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Well-Defined Organic Nanotubes from Multicomponent Bottlebrush Copolymers

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Abstract: Bottlebrush copolymers are comblike macromolecules with densely grafted polymeric branches that adopt a cylindrical shape in solutions. We demonstrate a new method for the preparation of organic nanotubes by single molecule templating of core−shell bottlebrush copolymers. Multicomponent bottlebrush copolymers with well-defined structural parameters are synthesized by a combination of different living polymerization methods. Tubular structures can be prepared by cross-linking the shell layer and selectively etching out the core. The shape and size of original bottlebrush macromolecules are preserved during these transformations, which leads to the formation of well-defined organic nanotubes. The length and diameter of nanotubes are dictated by the length of the backbones and branches of the polymeric precursors, respectively. Water-soluble nanotubes with a hydrophobic interior can be prepared from bottlebrush copolymers with triblock copolymer branches. Herein, we outline molecular design strategies to fabricate nanotubes with controlled lengths, open pores, and different solubility characteristics.

Introduction

Organic tubular structures of nanometer dimensions have become a focus of many research efforts inspired by the functional utility of similar assemblies in biological systems.[1−3] A variety of synthetic nanotubes have been prepared for potential use in selective ion transport, biosensor applications, chemical catalysis, nanocomposite synthesis, etc. Structurally well-defined nanotubes can also be considered as building blocks for the preparation of higher order nanostructured materials and nanodevices. Synthetic efforts to construct organic nanotubes have mainly focused on the self-assembly of smaller building blocks, such as cyclic peptides, dendrons, or organic macrocycles.[4−8] In these approaches, hydrogen bonding, π-stacking, and other interactions between small structural units lead to their organization into tubular stacks, albeit of uncontrolled lengths. Other methods of generating nanotubes are based on helical polymer precursors[9−11] and on cylindrical microstructures obtained by block copolymer self-assembly.[12−14] These methods have been used to prepare a variety of fascinating tubular structures that continue to enrich our understanding of supramolecular organization and provide inspiration for future endeavors in the field. However, the lack of length control, which often results in the formation of infinitely long or polydisperse tubular assemblies, unavoidably limits the scope and potential utility of organic nanotubes. In addition, tubular structures formed from cyclic or helical precursors are usually limited to maximum pore sizes of 1−2 nm. Access to dimensionally and functionally well-controlled nanotubes will significantly broaden their use in biomedical applications and pave exciting new avenues in nanotechnology. In this report, we demonstrate a new method for the preparation of organic nanotubes with controlled lengths and functionalities by templating individual bottlebrush macromolecules that adopt cylindrical conformations in solution.

Bottlebrush copolymers are a class of shape-persistent macromolecules that possess a highly branched comblike architecture. Steric repulsion between densely grafted polymeric branches causes the backbone to adopt an extended conformation.[15−18] When polymeric side chains are much shorter than the backbone, these macromolecules take on cylindrical shape[19]

