Supporting Information

Synthesis and visualization of molecular brush-*on*-brush based hierarchically branched structures

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Contents:

1. Materials

Methyl methacrylate (MMA, 99.8+%, TCI), 2-(trimethylsilyloxy)ethyl methacrylate (HEMA-TMS, 96%, Aldrich), *n*-butyl acrylate (*n*BA, 99+%, TCI), *tert*-butyl acrylate (*t*BA,98+%, TCI), methyl acrylate (MA, 99+%, TCI), benzyl methacrylate (BzMA, 96%, Aldrich), styrene (St, 99.5%, Acros) were passed through a basic alumina column to remove the inhibitors before use. Cumyl dithiobenzoate (CDB, 99%, Aldrich), 2-cyano-2-propyl benzodithioate (CPBDT, 97%, Aldrich), dimethylformamide (DMF, 99.5%, Acros), tetrahydrofuran (THF, HPLC grade, 99.9%, Aldrich), anisole (99%, Acros), $CuBr_2$ (99.999%, Aldrich), α-bromoisobutyryl bromide (BIBB, 98%, Aldrich), 2,6-di-tert-butylphenol (DTBP, 99%, Aldrich), tetrabutylammonium fluoride solution (TBAF, 1.0 M in THF, ~5% water contained, Aldrich), potassium fluoride (KF, 99+%, Aldrich), 4,4′-dinonyl-2,2′-dipyridyl (dNbpy, 97%, Aldrich), tris[2-(dimethylamino)ethyl]amine (Me_6TREN, 97%, Aldrich) and *N*,*N*′,*N*″,*N*‴-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were used as received. CuBr (99.999%, Aldrich) was purified according to previously reported procedure.[1] Copper wire (Cu^0, diameter 1.0 mm, 99.9+%, Aldrich) was cleaned by successive washing and sonication in the mixture of methanol and hydrochloric acid, methanol, and acetone, and stored in an inert atmosphere. 2,2′-Azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich) was recrystallized from methanol prior to use. Anhydrous THF (HPLC grade, 99.9%, Aldrich) was prepared from a J.C. Meyer solvent purification system. All other solvents were used as received.

2. Characterization

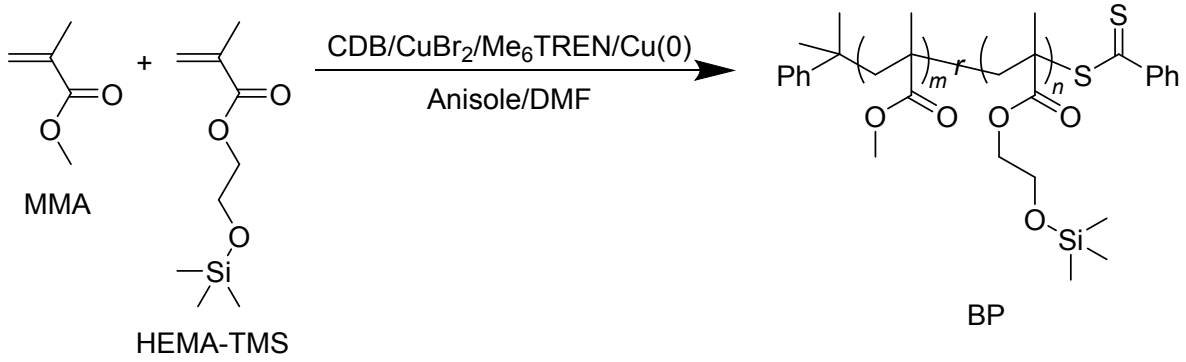
The molecular weight and dispersity were measured on a TOSOH Bioscience EcoSEC HKC08320 GPC with differential refractive index (RI) detector and a TSKgel GMHHR-M column. The measurements were run at a flow rate of 1 mL/min at 40 °C with THF solvent and the data were calibrated using linear polystyrene standards. AFM height images were acquired using a Bruker Dimension Fastscan AFM in “peak-force” mode with the FastScan-B tips from Bruker. AFM samples were prepared by spin-coating 20-100 μg/mL chloroform solution of polymers onto a freshly cleaved mica substrate. ^{1}H nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on an Agilent DD2 spectrometer (400 or 500 MHz) and chemical shifts were reported in ppm based on the solvent resonance standard (7.26 ppm for $CDCl_3$, 5.32 ppm for CD_2Cl_2, 3.31 ppm for CD_3OD).

3. Preparation of backbone precursor (BP)

Table S1. Structural parameters of BP.

Samples	m[a]	n[a]	$M_{n,GPC}$ ($\times 10^5$ Da)[b]	$M_{n,theo}$ ($\times 10^5$ Da)[c]	$Đ$[b]
BP-1	1021	113	1.22	1.25	1.18
BP-2[d]	1152	12	1.17	-	1.14

[a] m and n are the numbers of unit of MMA and HEMA-TMS, determined by ^{1}H-NMR, in the backbone, respectively. [b] The experimental number-average molecular weight ($M_{n,GPC}$) and dispersity ($Đ$) were obtained from THF GPC with linear polystyrene standard. [c] The theoretical number-average molecular weight ($M_{n,theo}$) was calculated according to equation: $M_{n,theo} = M_{n,MMA} \times m + M_{n,HEMA\text{-}TMS} \times n$, where $M_{n,MMA}$ and $M_{n,HEMA\text{-}TMS}$ are the molecular weight of MMA and HEMA-TMS, respectively. [d] The DPs were calculated from the polystyrene standard curves.



Scheme S1. Synthetic route to BP.

Synthesis of BP-1 (m = 1021, n = 113, Table S1). 304.5 mg of CDB (1.11 mmol) was dissolved in 15 mL of anisole, labeled as stock solution A; 5.0 mg of $CuBr_2$ (2.23×10^{-2} mmol) and 15.5 mg of Me_6TREN (6.71×10^{-2} mmol) were dissolved in 5 mL of DMF, labeled as stock solution B. 17.81 g of MMA (177.9 mmol), 4.0 g of HEMA-TMS (19.77 mmol), 1.3 mL of stock solution A (27.0 mg of CDB), 2.2 mL of stock solution B (2.2 mg of $CuBr_2$ and 6.8 mg of Me_6TREN) were fed into a 100 mL Schlenk flask. The mixture was deoxygenated through sparging with nitrogen for 30 min. A freshly cleaned Cu^0 wire (length of 25 cm and diameter of 1.0 mm) was added into the reaction flask under N_2 protection, followed by N_2 sparging for additional 15 min. The reaction proceeded in a 80 °C oil bath for 12 h. Aliquots were taken for the GPC and ^{1}H-NMR analyses. The monomer conversion determined by ^{1}H-NMR was 56.7%, offering BP-1, $PMMA_{1021}$-*r*-$P(HEMA\text{-}TMS)_{113}$, assuming an equal reactivity of MMA and HEMA-TMS in the free radical polymerization. The reaction media was quenched by adding THF and vigorous stirring to fully oxidize the remaining CuBr activator. The

solution was passed through a column filled with neutral alumina to remove catalyst before being precipitated in hexanes twice. The solid product was dried under vacuum. 11.5 g of BP-1 was obtained with an isolated yield of 53%. Results determined by THF GPC and ^{1}H-NMR were $M_{n,GPC}$ = 1.22×10^5 Da, $Đ$ = 1.18, $M_{n,theo}$ = 1.25×10^5 Da.

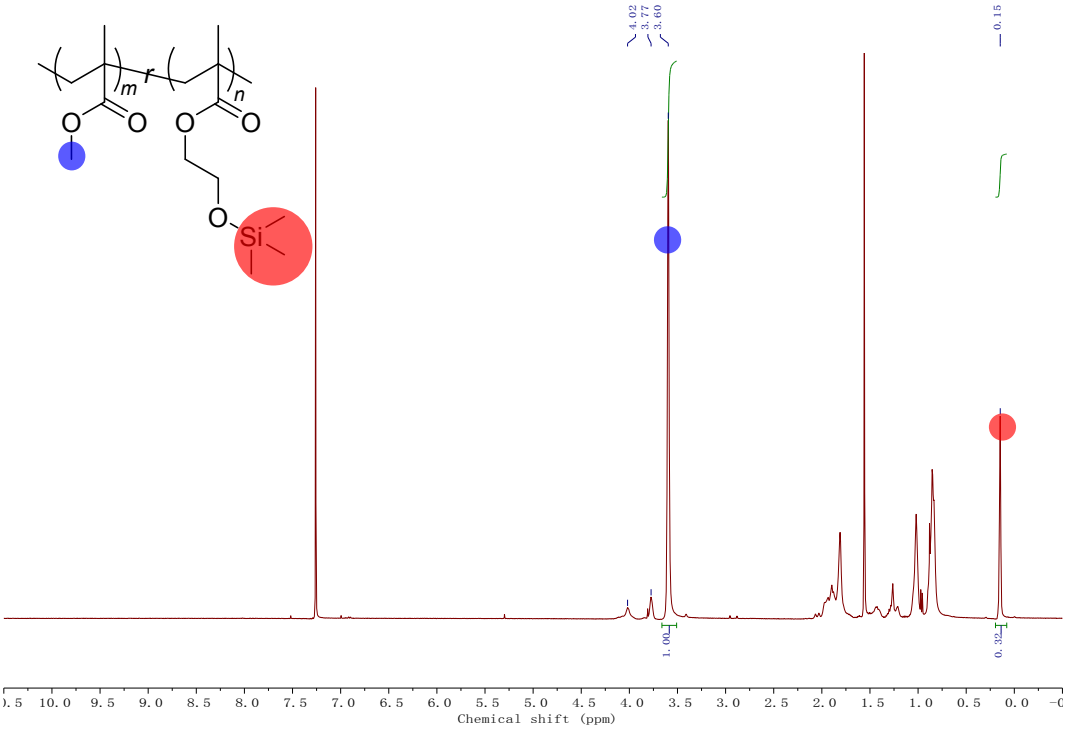


Figure S1. ^{1}H-NMR spectrum of BP-1 (m = 1021, n = 113, 400 MHz, $CDCl_3$).

Synthesis of BP-2 (m = 1152, n = 12, Table S1). 100 g of MMA (998.8 mmol), 2.0 g of HEMA-TMS (10.08 mmol), 44.7 mg of CPBDT (0.2 mmol), 3.3 mg of AIBN (2.01×10^{-2} mmol) and10 mL of toluene were added into a 250 mL Schlenk flask. The reaction medium was deoxygenated though sparging with nitrogen for 30 min. The reaction proceeded in a 65 °C oil bath for 19 h. Aliquots were taken for the GPC analysis. PMMA$_{1152}$-*r*-P(HEMA-TMS)$_{12}$ was determined from the polystyrene standard calibration curve, assuming an equal reactivity of MMA and HEMA-TMS in the free radical polymerization. The reaction solution was precipitated in hexane twice and the resulted solid polymers were dried under vacuum. 26.0 g of BP-2 was obtained with an isolated yield of 25.48%. Results determined by THF GPC were $M_{n,GPC}$ = 1.17×10^5 Da, $Đ$ = 1.18.

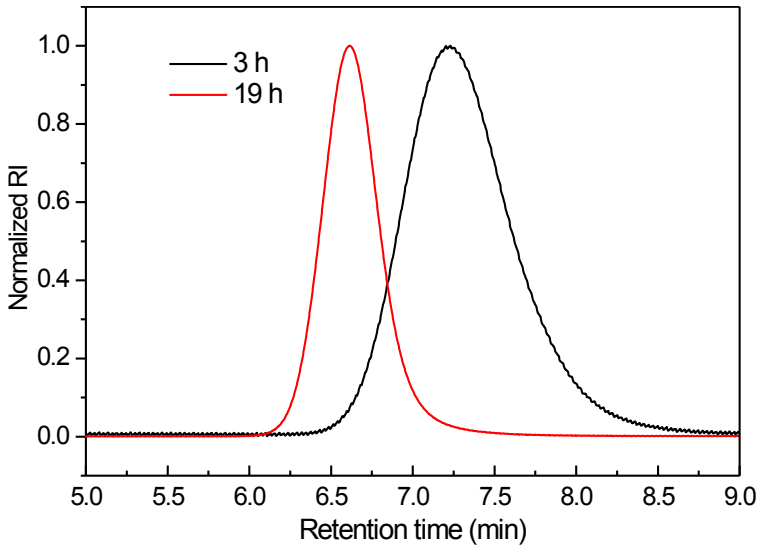


Figure S2. GPC traces during the synthesis of BP-2.

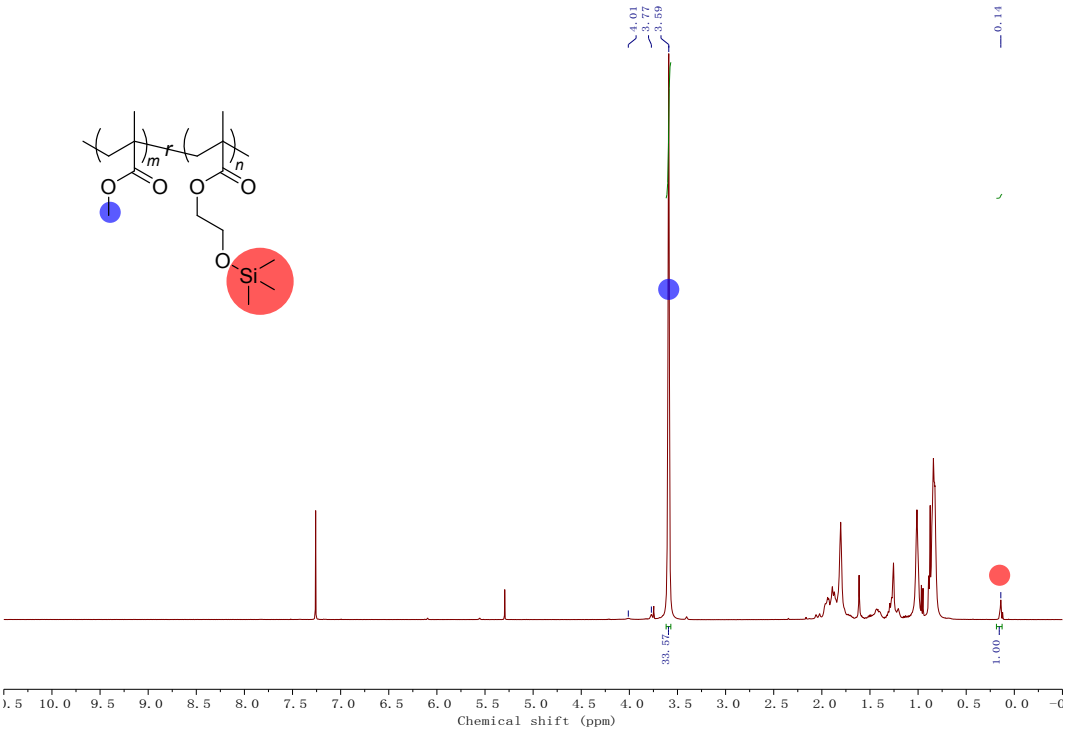


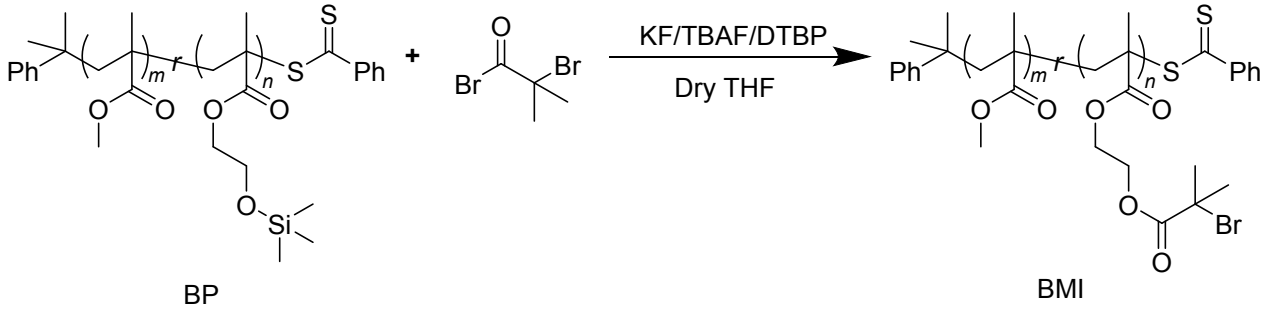
Figure S3. ^{1}H-NMR spectrum of BP-2 (m = 1152, n =12, 400 MHz, $CDCl_3$).

