^{13}C NMR spectrum (Figure S1, Supporting Information). It was further confirmed by UV−vis spectroscopy where a strong UV absorbance peak at ~306 nm characteristic of the DIBO unit was observed (Figure S2a, Supporting Information).[44] The MALDI-TOF mass spectrum (Figure 1b) displays a single peak at m/z 1145.16 that agrees well with the calculated monoisotopic molecular mass for alkyne−(VPOSS)−DIBO (1145.08 Da). The presence of one DIBO group and one terminal alkyne group can be used to install two (or more) different immiscible blocks onto the VPOSS cage using SPAAC and Cu(I)-catalyzed azide−alkyne cycloaddition (CuAAC), respectively. The vinyl groups on the VPOSS periphery can be used for surface chemistry diversification on POSS via thiol−ene "click" coupling (TECC). The possibility to do three sequential "click" reactions shall greatly expand the scope of POSS-based shape amphiphiles. We anticipate that different macromolecules including dendrimers, cyclic polymers, branched polymers, and other molecular nanoparticles can be readily incorporated to prepare even more complex POSS-based shape amphiphiles. In this work, we demonstrate the utility of this precursor by the preparation of a model MHGS possessing two different POSS heads and a model MTGS possessing two different polymer tails.

To utilize the sequential "click" approach, it is important that each of the "click" reactions is highly selective, and no side reactions would occur. We have recently demonstrated the compatibility of CuAAC reaction with the vinyl groups on POSS.[28] Yet, it remains uncertain whether the presence of a highly reactive DIBO unit may lead to any side reactions during the first copper-free "click" reaction. It was examined by the SPAAC between alkyne−(VPOSS)−DIBO and an azide-functionalized poly(ε-caprolactone)[48] (PCL−N_3, $M_{n,\text{NMR}}$ = 2.8 kg/mol, $M_{n,\text{SEC}}$ = 3.4 kg/mol, PDI = 1.12, see Figure S3, Supporting Information, for MALDI-TOF mass spectrum) in the absence of copper catalyst. Simply mixing two components in a common solvent (such as $CHCl_3$ or THF) for about one hour led to complete reaction, as shown by the FT-IR spectrum of the crude product which displays no absorption of the azide group at around 2100 cm^{-1} (Figure S4, Supporting Information). The VPOSS−PCL conjugate was then obtained in a good yield of 89%. The success of the cycloaddition was also directly evidenced by the UV−vis absorbance profile. The complete disappearance of the strong absorbance for the alkyne group in DIBO at ~306 nm ($\varepsilon_{\text{alkyne-(VPOSS)-DIBO}}$ = 36080 L·mol^{-1}·cm $^{-1}$ vs $\varepsilon_{\text{alkyne-(VPOSS)-PCL}}$ = 0 L·mol^{-1}·cm $^{-1}$) in the UV−vis absorbance spectrum (Figure S2, Supporting Information) indicates the successful coupling of VPOSS with a PCL tail in a high conversion.[43,44] In the ^{1}H NMR spectrum, the proton (c) of the precursor alkyne−(VPOSS)−DIBO at δ 5.59 ppm completely shifts to a new resonance at δ 6.23 ppm (Figure 2a), suggesting a complete reaction of the DIBO unit. Notably, according to ref 49, there should be another characteristic resonance attributed to the proton (c) at δ 6.00 ppm. However, it overlaps with those of the vinyl protons of VPOSS and thus could not be distinguished.[49] We expect that it

