

Versatile Grafting Approaches to Star-Shaped POSS-Containing Hybrid Polymers using RAFT Polymerization and Click Chemistry

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Supplementary Information

Table of Contents

Experimental Materials and Characterization.....	S2
General Procedure for 8P-POSS.....	S4
General Procedure for 8CTAs-POSS.....	S7
Synthesis Route for PMMA-g/t-POSS Hybrid.....	S13
Synthesis of PMMA-g/f-POSS hybrid.....	S14
Multifunctional RAFT Agents Used in the Synthesis of Star Polymers.....	S16
Table S1~S3.....	S16
Figure S10~S14.....	S18
References.....	S21

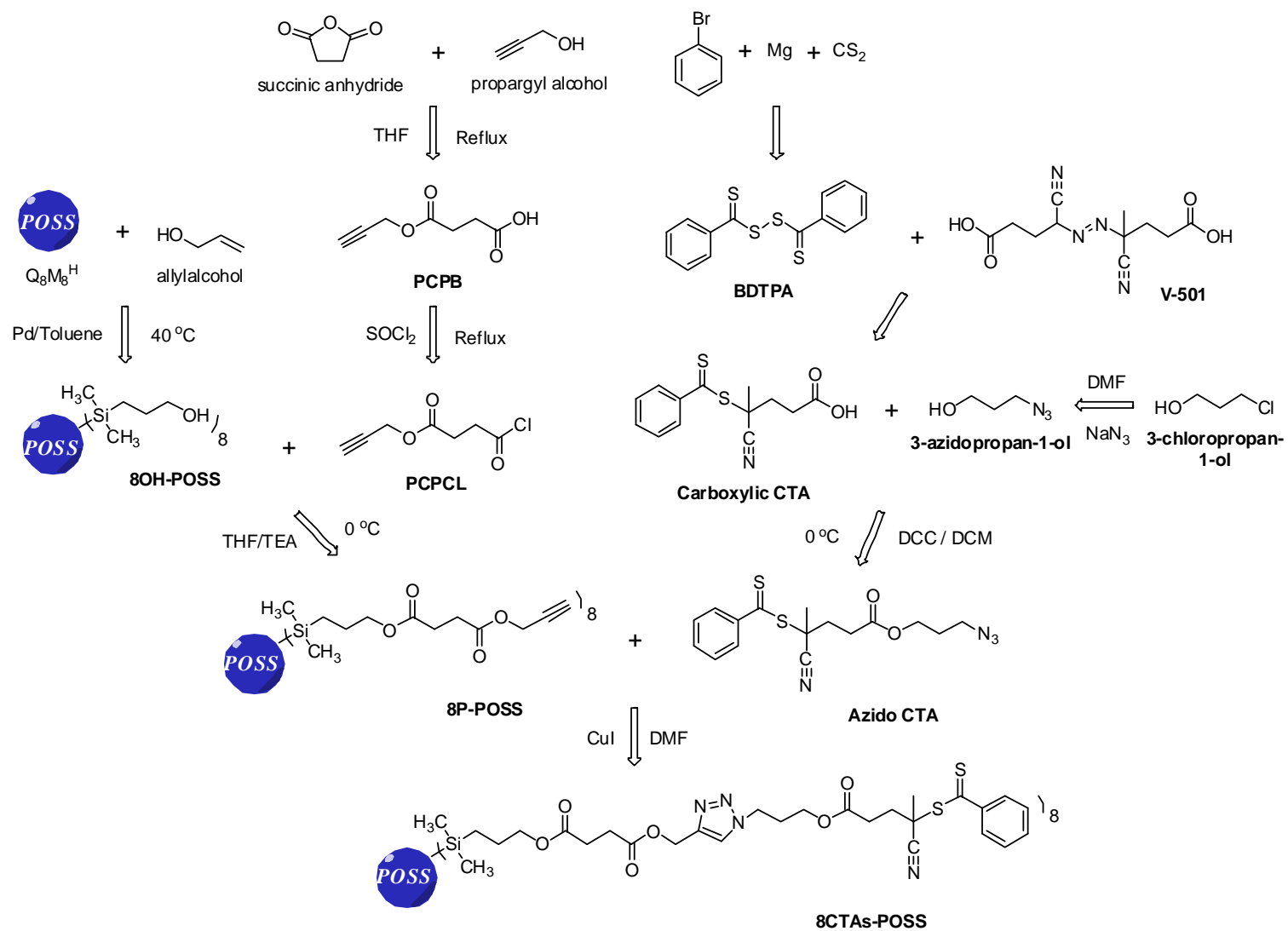
Experimental Materials

Succinic anhydride (99%), propargyl alcohol (99%), bromobenzene (99%, pure), magnesium (99.9+%), sodium azide (99%), 1-chloro-3-hydroxypropane (98%), N, N'-dicyclohexylcarbodiimide (DCC) (99%), 4-dimethylaminopyridine (99%), allyl alcohol (99+%) and Copper(I) Iodide (98%) were purchased from Acros. 4,4'-Azobis(4-cyanovaleric acid) (V501) was purchased from Sigma-Aldrich. Carbon disulphide (99.9%) was purchased from Panrea. N,N-dimethylformamide (DMF; Sigma-Aldrich), tetrahydrofuran (THF; Acros), dichloromethane (DCM; Acros) and triethylamine (TEA; Acros) were vacuum-distilled prior to use.

Characterization

FT-IR spectra were obtained with a Nicolet Avatar 320 FTIR spectrometer; 32 scans were collected at a spectral resolution of 1 cm^{-1} . The sample for FTIR measurement was prepared by deposition of solutions on salt plates. ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were obtained in $\text{CDCl}_3\text{-d}_3$ or DMSO-d_6 on a Varian 500 MHz spectrometer model Unity INOVA. The internal solvent peak was used to calibrate the chemical shift in the NMR data. Gel permeation chromatography (GPC) analysis was performed on a JASCO HPLC Gulliver 900 with a combination of KF-803L (30 cm, exclusion limit: 7.0×10^4 , polystyrene) and KF-804 (30 cm, exclusion limit: 4.0×10^5 , polystyrene) columns (linear calibration down to $M_n = 100$) with THF as an eluent at $35\text{ }^\circ\text{C}$. Calibration was achieved with commercial polystyrene standards ranging from 300 to 10^6 g mol^{-1} . For GPC characterization of the HF-etched sample, the PMMA-g/f-POSS hybrids were dissolved in THF prior to etching. After HF-etching, the products in THF were used directly for GPC measurements. Thin-layer chromatography (TLC) was performed on a silica gel sheet coated with silica gel 60 F₂₅₄ from E. Merck, visualized by UV light. Column chromatography was performed on silica gel 60 N (Kanto Chemical CO., INC, Cat. No. 37563-79, 40-50 μm). Elemental analyses (EA) were run on a PerkinElmer model 2400 CHN analyzer.

Scheme S1. Synthesis route for 8P-POSS and 8CTAs-POSS.



General Procedure for 8P-POSS

Preparation of 3-propargyl carbonyl propionic Acid (PCPA): Propargyl alcohol (10g, 0.18 mol), succinic anhydride (21.6g, 0.22mol), 17.2 mL (0.23 mol) pyridine and 36 mL (0.23 mol) triethyl amine were dissolved in 200 mL of dry THF. The mixture was stirred at 80 °C for 24h. The mixture was evaporated under vacuum and then dissolved in dichloromethane and washed with chilled 1 M HCl. After extracting three times, the organic phase was dried over Na₂SO₄, filtered, and evaporated. The product was crystallized from toluene (yield: 48 %).

¹H NMR (CDCl₃): δ = 2.49 (s, 1H, CH≡C-), 2.64 (m, 4H, COOH-CH₂-CH₂-COOH), 4.72 (d, 2H, CH≡C-CH₂-O-), 11.36 (s, 1H, COOH) ppm. ¹³C NMR (CDCl₃): δ = 29.35 (COOH-CH₂-CH₂-COOH), 52.48 (CH≡C-CH₂-O-), 75.59 (CH≡C-), 78.77 (CH≡C-CH₂-), 171.98 (CH₂-COOH-CH₂-), 178.34 (-CH₂-COOH) ppm.