4. Preparation of backbone macroinitiator (BMI)

Table S2. Structural parameters of BMI.

Samples	m[a]	n[a]	$M_{n,GPC}$ ($\times10^5$ Da)[b]	$M_{n,theo}$ ($\times10^5$ Da)[c]	$Đ$[b]	Precursors[d]
BMI-1	1021	113	1.21	1.33	1.14	BP-1
BMI-2	1152	12	1.03	1.18	1.13	BP-2

[a] m and n are the numbers of unit of MMA and (2-bromoisobutyryloxy)ethyl methacrylate (BIBEM) in the backbone, respectively, because of the quantitative transportation from HEMA-TMS to BIBEM repeating units, determined by ^{1}H-NMR. [b] $M_{n,GPC}$ and $Đ$ were obtained from THF GPC with linear polystyrene standards. [c] Calculated according to equation: $M_{n,theo} = M_{n,MMA} \times m + M_{n,BIBEM} \times n$, where $M_{n,MMA}$ and $M_{n,BIBEM}$ are the molecular weight of MMA and BIBEM, respectively. [d] BMI-1 and BMI-2 were derived from BP-1 and BP-2, respectively.



Scheme S2. Synthetic route to BMI.

Synthesis of BMI-1 (m = 1021, n = 113, Table S2). 3.0 g of BP-1 (2.71 mmol of TMS group), 0.2 g of KF (3.52 mmol), 72.57 mg of DTBP (0.35 mmol), and 45 mL of dry THF were added in a 100 mL flask under nitrogen protection. 27 μL of TBAF solution (1 M in THF, 2.71×10^{-2} mmol TBAF) was added at 0 °C within 10 min and 1.67 mL of BIBB (13.55 mmol) was dropwise added within 5 min. The reaction was warmed up to room temperature and proceeded for 16 h. The solid was filtered out and the filtrate was precipitated into methanol/water (7/3 v/v). The polymer was re-dissolved in THF, and the solution was passed through a column filled with basic alumina before being precipitated in hexane twice. The solid product was dried under vacuum. 1.8 g of $PMMA_{1021}$-r-$P(BIBEM)_{113}$, i.e., BMI-1, product was obtained with 58% yield. Results determined by THF GPC and ^{1}H-NMR were $M_{n,GPC} = 1.21\times10^5$ Da, $Đ = 1.14$, $M_{n,theo} = 1.33\times10^5$ Da.

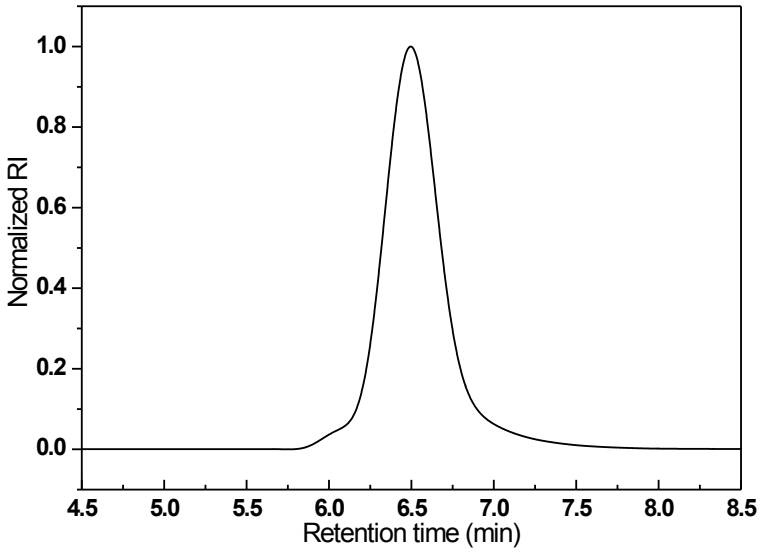


Figure S4. GPC trace of BMI-1.

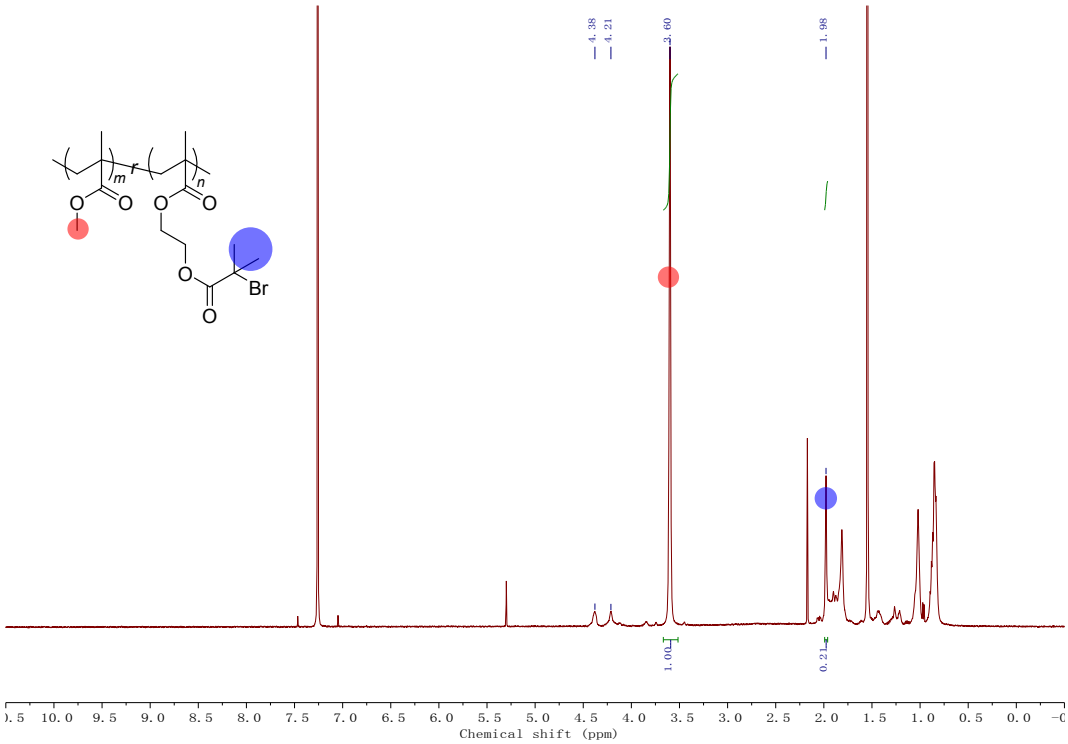


Figure S5. ^{1}H-NMR spectrum of BMI-1 (m = 1021, n =113, 400 MHz, $CDCl_3$).

Synthesis of BMI-2 (m = 1152, n = 12, Table S2). 9.7 g of BP-2 (1 mmol of TMS group), 75.8 mg of KF (1.3 mmol), 20.7 mg of DTBP (9.69×10^{-2} mmol) and 114 mL of dry THF were added in a 250 mL flask under nitrogen protection. 10 μL of TBAF solution (1 M in THF, 0.1 mmol of TBAF) was added at 0 °C within 10 min and 1.24 mL of BIBB (10 mmol) was dropwise added within 5 min. The reaction was warmed up to room temperature and proceeded for 16 h. The solid was filtered out and the filtrate was precipitated into methanol/water (7/3 v/v). The polymer was re-dissolved in THF, and

the solution was passed through a column filled with basic alumina before being precipitated in hexane twice. The solid product was dried under vacuum. The 5.9 g of $PMMA_{1152}$-*r*-$P(BIBEM)_{12}$, i.e., BMI-2, product was obtained with 59.97% yield. Results determined by THF GPC and ^{1}H-NMR were $M_{n,GPC}$ = 1.03×10^5 Da, $Đ$ = 1.13, $M_{n,theo}$ = 1.18×10^5 Da.

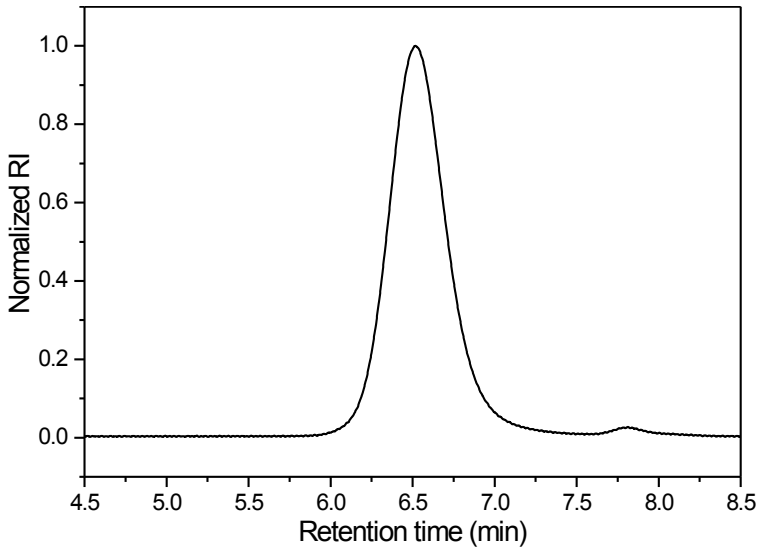


Figure S6. GPC trace of BMI-2.

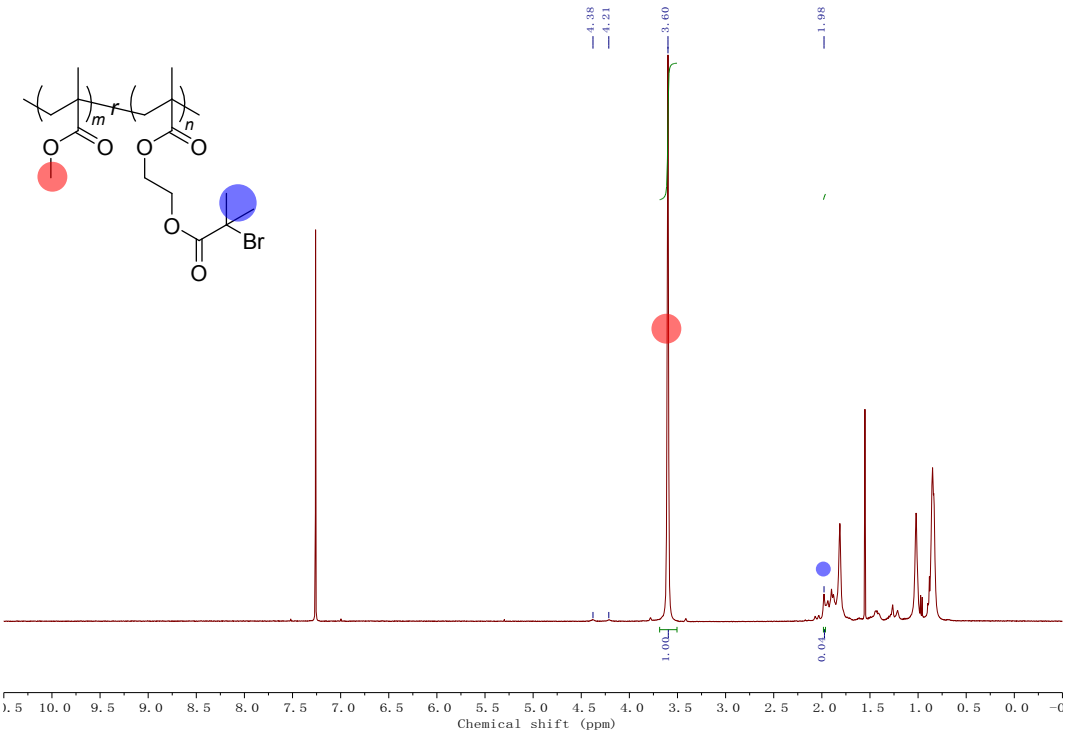


Figure S7. ^{1}H-NMR spectrum of BMI-2 (*m* = 1152, *n* =12, 400 MHz, $CDCl_3$).

5. Preparation of TMS-protected molecular brush (PMB) with primary side chains

Table S3. ATRP reaction conditions for the preparation of PMB.

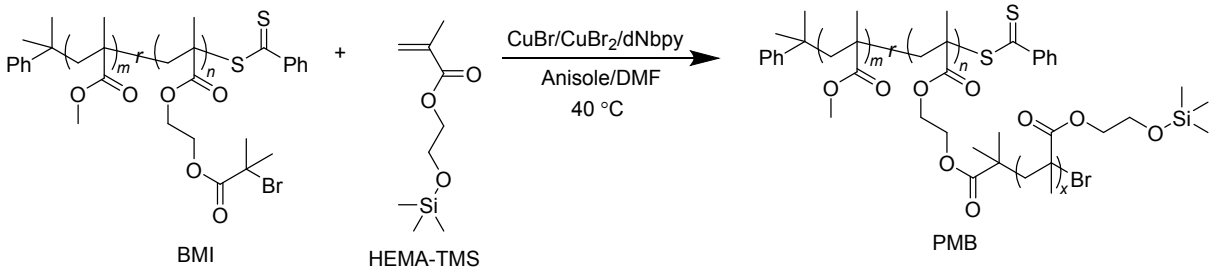
Samples[a]	MI[b]	$[M]_0$[c]	$[CuBr]_0$	$[CuBr_2]_0$	$[dNbpy]_0$	Time (min)	Conv.(%)[d]
PMB-1	BMI-1	600	1.2	0.4	3.2	160	5.48
PMB-2	BMI-1	855	1.6	0.4	4	150	7.50
PMB-3[c]	BMI-2	500	0.8	0.2	2	360	6.15

[a] All ATRP polymerizations of HEMA-TMS were carried out under nitrogen protection at 40 °C; Anisole/DMF/monomer = 0.1 mL/0.01 mL/1 g; The initial Br sites $[Br]_0$ in macroinitiator (MI) was denoted as 1. [b] Macroinitiator used for the preparation of molecular brush with primary side chains of TMS groups. [c] M represents the monomer, that is, HEMA-TMS. [d] The monomer conversion was determined by gravimetry.

Table S4. Structural parameters of PMB.

Samples	m[a]	n[a]	x[a]	$M_{n,GPC}$ ($\times 10^5$ Da)[b]	$M_{n,theo}$ ($\times 10^5$ Da)[c]	$Đ$[b]	Grafting density[d]
PMB-1	1021	113	33	3.94	8.88	1.14	0.1
PMB-2	1021	113	64	5.98	15.96	1.10	0.1
PMB-3	1152	12	30	1.67	1.91	1.15	0.01

[a] m and n are the numbers of unit of MMA and BIBEM in the backbone, respectively; x is the degree of polymerization (DP) of the primary side chains determined by gravimetry; [b] $M_{n,GPC}$ and $Đ$ were obtained from THF GPC with linear polystyrene standards. [c] Calculated according to the equation: $M_{n,theo} = M_{n,MMA} \times m + M_{n,BIBEM} \times n + M_{n,HEMA\text{-}TMS} \times x \times n$, where $M_{n,BIBEM}$ and $M_{HEMA\text{-}TMS}$ is the molecular weight of BIBEM and HEMA-TMS, respectively. [d] Grafting density of backbone = $n/(m+n)$.



Scheme S3. Synthetic route to PMB.

Synthesis of PMB-1 (m = 1021, n = 113, x = 33, Table S4). 243.8 mg of BMI-1 (0.2 mmol of Br), 25.0 g of HEMA-TMS (123.56 mmol), 269.3 mg of dNbpy (0.65 mmol), 18.4 mg of $CuBr_2$ (8.23×10^{-2} mmol), 2.5 mL of anisole and 0.25 mL of DMF were mixed in a 50 mL Schlenk flask. After three cycles of freeze-pump-thaw, 35.5 mg of CuBr (0.24 mmol) was added to the frozen reaction mixture.