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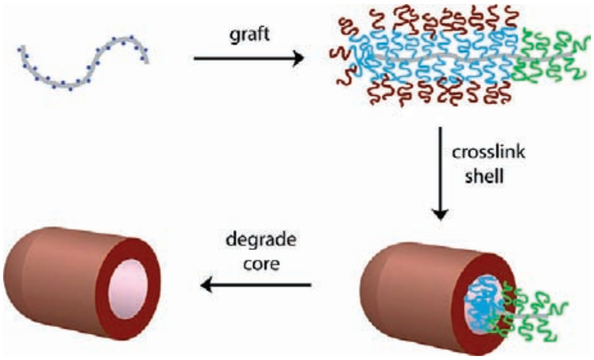
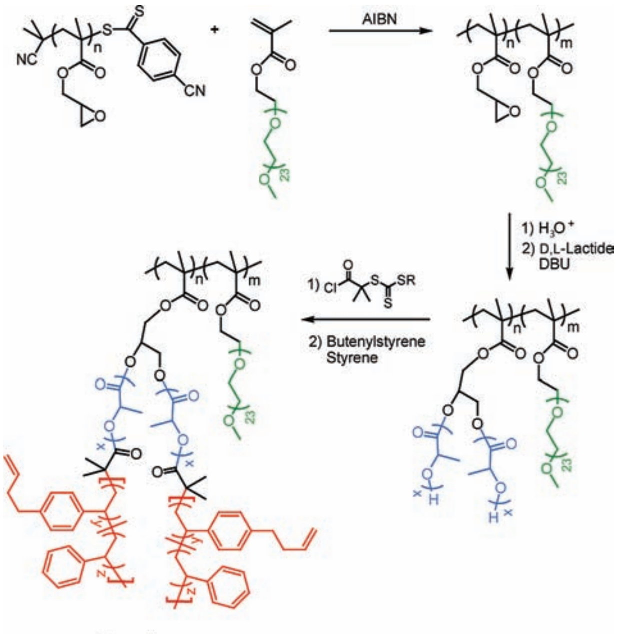


Figure 1. Synthetic pathway to well-defined organic nanotubes from multicomponent bottlebrush copolymers.

that can be visualized by atomic force microscopy (AFM).[20] A variety of single-component and core−shell bottlebrush copolymers have been synthesized by grafting-from and grafting-through methods.[19,21−25] Previous attempts to prepare porous objects from bottlebrush copolymers resulted only in spherical nanostructures and the shape of precursor molecules could not be maintained.[26]

The proposed synthetic pathway to well-defined organic nanotubes is illustrated in Figure 1. A diblock copolymer bottlebrush is synthesized first, where one of the blocks contains copolymer branches with inner (blue) and outer (red) segments. The other block serves as a sacrificial “stopper” (green) and contains branches with removable segments only. In the subsequent steps, the outer segments are cross-linked while the inner degraded, providing a tubular structure. The “stoppers” are used to prevent the outer segments from curving around the edges to form closed shells. In this approach, the length of the tube is determined by the size of the backbone and the pore size is dictated by the length of the inner branch segments. Both of these structural parameters can be controlled to the highest degree during synthesis of polymeric precursors. In addition, functional composition of the shell determines solubility characteristics of the prepared nanotubes. Herein, we outline molecular design strategies for the preparation of well-defined organic nanotubes from tailor-made multicomponent bottlebrush copolymers. The new method allows for the exact structural and functional control of the prepared nanoobjects in unprecedented fashion.

Results and Discussion



Copolymer	n	m	x	y	z
1	225	31	15	26	32
2	526	26	26	30	36
3	526	26	26	18	23

Figure 2. Synthesis of multicomponent bottlebrush copolymers.

Polymer Synthesis. Multicomponent bottlebrush copolymers were synthesized by a combination of living radical and ring-opening polymerization techniques (Figure 2). The targeted structures had polylactide (PLA) as a degradable core, polyethylene oxide (PEO) brush as a “stopper” on one side, and poly(4-(3-butenyl)styrene) as a cross-linkable shell. Controlling the length of prepared tubular structures is central to our synthetic methodology. Therefore, we utilized a grafting-from[27,28] approach that allows for the preparation of a well-defined backbone. Poly(glycidyl methacrylate) (PGM) backbones with extremely narrow molecular weight distributions ($M_w/M_n < 1.1$) were prepared by reversible addition−fragmentation chain transfer (RAFT) polymerization[29] mediated by 2-cyanoprop-2-yl 4-cyanodithiobenzoate (CPD).[30] The “stopper” was added by a grafting-through[31] method with PEO methacrylate (PEO-MA, $M_n = 1$ kg/mol) as a macromonomer. Well-defined block copolymers with narrow molecular weight distributions were obtained (Supporting Information, Table S1). Poly(GM-*b*-PEOMA) block copolymers, despite larger size, eluted slower than the precursor PGM during size exclusion chromatography (SEC) analysis (Supporting Information, Figure S1). This behavior was attributed to the interaction of PEO block with the SEC columns. Pendant epoxide groups of PGM were then hydrolyzed to provide diols, which served as initiators for subsequent polymerization of racemic lactide.[32] By NMR end group analysis, we compared the intensity of the PLA methine

