Supporting Information

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S1. Materials and Methods.

Tris(pentafluorophenyl)borane, 1,1,3,3-tetramethyldisiloxane, tetraethylorthosilicate, cyclohexane, dichloromethane, methanol, tetramethylammonium hydroxide, tetrahydrofuran (THF), sec-butyl lithium (1.3 M solution in cyclohexane), styrene, hexamethylcyclotrisiloxane (D3), n-BuLi (2.5 M solution in hexane), 1，3，5-trimethyl-1,3,5-tris (3,3,3-trifluoropropyl) cyclotrisiloxane (F3), chlorodimethylvinylslane, trimethylchlorosilane (TMCS) were purchased through InnoChem, Inc., China. Styrene was dried over CaH_2 for 24 h and subsequently distilled under reduced pressure prior to polymerization. 1，3，5-trimethyl-1,3,5-tris (3,3,3-trifluoropropyl) cyclotrisiloxane (F3) was distilled over CaH_2 prior to polymerization. Tetrahydrofuran (THF) was dried over sodium prior to use. Infrared (IR) spectra were recorded on an IR spectrometer at the transmission mode for liquid products in liquid cells. ^1H NMR spectra were recorded in $CDCl_3$ on 300 MHz NMR spectrometer. The ^1H NMR were referenced to residual solvent signals at 7.26 ppm ($CHCl_3$). ^{29}Si NMR spectra proton was decoupled and recorded in $CDCl_3$ with a 60 s delay at 120 MHz. Gel-permeation chromatography (GPC) analysis was conducted on a Viscotek GPC/SEC 270 max with RI/UV/viscosity/light scattering as the detectors. Single-crystal X-ray diffraction was collected on the Bruker APEX II diffractometer at -100°C, and then the data was solved and refined by the Bruker APEX II software package. The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum was collected on a Bruker Autoflex III with 2,5-dihydroxybenzoic acid as the matrix. Raman spectra were recorded on a LabRAM HR Evolution at 532 nm. Atomic force microscope (AFM) images were captured on a Bruker Dimension Icon with ScanAsyst. Viscosity was measured on a NDJ-5S Digital Viscometer with the spinning speed of 30r/min.

Curing was performed by mixing the relative amount of different components and catalyst in CH_2Cl_2 , and the solvent was then removed under high vacuum. For square examples, the mixture was then poured to a mold, and transferred to the oven for curing.

S2. Reaction Procedure：

Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (51.2mg, 0.1mmol, around 1400 ppm relative to the total weight of starting materials) was dissolved in 900 ml cyclohexane in a 2000 ml two-neck glass bottle. A mixture of 1,1,3,3-tetramethyldisiloxane (26.866 g, 0.2mol) and tetraethylorthosilicate (20.833 g, 0.1mol) in 100 ml cyclohexane was slowly added to the catalyst solution via a syringe over 2 h on a syringe pump. After the addition, 2g activated carbon and 3~4 drops triethylamine was added to the reaction mixture to deactivate the catalyst, and then the mixture was filtered and the solvent was removed using a rotovap. The product was concentrated and dried under an oil pump to give a colorless liquid mixture mixed with small amount of solids (36.61g). The mixture were purified by fractional distillation at reduced pressures to obtain a white solid (1.947g, yield 5.3%). Needle-like crystals were obtained by sublimation of the solids in a vial, and was then characterized a spirocyclosiloxane compound by single-crystal X-ray diffraction experiment (see Fig. S19B). The remaining mixture was purified by repeated precipitation with the methanol / CH_2Cl_2 = 10:1 to given colorless liquid with the viscosity of 10360 mPa·s (**HBP-1**, 10.67g, yield 33.3%).

HBP-1: colorless liquid, IR: 2962, 2361, 2338, 1256, 1084, 1009, 848,790 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.10 (m); ^{29}Si NMR (120 MHz, $CDCl_3$, ppm) δ -7, -20, -103,-109.

Spirocyclosiloxane: white solid, IR (ATR): 2962, 2361, 2338, 1256, 1084, 1009, 848,790 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.10 (m); ^{29}Si NMR (120 MHz, $CDCl_3$, ppm) δ -6, -20, -95,-103.

S3. ^{1}H/^{29}Si NMR

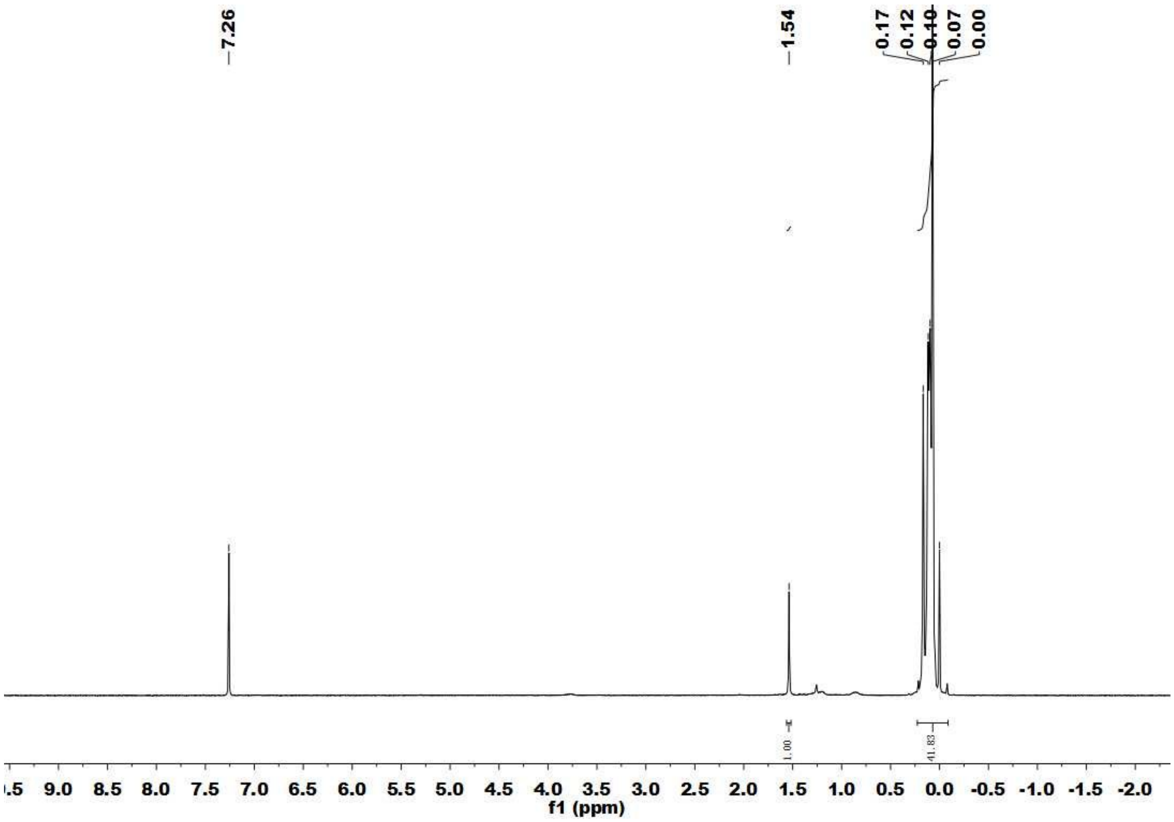


Fig. S1 ^{1}H-NMR of **HBP-1**. The peaks at 7.26 and 1.54 ppm refers to the residual $CHCl_3$ and H_2O molecules in the $CDCl_3$ solvent.

