3148 *Macromolecules* **2010**, *43*, 3148–3152
DOI: 10.1021/ma902830f

Macromolecules
COMMUNICATION TO THE EDITOR

A "Click Chemistry" Approach to Linear and Star-Shaped Telechelic POSS-Containing Hybrid Polymers

Weian Zhang[†,‡] and Axel H. E. Müller[*,†]

[†]*Makromolekulare Chemie II, Universität Bayreuth,*
D-95440 Bayreuth, Germany, and [‡]*Laboratory for Advanced*
Materials, Department of Chemistry, East China University of
Science and Technology, 130 Meilong Road, Shanghai 200237,
P. R. China

Received December 23, 2009
Revised Manuscript Received February 17, 2010

In 1960, the term "telechelic", originating from the Greek words "*tele*" (far, distant) and "*chele*" (crab claw), was first introduced into polymer science, defining oligomers or polymers possessing reactive groups at both chain ends, which can be used as cross-linking agents or a chain extenders.[1] When there is only one reactive group at the end of a linear polymer chain, such end-functional polymers have been named "mono-telechelic" or "semi-telechelic".[2,3] However, since the inset "*tele*" is meaningless in such a structure, we prefer to name these end-functional polymers "monochelic". Nowadays, with the great progress in polymer synthesis, polymers with all kinds of special groups at the end of the polymer chain are called "telechelic polymers". These special groups can be reactive or unreactive and organic or inorganic, and the topological structures of telechelic polymers could be linear, star, randomly branched, comb-shaped, etc.[4−8]

Polyhedral oligomeric silsesquioxanes (POSS) have attracted a great deal of attention in materials fields because of their unique nanoscale cage-shaped structure and a good solubility.[9−13] POSS can be easily incorporated into polymeric matrices to prepare novel polymer hybrids with promising properties such as thermal and flammability resistance or special surface properties.[14−29] In the past, POSS-containing polymer hybrids have been mostly prepared by conventional chemical copolymerization, cross-linking, or physical blending, which is difficult to afford hybrids with a well-defined topological structure. Recently, with the new living/controlled polymerization techniques emerging in polymer science, many novel POSS-containing hybrid polymers with well-defined topological structure have been prepared. For example, star-shaped block copolymers containing a POSS core were synthesized via atom transfer radical polymerization (ATRP).[30,31] Nowadays, much interest has also focused on the preparation of telechelic POSS-containing polymer hybrids. Ditelechelic and monochelic POSS-containing hybrid polymers were prepared by urethane formation between α,ω-hydroxyl-functional polymers and isocyanate-monofunctional POSS molecules.[32,33] Monochelic ("tadpole-shaped") POSS-containing polymer hybrids were also synthesized using controlled/living radical polymerization techniques, such as ATRP and reversible addition−fragmentation chain transfer (RAFT) polymerization. Fukuda et al. developed an efficient method to modify the monofunctional POSS molecule as ATRP initiators which were successfully used to produce well-defined, monochelic POSS-containing hybrid polymers.[34,35] Recently, we prepared a series of monochelic POSS-containing hybrid homopolymers and block copolymers using a POSS-modified chain transfer agent via RAFT polymerization, and the self-assembly of these polymer hybrids was also studied.[36,37]

Recently, the Cu(I)-catalyzed 1,3-dipolar cycloaddition of azides and alkynes named "click chemistry" has emerged as an attractive and promising tool to construct novel polymers with well-defined architectures, since it can be performed with a good tolerance of functional groups and at mild reaction conditions such as room temperature and in aqueous solution.[38−40] When "click chemistry" is combined with living/controlled radical polymerization techniques, it becomes an even more powerful tool in materials science.[41−49] "Click chemistry" was also used to construct POSS-containing polymer hybrids.[50,51] For example, Liu et al. used octa-azido-modified POSS as the core of star-shaped polymers.[52]

In this contribution, "click chemistry" is applied in the preparation of telechelic POSS-containing polymer hybrids by combining with ATRP. Monochelic and telechelic bromo-terminated polystyrenes were prepared by ATRP using mono-, di-, and pentafunctional initiators. Subsequently, the bromine end-groups were substituted by azide groups to generate azido-terminated polymers. Finally, "click" reactions were performed between azido-terminated polystyrenes and alkyne-functionalized POSS to produce monochelic, di- and penta-telechelic POSS-containing hybrid polystyrenes. This provides a simple and versatile strategy to prepare monochelic and telechelic POSS-containing polymer hybrids.

