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NOTE

Facile Synthesis of Thermally Stable Core−Shell Gold Nanoparticles via Photo-Cross-Linkable Polymeric Ligands

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Polymer/nanoparticle hybrid materials have attracted significant attention in a variety of applications including photonic bandgap materials, nanostructured solar cells, light-emitting diodes, and memory devices.[1−4] In addition, the bulk properties of polymeric materials such as mechanical strength, conductivity, and rheological properties can be greatly enhanced by introducing nanoparticles into the polymer matrix.[5−8] For all of these applications, it is a critical requirement to achieve compatibility between the nanoparticles and polymers, suppressing macrophase separation of nanoparticles and inducing a complete dispersion of the particles within the polymer matrix. A promising strategy for improving dispersion is to modify the interface between the nanoparticle surface and the polymer matrix by introducing a compatibilizing polymeric shell to the inorganic nanoparticle core. Several research groups have successfully shown that the dispersion of the nanoparticles as well as their precise location within a composite blend can be achieved by tuning the enthalpic interaction between the nanoparticles and matrix through the judicious choice of the polymer chains in the shell including homopolymers, random copolymers, block copolymers, or mixtures of different polymers.[8−29]

From the wide range of nanoparticles used in the preparation of nanocomposites, gold nanoparticles (Au NPs) have attracted significant research interest due to their potential applications in catalyst, sensors, and biomedicine and the ability to accurately control their size from 1 to 100 nm.[30−32] Another advantage of Au nanoparticles is the tunability of the surface through the facile grafting of thiol end groups (-SH) to yield a controlled polymer ligand areal density on the gold nanoparticle surface.[33] In addition, the strong contrast between Au NPs and polymers under electron microscopy as well as their ability of light absorption in the visible regime makes them well suited for model studies on the effect of nanoparticles in compatibilizing polymer blends. Despite these advantages, a major challenge with all studies involving thiol ligand stabilized Au nanoparticles is the reversible nature of the Au−thiol bond, which allows ligand escape above 60 °C.[34] This serious limitation prevents their use in most of aforementioned applications. In recent studies, the stability of the Au−thiol bond could be improved through the shell cross-linking of polymeric micelles surrounding the Au NPs or the introduction of more than two thiol-anchoring groups at the polymer chain ends.[35−37] However, these methods still suffer from a lack of thermal stability and require multistep synthetic approaches. Matyjaszewski recently demonstrated the synthesis of stable polymer coated Au NPs by a "grafting-from" approach involving the formation of copolymer brushes consisting of monomers and cross-linkers.[38] However, the degree of control with this one-step procedure is limited, and the thermal stability of the resulting nanoparticles was increased to only 110 °C.

Herein, we report a simple, yet powerful strategy for preparing thermally stable Au NPs by introducing photo-cross-linkable azide groups (-N_3) into the polymeric ligands attached to the Au core. Thiol end-functionalized block copolymers consisting of polystyrene (PS) and azido-polystyrene (PS-N_3) blocks were prepared by reversible addition−fragmentation chain transfer (RAFT) polymerization technique, and the resulting polymer-grafted Au NPs were efficiently cross-linked by exposure to UV light. Consequently, it was observed that the cross-linked Au NPs were thermally stable in both solution and nanocomposite films at elevated temperatures. The selection of azido groups as the photo-cross-linkable units in this strategy was driven by prior success in utilizing these units for the fabrication of various polymeric nanostructures, such as multilayers or vertically aligned block copolymers.[39−42] Although it is known that photolysis of benzyl azides can lead to their rearrangement to imines,[43,44] we demonstrated that they can be effectively used as cross-linkers in the polymer system via UV irradiation or heating. In this case, it was suggested that the bimolecular coupling reaction can be facilitated by triplet sensitization of the azide unit instead of the normal rearrangement of singlet nitrenes to the imine.[45] A second critical aspect of the ligand design was that the short PS-N_3 block is placed adjacent to the thiol group, and hence Au cores can be protected, in principle, by cross-linked shells after *in situ* photo-cross-linking to give core−shell nanostructures with well-defined linear polymer chains surrounding a cross-linked polymer shell (Scheme 1a).

