

# MAGNETIC / SEMICONDUCTING NANOCYLINDERS VIA POLYCHELATES OF CYLINDRICAL CORE-SHELL POLYMER BRUSHES

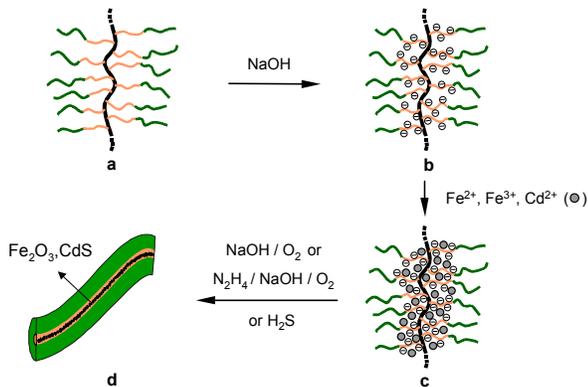
Mingfu Zhang, Markus Drechsler and Axel H. E. Müller

Makromolekulare Chemie II  
Universität Bayreuth  
D-95440 Bayreuth, Germany

## Introduction

There has been growing interest in the synthesis of inorganic nanoparticles using polymer templates, since the obtained hybrid materials integrate the promising properties of both components. Various polymer templates,<sup>1,2</sup> such as porous polymers, block copolymer films, and polymeric micelles have been used. In particular, single molecule polymer templates attracted more and more attention recently,<sup>3</sup> since isolated nanocomposites based on single molecules can be obtained which have many potential applications. However, in most reported cases nanoparticles are fabricated around single molecular templates thus the nanoparticles are naked and may lack stability. In this paper we report the use of a peculiar single polymer molecule template, a cylindrical polymer brush with poly(acrylic acid) (PAA) core and poly(*n*-butyl acrylate) (*Pn*BA) shell, in fabricating magnetic or semiconducting nanoparticles within the PAA core of the polymer brush (Scheme 1). Besides the size control, the stabilization and directed distribution of the nanoparticles can be achieved as well.

The polymer brush, which was used as a template, has a backbone of poly(2-hydroxyethyl methacrylate) with degree of polymerization (DP) of 1500 and one block copolymer (25 AA units inside and 61 *n*BA units outside) side chain per backbone monomer unit, defined as [AA<sub>25</sub>-*n*BA<sub>61</sub>]<sub>1500</sub>.<sup>4</sup>



**Scheme 1.** Synthetic route to magnetic or semiconducting nanocylinders: (a) polymer brush; (b) neutralized polymer brush with poly(sodium acrylate) core ( $\text{Na}^+$  is not shown); (c) polychelate of the polymer brush and metal ion; and (d) hybrid magnetic/semiconducting nanocylinder.

## Experimental

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

**Instrumentation.** The absolute molecular weight of the polymer backbone was obtained by membrane osmometry. The DP of the side chain was calculated from the monomer conversion of polymerizations obtained by gas chromatography. The detailed polymer synthesis and characterization have been reported previously.<sup>4</sup>

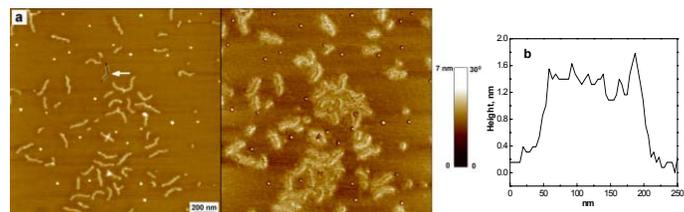
Scanning force microscopy (SFM) images were recorded on a Digital Instruments Dimension 3100 microscope operated in Tapping Mode on mica. Transmission electron microscopy (TEM) images were taken on a LEO 922 OMEGA electron microscope operated at 200 kV using carbon or Formvar/carbon coated copper grids. Electron diffraction (ED) measurements were carried out on a Philips CM 20 TEM operated at 200 kV. Energy dispersive X-ray (EDX) analysis was performed on a LEO 1530 field emission scanning electron microscope using X-ray detector. UV/vis spectra were recorded on a Perkin-Elmer Lambda 15 UV/vis spectrophotometer.