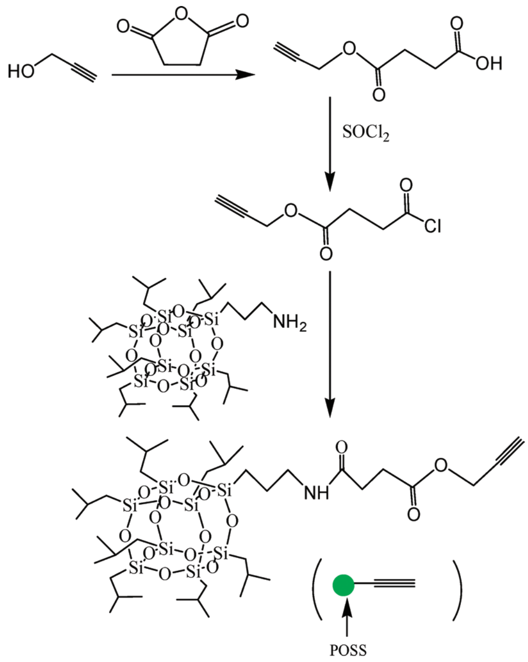
Results and Discussion. We first prepared alkyne-functionalized POSS (alkyne-POSS), which was further used in modifying the end-groups of various polystyrenes to afford telechelic POSS-containing hybrid polystyrenes via "click chemistry". In the preparation of alkyne-POSS (Scheme 1), we did not choose the commercially available propargylic acid as the precursor, but 3-propargylcarbonylpropionic acid (PCPA), since PCPA can effectively increase the polarity of alkyne-POSS. In our past work on POSS-containing hybrids a major problem we encountered is the removal of unreacted POSS. Sometimes, the precipitation is ineffective because due to its molecular weight of about 1000, the unreacted POSS coprecipitates with the product. Here PCPA was used to modify aminopropylheptaisobutyl-POSS to produce alkyne-POSS, which effectively enhances the solubility, being dissolved in polar to nonpolar solvents, such as *n*-hexane and DMF.

The FTIR spectra of PCPA and 3-propargylcarbonylpropionic chloride (PCPCl) are shown in the Supporting Information (Figure S1). Comparing the spectra of PCPCl and PCPA, it can be seen that the broad band from 2225 to 3251 cm^{-1} disappears in the spectrum of PCPCl, and a new band appears at 1785 cm^{-1}, which is assigned to the stretching vibration of carbonyl chloride. Moreover, the peak at 3291 cm^{-1}, ascribed to the stretching vibration of the alkyne group, is almost unchanged. This indicates that PCPA was successfully synthesized and transformed into PCPCl, which is also confirmed by ^{1}H NMR (Figure S2). The signals at δ = 2.50 (a), 2.72 (c, d), and 4.73 ppm (b) are respectively

---

*Corresponding author. E-mail: Axel.mueller@uni-bayreuth.de.

Scheme 1. Synthesis of 3-Propargylcarbonyl-*N*-(3-(heptaisobutyl polyhedral oligomeric silsesquioxane) propyl)propanamide (Alkyne-POSS)



assigned to the methine proton ($-OCH_2CC\mathit{H}$) and methylene protons of PCPA ($-OCO(C\mathit{H}_2)_2COOH$ and $-OC\mathit{H}_2CCH$). Compared to the ^{1}H NMR of PCPA, the overlapping signal at 2.72 ppm was detached into two independent signals at 2.72 and 3.23 ppm in the ^{1}H NMR of PCPCl; moreover, the integral area of these two signals are well equal, which confirms that PCPA is successfully transformed into PCPCl.

Alkyne-POSS was prepared by amide formation between aminoheptaisobutyl-POSS and freshly prepared PCPCl. The resulting product was easily purified by precipitating the reaction solution into a mixture of water/methanol (v/v, 1/4). The ^{1}H NMR spectrum of alkyne-POSS is shown in Figure 1. The signals at δ = 4.71 (i), 2.75 (g), and 2.50 ppm (h, j) are respectively assigned to the resonance of the methylene protons ($-COOC\mathit{H}_2CCH$, $-NHCOC\mathit{H}_2CH_2COO-$, $-NHCOCH_2C\mathit{H}_2COO-$) and methine proton ($-COOCH_2CC\mathit{H}$) originating from PCPA. The signals at δ = 0.98 ppm (a), 1.87 ppm (b), 0.62 ppm (c, d), 1.61 ppm (e), and 3.26 ppm (f) are respectively assigned to the methyl, methine, and methylene protons originating from POSS. Moreover, the integration area ratio of the peaks a:b:(c + d):e:f:g:(h + j):i is almost equal to 42:7:16:2:2:2:3:2, indicating that alkyne-POSS has a higher purity. In addition, compared to the FTIR spectrum of POSS-NH$_2$, a new band appears at 3293 cm^{-1} in the spectrum of alkyne-POSS (Figure S3), which is assigned to the stretching vibration of the alkyne group. The bands at 1743, 1645, and 1554 cm^{-1} are due to the formation of amide group. Based on the results of ^{1}H NMR and FTIR, alkyne-POSS with high purity was successfully prepared. The solubility of alkyne-POSS was also studied, and we found it not only dissolves in nonpolar solvents, such as *n*-hexane, but also in strongly polar solvents, such as DMF and methanol.

