Supporting information

For

# Two-dimensional controlled syntheses of polypeptide molecular brushes *via N*-carboxyanhydride ring-opening polymerization and ring-opening metathesis polymerization

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## Experimental section

### Materials

Ethyl acetate, *n*-hexane, diethyl ether, methanol, dichloromethane (DCM, anhydrous, ≥ 99.8%), *N,N*-dimethylformamide (DMF, anhydrous, ≥ 99.8%), *N,N*-dimethylacetamide (DMAc, anhydrous, ≥ 99.8%), potassium hydroxide (KOH, ≥ 97%), sodium chloride (NaCl, ≥ 99%), potassium carbonate ($K_2CO_3$, ≥ 99%), β-benzyl-L-aspartate (≥ 99%), bis(trichloromethyl) carbonate (≥ 98%), 1,8-diaminooctane, acetyl anhydride, *exo*-5-norbornenecarboxylic acid, *N*-hydroxysuccinimide, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) hydrochloride, *N*-Boc-ethylenediamine, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][$BF_4$]), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([bdmim][$BF_4$]) were purchased from Sigma-Aldrich company (USA). All chemicals were used without further purification, unless otherwise noted. Nanopure water (18.2 MΩ·cm) was acquired by means of a Milli-Q water filtration system, Millipore Corp. (St. Charles, MO). The modified Grubbs 2$^{nd}$ generation catalyst was synthesized according to the literature report.[1]

### Instrumentation

$^1$H and $^{13}$C NMR spectra were recorded on a Varian Inova 500 spectrometer interfaced to a UNIX computer using VnmrJ software. Chemical shifts were referenced to the solvent resonance signals. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) spectra were recorded on an IR Prestige 21 system (Shimadzu Corp.) and analysed using IRsolution v. 1.40 software.

DMF-based size-exclusion chromatography (SEC) was conducted on a Waters (Waters Chromatography, Inc., Milford, MA) system equipped with an isocratic pump model 1515, a differential refractometer model 2414, a PD2020 dual-angle (15° and 90°) light scattering detector (Precision Detectors, Inc.), and a four-column set of 5 μm Guard (50 × 7.8 mm), Styragel HR 4 5 μm DMF (300 × 7.8 mm), Styragel HR 4E 5 μm DMF (300 × 7.8 mm), and Styragel HR 2 5 μm DMF (300 × 7.8 mm). The system was equilibrated at 70 °C in pre-filtered DMF (containing 0.05 mol/L LiBr), which served as the polymer solvent and eluent (flow rate set to 1.00 mL/min). Polymer solutions were prepared at a known concentration (3.0 – 5.0 mg/mL) and an injection volume of 200 μL was used. Data collection and analysis were performed with Precision Acquire software and Discovery 32 software, respectively. Inter-detector delay volume and the light

scattering detector calibration constant were determined by calibration using a nearly monodispersed polystyrene (PS) standard (Polymer Laboratories, Amherst, MA, $M_p$ = 90 kDa, $M_w/M_n$ < 1.04). The differential refractometer was calibrated with stand PS material (SRM 706 NIST), of known specific refractive index increment dn/dc (0.185 mL/g). The dn/dc values of the analyzed polymers were then determined from the differential refractometer response. The system was calibrated with PS standards ranging from 1480 to 1233000 Da and poly(ethylene oxide) (PEO) standards (Polymer Laboratories, Amherst, MA) ranging from 1010 to 723500 Da.

Thermogravimetric analysis (TGA) was performed under an argon atmosphere using a Mettler-Toledo model TGA/SDTA851$^e$ (Mettler-Toledo, Inc., Columbus, OH), with a heating rate of 10 °C/min. Measurements were analyzed using Mettler-Toledo STAR$^e$ v. 7.01 software. Glass transition temperatures ($T_g$) were measured by differential scanning calorimetry (DSC) on a Mettler-Toledo DSC822®, with a heating rate of 10 °C/min. Measurements were analyzed using Mettler-Toledo STAR$^e$ v. 7.01 software. The $T_g$ was taken as the midpoint of the inflection tangent, upon the second heating scan.