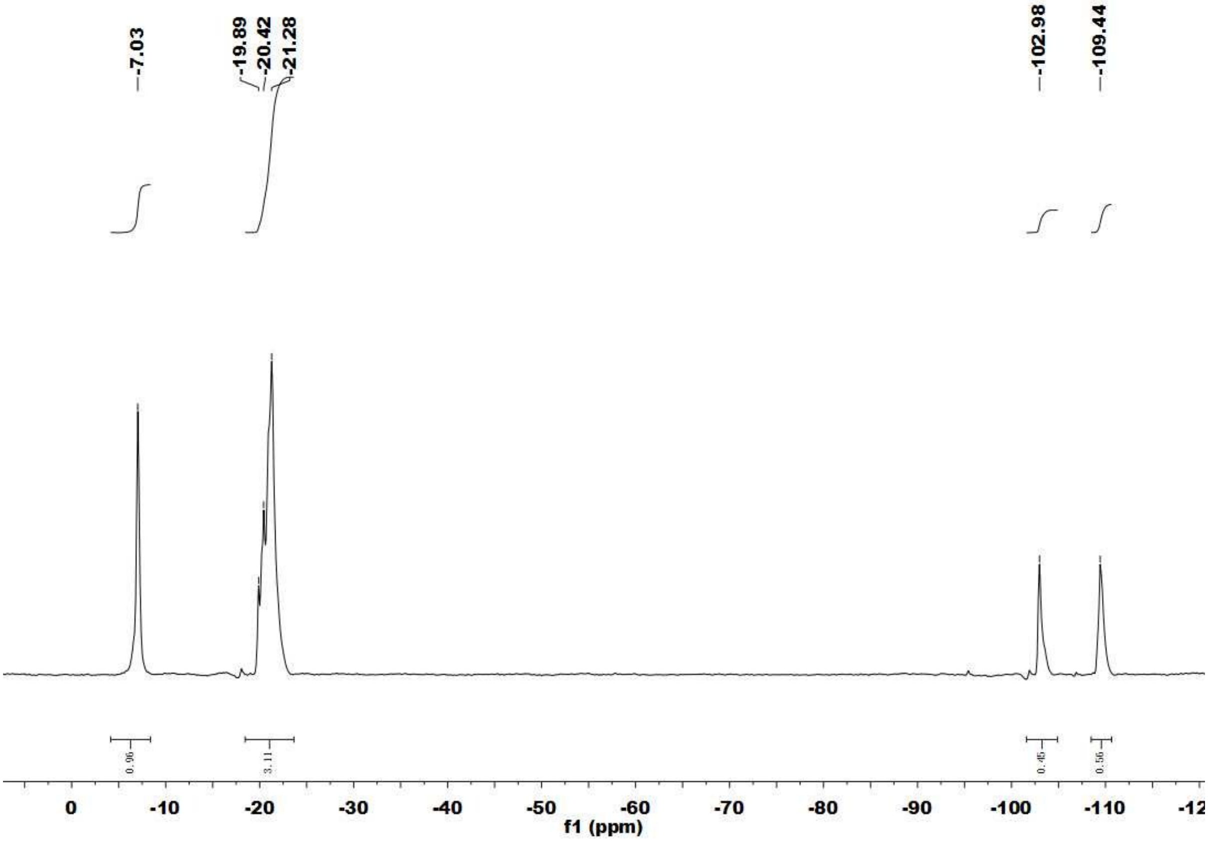


Fig. S2 ^{29}Si-NMR of **HBP-1**. It is known that the constrain in 6-memebered cyclotrisiloxane ring leads to around 10 ppm downfield shifting of relative signals in ^{29}Si-NMR[1], and therefore the signals at -7 ppm and -102 ppm are assigned to the D and Q units in the cyclotrisiloxane rings, and the peaks at -21 ppm and -109 ppm are assigned to the D and Q units not in the cyclotrisiloxane rings. This clearly shows the existence of significant amount of cyclotrisiloxane units in 1. Based on the dendritic form of 1 in Figure 1, it can be derived that the $Q_{non\text{-}6}/Q_6 = \frac{2 * 3^n - 1}{2 * 3^n} = 1 - \frac{1}{2 * 3^n}$, $D_{non\text{-}6}/D_6 = \frac{12 * 3^n - 4}{4 * 3^n} = 3 - \frac{1}{3^n}$, with n representing the generation number (Qnon-6 and Q6 refer to the Q Si atoms not in and in the six-membered rings respectively) . Given the Mw of HBP-1 around 18962, the average of n should be around 2 (molecular weight of the structure in Scheme 1 is 12484 when n =2). When n=2, the ratios are respectively around 0.94 for $Q_{non\text{-}6}/Q_6$ and 2.89 for $D_{non\text{-}6}/D_6$. In fact, the measured relative ratios in ^{29}Si-NMR are 0.96 and 3.11 respectively. This indicates around 90% of the intramolecular cyclics are the highly constrained cyclotrisiloxane units. Since the polymer is made by one step synthesis, structural defects are unavoidable, and together with the intrinsic NMR integration derivations, this explains the slight discrepancy between the calculated and experimental sets of data. The ratio of D silicon atoms in the cyclotrisiloxane rings versus those not the in the rings is around 1:3.2. Therefore there is around 23.8% chance for D units to close into a cyclotrisiloxane ring, and in other words, the possibility of forming spirotrisiloxanes with two cyclotrisiloxane rings on one silicon atom is estimated to be 23.8%*23.8%=5.7%, and this actually matches very well with around 5.3% isolation yield of the spirocyclosiloxanes from the reaction mixture. Structure candidates of **HBP-1**, which are good for ^{1}H-NMR and MALDITOF MS analysis but fail in the ^{29}Si-NMR analysis. The structure of A had minimal amount of Q silicon atoms in the cyclotrisiloxane unit (Q_6), while structure B had minimal amount of Q silicon atoms not in the cyclotrisiloxane unit ($Q_{non\text{-}6}$), and none of this matched the measured $Q_{non\text{-}6}/Q_6$ ratio of around 1 in ^{29}Si-NMR. They didn't pass the similar analysis on the D region either. A mixture of A and B of 1:1 molar ratio matched the ^{29}Si NMR result, but this assumption didn't warrant any chemical sense, neither didn't explain the unimodal distribution of the product peak in the GPC result.

Fig. S3 ^{1}H-NMR of the spirocyclolsiloxane solids. The peaks at 7.26 and 1.54 ppm refer to the residual $CHCl_3$ and H_2O molecules in the $CDCl_3$ solvent.

