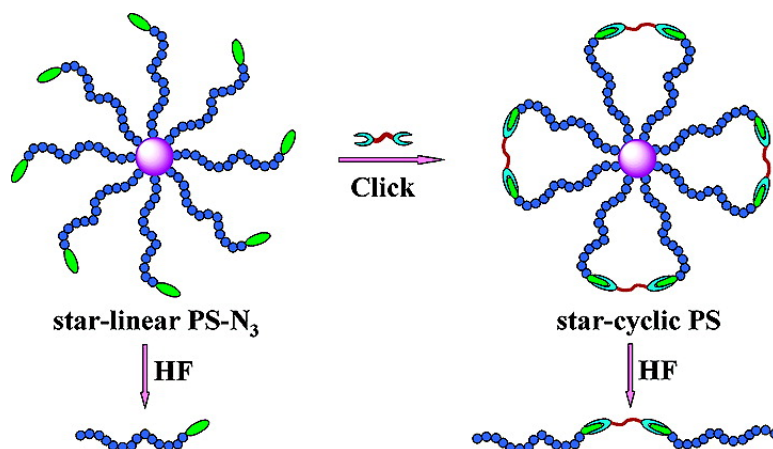


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Articles

Synthesis of Organic/Inorganic Hybrid Quatrefoil-Shaped Star-Cyclic Polymer Containing a Polyhedral Oligomeric Silsesquioxane Core

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ABSTRACT: We report the synthesis of quatrefoil-shaped star-cyclic polystyrene, *star-cyclic* PS, containing a polyhedral oligomeric silsesquioxane (POSS) core via the combination of atom transfer radical polymerization (ATRP) and click chemistry techniques. The obtained *star-cyclic* PS represents a new chain topology in the category of nonlinear-shaped polymers. Using octa(3-chloropropyl) polyhedral oligomeric silsesquioxane, POSS-(Cl)₈, as the starting material, its azidation and subsequent click reaction with a slight excess of propargyl 2-bromobutyrate afforded octafunctional initiator, POSS-(Br)₈. 8-arm *star-linear* PS-*N*₃ was obtained by the azidation of *star-linear* PS-Br, which was synthesized by the ATRP of styrene using POSS-(Br)₈ as the initiator. Model reaction between α,ω -diazido-terminated PS (*N*₃-PS-*N*₃) and difunctional propargyl ether confirmed that bimolecular click cyclization reaction can effectively occur under highly dilute conditions. Next, intramolecular click ring closure of *star-linear* PS-*N*₃ was conducted under highly dilute conditions, using propargyl ether as the difunctional linker and CuBr/PMDETA as the catalyst, affording quatrefoil-shaped *star-cyclic* PS. Gel permeation chromatography (GPC), ¹H NMR, and FT-IR analysis confirmed the complete consumption of azide moieties in *star-linear* PS-*N*₃ and that the coupling reaction proceeded via the intramolecular manner. Differential scanning calorimetry (DSC) results revealed that *star-cyclic* PS possesses higher glass transition temperature (*T*_g) than that of *star-linear* PS, possibly due to the ring topology of PS arms in the former.

Introduction

The synthesis of polymers with varying chain topologies has always been the focus of polymer chemistry field due to that chain architectures play an important role in determining macromolecular properties and functions in bulk and solution states.^{1–3} In the past decade, a variety of polymers with intriguing topologies, such as cyclic,^{4–6} linear-cyclic,^{7,8} linear-dendritic,^{9,10} dendronized,^{11–13} Y-shaped,^{14,15} H-shaped,^{16–18} ABC miktoarm star,^{18–21} hyperbranched,^{22–28} and dendritic polymers^{29–32} have been prepared, partially due to the boom of controlled radical polymerization techniques and new concepts (click reaction, Diels–Alder reaction) “borrowed” from modern organic chemistry.

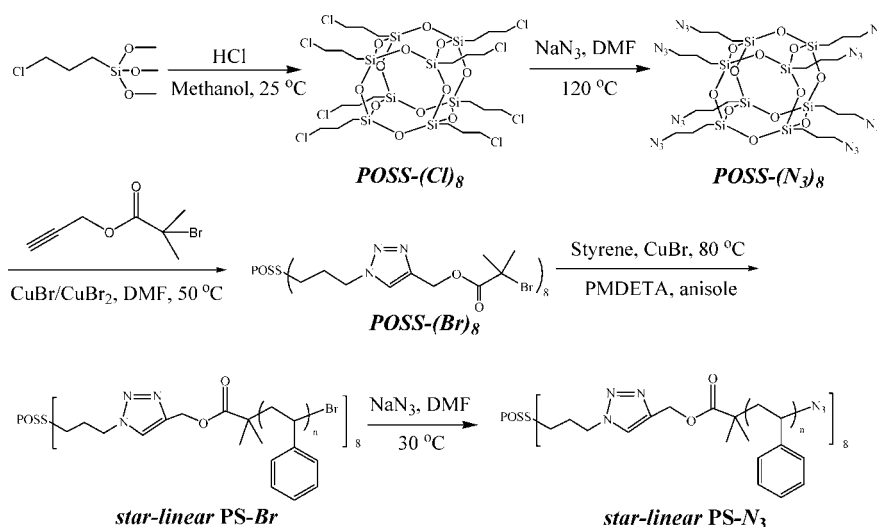
Macrocylic polymers represent the simplest nonlinear-shaped chain architecture consisting of only one type of monomer repeating units. Recent developments in this area focused on the fabrication of nonlinear polymers embedding with cyclic motifs. Based on their previous experiences in preparing cyclic polymers, Deffieux et al. prepared “tadpole-shaped” linear-cyclic,⁷ “eight-shaped” bicyclic,³³ and macrotricyclic polymers³⁴ by living anionic or cationic polymerization techniques. Tezuka et al.^{35,36} synthesized bicyclic and tricyclic polymers, as well as monocyclic polymers covalently attached with single, double, and triple linear tails at predetermined positions via electrostatic self-assembly between terminally ionized linear precursors and multifunctional coupling agent bearing opposite charges, and the subsequent covalent fixation.³⁷

