Supporting Information

Well-Defined Bilayered Molecular Cobrushes with Internal Polyethylene Blocks and ω-Hydroxyl-Functionalized Polyethylene Homobrushes

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Experimental section

Chemicals

s-Butyllithium (*s*-BuLi) (1.4 M in cyclohexane, Aldrich), *n*-butyllithium (*n*-BuLi) (1.6 M in hexane, Aldrich), *di*(*n*-butyl)magnesium (2.5 M in cyclohexane, Aldrich), calcium hydride (CaH₂) (95%, Aldrich), 5-norbornene-2-carboxylic acid (98%, mixture of *endo* and *exo* isomers, predominantly endo, Aldrich), *N*,*N'*-dicyclohexylcarbodiimide (DCC) (> 99%, Aldrich), 4- (dimethylamino)pyridine (DMAP) (> 99%, Aldrich), trimethylamine *N*-oxide dehydrate (TAO) (> 99%, Aldrich), tert-butyldimethylsilyl chloride (97%, Aldrich), borane-tetrahydrofuran complex (BH₃·THF) (1.0 M in tetrahydrofuran, Aldrich), imidazole (> 99%, Aldrich), and tetrabutylammonium fluoride solution (1.0 M in THF, Aldrich) were used as received. Styrene (99%, Aldrich), 1,1-diphenylethylene (DPE) (97%, Aldrich) and allyl alcohol (> 99%, Aldrich) were distilled over CaH₂ and were degassed by 3 cycles of freeze-pump-thaw before use. Grubbs catalyst (1st generation) (97%, Aldrich) was diluted with fresh toluene to 5 mM solution before use. Tetrahydrofuran (>99%, Aldrich), toluene (>99%, Aldrich) and cyclohexane (>99%, Aldrich) were distilled over sodium/benzophenone before use. The dimethylsulfoxonium methylide solution (0.82 M) was prepared according to our previous work.¹

Instruments

High temperature gel permeation chromatography (HT-GPC) measurements were performed on a Viscotek HT-GPC module 350 instrument equipped with a two-angle light scattering detector, a viscometer and a refractive index detector. Two PLgel 10 µm MIXED-B columns were employed for separation with 1,2,4-trichlorobenzene (TCB) as eluent (0.8 mL/min at 150 °C). The RI detector was calibrated with polystyrene standards (from 1050 to 1900000 g/mol) and the tri-detector system with one PS standard ($M_w = 120\ 000$, PDI = 1.06). Proton and carbon-13 nuclear magnetic resonance spectroscopy (¹H and ¹³C NMR) were carried out on a Bruker AVANCE III-600 spectrometer. Differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo DSC1/TC100 system in an inert nitrogen atmosphere. The samples were heated from room temperature to 160 °C, cooled to -110 °C and finally heated again to 160 °C at a heating/cooling rate of 10 °C/min. The second heating curve was used to determine the melting point (T_m) and crystallinity degree (X_c).

Synthesis of allyl-terminated PS (PS-allyl)

All flasks were connected to a vacuum line, heated with a heat gun and dried with argon/vacuum for more than 5 times. 15 mL of styrene (131 mmol) was distilled into the polymerization flask from *di*(*n*-butyl)magnesium followed by distillation of 100 mL of cyclohexane from DPELi (adduct of DPE and *s*-BuLi) at room temperature under high vacuum. The flasks were charged with argon. Against an argon flow, 7.2 mL of *s*-BuLi (1.4 M in cyclohexane) was added to the reaction flask. The red color indicated the start of the polymerization. After 4 h, 2.5 mL of DPE (13.8 mmol) was added into the solution followed by 0.5 mL of dry and degassed THF. 24 h later, 1.5 mL of allyl bromide (17.4 mmol) was added against an argon flow to quench the living DPE-capped polystyryllithium leading to PS-allyl. After removing the cyclohexane in a rotary evaporator, the product was dissolved in THF and then precipitated in excess methanol twice to give a white solid powder of PS-allyl ($M_{n, GPC} = 1800$ g/mol, PDI = 1.10, $M_{n, NMR} = 1900$ g/mol, PS standards).