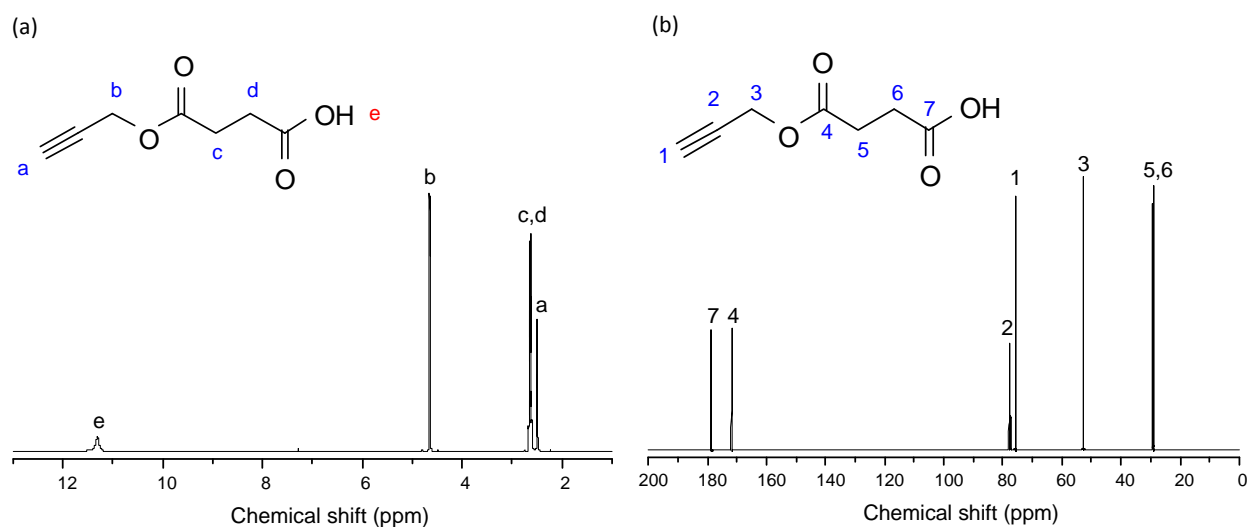
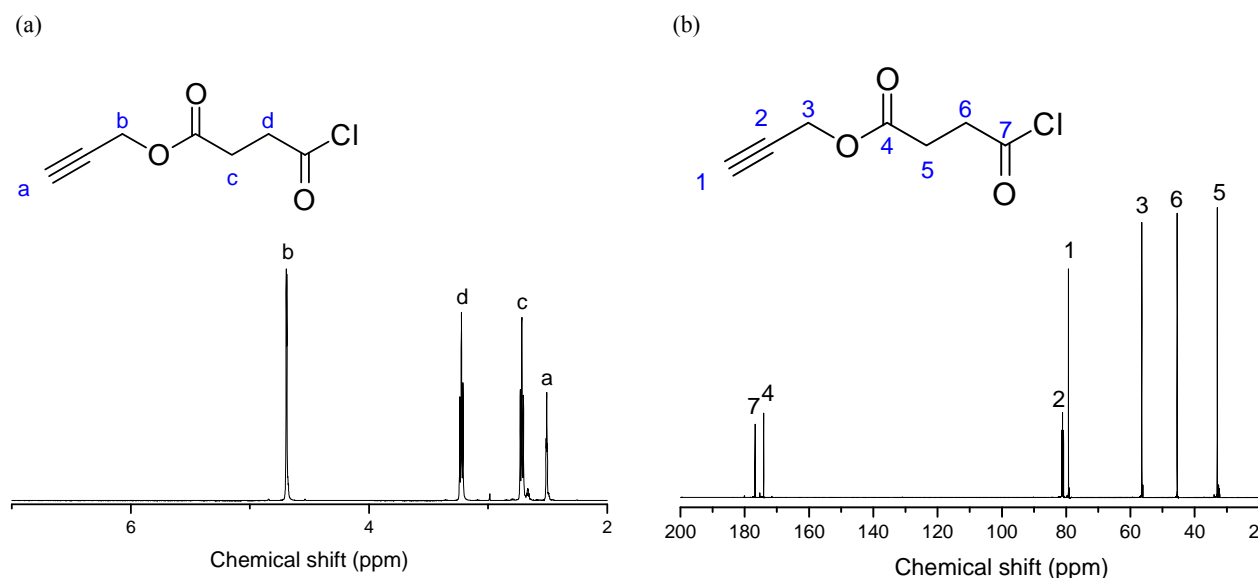


Figure S1. (a) ¹H-NMR and (b) ¹³C-NMR of spectra of PCPA.

Preparation of 3-propargylcarbonyl propionic chloride (PCPCI): 3-Propargylcarbonyl propionic chloride (PCPCI) was prepared from PCPA as follows: PCPA (10.0 g, 0.18 mol) was introduced into a dried Schlenk flask and mixed with 25 ml of anhydrous dichloromethane. Freshly distilled thionyl chloride (20 mL) was added dropwise to the PCPA mixture solution over 30 min.

Then the reaction mixture was heated at reflux for 5 h. The solvent was removed by first distilling at atmospheric pressure, and then under a vacuum overnight at room temperature, leaving the product as a yellow and highly viscous liquid, which distilled under vacuum (6.7×10^{-2} Pa) at 120 °C to give a colorless viscous product (yield 91 %).

^1H NMR (CDCl_3): δ = 2.51 (s, 1H, $\text{CH}\equiv\text{C}-$), 2.71 (t, 2H, $-\text{COO}-\text{CH}_2-\text{CH}_2-$), 3.22 (t, 2H, $\text{CH}_2-\text{CH}_2-\text{COOCl}$), 4.69 (s, 2H, $\text{CH}\equiv\text{C}-\text{CH}_2-$) ppm. ^{13}C NMR (CDCl_3): δ = 32.88 ($-\text{COO}-\text{CH}_2-\text{CH}_2-$), 45.41 ($-\text{CH}_2-\text{CH}_2-\text{COOCl}$), 56.69 ($\text{CH}\equiv\text{C}-\text{CH}_2-$), 79.20 ($\text{CH}\equiv\text{C}-$), 80.93 ($\text{CH}\equiv\text{C}-\text{CH}_2$), 174.09 (CH_2-COOCl), 176.67 ($-\text{COO}-\text{CH}_2$) ppm.



Preparation of Octakis(dimethylsilyloxy)hydroxypropyl silsesquioxane (8OH-POSS):

8OH-POSS was synthesized according to our previous reports.¹⁻³ $\text{Q}_8\text{M}_8^{\text{H}}$ (3 g, 2.95 mmol) was dissolved in anhydrous toluene in a 100 mL round-bottom flask under argon. Allyl alcohol (1.71g, 29.46 mmol) was added in 25% excess to the $\text{Q}_8\text{M}_8^{\text{H}}$. Karstedt's catalyst [$\text{Pt}(\text{dvs})$] (0.6 mL of 6 mmol solution in toluene) was added, and an immediate increase from room temperature to 35 °C was observed. The reaction was monitored by ^1H NMR. After 2 h, the disappearance of the Si-H proton shift δ = 4.72 ppm) confirmed that the hydrosilylation had gone to completion. The reaction mixture was concentrated under reduced pressure, and the excess starting allyl alcohol was

removed by vacuum distillation giving a white waxy solid (yield: 95 %. $M_w = 1500 \text{ g mol}^{-1}$).

^1H NMR (CDCl_3): $\delta = 0.17$ (m, 6H, $-\text{Si}(\text{CH}_3)_2-$), 0.62 (m, 2H, $\text{Si}-\text{CH}_2-\text{CH}_2-$), 1.64 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 3.59 (m, 3H, $-\text{CH}_2-\text{CH}_2-\text{OH}$) ppm. ^{13}C NMR (CDCl_3): $\delta = 0.021$ ($-\text{Si}(\text{CH}_3)_2-$), 13.86 ($\text{Si}-\text{CH}_2-\text{CH}_2-$), 26.68 ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 65.49 ($-\text{CH}_2-\text{CH}_2-\text{OH}$) ppm.

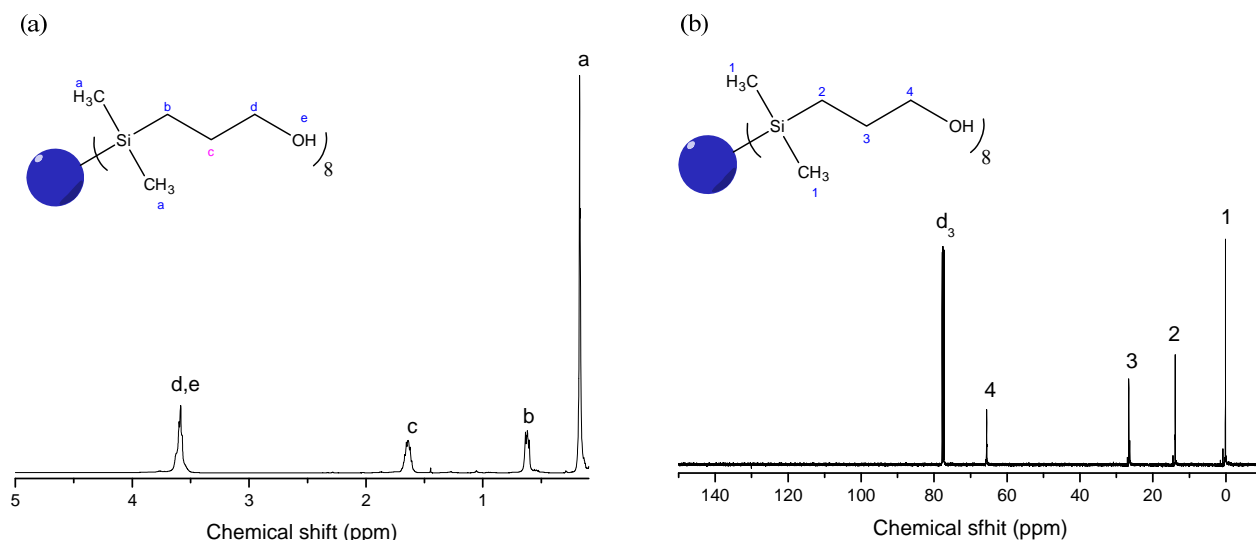


Figure S3. (a) ^1H -NMR and (b) ^{13}C -NMR of spectra of 8OH-POSS.

