# Molecular Bottlebrushes: New Opportunities in Nanomaterials Fabrication

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ABSTRACT: This Viewpoint highlights the ability of molecular bottlebrushes to serve as highly tunable building blocks for creating nanostructured materials via molecular templating, solution aggregation, and melt self-assembly. Recent achievements in the synthesis of discrete nano-objects, micellar structures, and periodic nanomaterials from bottlebrush copolymers are emphasized, and future opportunities in this area of polymer science are briefly discussed.
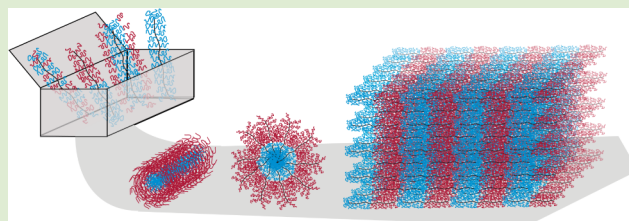
The shape-persistent nature, remarkable spatial dimensions, and tunable architecture of molecular bottlebrushes have forged new facets of bottom-up nanomaterials fabrication, providing access to nanostructures often unattainable from linear polymers. As a class of comb/graft copolymers, molecular bottlebrushes (also referred to as cylindrical polymer brushes, poly(macromonomers), or molecular brushes) are composed of a long polymeric backbone with densely grafted polymeric side chains.[1] When the backbone is longer than the side chains, these macromolecules take on a persistent, cylindrical shape, which is brought about by the steric repulsion between the polymeric side chains forcing the backbone to adopt a nearly extended conformation.[2−4] Because the rigid nature of these cylindrical brushes is caused by the molecular architecture rather than a specific chemical structure, a wide spectrum of chemically distinct bottlebrushes can be generated from a variety of traditional monomers. The synthesis, characterization, and various applications of molecular bottlebrushes have been carefully reviewed elsewhere.[5−7] This Viewpoint article offers a perspective on the framework, including some unique aspects, of nanomaterials fabrication with bottlebrush copolymers.

The interest in the bottlebrush architecture was rekindled since a rigorous characterization study by Schmidt et al. on solution structure of "rodlike combs",[8] which were synthesized by conventional radical polymerization of macromonomers.[9,10] The advent of controlled/living radical polymerization techniques and a seminal work by Matyjaszewski et al. on the grafting-from synthesis of molecular brushes by atom transfer radical polymerization (ATRP)[11] opened access to a great variety of bottlebrush structures with well-regulated dimensions. Currently, bottlebrush copolymers are routinely synthesized by three different methods (Figure 1): grafting-through (polymerization of macromonomers), grafting-to (coupling of side chains to the backbone), and grafting-from (synthesis of side chains from a backbone polyinitiator). The grafting-though method, which has long been a domain of conventional radical polymerizations with poor length control, has been recently reenergized by the discovery of highly active ruthenium
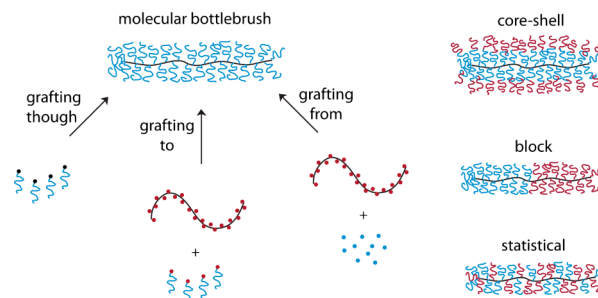

Figure 1. Synthesis and various architectures of molecular bottlebrushes.