Synthesis and titration of macroinitiator of PS₃B

In a 50 mL Schlenk flask, 5.0 g of dry PS-allyl (2.63 mmol) was dissolved in 20 mL of freshly distilled toluene at 0 °C followed by addition of 0.8 mL of BH_3 ·THF solution in THF (1.0 M) to afford the macroinitiator for the polyhomologation, PS₃B. The mixture was kept in a glove box (argon atmosphere) at room temperature for 10 days.

The titration of the initiator was performed by a small scale polyhomologation process. 1 mL of PS₃B solution was added into 15 mL of dimethylsulfoxonium methylide solution in

toluene (0.82 M) at 80 °C. 20 min later, 0.3 g TAO was added to the solution and the solution was kept at 80 °C for 4 h. A white solid product, a mixture of PS-b-PE-OH and unreacted PS-allyl, was obtained by precipitating the solution into excess methanol. To remove the PS residual, the crude product was dissolved in hot toluene (80 °C) and was cooled down to room temperature affording a cloudy solution. By centrifugation, the cloudy solution was seperated into two phases, one was gel-like (PS-b-PE-OH) on the bottom and the other was clear/transparent solution (PS-allyl). The HT-GPC traces indicated a high purity of PS-*b*-PE-OH (Figure S1). From the ¹H NMR spectrum (Figure S2), the molecular weight $M_{\rm n, NMR} = 8570$ g/mol of PE block was calculated according to $M_{\rm n, PE} = 17.5 \times 14 \times 10^{-10}$ (area of the peaks at δ =1.20-1.45 ppm)/(area of the peaks at δ =6.40-6.85 ppm) (g/mol), where 17.5 is the averaged DP of the PS chain, 14 correspond to the molecular weight of -CH₂- in PE block, the peaks at δ =6.40-6.85 ppm corresponds to the five protons of the phenyl group in PS block and the peaks at δ =1.20-1.45 ppm to -CH₂- of thr PE block. By using this molecular weight ($M_{n, NMR} = 8570$ g/mol), the real concentration of PS₃B of 0.0067 mmol/mL was calculated according to $C_{PS3B} = 12.3/(612\times3)$ (mmol/mL), where C_{PS3B} is the concentration of PS₃B, 12.3 is amount of ylide in mole, 612 is the averaged DP of -CH₂- unit in PE block and 3 is functionality of macroinitiator. The lower concentration was supposed to be a consequence of the existence of impurity (oxygen and moisture) embedded in PS-allyl or that introduced during the operation.



Figure S1. HT-GPC traces of PS-*b*-PE-OH synthesized for the titration of the boron initiator (1,2,4-trichlorobenzene, 150 °C) (^{a.} the peak is negative due to the negative dn/dc and was shown in positive style for better comparison)



Figure S2. ¹H NMR spectrum of PS-*b*-PE-OH (toluene- d_8 , 90 °C) synthesized for the titration of the boron initiator (left: full spectrum, right: zoomed spectrum alone the y-axis)

Synthesis of macromonomer of PS-b-PE-Nor

The PS-*b*-PE-OH ($M_{n, HT-GPC-RI} = 6300$ g/mol, PDI = 1.16, $M_{n, NMR} = 5650$ g/mol, 1.6 g, yield: 66 % based on ylide) was synthesized in the same way as for titration by using 20 mL of PS₃B solution (0.0067 M in toluene) and 120 mL of dimethylsulfoxonium methylide solution (0.82 M in toluene, 100 mmol) (Figure S3).

1.0 g of dry PS-*b*-PE-OH (0.17 mmol) was dissolved in 20 mL of freshly distilled toluene at 80 °C followed by addition of 0.5 g of 5-norbornene-2-carboxylic acid (3.6 mmol), 1.0 g of DCC (4.9 mmol) and 0.01 g of DMAP (0.08 mmol). The reaction solution was stirred at 80 °C for 24 h. The white solid formed during the esterification reaction was removed by filtration and the filtrate was precipitated in methanol twice. The white solid product was dried under vacuum and characterized by HT-GPC (Figure 1) and ¹H NMR spectroscopy (Figure 2 in main text) ($M_{n, HT-GPC-RI} = 6\,450$ g/mol, PDI = 1.15, $M_{n, NMR} = 5\,750$ g/mol).



