

## CORE-SHELL CYLINDRICAL POLYMER BRUSHES WITH SILICA NANOWIRE CORE

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### Introduction

Cylindrical polymer brushes (CPB's) or 'bottlebrush' polymers, which possess linear side chains or dendritic side groups densely grafted from a linear main chain, have attracted considerable experimental and theoretical interest over the past decade, owing to the possibility of forming extended chain conformations and their peculiar solution and bulk properties.<sup>[1-3]</sup> Due to the modern progress in living/controlled polymerizations well-defined core-shell CPB's with block copolymer side chains, as one of the advanced CPB architectures have gained growing interest.<sup>[4-8]</sup> When the diblock copolymer side chains include block segment combinations of soft-hard, hydrophilic-hydrophobic and crystalline-amorphous, the core-shell CPB's resemble intramolecular phase-separated cylindrical micelles. Schmidt et al.<sup>[4]</sup> succeeded in the synthesis of CPB's with a hydrophilic poly(2-vinylpyridine) core and a hydrophobic polystyrene (PS) shell via the radical polymerization of P2VP-*b*-PS macromonomers. Matyjaszewski et al.<sup>[5]</sup> reported the synthesis of CPB's with a crystallizable poly( $\epsilon$ -caprolactone) (PCL) core and an amorphous poly(*n*-butyl acrylate) (PnBA) shell using a combination of ATRP and ring-opening polymerization. Recently, we have synthesized various core-shell CPB's<sup>[1, 6-7]</sup> that can be divided into two basic groups, acrylic acid (AA)- and trimethylsilyl (TMS)- based brushes, according to the composition and function of the core as template to prepare one-dimensional (1D) inorganic nanostructures. The preparation of the AA-based amphiphilic core-shell CPB's and the fabrication of semiconductor and magnetic nanocylinders have been already reported by us.<sup>[9-10]</sup> In this contribution, we present the synthesis of a TMS-based core-shell CPB,  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$ , which has a crosslinked silsesquioxane network in the core. It was successfully used for the templated formation of silica nanowires on mica.

### Experimental

**Materials.** All reagents were of analytical grade and used without further purification.

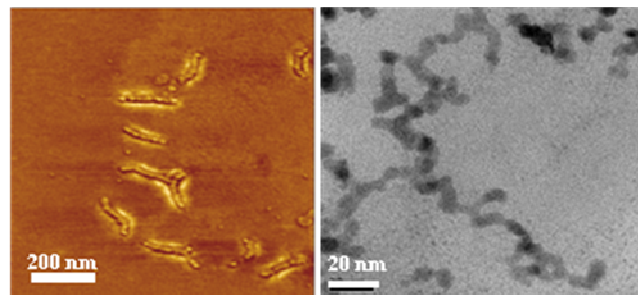
**Instrumentation.** The absolute molecular weight of the macroinitiator backbone poly(2-bromoisobutyryloxyethyl methacrylate) (PBIEM) was obtained by the combination of GPC and static light scattering. The DP of the side chain was calculated from the monomer conversion of polymerizations obtained by <sup>1</sup>H NMR.

Atomic force microscopy (AFM) images were recorded on mica using a Digital Instruments Dimension 3100 microscope operated in Tapping Mode. Transmission electron microscopy (TEM) images were taken on a LEO 922 OMEGA electron microscope operated at 200 kV using carbon coated copper grids. Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA 851. The measurements were performed under airflow of 50 ml/min with heating from 30 °C to 700 °C (rate: 10 °C/min). The Fourier Transform Infrared Spectroscopy (FTIR) measurements were undertaken on a Bruker EQUINOX 55/S infrared spectrometer.

**Synthesis of hybrid CPB  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  and the fabrication of silica nanowires.** The sequential ATRP of 3-(trimethoxysilyl)propyl acrylate (TMSPA) and oligo(ethylene glycol) methacrylate (OEGMA) from the macroinitiator backbone was conducted in benzene at 80 °C and the reaction mixtures were purified under N<sub>2</sub> via ultrafiltration in benzene as well. For the condensation of the trimethoxysilyl (TMS) moieties in the brush core, 445 mg of the core-shell CPB  $[\text{TMSPA}_{20}\text{-b-OEGMA}_{57}]_{3200}$  (containing 0.278 mmol of TMS groups) in 20 ml of benzene, was dialyzed against methanol. Then the brush solution was diluted to 200 ml, and 20 ml of aqueous ammonia solution (12 wt %) was added under stirring. After 24 hours, the excess ammonia and water were removed by dialysis to obtain  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  core-shell hybrid CPB (with crosslinked silsesquioxane network in the core) solution in methanol. For the preparation of silica nanowires on mica, the hybrid brushes were dip-coated onto mica, which was kept at 700 °C for 30 min in the presence of air.

