

Synthesis and Self-Assembly Behavior of POSS-embedded Hyperbranched Polymers

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1. Materials

Octavinyl POSS (98%, Hybrid Plastics), 4-(dimethyl-amino)-pyridine (DMAP, 99%, Aldrich), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 99%, Energy Chemical), dithiothreitol (DTT, 99%, J&K), 3,3'-dithiodipropionic acid (99%, Energy Chemical), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, J&K), triethylamine (TEA, 99%, Beijing Chemical Works), hydrochloric acid, acetone, hexane and ether (reagent grade, Beijing Chemical Works), tetrahydrofuran (THF), *N,N*-dimethyl formamide (DMF) and dichloromethane (CH₂Cl₂) were purified by stirring over calcium hydride for 24 h followed by distillation.

2. Characterizations

¹H and ¹³C NMR spectra were obtained on a Bruker DRX-400 spectrometer in chloroform-d using tetramethylsilane (TMS) as internal reference. Thermogravimetric analysis (TGA) measurements were performed on a TA Instruments, Inc., MDSC-2910. The temperature program was from 60 to 700 °C with an increasing rate of 10 °C min⁻¹ in a flow of air. The differential scanning calorimetric (DSC) analysis was performed on a NETZSCH DSC differential scanning calorimeter under a nitrogen atmosphere, in which the sample was heated to 200 °C at the rate of 10 °C min⁻¹, cooled to 0 °C at the rate of 10 °C/min, and then heated to 200 °C at the rate of 10 °C min⁻¹. X-ray diffraction (XRD) data were obtained with a graphite monochromatic device and Cu K α radiation $\lambda = 0.15406$ nm on the Rigaku D/max 2500, operated in the $\theta : 2\theta$ mode primarily in the 3-80° (2 θ) range and step-scan of $2\theta = 0.04^\circ$. The tube voltage was 40 kV, and the tube current was 200 mA. Dynamic light scattering (DLS) data were obtained in THF on a commercial laser light scattering spectrometer (ALV/DLS/SLS-5022F) equipped with a multi- τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser ($\lambda_0=632.8$ nm) was used. The laser light scattering cell is held in a thermostat index matching vat filled with purified and dust-free toluene, with the temperature controlled to within 0.1 °C. MALDI-TOF-MS measurement was carried out using a Bruker BIFLEX III equipped with a 337 nm nitrogen laser. Gel permeation chromatography (GPC) measurements were carried out on GPCmax VE-2001 (Viscotek) equipped with a Viscotek TriSEC Model 302 triple detector array (refractive index detector, viscometer detector, and laser light scattering detector) using two I-3078 Polar Organic Columns. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL min⁻¹. Molecular weights (M_n and M_w) and polydispersity indexes (PDIs) were obtained using the workstation software equipped with the system by the processing method for dendritic polymers based on a working curve of polystyrene standards.

3. Syntheses of the AB₇ monomer, HB-POSS and HB-POSS-PEG₃₅₀ polymers

Synthesis of (vinyl)₇-POSS-SS-POSS-(vinyl)₇. (vinyl)₇-POSS-OH (0.78 g, 1.2 mmol), 3,3'-dithiodipropionic acid (108 mg, 0.5 mmol), EDCI (0.23 g, 1.2 mmol) and DMAP (22.9 mg, 0.2 mmol) were added to a 50 mL round-bottomed flask equipped with a magnetic stirring bar, followed by the addition of 25 mL of freshly dried DMF to fully dissolve all the solids. The solution was cooled to 0 °C for 15 min and allowed to the room temperature, and then further stirred for another 24 h to complete the reaction. After removing DMF, CH₂Cl₂ was added to dissolve the solids, and then washed with 2M HCl aqueous solution, saturated NaCl aqueous solution and DI water for three times and dried over anhydrous Na₂SO₄. Then the final product was precipitated into cold methanol several times to remove the excess (vinyl)₇-POSS-OH to afford a white powder, (vinyl)₇-POSS-SS-POSS-(vinyl)₇, (615 mg, 83.4%) after obtained in vacuo.

