

## Letters

### Effect of the Casting Solvent on the Morphology of Poly(styrene-*b*-isoprene) Diblock Copolymer/Magnetic Nanoparticle Mixtures

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We investigate the effect of the casting solvent on the phase behavior of a cylinder-forming poly(styrene-*b*-isoprene) (PS-*b*-PI) diblock copolymer mixed with marginally selective  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. Notably, for the mixtures of PS-*b*-PI/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles cast with toluene, which is a neutral solvent for both PS and PI blocks, the latticelike aggregates of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, originating from magnetic dipole interactions, induce an intriguing transition from hexagonal cylinders to body-centered cubic spheres via undulated cylinders whereas the neat block copolymer does not show such an order–order transition. In contrast, when PI-selective hexane is used, the nanoparticles are selectively incorporated into the PI domains, and the microphase-separated hexagonal cylinder morphology gradually loses its long-range order upon increasing the nanoparticle concentration. The structural information obtained from small-angle X-ray scattering is also in good agreement with transmission electron microscopy images and differential scanning calorimetry results.

The fabrication of patterned arrays of nanoparticles (NPs) has been extensively investigated for their potential applications in memory devices.<sup>1–3</sup> Significant efforts have been devoted in recent years to combine block copolymers (BCPs) and NPs to integrate properties of disparate materials.<sup>4–7</sup> NPs can be sequestered into certain domains of self-assembled BCPs,<sup>8,9</sup> and

the selective decoration of NPs in a microphase-separated BCP on a length scale of tens of nanometers can provide intriguing structures.<sup>10–12</sup>

For the BCPs self-assembled into a wide range of ordered nanostructures, the addition of NPs can alter the characteristic

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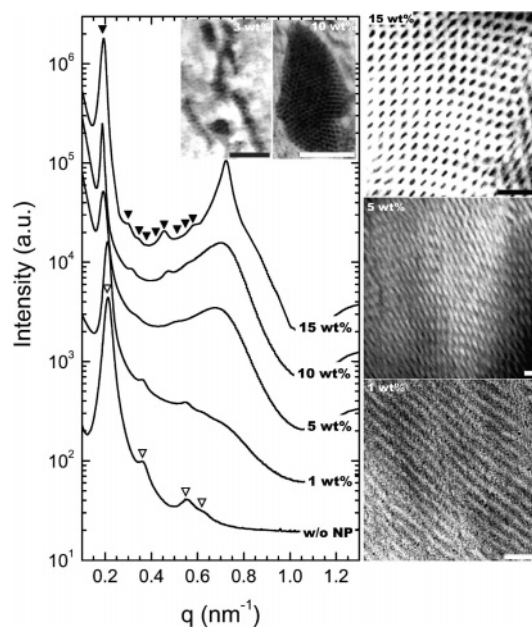
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dimensions, or even the morphology, of the ordered BCP structures because the BCP is often weakly bound to the NPs.<sup>13–15</sup> Furthermore, when magnetic NPs are used for the NP/BCP hybrids, magnetic interactions among magnetic NPs can sometimes cause clustering.<sup>16–18</sup> Consequently, the novel change in the ordered morphology of block copolymers triggered by the existence of NPs aggregates is expected,<sup>19</sup> and the fascinating nature of morphological transformation has stimulated both fundamental and applied research.

In the present study, we report the phase behavior of polystyrene-*block*-polyisoprene (PS-*b*-PI) diblock copolymer/magnetic NP mixtures with different casting solvents. To the best of our knowledge, this is the first effort to address the phase behavior upon the incorporation of NPs into the PS-*b*-PI. Monodisperse  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs of 7 nm diameter with surfaces modified with oleic acid have been synthesized,<sup>2</sup> and a PS-*b*-PI, denoted as SI(39-12) with  $M_{PS} = 39\ 200$  g/mol and  $M_{PI} = 12\ 100$  g/mol, was prepared by anionic polymerization.<sup>20</sup> Mixtures of NPs and SI(39-12) with different NP concentrations were prepared by solution casting using either toluene or hexane as a casting solvent and were then annealed above the glass-transition temperature ( $T_g$ ) of the PS block.

It should be noted here that the values of the interfacial tension, which are in turn related to the values of the surface tension ( $\gamma_{PS} = 40.7$  dyn/cm,  $\gamma_{PI} = 30.5$  dyn/cm, and  $\gamma_{\text{octadecene}} = 28.1$  dyn/cm at 20 °C) and the polarities of the two contiguous phases through the harmonic mean equation,<sup>21,22</sup> are calculated to be  $\gamma_{PS/NP} = 7.38$  dyn/cm and  $\gamma_{PI/NP} = 0.33$  dyn/cm. This implies that the NPs are more miscible with the PI block than with the PS block. Different thermodynamic justification of the preferential interaction of NPs with the PI block is also provided in the Supporting Information (Figure 1S).

