

Morphologies of block copolymer/metal salt hybrids via metal-ligand coordination

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1 Introduction

Organic-inorganic hybrids with well-ordered periodic nanostructures have been attracting much attention due to their high potential for nano-applications. Recently, we have reported a facile preparation procedure of macroscopically homogeneous block copolymer/metal salt hybrids via solvent casting by using a solvent with coordination ability, which provides nanophase-separated structures composed of an organic phase and a metal containing hybrid phase via metal-ligand coordination [1,2]. Here we report a systematic study of morphologies of polystyrene-*b*-polyvinylpyridine (PS-PVP) block copolymer/metal salt hybrids, where polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP) or polystyrene-*b*-poly(2-vinylpyridine) (PS-P2VP) was used as PS-PVP for experiments.

2 Experiments

PS-P4VP ($M_n=54k$, PDI=1.13, $\phi_S=0.62$) and PS-P2VP ($M_n=54k$, PDI=1.20, $\phi_S=0.61$) were synthesized via living radical RAFT polymerization. Hybrid samples were prepared by mixing PS-PVP and $FeCl_3$ in a solvent of pyridine, followed by solvent casting (50°C, 24h) and thermal treatment (170°C, 24h). Blend molar ratio of $FeCl_3$ to pyridine unit in PVP block was varied from 0 to 0.6, which was described as X. The hybrids were characterized by FT-IR spectroscopy and DSC measurements. Their morphologies were investigated by 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 and DSC measurements revealed metal-ligand coordination between $FeCl_3$ and pyridine rings in PVP blocks, suggesting selective incorporation of $FeCl_3$ into PVP nanodomains.

Figure 1 shows 1D-SAXS profiles of neat PS-PVPs and the hybrids. As for the neat PS-PVPs (PS-P4VP and PS-P2VP), they represented the same PVP cylindrical morphologies, though different interdomain distance and domain sizes were observed between PS-P4VP and PS-P2VP. This is due to the difference in the strength of repulsive force between PS and PVP. On the other hand, hybrids of PS-P4VP/ $FeCl_3$ represent different morphologies from PS-P2VP/ $FeCl_3$, even though the molecular weights and the compositions of the parent block copolymers are the same. Such morphological differences were also confirmed by TEM observations.

Comparing these two hybrids, morphology transition occurred more easily in PS-P2VP/ $FeCl_3$ hybrids. Moreover, interdomain distance drastically increased in PS-P2VP/ $FeCl_3$ hybrids as X increased. These results can be explained by the difference of chain conformations in hybrids; in other words, P2VP chains can be extended considerably due to complex formation with $FeCl_3$, while P4VP chains may be inhibited to extend the chain dimension owing to cross-linking via metal-ligand coordination with $FeCl_3$ [3].

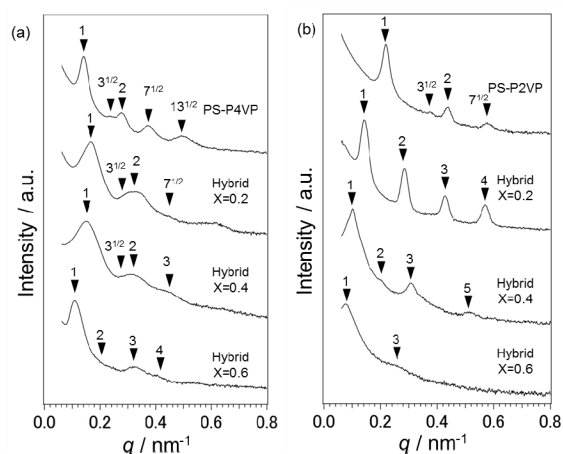


Fig. 1: 1D-SAXS profiles of (a) PS-P4VP/ $FeCl_3$ hybrids and (b) PS-P2VP/ $FeCl_3$ hybrids.

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