Octakis(dimethylsilyloxy)propargyl carbonyl-silsesquioxane (8P-POSS): 8OH-POSS (3 g, 2.00 mmol, 1.0 equiv) was dissolved in 30 mL of absolute THF, and distilled with triethylamine (TEA) (2.02g, 20 mmol, 10 equiv). A solution of PCPCl (3.49g, 20 mmol, 10 equiv) in 10 mL of absolute THF was slowly added to the above 8OH-POSS solution at 0°C . After stirring for 24 h at room temperature under nitrogen, the mixture solution was filtered. The filtrate was concentrated by rotary evaporation. The resulting oily residue was purified by column chromatography (silica gel, eluent: ethyl acetate/hexane (1:1)) to give the product. Yield: 89 %. $M_w = 2679 \text{ g mol}^{-1}$.

^1H NMR (CDCl_3): $\delta = 0.18$ (m, 6H, $-\text{Si}(\text{CH}_3)_2-$), 0.61 (m, 2H, $\text{Si}-\text{CH}_2-\text{CH}_2-$), 1.68 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 2.51 (s, 1H, $-\text{C}\equiv\text{CH}$), $2.73\sim 2.61$ (m, 4H, $-\text{COO}-\text{CH}_2-\text{CH}_2-\text{COO}-$), 4.05 (t, 2H, $\text{CH}_2-\text{CH}_2-\text{COO}-$), 4.71 (s, 2H, $-\text{COO}-\text{CH}_2-\text{C}\equiv\text{CH}$) ppm. ^{13}C NMR (CDCl_3): $\delta = 0.15$ ($-\text{Si}(\text{CH}_3)_2-$), 14.01 ($\text{Si}-\text{CH}_2-\text{CH}_2-$), 22.67 ($\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 29.60 ($-\text{COO}-\text{CH}_2-\text{CH}_2-\text{COO}-$), 52.59 ($-\text{COO}-\text{CH}_2-\text{C}\equiv\text{CH}$), 67.74 ($\text{CH}_2-\text{CH}_2-\text{COO}-$), 75.53 ($-\text{C}\equiv\text{CH}$), 77.68 ($-\text{CH}_2-\text{C}\equiv\text{CH}$), 176.56 ($-\text{COO}-\text{CH}_2-\text{CH}_2-\text{COO}-$) ppm.

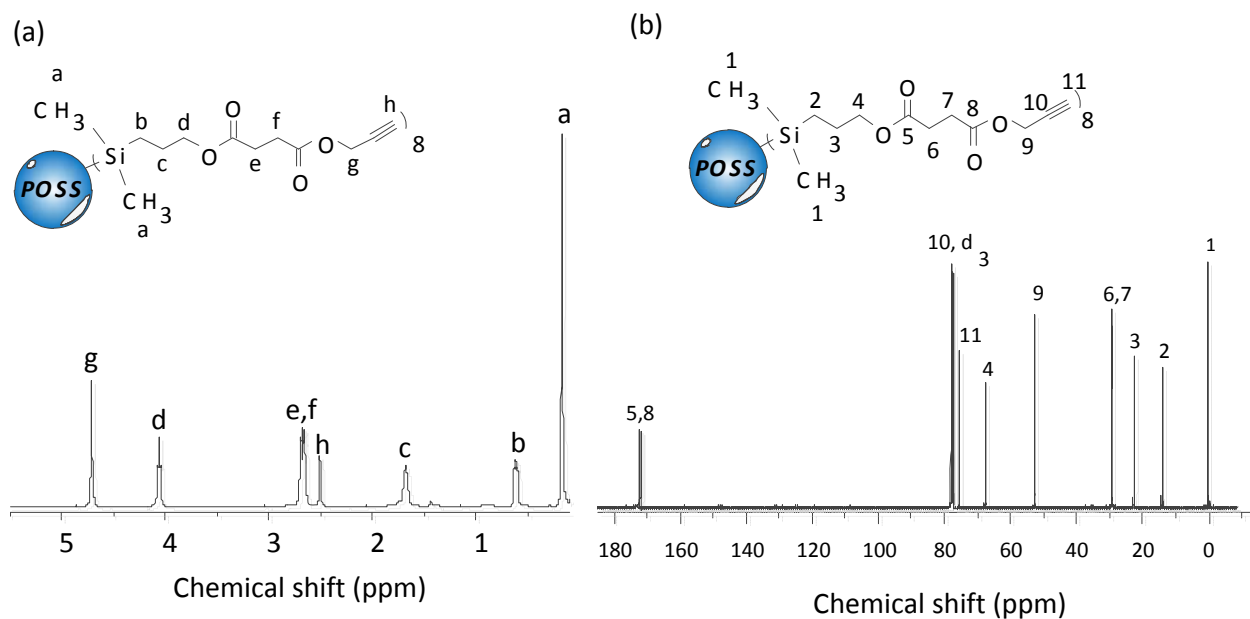


Figure S4. (a) ^1H -NMR and (b) ^{13}C -NMR of spectra of 8OH-POSS.

General Procedure for 8CTAs-POSS

Preparation of Di(thiobenzoyl) Disulfide: Di(thiobenzoyl) disulfide was synthesized according to Sumerlin's report.⁴ Bromobenzene (12.6 mL) in 90 mL of dry THF was added dropwise to magnesium turnings (3g, 0.12 mol) in 100 mL of dry THF with stirring under nitrogen. After the magnesium had finished reacting, the solution was cooled to 0 °C and carbon disulfate (9.15g, 0.12 mol) was added dropwise to the Grignard mixture with cooling. The Grignard reagent was then hydrolyzed by the slow addition of water (20 mL). The magnesium salts were removed by filtration and washed with water. To this, 200 mL of a 1.0 N HCl solution was added changing the color to a vibrant pink. The pink solution was transferred to a 1L separating funnel and washed with 150 mL of ethyl ether. The colorless aqueous layer was discarded. The red ether layer was washed with 350 mL of a 1.0 N NaOH solution and the yellow ether layer discarded. The dark red aqueous layer was washed with 150 mL of ethyl ether and the yellow ether layer discarded, leaving a dark red solution of the sodium salt of dithiobenzoic acid.

A solution of the sodium salt of dithiobenzoic acid (350 mL) was placed in 1L round-bottomed flask equipped with an addition funnel, and a reflux condenser. A solution of potassium ferricyanide

(III) (21.4g, 0.065mol) in 100 mL distilled water was added dropwise, to a vigorously stirred solution, over 1.5 h. The red precipitate was collected in a Buchner funnel by a vacuum filtration.

Yield: 4.88g.

^1H NMR (CDCl_3): δ = 7.47 (m, 4H, Ph- C_3 and C_5), 7.63 (m, 2H, Ph- C_4), 8.11 (m, 4H, Ph- C_2) ppm.

^{13}C NMR (CDCl_3): δ = 127.16 (Ph- C_2 and C_6), 128.71 (Ph- C_3 and C_5), 133.00 (Ph- C_4), 143.93 (Ph- C_1), 219.54 (Ph- $\text{C}=\text{S}$ -) ppm.

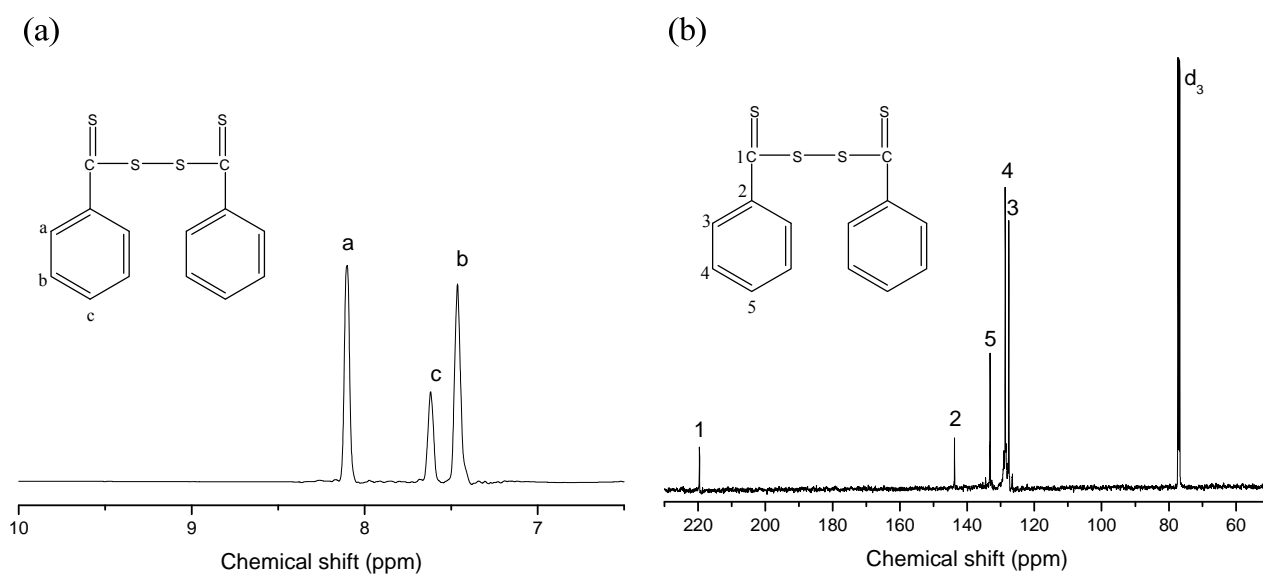


Figure S5. (a) ^1H -NMR and (b) ^{13}C -NMR of spectra of Di(thiobenzoyl) Disulfide.