## Experimental procedures

### Synthesis of *exo-N*-(8-aminooctyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide (NB-amine initiator, 1)

A mixture of *exo*-5-norbornenecarboxylic acid (1.50 g, 10.8 mmol), *N*-hydroxysuccinimide (1.58 g, 14.7 mmol) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) hydrochlorid (2.68 g, 14.1 mmol) was stirred in dry dichloromethane (DCM) (30 mL) for 8 hours at room temperature. The solvent was evaporated in vacuum and the crude reaction mixture was purified by flash chromatography (ethyl acetate : *n*-hexane = 1 : 2). The solution of the activated ester in dry DCM (60 mL) was added dropwise over 1 h period to a vigorously stirred solution of 1,8-diaminooctane (7.8 g, 54 mmol) in dry DCM (30 mL). The solution was stirred overnight at room temperature and quenched with concentrated potassium hydroxide solution (20 mL). The product was extracted with ethyl acetate (3 × 150 mL), the organic fractions were collected and washed with basic water (pH = 14, 20 mL) and finally basic brine (20 mL). The organic phase was dried over potassium carbonate and the product purified by flash chromatography (silica, eluent: methanol/chloroform/$NH_4OH_{aq,\ conc.}$ = 100/800/10) upon removal of the volatiles under reduced pressure, and the residual methanol was removed by azeotropic distillation with DCM (3 × 30 mL). The targeted

compound appeared as a light yellow oil (2.45 g, 86 %). $^{1}$H NMR (500 MHz, $CDCl_3$, ppm): δ 1.20-1.33 (12H), 1.35-1.42 (2H), 1.42-1.51 (2H), 1.69 (d, *J* = 8.3 Hz, 1H), 1.87 (dt, *J* = 8.1, 3.8 Hz, 1H), 1.91-1.96 (1H), 2.60-2.67 (2H), 2.84-2.89 (2H), 3.18-3.24 (2H), 5.51 (1H), 6.06 (dd, *J* = 5.6, 3.1 Hz, 1H), 6.10 (dd, *J* = 5.6, 3.1 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$, ppm): δ 27.0, 27.1, 29.4, 29.6, 29.9, 30.7, 34.0, 39.8, 41.7, 42.4, 45.0, 46.5, 47.4, 136.2, 138.4, 175.7. FTIR ($cm^{-1}$): 3300-2900, 2852, 1643, 1537, 1454, 1440, 1244. HRMS: calculated $[M+H]^+$ for $C_{15}H_{24}N_2O_3$: 265.2280, found: 265.2270.

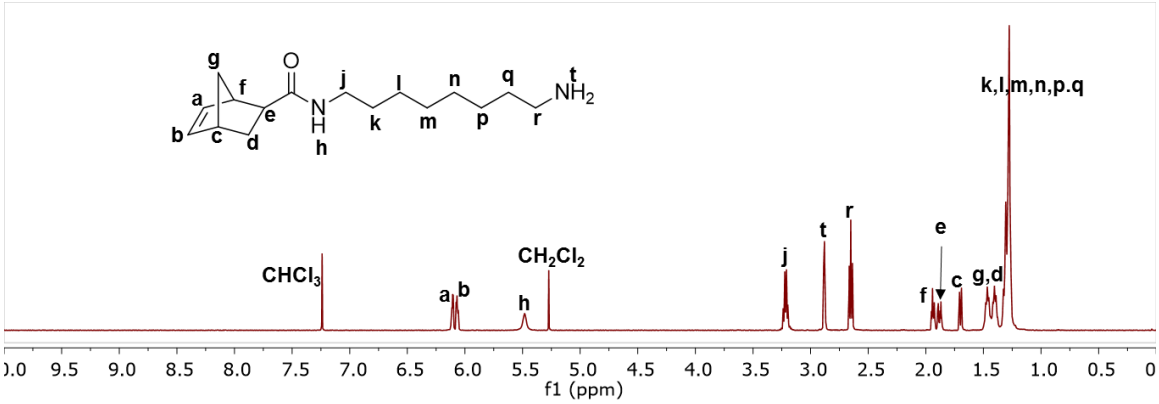
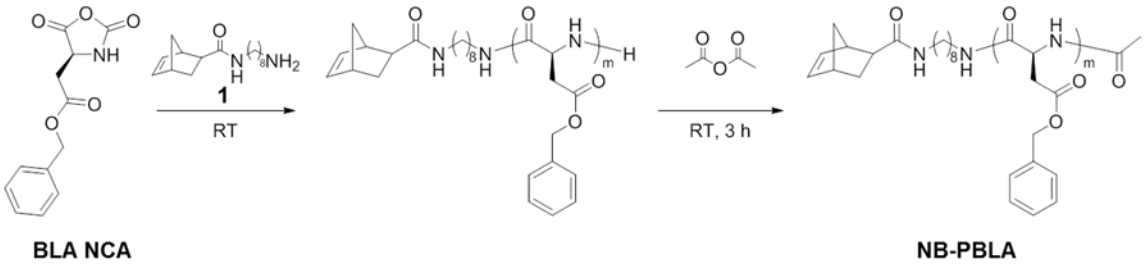



