

Electronic Supplementary Information for:

Engineering the Morphology of Hydrogen-Bonded Comb-Shaped Supramolecular Polymers: From Solution Self-Assembly to Confined Assembly

Senbin Chen,^{*a} Zhen Geng,^a Xihuang Zheng,^a Jiangping Xu,^a Wolfgang H. Binder,^{*b} Jintao

Zhu^{*a}

^a Key Laboratory of Materials Chemistry for Energy Conversion and Storage of Ministry of Education (HUST), School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China

^b Chair of Macromolecular Chemistry, Faculty of Natural Science II (Chemistry, Physics and Mathematics), Martin Luther University Halle-Wittenberg, von-Danckelmann-Platz 4, Halle (Saale) D-06120, Germany.

Correspondence to: jtzhu@mail.hust.edu.cn (J. Z.)

wolfgang.binder@chemie.uni-halle.de (W. H. B.)

senbin@hust.edu.cn (S. C.)

Table of Contents:

Materials.....	S3
Characterization methods	S3
Synthesis of Ba-functionalized styrene (BaSt, Figure S1)	S4
Self-initiated RAFT copolymerization of St with BaSt to afford P(St-co-BaSt)	S6
Preparation of supramolecular polymer particles via emulsion-solvent evaporation method ...	S7
References.....	S8

Materials

All chemicals were purchased from Alfa Aesar or Sigma-Aldrich. Styrene was purified by vacuum distillation at room temperature. Unless otherwise indicated, the other chemicals were used without further purification. The Hamilton wedge functionalized PDMS (e.g., HW-PDMS) was synthesized according to our previous report.¹

Characterization methods

¹H and ¹³C NMR spectra were recorded on a Varian unity Inova 500 (500 MHz) NMR spectrometer using CDCl₃, DMSO-d₆ or THF-d₈ as solvent.

Polymers were analyzed by size exclusion chromatography (SEC), running in THF at 35°C (flow rate: 1 mL·min⁻¹) and recorded on a GPCmax VE 2001 from Viscotek™, equipped with a column set of a H_{HR}-H Guard-17369 column, a CLM30111 column and a G2500H_{HR}-17354 column. The number-average molecular weight of all the polymers was derived from a calibration curve based on polystyrene using IR signal.

Transmission electron microscopy (TEM) analyses were conducted with an HT7700 electron microscope with a CCD camera operating at an acceleration voltage of 120 kV. The samples (~5 μL) were drop-casted onto a Cu grid coated with a carbon film and air-dried before the measurement.

Scanning electron microscopy (SEM) measurements were performed on an F-SEM (Nova Nano SEM 450) operated at an acceleration voltage of 10 kV. For preparing the samples for SEM, ~5 μL samples was drop-casted onto the silicon wafers.

Synthesis of Ba-functionalized styrene (BaSt, Figure S1)

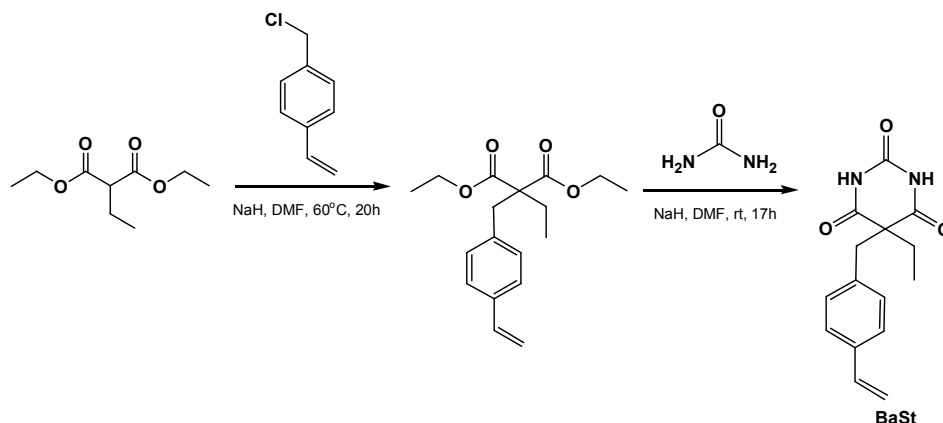


Figure S1: Synthetic route for the BaSt.

Sodium hydride (0.43 g of 60% dispersion in mineral oil, 10 mmol) was suspended in DMF (4 mL). Then, diethyl 2-ethylmalonate (2.1g, 11 mmol) was added dropwise at 0 °C. After the addition, the mixture was left stirring for 30 min until a clear, yellowish solution was obtained and no more gas release was observed. After cooling to 0 °C again, 4-chlorostyrene (1.5 g, 1.3 mL, 11 mmol) in DMF (5 mL) was added dropwise and the mixture was heated to 60 °C for 20 h; then, it was cooled to room temperature (rt) and water (40 mL) was added. The organic phase was extracted with diethyl ether (2 x 30 mL), washed with water (2 x 30 mL), and evaporated to afford a yellow oil **1** which was used directly for the next step without further purification.