Synthesis of (vinyl)₇-POSS-SH. Briefly, (vinyl)₇-POSS-SS-POSS-(vinyl)₇ (615 mg, 0.41 mmol) was dissolved in 20 mL of THF containing 1 mL of TEA, and then added DTT (32 mg, 0.2 mmol) to the solution at room temperature. The reaction was kept under an argon atmosphere to minimize free thiol oxidation. After stirring for 12 h, the mixture was concentrated under reduced pressure and separated chromatographically on silica gel with CH₂Cl₂/hexane (v/v = 1/4) to afford a white solid, (vinyl)₇-POSS-SH, (425 mg, 69.2%) after obtained in vacuo.

Photopolymerization of POSS-embedded hyperbranched polymers, HB-POSS polymers. (vinyl)₇-POSS-SH (80 mg, 0.11 mmol) and DMPA (4 mg, 0.015 mmol) were dissolved in 10 mL of THF. This solution was divided into 3 glass vials and degassed by bubbling nitrogen for 20 min. After irradiation under a 365 nm UV lamp at room temperature for their allotted time (0.5 h, 1 h and 4 h), each product was precipitated into cold methanol several times to remove the by-products to afford the yellowish powder after obtained in vacuo.

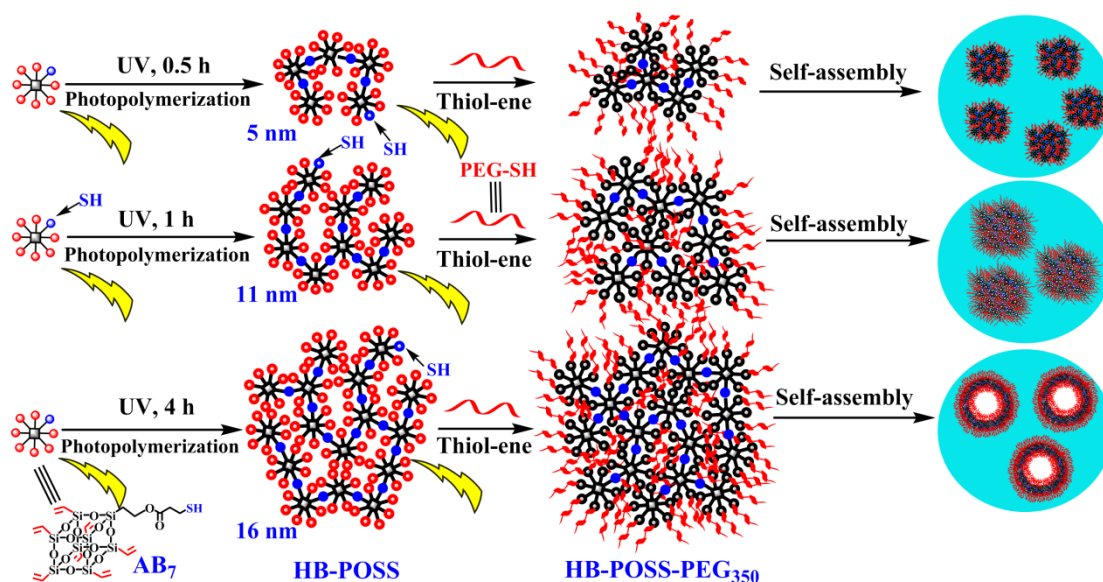
Synthesis of amphiphilic polymers, HB-POSS-PEG₃₅₀ polymers. Typically, a HB-POSS polymer, PEG-SH ($M_n=350$) and DMPA were dissolved in 10 mL of THF. After irradiation under a 365 nm UV lamp at room temperature for 3 h to make sure no vinyl groups existed. The product was precipitated into ether several times and further purified by ultrafiltration (MWCO 1000) to afford the yellowish products.

