

Supporting information

Synthesis and Direct Visualization of Dumbbell-shaped Molecular Brushes

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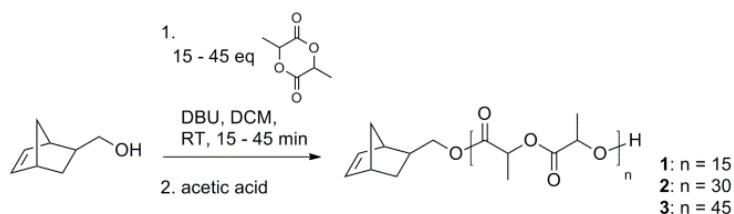
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Experimental Section

Materials. All Chemicals and reagents were purchased from Aldrich Chemical Co. and used as received, unless otherwise noted. DL-lactide was recrystallized twice from hexanes/ethyl acetate before use. Dichloromethane was distilled over CaH_2 and stored under N_2 before use. Toluene was purified by passage through solvent purification system (JC Meyer Solvent Systems) connected to a glove box without degassing before conducting ROMP. Modified 2nd generation Grubbs' catalyst $((\text{H}_2\text{IMes})(\text{pyr})_2(\text{Cl})_2\text{RuCHPh})$ was prepared according to reported method.¹

Characterization Methods. ^1H NMR and ^{13}C NMR spectra were recorded on Varian Inova 300 MHz or Varian Mercury 300 MHz spectrometers interfaced to a UNIX computer using VnmrJ software. Chemical shifts were referred to the solvent resonance signals. IR spectra were recorded on an IR Prestige 21 system (Shimadzu Corp., Japan) and analyzed using IRsolution v. 1.40 software. Gel permeation chromatography (GPC) was performed on a Waters Chromatography, Inc., 1515 isocratic HPLC pump equipped with an inline degasser, a model PD2020 dual angle (15° and 90°), static light scattering detector (Precision Detectors, Inc.), a model 2414 differential refractometer (Waters, Inc.), and four PL_{gel} polystyrene-co-divinylbenzene gel columns (Polymer Laboratories, Inc.) connected in series: 5 μm Guard (50×7.5 mm), 5 μm Mixed C (300×7.5 mm), 5 μm 10^4 (300×7.5 mm), and 5 μm 500 Å (300×7.5 mm) using the Breeze (version 3.30, Waters, Inc.) software. The instrument was operated at 35 °C with THF as eluent (flow rate set to 1.0 mL/min). Polymer solutions were prepared at a known concentration (*ca.* 3 mg/mL) and an injection volume of 200 μL was used. Data collection was performed with Precision Acquire 32 Acquisition program (Precision Detectors, Inc.) and analyses were carried out using Discovery32 software (Precision Detectors, Inc.). A system calibration curve generated from plotting molecular weight as a function of retention time

for a series of broad polydispersity poly(styrene) standards was used to determine the macromonomer molecular weight values, and the brush absolute molecular weight values were determined using dn/dc values that were calculated for each sample as 0.041 or 0.042 mL/g. Glass transition temperatures (T_g) were measured by differential scanning calorimetry on a Mettler-Toledo DSC822^e (Mettler-Toledo, Inc., Columbus, OH), with a heating rate of 10 °C/min. Measurements were analyzed using Mettler-Toledo Star^e v. 10.00 software. The T_g was taken as the midpoint of the inflection tangent, upon the third heating scan. Thermogravimetric analysis was performed under N₂ atmosphere using a Mettler-Toledo model TGA/DSC 1, with a heating rate of 5 °C/min. Measurements were analyzed using Mettler-Toledo Star^e v. 10.00 software. Atomic force microscopy (AFM) imaging was performed using a MFP-3D system (Asylum Research, Santa Barbara, CA) in tapping mode using standard silicon tips (SCANASYST-AIR, from Bruker, 115 μM, spring constant 0.4 N m⁻¹). Samples were prepared by spin casting dilute solutions (*ca.* 0.002 mg/mL) in chloroform onto freshly cleaved mica at 3000 rpm.



Scheme S1. Syntheses of macromonomers, NB-PLA₁₅, 1; NB-PLA₃₀, 2; NB-PLA₄₅, 3.

Representative procedure for the synthesis of NB-PLA macromonomers.