**Figure S1**. $^{1}$H NMR spectrum of **1** in $CDCl_3$.

### Synthesis of β-benzyl-L-aspartate *N*-carboxyanhydride (BLA NCA) monomer

In a 250-mL three-necked round bottom flask equipped with a magnetic stirrer, condenser and $N_2$ inlet, BLA NCA monomer was synthesized from β-benzyl-L-aspatate (5.0 g, 22 mmol, 2 equiv.) and bis(trichloromethyl) carbonate (3.3 g, 11 mmol, 1 equiv.) in 100 mL dry ethyl acetate at 80 °C under $N_2$ flow for 3 h.[2] The reaction solution became clear around 1 h after the addition of bis(trichloromethyl) carbonate. After cooling to room temperature, the reaction mixture was concentrated into a white solid, which was further purified by recrystallization with ethyl acetate/*n*-hexane 1:1 (v/v) three times, and dried in vacuum to obtain a white needle-like crystal (3.5 g, yield: 63%). The product was stored in a -20 °C freezer under $N_2$ atmosphere. $^{1}$H NMR (500 MHz, DCM-$d_2$, ppm): δ 2.91 (dd, *J* = 8.4 Hz, *J* = 17.8 Hz, 1H, CHC*H*$_2$COO), 3.07 (dd, *J* = 3.4 Hz, *J* = 17.8 Hz, 1H, CHC*H*$_2$COO), 4.60 (ddd, *J* = 3.4 Hz, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H, C*H*CH$_2$COO), 5.18 (2H, COOC*H*$_2$), 6.32 (1H, CON*H*CH), 7.37 (5H, Ar*H*). $^{13}$C NMR (125 MHz, DCM-$d_2$, ppm): δ 34.9, 53.6, 66.3, 128.2, 128.2, 128.5, 135.5, 152.2, 169.3, 171.0. FTIR ($cm^{-1}$): 3450-3100, 3030, 2971, 2941, 2900, 1833, 1782, 1725, 1258, 1173, 1110, 923, 747. HRMS: calculated $[M-H]^-$ for $C_{12}H_{11}NO_5$: 248.0559, found: 248.0561.

**Synthesis of PBLA macromonomer initiated by NB-amine initiator, 1, with direct chain-end modification after polymerization**




**Scheme S1**. Synthetic route of NB-PBLA from ROP of BLA NCA using the $N_2$ flow method, followed by direct chain-end modification with acetic anhydride without the need to isolate polypeptide after polymerization.

NB-PBLA macromonomers with different chain lengths were synthesized in a similar approach and the detailed synthesis of NB-PBLA$_{10}$ is described here. In a 25-mL flame-dried Schlenk flask equipped with a magnetic stir bar, NB-amine, **1**, (106 mg, 0.401 mmol, 1 equiv.) was added into a solution of BLA NCA (1.0 g, 4.0 mmol, 10 equiv.) in 10 mL anhydrous DMF solution. The reaction mixture was stirred at a rate of 400 rpm under continuous $N_2$ flow (100 mL/min) at room temperature. The Schlenk flask was capped with a rubber septum with a needle outlet connected to a drying tube. FTIR was used to monitor the process of reaction and over 99% of BLA NCA monomer was consumed in 12 h. Then acetic anhydride (205 mg, 2.00 mmol, 5 equiv.) was added into the reaction mixture dropwise *via* syringe and the reaction was allowed to proceed at room temperature for 3 h. After evaporation of DMF *in vacuo*, the crude product was re-dissolved into DCM (30 mL) and precipitated into diethyl ether (300 mL) at 0 °C under vigorous stirring (3×). A white powder was obtained after centrifuging and drying *in vacuo* at room temperature (613 mg, yield: 75 %). $^1$H NMR (500 MHz, DMSO-d$_6$, ppm): $\delta$ 1.18 (br, 12H, CH$_2$C*H*$_2$CH$_2$), 1.33 (br, 4H, CONHC*H*$_2$), 1.64 (1H), 1.75 (1H), 1.79 (3H, COC*H*$_3$), 2.00 (1H), 2.61 (br, 10H, CHC*H*$_2$CO), 2.81 (br, 10H, CHC*H*$_2$CO; br, 4H), 4.62 (br, 10H, COC*H*NH), 5.03 (br, 20H, COOC*H*$_2$Ar), 6.10 (2H, NB alkenyl protons), 7.31 (br, 50H, Ar*H*), 8.16 (br, 12H, N*H*). $^{13}$C NMR (125 MHz, DMSO-d$_6$, ppm) $\delta$ 22.5, 26.2, 26.4, 28.7, 28.9, 29.2, 29.8, 35.8, 38.6, 41.0, 43.0, 45.6, 46.9, 49.6, 65.8, 127.9, 128.0, 128.4, 136.0, 136.3, 137.7, 169.4, 169.7, 169.8, 170.1, 170.3, 170.7, 174.3. FTIR (cm$^{-1}$): 3300-2850, 1732, 1634, 1526, 1454, 1383, 1356, 1215, 1163, 970, 908, 735, 694. SEC: PEO standard: $M_n$ = 1.2

