

Supporting Information

for

Highly Asymmetric Phase Behaviors of Polyhedral
Oligomeric Silsesquioxanes Based Multi-Headed
Giant Surfactants

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1. Materials and Methods

1.1. Chemicals and Solvents.

All the chemicals and solvents were used as received unless otherwise stated. Dichloromethane (certified ACS, DCM, Fisher Scientific), chloroform (certified ACS, Fisher Scientific), ethyl acetate (certified ACS, Fisher Scientific), methanol (MeOH, reagent grade, Fisher Scientific), hexanes (certified ACS, Fisher Scientific), *N,N*-dimethylformamide (anhydrous, 99.8%, Sigma-Aldrich), 1,3-dibromo-2-propanol (95%, Sigma-Aldrich), 4-pentynoic acid (98%, Acros Organics), *N,N'*-diisopropyl carbodiimide (DIPC, 99%, Acros Organics), 4-dimethylaminopyridine (DMAP, $\geq 99\%$, Sigma-Aldrich), copper(I) bromide (98%, Acros Organics), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Sigma-Aldrich), *N,N,N',N'',N''*-pentamethyl diethylenetriamine (PMDETA, 99%, Sigma-Aldrich), trifluoromethanesulfonic acid (99%, Acros Organics), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiofenone (Irgacure 2959, 98%, Sigma-Aldrich), 1-thioglycerol ($\geq 97\%$, Sigma-Aldrich), sodium azide (NaN_3 , 99%, Sigma-Aldrich).

VPOSS-alkyne,¹ VPOSS-COOH,² adapter molecule with one alkyne group and four hydroxyl groups **2**,³ azide-functionalized PS ($\text{PS}_n\text{-N}_3$),⁴ DPOSS- PS_n ,⁴ and 3DPOSS- PS_n ⁴ were synthesized as reported.

1.2. Characterizations

Nuclear Magnetic Resonance (NMR) Spectroscopy. All the ^1H and ^{13}C NMR spectra were obtained in CDCl_3 (Sigma-Aldrich, 99.8% D) using Varian Mercury 300 MHz NMR or 500 MHz NMR spectrometers. All ^1H NMR spectra were referenced to the peak of residual proton impurities in CDCl_3 at $\delta = 7.27$ ppm and all ^{13}C NMR spectra were referenced to the peak of $^{13}\text{CDCl}_3$ at $\delta = 77.00$ ppm. All NMR data were processed using the ACDLABS 12.0 software (Academic Edition).

Fourier-Transform Infrared (FTIR) Spectroscopy. Infrared spectra of the chemicals were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting sample films on KBr plates at room temperature. The data were processed using the Win-IR software.

Size Exclusion Chromatography (SEC). SEC analyses for the synthesized hybrid polymers were performed on a Waters 150-C Plus instrument equipped with three HR-Styrigel columns [100 Å, mixed bed (50/500/103/104 Å), mixed bed ($10^3, 10^4, 10^6$ Å)], and a triple detector system. The three detectors included a differential viscometer (Viscotek 100), a laser light scattering detector (Wyatt Technology, DAWN EOS, $\lambda = 670$ nm), and a differential refractometer (Waters 410). THF was used as the eluent with a flow rate of 1.0 mL/min at room temperature. Data processing was accomplished using the software on a workstation equipped with this system.

Matrix-assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) Mass Spectroscopy. All MALDI-TOF mass spectra were obtained on a Bruker Ultraflex III TOF/TOF mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with a Nd:YAG laser emitting at 355 nm. *Trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyli-dene]-malononitrile (DCTB, >98%, Sigma-Aldrich) was dissolved in THF (20.0 mg/mL) as the matrix solution. Sodium trifluoroacetate (NaTFA , 98%, Sigma-Aldrich), potassium trifluoroacetate (KTFA , 98%,

Sigma-Aldrich), or silver trifluoroacetate (AgTFA, 98%, Sigma-Aldrich) was dissolved in MeOH/CHCl₃ (v/v = 1/3) at 10.0 mg/mL and used as the cationizing agent solution. The matrix and cationizing agent solutions were mixed in a 10/1 (v/v) ratio. Samples were typically dissolved in THF at 5.0 mg/mL. To prepare the samples, 0.5 μ L of the matrix and cationizing agent mixture solution was deposited on the wells of a 384-well ground-steel sample plate and allowed to dry, followed by depositing 0.5 μ L of the sample solution on a spot of the dried matrix and cationizing agent, and a second deposition of 0.5 μ L of the matrix and cationizing agent mixture solution on top of the dried sample. The sample plate was loaded into the MALDI-TOF mass spectrometer and the spectra were measured in the reflection mode. The mass scale was calibrated with polystyrene or poly(methyl methacrylate) standards with molecular weight regions under consideration. Data analyses were conducted using the Bruker's flexAnalysis software.

2. Synthesis of XDPOSS-PS_n

2.1. Synthesis of 2DPOSS-PS_n



Scheme S1. synthesis route for adapter molecule (**Compound 1**).

Preparation of Compound 1. To a 100 mL round-bottomed flask equipped with a magnetic stirring bar were added 4-pentynoic acid (0.500 g, 5.10 mmol), 1,3-dibromo-2-propanol (1.22 g, 5.61 mmol), and DMAP (0.063 g, 0.50 mmol), followed by the addition of 30 mL freshly dried CH₂Cl₂ to fully dissolved the solids. The flask was capped with a rubber septum and cooled to 0 °C. With stirring, DIPC (0.836 g, 6.63 mmol) was added dropwise into the flask via syringe. The resulting mixture was stirred for 12 h at room temperature. After that, the white precipitate was filtered out, and the filtrate was evaporated by rotary evaporation. The crude product was purified by flash column chromatography on silica gel using the eluent (ethyl acetate/hexane) to afford the product (1.32 g) as pale yellow oil. Yield: 87%. ¹H NMR (CDCl₃, 500 MHz, ppm): ¹H NMR (500 MHz, Chloroform-*d*) δ 5.21 – 5.15 (m, 1H), 3.62 (d, 4H), 2.68 - 2.50 (m, 4H), 2.00 (t, 1H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 170.75, 82.10, 71.05, 69.20, 33.82, 31.28, 14.10.

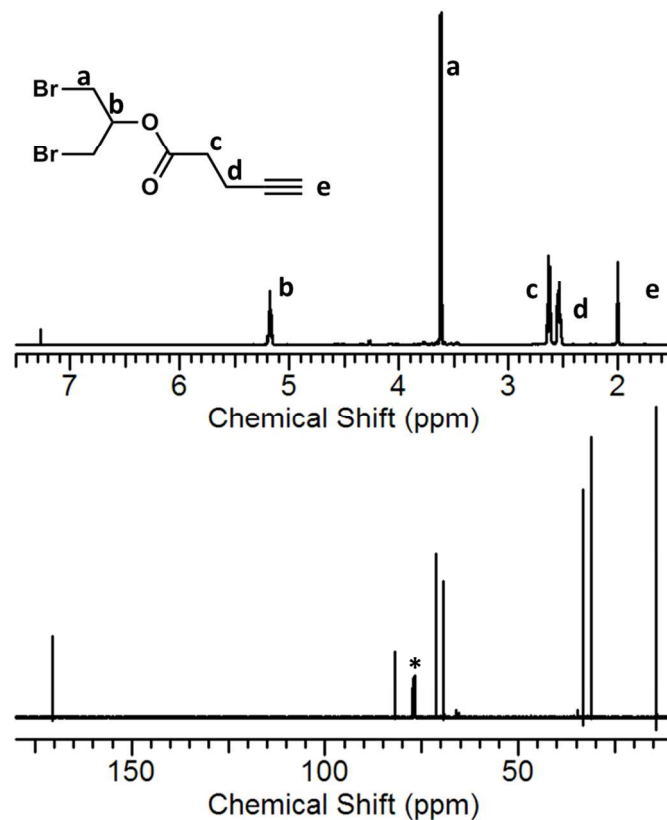
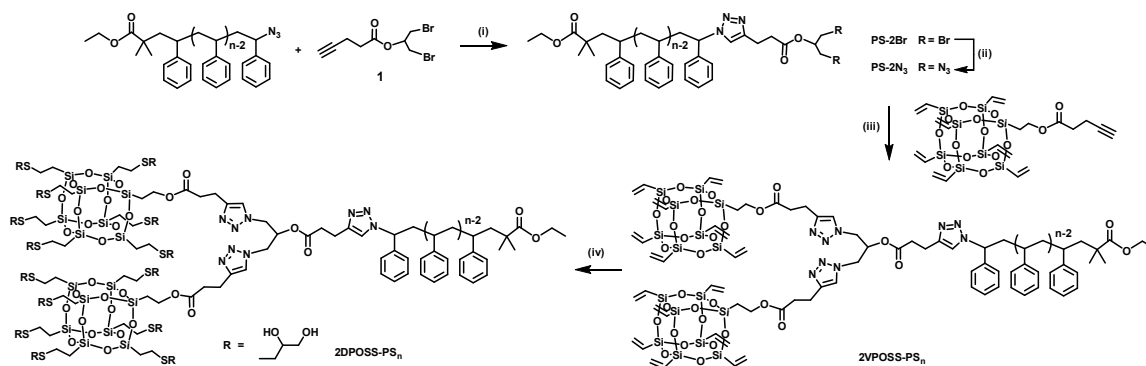


