

Well-defined polyethylene-based random, block and bilayered molecular comb brushes

Hefeng Zhang,^{1,2} Zhen Zhang,^{1,2} Yves Gnanou,² Nikos Hadjichristidis^{1,2*}

King Abdullah University of Science and Technology (KAUST), Thuwal 23955, Saudi Arabia

¹ Physical Sciences and Engineering Division, Catalysis Center, Polymer Synthesis Laboratory,

² Physical Sciences and Engineering Division

* Corresponding author, E-mail: nikolaos.hadjichristidis@kaust.edu.sa

Experiments

Chemicals

Trimethylsulfoxonium iodide (98 %, Alfa Aesar), benzyltri-*n*-butylammonium chloride (98%, Alfa Aesar) and trimethylamine *N*-oxide dihydrate (TAO·2H₂O) (>99%, Fluka), triethylborane (1.0 M in tetrahydrofuran, 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), phosphazene base P2-*t*-Bu solution (P2) (1 M in tetrahydrofuran, Aldrich) and poly(ethylene oxide) methyl ether (PEO) ($M_n = 2\,000$ g/mol and 5 000 g/mol, Aldrich) were used as received. Grubbs Catalyst (1st Generation) (97%, Aldrich) was dissolved in toluene (50 mM) before use. Sodium hydride (NaH) (60% in mineral oil, Aldrich) was washed by hexane before use. Celite 545[®] (Aldrich) was dried at 150 °C for 48 h before use. Tetrahydrofuran (THF) (99%, Fisher), cyclohexane and toluene (99.7%, Fluka) were distilled from sodium/benzophenone before use. ϵ -Caprolactone (>99%, Aldrich) was distilled from CaH₂ before use.

Instruments

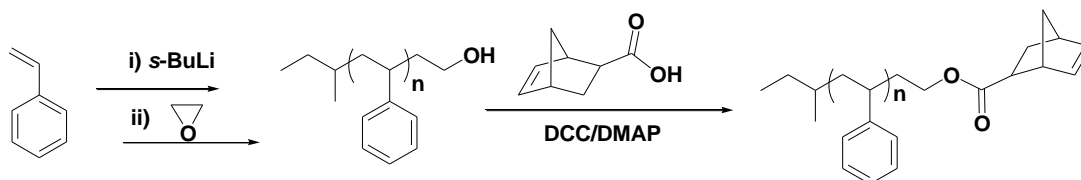
High temperature gel permeation chromatography (HT-GPC) measurements were carried out on a Viscotek HT-GPC module 350 instrument with two PLgel 10 μ m MIXED-B columns equipping with a reflective index detector, a light scattering detector ($\lambda = 670$ nm) and a viscometer. 1,2,4-Trichlorobenzene (TCB) was used as eluent (0.8 mL/min) at 150 °C. The tri-detector HT-GPC system was calibrated with PS standard ($M_w = 115 \times 10^3$ g/mol, PDI = 1.05). The polydispersity indexes (PDI) of macromonomers were determined by RI trace after calibrated with PS standards with molecular weights (M_p) from 560 g/mol to 1.9×10^6 g/mol (PDIs < 1.15). GPC measurements using THF as eluent were carried out on a Viscotek GPCmax module 305 instrument with two columns of Styragel HR 4 and Styragel HR 2 (1.0 mL/min, 35 °C). Proton nuclear magnetic resonance spectra (¹H NMR) were recorded on a Bruker AVANCE III-600 spectrometer. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1/TC100 system with an inert nitrogen atmosphere. The samples were heated from

room temperature to 160 °C, cooled to -80 °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 glass transition temperature (T_g), melting point (T_m) and enthalpy. Atomic force microscopy (AFM) images were recorded on an Agilent 5500 instrument operated in tapping mode, using the silicon tips of RTESPA (Bruker). A drop of polymer solution (0.05 mg/mL in toluene, 80 °C) was dropped on a clean silica wafer (~80 °C) and dried on the vacuum for 1 h before visualization.

Synthesis of macromonomers

The PE macromonomers were synthesized according to our previous work.¹

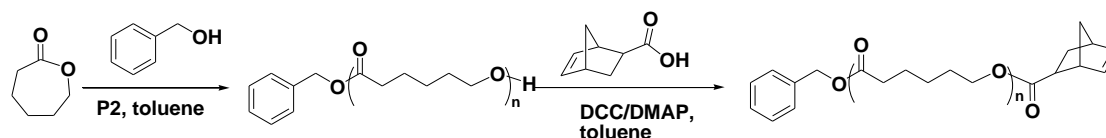
Polystyrene macromonomer (PS₂₅₀₀-Nor) (Scheme S1): 25 mL of styrene (0.22 mol) was distilled from *n*-dibutylmagnesium into polymerization flask through the vacuum line followed by 150 mL of cyclohexane from polystyryllithium (PSLi) solution. After warmed up to room temperature, 7 mL of *s*-BuLi (1.4 M in cyclohexane, 9.8 mmol) was added into the solution. The polymerization solution was kept at room temperature for 4 h and quenched by ethylene oxide (EO) gas dried by NaH. After removed cyclohexane on a rotary evaporator, the product was dissolved in 50 mL of THF and precipitated in methanol. After filtration and dried at vacuum, white solid product (PS-OH) was obtained (21.5 g, yield: 95%, $M_n = 2\,400$ g/mol, PDI = 1.05). 10 g of dry PS-OH (4.2 mmol) was dissolved in 150 mL of freshly distilled toluene followed by adding 5 g of 5-norbornene-2-carboxylic acid (36 mmol), 10 g of DCC (48 mmol), 0.5 g of DMAP (4.1 mmol). The solution was stirred at 90 °C for 24 h. After reaction, the solution was filtered to remove the white solid and the filtrate was precipitated in methanol for three times from toluene. The product of PS-Nor was filtered and dried under vacuum (9.5 g, $M_n = 2500$ g/mol, PDI = 1.05).



Scheme S1. Synthesis of PS-Nor by anionic polymerization followed by esterification reaction

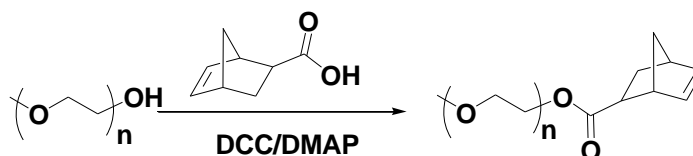
Polycaprolactone macromonomer (PCL-Nor) (Scheme S2): 0.3 mL of P2 (1 M in THF, 0.30 mmol) was added into a flask and pumped to remove the THF. 10 mL of dry toluene and 0.3 mL of benzyl alcohol (2.89 mmol) was introduced followed by 20 mL of dry caprolactone (CL) (0.18 mol). The solution was stirred at room temperature for 3 min and then quenched by 1 mL of acetic acid. The resulting solution was precipitated in methanol and the resulting white solid was dried on the vacuum (10.0g, $M_{n, NMR} = 2\,910$ g/mol, $PDI_{GPC} = 1.05$). 7 g of the resulting PCL (2.41 mmol) was dissolved in 100 mL of toluene followed by 4 g of 5-norbornene-2-carboxylic acid (28.8 mmol), 8 g of DCC (38.4 mmol), 0.5 g of DMAP (4.1 mmol). The solution was stirred at 90 °C for 24 h. After reaction, the solution was filtered to

remove the yellow solid and precipitated in methanol 3 times from toluene. The resulting solid product of PCL-Nor was dried on the vacuum (6.0 g, yield: 86%, $M_n = 3030$ g/mol, PDI = 1.05).



Scheme S2. Synthesis of PCL-Nor by ring opening polymerization followed by esterification reaction

Poly(ethylene oxide) macromonomer (PEO-Nor) (Scheme S3): 5 g of PEO ($M_n = 2\ 000$ g/mol, PDI = 1.09, 2.5 mmol) was dissolved in 100 mL of toluene followed by 4 g of 5-norbornene-2-carboxylic acid (28.8 mmol), 8 g of DCC (38.4 mmol), 0.5 g of DMAP (4.1 mmol). The solution was stirred at 90 °C. 24 h later, the solution was filtered to remove the white solid and precipitated in cold petroleum ether after concentrated. The white solid product of PEO-Nor was dried on the vacuum (4.0 g, $M_n = 2\ 100$ g/mol, PDI = 1.10).



Scheme S3. Synthesis of PEO-Nor by esterification reaction

PE-*b*-PCL-Nor (Scheme 3 in main text): 0.60 g of PE-OH ($M_{n,NMR} = 870$ g/mol, PDI = 1.07, 69 μ mol) was dissolved in 3 mL of hot toluene (80 °C) followed by adding 1.0 mL of ϵ -caprolactone (9.0 mmol) and 0.05 mL P2 (2 M in THF, 0.10 mmol). The resulting polymerization solution was kept at 80 °C for 14 h and then quenched by 0.1 mL acetic acid. The product PE-*b*-PCL was precipitated in methanol 3 times from hot toluene and dried on the vacuum ($M_{n,NMR} = 2\ 420$ g/mol, 1.1 g, yield: 67%). 1.0 g PE-*b*-PCL was dissolved in 20 mL of hot toluene (80 °C) followed by 1.0 g 5-norbornene-2-carboxylic acid (5.8 mmol), 1.5 g DCC (7.3 mmol) and 0.5 g DMAP (4.1 mmol). The reaction solution was kept at 80 °C for 24 h. The resulting solution was filtered at 80 °C to remove the white salt and the filtrate was precipitated in methanol for 3 times from the hot toluene. The white product of PE-*b*-PCL-Nor was obtained and dried on the vacuum ($M_n = 2\ 580$ g/mol, 0.7 g, yield: 70%).

