

One-Shot Synthesis and Melt Self-Assembly of Bottlebrush Copolymers with a Gradient Compositional Profile

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ABSTRACT: Morphological control plays a central role in soft materials design. Herein, we report the synthesis of a gradient bottlebrush architecture and its role in directing molecular packing in the solid state. Bottlebrush copolymers with gradient interfaces were prepared via one-shot ring-opening metathesis polymerization of *exo*- and *endo*-norbornene-capped macromonomers. Kinetic studies revealed a gradient compositional profile separating the two blocks along the backbone. Side-chain symmetric gradient bottlebrush copolymers exhibited a strong tendency to assemble into cylindrical microstructures, in contrast to their block copolymer analogs with sharp interfaces. Such exquisite architectural control of the interfacial composition affords a delicate handle to direct macromolecular assembly.

Block copolymer self-assembly in the solid state is a robust and versatile method for fabricating materials with nanoscale morphologies containing lamellar, cylindrical, spherical, or continuous network domains, which are of interest in a variety of applications as membranes, templates for nanomaterial synthesis and surface patterning, photonic bandgap materials, and catalyst supports.¹⁻⁶ A promising strategy to control the assembly of linear block copolymers has been the incorporation of gradient, or tapered, interfaces between the two blocks. This allows for the precise control of interfacial interactions independent of polymer chemistry and molecular weight.⁷⁻¹¹ On the other hand, polymer architecture can be used as a powerful tool for the refinement of materials structure and properties without changing the chemistry of the monomer building blocks. The combination of gradient interfacial manipulation with polymer architectural refinement can unleash another level of morphological control. However, gradient interfaces have only been studied in linear copolymers so far,⁹ partly due to synthetic challenges associated with the access to such branched and multi-dimensional systems. Herein, we report a “user-friendly” one-shot synthesis of bottlebrush copolymers with a side chain compositional gradient along the backbone through ring-opening metathesis polymerization (Figure 1) and investigate their melt self-assembly.

Bottlebrush copolymers have recently emerged as a new class of materials characterized by a comb-like architecture with densely grafted polymeric side chains.¹²⁻¹³ Two-component bottlebrush copolymers can be designed to contain homopolymer side chains distributed along the backbone in a blocky¹⁴⁻¹⁸ or statistical¹⁶ fashion, or block copolymer side chains connected to the backbone via end groups (core-shell)¹⁹⁻²³ or junction points (Janus-type)²⁴⁻²⁵. Melt self-assembly of the vast majority of two-component bottlebrush copolymers results in lamellar morphologies, even for highly compositionally asymmetric systems.¹⁴ Examples of non-lamellar

morphologies were obtained from block and Janus type bottlebrush copolymers with large side chain asymmetries.^{24, 26-27}

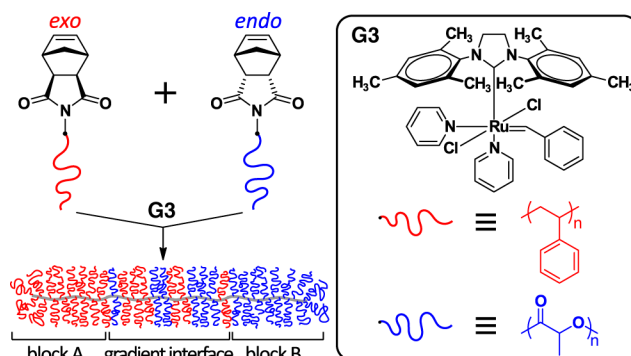


Figure 1. One-shot synthesis of gradient bottlebrush block copolymers by ring-opening metathesis polymerization.

Reports of bottlebrush copolymers with a gradient change in structural parameters along the backbone are exceedingly rare. Bottlebrush copolymers with a gradient in grafting density were synthesized by Matyjaszewski et al. using a grafting-from approach,²⁸⁻²⁹ and recently by Grubbs et al. using a grafting-through approach.³⁰⁻³¹ Choi et al. reported the synthesis of cone-shaped dendronized polymers by polymerizing two dendronized macromonomers with vastly different reactivities.³² Recently, Matson et al. reported the synthesis of tapered bottlebrush copolymers by sequential polymerization of varying length macromonomers.³³ In this communication, we show that (1) a gradient interface can be installed into the bottlebrush block copolymer architecture by exploiting reactivity differences of *exo*- and *endo*-norbornene groups, and (2) such interfacial manipulation has a profound effect on pol-

mer self-assembly producing non-lamellar morphologies from side chain symmetric copolymers.