A flame-dried 250-mL Schlenk flask equipped with a magnetic stir bar was charged with *exo*-5-norborene-2-methanol (1 eq.), *DL*-lactide (15-45 eq.), and dry dichloromethane (20 eq. to *DL*-lactide). The flask was sealed with a rubber septum and allowed to stir at room temperature for 20 min to ensure homogeneous mixing. Then, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU, 1.2

eq.) was quickly added to the mixture to initiate the polymerization. After 15-45 min reaction time at room temperature, the reaction was quenched by adding several drops of acetic acid. The reaction was further stirred for 10 min before the reaction mixture was concentrated under vacuum. The polymer solution was precipitated from dichloromethane into cold methanol (3×) and dried under vacuum, overnight to yield a white solid. IR (cm⁻¹): 3495-3086, 3024-2916, 1743, 1450, 1365, 1265, 1188, 1080. ¹H NMR (300 MHz, CDCl₃, ppm) δ 6.09 (s, norbornenyl alkenyl protons), 5.25-5.06 (br, >CHCH₃ of PLA backbone), 4.14-3.96 (m, -CH₂OC(O)-) of NB group), 2.82 (s, 1H, allylic proton of NB group), 2.69 (s, 1H, allylic proton of NB group), 1.67-1.45 (br, -CH₃ of PLA backbone), 1.40-1.13 (m, -CH< and >CHCH₂CH< of NB group). ¹³C NMR (75 MHz, CDCl₃, ppm) δ 169.5, 136.9, 135.9, 68.9, 67.9, 66.7, 44.9, 43.4, 41.5, 37.9, 29.4, 16.5.

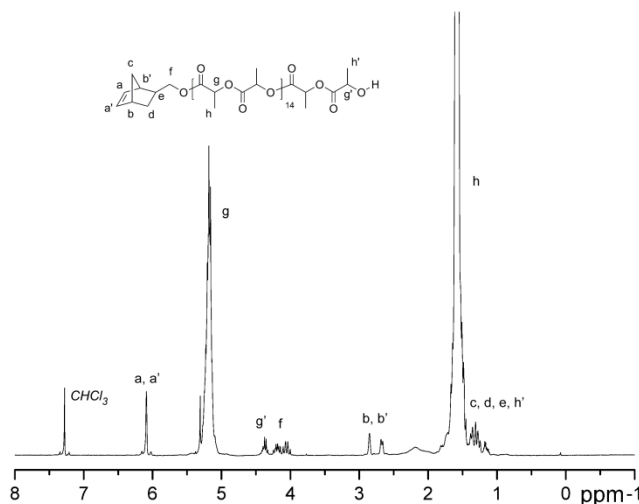


Figure S1. ¹H NMR (300 MHz, CDCl₃) spectrum of NB-PLA₁₅, **1**.

NB-PLA₁₅, 1. >99 % monomer conversion with 52 % isolation yield. $M_n^{\text{theo.}} = 2300$ Da, $M_n^{\text{GPC}} = 2000$ Da, PDI = 1.20, $T_g = 33$ °C, TGA in Ar: 220-360 °C, 94% mass loss.

NB-PLA₃₀, 2. >99 % monomer conversion with 57 % isolation yield. $M_n^{\text{theo.}} = 4400$ Da, $M_n^{\text{GPC}} = 4700$ Da, PDI = 1.11, $T_g = 48$ °C, TGA in Ar: 260-390 °C, 90% mass loss.

NB-PLA₄₅, 3. >99 % monomer conversion with 65 % isolation yield. $M_n^{\text{theo.}} = 6800$ Da, $M_n^{\text{GPC}} = 7000$ Da, PDI = 1.10, $T_g = 53$ °C, TGA in Ar: 270-390 °C, 86% mass loss.

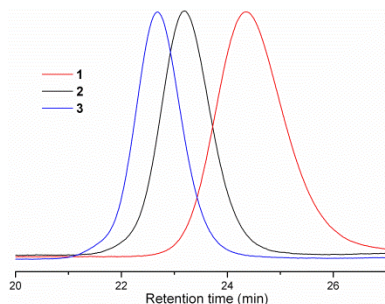
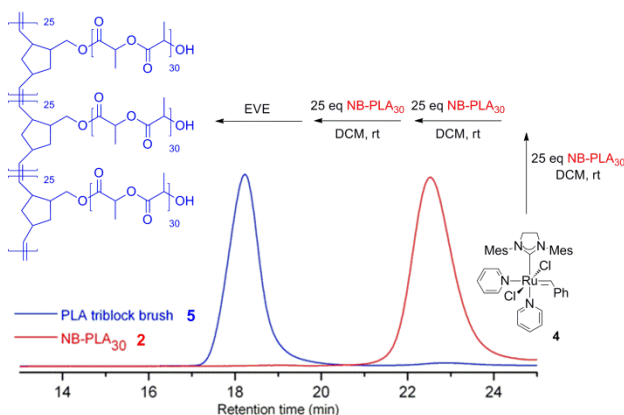


Figure S2. GPC traces of NB-PLA₁₅, **1**; NB-PLA₃₀, **2**; NB-PLA₄₅, **3**.



Scheme S2. Preliminary study of synthesizing of triblock brush copolymer **5**.

Representative procedure for the synthesis of triblock brush copolymers.