The synthetic strategies for monochelic, di- and pentatelechelic POSS-containing hybrid polymers are shown in Scheme 2. They consist of three steps. Polystyrenes with different numbers of bromo-terminal initiating groups were synthesized using their corresponding ATRP initiators. Subsequently, the bromine groups were transformed into azide groups using sodium azide in DMF via nucleophilic substitution. Finally, the click coupling occurs between the azido-terminated polystyrenes and alkyne-POSS to afford mono-, di-, and pentafunctional POSS-containing hybrid polystyrenes.

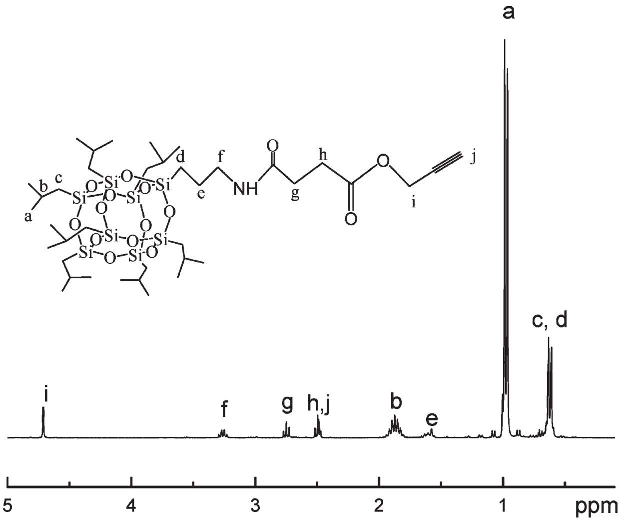


Figure 1. ^{1}H NMR of alkyne-POSS.

Here, the preparation method of the ditelechelic POSS-containing hybrid polystyrene (PS-POSS$_2$), as a representative, is detailed. Dibromo-terminated polystyrene was synthesized by ATRP using diethyl 2,6-dibromoheptanedioate as initiator and CuBr/PMDETA as the catalyst. The polymerization was conducted in toluene at 70 °C, and small samples (about 0.1 mL) were taken from the reaction flask at intervals to check the conversion, which was measured by ^{1}H NMR by comparing the peaks of the vinyl protons at 5.79 ppm and those of aromatic protons at 7.33 ppm. To avoid the coupling reaction between two polystyrene chains, the polymerization was quenched at low conversion of styrene, and the dibromo-terminated polystyrene (PS-Br$_2$) with a low polydispersity was obtained. The molecular weights and polydispersity indices (PDI) of all polymers are listed in Table 1, and the symmetrical GPC curve is shown in Figure 2. Figure 3a shows the ^{1}H NMR of PS-Br$_2$. The signals in the range from 1.16 to 2.15 ppm and from 6.31 to 7.45 ppm are respectively assigned to the protons of the chain backbone and the phenyl rings of polystyrene. The proton signal of the methine neighboring to the terminal bromine is still discerned at about 4.43 ppm due to the low molecular weight of polystyrene.

The terminal bromine atoms of PS-Br$_2$ were easily transformed into azide groups to produce diazido-polystyrene, PS-(N$_3$)$_2$, via nucleophilic substitution. The reaction was performed in DMF at room temperature. The typical ^{1}H NMR of PS-(N$_3$)$_2$ is shown in Figure 3b, it can be seen that the signal at 4.43 ppm has completely disappeared, and a new signal peak appears at about 3.95 ppm, which is ascribed to the methine adjacent to the terminal azide group of PS-(N$_3$)$_2$. Unfortunately, this proton signal is not clearly separated, since it partly overlaps with the signals of the methylene protons derived from the ATRP initiator. In addition, FT-IR was also used to characterize the terminal azido group. Compared to the FT-IR spectrum of PS-Br$_2$, an obvious peak at 2092 cm^{-1} appears in the spectrum of PS-(N$_3$)$_2$, which is assigned to the stretching vibration of terminal azido groups. On the basis of NMR and FT-IR, the nucleophilic substitution was effectively conducted, and the terminal bromo groups were completely transformed into azido groups.