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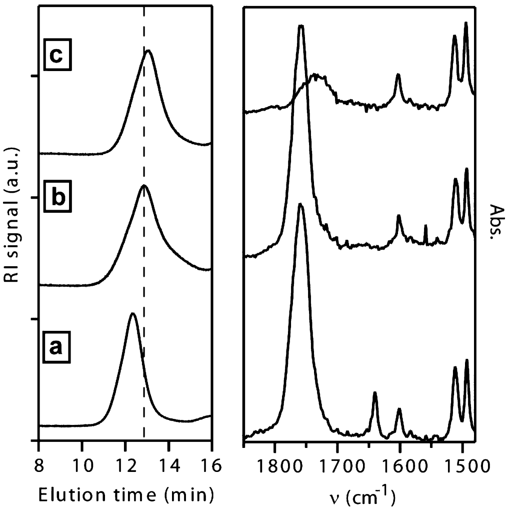

Figure 3. SEC (left) and IR (right) characterization of bottlebrush copolymer **1** as synthesized (a), after shell cross-linking (b), and after PLA degradation (c).

end group signal at 4.35 ppm to the PEO methoxy end group signal at 3.38 ppm (Supporting Information, Figure S2). The obtained ratio was approximately double of that calculated for PGM epoxy groups of the precursor and PEO end groups. These results suggested that the initiation efficiency for the polymerization of lactide was near quantitative (>90%), which led to the formation of extremely dense polylactide brushes (~2 branches per repeat unit). The hydroxyl end groups of PLA side chains were then modified to introduce trithiocarbonate functionalities,[33] and the shell was grown by RAFT copolymerization of styrene and 4-(3-butenyl)styrene. The latter was reported to polymerize through the styrenic double bond exclusively,[34,35] thus leaving pendant olefinic groups available for further reactions. SEC analysis of polymers after each step evidenced efficient reinitiation and formation of well-defined copolymers (Supporting Information, Figure S1). Structural parameters for the synthesized bottlebrush copolymers are provided in Figure 2 (see also Supporting Information, Table S1). Accurate estimation of molecular weight distributions of the bottlebrush copolymers was complicated by the presence of non-size-exclusion effects during SEC analysis (in particular for those with long backbones).[36] When measured relative to polystyrene standards, polydispersity indexes were in the range of 1.4−2.0, while those measured by light scattering detector were close to 1.1.

Intramolecular Cross-Linking. The synthesized multicomponent bottlebrush copolymers were then treated with Grubbs generation I catalyst under dilute conditions in order to cross-link the shell layer via cross-metathesis of olefinic groups. The successful outcome of this reaction was confirmed by IR spectroscopy, where peaks at 1640 and 910 cm^{-1} corresponding to vinyl group vibrations completely disappeared, while a new peak emerged at 965 cm^{-1}, corresponding to a trans double bond vibration (Figure 3 and Supporting Information, Figure S3). These results indicate that almost all of the vinyl groups have reacted and, therefore, a shell with very high cross-linking density was obtained. NMR signals of cross-linked bottlebrushes dispersed in chloroform were very broad suggesting that a rigid structure was formed. In addition, SEC peaks of bottlebrush copolymers shifted to longer elution times after cross-linking, which was attributed to the formation of a relatively smaller, more compact structure (Figure 3).[37] Differential scanning calorimetry characterization of bottlebrush copolymers also suggested the formation of rigid macromolecules upon intramolecular cross-linking. Original copolymers exhibited only one glass transition at 60 °C (Supporting Information, Figure S4). The close proximity of glass transition temperatures (T_g) of PLA brushes (54 °C)[38] and a copolymer of styrene and 4-(3-butenyl)styrene constituting the shell (59 °C)[39] made it impossible to identify two separate transitions. Upon intramolecular cross-linking of the bottlebrush copolymers, no glass transition could be detected up to 220 °C, indicating the formation of rigid polymer structures.