catalysts for controlled ring-opening metathesis polymerization of norbornene-functionalized macromonomers.[12−14] The grafting-to method has been dramatically improved with the use of new chemical coupling reactions, such as click chemistry, although high coupling efficiencies are often reserved for a limited variety of side chains.[15−18] The grafting-from synthesis has relied on controlled radical and ring-opening polymerizations for side chain growth to produce a diverse array of well-defined bottlebrush copolymers.[19−22] Often, a combination of different methods is used to synthesize molecular brushes with multiple compartments, such as core−shell, block, and statistical bottlebrushes (Figure 1). With such a variety of polymerization tools available for the synthesis of bottlebrush copolymers, a multitude of structures can be generated with different properties, strategically placed functional groups/components, and well-controlled dimensions. Such molecules have been tailored to exhibit specific properties for the utilization as molecular pressure sensors,[23] pH-sensitive molecular probes,[24] supersoft elastomers,[25] and therapeutic delivery vehicles.[26−28]

The unique shape and easily controlled dimensions (from tens to hundreds of nanometers) of molecular bottlebrushes render them particularly useful as molecular building blocks for generating nanostructured materials by (1) single-molecule manipulation to create well-defined nano-objects, (2) solution self-assembly to produce larger aggregates with different morphologies, and (3) melt self-assembly to fabricate periodic nanomaterials with large domain spacings. In each of these applications, the peculiar properties of bottlebrush copolymers enable the synthesis of previously inaccessible materials in a controlled and predictable fashion.

The molecular templating method based on bottlebrush copolymers combines excellent dimensional control of solid templating methods and scalability of self-assembly approaches to provide a robust platform for the construction of 1D nano-objects with tunable dimensions (Figure 2). A molecular
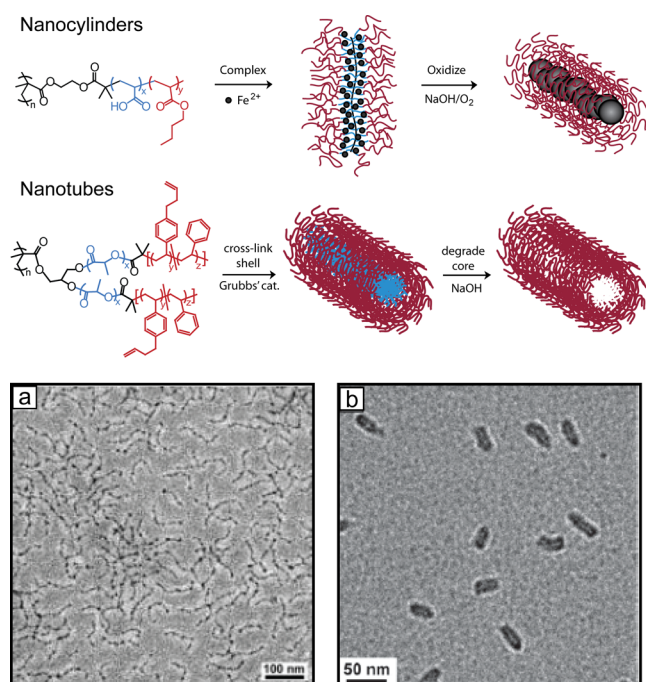

Figure 2. Molecular templating based on core−shell bottlebrush copolymers: chemical design and TEM images of (a) hybrid nanocylinders (Reprinted with permission from ref 30. Copyright 2004 Wiley.), and (b) organic nanotubes (from ref 36).

bottlebrush can be viewed as a covalently preassembled cylindrical polymer micelle. In contrast to an actual polymer micelle, which is formed by the self-assembly of an amphiphilic block copolymer in a discriminating solvent, a cylindrical polymer brush can be synthesized to contain only one polymer component, its dimensions are predetermined by the lengths of the backbone and the side chains, and its cylindrical structure is not easily perturbed by the incorporation of additional functional groups. Even though covalently built molecular brushes cannot take advantage of the dynamic nature of self-assembly, they can serve as very robust molecular templates that can be conveniently manipulated in different chemical environments. For example, core−shell bottlebrush copolymers can serve as precursors for inorganic−organic hybrid materials where the core layer is used for binding inorganic salts or nanoparticles and the shell layer serves as a protective corona (Figure 2). The dimensions of the obtained nanocylinders are