The click cycloaddition of between PS-(N$_3$)$_2$ and alkyne-POSS was carried out at 80 °C for 24 h using CuBr/PMDETA

Scheme 2. Synthesis of POSS-Functional Polystyrenes by Combination of ATRP and "Click Chemistry"

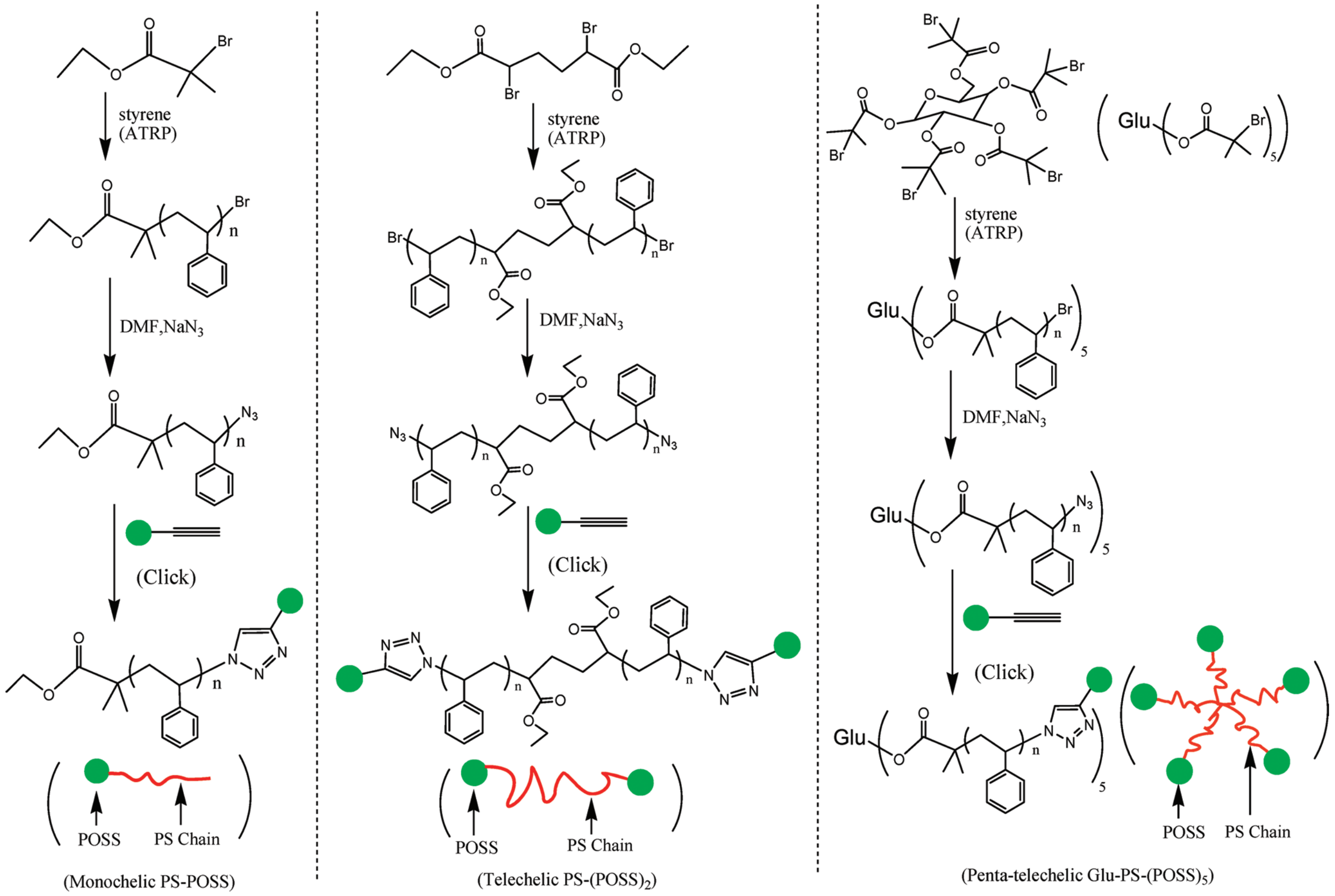


Table 1. GPC Characterization of Mono-, Di-, and Pentafunctional Polystyrenes before and after Click Reaction