Figure S1. ^1H NMR and ^{13}C NMR spectra of click adapter Compound 1. Resonance peaks in are assigned. Asterisks indicate corresponding signals from CDCl_3 solvent.



Scheme S2. Synthetic scheme of 2DPOSS- PS_n . Reagents and conditions: (i) CuBr , PMDETA, toluene, r.t., overnight, $\sim 83\%$; (ii) NaN_3 , DMF, 80°C , 24 h, $>90\%$; (iii) CuBr , PMDETA, toluene, r.t., overnight, $\sim 80\%$; (iv) 1-thioglycerol, Irgacure 2959, THF, $h\nu$, 10 min, $\sim 70 - 85\%$.

Preparation of PS₃₈-2N₃. To a 100 mL Schlenk flask equipped with a magnetic stirring bar were added **PS₃₈-N₃** ($M_{n,NMR} = 4.00$ kg/mol, $D = 4.07$, 400 mg, 0.10 mmol), compound **1** (44.8 mg, 0.15 mmol), CuBr (0.05 eq per azide group), and 20 mL toluene. The solution was degassed by three freeze-pump-thaw cycles before the addition of PMDETA (1 eq per azide group) under the protection of nitrogen gas. The mixture was degassed by one more freeze-pump-thaw cycle and then stirred at room temperature for 12 h. After that, the solution was directly transferred onto a silica gel column. Toluene was used to remove any unreacted molecules. Then, CH₂Cl₂ was used to flash the product out of the column. After removal of solvent, the crude product was dissolved in THF and precipitated in cold methanol. The product was collected by vacuum filtration and directly used for next step reaction. The white solid **PS₃₈-2Br** was added to a 50 mL round-bottomed flask equipped with a magnetic stirring bar and anhydrous DMF (10 mL). The mixture was stirred at 80 °C overnight before allowing cooling to room temperature, followed by the addition of 20 mL CH₂Cl₂. The resulting mixture was washed with water (50 mL × 2), brine (50 mL), dried over Na₂SO₄, concentrated by rotary evaporation, and precipitated into cold methanol. The white solids were collected and dried *in vacuo* to afford **PS₃₈-2N₃** (322 mg). Two steps yield: 75%. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.50 - 6.40 (m, 190H), 5.21 - 5.00 (m, 2H), 3.75 - 3.60 (m, 2H), 3.40 (d, 4H), 3.02 - 2.64 (m, 4H), 2.60 - 0.90 (m, 114H), 1.10 - 0.82 (m, 9H). SEC: $M_{n,SEC} = 4.25$ kg/mol, $M_{w,SEC} = 4.46$ kg/mol, $D = 1.05$. A series of **PS_n-2N₃** samples with different molecular weights can be similarly obtained with similar yields.

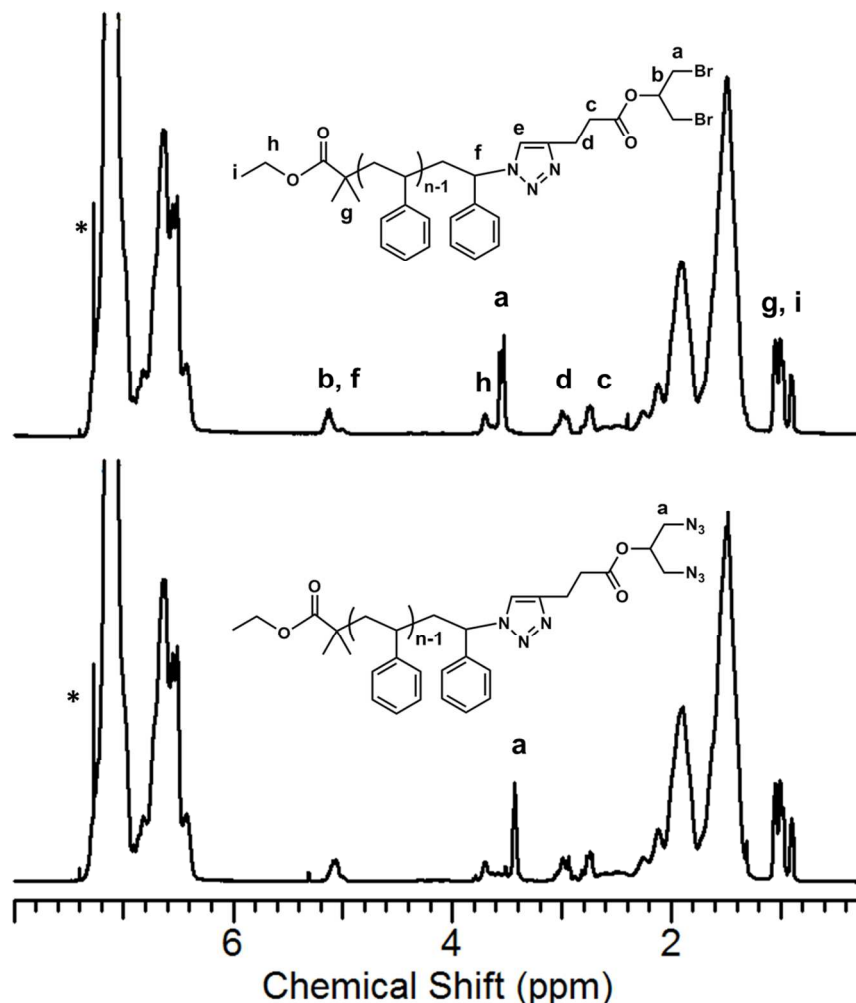


Figure S2. ^1H NMR spectra of **PS₃₈-2Br** and **PS₃₈-2N₃**.