controlled by the size of the bottlebrush copolymer template. Schmidt et al. demonstrated the use of amphiphilic core−shell poly(macromonomers) as templates for creating gold nano-wires, although length control could not be achieved.[29] Müller et al. designed a strategy to produce superparamagnetic nanocylinders by using core−shell bottlebrush copolymers with a poly(acrylic acid) core and a poly(n-butyl acrylate) shell (Figure 2).[30] Oxidation of the complexed salts inside the core produced magnetic nanoparticle aggregates, whose dimensions replicated those of the precursor bottlebrushes. Core−shell bottlebrush copolymer templates have also been used to generate magnetite[31] and CdSe[32] nanoparticle arrays, and CdSe[33] and silica[34] nanowires.

Porous nanostructures can be produced by peripheral cross-linking and subsequent core removal of core−shell bottle-brushes (Figure 2b). Wooley et al. used molecular brushes with a polyisoprene core and a poly(acrylic acid) shell to generate hollow spherical nanocages.[35] Our group has developed a method for the synthesis of organic nanotubes with well-controlled dimensions from multicomponent molecular bot-tlebrushes.[36] Poly(4-butenylstyrene) shell was used to fixate the cylindrical shape of the bottlebrush copolymer precursors, while polylactide (PLA) core removal provided a pore running through the center of the cylindrical nanoparticles (Figure 2). Poly(ethylene oxide) or PLA stoppers were used at either or both ends of the bottlebrush to produce nanotubes with open ends.[36,37] The nanotube length was in close agreement with the expected end-to-end distances of the fully stretched bottlebrush backbones. This approach was further expanded for the preparation of tubular nanostructures with favorable solubility characteristics or with functionalized interior surfaces by utilizing molecular brushes with triblock copolymer side chains.[38] The prepared amphiphilic nanotubes were exploited for cellular internalization[39] and selective molecular transport.[40] A similar strategy was employed by Müller et al. to prepare water-soluble organo-silica hybrid nanotubes.[41]

The molecular templating strategy relies on the availability of strategically compartmentalized bottlebrush copolymer pre-cursors. The shape of molecular brushes is dictated by the topology of the backbone and the length and chemistry of the side chains. Cyclic,[42−44] star,[45,46] and dumbbell-shaped[47] molecular brushes, as well as dendronized polymers,[48] have been recently synthesized by the appropriate choice of the backbone and branches and can potentially serve as templates for creating uniquely shaped nano-objects.

Compared to solution self-assembly of linear block copolymers, the aggregation of amphiphilic bottlebrush copolymers in a selective solvent is distinguished in two ways. First, due to their large molecular size, the assemblies generated from the supramolecular organization of bottlebrush copolymers are in the size regime not accessible by linear copolymers. Micellar aggregates with diameters from fifty to several hundred nanometers have been reported for brush−brush and brush−coil block copolymers.[26,49,50] Second, due to the unique architecture of bottlebrush copolymers, some new modes of assembly have been observed leading to morpholog-ically different aggregates. Wooley et al. reported solution aggregation of a molecular brush with amphiphilic triblock copolymer branches to generate one-dimensional 92 ± 21 nm long assemblies with 4−5 molecular brushes present per aggregate.[51] The authors hypothesized that the linear nanostructures were produced via end-to-end interactions between hydrophobic cores of individual molecular brushes.

