

## Importance of End-Group Structure in Controlling the Interfacial Activity of Polymer-Coated Nanoparticles

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The ability to control nanoparticle location precisely within polymer matrices is becoming increasingly important and a critical prerequisite for most applications of polymer nanocomposites that ultimately require integration of nanoscale components into macroscopic objects.<sup>1–4</sup> However, success in controlling their precise location within a domain remains limited due to the inherently high surface area of nanoparticles and general incompatibility of unfunctionalized systems with the surrounding polymer matrix. To overcome this phase separation, surface-functionalized nanoparticles are a powerful tool for controlling the structure of such hybrid polymer nanocomposites. By specifically tailoring the shell/surface layer of the nanoparticle, the interfacial activity of nanoparticles within a polymeric matrix can be regulated independently of the inorganic core.<sup>5–8</sup> A recent strategy for controlling the location of Au nanoparticles in a block copolymer or polymer blend involves tuning the surface properties of the Au core by attachment of a random copolymer corona. Synthesis of the desired random copolymers can be accomplished by reversible addition fragmentation chain transfer (RAFT) polymerization which allows a wide range of random copolymers with narrow polydispersity (PDI) and controlled end groups to be prepared.<sup>9</sup> Polymers synthesized by RAFT are interesting for use in functionalizing metals such as gold and silver via the “grafting-to” approach due to the presence of thiocarbonylthio chain end(s).<sup>10</sup> However, despite the many advantages of using RAFT polymers for coating nanoparticles, synthesis of core–shell nanoparticles with densely packed polymeric ligands cannot be guaranteed due to the potential for steric hindrance of the thiol end group adjacent to the monomer repeating unit.

In this Communication, we investigate the effect of steric environment and nature of thiol end groups on the formation and structure of core–shell type nanoparticles. A simple procedure to modify the end group of RAFT polymers was developed which enables a densely packed polymeric shell to be formed on the nanoparticle surface. Finally, the critical importance of controlling the molecular structure of the shell is demonstrated by observing the dramatic change in nanoparticle position within a polymer matrix due to small changes in the nature of the surface layer.

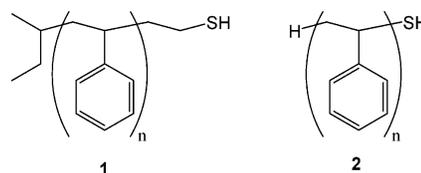
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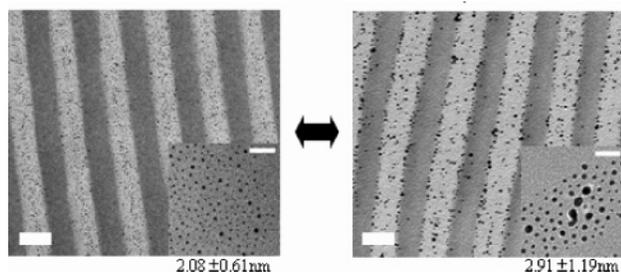


**Figure 1.** Structure of thiol-terminated polystyrene derivatives prepared by either anionic polymerization, **1**, or RAFT polymerization, **2**.

Our model system, consisting of poly(styrene-*b*-2-vinylpyridine) (PS-*b*-P2VP) diblock copolymer matrix and PS-coated gold nanoparticles, is employed to investigate the effect of molecular structure and surface chemistry on the directed assembly of Au nanoparticles. Of particular interest is surface coverage of the gold nanoparticles by PS chains which is a critical factor in determining the nanoparticle location within a PS-*b*-P2VP matrix due to strong favorable interactions between the bare gold surface and P2VP block. Therefore, the degree of packing of polymeric ligands on the nanoparticle surface can be visualized by the change in nanoparticle location. For example, nanoparticles having a densely packed monolayer of PS ligands above the critical value ( $\Sigma_c$ ) are located within the PS domain of PS-*b*-P2VP template; otherwise, nanoparticles are localized at the PS/P2VP interface.<sup>7</sup>