**Synthesis Of Magnetic Nanocylinders.** 403 mg of the polymer brush, [AA<sub>25</sub>-*n*BA<sub>61</sub>]<sub>1500</sub> (containing 1.06 mmol of AA), was dissolved in a mixture of methanol and chloroform (250 mL, *v/v* = 1/1). Then NaOH (0.95 mmol, in 7.4 mL methanol containing 2 vol.% water) solution was added to neutralize the core of the polymer brush. Afterwards, FeCl<sub>3</sub> (0.35 mmol, in 1.8 mL methanol) was added. To remove the uncoordinated Fe<sup>3+</sup> ions, ultracentrifugation and precipitation (via concentration) were carried out to separate the Fe<sup>3+</sup>-loaded polymer brush from solution. The precipitate was dissolved in mixture of methanol and chloroform (300 mL, *v/v* = 1/1) and the obtained solution was degassed and put under N<sub>2</sub>. Addition of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (N<sub>2</sub>H<sub>4</sub>/FeCl<sub>3</sub> = 20) resulted in a color change from brown to yellowish-green, indicating the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>. Subsequent addition of NaOH (0.13 M in methanol containing 2 vol.% water, NaOH/FeCl<sub>3</sub>=10) caused the color changing from yellowish-green to olive-green, indicating the formation of Fe(OH)<sub>2</sub>. Finally, the reaction mixture was bubbled with air. The color of the mixture turned brown instantly, due to the formation of iron oxide nanoparticles. When FeCl<sub>2</sub> was used, the reduction step by N<sub>2</sub>H<sub>4</sub> was skipped.

**Synthesis Of Semiconducting Nanocylinders.** 29.7 mg of the polymer brush, [AA<sub>25</sub>-*n*BA<sub>61</sub>]<sub>1500</sub> (containing 0.077 mmol of AA), was dissolved in 20 mL of methanol/chloroform mixture (*v/v* = 1/1). Then 75  $\mu\text{L}$  of 1.0 M NaOH aqueous solution was added to neutralize the polymer core. Afterwards, 0.042 mmol of CdAc<sub>2</sub>·2H<sub>2</sub>O (0.133 M solution in methanol) was added. To remove the uncoordinated Cd<sup>2+</sup> ions, precipitation was carried out by addition of water. The precipitate was then dispersed in 30 mL of methanol/chloroform mixture (*v/v* = 1/1) and a turbid dispersion of the polychelate of the polymer brush and Cd<sup>2+</sup> ion was obtained. Introduction of H<sub>2</sub>S into the turbid dispersion of the polychelate produced CdS nanoparticles within the polymer brush, indicated by the instant color change to yellow. Finally a clear solution of semiconducting nanocylinder was obtained.

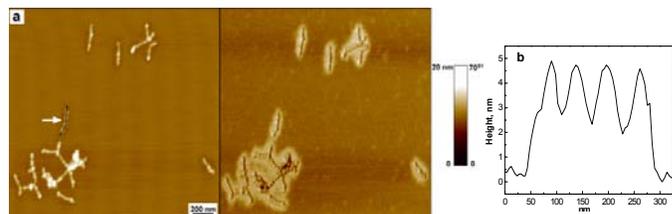
## Results and Discussion

The well-defined core-shell structure of the polymer brush can be directly visualized on the SFM phase image, as shown in Figure 1.



**Figure 1.** (a) SFM image of the polymer brush (left: height image; right: phase image); and (b) cross section of one brush molecule indicated by the arrow in the height image (along the black solid line).

**Magnetic Nanocylinders.** As shown in Scheme 1, the synthesis of inorganic nanoparticles proceeds in three steps: neutralization of the PAA polymer core; loading of metal ions into the polymer core via coordination between carboxylate groups and metal ions (the composite of the polymer brush and metal ion is named as polychelate); and particle formation.