In another study, Deffieux et al. synthesized macrocyclic molecular brushes with randomly distributed polyisoprene and polystyrene side chains.[44] In a selective solvent for polyisoprene branches, these macrocyclic molecular brushes aggregated into supramolecular tubular nanostructures with lengths up to 700 nm (Figure 3). Wu et al. recently reported a different approach
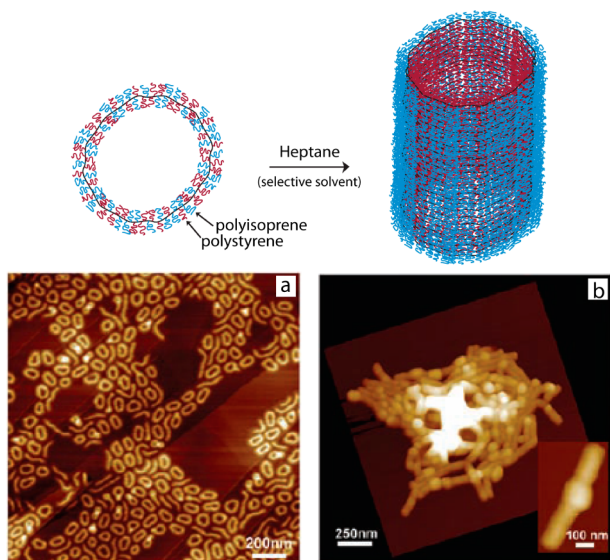

Figure 3. Self-assembly of cyclic molecular brushes with randomly distributed side chains in a selective solvent. AFM images of (a) macrocyclic brushes and (b) nanotubes. (From ref 44. Reprinted with permission from AAAS.)

for the fabrication of polymeric nanoscale networks from bottlebrush copolymers.[52] Long molecular brushes, utilized as nanofibers, were intra- and intermolecularly cross-linked in solution, providing porous nanostructured networks with an average pore size of 6−9 nm.

Melt self-assembly of linear block copolymers has been a dependable tool for producing periodic nanostructured soft materials.[53] The limitations in domain spacings arising from the high entanglement density of long linear block copolymers can be circumvented by the use of molecular brushes. Due to their comb-like molecular architecture, the melt dynamics of bottlebrush copolymers do not appear to be hindered by interchain entanglement.[54,55] Thus, melt self-assembly of bottlebrush block copolymers provides easy access to ordered nanomaterials with large domain spacings ($d > 100$ nm, Figure 4) exhibiting photonic properties. Bowden et al. has reported the formation of large domain nanostructures from a series of brush−brush and brush−linear block copolymers, as evidenced by scanning electron microscopy.[56,57] Our group has demonstrated a grafting-from synthesis and melt self-assembly of polystyrene−polylactide bottlebrush block copolymers to produce highly ordered periodic materials with domain spacings as large as 160 nm (obtained by ultrasmall-angle X-ray scattering, USAXS).[58] Predominantly lamellae morphologies were observed even for highly asymmetric bottlebrush block copolymers ($f_{PLA} = 0.3$) where the asymmetry was achieved by different length backbones. Interestingly, the obtained d-spacings coincided with the calculated end-to-end distances of a bottlebrush backbone, assuming a fully stretched conformation (Figure 4). Grubbs et al. also has shown that the domain spacings for poly(n-butyl acrylate)−polylactide bottle-
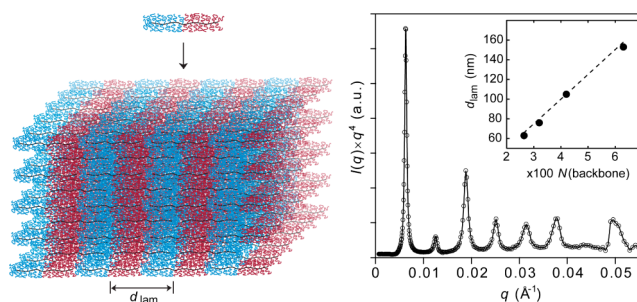

Figure 4. Melt self-assembly of bottlebrush block copolymers into lamellae microstructures (left), and USAXS spectrum of a PS-PLA bottlebrush copolymer with a methacrylate backbone (right). The inset shows the dependence of lamellae spacing on the length of the backbone (dots: experimental data; dotted line: end-to-end distance of a fully stretched backbone) from ref 58.

