Self-Organization of Homopolymer Brush- and Mixed Homopolymer Brush-Grafted Silica Nanoparticles in Block Copolymers and Polymer Blends

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ABSTRACT: In this report, hierarchical self-organization of poly(*tert*-butyl acrylate) (PtBA) brush- and mixed PtBA/polystyrene (PS) brush-grafted silica nanoparticles (NPs) in PtBA-*b*-PS block copolymer and PtBA/PS polymer blend matrices having different molecular weights was investigated using transmission electron microscopy (TEM). Driven by the entropic interactions between the brushes and the polymer matrices (i.e., wet- and dry-brush effects), various morphologies were observed. First, PtBA brush-grafted 67 nm silica NPs could induce an onion-like structure in a low molecular weight block copolymer matrix because of the wet-brush effect, low particle curvature, and low bending rigidity of the block copolymer lamellae. On the contrary, PtBA brush-grafted 23 nm silica NPs could not induce the onion-like structure, primarily owing to the high particle curvature and high bending penalty of the block copolymer lamellae. Second, the attempt to use ordered block copolymer lamellae to direct microphase separation of mixed homopolymer brushes with a goal of achieving ordered nanopatterns was unsuccessful, likely because the mixed PtBA/PS brushes on NPs underwent microphase separation prior to the ordering of block copolymers during the solution-casting process. Third, in polymer blends, the wet- and dry-brush entropic effects played an important role. In the wet-brush regime, the hairy NPs were uniformly distributed in the preferred polymer phase. In the dry-brush regime, the hairy NPs were driven to the interfaces of immiscible PtBA/PS domains. The knowledge gained on hierarchical self-organization of homopolymer brush- and mixed homopolymer brush-grafted NPs in block copolymer and polymer blend matrices will help us design better polymer nanocomposites with precisely controlled locations of NPs.

Keywords: Mixed homopolymer brushes, diblock copolymers, polymer blends, wet and dry brushes, entropic effect

1. Introduction

Polymer nanocomposites have attracted great attention in research recently because of their potential to improve mechanical, optical, and electrical properties with synergistic integration of inorganic nanoparticles (NPs) and polymer matrices.[1, 2] However, facile dispersion of inorganic NPs in polymer matrices has been challenging for achieving the full potential of polymer nanocomposites. Polymer brushes covalently tethered to inorganic NPs have been proved to be an effective strategy to prevent van der Waals attraction and thus agglomeration of nanoparticles. By using grafting from or grafting to methods, a rich variety of homopolymer, block copolymer, and mixed homopolymer chains have been grafted on the particle, producing various hairy nanoparticles.[3, 4]

Currently, most theoretical and experimental work focuses on homopolymer brush-grafted particles in various polymer matrices, including homopolymers, block copolymers, and polymer blends. For nanocomposites with inorganic NPs and homopolymer matrices, early theoretical studies showed that the interaction between polymer brush-grafted particles and the homopolymer matrix having the same chemical structure is an entropic-driven process. High grafting density and long brush length, where $\sigma(N)^{1/2} > 1$ (σ and N are the grafting density and degree of polymerization of the brush chains, respectively), can effectively deplete the van der Waals attraction among particles, resulting in a better dispersion in polymer matrix.[5] For polymer brushes having different chemical structure from the matrix polymer, the enthalpic effect can play an important role in addition to the entropic effect. If the Flory-Huggins interaction parameter of the matrix polymer with the grafted brushes is negative ($\chi < 0$), the dispersed hairy NPs are stable in the polymer matrix.[6] Recent computational simulations showed that, besides the graft length and grafting density, the graft flexibility and the graft

polydispersity, as well as the curvature and shape of the substrate, could also affect the dispersion of NPs in the homopolymer matrix.[7-9] Inspired by theoretical predictions, extensive experimental studies have been carried out to investigate the nanocomposites with polymer-grafted NPs. By varying the parameters of the grafts, substrate and matrix polymer, dispersion of NPs can be controlled, and the properties of nanocomposites can be tailored.[2]

The interaction between homopolymer-grafted hairy NPs and block copolymers have attracted much attention. When the particle size is smaller than the domain size, the spatial distribution of NPs can be precisely tailored in block copolymer matrices. Computational simulations predicted that the added NPs could locate either in one block phase or at the interface, depending on the particle size and the enthalpic effect,[10-12] and these unique nanocomposites could provide special mechanical and optical properties.[13, 14] These theoretical predictions were later confirmed by experimental studies.[15, 16] In addition, NPs can also alter the morphology and orientation of block copolymer microdomains. According to a simulation study, the size of NPs played an important role in tailoring the morphology of nanocomposite.[17] If the NP size is large compared with polymer chain end-to-end distance, the NPs will influence the formation of block copolymer phase structure. Such prediction was confirmed by experimental studies for nanocomposites with NPs having different sizes.[18, 19] Moreover, block copolymer colloids with novel nanostructures were recently reported by applying polymer-coated gold nanoparticles.[20]

