

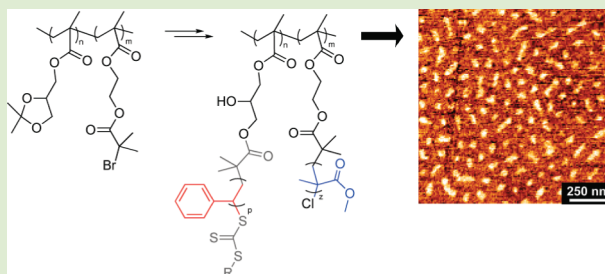
Tandem RAFT-ATRP Synthesis of Polystyrene–Poly(Methyl Methacrylate) Bottlebrush Block Copolymers and Their Self-Assembly into Cylindrical Nanostructures

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S Supporting Information

ABSTRACT: A polystyrene–poly(methyl methacrylate) (PS-PMMA) bottlebrush block copolymer with asymmetric branches was synthesized by grafting from a symmetrical backbone containing a novel dual vinyl initiation system and characterized by atomic force microscopy (AFM) and small-angle X-ray scattering (SAXS). The block copolymer backbone was prepared by sequential reversible addition–fragmentation chain transfer (RAFT) copolymerization of solketal methacrylate (SM) and 2-(bromoisobutryl)ethyl methacrylate (BIEM). From the poly-(BIEM) segment, PMMA branches of 26 units were grafted by atom transfer radical polymerization (ATRP). Solketal groups were then subjected to hydrolysis and functionalized with a RAFT agent. Subsequently, from RAFT sites of the poly(SM) segment, polystyrene branches of 45 units were grafted to yield the final bottlebrush block copolymer. The resulting polymer was found to have a vertically oriented cylindrical morphology by AFM with an average cylinder diameter of 45 nm; morphology was also confirmed by SAXS analysis.



Bottlebrush copolymers, or molecular brushes, are comb-like macromolecules with short polymeric branches densely grafted along a long polymeric backbone.^{1,2} Steric crowding of the side chains forces the backbone to acquire a nearly stretched conformation, with bottlebrush macromolecules adopting a cylindrical shape. Recently, diblock bottlebrush block copolymers, comprised of two distinct sets of branches, have been synthesized and shown to self-assemble into remarkably ordered periodic nanomaterials with large domain spacings ($d_{\text{lam}} > 70$ nm).^{3–5} Such a high degree of supramolecular order was attributed to enhanced mobility in bottlebrush copolymer melts due to a low density of entanglements despite their extremely high molecular weights ($M_n > 1$ million Da).^{6,7} Bottlebrush block copolymer self-assembly provides access to ordered nanomaterials with large periodicities, which are required for the preparation of a variety of advanced materials, such as ultrafiltration membranes^{8,9} and photonic band gap materials.¹⁰

There are three major synthetic strategies for the preparation of bottlebrush block copolymers: “grafting-through,”^{4,5} “grafting-to,”^{11,12} and “grafting-from.”¹³ Controlled radical polymerization techniques, such as atom transfer radical polymerization (ATRP)¹⁴ and reversible addition–fragmentation chain transfer (RAFT),¹⁵ have allowed access to bottlebrush copolymers by a “grafting-from” method, where side chains are produced by a polymerization initiated from active sites along a well-defined backbone.^{13,16–19} Most commonly, bottlebrush copolymers with two chemically distinct side chains are prepared by mutually compatible polymerization techniques, for example, ring-opening polymerization of lactones and radical polymerization of vinyl

monomers.^{3,20} Such approaches impose limitations on the diversity of side chain composition and thus on the functionality of obtained nanomaterials. Herein, we report a new method for producing diblock bottlebrushes where side chains are assembled from any two vinyl monomers amenable to controlled radical polymerization. We demonstrate the utility of the new protocol by synthesizing an asymmetric polystyrene–poly(methyl methacrylate) (PS-PMMA) bottlebrush block copolymer. Linear PS-PMMA diblock copolymers have been well-studied in regard to their thin film morphology.^{21,22} By employing architectural parameters determined in our previous work,⁸ we targeted the preparation of a cylindrical morphology due to its utility in the fabrication of templates for nanowires, nanopatterns, and nanoporous membranes.^{23–25} We show that asymmetric PS-PMMA bottlebrush block copolymers prepared by the new methodology phase separate to produce an ordered cylindrical morphology in bulk and thin films.