Sodium hydride (1.20 g of a 60% w/w dispersion in mineral oil, 30 mmol) was added to DMF (5 mL), and the above solution was added dropwise a solution of urea (1.2 g, 19 mmol) in DMF (10 mL) at 0 °C. After the gas release, all the obtained **1** was dissolved in DMF (5 mL) and added dropwise. The mixture was then left stirring at rt during 17 h. Subsequently, NaHCO₃ solution (5 %) was added, following extracted with ethyl acetate (3 x 100 mL), and the organic phase was

collected and washed with a 1 M solution of hydrochloric acid (3 x 50 mL), dried with MgSO₄. The solvent was evaporated and the resulting BaSt as a white solid (0.6 g, 20 % yield for two steps).

¹H NMR (DMSO-d₆) δ (ppm): 11.36 (s, 2H), 7.35 (d, 2H), 6.96 (d, 2H), 6.69 (d, 1H), 6.65 (d, 1H), 5.80 (d, 1H), 5.23(d, 1H), 3.07 (s, 2H), 1.96 (q, 2H), 0.75 (t, 3H).

¹³C NMR (DMSO-d₆) δ (ppm): 172.92, 149.80, 136.58, 136.49, 135.44, 129.87, 126.59, 114.74, 58.20, 43.97, 31.92, 9.62.

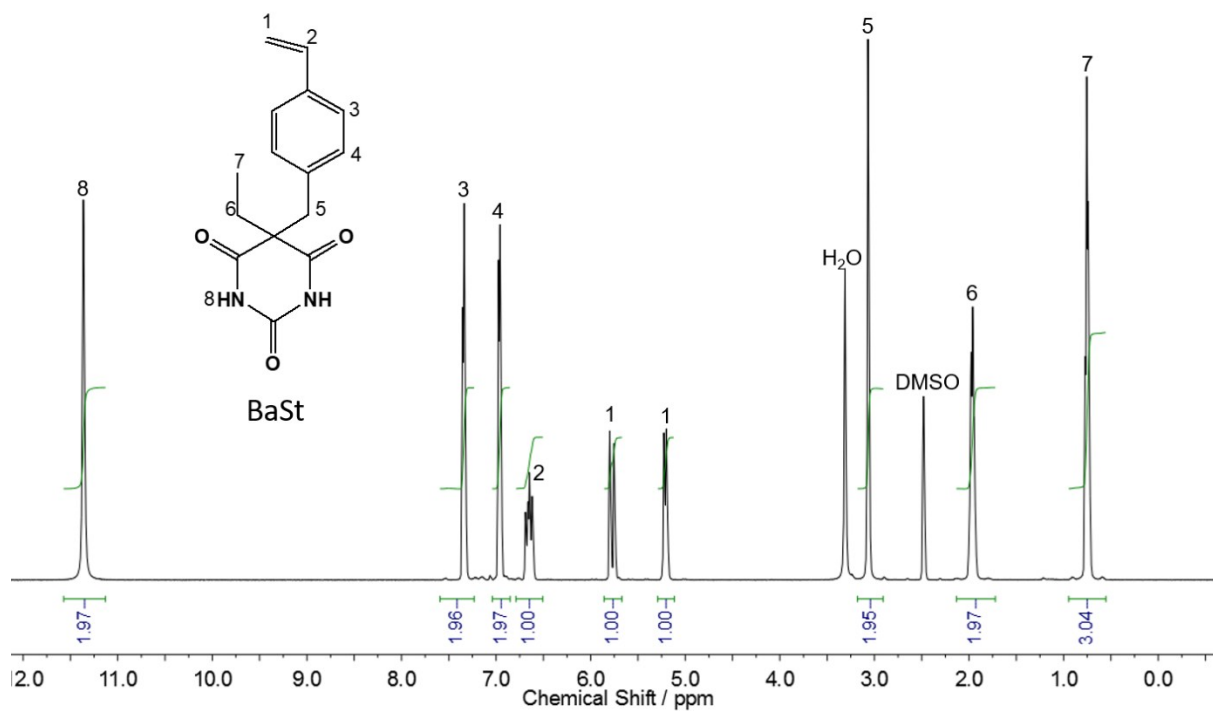


Figure S2: ¹H NMR of BaSt recorded in DMSO-d₆ at 27 °C.