Preparation of 4-cyano-4-(thiobenzoyl) sulfonyl pentanoic acid (CTB; RAFT chain transfer agents (CTAs)): Bis (thiocarbonyl) disulfide (18.6g, 0.06 mmol, 1.0 equiv) and 4, 4'-azo-bis-(4-cyanovaleric acid) (16.69 g, 0.06 mol, 1.0 equiv) were refluxed in ethyl acetate at 85 °C for 12 h, under nitrogen, in a free radical reaction. The solvent was then removed by rotary evaporation and the crude product was purified by column chromatography (silica gel, eluent: ethyl acetate/hexane (2:8)) to give the red oily product. The oily product was further recrystallized in benzene to obtain the final product (yield: 75%).

^1H NMR (CDCl_3): δ = 1.96 (s, 3H, - $\text{S}-\text{C}(\text{CH}_3)-\text{CN}$), 2.35 to 2.80 (m, 4H, - $\text{CH}_2-\text{CH}_2-\text{COOH}$), 7.40

(m, 2H, Ph-C₂ and C₆), 7.57 (m, 1H, Ph-C₄), 7.90 (m, 2H, Ph-C₃ and C₅) ppm. ¹³C NMR (CDCl₃): δ = 24.89 (-S-C(CH₃)-CN), 29.84 (-CH₂-CH₂-COOH), 33.48 (-CH₂-CH₂-COOH), 46.16 (-S-C(CH₃)-CN), 119.02 (C≡N), 127.16 (Ph-C₂ and C₆), 128.97 (Ph-C₃ and C₅), 133.51 (Ph-C₄), 145.29 (Ph-C₁), 177.26 (C=O), 222.69 (Ph-C=S-) ppm.

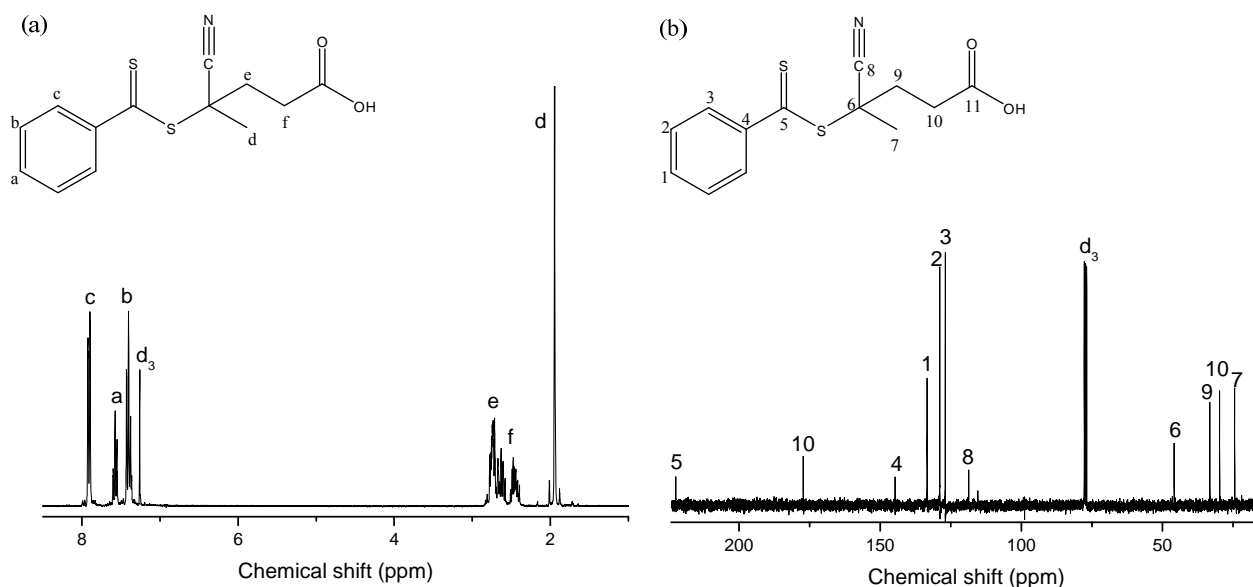


Figure S6. (a) ¹H-NMR and (b) ¹³C-NMR of spectra of CTB.

Preparation of 3-Azidopropanol: 3-Chloro-1-propanol (10.0g, 0.11 mol) and sodium azide (17.18g, 0.26 mol) were reacted in H₂O (100 mL) at 95 °C for 24 h. The reaction mixture was cooled to room temperature, poured into 400 mL of ethyl ether, and extracted with a saturated aqueous 800 mL of NaCl solution. The organic layer was separated, dried over MgSO₄, and filtered. The supernatant was concentrated to obtain the product (yield: 98%).

¹H NMR (CDCl₃): δ = 1.86 (m, 2H, OH-CH₂-CH₂-CH₂-N₃), 3.46 (t, 2H, -CH₂-CH₂-N₃), 3.76 (t, 2H, OH-CH₂-CH₂-) ppm. ¹³C NMR (CDCl₃): δ = 31.83 (OH-CH₂-CH₂-CH₂-N₃), 48.65 (-CH₂-CH₂-N₃), 59.56 (OH-CH₂-CH₂-) ppm.

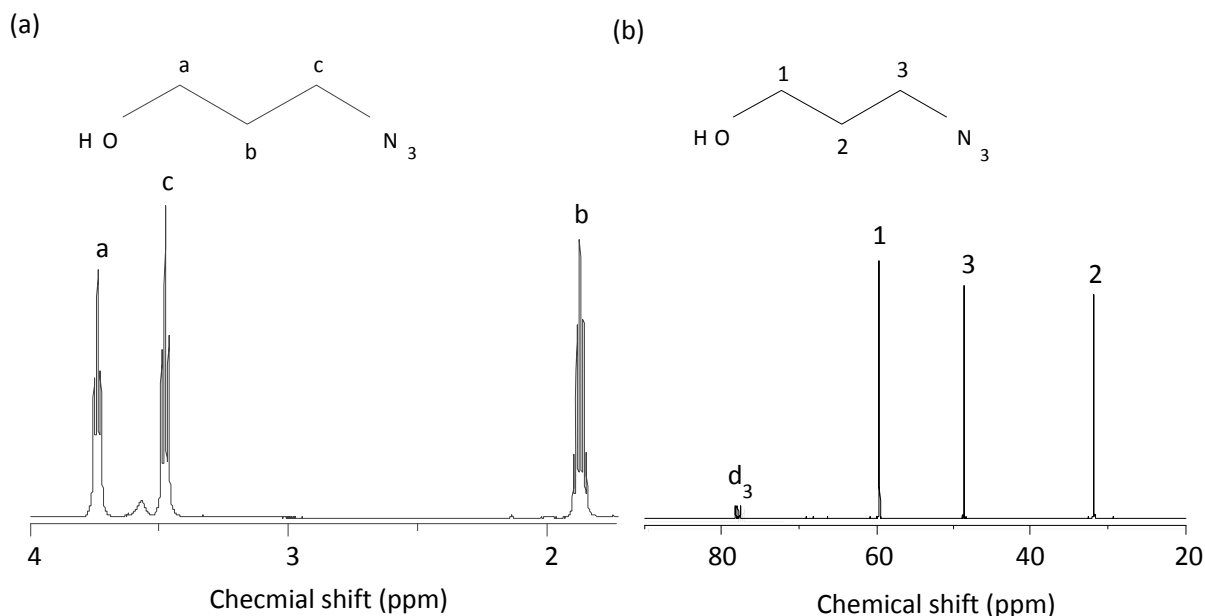


Figure S7. (a) ^1H -NMR and (b) ^{13}C -NMR of spectra of 3-Azidopropanol.

Preparation of 3-azidopropyl 4-cyano-4-((phenylcarbonothioyl)thio)butanoate (Azido-CTAs):

CTB (1g, 3.77 mmol, 1.0 equiv) and 3-Azidopropanol (0.38g, 3.77 mmol, 1.0 equiv) were dissolved in 20 mL of dry dichloromethane in a 100 mL round bottom flask and cooled to approximately 0 °C. A solution of N,N'-Dicyclohexylcarbodiimide (DCC) (0.78g, 3.77mmol, 1.0 equiv) in 10 mL of dry dichloromethane was added dropwise, and the reaction mixture was allowed to warm to room temperature and stir for 24h. The white solid was filtrated, and the organic layer was washed with a 10% sodium bicarbonate solution, water, and a saturated NaCl solution. The resulting oily residue was purified by column chromatography (silica gel, eluent: ethyl acetate/hexane (2:8)) to give the product (yield: 49%).