PS-PMMA bottlebrush block copolymers were prepared by a synthetic strategy outlined in Figure 1. First, a diblock copolymer backbone was synthesized, where one block contained pendant ATRP initiating sites and the other block was transformed to contain pendant RAFT agent groups. ATRP initiating sites were directly introduced into the backbone by RAFT polymerization of 2-(bromoisobutryl)-ethyl methacrylate (BIEM).²⁶ On the other hand, there are no direct methods to introduce RAFT containing monomers into a

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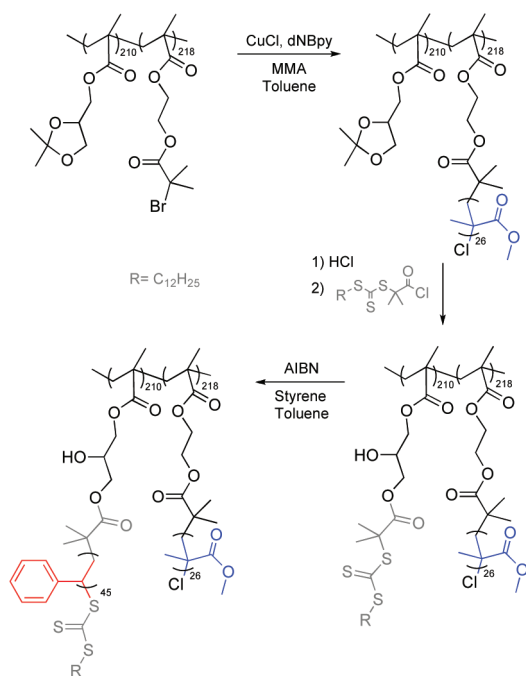


Figure 1. Synthesis of PS-PMMA bottlebrush block copolymers.

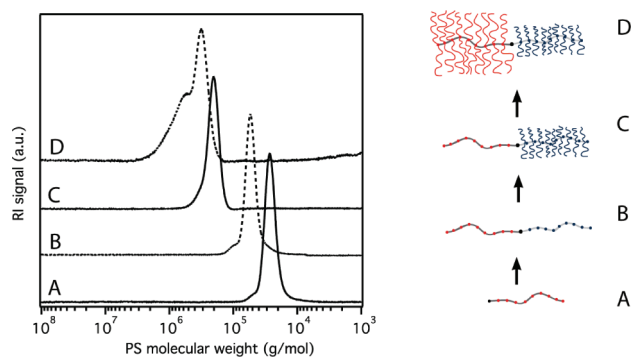


Figure 2. GPC (RI detector) traces of (A) poly(SM), (B) poly(SM-*b*-BIEM), (C) poly(SM-*b*-(BIEM-*g*-MMA)), and (D) poly((SM-*g*-PS)-*b*-(BIEM-*g*-MMA)).

backbone by living radical techniques without producing a hyperbranched polymer.²⁷ Therefore, we chose to introduce pendant RAFT groups post polymerization by reaction with hydroxy groups of the hydrolyzed poly(solketal methacrylate) block. PMMA and PS branches were grafted onto the backbone by ATRP and RAFT, respectively. It must be noted that the RAFT end group of the diblock copolymer backbone will likely participate in the subsequent grafting-from syntheses and produce one side chain composed of a PMMA-PS block copolymer. However, due to the fact that it is only 1 among 200 side chains in the final bottlebrush copolymer, we do not expect it to have a significant impact on polymer physical properties.

The backbone precursor was synthesized by sequential RAFT copolymerization of solketal methacrylate (SM) and 2-(bromoisobutyryl)ethyl methacrylate with 2-cyano-2-propylbenzodithioate as a chain transfer agent, following a procedure previously reported by our group.³ The backbone diblock copolymer was prepared to contain a poly(SM) block with an average of 210 repeat units and a poly(2-(bromoisobutyryl)-

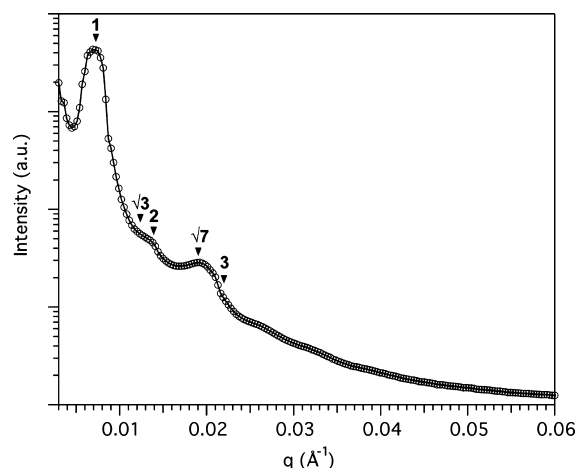


Figure 3. SAXS characterization (25 °C) of the PS-PMMA bottlebrush block copolymer after annealing (230 °C for 16 h). Triangles indicate expected reflections for a hexagonally packed cylinders morphology.

ethyl methacrylate) block with an average of 218 units. The polymer had a low polydispersity index (PDI) of 1.09 (Figure 2 and Table S1 in the Supporting Information).