In the matrices of polymer blends, NPs mainly behave as the Pickering surfactants, which locate at the interfaces of different phases, improving the stability of immiscible blends.[21] Distinct phase structures were predicted by a computer simulation to exist at the early stage of phase formation, causing the macrophase separation kinetics of immiscible polymer blends to be

substantially slowed down.[22] The change of polymer blend phase diagrams with addition of NPs has been examined by theoretical investigation, and the morphology of immiscible polymer mixture could be controlled by the size and volume fraction of NPs.[23] For experimental studies, extensive work was conducted for polymer blends with addition of nanoclays.[21] Enhanced miscibility of polymer phases were observed, and mechanical, electrical, and thermal properties of the polymer matrices were improved. Recently, the performance of polymer brush-grafted gold NPs and polymer Janus NPs in polymer blends were investigated.[24, 25] The domain size of the dispersed polymer phase was dramatically reduced with the addition of NPs. Compared with block copolymer compatibilizers, hairy NPs presented more efficient compatibilization.

Research work on block copolymer and mixed homopolymer brush-grafted hairy particles in various polymer matrices has just begun. Using a grafting-from method, poly(*tert*-butyl acrylate) (PtBA) and polystyrene (PS) were grown from the Y-initiator immobilized on the surface of silica particles.[26-28] These hairy particles can demonstrate environmental responsiveness under different solvent conditions.[29] More recently, entropy-driven self-assembly of symmetric PtBA/PS brush-grafted 67 nm silica nanoparticles in PtBA and poly(cyclohexyl methacrylate) (PCHMA) matrices having various molecular weights was reported.[30] Here, the PtBA matrix is compatible with the PtBA brush chains and PCHMA is compatible with the PS brush chains. When the molecular weight of the PtBA matrix is lower than that of the PtBA brush chains, PtBA brush chains will be swollen by the PtBA matrix chains. Meanwhile, the PS brush chains will collapse, forming isolated domains on the mixed brush-grafted silica particles. This is the wet-brush scenario.[2, 30] As a result, the mixed brush-grafted particles can be well-dispersed in the PtBA homopolymer matrix.

When the molecular weight of the *Pt*BA matrix is higher than that of the *Pt*BA brush chains, *Pt*BA and PS brush chains remain intact due to the dry-brush scenario,[2, 30] forming the pristine morphology with bicontinuous microphase separated *Pt*BA and PS domains on silica particles. Consequently, mixed brush-grafted particles aggregated together in the high molecular weight *Pt*BA matrix. For the PCHMA matrix having various molecular weights, a similar situation is obtained, but having a reverse phase morphology. Namely, in a low molecular weight PCHMA matrix, PS brush chains are swollen and *Pt*BA brush chains collapse, forming isolated *Pt*BA domains due to the wet-brush scenario. As a result, the mixed brush-grafted silica particles can be dispersed in the low molecular weight PCHMA matrix. In a high molecular weight PCHMA matrix, the dry-brush scenario is formed and the mixed brush-grafted silica particle aggregate together.

In this study, we continue to investigate the self-assembly behavior of mixed *Pt*BA/PS brush-grafted silica particles in *Pt*BA-*b*-PS diblock copolymer and *Pt*BA/PS blend matrices. For the symmetric diblock copolymer matrix, it would be interesting to see if the ordered lamellar structure of the diblock copolymer can influence or template the nanopattern formation from the mixed *Pt*BA/PS brush chains. If yes, a new nanoscale ring pattern, rather than the pristine random worm-like bicontinuous structure, will form on the 67 nm silica particles. For the polymer blend matrix, we intend to study the entropic interaction condition for the formation of Pickering emulsions using mixed brush-grafted 67 nm silica particles. In both types of matrices, *Pt*BA homopolymer-grafted silica particles are used as controls.

2. Experimental

2.1. Materials

PtBA brush-grafted 67 nm silica nanoparticles were prepared by atomic transfer radical polymerization (ATRP) of *tert*-butyl acrylate from the surface immobilized Y-initiator bearing an ATRP initiator and an alkoxyamine moiety. Mixed PtBA/PS brush-grafted 67 nm silica NPs were prepared by surface-initiated nitroxide-mediated radical polymerization (NMRP) of styrene from the corresponding PtBA brush-grafted 67nm silica nanoparticles. The synthesis details can be found in our previous report.[27] The synthesis of PtBA brush-grafted 23 nm silica NPs followed a procedure similar to that reported in the literature.[31] The characterization data of all polymer brush-grafted silica nanoparticles are summarized in Table 1. PtBA-*b*-PS block copolymers were synthesized by sequential reversible addition-fragmentation chain transfer (RAFT) polymerization of *tert*-butyl acrylate and styrene. The characterization data of different PtBA-*b*-PS block copolymers are listed in Table 2. The PtBA homopolymer with a number-average molecular weight (M_n) of 5 kDa was synthesized by ATRP. Other PtBA and PS homopolymers were purchased from Polymer Source Inc. (Toronto, Ontario, CA). The characterization data of all homopolymers used in this study are listed in Table 3.