	$10^3 M_{n,th}$	$10^3 M_{n,GPC}$[c]	M_w/M_n[c]
PS-Br	5.25[a]	5.43	1.25
PS-POSS	6.26[b]	6.94	1.10
$PS-Br_2$	4.52[a]	4.50	1.14
$PS-(POSS)_2$	6.54[b]	7.49	1.22
$Glu-PS-Br_5$	12.1[a]	10.7	1.10
$Glu-PS-(POSS)_5$	17.2[b]	17.1	1.21

[a] $M_{n,th} = [M]_0 x/[I]_0 \times M_{styrene} + M_{initiator}$, where x is the monomer conversion. [b] Estimated as $M_{n,th} = M_{n,th}(PS\text{-}Br_n) + n \times M_{alkyne\text{-}POSS}$, where m is 1, 2 and 5, respectively. [c] Measured by GPC calibrated with linear PS standards.

as catalyst and DMF as solvent. To complete the coupling reaction, the initial molar ratio of alkyne-POSS to $PS-(N_3)_2$ was 2/1. The unreacted excess alkyne-POSS is removed by precipitating the polymer into *n*-hexane to obtain ditelechelic POSS-containing polystyrene, $PS-POSS_2$. The ^1H NMR of $PS-POSS_2$ is shown in Figure 3c. Except for the proton signals of the styrene units in the range from 1.16 to 2.15 ppm and from 6.31 to 7.45 ppm, the signals at $\delta = 0.97$ and 0.62 ppm are respectively assigned to the methyl protons ($-Si-CH_2CH(CH_3)_2$) and methylene protons ($-Si-CH_2-CH(CH_3)_2$ and $-Si-CH_2CH_2CH_2-NH-$) originating from alkyne-POSS. Moreover, the signals at $\delta = 5.55$ (g) and 5.08 (f) ppm are respectively assigned to the methine proton and the methylene protons adjacent to the triazole ring, which indicates the triazole formation. Moreover, the ratio of POSS to PS estimated using the integration area ratio of the methylene protons of POSS (c, d) and of the styryl protons of PS (m) is 1.87, which is close to the theoretical value of 2. FT-IR also confirmed that $POSS-PS_2$ was successfully prepared. Compared to the FT-IR spectrum of $PS-(N_3)_2$, the band at 2092 cm^{-1} of the azide stretching vibration has completely disappeared, and a new band appears at 1107 cm^{-1} in the spectrum of $PS-POSS_2$, which is assigned to the stretching vibration of Si−O−Si. From the GPC traces of $PS-POSS_2$ (Figure 2), we can find the curve of $PS-POSS_2$ obviously shifts to lower elution volumes, indicating that $PS-POSS_2$ has a higher molecular weight. Moreover, the GPC trace of $PS-POSS_2$ is perfectly symmetric without a shoulder on its right side. This suggests that click coupling is complete.

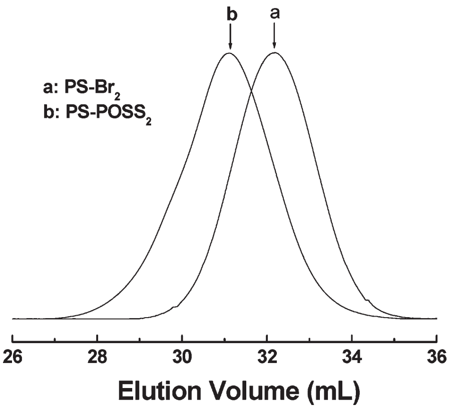


Figure 2. Evolution of GPC chromatograms for $PS-Br_2$ and $PS-POSS_2$.

The preparation procedure of monochelic POSS-containing hybrid polystyrene (PS-POSS) is similar to that of ditelechelic