kDa, $M_w$ = 1.4 kDa, $Đ$ = 1.13, PS standard: $M_n$ = 6.5 kDa, $M_w$ = 6.8 kDa, $Đ$ = 1.05. DSC: $T_g$ = 50 °C. TGA in $N_2$: 20-218 °C, 1% mass loss; 218-269 °C, 38% mass loss; 269-380 °C, 26% mass loss; 380-500 °C, 13% mass loss; 22% mass remaining above 500 °C.

NB-PBLA$_{20}$ was synthesized by the same approach with the reaction concentration diluted to 50 mg/mL for BLA NCA monomer and the recovery yield of the target polypeptide macromonomer was 68%. $^1$H NMR (500 MHz, DMSO-$d_6$, ppm): δ 1.17 (br, 12H, $CH_2CH_2CH_2$), 1.32 (br, 4H, CONHC$H_2$), 1.63 (1H), 1.75 (1H), 1.79 (3H, COC$H_3$), 2.00 (1H), 2.61 (br, 20H, CHC$H_2$CO), 2.80 (br, 20H, CHC$H_2$CO; br, 4H), 4.61 (br, 20H, COC$H$NH), 5.03 (br, 40H, COOC$H_2$Ar), 6.10 (2H, NB alkenyl protons), 7.28 (br, 100H, Ar$H$), 8.16 (br, 22H, N$H$). FTIR (cm$^{-1}$): 3300-2850, 1732, 1659, 1537, 1454, 1385, 1358, 1215, 1165, 988, 908, 735, 696. SEC: PEO standard: $M_n$ = 1.6 kDa, $M_w$ = 1.9 kDa, $Đ$ = 1.13, PS standard: $M_n$ = 8.1 kDa, $M_w$ = 8.8 kDa, $Đ$ = 1.10. DSC: $T_g$ = 46 °C. TGA in $N_2$: 20-203 °C, 1% mass loss; 203-254 °C, 36% mass loss; 254-390 °C, 24% mass loss; 390-500 °C, 9% mass loss; 30% mass remaining above 500 °C.

NB-PBLA$_{50}$ was synthesized by changing the reaction solvent from neat DMF to the mixture of DMF : DCM = 1 : 9 (v/v) and the reaction concentration of BLA NCA monomer was diluted to 50 mg/mL. Without the utilization of $N_2$ flow method during the reaction, the polymerization time extended to 48 h and the recovery yield of the target polypeptide macromonomer was 67%. $^1$H NMR (500 MHz, DMSO-$d_6$, ppm): δ 1.17 (br, 12H, $CH_2CH_2CH_2$), 1.33 (br, 4H, CONHC$H_2$), 1.64 (1H), 1.75 (1H), 1.79 (3H, COC$H_3$), 2.00 (1H), 2.60 (br, 50H, CHC$H_2$CO), 2.82 (br, 50H, CHC$H_2$CO; br, 4H), 4.62 (br, 50H, COC$H$NH), 5.01 (br, 100H, COOC$H_2$Ar), 6.10 (2H, NB alkenyl protons), 7.27 (br, 250H, Ar$H$), 8.18 (br, 52H, N$H$). FTIR (cm$^{-1}$): 3300-2850, 1732, 1657, 1547, 1454, 1387, 1358, 1256, 1165, 988, 908, 737, 696. SEC: PEO standard: $M_n$ = 3.4 kDa, $M_w$ = 3.9 kDa, $Đ$ = 1.15, PS standard: $M_n$ = 15.7 kDa, $M_w$ = 17.3 kDa, $Đ$ = 1.11. DSC: $T_g$ = 45 °C. TGA in $N_2$: 20-232 °C, 4% mass loss; 232-313 °C, 41% mass loss; 313-411 °C, 24% mass loss; 411-500 °C, 5% mass loss; 26% mass remaining above 500 °C.