The reaction flask was sealed and further deoxygenated by evacuation/back-filling with nitrogen three times. The reaction proceeded in a 40 °Coil bath for 2 h 40 min and the monomer conversion determined by gravimetry was 5.48%, offering the molecular brush PMB-1 with DP = 33 of primary side chains (P[MMA_{1021}-*r*-(BIBEM-*g*-HEMA-TMS_{33})$_{113}$]) by assuming 100% site-initiating efficiency in backbones. The reaction was quenched by cooling down to 0 °C and addition of aerated THF. The catalyst was removed by passing reaction mixture through a neutral alumina column. The crude product was transferred into 100 mL pre-weighed flask and followed by flushing air overnight to remove remaining monomer. The product was used for next step without further purification. Results determined by THF GPC and gravimetry were $M_{n,GPC}$ = 3.94×10^5 Da, $Đ$ = 1.14, $M_{n,theo}$ = 8.88×10^5 Da.

Note: BMIs have a dithioester moiety at one of the two chain ends, which will be further activated by CuBr during the preparation of PMBs, leading to an extra "primary side chain". Also, the dithioester moiety could statistically exist at every chain end, including chain ends of backbone and primary side chain. For simplicity, the dithioester moiety was shown at a backbone end and the dithioester-derived "side chain" was not shown in Scheme S3. Despite this, the proposed PMBs parameter was still valid. For example, the calculated DP of the primary side chain remained constant when the dithioester-derived "primary side chain" was included in the 113 primary side chains grown from initiating sites of BMI-1.

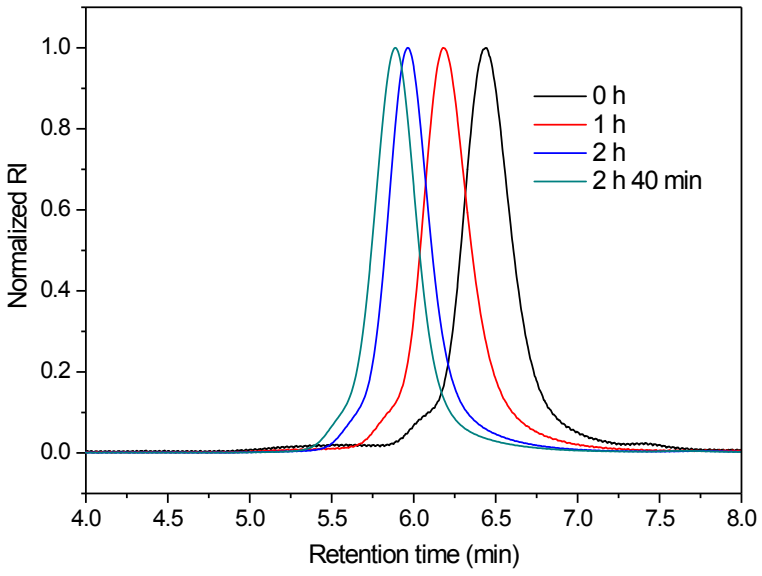


Figure S8. GPC traces during the synthesis of PMB-1.

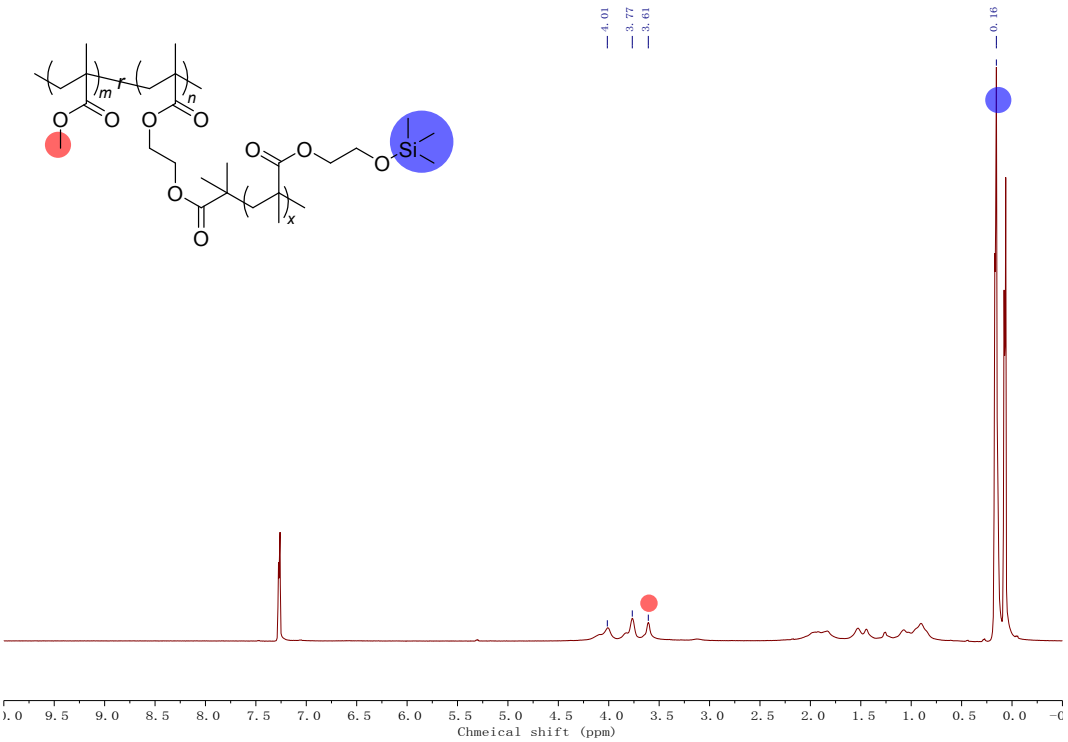


Figure S9. ^{1}H-NMR spectrum of PMB-1 (m = 1021, n = 113, x = 33, 400 MHz, $CDCl_3$).

Synthesis of PMB-2 (m = 1021, n = 113, x = 64, Table S4). 102.6 mg of BMI-1 (8.66×10^{-2} mmol), 15.0 g of HEMA-TMS (74.13 mmol), 151.5 mg of dNbpy (0.37 mmol), 8.3 mg of $CuBr_2$ (3.7×10^{-2} mmol), 1.6 mL of anisole and 0.16 mL of DMF were mixed in a 25 mL Schlenk flask. After three cycles of freeze-pump-thaw, 21.3 mg of CuBr (0.14 mmol) was added to the frozen reaction mixture. The reaction flask was sealed and further deoxygenated by evacuation/back-filling with nitrogen three times. The reaction proceeded in a 40 °C oil bath for 2.5 h and the monomer conversion determined by gravimetry was 7.5%, offering the molecular brush PMB-2 with DP = 64 of primary side chains (P[MMA_{1021}-*r*-(BIBEM-*g*-HEMA-$TMS_{64})_{113}$]) by assuming 100% site-initiating efficiency in backbones. The reaction was quenched by cooling down to 0 °C and addition of aerated THF. The catalyst was removed by passing reaction mixture through a neutral alumina column. The crude product was transferred into 100 mL pre-weighed flask and followed by flushing air overnight to remove remaining monomer. The product was used for next step without further purification. Results determined by THF GPC and gravimetry were $M_{n,GPC}$ = 5.98×10^5 Da, $Đ$ = 1.10, $M_{n,theo}$ = 1.59×10^6 Da

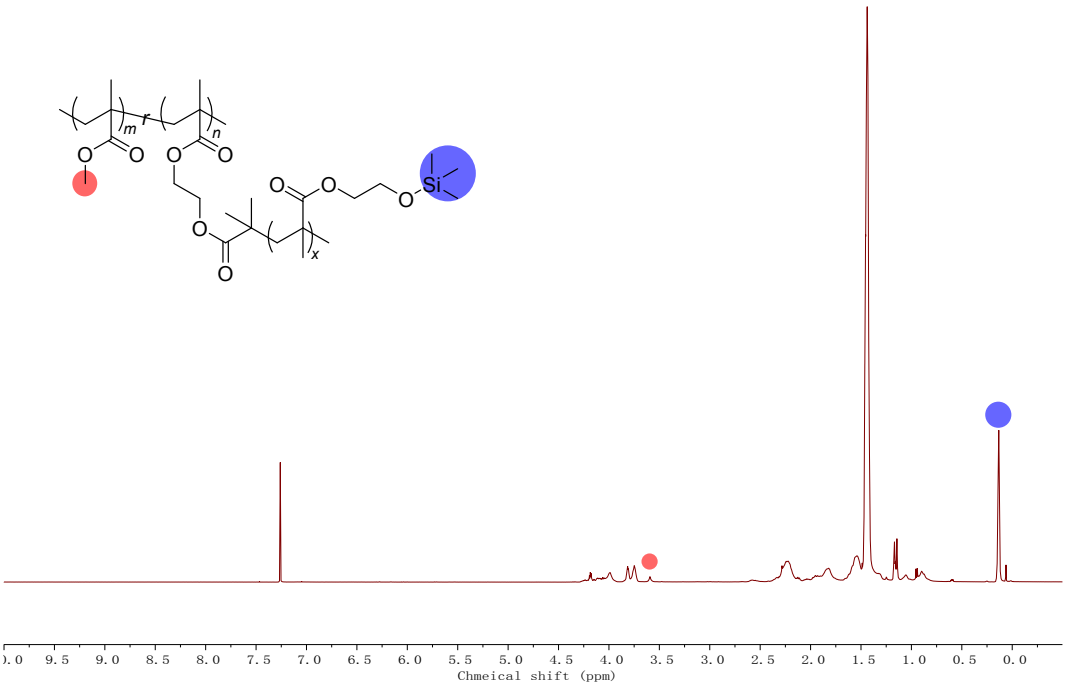


Figure S10. ^{1}H-NMR spectrum of PMB-2 (m = 1021, n = 113, x = 64, 400 MHz, $CDCl_3$).

Synthesis of PMB-3 (m = 1152, n = 12, x = 30, Table S4). 2.0 g of BMI-2 (0.19 mmol of Br), 20.0 g of HEMA-TMS (98.85 mmol), 161.6 mg of dNbpy (0.39 mmol), 8.8 mg of $CuBr_2$ (3.95×10^{-2} mmol), 20 mL of anisole were mixed in a 100 mL Schlenk flask. After three cycles of freeze-pump-thaw, 22.7 mg of CuBr (0.15 mmol) was added to the frozen reaction mixture. The reaction flask was sealed and further deoxygenated by evacuation/back-filling with nitrogen three times. The reaction proceeded in a 40 °C oil bath for 6 h and the monomer conversion determined by gravimetry was 6.15%, offering the molecular brush PMB-3 with DP = 30 of primary side chains (P[MMA_{1152}-*r*-(BIBEM-*g*-HEMA-TMS_{30})$_{12}$]) by assuming 100% site-initiating efficiency in backbones. The reaction was quenched by cooling down to 0 °C and addition of aerated THF. The catalyst was removed by passing reaction mixture through a neutral alumina column. The crude product was precipitated in hexane once. The product was used for next step without further purification. It should be noted that some monomers remained in the crude product according to ^{1}H-NMR. Results determined by THF GPC and gravimetry were $M_{n,GPC}$ = 1.67×10^5 Da, $Đ$ = 1.15, $M_{n,theo}$ = 1.91×10^5 Da.

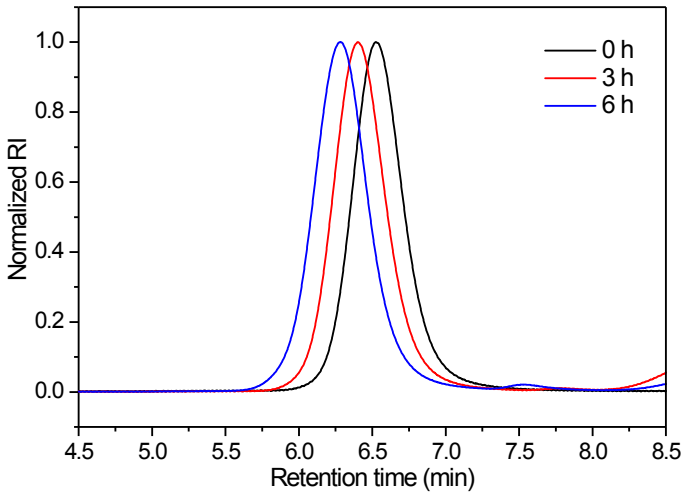


Figure S11. GPC traces during the synthesis of PMB-3.

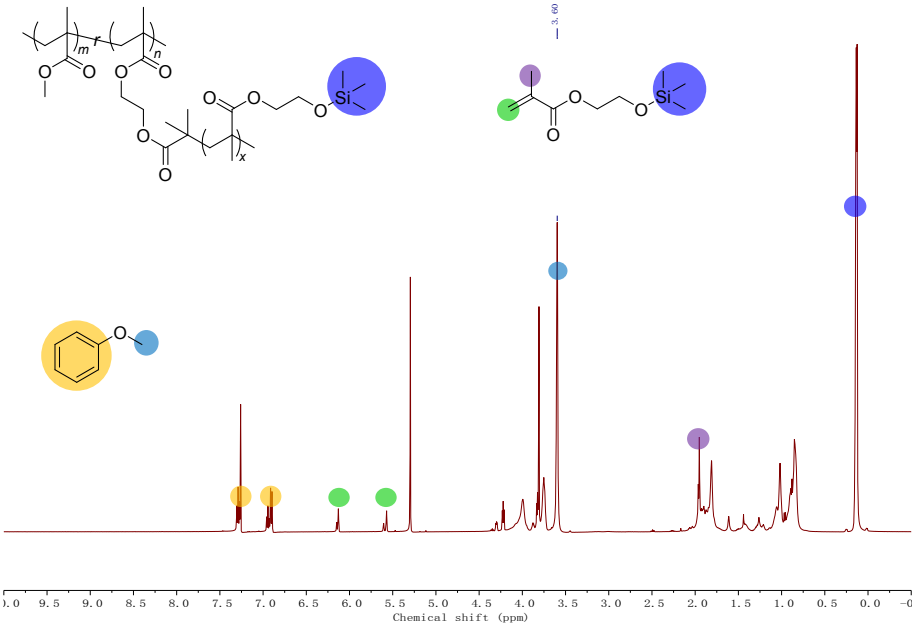


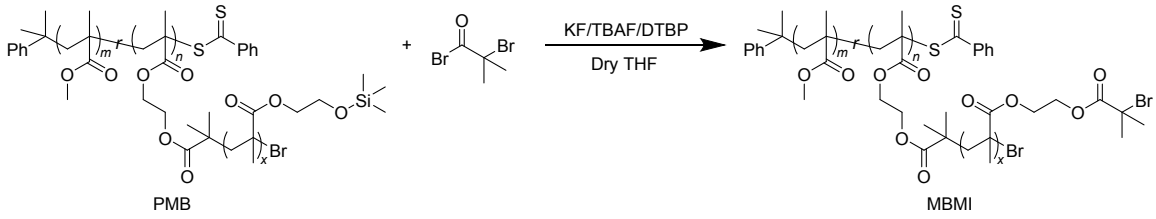
Figure S12. ^{1}H-NMR spectrum of PMB-3 with a little residual monomers and anisole (m = 1152, n = 12, x = 30, 400 MHz, $CDCl_3$).

6. Preparation of molecular brush macroinitiator (MBMI) with primary side chains

Table S5. Structural parameters of MBMI.

Samples	m^a	n^a	x^a	$M_{n,GPC}$ ($\times10^5$ Da)^b	$M_{n,theo}$ ($\times10^5$ Da)^c	$Đ^b$	Precursors^d
MBMI-1	1021	113	33	4.40	11.46	1.24	PMB-1
MBMI-2	1021	113	64	5.73	21.52	1.17	PMB-2
MBMI-3	1152	12	30	1.79	2.92	1.18	PMB-3

[a] m and n are the numbers of unit of MMA and BIBEM in the backbone, respectively; x is the DP of the primary side chains because of the quantitative transportation from HEMA-TMS to BIBEM derived repeating units, determined by ^{1}H-NMR; [b] $M_{n,GPC}$ and $Đ$ were obtained from THF GPC with linear polystyrene standards. [c] Calculated according to the equation: $M_{n,theo} = M_{n,MMA} \times m + M_{n,BIBEM} \times n + M_{n,BIBEM} \times x \times n$. [d] MBMI-1, MBMI-2 and MBMI-3 are derived from PMB-1, PMB-2 and PMB-3, respectively.