ROMP of macromonomers monitored by ^1H NMR

Taking the PCL₃₀₃₀-Nor for example, 0.06 g of PCL₃₀₃₀-Nor (20 μ mol) was added into a NMR tube and degassed by pumping/argon for 3 times. 0.5 mL of toluene-*d*₈ was added followed by 20 μ L of Grubbs catalyst (1st generation) (50 mM in toluene, 1 μ mol). The tube was immediately put into NMR instrument (the instrument was stabilized at 80 °C before use) and the spectra were collected at different time.

ROMP of macromonomers for the synthesis of PE-based random molecular combbrushes

The random molecular combbrushes were synthesized by ROMP of mixtures of PE-Nor and other macromonomers. Taking the synthesis of P(PE₇₄₀)₇₂-*co*-P(PCL₃₀₃₀)₃₄ (entry 2, Table 2) for example, 0.08 g of PE₇₄₀-Nor (108 μmol) and 0.14 g of PCL-Nor (46 μmol) were dissolved into 1 mL of hot toluene (90 °C) in a Schlenk flask to give a clear and transparent solution. The resulting solution was put into oil bath at 80 °C followed by adding 30 μL of Grubbs catalyst (1st generation) in toluene (50 mM, 1.5 μmol) against an argon flow. 5 h later, 0.5 mL of vinyl ethyl ether was added to quench the polymerization. To remove the catalyst, the solution was passed through an aluminum oxide column using hot toluene (90 °C) as eluent. The filtrate was concentrated and precipitated in cold methanol giving the white product of P(PE₇₄₀)₇₂-*co*-P(PCL₃₀₃₀)₃₄ (0.12 g, yield: 55%, $M_{w, HT-GPC-LS} = 156\,700$ g/mol, $PDI_{HT-GPC-LS} = 1.06$).

Synthesis of PE-based block molecular combbrushes by sequential ROMP of macromonomers

Taking the synthesis of P(PCL₅₁₀₀)₃₅-*b*-P(PE₇₀₀)₅₅ (entry 4, Table 3) for example, 0.3 g of dry PCL₅₁₀₀-Nor (59 μmol) was dissolved into 2 mL of toluene. The solution was put into oil bath at 80 °C. 40 μL of Grubbs 1st generation catalyst in toluene (50 mM, 2 μmol) was added against argon flow. 2 h later, 0.5 mL of polymerization solution was transferred to a flask with 2 mL of toluene and 0.5 mL of vinyl ethyl ether. To the polymerization flask, 0.5 mL of PE₇₀₀-Nor solution in toluene (0.10 g/mL) (71 μmol) was added. After 3 h, 0.5 mL of vinyl ethyl ether was added to quench the polymerization. The catalysts in both PCL brush and PE-*b*-PCL brush solution were removed by passing the solution through an aluminum oxide column using hot toluene (90 °C) as eluent. The filtrates were precipitated in methanol giving white product. For the fractionation, the product (0.3 g) was dissolved in 40 mL of hot toluene (90 °C) and cooled naturally. The resulting turbid solution was centrifuged leading to a clear and transparent solution with a gel-like phase on the bottom. The gel-like phase was collected and dried on the vacuum giving the target product of P(PCL₅₁₀₀)₃₅-*b*-P(PE₇₀₀)₅₅ (0.18 g, yield: 60%, $M_{w, HT-GPC-LS} = 216\,400$ g/mol, $PDI_{HT-GPC-LS} = 1.20$).

Synthesis of PE-based bilayered molecular combbrushes by ROMP of a block macromonomer of PE-*b*-PCL-Nor

For the synthesis of bilayered molecular combbrush of P(PE₈₇₀-*b*-PCL₁₅₅₀)₄₃, 0.26 g of PE₈₇₀-*b*-PCL₁₅₅₀-Nor (102 μmol) was dissolved into 1.5 mL of hot toluene (80 °C) followed by injecting 50 μL of Grubbs catalyst (1st generation) (50 mM, 2.5 μmol) against an argon flow. The polymerization solution was kept at 80 °C in the oil bath for 24 h and quenched by 0.5 mL of vinyl ethyl ether. The catalyst was removed by passing through a hot aluminum oxide column using hot toluene (90 °C) as eluent. The solution was concentrated and precipitated in methanol. The resulting product was dried on the vacuum (0.15 g, yield: 57%, $M_{w, HT-GPC-LS} = 112\,100$ g/mol, $PDI_{HT-GPC-LS} = 1.14$).

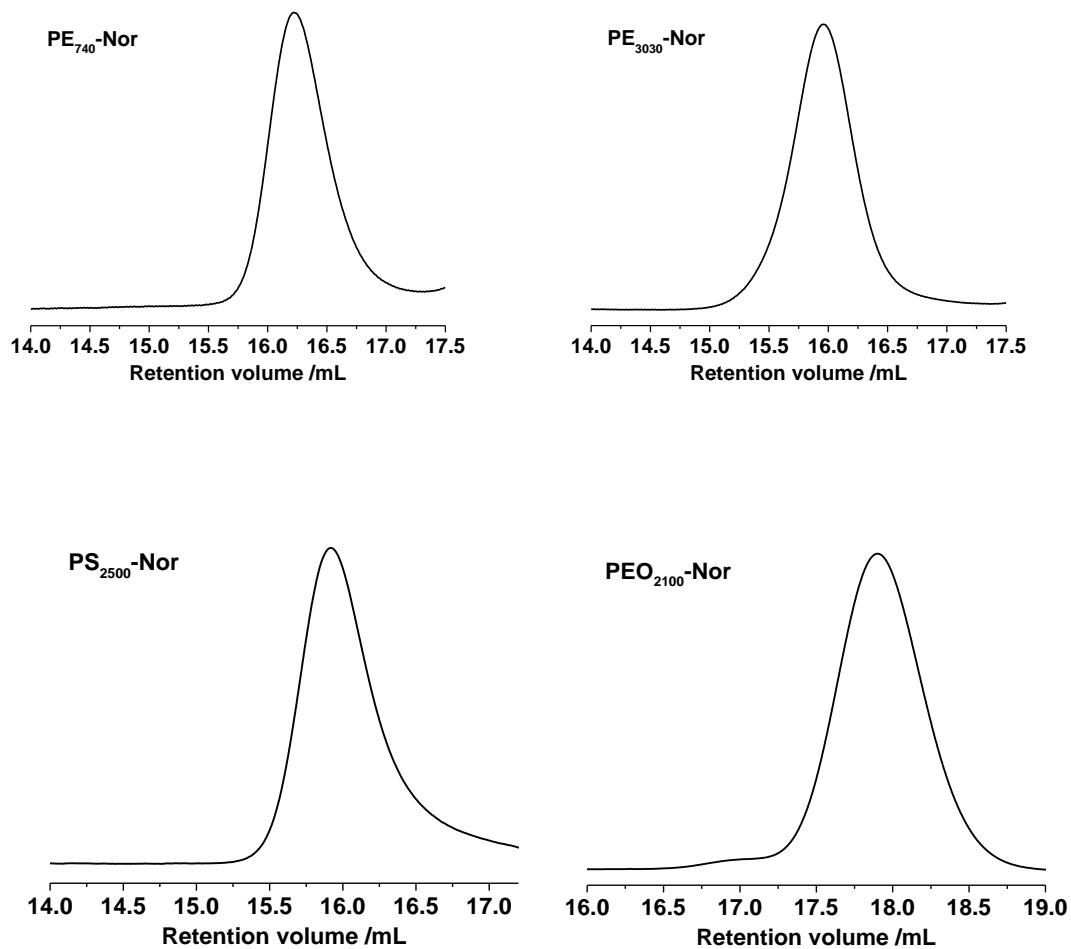


Figure S1. Macromonomers of PE₇₄₀-Nor, PS₂₅₀₀-Nor and PCL₃₀₃₀-Nor measured by HT-GPC (TCB, 150 °C), as well as PEO₂₁₀₀-Nor by general GPC (THF, 35 °C)