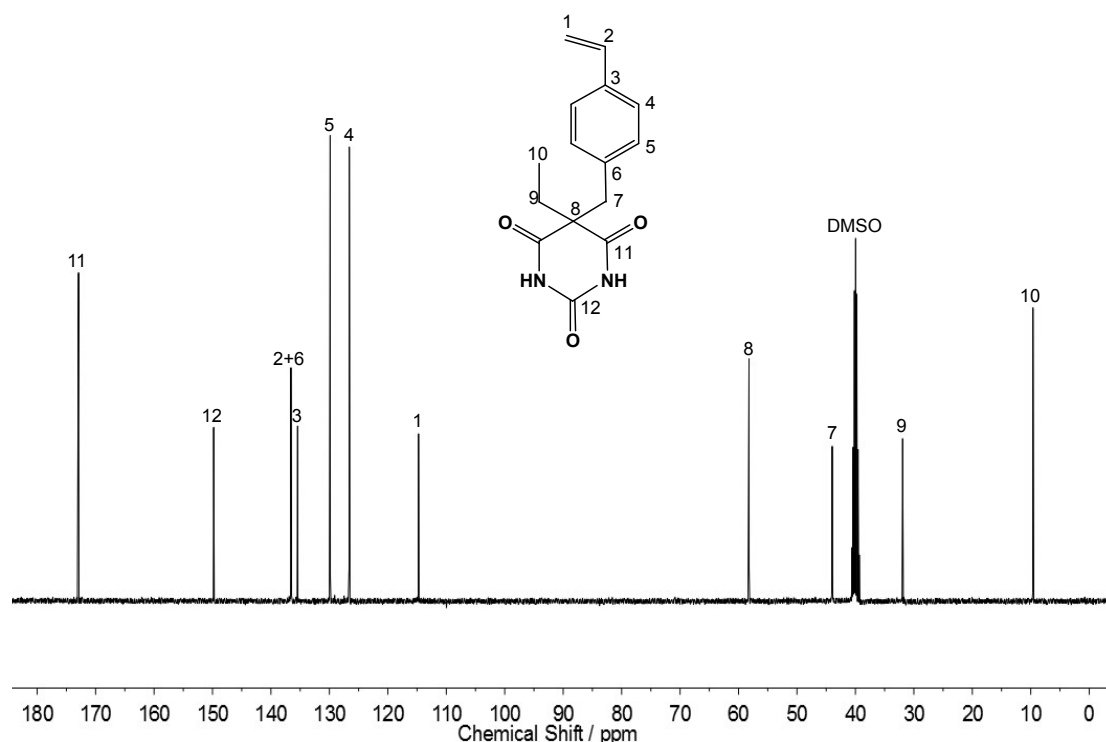


Figure S3: ^{13}C NMR of BaSt recorded in DMSO-d_6 at 27 °C.

Self-initiated RAFT copolymerization of St with BaSt to afford P(St-co-BaSt)

The copolymerization of St with BaSt was carried out using DBTTC as chain transfer agent at 120 °C without initiator. Typically, solution copolymerization of St (1.04 g, 1.14 mL, 1.0×10^{-2} mol) with BaSt (0.272 g, 1.0×10^{-3} mol) was carried out using DBTTC (5.8 mg, 2.0×10^{-5} mol) and DMF (1.2 mL), both as solvent and also as internal reference for the measurement of co-monomer consumption via ^1H NMR. A stock solution was typically transferred into a flask sealed with rubber septum, deoxygenated by nitrogen bubbling for ~30 min at 0 °C, then immersed in an oil bath thermostated at 120 °C. The reaction was stopped by plunging the flask into liquid nitrogen. The polymer was subsequently precipitated twice into MeOH in order to eliminate residual co-monomer. The obtained copolymer was dried under vacuum and characterized by ^1H NMR and SEC. The final co-monomer molar ratio of the pure poly(St-co-BaSt) was finally evaluated by ^1H NMR (THF-d_8) from the relative integration of the characteristic methyl group protons from poly(BaSt) backbone ($\text{CH}_3\text{-CH}_2\text{-}$, 3mH, $\delta = 0.8$ ppm, with m being the degree of polymerization), the characteristic aromatic protons of the poly(St) backbone and characteristic

aromatic protons of DBTTC (phH , $(5n + 5)H$, $\delta = 5.8 - 7.3$ ppm, with n being the degree of polymerization).

Table S1: Properties of the RAFT-made P(St-co-BaSt) copolymers.