brush block copolymers were in close agreement with the contour length of a single polymer chain.[59] These observations suggest interdigitated packing of bottlebrush block copolymers, but more studies are necessary to understand the phenomenon. The morphology of blocky bottlebrushes can be manipulated by perturbing their cylindrical shape with the use of different length branches on each side of the bottlebrush. Such asymmetric molecules have been shown to pack into cylindrical microstructures, which upon removal of the minority PLA component provide nanoporous materials with enlarged pores ($d_{pore} > 50$ nm),[60] difficult to achieve from linear block copolymer precursors. On the other hand, Grubbs et al. also demonstrated that melt self-assembly of bottlebrush copolymers with PLA and poly(n-butyl acrylate) side chains randomly distributed along the backbone produced lamella microstructures with much smaller d-spacings (14 nm).[59] The magnitudes of the observed d-spacings and their independence of the bottlebrush backbone length suggested that the backbones were aligned parallel to the interface, unlike the perpendicular arrangement envisioned for blocky bottlebrushes. These studies vividly illustrate the ability to manipulate the materials morphology by the tunable bottlebrush architecture.

The access to well-defined multicomponent bottlebrush copolymers has been facilitated by tremendous progress in synthetic polymer chemistry in the past couple of decades. Despite being a new kid on the block, molecular brushes have helped to circumvent a number of challenges in materials synthesis and led to the fabrication of well-defined nano-objects, organic nanotubes, and photonic and nanoporous materials. However, many challenges and opportunities remain. A better fundamental understanding of the bottlebrush self-assembly process is necessary, which will facilitate the access to new morphologies and enable a rational design of hierarchical nanostructures. New synthetic methods for the preparation of more sophisticated bottlebrushes can lead to the development of highly compartmentalized nanoparticles that can address ongoing problems in drug delivery, catalysis, and molecular separations. With so many exciting opportunities, bottlebrush copolymers are poised to continue their rapid ascent to the top shelf of a materials scientist's toolbox.

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Notes

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REFERENCES

(1) Wintermantel, M.; Gerle, M.; Fischer, K.; Schmidt, M.; Wataoka, I.; Urakawa, H.; Kajiwara, K.; Tsukahara, Y. *Macromolecules* **1996**, *29*, 978.

(2) Zhang, B.; Grohn, F.; Pedersen, J. S.; Fischer, K.; Schmidt, M. *Macromolecules* **2006**, *39*, 8440.

(3) Rathgeber, S.; Pakula, T.; Wilk, A.; Matyjaszewski, K.; Beers, K. L. *J. Chem. Phys.* **2005**, *122*, 124904.

(4) Lecommandoux, S.; Checot, F.; Borsali, R.; Schappacher, M.; Deffieux, A.; Brulet, A.; Cotton, J. P. *Macromolecules* **2002**, *35*, 8878.

(5) Lee, H.-i.; Pietrasik, J.; Sheiko, S. S.; Matyjaszewski, K. *Prog. Polym. Sci.* **2010**, *35*, 24.

(6) Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K. *Prog. Polym. Sci.* **2008**, *33*, 759.

(7) Zhang, M. F.; Muller, A. H. E. *J. Polym. Sci., Polym. Chem.* **2005**, *43*, 3461.

(8) Wintermantel, M.; Schmidt, M.; Tsukahara, Y.; Kajiwara, K.; Kohjiya, S. *Macromol. Rapid Commun.* **1994**, *15*, 279.

(9) Tsukahara, Y.; Mizuno, K.; Segawa, A.; Yamashita, Y. *Macromolecules* **1989**, *22*, 1546.

(10) Tsukahara, Y.; Tsutsumi, K.; Yamashita, Y.; Shimada, S. *Macromolecules* **1990**, *23*, 5201.

