Hybrids Composed of Block Copolymers and Semiconductor Nanoparticles via Hydrogen Bonding

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1 Introduction
Organic-inorganic hybrids with well-ordered periodic nanostructures have been attaining much attention due to their high potential for nanoapplications. Block copolymer/semiconductor nanoparticle hybrids are one of good candidates to achieve such nanomaterials with high functionality. However, it is not easy to incorporate semiconductor nanoparticles into a specific phase of nanophase-separated structures of block copolymers, since there exist large repulsive forces between semiconductor nanoparticles and organic block copolymers. In this report, simple incorporation procedure of semiconductor nanoparticles into nanophase-separated block copolymers will be provided. Effects of block copolymer molecular weight on morphologies of block copolymer/semiconductor nanoparticle hybrids via hydrogen bonding were also investigated in detail.

2 Experiment
Two polystyrene-b-poly(4-vinylpyridine) (PS-P4VP) block copolymers with exactly the same PS chain length ($M_n(PS) = 39k$) but with different P4VP chain length ($M_n(P4VP) = 41k, 4k$) were synthesized via RAFT polymerization. Nanophase-separated hybrids were prepared by mixing each PS-P4VP and hydroxy-capped nanoparticles made of cadmium selenide (h-CdSe). FT-IR measurements were carried out to identify hydrogen bonding in hybrids. Morphologies of hybrids were observed by both transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS).

3 Results and Discussion
Although the data is not shown in this report, FT-IR spectroscopy revealed presence of hydrogen bonding between hydroxy groups on h-CdSe and pyridine groups on PS-P4VP, which indicates selective incorporation of h-CdSe into P4VP nanodomains.

TEM images and SAXS profiles of hybrids were provided in Figures 1 and 2. Hybrids composed of PS-P4VP(41k) and h-CdSe represent uniform morphologies of a single nanophase-separated structure such as lamellae in Figure 1a, where domain spacing expansion and morphology transition induced by addition of h-CdSe were also observed. (The data is not shown.) On the other hand, nonuniform morphologies, i.e., macrophase separation accompanied by overflow of h-CdSe from nanophase-separated domains, were observed in hybrids of PS-P4VP(4k)/h-CdSe, as shown in Figures 1 and 2.

These results are attributed to the stoichiometric balance of functional groups.[1]

Figure 1. Schematic illustrations and TEM images of hybrids: (a) PS-P4VP(41k)/h-CdSe; (b) PS-P4VP(4k)/h-CdSe.

Figure 2. SAXS profiles of PS-P4VP(41k)/h-CdSe (top) and PS-P4VP(4k)/h-CdSe (bottom).

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