4. Hydrophilic fractions of the amphiphilic HB-POSS-PEG₃₅₀ polymers. The vinyl peaks completely disappeared after thiol-ene click treatment of HB-POSS using PEG-SH, demonstrating all the vinyl groups of the HB-POSS were successfully substituted by PEG shells. So we deduced the graft ratio of PEG arms should be

~100%. Consequently, number of PEG arms in HB-POSS-PEG can be calculated by the equation of ' $N_{\text{PEG}} = 6n+1$ ' (n is average number of repeat unit) from the corresponding vinyl groups in the HB-POSS polymers. For the HB-POSS polymers obtained after UV irradiation for 0.5, 1 and 4 hours, the average numbers of repeat unit are 4.3, 9.4 and 13.6, respectively. Therefore the corresponding HB-POSS-PEGs possess 26.8, 57.4 and 82.6 PEG arms. The hydrophilic fraction may be approximately determined by the equation of ' $H\% = (N_{\text{PEG}} \times M_{n,\text{PEG}}) / (N_{\text{PEG}} \times M_{n,\text{PEG}} + M_{n,\text{HB-POSS}})$ ', so the corresponding hydrophilic fractions of the three amphiphiles are 74.7%, 74.3% and 74.2%, respectively.

5. Self-assembly behaviors of the amphiphilic HB-POSS-PEG₃₅₀ polymers.

A typical self-assembly aggregate solution was prepared as following: HB-POSS-PEG₃₅₀ (5 mg) was first dissolved in THF (1 mL), which is a good solvent for both the POSS and PEG components. Then deionzied water (4 mL) was added dropwise into the solution at the rate of 0.05 mL/min via a syringe pump. The colloidal dispersion was further stirred for another 2 h and the temperature was fixed at 30 °C during the self-assembling process. The organic solvent (THF) was removed by dialysis (MW cutoff, 1 kDa) against deionzied water for 2 days.



Scheme S1 Schematic illustration of synthesis and self-assembly behavior of POSS-embedded hyperbranched polymers starting from an AB₇ monomer.