Scheme S4. Synthetic route to MBMI.

Synthesis of MBMI-1 (m = 1021, n =113, x = 33, Table S5). 2.7 g of PMB-1 (12.28 mmol of TMS group), 0.9 g of KF (15.96 mmol), 0.3 g of DTBP (1.59 mmol), and 27 mL of dry THF were added in a 50 mL flask under nitrogen protection. 122.8 μL of TBAF solution (1 M in THF, 0.122 mmol of TBAF) was added at 0 °C within 10 min and 7.6 mL of BIBB (61.44 mmol) was dropwise added over a course of 5 min. The reaction was allowed to warm up to room temperature and kept for 16 h. The reaction mixture was filtered, precipitated in methanol, passed through a neutral alumina column after being re-dissolved in THF and re-precipitated in hexane twice. The solid product MBMI-1 was obtained after drying under vacuum with the composition of P[MMA_{1021}-*r*-(BIBEM-*g*-$BIBEM_{33}$)$_{113}$] according to ^{1}H-NMR. Results determined by THF GPC and ^{1}H-NMR were $M_{n,GPC} = 4.40\times10^5$ Da, $Đ = 1.24$, $M_{n,theo} = 1.17\times10^6$ Da.

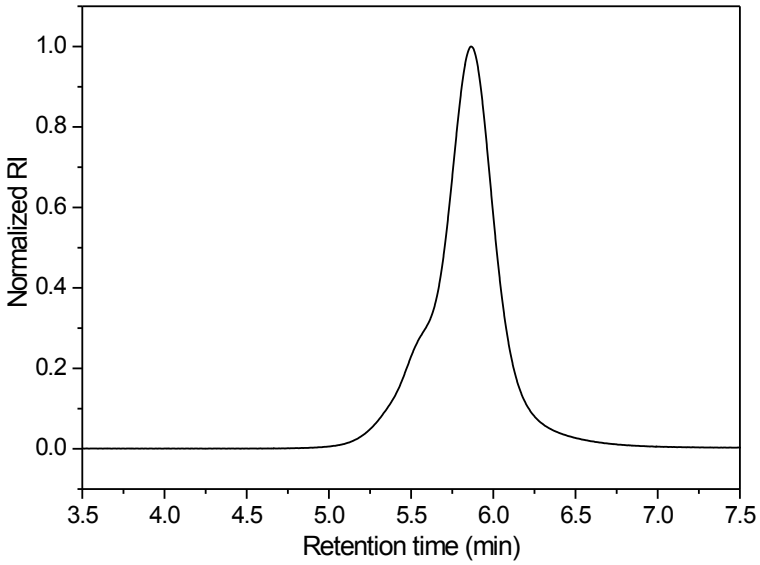


Figure S13. GPC trace of MBMI-1.

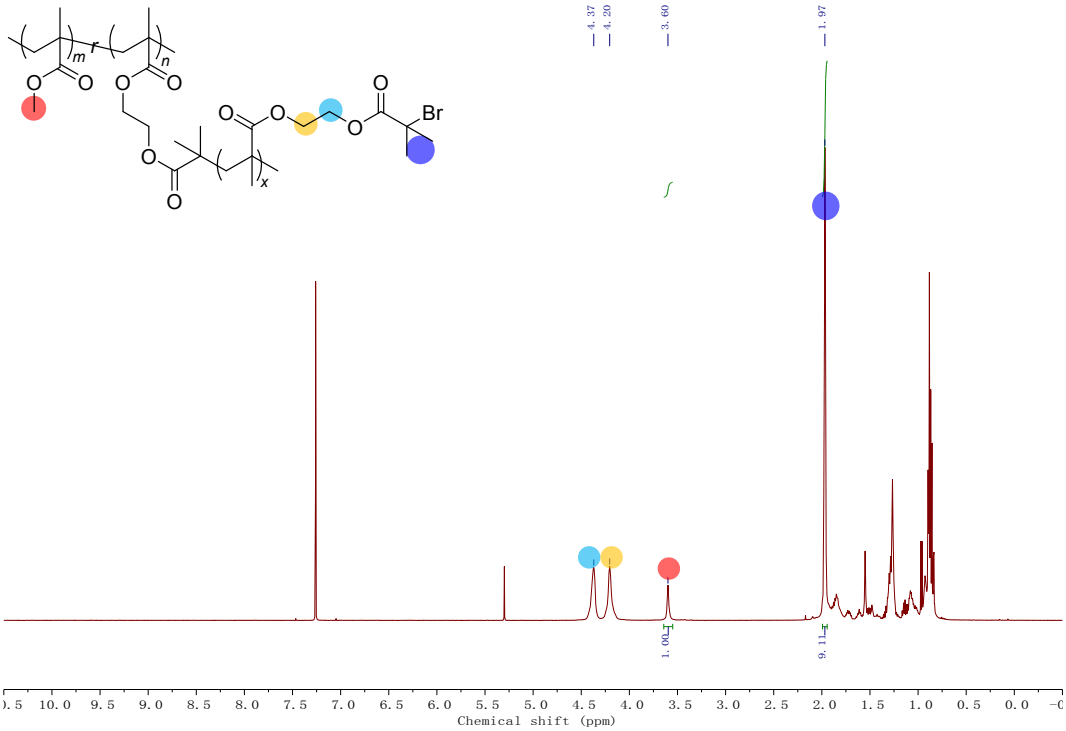


Figure S14. ^{1}H-NMR spectrum of MBMI-1 (m = 1021, n = 113, x = 33, 400 MHz, $CDCl_3$).

Synthesis of MBMI-2 (m = 1021, n =113, x = 64, Table S5). 1.8 g of PMB-2 (8.36 mmol TMS group), 0.6 g of KF (10.86 mmol), 0.2 g of DTBP (1.08 mmol), and 17 mL of dry THF were added in a 50 mL flask under nitrogen protection. 83.6 μL of TBAF solution (1 M in THF, 8.361×10^{-2} mmol TBAF) was added at 0 °C within 10 min and 5.2 mL of BIBB (41.8 mmol) was dropwise added over a course of 5 min. The reaction was allowed to warm up to room temperature and kept for 16 h. The reaction mixture was filtered, precipitated in methanol/water (7/3 v/v), passed through a neutral

alumina column after being re-dissolved in THF, and re-precipitated in hexane twice. The solid product MBMI-2 (0.7 g) was obtained after drying under vacuum with the composition of P[MMA_{1021}-*r*-(BIBEM-*g*-$BIBEM_{64}$)$_{113}$] according to ^{1}H-NMR. Results determined by THF GPC and ^{1}H-NMR were $M_{n,GPC}$ = 5.73×10^5 Da, $Đ$ = 1.17, $M_{n,theo}$ = 2.15×10^6 Da.

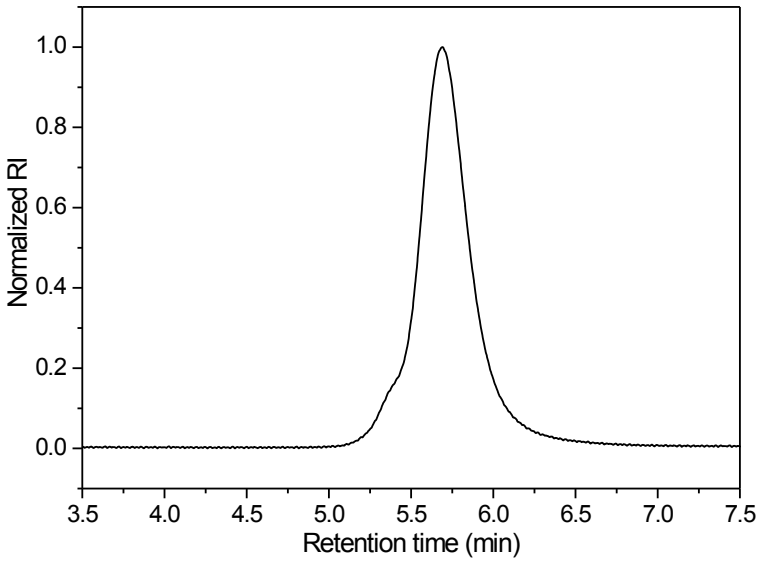


Figure S15. GPC trace of MBMI-2.

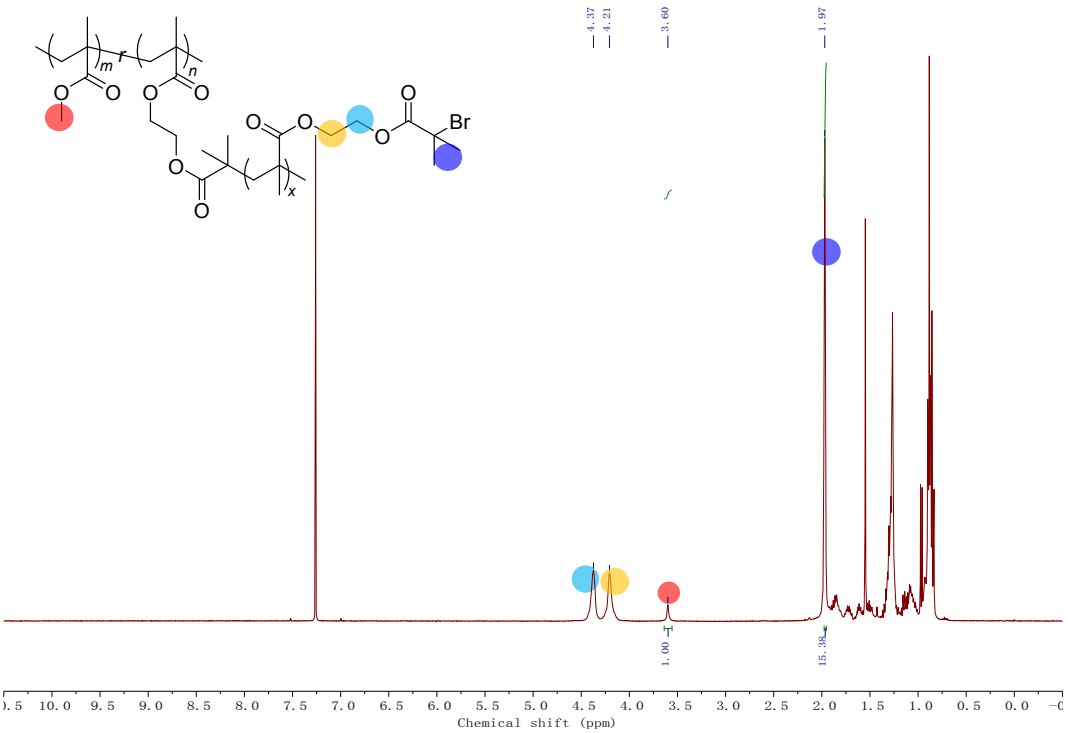


Figure S16. ^{1}H-NMR spectrum of MBMI-2 (*m* = 1021, *n* = 113, *x* = 64, 400 MHz, $CDCl_3$).

Synthesis of MBMI-3 (*m* = 1152, *n* =12, *x* = 30, Table S5). 3.9 g of PMB-3 (7.33 mmol TMS group), 0.6 g of KF (9.52 mmol), 0.2 g of DTBP (0.73 mmol), and then 40 mL of dry THF were added in a 100 mL flask under nitrogen protection. 73 μL of TBAF solution (1 M in THF, 7.33×10^{-2} mmol TBAF) was added at 0 °C within 10 min and 4.5 mL of BIBB (36.65 mmol) was dropwise added over a course of 5 min. The reaction was allowed to warm up to room temperature and kept for 16 h. The reaction mixture was filtered, precipitated in methanol, passed through a neutral alumina column after being re-dissolved in THF and re-precipitated in hexane twice. The solid product MBMI-3 (3.9 g) was obtained after drying under vacuum with the composition of P[MMA_{1152}-*r*-(BIBEM-*g*-$BIBEM_{30}$)$_{12}$] according to ^{1}H-NMR. Results determined by THF GPC and ^{1}H-NMR were $M_{n,GPC} = 1.79\times10^5$ Da, $Đ = 1.18$, $M_{n,theo} = 2.92\times10^6$ Da.

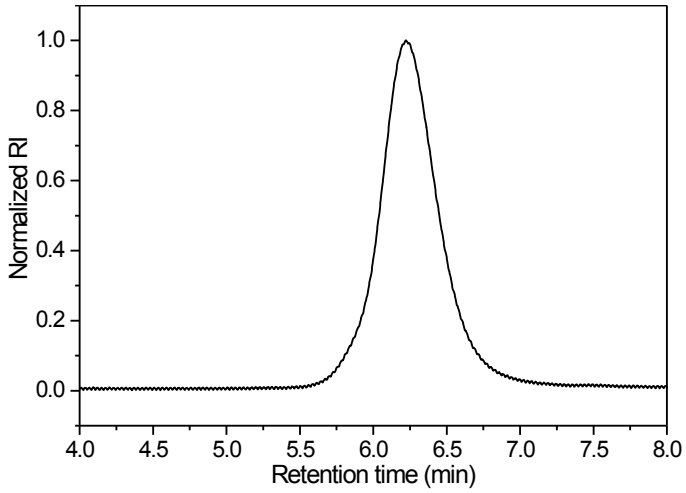


Figure S17. GPC trace of MBMI-3.

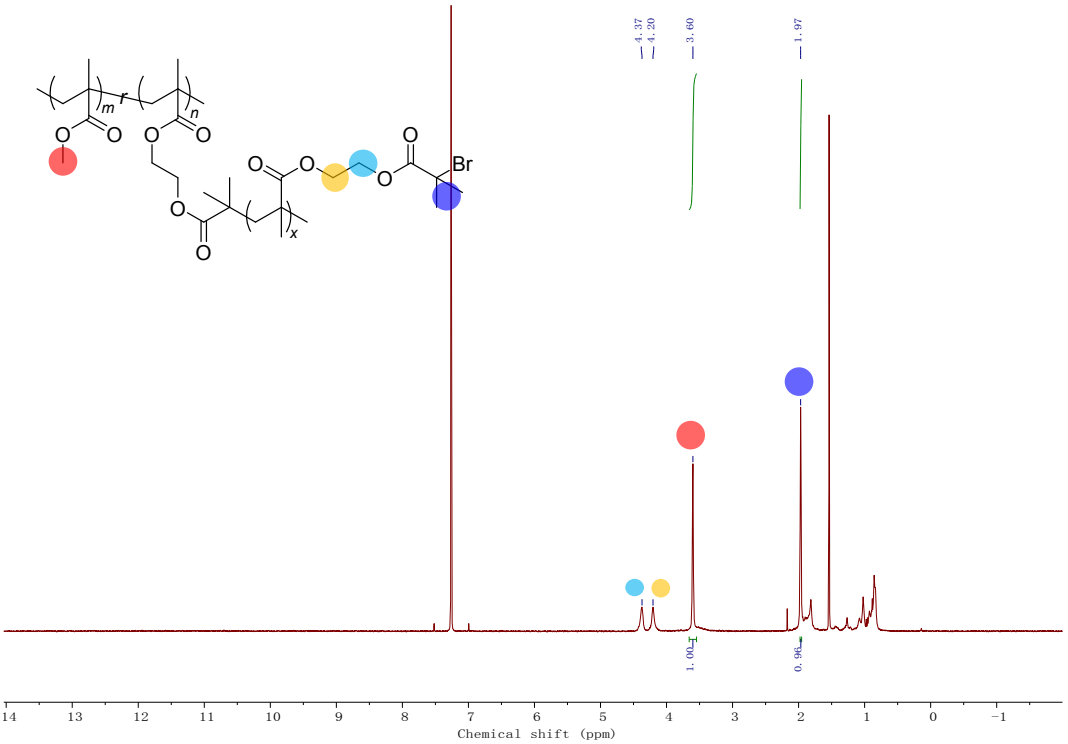


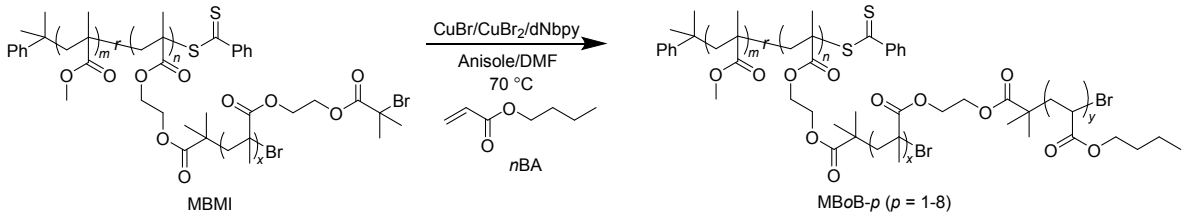
Figure S18. ^{1}H-NMR spectrum of MBMI-3 (m = 1152, n = 12, x = 30, 400 MHz, $CDCl_3$).

