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Synthesis and Direct Visualization of Dumbbell-Shaped Molecular Brushes

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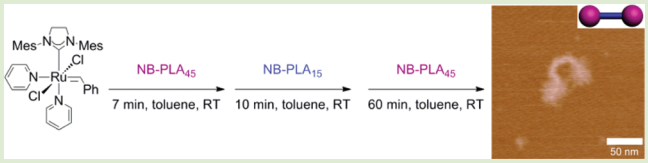
Supporting Information

ABSTRACT: Dumbbell-shaped triblock molecular brushes were synthesized by ring-opening metathesis polymerization (ROMP) of poly(lactide) macromonomers with terminal norbornene groups (NB-PLA) in a sequential addition manner. By changing the macromonomer size and the feed ratio of Grubbs' catalyst to macromonomer, the dimensions of the "ball" and "bar" of the dumbbell-shaped molecular brushes were controlled. The growth and production of well-defined structures were verified by gel permeation chromatography (GPC), and the final dumbbell-shaped architectures were visualized by atomic force microscopy (AFM). This synthetic methodology represents a rapid and convenient route to unique macromolecular topologies.



The construction of nanoscale polymeric architectures with complex and well-defined structures is of great interest because it enables the fabrication of soft materials with tunable properties and functionalities.[1] Molecular brushes represent a unique class of densely grafted polymers with control over the grafting densities, as well as the compositions and lengths of both the brush polymer backbone and the side chains, to affect their shapes and sizes from macromolecular to nanoscopic dimensions.[2] Due to their worm-like or cylindrical conformations caused by the steric repulsion among densely distributed side chains, molecular brushes have been explored in various applications, such as photonic materials,[3] templates for inorganic nanowires,[4] supersoft elastomers,[5] and nanocarriers for nanomedicine.[6] By employing various controlled/living polymerization methodologies, numerous molecular brush polymer architectures, such as cyclic,[7] tubular,[8] dumbbell-,[9] tadpole-,[10] and star-like,[11] have been synthesized and directly visualized by atomic force microscopy (AFM).

We are particularly interested in heterografted block brush copolymers, having differential side chains distributed along the backbone, because such macromolecules with increased complexities and defined three-dimensional morphologies may better mimic some features of biomacromolecules, compared to their linear block copolymer counterparts, and lead to unusual hierarchical nanoassemblies in aqueous medium[12] and in the bulk.[3c] The backbone-based block brush copolymers can be synthesized by three strategies: "grafting-onto", "grafting-from", and "grafting-through". The first two strategies include the preparation of long and well-defined block copolymer backbones, decorated with orthogonal functionalities, followed by coupling presynthesized side chains ("grafting onto"),[13] or by growing different side chains using orthogonal polymerizations[3b,8a,14] or selective protection/deprotection methodologies ("grafting from").[8b] The "grafting-through" approach allows for variation in the side chain composition and structure in a straightforward manner that involves sequential polymerizations of macromonomers, and is analogous to the standard procedures for the growth of typical linear block copolymers. Steric effects and relatively low concentration of the polymerizable functionality can pose challenges for "grafting-through" polymerizations, however, ring-opening metathesis polymerization (ROMP) has been proven to be an effective chemistry to polymerize norbornene groups in macromolecules to form molecular brush polymers.[15] Moreover, due to the high activity of Ru-based olefin metathesis catalysts, high tolerance of the catalyst to functional groups, and the living characteristics,[16] ROMP displays advantages and conveniences toward preparing block brush copolymers. It allows fast polymerization with high macromonomer conversion, facile incorporation of a variety of functional polymers into molecular brush frameworks, and precise control over the macromolecular architecture, by controlling the lengths and structures of backbones and side chains independently.

Driven by our interest in developing facile synthetic methodologies to achieve increasingly sophisticated macromolecules, herein, we report the novel synthesis of triblock dumbbell-shaped molecular brushes *via* ROMP by sequential additions of macromonomers in a one-pot "grafting-through" manner. Although macromolecules with backbone multiblock structures, or even dumbbell/pom-pom shapes have been constructed by combining various controlled polymerizations,[9,14b,17] this work represents an advance in synthetic techniques to allow for the facile preparation of brush polymers

