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Design and Fabrication of Janus Nanoparticles for Interfacial Distribution in Block Copolymers

Qiuyan Yang, Katja Loos*

Hybrid composites with highly ordered structures show promise for applications in various fields and thus there is great interest in their fabrication. In this context, Janus nanoparticles (JNPs) are synthesized with the aim of further incorporating them into polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) block copolymers to fabricate hybrid composites. It is observed that the dispersed JNPs are located at the boundary of the two morphological phases in PS-*b*-P2VP. The orientation of the lamellar structure in the bottom and free surface region of the block copolymer (BCP) composites shows a distinct difference as the composition of the JNPs is adjusted. The processing conditions of the nanoparticle/BCP composites are found to play an important role in achieving the desired structures.

1. Introduction

Incorporating nanoparticles (NPs) into polymeric materials is a practical pathway to develop engineered plastics with improved mechanical, optical, electrical, magnetic, and other properties. It is also one of the most attractive ways to obtain well-defined structures at different length scales by controlling the spatial organization of NPs inside polymers.^[1–13] The ability to control the length, spatial, and orientational organization of block copolymer (BCP) morphologies (from spherical to cylindrical, bicontinuous, and lamellar structures) makes BCP materials attractive as templates for manipulating the spatial location of inorganic NPs at various lengths, from the micro to the nano scale. Even though several general strategies based on the understanding of complex BCP-particle interactions have been proposed, precisely controlling the location of NPs in polymer matrices remains an obstacle in fabricating BCP-NP functional materials.^[2]

Of particular interest is controlling the assembly of inorganic or metallic NPs at the interface between different phase domains of BCPs, to achieve a high degree of order and even responsive behavior.^[14] These types of highly ordered hybrid materials have potential applications in flexible sensors,^[15–19] tunable plasmonic nanostructures for surface-enhanced Raman scattering,^[20–23] ultrafast switches and organic memory devices,^[24,25] and advanced photovoltaic devices.^[26,27]

For the purpose of interfacial localization of NPs inside BCPs with enhanced stability, particles with amphiphilic surface properties are preferably used, such as NPs grafted with a mixture of ligands,^[28–30] random copolymer-anchored NPs,^[29] or Janus-type NPs.^[31] Janus nanoparticles (JNPs) with two chemically different grafting compartments are especially reported to strongly adsorb and orient to the interface due to their higher interfacial activity and their stronger amphiphilicity compared to homogeneous polymer-grafted NPs.^[32–41] In addition, the orientation and off-center position of JNPs at the interfaces of BCP composites are also reported to be tunable, which is usually governed by an intricate balance of enthalpic and entropic interaction.^[38–41] However, as experimental studies on the incorporation of JNPs in BCP scaffolds are rare, it is difficult to draw a firm conclusion about which of the three types of amphiphilic particles is better for interfacial location just yet. To compare

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and thus reach a conclusion, more thorough studies on JNPs are needed. In addition, establishing a more detailed knowledge of the effect of JNPs on their position in BCP scaffolds is still needed to create nanocomposites with the desired structures.

In this paper, polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) is used as the scaffold for the incorporation of silica JNPs, which were surface functionalized by PS and P2VP on opposite hemispheres. The distribution and location of the JNPs inside PS-*b*-P2VP in both bulk and thin films, as well as the resulting change in phase orientation of the BCPs, are investigated and discussed in detail. In fact, as the location of the NPs in the BCPs and the overall structure of the hybrids are ultimately controlled by thermodynamics, the processing conditions of BCP-JNP composites can play an important role in achieving the desired structures and functional properties and thus influence structure-property relations.^[2] Therefore, the influence of various processing parameters on the resulting composite structure is also discussed in order to get better control over the structure and properties of BCP-JNP composites in the future.