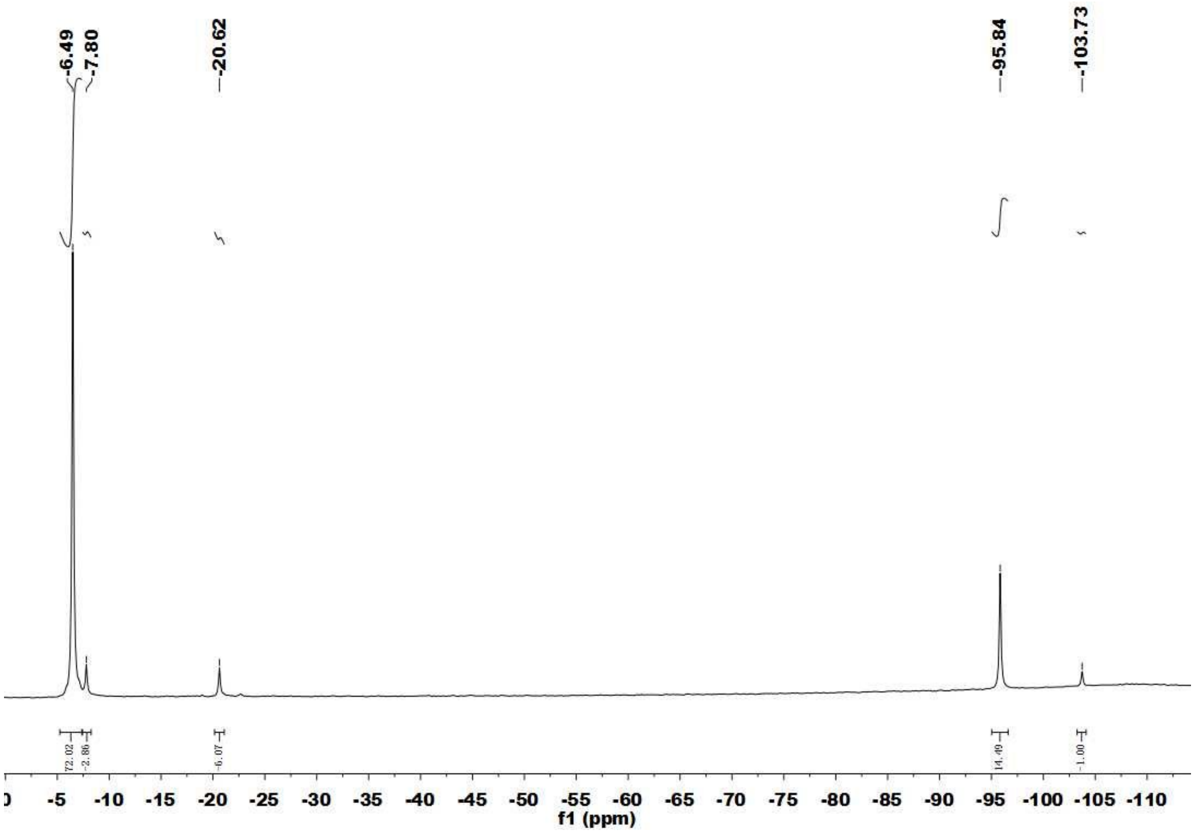


Fig. S4 ^{29}Si-NMR of the spirocyclolsiloxane solids. The peaks at -7.80, -20.62 and -103.73 refer to residual impurities.

S4. IR

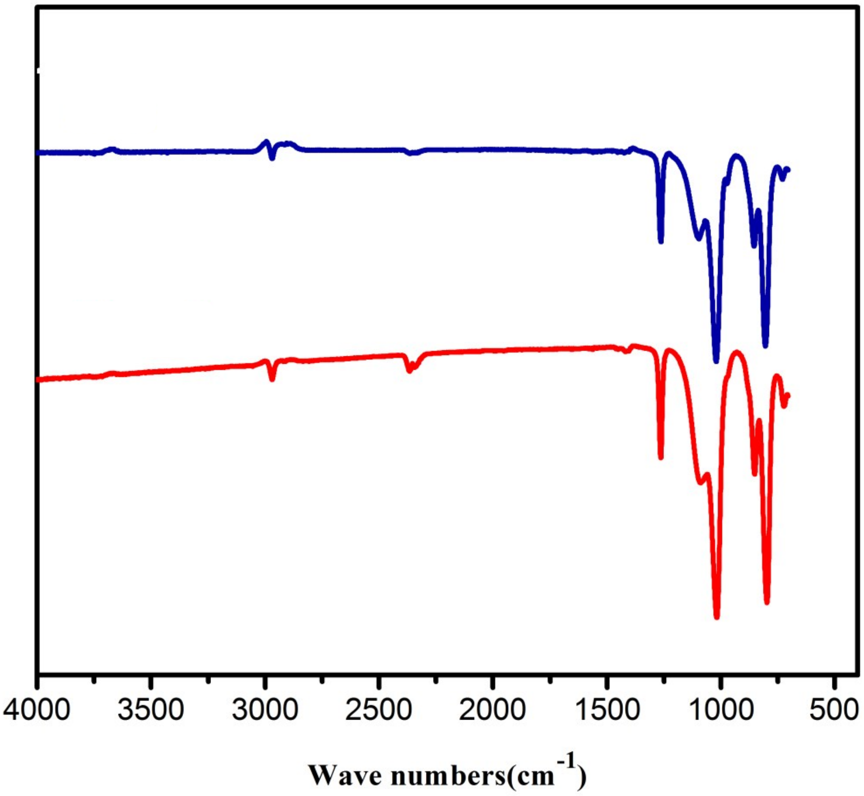


Fig. S5 IR of **HBP-1** (red line) and the spirocyclosiloxane solids (Blue line)

S5. GPC of the HBP-1 and TMS-terminating PDMS sample

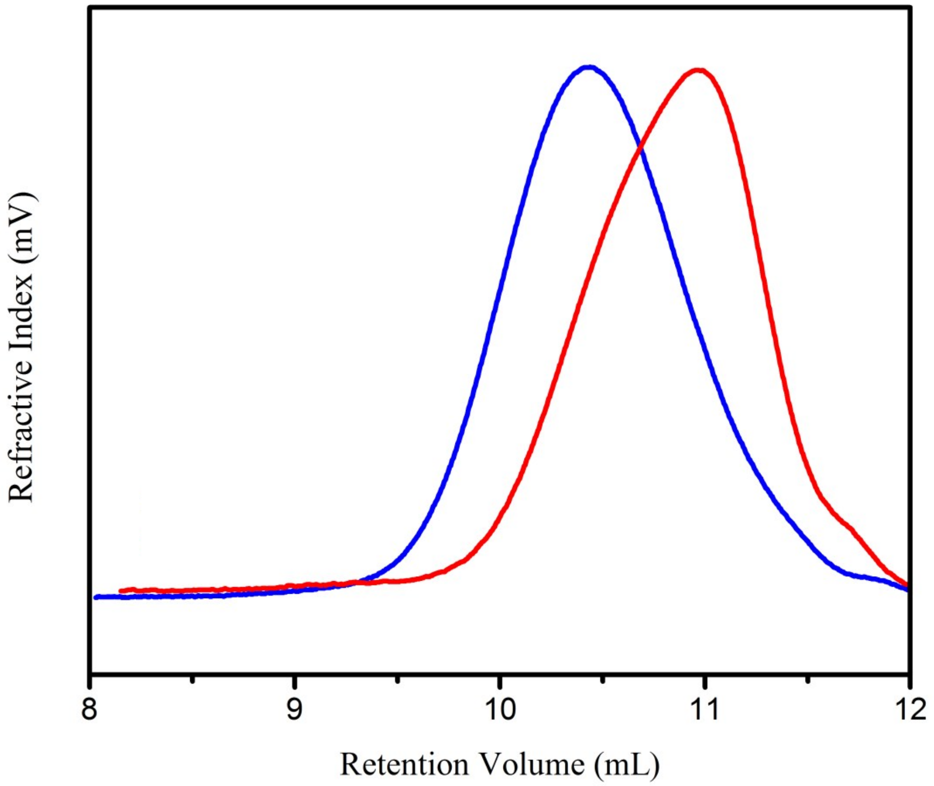


Fig. S6 GPC of **HBP-1** and a linear polydimethylsiloxane (PDMS) polymer in toluene with the absolution Mw determined. The Figure 1A, in which the curves of viscosity/Mw of **HBP-1** and PDMS are compared, was then derived based on the GPC result.

