

## Supplementary Information

### Well-defined polyethylene molecular brushes by polyhomologation and ring opening metathesis polymerization

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#### Experimental section

##### Chemicals

Trimethylsulfoxonium iodide (98 %, Alfa Aesar), Benzyl tri-*n*-butylammonium chloride (98 %, Alfa Aesar), trimethylamine *n*-oxide dihydrate (TAO·2H<sub>2</sub>O) (>99%, Fluka) and triethylborane (1.0 M in tetrahydrofuran, Aldrich) were used as received. Grubbs Catalyst (1<sup>st</sup> Generation) (97%, Aldrich) was dissolved in freshly distilled toluene (5 mM). 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) were used as received. Sodium hydride (NaH) (60 % in mineral oil, Aldrich) was washed with hexane (97 %, Aldrich). Celite<sup>®</sup>545 (Aldrich) was dried at 150 °C for 48 h. Polyethylene (PE) standard ( $M_p = 119\ 600$  g/mol, PDI = 1.20) (received from ExxonMobil) was used as received.

##### Instruments

High temperature gel permeation chromatography (HT-GPC) measurements were carried out with a Viscotek HT-GPC module 350 instrument with two PLgel 10 μm MIXED-B columns. 1,2,4-trichlorobenzene (TCB) was used as eluent at a flow rate of 0.8 mL/min at 150 °C. The system was calibrated by PS standards. <sup>1</sup>H NMR spectra were recorded with a Bruker AVANCE III-600 spectrometer. Fourier-transform infrared spectra (FTIR) (transmission) were obtained with a Nicolet Magna 6700 FT spectrometer. Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC1/TC100 system in an inert atmosphere (nitrogen). The samples were heated from room

temperature to 160 °C, cooled to -60 °C and finally heated again to 160 °C with a heating/cooling rate of 10 °C/min. The second heating curve was used to determine the melting temperature ( $T_m$ ) and degree of crystallinity ( $X_c$ ).

### **Synthesis of the hydroxyl-terminated PE (PE-OH) by polyhomologation**

Dimethylsulfoxoniummethylide, the monomer for polyhomologation, was prepared according to the Corey's method followed by switching the solvent from THF to toluene.<sup>1, 2</sup> In a typical process, 13.5 g of NaH (dispersed in mineral oil, 60% by weight) was introduced into a three-necked flask connected with a condenser and argon/vacuum line and washed with dry hexane (40 mL  $\times$  3). The residual solid was dried under vacuum. 200 mL of freshly distilled THF was added, followed by the addition of 40 g of dry trimethylsulfoxonium chloride. The mixture was heated and refluxed at 70 °C until the gas ceased (4-5 h). The THF was removed under low pressure followed by transferring 50 mL of toluene into the flask and stirred for 0.5 h. The resulting turbid solution was filtered through a dry Celite® 545 column. The flask and the filtration cake were washed with 150 mL toluene. A clear and transparent solution with a light yellow color was obtained. All the operations were performed under argon. The concentration of ylide was determined by titration with a standard hydrochloric acid aqueous solution (1.12 mmol/mL; yield: 72 %).

100 mL of freshly distilled toluene and 100 mL of the resulting ylide (1.12 M) solution in toluene was transferred into a flask followed by addition of 0.4 mL of triethylborane solution in THF (1.0 M). The solution was stirred at 80 °C. After 20 min, 0.1 mL of reaction solution was taken out and added into 10 mL of water. The resulting mixture was neutral (pH paper) indicating that all ylide was consumed. 1.0 g of TAO $\cdot$ 2H<sub>2</sub>O was added into the reaction solution and stirred at 80 °C overnight. The solution was concentrated (rotor evaporator) and precipitated in methanol twice. The white solid (PE-OH) was dried under vacuum and characterized by <sup>1</sup>H NMR and HT-GPC (1.1 g, 70 %,  $M_{n, NMR} = 1230$  g/mol,  $PDI_{HT-GPC} = 1.05$ ). Another two PE-OHs with different molecular weights of  $M_{n, NMR} = 640$  g/mol ( $PDI = 1.05$ ) and  $M_{n, NMR} = 1500$  g/mol ( $PDI = 1.10$ ) were also prepared by using appropriate ratios of ylide to triethylborane in the same way.