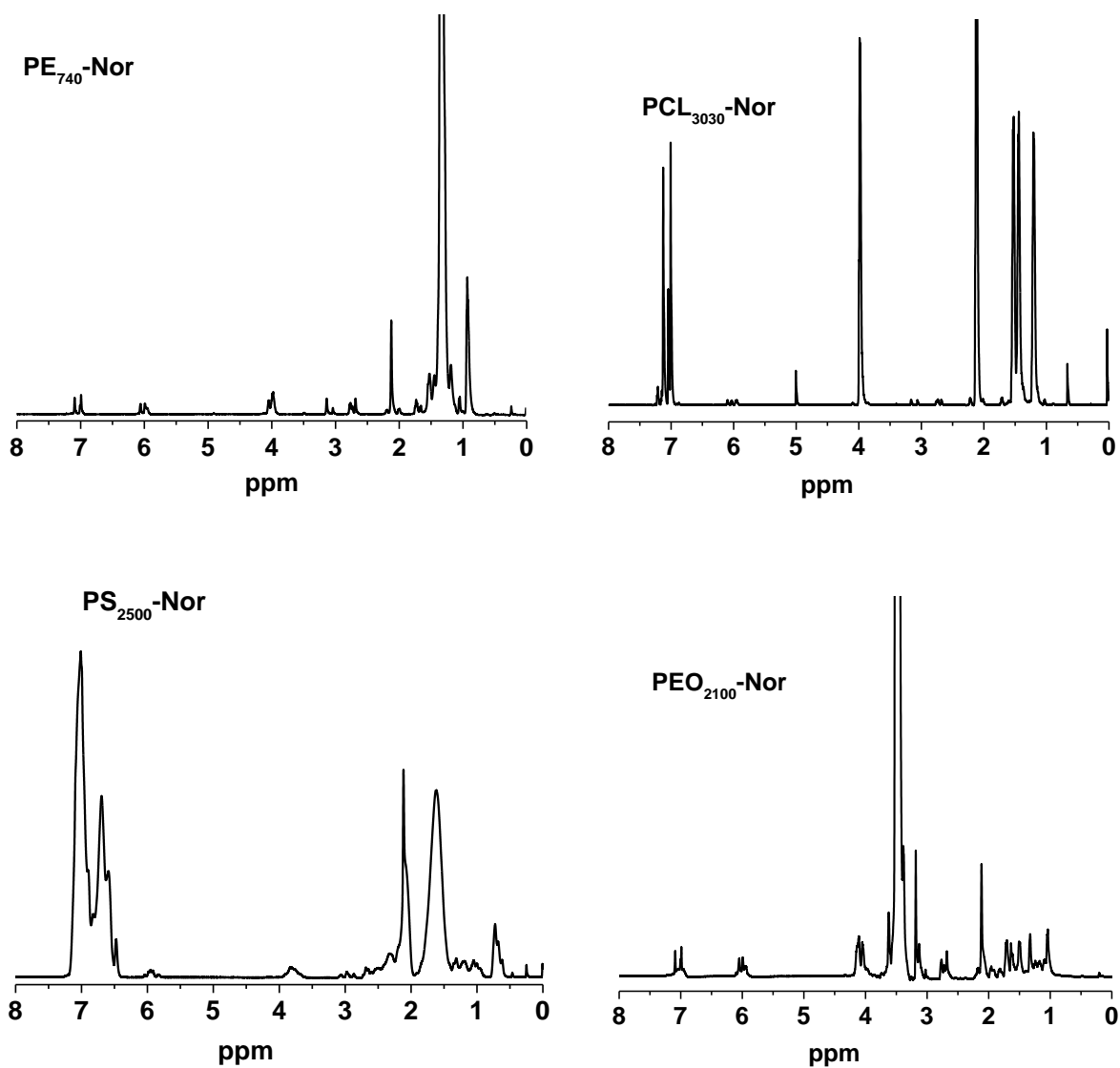


Figure S2. ^1H NMR spectra of macromonomers (toluene- d_8 , 80 °C)

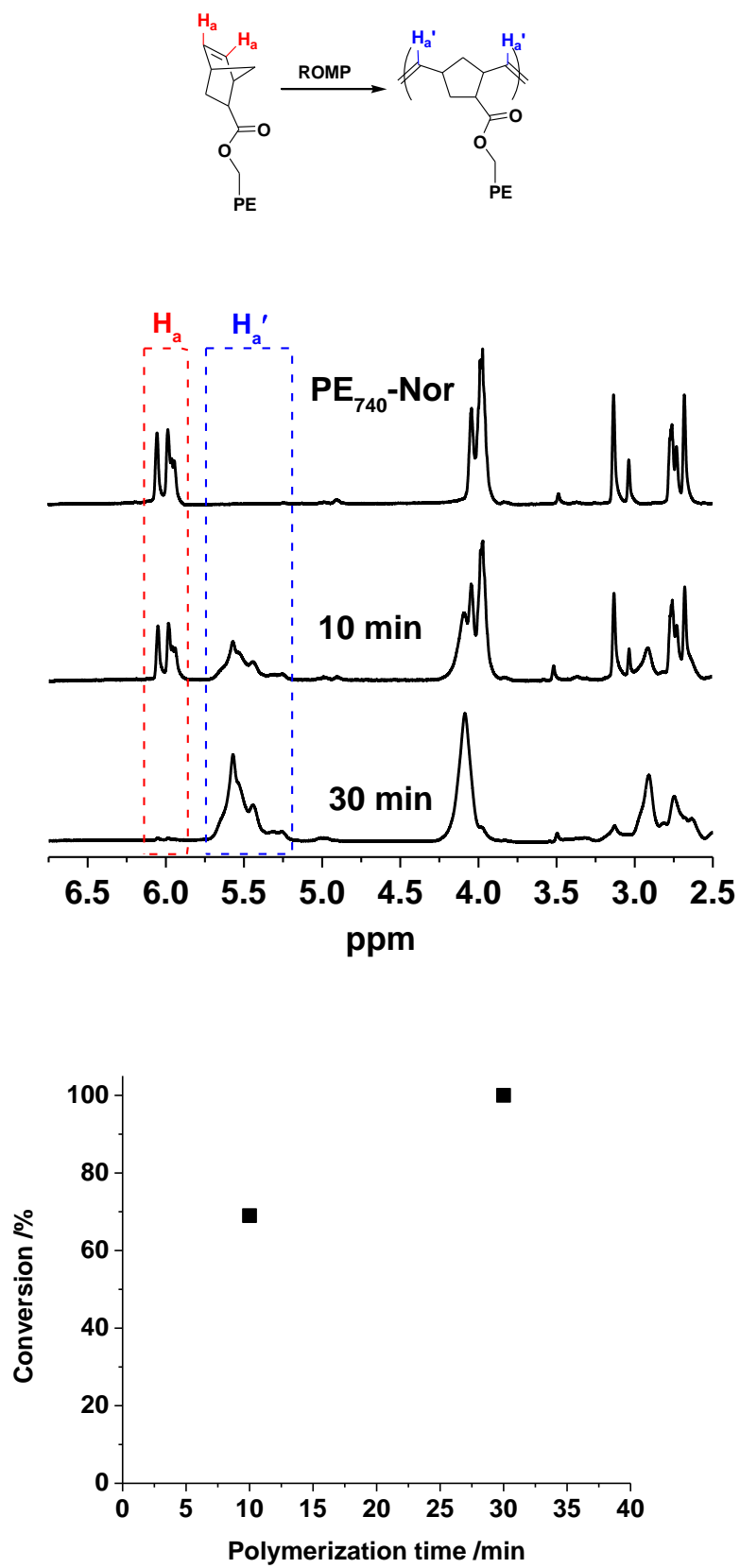


Figure S3. ROMP of PE₇₄₀-Nor monitored by 1H NMR (toluene- d_8 , 80 °C)

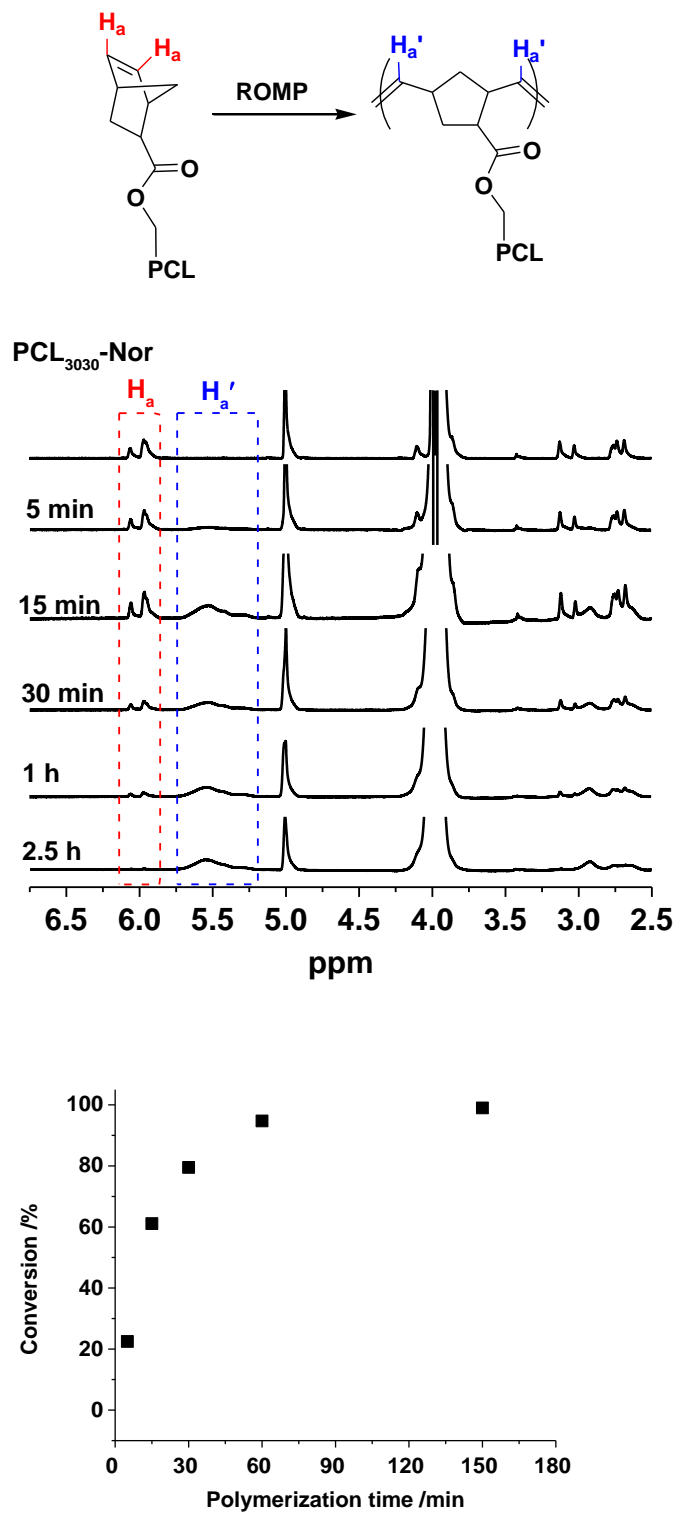


Figure S4. ROMP of $\text{PCL}_{3030}\text{-Nor}$ monitored by ^1H NMR (toluene- d_8 , 80 °C)