^1H NMR (CDCl_3): δ = 1.96~1.84 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 1.94 (s, 3H, $-\text{S}-\text{C}(\text{CH}_3)-\text{CN}$), 2.68~2.36 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{COO}-$), 3.41 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{N}_3$), 4.20 (t, 2H, $-\text{COO}-\text{CH}_2-\text{CH}_2-$), 7.39 (m, 2H, Ph- C_3 and C_5), 7.56 (Ph- C_4), 7.91 (m, 2H, Ph- C_2 and C_6) ppm. ^{13}C NMR (CDCl_3): δ = 24.53 ($-\text{S}-\text{C}(\text{CH}_3)-\text{CN}$), 28.20 ($\text{CH}_2-\text{CH}_2-\text{COO}-$), 30.00 ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 33.62 ($-\text{CH}_2-\text{CH}_2-\text{COOH}$), 45.91 ($-\text{S}-\text{C}(\text{CH}_3)-\text{CN}$), 48.18 ($-\text{CH}_2-\text{CH}_2-\text{N}_3$), 62.28 ($-\text{COO}-\text{CH}_2-\text{CH}_2-$), 118.68 ($-\text{C}\equiv\text{N}$), 126.87 (Ph- C_2 and C_6), 128.68 (Ph- C_3 and C_5), 133.24 (Ph- C_4), 144.63 (Ph- C_1),

171.43 (CH₂-COO-), 222.38 (Ph-C=S) ppm.

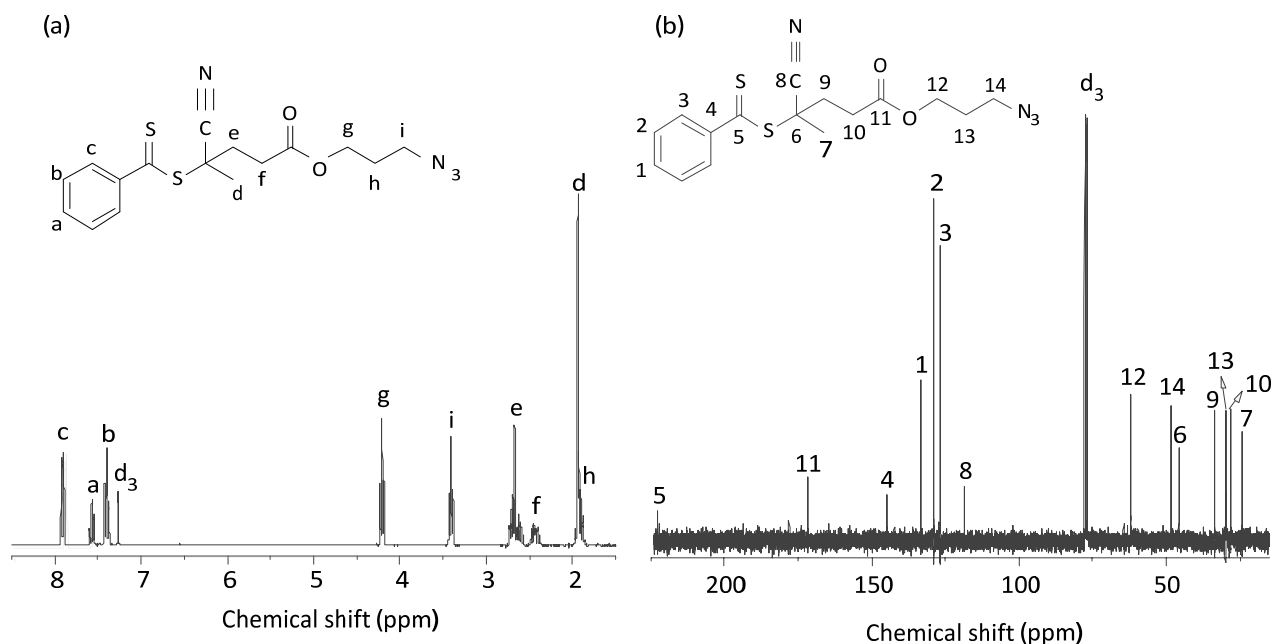


Figure S8. (a) ¹H-NMR and (b) ¹³C-NMR of spectra of Azido-CTAs.

Preparation of Octakis(dimethylsilyloxy)-4-cyano-4-((phenylcarbonothioyl)thio)butanoate-silsesquioxane (8CTAs-POSS): 8P-POSS (2g, 0.72mmol, 1.0 equiv) and azido-CTAs (2.61g, 7.20 mmol, 10 equiv) in 10 mL of DMF was purged with nitrogen and transferred via cannula to a vial containing CuBr (21.6 mg, 0.15 mmol) under a nitrogen environment. The reaction mixture stirred at room temperature in the absence of oxygen for 24h. The reaction mixture was exposed to air, and the solution was passed through a column of neutral alumina. DMF was evaporated under vacuum (6.7×10^{-2} Pa) system at 40 °C to obtain a red viscous oil. The resulting oily residue was purified by column chromatography (silica gel, eluent: methanol/dichloromethane (1:9)) to give the product. Yield: 91%.

¹H NMR (CDCl₃): δ = 0.18 (m, 6H, -Si-(CH₃)₂-), 1.96~1.93 (s, 3H, -S-C(CH₃)-CN; m, 2H, -CH₂-CH₂-CH₂-), 2.47~2.19 (-COO-CH₂-CH₂-), 2.76~2.57 (m, 4H, -COO-CH₂-CH₂-COO-; m, 2H, -S-C(CH₃)-CN), 4.09 (t, 2H, -CH₂-CH₂-COO-), 4.18 (t, 2H, -CH₂-CH₂-COO-), 4.49 (t, 2H, -C-CH₂-CH₂-), 5.25 (s, 2H, -COO-CH₂-N-), 7.42 (m, 2H, Ph-C₃ and C₅), 7.58 (m, 1H, Ph-C₄), 7.93 (7.75, 1H, -N-C=C-), 7.91 (m, 2H, Ph-C₂ and C₆) ppm. ¹³C NMR (CDCl₃): δ = 0.15 (-Si-(CH₃)₂-),

13.83 (-Si-CH₂-CH₂-), 22.22 (-CH₂-CH₂-CH₂-), 24.21 (-S-C(CH₃)-CN), 28.94 (-COO-CH₂-CH₂-), 29.24 (-COO-CH₂-CH₂-COO-), 29.73 (-CH₂-CH₂-CH₂-), 33.31 (CH₂-CH₂-C(CN)-), 45.69 (-S-C(CH₃)-CN), 47.66 (-C-CH₂-CH₂-), 57.72 (-COO-CH₂-N-), 61.77 (-CH₂-CH₂-COO-), 67.26 (-CH₂-CH₂-COO-), 118.54 (-C≡N), 124.04 (-N-CH=C-), 126.58 (Ph-C₂ and C₆), 128.58 (Ph-C₃ and C₅), 133.13 (Ph-C₄), 142.66 (-CH-C-CH₂), 144.66 (Ph-C₁), 171.27 (-COO-CH₂-CH₂-COO-), 172.27 (-COO-CH₂-), 222.56 (Ph-C=S) ppm. M_w = 5546 g mol⁻¹.