Preparation of 2VPOSS-PS₃₈. To a 100 mL Schlenk flask equipped with a magnetic stirring bar were added **PS₃₈-2N₃** (240 mg, 0.056 mmol), **VPOSS-alkyne** (87 mg, 0.119 mmol, 1.05 eq per azide group), CuBr (0.05 eq per azide group), and 20 mL toluene. The solution was degassed by three freeze-pump-thaw cycles before the addition of PMDETA (1 eq per azide group) under the protection of nitrogen gas. The mixture was degassed by one more freeze-pump-thaw cycle and then stirred at room temperature for 12 h. After that, the solution was directly transferred onto a silica gel column. CH₂Cl₂ was used to remove any unreacted VPOSS-alkyne. Then, a mixture of CH₂Cl₂ and ethyl acetate (v/v = 1/1) was used to flash the product out of the column. After removal of solvent, the crude product was dissolved in THF and precipitated in cold methanol. The product was collected by vacuum filtration and dried *in vacuo* to afford **2VPOSS-PS₃₈** as a white powder (248 mg). Yield: 77%. ^1H NMR (CDCl₃, 500 MHz, ppm): δ 7.50 - 6.40 (m, 190H), 6.20 - 5.90 (m, 42H), 5.40 - 5.08 (m, 2H), 4.40 - 4.30 (m, 4H), 4.30 - 4.20 (m, 4H), 3.75 - 3.60 (m, 2H), 3.02 - 2.64 (m, 14H), 2.40 - 1.38 (m, 114H), 1.37 - 0.82 (m, 9H), 0.81 - 0.74 (m, 4H). SEC: $M_{n,\text{SEC}} = 5.85$ kg/mol, $M_{w,\text{SEC}} = 6.13$ kg/mol, $D = 1.05$. A series of **2VPOSS-PS_n** samples with different molecular weights can be similarly obtained from **VPOSS-alkyne** and different **PS_n-2N₃** samples with similar yields.

Preparation of 2DPOSS-PS₃₈. To an open vial without a stirring bar were added **VPOSS-3PS₁₁** (150 mg, 0.026 mmol), 1-thioglycerol (10.0 eq per VPOSS cage), Irgacure 2959 (0.10 eq per VPOSS cage, or 0.014 eq per vinyl group), and a minimum amount of THF (~ 2 mL) to fully dissolve the solids. The reaction was completed after irradiation by 365 nm UV light for 20 min. The resulting mixture was then purified by repeated precipitations from concentrated THF solutions into cold MeOH/water mixture (v/v = 1/2), collected by centrifugation, and dried *in vacuo* to afford **2DPOSS-PS₃₈** as a white powder (142 mg). Yield: ~75%. ^1H NMR (d⁶-DMSO, 500 MHz, ppm): δ 7.50 - 6.40 (m, 190H), 5.40 - 5.08 (m, 2H), 4.40 - 4.30 (m, 4H), 4.30 - 4.20 (m, 4H), 3.95 - 3.80 (m, 2H), 3.60 - 3.40 (m, 42H), 2.95 - 2.80 (m, 6H), 2.70 - 2.50 (m, 56H), 2.40 - 1.38 (m, 114H), 1.37 - 0.82 (m, 9H), 0.81 - 0.74 (m, 4H). SEC: $M_{n,\text{SEC}} = 7.20$ kg/mol, $M_{w,\text{SEC}} = 7.56$ kg/mol, $D = 1.06$. A series of **2DPOSS-PS_n** samples with different molecular weights can be similarly obtained from different **2VPOSS-PS_n** samples with similar yields.

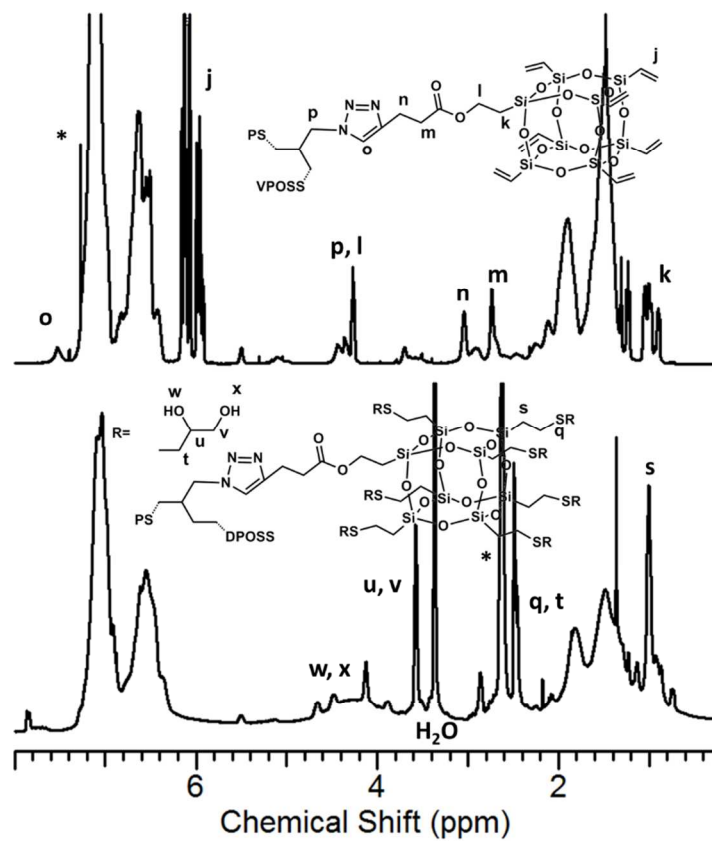


Figure S3. ^1H NMR spectra of 2VPOSS-PS₃₈ and 2DPOSS-PS₃₈.

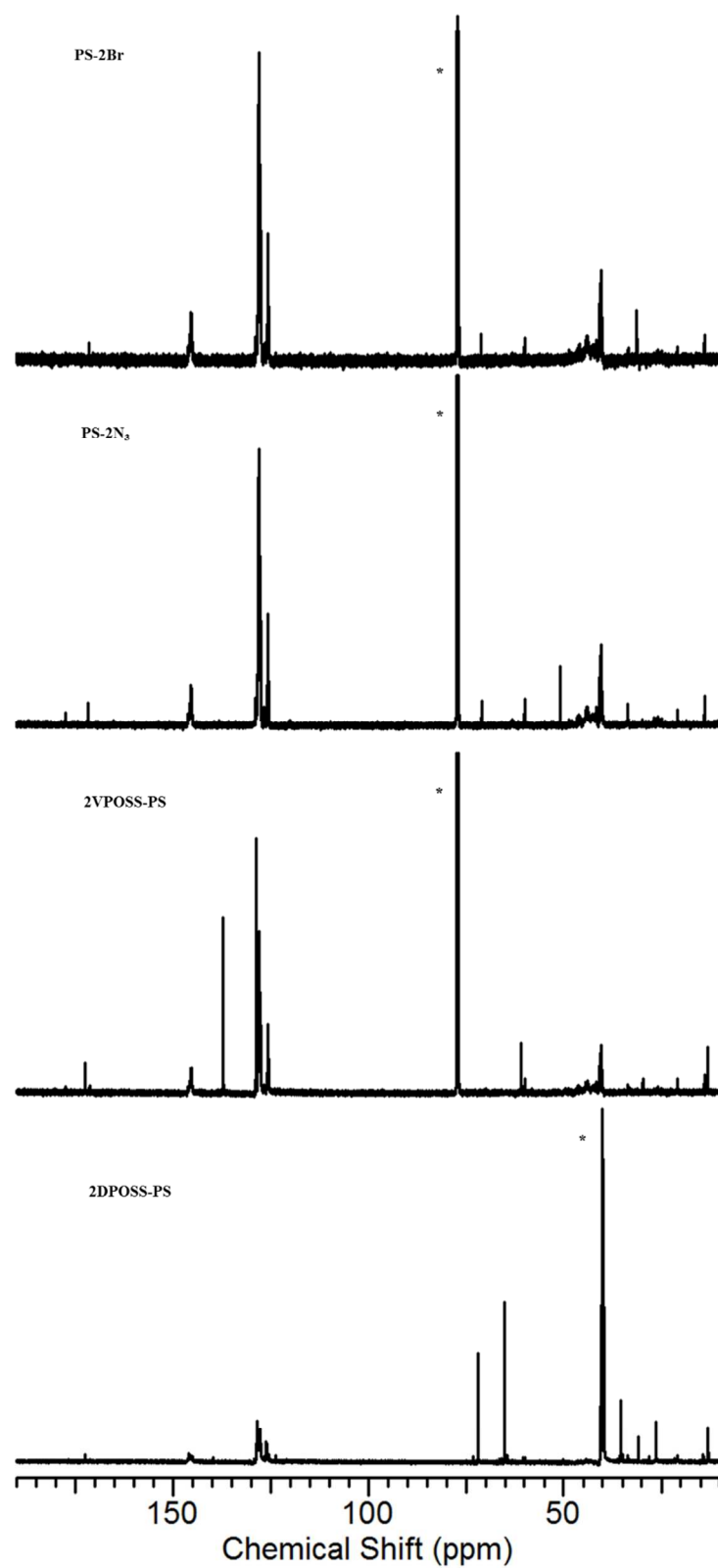


Figure S4. ^{13}C NMR spectra of **PS₃₈-2Br**, **PS₃₈-2N₃**, **2VPOSS-PS₃₈** and **2DPOSS-PS₃₈**. After the thiol-ene reaction, characteristic resonance peaks from vinyl carbons disappeared. Asterisks indicate corresponding signals from CDCl_3 .