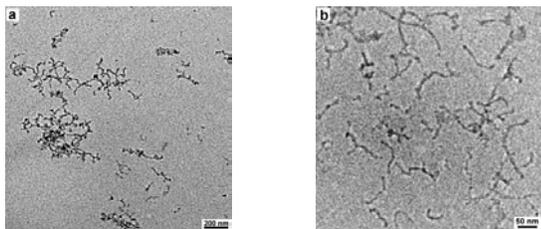


**Figure 2.** (a) SFM image of the polychelate of the polymer brush and Fe<sup>3+</sup> ion; and (b) cross section of one polymer brush molecule indicated by the arrow in the SFM height image (along the black solid line).

Various analytical techniques, such as FT-IR, UV/vis, TEM and SFM confirmed the successful coordination between iron ions and carboxylate groups in the polymer core,<sup>5</sup> besides the apparent color change upon loading of iron ions. Figure 2 shows a typical SFM image of the polychelate. Both the morphology and the size of the polymer brush changed significantly after the

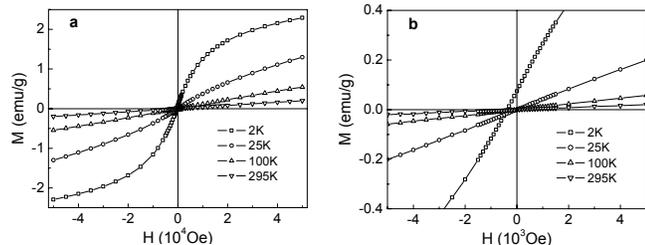
loading of  $\text{Fe}^{3+}$  ions. A peculiar pearl necklace structure was observed for the polychelate, resulting from the cross-linking of side chains via bridging multivalent  $\text{Fe}^{3+}$  ions.<sup>5,6</sup> A large increase in the height of the polymer brush was also observed, indicated by the cross section analysis.

Formation of magnetic iron oxide nanoparticles within the polymer brush was confirmed by SFM, TEM and magnetization measurements. SFM measurements show that the morphology and size of the hybrid magnetic nanocylinders are very similar to those of the pure polymer brushes, indicating that the particles must be very small so they did not change the dimension of the polymer template significantly. **Figure 3** shows TEM images of the magnetic nanocylinders. The wire-like objects correspond to the assemblies of iron oxide nanoparticles, since the polymer is invisible.



**Figure 3.** Non-stained TEM images of the magnetic nanocylinders (hybrids of polymer brushes and iron oxide nanoparticles)

The as-prepared hybrid nanocylinders contain 6.1 wt.% of iron oxide, determined by thermogravimetric analysis (TGA). These hybrid nanocylinders show typical superparamagnetic behavior, as shown by the magnetization measurements. **Figure 4** shows the magnetization curves of the hybrid nanocylinders at different temperatures. Above 25 K, no hysteresis was observed, so the hybrid nanocylinders are superparamagnetic. Only at very low temperature (2K) which is below the blocking temperature, a coercivity (370 Oe) was observed and the nanocylinders are ferrimagnetic.

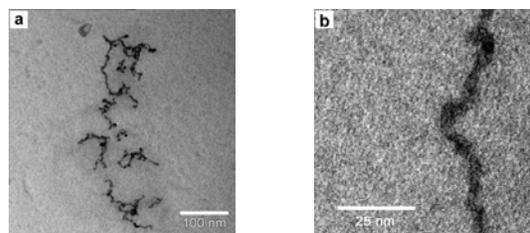


**Figure 4.** Magnetization of the magnetic nanocylinders ( $M$ ) versus applied magnetic field ( $H$ ); (b) magnified plot of the central part of (a).

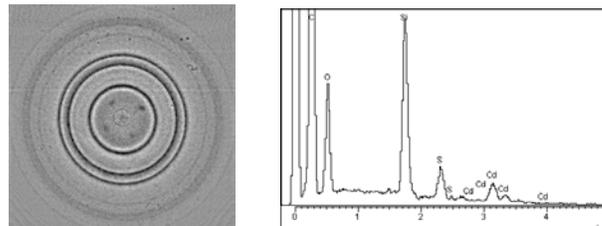
When  $\text{FeCl}_2$  was used, the obtained hybrid nanocylinders show very similar magnetic behavior to that obtained from  $\text{FeCl}_3$ .