It is worthy of noting that in the above examples, linear precursors were typically synthesized via living anionic or cationic polymerizations. Though structurally well-defined in their cases, the exploration of more convenient and mild synthetic conditions is still desirable. In this context, the application of controlled radical polymerizations, such as nitroxide-mediated radical polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition–fragmentation chain transfer (RAFT) polymerization, as well as the concept of “click chemistry” can be quite helpful. Grayson and co-workers^{4,5} prepared α -alkynyl- ω -azido polystyrene (PS) by ATRP, and macrocyclic PS can be obtained with high efficiency by an intramolecular click ring closure reaction. Winnik et al.³⁸ and our research group^{39,40} independently synthesized macrocyclic poly(*N*-isopropylacrylamide) (PNIPAM) by the combination of click reaction and RAFT or ATRP techniques. Recently, Pan et al.⁸ synthesized “tadpole-shaped” polymers consisting of linear PNIPAM and cyclic PS by coupling RAFT and click reactions. They also successfully synthesized bicyclic polymers consisting of PS and poly(ϵ -caprolactone) rings by coupling ATRP, click, and ring-opening polymerization (ROP) techniques.⁴¹

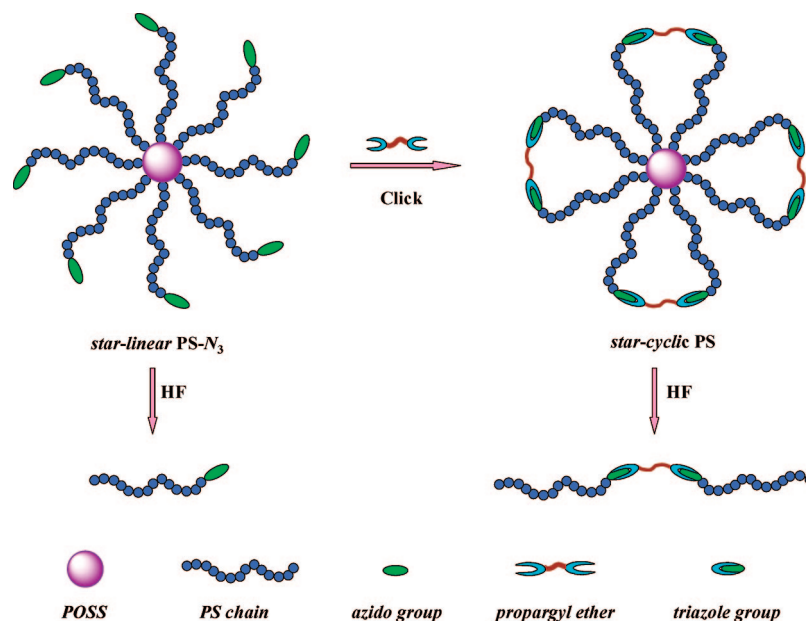
To the best of our knowledge, the synthesis of star polymers with macrocyclic arms has not been reported yet. Herein we report a proof-of-concept example of the synthesis of quatrefoil-shaped star-cyclic polystyrene, *star-cyclic* PS, containing polyhedral oligomeric silsesquioxane (POSS) core via the combination of ATRP and click reactions (Schemes 1 and 2). 8-arm *star-linear* PS (*star-linear* PS-*N*₃) bearing eight terminal azide functionalities was prepared by ATRP of styrene using POSS-

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Scheme 1. Schematic Illustration for the Preparation of Octa(3-azidopropyl)polyhedral Oligomeric Silsesquioxane, POSS-(N₃)₈, POSS-Based Octafunctional ATRP Initiator, POSS-(Br)₈, and POSS-Based 8-Arm Star Polystyrene, *star-linear* PS



Scheme 2. Schematic Illustration for the Synthesis of POSS-Based Quatrefoil-Shaped *star-cyclic* PS from 8-Arm *star-linear* PS-N₃ via Intramolecular Click Ring Closure with Propargyl Ether under Extremely Dilute Conditions



based octafunctional initiator, followed by the subsequent azidation reaction. Under click conditions, difunctional linker propargyl ether was slowly added via a syringe pump into the extremely dilute solution of *star-linear* PS-N₃, leading to high efficiency preparation of quatrefoil-shaped *star-cyclic* PS bearing an inorganic POSS core.

Experimental Section

Materials. Styrene (St, 99.5%, Beijing Chemical Factory) was successively washed with aqueous NaOH (5.0 wt %) and water, then distilled over CaH₂ at reduced pressure. CH₂Cl₂, anisole, and triethylamine (TEA) were distilled over CaH₂. Sodium azide (NaN₃), copper(I) bromide (CuBr, 98%), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), propargyl alcohol, propargyl ether, dimethyl 2,6-dibromoheptanedioate, and 2-bromoisobutyryl bromide were purchased from Aldrich and used as received. Merrifield resin was purchased from GL Biochem (Shanghai) Ltd. and used as received. Hydrofluoric acid (HF), 3-chloropropyltrimethoxysilane, and all other chemicals were purchased from Sinopharm Chemical Reagent Co. and used as received. Azido-functionalized Merrifield resin was prepared according to literature

procedures.^{42,43}

Sample Preparation. Synthetic schemes employed for the preparation of *star-linear* PS-N₃ and *star-cyclic* PS were shown in Schemes 1 and 2.

Synthesis of Octafunctional POSS-(Cl)₈. According to literature procedures,⁴⁴ a mixture of methanol (1.8 L), 3-chloropropyltrimethoxysilane (79.5 g, 0.4 mol), and concentrated HCl (90 mL) was allowed to stir at room temperature for 5 weeks. POSS-(Cl)₈ was obtained as a white powder after suction filtration and washing with deionized water (14.5 g, yield: 28%). ¹H NMR (CDCl₃, δ, ppm, TMS): 0.74–0.88 (2H, Si–CH₂–), 1.80–1.96 (2H, Si–CH₂CH₂–), 3.49–3.62 (2H, Si–CH₂CH₂CH₂Cl). ¹³C NMR (CDCl₃, δ, ppm): 9.4 (Si–CH₂–), 26.3 (Si–CH₂CH₂–), 47.1 (Si–CH₂CH₂CH₂Cl). ²⁹Si NMR (CDCl₃, δ, ppm): –67.1 (Si–CH₂–).