	Mn	Mw	PDI	Rh	Mark-Houwink a	Mark-Houwink logK
HBP-1	5463	18965	3.471	2.2	0.522	-3.509
PDMS	6058	20552	3.393	3.2	0.551	-3.181

S6. MALDITOF Data of the PDMS Sample

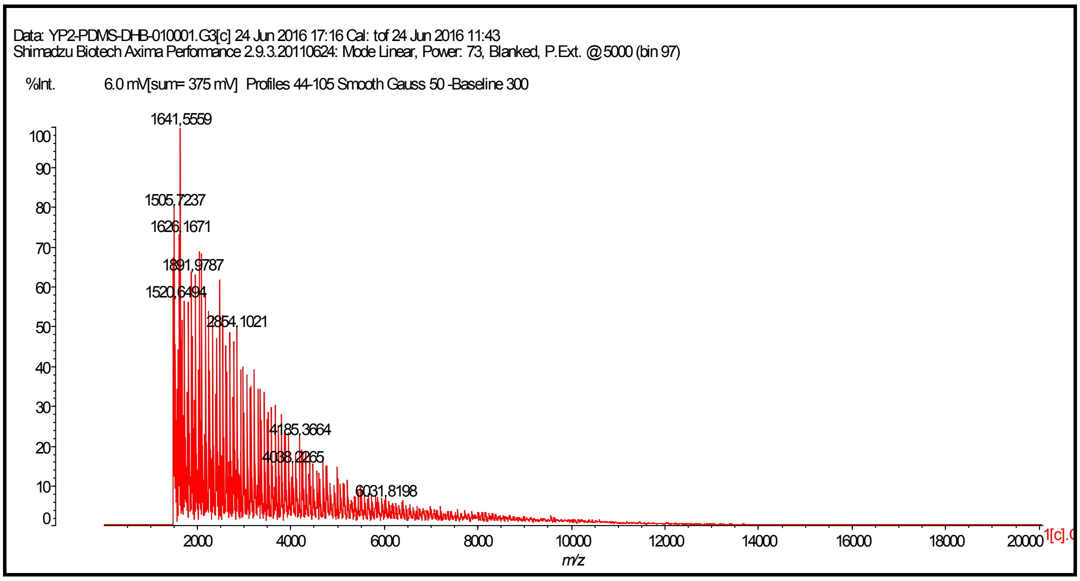


Fig. S7 MALDI-TOF mass spectrum of the PDMS sample. Although GPC gave a Mn of 6058 and Mw of 20552, the MALDI-TOF data showed the intensity distribution decreasing from ~1600 to higher values. This result showed that the MALDI-TOF intensity distribution curve of polysiloxane samples doesn't necessarily exactly match the real molecular weight distribution. Therefore the MALDI-TOF intensity distribution curve in Figure 2 of the main text for **HBP-1** didn't violate the molecular weight distribution data obtained from GPC analysis.

S7. Quantum Calculation of the Raman Vibration of HBP-1 and the Assignments of the Peaks of Experimental Data.

Assignment of the vibration peaks in Raman spectrum for the cyclotrisiloxane units

The geometry optimization and Raman intensity were done on hexamethylcyclotrisiloxane (D3) as the model compound at the B3LYP/6-31G(d) level using Gaussian 09 software package. The D3 results were first analyzed to show that the peaks at 457 and 586 cm^{-1} correspond to characteristic silicon and oxygen atoms breathing modes in the cyclotrisiloxane ring, and the peaks in **HBP-1** before curing were therefore assigned relatively, and were used to monitor the curing process of **HBP-1**.

	D3		**HBP-1**
Silicon Atom Breathing	441(cal.)	457(exp.)	449(exp.)
Oxygen Atom Breathing	568(cal.)	586(exp.)	595(exp.)

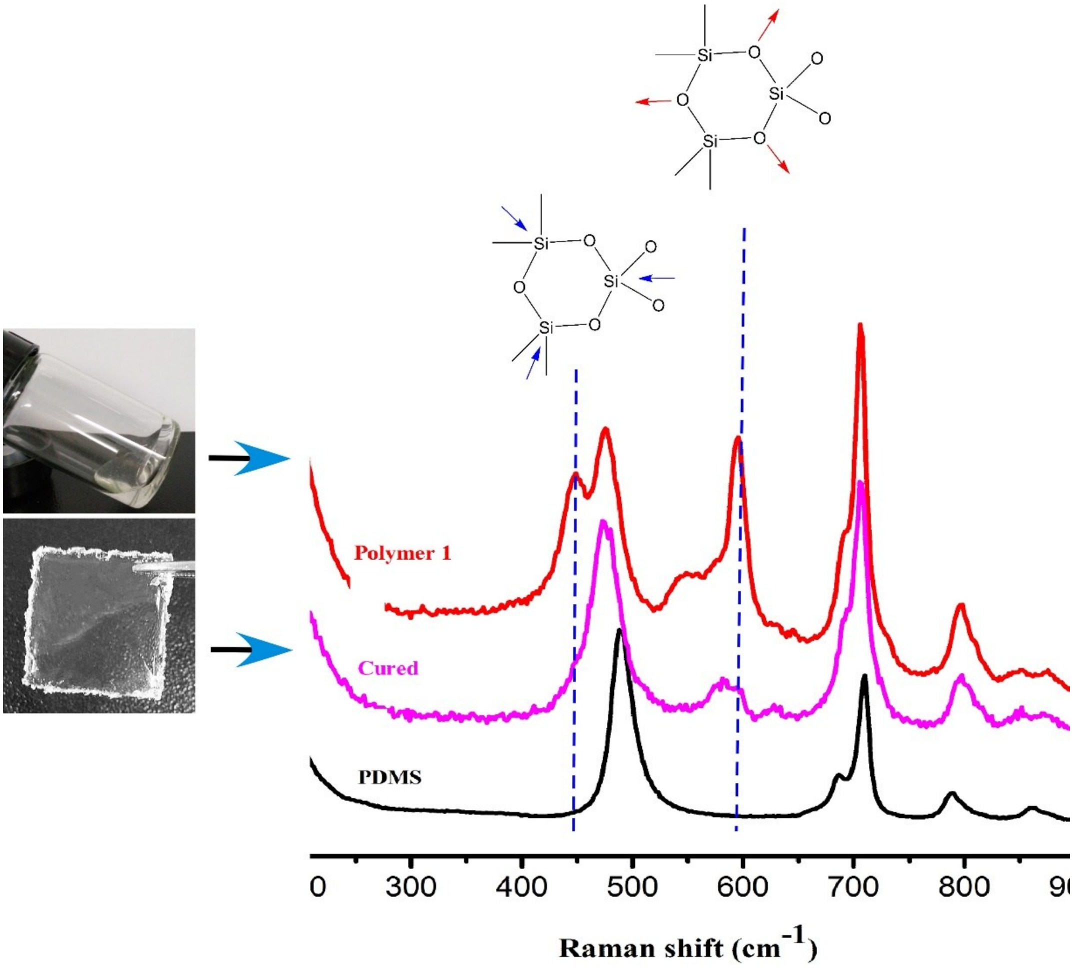


Fig. S8 Raman spectrum comparison between those of **HBP-1** (polymer 1) and its cured product. The two peaks at 449 and 595 cm^{-1}, corresponding to the breathing modes of silicon and oxygen atoms in the cyclotrisiloxane rings, disappeared after the curing by tetrabutylammonium hydroxide.