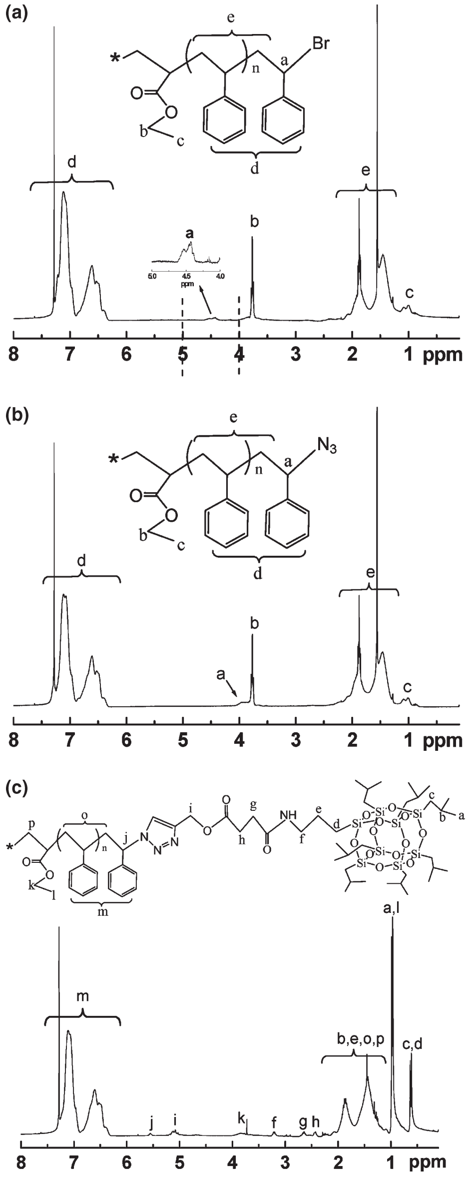


Figure 3. ^1H NMR of PS-Br_2 (a), PS-$(N_3)_2$ (b), and PS-$POSS_2$ (c).

PS-$POSS_2$. The monobromo-terminated polystyrene (PS-Br) was prepared using ethyl 2-bromoisobutyrate (EBiB) as initiator. The synthetic steps were characterized by FT-IR and ^1H NMR, which are respectively shown in Figures S4 and S5. In the spectrum of PS-POSS, it is also seen that the stretching vibration peak of the azido group at 2092 cm^{-1} has disappeared, and a new peak at 1107 cm^{-1} appears, corresponding to the stretching vibration of Si$-$O$-$Si. In the ^1H NMR spectrum of PS-POSS, the signals of the characteristic protons derived from POSS are shown at $\delta = 0.98$ and 0.62 ppm. The proton signals at $\delta = 5.55$ and 5.08 ppm are respectively assigned to the methylene protons adjacent to the triazole ring, which also can be clearly discerned. GPC shows that PS-POSS has a higher molecular weight compared to PS-Br (Figure S6). All of results confirm that monochelic PS-POSS was also successfully prepared.

The star-shaped, penta-telechelic POSS-containing hybrid polystyrene, PS-$POSS_5$, was prepared by click reaction between alkyne-POSS and penta-azido-terminated polystyrene, PS-$(N_3)_5$. The latter was synthesized from pentabromo-terminated (PS-Br_5), which was prepared using a pentabromofunctionalized ATRP initiator derived from glucose.[53]

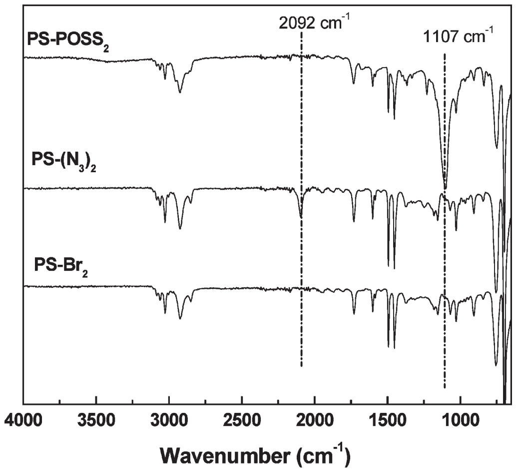


Figure 4. FTIR of of PS-Br_2, PS-$(N_3)_2$, and PS-$POSS_2$.

The formation of the triazole ring was also confirmed by FT-IR and ^1H NMR, which are respectively displayed in Figures S7 and S8. In the preparation of PS-Br_5, star$-$star coupling can occur much more easily. We found that cross-linking occurs in this system at conversions above 12%. Thus, polymerization was quenched at relatively low conversion. But even at a conversion as low as 4.2%, we still can find a small shoulder toward lower elution volumes in the GPC curve of PS-Br_5 in Figure S9. After click coupling, this shoulder became more significant. This might stem from further coupling of the PS stars, although a mechanisms for such a coupling reaction is difficult to conceive. We could also consider the formation of aggregates of two or more hybrid molecules in THF, but this not very probable, given the good solubility of both polystyrene and heptaisobutyl-POSS.