The advent of highly active ruthenium based Grubbs' catalysts enabled efficient grafting-through synthesis of bottlebrush copolymers by direct ring-opening metathesis polymerization (ROMP) of macromonomers with reactive end groups. The most commonly used ROMP-active functional group has been norbornene due to its high ring-strain and ease of preparation, but its reactivity can vary widely depending on the stereochemistry and the nature of the anchoring group.^{16-17, 30, 34-35} Out of the two configurations possible for disubstituted norbornenes (*exo* and *endo*), *exo*-norbornene is almost exclusively selected when synthesizing bottlebrush polymers because of its superior ROMP reactivity compared to its *endo* counterpart.³⁶⁻³⁷ Intentional use of the less reactive *endo*-norbornene group is rare. For example, O'Reilly et al. used much higher reactivity of *exo*-norbornene to surgically insert individual units during polymerization of slower *endo*-norbornene-based monomer.³⁸ A recent study by Grubbs et al. evaluated reactivities of various *exo*- and *endo*-substituted norbornenes to produce bottlebrush copolymers with controlled grafting densities.³⁰ We hypothesized that one-shot polymerization of a simple mixture of two sets of macromonomers (MM) with easily synthetically accessible *exo*- and *endo*-norbornene end groups can afford bottlebrush copolymers with gradient compositional profile along the backbone. While many types of gradients can potentially be installed by this route, we first focused on a compositional gradient, where side chain length and grafting density were kept uniform along the bottlebrush backbone.

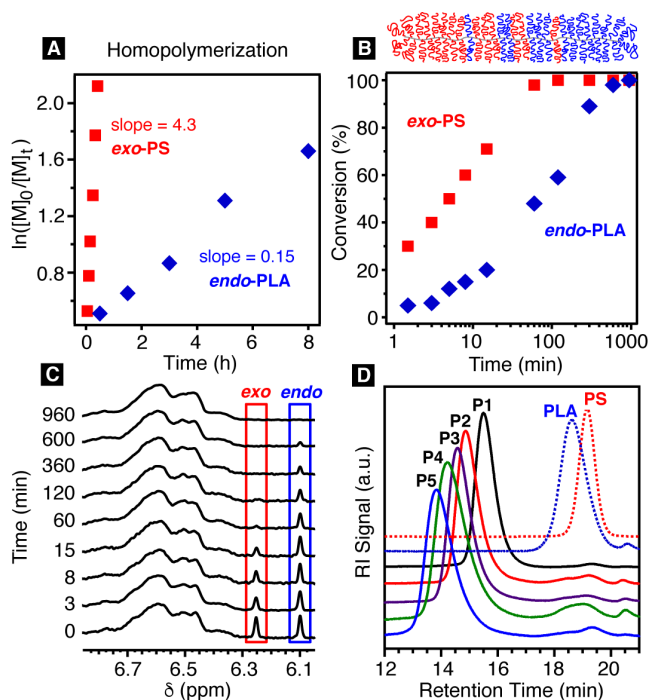


Figure 2. Kinetic analysis of (A) homopolymerization and (B) one-shot copolymerization of *exo*-PS and *endo*-PLA ($[MM] = 25$ mM, $[MM]:[G3] = 100:1$, RT), (C) NMR analysis, and (D) SEC characterization of the gradient copolymers.

Exo-norbornene capped polystyrene macromonomer (*exo*-PS) and *endo*-norbornene capped polylactide macromonomer (*endo*-PLA) with comparable molecular weights (2.1 kg/mol) were synthesized by previously reported procedures³⁹⁻⁴⁰ (Supporting Infor-

