Photon Factory Activity Report 2012 #30 (2013) **B**

BL-15A/6A/2012G176

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]

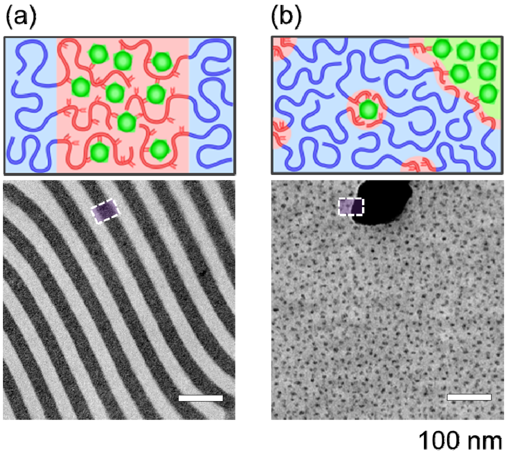

Figure 1. Schematic illustrations and TEM images of hybrids: (a) PS-P4VP(41k)/h-CdSe; (b) PS-P4VP(4k)/h-CdSe.

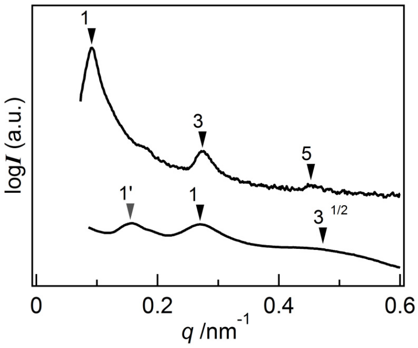

Figure 2. SAXS profiles of PS-P4VP(41k)/h-CdSe (top) and PS-P4VP(4k)/h-CdSe (bottom).

Acknowledgement

Use of synchrotron X-ray source was supported by Photon Factory, KEK, in Tsukuba, Japan. (No. 2012G176 for A.N.) The authors thank Dr. Yuya Shinohara at the University of Tokyo for his assistance in SAXS measurements. A.N. is grateful for financial support of KAKENHI grant no. 23655123 (A.N.), and no. 24685035 (A.N.) from JSPS, Japan.

References

[1] A. Noro, K. Higuchi, Y. Sageshima, and Y. Matsushita, *Macromolecules* **45**, 8013-8020 (2012). (Ranked among the Top 20 most read articles in Macromolecules (Oct, 2012))

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