

Creating Surfactant Nanoparticles for Block Copolymer Composites through Surface Chemistry

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A simple strategy to tailor the surface of nanoparticles for their specific adsorption to and localization at block copolymer interfaces was explored. Gold nanoparticles coated by a mixture of low molecular weight thiol end-functional polystyrene (PS-SH) ($M_n = 1.5$ and 3.4 kg/mol) and poly(2-vinylpyridine) homopolymers (P2VP-SH) ($M_n = 1.5$ and 3.0 kg/mol) were incorporated into a lamellar poly(styrene-*b*-2-vinylpyridine) diblock copolymer (PS-*b*-P2VP) ($M_n = 196$ kg/mol). A library of nanoparticles with varying PS and P2VP surface compositions (F_{PS}) and high polymer ligand areal chain densities was synthesized. The location of the nanoparticles in the PS-*b*-P2VP block copolymer was determined by transmission electron microscopy. Sharp transitions in particle location from the PS domain to the PS/P2VP interface, and subsequently to the P2VP domain, were observed at $F_{PS} = 0.9$ and 0.1 , respectively. This extremely wide window of F_{PS} values where the polymer-coated gold nanoparticles adsorb to the interface suggests a redistribution of PS and P2VP polymers on the Au surface, inducing the formation of amphiphilic nanoparticles at the PS/P2VP interface. In a second and synthetically more challenging approach, gold nanoparticles were covered with a thiol terminated random copolymer of styrene and 2-vinylpyridine synthesized by RAFT polymerization. Two different random copolymers were considered, where the molecular weight was fixed at 3.5 kg/mol and the relative incorporation of styrene and 2-vinylpyridine repeat units varied ($F_{PS} = 0.52$ and 0.40). The areal chain density of these random copolymers on Au is unfortunately not high enough to preclude any contact between the P2VP block of the block copolymer and the Au surface. Interestingly, gold nanoparticles coated by the random copolymer with $F_{PS} = 0.4$ were dispersed in the P2VP domain, while those with $F_{PS} = 0.52$ were located at the interface. A simple calculation for the adsorption energy to the interface of the nanoparticles with different surface arrangements of PS and P2VP ligands supports evidence for the rearrangement of thiol terminated homopolymers. An upper limit estimate of the adsorption energy of nanoparticles uniformly coated with a random arrangement of PS and P2VP ligands where a 10% surface area was occupied by P2VP -mers or chains was $\sim 1 k_B T$, which indicates that such nanoparticles are unlikely to be segregated along the interface, in contrast to the experimental results for nanoparticles with mixed ligand-coated surfaces.

Introduction

The ability to control the chemical composition and structure of block copolymers allows these materials to be ideal templates for hierarchical supramolecular control over the size, particle density, and spatial location of inorganic nanoparticles. In turn, the interesting photonic, magnetic, electrical, and catalytic properties of the nanoparticles^{1–4} add significant functionality to hybrid inorganic nanoparticle/block polymer nanocomposites. Such design flexibility has been exploited in the efficient fabrication of novel functional materials such as nanostructured solar cells, photonic band gap materials, highly efficient catalysts,

and high density magnetic storage media.^{5–14} However, despite the importance of controlling the arrangement of nanoparticles within the periodic structure of the block copolymer, establishing such control has been difficult.^{5,6,9,10} Of particular interest is controlling the assembly of nanoparticles at the interface between different polymer domains. Russell and co-workers¹⁵ showed that the orientation of block copolymer domains in thin films could be controlled by introducing surface active nanoparticles that preferentially segregate to the surface of high surface energy

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domains. Emrick et al.¹⁶ demonstrated the fabrication of an array of cross-linked CdSe quantum dots at an oil/water interface. Aside from useful applications associated with nanoparticle arrays formed at an interface, nanoparticles segregated to an interface between immiscible fluids can have a tremendous impact on the microstructure and physical properties. Cates and co-workers¹⁷ suggested that two-phase mixtures with nanoparticle additives can stabilize bicontinuous emulsions of small molecule liquids. This work assumes such emulsions to be metastable, stabilized by the jamming of neutral nanoparticles bound to the liquid/liquid interfaces. Chung et al.¹⁸ observed that the interfacial segregation of short polymer-coated silica nanoparticles stabilized a bicontinuous structure for blends of poly(methyl methacrylate) and poly(styrene-*r*-acrylonitrile). Recently, Kim et al.¹⁹ showed that stable bicontinuous morphologies with nanoscale dimensions below 100 nm can be easily fabricated by exploiting nanoparticles that strongly bind to and alter the interface between diblock copolymer domains. This method offers an alternative route to bicontinuous polymer-based nanostructures that are not easy to access with conventional methods^{20,21} but that offer advantages for many applications such as transport membranes, catalysts, and photovoltaic films.

Recently, there has been a growing interest to control the nanoparticle location within block copolymer domains.^{22–30} On the basis of theoretical predictions for inorganic–organic nanocomposites by Balazs and co-workers,^{23,24,26} Bockstaller et al.²⁵ demonstrated a hierarchical pattern formation of silica and gold nanoparticles coated by short organic molecules using binary mixtures of nanoparticles and block copolymers. More recently, Kim et al.^{28,30} and Chiu et al.²⁷ showed that the nanoparticle location within an A–B block copolymer template can be controlled by changing the enthalpic interaction between the block copolymer and the polymer-coated nanoparticles. The important factor in determining the stable incorporation of the nanoparticles within a block copolymer matrix is the compatibility of the nanoparticles with the block copolymer domains. However, a better understanding of the interaction between the surface modified particles, ligands on the surface, and the polymer matrix is required to achieve precise control over particle location. For example, information regarding the change in particle location as a function of the surface composition of nanoparticles is

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important, but as yet, not available. In addition, a model system is required to systematically examine the factors that control nanoparticle location. The model system designed for this study has a number of advantages for investigating the interaction between nanoparticles and block copolymer domains. First, the parameters governing the interactions between polymer ligands and polymer matrices of polystyrene (PS) and poly(2-vinylpyridine) (P2VP) are well-understood, such as the Flory–Huggins parameter and the interfacial tension.^{31–33} Second, a high areal chain density of thiol end-functional short chains can be grafted to the surface of gold nanoparticles, and the resulting core–shell structures are readily characterized by transmission electron microscopy, thermal gravimetric analysis, elemental analysis, and NMR.

In this paper, two different methods to control the location of polymer-coated gold nanoparticles within polystyrene-*b*-poly(2-vinylpyridine) block copolymer (PS-*b*-P2VP) domains are explored. In the first case, the surface modification of the nanoparticles involves adsorption of a mixture of two different homopolymer ligands, thiol terminated polystyrene and thiol terminated poly(2-vinylpyridine). This case is compared with nanoparticles that have a surface coating composed of random copolymers prepared from the same two monomers, styrene and 2-vinylpyridine. With these isomeric materials, the adsorption of nanoparticles to the interface as a function of the fractional PS and P2VP surface coverage for each approach is investigated. From our results, we determine the conditions necessary for the segregation of polymer-coated nanoparticles to the interface. By comparing the segregation behavior of particles coated with random PS-P2VP copolymers to those coated with mixtures of PS and P2VP homopolymers, we also address the question as to whether ligands are mobile on the particle surface, allowing them to optimize their interaction with the two domains of the block copolymer.

Experimental Procedures

Synthesis of Thiol Terminated PS and P2VP by Living Anionic Polymerization. A thiol terminated PS homopolymer (PS-SH) was synthesized by living anionic polymerization using benzene as the solvent at 30 °C.^{12,34} Polymerization of styrene was initiated by sec-butyl lithium and allowed to proceed for 3 h under nitrogen. Polystyryl anions were then titrated by ethylene sulfide, after which the sulfide ends were protonated by acidic methanol. Two different PS-SH ligands with respective molecular weights of 1.5 and 3.4 kg/mol were synthesized with a low polydispersity (PDI < 1.15). Two thiol terminated P2VP chains (P2VP-SH) with molecular weights of 1.5 and 3 kg/mol were synthesized by living anionic polymerization following the same procedure described for the synthesis of PS-SH.