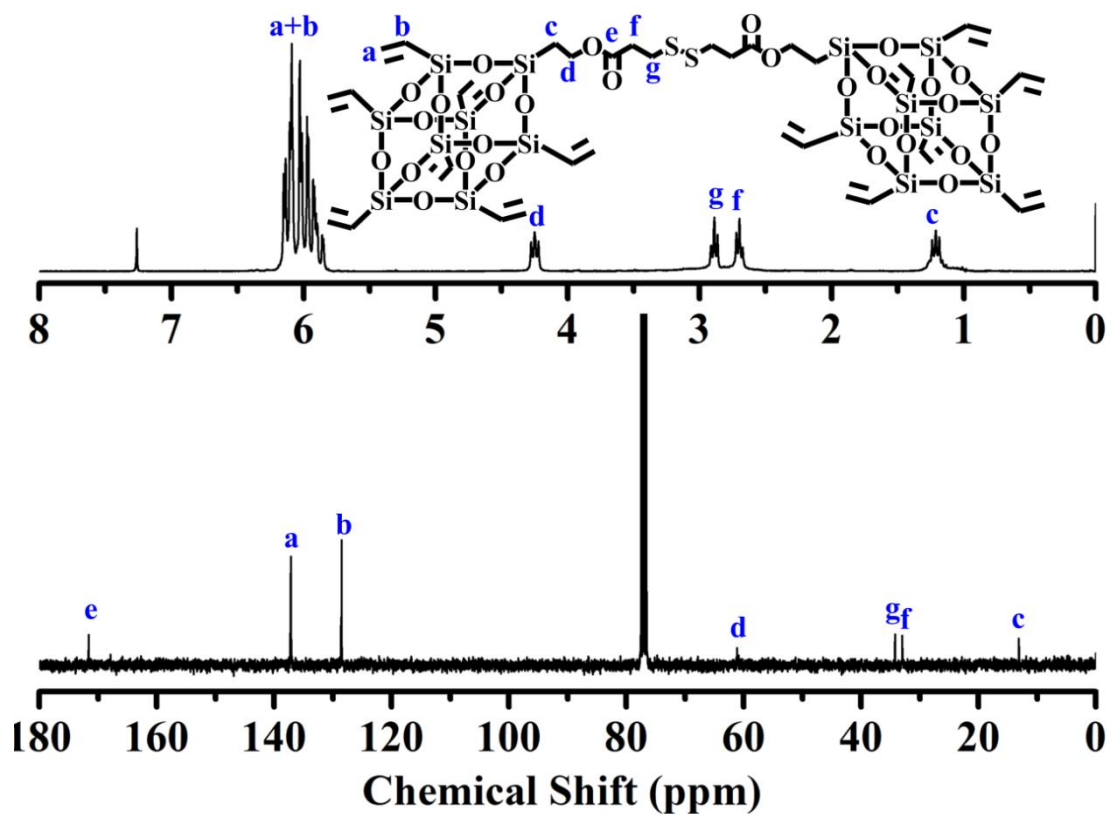


Fig. S1 ^1H and ^{13}C NMR spectra of the intermediate, (vinyl) $_7$ -POSS-SS-POSS-(vinyl) $_7$ at CDCl_3 .

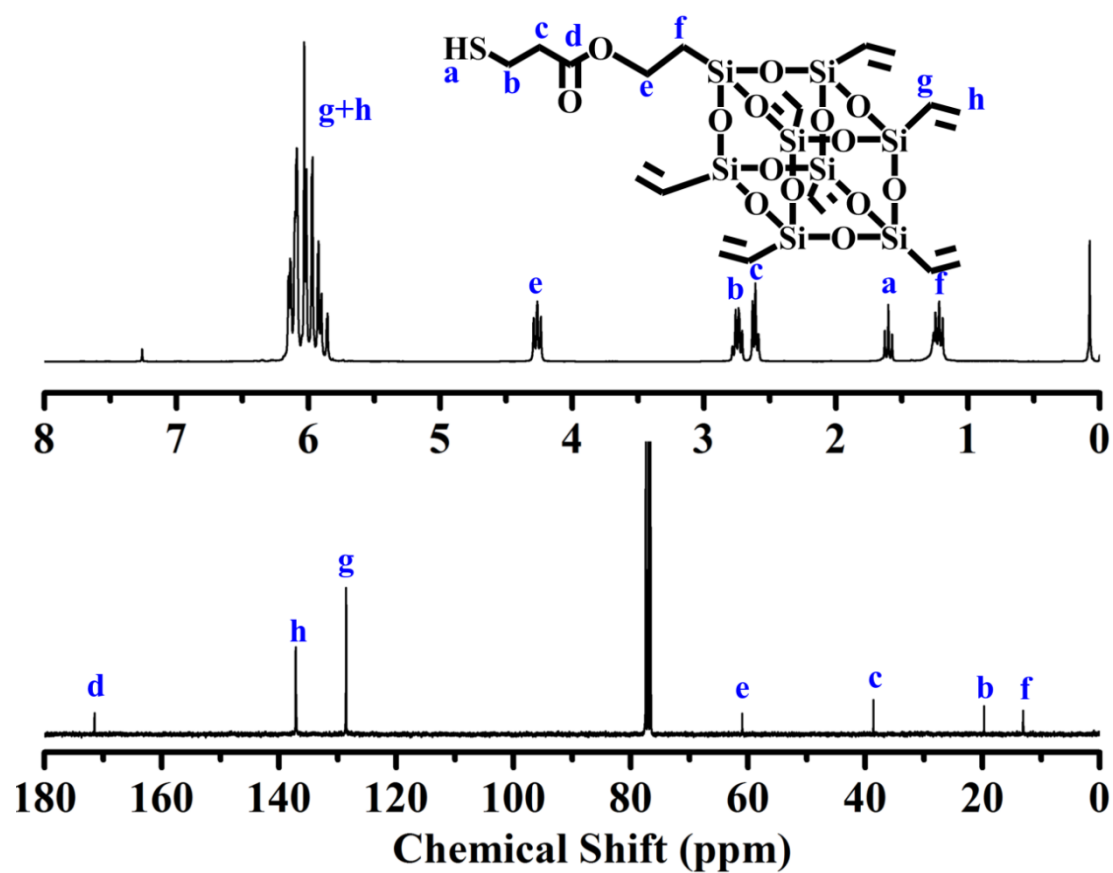


Fig. S2 ^1H and ^{13}C NMR spectra of the monomer, (vinyl) $_7$ -POSS-SH at CDCl_3 .