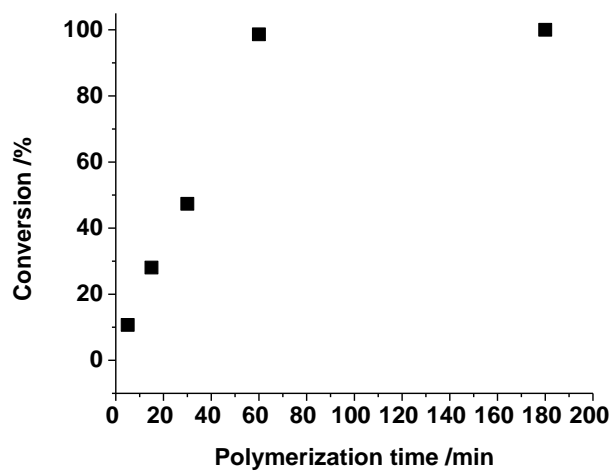
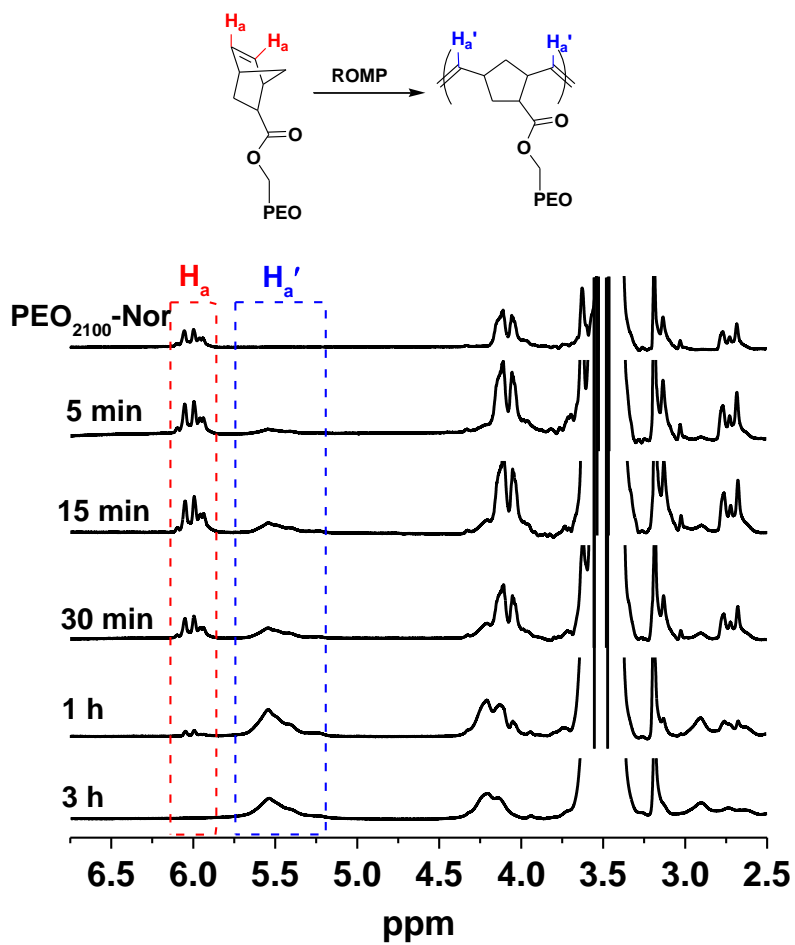


Figure S5. ROMP of PEO₂₁₀₀-Nor monitored by ¹H NMR (toluene-*d*₈, 80 °C)

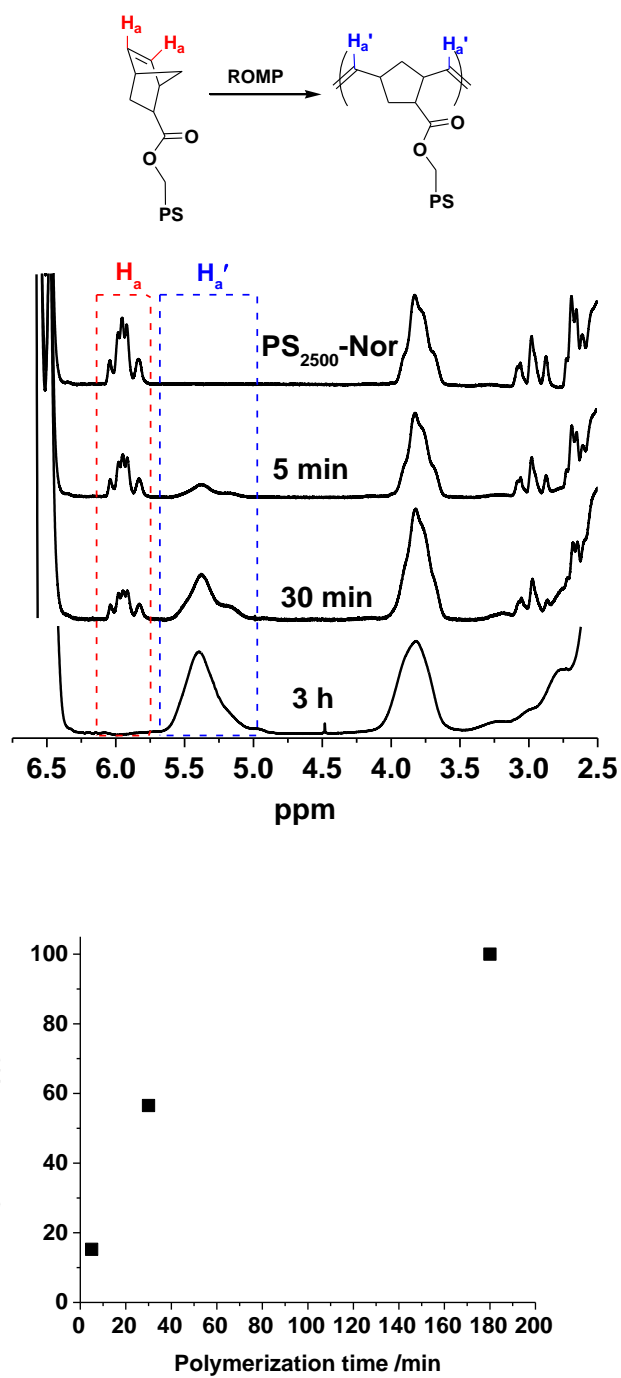


Figure S6. ROMP of PS₂₅₀₀-Nor monitored by ¹H NMR (toluene-*d*₈, 80 °C)

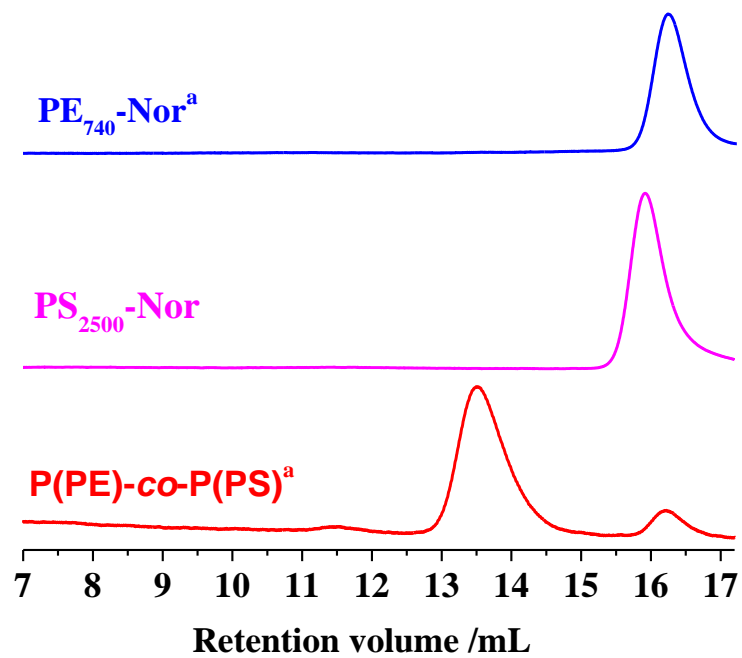


Figure S7. Monitoring the synthesis of $P(PE_{740})_{128}\text{-co-P}(PS_{2500})_{13}$ (entry 3, Table 2) by HT-GPC (TCB, 150 °C, ^a the peaks are negative and shown as positive for better comparison)

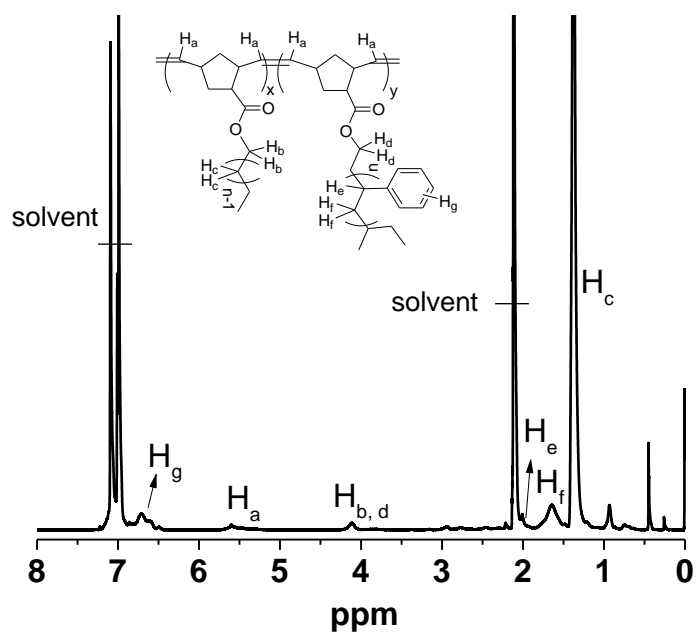
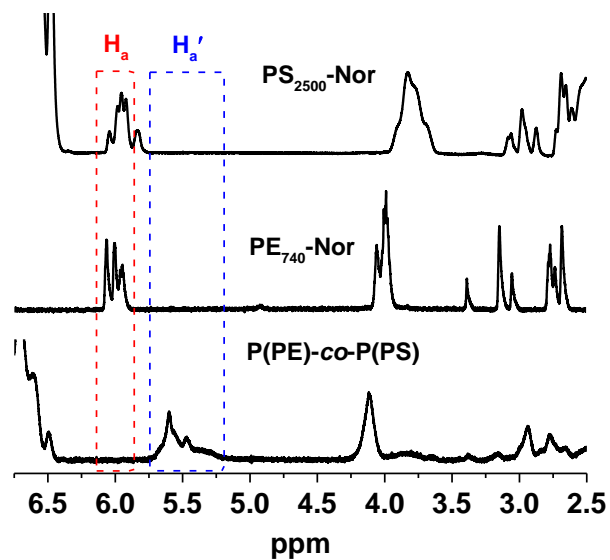