Synthesis of Thiol Terminated Random Copolymer of Styrene and 2-Vinylpyridine. Thiol terminated random copolymers of styrene and 2-vinylpyridine (PS-*r*-P2VP-SH) were synthesized via living radical polymerization of a reversible addition fragmentation transfer (RAFT) method.^{35–37} The scheme for the preparation of

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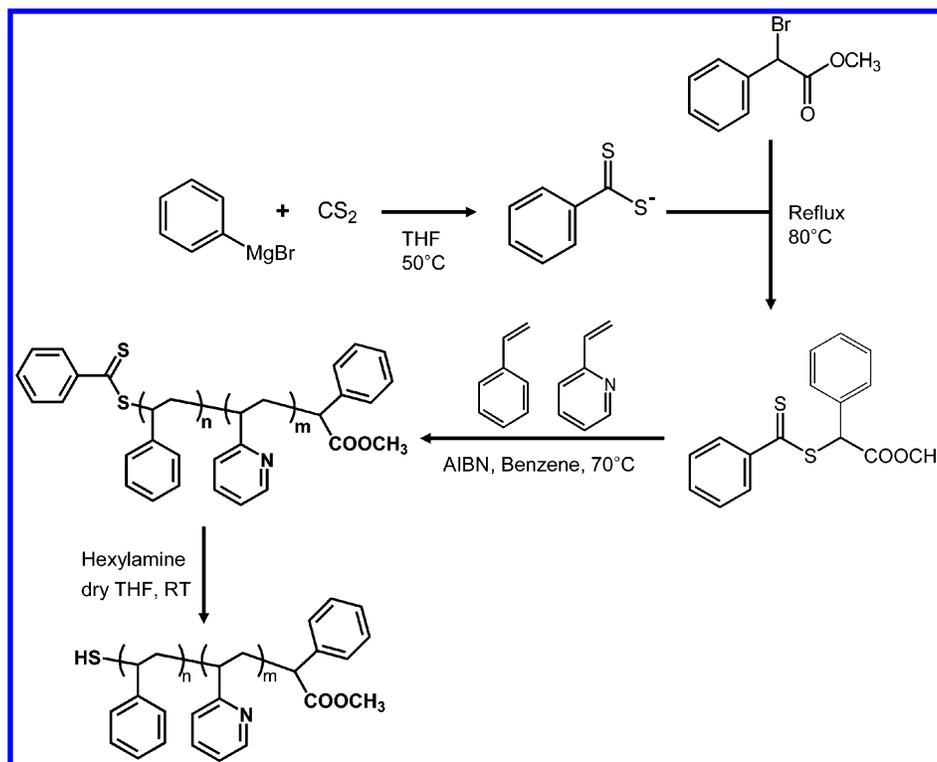


Figure 1. Schematic for synthesis of RAFT initiator and polymerization.

PS-*r*-P2VP-SH is shown in Figure 1. Dithioester RAFT agent was prepared following the procedure described elsewhere.³⁸

RAFT Polymerization. Two different compositions of PS-*r*-P2VP were synthesized as follows: styrene and 2-vinylpyridine (2-VP) monomers were purified by distillation prior to use. The styrene monomer (4.97 g, 0.048 mol), 2-VP monomer (5.09 g, 0.048 mol), AIBN (0.012 g, 0.073 mmol), and dithioester RAFT agent (0.153 g, 0.47 mmol) were dissolved in benzene (5 g). The reaction mixture was degassed by three freeze–pump–thaw cycles. The reaction was carried out at 70 °C for 2 h under vacuum. It should be noted that the conversion was kept as low as 0.15 to ~0.20 to prevent the composition drift caused by the difference in the reactivity ratio of the styrene and 2-VP monomers.³⁹ The M_n and PDI of PS-*r*-P2VP were 3.5 kg/mol and 1.1, respectively. The composition of PS-*r*-P2VP was found to be 0.40 mol fraction of styrene (F_{PS}) by proton NMR. By the same procedure, another PS-*r*-P2VP with $F_{PS} = 0.52$ by proton NMR was synthesized, resulting in M_n of 3.5 kg/mol and PDI of 1.1. The M_n as well as PDI of PS-*r*-P2VP after reaction were measured by size exclusion chromatography (SEC). The M_n was confirmed by proton NMR estimated from the ratio of the peak area of initiator to that of PS.

Thiol Terminated PS-*r*-P2VP (PS-*r*-P2VP-SH). The dithioester terminal group of PS-*r*-P2VP was cleaved by reaction with hexylamine to produce PS-*r*-P2VP-SH, as described by Deletre and Levesque.⁴⁰ RAFT terminated PS-*r*-P2VP (1 equiv) was dissolved in dry THF under a N_2 atmosphere. Then, hexylamine in excess (2 equiv) was added to the polymer solution under N_2 , and the reaction was carried out at room temperature overnight with the initial light red color changing to yellow. The polymer was precipitated into cold hexane (<0 °C), and the purified random copolymer was analyzed by proton NMR spectroscopy. However, SEC showed a shoulder in the higher molecular weight region next to the original peak of PS-*r*-P2VP. The presence of the secondary peak is most likely due to the oxidative coupling of thiols, which results in the formation of a disulfide bridge between two polymer chains.⁴¹ The

fraction of these disulfide coupled PS-*r*-P2VP chains with F_{PS} of 0.4 was 0.14, obtained by deconvoluting the SEC peaks. To suppress the disulfide formation, a few drops of an aqueous solution of $Na_2S_2O_4$ were mixed with the solution as described in the work of Lima et al.,⁴² and the reaction was allowed to proceed at room temperature overnight under N_2 .

Synthesis of Au Nanoparticles. Gold nanoparticles coated with a mixture of PS-SH and P2VP-SH (Au-PS,P2VP) were synthesized using a one-phase method.⁴³ Two different pairs of PS-SH and P2VP-SH ligands were used to stabilize the Au nanoparticles. The first pair consisted of PS-SH with M_n of 1.5 kg/mol and P2VP-SH with M_n of 1.5 kg/mol, and the second pair consisted of PS-SH with M_n of 3.4 kg/mol and P2VP-SH with M_n of 3.0 kg/mol. First, PS-SH and P2VP-SH ligands and gold precursors ($HAuCl_4$) together with various ratios of PS-SH to P2VP-SH were dissolved into dry THF and mixed for 15 min under a nitrogen atmosphere. Next, gold nanoparticles were synthesized by adding a reducing agent, superhydride (1.0 M $Li(C_2H_5)_3BH$ in THF from Sigma-Aldrich), dropwise under nitrogen. The addition of the reducing agent was continued dropwise until no more gas was evolved. The polymer-coated gold particles were separated from unattached PS thiol and P2VP thiol chains by centrifugation followed by membrane filtration (MWCO 30 000 Da, Millipore, Inc.) using dimethyl formamide (DMF) as the solvent. Finally, those particles were redispersed in dioxane and washed by membrane filtration at least 3 times and subsequently washed with methanol to remove ungrafted ligands as well as any residual reducing agent. To achieve Au-PS,P2VP nanoparticles with a given fraction F_{PS} of PS-SH ligands required that the Au-PS,P2VP synthesis use a mole fraction f_{PS} of PS-SH in solution that was smaller than F_{PS} . Representative values of f_{PS} and F_{PS} are given in Table 1.

The synthesis of Au nanoparticles coated by PS-*r*-P2VP-SH (Au-PS-*r*-P2VP) was accomplished following the same one-phase

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Table 1. Representative Values of f_{PS} , Fraction of PS-SH Ligands in Nanoparticle Synthesis Solution, and F_{PS} , PS Fraction on Nanoparticle Surface

f_{PS}	0	0.1	0.2	0.3	0.5	0.75	0.8	0.9	1.0
F_{PS}	0	0.14	0.29	0.49	0.67	0.88	0.90	0.93	1.0

procedure, and these nanoparticles were sequentially washed by membrane filtration as described for the synthesis of Au-PS,P2VP particles.