Figure 1 shows the intriguing structural change of SI(39-12)/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NP mixtures at different NP concentrations cast with toluene, measured with both synchrotron small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). SAXS profiles demonstrate that the hexagonal cylinder (hex) morphology of a neat SI(39-12) with a  $q/q^*$  ratio of  $1:\sqrt{3}:\sqrt{7}:\sqrt{9}$  (the lower trace ( $\nabla$ ) in Figure 1 and  $q^* = 2\pi/d_{100}$ ) first transforms into suppressed ordered morphology up to the NP loading of 5 wt %, and a well-developed body-centered cubic (bcc) phase is finally obtained for the 15 wt % NP with a  $q/q^*$  ratio of  $1:\sqrt{2}:\sqrt{3}:\sqrt{4}...$  (the upper trace ( $\blacktriangledown$ ) in Figure 1). The TEM micrographs, in which the PI domains stained with OsO<sub>4</sub> appear dark while the PS domains are bright, again reveal the clear morphological transition of the hex in the [100] direction at 1 wt % NP  $\rightarrow$  undulated hex with 5 wt % NP  $\rightarrow$  bcc in the [001] direction for 15 wt % NP.<sup>23</sup> This implies that the block copolymer microstructure, whether it is hex or bcc, can be tuned



**Figure 1.** SAXS profiles for SI(39-12)/NP mixtures cast with toluene as a function of NP concentration. The lower trace ( $\nabla$ ) of neat SI(39-12) represents the peaks with a ratio of  $1:\sqrt{3}:\sqrt{7}:\sqrt{9}$  corresponding to the hex phase. The upper trace ( $\blacktriangledown$ ) with 15 wt % NPs shows the well-developed bcc phase with a peak ratio of  $1:\sqrt{2}:\sqrt{3}:\sqrt{4}...$  Cross-sectional TEM images of SI(39-12)/NP mixtures (1, 5, and 15 wt %) (PI domains are shown in black by the OsO<sub>4</sub> staining) are also shown. In particular, the block copolymer morphology with 15 wt % NPs is in good agreement with the bcc [001] direction. The TEM images in the inset of the SAXS profiles also show the magnetic strings with 3 wt % NPs and self-assembled NP lattices for 10 wt % NP loading. All scale bars are 100 nm.

by simply changing the concentration of coexisting magnetic NPs without altering the block copolymer composition.

The coexisting NP aggregates revealed by the intercorrelation at around  $q = 0.73\ \text{nm}^{-1}$  are identified as magnetic strings for the 3 wt % NP and the hexagonally packed lattices above the 10 wt % NPs formed by the magnetic dipole interactions,<sup>24</sup> as represented in the TEM images in the inset of Figure 1. The presence of NP aggregates with chainlike morphology or latticelike NPs, which enhances the effect of magnetostatic interactions,<sup>25</sup> causes the fluctuation between PS and PI interfaces, and the undulated cylinders eventually favor the formation of the bcc lattice. To the best of our knowledge, this type of morphological transition of a block copolymer triggered by coexisting latticelike NP aggregates has never been reported before. It should also be emphasized at this point that the SI(39-12) with  $f_{PS} = 75\%$  is located in the vicinity of bcc and hex in the block copolymer phase diagram ( $f_{PS} = 77\%$ ),<sup>26</sup> which makes the morphological transition from the hex to the bcc rather easy.

In contrast, when the same SI(39-12)/NP mixtures are cast with hexane, Figure 2 shows that the higher-order peaks corresponding to the hex morphology are maintained at lower particle loadings. In striking difference from the unique morphological transition from the hex to the bcc shown with toluene casting solvent, the high NP loading above 10 wt % induces the disordered morphology of the block copolymer upon extensive aggregation of NPs. The TEM image with 1 wt % NP