7. Preparation of molecular brush-*on*-brush (MB*o*B) with secondary side chains of polyacrylate

Table S6. ATRP reaction conditions for the preparation of MB*o*Bs.

Samples	I[a]	M[b]	Ligand	$[M]_0/[I]_0/[CuBr]_0/[CuBr_2]_0/[L]_0$	Anisole/DMF/M	T (°C)	Conv.(%)[c]	Time (h)
MB*o*B-1	MBMI-1	*n*BA	dNbpy	350/1/0.78/0.09/1.75	0.1/0.01/1	70	5.01	12.5
MB*o*B-2	MBMI-1	*n*BA	dNbpy	500/1/1.12/0.12/2.5	0.1/0.01/1	70	4.31	21
MB*o*B-3	MBMI-1	*n*BA	dNbpy	800/1/1.9/0.1/4	0.1/0.01/1	70	6.86	15.5
MB*o*B-4	MBMI-1	*n*BA	dNbpy	1500/1/1.9/0.1/4	0.1/0.01/1	70	4.73	41.5
MB*o*B-5	MBMI-2	*n*BA	dNbpy	357/1/1.35/0.15/3	0.1/0.01/1	70	6.18	20
MB*o*B-6	MBMI-2	*n*BA	dNbpy	238/1/0.54/0.08/1.54	0.1/0.01/1	70	11.34	16
MB*o*B-7	MBMI-2	*n*BA	dNbpy	476/1/1.8/0.2/4	0.1/0.01/1	70	7.60	24.5
MB*o*B-8	MBMI-2	*n*BA	dNbpy	800/1/1.9/0.1/4	0.1/0.01/1	70	5.73	20
MB*o*B 9	MBMI-3	*t*BA	PMDETA	1000/1/0.9/0.1/1	0.5/0.02/1	60	3.34	11
MB*o*B-10	MBMI-3	*t*BA	PMDETA	1000/1/0.9/0.1/1	0.5/0.02/1	60	5.29	23
MB*o*B-11	MBMI-3	MA	PMDETA	1000/1/0.9/0.1/1	0.5/0.02/1	65	9.20	8
MB*o*B-12	MBMI-3	BzMA	dNbpy	1000/1/0.8/0.2/2	0.5/0.02/1	40	3.87	3
MB*o*B-13	MBMI-3	MMA	dNbpy	1000/1/0.8/0.2/2	0.5/0.02/1	40	5.58	3
MB*o*B-14	MBMI-3	St	dNbpy	1000/0.9/0.1/2	0.5/0.02/1	90	1.42	3

[a] Macroinitiators; [b] Monomers.



Scheme S5. Synthetic route to MB*o*B-*p* (*p* = 1-8) with secondary side chains of poly(*n*BA).

Synthesis of MBoB-1 (*m* = 1021, *n* = 113, *x* = 33, *y* = 18, Scheme S5 and Table 1 in main text). 70.2 mg of MBMI-1 (0.22 mmol of Br), 10 g of *n*BA (78.02 mmol), 159.4 mg of dNbpy (0.39 mmol), 4.4 mg of $CuBr_2$ (1.95×10^{-2} mmol), 1 mL of anisole and 100 μL of DMF were mixed in a 25 mL Schlenk flask. The reaction mixture was subjected to three freeze-pump-thaw cycles and then 25.2 mg of CuBr (0.17 mmol) was added in the frozen reaction mixture during the final cycles. The reaction flask was further deoxygenated by cycles of evacuation/back-filling with nitrogen gas three times, and immersed in a 70 °C oil bath for 12.5 h. The monomer conversion determined by gravimetry was 5.01%, resulting in MB*o*B-1 with DP = 18 of the secondary side chains by assuming 100% site-initiating efficiency in the primary side chains. The polymer was purified by dialysis against acetone for 48 h and the solvent was refreshed every 12 h. The polymer product was obtained upon drying under vacuum at room temperature and the composition was P{MMA_{1021}-*r*-[BIBEM-*g*-(BIBEM-*g*-$nBA_{18})_{33}]_{113}$}. Results determined by THF GPC and gravimetry were $M_{n,GPC} = 1.07\times10^6$ Da, $Đ = 1.32$, $M_{n,theo} = 9.77\times10^6$ Da. The syntheses of MB*o*Bs-2, 3 and 4 were similar as just mentioned here.

Note: MBMIs have a terminal bromide group at every primary side chain end, which will be further activated by CuBr during the following preparation of MB*o*Bs, leading to an extra "secondary side chain". Also, the dithioester moiety could statistically exist at every chain end, including chain ends of backbone and primary/second side chain. For simplicity, the dithioester moiety was only depicted at a backbone end and the dithioester-derived "primary side chain" and primary side chain end-derived "secondary side chain" were not shown in Scheme S5.

Fraction of intermolecular coupling (f_{ic}) of representative MBoBs. To quantify the f_{ic} of representative MB*o*B-*p* (*p* = 1-3), the deconvolution of GPC curve for MB*o*Bs was conducted with the coefficient of determination (R^2), and the corresponding results were directly shown in Figure S19-21. $f_{ic} = [A_{sp}/(A_{sp} + A_{mp})]\times100\%$, where A_{sp} and A_{mp} represent the areas of the shoulder and main peaks, respectively.

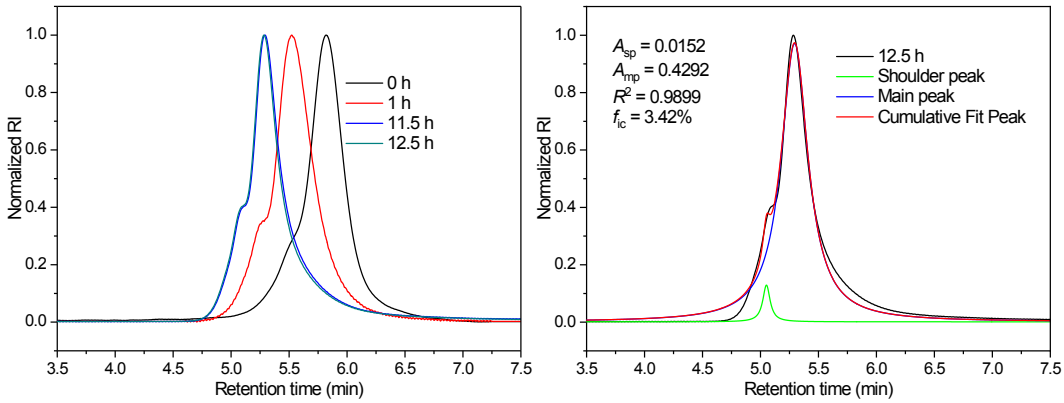


Figure S19. (a) GPC traces during the synthesis and (b) deconvolution of GPC curve at the final reaction time of MB*o*B-1.

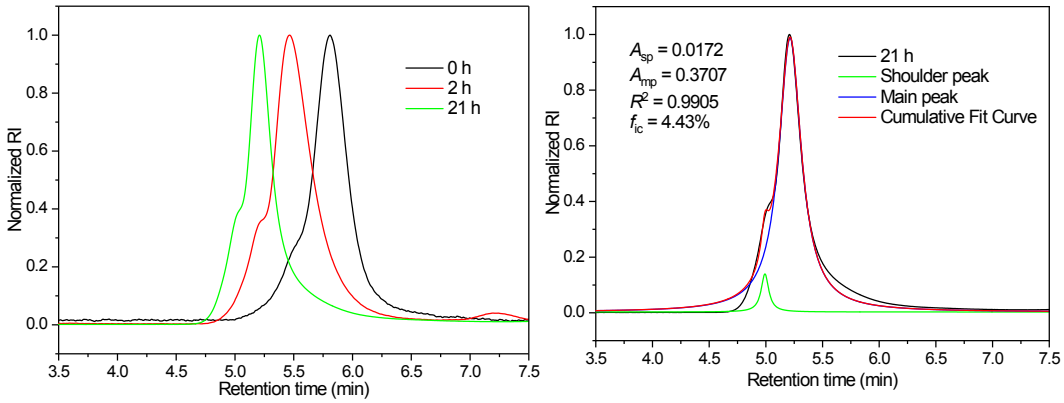


Figure S20. (a) GPC traces during the synthesis and (b) deconvolution of GPC curve at the final reaction time of MB*o*B-2.

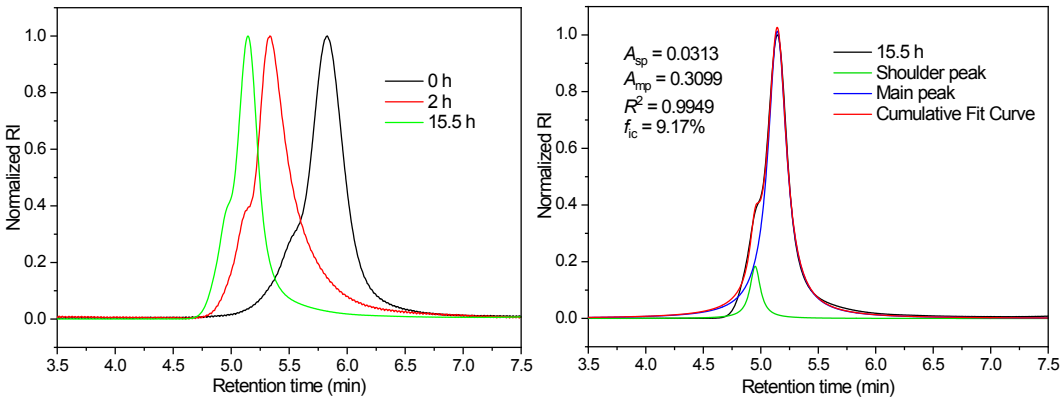


Figure S21. (a) GPC traces during the synthesis and (b) deconvolution of GPC curve at the final reaction time of MB*o*B-3.

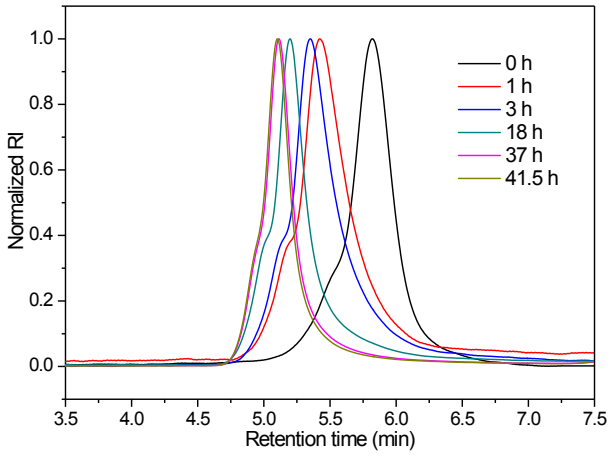


Figure S22. GPC traces during the synthesis of MB*o*B-4.

Synthesis of MB*o*B-5 (*m* = 1021, *n* = 113, *x* = 64, *y* = 22, Scheme S5 and Table 1 in main text). 52.0 mg of MBMI-2 (0.1 mmol of Br), 8.0 g of *n*BA (62.41 mmol), 127.5 mg of dNbpy (0.31 mmol), 3.5 mg of $CuBr_2$ (1.56×10^{-2} mmol), 0.8 mL of anisole, and 80 μL of DMF were mixed in a 25 mL Schlenk flask. The reaction mixture was subjected to three freeze-pump-thaw deoxygenating cycles and then 20.2 mg of CuBr (0.14 mmol) was added in the frozen reaction mixture during the final cycles. The reaction flask was further deoxygenated by cycles of evacuation/back-filling with nitrogen gas three times, and immersed in a 70 °C oil bath for 20 h. The monomer conversion determined by gravimetry was 6.18%, resulting in MB*o*B-5 with DP = 22 of the secondary side chains by assuming 100% site-initiating efficiency in the primary side chains. The polymer was purified by dialysis against acetone for 48 h and the solvent was refreshed every 12 h. The polymer product was obtained upon drying under vacuum at room temperature and the composition was P{MMA_{1021}-*r*-[BIBEM-*g*-(BIBEM-*g*-*n*BA_{22})$_{64}$]$_{113}$}. Resutls determined by THF GPC and gravimetry were $M_{n,GPC}$ = 1.48×10^6 Da, $Đ$ = 1.14, $M_{n,theo}$ = 2.25×10^7 Da. The syntheses of MB*o*Bs-6, 7 and 8 were similar as mentioned in the preparation of MB*o*B-5.

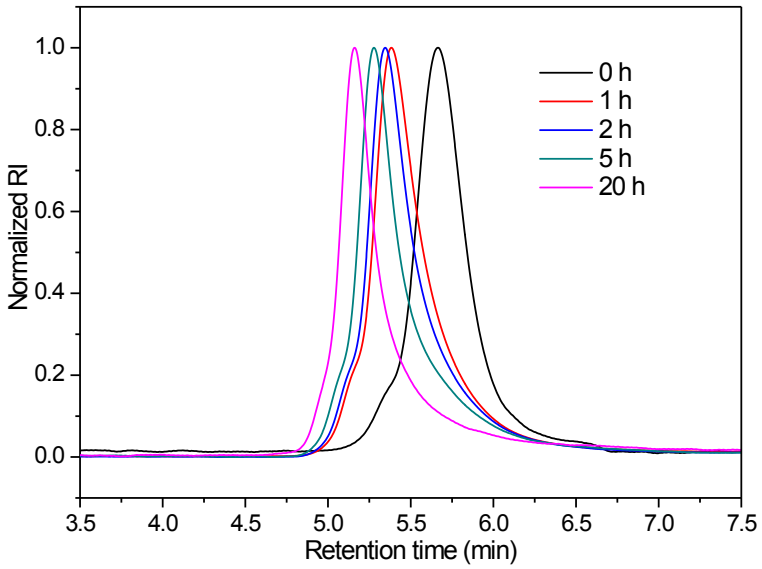


Figure S23. GPC traces during the synthesis of MB*o*B-5.

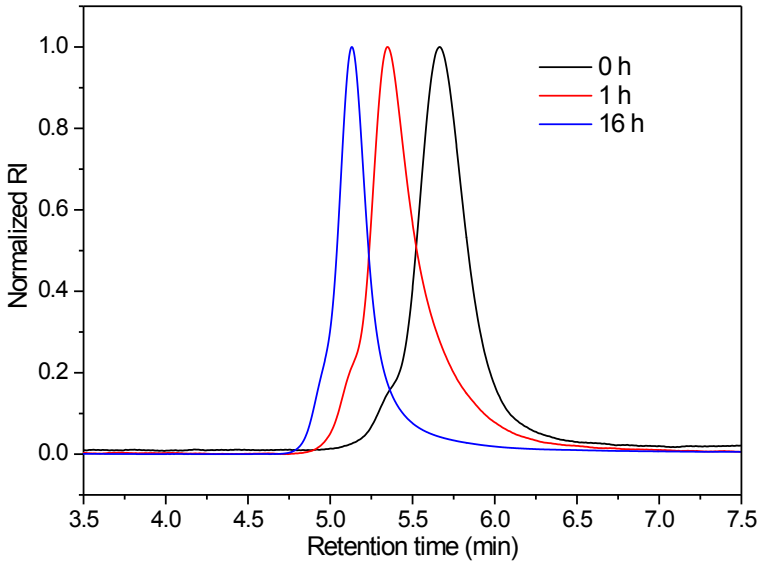


Figure S24. GPC traces during the synthesis of MB*o*B-6.