A low molecular weight P(S-*b*-S-N_3)-SH block copolymer was synthesized by RAFT polymerization (Scheme 1b) with the total molecular weight (M_n) being ∼3000 g/mol, which allows a large number of polymer chains to be grafted to the gold surface, according to previous studies.[13,14] The block molecular weights were 2000 and 900 g/mol for PS and PS-N_3 block, respectively (Figure S1). Therefore, it can be regarded that there are 9−10 cross-linkable units per polymer chain. As a control experiment, PS-SH was also synthesized with the same molecular weight, ∼3000 g/mol, and the polydispersities (PDIs) of both polymers were narrow (1.09 and 1.11 for PS-SH and P(S-*b*-S-N_3)-SH, respectively (Figure S1)). The PS-SH and P(S-*b*-S-N_3)-SH coated Au NPs, denoted as PS-Au and P(S-*b*-S-N_3)-Au, respectively, were synthesized by the two-phase method,[13,14] and the unbound polymers and residual reducing agents were then removed by membrane filtration. The size of Au core measured by transmission

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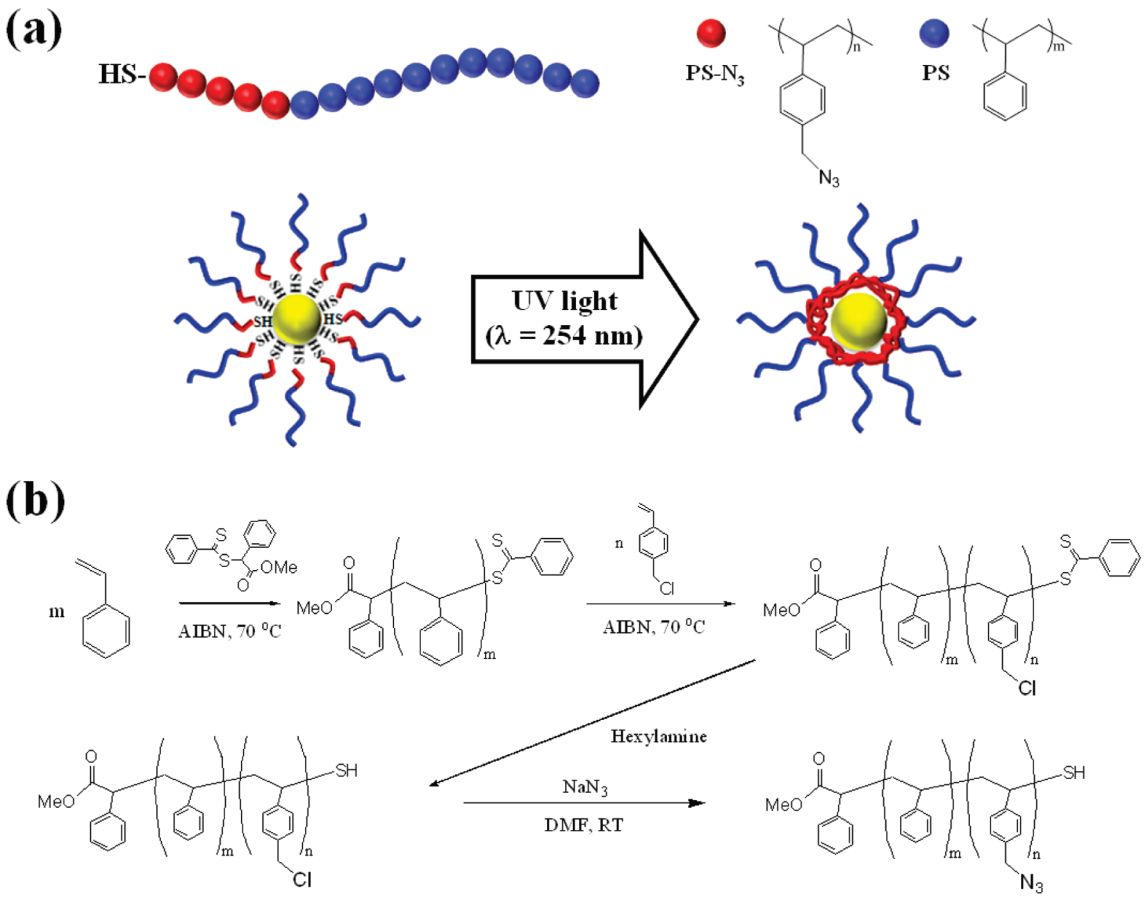
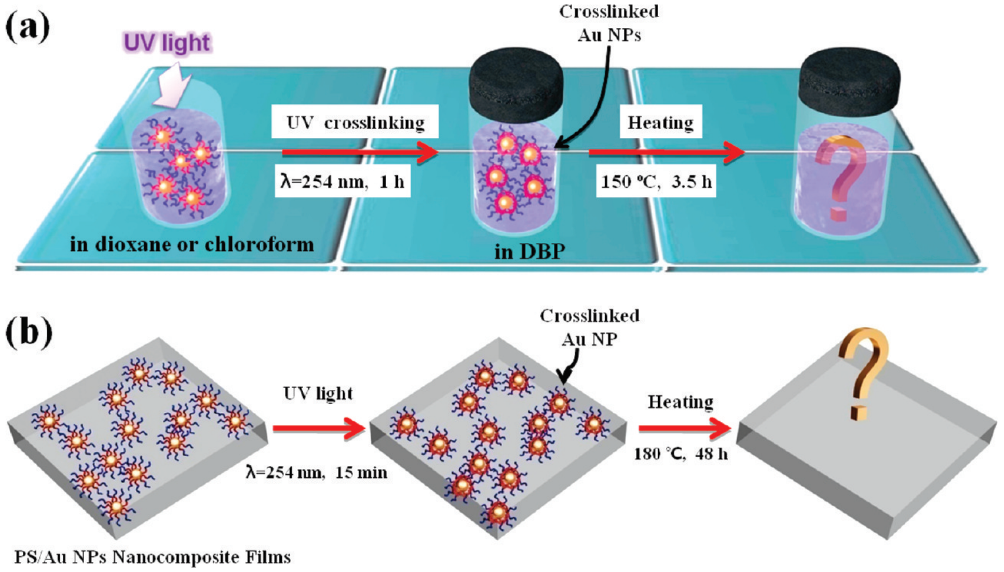
Scheme 1. Schematic Illustration for (a) the Design of Shell-Protected Au NPs via UV Cross-Linking Reaction of Azido (-N_3) Group and (b) the Synthesis of Photo-Cross-Linkable P(S-*b*-S-N_3)-SH Block Copolymer by RAFT Polymerization



