Controlled specific placement of nanoparticles into microdomains of block copolymer thin films

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Conceptually attractive hybrid materials composed of nanoparticles and elegant block copolymers have become important for diverse applications. In this work, controlled specific placement of nanoparticles such as Au and titania (TiO2) into microphase separated domains in poly(styrene)-b-poly(2-vinylpyridine) (PS-b-P2VP) block copolymer thin films was demonstrated. The effect of nanoparticle surface functionality on the spatial location of particles inside polymer film was observed by transmission electron microscopy. It was revealed that the location of nanoparticles was highly dependent on the surface ligand property of nanoparticle. In addition, the microphase separation behavior of thin block copolymer film was also affected by the nanoparticle surface functional groups. This study might provide a way to understand the properties and behaviors of numerous block copolymer/nanoparticle hybrid systems.

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1. Introduction

Block copolymers (BCPs), owing to their ability to form periodically ordered nanostructures and the capability to tune the size of the microdomains by varying molecular weight and composition, have received a tremendous attention as an emerging material for nanoscale applications. In this work, controlled specific placement of nanoparticles such as gold (Au) and titania (TiO2) into microphase separated domains in poly(styrene)-b-poly(2-vinylpyridine) (PS-b-P2VP) block copolymer thin films was demonstrated. The effect of nanoparticle surface functionality on the spatial location of particles inside polymer film was observed by transmission electron microscopy. It was revealed that the location of nanoparticles was highly dependent on the surface ligand property of nanoparticle. In addition, the microphase separation behavior of thin block copolymer film was also affected by the nanoparticle surface functional groups. This study might provide a way to understand the properties and behaviors of numerous block copolymer/nanoparticle hybrid systems.

To date, extensive experimental and theoretical investigations on BCP/NPs hybrids were conducted to reveal the profound properties and to explore the possibility of practical applications [9–20]. However, despite the importance of controlling spatial arrangement of NPs in the regular periodic structure of the BCPs, achieving such control over large area has been challenging. Balazs et al. provided the basis of theoretical predictions for BCP/NP nanocomposites [21,22]. Russell et al. have shown that the microdomain orientation of BCP could be tuned by introducing surface functional NPs that preferentially segregate to the surface of high surface energy microdomains [20]. Emrick et al. demonstrated the precise placement of an array of cross-linked CdSe quantum dots at an oil/water interface [23]. Kim et al. and Chiu et al. showed that

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the NP location within diblock copolymer template can be controlled by changing the enthalpic interaction between the matrix and polymer coated NPs [17,24].

Still, a better understanding of the interaction between surface functional NPs, ligands on the surface, and the BCP continuous phase is critical to collect more precise information regarding BCP/NP hybrids. Consequently, in this work, the controlled specific placement of spherical Au and cylindrical TiO$_2$ NPs into poly(styrene)-b-poly(2-vinylpyridine) (PS-b-P2VP) copolymer was examined. The dependence of spatial location of NPs on surface ligands and shape of NPs was investigated systematically. Furthermore, the effect of NP surface functionality on microphase separation behavior of BCP was observed by cross-sectional transmission electron microscopy (TEM). This work will provide fundamental information concerning the general behavior of BCP/NP hybrids systems, thus making it possible to design unique hybrid systems.

2. Experimental

2.1. Materials

Two types of poly(styrene)-b-poly(2-vinylpyridine) BCPs having the same blocks and different compositions, PS-b-P2VP (lamellar) (number average molecular weight: $M_n$, PS = 25 kg/mol, P2VP = 23 kg/mol, $M_n/M_w = 1.08$) and PS-b-P2VP (cylinder) (number average molecular weight: $M_n$, PS = 32 kg/mol, P2VP = 12 kg/mol, $M_n/M_w = 1.07$) were purchased from Polymer Source (Quebec, Canada) and used without further purification. Common solvents, toluene and tetrahydrofuran (THF) were dried by a conventional method.