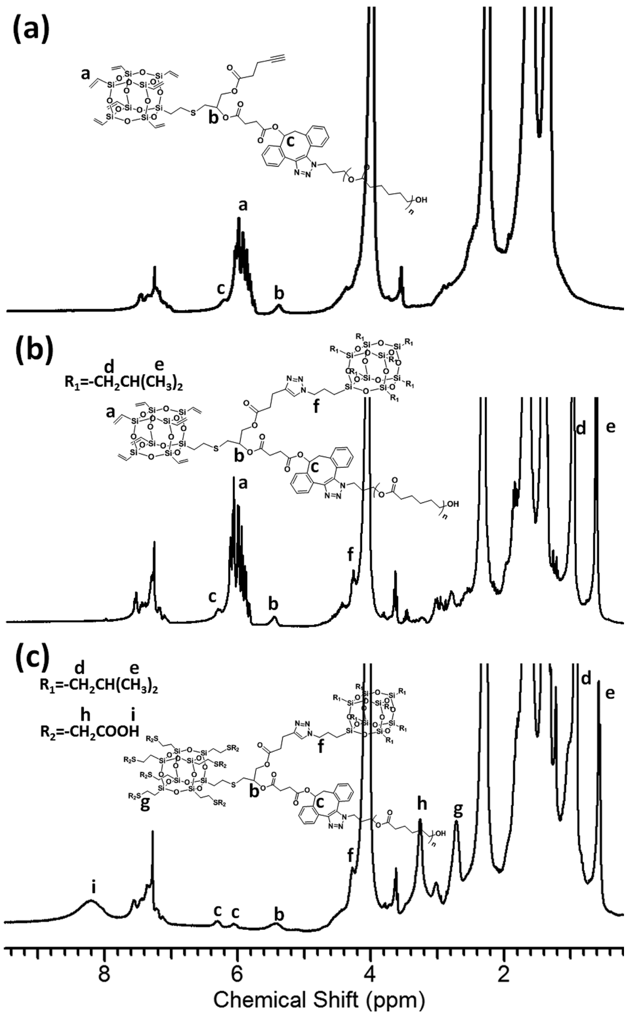


Figure 2. ^{1}H NMR spectra of (a) alkyne−(VPOSS)−PCL, (b) BPOSS−(VPOSS)−PCL, and (c) BPOSS−(APOSS)−PCL.

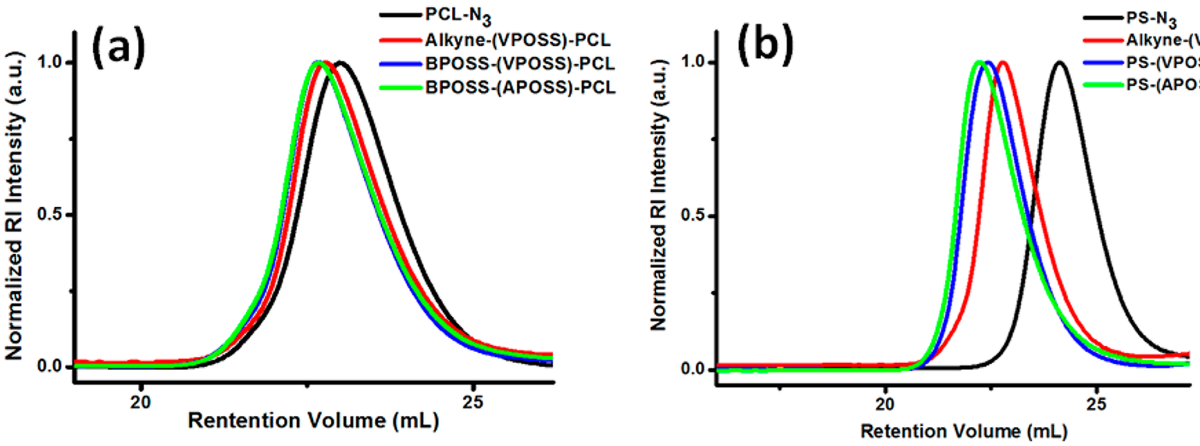


Figure 3. SEC overlays for polymers: (a) PCL−N_3 (black curve), alkyne−(VPOSS)−PCL (red curve), BPOSS−(VPOSS)−PCL (blue curve), and BPOSS−(APOSS)−PCL (green curve) and (b) PS−N_3 (black curve), alkyne−(VPOSS)−PCL (red curve), PS−(VPOSS)−PCL (blue curve), and PS−(APOSS)−PCL (green curve).