Table 1. Molecular characterization of polymer brushes grafted on silica nanoparticles

Samples	PtBA M_n (kDa), DI, and DP ^c	σ_{PtBA} ^d (chains/nm ²)	PS M_n (kDa), DI, and DP ^d	σ_{PS} ^d (chains/nm ²)	PtBA brush volume ratio ^e
HB-1 ^a	22.2, 1.19, 173	0.54	—	—	—
HB-2 ^a	36.6, 1.12, 286	0.53	—	—	—
MB-1 ^b	22.2, 1.19, 173	0.54	11.0, 1.24, 105	0.12	90%
MB-2 ^b	22.2, 1.19, 173	0.54	23.4, 1.17, 224	0.31	63%
MB-3 ^b	24.0, 1.14, 188	0.62	30.3, 1.16, 291	0.52	50%

^a Samples HB-1 and HB-2 are PtBA homopolymer brushes grafted on 67 and 23 nm silica nanoparticles, respectively.

^b Samples MB-1, MB-2 and MB-3 are PtBA/PS mixed brushes grafted on 67 nm silica nanoparticles.

^c The number-average molecular weight (M_n), dispersity index (DI), and degree of polymerization (DP) of polymer brushes are determined by size exclusion chromatography (SEC).

^d σ is polymer brush grafting density, which is calculated based on particle size, thermogravimetric analysis (TGA) data, and molecular weight of the brushes.

^e Brush volume ratio is calculated based on density values of PzBA (1.008 g/cm³) and PS (1.052 g/cm³).

Table 2. Molecular characterization data of PtBA-*b*-PS block copolymers

Samples	M _{n,SEC} (kDa) and DI of PtBA ^a	DP and M _{n,NMR} (kDa) of PtBA ^b	M _{n,SEC} (kDa) and DI of PtBA- <i>b</i> -PS ^a	DP of PS ^b	PtBA volume fraction ^c
BCP-1	7.7, 1.17	55, 7.0	15, 1.12	77	47.8%
BCP-2	13.2, 1.11	98, 12.5	26, 1.16	127	49.8%
BCP-3	25.7, 1.11	210, 26.9	50.4, 1.13	300	47.5%

^a The number-average molecular weight (M_{n,SEC}) and dispersity index (DI) were determined by size exclusion chromatography (SEC) relative to polystyrene standards.

^b The degree of polymerization (DP) and number-average molecular weight (M_{n,NMR}) are obtained from NMR data.

^c PtBA volume ratio is calculated based on density values of PtBA (1.008 g/cm³) and PS (1.052 g/cm³).

Table 3. Molecular characterization data of PtBA and PS homopolymers

	PtBA-1	PtBA-2	PtBA-3	PS-1	PS-2	PS-3
M _n (kDa)	5	23	65	4.8	21	61
DI	1.07	1.15	1.16	1.07	1.04	1.05

2.2. Characterization method and instrumentation:

To study the morphology of homopolymer brush-grafted silica nanoparticles, hairy NPs were dispersed in chloroform at a concentration of 0.01 mg/mL. About 5 μ L of the dispersion was drop-cast onto carbon-coated TEM grids. After chloroform was evaporated, the TEM grid with sample was thermally annealed at 120 °C for 3 h under the protection of dry nitrogen. To study the morphology of polymer brush-grafted silica NPs in the matrices of block copolymers and polymer blends, the hairy NPs were introduced by using two different ways. For the block copolymer matrices, about 8 mg of a block copolymer with 5 wt.% of hairy NPs were dissolved together in 0.1 mL of chloroform. The dispersion were added into a 6 mm diameter alumina pan (Thermal Support, TA style hermetically sealed pan). After evaporation of chloroform, a uniform polymer composite film was formed inside the pan. The film was then annealed in the chloroform vapor at room temperature in a closed jar overnight, followed by thermal annealing in dry nitrogen at 120 °C for 3 h. The polymer composite film was separated from the alumina pan by dissolving the alumina pan using a 0.1 M hydrochloric acid solution. After sputtering the sample surfaces with gold (Anatech Ltd., Hummer 6.2 Sputtering System), the composite

sample was embedded in epoxy resin (SPI-PON 812) for microtoming. Thin sections (~70 nm thickness) were obtained by cross-sectional ultramicrotoming using a Leica EM UC-6 microtome with a diamond knife at room temperature. For polymer blend matrices, 4 mg of the polymer blend of PtBA (65 wt.%) and PS (35 wt.%) with 1.5 wt.% of hairy NPs were dissolved in 2 mL of chloroform. About 5 μ L of the dispersion was drop-cast onto a carbon-coated 200 mesh TEM grid. After drying, the grid was thermally annealed at 120 °C for 3 h in dry nitrogen. All the TEM grids with drop-cast samples were stained by RuO₄ vapor at room temperature for 15 min. TEM was carried out on an FEI Tecnai T12 electron microscope at an accelerating voltage of 100 kV, and bright-field images were recorded using a bottom-mounted Gatan CCD camera.