In summary, alkyne-POSS with good solubility was successfully synthesized using aminopropylheptaisobutyl polyhedral oligomeric silsesquioxane (POSS). Mono-, di-, and penta-telechelic POSS-containing polystyrenes were respectively prepared by the combination of ATRP and "click chemistry". The properties and morphologies of these hybrids are under investigation. Here, we provide a simple and versatile method to prepare telechelic POSS-containing hybrid polymers.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (No. 50503013). W.Z. also acknowledges support by the Alexander von Humboldt Foundation.

Supporting Information Available: Experimental part, FTIR, ^1H NMR spectra of PCPA, PCPCl, PS-Br, PS-N_3, PS-POSS, PS-Br_5, PS-$(N_3)_5$ and PS-$POSS_5$, and GPC traces of PS-Br, PS-POSS, PS-Br_5, and PS-$POSS_5$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Uraneck, C. A.; Hsieh, H. L.; Buck, O. G. *J. Polym. Sci.* **1960**, *46*, 535–539.
(2) Jerome, R.; Henrioulle-Granville, M.; Boutevin, B.; Robin, J. J. *Prog. Polym. Sci.* **1991**, *16*, 837–906.
(3) Tezuka, Y. *Prog. Polym. Sci.* **1992**, *17*, 471–514.
(4) Tezuka, Y.; Oike, H. *J. Am. Chem. Soc.* **2001**, *123*, 11570–11576.
(5) Hofmeier, H.; Hoogenboom, R.; Wouters, M. E. L.; Schubert, U. S. *J. Am. Chem. Soc.* **2005**, *127*, 2913–2921.
(6) Okamura, H.; Terauchi, T.; Minoda, M.; Fukuda, T.; Komatsu, K. *Macromolecules* **1997**, *30*, 5279–5284.