Synthesis of POSS-(N₃)₈. POSS-(N₃)₈ was prepared via azidation of POSS-(Cl)₈. A typical procedure was as follows. Into a 100 mL round-bottom flask, NaN₃ (6.5 g, 0.1 mol), POSS-(Cl)₈ (3.0 g, 2.9 mmol), and DMF (50 mL) were added. The flask was then immersed into an oil bath thermostated at 120 °C. After stirring for 2 days, the solvents were removed at reduced pressure. The

residues were dissolved in THF and passed through a neutral alumina column to remove residual sodium salts. A colorless viscous liquid was obtained (2.5 g, yield: 79%) after drying in a vacuum oven overnight at room temperature, and it is safe to store POSS-(N_3)₈ in a desiccator at room temperature. ¹H NMR (CDCl₃, δ, ppm, TMS): 0.61–0.84 (2H, Si–CH₂–), 1.54–1.83 (2H, Si–CH₂CH₂–), 3.24–3.47 (2H, Si–CH₂CH₂CH₂N₃). ¹³C NMR (CDCl₃, δ, ppm): 9.8 (Si–CH₂–), 22.8 (Si–CH₂CH₂–), 53.6 (Si–CH₂CH₂CH₂N₃). ²⁹Si NMR (CDCl₃, δ, ppm): –69.1 (Si–CH₂–).

Preparation of Propargyl 2-Bromoisobutyrate. Propargyl 2-bromoisobutyrate was prepared by the esterification reaction of propargyl alcohol with 2-bromoisobutyryl bromide. In a typical example, propargyl alcohol (11.6 mL, 0.2 mol), triethylamine (27.8 mL, 0.2 mol), and 100 mL of CH₂Cl₂ were added into a 250 mL three-neck round-bottom flask. The mixture was cooled to 0 °C and 2-bromoisobutyryl bromide (24.7 mL, 0.2 mol) was added dropwise over 2 h. The reaction mixture was stirred overnight at room temperature. After removing insoluble salts by suction filtration, the filtrate was further purified by passing through a silica gel column using CH₂Cl₂ as the eluent. After removing all the solvents by a rotary evaporator, the obtained residues were distilled under reduced pressure, yielding a colorless liquid (30.8 g, yield: 75%). ¹H NMR (CDCl₃, δ, ppm, TMS): 4.7 (2H, –CH₂O), 2.5 (1H, CH≡C–), and 1.9 (6H, –C(CH₃)₂Br).

Synthesis of POSS-(Br)₈. Octafunctional ATRP initiator, POSS-(Br)₈, was prepared via click reaction of POSS-(N_3)₈ with a slight excess of propargyl 2-bromoisobutyrate. In a typical procedure, DMF (20 mL), CuBr₂ (0.782 g, 3.5 mmol), propargyl 2-bromoisobutyrate (3.3 g, 16.1 mmol), PMDETA (0.73 mL, 3.5 mmol), and POSS-(N_3)₈ (2.0 g, 1.84 mmol) were added to a 50 mL Schlenk tube. After one brief freeze–thaw cycle, CuBr (0.201 g, 1.4 mmol) was introduced under the protection of N₂ flow. The reaction tube was carefully degassed by three freeze–pump–thaw cycles, sealed under vacuum, and placed in an oil bath thermostated at 50 °C. After the reaction was stirred for 12 h, azido-functionalized Merrifield resin (2.5 g, ~1.4 mmol/g) was added, and the suspension was allowed to stir for another 8 h at 50 °C. After cooling to room temperature, the flask was exposed to air, followed by suction filtration. After removing all the solvents at reduced pressure, the residues were dissolved in CH₂Cl₂ and passed through a neutral alumina column to remove copper catalysts. A colorless viscous liquid was obtained (3.92 g, yield: 78%). ¹H NMR (CDCl₃, δ, ppm, TMS): 7.7–8.0 (1H, CH in 1,2,3-triazole), 5.2–5.4 (triazole-CH₂O–), 4.2–4.5 (CH₂CH₂CH₂-triazole–), 1.6–2.1 (CH₂CH₂CH₂-triazole–, –C(CH₃)₂Br), 0.4–0.7 (CH₂CH₂CH₂-triazole–).

Preparation of 8-Arm Star Polymer (star-linear PS-Br) via ATRP. General procedures employed for the preparation of star-linear PS-Br are as follows. The mixture containing styrene (22.5 g, 0.216 mol), PMDETA (0.3 mL, 1.44 mmol), and anisole (40 mL) was deoxygenated by bubbling with nitrogen for ~30 min. CuBr (0.21 g, 1.44 mmol) was then introduced under the protection of N₂ flow. The reaction mixture was stirred for ~10 min to allow the formation of CuBr/PMDETA complex. Then the octafunctional ATRP initiator POSS-(Br)₈ (0.49 g, 0.18 mmol) was introduced under the protection of N₂ flow to start the polymerization. The reaction mixture was stirred at 80 °C under N₂ atmosphere. After 8 h, the monomer conversion was determined to be 23% by ¹H NMR analysis. The polymerization was then quenched by the addition of CuBr₂. The mixture was diluted with 10 mL CH₂Cl₂ and passed through a neutral alumina column to remove copper catalysts. After removing most of the solvents, the solution was precipitated into an excess of methanol. The above dissolution–precipitation procedure was repeated for three times, yielding a white solid (4.8 g, yield: 21%; $M_{n, GPC}$ = 23.4 kDa, M_w/M_n = 1.08).

Preparation of 8-Arm Star-Linear PS- N_3 . Into a 100 mL round-bottom flask were added star-linear PS-Br (1.0 g), DMF (15 mL), and NaN₃ (0.163 g, 2.5 mmol). The reaction mixture was allowed to stir at 30 °C for 12 h. After removing DMF under reduced pressure, the residues were dissolved in CH₂Cl₂ and passed through a neutral alumina column to remove residual sodium salts. The eluents were concentrated and then precipitated into an excess of

methanol. The obtained product was dried in a vacuum oven overnight at room temperature (0.9 g, yield: 91%; $M_{n, GPC}$ = 23.4 kDa, M_w/M_n = 1.08).