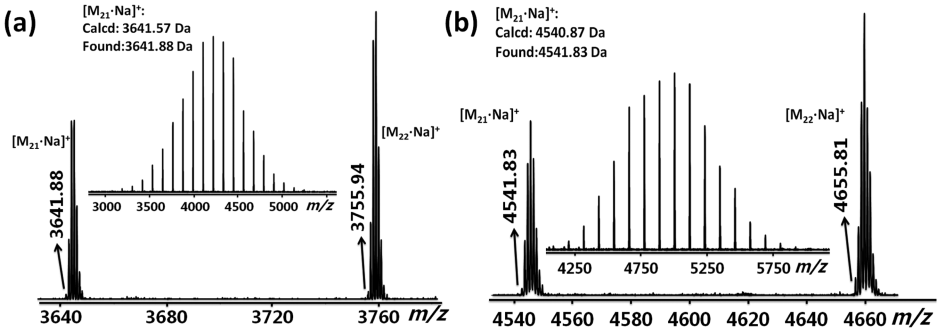


Figure 4. MALDI-TOF mass spectra of (a) alkyne−(VPOSS)−PCL and (b) BPOSS−(VPOSS)−PCL. Both spectra were obtained in reflection mode with monoisotopic resolution. The insets show the corresponding full spectra.

Table 1. Summary of Molecular Weight Characterizations

sample	molecular formula[a]	M (calcd)[b] (Da)	m/z (obsd)[c]	$M_{n,NMR}$ (g/mol)	$M_{n,SEC}$ (g/mol)	PDI
alkyne−(VPOSS)−PCL	$C_{173}H_{267}N_3NaO_{61}SSi_8$	3641.57	3641.88	4.0 k	4.2 k	1.09
BPOSS−(VPOSS)−PCL	$C_{204}H_{336}N_6NaO_{73}SSi_{16}$	4540.87	4541.83	4.7 k	5.2 k	1.07
BPOSS−(APOSS)−PCL	-	-	-	5.0 k	5.2 k	1.08
PS−(VPOSS)−PCL	-	-	-	7.6 k	8.1 k	1.05
PS−(APOSS)−PCL	-	-	-	7.9 k	8.5 k	1.03

[a] The molecular formula. [b] The calculated monoisotopic molecular weights. [c] The experimentally observed m/z.

should be observed once the vinyl groups have completely reacted in the following steps. The characteristic protons on PCL backbones at resonances of δ 3.96, 3.52, 2.21, 1.55, and 1.31 ppm can be clearly assigned as shown in Figure 2b. The integrity of the VPOSS cage after the first SPAAC reaction is demonstrated by vinyl protons in the range of δ 6.12−5.81 ppm in the ^{1}H NMR spectrum (Figure 2a) as well as sp^2 carbons of vinyl groups at resonances of δ 137.27 and 128.24 ppm in the ^{13}C NMR spectrum (Figure S5a, Supporting Information). The SEC diagram of alkyne−(VPOSS)−PCL (M_n = 4.2 kg/mol, PDI = 1.09) (Figure 3a) illustrates a monomodal symmetric peak at a lower retention volume than that of PCL−N_3, which is consistent with the increased molecular weight. Moreover, the MALDI-TOF mass spectrum (Figure 4a) shows only one single narrow distribution with molecular weights in accordance to the proposed structure. A representative monoisotopic mass peak at m/z 3641.88 for alkyne−(VPOSS)−PCL (Na^+ adduct) is in close match with the calculated molecular mass of 3641.57 Da for 21-mer of the formula $[C_{173}H_{267}N_3NaO_{61}SSi_8]^+$ (Figure 4 and Table 1). These results unambiguously confirm the molecular structure and uniformity of the conjugate.