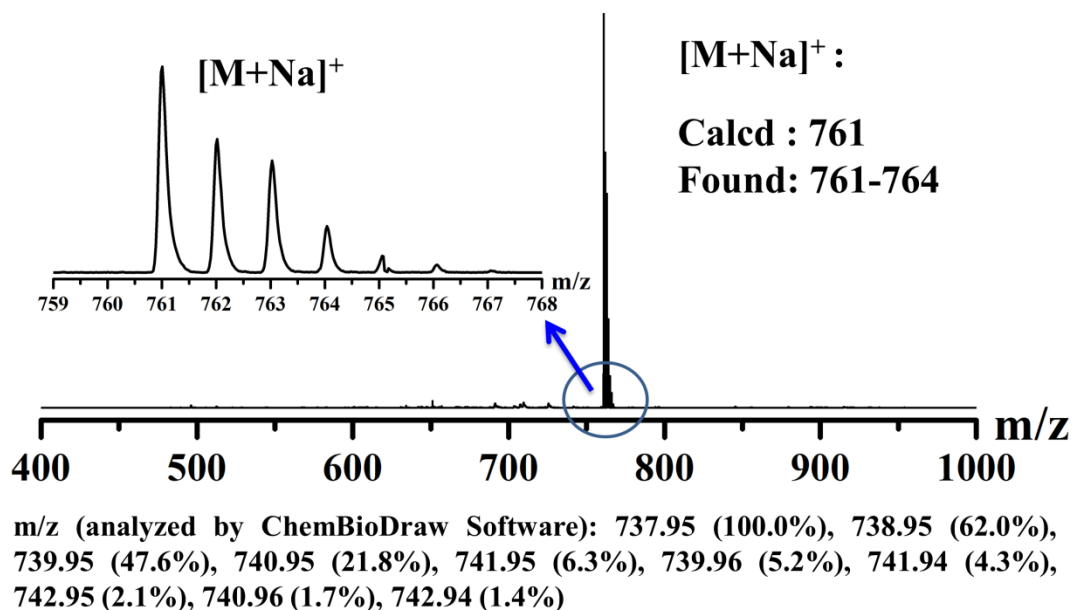


Fig. S3 MALDI-TOF curve of the monomer, (vinyl)₇-POSS-SH.