mation). Homopolymerization of these two macromonomers in the presence of a pyridine-modified 3rd generation Grubbs' catalyst (G3) at $[MM] = 25$ mM and $[MM]:[G3] = 100:1$ showed significantly different ROMP reactivities, with *exo*-PS macromonomer polymerizing 29 times faster than *endo*-PLA (Figure 2A). The vast reactivity difference between the two macromonomers during copolymerization was also corroborated by the calculated reactivity ratios ($r_1 = 5.0$ and $r_2 = 0.19$, see Supporting Information). When mixed in equimolar amounts (25 mM), both macromonomers smoothly copolymerized to completion in 16 h (Figure 2B). ¹H NMR analysis of aliquots taken at different reaction times allowed us to monitor the consumption of each macromonomer independently by watching the disappearance of the *exo*-norbornene olefin signal at 6.25 ppm and *endo*-norbornene olefin signal at 6.10 ppm (Figure 2C). At 40% *exo*-PS conversion, there is still ~95% *endo*-PLA unreacted, and by the time *exo*-PS is depleted, ~50% of *endo*-PLA remains, which continues polymerization until all norbornene groups are eventually consumed. Thus, the produced gradient bottlebrush copolymers had a PS-rich end of the molecule and a PLA-rich end of the molecule, with about half of the molecule in the middle featuring a gradient transition from PS branches to PLA branches, as illustrated in the cartoon in Figure 2. Size exclusion chromatography (SEC) analysis of the final copolymers evidenced almost complete disappearance of the starting macromonomers, and the formation of bottlebrush copolymers with low dispersities ($\bar{D} < 1.25$, Figure 2D and Table 1), consistent with the living nature of ROMP. A similar gradient was installed when *endo*-capped poly(methyl methacrylate) macromonomer was used in conjunction with *exo*-PS, confirming generality of the developed approach (Figure S9).

Table 1. Structural parameters of gradient bottlebrush copolymers.^a

Polymer	f_{PS}^b	$N_{backbone}$	M_n (g/mol) ^c	$\bar{D}^d$	d (nm) ^e
P1	0.56	54	1.1×10^5	1.13	21
P2	0.56	95	1.7×10^5	1.17	27
P3	0.56	130	2.8×10^5	1.19	30
P4	0.58	172	3.7×10^5	1.24	38
P5	0.56	212	4.4×10^5	1.21	47
P6 (block)	0.55	136	2.8×10^5	1.19	52
P7 (stat) ^f	0.54	135	3.1×10^5	1.08	N/A

^aPrepared using PS and PLA macromonomers with $M_n = 2.1$ kg/mol; ^bVolume fraction of PS determined by using the following densities: $D_{PS} = 1.04$ g/cm³ and $D_{PLA} = 1.25$ g/cm³; ^cMeasured by SEC-LS; ^dMeasured by SEC with linear PS calibration; ^eSpacing obtained from SAXS as $d = 2\pi/q^*$; ^fPrepared using 2.5 kg/mol PLA macromonomer.

Structural characteristics of a series of nearly symmetrical bb(PS-*grad*-PLA) bottlebrush copolymers (P1-P5) with different backbone lengths synthesized by one-shot copolymerization of *exo*-PS and *endo*-PLA macromonomers at different monomer-to-initiator ratios are summarized in Table 1. At the same time, bottlebrush copolymers bb(PS-*block*-PLA) (P6) and bb(PS-*stat*-PLA) (P7) with a blocky and statistical distributions of side chains along the backbone, respectively, were prepared as described in the literature (Supporting Information).¹⁶ Polymer samples were then pressed into disks and annealed at 180 °C for 20 h for small-angle X-ray

scattering (SAXS) analysis. Self-assembly of copolymers **P3** (gradient), **P6** (block), and **P7** (statistical) was investigated first in order to assess the effect of the gradient interface on molecular packing in the solid state. These three copolymers have similar molecular weights, component volume fractions, side chain and backbone lengths (Table 1), and only differ in the way PS and PLA side chains are arranged along the backbone. Their drastically different solid state behavior was revealed by SAXS analysis (Figure 3). As expected,⁴¹ bb(PS-*block*-PLA) copolymer **P6** ordered into a lamellar morphology with a domain spacing of 52 nm, evidenced by a number of higher order reflections at multiples of the primary scattering peak q^* . bb(PS-*stat*-PLA) copolymer **P7** did not exhibit a highly-ordered morphology, featuring SAXS profile with a broad peak corresponding to a characteristic distance of 12 nm, which is approximately two times diameter of the bottlebrush and is consistent with microphase separation due to dissimilar side chain segregation on opposite sides of the backbone.¹⁶ On the other hand, bb(PS-*grad*-PLA) copolymer **P3**, prepared by one-shot ROMP of *exo*-PS and *endo*-PLA, showed a strong primary scattering peak corresponding to a d -spacing of 30 nm, and higher order reflections at $2q^*$ and $\sqrt{7}q^*$, indicative of a non-lamella morphology. Transmission electron microscopy (TEM) analysis of **P3** (Figure 3) evidenced the formation of an ordered morphology with microdomains that did not resemble traditional lamellar or cylindrical block copolymer phases.