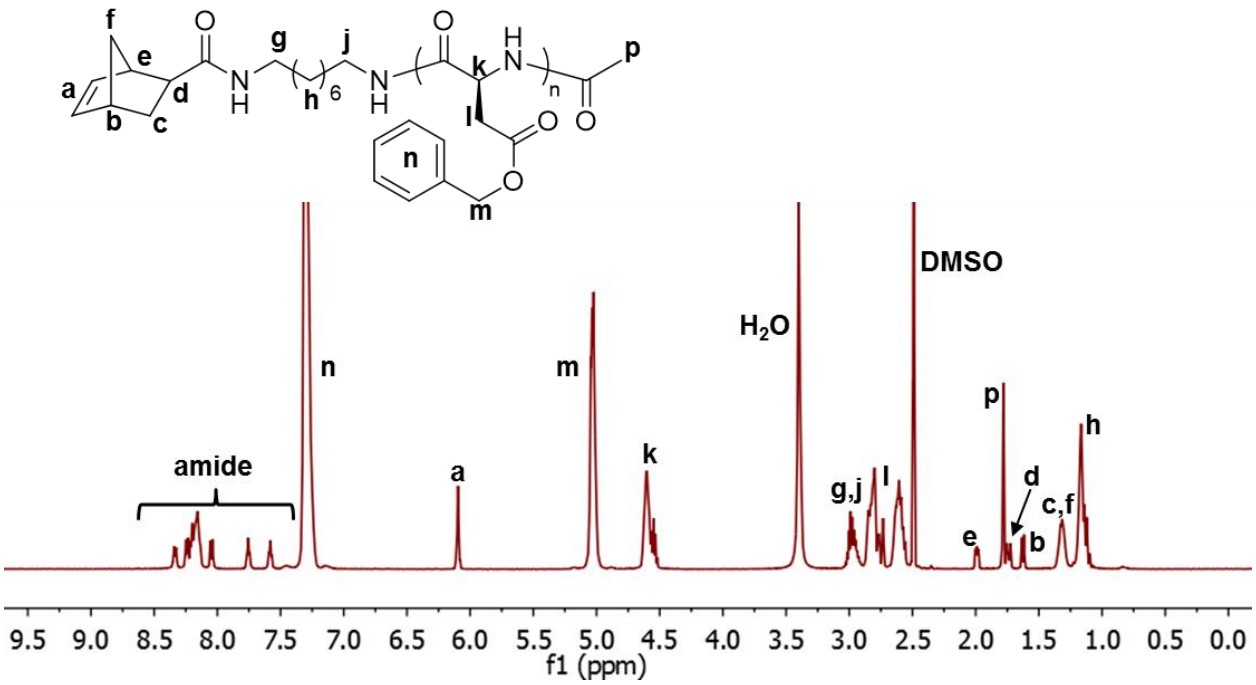
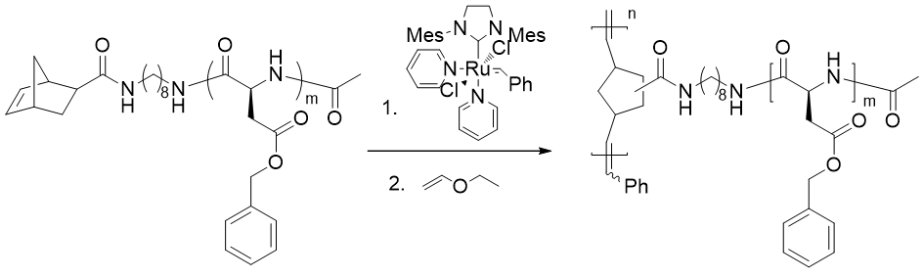



**Figure S2**. $^{1}$H NMR spectrum of NB-PBLA in DMSO.

**Syntheses of poly-(norbornene-*graft*-poly(β-benzyl-L-aspartate) (P(NB-*g*-PBLA)) brushes *via* ring-opening metathesis polymerizations (ROMPs) in solvent mixtures of DCM and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][$BF_4$])**