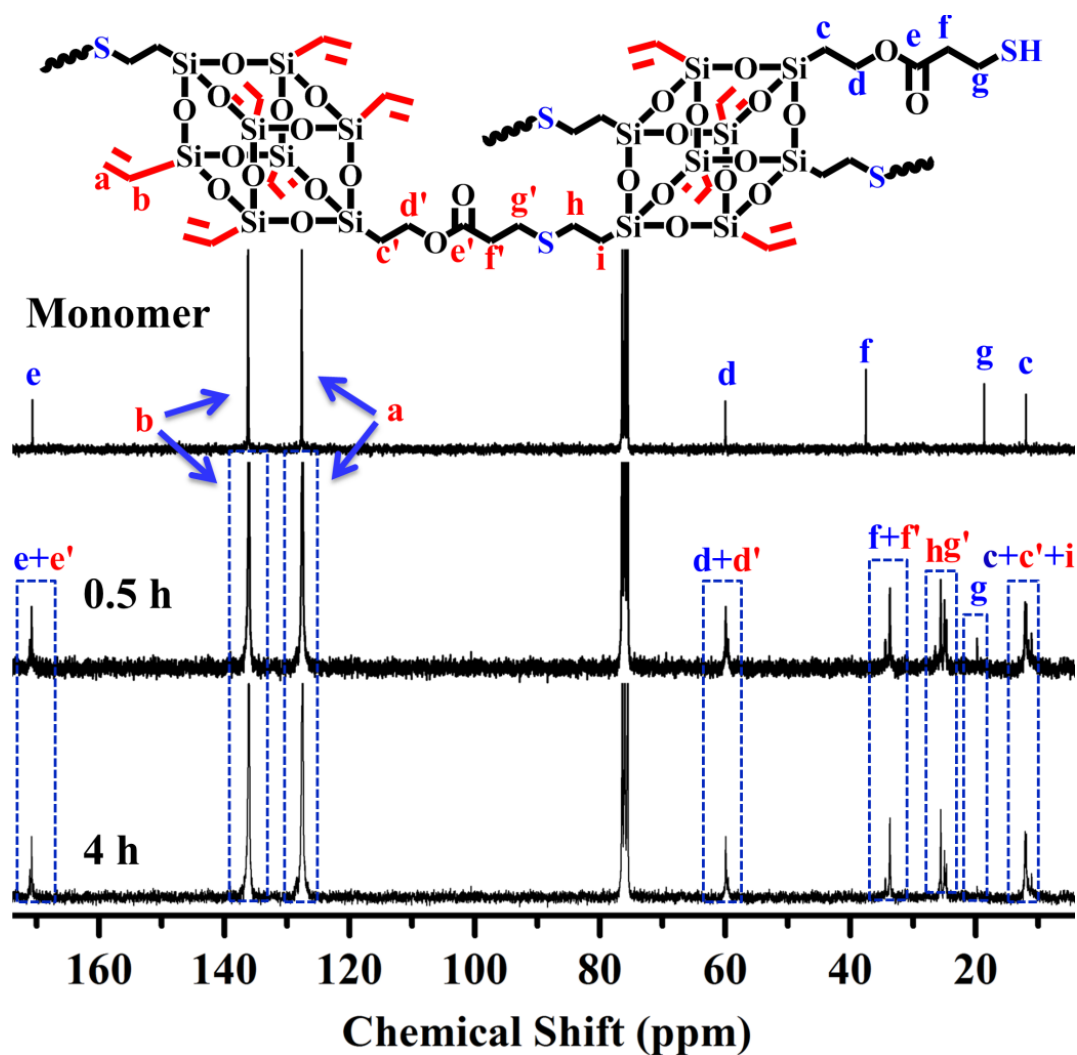


Fig. S4 Comparison of ¹³C NMR spectra of the (vinyl)₇-POSS-SH monomer before and after UV irradiation for 0.5 and 4 hours at CDCl₃.