PMMA side chains were grafted from α -bromo ester groups of poly(BIEM) by using conditions previously reported by Neugebauer et al.²⁸ From ¹H NMR analysis (Figure S3, Supporting Information), the average branch length was determined to be 26 repeat units by comparing the PMMA methyl ester peak at 3.62 ppm to the poly(SM) methylene peak at 4.34 ppm. Initiation efficiency of 68% was calculated by using a PMMA end-group methyl ester peak at 3.8 ppm, which is consistent with previous reports on PMMA grafting by ATRP.²⁸ A clean shift of the GPC peak to lower elution times and a low bottlebrush PDI of 1.21 (Figure 2c), evidenced the lack of major side reactions.

The installation of the RAFT initiation sites for grafting PS brushes first required deprotection of diol groups along the poly(SM) backbone, which was accomplished under acidic conditions in THF. Complete deprotection was confirmed by the disappearance of solketal peaks in the ¹H NMR spectrum (Figure S4, Supporting Information). A carboxylic acid-containing RAFT agent, *S*-1-dodecyl-*S'*-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate,²⁹ was transformed into an acid chloride and then attached to pendant hydroxyl groups of the hydrolyzed poly(SM) block in DMF. The successful outcome of the esterification was confirmed by ¹H NMR analysis (Figure S5, Supporting Information). The number of grafted RAFT groups was calculated by comparing a new peak at 3.28 ppm, corresponding to methylene protons adjacent to the trithiocarbonate group, to the PMMA methyl ester peak at 3.62 ppm. Under optimized conditions, by using an excess of RAFT agent acid chloride, 183 RAFT groups were successfully grafted to the polymer, corresponding to an average of 87% of poly(SM) repeat units having a single RAFT agent (43% conversion of hydroxy groups).

Grafting of PS side chains onto the bottlebrush backbone was accomplished by RAFT polymerization. To minimize the recombination of polystyrene radicals, the reaction was conducted in toluene as a solvent and was stopped at low conversions (<15%). The grafted PS branch length was determined from a ¹H NMR spectrum (Figure S6, Supporting Information) by comparing the signal at 3.25 ppm, representing

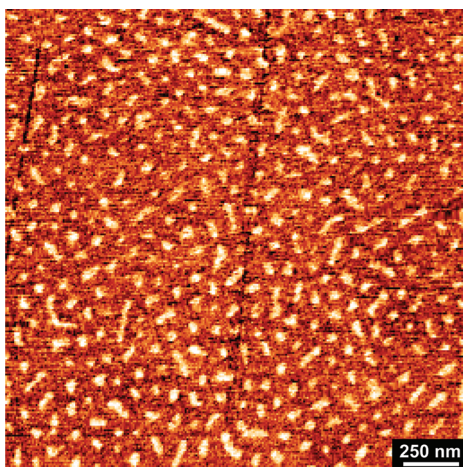


Figure 4. AFM characterization of a PS-PMMA bottlebrush block copolymer thin film spin coated on a silicon wafer and annealed at 230 °C.

methylene protons adjacent to the trithiocarbonate group, to the polystyrene aromatic signal at 6.3–7.2 ppm. Polystyrene side chains were found to be 45 units long on average with a final polymer PDI of 1.30 (Figure 2d). By comparing PS chains trithiocarbonate end-group signal at 3.25 ppm and PMMA chains end-group peak at 3.8 ppm, we determined the initiation efficiency for RAFT grafting to be 83%. GPC trace of the final polymer shifted to lower elution times, indicating an increase in molecular weight, albeit with an appearance of a high molecular weight shoulder, which could be attributed either to polymer aggregation due to remaining hydroxy groups or, more likely, to bimolecular coupling of PS radicals. The final PS-PMMA diblock bottlebrush block copolymer was determined to have a PMMA volume fraction of 41%.

Bulk morphology of the synthesized PS-PMMA bottlebrush block copolymer (melt-pressed and annealed at 230 °C) was characterized by small-angle X-ray scattering (Figure 3). The presence of a strong primary scattering peak at $q = 0.0072 \text{ \AA}^{-1}$, corresponding to a d -spacing of 87 nm, indicated microphase separation of PS and PMMA domains of the block copolymer. A number of higher order reflections were also observed, with the most intense peak located at $\sqrt{7}q$, consistent with a well-ordered hexagonally packed cylinders morphology. We attribute the formation of a cylindrical morphology to the structural asymmetry of the synthesized bottlebrush block copolymer, where PS branches on one side of the molecular brush were much longer than PMMA branches on the other, preventing bottlebrush macromolecules from packing into microstructures with flat interfaces. The results are consistent with our previous observations on the microphase separation of polystyrene–polylactide bottlebrush block copolymers⁸ and suggest a general trend in the packing of such highly branched macromolecules. This is the first example of an asymmetric bottlebrush block copolymer self-assembling into a well-ordered cylindrical morphology identifiable by SAXS analysis.