### **Synthesis of norbornyl PE macromonomers (PE-MM)**

Norbornyl PE-MM were synthesized by reacting PE-OH with 5-norbornene-2-carboxylic acid in presence of DCC and DMAP.<sup>3</sup> 1.0 g of PE-OH ( $M_{n, NMR} = 640$  g/mol,  $PDI = 1.05$ ) was dissolved in 20 mL freshly distilled toluene followed by addition of 2.0 g of 5-norbornene-2-carboxylic acid, 2.0 g of DCC and 0.1 g

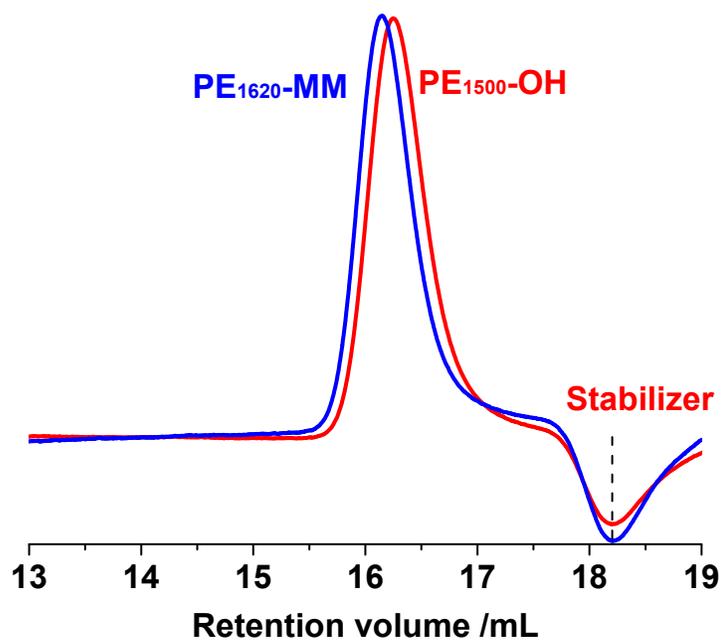
of DMAP. The reaction solution was stirred at 80 °C for 24 h. The white solid formed during the esterification reaction was removed by filtration. The filtrate was precipitated in methanol twice giving a white solid product. The resulted norbornyl PE-MM was characterized by HT-GPC, <sup>1</sup>H NMR and FTIR. Another two PE-MMs with different molecular weight of 1350 and 1620 g/mol have been prepared in the same way by using the corresponding PE-OH precursors.

### **Synthesis of PE molecular brushes by ring opening metathesis polymerization of PE-MMs**

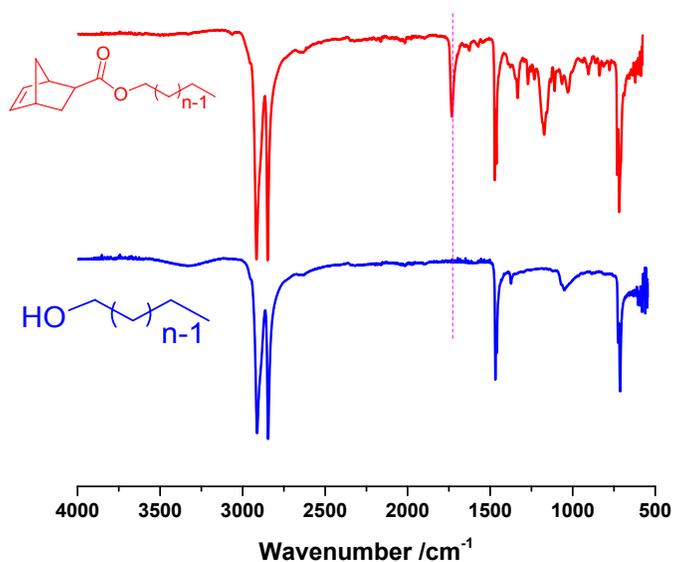
In a general process, 0.30 g of PE<sub>760</sub>-MM (0.39 mmol) was added into a Schlenk flask which was connected to a vacuum/argon line and pumped. 5 mL of toluene (over sodium/benzophenone) was distilled into the flask. After heating to 60 °C to dissolve the PE-MM, the solution was degased by freezing (liquid nitrogen)/pumping (10 min)/heating (60 °C) for 3 times. To the resulting clear and transparent solution at 60 °C, 1 mL of Grubbs 1<sup>st</sup> generation catalyst solution (5 mM in toluene, 5 μmol) was added and stirred at 50 °C for 8 h. 0.2 mL of vinyl ether was added and left to react for 10 min. The resulted solution was passed through a basic aluminum oxide column at 80 °C. The filtrate was concentrated (rotor evaporator) and precipitated in methanol giving a white solid product. The resulted product was dried under vacuum at room temperature (0.15 g, 50 %,  $M_{w,LS} = 50\ 600$  g/mol, PDI = 1.18). The other PE molecular brushes were synthesized in the same way using appropriate ratios of catalyst to the corresponding PE-MMs.

