Summary

Core-shell cylindrical polymer brushes with poly(*t*-butyl acrylate)-*b*-poly(*n*-butyl acrylate) (P*t*BA-*b*-P*n*BA) diblock copolymer side chains were synthesized via the "grafting from" technique using a combination of anionic polymerization (for the synthesis of the backbone) and atom transfer radical polymerization (ATRP, for the synthesis of the side chains). The formation of well-defined brushes was confirmed by ^{1}H-NMR and GPC. The selective hydrolysis of the P*t*BA block of the side chains resulted in novel amphiphilic core-shell cylindrical polymer brushes with poly(acrylic acid)-*b*-poly(*n*-butyl acrylate) (PAA-*b*-P*n*BA) side chains. The characteristic core-shell cylindrical structure of the brushes was directly visualized on mica by scanning force microscopy (SFM). Amphiphilic brushes with 1500 block copolymer side chains and a length distribution of $l_w/l_n = 1.04$ at a total length $l_n = 179$ nm were obtained. These amphiphilic polymer brushes can be regarded as unimolecular cylindrical micelles, because of the core-shell structure and the amphiphilicity of side chains.

The amphiphilic brushes can be used as single molecular templates for the synthesis of inorganic nanoparticles, because the carboxylic acid groups (or carboxylate groups, after neutralization) in the polymer core can coordinate with various metal ions.

The hydrophilic core of polymer brushes, poly(acrylic acid), was neutralized by NaOH and afterward iron cations (Fe^{3+} and Fe^{2+}) were loaded into the polymer core via ion exchange. The formation of the polychelates of polymer brushes and iron cations was confirmed and characterized by various techniques such as Fourier transform infrared spectroscopy (FTIR), UV/vis spectroscopy, transmission electron microscopy (TEM) and SFM. A peculiar "pearl necklace" morphology was observed for the polychelates, which is caused by the physical cross-linking of the side chains via multivalent iron cations. Formation of crystalline α-Fe_2O_3 (hematite) was observed during the He-Ne laser irradiation in the confocal Raman microscopy measurement of the polychelate containing Fe^{3+} ions.

Magnetic nanoparticles were successfully produced from the coordinated iron cations within polymer brushes via single molecule templating technique, as confirmed by various techniques such as SFM, TEM, and UV/visible spectroscopy. Superconducting quantum interference device (SQUID) magnetization measurements show that the hybrid nanocylinders are superparamagnetic at room temperature. The polymer shell provides not only the stability of the nanoparticles but also the solubility of the hybrid nanocylinders.

After the formation of the magnetic nanoparticles, the carboxylate coordination sites within the polymer brushes are liberated and ready for further coordination with more iron ions, thus it is possible to increase the amount and/or particle size of the nanoparticles by multi-cycles of iron ion loading and particle formation. The as-prepared hybrid nanocylinders combine the promising properties of polymers and superparamagnetic nanoparticles, and may find potential applications such as in ferrofluids.

Similarly, using the amphiphilic core-shell cylindrical polymer brush with PAA core and P*n*BA shell as template, wire-like assemblies of CdS nanoparticles were successfully synthesized under mild solution conditions, as confirmed by various characterization techniques. Quantum confinement of the CdS nanoparticles was observed, indicated by the blue shift of the absorbance edge in UV/visible spectrum.

The technique using a single cylindrical molecule as template for inorganic nanoparticle fabrication presented in this thesis is not restricted to magnetic/semiconductor nanoparticles, but can also be used for the preparation of a number of metal, metal oxide, and metal chalcogenide nanoparticles.