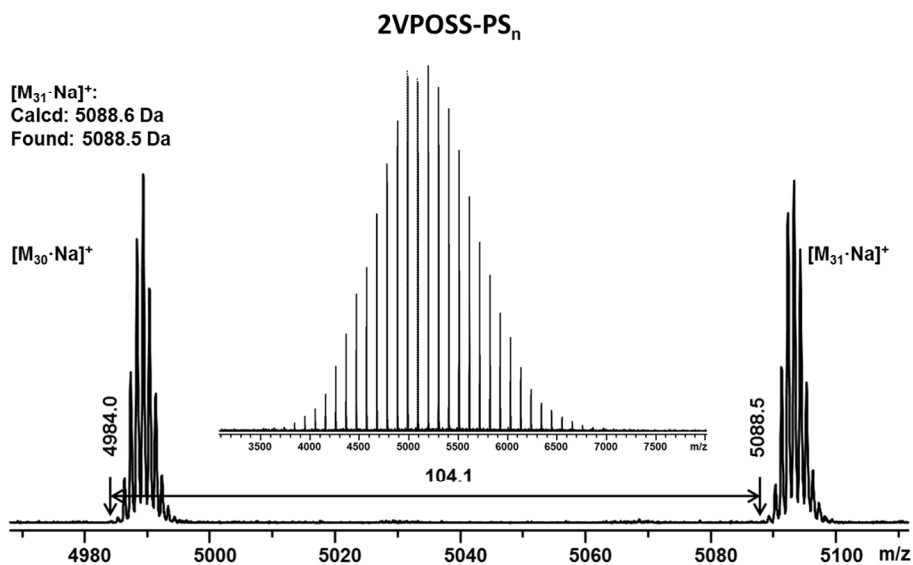


Figure S5. MALDI–TOF mass spectrum of 2VPOSS-PS_n with monoisotopic resolution. The inset showed the full spectrum.

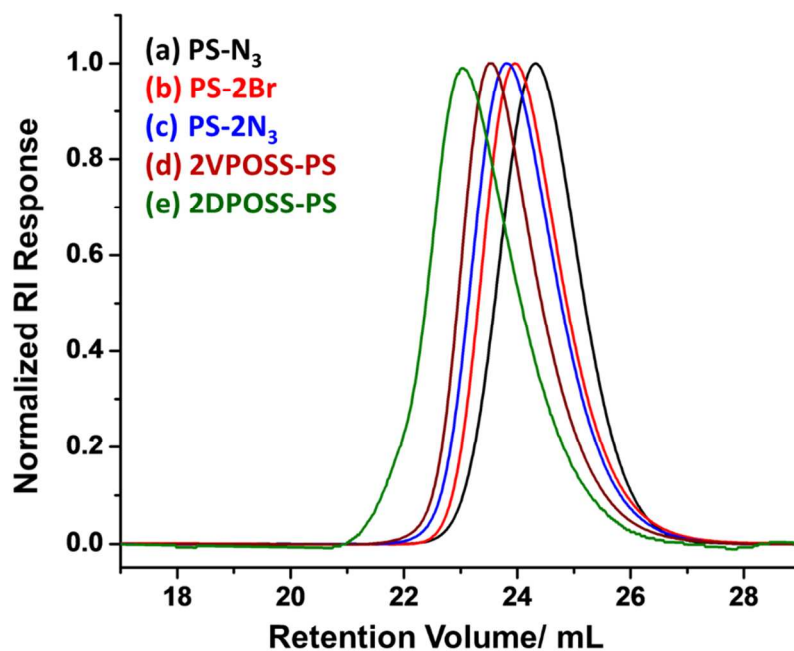


Figure S6. Normalized SEC overlay of PS_n-N₃ (black curve), PS_n-2Br (red curve), PS_n-2N₃ (blue curve), 2VPOSS-PS_n (magenta curve), and 2DPOSS-PS_n (green curve).

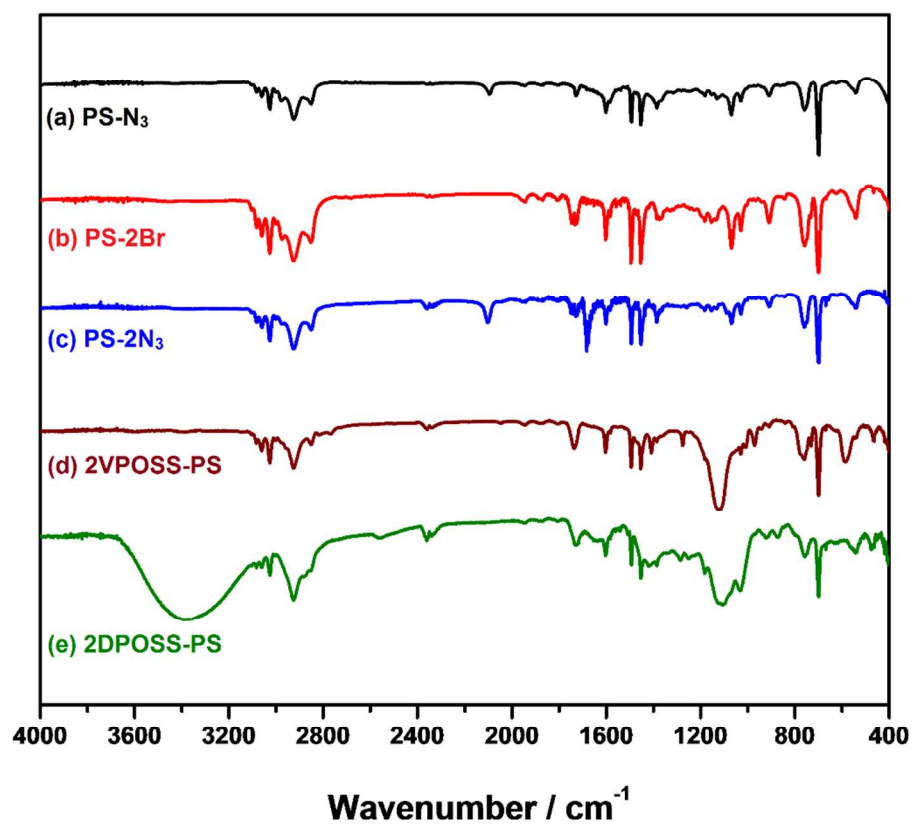
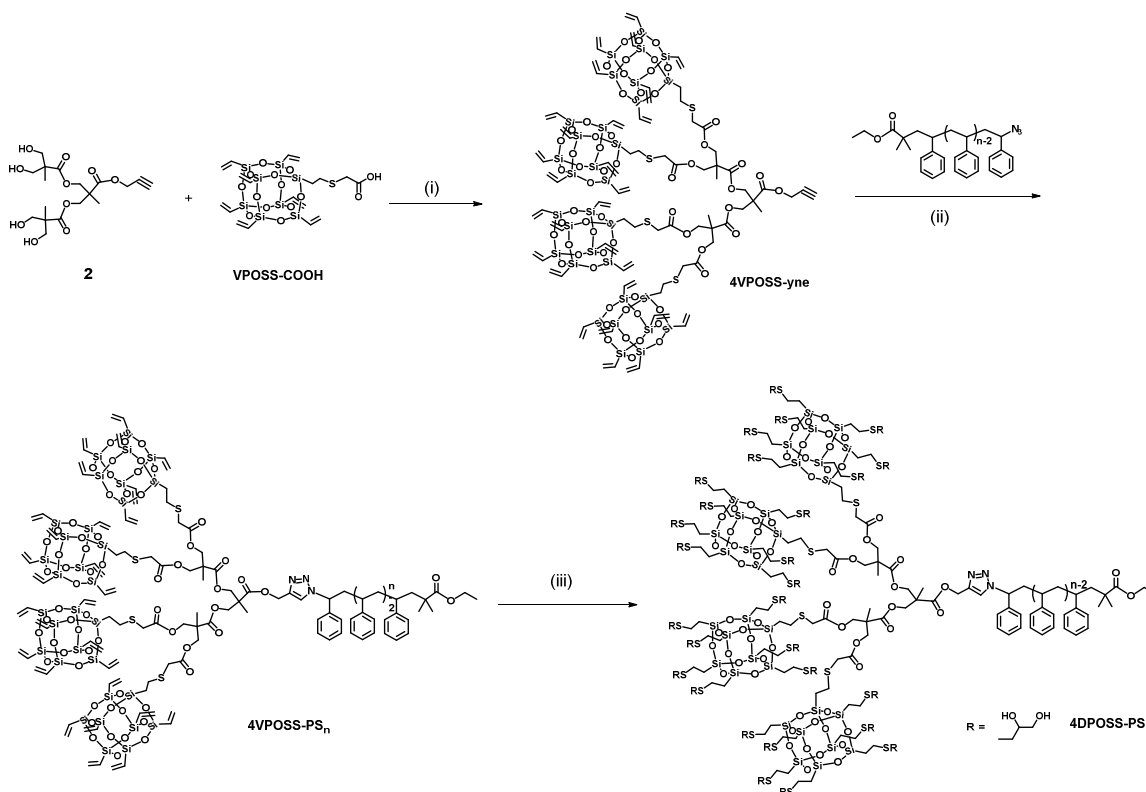