### ***In situ* monitoring the ring opening metathesis polymerization of PE-MM**

0.025 g of PE<sub>1620</sub>-MM (15 μmol) was added into a NMR tube followed by adding 0.75 mL of toluene-*d*<sub>8</sub> and heating to 80 °C to give a clear and transparent solution. After the characterization by <sup>1</sup>H NMR at 80 °C, the solution was degased by freezing (liquid nitrogen)/pumping (10 min)/heating (80 °C) for 3 times. 0.1 mL of Grubbs catalyst (1<sup>st</sup> generation) solution in toluene (5 mM, 0.5 μmol) was added and the <sup>1</sup>H NMR spectra were collected at different polymerization time at 80 °C.



**Figure S1.** Monitoring the synthesis of PE-OH and norbornyl PE-MM by high temperature gel permeation chromatography (HT-GPC, TCB, 150 °C). Both peaks are negative ( $dn/dc_{PE} < 0$ ) but are shown in a positive style for better comparison.



**Figure S2.** FTIR spectra of PE-OH ( $PE_{1500-OH}$ ) and norbornyl PE-MM ( $PE_{1620-MM}$ )

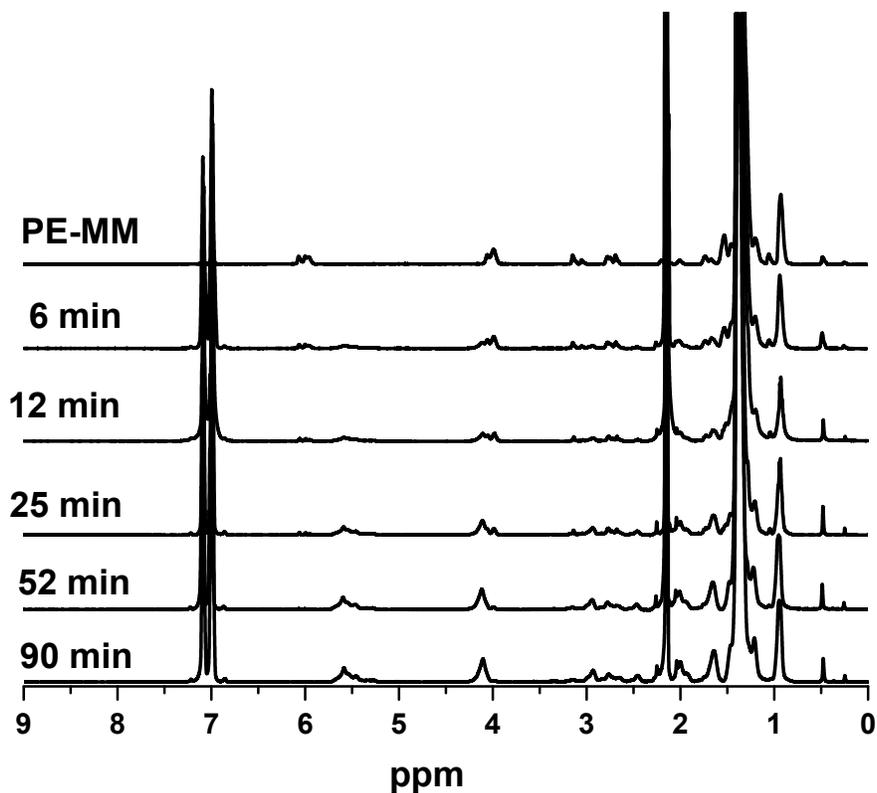