Sample	CTA	[M]/		Time h	Conv ^b %	F_{BaSt}^c	$M_{n, th}^d$	$M_{n, NMR}^e$	$M_{n, SEC}^f$	\bar{D}^f
		[CTA]	f_{BaSt}^a				g/mol	g/mol	g/mol	
P(St ₆₀ -co-BaSt ₆)	DBTTC	550	0.091	5	12.0	0.091	8100	6500	5800	1.38
P(St ₉₄ -co-BaSt ₉)	DBTTC	550	0.091	10	21.9	0.090	14300	12600	11700	1.38
P(St ₁₅₃ -co-BaSt ₁₅)	DBTTC	550	0.091	15	34.0	0.090	22200	20400	19500	1.35
P(St ₁₈₁ -co-BaSt ₁₈)	DBTTC	550	0.091	20	40.8	0.089	26700	24100	23800	1.33

Note: ^a: Initial molar fraction of BaSt in the co-monomer mixture. ^b: Overall co-monomer conversion from ¹H NMR. ^c: Molar fraction of BaSt in the final copolymers, P(St-co-BaSt), calculated from ¹H NMR. ^d: Number-average molecular weight was evaluated from the following equation: $M_{n, th} = Conv \times ([M]/[CTA]) \times m_M + m_{CTA}$. ^e: Determined from relative integration of protons from ¹H NMR. ^f: From RI signals of SEC in THF (PS calibration).

Preparation of the supramolecular polymer particles via the emulsion-solvent evaporation method

The supramolecular polymer particles were prepared by using the emulsification method,² followed by the solvent evaporation at 30 or 90 °C, respectively. P(St₁₈₁-co-BaSt₁₈) and HW-PDMS₇₈ were mixed together with desired molar ratio (1/1, 3/1, 6/1 and 10/1, respectively), and then the P(St₁₈₁-co-BaSt₁₈)/HW-PDMS₇₈ mixture was dissolved in chloroform with the concentration of 10 g/L, followed by the stirring overnight to complete the hydrogen bonding association. Subsequently, 0.1 mL of the prepared P(St₁₈₁-co-BaSt₁₈)/HW-PDMS₇₈ solution

was emulsified with 1.0 mL of PVA aqueous solution (3 g/L) by ultrasonication (total time: 5 min) in a vial placed in the ice-water bath. Chloroform was then allowed to evaporate in an open vial at 30 °C for 24 h or 90 °C for 2 h, eventually leading to the solidification of polymers and segregation of the building blocks within the confined spaces. The particles were thus obtained through centrifugation of the resulting suspension to eliminate the redundant PVA, and finally the obtained particles were dispersed in distilled water and subjected to TEM and SEM investigations. To selectively remove the HW-PDMS building block, the particles were dispersed in excess hexane (1mL) under sonication for 1 h; then, centrifugation was applied to remove hexane and HW-PDMS₇₈, washed with hexane for 2 times. The particles were then dispersed in distilled water again and subjected to TEM and SEM investigations. In order to elucidate the effect of H-bonding on the internal structures, the particles (**Figure S4**) generated from pristine P(St₁₈₁-co-BaSt₁₈) was prepared under the same procedure except without adding HW-PDMS₇₈.

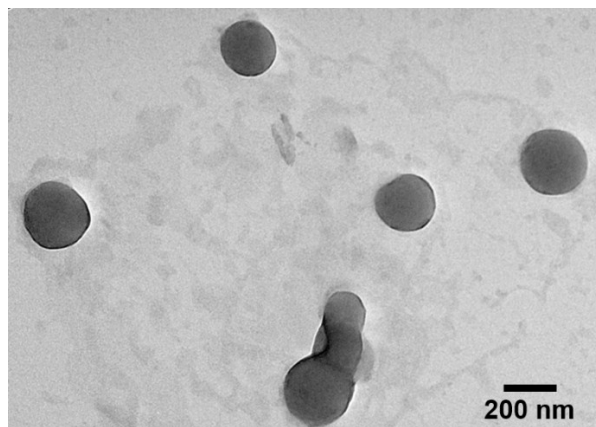


Figure S4: TEM image of pristine P(St₁₈₁-co-BaSt₁₈) under the 3D confinement.

References

- (1) S. Chen, T. Yan, M. Fischer, A. Mordvinkin, K. Saalwächter, T. Thurn-Albrecht, W. H. Binder, Opposing Phase-Segregation and Hydrogen-Bonding Forces in Supramolecular Polymers. *Angew. Chem. Int. Ed.*, 2017, **56**, 13016.
- (2) H.-Q. Peng, J.-F. Xu, Y.-Z. Chen, L.-Z. Wu, C.-H. Tung, Q.-Z. Yang, Water-dispersible nanospheres of hydrogen-bonded supramolecular polymers and their application for mimicking light-harvesting systems. *Chem. Commun.*, 2014, **50**, 1334.