Preparation of α,ω -Diazido-Terminated PS (N_3 -PS- N_3).^{45,46} General procedures employed for the preparation of α,ω -dibromo-terminated PS (Br-PS-Br) are as follows (Scheme S1). The mixture containing styrene (20.8 g, 0.2 mol), PMDETA (43 mg, 0.25 mmol), and anisole (40 mL) was deoxygenated by bubbling with nitrogen for ~30 min. CuBr (36 mg, 0.25 mmol) was then introduced under the protection of N₂ flow. The reaction mixture was stirred for ~10 min to allow the formation of CuBr/PMDETA complex. After thermostating at 75 °C, difunctional ATRP initiator, dimethyl 2,6-dibromoheptanedioate (0.173 g, 0.5 mmol), was introduced under the protection of N₂ flow to start the polymerization. The reaction mixture was stirred at 75 °C under N₂ atmospheres. After 8 h, monomer conversion was determined to be 32% by ¹H NMR analysis. The polymerization was quenched by the addition of CuBr₂. The mixture was diluted with 20 mL CH₂Cl₂ and passed through a neutral alumina column to remove copper catalysts. After removing most of the solvents, the solution was precipitated into an excess of methanol. The above dissolution–precipitation procedure was repeated for three times, yielding a white powder (6.29 g, yield: 30%; $M_{n, GPC}$ = 6.9 kDa, M_w/M_n = 1.11).

Into a 100 mL round-bottomed flask were added linear Br-PS-Br (1.0 g), DMF (15 mL), and NaN₃ (0.325 g, 5 mmol). The reaction mixture was allowed to stir at 30 °C for 12 h. After all the solvents were removed under reduced pressure, the residues were dissolved in CH₂Cl₂ and passed through a neutral alumina column. The eluents were concentrated and then precipitated into an excess of methanol. The obtained product was dried in a vacuum oven overnight at room temperature (0.91 g, yield: 92%; $M_{n, GPC}$ = 6.8 kDa, M_w/M_n = 1.11).

Preparation of Cyclic PS via Bimolecular Click Cyclization (Scheme S1). PMDETA (0.145 mL, 0.694 mmol), linear N_3 -PS- N_3 (0.1 g, 29.4 μ mol azide moiety), and 2 L of DMF were added into a 3 L three-neck round-bottomed flask. After the flask was deoxygenated by bubbling with nitrogen for 1 h, CuBr (0.1 g, 0.694 mmol) was introduced into the flask under the protection of N₂ flow. After the flask was thermostated at 90 °C, freshly degassed mixture of propargyl ether (1.5 mg, 16 μ mol) and 20 mL of DMF was added into the reaction flask via a syringe pump at a rate of 0.5 mL/h. After the addition was completed, the reaction mixture was allowed to stir for another 6 h at 90 °C. After all the solvents were removed at reduced pressure, the residues were dissolved in CH₂Cl₂ and passed through a neutral alumina column to remove copper catalysts. The eluents were concentrated and precipitated into an excess of methanol. The above dissolution–precipitation cycle was repeated twice. After drying in a vacuum oven overnight at room temperature, the product was obtained as a white powder (0.07 g, yield: 69%; $M_{n, GPC}$ = 5.4 kDa, M_w/M_n = 1.12).

Synthesis of Quatrefoil-Shaped star-cyclic PS. General procedures employed for the preparation of star-cyclic PS were as follows. PMDETA (0.145 mL, 0.694 mmol), star-linear PS- N_3 (0.2 g, 48 μ mol azide moiety), and 1.5 L DMF were added into a 2.5 L three-neck round-bottomed flask. After the mixture was thoroughly deoxygenated by bubbling with nitrogen for 1 h, CuBr (0.1 g, 0.694 mmol) was introduced into the flask under the protection of N₂ flow. After the flask was thermostated at 90 °C, a previously degassed mixture of propargyl ether (3 mg, 32 μ mol) and 20 mL of DMF was added into the flask via a syringe pump at a rate of 0.5 mL/h. After the addition was completed, the reaction mixture was allowed to stir for another 2 h at 90 °C. After all the solvents were removed at reduced pressure, the residues were dissolved in CH₂Cl₂ and passed through a neutral alumina column to remove copper catalysts. The eluents were concentrated and precipitated into an excess of methanol. The above dissolution–precipitation cycle was repeated twice. After drying in a vacuum oven overnight at room temperature, the product was obtained as a white powder (0.13 g, yield: 65%; $M_{n, GPC}$ = 20.6 kDa, M_w/M_n = 1.14). To further investigate the formation of intermediate cyclization products, another experiment was conducted under the same reaction condi-

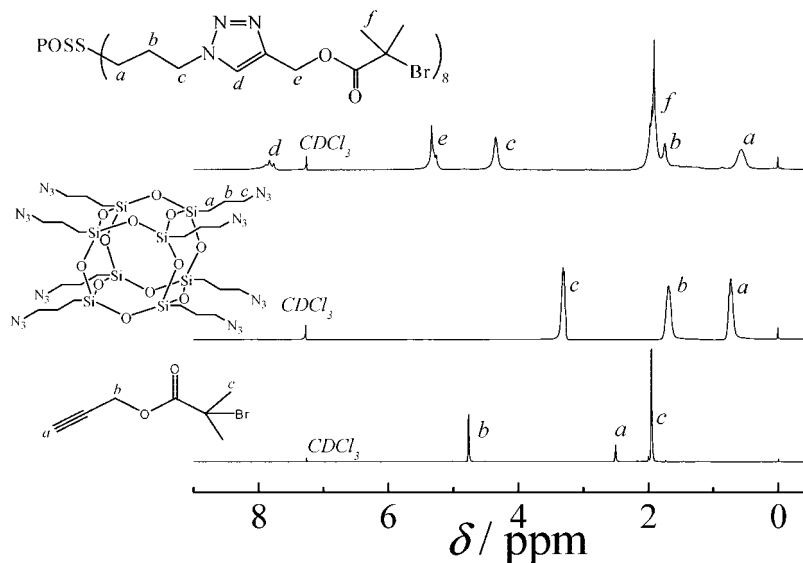


Figure 1. ^1H NMR spectra obtained for propargyl 2-bromoisobutyrate, $\text{POSS}-(\text{N}_3)_8$, and POSS -based octafunctional ATRP initiator, $\text{POSS}-(\text{Br})_8$, in CDCl_3 .

tion as described above except that the amount of propargyl ether was reduced to 1.5 mg (16 μmol , ~ 0.66 equiv. relative to azide moieties). GPC analysis of the product gave an $M_{n,\text{GPC}}$ of 21.8 kDa and an M_w/M_n of 1.16.