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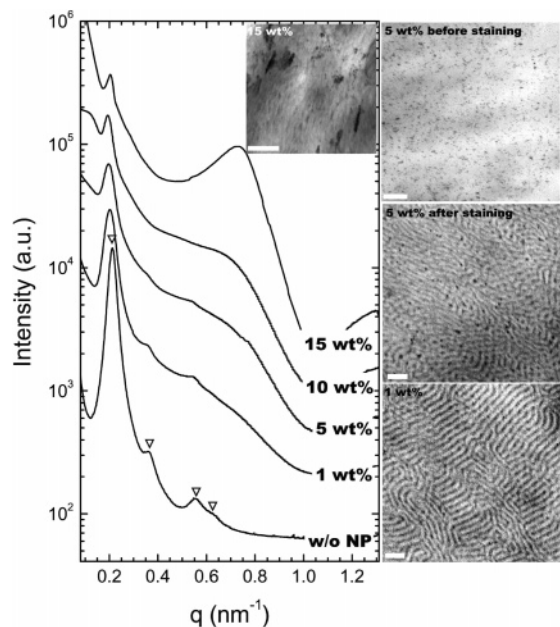
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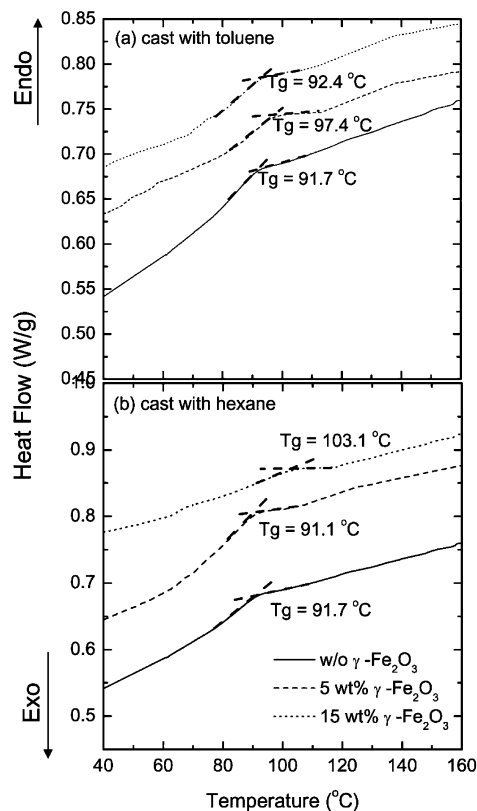
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**Figure 2.** SAXS profiles for SI(39-12)/NP mixtures cast with hexane as a function of NP concentration. The lower trace ( $\nabla$ ) of neat SI(39-12) again indicates the hex phase, and the block copolymer loses its long-range order as the NP concentration is increased. Cross-sectional TEM images of SI(39-12)/NP mixtures (1, 5, and 15 wt %) are also shown. Darker spots in each TEM micrograph represent the dispersed NPs of 7 nm diameter. The TEM image in the inset of the SAXS profiles shows the formation of NP strings coexisting with disordered block copolymer micelles. All scale bars are 100 nm.

concentration also shows the hex phase with NPs being randomly incorporated into the PI cylinders. At 5 wt % NP loading, the TEM image taken before the  $\text{OsO}_4$  staining clearly shows the well-dispersed NPs without extensive aggregation of NPs, and although it is difficult to locate entire NPs because of the reduced contrast of  $\gamma\text{-Fe}_2\text{O}_3$  NPs upon staining, it appears that the NPs selectively disperse within the PI domains. In other words, we can easily disperse NPs into the PI domains simply by using a PI-selective solvent. Upon further increases in NP concentration, NPs are finally aggregated, and the hex morphology gradually loses its long-range order. We also obtained a rather broad and suppressed particle correlation peak in the high- $q$  range, and no evidence of ordered NP arrays is observed in the TEM, contrary to the situation for SI(39-12)/NP mixtures cast with toluene, clearly indicating the effect of the structure of aggregated magnetic NPs on the block copolymer morphology.

Differential scanning calorimetry (DSC) measurements were also performed, and the DSC thermograms of three representative samples with neat SI(39-12) and SI(39-12)/NP mixtures with 5 and 15 wt % NPs are shown in Figure 3. The small change in the heat flow at around 91.7 °C corresponds to the glass-transition temperature of the PS block ( $T_{g,PS}$ ).  $T_{g,PS}$  of a SI(39-12) mixed with 5 wt % NPs, cast with toluene, increases by 5.7 °C as compared with that of a neat SI(39-12). This increase in  $T_{g,PS}$  is attributed to the NP aggregates, which hinder the molecular motion of PS domains via a binding effect.<sup>27,28</sup> Upon further increases in NP concentration, the  $T_{g,PS}$  comes back to a lower value corresponding to the value for the neat SI(39-12), implying