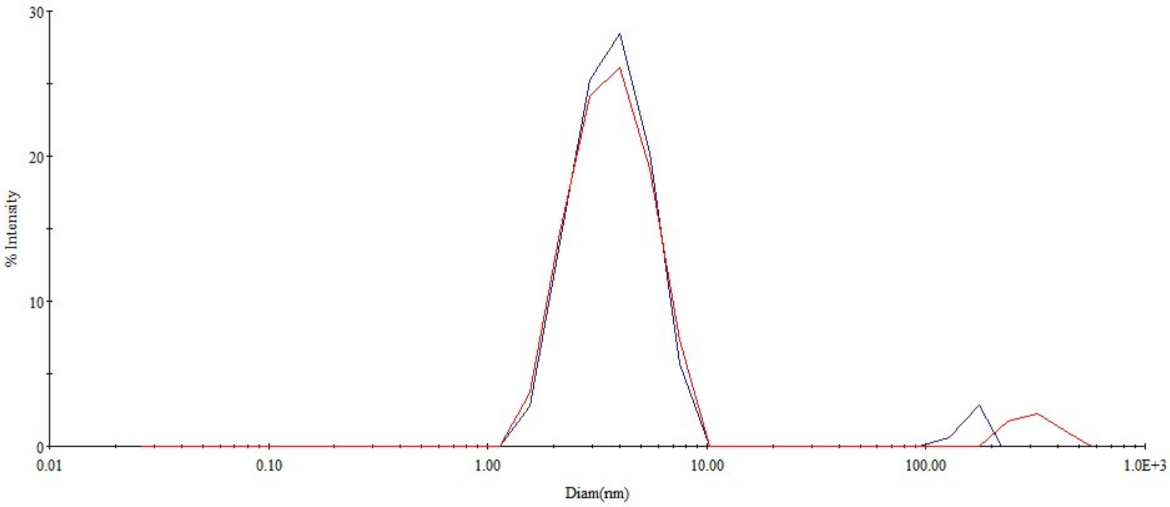
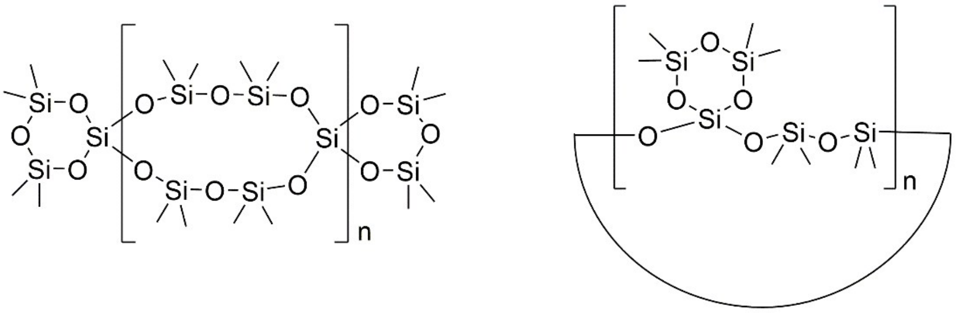


Fig. S9 Dynamic light scattering of **HBP-1**, showing the diameter of 4.8 nm. There are some aggregation peaks at several hundreds nanometers.



A

B

Fig. S10 ^{29}Si-NMR analysis of **HBP-1** in Fig. S2 to rule these possible structures (A) and (B)

S8. Synthesis of Janus type block JHBP-1:

Solution **1**. (0.19 ml, 1.3 M solution in cyclohexane, 0.25mmol) Sec-butyl lithium was added to a solution of (0.575ml, 5mmol) styrene in 10ml THF at −78 ℃, and then the solution was stirred for 30 min under N$_2$ atmosphere. Then (223mg, 1mmol) D$_3$ was added. After 10 min, the reaction temperature was increased to room temperature as the solution **1**.

Solution **2**. (0.1 ml, 2.5 M solution in hexane, 0.25mmol) n-BuLi was first added to one reaction flask under the protection of N$_2$ with (5mmol) in 10 THF. (0.2811g, 0.6 mmol) 1，3，5-Trimethyl-1,3,5-tris (3,3,3-trifluoropropyl) cyclotrisiloxane (F3) to the solution at 0℃. After 1 hour, another portion F3 (2.0616g, 4.4 mmol) was added. The solution was stirred at 0℃ as the solution **2**.

JHBP-1. Solution **1** and **2** were mixed at room temperature, followed immediately by addition of **HBP-1** (0.345 g) in 5 mL THF solution was added into the reactor. After 3 h, the polymerization was terminated with excessive chlorodimethylvinylslane. After filtration, the solution was added 50 ml MeOH and a white and fully precipitate formed, which was collected and dried as **JHBP-1** with an isolation yield of around 40%.

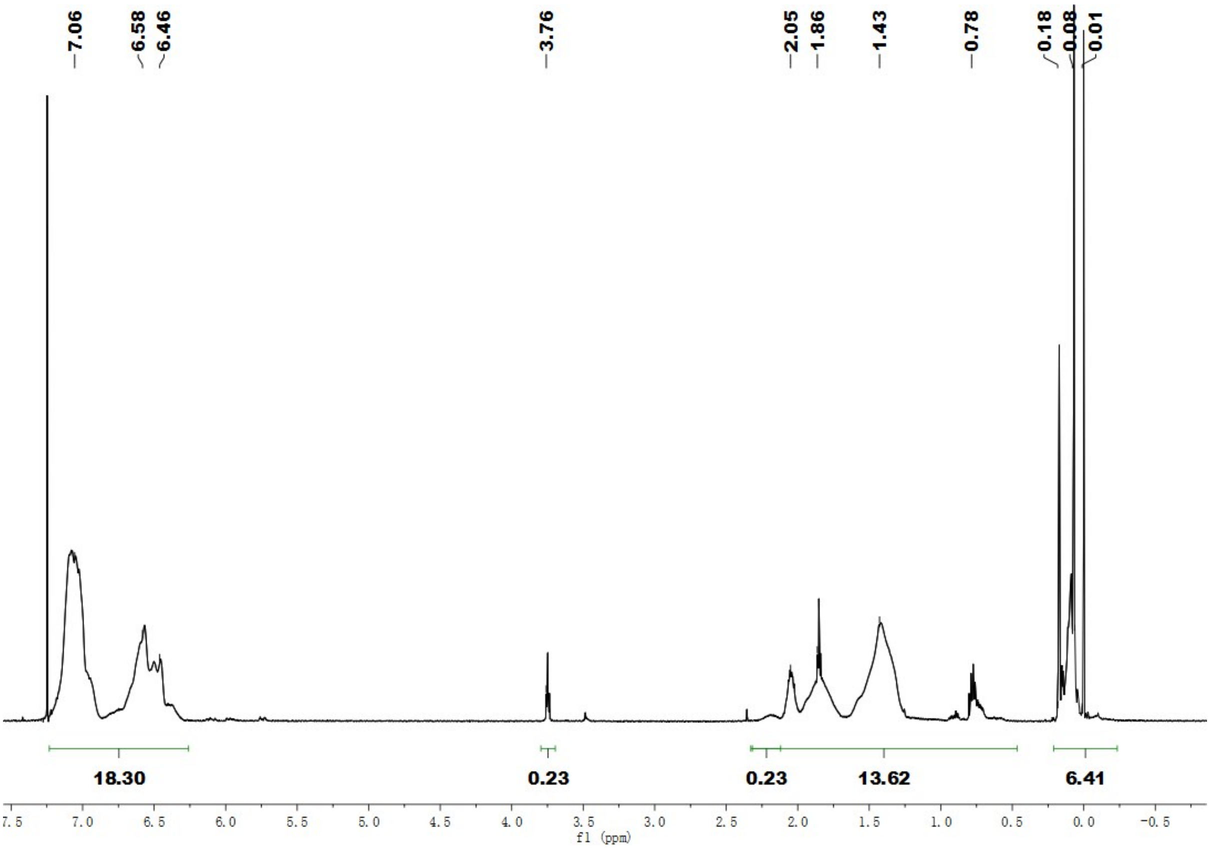
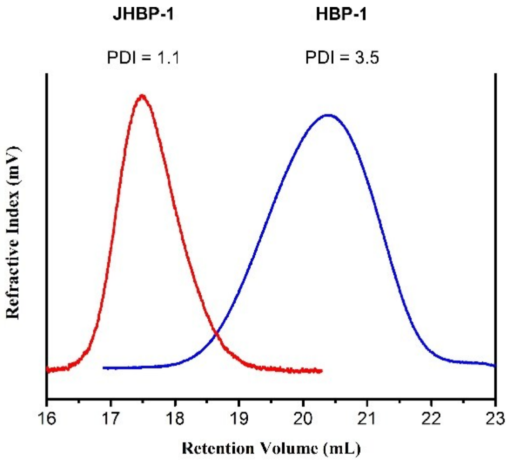