Cleavage of Star-Linear PS- N_3 and Star-Cyclic PS. Typical procedure for the cleavage of *star-linear* PS- N_3 and *star-cyclic* PS was as follows. 50 mg POSS -containing star polymer was dissolved in 2 mL of THF, then 20 μL HF solution (40 wt %) (**Caution! hydrofluoric acid is extremely corrosive**) was added to the solution. After stirring at 50 $^\circ\text{C}$ for 4 h and then removing all the solvents, the residues were dissolved in 0.5 mL CH_2Cl_2 and precipitated into an excess of methanol. The sediments were collected and dried in a vacuum oven overnight at room temperature, yielding a white powder (34 mg, yield: $\sim 70\%$).

Characterization. Nuclear Magnetic Resonance (NMR) Spectroscopy. All ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a Bruker AV300 NMR spectrometer operated in the Fourier transform mode. CDCl_3 was used as the solvent.

Fourier Transform Infrared (FT-IR) Spectroscopy. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. The spectra were collected at 64 scans with a spectral resolution of 4 cm^{-1} .

Gel Permeation Chromatography (GPC). The molecular weight and molecular weight distributions of the polymers synthesis in this article were determined by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30 $^\circ\text{C}$). It uses a series of three linear Styragel columns (HT2, HT4, and HT5) or two linear Styragel columns (HR2 and HR4) at an oven temperature of 45 $^\circ\text{C}$. The eluent was THF at a flow rate of 1.0 mL/min. A series of low polydispersity polystyrene standards were employed for the GPC calibration.

Differential Scanning Calorimetry Thermograms (DSC). DSC measurements were conducted on a DSC TA-60WS thermal analysis system (Shimadzu, Japan). Samples were first heated from 20 to 150 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$ under nitrogen atmosphere, followed by cooling to 20 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C}/\text{min}$ after stopping at 150 $^\circ\text{C}$ for 3 min, and finally heating to 150 $^\circ\text{C}$ at the rate of 10 $^\circ\text{C}/\text{min}$. Glass transition temperature (T_g) was determined as the midpoint of the transition of the final heating process.

Results and Discussion

Synthesis of Star-Linear PS and Star-Cyclic PS. 8-Arm *star-linear* PS- N_3 was prepared from a POSS -based octafunctional initiator via ATRP, followed by azidation (Scheme 1).

Subsequently, quatrefoil-shaped *star-cyclic* PS was obtained from the star linear precursor via intramolecular click ring closure using propargyl ether as the coupling agent under highly dilute conditions (Scheme 2).

Synthesis of $\text{POSS}-(\text{Br})_8$. Star polymers can be prepared via the “arm-first” or “core-first” strategy. Generally speaking, the former can afford star polymers with relatively large number of arms, whereas the actual attached number of arms is often not accurate. Whereas in the latter approach, star polymers are prepared from a multifunctional core, and the number of arm can be accurately controlled by selecting core molecules with predetermined functionality and proper chain growth techniques, such as controlled radical polymerization or ROP.^{47–58} In the current case, the target polymer is quatrefoil-shaped *star-cyclic* PS, thus the “core-first” strategy is chosen. A POSS -based octafunctional ATRP initiator was synthesized at first. POSS possesses a cube-octameric frame structure represented by the formula of $\text{R}_8\text{Si}_8\text{O}_{12}$ with an inorganic core (~ 1 nm) surrounded with eight organic groups.

Previously, Laine et al.⁴⁸ and He et al.⁵³ reported the synthesis of POSS -based octafunctional ATRP initiator. However, their synthesis typically involved multistep procedures and the overall yield is not high. Here we incorporated into the synthesis of POSS -based multifunctional initiator with click reaction, which was well-known for its high efficiency and quantitative yield.

The click reaction of $\text{POSS}-(\text{N}_3)_8$ with propargyl 2-bromoisobutyrate led to the formation of $\text{POSS}-(\text{Br})_8$. It should be pointed out that both CuBr and CuBr_2 were added into the reaction mixture during click reaction. If only CuBr was used, the reaction system was also an ATRP environment for propargyl 2-bromoisobutyrate. The possible generation of free radicals from propargyl 2-bromoisobutyrate, and the coupling of radical will lead to the loss of Br functionality. The addition of CuBr_2 can effectively prohibit the generation of radicals. Moreover, the presence of Cu^{2+} will not influence the proceeding of click reaction between $\text{POSS}-(\text{N}_3)_8$ and propargyl 2-bromoisobutyrate.

^1H NMR spectra of $\text{POSS}-(\text{N}_3)_8$, propargyl 2-bromoisobutyrate, and POSS -based octafunctional ATRP initiator, $\text{POSS}-(\text{Br})_8$ were shown in Figure 1. Compared to those of the two precursors, we can clearly observe the appearance of new signals at 4.3, 5.3, and 7.9 ppm (peaks c, d, and e) in the NMR spectrum of $\text{POSS}-(\text{Br})_8$ resulting from click reaction (Figure 1c), these signals are ascribed to methylene protons in $\text{CH}_2\text{CH}_2\text{CH}_2$ -

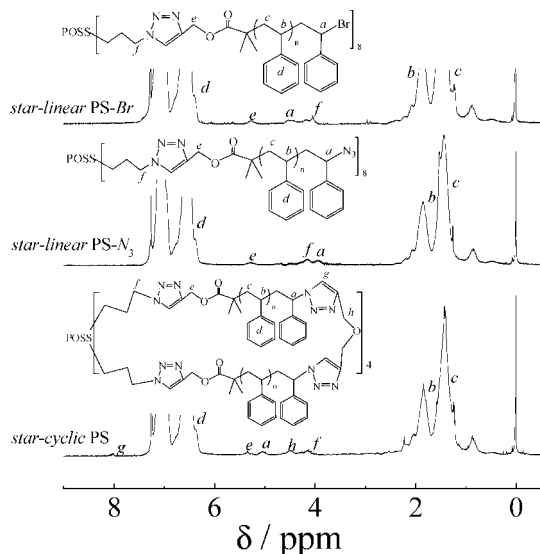


Figure 2. ^1H NMR spectra obtained for POSS-based 8-arm *star-linear* PS-Br, *star-linear* PS- N_3 , and *star-cyclic* PS in CDCl_3 .

triazole, triazole- CH_2O -, and $-\text{CH}$ in 1,2,3-triazole, respectively. On the other hand, signals at 2.5 and 4.7 ppm (Figure 1a, peaks *a*, *b*) in the spectrum of propargyl 2-bromoisobutyrate and signals at 3.3 ppm (Figure 1b, peak *c*) in the spectrum of POSS- $(\text{N}_3)_8$ completely disappeared in the spectrum of POSS- $(\text{Br})_8$. Moreover, the integral ratio of peak *c* and that of *e* is close to 1:1. All of this indicates that we successfully obtained POSS-based octafunctional ATRP initiator, POSS- $(\text{Br})_8$.