Preparation for PS-*b*-P2VP/Polymer-Coated Au Nanoparticle Composites. To prepare the nanocomposite samples, a 1 wt % block copolymer solution in dichloromethane, a neutral solvent for PS and P2VP, was mixed with Au-PS,P2VP or Au-PS-*r*-P2VP (15 wt % relative to the block copolymer). The nanoparticle/block copolymer composite was prepared by solvent casting a mixture of polymer-coated Au nanoparticles and PS-*b*-P2VP block copolymer in dichloromethane onto an epoxy substrate and then annealing under a saturated solvent atmosphere at 25 °C for at least a day.²⁷ All solvent in the sample was allowed to evaporate slowly over an additional day and subsequently dried in the air overnight and further under vacuum for 4 h. This resulted in a 10–20 μm thick film of a nanoparticle/block copolymer composite being obtained.

Characterization. The size of the polymer-coated gold nanoparticles as well as the location of these particles in the PS-*b*-P2VP matrix were determined by transmission electron microscopy (TEM) using a FEI Tecnai G2 microscope operated at 200 kV. Gold nanoparticles coated by polymer chains were dissolved at a very low concentration in dichloromethane or THF. A 20–30 nm thick carbon film-coated TEM grid was dipped into the solution for 1 s, dried in the air, and then examined by TEM. Samples of gold nanoparticle-block copolymer composites were prepared for cross-sectional TEM by microtoming epoxy supported thick films into 25–40 nm slices that were then stained by exposing them to iodine vapor that selectively stained the P2VP domains.

The gold core diameter distribution was obtained from TEM image analysis. These data were used to calculate the average surface area per gold nanoparticle as well as the total surface area per unit mass of gold. Weight fractions of gold and polymer ligands were measured by thermal gravimetric analysis (TGA). These numbers were confirmed by elemental analysis. The weight fractions of the polymer chains were converted into volume fractions using the density of the polymer ($\sim 1.05 \text{ g/cm}^3$) and the density of the gold particles ($\sim 19.3 \text{ g/cm}^3$). The number of polymer ligands per mass of gold particles divided by the surface area per mass of gold particles, determined from the histogram of particle sizes, gives the average chain areal density of polymer ligands on the particle surface.^{19,28}

Results and Discussion

The location of nanoparticles within a block copolymer matrix is primarily influenced by the compatibility of the nanoparticles with each constituent of the block copolymer microstructure. Therefore, surface modification of the nanoparticles is necessary not only to stabilize them against aggregation but also to tune their interactions with each block copolymer domain. When the particle surface is roughly neutral with respect to the blocks, nanoparticles tend to be found at the block copolymer interface since displacing them into either block involves a free energy penalty consisting of the interfacial energy of the block copolymer times the projected area of the adsorbed particle.

In this paper, two different approaches for tailoring the surface properties of nanoparticles were explored to control the nanoparticle location within the PS-*b*-P2VP domains. The first approach was to use a mixture of thiol terminated PS (PS-SH) and P2VP (P2VP-SH) homopolymers to control the surface properties of the nanoparticle. PS-SH and P2VP-SH were synthesized by living anionic polymerization. The second approach was to use a thiol terminated random copolymer of styrene and 2-vinylpyridine (PS-*r*-P2VP-SH). Monodisperse PS-

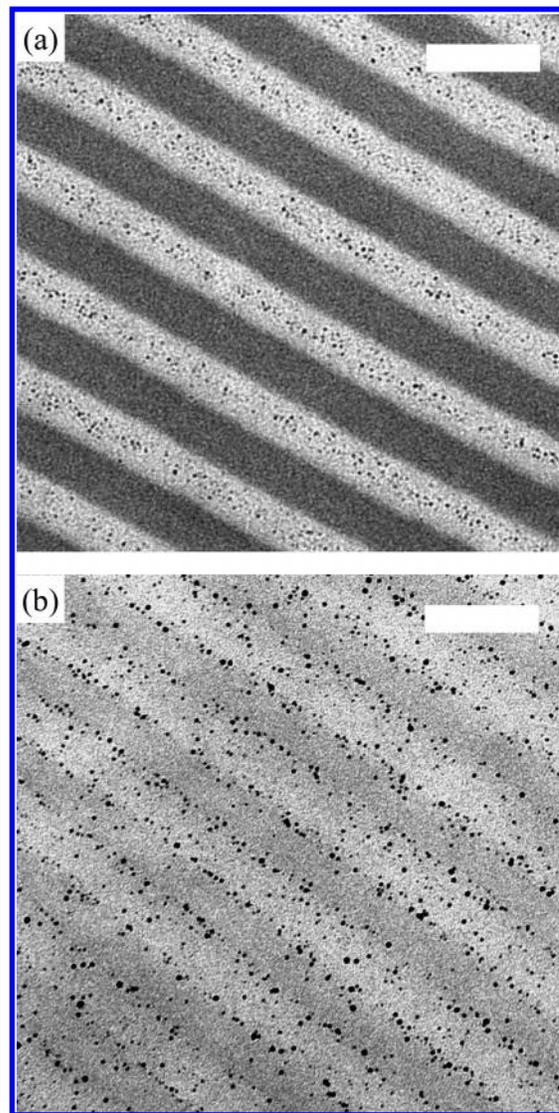


Figure 2. Cross-sectional TEM images of PS-*b*-P2VP block copolymer ($M_n = 196 \text{ kg/mol}$) containing gold nanoparticles whose surfaces are covered by (a) only PS chains and (b) a mixture of PS and P2VP chains. The fraction (F_{PS}) by PS chains on the Au surface in panel b is 0.80. Scale bar is 100 nm.

r-P2VP-SH is synthesized by controlled radical polymerization using the RAFT method.

To study the first method, two different particles were initially prepared with either the surface coated by only PS-SH or with a mixture of PS-SH and P2VP-SH chains. The fractions of PS chains (F_{PS}) and P2VP chains ($1 - F_{PS}$) on the particle surfaces were measured by proton NMR and elemental analysis. The two particles were mixed with a symmetric PS-*b*-P2VP diblock copolymer yielding a molecular weight (M_n) of 196 kg/mol to produce a nanoparticle weight fraction of approximately 0.15. Cross-sectional morphologies were observed by TEM as shown in Figure 2. Gold nanoparticles coated only by PS chains were clearly observed to be located near the center of the PS domains, which is the bright phase in the TEM micrographs owing to the selective staining of the P2VP domain by iodine. In contrast to PS-coated nanoparticles, nanoparticles coated by a mixture PS-SH and P2VP-SH with a F_{PS} of 0.80 were segregated near the PS/P2VP interface (Figure 2b). Clearly, gold particles coated by a mixture of PS and P2VP ligands are less selective for the PS and P2VP domains and are localized near the interface.