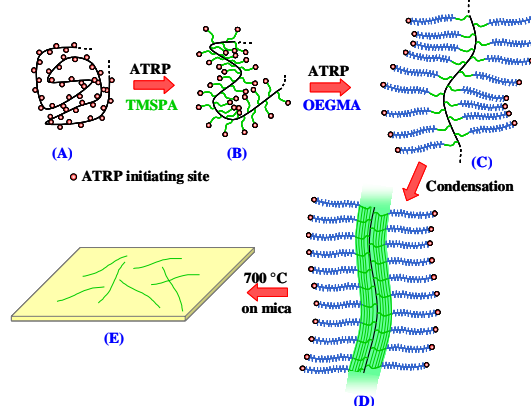
### Results and Discussion

**Synthesis of CdS and CdSe hybrid nanowires.** The AA-based amphiphilic core-shell CPB's possess a PAA core and a hydrophobic shell, like PS or PnBA, which can be directly visualized by AFM.<sup>[7]</sup> The PAA core renders them the ability to load and align inorganic nanoparticles one-dimensionally within the brush. For instance, amphiphilic brushes were successfully used as templates to fabricate CdS<sup>[9]</sup> and CdSe<sup>[11]</sup> nanocylinders, as shown in the AFM and TEM images in Figure 1. The hydrophilic core imposes strict control on the nanocylinder dimension and the hydrophobic shell protects them from the agglomeration and precipitation in solution.

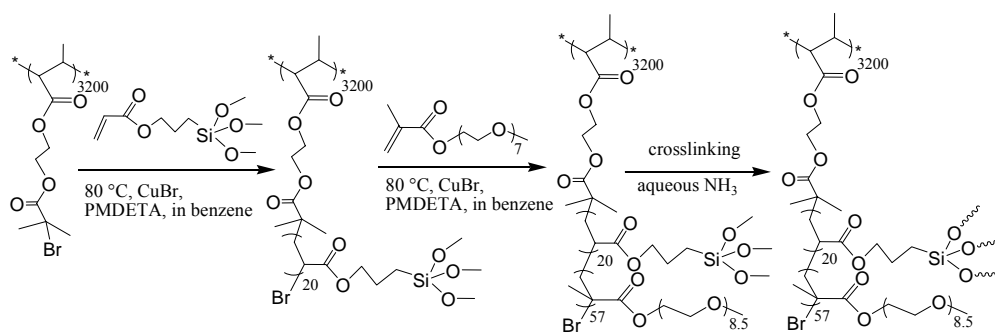


**Figure 1.** Hybrid of the core-shell CPB,  $[(\text{AA})_{25}\text{-b-(nBA)}_{61}]_{1500}$ , and CdSe nanoparticles. a) AFM Tapping Mode phase image, dip-coated from dilute CH<sub>3</sub>OH/CHCl<sub>3</sub>(1/1) solution on mica (range: 25°). b) Non-stained TEM image.

**Synthesis of the hybrid brush  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  and SiO<sub>2</sub> nanowires.** The schematic synthesis route is illustrated and outlined in Figures 2 and 3. Due to the moisture sensitivity of the TMS groups in monomer TMSPA, sequential ATRP's of TMSPA and OEGMA initiated by the pendant  $\alpha$ -bromoester groups along the macroinitiator backbone were carried out in benzene. As a consequence, the functional TMS moieties were arranged into a 1D manner originating from the cylindrical shape of the brush. The linear core was then frozen by the crosslinked silsesquioxane network via the condensation of TMS groups, rendering the rigid  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  core-shell hybrid CPB's. We can take advantage of the fixed linear core of the hybrid CPB for the formation of silica nanowires and the shell for suppressing the intermolecular coupling reactions. At the end, uniform silica nanowires were obtained by the simultaneous removal of the polymer template via pyrolysis at 700 °C. In our synthesis, the brush backbone has a DP of 3,200 and each copolymer side chain consists of 20 TMSPA units in the core block and 57 OEGMA units in the shell block on average.

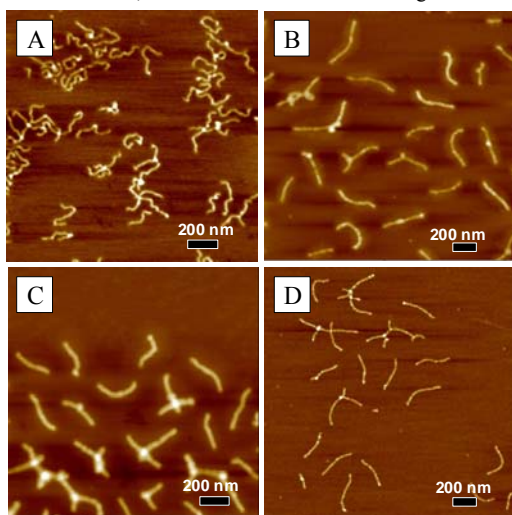


**Figure 2.** Schematic illustration for the synthesis of  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  core-shell hybrid CPB's and the templated formation of SiO<sub>2</sub> nanowires on mica: a) macroinitiator backbone with DP=3200; b)  $[\text{TMSPA}_{20}]_{3200}$  CPB with PTMSPA homopolymer side chains; c)  $[\text{TMSPA}_{20}\text{-b-OEGMA}_{57}]_{3200}$  core-shell CPB with PTMSPA-*b*-OEGMA diblock copolymer side chains; d)  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  core-shell hybrid CPB; e) SiO<sub>2</sub> nanowires prepared on mica via pyrolysis at 700 °C.