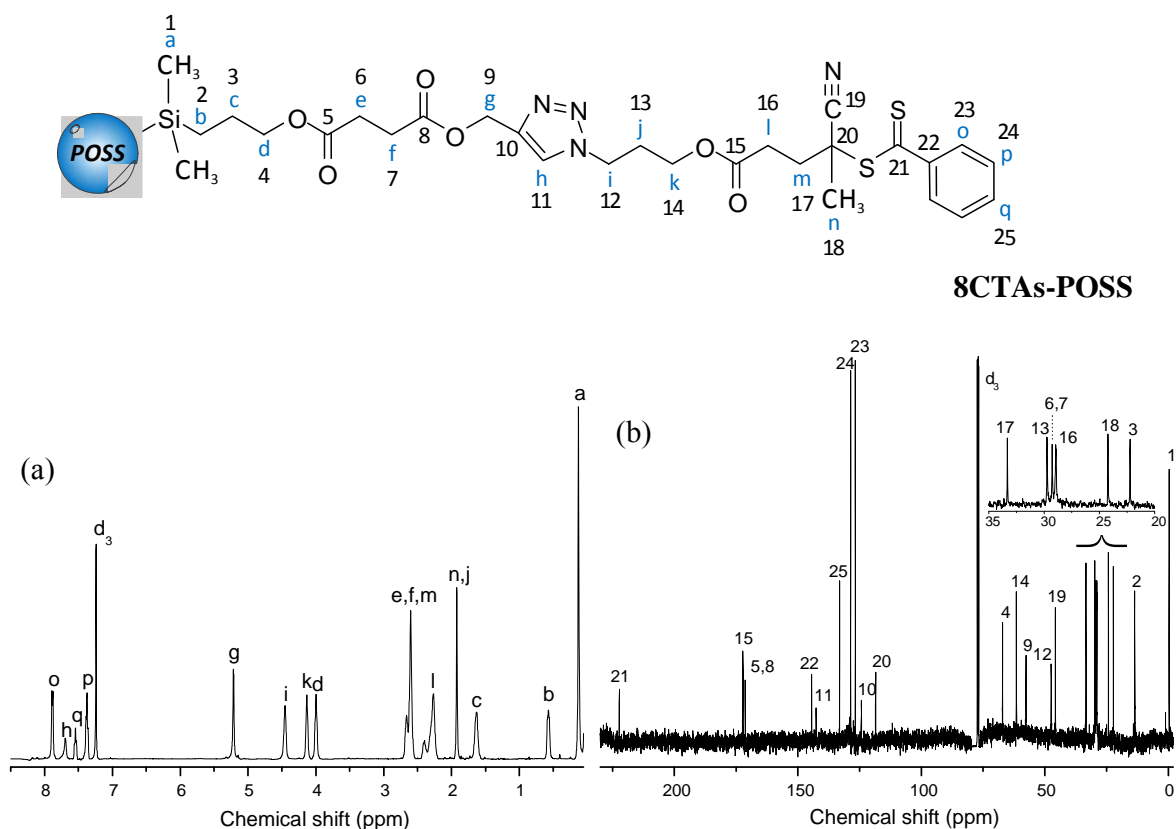
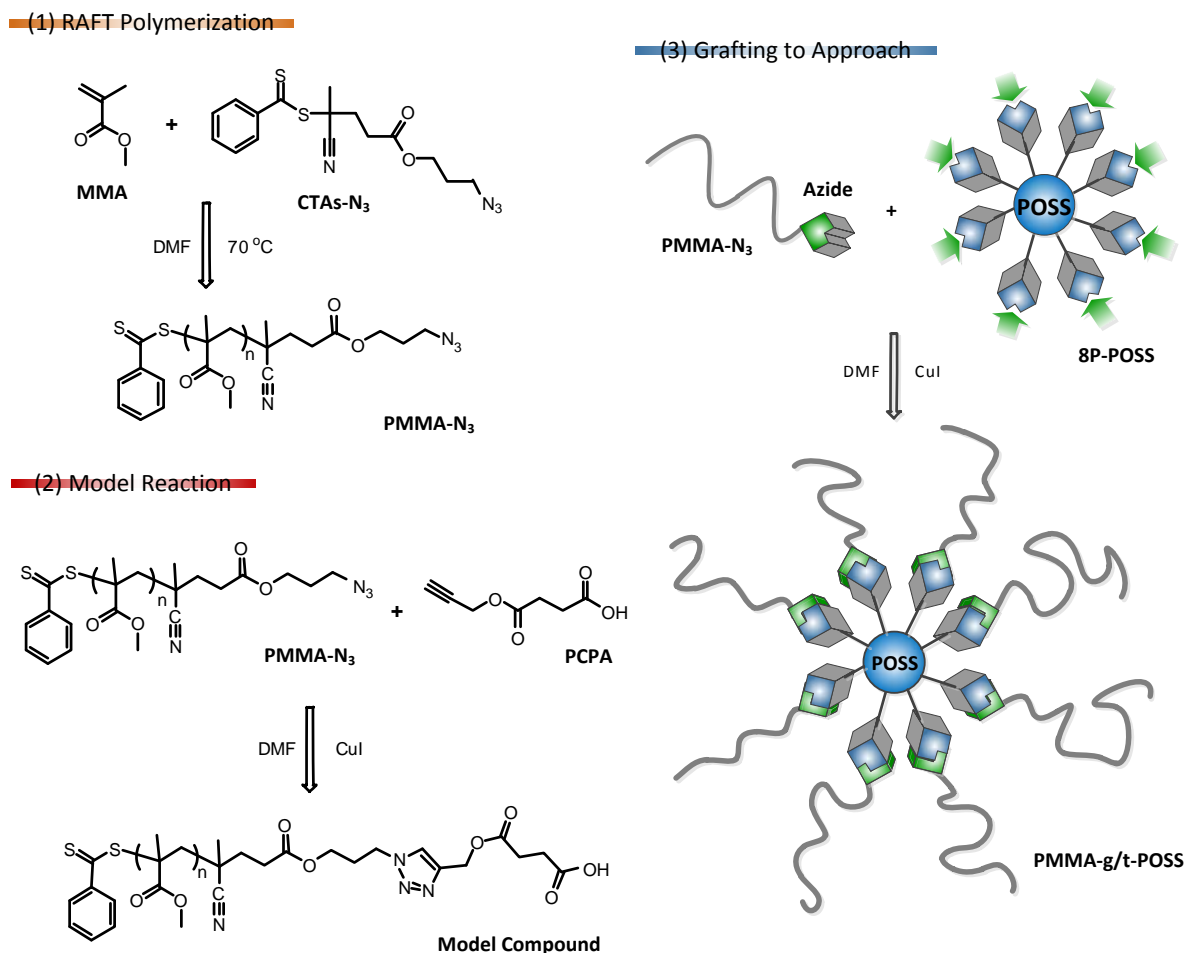


Figure S9. (a) ¹H-NMR and (b) ¹³C-NMR of spectra of 8CTAs-POSS.

Scheme S2. Synthesis route for PMMA-g/t-POSS hybrid.



General Procedure for RAFT Polymerization of MMA with Azido-CTAs (azido-terminated polymer, PMMA-N₃) [Scheme S2 (a)]

Polymerizations were conducted in DMF using AIBN as the primary radical source and azido-CTA as the functional chain transfer agent. In typical polymerization (run 1 of Table S1), MMA (3g, 30.0 mmol, 50 equiv), azido-CTAs (0.217g, 0.6 mmol, 1.0 equiv), and AIBN (2088 mg, 0.12 mmol, 0.2 equiv) were added to a glass tube with a magnetic stirring bar, and DMF was added until the total concentration was 4 M. The tubes were subjected to three cycles of freeze-pump-thaw to remove oxygen. The tube was subsequently immersed into an oil bath preheated to 70 °C. After 24 h, the polymerization was quenched by placing the tube into an ice-water bath. The polymerization solution was drawn and dissolved into CDCl₃ to check ¹H-NMR, and the monomer conversion was

determined to be 95.6 % comparing the integrated areas of characteristic signals of monomer and polymer. After precipitating into a large amount of methanol, azido-terminated PMMA was isolated, and its molecular weight and polydispersity (PDI) were obtained by gel permeation chromatography (GPC) in Table S2. Other polymers were synthesized according to a similar approach.

Model Click Reaction for Azido-terminated Polymer [Scheme S2 (b)]

The low-molecular-weight azido-terminated PMMA was reacted with PCPA which has same alkyne structure as 8P-POSS. A solution of PMMA-N₃ (PMMA-N₃ (50) M_n = 4676 g mol⁻¹; 1g, 0.214 mmol, 1.0 equiv) in 10 mL of DMF, PCPA (0.05g, 0.321mmol, 1.5 equiv) was purged with nitrogen and transferred via cannula to a vial containing CuI (4.6 mg, 0.032 mmol) under a nitrogen environment. The reaction mixture stirred at room temperature in the absence of oxygen for 24 h. The reaction mixture was exposed to air, and the solution was passed through a column of neutral alumina. The polymer was precipitated into methanol and dried under vacuum.

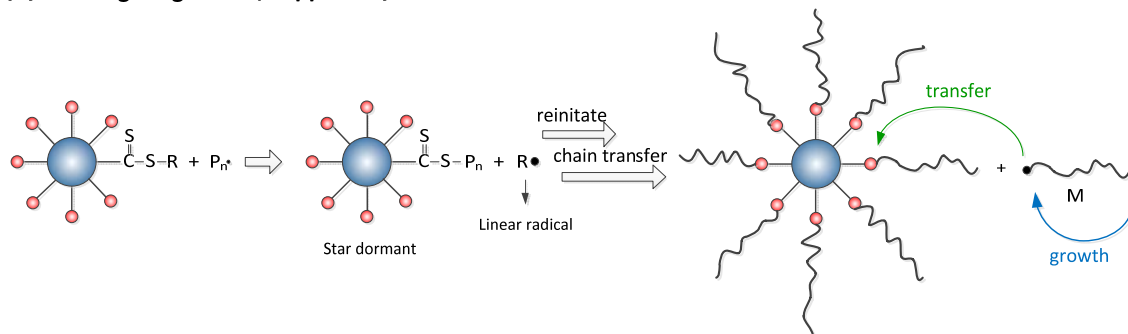
General Procedure for “Grafting to “ Approach [Scheme S2 (c)]

8P-POSS (0.05g, 0.018 mmol, 1.0 equiv) and PMMA-N₃ (0.144 mmol, 8.0 equiv) were dissolved in 10 mL of DMF and purged with nitrogen and transferred via cannula to a vial containing CuI (2.05 mg, 0.014 mmol) under a nitrogen environment. The reaction mixture stirred at room temperature in the absence of oxygen for 24 h. The reaction mixture was exposed to air, and the solution was passed through a column of neutral alumina. The polymer was precipitated into methanol and dried under vacuum.