Fig. 1. Bright-field TEM micrographs of (A) drop-cast HB-1 particles and microtomed thin sections of HB-1 particles in *PtBA-b-PS* diblock copolymer matrices: (B) BCP-1, (C) BCP-2, and (D) BCP-3. All composite samples are stained by RuO_4 for 15 min.

3. Results and Discussion

3.1. *PtBA brush-grafted silica nanoparticles in *PtBA-b-PS* block copolymer matrices*

Fig. 1A shows a monolayer of *PtBA* brush-grafted 67 nm silica nanoparticles (HB-1) on the carbon-coated TEM grid. The M_n of *PtBA* brushes was 22.2 kDa. These silica particles packed in a nearly hexagonal pattern as a result of interparticle interactions facilitated by *PtBA*

brushes. A ~5 nm thick, grey thin layer was seen covering the surface of silica particles, which could be attributed to the collapsed *PtBA* brushes after evaporation of chloroform. In the interstitial space between adjacent particles, some *PtBA* brush bundles were highly stretched and connected as bridges. Figs. 1B-D show the morphology of HB-1 hairy NPs in the matrices of *PtBA-*b*-PS* block copolymers having various molecular weights. The dark layers were PS due to the staining of RuO₄, and the white layers were the unstained *PtBA*. Although these block copolymers were nearly symmetric (i.e., nearly 50 vol.%, see Table 2), the PS layers appeared thicker than the *PtBA* domains in the TEM images. This could be explained by the following. First, the cross-sections were very likely cut at an angle to the lamellar normal. Namely, the *PtBA/PS* interfaces in the thin section were tilted at an angle with respect to the viewing direction. Second, RuO₄ stained the PS domains throughout the entire film. When the samples with a tilted alternating lamellar structure was viewed under TEM, the dark/stained PS domains would produce a thicker projection than the unstained *PtBA* domains. This phenomenon had also been observed in our previous report.[32] For the BCP-1 matrix with the lowest molecular weight, the 67 nm HB-1 particles were able to induce an onion-like structure around them. As the molecular weight gradually increased for BCP-2 and BCP-3, the HB-1 particles could not induce the onion-like structure anymore. Instead, the block copolymer lamellae passed directly through the embedded particles with only slight bending. This could be explained by the bending rigidity of the block copolymer lamellae. When the molecular weight was low (e.g., 15 kDa for BCP-1), the bending rigidity of the block copolymer lamellae was low enough to allow wrapping around the HB-1 particles, because the *PtBA* blocks in the BCP-1 were compatible with the *PtBA* brushes on the HB-1 particles. When the molecular

weight was higher than 26 kDa, the bending rigidity of the block copolymer became high, and thus the lamellae passed directly around the HB-1 particles.

Fig. 2. Bright-field TEM micrographs of (A) drop-cast HB-2 particles and microtomed thin sections of HB-2 particles in *PtBA-*b*-PS* diblock copolymer matrices of (B) BCP-1, (C) BCP-2, and (D) BCP-3. All composite samples are stained by RuO_4 for 15 min.

Changing the particle size would change the surface curvature. Fig. 2 shows HB-2 particles (23 nm silica NP core, see Fig. 2A) in *PtBA-*b*-PS* block copolymer matrices with various molecular weights. Intriguingly, the HB-2 particles always agglomerated in the block

copolymer matrices, regardless of their different molecular weights. Assuming that the PtBA brush density was the same as the bulk (1.008 g/cm^3) and taking account of the PtBA brush molecular weight of 36.6 kDa, the grafting density of 0.53 chains/nm^2 , and the average silica core radius of 11.5 nm, the PtBA brush layer thickness was calculated to be 12.7 nm. Therefore, the HB-2 particle diameter was 48.4 nm, which was consistent with the average distance (45-50 nm) between neighboring particles in Fig. 2A. This particle size was larger than the thicknesses of all the PtBA layers in block copolymers, i.e., 8.6 nm for BCP-1, 11.5 nm for BCP-2, and 17.5 nm for BCP-3 (obtained from small-angle X-ray scattering results[32]). On one hand, it was unfavorable for the block copolymer lamellae to wrap around such small HB-2 particles due to their high curvature. On the other hand, it was impossible for the HB-2 particles to reside in the PtBA layers without getting into direct touch with PS lamellae. As a result, the unfavorable interactions between the PS blocks and the PtBA brushes led to macrophase separation of the HB-2 particles in all the diblock copolymers. This situation was different from other studies, where the hairy particles were smaller than the miscible lamellar thickness.[18, 33] In those studies, the hairy particles could exclusively reside in the miscible lamellae of the block copolymers, no matter in the center of the lamella or at the interfaces.