Figure S8. Full ^1H NMR spectrum of $\text{P(PE}_{740})_{128}\text{-co-P(PS}_{2500})_{13}$, (entry 3, Table 2, fingerprints of PE and PS blocks) and magnified spectrum in directions x and y (disappearance of the norbornene cyclic protons and appearance of the internal double bond protons of the cobrush, spectra taken in toluene- d_8 at 80 °C)

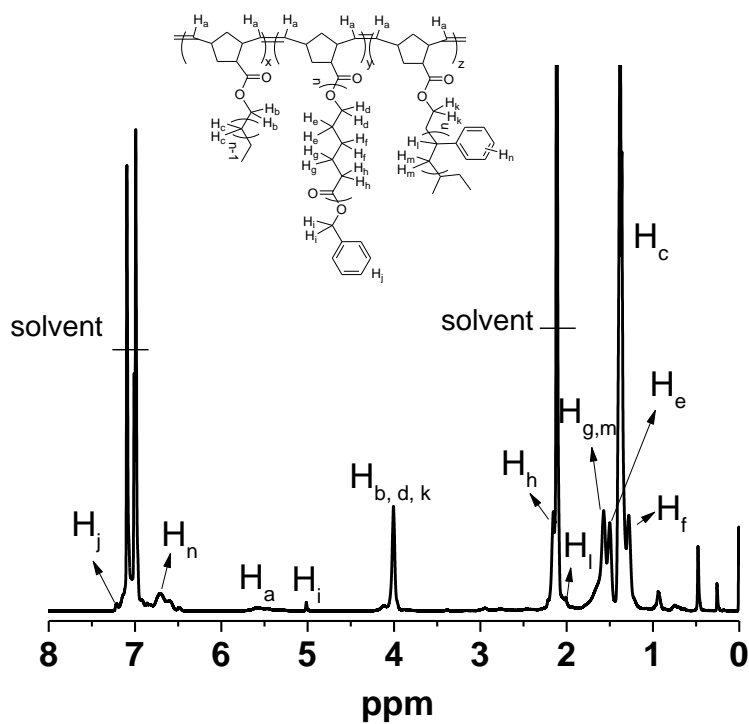
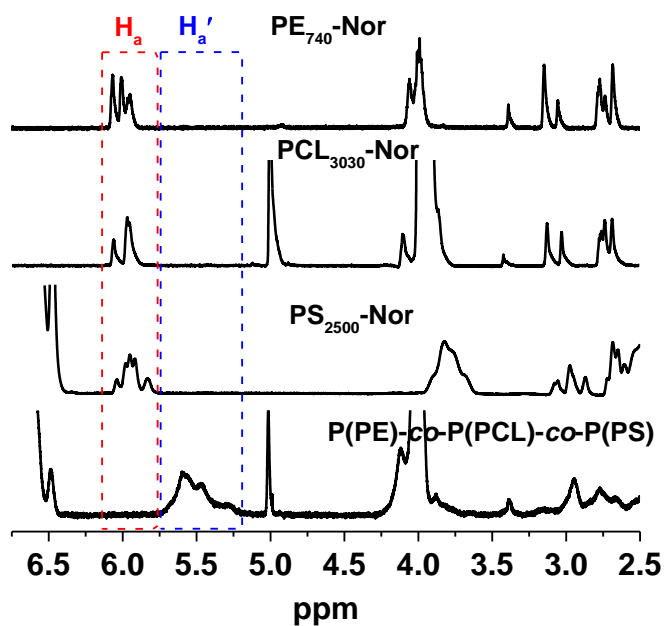


Figure S9. Full ^1H NMR spectrum of $\text{P}(\text{PE}_{740})_{144}\text{-co-P}(\text{PCL}_{3030})_{22}\text{-co-P}(\text{PS}_{2500})_{15}$, (entry 4, Table 2, fingerprints of PE, PCL and PS blocks) and magnified spectrum in directions x and y (disappearance of the norbornene cyclic protons and appearance of the internal double bond protons of the cobrush, spectra taken in $\text{toluene-}d_8$ at $80\text{ }^\circ\text{C}$)

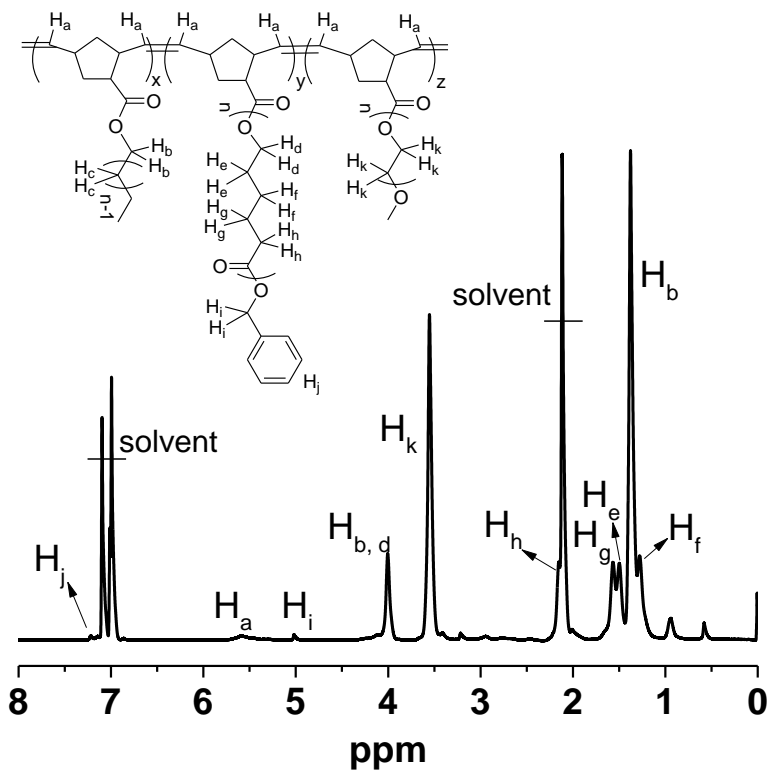
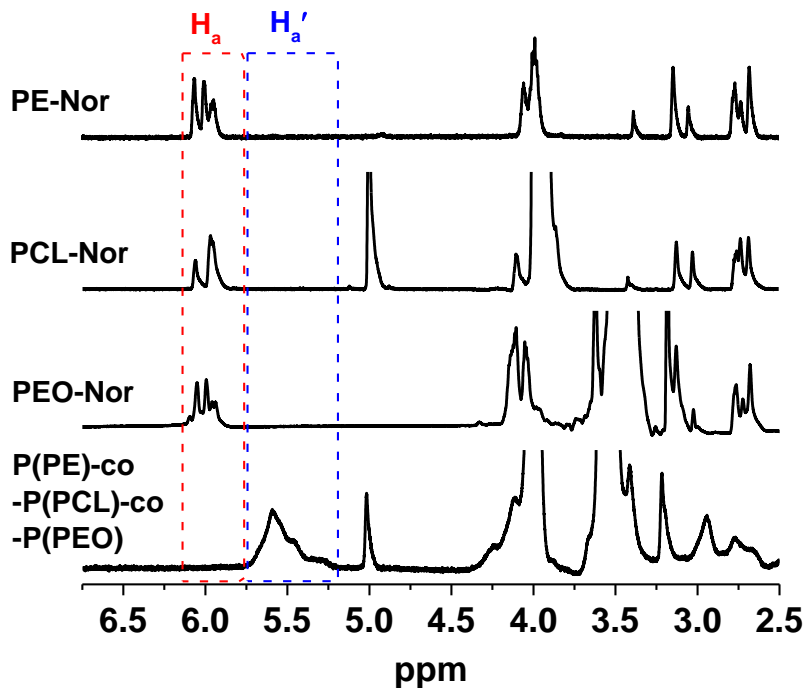


Figure S10. Full ^1H NMR spectrum of P(PE)-co-P(PCL)-co-P(PEO), (entry 5, Table 2, fingerprints of PE, PCL and PEO blocks) and magnified spectrum in directions x and y (disappearance of the norbornene cyclic protons and appearance of the internal double bond protons of the cobrush, spectra taken in toluene- d_8 at 80 °C)

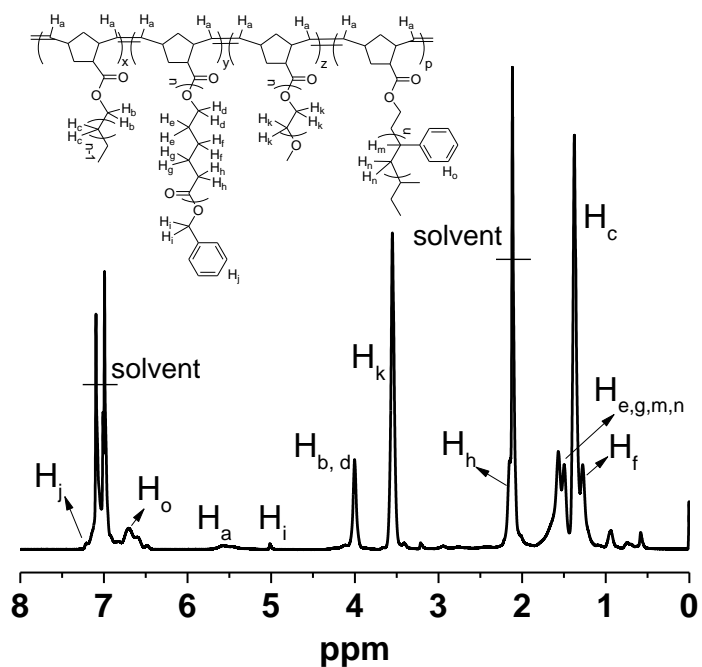
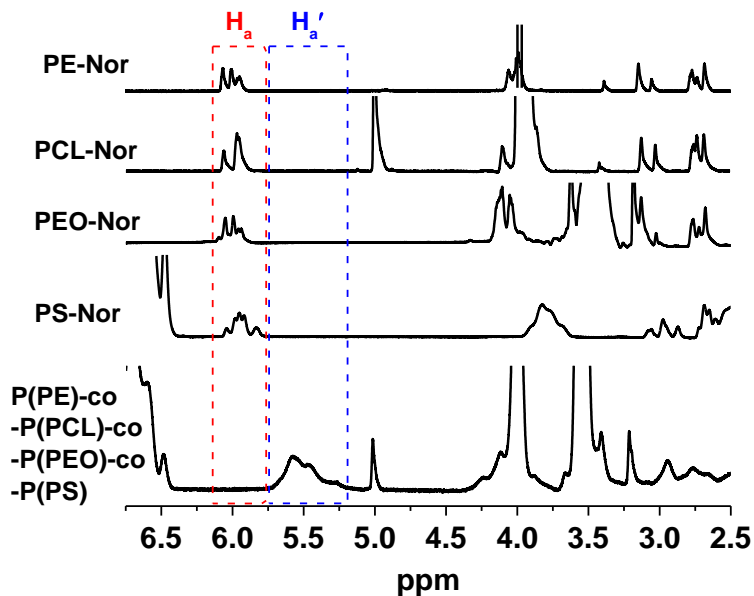