Gold (Au) and titania (TiO$_2$) NPs were prepared by established procedures [25–27]. For example, polystyrene-functionalized gold NPs (Au(PS)), with an average gold diameter of 4 nm, were prepared according to the Brust–Schiffrin method, by reduction of hydrogen tetrachloroaurate with sodium borohydride using polystyrenethiol as ligand [27]. An aqueous solution of hydrogen tetrachloroaurate was mixed with a solution of tetraoctylammonium bromide in toluene. The two-phase mixture was vigorously stirred until all the tetrachloroaurate was transferred into organic phase and polystyrenethiol was then added to the organic phase. An aqueous solution of sodium borohydride was slowly added with vigorous stirring. After further stirring for 3 h the organic phase was separated, evaporated in a rotary evaporator and mixed with ethanol to remove excess thiol. It is desirable to store the gold nanoparticle precursor at low temperature (approximately $-20 \, ^\circ C$) to suppress oxidation/reduction reactions. The molecular weight of the PS ligand was 1 kg/mol, and the density of the Au(PS) was 19.3 g/cm$^3$. Polystyrene-functionalized gold NPs (Au(PS)) were prepared by ligand exchange to prepare dodecanethiol-covered Au NPs (Au(DDT)) [28–30]. Titanium tetraisopropoxide was added to oleic acid at room temperature. Then, the resulting mixture was gradually heated to 270 °C for a period of 20 min and kept at this temperature for 2 h. The solution was then cooled to room temperature, and excess ethanol was added to yield a white precipitate. The average diameter and length of prepared titania were 8 nm and 30 nm, respectively. The surface of titania was covered with oleic acid functionality [25,26]. The approximate density and dielectric constant of titania nanorods were 4.3 g/cm$^3$ and 50. The NP surface was coated onto silicon wafer at 2000 rpm for 60 s from the BCP/NP mixture solution. The dried hybrid thin films were thermally annealed at well-above glass transition temperatures of both blocks, 170 °C for 48 h.

2.3. Instrumentations

Bright field TEM experiments were performed with a JEOL 200CX TEM operated at an accelerating voltage of 200 kV. First, the thin BCP/NP films were spin coated onto a silicon wafer having a 250 nm thick silicon oxide layer. The oxidized silicon layer was etched with a 5% hydrofluoric acid aqueous solution. The separated polymer thin film was retrieved with a copper grid and examined by TEM. To prepare cross-sectional TEM specimens, a thin layer of carbon was evaporated onto the film surface before embedding in epoxy resin to prevent the diffusion of the epoxy resin into hybrid thin film. The thin film was then embedded in an epoxy resin and cured at 60 °C for 18 h. The films were removed from the substrate by dipping into liquid N$_2$. Ultrathin sections (60 nm) were collected at room temperature using a Leica Ultracut Microtome, equipped with a diamond knife. The thin sections were exposed to iodine vapor for 30 min to enhance the contrast.

<p>| Table 1 |
| Physical and surface properties of nanoparticles used in this study. |</p>
<table>
<thead>
<tr>
<th>NP</th>
<th>Average size (nm)</th>
<th>Density (g/cm$^3$)</th>
<th>Surface property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (PS)</td>
<td>4</td>
<td>19.3</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>Au (DDT)</td>
<td>4</td>
<td>19.5</td>
<td>Dodecanethiol</td>
</tr>
<tr>
<td>TiO$_2$ (OA)</td>
<td>8 (radius) 30 (length)</td>
<td>4</td>
<td>Oleic acid</td>
</tr>
</tbody>
</table>

Fig. 1. TEM images of nanoparticles (a) Au(PS) and (b) TiO$_2$ (OA). Scale bar 20 nm.
3. Results & discussion

To examine the effect of NP surface ligand on spatial distribution of NPs into BCP domain, two types of surface ligands—PS and DDT were introduced on Au NPs. PS ligand shows a selectively favorable interaction with PS domain, but DDT ligand provides a similar affinity to both blocks. In order to investigate the BCP composition effect, two types of BCPs, PS-\textit{b}-P2VP (L) (lamellar; PS: P2VP = 52: 48) and PS-\textit{b}-P2VP (C) (cylinder; PS: P2VP = 71: 29), were compared.

Achieving a uniform dispersion of NPs in the polymer matrix can be challenging. However, the ligands attached to the NPs can be tailored to interact favorably with the polymer matrix, so that ligand/matrix interactions are more favorable than ligand/ligand interactions\cite{11,31}. In this way, homogeneous dispersions of NPs in a polymer matrix can be realized. Fig. 2 shows TEM images of PS-\textit{b}-P2VP (L)/Au(PS) and PS-\textit{b}-P2VP (L)/Au(DDT) thin films with an average thickness of approximately 50 nm containing 1 vol.% NPs. The images were taken without staining to monitor clearly the homogeneous distribution of NPs inside the polymer matrix. It is clear that uniform dispersion of NPs into BCP was accomplished for both ligands. The uniform distribution of NPs in the host polymer is a key to ensure uniformity of properties, from the mechanical to the electrical properties of the nanocomposite. To this end, the Au NPs were functionalized with both PS and DDT ligands that would be expected to disperse the NPs. In this case, the enthalpic advantage for dispersing the particles is zero (PS) or small (DDT) due to interactions between the ligand and host polymer, and any entropy loss arising from packing the NPs in the polymer matrix must be minimized. For this study, the NPs were considerably small so that configurational entropic losses of the polymer to incorporate the NPs were very small; consequently, a uniform dispersion was achieved.