*3.2. Mixed PtBA/PS brush-grafted silica nanoparticles in PtBA-*b*-PS block copolymer matrices*

Mixed brush particles, MB-1, and the blends with different PtBA-*b*-PS matrices are shown in Fig 3. Because the grafted PtBA brush chains on MB-1 particles are longer and denser than the grafted PS brush chains, the dark PS brush chains organized into isolated domains (short cylinders) in the continuous bright PtBA phase. This is consistent with the low volume fraction of PS, i.e., 10 vol.%. From the side view of the brushes (i.e., at the edges of

silica cores), the bright PtBA phase covered the dark PS domains, revealing the vertical phase separation.

Fig. 3. Bright-field TEM micrographs of (A) drop-cast MB-1 particles and microtomed thin sections of MB-1 particles in diblock copolymer matrices of (B) BCP-1, (C) BCP-2, and (D) BCP-3. All samples are stained by RuO_4 for 15 min.

When MB-1 particles were embedded in the low molecular weight BCP-1 matrix, an onion-like structure was observed around the nanoparticles, similar to the case for HB-1 in

BCP-1. However, the isolated PS domain structures were mostly unperturbed on the MB-1 particles. Again, this onion-like morphology around the MB-1 particles could be attributed to the longer P α BA brush chains on MB-1, which were compatible with the P α BA block in BCP-1.

Fig. 4. Bright-field TEM micrographs of (A) drop-cast MB-2 particles and microtomed thin sections of MB-2 particles in diblock copolymer matrices of (B) BCP-1, (C) BCP-2, and (D) BCP-3. All samples are stained by RuO₄ for 15 min.

Subsequently, the relatively low bending rigidity of the lamellae of BCP-1 allowed the formation of onion-like morphology. When the MB-1 particles were embedded in higher molecular

weight diblock copolymer matrices, BCP-2 and BCP-3, no onion-like structures were observed. Instead, the block copolymer lamellae passed directly around the particles. With increasing the molecular weight, the bending rigidity of the block copolymer lamellae became so high that the onion-like structure would not be allowed. For the MB-1 particles in Figs. 3C and D, the isolated PS domains did not change their morphology as compared to that in Fig. 3A. This was understandable because the isolated PS domains were largely covered by the longer *Pt*BA brush chains and would not have a chance to interact with the PS blocks in the BCP-1.

To enable the interaction between PS brush chains in mixed brush particles and PS blocks in the block copolymer matrix, it was desired to increase the length of the PS brush chains to be comparable with that of the *Pt*BA brush chains. MB-2 particles with similar PS and *Pt*BA brush chain lengths were chosen for this purpose, and the morphology of solution-cast neat hairy particles is shown in Fig. 4A. Different from the MB-1 particles (Fig. 3A), alternating wedge-shaped dark PS and bright *Pt*BA domains radiated out from the silica core, forming bridges among adjacent particles with a hexagonal packing.[27] This could be attributed to similar lengths of the PS and *Pt*BA brush chains. The detailed 3D structure of this self-assembled monolayer film had been reported in a previous publication.[34]

If the *Pt*BA/PS blocks in the diblock copolymers can strongly interact with the mixed *Pt*BA/PS brushes on MB-2, one interesting situation may occur. Namely, the mixed *Pt*BA/PS brushes on the silica particles may conform to the alternating *Pt*BA/PS lamellae in the block copolymer matrix, forming circular stripes on the silica particles. To see if this could be possible, the MB-2 particles were embedded into the block copolymer matrices having different molecular weights by solution-casting. Figs. 4B-D shows the morphology of MB-2 particles embedded in *Pt*BA-*b*-PS matrices with different molecular weights. For the BCP-1 matrix (Fig.