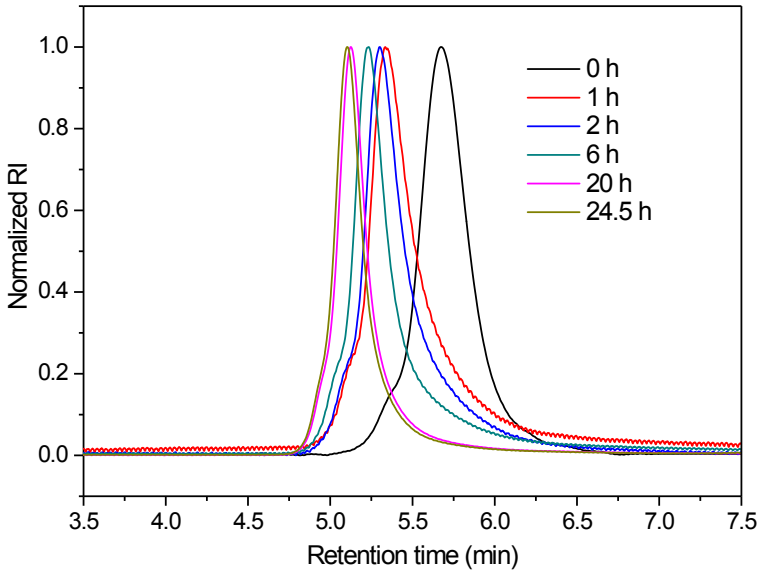


Figure S25. GPC traces during the synthesis of MB*o*B-7.

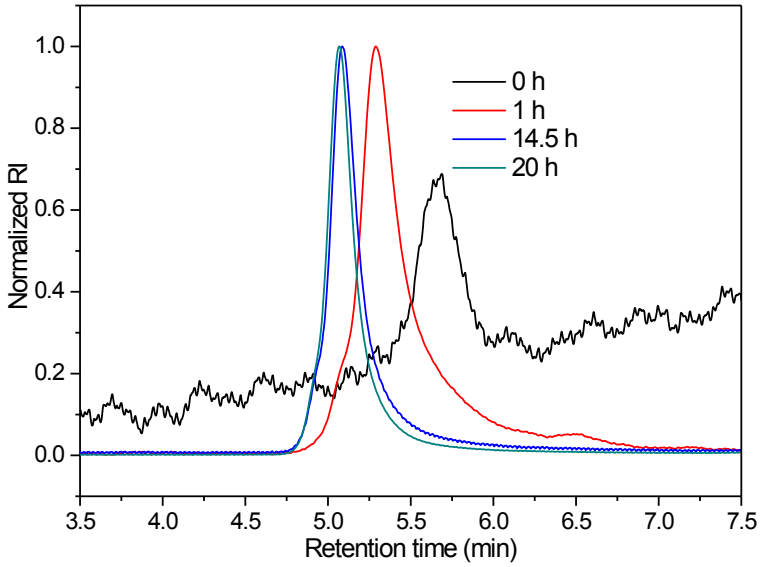
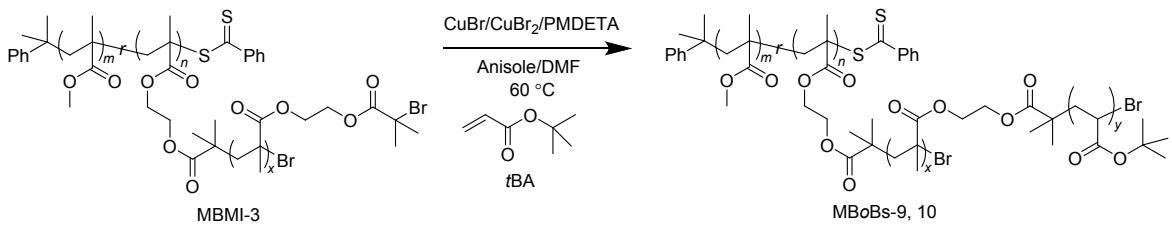


Figure S26. GPC traces during the synthesis of MB*o*B-8.



Scheme S6. Synthetic route to MB*o*B with secondary side chains of poly(*t*BA).

Synthesis of MBoBs-9, 10 (*m* = 1152, *n* = 12, *x* = 30, *y* = 33 and 53, Scheme S6 and Table 1 in main text). 237.5 mg of MBMI-3 (0.39 mmol of Br), 50.0 g of *t*BA (390.1 mmol), 67.6 mg of

PMDETA (0.39 mmol), 8.7 mg of $CuBr_2$ (3.9×10^{-2} mmol), 25.0 mL of anisole and 1 mL of DMF were mixed in a 100 mL Schlenk flask. The reaction mixture was deoxygenated through sparging with nitrogen for 30 min and then 50.0 mg of CuBr (0.35 mmol) was added in the reaction mixture under nitrogen protection, followed by nitrogen sparging for additional 15 min. The reaction flask was immersed in a 60 °C oil bath for 23 h. The monomer conversions determined by gravimetry were 3.34% at 16 h and 5.29% at 23 h, respectively offering MB*o*B-9 with DP = 33 and MB*o*B-10 with DP = 53 of the secondary side chains by assuming 100% site-initiating efficiency in the primary side chains. The polymer was purified by precipitation in methanol/water (7/3 v/v) twice and then dried under vacuum at room temperature. Results determined by THF GPC and gravimetry were $M_{n,GPC}$ = 4.46×10^5 Da, $Đ$ = 1.11, $M_{n,theo}$ = 1.81×10^6 Da for MB*o*B-9 and $M_{n,GPC}$ = 5.54×10^5 Da, $Đ$ = 1.13, $M_{n,theo}$ = 2.73×10^6 Da for MB*o*B-10.

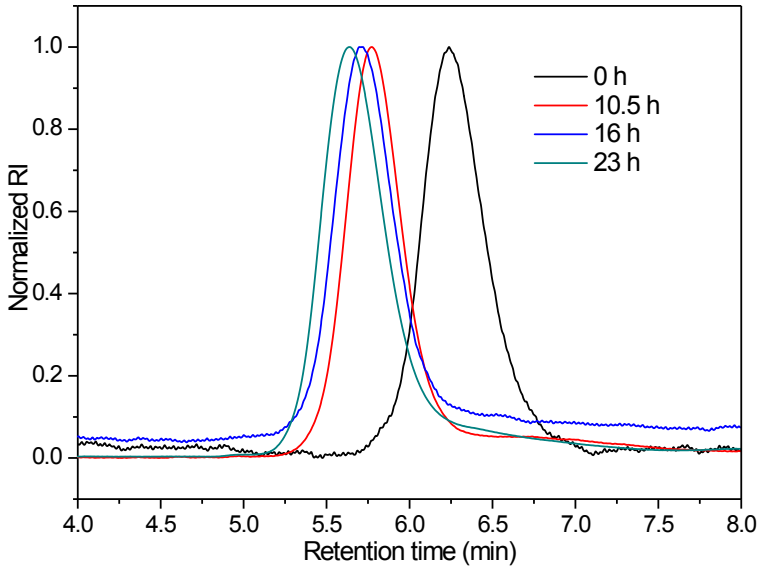
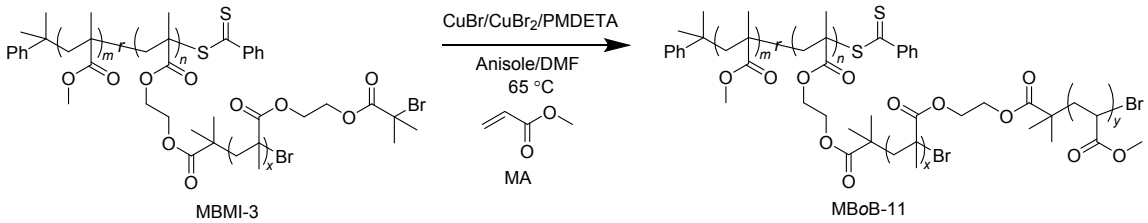


Figure S27. GPC traces during the synthesis of MB*o*B-9 (at 16 h) and MB*o*B-10 (at 23 h).



Scheme S7. Synthetic route to MB*o*B-11 with secondary side chains of poly(MA).

Synthesis of MBoB-11 (*m* = 1152, *n* = 12, *x* = 30, *y* = 92, Scheme S6 and Table 1 in main text). 212.0 mg of MBMI-3 (0.34 mmol of Br), 30.0 g of MA (348.4 mmol), 60.4 mg of PMDETA (0.34

mmol), 7.8 mg of $CuBr_2$ (3.4×10^{-2} mmol), 15 mL of anisole and 1 mL of DMF were mixed in a 100 mL Schlenk flask. The reaction mixture was deoxygenated through sparging with nitrogen for 20 min and then 40.0 mg of CuBr (0.31 mmol) was added in the reaction mixture, followed by nitrogen sparging for additional 10 min. The reaction flask was immersed in a 65 °C oil bath for 8 h. The monomer conversion determined by gravimetry was 9.2% at 8 h, offering MB*o*B-11 with DP = 92 of the secondary side chains by assuming 100% site-initiating efficiency in the primary side chains. The polymer was purified by precipitation in hexane twice and then dried under vacuum at room temperature. Results determined by THF GPC and gravimetry were $M_{n,GPC}$ = 5.08×10^5 Da, $Đ$ = 1.17, $M_{n,theo}$ = 3.07×10^6 Da.

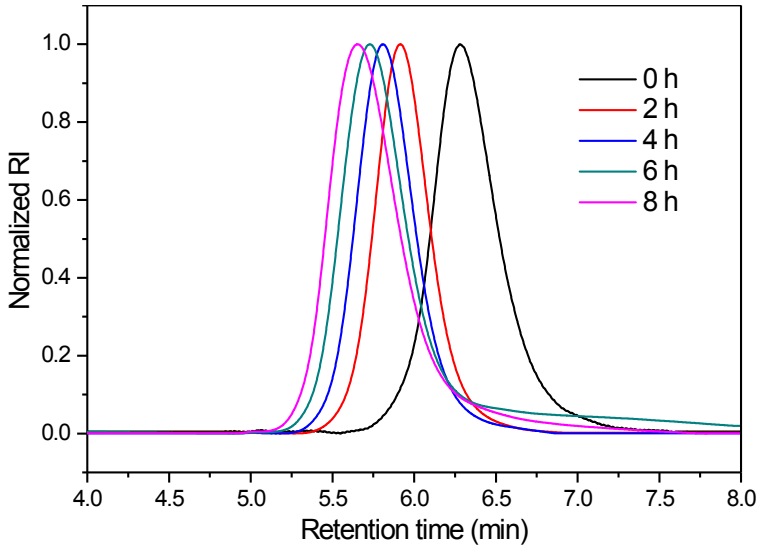
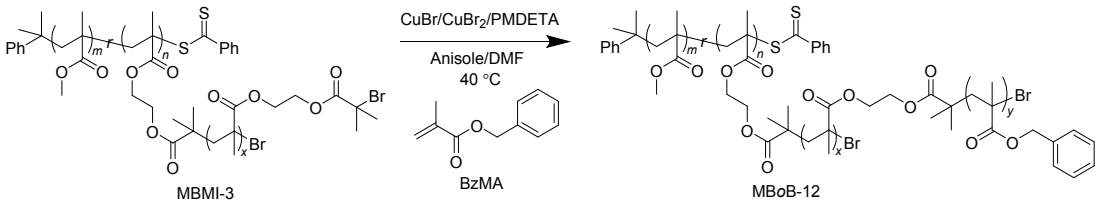


Figure S28. GPC traces during the synthesis of MB*o*B-11.

8. Preparation of MB*o*Bs with secondary side chains of polymethacrylate



Scheme S8. Synthetic route to MB*o*B-12 with secondary side chains of poly(BzMA).

Synthesis of MBoB-12 ((m = 1152, n = 12, x = 30, y = 38, Scheme S8 and Table 1 in main text). 345.5 mg of MBMI-3 (0.56 mmol of Br), 100.0 g of BzMA (567.5 mmol), 463.5 mg of dNbpy (1.13 mmol), 25.3 mg of $CuBr_2$ (0.11 mmol), 50 mL of anisole and 2 mL of DMF were mixed in a 250 mL Schlenk flask. The reaction mixture was deoxygenated through sparging with nitrogen for 30 min and

then 65.1 mg of CuBr (0.45 mmol) was added in the reaction mixture, followed by nitrogen sparging for additional 15 min. The reaction flask was immersed in a 40 °C oil bath for 3 h. The monomer conversion determined by gravimetry was 3.87% at 8 h, offering MB*o*B-12 with DP = 38 of the secondary side chains by assuming 100% site-initiating efficiency in the primary side chains. The polymer was purified by precipitation in methanol twice and then dried under vacuum at room temperature. Results determined by THF GPC and gravimetry were $M_{n,GPC}$ = 4.72×10^5 Da, $Đ$ = 1.15, $M_{n,theo}$ = 2.62×10^6 Da.

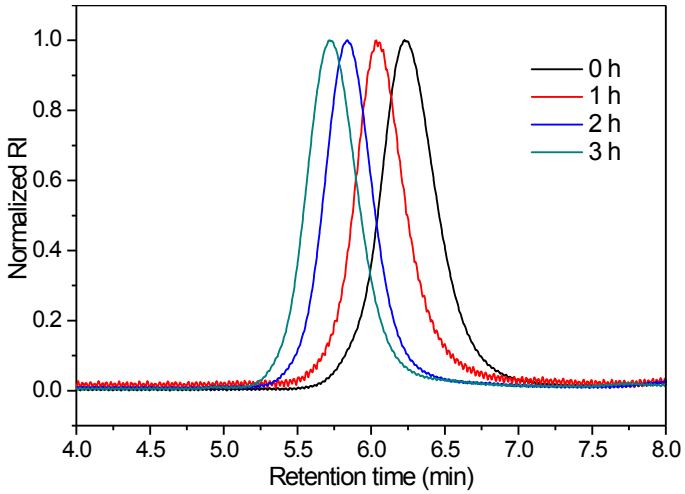
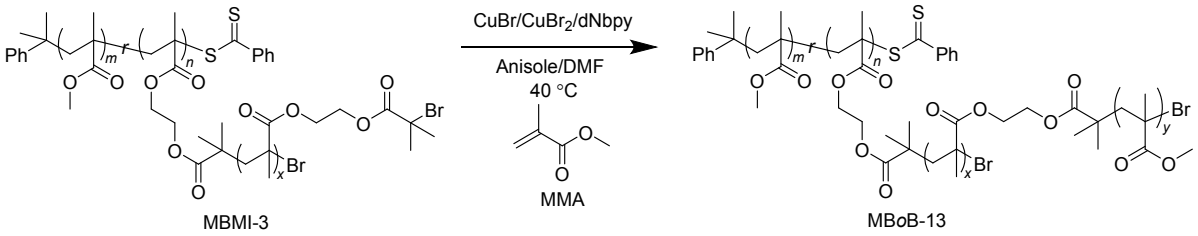


Figure S29. GPC traces during the synthesis of MB*o*B-12.



Scheme S9. Synthetic route to MB*o*B-13 with secondary side chains of poly(MMA).

Synthesis of MBoB-13 (*m* = 1152, *n* = 12, *x* = 30, *y* = 56, Scheme S9 and Table 1 in main text). 300.0 mg of MBMI-3 (0.5 mmol of Br), 50.0 g of MMA (499.4 mmol), 408.0 mg of dNbpy (0.99 mmol), 22.0 mg of $CuBr_2$ (0.099 mmol), 25 mL of anisole and 1 mL of DMF were mixed in a 100 mL Schlenk flask. The reaction mixture was deoxygenated through sparging with nitrogen for 30 min and then 57.3 mg of CuBr (0.39 mmol) was added in the reaction mixture, followed by nitrogen sparging for additional 15 min. The reaction flask was immersed in a 40 °C oil bath for 3 h. The monomer conversion determined by gravimetry was 5.58% at 3 h, offering MB*o*B-13 with DP = 56 of the secondary side chains by assuming 100% site-initiating efficiency in the primary side chains. The

polymer was purified by precipitation in hexane twice and then dried under vacuum at room temperature. Results determined by THF GPC and gravimetry were $M_{n,GPC}$ = 5.12×10^5 Da, $Đ$ = 1.23, $M_{n,theo}$ = 2.23×10^6 Da.