AFM analysis of the bottlebrush copolymers before and after cross-linking confirmed that the cylindrical shape of the molecules was preserved (Figure 4). From cross-sectional profiles taken across the molecules adsorbed on mica, it is evident that upon shell cross-linking the height of molecular undulations increased from 4.5 to 8.5 nm for copolymer **1**, and from 5 to 11 nm for copolymer **2**. This is consistent with previous observations that bottlebrush copolymers spread out when adsorbed onto a mica surface.[20] After cross-linking, such spreading is not possible and, therefore, the height of undulations increases. Larger cross-sectional distances obtained for copolymer **2** is consistent with the fact that it contains longer branches than copolymer **1**.

Nanotube Synthesis. Bottlebrush copolymers with cross-linked shells were then treated in acidic dioxane in order to etch out PLA chains from the core. Complete removal of PLA was confirmed by the disappearance of the characteristic PLA carbonyl stretch peak (1759 cm^{-1}) in the IR spectrum (Figure 3). A small new peak appeared at 1720 cm^{-1} after PLA degradation, which was attributed to the carboxylic acid group of the last hydrolyzed PLA unit that remained attached to the shell. Most importantly, after PLA core removal (~20% weight loss), the SEC elution time of the polymer remained almost the same, indicating that the overall size of the structure was preserved (Figure 3c). When PLA etching was carried out without prior cross-linking, complete polymer degradation to small molecular weight side chains was observed.

The formation of tubular structures was characterized by transmission electron microscopy (TEM). Clearly distinguishable were small channels running through almost every cylindrical nanoparticle (Figure 5). The contrast in TEM images, conducted without prior staining, was attributed to the presence of residual Grubbs catalyst in the shell layer. Consistent with the SEC analysis, the size of the prepared nanotubes seemed to agree quite well with the size of the original bottlebrush copolymer precursors, visualized by AFM. The cylindrical shape of the precursor copolymers was also preserved after their transforma-

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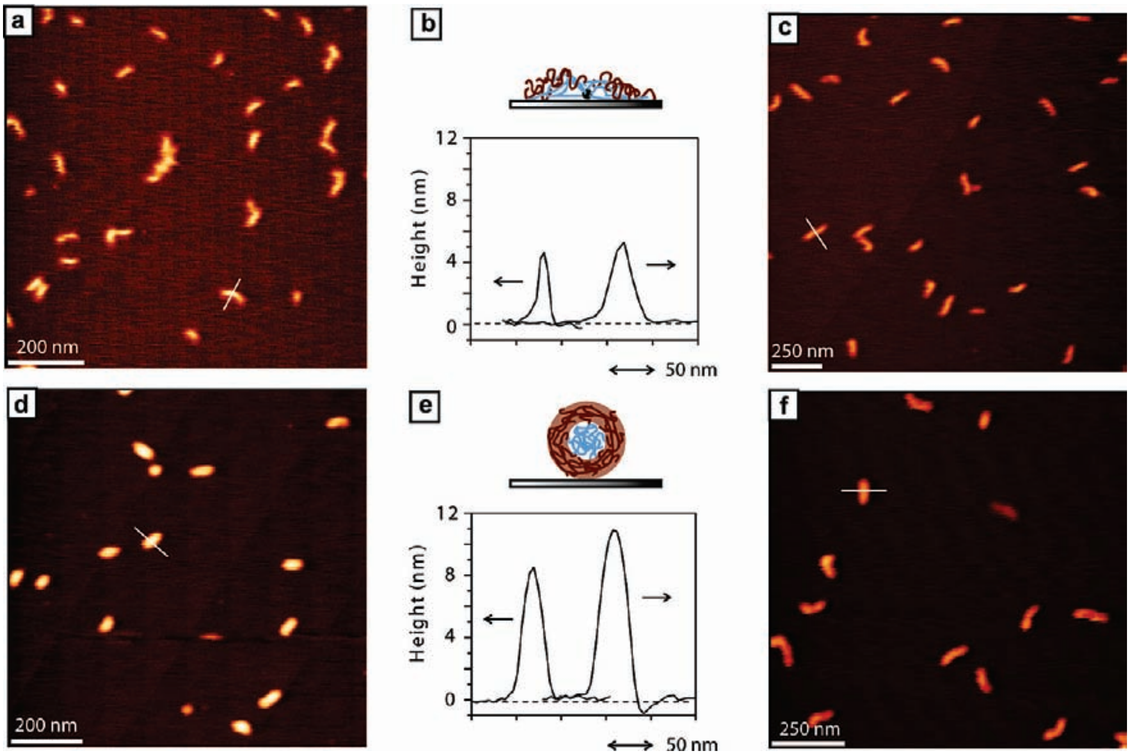