Figure S7. FT-IR spectra of $\text{PS}_n\text{-N}_3$ (black curve), $\text{PS}_n\text{-2Br}$ (red curve), $\text{PS}_n\text{-2N}_3$ (blue curve), 2VPOSS-PS_n (magenta curve), and 2DPOSS-PS_n (green curve).

2.2. Synthesis of 4DPOSS-PS_n



Scheme S3. Synthetic scheme of 4DPOSS-PS_n. Reagents and conditions: **(i)** DIPC, DMAP, DCM, r.t., overnight, ~ 50%; **(ii)** CuBr, PMDETA, toluene, r.t., overnight, ~ 80%; **(iii)** 1-thioglycerol, Irgacure 2959, THF, *hν*, 10 min, ~70 - 85%.

Preparation of 4VPOSS-yne. To a 100 mL round-bottomed flask equipped with a magnetic stirring bar were added **2** (0.400 g, 0.90 mmol), VPOSS-COOH(2) (3.24 g, 4.47 mmol), and DMAP (0.063 g, 0.50 mmol), followed by the addition of 50 mL freshly dried CH₂Cl₂ to fully dissolved the solids. The flask was capped with a rubber septum and cooled to 0 °C. With stirring, DIPC (0.643 g, 5.10 mmol) was added dropwise into the flask via syringe. The resulting mixture was stirred for 24 h at room temperature. After that, the white precipitate was filtered out, and the filtrate was evaporated by rotary evaporation. The crude product was purified by flash column chromatography on silica gel using the eluent (ethyl acetate/hexane) to afford the product (1.53 g) as white solid. Yield: 52%. ¹H NMR (CDCl₃, 500 MHz, ppm): ¹H NMR (500 MHz, Chloroform-*d*) δ 6.41 – 5.61 (m, 84H), 4.73 (dd, *J* = 2.3, 1.1 Hz, 2H), 4.31 (m, 4H), 4.26 (s, 8H), 3.24 (s, 8H), 2.91 – 2.64 (m, 8H), 2.53 (m, 1H), 1.29 (s, 3H), 1.26 (s, 6H), 1.14 – 1.05 (m, 8H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 171.74, 171.36, 169.72, 137.02 (t, *J* = 6.5 Hz), 129.63–124.85 (m), 65.78, 46.63, 34.66, 33.93 (d, *J* = 183.6 Hz), 26.88, 25.27, 17.61 (d, *J* = 16.9 Hz), 17.54, 12.52.

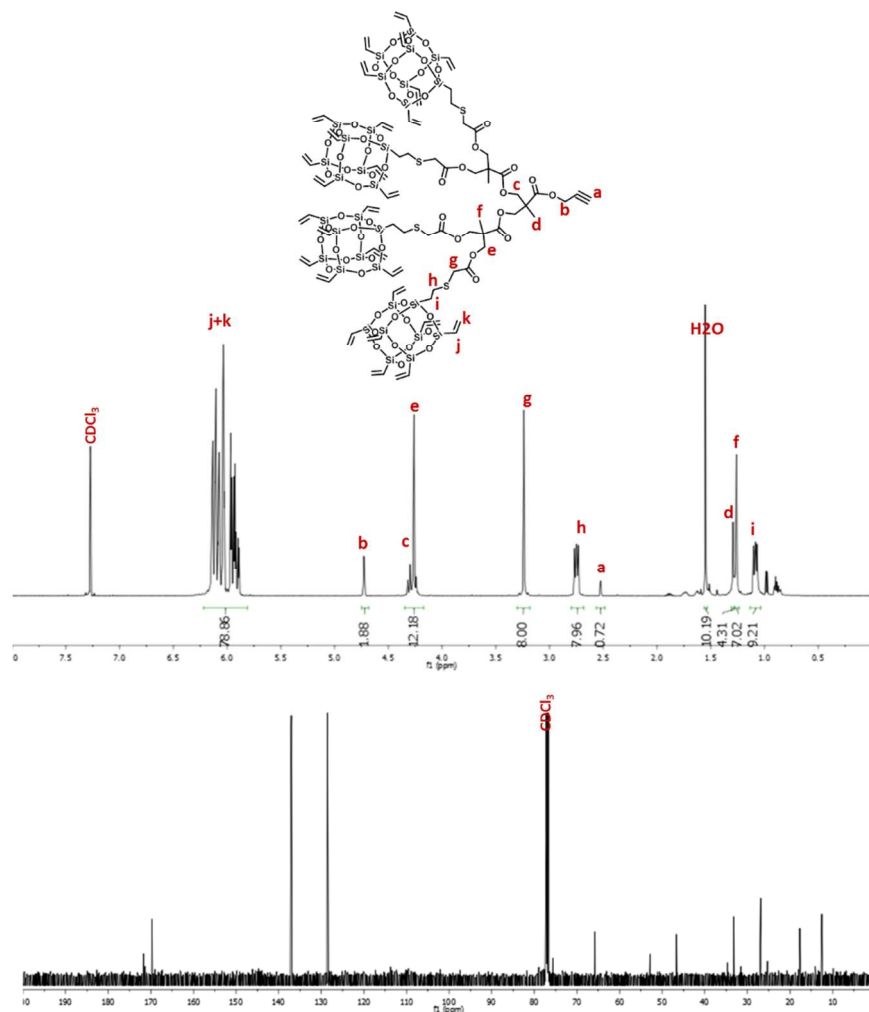


Figure S8. ¹H NMR and ¹³C NMR spectra of **4VPOSS-yne**. Resonance peaks in are assigned. Asterisks indicate corresponding signals from CDCl₃ solvent.