Fig. S11 ^{1}H-NMR of **JHBP-1** in $CDCl_3$.



	Mn	Mw	PDI	Rh	Mark-Houwink a	Mark-Houwink logK
JHBP-1	146,221	163,181	1.116	10.978 nm	0.594	-3.367

Fig. S12 GPC result of **JHBP-1** in toluene. The blue line for HBP-1 was added for a visual comparison of the PDI reduction.

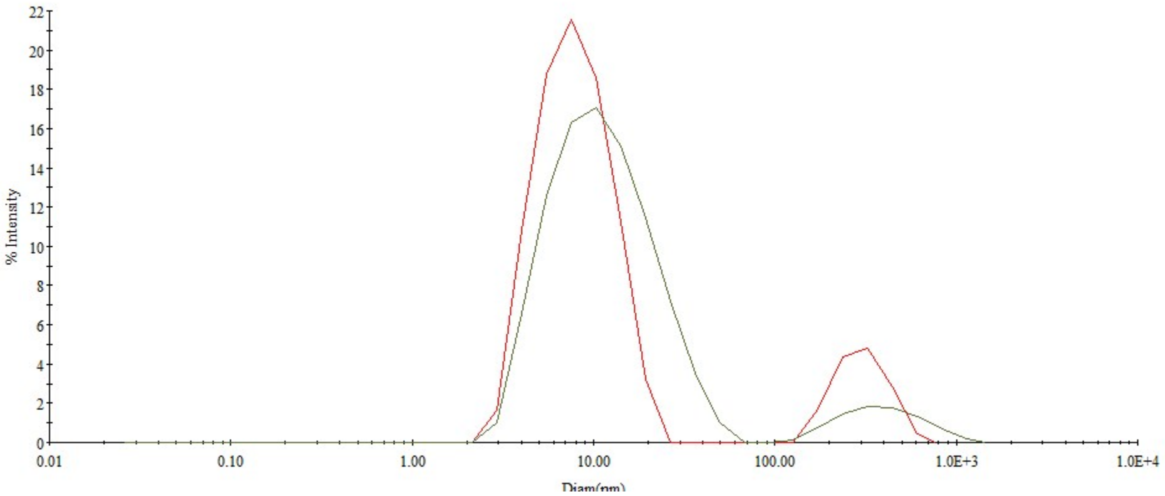
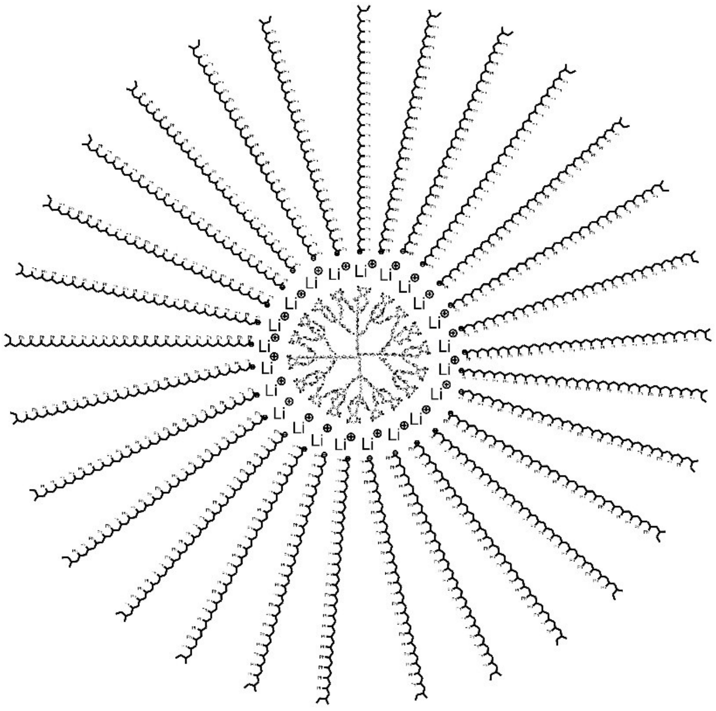


Fig. S13 Dynamic light scattering of **JHBP-1** at 10 mg/ml in $CHCl_3$.

S9. Polystyrene-Polysiloxanes block polymer:

Styrene (2.08 g, 20 mmol) was dissolved in anhydrous THF (20 mL) and initiated with 0.8 mL sec-butyllithium (1 mmol, 1.3 M solution in cyclohexane) at -78 ℃ under N_2 atmosphere for 30 minutes. The solution was then warmed up to ambient temperature, and **HBP-1** (0.69 g) in 5 mL THF solution was added into the reactor. After 3 h, the polymerization was terminated with excessive trimethylchlorosilane (TMCS). After removing LiCl precipitate the product was dried under vacuum 3 h at 150 ℃, the product polymer **PSt-HBP-1** was purified by precipitation in methanol/CH_2Cl_2 mixtures with an isolation yield around 70%. The structure of **PSt-HBP-1** was estimated as the following based $^1H/^{29}Si$-NMR and GPC analysis.