Scheme 2. Schematic Illustration for the Test of Thermal Stability of Cross-Linked P(S-*b*-S-N_3)-Au NPs in (a) Solution and (b) Nanocomposite Thin Film



electron microscopy (TEM) was observed to be 2.80 and 2.62 nm for PS-Au and P(S-*b*-S-N_3)-Au NPs, respectively (Figure S2). During the synthesis of these Au NPs, the mole feed ratio of polymer ligands to Au atoms was 0.30, which results in an areal chain density of PS-Au and P(S-*b*-S-N_3)-Au NPs of 1.3 and 1.4 chains/nm^2, respectively, as determined by thermogravimetric analysis (TGA). It should be noted that both the areal chain densities of PS-Au and P(S-*b*-S-N_3)-Au NPs are not high enough to completely cover the Au particle surface.[13]

The cross-linking reaction and the subsequent evaluation of thermal stability for the P(S-*b*-S-N_3)-Au NPs were performed in both solution and nanocomposite thin films, as illustrated in Scheme 2. For the solution test, ca. 0.1 wt % of P(S-*b*-S-N_3)-Au NPs was first dispersed in UV transparent, good solvents for PS

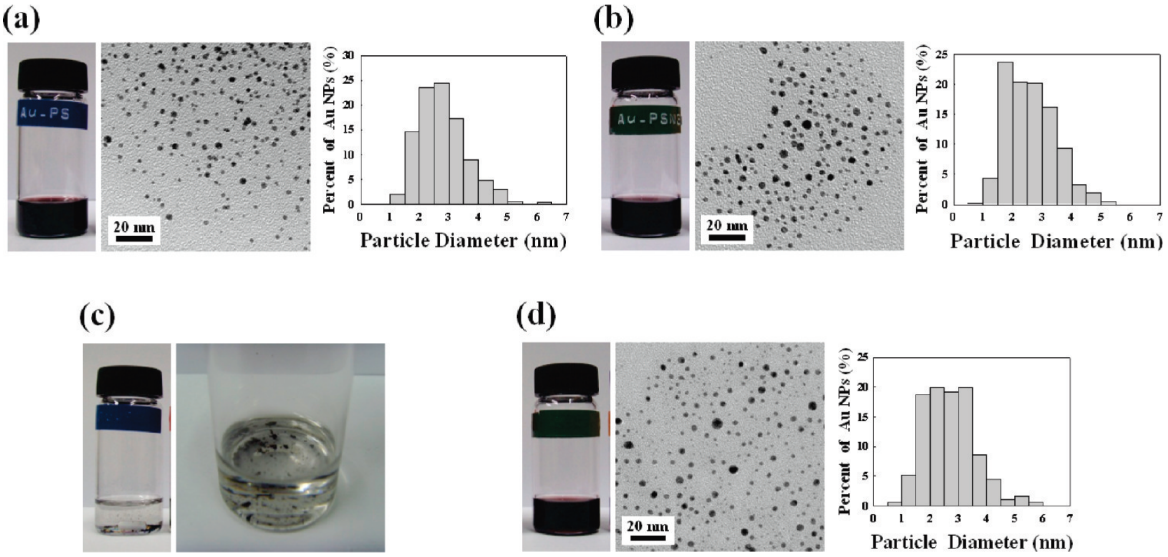


Figure 1. TEM images and the size distribution of (a) PS-Au NPs and (b) cross-linked P(S-*b*-S-N_3)-Au NPs before heating. (c) Photograph image of PS-Au NPs in DBP solution after heating to 150 °C for 3.5 h. (d) TEM images and the size distribution of cross-linked P(S-*b*-S-N_3)-Au NPs after heating to 150 °C for 3.5 h. Photograph images in (a), (b), and (d) correspond to Au NPs in DBP solutions. The number of analyzed Au NPs is 600−1000.

such as dioxane or chloroform. The solutions were then exposed to UV light ($\lambda = 254$ nm) for ~1 h under ambient conditions, using a hand UV lamp (intensity of ~2 mW/m^2). The cross-linked Au NPs were separated by centrifugation and dried in vacuo overnight. To test the thermal stability of these Au NPs in solution, dibutyl phthalate (DBP) was chosen as a nonvolatile, PS selective solvent (bp = 340 °C). After the cross-linked nanoparticles were dispersed in DBP, the solution was heated to 150 °C for several hours.

For the nanocomposite test, a 2 wt % toluene solution of nonfunctionalized PS homopolymer (M_n = 56 500 g/mol and PDI = 1.07) was mixed with un-cross-linked P(S-*b*-S-N_3)-Au NPs or PS-Au NPs (10 wt % relative to PS). Nanocomposite films with a thickness of 80−100 nm were then prepared by spin-coating on a silicon substrate having a 100 nm SiO_2 layer. To cross-link the P(S-*b*-S-N_3)-Au NPs, the nanocomposite films were exposed to the UV light for 15 min under vacuum. Then, the films were annealed at 180 °C for 48 h under vacuo, and the nanocomposite films were examined by TEM with the films being lifted off by etching away the SiO_2 with a dilute hydrogen fluoride (HF) solution.

Figure 1 shows TEM micrographs for DBP solutions of Au NPs before and after heating. For un-cross-linked PS-Au NPs, it is apparent that all nanoparticles were aggregated and precipitate upon heating due to the dissociation of the Au−thiol bonds, as can be seen from the before and after photograph images in Figure 1a,c. In direct contrast, the cross-linked Au NPs exhibit remarkable thermal stability with the color of DBP solutions remaining unchanged before and after heating and TEM analysis showing very similar diameters for the Au NPs, 2.62 and 2.71 nm, respectively (Figure 1b,d). To quantitatively confirm the thermal stability of cross-linked Au NPs, the UV−vis spectra were collected for both solutions during heating (Figure S3). Before heating, the both solutions exhibited the distinct surface plasmon absorption band near ~530 nm. When the solutions were heated, it can be clearly observed that the absorption peaks from cross-linked Au NPs did not change whereas they completely disappeared in PS-Au NPs solution due to the aggregation of Au NPs. These results indicate that the PS-N_3 blocks in P(S-*b*-S-N_3)-Au NPs could be successfully cross-linked via UV irradiation, and the dissociation of Au and thiol bond was completely suppressed due to the presence of the cross-linked PS-N_3 shell.

