HYBRID OF MAGNETIC NANOPARTICLES WITH DOUBLE-HYDROPHILIC CORE-SHELL CYLINDRICAL POLYMER BRUSHES

Youyong Xu, Markus Drechsler, Jiayin Yuan, and Axel H. E. Müller

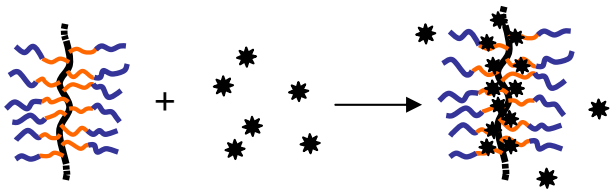
Makromolekulare Chemie II and Bayreuth Zentrum für Kolloide und Grenzflächen; Universiät Bayreuth, 95440 Bayreuth, Germany

Introduction

One-dimensional (1-D) nanostructures have drawn much research interest[1]. Template-directed synthesis has proved to be an effective method to prepare 1-D nanomaterials. Among different one-dimensional templates, cylindrical polymer brushes show distinct advantages. By controlled synthesis, it is possible to get narrowly distributed and well-defined single molecular cylindrical brushes[2]. Several examples have shown the possibilities of making metal[3] and semiconductor[4] 1-D nanostructures within the core of core-shell cylindrical polymer brushes.

As part of our continuous efforts on making nano-hybrids of magnetic nanoparticles with cylindrical polymer brushes, our group has previously reported the synthesis and characterization of a hybrid of superparamagnetic maghemite nanoparticles with amphiphilic core-shell cylindrical polymer brushes[5]. Because of the amphiphilicity of the template brushes, a mixed solvent of methanol and chloroform should be used, which caused some difficulties for the work-up and instability of the hybrid in the solution. At the same time, because of steric problems, the magnetic nanoparticles, which were generated in-situ in the core of the brushes, were very small.

In this contribution, we prepared water-soluble double hydrophilic core-shell cylindrical brushes, which served as new templates for the magnetic hybrids. The core of the brush is poly(methacrylic acid) (PMAA) and the shell is poly(oligoethylene glycol methacrylate) (POEGMA). Since the carboxylic groups strongly interact with the magnetite nanoparticles, we have developed a new strategy for the preparation of magnetic nanocylinders. As shown in Scheme 1, as-prepared core-shell cylindrical brushes and magnetic nanoparticles were put together and the magnetic nanoparticles could be introduced into the core of the brushes. TEM and AFM were employed to characterize the hybrids. Some magnetic properties were also analyzed.



Scheme 1. Strategy for the synthesis of magnetic cylindrical hybrids.

Experimental

Materials. Poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) (PBIEM), which served as the macroinitiator for the brushes, were prepared by the procedure described in our former work[6]. It has *DP* of 1500 and Polydispersity of 1.08. OEGMA (MW=450) and *tert*-butyl methacrylate were purchased from Aldrich and were subjected to basic Alumina column before use. Iron (III) chloride, Iron (II) chloride, trifluoroacetic acid and HMTETA were all from Aldrich and used as they were. All the other solvents were used as received.

Instrumentation. **^{1}H NMR** spectra were recorded on a Bruker 250 AC spectrometer using either $CDCl_3$ or D_2O as solvent. **GPC** measurements were performed on a set of 30 cm SDV-gel columns of 5 mm particle size having a pore size of 10^5, 10^4, 10^3 and 10^2Å with RI and UV (λ=254 nm) detection. GPC was measured at an elution rate of 1 ml/min with THF as solvent. Polystyrene standards were used. **TEM** Images were taken with a Zeiss CEM 902, which was operated at 80 kV. **Cryo-TEM** measurements were performed on a Zeiss EM922 EFTEM with an acceleration voltage of 200kV. **AFM** measurements were carried out on Digital Instruments Dimension 3100 microscope operated in tapping mode.

Synthesis of core-shell brushes. Graft-from strategy was used to prepare PtBMA and PtBMA-b-POEGMA brushes, using consecutive ATRP reactions. Then by hydrolysizing the PtBMA core with trifluoroacetic acid, PMAA-b-POEGMA (termed as $[MAA_{60}$-b-$OEGMA_{200}]_{1500}$) core-shell brush was obtained.

Synthesis of magnetite nanoparticles and hybrids. Magnetite nanoparticles were prepared by the co-precipitation procedure described in literature[7]. TEM measurements show that the diameter of the particles is around 10 nm. The hybrid was prepared by mixing an aqueous solution of the brush with magnetite nanoparticles and heating them at 50 °C over the night.