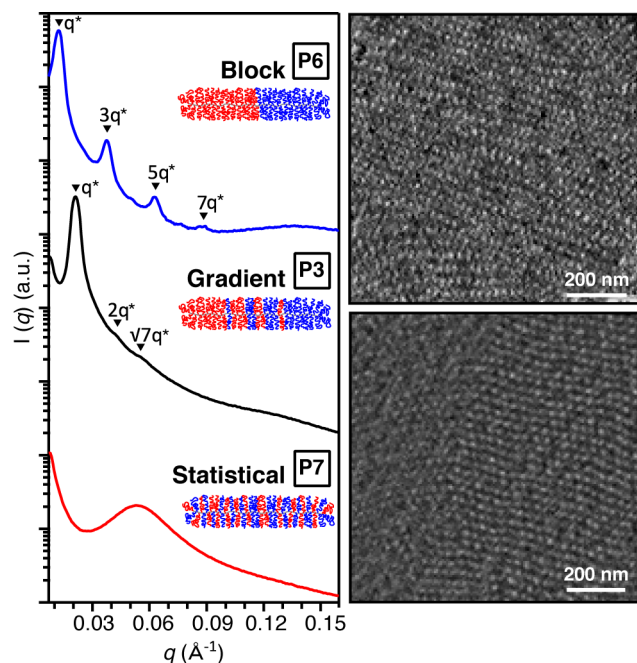


Figure 3. SAXS characterization (left) of block (**P6**, top), gradient (**P3**, middle) and statistical (**P7**, bottom) bottlebrush copolymers with similar backbone and side chain lengths, and TEM images of **P3** (right).

For additional investigation of the sample morphology, we shear aligned **P3** copolymer in a channel die and etched out the PLA domains under basic conditions (Figure 4A).⁴² ^1H NMR analysis indicated that only $\sim 40\%$ of PLA was removed by this method (Figure S13), even after prolonged periods of time (1 week). We attributed this to the inability of the etching solution to wet the mixed PS/PLA phase in the interfacial regions, with the degradation taking place solely in the PLA-rich phase. Both SAXS (Figure

4B) and scanning electron microscopy (SEM, Figures 4C and 4D) analyses of the fractured samples were indicative of hexagonally packed cylindrical morphology (Figure 4). SEM images of the fractured monolith surfaces parallel and perpendicular to the alignment direction clearly showed the presence of straight channels and hexagonally packed pores, respectively, with an average pore diameter of 15 nm.

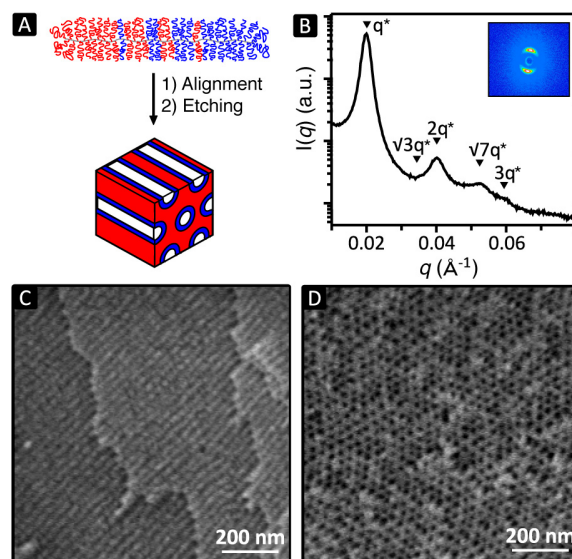


Figure 4. (A) formation of cylindrical nanopores from gradient bottlebrush copolymers, (B) SAXS analysis of shear aligned and etched copolymer **P3**, and SEM characterization of monoliths fractured parallel (C) and perpendicular (D) to the alignment direction.