Further evidence for the formation of thermally stable Au NPs can be provided by the stability testing of Au NPs when heated in a polymer matrix at elevated temperatures. The reactive and control nanoparticles of P(S-*b*-S-N_3)-Au NPs and PS-Au NPs were separately added to a PS matrix to produce thin film nanocomposites. The P(S-*b*-S-N_3)-Au NPs/PS film was then exposed to UV light to cross-link the shell of Au NPs and then heated to 180 °C for 48 h under vacuum. As a comparison, the nonfunctionalized PS-Au NPs/PS films were heated under the same conditions at 180 °C, and as shown in Figure 2, the nanocomposite films containing the nonfunctionalized PS-Au NPs exhibited a significant degree of aggregation after heating (Figure 2a,c). In contrast, when P(S-*b*-S-N_3)-Au NPs were dispersed in the nanocomposite films and then cross-linked before heating, the size of Au NPs did not change (Figure 2b, d). As a control experiment, the nanocomposite films containing P(S-*b*-S-N_3)-Au NPs were heated to 180 °C for 48 h without UV cross-linking. In this case, we found that the degree of aggregation is retarded comparing to the nonfunctionalized PS-Au NPs/PS films, as the azide group is also thermally reactive and the partial cross-linking may occur during heating to 180 °C. However, the size of Au NPs significantly increases to 7.17 nm, confirming that the UV cross-linking is required for enhanced thermal stability of Au NPs (Figure S4). In agreement with the results for the solution experiments, these results indicate that the photochemical cross-linking of the azide functionalized NPs gives core−shell nanostructures that are thermally stable in nanocomposite films.

Since the cross-linked Au NPs were stable upon heating in both solution and melt states, they can now be used in various processes that require stability during thermal treatment. For example, in nanoparticle/polymer nanocomposites, it is a prerequisite that the surface chemistry of Au NPs be precisely tuned by the polymeric ligands, thus ensuring the complete dispersion of nanoparticles within a polymer matrix. In our cross-linked Au NPs, the polymeric ligands consist of two parts: the cross-linked shell resulting from photo-cross-linking of the PS-N_3 block and the outer brush layer corresponding to the PS blocks. In this case, it can be expected that the interfacial interactions of the cross-linked PS-N_3 shell with surrounding polymers will be different from that of a pure PS brush due to the existence of polar nitrogens in the cross-linked structure (Figure S5).[42] This difference

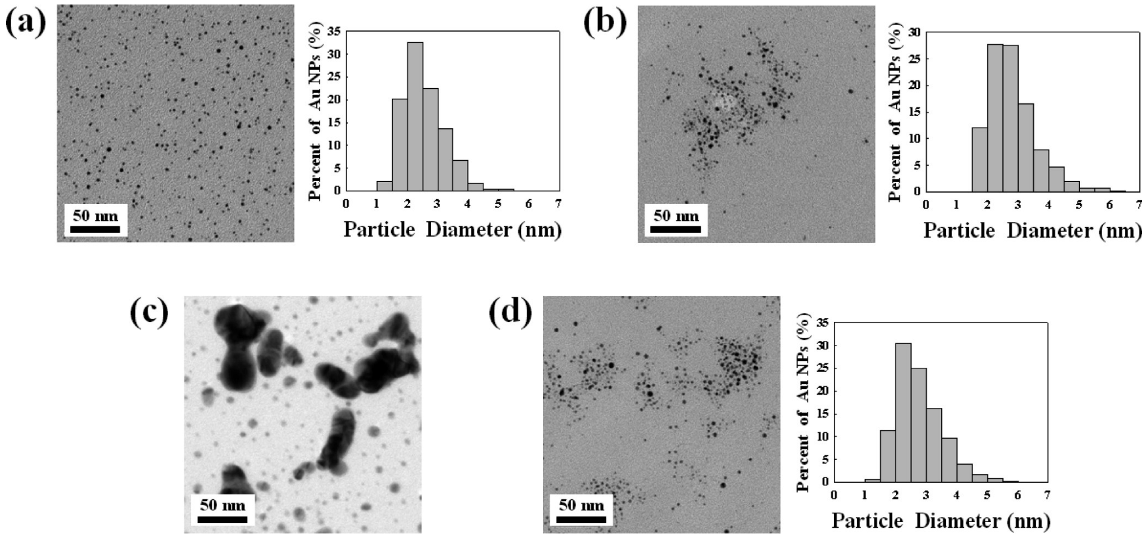


Figure 2. TEM images and the size distribution of Au NPs in (a) PS/PS-Au NPs and (b) PS/cross-linked Au NPs nanocomposite films before annealing and (c) PS/PS-Au NPs and (d) PS/cross-linked Au NPs nanocomposite films after annealing at 180 °C for 48 h. The size distribution is not given in (c) due to the significant aggregation of PS-Au NPs.