Figure 4. AFM characterization of bottlebrush copolymers as synthesized (a−c) and after shell cross-linking (d−f). (a) AFM height image of a pristine copolymer **1** adsorbed on a mica surface; (b) cross-sectional profiles for pristine copolymers **1** and **2** obtained from the corresponding AFM data; (c) AFM height image of a pristine copolymer **2** adsorbed on a mica surface; (d) AFM height image of a shell-cross-linked copolymer **1**; (e) cross-sectional profiles for cross-linked copolymers **1** and **2**; (f) AFM height image of a shell-cross-linked copolymer **2**.

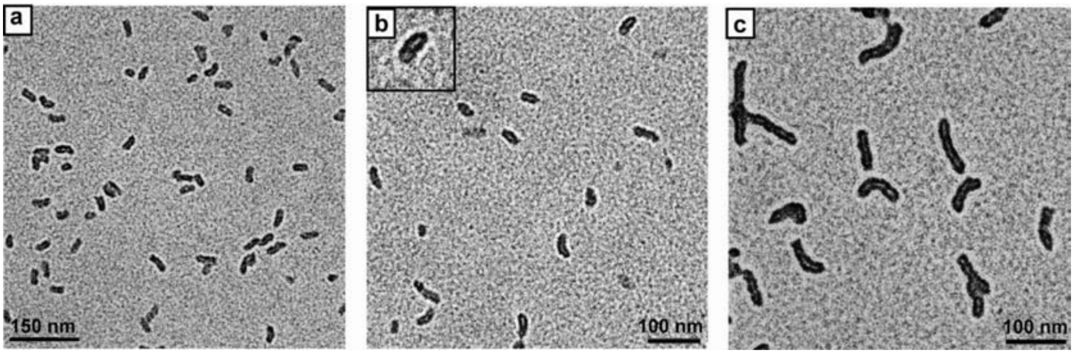

Figure 5. TEM characterization of organic nanotubes prepared from copolymer **1** (a, b) and copolymer **2** (c).

tion into nanotubes. Copolymer **1**, which contained 225 repeat units in the backbone, provided 36 ± 6 nm long nanotubes; while copolymer **2**, with 526 backbone units, resulted in longer nanotubes with $L = 86 \pm 7$ nm. The lengths and corresponding standard deviations of the nanotubes were obtained by analyzing 100 nanoparticles from TEM images. The overall length of the nanotubes was consistently close to but smaller than the length of a fully extended zigzag backbone of the precursor (56 nm for **1**; 131 nm for **2**). Polydispersity indexes of nanotubes obtained from SEC with a light scattering detector were lower than 1.1. The narrow size distribution of the prepared nanotubes was a reflection of low polydispersities of the bottlebrush copolymer backbones. The synthesized organic nanotubes contained pores of 3−5 nm in diameter, and shell thicknesses of 5−7 nm.