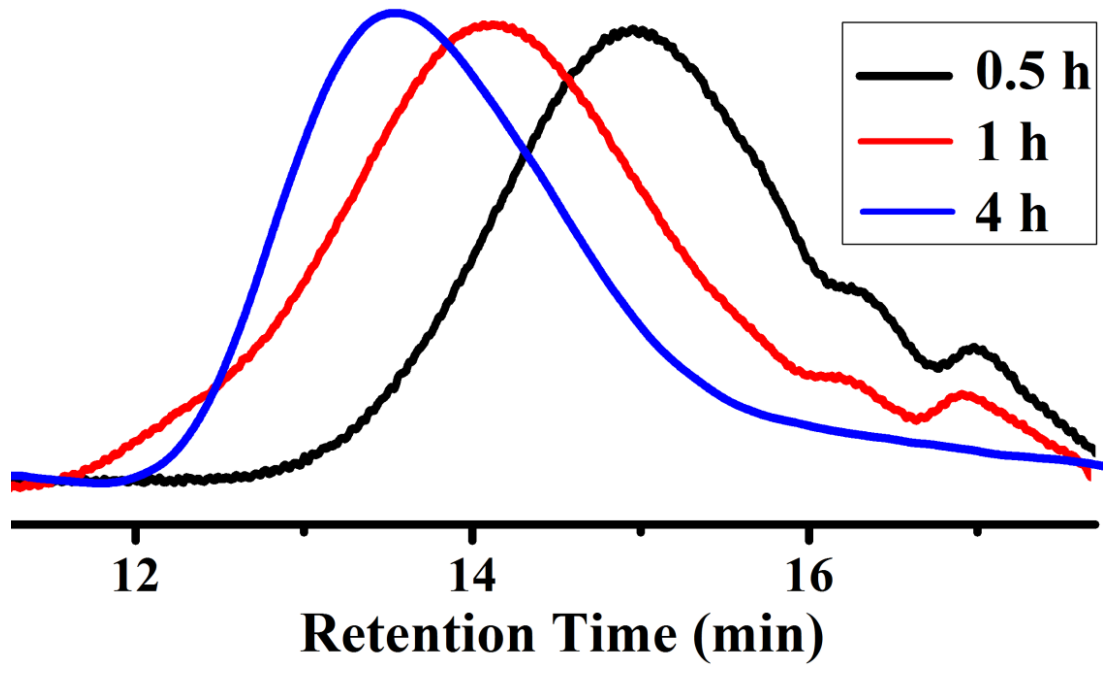


Fig. S5 GPC curves of the HB-POSS polymers.

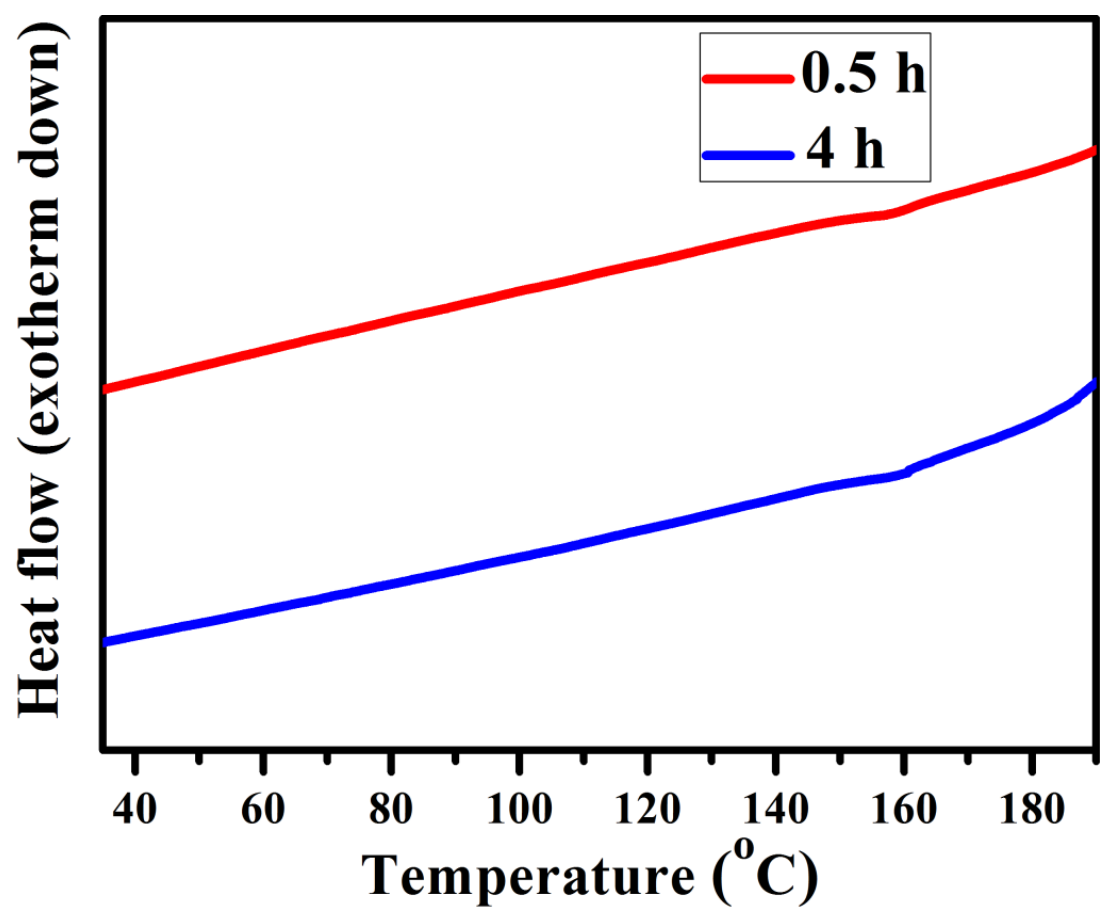


Fig. S6 DSC curves of the HB-POSS polymers.