**Figure 3.** Synthetic route to the  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  hybrid. a) PBIEM macroinitiator; b)  $[\text{TMSPA}_{20}]_{3200}$  CPB; c)  $[\text{TMSPA}_{20}\text{-b-OEGMA}_{57}]_{3200}$  core-shell CPB; d)  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  hybrid.

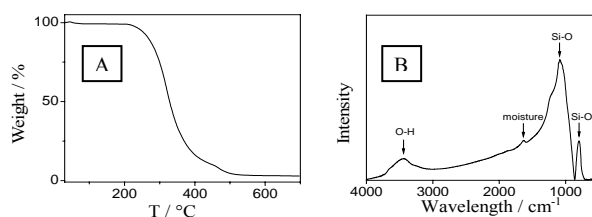
**Visualization by AFM.** Molecular visualization of the CPB's and  $\text{SiO}_2$  nanowires on mica by AFM was undertaken to verify the success of the synthetic strategy for each step in the process. In all cases, AFM revealed individual wormlike structures lying flat on the substrate. The typical AFM height images of the  $[\text{TMSPA}_{20}]_{3200}$  and  $[\text{TMSPA}_{20}\text{-b-OEGMA}_{57}]_{3200}$  CPB's on mica are shown in Figure 4a and 4b, respectively. It clearly illustrates that the latter are more stretched and less curved than the former, due to the introduction of a long and bulky POEGMA block, which enhanced the repulsions among the side chains. In order to make rigid rod-like cylinders, crosslinking was then carried out via the condensation of the TMS groups in the core region to form  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  core-shell hybrid CPB's which possess a silsesquioxane crosslinked network in the core. (Figure 4c) The function of the crosslinked silsesquioxane network is to fix and stiffen the well-designed cylindrical shape, and generate the uniform template of the silica nanowires, which was simply achieved by the pyrolysis of the hybrid brush on mica at  $700\text{ }^\circ\text{C}$ . Figure 4d shows the AFM height image of the obtained silica nanowires on mica, which were uniform in both length and diameter.



**Figure 4.** AFM height images of a)  $[\text{TMSPA}_{20}]_{3200}$  CPB's (height scale: 4nm), b)  $[\text{TMSPA}_{20}\text{-b-OEGMA}_{57}]_{3200}$  core-shell CPB's (height scale: 15nm), c)  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  core-shell hybrid CPB's (height scale: 20nm), and d)  $\text{SiO}_2$  nanowires on mica (height scale: 4nm).

**Silica nanowires.** The silicon content in the hybrid CPB was determined by TGA measurement of the bulk material of the hybrid brush in the presence of air. The weight loss, as pictured in Figure 5a, keeps constant above  $530\text{ }^\circ\text{C}$ , leaving a residue of 3.53%, very close to the theoretical calculated  $\text{SiO}_2$  amount (3.95%). This implies that above  $530\text{ }^\circ\text{C}$  all polymers were completely decomposed. Furthermore, the residue was examined by FTIR. Only the characteristic vibration of the O-H bond in the Si-O-H and Si-O bond in the Si-O-Si groups were observed, as shown in Figure 5b. The disappearance of the

C-H vibration between  $2800$  and  $3000\text{ cm}^{-1}$  confirms the complete removal of the methylene group directly attached to the Si atom in the hybrid brush, which converts the silsesquioxane network in the core to pure silica.



**Figure 5.** a) TGA curve of bulk  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  core-shell hybrid CPB. b) FTIR spectrum of the residue of the hybrid brush after TGA.

## Conclusions

Well-defined  $[(\text{SiO}_{1.5}\text{-PA})_{20}\text{-b-OEGMA}_{57}]_{3200}$  hybrid CPB's with a silsesquioxane crosslinked network in the PTMSPA core and a POEGMA shell were successfully synthesized. The bulky POEGMA block and the frozen core force the CPB's to become rigid. The hybrid brushes were subsequently employed as template to fabricate uniform silica nanowires ( $L = 276\text{ nm}$ ,  $\text{PDI} = 1.06$ ), on mica via pyrolysis at  $700\text{ }^\circ\text{C}$ .

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