Figure S3. Synthesis of PS-*b*-PE-OH monitored by HT-GPC (1,2,4-trichlorobenzene, 150 °C) (^a the peak is negative due to the negative dn/dc and is shown in positive style for better comparison) (left: the product of PS-*b*-PE-OH collected from the gel-like phase on the bottom after centrifugation in a comparison with the precursor of PS-allyl and crude product, right: the polymer collected from the clear/transparent solution phase after centrifugation by removing the solvent)

Synthesis of bilayered molecular cobrush with PE internal blocks, P(PE-b-PS)

0.6 g PS-*b*-PE-Nor (104.3 µmol) was dissolved in 5 mL of freshly distilled toluene at 80 °C followed by addition of 0.4 mL of Grubbs 1st generation catalyst (5 mM in toluene, 2.0 µmol). The polymerization solution was kept at 80 °C for 24 h. 0.2 mL of vinyl ethyl ether was added to quench the polymer. The solution was passed through a silica gel column and then precipitated in excess methanol affording white solid product ($M_{w, HT-GPC-LS} = 323\ 000\ g/mol$, PDI = 1.36, 0.41 g).



Figure S4. Monitoring the synthesis of P(PE-*b*-PS) by ¹H NMR (full spectra) (toluene- d_8)

Synthesis of *tert*-butyl(allyloxy)dimethylsilane (TBDMS-allyl)²

20 mL of allyl alcohol (294 mmol), 37.7 g of *tert*-butyldimethylsilyl chloride (250 mmol) and 20.4 g of imidazole (300 m mol) were transferred into 100 mL of DMF in a Schlenk flask charged with an argon atmosphere. The solution was stirred at room temperature for 48 h giving two clear/transparent liquid phases. After washed with water and aqueous NaHCO₃, the organic phase was dried over anhydrous MgSO₄ and was distilled under reduced pressure from CaH₂ affording a clear/transparent liquid product (35 mL, yield: 66%). The successful synthesis of *tert*-butyl(allyloxy)dimethylsilane was confirmed by both ¹H and ¹³C NMR spectra (Figure S5).



Figure S5. ¹H (left) and ¹³C NMR (right) spectra of allyl-TBDMS

Synthesis and titration of tri[3-(tert-butyldimethylsilyloxyl)propyl]borane

10 mL of tert-butyl(allyloxy)dimethylsilane (11.4 mmol) was transferred into a Schlenk flask with 10 mL of toluene against an argon flow and the solution was degassed by freeze-pump-thaw three times. After cooled to 0 °C with an ice bath, 3 mL of BH₃·THF solution (3 mmol) was added drop by drop. The mixture was naturally warmed up to room temperature and was stirred for 72 h resulting in the initiator, tri[3-(*tert*-butyldimethylsilyloxyl)propyl]borane.

To titrate the concentration of the initiator, 1 mL of tri[3-(tertbutyldimethylsilyloxyl)propyl]borane was added to 55 mL of dimethylsulfoxonium methylide (0.80 M in toluene, 44.0 mmol) at 90 °C. 30 min later, the polyhomologation finished (indicated by the neutral pH of the polymerization solution) and 0.3 g TAO was added into the solution against an argon flow. 3 h later, the solution was precipitated in excess methanol giving white solid product. The product was characterized by HT-GPC ($M_n = 1$ 1800 g/mol, PDI = 1.35) (Figure S6). The molecular weight was calculated from ¹H NMR spectrum by using the area ratio of peak a to peak c ($M_{n, NMR} = 6500 \text{ g/mol}$) (Figure S7). So the concentration of the tri[3-(*tert*-butyldimethylsilyloxyl)propyl]borane was found to be 0.032 mmol/mL according to $C_{tri[3-}$ $n_{\text{ylide}}/[3 \times (M_{\text{n}})]$ TBDMS-PE-OH/14)×Vtri[3-(tert-(tert-butyldimethylsilyloxyl)propyl]borane =NMR, butyldimethylsilyloxyl)propyl]borane], where $C_{\text{tri}[3-(tert-butyldimethylsilyloxyl)propyl]borane}$ is the concentration of the initiator. tri[3-(*tert*-butyldimethylsilyloxyl)propyl]borane, *n*_{vlide} is the amount of dimethylsulfoxonium methylide used for the polyhomologation, $M_{n, NMR, TBDMS-PE-OH}$ is the