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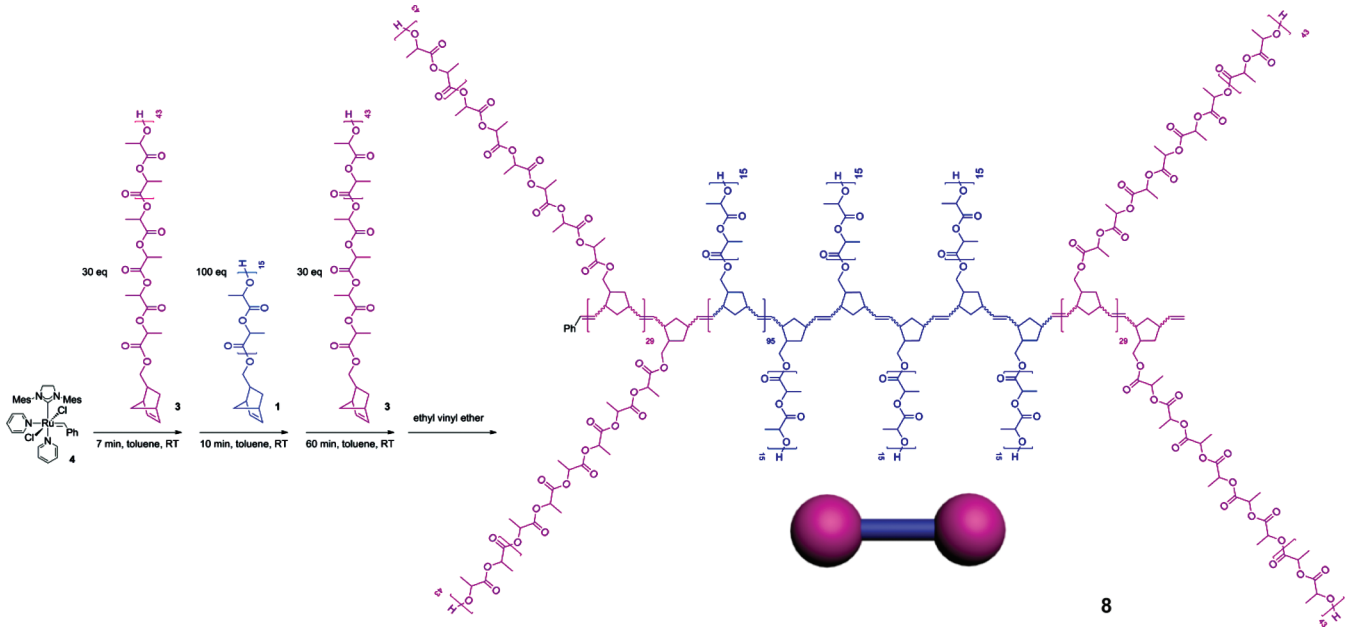
Scheme 1. Synthesis of Triblock Molecular Brush 8 by Sequential Addition of 3 and 1 *via* ROMP



with densely grafted side chains along the entire backbone with three different block segments, as ABA or asymmetric ABC triblock copolymer nanostructures.

Three poly(DL-lactide) macromonomers having terminal norbornene groups, with degrees of polymerization (DP) of 15, 30, and 45 (NB-PLA$_{15}$, **1**; NB-PLA$_{30}$, **2**; NB-PLA$_{45}$, **3**), and low polydispersity indices (PDI) of 1.20, 1.11, and 1.10, respectively, were synthesized by 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU)-catalyzed ring-opening polymerization (ROP) of DL-lactide in dichloromethane (DCM) at room temperature (Scheme S1 in the Supporting Information).[18] For this initial demonstration of dumbbell synthesis and characterization studies, the same composition, PLA, of side chains was chosen to avoid the potential differential segregation or aggregation of block brush copolymer components on the substrate during AFM characterization. In addition, PLA is a hydrolytically degradable material, which is of interest as an environmentally- and biologically benign building block. Convenient and precise control of the macromonomer lengths and chain ends were important to achieve well-defined side chains of the dumbbell-shaped brush copolymers. The DBU-catalyzed ROP allowed for accurate tuning of the macromonomer structures, due to the high monomer conversion (>99%) and *ca.* quantitative initiation efficiency, as verified by agreement of DP values calculated from monomer conversion and chain end analysis by ^{1}H NMR spectroscopy, involving comparison of integration values of the NB group vinyl protons (6.05−6.10 ppm) and methine protons (5.09−5.25 ppm) of PLA (Figure S1 in Supporting Information).