4B), the block copolymer lamellae passed around the MB-2 particles with limited interactions. Namely, some *Pt*BA/PS brush chains were connected with the *Pt*BA/PS lamellae, especially at two poles of the particle along the lamellar direction. On the particle surface, the PS brush chains formed isolated domains with non-spherical cross-sections, regardless of well-organized PS lamellae around them (see the right most particle in Fig. 3B). Note that due to the different grafting densities (0.54 chains/nm^2 for *Pt*BA and 0.31 chains/nm^2 for PS, see Table 1), the volume fractions for the PS and *Pt*BA brushes were 37 vol.% and 63 vol.%, respectively, even though both brush chains were of similar length. The smaller PS volume fraction resulted in isolated PS-brush domains in the *Pt*BA-brush matrix. From the observation in Fig. 4B, the self-assembled morphologies of the *Pt*BA/PS mixed brushes on MB-2 particles and *Pt*BA/PS lamellae in BCP-1 were mostly unperturbed, although they were in intimate contact. This can be explained by the following. At the beginning of solution-casting, the microphase separation has already occurred for the *Pt*BA/PS mixed brushes on MB-2, because the local concentrations of PS and *Pt*BA brush chains are high due to the covalent tethering. Similar microphase separation in a good solvent (DMF) was observed for PAA/PS mixed brushes derived from MB-2, as reported in our recent publication.[35] On the contrary, there is no microphase separation in the dilute chloroform solution for BCP-1. Upon evaporation of chloroform, the BCP-1 starts to microphase separate when the concentration is above certain critical value. The ordering of the BCP-1 could not affect the existing microphase separated morphology of the *Pt*BA/PS mixed brushes on MB-2. Even after solvent and thermal annealing, the interactions between the mixed brushes and the diblock copolymer may still be too weak to alter the pre-existing morphology of microphase separated *Pt*BA/PS mixed brushes on MB-2. For

BCP-2 and BCP-3 matrices, similar situation took place as the MB-2 in BCP-1, regardless of different molecular weights for the block copolymers (see Figs. 4C and D).

To achieve ordered microphase separation (i.e., circular stripes) of mixed brushes on silica particles using diblock copolymer lamellae as template, we propose the following strategy. On the basis of our previous study,[36] symmetric *PtBA*/*PS* mixed brushes with $M_{n,PtBA} = 10.4$ kDa/ $\sigma_{PtBA} = 0.32$ chains/nm² and $M_{n,PS} = 11.9$ kDa/ $\sigma_{PS} = 0.34$ chains/nm² are disordered after thermally annealing at 120 °C. However, the BCP-1 with $M_{n,PtBA} = 7.7$ kDa and $M_{n,PS} = 7.3$ kDa is ordered after thermal annealing at 120 °C (see Figs. 3B and 4B). Comparing these results, it is clear that mixed brushes should have a lower order-to-disorder transition temperature (T_{ODT}) than the corresponding diblock copolymer having the same block lengths. Based on our recent report,[32] this is attributed to the crossover interphase zone between the *PtBA* and *PS* mixed brushes when they microphase separate laterally. If this is the case, it is possible to heat the MB-2/block copolymer blends to a high enough temperature that the mixed brushes will undergo an order-to-disorder transition, whereas the diblock copolymer is still in the ordered state. Upon slow cooling back to room temperature, the ordered diblock copolymer lamellae may be able to dictate the ordered structure formation of mixed brushes on the silica NPs. Following this idea, we have carried out corresponding studies. Unfortunately, after annealing the MB-2/BCP-1 blend at 160 °C for 30 min, no significant difference is observed for the brush morphology, as compared to that in Fig. 4B (data not shown). Further annealing the sample above 160 °C and/or for a longer time will cause the formation of many nano-sized bubbles in the blend, indicating significant thermal degradation of *PtBA* (i.e., cleavage of the *tBA* side groups from the main chain[32]). Therefore, it is impossible for the MB-2/BCP-1 blend to achieve ordered microphase separation (i.e., circular stripes) of mixed brushes on silica particles.

More thermally stable mixed brushes (e.g., *Pn*BA/PS) need to be synthesized and investigated in the future.

Fig. 5. Bright-field TEM micrographs of (A) drop-cast MB-3 particles and microtomed thin sections of MB-3 particles in diblock copolymer matrices of (B) BCP-1, (C) BCP-2, and (D) BCP-3. All samples are stained by RuO_4 for 15 min.

Given what was learned for MB-1 and MB-2 particles in different block copolymer matrices, it would be interesting to see what would happen when further increasing the length for

the PS brush chains. Fig. 5A shows the morphology of a monolayer of MB-3 particles cast from chloroform. For MB-3 particles, PS brush chains had a higher degree of polymerization ($DP = 291$) than *Pt*BA brush chains ($DP = 188$), whereas the overall volume fraction of *Pt*BA was close to 50 vol.%. These features resulted in both vertical and lateral microphase separation, i.e., the longer PS brush chains in the top layer (i.e., the dark rings in the image) and bicontinuous *Pt*BA/PS domains in the bottom layer.

Figs. 5B-D show the morphology of MB-3 particles embedded in *Pt*BA-*b*-PS matrices with different molecular weights. Supposedly, the longer PS brush chains should be able to induce the onion-like structure in BCP-1, similar to the case of MB-1 in MCP-1. However, the BCP-1 lamellae passed around the MB-3 particles without forming any onion-like structure (Fig. 5B). We speculate that the PS brush chains were not long enough to completely shield the *Pt*BA brush chains, and the unfavorable interactions between the *Pt*BA brush chains in MB-3 and PS blocks in the matrix prevented the formation of the onion-like structure. Note that it was somewhat difficult to synthesize even longer PS brush chains than 35 kDa using the NMRP technique in our mixed brush system.