2. Results and Discussion

2.1. Synthesis of Janus Nanoparticles

Figure 1 demonstrates a typical procedure for the preparation of Janus nanoparticles coated with poly(2-vinylpyridine) (P2VP) on one hemisphere and polystyrene (PS) on the other. Firstly, negatively charged $-\text{COOH}$ surface functionalized PS spheres (200 nm) were surrounded by positively charged $-\text{NH}_2$ surface functionalized silica particles (10 nm) to form core/satellite hierarchical structures. These hierarchical structures were further stabilized via a carbodiimide-assisted coupling between the $-\text{COOH}$ groups from the surface of PS spheres with the $-\text{NH}_2$ groups from the surface of silica particles. The TEM image in Figure 2 indicates the successful preparation of such PS/silica hierarchical composites. In the following step (Figure 1b), carbon dioxide (CO_2) was applied to soften the PS template and thus to allow the target silica particles to be embedded inside the PS templates. The NP embedding depth into the PS template was adjustable by controlling the pressure or the temperature of CO_2 .^[42] In this way, one hemisphere of

Figure 1. Preparation of Janus silica nanoparticles coated with PS (gray side) and P2VP (dark gray side): (a) 200 nm/10 nm PS/silica hierarchical composites are prepared by a carbodiimide-assisted coupling method; (b) supercritical CO_2 treatment; (c) P2VP is attached by glutaraldehyde and further P2VP- NH_2 surface modification procedures on the exposed hemisphere are conducted to achieve JNPs. The bigger sphere here refers to the $-\text{COOH}$ surface functionalized PS template and the smaller spheres are $-\text{NH}_2$ surface functionalized silica nanoparticles.

Figure 2. TEM images of 200 nm/10 nm PS-COOH/silica-NH₂ hierarchical composites.

the target particles can be protected by embedding them inside the PS template.

Subsequently, it is possible to further modify the still exposed hemisphere with P2VP to fabricate various types of nanosized silica Janus particles, as shown in Figure 1c. As control experiments, silica particles fully coated by various ligands (including -NH₂, -CHO, and P2VP, as listed in Table 1 in the Experimental Section) were also prepared via the same procedure. The first step (the reduction reactions on the exposed hemisphere of silica NPs by glutaraldehyde) was performed in an aqueous environment, which could even render the formation of

the imines unnecessary.^[43,44] It has been reported that this reaction type possibly proceeds via reduction of the hemiaminal species.^[45] Generally, intermediate formation and reduction by sodium cyanoborohydride occurs sequentially in one pot and reactions can be completely finished in quite short times. This was confirmed by using TGA measurements (see Figure S1, Supporting Information) as no obvious differences were observed when decreasing the reaction time from 24 h to 2 h, even though there was a slight difference in the overall weight loss of the samples. The random weight loss below 150 °C could be attributed to residual solvent attracted by hydrophilic functional groups on the silica NPs. The subsequent modification by P2VP was conducted in methanol in which both NPs and P2VP-NH₂ ligands can be well dissolved. As shown in Figure S2 in the Supporting Information, the weights of the ligands on the surface of the silica NPs increased step by step with each step of the reaction, indicating the successful surface modification of aldehyde ligands and subsequently P2VP on the silica NPs. However, because of the strong absorption of bulk silica in FTIR spectra, the typical absorption bands of aldehyde and P2VP overlapped with these broad peaks, but are still visible in Figure S3 in the Supporting Information.

Finally, PS templates can be removed by dissolving methods in organic solvents (such as toluene, DMF, and THF). In this way, PS chains will be covalently attached on the other side of the JNPs due to the carbodiimide-assisted coupling between silica particles and the PS template (Figure 1c). By following the same surface modification procedure mentioned above, P2VP and PS-coated silica JNPs can thus be obtained.

Figure 3a shows the FTIR spectra of the JNPs synthesized via the embedding treatment at 40 °C, at 60 bar in CO₂. Absorption peaks of aromatic C-C stretching were observed in the region between 1400 and 1500 cm⁻¹ as well as from 1500 to 1600 cm⁻¹ in the spectra of the Janus particles, which can be attributed to the presence of PS or P2VP, respectively. To be honest, it is hard to distinguish the contribution of PS and P2VP solely by FTIR measurements, because the features of the absorption peaks (aromatic C-C stretching) of PS and P2VP always appear at similar wavenumber regions and the typical absorptions of the C-N stretch in P2VP were overlapped by the strong absorption of silica (Figure S4, Supporting Information).

However, the TGA curves in Figure 3b demonstrate the successful synthesis of P2VP and PS-coated silica JNPs. The total weight loss of silica NPs with further functionalization by P2VP demonstrated an increase compared to that of silica NPs that were partially modified with PS, indicating P2VP successfully reacted with the exposed side of the silica particles. In addition, a delay of the second terrace in the region between 400 and 500 °C was observed in Figure 3b when comparing the red TGA curve

Table 1. The surface composition of synthesized silica particles.