Preparation of 4VPOSS-PS₃₈. To a 100 mL Schlenk flask equipped with a magnetic stirring bar were added **PS₃₈-N₃** ($M_{n,NMR} = 3.95$ kg/mol, $D = 1.05$, 220 mg, 0.056 mmol), **4VPOSS-yne** (193 mg, 0.059 mmol, 1.05 eq per azide group), CuBr (0.05 eq per azide group), and 20 mL toluene. The solution was degassed by three freeze-pump-thaw cycles before the addition of PMDETA (1 eq per azide group) under the protection of nitrogen gas. The mixture was degassed by one more freeze-pump-thaw cycle and then stirred at room temperature for 12 h. After that, the solution was directly transferred onto a silica gel column. CH₂Cl₂ was used to remove any unreacted VPOSS-alkyne. Then, a mixture of CH₂Cl₂ and ethyl acetate (v/v = 1/1) was used to flash the product out of the column. After removal of solvent, the crude product was dissolved in CH₂Cl₂ and precipitated in cold methanol. The product was collected by vacuum filtration and dried *in vacuo* to afford **4VPOSS-PS₃₈** as a white powder (290 mg). Yield: ~73%. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.50 - 6.40 (m, 180H), 6.28 - 5.80 (m, 84H), 5.25 - 5.00 (m, 2H), 4.43 - 4.05 (m, 14H), 3.80 - 3.45 (m, 6H), 3.24 (s, 8H), 3.00 - 2.80 (m, 2H), 2.80 - 2.60 (m, 8H), 2.40 - 1.15 (m, 110H), 1.20 - 0.74 (m, 40H). SEC: $M_{n,SEC} = 9.5$ kg/mol, $M_{w,SEC} = 9.9$ kg/mol, $D = 1.04$. A series

of **4VPOSS-PS_n** samples with different molecular weights can be similarly obtained from **4VPOSS-yne** and different **PS_n-N₃** samples with similar yields.

Preparation of 4DPOSS-PS₃₈. To an open vial without a stirring bar were added **4VPOSS-PS₃₈** ($M_{n,NMR} = 7.18$ kg/mol, $\bar{D} = 1.02$, 140 mg, 0.019 mmol), 1-thioglycerol (10.0 eq per VPOSS cage), Irgacure 2959 (0.10 eq per VPOSS cage, or 0.014 eq per vinyl group), and a minimum amount of THF (~ 2 mL) to fully dissolve the solids. The reaction was completed after irradiation by 365 nm UV light for 20 min. The resulting mixture was then purified by repeated precipitations from concentrated THF solutions into cold MeOH/water mixture (v/v = 1/2), collected by centrifugation, and dried *in vacuo* to afford **4DPOSS-PS₃₈** as a white powder (123 mg). Yield: ~65%. ^1H NMR (CD_3OD , 500 MHz, ppm): δ 7.50 - 6.40 (m, 169H), 5.25 - 5.00 (m, 2H), 4.43 - 4.05 (m, 14H), 3.80 - 3.50 (m, 84H), 3.30 (s, 8H), 2.76 - 2.48 (m, 112H), 2.20 - 1.25 (m, 114H), 1.20 - 0.74 (m, 40H). SEC: $M_{n,SEC} = 10.5$ kg/mol, $M_{w,SEC} = 10.8$ kg/mol, $\bar{D} = 1.03$. A series of **4DPOSS-PS_n** samples with different molecular weights can be similarly obtained from different **4VPOSS-PS_n** samples with similar yields.

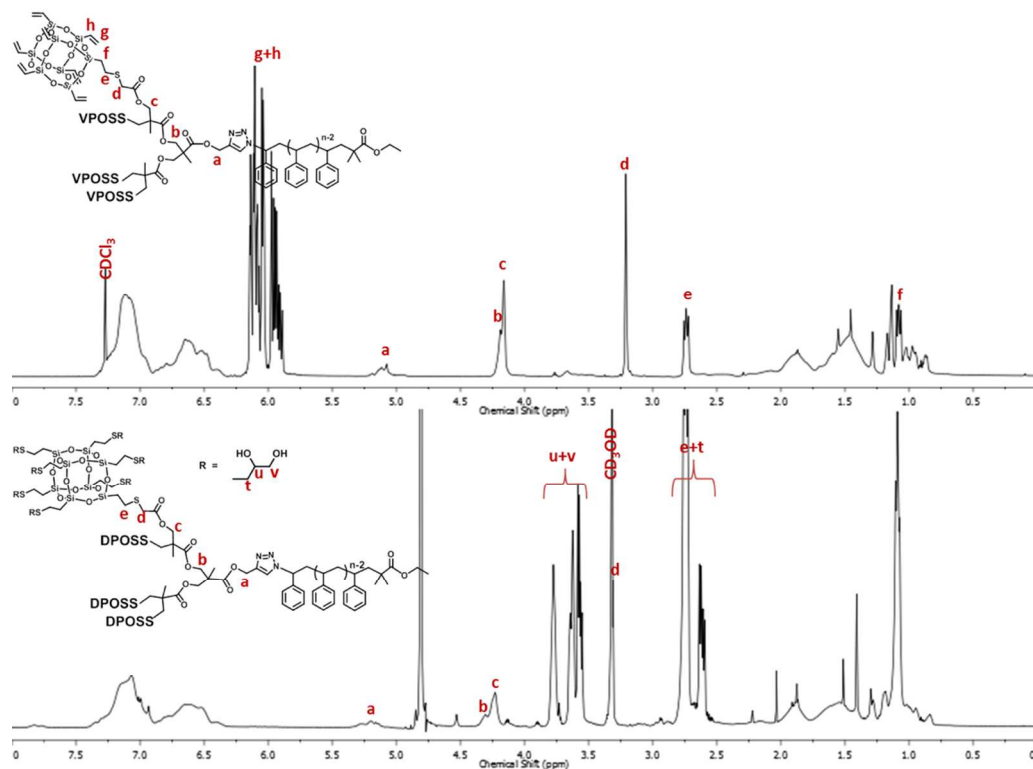


Figure S9. ^1H NMR spectra of **4VPOSS-PS₃₈** and **4DPOSS-PS₃₈**.

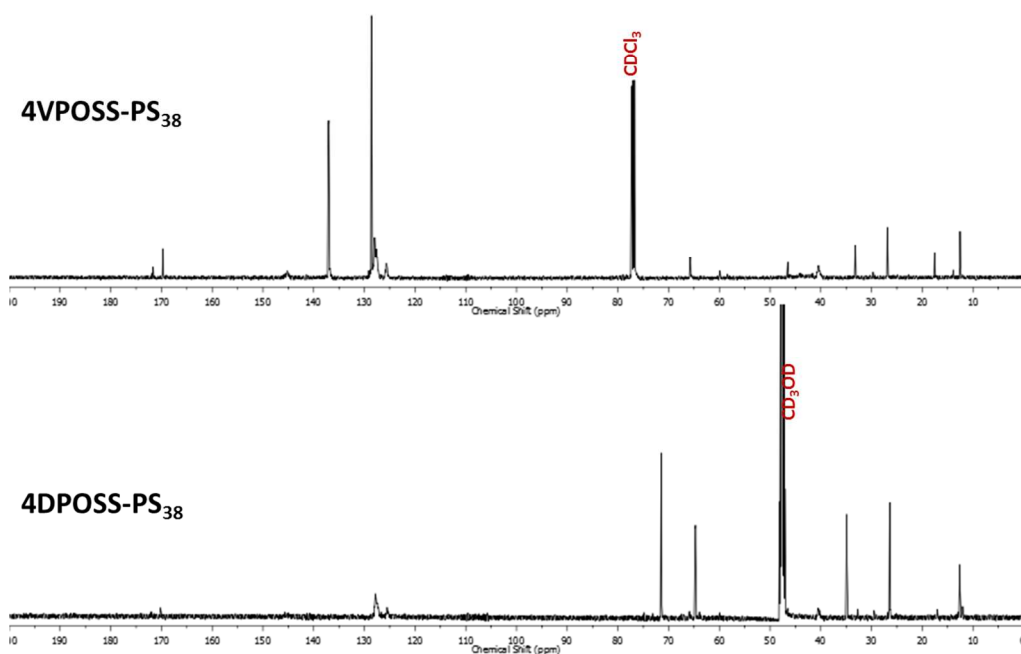


Figure S10. ^{13}C NMR spectra of 4VPOSS-PS₃₈ and 4DPOSS-PS₃₈.