Alkyne−(VPOSS)−PCL can now serve as a common macromolecular precursor to a variety of MHGS/MTGS following sequential "click" functionalization by CuAAC and TECC. To prepare MHGS possessing two different POSS heads, an isobutyl-functionalized POSS (BPOSS) and a carboxylic acid-functionalized POSS (APOSS) were chosen. We have previously shown that a molecular Janus particle can be constructed by linking APOSS with BPOSS and that the resulting dumbbell molecule self-assembles into a unique lamellar crystal.[21] We expect intriguing hierarchical structure formation from the MHGS, BPOSS−(APOSS)−PCL, since the three components are strongly microphase separated.[16,21,50] The incorporation of BPOSS was carried out between BPOSS−N_3 and alkyne−(VPOSS)−PCL under a typical CuAAC condition.[14,28,30] The structure of the product, BPOSS−(VPOSS)−PCL, was fully characterized. In the FT-IR spectrum, the disappearance of the strong characteristic vibrational band for the azide group at 2091 cm^{-1} suggests the complete consumption of the BPOSS−N_3 (Figure S6, Supporting Information). In the ^1H NMR spectrum (Figure 2b), the resonant peaks from the seven isobutyl groups on the BPOSS cage appear at δ 0.87 and 0.53 ppm, and the methylene protons adjacent to the azide group shift from 3.27 ppm in BPOSS−N_3[51] to 4.21 ppm in BPOSS−(VPOSS)−PCL due to the formation of a triazole ring. The characteristic peaks corresponding to isobutyl chains on the BPOSS cage can be clearly assigned in the ^{13}C NMR spectrum at δ 25.64, 24.86, 23.80, and 22.37 ppm (Figure S5b, Supporting Information). Moreover, the MALDI-TOF mass spectrum of BPOSS−(VPOSS)−PCL (Figure 4b) further shows a unimodal narrow molecular weight distribution with peak mass shift of m/z = 899.95 relative to its precursor alkyne−(VPOSS)−PCL ($[M_{21}\bullet Na]^+$), which corresponds to the precise "click" addition of one BPOSS−N_3 molecule (899.30 Da). The increased molecular weight is also confirmed by the shift in elution volume of BPOSS−(VPOSS)−PCL as compared to that of alkyne−(VPOSS)−PCL in the SEC chromatogram (Figure 3a). All of the above evidence confirms the structure of the desired product.

Recently, TECC reaction has been demonstrated to be a very powerful tool for simultaneous, multiple-site functionalization of the VPOSS cage[14,16,21,28] because it is highly efficient, rapid, regiospecific (anti-Markovnikov addition), and compatible with a wide range of experimental conditions.[52−55] In this work, 2-mercaptoacetic acid was selected to convert the VPOSS cage into a hydrophilic cage that could lead to strong microphase separations from both BPOSS and PCL segments. The complete functionalization is revealed by the disappearance of the vinyl protons in the resonance range of δ 5.72−6.07 ppm in the ^1H NMR spectrum (Figure 2c) and sp^2 carbon signals at δ 137.28 and 128.27 ppm (Figure S5c, Supporting Information) in the ^{13}C NMR spectrum of BPOSS−(APOSS)−PCL. The successful introduction of multiple carboxylic acid groups onto the VPOSS surface was confirmed by the observation of broad characteristic resonances appearing in the range of δ 8.93−8.32 ppm [the protons (i) in Figure 2c] in the ^1H NMR spectrum and a strong absorbance band at around 3200 cm^{-1} in the FT-IR spectrum (Figure S6, Supporting Information). It is also worth noting that two distinct chemical shifts at δ 6.24 and 5.99 ppm corresponding to the proton (c) can be observed at this time due to the disappearance of the vinyl groups. In addition, the SEC overlay shows a single symmetric distribution for BPOSS−(APOSS)−PCL (M_n = 5.2 kg/mol, PDI = 1.08) shifted to a slightly lower retention volume relative to that of BPOSS−(VPOSS)−PCL (M_n = 5.2 kg/mol, PDI = 1.07) due to a small increase in molecular weight and the change in amphiphilicity of the macromolecule. Therefore, it can be concluded that the model MHGS with two different POSS heads has been successfully synthesized via a sequential triple "click" reaction of SPAAC, CuAAC, and TECC.