Synthesis of Star-Linear PS- N_3 . The advent of controlled radical polymerization techniques, such as NMP, ATRP, and RAFT, has rendered the preparation of well-defined star polymers much easier, starting from proper multifunctional initiators with known number of initiating sites.^{47–58} A variety of star polymers with varying number of arms have been prepared via ATRP “grafting-from” strategy. Starting from POSS-based octafunctional ATRP initiator, organic/inorganic nanocomposite star polymers have been recently prepared by He et al.⁵³

The obtained POSS- $(\text{Br})_8$ was then used as multifunctional initiator for the ATRP of styrene in anisole, employing CuBr/PMDETA as the catalyst. This polymerization system has been proved quite successful for styrene; moreover, a high degree of end Br functionality can be achieved if monomer conversions were kept relatively low. In our case, the monomer conversion was controlled to be 23%. ^1H NMR spectrum of the obtained *star-linear* PS-Br was shown in Figure 2, together with the peak assignments. The spectrum clearly revealed the presence of characteristic signals of PS segments and the terminal groups, except for the methine proton in 1,2,3-triazole rings, which were located at the surface of POSS core within the star polymer. On the basis of integral ratio of peak *e* (5.3 ppm) to that of peaks *b* + *c* (0.7~2.4 ppm), the actual DP of the PS arm was calculated to be ~ 35 . THF GPC trace of *star-linear* PS-Br (Figure 3) exhibited a monodisperse and relatively symmetric peak, reporting a number-average molecular weight, M_n , of 23.4 kDa and a polydispersity, M_w/M_n , of 1.08.

To further reveal the chemical structure of *star-linear* PS-Br, especially the number of arms, the core of *star-linear* PS-Br was etched off by HF in THF, leading disintegration of star polymers into individual linear PS chains. THF GPC trace of the cleaved product (Figure 3) exhibited a relatively symmetric peak with a slight shoulder at the higher molecular weight (MW) side, reporting a polydispersity, M_w/M_n , of 1.26 and an M_n of 4.1 kDa, which was in reasonable agreement with the DP of

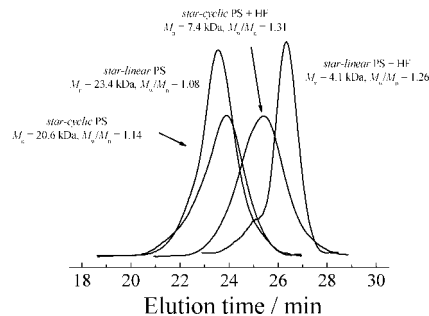


Figure 3. THF GPC traces recorded for POSS-based *star-linear* PS, *star-cyclic* PS, and the corresponding product cleaved from star polymers by treating with HF at 40 °C in THF.

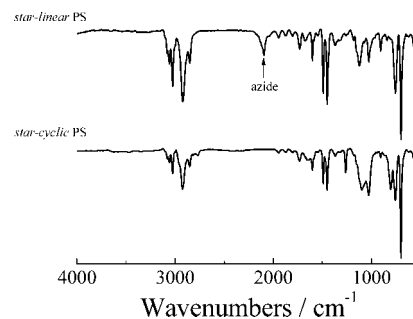


Figure 4. FT-IR spectra obtained for POSS-based 8-arm *star-linear* PS- N_3 and *star-cyclic* PS.

PS arms (~ 35) calculated from ^1H NMR (Figure 2). The slight shoulder at the higher MW side in the GPC elution peak of *star-linear* PS-Br might be ascribed to inter- or intrastar coupling of growing radicals. Laine et al.⁴⁸ also observed similar results during the preparation of star polymers from POSS-based octafunctional ATRP initiator. They confirmed that the coupling of growing species decreased the average number of arms to ~ 7 .

Fortunately, the higher MW impurity resulting from intra- or interstar coupling was considerably small (<10% by curve fitting), and the main elution peak is quite symmetric and narrow-disperse, i.e., most of star polymer molecules still possess an arm number of ~ 8 . We can also calculate from Figure 3 that the M_n of *star-linear* PS-Br is ca. 6 times that of the cleaved product (linear PS arm). This can be explained by the star topology of *star-linear* PS-Br, GPC analysis of which tends to give smaller values compared to that of linear polymers with comparable MW, as star polymers typically possess smaller hydrodynamic volumes.

The terminal Br functionality of *star-linear* PS-Br was then readily converted to azide moiety by reacting with NaN_3 at ambient temperature. From ^1H NMR spectra (Figure 2), it can be seen that after azidation, the resonance signal of methine proton in $-\text{CH}(\text{Ph})\text{Br}$ of *star-linear* PS-Br shifted from 4.5 ppm to 3.9 ppm, the latter was ascribed to $-\text{CH}(\text{Ph})\text{N}_3$ of *star-linear* PS- N_3 . This suggested that the azidation reaction is complete. Moreover, FT-IR spectrum of *star-linear* PS- N_3 shown in Figure 4 revealed the presence of absorbance peak at $\sim 2100\text{ cm}^{-1}$, which is characteristic of the terminal azide group.

Synthesis of star-cyclic PS. At early stages, cyclic polymers have been prepared by the coupling reaction of α,ω -difunctional polystyryl anions with difunctional electrophiles such as α,α' -dibromo-*p*-xylene and dichlorodimethylsilane under highly dilute conditions. Tezuka et al.³⁶ further developed this strategy by employing electrostatic self-assembly and the subsequent covalent fixation technique, and successfully prepared bicyclic and tricyclic polymers. Grayson and co-workers^{4,5} prepared

macrocyclic PS from α -alkynyl- ω -azido PS in highly dilute solution via intramolecular click cyclization reaction. Matyjaszewski et al.^{45,46} investigated the click coupling reaction between α,ω -diazido-terminated PS and propargyl ether at a relatively high concentration and observed the formation of a small amount of bimolecular cyclization product. Inspired by the above work, we suppose that the obtained 8-arm *star-linear* PS- N_3 can be further converted to quatrefoil-shaped star-cyclic polymer possessing four PS rings and one POSS core by employing difunctional propargyl ether as the coupling agent in extremely dilute solution under click conditions (Scheme 2).