Additional TEM experiments were performed to determine whether a migration/segregation of the NPs to the film/air surface (white) occurred before thermal annealing. Such a nonuniform distribution of NPs would, of course, distort the movement of the NPs during annealing. Cross-sectional TEM images of PS-\textit{b}-P2VP (L)/Au(PS) and PS-\textit{b}-P2VP (L)/Au(DDT) thin films with an average thickness of approximately 300 nm containing 1 vol.% NPs were presented in Fig. 3. Regardless of the viewing angle, the NPs appear to be uniformly dispersed throughout the film before thermal annealing. Remarkably, occasional aggregations of Au(DDT) NPs are observed within restricted narrow ranges in Fig. 3b. This is attributed to the significant ligand/ligand interactions between Au(DDT) NPs. For Au(DDT) NPs, the DDT groups can be introduced by ligand exchange with mercapto-undecanol. Thus trace amount of mercapto-undecanol precursor can remain after the washing process. This functional group can form hydrogen bonding with the P2VP block. In addition, attractive interaction is accessible between mercapto-undecanol groups on Au(DDT) NPs, because it can be more favorable than ligand/polymer interactions when the interparticle distances are close. Therefore, fragmentary aggregations of Au(DDT) can be induced locally\cite{30,32}. Considering the observations from Figs. 2 and 3, it is clear that Au NPs were homogeneously dispersed into the host BCP matrix.

Subsequently, we proceeded to monitor the spatial locations of Au NPs inside the PS-\textit{b}-P2VP (L) matrix after thermal annealing to obtain an equilibrium microphase separated morphology. Fig. 4 displays cross-sectional TEM images of PS-\textit{b}-P2VP (L)/Au(PS) and PS-\textit{b}-P2VP (L)/Au(DDT) thin films annealed at 170 °C for 48 h. To enhance contrast, TEM specimens were exposed to iodine vapor for a short time. Because...
iodine vapor can be adsorbed to P2VP groups, P2VP looks darker after staining.

For the PS-b-P2VP (L)/Au(PS) hybrid film, Au(PS) NPs were exclusively located within PS domains. As the surface of Au NPs was entirely covered with PS ligand, the Au(PS) NPs were dominantly located in the center of PS microdomain. Kim et al. demonstrated that the location and population of NPs in a specific microdomain of BCP can be tuned by varying surface ligand [33]. Coagulation of NPs was unremarkable throughout the films. It is obvious that no migration/segregation happened during thermal annealing. Without external forces or fields, the coagulation or segregation of Au(PS) NPs is energetically nonadvantageous, because ligand/matrix interaction is ideal. For PS-b-P2VP (L)/Au(DDT), the aggregation of Au(DDT) NPs is not conspicuous, either. This fact indicates that the coagulation of TiO2 (OA) NPs is energetically advantageous. On the other hand, it can be inferred that the partial rotation of the microdomain induced by NPs was observed regardless of BCP compositions.

To systematically investigate the effect of NP shape, TiO2 nanorods (8 nm diameter & 30 nm length) were employed into the PS-b-P2VP (C) polymer. The surface functional group of titania is oleic acid (OA). Fig. 6a shows the cross-sectional TEM image of PS-b-P2VP (C)/TiO2 (OA) hybrid thin films. In spite of the relatively large size of TiO2 and surface ligands, only a small amount of aggregation of TiO2 (OA) NPs is evident. Still, TiO2 (OA) NPs are fairly well-dispersed within the polymer matrix. Fig. 6b exhibits the cross-section of the PS-b-P2VP (C)/TiO2 (OA) thin film thermally annealed at 170 °C for 48 h. The degree of coagulation increased, but the segregation of TiO2 (OA) NPs is not conspicuous. This fact indicates that the coagulation of TiO2 (OA) NPs is energetically advantageous. On the other hand, it can be inferred
that entropic requirement for driving TiO₂ (OA) NPs to the film/air interface is relatively large size. When the interfacial energy between ligand of NPs and polymer is comparable, nanorods require more energy (torque) than sphere to migrate within BCP. Unless the titania nanorods can obtain this energy from environment, they tend to stay, forming coagulation rather than rotate or migrate [35]. Based on these facts, it can be concluded that small sized spherical NPs is more advantageous for migration/segregation than large cylindrical NPs. Because there was no remarkable migration/segregation, rotation of the BCP microdomain is not striking.

4. Conclusion

The precise control over spatial distribution of nanoparticles was demonstrated by varying shape and surface ligands of nanoparticles. For spherical gold nanoparticles, no migration occurred, when the surface ligand/polymer interaction is favorable. On the contrary, for the case of less favorable ligand/polymer interaction, entropy driven migration/segregation of nanoparticles to the top surface happened. This phenomenon was universal regardless of block copolymer composition. For large cylindrical titania nanoparticles, coagulation of titania nanoparticles within the block copolymer microdomain was prevalent without migration/segregation. In this case, entropy driven migration was found to be difficult. This study provides fundamental information regarding block copolymer/nanoparticle hybrid systems, leading to a more elegant design of emerging nanocomposites.

References