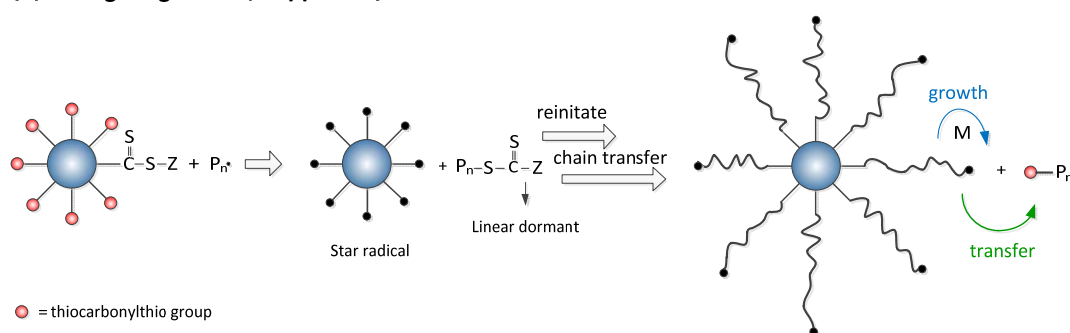
Multifunctional RAFT Agents Used in the Synthesis of Star Polymers

Scheme S3. Multifunctional RAFT agents used in the synthesis of star polymers

(A) Convergent growth (Z-approach)



(B) Divergent growth (R-approach)



There are two types of multifunctional RAFT agents used in the synthesis of star polymer: (A) the multifunctional RAFT agents with the Z-group as a part of the core will allow the growth of arms away from the core during polymerization. (B) For those RAFT agents with the R-group as a part of core, chain growth must occur on the surface of core.

General Procedure for ‘‘Grafting from’’ Approach (Synthesis of PMMA-g/f-POSS hybrid)

MMA graft polymerization from 8CTAs-POSS was conducted in DMF using AIBN as the primary radical source and 8CTA-POSS as the functional chain transfer agent. In typical polymerization (run 1 of Table S2), MMA (3g, 30.0 mmol, 50 equiv), 8 CTAs -POSS (0.37g, 0.075 mmol, 0.125 equiv), and AIBN (2.61 mg, 0.015 mmol, 0.025 equiv) were added to a glass tube with a magnetic stirring bar, and DMF was added until the total concentration was 4 M. The tubes were subjected to three cycles of freeze-pump-thaw to remove oxygen. The tube was subsequently immersed into an oil bath preheated to 70 °C. After 24 h, the polymerization was quenched by placing the tube into an ice-water bath. The polymerization solution was drawn and dissolved into CDCl₃ to check ¹H-NMR, and the monomer conversion was determined to be 89.4 % by comparing the integrated areas of characteristic signals of monomer and polymer. After precipitating into a large amount of methanol, star PMMA was isolated, and its molecular weight and polydispersity (PDI) were obtained by gel permeation chromatography (GPC) in Table S3. Other star polymers were synthesized according to a similar approach.

Table 1. GPC and EA characterization of POSS derivative.

Sample	Theoretical M _w	Calculated M _w ^a	Theoretical			Calculated		
			Elem. Anal.			Elem. Anal.		
			C	N	H	C	N	H
8OH-POSS	1 483	1 500	32.4	0	7.2	31.5	0	7.9
8P-POSS	2 588	2 779	43.2	0	5.9	42.8	0	6.2
8CTA-POSS	5 488	5 546	49.0	8.2	5.4	48.5	7.5	5.8

^a Calculated from GPC.

Table S2. RAFT polymerization of MMA mediated by azido-CTAs.

Sample	[M] : [CTA] : [I]	M_n (th)	M_n (GPC)	M_w (GPC)	PDI (M_w/M_n)	M_n (NMR) ^a
PMMA-N ₃ (50)	50 : 1 : 0.2	5 126	4 676	5 611	1.20	4 700
PMMA-N ₃ (75)	75 : 1 : 0.2	7 412	7 564	8 926	1.18	7 200
PMMA-N ₃ (150)	150 : 1 : 0.2	14 732	12 221	14 910	1.22	13 500
PMMA-N ₃ (230)	230 : 1 : 0.2	22 235	21 307	26 634	1.25	20 300

^a Calculated from ¹H-NMR.

Table S3. RAFT polymerization of MMA mediated by 8CTAs-POSS.

Sample	[M] : [CTA] : [I]	M_n (arm) (th)	M_n (arm) (GPC) ^a	PDI _(star)	M_n (arm) (Hydrolysis) ^b	M_w (arm) (Hydrolysis) ^b	PDI _(arm) ^b
PMMA-g/f-POSS	75 : 1 : 0.2	7 120	8 180	1.29	7 900	8 769	1.11
PMMA-g/f-POSS	150 : 1 : 0.2	13 712	10 480	1.35	14 200	16 330	1.15
PMMA-g/f-POSS	230 : 1 : 0.2	21 900	13 200	1.21	22 100	25 857	1.17

^a The number-average molecular weight of the arm in the PMMA-g/f-POSS M_n (arm) (GPC), calculated from GPC based on eq S1.

^b GPC measurement of the hydrolysis product.

$$M_n(\text{star}) (\text{GPC}) = M_n(\text{arm}) (\text{GPC}) \times 8 + M_{8\text{CTAs-POSS}} \dots \text{eq S1}$$

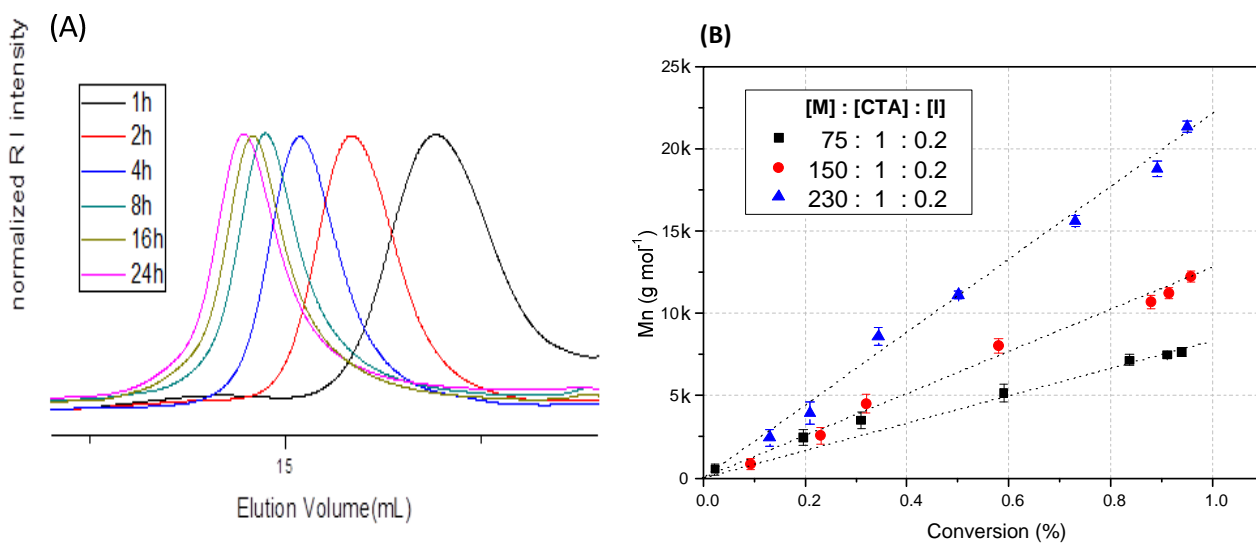


Fig. S10. (A) GPC traces as a function of time for the RAFT polymerization of MMA with azido-CTAs ($[M]_0 : [CTAs] : [AIBN] = 150 : 1 : 0.2$) (B) number-average molecular weight (M_n) vs monomer conversion for the RAFT polymerization of MMA with azido-CTAs.

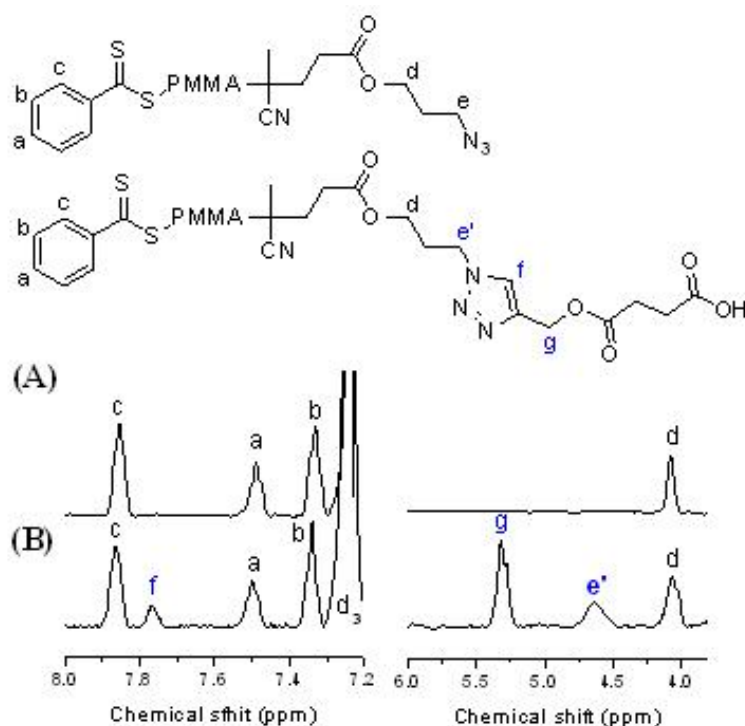


Fig. S11. $^1\text{H-NMR}$ spectra of peak assignments for (A) PMMA- N_3 and (B) the product after coupling with PCPA.