Nanoparticles	Surface modification	
	Functional end group	Embedment in CO ₂
SiO ₂ -NH ₂	-NH ₂ fully coated	No
SiO ₂ -CHO	-CHO fully coated	No
SiO ₂ -P2VP	-P2VP fully coated	No
PS-SiO ₂ -60	-PS partially coated	40 °C, 60 bar
JNPs-50	-PS partially coated	40 °C, 50 bar
	-P2VP partially coated	
JNPs-60	-PS partially coated	40 °C, 60 bar
	-P2VP partially coated	
JNPs-66	-PS partially coated	40 °C, 66 bar
	-P2VP partially coated

Figure 3. FTIR spectra (a) and TGA curves (b) of silica nanoparticles with various surface functionalizations.

with the blue one. This phenomenon can be considered as the contribution of P2VP on the final Janus silica NPs, which has a higher thermal degradation temperature, as shown in Figure S5 in the Supporting Information.

2.2. Nanoparticles and PS-*b*-P2VP Composite Thin Films

JNPs were dispersed into a PS-*b*-P2VP solution in toluene to prepare mixtures with different fractions (1 to 10 wt%) of nanoparticles. The fraction of NPs was calculated by the mass ratio between the NPs and the block copolymer in solution. The hybrid thin films of JNPs were spin-coated from a PS-*b*-P2VP solution with the JNP fraction from 1 to 10 wt% (a mass ratio between JNPs and PS-*b*-P2VP) and subsequently annealed in chloroform vapor.

In the presence of 1 wt% JNPs-60, the overall phase separation proceeded gradually with the increase of annealing time inside chloroform vapor, as demonstrated in Figure S6 in the Supporting Information. Well-ordered fingerprint structures of BCPs were formed after annealing samples for 115 min (Figure 4), even though less NPs could be observed on the surface of the BCP film via AFM or inside the BCP from the TEM images in

Figure S7 in the Supporting Information), probably due to the quite low fraction of NPs and the aggregation. It was also found that only partially lamellar structures formed as the fraction of JNPs-60 increased to 10 wt% (Figure 4c). However, by prolonging the annealing time for composite films with 5 wt% JNPs-60 to 120 min, defined structures could be obtained as shown in Figure S8 in the Supporting Information, indicating that phase separation of BCP-JNPs composites requires a longer time to reach ordered structures. A similar phenomenon has also been reported in the literature via simulation methods.^[39] This demonstrates that the strong interactions between polymer blocks and sphere surfaces keep the JNPs attaching to the interface during the process, which depressed the evolution of nanocomposites and leads to sluggish kinetics in comparison to those of the pure diblock copolymers.^[39]

Figure 5 demonstrates the distribution of various types of NPs inside PS-*b*-P2VP films, including $\text{SiO}_2\text{-NH}_2$ NPs, $\text{SiO}_2\text{-P2VP}$ NPs, and JNPs (information on the particles is shown in Table 1 in the Experimental Section and JNPs-60 and JNPs-66 refer to JNPs which are prepared with a CO_2 embedding process at 40 $^{\circ}\text{C}$ with a pressure of 60 bar for 140 min, and 66 bar for 2 h, respectively).

Figure 4. AFM surface profiles of JNPs-60 inside PS-*b*-P2VP 80 nm thin films: (a) 1 wt% JNPs-60 in a BCP film, as-spun; (b) 1 wt% JNPs-60 in a BCP film annealing in chloroform vapor at 27 $^{\circ}\text{C}$ for 115 min; (c) 10 wt% JNPs-60 in a BCP film annealed in chloroform vapor at 27 $^{\circ}\text{C}$ for 115 min.

Figure 5. (a,b) AFM surface profiles and (c,d) TEM images of various nanoparticles inside the PS-*b*-P2VP 80 nm thin films annealed in chloroform vapor at 27 °C: (a) 10 wt% SiO₂-NH₂ nanoparticles; (b) 10 wt% SiO₂-P2VP nanoparticles; (c) 5 wt% JNPs-60 nanoparticles, inset is the zoomed-in TEM image from (c); (d) 10 wt% JNPs-66 nanoparticles.