Fig. 6. Bright-field TEM micrographs of HB-1 NPs in polymer blend matrices of (A) *Pt*BA-1/PS-1, (B) *Pt*BA-2/PS-2, and (C) *Pt*BA-3/PS-3. All samples are stained by RuO_4 for 15 min.

3.3. PtBA brush-grafted silica particles in PtBA/PS blend matrices

Before the investigation of mixed brush particles in PtBA/PS blends, we first investigate the PtBA homopolymer brushes in PtBA/PS blends. Fig. 6 shows the HB-1 embedded in the PtBA/PS blends having different molecular weights. Here, the PS content was fixed at 35 wt.% for all the blends, and thus PS formed the minor phase. Instead of the method of microtoming bulk blend samples for sample preparation, the drop-casting method was adopted because it was a facile and effective method, as we reported before.[30] For all three blends, the HB-1 particles always resided in the PtBA phases due to the compatibility of PtBA brushes with the PtBA matrices. However, there were some differences for blends with different molecular weights as compared to that of the PtBA brushes on HB-1. When the molecular weight of the PtBA homopolymer in the blends was not higher than that of the PtBA brushes on HB-1, the wet-brush scenario was formed,[30] where the PtBA homopolymer wetted the PtBA brush chains and helped the dispersion of HB-1 particles in the PtBA matrices (see Figs. 6A and B). When the molecular weight of the PtBA homopolymer in the blends was higher than that of the PtBA brush chains on HB-1, the dry-brush scenario was formed,[30] where the PtBA matrix started to repel the PtBA brush chains on HB-1 particles. As a result, a significant amount of HB-1 particles are located near the PtBA/PS interfaces in the PtBA matrix (Fig. 6C).

Fig. 7. Bright-field TEM micrographs of HB-2 NPs in polymer blend matrices of (A) PtBA-1/PS-1, (B) PtBA-2/PS-2, (C) and PtBA-3/PS-3. All samples are stained by RuO₄ for 15 min.

When the silica core size decreased from 67 nm (HB-1) to 23 nm (HB-2), the dispersion of homopolymer brush particles in various PtBA/PS blends was investigated, and results are shown in Fig. 7. Again, HB-2 particles dispersed well in the PtBA phases when the molecular weight of the PtBA homopolymer in the blends was lower than that of the PtBA brush chains (Figs. 7A and B). This was attributed to the web-brush scenario. When the molecular weight (65 kDa) of the PtBA homopolymer in the blend was higher than that (36.6 kDa) of the PtBA brush chains, most HB-2 particles still dispersed relatively well in the PtBA matrix with only a few particles near the PtBA/PS interfaces (Fig. 7C). This could be attributed to the high curvature effect of the hairy particles, as we recently reported.[30] When the particle core was small, the grafted brush chains became more splayed in the corona region, leaving space for the PtBA matrix chains to partly penetrate into it. As a result, the compatibility between PtBA brush chains grafted on small NPs and the PtBA matrix was improved. Note that there were some 20 nm dark dots in the PS domains in Fig 7. We consider that they were not the HB-2 particles and could be attributed to the reduced RuO₂ particles after RuO₄ staining. These

nano-sized dark dots were also observed in the PS domains in other solution-cast samples (see Figs. 8-10 later).

Fig. 8. Bright-field TEM micrographs of MB-1 NPs in polymer blend matrices of (A) PtBA-1/PS-1, (B) PtBA-2/PS-2, (C) and PtBA-3/PS-3. All samples are stained by RuO₄ for 15 min.

3.4. *PtBA/PS mixed brush-grafted silica particles in PtBA/PS blend matrices*

Fig. 8 shows the morphology of MB-1 particles embedded in different *PtBA/PS* blends. Because *PtBA* brush chains (DP=173) were longer than *PS* brush chains (DP=105), *PtBA* brush chains dictated the interaction with the surrounding matrix. Therefore, MB-1 particles exhibited similar behavior in polymer blend matrices as the HB-1 particles. Namely, all the MB-1 particles resided in the *PtBA* homopolymer domains for different blends. However, there were distinct differences due to the unfavorable interactions between the matrix homopolymer chains and the *PS* brush chains as the matrix homopolymer chains penetrated the *PtBA* brush chains on silica particles. When the molecular weight (5 kDa) of the *PtBA* matrix was lower than that (22.2 kDa) of the *PtBA* brush chains, MB-1 NPs disperse relatively well in the *PtBA* matrix because of the wet-brush scenario (Fig. 8A). When the molecular weight (23 kDa) of the *PtBA* matrix was similar to that of the *PtBA* brush chains, there were a significant amount of MB-1 particles that accumulated at the *PtBA/PS* interfaces as a result of the dry-brush scenario (Fig. 8B). When the molecular weight (65 kDa) of the *PtBA* matrix was higher than that of the *PtBA* brush chains (the dry-brush scenario), the MB-1 NPs tended to form certain aggregates around the *PS* domains (Fig.