A model MTGS can be similarly synthesized from alkyne−(VPOSS)−PCL using another azido-functionalized polymer, such as PS−N_3.[14,28,30] As expected, the occurrence of a new characteristic resonance at δ 5.02 ppm (the proton (c)) in the ^1H NMR spectrum of PS−(VPOSS)−PCL suggests the efficient and successful coupling of the PS chain via CuAAC reaction (Figure S7a, Supporting Information). In addition, the resonances at the aromatic region of the ^{13}C NMR spectrum of PS−(VPOSS)−PCL further confirm the successful installation of a PS tail onto the VPOSS cage (Figure S8a, Supporting Information). The SEC chromatogram of PS−(VPOSS)−PCL (Figure 3b) exhibits a monomodal, symmetric peak with a narrow molecular weight distribution (M_n = 8.1 kg/mol, PDI = 1.05). There is a clear shift in retention volume compared to that of PS−N_3 (M_n = 3.7 kg/mol, PDI = 1.05), consistent with the molecular weight increase as a result of polymer conjugation. The subsequent TECC of the VPOSS cage using 2-mercaptoacetic acid is as reliable and robust as usual, yielding the proposed MTGS, PS−(APOSS)−PCL. The ^1H NMR resonances in the range of δ 6.09−5.82 ppm, corresponding to the vinyl protons, completely disappeared after 15 min of irradiation, and the resonances for new protons at the thiol−ether linkages can be clearly observed at δ 3.25 and 2.70 ppm (Figure S7b, Supporting Information). Meanwhile, the broad resonance at around δ 8.81 ppm in the ^1H NMR spectrum can be assigned to the protons of carboxylic acid groups on the POSS head. Again, from the SEC overlay shown in Figure 3b, it is evident that the SEC trace of the final product, PS−(APOSS)−PCL (M_n = 8.5 kg/mol, PDI = 1.03), shifted to a smaller retention volume after the TECC reaction. In Figure 3, it is also noted that the retention volume change upon TECC is larger for PS−(VPOSS)−PCL than that for BPOSS−(VPOSS)−PCL, which indicates that the hydrodynamic volume of MTGS increases to a larger extent upon the introduction of amphiphilicity than that of MHGS. Although we were unable to obtain a MALDI-TOF mass spectrum of the final product due to the high compositional heterogeneity, all the evidence proved that the model MTGS with two different polymeric tails (PS and PCL) have been successfully synthesized. We anticipate that, in combination with the "click" adaptor and other polymeric motifs of more complex architecture (such as cyclic polymers and block copolymers), the sequential triple "click" approach can be very powerful and versatile in creating shape amphiphiles with unusual architecture and compositions.

In summary, we have successfully developed sequential triple "click" strategy based on the reactivity difference between DIBO and terminal alkyne groups and demonstrated by the synthesis of model MHGS and MTGS that it is a general, robust, and efficient methodology. The important molecular parameters of each block in MHGS/MTGS, including chemical composition, molecular weight, and polydispersity, could be rigorously controlled and systematically varied. This method is being applied to establish libraries of POSS-based shape amphiphiles of complex structures for a systematic study of their self-assembly principles and hierarchical structure formation in the bulk, thin film, and solutions. It expands the scope of POSS-based shape amphiphiles and offers numerous new possibilities for macromolecular assembly. The method also has general implications for application in the synthesis of shape amphiphiles based on other molecular nanoparticles, such as C_{60}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information on 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: yl48@zips.uakron.edu (Y.L.). Fax: +1 330 972 8626. Tel.: +1 330 256 9458. E-mail: wz8@uakron.edu (W.-B.Z.).

Fax: +1 330 972 8626. Tel.: +1 330 990 9801. E-mail: scheng@uakron.edu (S.Z.D.C.). Fax: +1 330 972 8626. Tel.: +1 330 972 6931.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (DMR-0906898) and the Joint-Hope Education Foundation. We thank Ms. Kai Guo and Prof. Chrys Wesdemiotis for their help with the MALDI-TOF mass characterizations.

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