Figure S11. Full ^1H NMR spectrum of P(PE)-*co*-P(PCL)-*co*-P(PEO)-*co*-P(PS) (entry 6, Table 2, fingerprints of PE, PCL, PEO and PS blocks) and magnified spectrum in directions x and y (disappearance of the norbornene cyclic protons and appearance of the internal double bond protons of the cobrush, spectra taken in toluene- d_8 at 80 °C)

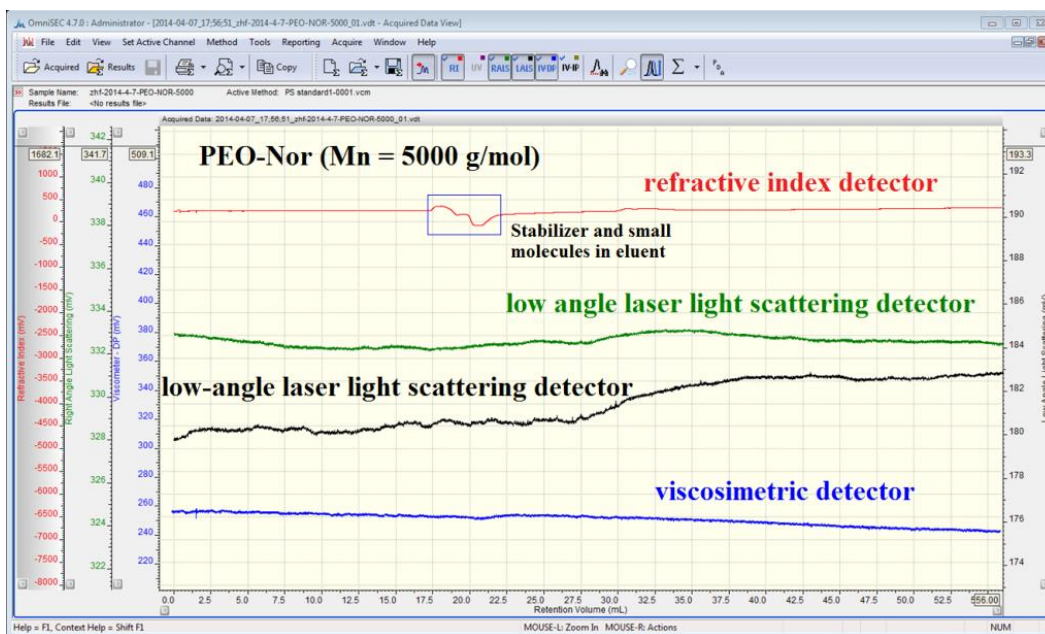


Figure S12. GPC traces of PEO-Nor ($M_n = 5000$ g/mol), indicating a strong absorption by the column, measured by high temperature GPC system with refractive index, light scattering and viscosimetric detectors (1,2,4-trichlorobenzene, 150 °C, sample concentration: 2.0 mg/mL, inject volume: 0.2 mL).

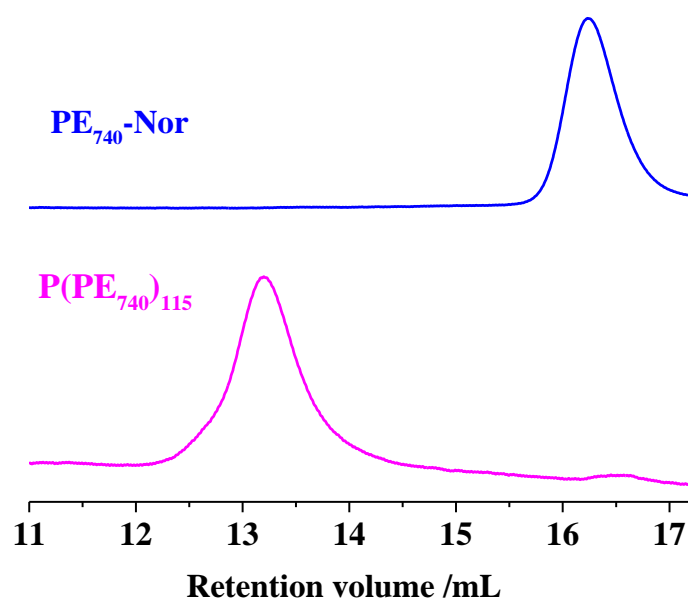


Figure S13. Monitoring the synthesis of $P(PE_{740})_{115}$ (entry 1, Table 2) by HT-GPC (TCB, 150 °C, the peaks are negative and shown as positive for better comparison)

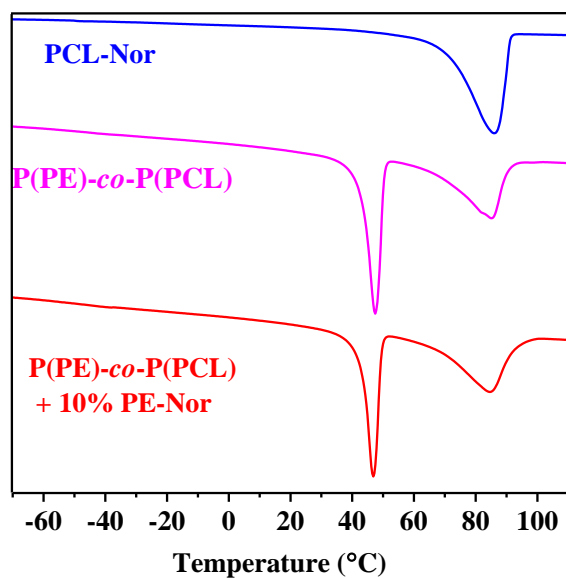


Figure S14. DSC traces of PE₇₄₀-Nor, random molecular cobrush of P(PE₇₄₀)₇₂-co-P(PCL₃₀₃₀)₃₄ and their mixture (PE-Nor content: 10% in weight) (N₂, 10 °C/min, second cycle)

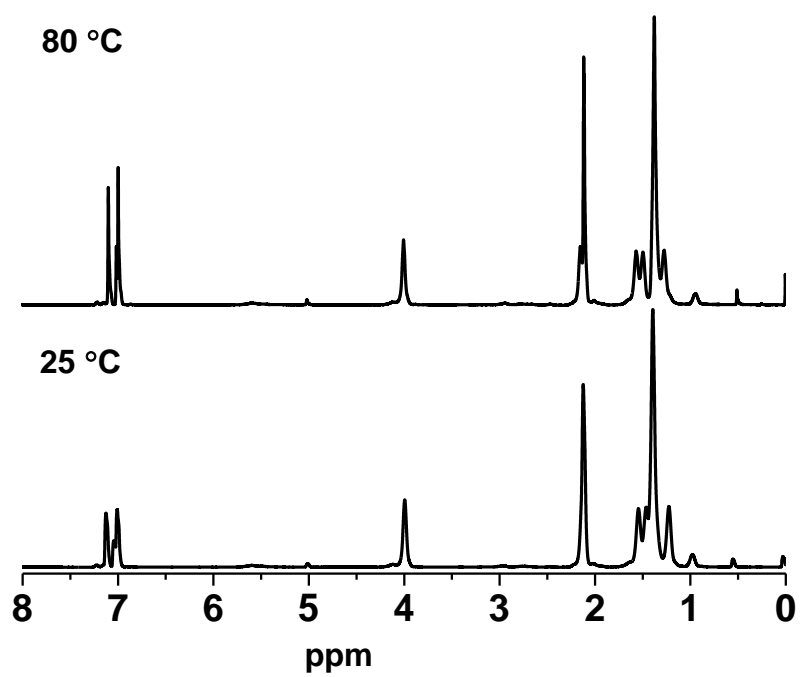


Figure S15. Comparison of ¹H NMR spectra of P(PE₇₄₀)₇₂-co-P(PCL₃₀₃₀)₃₄ (entry 2, Table 2) in toluene-*d*₈ at room temperature and 80 °C