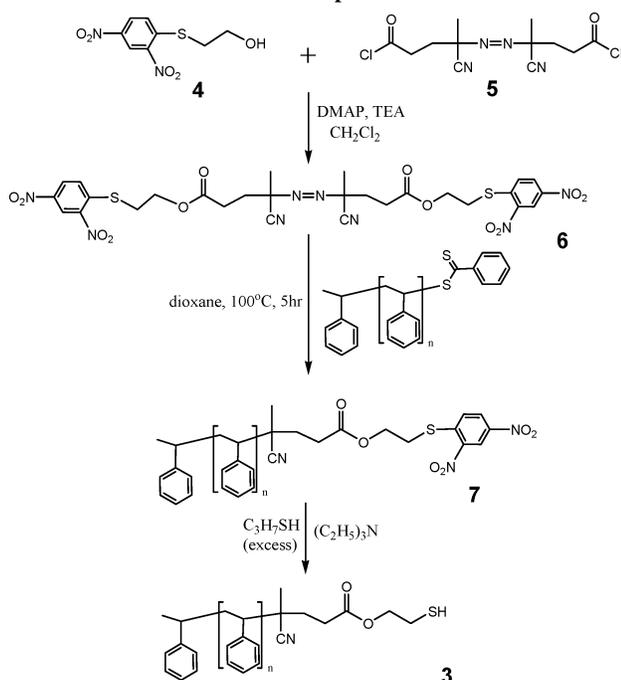
To investigate the importance of the steric environment and nature of the end group, two different polymers were synthesized by living anionic polymerization and RAFT polymerization. A PS chain was synthesized by anionic polymerization and terminated by reaction with ethylene sulfide to give the desired primary thiol end group (PS-SH, **1**  $M_n = 2.5$  kg/mol; PDI = 1.1).<sup>17</sup> The corresponding secondary derivative (PS-*sec*-SH, **2**) which has a secondary thiol end group adjacent to the phenyl ring ( $M_n = 3.5$  kg/mol, PDI = 1.1) was prepared by RAFT polymerization followed by amidation of the terminal dithio ester (Figure 1). Synthesis of PS-coated Au nanoparticles from either of these polymeric ligands was accomplished using a two-phase system<sup>11</sup> and purified to remove any unbound thiol polymer chains and residual reducing agent.<sup>7</sup> The primary PS-SH **1**-coated Au nanoparticles were synthesized with an initial mole feed ratio of PS ligands to Au atoms of  $f_{PS} = 0.30$  to produce an areal chain density ( $\Sigma$ ) as determined by TGA of 2.4 chains/nm<sup>2</sup>. With a similar initial condition of  $f_{PS} (=0.33)$ , the PS-*sec*-SH **2**-coated Au nanoparticles were synthesized and found to give an areal density,  $\Sigma$ , of only 1.3 chains/nm<sup>2</sup>. The PS-SH **1**- and PS-*sec*-SH **2**-coated nanoparticles were then blended with a symmetric PS-*b*-P2VP diblock copolymer of total  $M_n \sim 197$  kg/mol. Nanoparticle core size and location were determined by transmission electron microscopy (TEM), and the P2VP domains were stained selectively using an iodine vapor.

In Figure 2, we show cross-sectional TEM images of PS-*b*-P2VP block copolymer containing (a) PS-SH **1**-coated gold nanoparticles and (b) PS-*sec*-SH **2**-coated gold nanoparticles synthesized under the similar initial condition of  $f_{PS} \sim 0.3$ . From Figure 2a, it is clear that the higher areal density nanoparticles derived from **1** are fully dispersed into the PS domains (light regions). In direct contrast, lower areal density nanoparticles prepared from the sterically hindered, secondary thiol, **2**, are localized at the interface between the PS-*b*-P2VP blocks (Figure 2b). The dramatic difference in nanoparticle distribution between the two PS-coated systems is attributed to the change in areal density as the nature of the thiol chain end is varied. The strong



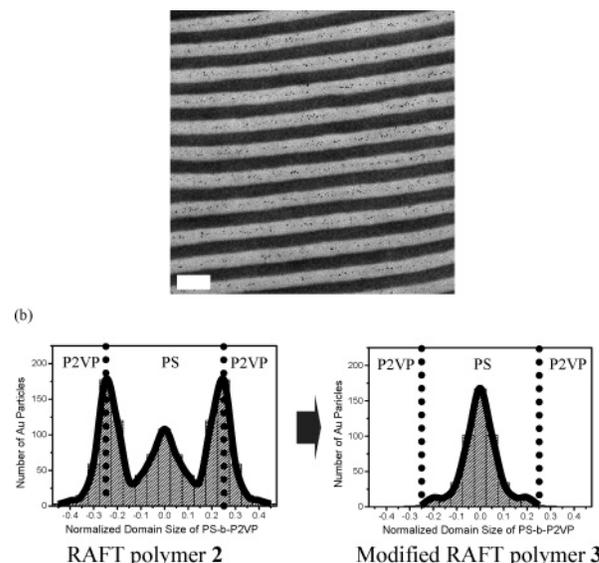
**Figure 2.** Cross-sectional TEM images of PS-*b*-P2VP block copolymer containing gold nanoparticles whose surfaces are covered with two different PS homopolymers synthesized by (a) living anionic polymerization and (b) RAFT controlled radical polymerization. Scale bar is 50 nm in the main window and 20 nm in the small window.