Fig. 9. Bright-field TEM micrographs of MB-2 NPs in polymer blend matrices of (A) PtBA-1/PS-1, (B) PtBA-2/PS-2, and (C) PtBA-3/PS-3. All samples are stained by RuO₄ for 15 min.

8C). For individual MB-1 NPs, isolated PS domains were seen on the surface of the silica core, resembling the morphology of neat MB-1 particles seen in Fig. 3A.

When the MB-2 particles were embedded in different PtBA/PS blends, the morphology is shown in Fig. 9. Intriguingly, most MB-2 particles were located in the dark PS domains. Note that the brush length of PS (DP=224) were slightly longer than that of PtBA (DP=173), although the PtBA brushes had a higher volume fraction of 63 vol.%. It was the longer PS brush chains that caused the MB-2 particles to preferably reside in the PS domains. When the molecular weight (4.8 kDa) of the PS homopolymer was smaller than that (23.4 kDa) of the PS brush chains, the MB-2 particles located inside the PS domain (Fig. 9A). When the molecular weight (21 kDa) of the PS homopolymer was similar to that of the PS brush chains, the MB-2 NPs tended to locate near the PS/PtBA interface (Fig. 9B). When the molecular weight (61 kDa) of the PS homopolymer was higher than that of the PS brushes, significant particle aggregation took place with many of them located at the PS/PtBA interface (Fig. 9C). The situations in Figs. 9B and C could be ascribed to the dry-brush scenario.

Fig. 10. Bright-field TEM micrographs of MB-3 NPs in polymer blend matrices of (A) *Pt*BA-1/PS-1, (B) *Pt*BA-2/PS-2, and (C) *Pt*BA-3/PS-3. All samples are stained by RuO₄ for 15 min.

Fig. 10 shows the morphology of MB-3 particles in different polymer blend matrices. Again, the MB-3 particles resided in PS domains for all blends because of the longer PS brush chains. In Figs. 10A and B, the molecular weights (4.8 and 21 kDa) of the PS matrices were smaller than that (30.3 kDa) of the PS brush chains. As a result, MB-3 nanoparticles were well-dispersed in the PS homopolymer phase because of the wet-brush scenario. For individual MB-3 particles, isolated white *Pt*BA nanodomains could be observed, instead of the original bicontinuous *Pt*BA/PS structure (Fig. 5A). It was possible that penetration of the matrix PS chains into the *Pt*BA/PS mixed brushes caused isolation of *Pt*BA brush domains on MB-3 particles. In Fig 10C, the molecular weight (61 kDa) of the PS matrix was higher than that of the brush chains. Owing to the dry-brush effect, the MB-3 particles were pushed to the interface between *Pt*BA and PS domains.

4. Conclusions

In summary, the self-organization behavior of two *Pt*BA homopolymer brush-grafted silica NP samples (67 and 23 nm silica cores) and three mixed *Pt*BA/PS brush-grafted 67 nm silica NP samples (longer *Pt*BA, nearly symmetric, and longer PS brush chains) was studied in the matrices of *Pt*BA/PS diblock copolymers and polymer blends with different molecular weights. Delicate entropic interactions between the homopolymer/mixed brushes and the block copolymer/polymer blend matrices, i.e., wet- and dry-brush scenarios, played an important role in the self-organization. A few important lessons have been learned through this study.

First, the *Pt*BA homopolymer brush-grafted 67 nm silica NPs could induce the onion-like structure in a low molecular weight block copolymer matrix, as a result of low curvature of the particles and low bending rigidity of the block copolymer lamellae. Neither small NPs (23 nm silica core) nor high molecular weight diblock copolymers were able to induce the onion-like structure. Similarly, the onion-like structure could also be induced by *Pt*BA/PS mixed brush particles with much longer *Pt*BA brush chains (i.e., MB-1).

Second, block copolymer lamellar matrices could not dictate the microphase separation of mixed brushes grafted on 67 nm silica NPs to achieve ordered lamellar pattern on spherical particles. This was primarily attributed to the fact that the microphase separation of mixed brushes took place before the microphase separation of the block copolymers during the solution-casting process.

Third, for homopolymer/mixed brush particles in polymer blends, the molecular weights of the binary blends were important. In a low molecular weight blend (web-brush scenario), the hairy NPs adopted uniform dispersion in the preferred domains. In a high molecular weight blend (dry-brush scenario), the hairy NPs tended to segregate to the interfaces. The results and lessons learned from this study can facilitate the design and preparation of polymer-hairy NP nanocomposites with tailored structures and properties.

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Graphical Abstract

Self-Organization of Homopolymer Brush- and Mixed Homopolymer Brush-Grafted Silica Nanoparticles in Block Copolymers and Polymer Blends

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