**Scheme S2**. Synthesis of P(NB-*g*-PBLA) from ROMP of NB-PBLA with the modified Grubbs 2nd generation catalyst.

The polypeptide molecular brush, P(NB-*g*-PBLA), was synthesized *via* a "grafting through" strategy, by using the ROMP of NB-PBLA macromonomers. As a representative reaction, to a 10-mL flame-dried Schlenk flask equipped with a magnetic stir bar under $N_2$ atmosphere, was added the macromonomer NB-$PBLA_{10}$ (300 mg, 125 μmol, 50 equiv.) and 3 mL of solvent mixture with DCM : [bmim][$BF_4$] = 9 : 1 (v/v). The mixture was stirred at room temperature until the macromonomer dissolved, and the solution was then deoxygenated through three cycles of freeze-pump-thaw and back-filled with $N_2$. After the last cycle, the stock solution of the modified Grubbs 2nd generation catalyst (1.8 mg, 2.5 μmol, 1 equiv.) in 0.05 mL anhydrous DCM (deoxygenated through three cycles of freeze-pump-thaw) was added quickly *via* an airtight syringe. The reaction mixture was allowed to stir for 3 h at room temperature before quenching the polymerization by addition of ethyl vinyl ether (EVE, 20 μL) in DCM (80 μL), and was further allowed to stir for 30 min at room temperature. The polymer product was isolated by precipitation of the reaction mixture into methanol (40 mL), collected through centrifugation, dissolved in DMF (10 mL), precipitated again in methanol (40 mL), and, finally, precipitated into diethyl ether (40 mL). The precipitate was collected through centrifugation and kept under vacuum overnight to obtain the target product (225.2 mg, yield: 75% based on 95% conversion of NB-$PBLA_{10}$). $^1$H NMR (500 MHz, DMSO-$d_6$, ppm): δ 1.11 (br, 600H, $CH_2CH_2CH_2$), 1.28 (br, 200H, CONHC$H_2$), 1.79 (150H, COC$H_3$), 1.79 (br, 100H), 2.27 (br, 50H),

2.61 (br, 500H, CHC$H_2$CO), 2.81 (br, 500H, CHC$H_2$CO; br, 200H), 4.62 (br, 500H, COC$H$NH), 5.03 (br, 1000H, COOC$H_2$Ar, br, 100H, NB alkenyl protons), 7.27 (br, 2500H, Ar$H$), 8.16 (br, 600H, N$H$). $^{13}$C NMR (125 MHz, DMSO-$d_6$, ppm): $\delta$ 22.6, 26.4, 26.5, 28.8, 28.9, 29.4, 35.8, 42.6, 49.7, 65.8, 66.0, 127.9, 128.0, 128.5, 135.9, 136.0, 169.6, 169.9, 170.0, 170.2, 170.3, 170.8, 170.9. FTIR ($cm^{-1}$): 3300-2900, 1738, 1634, 1526, 1454, 1379, 1217, 1163, 1094, 970, 908, 737, 696. SEC: $M_n$ = 144.3 kDa, $M_w$ = 166.0 kDa, $Đ$ = 1.15 (laser detector, dn/dc = 0.0790 mL/g), PEO standard: $M_n$ = 29.2 kDa, $M_w$ = 38.1 kDa, $Đ$ = 1.31, PS standard: $M_n$ = 97.2 kDa, $M_w$ = 122.8 kDa, $Đ$ = 1.26. DSC: $T_g$ = 122 °C. TGA in $N_2$: 20-200 °C, 2% mass loss; 200-266 °C, 28% mass loss; 266-384 °C, 26% mass loss; 384-500 °C, 10% mass loss; 34% mass remaining above 500 °C.

**Syntheses of P(NB-*g*-PBLA) brushes *via* ROMPs in solvent mixtures of DCM and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([bdmim][$BF_4$])**