**Scheme 1. RAFT Synthesis of PS, **3**, with Primary Thiol End Group**



interaction between the bare gold surface and P2VP block becomes critical as the surface coverage decreases and leads to the directed localization of the nanoparticle instead of in the PS domain. In addition, the core diameter of PS-*sec*-SH **2**-coated nanoparticles is found to be slightly larger and more polydisperse than that of PS-SH **1**-derived materials, indicating that the PS-*sec*-SH **2** ligands are less effective in stabilizing the formation of Au nanoparticle even at lower  $f_{PS}$ .<sup>7,12</sup> It should be noted that the areal chain density,  $\Sigma$ , of PS-*sec*-SH **2**-coated nanoparticles does not increase significantly with a further increase of  $f_{PS}$ . Therefore, the directed localization of Au nanoparticles coated with RAFT-derived, secondary PS-*sec*-SH **2** ligands to the PS domain in PS-PVP block copolymers is not possible even at higher initial concentrations,  $f_{PS} = 0.5$ , of **2**. We believe that the steric crowding from secondary thiol end group adjacent to phenyl ring hinders the efficient binding of PS-*sec*-SH **2** to the Au surface. As a result, it is important to consider the chemical and steric environment of the polymeric chain end when designing polymeric ligands for nanoparticle positioning within a block copolymer matrix.

To prove our hypothesis and achieve the densely packed monolayer on the particle surface with RAFT-derived polymers, the RAFT starting polymer was modified by radical exchange to give a primary thiol end group (PS-*pri*-SH **3**), as shown in



**Figure 3.** TEM image of Au nanoparticles modified by **3** in a PS-*b*-P2VP matrix. Scale bar is 100 nm. Histograms of particle positions are obtained from the TEM micrographs in Figure 2b (before the end-group modification) and Figure 3a (after end-group modification). Interfaces of the PS domain are at  $-0.25$  and  $+0.25$  and data are averaged at a given position relative to zero.

Scheme 1. The synthetic strategy<sup>13,14</sup> begins with preparation of  $\alpha$ -(2,4-dinitrophenylthio)ethanol, **4**, and 4,4'-azobis(4-cyanopentanoic acid chloride), **5**, followed by coupling in the presence of *N,N*-dimethylaminopyridine and triethylamine to give the protected thiol-AIBN derivatives, bis(2-(2,4-dinitrophenylthio)ethyl) 4,4'-(diazene-1,2-diyl)bis(4-cyanopentanoate), **6**, in 65% yield. Using conditions developed by Perrier,<sup>15</sup> the dithioester chain end of the starting RAFT PS polymer (1 equiv) was heated at 100 °C in dioxane with a large excess of **6** (25 equiv). This results in exchange of the dithioester chain end with the AIBN fragment containing a 2,4-dinitrophenyl-protected primary thiol group to give the polymer **7**, which could be easily purified by either precipitation or flash chromatography. Characterization of **7** by MALDI mass spectrometry and GPC with both RI and UV detection showed that the exchange of chain ends was essentially quantitative under these reaction conditions. Deprotection of **7** with an excess of propanethiol in the presence of triethylamine gave the desired primary thiol chain end, **3**. Characterization of **3** again showed essentially quantitative conversion of the chain ends with a molecular weight comparable to the anionically prepared PS-*sec*-SH, **1**. It should be noted that during workup and storage minor amounts of the coupled disulfide product was observed. These dimerized products would be efficiently converted back to the thiol precursors by treatment with DL-dithiothreitol.<sup>16</sup>

The RAFT-derived primary thiol polymer, **3**, was then used to prepare polystyrene-coated Au nanoparticles which were incorporated into the PS-*b*-P2VP template under the same conditions as above. Figure 3 shows the TEM image of Au nanoparticles coated with **3** dispersed into the PS-*b*-P2VP block copolymers. Clearly, the particles are now localized within the PS domain, and the histogram in Figure 3b illustrates the dramatic change in the particle distribution within a PS-*b*-P2VP after the end-group modification by Scheme 1.

The change in the nature of the thiol end group from secondary to primary by end-group modification enables the formation of Au nanoparticles covered with the densely packed monolayer of **3** ( $\Sigma \sim 2.3$  chains/nm<sup>2</sup>; cf. 2.4 chains/nm<sup>2</sup> for **1**)

enough to shield the bare Au surface from interacting with the P2VP block.

In conclusion, we have investigated the effect of changing the nature and steric environment for thiol-terminated PS ligands during the formation of Au nanoparticles and their subsequent directed self-assembly in a block copolymer matrix. Polymeric ligands derived from RAFT polymers which contain secondary thiol groups were found not to be sufficiently surface active to screen further interactions with the Au surface. To overcome this deficiency, a simple and robust strategy to modify RAFT polymers leading to more active polymeric ligands was developed. These materials allowed the synthesis of nanoparticles densely covered with ligands, which could then be used to direct the location of the nanoparticles in a heterogeneous matrix.

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**Supporting Information Available:** Experimental details for small molecules and polymers 1–7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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