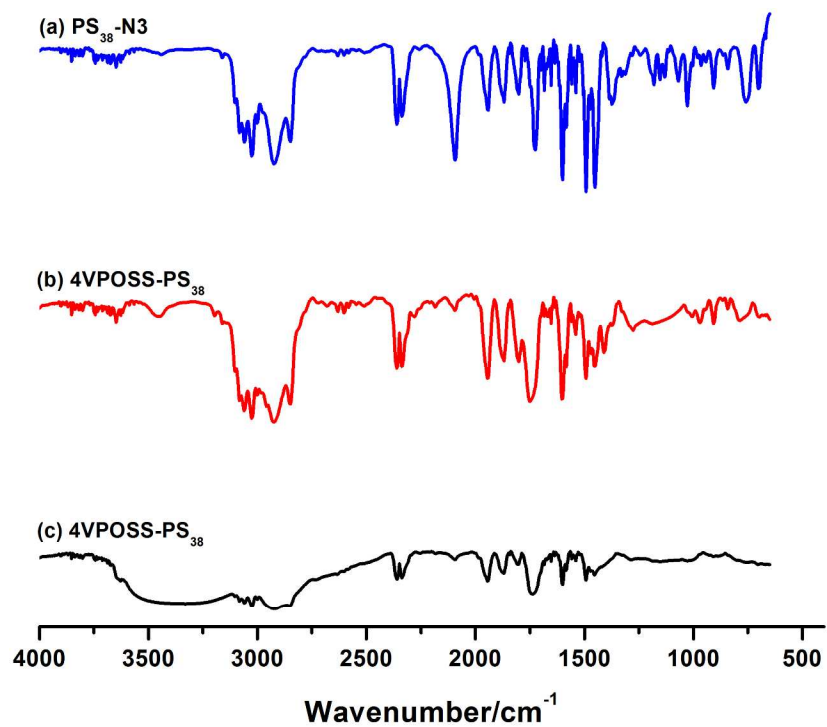


Figure S11. FT-IR spectra of PS_n-N₃ (blue curve), 4VPOSS-PS_n (red curve), and 4DPOSS-PS_n (black curve).

3. Supplementary figures for structure characterization.

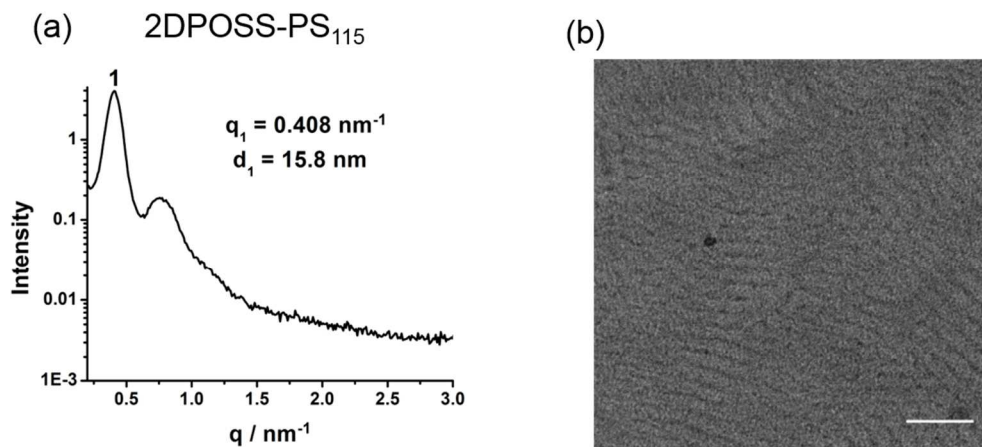


Figure S12. SAXS (a) and BF-TEM (b) of ill-defined HEX structure of 2DPOSS-PS₁₁₅. Scale bar: 50 nm.

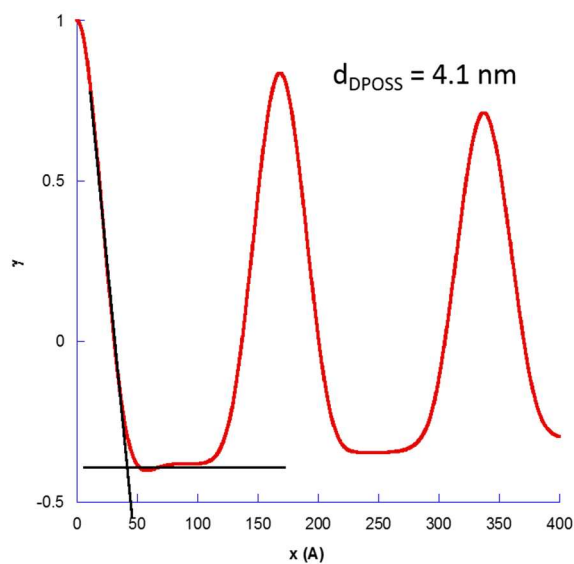


Figure S13. Correlation function analysis of the SAXS profiles obtained from 3DPOSS-PS₉₆. The size of DPOSS domains d_{DPOSS} determined from this analysis is also shown.

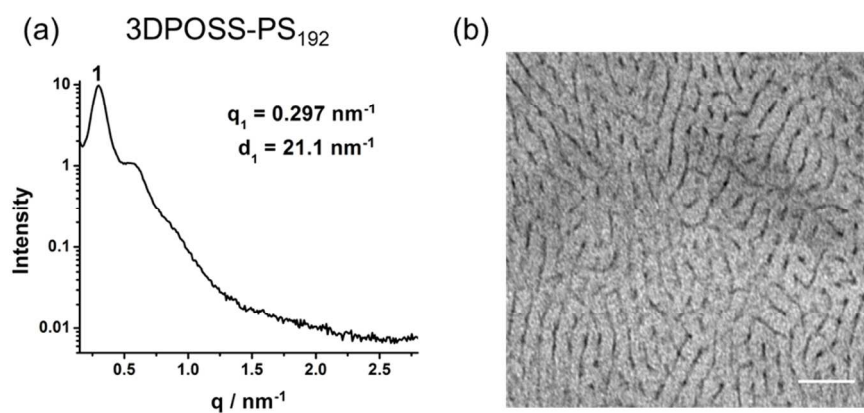


Figure S14. SAXS (a) and BF-TEM (b) of ill-defined PFL structure of 3DPOSS-PS₁₉₂. Scale bar: 50 nm.

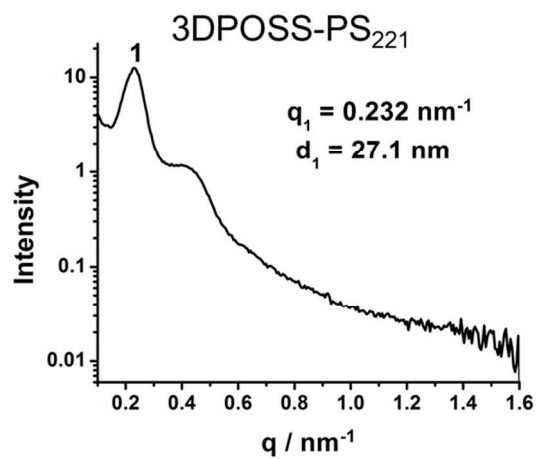


Figure S15. SAXS profile of ill-defined PFL structure of 3DPOSS-PS₂₂₁.