Despite the aggregation of NPs inside block copolymers (shown as an irregular white region in Figure S9 in the Supporting Information), the monodispersed particles of both SiO₂-NH₂ and SiO₂-P2VP NPs (the white dots in the AFM images from Figure 5a and 5b) were observed to disperse just in one of the domains. Also, as expected, both dispersed JNPs-60 and JNPs-66 (the black dots in the TEM images from Figure 5c and 5d) were found to be located at the boundary between the two phases.

However, aggregation of all types of NPs was found to be the main problem for distributing the NPs evenly inside the BCP films and thus hindered preparation of the highly ordered hybrid materials in Figure 5. The solvent seems to play an important role in the dispersion of NPs as well as the subsequent annealing processes, especially for Janus-type particles. In the case of toluene, in which the PS-*b*-P2VP copolymer exists as spherical micelles with a PS corona and a P2VP core due to the favorable interaction with the PS domains,^[46–48] NPs may have similar tendencies to form micelle-like structures inside

the BCP solution upon competitive interactions between NPs, block copolymer, and also toluene. This might also be the reason why the NPs were already observed to be aggregated (shown as irregular white regions in Figure S9 and S10 in the Supporting Information) in the as-spun films, even though JNPs-60 can disperse well in toluene without the presence of BCPs (Figure S11, Supporting Information). Chloroform is believed to be a better solvent for PS-*b*-P2VP and transparent solutions were prepared by dissolving PS-*b*-P2VP copolymers in chloroform. However, the chloroform vapor annealing process greatly enhanced the phase separation of BCPs but did not work quite as effectively to evenly distribute NPs inside the composite films. We also tried to use chloroform as a solvent to disperse particles in BCP solutions for spin-coating but still encountered the aggregation problems of NPs inside the films (Figure S12, Supporting Information), which can be attributed to the fast movement of particles and also the high evaporation rate of chloroform during the spin-coating process.

The kinetically trapped solvent vapor annealing (SVA) method holds the advantage of generating novel structures in non-equilibrium states. However, in solvent-based processes, a selective solvent can promote a wide variety of morphologies but may thus trap JNPs in one domain of the composite instead of at the boundary, whereas a neutral solvent can be more beneficial in distributing particles inside BCPs than a selective solvent but may result in challenges to obtaining ordered structure of BCPs.^[49] Therefore, more investigations on the influence of various processing parameters on the resulting composite structures are still required in the future to get better control over the structures and properties of BCP-JNP composites.

2.3. Incorporation of Nanoparticles in Bulk PS-*b*-P2VP

The distribution and the location of Janus silica NPs inside the BCP bulk were also investigated in detail by observing their cross-sectional structures by TEM. As shown in Figure 6a, when the PS-*b*-P2VP samples were drop-casted

and annealed in a chloroform vapor atmosphere, ordered lamellar structures were obtained in bulk samples except in the regions closed to the free surface and the substrate. Figure 6b–d demonstrate the cross-sectional structures of BCP-JNPs composites, where JNPs-66, JNPs-60, and JNPs-50 refer to JNPs which are prepared with a CO₂ embedding process at 40 °C with a pressure of 66 bar, 60 bar, and 50 bar, respectively. As discussed in our previous work,^[42] the embedding degree of the target silica NPs increases with the applied CO₂ pressure. A higher embedding degree will result in less exposed surface areas of immobilized silica NPs and thus a lower ratio of P2VP functionalization on the final obtained JNPs, i.e., the fraction of P2VP on the JNPs will ideally follow an order of JNPs-66 < JNPs-60 < JNPs-50. Despite the aggregation problems of NPs, the dispersed Janus-type NPs were observed to be located at the boundary between PS and P2VP domains (shown as the dark dots in Figure 6). However, no obvious differences in the position of located JNPs with respect to the center of phase boundary were found with the

Figure 6. Cross-sectional TEM images of different 5 wt% JNPs in the PS-*b*-P2VP bulk samples annealed under chloroform vapor atmosphere at 27 °C for one week: (a) bulk BCP; (b) JNPs-66; (c) JNPs-60; (d) JNPs-50.

adjustment of the Janus balances (the composition ratio between PS and P2VP on the surface of JNPs). This could have several possible reasons, including the strong amphiphilicity of the three types of JNPs, the high molecular weight of PS ($\bar{M}_n = 97.8 \text{ kg mol}^{-1}$ and $\bar{M}_w = 574.1 \text{ kg mol}^{-1}$ from GPC measurements of the PS spherical templates dissolved in DMF) and P2VP ($\bar{M}_n = 135.6 \text{ kg mol}^{-1}$, PDI = 1.04 as bought) on the JNPs' surfaces, and the relatively small surface area difference between the coated PS and P2VP under the given synthetic conditions.