(7) Kujawa, P.; Segui, F.; Shaban, S.; Diab, C.; Okada, Y.; Tanaka, F.; Winnik, F. M. *Macromolecules* **2006**, *39*, 341–348.
(8) Kim, S. D.; Torkelson, J. M. *Macromolecules* **2002**, *35*, 5943–5952.
(9) Sprung, M. M.; Guenther, F. O. *J. Am. Chem. Soc.* **1955**, *77*, 3990–3996.
(10) Brown, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 4317–4324.
(11) Lichtenhan, J. D.; Schwab, J. J.; Feher, F. J.; Soulivong, D. U.S. Patent 5942638, **1999**.
(12) Pielichowski, K.; Njuguna, J.; Janowski, B.; Pielichowski, J. *Adv. Polym. Sci.* **2006**, *201*, 225–296.
(13) Laine, R. M. *J. Mater. Chem.* **2005**, *15*, 3725–3744.
(14) Constable, G. S.; Lesser, A. J.; Coughlin, E. B. *Macromolecules* **2004**, *37*, 1276–1282.
(15) Lee, A.; Xiao, J.; Feher, F. J. *Macromolecules* **2005**, *38*, 438–444.
(16) Cho, H. J.; Hwang, D. H.; Lee, J. I.; Jung, Y. K.; Park, J. H.; Lee, J.; Lee, S. K.; Shim, H. K. *Chem. Mater.* **2006**, *18*, 3780–3787.
(17) Kang, J. M.; Cho, H. J.; Lee, J.; Lee, J. I.; Lee, S. K.; Cho, N. S.; Hwang, D. H.; Shim, H. K. *Macromolecules* **2006**, *39*, 4999–5008.
(18) Chou, C. H.; Hsu, S. L.; Dinakaran, K.; Chiu, M. Y.; Wei, K. H. *Macromolecules* **2005**, *38*, 745–751.
(19) Kopesky, E. T.; Haddad, T. S.; Cohen, R. E.; McKinley, G. H. *Macromolecules* **2004**, *37*, 8992–9004.
(20) Abad, M. J.; Barral, L.; Fasce, D. P.; Williams, R. J. J. *Macromolecules* **2003**, *36*, 3128–3135.
(21) Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, B. D. *Angew. Chem., Int. Ed.* **2008**, *47*, 4137–4140.
(22) Xu, H. Y.; Kuo, S. W.; Lee, J. S. Y.; Chang, F. C. *Macromolecules* **2002**, *35*, 8788–8793.
(23) Kotal, A.; Si, S.; Paira, T. K.; Mandal, T. K. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1111–1123.
(24) Strachota, A.; Whelan, P.; Kriz, J.; Brus, J.; Urbanova, M.; Slouf, M.; Matejka, L. *Polymer* **2007**, *48*, 3041–3058.
(25) Liu, H. Z.; Zheng, S. X.; Nie, K. M. *Macromolecules* **2005**, *38*, 5088–5097.
(26) Knight, P. T.; Lee, K. M.; Qin, H.; Mather, P. T. *Biomacromolecules* **2008**, *9*, 2458–2467.
(27) Markovic, E.; Matisons, J.; Hussain, M.; Simon, G. P. *Macromolecules* **2007**, *40*, 4530–4534.
(28) Paul, R. K., U.; Swift, M. C.; Esker, A. R. *Langmuir* **2008**, *24*, 5079–5090.
(29) Hottle, J. R.; Deng, J.; Kim, H.-J.; Farmer-Creely, C. E.; Viers, B. D.; Esker, A. R. *Langmuir* **2005**, *21*, 2250–2259.
(30) Costa, R. O. R.; Vasconcelos, W. L.; Tamaki, R.; Laine, R. M. *Macromolecules* **2001**, *34*, 5398–5407.
(31) Pyun, J.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 217–220.
(32) Kim, B. S.; Mather, P. T. *Macromolecules* **2002**, *35*, 8378–8384.
(33) Cardoern, G.; Coughlin, E. B. *Macromolecules* **2004**, *37*, 5123–5126.
(34) Ohno, K.; Sugiyama, S.; Koh, K.; Tsujii, Y.; Fukuda, T.; Yamahiro, M.; Oikawa, H.; Yamamoto, Y.; Ootake, N.; Watanabe, K. *Macromolecules* **2004**, 8517–8522.
(35) Koh, K.; Sugiyama, S.; Morinaga, T.; Ohno, K.; Tsujii, Y.; Fukuda, T.; Yamahiro, M.; Iijima, T.; Oikawa, H.; Watanabe, K.; Miyashita, T. *Macromolecules* **2005**, *38*, 1264–1270.
(36) Zhang, W. A.; Liu, L.; Zhuang, X. D.; Li, X. H.; Bai, J. R.; Chen, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 7049–7061.
(37) Zhang, W. A.; Fang, B.; Walther, A.; Müller, A. H. E. *Macromolecules* **2009**, *42*, 2563–2569.
(38) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599.
(39) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.
(40) Lewis, W. G.; Magallon, F. G.; Fokin, V. V.; Finn, M. G. *J. Am. Chem. Soc.* **2004**, *126*, 9152–9153.
(41) Lutz, J.-F.; Boerner, H. G. *Prog. Polym. Sci.* **2008**, *33*, 1–39.
(42) Goldmann, A.; Quémener, D.; Millard, P.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C.; Müller, A. H. E. *Polymer* **2008**, *49*, 2274–2881.
(43) Goldmann, A.; Walther, A.; Nebhani, L.; Joso, R.; Ernst, D.; Loos, K.; Barner-Kowollik, C.; Barner, L.; Müller, A. H. E. *Macromolecules* **2009**, *42*, 3707–3714.
(44) Helms, B.; Mynar, J. L.; Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15020–15021.
(45) Iha, R. K.; Wooley, K. L.; Nystrm, A. M.; Burke, D. J.; Kade, M. J.; Hawker, C. J. *Chem. Rev.* **2009**, *109*, 4961–6540.
(46) Agut, W.; Taton, D.; Lecommandoux, S. *Macromolecules* **2007**, *40*, 5653–5661.
(47) Vogt, A. P.; Sumerlin, B. S. *Macromolecules* **2006**, *39*, 5286–5292.
(48) Ladmiral, V.; Mantovani, G.; Clarkson Guy, J.; Cauet, S.; Irwin Jacob, L.; Haddleton David, M. *J. Am. Chem. Soc.* **2006**, *128*, 4823–4830.
(49) Topham, P. D.; Sandon, N.; Read, E. S.; Madsen, J.; Ryan, A. J.; Armes, S. P. *Macromolecules* **2008**, *41*, 9542–9547.
(50) Gungor, E.; Bilir, C.; Durmaz, H.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5947–5953.
(51) Ak, M.; Gacal, B.; Kiskan, B.; Yagci, Y.; Toppare, L. *Polymer* **2008**, *49*, 2202–2210.
(52) Ge, Z. S.; Wang, D.; Zhou, Y. M.; Liu, H. W.; Liu, S. Y. *Macromolecules* **2009**, *42*, 2903–2910.
(53) Plamper, F. A.; Becker, H.; Lanzendörfer, M.; Patel, M.; Wittemann, A.; Ballauff, M.; Müller, A. H. E. *Macromol. Chem. Phys.* **2005**, *206*, 1813–1825.