At first, we conducted a model bimolecular cyclization reaction between α,ω -diazido-terminated PS (N_3 -PS- N_3) and propargyl ether under highly dilute conditions (Scheme S1, see the Supporting Information). N_3 -PS- N_3 was obtained via ATRP of styrene using dimethyl 2,6-dibromoheptanedioate as the difunctional initiator, followed by end group functionalization with NaN_3 . During bimolecular cyclization reaction under high dilution, the amount of propargyl ether employed was in a slightly molar excess relative to that of azide moiety in N_3 -PS- N_3 to ensure the complete consumption of azide moieties. The products before and after click cyclization were characterized by FT-IR, ^1H NMR, and GPC analysis (Figure S1–S3, see the Supporting Information).

The complete disappearance of characteristic azide absorbance peak at $\sim 2100\text{ cm}^{-1}$ in the FT-IR spectrum of *cyclic* PS as compared to that of N_3 -PS- N_3 indicates that all azide end functionalities have participated in the click reaction (Figure S1). ^1H NMR analysis of *cyclic* PS reveals the appearance of new peaks at $\delta = 7.6, 4.5,$ and 5.0 ppm , which clearly confirms the formation of 1,2,3-triazole moiety (Figure S2). Thus, both FT-IR and ^1H NMR results confirmed the efficient click reaction of terminal functionalities between N_3 -PS- N_3 and propargyl ether.^{5,45,46}

Compared to linear chains, cyclic ones possess a much smaller hydrodynamic volume in solution.^{5,40} Figure S3 shows GPC traces of N_3 -PS- N_3 and *cyclic* PS; compared to that of linear N_3 -PS- N_3 , elution peak of *cyclic* PS clearly shifts to the lower MW side. Moreover, we can not discern any shoulder peak at the higher MW side, this indicates the successful bimolecular cyclization reaction under highly dilute conditions.^{45,46} Based on the above FT-IR, ^1H NMR, and GPC results, we conclude that the bimolecular click cyclization reaction between N_3 -PS- N_3 and small molecule difunctional linker, propargyl ether, can effectively occur under highly dilute conditions.

In the current work, we attempted to transform 8-arm *star-linear* PS- N_3 into quatrefoil-shaped star-cyclic polymer possessing four PS rings and the POSS core (Scheme 2). Three design criteria should be noted to accomplish this task according to the unique conformation of *star-linear* PS- N_3 and the above model bimolecular cyclization reaction. First, the amount of alkynyl functionality of propargyl ether need to be in slight molar excess relative to that of azide moiety in *star-linear* PS- N_3 to ensure the complete click reaction of azide functionality at the terminal of PS arms, and a 33% molar excess was chosen in this work. Second, the method of introducing propargyl ether is crucial.⁵ If a slight excess of propargyl ether was added in one go, there existed the possibility of interstar click coupling and monoclicking of the coupling agent, i.e., without the formation of PS rings. We chose to slowly introduce propargyl ether via a syringe pump at a rate of 0.5 mL/h ($3.0\text{ mg propargyl ether in }20\text{ mL DMF}$). Such a slow addition rate can ensure that before the next drop of propargyl ether solution was introduced, propargyl ether in the previously added one has completely participated in the click reaction with azide functionality. Finally, the polymer concentration was kept extremely low ($1.3 \times 10^{-4}\text{ g/mL}$) during the click ring closure reaction at

$90\text{ }^\circ\text{C}$. This can greatly eliminate the possibility of interstar coupling reaction; once one propargyl ether molecule “click” reacted with an azide group, the remaining alkynyl group will preferentially react with a terminal azide group in the neighboring arms within the same star molecule. All the above factors will cooperatively contribute to the successful preparation of well-defined quatrefoil-shaped star-cyclic PS (Scheme 2).

Figure 2 shows the ^1H NMR spectrum of the obtained *star-cyclic* PS, together with the peak assignments. We can observe the appearance of two new resonance peaks *g* and *h* at 8.0 ppm and 4.5 ppm , respectively. These two peaks can be ascribed to the methine proton of 1,2,3-triazole ring (peak *g*) and methylene protons neighboring to 1,2,3-triazole (peak *h*), respectively. The latter actually came from the difunctional linker, propargyl ether. Moreover, peak *a* initially at 3.9 ppm in the spectrum of *star-linear* PS- N_3 completely shifted to 5.0 ppm after click ring closure. Thus, ^1H NMR results suggested the nearly complete click reaction of azide groups of *star-linear* PS- N_3 .

The intrastar arm-arm coupling reaction was further confirmed by FT-IR spectroscopy. From Figure 4, we can clearly observe the complete disappearance of characteristic azide absorbance peak at $\sim 2100\text{ cm}^{-1}$ for *star-cyclic* PS, as compared to that of *star-linear* PS- N_3 . Moreover, no absorbance peak in the region around 3310 cm^{-1} , which is characteristic of terminal alkyne groups, can be discerned in the spectrum of *star-cyclic* PS. This suggested the absence of alkynyl functionality within the star-cyclic molecule (Scheme 2).

Since ^1H NMR and FT-IR cannot determine whether the click coupling reaction proceeds via an intramolecular or intermolecular manner, GPC analysis was further employed to characterize *star-cyclic* PS (Figure 3). Interestingly, elution peak of *star-cyclic* PS revealed a monomodal peak, giving an M_n of 20.6 kDa and an M_w/M_n of 1.14 . The obtained M_n value of *star-cyclic* PS was considerably smaller than that of *star-linear* PS- N_3 (23.4 kDa). Most importantly, we can also clearly observe a slight shift to the lower MW side for *star-cyclic* PS, as compared to that of *star-linear* PS- N_3 . Early in the 1940s, Kramers et al.⁵⁹ and Zimm et al.⁶⁰ theoretically predicted that the ratio of average radius of gyration, $\langle R_g \rangle$, of a random coiled linear chain to that of a cyclic one should be 2.0 , and this conclusion has been confirmed by many experimental results. Deffieux et al.³⁴ reported that after cyclization, $M_{n,\text{GPC}}$ of tricyclic polymer was appreciably smaller than that of 3-arm star precursor. Thus, our results were in qualitative agreement with what they have observed, which is reasonable considering that cyclic PS within *star-cyclic* PS possesses lower hydrodynamic volume compared with that of linear PS arm of *star-linear* PS- N_3 .