(11) Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. *Macromolecules* **1998**, *31*, 9413.

(12) Li, Z.; Zhang, K.; Ma, J.; Cheng, C.; Wooley, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5557.

(13) Jha, S.; Dutta, S.; Bowden, N. B. *Macromolecules* **2004**, *37*, 4365.

(14) Xia, Y.; Kornfield, J. A.; Grubbs, R. H. *Macromolecules* **2009**, *42*, 3761.

(15) Gao, H.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2007**, *129*, 6633.

(16) Lahasky, S. H.; Serem, W. K.; Guo, L.; Garno, J. C.; Zhang, D. *Macromolecules* **2011**, *44*, 9063.

(17) Johnson, J. A.; Lu, Y. Y.; Burts, A. O.; Lim, Y. H.; Finn, M. G.; Koberstein, J. T.; Turro, N. J.; Tirrell, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 559.

(18) Sun, J.; Hu, J.; Liu, G.; Xiao, D.; He, G.; Lu, R. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1282.

(19) Lee, H.; Jakubowski, W.; Matyjaszewski, K.; Yu, S.; Sheiko, S. S. *Macromolecules* **2006**, *39*, 4983.

(20) Nese, A.; Li, Y. C.; Averick, S.; Kwak, Y.; Konkolewicz, D.; Sheiko, S. S.; Matyjaszewski, K. *ACS Macro Lett.* **2012**, *1*, 227.

(21) Bolton, J.; Rzayev, J. *ACS Macro Lett.* **2012**, *1*, 15.

(22) Zehm, D.; Laschewsky, A.; Liang, H.; Rabe, J. P. *Macromolecules* **2011**, *44*, 9635.

(23) Xu, H.; Sun, F. C.; Shirvanyants, D. G.; Rubinstein, M.; Shabratov, D.; Beers, K. L.; Matyjaszewski, K.; Sheiko, S. S. *Adv. Mater.* **2007**, *19*, 2930.

(24) Nese, A.; Lebedeva, N. V.; Sherwood, G.; Averick, S.; Li, Y.; Gao, H.; Peteanu, L.; Sheiko, S. S.; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 5905.

(25) Pakula, T.; Zhang, Y.; Matyjaszewski, K.; Lee, H.-i.; Boerner, H.; Qin, S.; Berry, G. C. *Polymer* **2006**, *47*, 7198.

(26) Yang, Y. Q.; Guo, X. D.; Lin, W. J.; Zhang, L. J.; Zhang, C. Y.; Qian, Y. *Soft Matter* **2012**, *8*, 454.

(27) Johnson, J. A.; Lu, Y. Y.; Burts, A. O.; Xia, Y.; Durrell, A. C.; Tirrell, D. A.; Grubbs, R. H. *Macromolecules* **2010**, *43*, 10326.

(28) Kano, A.; Yamano, T.; Choi, S. W.; Maruyama, A. *Adv. Mater. Res.* **2008**, *47−50*, 762.

(29) Djalali, R.; Li, S. Y.; Schmidt, M. *Macromolecules* **2002**, *35*, 4282.

(30) Zhang, M.; Estournes, C.; Bietsch, W.; Mueller, A. H. E. *Adv. Funct. Mater.* **2004**, *14*, 871.

(31) Xu, Y.; Yuan, J.; Fang, B.; Drechsler, M.; Muellner, M.; Bolisetty, S.; Ballauff, M.; Mueller, A. H. E. *Adv. Funct. Mater.* **2010**, *20*, 4182.

(32) Zhang, M. F.; Drechsler, M.; Muller, A. H. E. *Chem. Mater.* **2004**, *16*, 537.

(33) Yuan, J.; Drechsler, M.; Xu, Y.; Zhang, M.; Mueller, A. H. E. *Polymer* **2008**, *49*, 1547.