Figure S3. Full scale of  $^1\text{H}$  NMR spectra corresponding to Figure 3

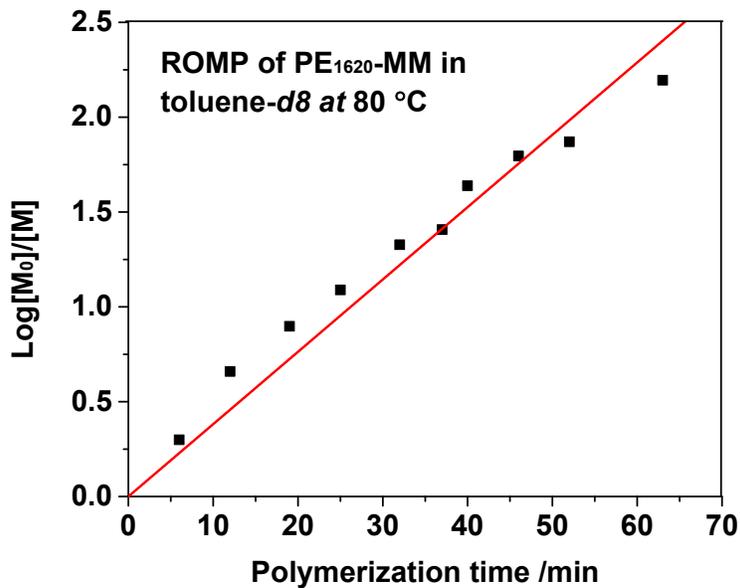
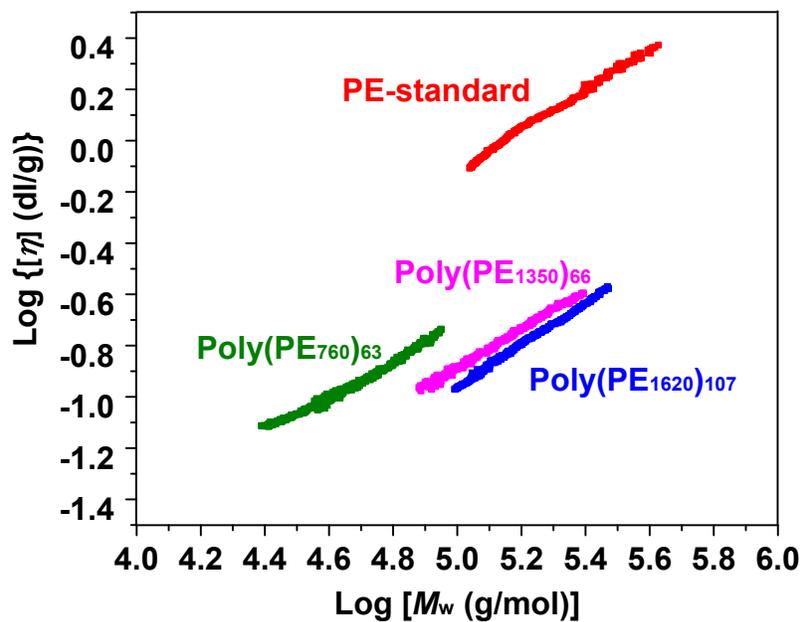
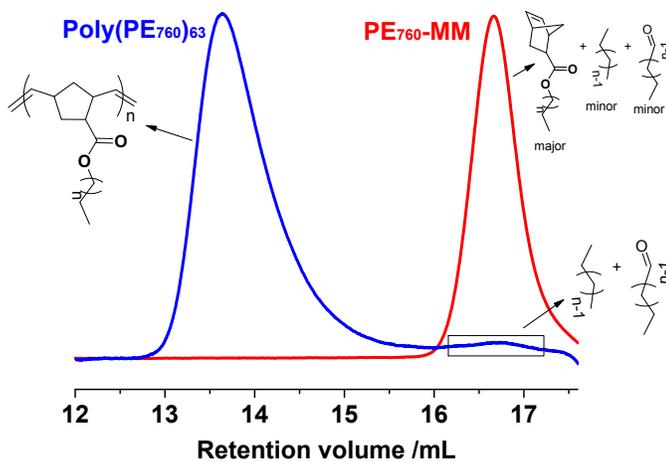


Figure S4. Kinetics of ROMP of PE macromonomer calculated from the *in situ*  $^1\text{H}$  NMR results ( $\text{PE}_{1620}\text{-MM}$  : Grubbs catalyst (1<sup>st</sup> generation) = 30 : 1 in mol,  $c_{\text{PE-MM}} = 33\text{ mg/mL}$  in toluene- $d_8$ )



**Figure S5.** Mark-Houwink-Sakurada plots of PE molecular brushes and a PE standard ( $M_p = 119\,600$  g/mol, PDI = 1.20) for comparison (HT-GPC system, TCB at 150 °C)



**Figure S6.** Unreacted non-OH terminated PE, after the ROMP of the PE-MM (inside the rectangular)

## References

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