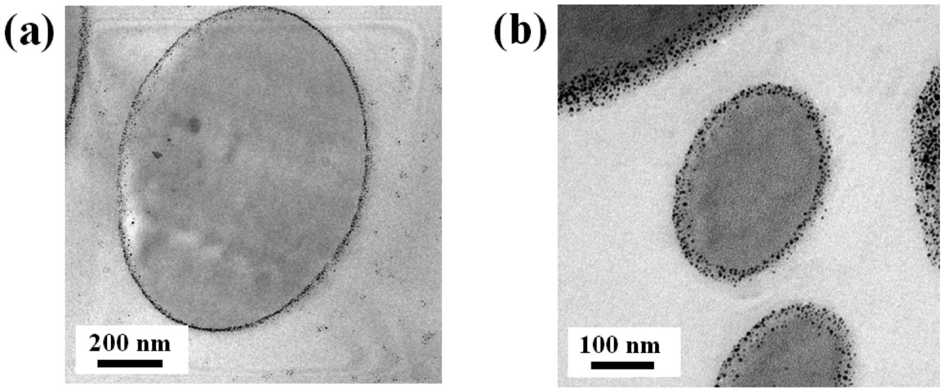


Figure 3. TEM images of PS/PMMA (50:50) blends after annealing at 180 °C for 48 h when (a) 5.0 wt % and (b) 10.0 wt % of cross-linked Au NPs was used as compatibilizers.

leads to a minor change in the dispersibility of the Au NPs in a polystyrene matrix (Figure 2b,d). Compared to well-dispersed PS-Au NPs in PS (Figure 2a), P(S-*b*-S-N_3)-Au NPs exhibit a less homogeneous dispersion of the nanoparticles in the PS film as shown in Figure 2b,d. Previously, it was demonstrated that PS-coated Au NPs with various areal chain density can be used to control the NP location in poly(styrene-*b*-2-vinylpyridine) (PS-*b*-P2VP) block copolymer templates.[13] As PS chain areal density in Au NPs decreases and the bare Au surface becomes exposed to the PS-*b*-P2VP chains, it was observed that the Au NPs are located at the PS-*b*-P2VP interface due to a favorable interaction between Au atoms and nitrogen atoms in P2VP. Analogously, the cross-linked Au NPs prepared in this study can be also applied to control the location of the nanoparticles in a polymer blend consisting of a PS domain and another polymer domain that interacts favorably with the inner PS-N_3 shell on the Au NPs, if the overall areal density of P(S-*b*-S-N_3) chains on the Au NPs is low enough. Indeed, the areal density of P(S-*b*-S-N_3) brushes on the Au particle surface (1.3−1.4 chains/nm^2) is lower than the critical areal density (~1.6 chains/nm^2) to determine the PS-Au particle location in the PS-*b*-P2VP matrix.[13,46] This balance of enthalpic interactions between (polar) cross-linked PS-N_3 shell and (nonpolar) outer PS brush may allow these stabilized systems to be interfacially active.

To test this possibility, blends of PS and PMMA were chosen as the polymer matrix. In this case, it can be expected that there is a favorable enthalpic interaction between cross-linked PS-N_3 shell and PMMA, as PMMA is more polar than PS. To prepare the nanocomposite samples, a 2 wt % solution of a blend of PS/PMMA (50:50 by volume) in dichloromethane was mixed with cross-linked Au NPs to produce a weight fraction of NPs of 5.0 and 10.0 wt %. The M_n and PDI are 56 500 g/mol and 1.07 for PS and 57 000 g/mol and 1.15 for PMMA, respectively. The solutions were then cast on NaCl substrates and then annealed at 180 °C for 48 h. To examine the morphology of these nanocomposites by TEM, the films were floated from the NaCl substrate, transferred to the epoxy supports, and microtomed (PS domains were stained with RuO_4).