As a representative reaction, to a 10-mL flame-dried Schlenk flask equipped with a magnetic stir bar under $N_2$ atmosphere, was added the macromonomer NB-$PBLA_{10}$ (300 mg, 125 μmol, 50 equiv.) and 3 mL of solvent mixture with DCM : [bdmim][$BF_4$] = 9 : 1 (v/v). The mixture was stirred at 40 °C until the macromonomer had dissolved, and the solution was then deoxygenated through three cycles of freeze-pump-thaw and back-filled with $N_2$. After the last cycle, the reaction mixture was heated to 40 °C and the stock solution of the modified Grubbs 2$^{nd}$ generation catalyst (1.8 mg, 2.5 μmol, 1 equiv.) in 0.05 mL anhydrous DCM (deoxygenated through three cycles of freeze-pump-thaw) was added quickly *via* an airtight syringe. The reaction mixture was allowed to stir for 3 h at 40°C before quenching the polymerization by adding EVE (20 μL) in DCM (80 μL), and was further allowed to stir for 30 min at 40 °C. The polymer product was isolated by precipitation of the reaction mixture into methanol (40 mL), collected through centrifugation, dissolved in DMF (10 mL), precipitated again in methanol (40 mL), and, finally, precipitated into diethyl ether (40 mL). The precipitate was collected by centrifugation and kept under vacuum overnight to obtain the target product (200.5 mg, yield: 70% based on 95% conversion of NB-$PBLA_{10}$). SEC: $M_n$ = 138.7 kDa, $M_w$ = 163.9 kDa, $Đ$ = 1.18 (laser detector, dn/dc = 0.0790 mL/g), PEO standard: $M_n$ = 51.6 kDa, $M_w$ = 62.2 kDa, $Đ$ = 1.21, PS standard: $M_n$ = 94.7 kDa, $M_w$ = 116.4 kDa, $Đ$ = 1.23. The $^1$H NMR, $^{13}$C NMR, FTIR spectra and thermal analyses results were similar to the polypeptide molecular brushes described above.

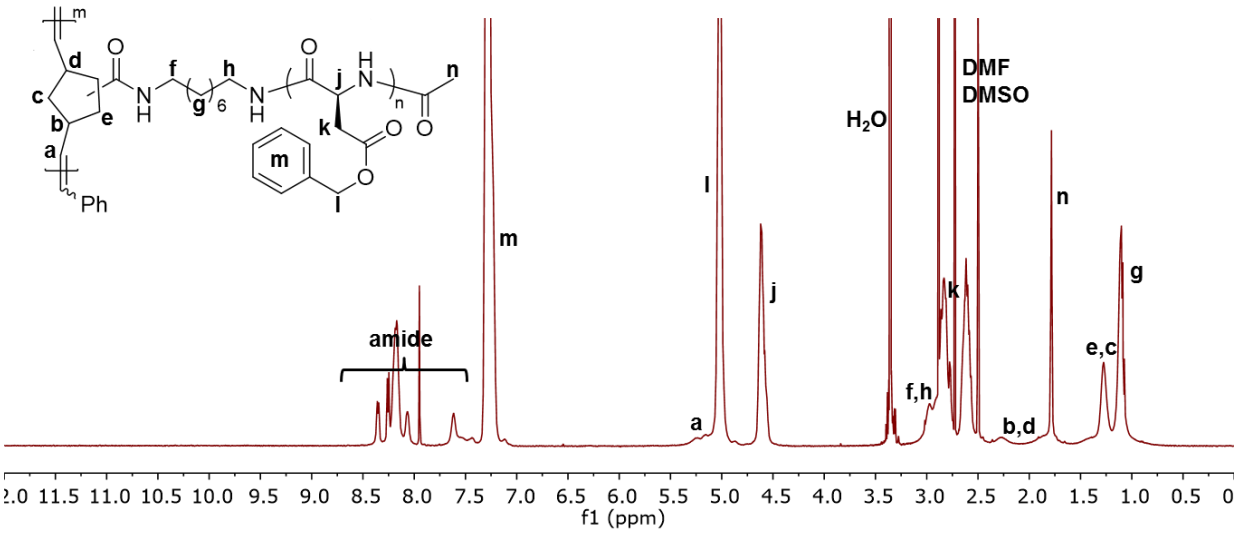
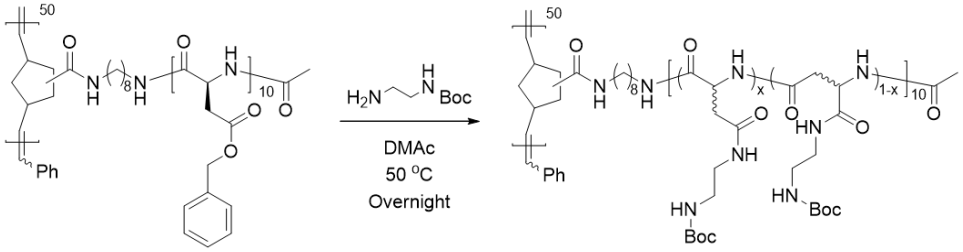