A preliminary study was then conducted to investigate the possibility of synthesizing triblock brush copolymers by three sequential additions of macromonomers to a solution of modified second generation Grubbs' catalyst (H$_2$IMes)-(pyr)$_2$(Cl)$_2$RuCHPh (**4**) as the initiator in DCM at room temperature (Scheme S2 in Supporting Information). Three portions of **2** (each portion with [**2**]/[**4**] = 25) were added sequentially with time intervals of 5, 10, and 20 min. The final macromonomer conversion was measured by gel permeation chromatography (GPC). It was shown that sequential additions of three portions of **2** could afford well-defined brush copolymer, **5**, with high overall macromonomer conversion (>90%) and low PDI (1.11), which demonstrated the living characteristics and high efficiency of ROMP of NB-terminated macromonomers. This approach toward triblock brush copolymers is attractive because the macromolecular architecture can be effectively controlled by adjusting the macromonomer sizes as well as the macromonomer to catalyst ratio, at each stage of the ROMP.

Based on this result, we attempted the synthesis of dumbbell-shaped brush copolymer having the "balls" and "bar" composed of **3** and **1**, respectively, by sequential polymerization of **3**, **1**, and then **3** again, at stoichiometries relative to **4** that would give DP(backbone) of 30, 100, and 30, respectively P(NB-*g*-PLA$_{45}$)$_{30}$-*b*-P(NB-*g*-PLA$_{15}$)$_{100}$-*b*-P(NB-PLA$_{45}$)$_{30}$, **8** (Scheme 1). To achieve precise control of the structure and dimensions of the triblock brush copolymers, avoiding either mixtures of macronomonomers being present or delays that may result in chain termination events, each portion of macromonomer solution must be added immediately after the consumption of the previous one. Therefore, a series of experiments was performed to determine the time required for each stage of ROMP for macromonomers **3** and **1**. ROMP was initiated by adding catalyst stock solution into macromonomer solution (*ca.* 100 mg/mL in toluene), and the molecular weights, PDIs and macromonomer conversions were measured by GPC. These kinetics studies revealed that the reactions of building up the first block (P(NB-*g*-PLA$_{45}$)$_{30}$, **6**, [**3**]/[**4**] = 30:1) and the second block (P(NB-*g*-PLA$_{45}$)$_{30}$-*b*-P(NB-*g*-PLA$_{15}$)$_{100}$, **7**, [**3**]/[**4**]/[**1**] = 30:1:100) finished in *ca.* 7 min with 91% macromonomer conversion, and *ca.* 10 min with overall 91% macromonomer conversion, respectively. The chain extensions were verified by GPC analyses with observation of the consumption of macromonomer(s) and the shifts of the GPC traces from retention times of the macromonomers to the brush copolymer, **6**, and the diblock brush copolymer, **7**, at increasingly shorter retention times, with less than 10% unreacted macromonomers remaining (Figure 1). With the extents of macromonomer conversion being quite similar, we

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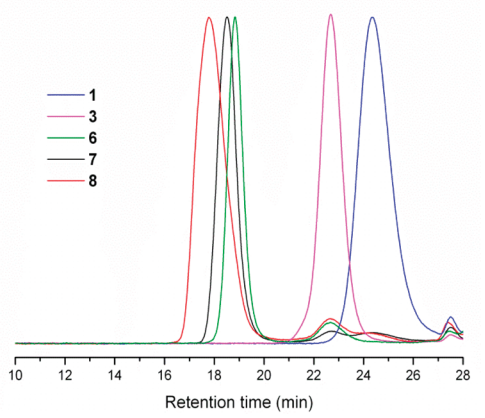

Figure 1. Representative GPC traces (RI detection) of macromonomers **1** and **3** after purification, and brush polymers **6**–**8** without purification.

had suspected that residual macromonomers may lack the polymerizable NB α-chain terminus. However, MALDI-tof mass spectrometry confirmed that >98% of the PLA macromonomers possessed the NB group. We, therefore, attribute the *ca.* 90% macromonomer conversion to a combination of the *ca.* 2% lacking NB groups and *ca.* 5% NB groups being of the endo isomer, which is substantially less reactive toward ROMP. The molecular weights of the first block (M_n^{GPC} = 230 kDa) and second block (M_n^{GPC} = 400 kDa) measured by GPC equipped with a dynamic light scattering detector were close to the theoretical M_n values (first block: $M_n^{theo.}$ = 177 kDa; second block: $M_n^{theo.}$ = 373 kDa) (Table 1). Moreover, the molecular weight distribution of the diblock brush copolymer remained monomodal and narrow. Next, with the polymerization times required to complete ROMP growth of the first (7 min) and second (10 min) blocks determined, we applied those time periods and investigated the synthesis of dumbbell-shaped brush copolymer by adding a third block macromonomer solution quickly into the polymerization mixture after the second block was constructed, without monitoring the reaction progress of each stage. After stirring at room temperature for 1 h, the third block was successfully chain extended to give **8**, as verified by the GPC peak shift to shorter retention time compared to **7**, high consumption of macromonomers with 91% total conversion, and agreement of theoretical molecular weight ($M_n^{theo.}$ = 550 kDa) and that measured by GPC (M_n^{GPC} = 660 kDa). The monomodal molecular weight distribution and low PDI of 1.14 indicated a well-defined structure for the dumbbell-shaped brush copolymer **8** (Figure 1).