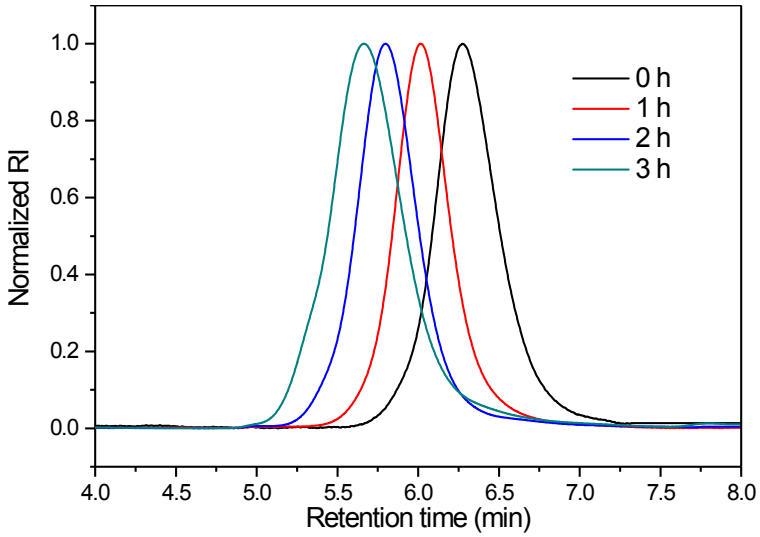
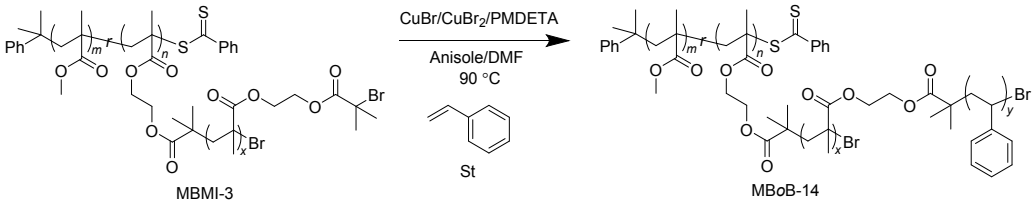


Figure S30. GPC traces during the synthesis of MB*o*B-13.

9. Preparation of MB*o*B with secondary side chains of polystyrene



Scheme S10. Synthetic route to MB*o*B-14 with secondary side chains of polystyrene.

Synthesis of MBoB-14 (*m* = 1152, *n* = 12, *x* = 30, *y* = 14, Scheme S10 and Table 1 in main text). 290.0 mg of MBMI-3 (0.47 mmol of Br), 50.0 g of St (478.4 mmol), 82.8 mg of PMDETA (0.47 mmol), 10.7 mg of $CuBr_2$ (0.047 mmol), 25 mL of anisole and 1 mL of DMF were mixed in a 100 mL Schlenk flask. The reaction mixture was deoxygenated through sparging with nitrogen for 30 min and then 61.8 mg of CuBr (0.43 mmol) was added in the reaction mixture, followed by nitrogen sparging for additional 15 min. The reaction flask was immersed in a 90 °C oil bath for 3 h. The monomer conversion determined by gravimetry was 1.42% at 3 h, offering MB*o*B-14 with DP = 14 of the secondary side chains by assuming 100% site-initiating efficiency in the primary side chains. The polymer was purified by precipitation in methanol twice and then dried under vacuum at room

temperature. Results determined by THF GPC and gravimetry were $M_{n,GPC}$ = 3.2×10^5 Da, $Đ$ = 1.14, $M_{n,theo}$ = 7.4×10^5 Da.

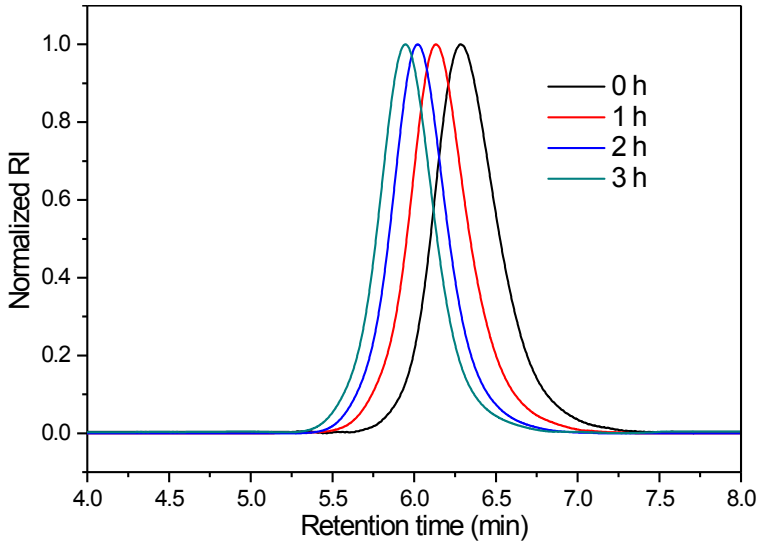
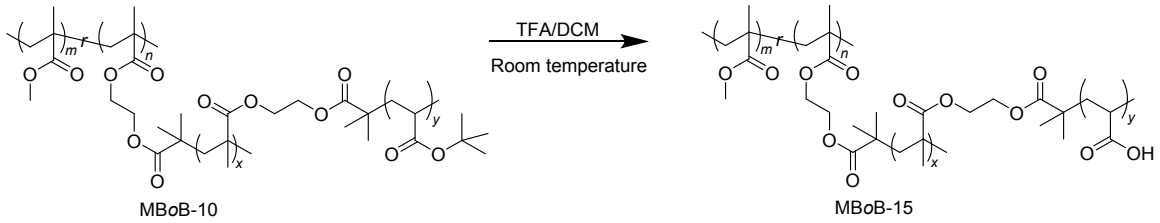


Figure S31. GPC traces during the synthesis of MB*o*B-14.

10. Preparation of MB*o*B with secondary side chains of poly(sodium acrylate)



Scheme S11. Synthetic route to MB*o*B-15 with secondary side chains of poly(sodium acrylate).

Synthesis of MBoB-15 (*m* = 1152, *n* = 12, *x* = 30, *y* = 53, Scheme S11 and Table 1 in main text). 0.3 g of MB*o*B-10 was dissolved in 6 mL of dichloromethane (DCM) under nitrogen protection and the reaction was cooled down to 0 °C. 1.5 mL of trifluoroacetic acid (TFA) was dropwise added over a course of 10 min. The reaction was allowed to warm up to room temperature and proceeded overnight. The product, i.e., MB*o*B-15, was purified by flushing air overnight and dried under vacuum.

The MB*o*B-15 was dissolved in aqueous solution of sodium decarbonate, which could give the aqueous MB*o*B with the secondary side chains of poly(sodium acrylate) as polyelectrolyte.

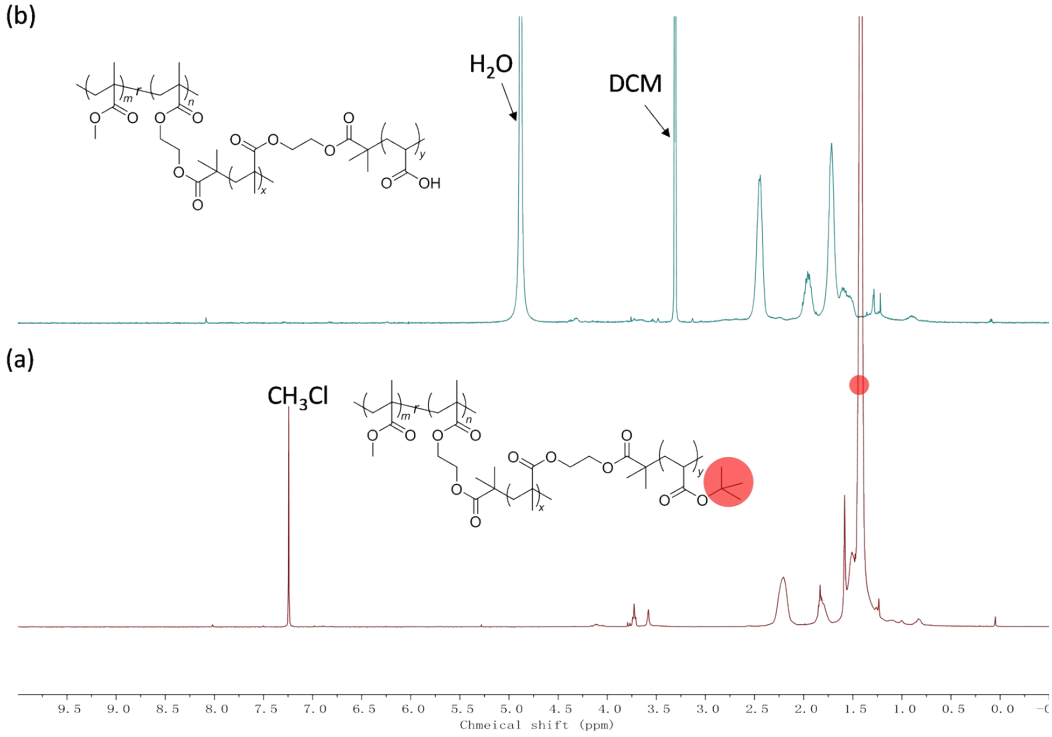
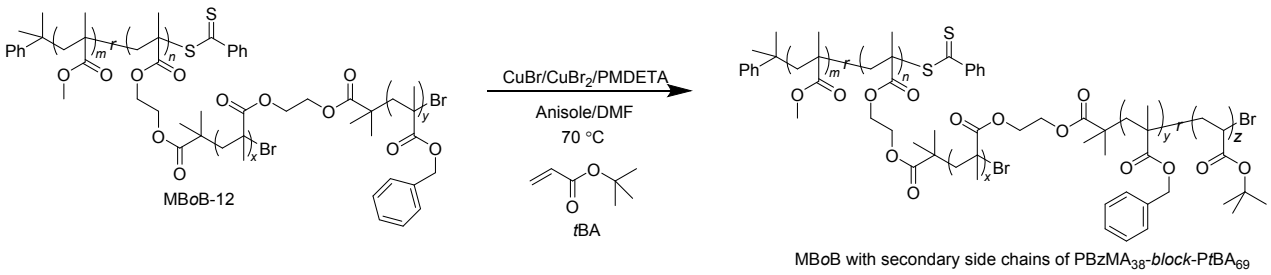


Figure S32. ^{1}H-NMR spectra of (a) MB*o*B-10 (400 MHz, $CDCl_3$) and (b) MB*o*B-15 (400 MHz, CD_3OD) derived from MB*o*B-10 (m = 1152, n = 12, x = 30, y = 53).

11. Preparation of MB*o*B with secondary side chains of di-block copolymers



Scheme S12. Synthetic route to MB*o*B with the secondary side chains of $PBzMA_{38}$-*block*-$PtBA_{69}$ di-block copolymers.

Synthesis of MB*o*B with the secondary side chains of $PBzMA_{38}$-*block*-$PtBA_{69}$ di-block copolymers (m = 1152, n = 12, x = 30, y = 53, Scheme S12 and Table 1 in main text). 0.6 g of MB*o*B-12 (0.078 mmol of Br), 10.0 g of *t*BA (78 mmol), 13.5 mg of PMDETA (0.078 mmol), 1.7 mg of $CuBr_2$ (7.8×10^{-3} mmol), 10 mL of anisole and 1 mL of DMF were mixed in a 25 mL Schlenk flask. The reaction mixture was deoxygenated through sparging with nitrogen for 20 min and then 10.0 mg of CuBr (0.07 mmol) was added in the reaction mixture, followed by nitrogen sparging for additional 15 min. The reaction flask was immersed in a 70 °C oil bath for 20 h. The monomer conversion

determined by gravimetry was 6.9% at 20 h, offering MB*o*B with the secondary side chains of PBzMA$_{38}$-*block*-P*t*BA$_{69}$ by assuming 100% site-initiating efficiency in the primary side chains. The polymer was purified by precipitation in methanol/water (7/3 v/v) twice and then dried under vacuum at room temperature. Results determined by THF GPC and gravimetry were $M_{n,GPC}$ = 5.38×10^5 Da, $Đ$ = 1.2, $M_{n,theo}$ = 5.81×10^6 Da.

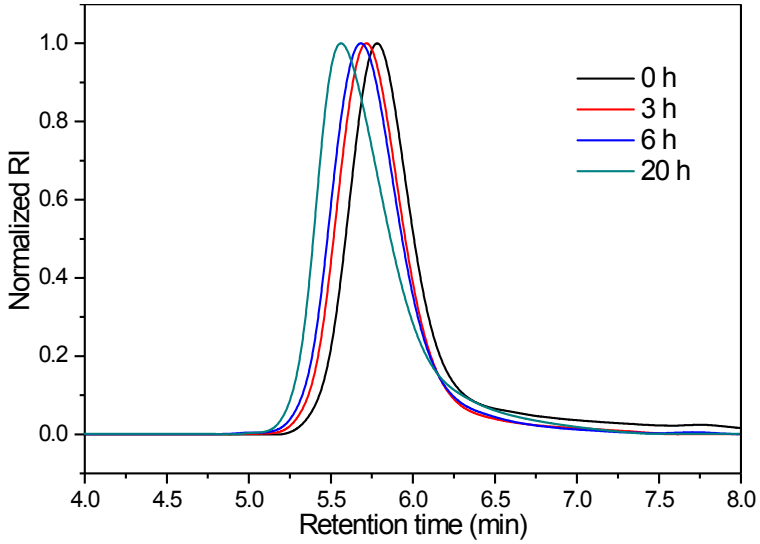


Figure S33. GPC traces during the synthesis of MB*o*B with the secondary side chains of PBzMA$_{38}$-*block*-P*t*BA$_{69}$ di-block copolymers.

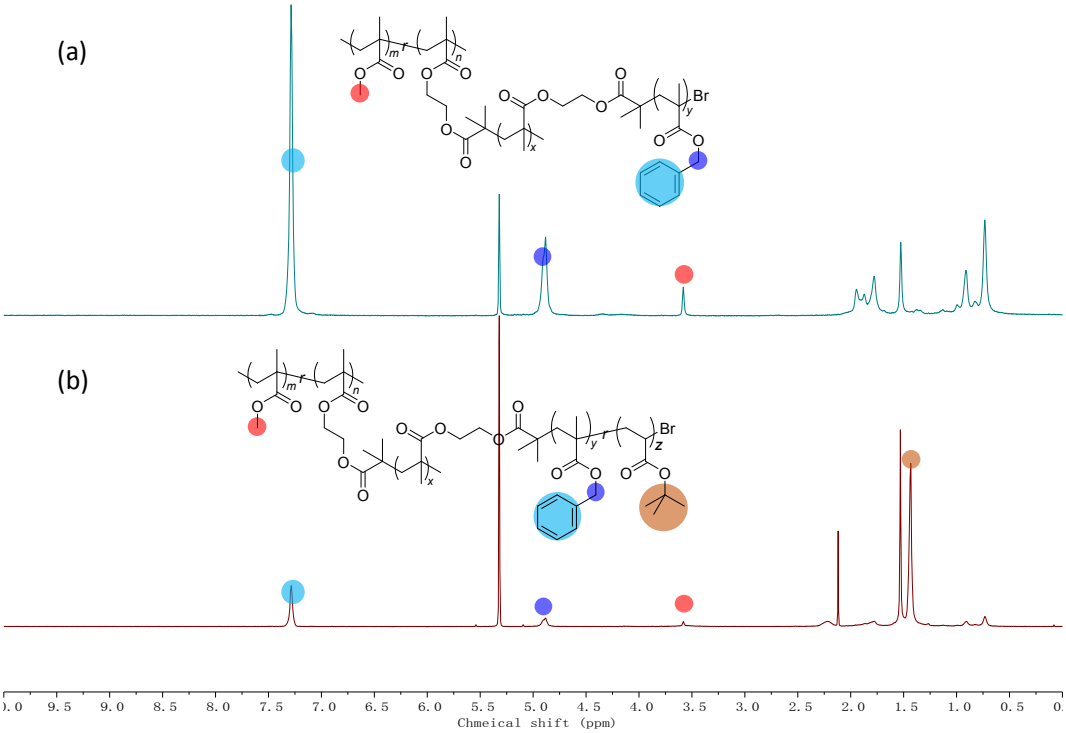


Figure S34. ^{1}H-NMR spectra of MB*o*Bs with the secondary side chains of (a) PBzMA$_{38}$ (MB*o*B-12) and (b) PBzMA$_{38}$-*block*-P*t*BA$_{69}$ (m = 1152, n = 12, x = 30, y = 38, z = 69, 400 MHz, $CDCl_3$).