It is worth mentioning that the orientation of the lamellar structures at the close to substrate regions turned from parallel to perpendicular (regarding to the substrate) in the presence of JNPs, as shown in Figure 7a–c. In particular, the multi-layers of JNPs-60 coated at the bottom rendered the selectivity of the substrate for P2VP^[50] to become relatively neutral. In the case of JNPs-50 (Figure 7d), which in principle contains the highest amount of P2VP on the surface, the orientation of the lamellas showed a trend to transfer from

perpendicular to parallel when compared to JNPs-60, which could be attributed to the higher loading of PS ligands on the JNPs-50 surface. Similar phenomena were also observed from the domain orientation change in the close free surface region in Figure S13 combining with Figure S14 in the Supporting Information. In the above results, JNPs functioned as a kind of surfactant, which would be interesting to control block copolymer nanodomain orientation.^[51–55] In turn, the unexpected result that JNPs induce an orientation change of BCP domains confirms the “amphiphilic” property and also the difference in the composition of these three types of JNPs.

For comparison, thermally annealed bulk composites samples (140 °C over a week) were prepared as well. However, long-range ordered structures were not formed in the given annealing time scale (Figure S15, Supporting Information). The BCP bulk sample also demonstrated different morphologies to the above mentioned SVA annealed BCP samples. In the free surface region, the lower surface tension block preferentially segregated to the free surface and

Figure 7. Cross-sectional TEM images of the bottom region in PS-*b*-P2VP bulk composite sample with or without 5 wt% Janus-type nanoparticles inside: (a) bulk BCPs; (b) JNPs-66; (c) JNPs-60; (d) JNPs-50. All samples were prepared by annealing under chloroform vapor atmosphere at 27 °C for a week.

Figure 8. Cross-sectional TEM images of 5 wt% JNPs-60 dispersed in the PS-*b*-P2VP bulk samples annealed by thermal heating at 140 °C for a week.

to from a parallel patterning.^[56] Only incomplete phase separation was achieved in the bulk region here due to the high molecular weight of such a BCP.

Although longer thermal annealing time is necessary to get a thermodynamic equilibrium state with highly ordered structures, other useful information can also be provided by the trapped non-equilibrium state of the BCP-JNP composites. For example, a detailed kinetic movement of BCP-JNP NPs is expected to be reflected by the snapshot captured on the location of JNPs. Figure 8 shows TEM images of JNPs-60 in bulk composites by thermal annealing at 140 °C for one week where long range order was not yet reached. More TEM images can be found in Figure S16 in the Supporting Information. The dispersed JNPs (small dark dots in the TEM images) were observed favorably anchoring at the boundaries between the two phases, as predicted by simulation experiments,^[39] although the aggregated clusters were located in one phase.

Despite all this, with the aim of achieving much better JNP localization at the boundary of domains, more efforts on how to minimize JNP aggregation and how to control the competition between JNP loadings at the domain interfaces and the bottom (or surface) are needed by researchers in this field.

3. Conclusions

Despite the aggregation problems of NPs, the dispersed Janus-type NPs were observed anchoring at the boundary of two phases inside the BCP scaffold in both thin film and bulk samples. In the presence of JNPs-60, selectively oxidized silicon substrates turned neutral for PS-*b*-P2VP and a transformation from a parallel to a perpendicular orientation of the lamellar structures occurred at the bottom

region in bulk samples, proving the “amphiphilic” properties of JNPs-60 for the block copolymer. JNPs-60 also demonstrated a preference to anchor at the boundary of two difference phases in the non-equilibrium state obtained via a thermal annealing approach. Parallel structures were retained when the content of P2VP on the JNPs was low, as in the case of JNPs-66 in the region close to the bottom of the material. However, JNPs-50, which in principle holds the highest amount of P2VP on the surface, favorably aggregated at the interface between the substrate and PS-*b*-P2VP. This also led to partial changes in the parallel structures in this region. Structures in the surface regions were also observed to change according to the type of applied JNPs.