**Figure 3.** Differential scanning calorimetry traces of neat SI(39-12) and SI(39-12)/NP mixtures (with 5 and 15 wt % NPs) cast with (a) toluene and (b) hexane.

that the NPs completely segregate out of the SI(39-12) as the NP volume fraction is increased (i.e., macroscopic phase separation between NPs and the BCP). However,  $T_{g,PS}$  of a SI(39-12) with 5 wt % NPs cast with hexane is not strongly influenced by the coexisting NPs, confirming the selective incorporation of NPs into the PI domains. However, higher NP concentration shows a significant increase in  $T_{g,PS}$  by 11.4 °C because the increased number density and length of NP strings disturb the long-range hex order of the SI(39-12). In other words, the PI cylinders cannot encapsulate these NP strings entirely, and as a result, it is quite likely that the PS chains are also in contact with the NPs, which in turn causes the increase in  $T_{g,PS}$ .

On the basis of the experimental results obtained so far, we could schematically represent the effect of the casting solvent on the morphology of SI(39-12)/ $\gamma\text{-Fe}_2\text{O}_3$  NP mixtures, as shown in Scheme 1. Because NPs are marginally selective with respect to the PI chains because of the oleate surface layers of NPs, the preparation condition of SI(39-12)/NP mixtures can suppress or enhance the weak interactions between NPs and PI chains competing against the relatively strong interactions among magnetic NPs. Because toluene is a neutral solvent for both blocks of PS-*b*-PI and hexane is a PI-selective solvent and the solvent evaporation rates of toluene and hexane are also quite different, the local structure of BCP/NP hybrids can be governed by the relative kinetics of the BCP ordering against the NP aggregation kinetics. Thus, when toluene is used as a casting solvent, PS, PI, and NPs are readily dissolved, and during the slow evaporation of toluene, the NPs favor self-aggregation rather than being selectively incorporated into the PI domains because of the strong particle–particle interactions. In contrast, when PI chains and NPs are dissolved in hexane while PS chains are just swollen, forming BCP micelles with PS block cores and PI block coronas at relatively high concentrations of BCP, NPs are well

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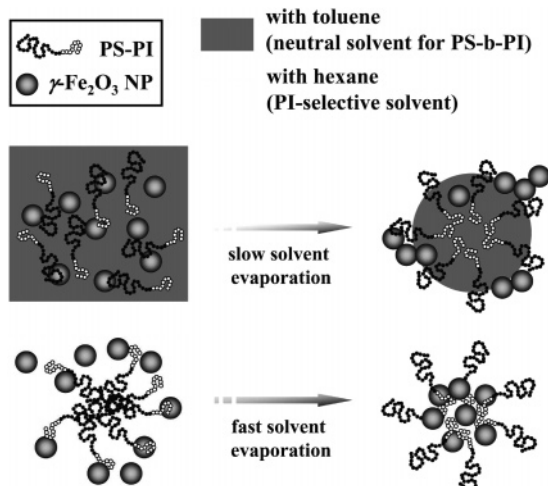
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**Scheme 1. Effect of the Casting Solvent on the Structural Development of SI(39-12)/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NP Mixtures**



mixed with the PI coronas. During the relatively fast evaporation of hexane, the facile inversion of micelles occurs, and this process is believed to retain NPs within the PI domains. This effective confinement of NPs within one domain in a block copolymer using a selective solvent can also be found or generalized with other block copolymer systems. (See Figure 2S in Supporting Information for PS-*b*-P4VP with both good and selective solvents.)

In summary, we investigated the effect of the casting solvent on the phase behavior of a cylinder-forming PS-*b*-PI diblock copolymer mixed with magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs. Two different

solvents, hexane and toluene, were tested to prepare film specimens by solution casting, and it is clearly shown that the competition of the interactions between NPs and BCP against the interactions of NP themselves leads to different hybrid morphologies. It is intriguing that the regular latticelike aggregate structure of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs induces the transition from the hex cylinders to the bcc spheres via undulated cylinders under the toluene casting condition while the neat block copolymer does not show such an order–order transition. In contrast, magnetic NPs are selectively incorporated into the PI domains under the hexane casting condition. This implies that when NPs are marginally selective with respect to one of the blocks and the interactions among NPs are relatively strong, the choice of relevant solvent, whether the solvent is neutral or selective for the BCP, is quite important to the selective incorporation of the NPs into one of the ordered domains.

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**Supporting Information Available:** Thermodynamic justification of the preferential interaction of NPs with the PI block. Effective confinement of NPs within one domain in a PS-*b*-P4VP by varying casting solvents. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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