The size of the shell layer was crucial to retaining the cylindrical shape of original macromolecules. For example, copolymer **3**, which contained shorter shell branches, transformed into spherical capsules upon cross-linking (Supporting Information, Figure S5). The obtained spherical nanoparticles were 150−200 nm in diameter, much larger than the size of original bottlebrush copolymer precursors. Such large structures might result from the cleavage of some branches from the backbone under the stress applied by shell cross-linking. At the same time, a thinner shell cannot maintain structural integrity of the cylindrical nanostructures and swells to larger size particles. Spontaneous cleavage of covalent bonds in large bottlebrush copolymers when adsorbed onto a surface has been previously documented.[40] We also observed a coexistence of large spherical capsules and nanotubes for some bottlebrush copolymers with intermediate shell thicknesses.

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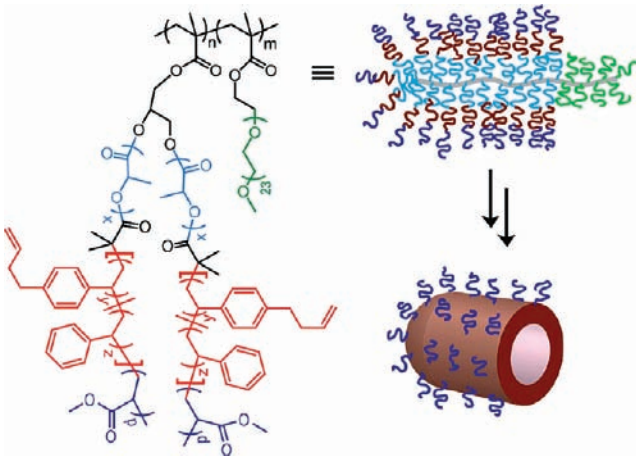

Figure 6. Molecular design and the corresponding bottlebrush copolymer used for the synthesis of core–shell nanotubes.

Nanotubes synthesized from copolymers **1** and **2** were easily dispersible in common organic solvents. The solubility of these nanostructures in organic solvents depends on many factors, including the strength of polymer–solvent vs polymer–polymer interactions. We also believe that the presence of loose chains at the nanotube surface contributes to their good solubility characteristics. From TEM analysis, some aggregation was observed for longer tubes, which is to be expected due to their large size and rigid structure. Also, if the prepared nanotubes are completely dried, they cannot be redispersed in any solvent. However, they can be stored in solutions for prolonged periods of time without any noticeable coagulation.

Water-Soluble Nanotubes. The solubility of organic nanotubes in aqueous media is important for their utilization in biomedical applications. We extended our new methodology to prepare amphiphilic nanotubes that contained hydrophobic interior and hydrophilic exterior and thus were easily dispersible in water. Such structures were synthesized from bottlebrush copolymers that contained branches with three segments: PLA core, cross-linkable shell layer, and an additional outmost layer to independently control the exterior surface chemistry of the nanotubes (Figure 6).

Bottlebrush copolymer **4** was synthesized from **1** by RAFT polymerization grafting of poly(methyl acrylate) (PMA) chains with 136 repeat units per branch. While PMA, used as the third layer, is not water-soluble itself, it can undergo hydrolysis under the conditions of PLA etching and provide hydrophilic poly(acrylic acid) coating. Copolymer **4** was cross-linked and etched under conditions similar to those used for **1**. AFM and TEM analyses of copolymer **4** before and after cross-linking showed that the shape of the original molecules was preserved and nanostructures with average length of 32 ± 6 nm were obtained (Figure 7). The aspect ratio of the prepared nanoobjects was noticeably smaller than for copolymer **1**, consistent with much longer side branches on copolymer **4**. Upon hydrolysis of the cross-linked nanostructures, PLA carbonyl stretch peak at 1759 cm^{-1} completely disappeared from the IR spectrum, indicating complete removal of the core. Concurrently, a new peak at 1717 cm^{-1} emerged and was assigned to the carbonyl stretch of carboxylic acid groups, produced by hydrolysis of methyl esters of the PMA brushes (Supporting Information, Figure S6). Quantitative characterization of the degree of hydrolysis was not possible due to the overlap between carbonyl stretch peaks of the original methyl esters of PMA and carbonyl stretch peak of hydrogen-bonded carboxylic acid. The prepared nanotubes were easily dispersed in methanol and water and were purified by dialysis against deionized water. TEM samples of the nanotubes were prepared by dip-coating directly from water. As shown in Figure 7, nanotubes appear to be well dispersed with almost no aggregation observed (see also Supporting Information, Figure S7). Thin channels could be identified inside most of the cylindrical nanoobjects. These nanostructures thus represent the first example of core–shell organic nanotubes with hydrophilic exterior and hydrophobic pores prepared by rational design strategies.