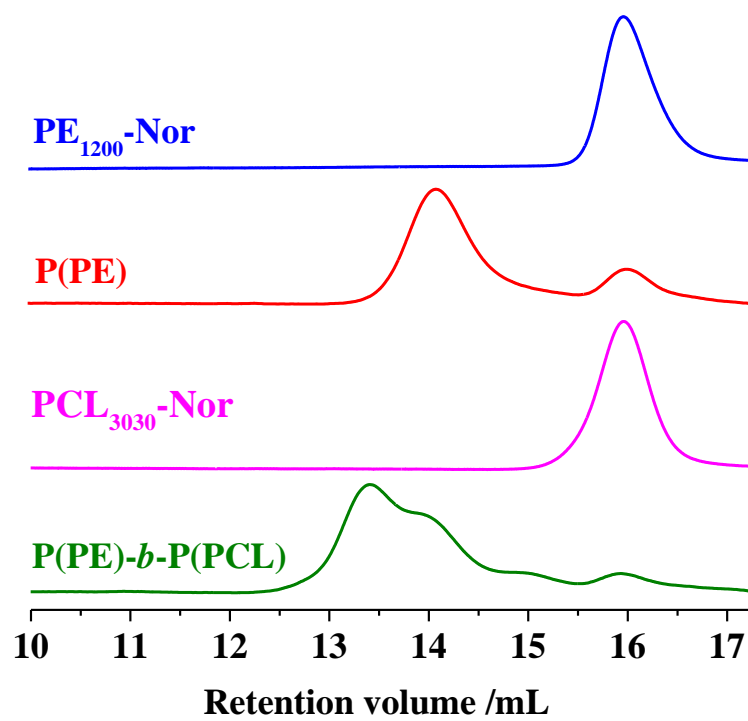


Figure S16. Non-quantitative initiation of macroinitiator of P(PE)=[Ru] for the second macromonomer of PCL₃₀₃₀-Nor

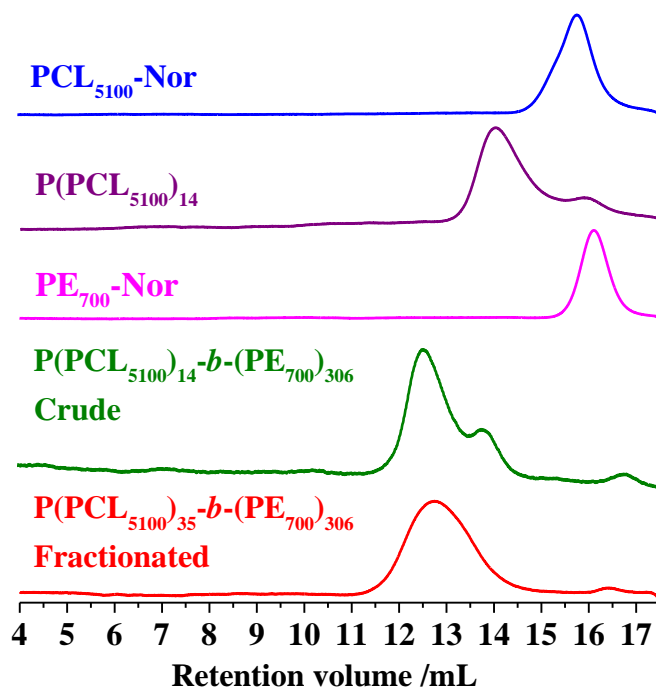


Figure S17. Monitoring the synthesis of P(PCL₅₁₀₀)₁₄-*b*-P(PE₇₀₀)₃₀₆ (entries 5 and 6, Table 3) by HT-GPC (TCB, 150 °C, all the peaks are negative and shown as positive for better comparison)

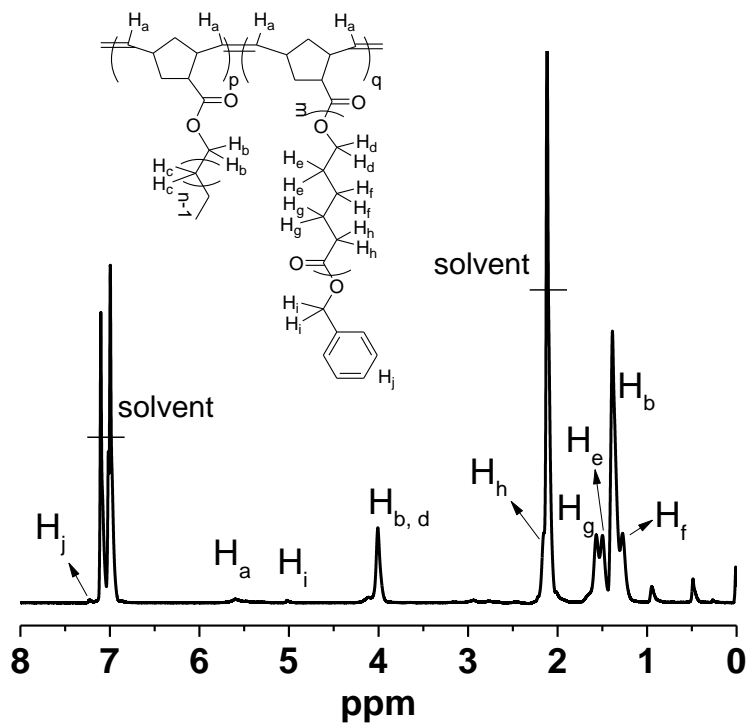
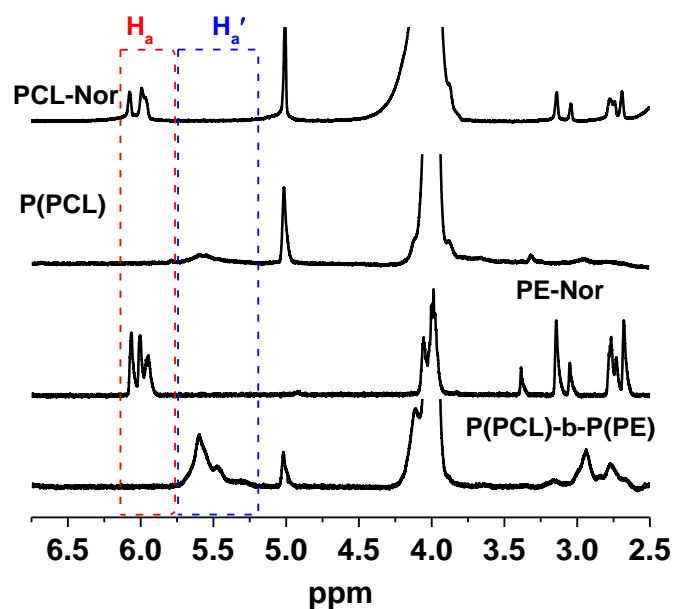


Figure S18. Full ^1H NMR spectrum of $\text{P}(\text{PCL}_{5100})_{35}\text{-}b\text{-P}(\text{PE}_{700})_{55}$, (entry 4, Table 3, fingerprints of PE and PCL) and magnified spectrum in directions x and y (disappearance of the norbornene cyclic protons and appearance of the internal double bond protons of the cobrush, spectra taken in toluene- d_8 at 80 °C)

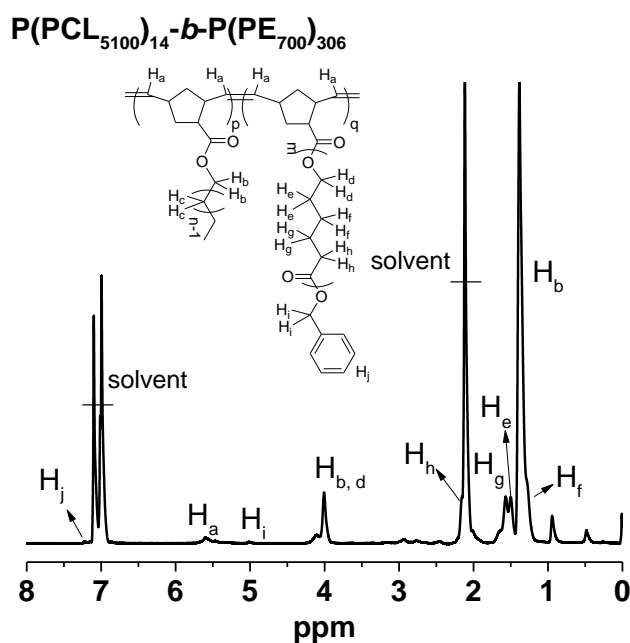
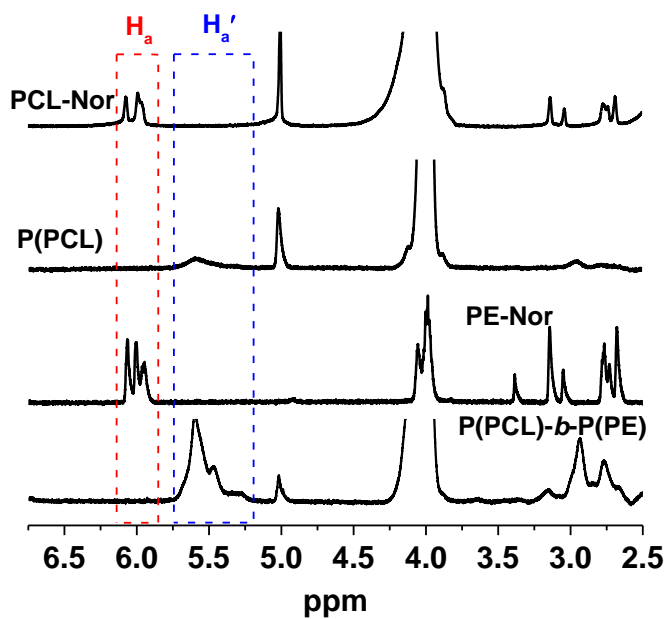


Figure S19. Full ^1H NMR spectrum of $\text{P}(\text{PCL}_{5100})_{14}\text{-}b\text{-P}(\text{PE}_{700})_{306}$, (entry 6, Table 3, fingerprints of PE and PCL) and magnified spectrum in directions x and y (disappearance of the norbornene cyclic protons and appearance of the internal double bond protons of the cobrush, spectra taken in toluene- d_8 at 80 °C)