In a glove box, toluene was added into vials containing pre-weighed macromonomer to yield solutions with macromonomer concentrations of *ca.* 100 mg/mL. A pre-determined amount of modified 2nd generation Grubbs' catalyst was added quickly into the vial of first block equipped with a stir bar. After *ca.* 7 min, the solution of second block was quickly added into the

polymerization mixture, followed by the addition of solution of third block after 10 min. The reaction was allowed to stir for another 1 h, and quenched by adding several drops of ethyl vinyl ether (EVE). The brush polymer was precipitated into cold methanol twice and dried under vacuum overnight to yield a white powder. IR (cm⁻¹): 3510-3055, 3008-2924, 1751, 1450, 1357, 1180, 1080. ¹H NMR (300 MHz, CD₂Cl₂, ppm) δ 6.09 (s, norbornenyl alkenyl protons), 5.25-5.06 (br, >CHCH₃ of PLA backbone), 4.14-3.96 (m, -CH₂OC(O)-) of NB group), 2.82 (s, 1H, allylic proton of NB group), 2.69 (s, 1H, allylic proton of NB group), 1.67-1.45 (br, -CH₃ of PLA backbone), 1.40-1.13 (m, -CH₃ and >CHCH₂CH< of NB group). ¹³C NMR (75 MHz, CDCl₃, ppm) δ 169.5, 136.9, 135.9, 68.9, 67.9, 66.7, 44.9, 43.4, 41.5, 37.9, 29.4, 16.5.

P(NB-*g*-PLA₄₅)₃₀-*b*-P(NB-*g*-PLA₁₅)₁₀₀-*b*-P(NB-PLA₄₅)₃₀, 8. 91 % macromonomer conversion with 77 % isolation yield. $M_n^{\text{theo.}} = 550$ kDa, $M_n^{\text{GPC}} = 660$ kDa, PDI = 1.14, $T_g = 52$ °C, TGA in Ar: 270-390 °C, 73% mass loss, 390-450 °C, 77% mass loss.

P(NB-*g*-PLA₄₅)₃₀-*b*-P(NB-*g*-PLA₁₅)₆₀-*b*-P(NB-PLA₄₅)₃₀, 9. 91 % macromonomer conversion with 76 % isolation yield. $M_n^{\text{theo.}} = 471$ kDa, $M_n^{\text{GPC}} = 583$ kDa, PDI = 1.10, $T_g = 53$ °C, TGA in Ar: 270-390 °C, 75% mass loss, 390-450 °C, 78% mass loss.

P(NB-*g*-PLA₄₅)₃₀-*b*-P(NB-*g*-PLA₁₅)₁₀₀-*b*-P(NB-PLA₃₀)₃₀, 10. 92 % macromonomer conversion with 75 % isolation yield. $M_n^{\text{theo.}} = 497$ kDa, $M_n^{\text{GPC}} = 562$ kDa, PDI = 1.12, $T_g = 52$ °C, TGA in Ar: 240-390 °C, 71% mass loss, 390-450 °C, 75% mass loss.

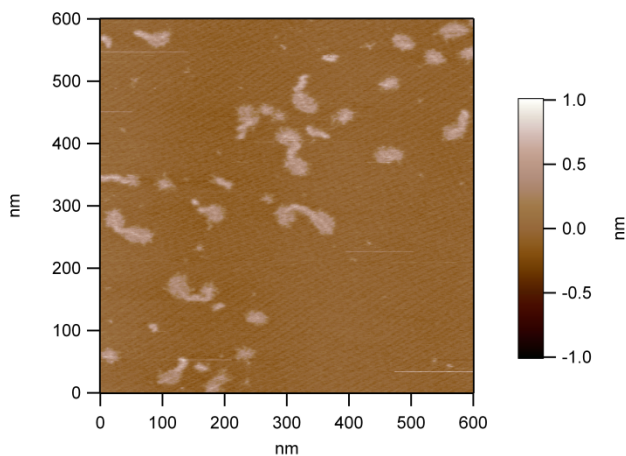


Figure S3. AFM height image of **8** showing coexistence of “intact” and “broken” dumbbells.

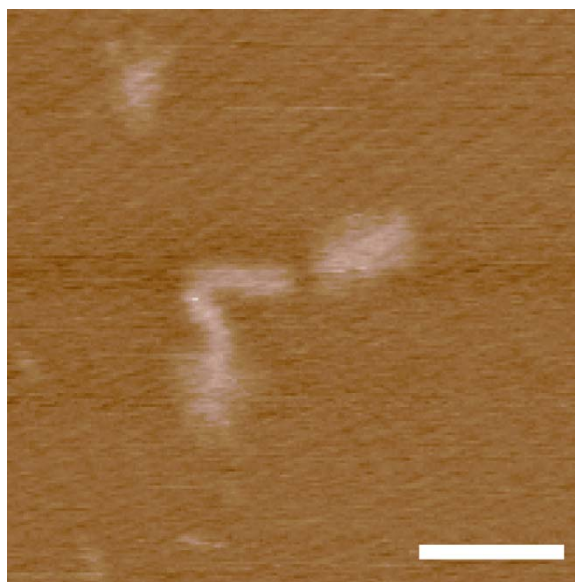


Figure S4. AFM height image of **8** showing chain scission occurred between first/third block and middle block. Scale bar = 50 nm.

(1) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 4035-4037.