**Semiconducting Nanocylinders.** Using the strategy shown in **Scheme 1**, semiconducting CdS nanoparticles were also produced within the core of the polymer brush.<sup>6</sup> SFM was used to monitor the morphology (and size) change of the polymer brush during the formation of CdS nanoparticles. Similarly, after loading of  $\text{Cd}^{2+}$  ions into the polymer core, a pearl necklace structure was observed which vanished when CdS nanoparticles formed via introduction of  $\text{H}_2\text{S}$  to the dispersion of the polychelate. Elemental analysis of the hybrid nanocylinders, which was carried out via an energy dispersive X-ray (EDX) analysis of a scanning electron micrograph, confirmed the presence of cadmium and sulfur with the average atom ratio of Cd/S of 1.1.

The TEM images shown in **Figure 5** provide a direct proof of the formation of CdS nanoparticles and their longitudinal distribution along the backbone of the polymer brush. Wire-like CdS nanoparticle assemblies with a diameter of 4-5 nm were clearly observed. The electron diffraction pattern (**Figure 6**) of the fabricated CdS nanoparticles shows a typical polycrystalline structure. The  $d$  spacings calculated from the rings in electron diffraction pattern are 3.29, 2.02, and 1.73 Å, corresponding to the reported  $d$  spacings for lattice planes (111), (220), and (311) of the cubic phase of CdS.

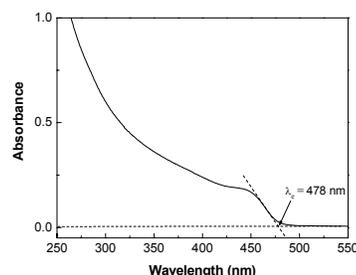


**Figure 5.** Non-stained TEM images of the semiconducting nanocylinders (hybrids of polymer brushes and CdS nanoparticles).



**Figure 6.** Electron diffraction pattern (left) and EDX spectrum (right) of the semiconducting nanocylinders.

**Figure 7** shows the UV/vis spectrum of the hybrid semiconducting nanocylinders. Since the pure polymer brush has no absorption in the observed wavelength range,<sup>5</sup> the absorption shown in **Figure 7** can be attributed exclusively to CdS nanoparticles. As expected, the absorbance edge ( $\lambda_c = 478$  nm) of CdS nanoparticles in the polymer brush is blue-shifted relative to that of bulk CdS ( $\lambda_c = 515$  nm), indicative of small particle size.



**Figure 7.** UV/vis spectrum of the semiconducting nanocylinders.

## Conclusions

Using an amphiphilic cylindrical polymer brush with PAA core and PnBA shell as a single molecular template, magnetic iron oxide and semiconducting cadmium sulfide nanoparticles were successfully synthesized within the core of the polymer brush. The as-prepared hybrid magnetic/semiconducting nanocylinders are soluble and stable in organic solvents and may find applications as one-dimensional nanostructured hybrid materials.

**Acknowledgements.** The authors would like to thank Dr. C. Estournes (University of Strasbourg) for the magnetization measurements. This work was supported by Deutsche Forschungsgemeinschaft (SFB 481).

## References

- (1) Ciebien, J.F.; Clay, R.T.; Sohn, B.H.; Cohen, R.E. *New J. Chem.* **1998**, *22*, 685.
- (2) Förster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195.
- (3) (a) Minko, S.; Kiriya, A.; Gorodyska, G.; Stamm, M. *J. Am. Chem. Soc.* **2002**, *124*, 10192; (b) Braun, E.; Eichen, Y.; Sivan, U.; Ben-Yoseph, G. *Nature* **1998**, *391*, 775.
- (4) Zhang, M.; Breiner, T.; Mori, H.; Müller, A.H.E. *Polymer* **2003**, *44*, 1449.
- (5) Zhang, M.; Teissier, P.; Krekhova, M.; Cabuil, V.; Müller, A.H.E. *Prog. Colloid Polym. Sci.*, in press.
- (6) Zhang, M.; Drechsler, M.; Müller, A.H.E. *Chem. Mater.*, in press.