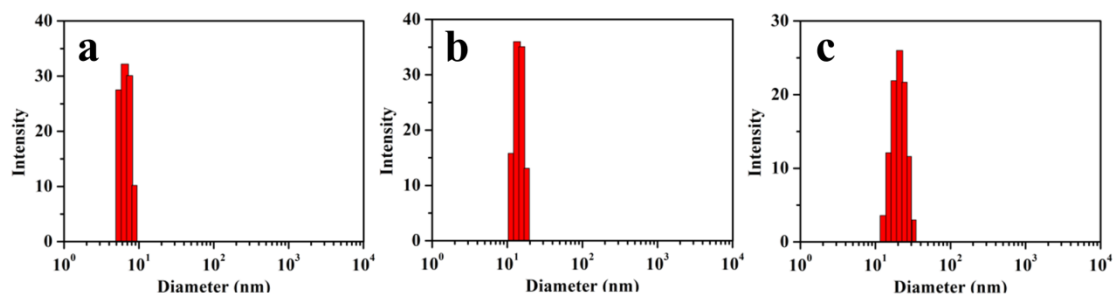


Fig. S7 DLS profiles of the HB-POSS polymers obtained after polymerization for (a) 0.5, (b) 1 and (c) 4 h in THF.

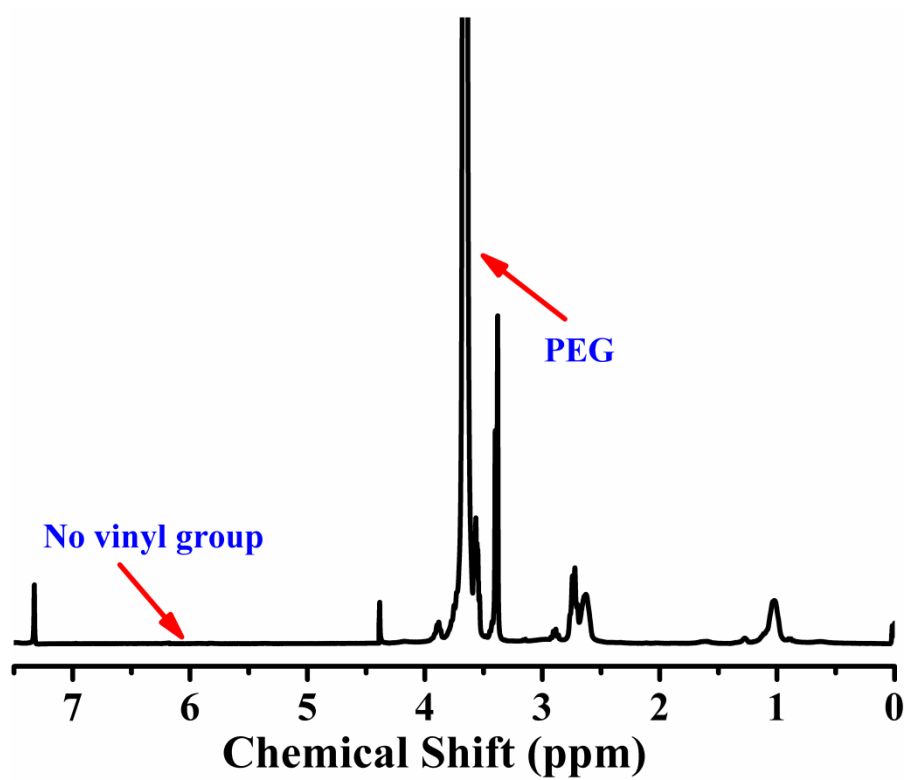


Fig. S8 ^1H NMR spectrum of the HB-POSS-PEG₃₅₀ with a HB-POSS core ($M_n = 11900$).