DOCTORAL THESIS

Metallo-block copolymers as precursors towards the synthesis of metal nanoparticles

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Abstract

The use of metal-containing block-copolymer to fabricate magnetic nanoparticles arranged in desired nanostructure has attracted immense attention in the field of materials science. As a result, a series of FePt-containing block copolymers were synthesized.

To begin with, a brief survey on the background of magnetic FePt NPs and the use of both organic and metal-containing block copolymer self-assembly was presented in chapter 1.

In chapter 2, a series of FePt-containing polymers were synthesized and characterized. The random copolymer **FePt-A** exhibited poor solubility and ill-characterized morphology in the bulk state self-assembly. The block copolymer **FePt-B2** showed incomplete complexation due to the bulky nature of the FePt-complexes **B5** used, whereas the block copolymer **FePt-C** resulted in insoluble polymeric materials after complexation. Fortunately, when using coordination linkage, **FePt-D**s were successfully synthesized and characterized with good solubility in common solvents. To retain the cylindrical (**FePt-D-Cy1/2**) and spherical (**FePt-D-Sp1/2**) morphologies of the neat block copolymer, the loading of bimetallic complexes **D1** was targeted at 20% of stoichiometry ratio to pyridine. The pyrolysis

of bulk samples generated fct FePt nanoparticles with size of 6-13 nm. The results showed the systematic tuning of size of nanoparticles by varying the molecular weight of block copolymers, and hence the total metal content by weight percentage in polymers.

In chapter 3, the thin film self-assembly of **FePt-D**s was further investigated to demonstrate the potential of our system for thin film fabrication. Three approaches were employed, the first method was solid state self-assembly in thin film, and the morphologies in thin film were consistent to those in the bulk state self-assembly. Solvent annealing of **FePt-D-Cy2** and **FePt-D-Sp1** showed improvement in the order and orientation of microdomains, despite the presence of some defects in order. With well-defined spherical morphology in **FePt-D-Sp1**, the pyrolysis in thin film was performed and the result showed the retention of spherical morphology with little defects. In the next stage, nanoimprint lithography directed self-assembly was employed to give the long range order. Both flattened and line array patterned molds were employed to imprint the polymers. The results showed alignment direction with the use of flattened mold. However, the results also showed the deformed and damaged patterns due to high adhesion force between the polymer and mold. Without an appropriate releasing agent covered on mold surface and a remedy to tribological problem, it would be hard to reliably obtain the morphology under the molds during

the press and release. Going to the last method, the solution state self-assembly of **FePt-D-Cy2** in THF/toluene mixture was demonstrated. By varying polymer concentrations and spinning rate, well-defined spherical micelles are possible to achieve with a better order and distribution. Solvent annealing with slightly selective solvent showed reduction in size distribution and domain size in the FePt spherical micelles with slightly improved packing. Although very nice packings in both solid and solution state self-assembly have not been achieved yet, this study still demonstrated the potential approach to use single bimetallic source-containing block copolymer to self-assemble into desired nanostructures for FePt nanoparticles synthesis.

Finally, chapters 4 and 5 presented the concluding remarks, future plans and the experimental details described in chapters 2 and 3.

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