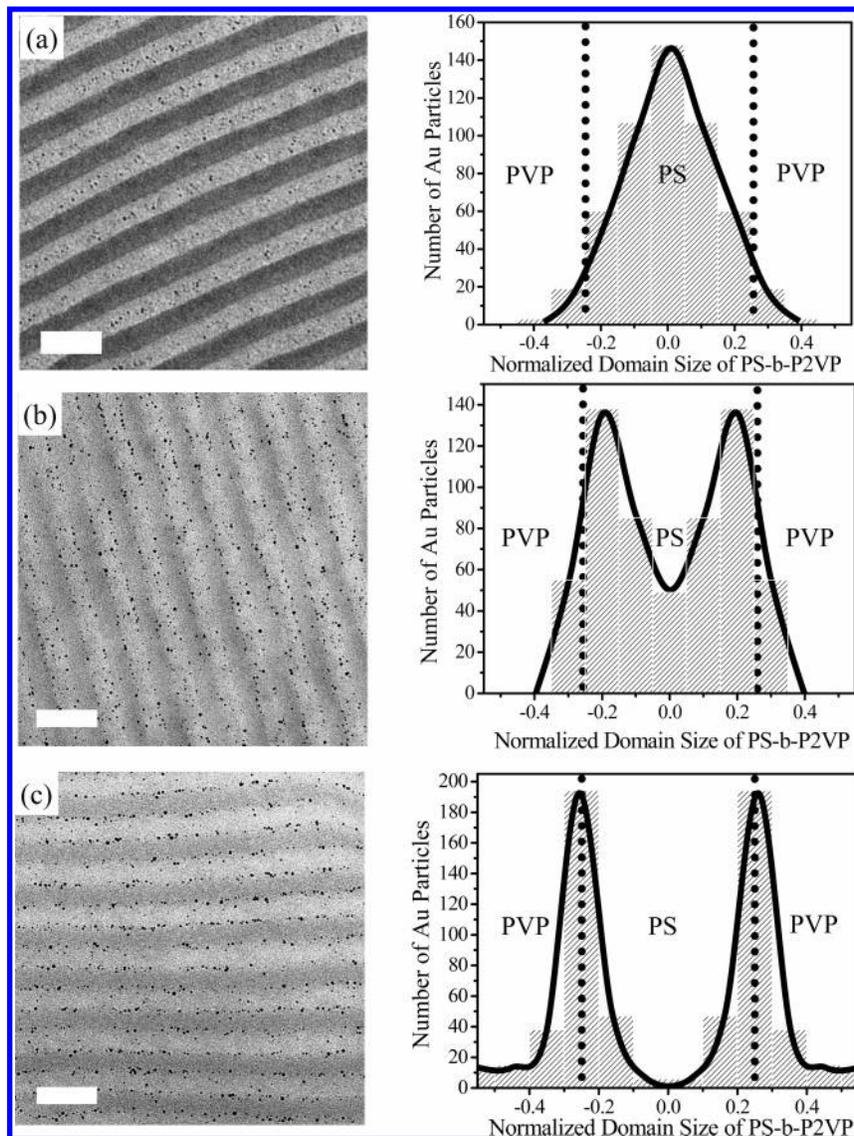


Figure 3. Cross-sectional TEM images showing the transition in location of Au nanoparticles coated with mixed ligands of PS-SH and P2VP-SH of $M_n = \sim 1.5$ kg/mol within the PS-*b*-P2VP block copolymer. The position of gold nanoparticles can be controlled from the center of the PS domains to the interface between PS and P2VP domains by varying the fraction of gold surface coverage by PS chains (F_{PS}). (a) Gold particles are dispersed near the center of the PS domain at $F_{PS} = 0.92$, (b) major portion of gold nanoparticles is located along the interface at $F_{PS} = 0.90$, (c) most particles are segregated to the interface at $F_{PS} = 0.80$. Histograms of particle positions from the TEM micrographs are shown next to the corresponding TEM image. Interfaces of the PS domain are at -0.25 and $+0.25$, and data are averaged at a given position relative to zero (i.e., number of particles at $-0.2 = (\text{number of particles at } -0.2 + \text{number of particles at } +0.2)/2$). Scale bar is 100 nm.

To systematically investigate this observation, the nanoparticle location within the block copolymer templates was studied as a function of the polystyrene surface coverage F_{PS} , and a library of nanoparticles was synthesized with different F_{PS} values by varying the initial mole ratios of PS-SH to P2VP-SH in the synthesis. It is important to note that the M_n (~ 1.5 kg/mol) of PS-SH is matched to that of P2VP-SH. Initially nanocomposite samples were prepared from nanoparticles with F_{PS} of 0.92, 0.90, and 0.80, and their location in the PS-*b*-P2VP domains was examined by TEM (Figure 3). From Figure 3a, it is clear that the particles with F_{PS} of 0.92 are located near the center of the PS domains (lighter regions). To visualize the particle distribution, the number of particles was counted as a function of particle location in the block copolymer domain, as shown in the corresponding histogram, which serves to quantitatively reinforce the qualitative impressions from visual inspection of the TEM micrographs. To obtain accurate statistics for the particle distribution, more than 500 nanoparticles were included in each

measurement, and the resulting histogram corresponding to the TEM image in Figure 3a confirms that particles with F_{PS} of 0.92 are dispersed near the center of the PS domain. As F_{PS} decreases from 0.92 to 0.90, the distribution of particles in PS-*b*-P2VP changes dramatically, as shown in Figure 3b, with the majority of particles being directed toward the interface between PS and P2VP domains. When F_{PS} further decreases to 0.80, virtually all the particles are located at the interface between PS and P2VP. While not shown in Figure 3, it is observed that the particles move to the P2VP domain as F_{PS} approaches 0. It is very interesting to note that gold nanoparticles having only 10% of their surface ligands that consist of very short P2VP chains ($F_{PS} = 0.90$) are bound to the interface between PS and P2VP domains.

To further explore the dependence of particle segregation on surface coating, a second and more extensive library of gold nanoparticles coated with a higher M_n of PS-SH (3.4 kg/mol) and P2VP-SH (3 kg/mol) was investigated. Once again, by varying

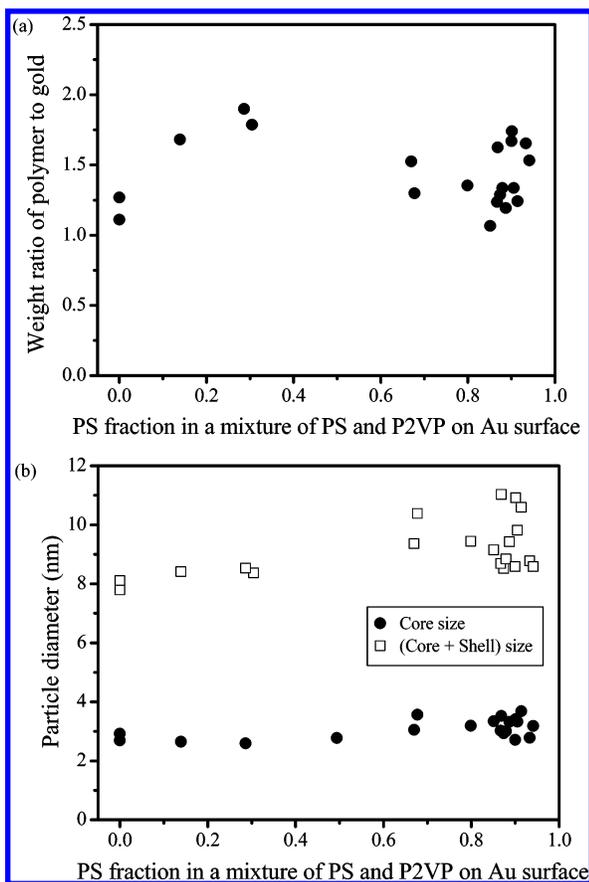


Figure 4. (a) Weight ratios of polymer shell to gold core in gold nanoparticles coated by a mixture of PS and P2VP chains ($M_n = \sim 3.4$ and 3 kg/mol, respectively) with various F_{PS} . (b) Particle core diameter and polymer shell thickness for various F_{PS} values.

the initial mole ratios of PS-SH to P2VP-SH, more than 20 sets of particles with a range of F_{PS} values were synthesized in THF using the one-phase method by varying the initial mole ratios of PS-SH to P2VP-SH during the synthesis. A stronger interaction of P2VP with the Au surface was observed during the synthesis of the Au nanoparticles with an important consequence that the initial mole ratio of polymer ligands to (gold atoms + polymer ligands) in the synthesis needed to be adjusted for different F_{PS} numbers to keep the areal density of polymer ligands on the nanoparticle surface constant. As a result, only nanoparticles having a polymer to gold weight ratio of approximately 1.5 were used to investigate the statistics of nanoparticle location as they have similar areal chain densities of polymer ligands on the nanoparticle surface. The polymer to gold weight ratio is measured by thermal gravimetric analysis, and the values are kept constant near 1.5 as a function of F_{PS} (Figure 4 a). In a previous study,²⁸ it was found that if the areal chain density (Σ) on nanoparticles coated only with PS ligands was less than a critical value, such PS-coated gold nanoparticles segregate to the PS/P2VP interface, owing to the favorable interaction between P2VP block chains and bare gold. To avoid binding of bare Au to the P2VP block in the current study, only nanoparticles with Σ values higher than the critical value of Σ were used, which is ~ 1.6 chains/nm² for gold particles coated by PS-SH with M_n of 3.4 kg/mol.