FTIR Result for 8P-POSS, Azido-CTAs and 8CTAs-POSS.

FTIR confirmed that CTAs-POSS was successfully prepared. Compared to the FTIR spectrum of 8P-POSS and azido-CTAs, the bands at 3285 cm^{-1} and 2097 cm^{-1} (i.e. the respective alkyne and azide stretching vibrations) have completely disappeared. The bands appearing at 1048 cm^{-1} and 1086 cm^{-1} in the spectrum of 8CTAs-POSS are assigned to the stretching vibration of C=S and Si-O-Si, respectively.

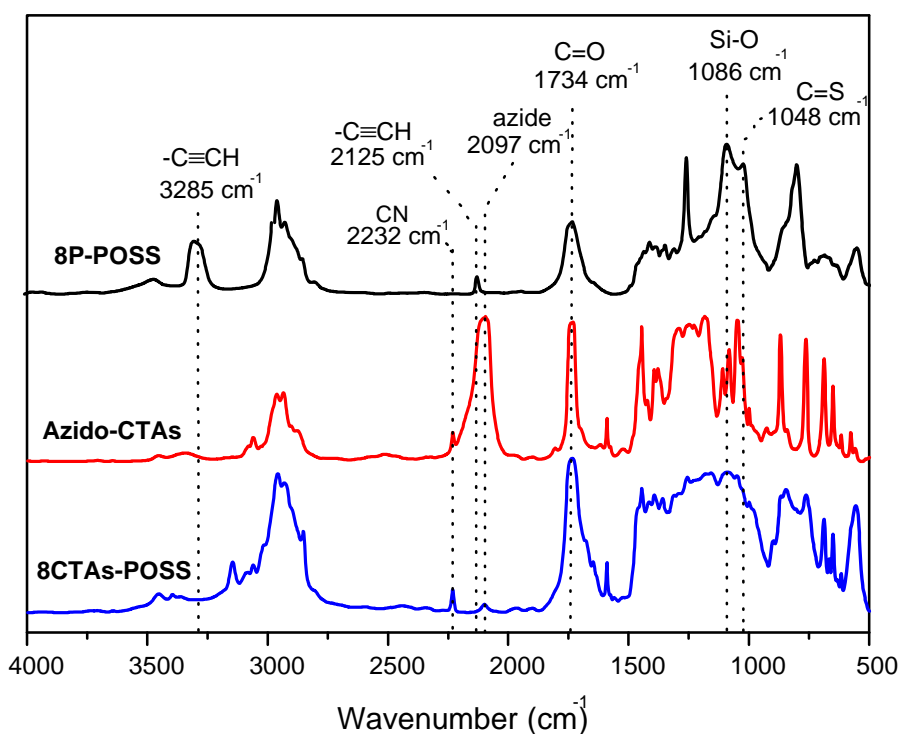


Fig. S12. FTIR spectra of 8P-POSS, Azido-CTAs and 8CTAs-POSS.

Table S4. FTIR wavenumber list

Sample	Position ν_s	Wavenumber (cm^{-1})
8P-POSS	-C≡CH	3285、2125
	C=O	1734
	Si-O	1086
Azido-CTAs	CN	2232
	azide	2097
	C=O	1734
	C=S	1048
8CTAs-POSS	CN	2232
	C=O	1734
	Si-O	1086
	C=S	1048

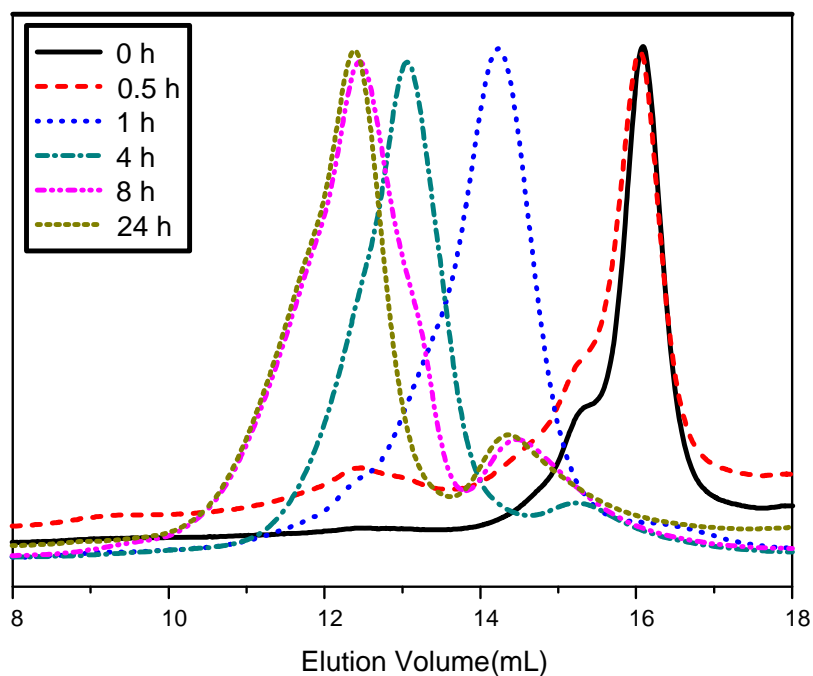


Fig. S13. GPC curve for the RAFT polymerization of MMA at 70 °C in DMF (4M) in the presence of 8CTAs-POSS ($[M]_0 : [CTAs] : [AIBN] = 150 : 1 : 0.2$).

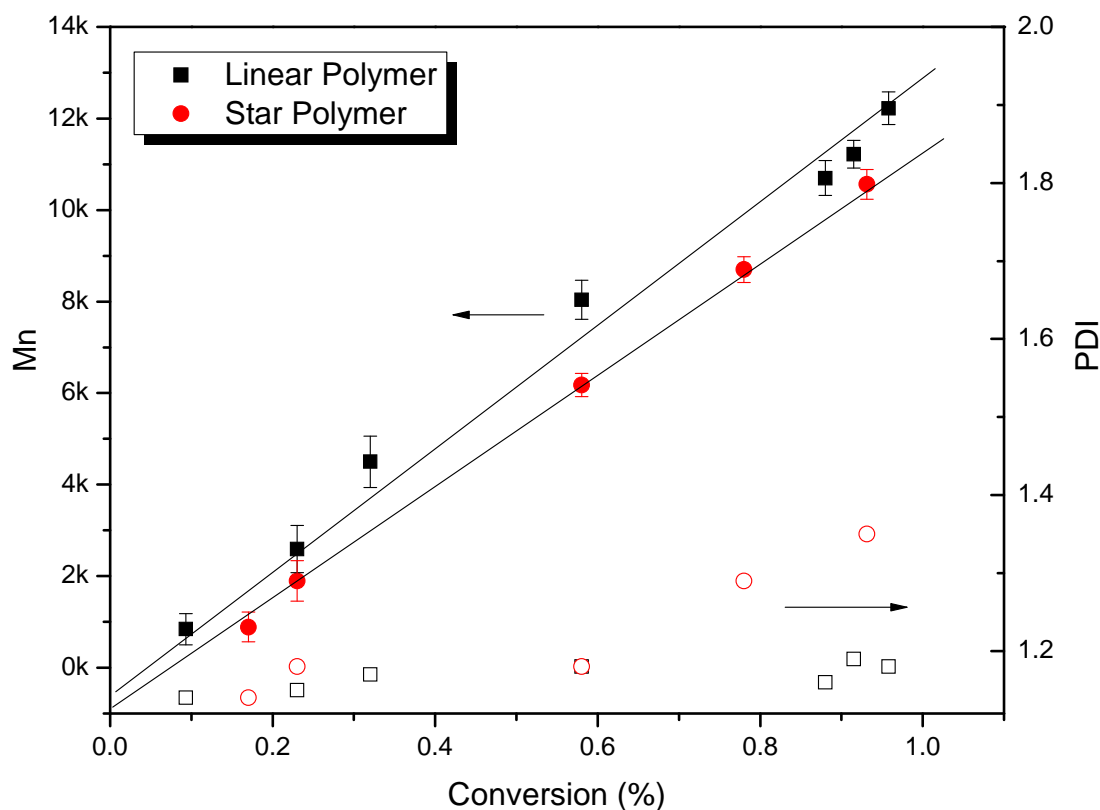


Fig. S14. Evolution of the molecular weight and PDIs with conversion for the RAFT polymerization of MMA at 70 °C in DMF in the presence of azido-CTAs and 8CTAs-POSS ($[M]_0 : [CTAs] : [AIBN] = 150 : 1 : 0.2$).

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