Unfortunately, the aggregation of all types of NPs was found to be the main problem for distributing NPs inside BCP films and thus was a barrier to preparing highly ordered hybrid materials. Solvents seemed to play an important role in dispersion of the NPs and also the subsequent annealing process. Actually, the location of NPs in BCPs and the overall structure of hybrids were ultimately controlled by thermodynamics, and the processing conditions of the NP and BCP composites play an important role in achieving the desired structures and functional properties. More investigations on the influence of various processing parameters on the resulting composite structure are still required to obtain better control over the structure and properties of BCP-JNP composites.

4. Experimental Section

4.1. Materials

Aqueous suspensions of 200 nm polystyrene microspheres functionalized with carboxyl groups (2.6 w/v%), and aqueous suspensions of 10 nm silica NPs were obtained from

Polyscience Inc. The amino terminated poly(2-vinyl pyridine) (P2VP-NH₂, $\bar{M}_n = 135.6 \times 10^3 \text{ g mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 1.04$) and PS-*b*-P2VP block copolymer (P5742-S2VP, $\bar{M}_n$ (PS) = 133 000 g mol⁻¹, $\bar{M}_n$ (P2VP) = 132 000 g mol⁻¹, $\bar{M}_w/\bar{M}_n = 1.15$) were purchased from Polymer Source, Inc. and used as received. Sodium cyanoborohydride (95%), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC, protein seq. grade), N-hydroxysuccinimide (NHS, 98%), monopotassium phosphate (>99.0%), 3-[N-morpholino] propanesulfonic acid (MOPS, ≥99.5%), 3-aminopropyltriethoxysilane (APTES), and glutaraldehyde solution (Grade I, 50% in H₂O) were purchased from Sigma-Aldrich. Hydrophilic polycarbonate membrane filters (pore size 100 nm, 0.1 microns with a diameter of 47 mm) were purchased from Sterlitech Corporation. All solvents were of analytical grade.

4.2. Preparation of Silica/PS Hierarchical Composites

The hierarchical composites were prepared by coupling -NH₂ groups functionalized with 10 nm silica particles with -COOH functionalized 200 nm PS spheres. Commercial bare silica NPs were functionalized with APTES by quickly adding 0.3 mL of APTES under vigorous stirring. An excess amount of silica-NH₂ spheres were dispersed in 10 mL of MOPS buffer (pH = 6.0, 0.025 M) and then the PS-COOH spheres were added to the solution. This suspension was sonicated for approximately 10 min to completely mix the spheres, because of the electrostatic forces and the presence of excess silica-NH₂, each negatively charged PS-COOH was surrounded by positively charged silica-NH₂ spheres. At this stage, 0.1 g of EDC and 0.03 g of NHS in 10 mL of MOPS buffer (pH = 6.4, 0.025 M) was added to the mixture, followed by slow rotation for 24 h. The colloidal solutions were centrifuged and washed with water several times to remove unreacted chemicals. In addition, the hierarchical composites were filtrated by using hydrophilic polycarbonate membranes with pore sizes of 0.1 micron to remove excess silica particles. A droplet of diluted hierarchical composite sample was dried on carbon coated copper grid for TEM imaging.

4.3. Embedding Treatment in CO₂

The prepared samples with hierarchical structures were first added to the reaction vessel (50 mL). Subsequently, the temperature of the sample was set to the desired value by a heating controller (Eurotherm controller, The Netherlands) and the set-up was refreshed with CO₂ for at least 10 s to flush the air inside. Subsequently, CO₂ was added using a membrane pump (Lewa, USA) to the cylinder until the desired pressure was reached. Most of the samples were allowed to be in continuous contact with CO₂. After the treatment, the pressure was slowly released by venting.

4.4. Preparation of PS and P2VP Coated Nanoparticles and Janus Silica Nanoparticles

Fully aldehyde group-coated silica NPs were prepared by modifying the amino groups of silica NPs with 600 μL of glutaraldehyde in 30 mL of PBS buffer (pH = 7.4, $10 \times 10^{-3} \text{ M}$) with reduction by 30 mg of sodium cyanoborohydride. A series of experiments

with 2 h, 6 h, 8 h, and 24 h reaction time were conducted to investigate the reaction time needed for complete conversion of amino groups. The results showed no obvious difference on the weight loss of the final products in TGA results, indicating reactions were already completely finished within 2 h. A high excess amount of glutaraldehyde was used here and the reactions were conducted in quite dilute solutions to avoid crosslinking. Samples were washed with PBS buffer and methanol, and were re-dispersed into 13.5 mL of methanol to further react with 1.5 mL of 2.0 w/v% amino functionalized poly(2-vinylpyridine) (P2VP-NH₂), reduced by 30 mg sodium cyanoborohydride. The washed samples were further dried under a vacuum overnight and dissolved in DMF to remove PS templates.