To fix Σ while varying F_{PS} over a wide range, the initial mole ratio of polymer ligands to gold atoms during the synthesis was increased to produce particles with lower F_{PS} values (higher P2VP fraction on the gold surface). The particle core size increases slightly from 2.8 to 3.1 nm as F_{PS} is increased as shown in Figure 4b. As a result, the total particle diameter of the particles, which

includes the polymer shell, also increases for fixed Σ values. However, previous work showed²⁸ that the effect of small variations in particle size on nanoparticle location is negligible as compared to that caused by Σ . The total polymer-coated Au particle diameter stays approximately constant at ~ 8 – 10 nm as F_{PS} is increased in Figure 4b.

Cross-sectional TEM images shown in Figure 5 illustrate representative examples of Au-PS,P2VP nanoparticles with different F_{PS} dispersed in the PS-*b*-P2VP lamellar diblock copolymer. From Figure 5a, it is clear that the nanoparticles with $F_{PS} = 0$ are located near the center of the P2VP domains (darker regions). As F_{PS} increases to 0.14, virtually all nanoparticles are segregated to the interface between PS and P2VP domains, as shown in Figure 5b. Au-PS,P2VP particles with F_{PS} of 0.30 and 0.68 stay bound to the interface as shown in Figure 5c,d, and the nanoparticles are directed to the PS domain at F_{PS} of 0.94 (Figure 5e). Of particular note is that segregation of Au-PS,P2VP particles at the PS/P2VP interface is observed over an extremely broad window of PS fraction on the Au surface. The fact that gold nanoparticles with only 10% coverage of very short P2VP chains induce strong binding to the interface is consistent with the results from similarly sized Au-PS,P2VP particles coated by shorter chains ($M_n = 1.5$ kg/mol) shown in Figure 3.

The interfacial segregation of Au nanoparticles coated with mixtures of PS and P2VP that contain as little as 10% of one or more of the polymer species raises very interesting questions about the distribution and mobility of PS and P2VP chains on the gold surface. It is reasonable that nanoparticles with an approximately neutral surface relative to the A and B polymers or blocks (i.e., nanoparticles with $F_{PS} = 0.50$) are bound to the interface as long as the interfacial tension between A and B polymers is large enough. However, a nanoparticle surface covered with a large majority of PS chains ($F_{PS} = 0.90$) is not really neutral since it would be attracted preferentially to the PS rather than to the P2VP block. Unless PS and P2VP can move on the Au particle surface and segregate to the PS and P2VP sides of the interface, it is difficult to see how the adsorption to the interface for such a coated nanoparticle could be strongly favorable energetically. In fact, the estimates later in this paper confirm this suspicion. Because directly measuring the rearrangement of ligands on 2.5 nm Au particles by imaging or scattering methods is extremely challenging, we need a means of preparing particles with a truly random surface incapable of rearranging.

To address this challenge, the following experiment was designed to probe the rearrangement of polymers on a Au particle surface. First, gold nanoparticles coated by a random copolymer of styrene and 2-vinylpyridine monomers (Au-PS-*r*-P2VP) with identical M_n as the polymer ligands on Au-PS,P2VP particles were prepared. A narrower window of F_{PS} values for Au-PS-*r*-P2VP particle segregation to the interface is expected since regardless of how the random copolymers are distributed on the Au surface, the surface remains uniform in composition.⁴⁴ Thiol terminated random copolymers of styrene and 2-vinylpyridine (PS-*r*-P2VP-SH) were prepared by controlled radical polymerization using RAFT methodology initiated by dithioester RAFT agent and AIBN. The polymer end group was then converted to a thiol group by reaction with a hexyl amine molecule to give two different PS-*r*-P2VP-SH copolymers with 0.4 and 0.52 mole fractions of styrene (F_{PS}). These random copolymer ligands were

(44) This may not be strictly true for short random copolymer chains since such chains will contain only about 30-mer units, and a random incorporation of monomers at an average rate will necessarily result in some chains with more and some chains with less PS content.

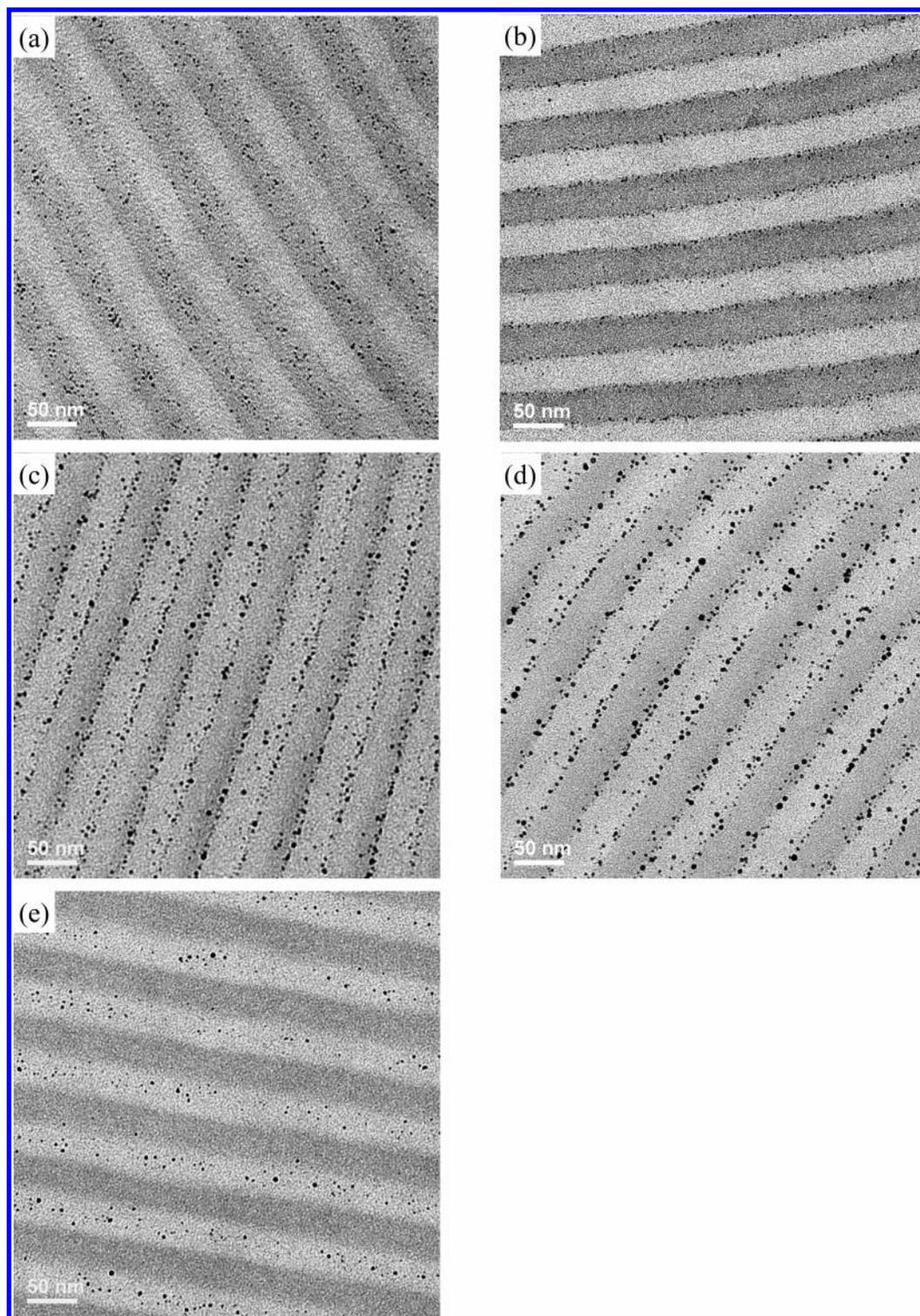


Figure 5. Cross-sectional TEM images showing the transition in Au nanoparticle location within PS-*b*-P2VP block copolymer for Au coated with PS and P2VP ligands with $M_n = \sim 3.4$ and 3 kg/mol, respectively. By varying F_{PS} , the position of gold nanoparticles can be controlled from the center of the PS domains, the interface between PS and P2VP domains, and finally to the center of the P2VP domain. (a) $F_{PS} = 0$, (b) $F_{PS} = 0.30$, (c) $F_{PS} = 0.67$, (d) $F_{PS} = 0.80$, and (e) $F_{PS} = 0.94$. Scale bar is 50 nm.

then used to stabilize gold nanoparticles, followed by dispersion into the same PS-*b*-P2VP block copolymer matrix.