Thin films of the PS-PMMA bottlebrush block copolymer were spin-coated on a freshly cleaned silicon wafer, annealed at 230 °C and analyzed by tapping-mode atomic force microscopy (AFM). Consistent with the SAXS data, AFM analysis revealed a collection of almost hexagonally packed dots (Figure 4), corresponding to cylindrical microdomains oriented normal to the surface. Such an orientation is consistent with the fact that

polymer d -spacing is larger than the film thickness (30–40 nm). PMMA domains were measured to have an average diameter of 45 nm.

In conclusion, PS-PMMA diblock bottlebrush copolymer was synthesized from a novel dual vinyl initiating system by combining both ATRP and RAFT polymerization techniques. The polymer was composed of a symmetric backbone and asymmetric branches with PS side chains longer than PMMA branches. This asymmetric bottlebrush block copolymer was found to self-assemble into a cylindrical morphology with a d -spacing of 87 nm, as identified by SAXS. AFM images of bottlebrush copolymer thin films were consistent with the formation of a vertically oriented cylindrical microstructure.

■ ASSOCIATED CONTENT

Supporting Information

Experimental section and ¹H NMR spectra of the synthesized copolymers (Figures S1–S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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■ REFERENCES

- Zhang, M.; Müller, A. H. E. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3461.
- Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K. *Prog. Polym. Sci.* **2008**, *33*, 759.
- Rzayev, J. *Macromolecules* **2009**, *42*, 2135.
- Xia, Y.; Olsen, B. D.; Kornfield, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 18525.
- Runge, M. B.; Bowden, N. B. *J. Am. Chem. Soc.* **2007**, *129*, 10551.
- Vlassopoulos, D.; Fytas, G.; Loppinet, B.; Isel, F.; Lutz, P.; Benoit, H. *Macromolecules* **2000**, *33*, 5960.
- Bailly, C.; Stephenne, V.; Muchtar, Z.; Schappacher, M.; Deffieux, A. *J. Rheol.* **2003**, *47*, 821.
- Bolton, J.; Bailey, T. S.; Rzayev, J. *Nano Lett.* **2011**, *11*, 998.
- Jackson, E. A.; Hillmyer, M. A. *ACS Nano* **2010**, *4*, 3548.
- Yoon, J.; Lee, W.; Thomas, E. L. *MRS Bull.* **2005**, *30*, 721.
- Tsarevsky, N. V.; Bencherif, S. A.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 4439.
- Gao, H. F.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2007**, *129*, 6633.
- Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. *Macromolecules* **1998**, *31*, 9413.
- Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921.
- Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379.
- Nese, A.; Kwak, Y.; Nicolay, R.; Barrett, M.; Sheiko, S. S.; Matyjaszewski, K. *Macromolecules* **2010**, *43*, 4016.
- Borner, H. G.; Beers, K.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. *Macromolecules* **2001**, *34*, 4375.
- Cheng, G. L.; Boker, A. A.; Zhang, M. F.; Krausch, G.; Muller, A. H. E. *Macromolecules* **2001**, *34*, 6883.
- Huang, K.; Canterbury, D. P.; Rzayev, J. *Macromolecules* **2010**, *43*, 6632.
- Lee, H. I.; Matyjaszewski, K.; Yu-Su, S.; Sheiko, S. S. *Macromolecules* **2008**, *41*, 6073.

- (21) Bang, J.; Jeong, U.; Ryu, D. Y.; Russell, T. P.; Hawker, C. J. *Adv. Mater.* **2009**, *21*, 4769.
- (22) Morkved, T. L.; Lu, M.; Urbas, A. M.; Ehrichs, E. E.; Jaeger, H. M.; Mansky, P.; Russell, T. P. *Science* **1996**, *273*, 931.
- (23) Thurn-Albrecht, T.; Schotter, J.; Kastle, C. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. *Science* **2000**, *290*, 2126.
- (24) Hillmyer, M. Nanoporous Materials from Block Copolymer Precursors. In *Block Copolymers II*; Abetz, V., Ed.; Springer: Berlin/Heidelberg, 2005; Vol. 190, p 137.
- (25) Stewart, S.; Liu, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 340.
- (26) Venkatesh, R.; Yajjou, L.; Koning, C. E.; Klumperman, B. *Macromol. Chem. Phys.* **2004**, *205*, 2161.
- (27) Vogt, A. P.; Gondi, S. R.; Sumerlin, B. S. *Aust. J. Chem.* **2007**, *60*, 396.
- (28) Neugebauer, D.; Sumerlin, B. S.; Matyjaszewski, K.; Goodhart, B.; Sheiko, S. S. *Polymer* **2004**, *45*, 8173.
- (29) Lai, J. T.; Filla, D.; Shea, D. *Macromolecules* **2002**, *35*, 6754.