The exposed hemispheres of the embedded silica NPs on the surface of 200 nm sized PS templates were firstly allowed to react with glutaraldehyde and then with P2VP-NH₂ to obtain Janus silica particles, following the same procedure mentioned above. All types of silica particles synthesized are shown in Table 1.

4.5. Preparation of PS-*b*-P2VP and Hybrid Composite Thin Film

Thin films of PS-*b*-P2VP were prepared by spin-coating of the polymer solution onto 1 × 1 cm silicon wafer. The obtained films were dried under a vacuum to remove the retained solvent before further solvent vapor annealing, especially when different solvent vapors were applied for annealing. However, the as-spin-coated samples were directly used for solvent vapor annealing if the solvent vapor was the same as that of the casting solvent. SVA treatments were conducted in a 60 mL glass container with solvent vapors by placing the spin-coated films at the bottom. One open small 4 mL bottle, which was typically filled with 2 mL of solvent, was placed inside this container to yield the solvent vapor. By closing the lid of the container and putting it inside a chamber with proper temperature control, the relative solvent vapor pressure inside the dish could roughly be adjusted, resulting in swelling of the films to different swelling ratios. Solvent vapor annealing was conducted in chloroform at 27 °C for different times to obtain well-ordered structures.

Thin films of the hybrid composites were cast from a mixture of PS-*b*-P2VP solution and the as-synthesized NPs (with a volume fraction of NPs from 1 to 10 wt%) and subsequently annealed under the same conditions described above.

Thin films of PS-*b*-P2VP and hybrid composites prepared by spin-coating were floated off silicon substrates by immersing the samples in 1 wt% NaOH aqueous solution for 30 min and then were dried onto copper grids for TEM imaging.

4.6. Preparation of PS-*b*-P2VP and Hybrid Composite Bulk Samples

Bulk PS-*b*-P2VP samples were prepared by drop-casting 2 w/v% polymer solution in *N,N*-dimethylformamide (DMF) onto silicon wafers, which were placed on top of a hot plate at 130 °C. Two parallel samples were annealed in a vacuum oven at 140 °C and in chloroform vapor atmosphere at 27 °C over a week, respectively.

A 2 w/v% PS-*b*-P2VP solution in DMF was mixed with a DMF solution of NPs at room temperature to give a solution with a typical NPs fraction of 5 wt% (referring to the weight of block copolymer). The effect of NPs loading (from 1 to 10 wt%) on the final structure of hybrid composites was also investigated. A bulk sample of the polymer-nanocomposite was quickly generated by drop-casting 400 μ L of the solution onto a silicon wafer at 130 °C, with further annealing in a vacuum oven at 140 °C or in chloroform vapor at 27 °C over a week.

Ultrathin sections (60–80 nm) for TEM were obtained by microtoming in epoxy (EpoFix, Electron Microscopy Sciences) embedded pieces of the bulk samples of PS-*b*-P2VP and hybrid composites using a Leica Ultracut UCT ultramicrotome equipped with a 35° DiATOME diamond knife.

4.7. Characterization

Atomic force microscopy (AFM) measurements were carried out on a Digital Instruments EnviroScope AFM equipped with a NanoscopeIIIa controller in tapping mode using Veeco RTESPW silicon cantilevers ($f_0 = 240\text{--}296$ kHz and $k = 20\text{--}80$ N m⁻¹ as specified by the manufacturer). AFM images were typically obtained with a scan range of 10 and 3 μ m² and a frequency of 0.5 Hz/line. Transmission electron microscopy (TEM) imaging was carried out on a Philips CM12 transmission electron microscope operating at an accelerating voltage of 120 kV. TEM images were recorded on a Gatan slow-scan CCD camera. Transmission FTIR measurements were performed under a vacuum on a Bruker FIS 66V/S spectrometer with a MIR DTGS detector in the range of 4000–700 cm⁻¹ at a normal resolution of 4 cm⁻¹. TGA measurements were performed on a Perkin-Elmer thermogravimetric analyzer under an air atmosphere in the temperature range 50–800 °C and with a heating rate of 10 °C min⁻¹.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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