Figure 6 presents cross-sectional TEM images of the PS-*b*-P2VP block copolymer containing gold nanoparticles whose surfaces are covered by a random copolymer of styrene and 2-VP with $F_{PS} = 0.52$ in panel a and a random copolymer of styrene and 2-VP with $F_{PS} = 0.40$ and high chain areal density (~ 1.8 chains/nm²) in panel b. While gold nanoparticles with $F_{PS} = 0.52$ are located along the interface as expected, the particles

with $F_{PS} = 0.40$ are clearly shown to be dispersed preferentially in the P2VP phase, a dramatically different result from the mixed ligand-coated particles with a lower PS surface coverage of $F_{PS} = 0.30$ that strongly segregate to the interface as shown in Figure 5c.

Figure 7 summarizes schematically the observed particle location as a function of F_{PS} for all sets of Au-PS,P2VP particles with $M_n = \sim 3$ kg/mol. It also shows the areal density Σ of the polymer chains on the gold nanoparticle surface. The Σ values

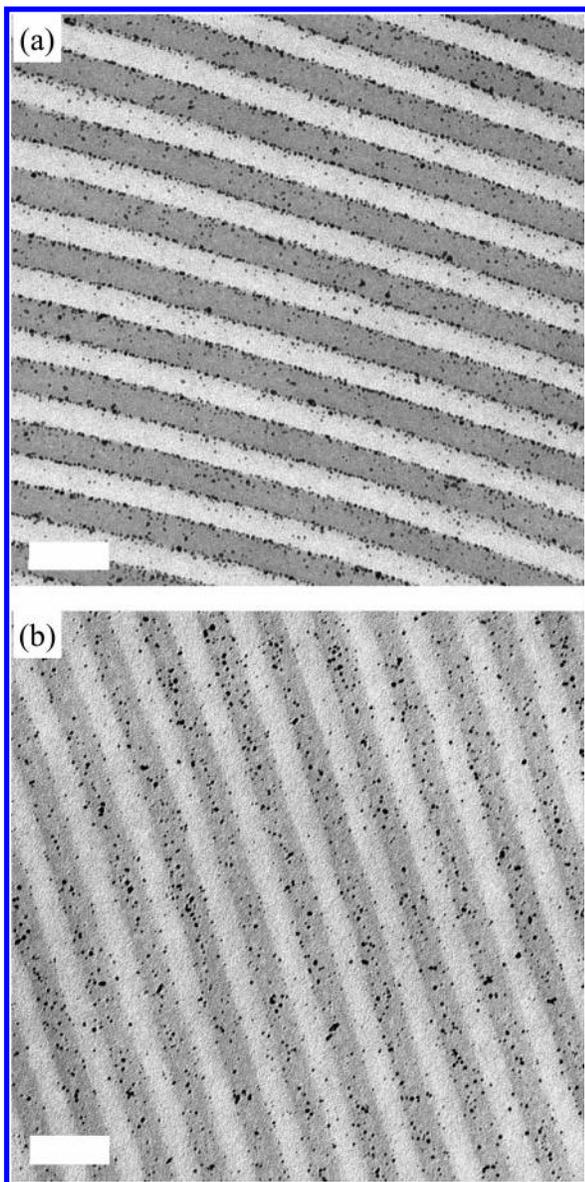


Figure 6. Cross-sectional TEM images of PS-*b*-P2VP block copolymer ($M_n = 196$ kg/mol) containing gold nanoparticles whose surfaces are covered by (a) a random copolymer of styrene and 2-VP with $F_{PS} = 0.52$ and (b) a random copolymer of styrene and 2-VP with $F_{PS} = 0.40$. Scale bar is 100 nm.

for the Au-PS,P2VP particles, between 2.1 and 3.5 chains/nm², are higher than the critical areal density of 1.6 chains/nm² for PS-coated Au nanoparticles in the same block copolymer.²⁸ Gold particles coated by a mixture of PS and P2VP segregate to the interface over an extremely broad range of F_{PS} values between 0.1 and 0.9 and move to the PS domain of PS-*b*-P2VP only when F_{PS} is larger than 0.9 or to the P2VP domain only when F_{PS} is smaller than 0.1. In stark contrast, Au-PS-*r*-P2VP particles remain in the P2VP domain and away from the interface even for $F_{PS} = 0.40$, as shown in Figure 6b. Au-PS-*r*-P2VP particles with $F_{PS} = 0.52$, however, are clearly segregated along the PS/P2VP interface consistent with the results of Figure 7. The chain areal density on these nanoparticles is ~ 1.6 chains/nm², close to the critical value for PS-SH chains of this length.^{28,45} However, all Au-PS particles synthesized with 3.4 kg/mol PS-SH with areal densities less than 1.6 chains/nm² down to the lowest values (~ 0.4 chains/nm²) at which the particles were stable in solution

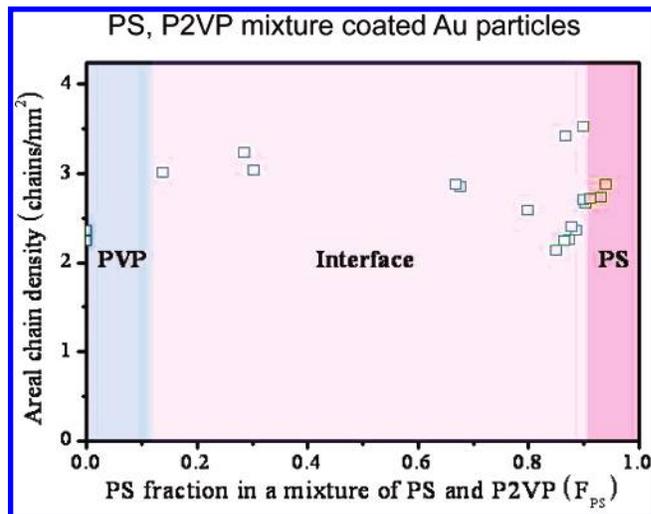


Figure 7. Location of gold particles coated by a mixture of PS and P2VP (Au-PS,P2VP) in a PS-*b*-P2VP template is shown as a function of F_{PS} for high areal chain density coverage. The Au-PS,P2VP particles adsorb to the interface for F_{PS} values between 0.1 and 0.9.

were segregated to the PS-*b*-P2VP interface. Even at the lowest areal chain densities few, if any, Au-PS particles were wholly in the P2VP block of the PS-*b*-P2VP. The fact that the Au-PS-*r*-P2VP particles remained in the P2VP domain $F_{PS} = 0.40$ thus is unlikely to be caused by the areal chain density being close to the critical value for PS-SH. Since the critical areal chain density for Au-PS was defined as the value where half the Au-PS particles were at the interface and half in the PS domain,^{28,45} the results for the Au-PS-*r*-P2VP particles with $F_{PS} = 0.52$ are also significant in that virtually all the Au-PS-*r*-P2VP particles are at the interface. In both cases, it seems probable that the chemical composition of the random copolymer ligand coating, and not its areal density, is determining the positioning of the nanoparticles in the block copolymer, but until higher areal density Au-PS-*r*-P2VP particles can be produced, the evidence cannot be said to be conclusive. Unfortunately, the synthesis of Au-PS-*r*-P2VP particles with areal chain densities much above the critical areal density (~ 1.6 chains/nm²) is extremely difficult, as reported in previous work.³⁰ Because of the crowding effect of PS-*r*-P2VP chains containing secondary thiol end groups adjacent to the benzene ring, in most cases, polymer ligands derived from RAFT polymers were found to form grafted layers on the Au particle surface significantly less dense than those that have a primary thiol end group. While a RAFT synthesis method for producing primary thiol end groups has been demonstrated,³⁰ it requires multiple steps and purifications that yield only small quantities of PS-*r*-P2VP primary thiols. Production of high areal chain density Au-PS-*r*-P2VP particles for a conclusive test thus will require an improved synthesis method.