To further demonstrate the versatility of making triblock brush copolymers by ROMP *via* macromonomer sequential additions, two more dumbbell-shaped brush copolymers: one with same size of "balls" but a shorter "bar" (P(NB-*g*-PLA$_{45}$)$_{30}$-*b*-P(NB-*g*-PLA$_{15}$)$_{60}$-*b*-P(NB-PLA$_{45}$)$_{30}$, **9**), the other with same "bar" size but asymmetric "balls" (P(NB-*g*-PLA$_{45}$)$_{30}$-*b*-P(NB-*g*-PLA$_{15}$)$_{100}$-*b*-P(NB-PLA$_{30}$)$_{30}$, **10**), were synthesized. The length of the backbone ("bar") was varied by alteration of the ratio of macromonomer to catalyst feed ([**1**]/[**4**]) during the second block growth, and the size of the "balls" was varied by alteration of the lengths of the macromonomers. These two triblock brush copolymers showed high macromonomer conversions, agreement of calculated and measured M_n values, and monomodal, narrow molecular weight distributions (Table 1).

Atomic force microscopy (AFM) is an effective characterization method to directly visualize molecular brushes. As shown in Figure 2, AFM images of these three triblock brush copolymers revealed dumbbell-shaped macromolecular architectures with "balls" consisting of **2** or **3** and "bars" made of **1**. Specifically, for **8** (Figure 2A, 2B), the width and length of the middle block were measured to be 18 ± 3 nm and 55 ± 9 nm, respectively, which are close to the calculated values (0.62 and 0.45 nm per monomeric unit for PNB backbone and PLA side

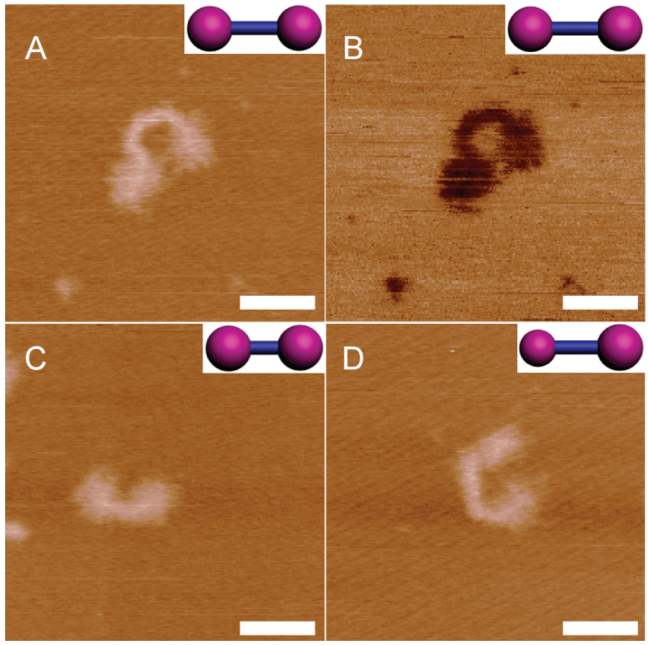

Figure 2. (A) AFM height image of **8**. (B) AFM phase image of **8**. (C) AFM height image of **9**. (D) AFM height image of **10**. (Samples were prepared by spin-casting dilute solutions onto freshly cleaved mica, scale bar = 50 nm, *z* scale = 2 nm).