**Figure S3**. $^{1}$H NMR spectrum of P(NB-*g*-PBLA) in DMSO.

**Post-polymerization modification of P(NB-*g*-PBLA) *via* aminolysis of PBLA**




**P(NB-*g*-PBLA)** **P(NB-*g*-PABEDA)**

**Scheme S3**. Aminolysis of PBLA side chain of P(NB-*g*-PBLA) molecular brush.

Following the highly reactive aminolysis reaction of PBLA with primary amines under basic conditions to produce the corresponding amide product, the post-polymerization modification was performed by using the polypeptide molecular brush and primary amine-derived reagents. In a 10-mL flame-dried Schlenk flask, P(NB-*g*-PBLA$_{10}$)$_{50}$ (100 mg, 0.758 μmol, 1 equiv., 500 equiv. for BLA repeat unit) was dissolved into anhydrous DMAc (2 mL). *N*-Boc-ethylenediamine (3.34 g, 20.9 mmol, 25000 equiv., 50 equiv. to BLA repeat unit) was dissolved into anhydrous DMAc (3 mL) and added into the reaction flask *via* syringe. The reaction was allowed to proceed at 50 °C overnight and the reaction solution was precipitated into diethyl ether (3×). The precipitate was collected through centrifugation and kept under vacuum to obtain the target product as a white powder (88.6 mg, yield: 73% based on 95% modification efficiency). $^1$H NMR (500 MHz, DMSO-d$_6$, 70 °C, ppm): δ 1.23 (br, 600H, CH$_2$C*H*$_2$CH$_2$), 1.38 (br, 4500H, NHC(C*H*$_3$)$_3$, br, 200H, CONHC*H*$_2$), 1.87 (s, 150H, COC*H*$_3$), 1.96 (br, 100H), 2.09 (br, 50H), 2.61 (br, 1000H, CHC*H*$_2$CO), 3.02 (br, 1000H, CH$_2$CONHC*H*$_2$), 3.14 (br, 1000H, CH$_2$C*H*$_2$NHCO), 4.55 (br, 500H, COC*H*NH), 5.17 (br, 100H, NB alkenyl protons), 6.51 (br, 500H, N*H*Boc), 8.03 (br, 1110H, N*H*). FTIR (cm$^{-1}$): 3300-2900, 1736, 1643, 1520, 1447, 1366, 1248, 1167, 1099, 974, 866, 660. SEC: $M_n$ = 152.5 kDa, $M_w$ = 180.1 kDa, $Đ$ = 1.18 (laser detector, dn/dc = 0.0938 mL/g), PEO standard: $M_n$ = 34.3 kDa, $M_w$ = 43.1 kDa, $Đ$ = 1.26, PS standard: $M_n$ = 112.8 kDa, $M_w$ = 139.1 kDa, $Đ$ = 1.23. DSC: $T_g$ = 129 °C. TGA in N$_2$: 20-202 °C, 1% mass loss; 202-264 °C, 37% mass loss; 264-389 °C, 12% mass loss; 389-500 °C, 10% mass loss; 40% mass remaining above 500 °C.

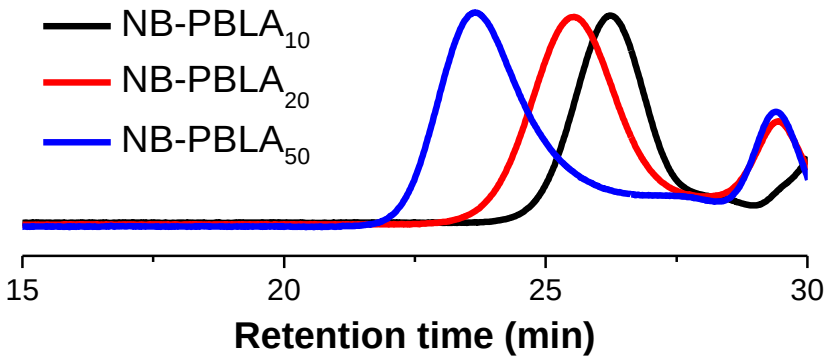



**Figure S4**. SEC traces for NB-PBLA$_{10}$ (black line), NB-PBLA$_{20}$ (red line) and NB-PBLA$_{50}$ (blue line).

## References

(1) Li, Z.; Ma, J.; Lee, N. S.; Wooley, K. L. *J. Am. Chem. Soc.* **2011**, *133*, 1228-1231.

(2) Habraken, G. J. M.; Peeters, M.; Dietz, C. H. J. T.; Koning, C. E.; Heise, A. *Polym. Chem.* **2010**, *1*, 514-524.