The previous experimental results suggest a hypothesis that there exists a nonrandom distribution of the PS and P2VP ligands on the Au-PS,P2VP surface. Theoretical considerations can support this hypothesis. One possibility is that such a distribution forms during synthesis as a result of a 2-D phase separation on the Au particle surface. Such a 2-D phase separation will depend on the product of $\chi_{PS-P2VP}$, the Flory-Huggins interaction parameter between PS and P2VP, and N , the degree of polymerization of the ligands. For a 2-D melt blend, this product is ~ 5.8 for the 3.4 kg/mol ligands but only 2.6 for the 1.5 kg/mol ones, both values being only modestly above the critical value $N\chi_{PS-P2VP} = 2$ for phase separation. The presence of the neutral solvent undoubtedly decreases $\chi_{PS-P2VP}$ from its melt value, so while the ligand-ligand repulsion during synthesis certainly

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contributes to a nonrandom distribution of PS and P2VP ligands on the Au surface, it is probably not the primary cause. The second possibility is that the ligands can redistribute on the Au surface once the particle is in contact with the block copolymer interface. The energetics of this redistribution of the PS and P2VP polymer ligands on the surface of Au-PS,P2VP nanoparticles when these nanoparticles are at the interface is estimated next. This estimate reveals the driving force for such a redistribution, showing that it should occur if the chains are mobile on the particle surface. The same calculation allows us to estimate an upper limit for the adsorption energies of nanoparticles with randomly placed PS and P2VP ligands as well as the adsorption energy for nanoparticles where the PS and P2VP ligands have redistributed optimally.

To support the hypothesis that the Au-PS,P2VP nanoparticles rearrange and become amphiphilic, calculations for the adsorption energy of random copolymer-coated nanoparticles to the interface based on the work of Pieranski were performed.⁴⁶ First, the effective Flory–Huggins parameter (χ) between random copolymer-coated gold nanoparticles and PS domains can be determined. χ can be estimated by the following equation derived from random copolymer theory:⁴⁷

$$\chi_{\text{PS-NP}} = \chi_{\text{PS-P2VP}}(1 - F_{\text{PS}})^2 \quad (1)$$

where $\chi_{\text{PS-NP}}$ is the Flory–Huggins interaction parameter between PS and Au nanoparticles with randomly placed PS and P2VP ligands, $\chi_{\text{PS-P2VP}}$ is the Flory–Huggins interaction parameter between PS and P2VP ($\chi_{\text{PS-P2VP}} = -0.033 + 63/T$), and F_{PS} is the polystyrene fraction in the randomly placed PS and P2VP ligands on the particle surface.³² A similar equation can be derived for $\chi_{\text{P2VP-NP}}$ by substituting F_{PS} for $(1 - F_{\text{PS}})$ in eq 1. Since symmetric PS-*b*-P2VP diblock copolymers in this system have a large degree of polymerization ($N_{\text{PS-P2VP}} = 1875$), the interfacial tension between PS and P2VP blocks in this strong segregation regime can be expressed as follows:⁴⁸

$$\gamma_{\text{PS-P2VP}} = k_{\text{B}}T\rho_c a \left(\frac{\chi}{6}\right)^{0.5} \quad (2)$$

where ρ_c is the segmental density of PS and P2VP polymers, k_{B} is Boltzmann's constant, T is the absolute temperature, and a is the statistical segment length of PS. The statistical segment length and segmental density for P2VP have not been measured but are assumed to be equal to those for PS due to the similarity in segment structure.³³ The adsorption energy of gold nanoparticles to the interface between PS and P2VP blocks (E_a) can be expressed as the following equation:⁴⁶

$$E_a/k_{\text{B}}T = (\pi R^2 \gamma_{\text{PS-P2VP}}/k_{\text{B}}T)(1 - |\cos(\theta)|)^2 \quad (3)$$

where R is the radius of a nanoparticle and $|\cos\theta| = |\gamma_{\text{PS-NP}} - \gamma_{\text{P2VP-NP}}|/\gamma_{\text{PS-P2VP}}$ is the ratio of the interfacial tension between nanoparticles and polymer matrix to that between PS and P2VP. Combining eqs 1–3, the adsorption energy is

$$E_a/k_{\text{B}}T = (\pi R^2 \gamma_{\text{PS-P2VP}}/k_{\text{B}}T)(1 - |1 - 2F_{\text{PS}}|)^2 \quad (4)$$

According to eq 4 the adsorption energy E_a for 4 nm radius Au nanoparticles with randomly placed PS and P2VP ligands with F_{PS} of 0.1 is approximately $1 k_{\text{B}}T$. Therefore, Au

nanoparticles with randomly placed PS and P2VP ligands with a surface coverage by P2VP of 0.1 are unlikely to be segregated along the interface. In contrast, Au nanoparticles with randomly placed PS and P2VP ligands, as well as high areal chain density Au-PS-*r*-P2VP nanoparticles, with F_{PS} of 0.4 have an adsorption energy of $22 k_{\text{B}}T$. It must be noted, however, that eq 4 obtained from the work of Pieranski⁴⁶ was originally calculated for a system where colloidal particles were adsorbed to the interface between two low molecular weight fluids. Therefore, the adsorption energy for our system is certainly overestimated since the entropic penalty due to chain stretching when there are particles at the interface is not included. Furthermore, the presence of ~ 20 vol % solvent at the time during the drying of the film when the glass transition temperature increases through room temperature (when the microstructure is frozen) dilutes some of the contacts between PS and P2VP chains at the interface, decreasing the adsorption energy. This estimate is therefore an upper limit. A much more sophisticated calculation based on a hybrid particle-field simulation⁴⁹ including solvent is required to consider all contributions. A recent strong segregation theory may be able to give an improved estimate of the interfacial tension between the particle and the block copolymer matrix from the fraction of nanoparticles adsorbed to the interface over the narrow range of surface compositions where this fraction is less than one and greater than zero.⁵⁰ We have not attempted to perform this due to the presence of solvent, which is not accounted for in the theory.

Similarly, the E_a of amphiphilic nanoparticles can be estimated as follows with the assumption that polymer ligands redistribute on the particle surface to minimize the unfavorable interaction between the particle surface and PS-*b*-P2VP

$$E_a/k_{\text{B}}T = (4\pi R^2 \gamma_{\text{PS-P2VP}}/k_{\text{B}}T)[1 - (1 - F_{\text{PS}})^2] \quad \text{for } F_{\text{PS}} \leq 0.5$$

$$E_a/k_{\text{B}}T = (4\pi R^2 \gamma_{\text{PS-P2VP}}/k_{\text{B}}T)[1 - F_{\text{PS}}^2] \quad \text{for } F_{\text{PS}} \geq 0.5 \quad (5)$$

For $F_{\text{PS}} \leq 0.5$, the fraction of the surface of the spherical particle surface is assumed to be a spherical cap of PS and the remaining portion, P2VP. The projected area of the base of the spherical cap is positioned exactly at the interface; a complementary model is adopted for $F_{\text{PS}} \geq 0.5$ (i.e., a spherical cap of P2VP). The adsorption energy from eqs 4 and 5 for both nanoparticles with a random surface and amphiphilic nanoparticles whose ligands can redistribute is plotted as a function of F_{PS} in Figure 8.