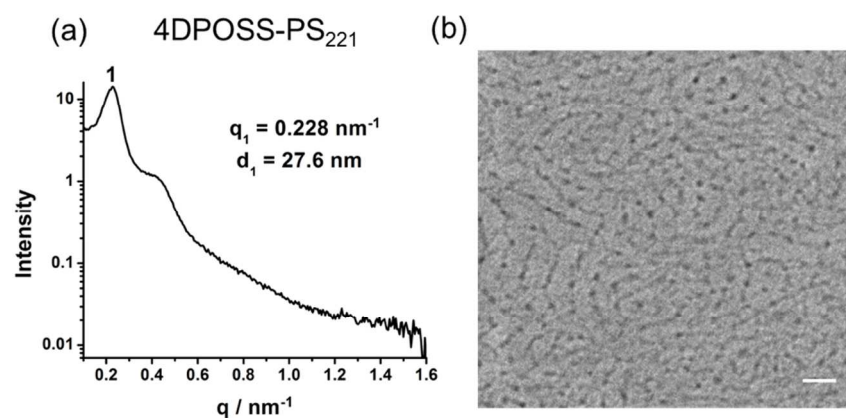


Figure S16. SAXS (a) and BF-TEM (b) of ill-defined PFL structure of 4DPOSS-PS₂₂₁. Scale bar: 50 nm.

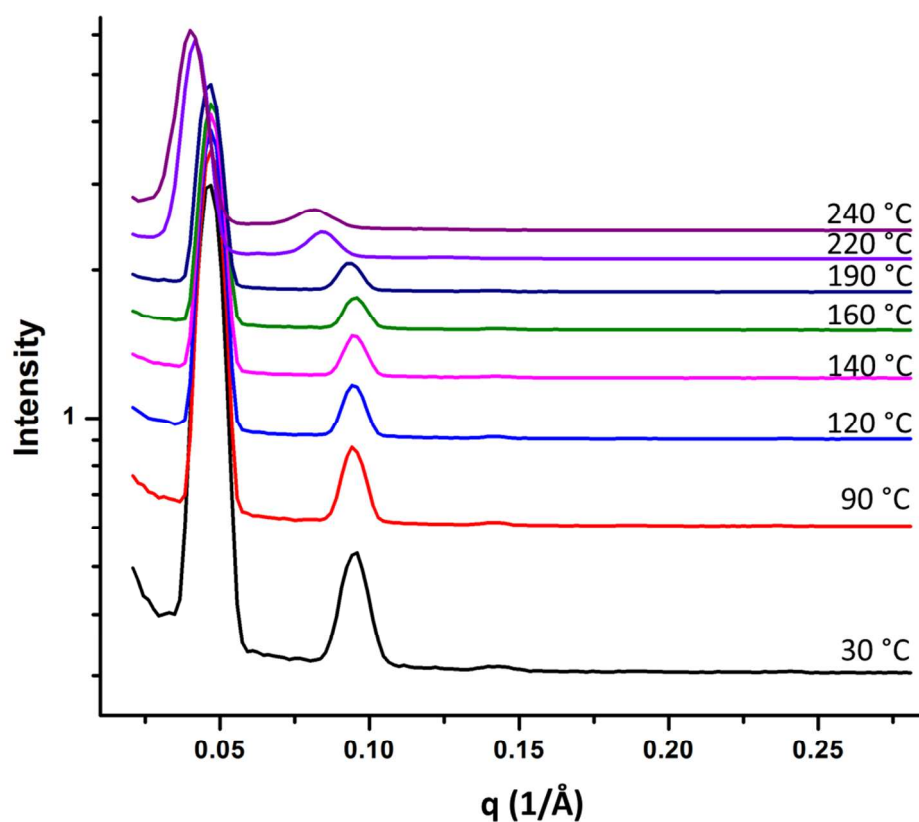


Figure S17. Varied-temperature SAXS profiles of 2DPOSS-PS₆₃ under heating processes. No order-order phase transitions or order-disorder phase transitions are observed before decomposition of the samples.

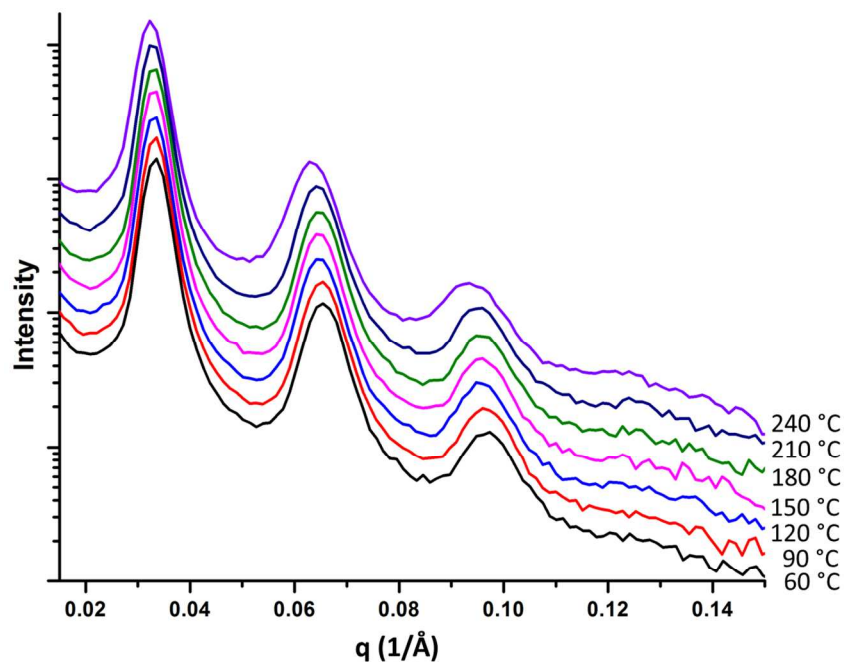


Figure S18. Varied-temperature SAXS profiles of 3DPOSS-PS₁₃₅ under heating processes. No order-order phase transitions or order-disorder phase transitions are observed before decomposition of the samples.

Table S1. Scaling relations of PS chain thickness L and repeat unit n in XDPOSS-PS _{n}

LAM structure

	DPOSS-PS _{n}	2DPOSS-PS _{n}	3DPOSS-PS _{n}	4DPOSS-PS _{n}
u^a	0.57	0.22	0.21	0.48
v^a	0.52	0.77	0.75	0.74

^a The scaling relations were fitted by power function: $L = un^v$.

Reference:

1. Yue, K.; Liu, C.; Guo, K.; Yu, X.; Huang, M.; Li, Y.; Wesdemiotis, C.; Cheng, S. Z. D.; Zhang, W.-B. Sequential “Click” Approach to Polyhedral Oligomeric Silsesquioxane-Based Shape Amphiphiles. *Macromolecules* **2012**, *45*, 8126-8134.
2. Li, Y.; Guo, K.; Su, H.; Li, X.; Feng, X.; Wang, Z.; Zhang, W.; Zhu, S.; Wesdemiotis, C.; Cheng, S. Z. D.; Zhang, W.-B. Tuning “Thiol-Ene” Reactions toward Controlled Symmetry Breaking in Polyhedral Oligomeric Silsesquioxanes. *Chem. Sci.* **2014**, *5*, 1046-1053.
3. Altin, H.; Kosif, I.; Sanyal, R. Fabrication of “Clickable” Hydrogels via Dendron–Polymer Conjugates. *Macromolecules* **2010**, *43*, 3801-3808.
4. Yue, K.; Liu, C.; Guo, K.; Wu, K.; Dong, X. H.; Liu, H.; Huang, M. J.; Wesdemiotis, C.; Cheng, S. Z. D.; Zhang, W. B. Exploring Shape Amphiphiles beyond Giant Surfactants: Molecular Design and Click Synthesis. *Polym. Chem.* **2013**, *4*, 1056-1067.