Table 1. Brush (Block) Copolymers 6–10

code	brush (co)polymers	[**3**]/[**4**]	[**1**]/[**4**]	[**3**]/[**4**]	[**2**]/[**4**]	convn[a]	M_n^{theo} (kDa)[b]	M_n^{GPC} (kDa)[c]	PDI
6	P(NB-*g*-PLA$_{45}$)$_{30}$	30				91	177	230	1.04
7	P(NB-*g*-PLA$_{45}$)$_{30}$-*b*-P(NB-*g*-PLA$_{15}$)$_{100}$	30	100			91	373	400	1.08
8	P(NB-*g*-PLA$_{45}$)$_{30}$-*b*-P(NB-*g*-PLA$_{15}$)$_{100}$-*b*-P(NB-PLA$_{45}$)$_{30}$	30	100	30		91	550	660	1.14
9	P(NB-*g*-PLA$_{45}$)$_{30}$-*b*-P(NB-*g*-PLA$_{15}$)$_{60}$-*b*-P(NB-PLA$_{45}$)$_{30}$	30	60	30		91	471	583	1.10
10	P(NB-*g*-PLA$_{45}$)$_{30}$-*b*-P(NB-*g*-PLA$_{15}$)$_{100}$-*b*-P(NB-PLA$_{30}$)$_{30}$	30	100		30	92	497	562	1.12

[a]Conversions of macromonomers were measured by comparing the peak areas of brush polymers and residual macromonomers of reaction mixture by GPC with RI detector. [b]Theoretical molecular weight, calculated from macromonomer to catalyst feed ratio × overall macromonomer conversion. [c]Determined by GPC using dual angle static light scattering detection and d*n*/d*c* values calculated for each sample as 0.041 or 0.042 mL/g.

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chain, respectively), suggesting a fully extended conformation due to the densely grafted side chains, as well as favorable interaction between the brush copolymers and mica substrate. The first and third blocks of **8** were of greater widths than was the central block. However, the measured widths, each of 34 ± 6 nm, were less than the theoretical value (*ca.* 41 nm) calculated for a fully extend conformation, which was attributed to less steric repulsion of side chains, as a result of a relatively small backbone DP value (DP = 30) compared to its side chains (DP = 45). For **9** (Figure 2C), with decreased backbone DP value of the middle block, the "bar" had a length of 28 ± 6 nm with the "balls" sizes remaining similar to those of **8**. Moreover, for **10** (Figure 2D), the third block, composed of **2**, had a width of 26 ± 3 nm, which correlated with the shorter PLA side chain length, compared to **3**.

Partial dumbbell-shaped structures were also observed by AFM (Figure S3 and S4 in Supporting Information). It was hypothesized that the partial dumbbells resulted from chain scission of the brush copolymer backbone, because fragments that could result only from breakage of the backbone were observed: single bars (Figure S3, Supporting Information) and broken dumbbells with pieces remaining in close proximity (Figure S4, Supporting Information). Chain scission could be caused by high bond tension generated from the repulsion of densely grafted side chains on mica, a high surface energy substrate.[19] Although dense grafting and steric crowding along vinylic polymer backbones has led to cleavage, chain scission has also been observed for cyclic brush copolymers having a polynorbornene backbone.[7b] However, because there is overlap between the diblock and triblock brush chromatograms by GPC, we could not confirm that all of the partial dumbbells were the result of chain scissions. Having unevenly distributed side chains along the backbone, these dumbbell-shaped molecular brushes may be interesting materials to achieve structure-directed chain scission of grafted polymers on substrates or even in solution.

In summary, triblock dumbbell-shaped molecular brushes with well-defined structures were synthesized *via* "grafting-through" ROMP by sequential additions of macromonomers bearing terminal norbornene groups. The dimensions of both the "balls" and the "bar" could be tuned, individually, by controlling the macromonomer sizes and the feeding ratios of side chains to catalyst, respectively. AFM characterization revealed the dumbbell-shaped architectures and allowed for direct measurements of the dimensions. With this strategy now demonstrated as a powerful methodology for the synthesis of multiblock brush copolymers, it can be applied to achieve various macromolecular architectures with tunable side chain compositions. In addition, by modification of the side chain termini, more advanced architectures can be derived. For instance, with the particular PLA materials employed here, their hydroxyl chain ends are easily modifiable to alter the surface of the molecular brushes, and their hydrolytic and enzymatic degradability could allow them to serve as biofriendly materials or could be used as sacrificial domains to build up more complicated hollowed nanostructures, delivery vehicles, *etc.*

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, Schemes S1 (syntheses of macromonomers) and S2 (preliminary study of synthesizing of triblock brush copolymer **5**), and Figures S1−S4 (NMR spectra, GPC traces, and AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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