Results and Discussion

In the synthesis of a polychelate of amphiphilic core-shell brushes with Cd^{2+} and Fe^{3+}, so-called pearl-necklace structructures had been observed, which were attributed to the insoloubility of the Cd and Fe salts of poly(acrylic acid).. Our brushes have a core of PMAA, which is pH-responsive. At low pH, the solubility of PMAA is poor, while at high pH, it is ionized and the solubility is good. Figure 1 shows the cryo-TEM images of the pure brush $[MAA_{60}$-b-$OEGMA_{200}]_{1500}$ at pH 4 and pH 7. From the image of pH 4, we can clearly see the pearl-necklace structures, most probably caused by the collapse of PMAA in the core of the brushes. At pH 7, no such structures could be found, because the PMAA chains are more extended in this environment. Similar pearl-necklace structures were also found in the polychelate of $[MAA_{60}$-b-$OEGMA_{200}]_{1500}$ with Fe^{3+}.

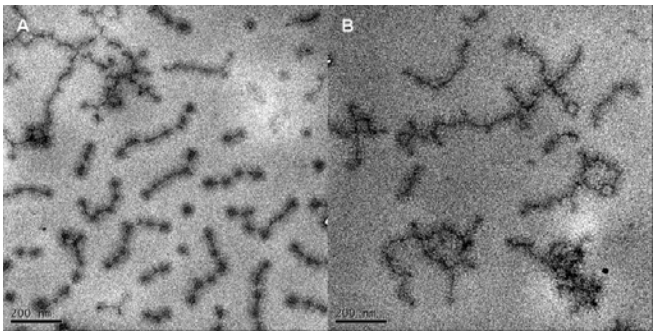


Figure 1. Cyro-TEM images of brush $[MAA_{60}$-b-$OEGMA_{200}]_{1500}$ at A) pH =4, and B) pH=7. The scale bars represent 200 nm.

To check the formation of the magnetic hybrids by introduction of magnetite particles into the core of the brushes, TEM and AFM were used. Figure 2 is the non-stained TEM image of the hybrid. Since the contrast of polymer without staining in TEM is quite low, we normally can not see the polymers. Only the particles could be seen. We can see some short chains of particles. This indicates that the particles went into the brushes and were aligned in the direction of the brushes.

The hybrid formed should have magnetic response due to the magnetic nanoparticles inside. Alignment of the hybrid cylinder was investigated. Solutions were dropped on a mica surface and a magnetic field was applied along the surface during the drying process. Without adding magnetic field, the hybrid cylinders were randomly distributed on the mica surface (figure 3A). In the presence of a magnetic field, we can see from figure 3B, there is alignment in the direction of the magnetic field.

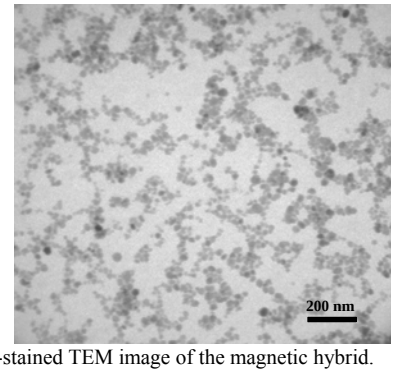


Figure 2. Non-stained TEM image of the magnetic hybrid.

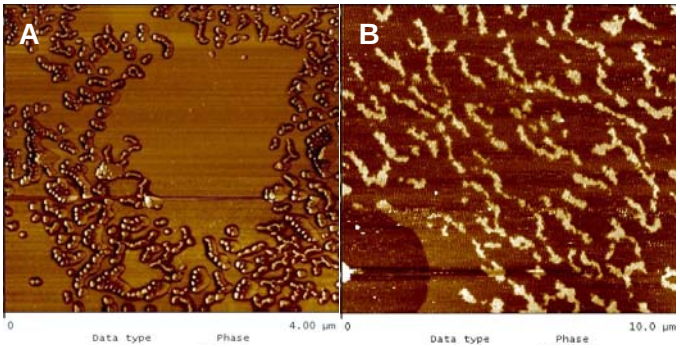


Figure 3. Cylindrical hybrid on mica surface: A) without magnetic field; B) with magnetic field (B=40 mT).

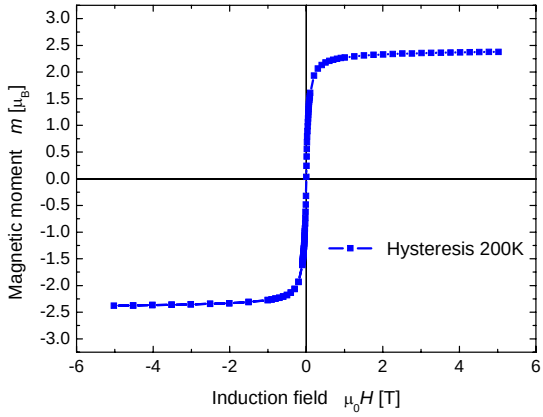


Figure 4. Magnetic hysteresis of cylindrical magnetic hybrid at 200 K.

SQUID measurements were carried out. The magnetization curve of the hybrid in Figure 4 shows the absence of a hysteresis, indicating that the magnetic cylindrical hybrids are superparamagnetic.

Conclusions

By a grafting-from method, we successfully prepared water soluble double hydrophilic core-shell cylindrical brushes. We obtained superparamagnetic cylindrical hybrids by introducing magnetite nanoparticles. The hybrids can be aligned on mica surface in presence of a magnetic field.

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