Domain spacings of bb(PS-*grad*-PLA) bottlebrush copolymers, calculated from the primary scattering peaks in SAXS, increased almost linearly with the number of repeat units in the bottlebrush backbone. This behavior is similar to that of bb(PS-*block*-PLA) bottlebrush copolymers, but the increase is much slower for gradient systems. In Figure 5, we compared d -spacings of gradient bottlebrush copolymers bb(PS-*grad*-PLA) synthesized in this work (diamonds) to those of bb(PS-*block*-PLA) bottlebrush block copolymers with similar side chain lengths of 2.4 kg/mol reported by Russell et al.⁴¹ (squares). It is evident that gradient bottlebrush copolymers consistently exhibit smaller domain spacings than their block copolymer counterparts with similar backbone and side chain lengths. For linear block copolymers with gradient interfaces, no change in domain spacing or morphology was observed when compared to block copolymer with similar chain lengths.¹⁰ From data presented in Figure 5A it also appears as if the behavior of gradient and block bottlebrush systems converge for the shortest backbone lengths. However, SAXS analysis of sample **P1** clearly revealed higher order reflections at $\sqrt{3}q^*$ and $2q^*$ consistent with non-lamellar packing (Figure 5B), as opposed to its block copolymer analog with the same size and domain spacing, which exhibits a lamellar morphology.⁴¹

Smaller domain spacings of gradient bottlebrush copolymers relative to their bottlebrush block copolymer counterparts can be attributed to either a different morphology (cylindrical for gradient, while lamellar for block systems), or to a tilt in the orientation of the backbone along the interface. It has been shown that for bottlebrush copolymers with statistically distributed side chains, the domain spacing is independent of the backbone length.¹⁶ This contrast in behavior has been explained by a different molecular ar-

rament at the domain interface with the bottlebrush backbones oriented perpendicular¹⁷ and parallel to the interface for block and statistical bottlebrush copolymer systems, respectively, which is also reflected in vastly different domain spacings observed for the two systems.¹⁶ So, it is reasonable to expect that orientation of the backbone at the domain interface plays a crucial role in determining the domain spacing and introducing interfacial curvature in the gradient bottlebrush copolymer assembly, although more studies are necessary to get insight into the molecular arrangement at the domain interface.

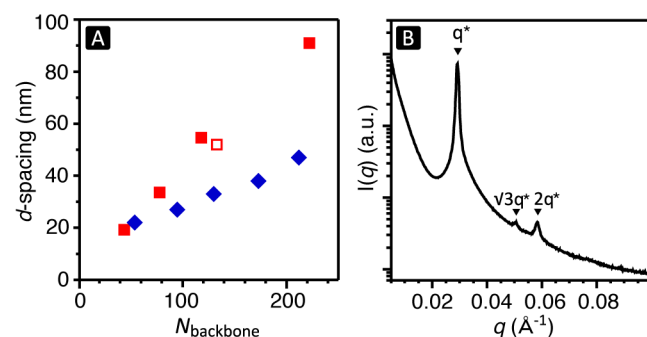


Figure 5. Backbone length dependence of the domain spacing for block (squares) and tapered (diamonds) bottlebrush copolymers (A), and SAXS profile of the smallest tapered copolymer **P1** (B). Filled squares are data from Ref. 14, open square is block copolymer **P6** prepared in this work.

In summary, the vast reactivity difference between easily accessible *exo*- and *endo*-norbornene functionalities enables the formation of bottlebrush copolymers with a gradient compositional profile along the backbone. Gradient bottlebrush copolymers bb(PS-*grad*-PLA) with symmetric composition and side chains form cylindrical morphologies, while their bottlebrush block copolymer counterparts bb(PS-*block*-PLA) with an abrupt change from PS to PLA branches along the backbone consistently pack into lamellar microstructures. In contrast to linear block copolymers, where the gradient interface has been mostly used to control the strength of interfacial interactions,^{10–11} in bottlebrush systems, it appears to change molecular packing and provides a new avenue for morphological control.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge on the ACS Publication website.

Experimental details for polymer synthesis, SEC, NMR and SAXS characterization (PDF).

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Notes

The authors declare no competing financial interest.

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