(34) Yuan, J. Y.; Xu, Y. Y.; Walther, A.; Bolisetty, S.; Schumacher, M.; Schmalz, H.; Ballauff, M.; Muller, A. H. E. *Nat. Mater.* **2008**, *7*, 718.

(35) Cheng, C.; Qi, K.; Khoshdel, E.; Wooley, K. L. *J. Am. Chem. Soc.* **2006**, *128*, 6808.

(36) Huang, K.; Rzayev, J. *J. Am. Chem. Soc.* **2009**, *131*, 6880.

(37) Huang, K.; Canterbury, D. P.; Rzayev, J. *Macromolecules* **2010**, *43*, 6632.

(38) Huang, K.; Canterbury, D. P.; Rzayev, J. *Chem. Commun.* **2010**, *46*, 6326.

(39) Huang, K.; Jacobs, A.; Rzayev, J. *Biomacromolecules* **2011**, *12*, 2327.

(40) Huang, K.; Rzayev, J. *J. Am. Chem. Soc.* **2011**, *133*, 16726.

(41) Muellner, M.; Yuan, J.-Y.; Weiss, S.; Walther, A.; Foertsch, M.; Drechsler, M.; Mueller, A. H. E. *J. Am. Chem. Soc.* **2010**, *132*, 16587.

(42) Xia, Y.; Boydston, A. J.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 5882.

(43) Zhang, K.; Lackey, M. A.; Wu, Y.; Tew, G. N. *J. Am. Chem. Soc.* **2011**, *133*, 6906.

(44) Schappacher, M.; Deffieux, A. *Science* **2008**, *319*, 1512.

(45) Schappacher, M.; Deffieux, A. *Macromolecules* **2000**, *33*, 7371.

(46) Matyjaszewski, K.; Qin, S. H.; Boyce, J. R.; Shirvanyants, D.; Sheiko, S. S. *Macromolecules* **2003**, *36*, 1843.

(47) Li, A.; Li, Z.; Zhang, S.; Sun, G.; Policarpio, D. M.; Wooley, K. L. *ACS Macro Lett.* **2012**, *1*, 241.

(48) Guo, Y.; van Beek, J. D.; Zhang, B.; Colussi, M.; Walde, P.; Zhang, A.; Kroeger, M.; Halperin, A.; Schlueter, A. D. *J. Am. Chem. Soc.* **2009**, *131*, 11841.

(49) Li, Z.; Ma, J.; Cheng, C.; Zhang, K.; Wooley, K. L. *Macromolecules* **2010**, *43*, 1182.

(50) Neiser, M. W.; Muth, S.; Kolb, U.; Harris, J. R.; Okuda, J.; Schmidt, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3192.

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

(52) Wu, D.; Nese, A.; Pietrasik, J.; Liang, Y.; He, H.; Kruk, M.; Huang, L.; Kowalewski, T.; Matyjaszewski, K. *ACS Nano* **2012**, *6*, 6208.

(53) Bates, F. S.; Fredrickson, G. H. *Phys. Today* **1999**, *52*, 32.

(54) Hu, M.; Xia, Y.; McKenna, G. B.; Kornfield, J. A.; Grubbs, R. H. *Macromolecules* **2011**, *44*, 6935.

(55) Vlassopoulos, D.; Fytas, G.; Loppinet, B.; Isel, F.; Lutz, P.; Benoit, H. *Macromolecules* **2000**, *33*, 5960.

(56) Runge, M. B.; Bowden, N. B. *J. Am. Chem. Soc.* **2007**, *129*, 10551.

(57) Runge, M. B.; Dutta, S.; Bowden, N. B. *Macromolecules* **2006**, *39*, 498.

(58) Rzayev, J. *Macromolecules* **2009**, *42*, 2135.

(59) Xia, Y.; Olsen, B. D.; Kornfield, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 18525.

(60) Bolton, J.; Bailey, T. S.; Rzayev, J. *Nano Lett.* **2011**, *11*, 998.