PEO "stoppers" were incorporated into the bottlebrush copolymer precursors in order to create nanotubes with one open end. For some, but not all, nanotubes, in particular for those prepared from copolymers **1** and **4**, two different ends could be distinguished by TEM, perhaps suggesting one open and one closed end (Figures 5b and 7c). While more detailed analysis and improved design of "stoppers" is necessary, this strategy represents a promising new way of rational fabrication of tubular structures with open pores.

Summary

We have demonstrated a new method for the fabrication organic nanotubes with controlled lengths and solubility characteristics. The synthetic strategy utilizes molecular engineering of multicomponent bottlebrush copolymers and single-molecule templating to produce well-defined nanostructures. Polymers were synthesized by a combination of RAFT polymerization and ring-opening polymerization. Shell cross-linking was achieved by cross-metathesis of pendant olefins of poly(4-(3-butenyl)-styrene), and a PLA core was selectively removed by acidic hydrolysis. The length and size distribution of the prepared nanotubes seemed to correlate with the length and polydispersity

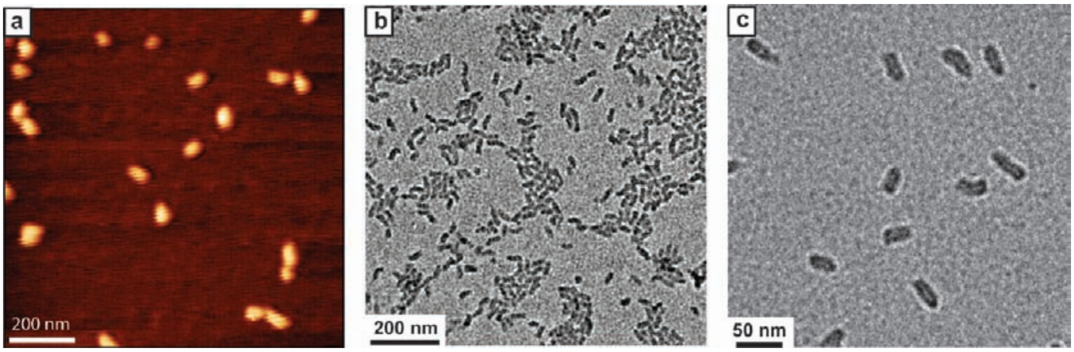

Figure 7. AFM and TEM characterization of core–shell nanotube synthesis from copolymer **4**: (a) AFM height image of a pristine copolymer adsorbed on a mica surface (*z*-scale = 10 nm), (b) TEM image of shell-cross-linked bottlebrush copolymers, and (c) TEM image of water-soluble nanotubes.

of the bottlebrush precursor's backbone. Rational design strategies can be utilized to prepare nanotubes with independently regulated interior and exterior surface chemistries. Water-soluble nanotubes were prepared from bottlebrush copolymers containing triblock copolymer branches. This new methodology will allow for the preparation of a variety of tubular structures with precise structural and functional control and enable their utilization in a range of applications as drug delivery vehicles and organic nanostructured building blocks.

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Supporting Information Available: Experimental details, Table S1, and Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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