12. Representative AFM of MB*o*Bs

Table S7. Molecular parameters of MB*o*Bs estimated from AFM.

Samples	m^a	n^a	x^a	y (M)[a]	Length (nm)[b]	Width (nm)[b]
MB*o*B-1	1021	113	33	18 (*n*BA)	331 ± 52	37 ± 7
MB*o*B-2	1021	113	33	22 (*n*BA)	336 ± 48	45 ± 6
MB*o*B-3	1021	113	33	54 (*n*BA)	363 ± 62	45 ± 6
MB*o*B-4[c]	1021	113	33	63 (*n*BA)	>320	>43
MB*o*B-5	1021	113	64	22 (*n*BA)	352 ± 61	69 ± 6
MB*o*B-7	1021	113	64	36 (*n*BA)	354 ± 41	77 ± 7

[a] *m* and *n* are the number of unit of MMA and BIBEM, respectively, in the backbone; *x* and *y* are the DPs of the primary and secondary side chains, respectively; M represents the monomer used in the secondary side chains. [b] Length = L_a ± SD and Width = W_a ± SD, where L_a and W_a represent number-average length and width of MB*o*Bs from AFM, respectively, depending on ~40 individual molecules; SD represents the standard deviation. [c] Length and width were underestimated due to the severe scission of backbone upon spin-coating on mica substrates.

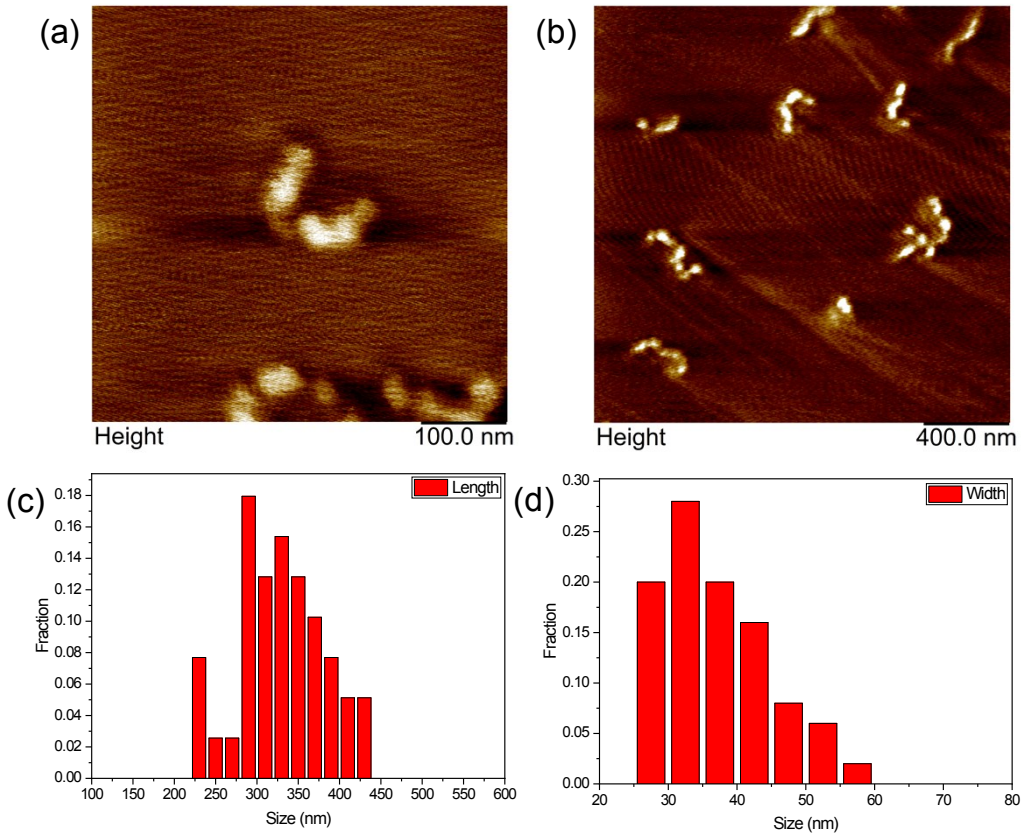


Figure S35. (a, b) AFM height images, (c) length distribution and (d) width distribution of MB*o*B-1.

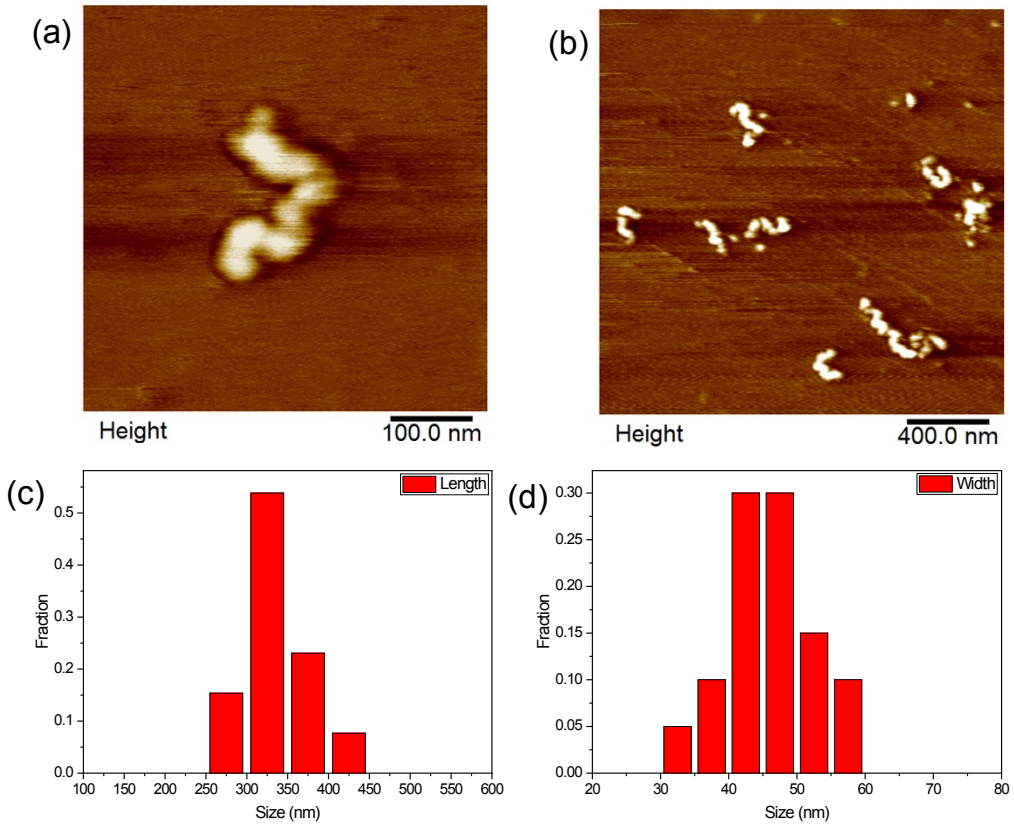


Figure S36. (a, b) AFM height images, (c) length distribution and (d) width distribution of MB*o*B-2.

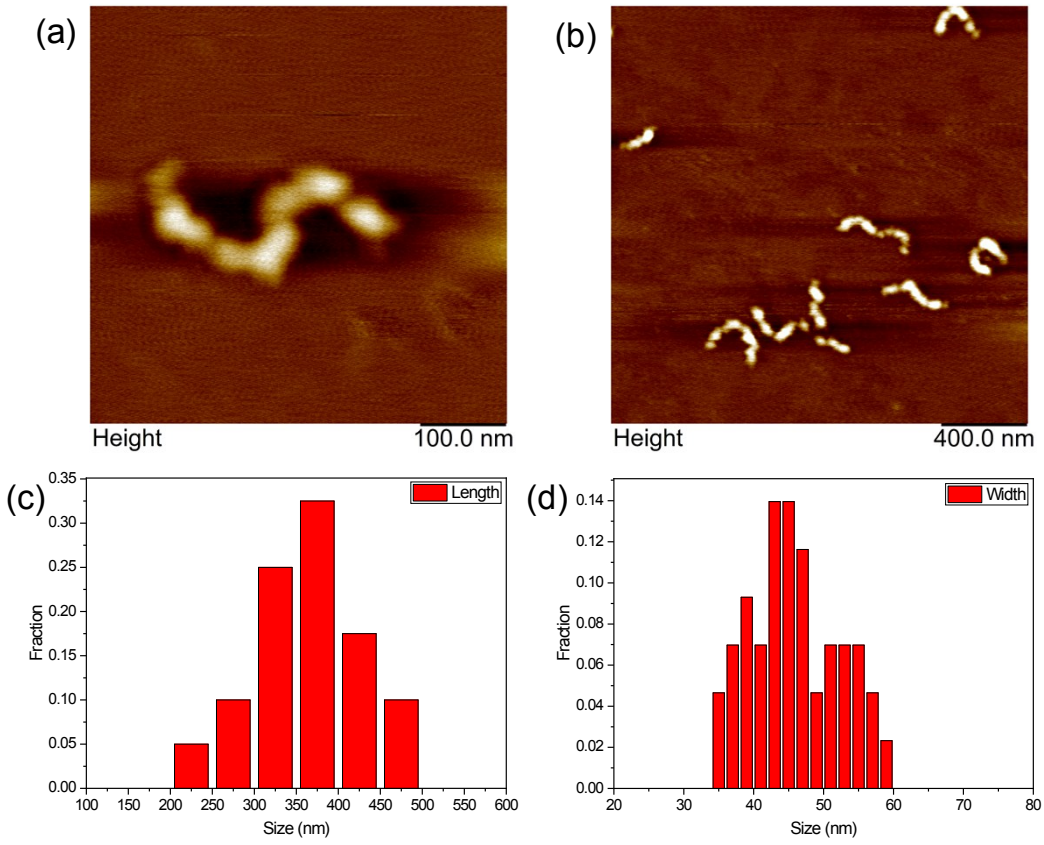


Figure S37. (a, b) AFM height images, (c) length distribution and (d) width distribution of MB*o*B-3.

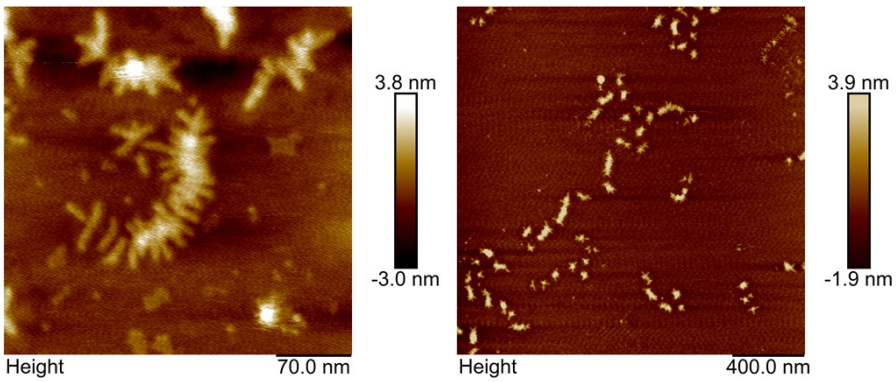


Figure S38. AFM height images of MB*o*B-4.

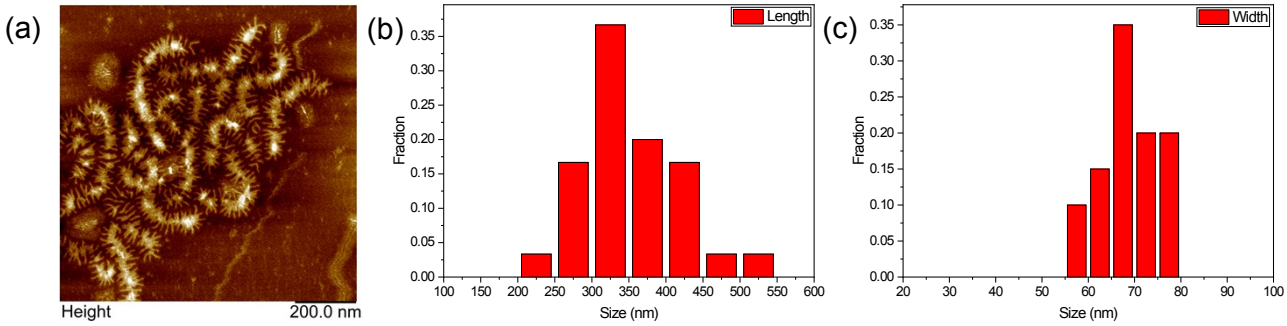


Figure S39. (a) AFM height images, (b) length distribution and (c) width distribution of MB*o*B-5.

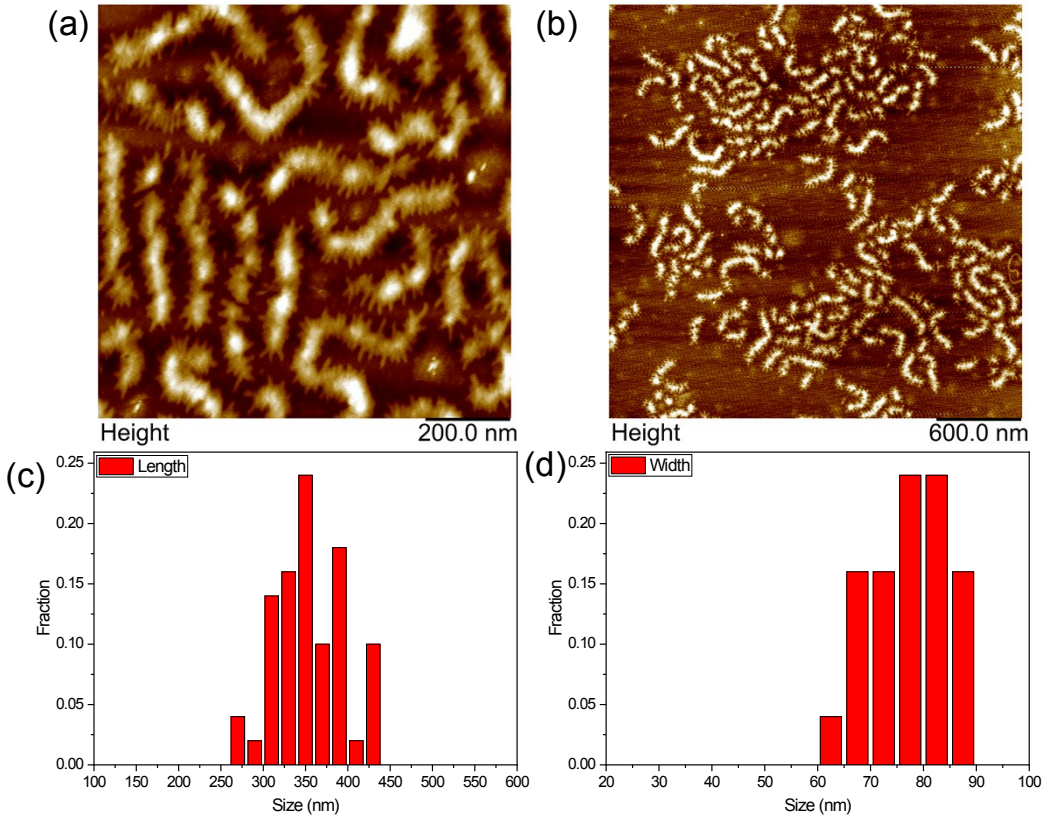


Figure S40. (a, b) AFM height images, (c) length distribution and (d) width distribution of MB*o*B-7.

13. References

1. X. Pang, L. Zhao, W. Han, X. Xin, Z. Lin Z., *Nat. Nanotechnol.*, 2013, **8**, 426-31.