The structure of **PSt-HBP-1**

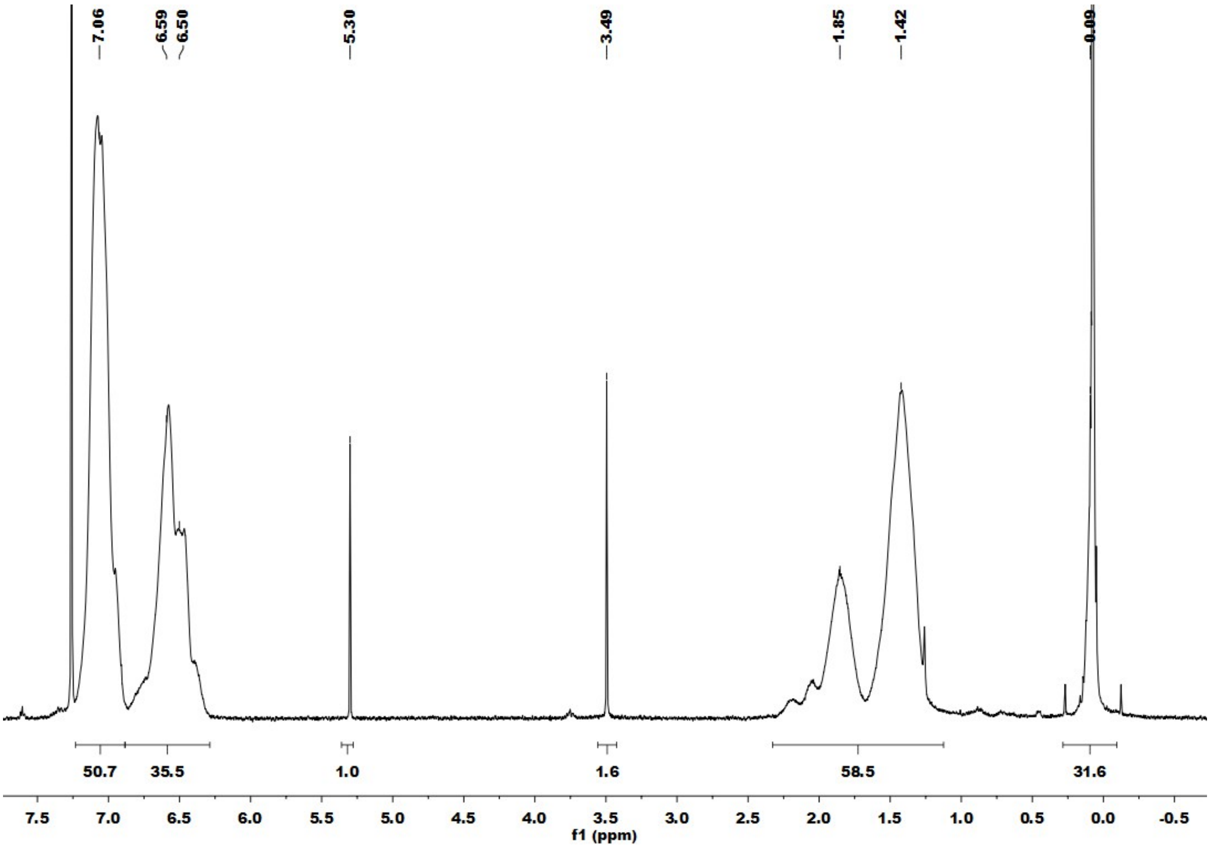


Fig. S14 ^{1}H-NMR of **PSt-HBP-1**. The peaks at 7.26, 5.3 and 3.5 ppm refer to the residues of $CHCl_3$, CH_2Cl_2 and MeOH.

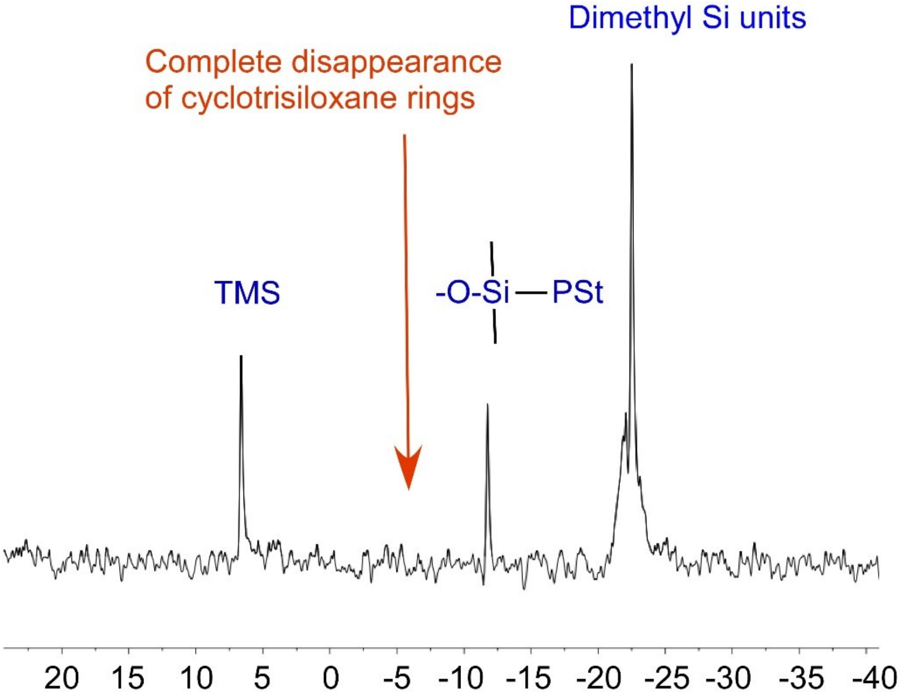
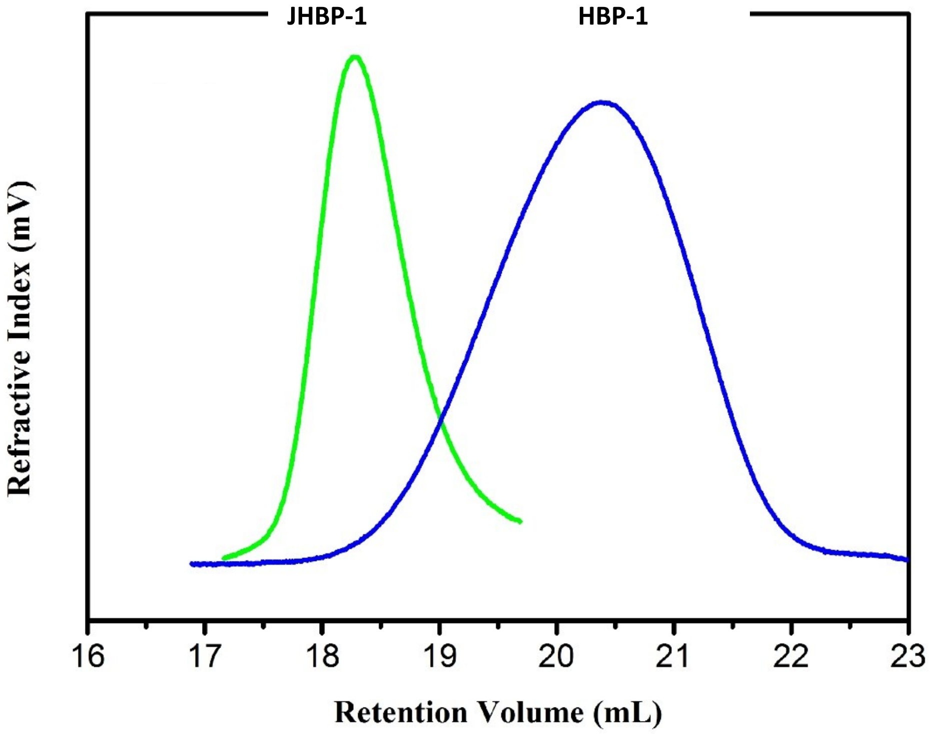


Fig. S15 ^{29}Si-NMR of **PSt-HBP-1**. The peak at 6.25 ppm correspond to the terminating Me_3Si groups and the peak at -11 ppm correspond to the D Si atom where the polystyrene arm is attached. The ratio of these two peaks matches the theoretical value of 1. The complete disappearance of peaks at -7 ppm indicate the complete ring opening by the polystyrene arms.