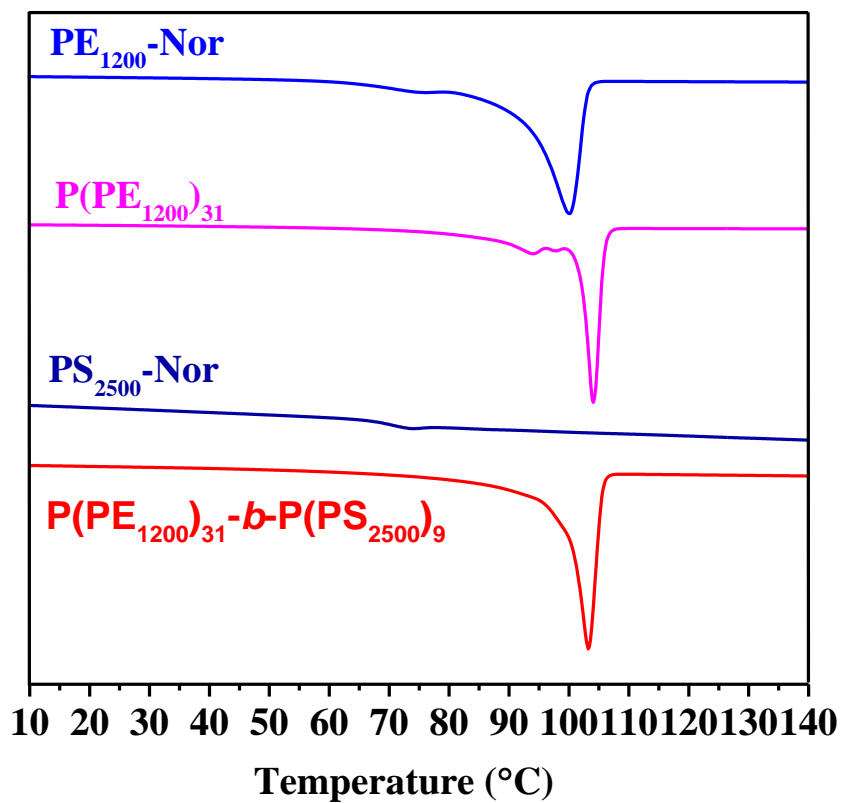


Figure S20. DSC traces of PE-based block molecular comb brushes of P(PE₁₂₀₀)₃₁-*b*-P(PS₂₅₀₀)₉ (entry 2, Table 3) (N₂, 10 °C/min, second cycle)

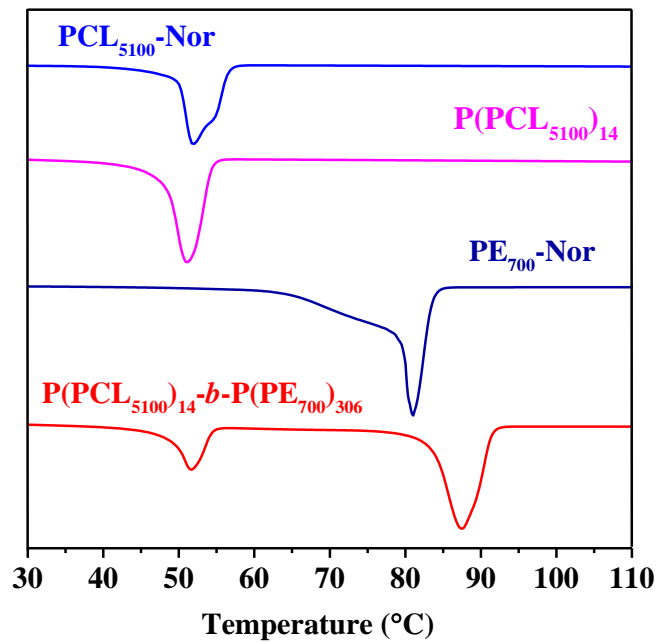


Figure S21. DSC traces of PE-based block molecular comb of P(PCL₅₁₀₀)₁₄-*b*-P(PE₇₀₀)₃₀₆ (entries 5 and 6, Table 3) (N₂, 10 °C/min, second cycle)

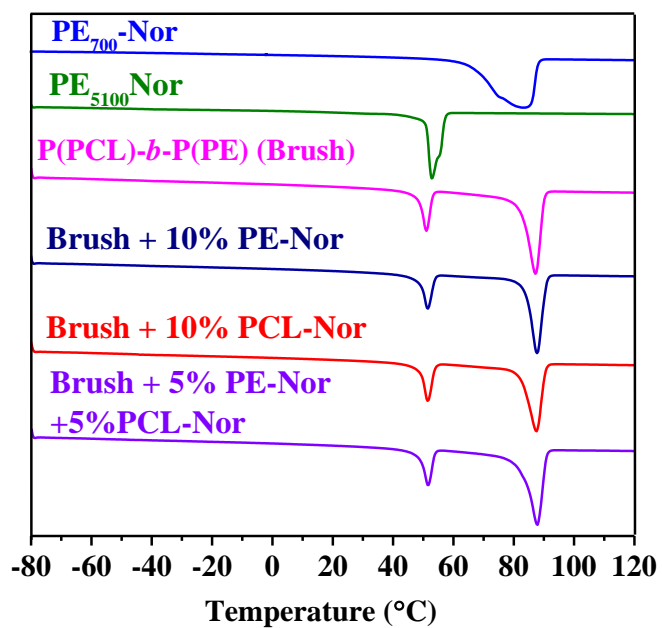


Figure S22. DSC traces of PE₇₀₀-Nor, PCL₅₁₀₀-Nor, block molecular cobrush of P(PCL₅₁₀₀)₁₄-*b*-P(PE₇₀₀)₃₀₆ and their mixtures (the ratios are based on weight) (N₂, 10 °C/min, second cycle)

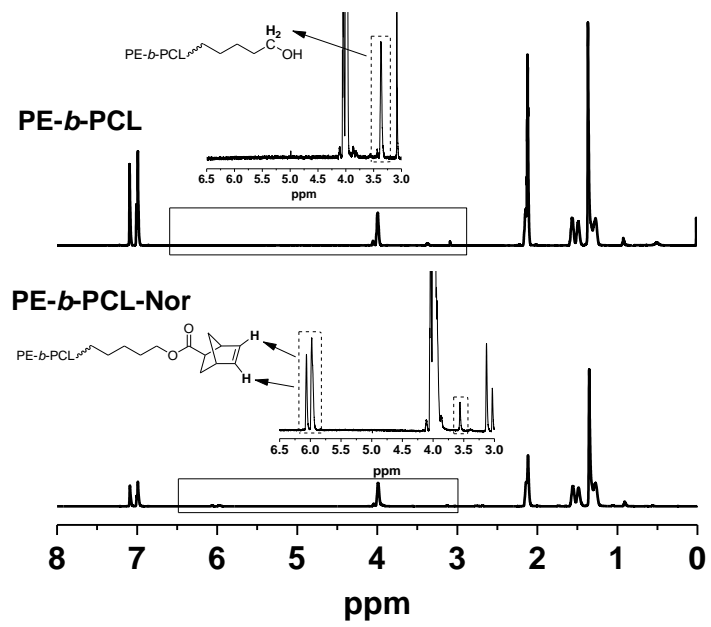


Figure S23. ^1H NMR spectra of $\text{PE}_{870}\text{-}b\text{-PCL}_{1550}$ and $\text{PE}_{870}\text{-}b\text{-PCL}_{1550}\text{-Nor}$

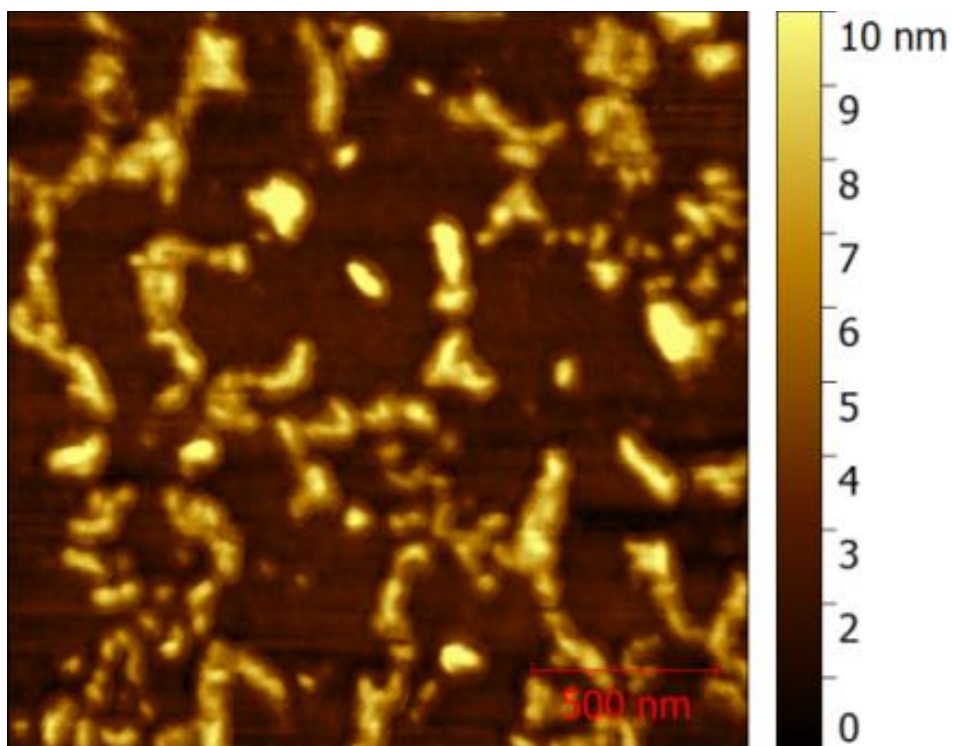


Figure S24. PE-based bilayered molecular comb brush of $P(\text{PE}_{870}\text{-}b\text{-PCL}_{1550})_{197}$ (entry 5, Table 4) visualized by AFM on silica wafer (tapping mode)

References

1. Zhang, H.; Gnanou, Y.; Hadjichristidis, N. *Polym. Chem.* **2014.** 5, 6431-6434.