The free energy driving force favoring redistribution of the PS and P2VP ligands on the Au particles at the interface can be found directly by subtracting eq 4 from eq 5 to yield

$$\Delta E_r/k_{\text{B}}T = (8\pi R^2 \gamma_{\text{PS-P2VP}}/k_{\text{B}}T)F_{\text{PS}}(1 - F_{\text{PS}}) \quad (6)$$

The magnitude of ΔE_r is substantial as shown in Figure 8, ranging from approximately $25 k_{\text{B}}T$ at $F_{\text{PS}} = 0.1$ to about $70 k_{\text{B}}T$ at $F_{\text{PS}} = 0.5$. While these numbers are undoubtedly overestimates, for the reasons discussed previously, they do show that the free energy favoring ligand redistribution for particles at the interface is substantial.

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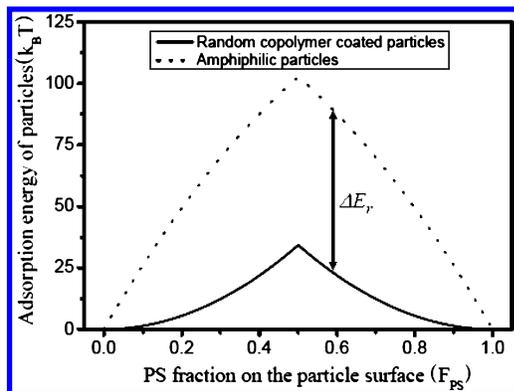


Figure 8. Adsorption energies for 4 nm radius random copolymer-coated nanoparticles (solid line) and amphiphilic nanoparticles (dotted line) from eqs 4 and 5 are plotted as a function of F_{PS} .

The fact that random copolymer-coated Au-PS-*r*-P2VP nanoparticles with $F_{PS} = 0.4$ do not segregate to the interface is consistent with the notion that eqs 4–6 are overestimates. The predicted adsorption energy for these particles is about the same as the amphiphilic Au-PS,P2VP nanoparticles with $F_{PS} = 0.1$, a surface composition that corresponds to the transition from the particles being in the P2VP and the nanoparticles segregating to the interface. Clearly, in both cases, the predicted adsorption energy is too large.

The question remains as to whether the PS and P2VP ligands are mobile enough on the Au surface to be able to redistribute in response to ΔE_r . Such redistribution can occur either by motion of the ligands on the Au surface (surface diffusion of the S terminal groups or the Au surface atoms themselves) for which there is some recent evidence^{51–54} or by exchange with ligands coming on and off the Au nanoparticles in solution.^{55–60} Logically, if the latter process can occur, it seems likely that surface diffusion, which should not require detachment of the S from the Au surface, would be even faster. To show that ligand exchange can occur under mild conditions with our PS-SH and P2VP-SH ligands, we conducted the following experiment. Au nanoparticles densely covered by PS-SH chains were dissolved into THF. At the same time, P2VP-SH chains in excess (10 equiv to that of PS-SH chains grafted to the gold particles) were added to the solution. After stirring for 1 h at 40 °C, half the amount of solution was taken and dried to yield A nanoparticles. The remaining solution was stirred further for 24 h at 40 °C to produce B nanoparticles. These two different nanoparticles were redispersed in a 1:1 mixture of immiscible toluene and acidic water solution (pH ~1). The B nanoparticles were found at the water/toluene interface (Figure 9b) instead of their original position (A nanoparticles) in the toluene phase (Figure 9a). The only logical explanation for the segregation of these nanoparticles to the water/toluene interface is that some of the P2VP-SH ligands exchange for some fraction of the PS-SH ligands originally on the surface of

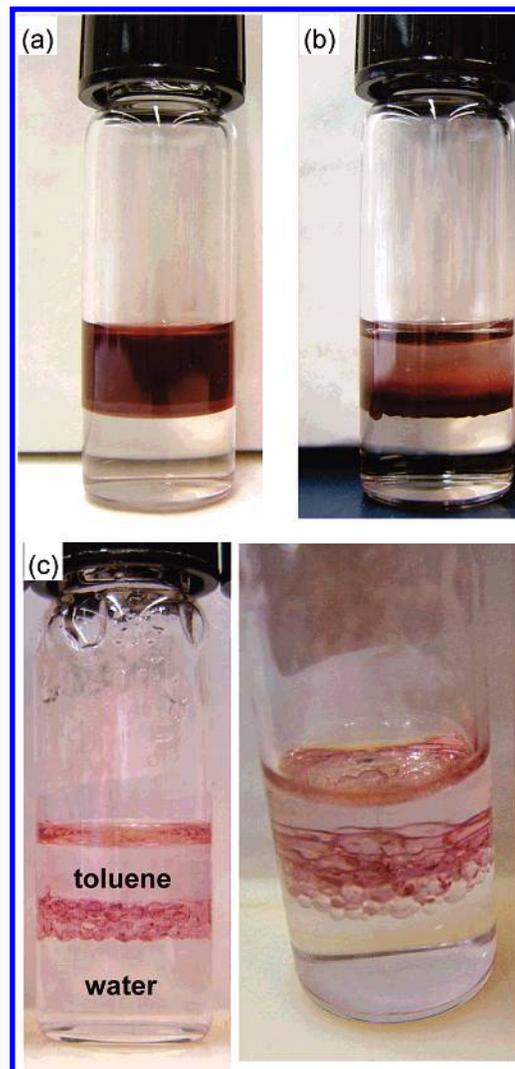


Figure 9. Solutions of Au-PS particles ($F_{PS} = 1$) in THF mixed with a large excess of thiol terminated P2VP chains were stirred at 40 °C for two different times: (a) 1 h and (b) 24 h, respectively. After solvent was evaporated, Au particles were redispersed into the immiscible toluene/acidic water solutions. Au particles after 1 h of stirring were dispersed in only toluene solution (panel a) in contrast to Au particles after 24 h stirring localized at the toluene/water interface (panel 9b). Panel c reveals the emulsified layer of water/toluene stabilized by an extremely small amount of Au particle surfactants between water and toluene.

the gold nanoparticles. If the P2VP-SH ligands are absent, the PS-coated Au nanoparticles remain in the toluene phase. To show that localization of such particles at the immiscible water/toluene interface is thermodynamically stable, the nanoparticles are used as surfactants for emulsification of toluene/water mixtures. Extremely small amounts of the surfactant (B) Au nanoparticles (~0.2 mg) were redispersed into the acidic water/toluene mixture (~2 mL), followed by vigorous shaking for 1 min. Figure 9c reveals the emulsified layer of water/toluene droplets stabilized by Au nanoparticle surfactants between water and toluene solutions. Therefore, it seems very likely that redistribution of PS-SH and P2VP on the surface of the nanoparticles can occur readily at the interface of the block copolymer and that the rearrangement of the polymer ligands on the gold nanoparticles coated by a mixture of PS-SH and P2VP-SH is the only reasonable explanation of the strong adsorption of Au-PS,P2VP nanoparticles to the PS-*b*-P2VP interface over the exceptionally wide range of surface compositions.

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Conclusion

In this study, we demonstrated that precise control of gold nanoparticle location within a PS-*b*-P2VP matrix can be achieved by tuning the enthalpic interaction between the polymer ligands on the nanoparticle surface and the block copolymer matrix. The surface properties of nanoparticles are tailored by coating the surface with a mixture of PS and P2VP homopolymers. Au-PS,P2VP nanoparticles showed a sharp transition in particle location from the PS domain to the interface at $F_{PS} = 0.9$ and from the P2VP domain to the interface at $F_{PS} = 0.1$. The extremely wide window of F_{PS} values for adsorption of Au-PS,P2VP-coated particles to the interface suggests redistribution of the PS and P2VP ligands on the Au surface, eventually inducing the formation of amphiphilic nanoparticles at the interface. A simple calculation

for the adsorption energy of random copolymer-coated nanoparticles supports the possibility of the rearrangement of thiol terminated polymers. The strategy of controlling the location of nanoparticles by coating them with a mixture of two polymer ligands is a simple and versatile method that can be extended to other inorganic-polymer hybrid materials.

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