number average molecular weight determined from ¹H NMR spectrum, 3 is the functionality of the initiator, tri[3-(*tert*-butyldimethylsilyloxyl)propyl]borane, 14 is molecular weight of the – CH₂– group, $V_{\text{tri}[3-($ *tert* $-butyldimethylsilyloxyl)propyl]borane}$ is the volume of the initiator, tri[3-(*tert*-butyldimethylsilyloxyl)propyl]borane, used for polyhomologation.



Figure S6. HT-GPC trace of TBDMS-O-PE-OH (titration of tri[3-(*tert*-butyldimethylsilyloxyl)propyl]borane) (1,2,4-trichlorobenzene, 150 °C) (^{a.} the peak is negative due to the negative dn/dc of PE block and was shown in positive style for better comparison).



Figure S7. ¹H NMR spectrum of TBDMS-O-PE-OH for titration of tri[3-(*tert*-butyldimethylsilyloxyl)propyl]borane

Synthesis of TBDMS-O-PE-OH and TBDMS-O-PE-Nor

15 mL of tri[3-(*tert*-butyldimethylsilyloxyl)propyl]borane (0.032 M in toluene, 0.47 mmol) was added into 190 mL dimethylsulfoxonium methylide solution in toluene (152 mmol) in a 500 mL Schlenk flask at 80 °C. After the polyhomologation finished in 30 min, 1.0 g TAO was added. 3

h later, the polymer was precipitated by adding the solution in excess methanol affording a white solid product ($M_{n, HT-GPC-RI} = 2.940$ g/mol, PDI = 1.12, $M_{n, NMR} = 1780$ g/mol, 1.9 g, yield: 91%).

1.5 g of dry TBDMS-O-PE-OH (0.84 mmol) was dissolved in 20 mL of freshly distilled toluene at 80 °C followed by addition of 0.5 g of 5-norbornene-2-carboxylic acid (3.6 mmol), 1.0 g of DCC (4.9 mmol) and 0.01 g of DMAP (0.08 mmol). The solution was stirred at 80 °C for 24 h. White solid formed and was removed by filtration. The filtrate was precipitated in methanol twice. The white solid product was dried under vacuum and measured by HT-GPC (Figure 5 in main text) and ¹H NMR (Figure 6 in main text) ($M_{n, HT-GPC-RI} = 2 900$ g/mol, PDI = 1.14, $M_{n, NMR}$ = 1 960 g/mol).

Synthesis of hydroxyl functionalized PE molecular brush of P(PE-O-TBDMS)

0.32 g TBDMS-O-PE-Nor (163.2 µmol) was dissolved in 5 mL of freshly distilled toluene at 80 °C followed by addition of 0.4 mL of Grubbs 1st generation catalyst (5 mM in toluene, 2.0 µmol). The polymerization solution was kept at 80 °C for 24 h. 0.2 mL of vinyl ethyl ether was added to quench the polymerization. The solution was passed through a silica gel column and the polymer precipitated in excess methanol affording a white solid product ($M_{w, HT-GPC-LS} = 175\ 000\ g/mol$, PDI = 1.19, 0.25 g).

Hydrolysis of P(PE-O-TBDMS) for P(PE-OH)

0.15 g of P(PE-O-TBDMS) (n_{TBDMS}: 0.077 mmol) was dissolved in 10 mL of freshly distilled toluene at 80 °C followed by 1.0 mL of tetrabutylammonium fluoride solution (1.0 M in THF, 1.0 mmol) for 48 h. After the reaction, the solution was concentrated and the polymer precipitated in excess methanol giving white solid product ($M_{w, HT-GPC-LS} = 162\ 300\ g/mol$, PDI = 1.22).

References

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- 2. Chan, S. S.; Kuo, S. W.; Chang, F. C. Macromolecules 2005, 38, 3099-3107