If cyclic PS were really formed by coupling *star-linear* PS- N_3 with propargyl ether under our conditions, we should observe a doubling of MW after etching off the POSS core from *star-cyclic* PS, as compared to that from *star-linear* PS- N_3 . To further confirm this, *star-cyclic* PS was treated with HF and the cleaved product was subjected to GPC analysis. From Figure 3, we can observe that the cleaved product of *star-cyclic* PS possessed a relatively symmetric elution peak, reporting an M_n of 7.4 kDa and an M_w/M_n of 1.31 , which was about 1.8 times that of the cleaved product from *star-linear* PS- N_3 . This result further confirmed the star-ring topology in *star-cyclic* PS, and we have indeed obtained quatrefoil-shaped star polymers.

To further investigate the formation of intermediate cyclization products during the synthesis of quatrefoil-shaped *star-cyclic* PS, we carried out another click cyclization experiment in which the amount of propargyl ether added was halved (~ 0.66 equiv of alkynyl relative to that of azide moieties). Theoretically, this will lead to partial intrastar arm-arm click coupling. Presumably, a mixture of mono-, di-, tri-, and tetra-

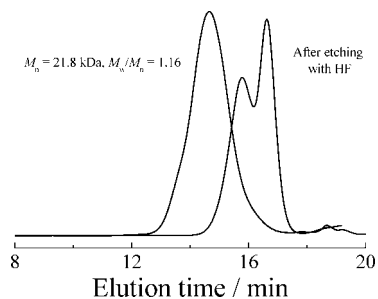


Figure 5. THF GPC traces recorded for the intrastar arm-arm click coupling product in the presence of 0.66 equiv of propargyl ether relative to that of azide moieties, and the corresponding product cleaved from the star polymer by treating with HF at 40 °C in THF.

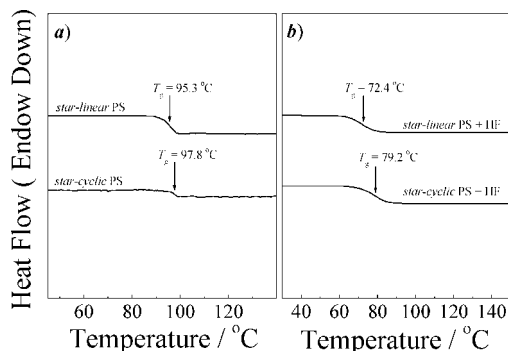


Figure 6. Differential scanning calorimetry thermograms recorded for (a) *star-linear* PS and *star-cyclic* PS, and (b) the corresponding products cleaved from star polymers by treating with HF at 40 °C in THF.

cyclic *star-cyclic* PS will be obtained. After etching off POSS with HF, the residues were subjected to GPC analysis. Figure 5 shows GPC traces recorded for click cyclization product before and after etching. We can clearly observe the presence of a double shoulder GPC elution peak after etching the cyclization product with HF. The peak molecular weights, M_p , of two shoulders are 7.6 kDa and 4.2 kDa, respectively, which can be ascribed to cyclic arms resulting from intrastar arm-arm click coupling and unreacted linear of the final product.

Based on the above characterization results from ^1H NMR, FT-IR, and GPC analysis and the formation of intermediate cyclization product when the amount of propargyl ether was halved, we conclude that quatrefoil-shaped *star-cyclic* PS was successfully prepared from the *star-linear* PS via intrastar click coupling reaction under highly dilute conditions. The obtained quatrefoil-shaped topology represents a novel chain topology in the category of nonlinear-shaped polymers.

DSC Studies of *star-linear* PS and *star-cyclic* PS. Glass transition temperature (T_g) is one of the basic physical parameters of polymers. It was known that MW (particularly at in the low range) and chain topology can considerably influence T_g value of a polymer. Moreover, it has been previously predicated and experimentally proven that cyclic polymers generally possess slightly higher T_g value than their linear counterparts.^{34,61}

DSC thermograms *star-linear* PS, *star-cyclic* PS, and their corresponding cleaved products were shown in Figure 6. A comparison of DSC curves of *star-linear* PS and *star-cyclic* PS revealed that the latter exhibited a slightly larger T_g (97.8 °C), with that of the former being 95.3 °C. The T_g increase might come from two possible contributions: (1) the formation of PS rings around the POSS core increased the MW of PS due to click coupling; (2) intrastar ring closure reaction eliminates free chain terminals for PS arms in *star-linear* PS, which will reduce the chain mobility due to the absence of chain

ends. After etching with HF, T_g values for the cleaved products from *star-linear* PS and *star-cyclic* PS were determined to be 72.4 and 79.2 °C, respectively. Compared to those of *star-linear* and *star-cyclic* polymers, cleaving with HF resulted in the decrease of overall MW and the increase of chain mobility due to freeing of chain ends covalently attached at the POSS surface; moreover, the presence of inorganic POSS moiety within *star-linear* PS and *star-cyclic* PS can also elevate their T_g values.^{62,63} All of these effects will contribute to the decrease of T_g for the cleaved products.

Conclusion

In summary, we report the synthesis of quatrefoil-shaped *star-cyclic* polystyrene, *star-cyclic* PS, containing polyhedral oligomeric silsesquioxane (POSS) core via the combination of atom transfer radical polymerization (ATRP) and click chemistry. The obtained *star-cyclic* PS represents a new chain topology in the category of nonlinear-shaped polymers. Gel permeation chromatography (GPC), ^1H NMR, and FT-IR analysis confirmed the complete consumption of azide moieties in *star-linear* PS- N_3 and that the coupling reaction proceeded via the intramolecular manner. Differential scanning calorimetry (DSC) results revealed that *star-cyclic* PS possesses higher glass transition temperature (T_g) than that of *star-linear* PS. Containing an inorganic POSS core, *star-cyclic* PS can also be considered as organic/inorganic hybrid nanocomposites. Overall, the combination of click chemistry and controlled radical polymerization techniques has emerged to be a powerful tool in designing and synthesis of polymeric materials with unique chain architectures.

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Supporting Information Available: Figures showing ^1H NMR, FT-IR, and GPC characterization results for the model bimolecular cyclization reaction and a scheme showing the synthetic routes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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