	Mn	Mw	PDI	Rh	Mark-Houwink a	Mark-Houwink logK
PSt-HBP-1	93,592	99,686	1.065	6.872 nm	0.669	-4.024

Fig. S16 GPC curve comparison between **HBP-1** and **PSt-HBP-1** and the relative result. The blue line for **HBP-1** was added for a visual comparison of the PDI reduction.

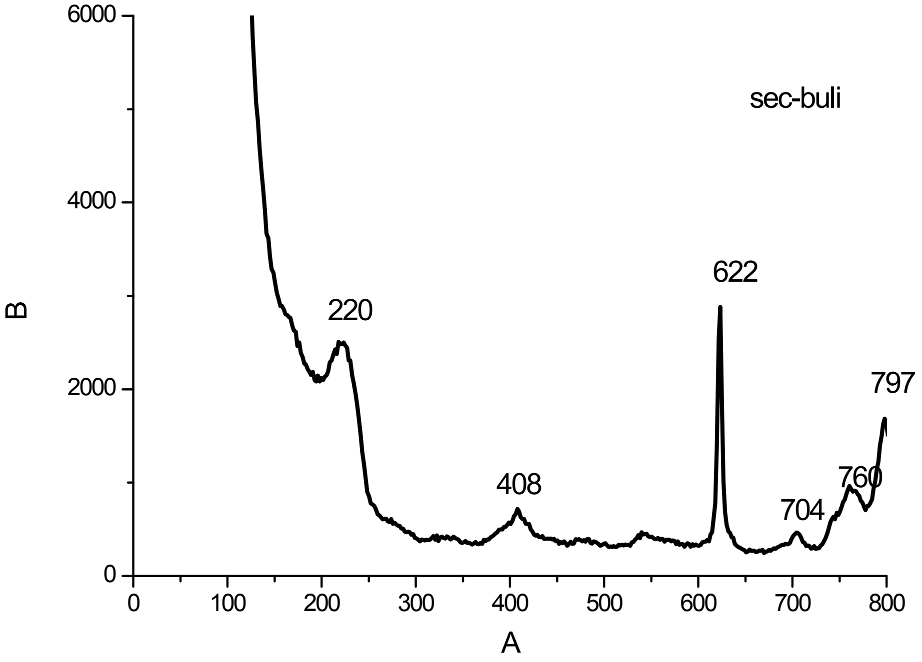


Fig. S17 Raman spectrum of **PSt-HBP-1**. The two peaks at 449 and 595 cm^{-1}, corresponding to the breathing modes of silicon and oxygen atoms in the cyclotrisiloxane rings, disappeared after the attachment of the polystyrene arms.

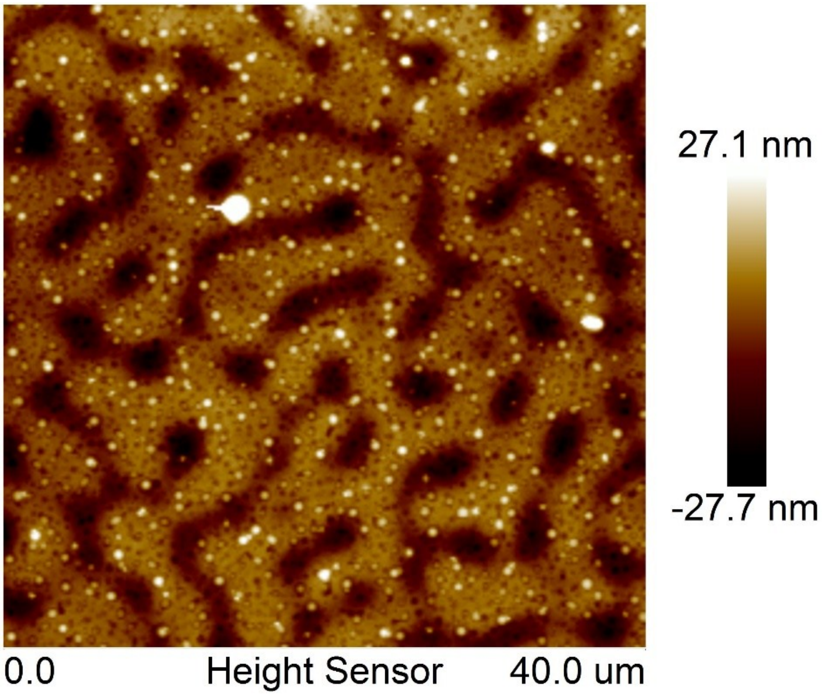


Fig. S18 The observed phase separation in addition to the cyclic assembly described in Figure 5 in the main text for **JHBP-1**.

S10. Other files

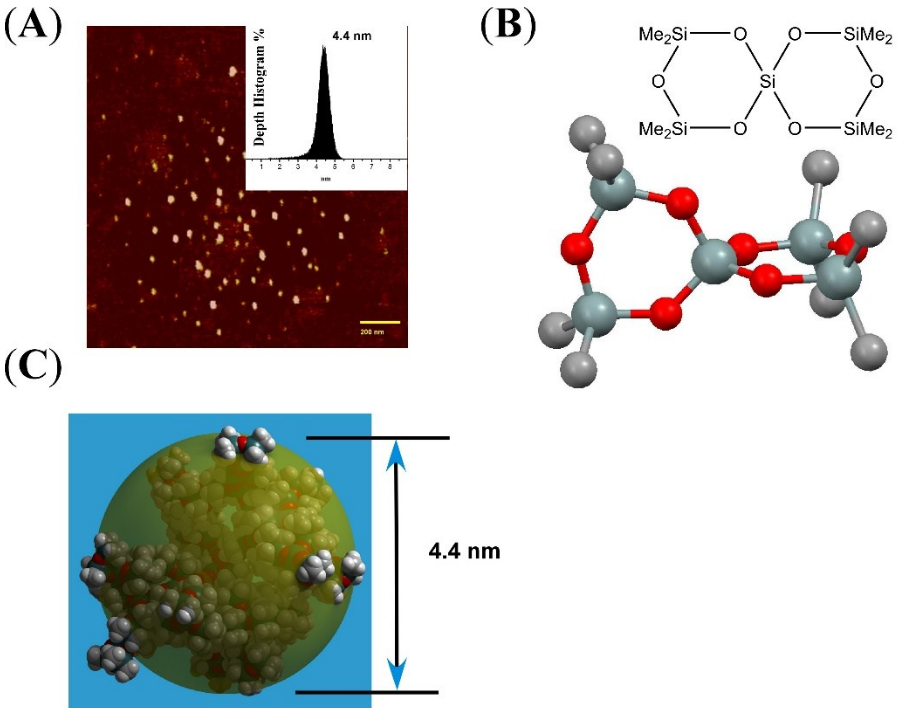


Fig. S19 (A) AFM image of **HBP-1** dispersed on the surface of mica with the depth histogram of the particles (the height of the particles). (B) Crystal structure of the solid isolated from the crude mixture. (C) The simulated molecular structure in scheme 1 with the van der waals surface shown. One dummy atom is placed at the central atom position and then its radius is gradually increased until the van der Waals surface of it encapsulates the majority of the atoms, and therefore the size of the dummy atom will be the same as that of the structure of **HBP-1**.

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[1] T. B. Casserly, K. K. Gleason, *J. Phys. Chem. B.,* 2005, ***109***, 13605-13610.