Figure 3 represents cross-sectional TEM images of PS/PMMA blends containing 5.0 and 10.0 wt % of cross-linked Au NPs. Because of the immiscibility between PS and PMMA, the morphology of polymer blends results in two distinct domains; i.e., droplets of one polymer domain are dispersed within the other polymer matrix. When 5.0 and 10.0 wt % of cross-linked Au NPs were mixed with the PS/PMMA blend, a dramatic localization of Au NPs is observed at the polymer/polymer interface. While cross-linked P(S-*b*-S-N_3)-Au NPs are clearly seen at the PS/PMMA interface regardless of a weight fraction of NPs in the blend, of particular interest is the observation that the interfacial width of the PS/PMMA blend indicated by the width of the gold nanoparticle layer increases as the wt % of Au nanoparticles increases (Figure 3). This indicates that the

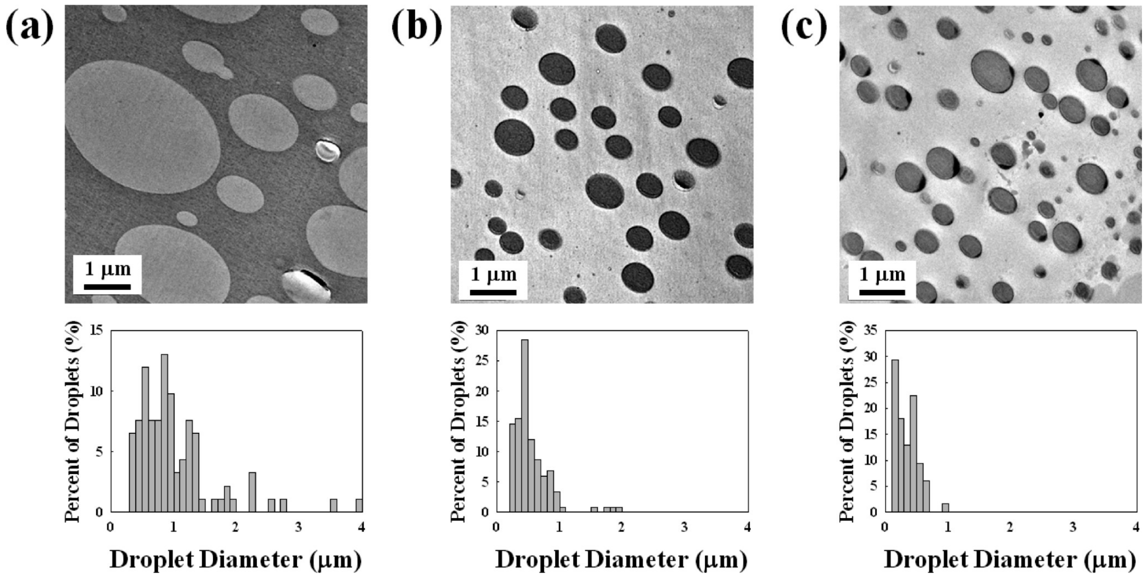


Figure 4. TEM images and the corresponding droplet size distribution of PS/PMMA(50:50) blends with cross-linked Au NPs as compatibilizer, after annealing at 180 °C for 48 h. The amounts of cross-linked Au NPs in blends are (a) 0.0, (b) 5.0, and (c) 10.0 wt %.

P(S-*b*-S-N_3)-Au NPs are nonselective to both the PS and PMMA phases but are localized to the interface to reduce the interfacial tension between the PS and PMMA phases and to avoid the entropic penalty of polymer matrix chains if the NPs are dispersed in either PS or PMMA domain. This feature suggests that the cross-linked Au NPs can function as compatibilizers in polymer blends. To promote small droplet phase sizes in polymer blends, block copolymers whose blocks are each miscible with one of the homopolymers have been widely used as compatibilizers.[47−53] For PS/PMMA blends, it has been well established that addition of PS-*b*-PMMA block copolymers as compatibilizers can effectively reduce the size of droplets, as they are located at the PS/PMMA interface thus reducing the interfacial tension and retarding droplet coalescence.[51−53] In this vein, the effect of cross-linked Au NPs as compatibilizers in PS/PMMA blends was examined by determining the size of droplets, as shown in Figure 4. Since the volume fractions of PS and PMMA are the same, both PS and PMMA droplets are observed in all samples. In the absence of cross-linked Au NPs, the droplet size spans from submicrometers to several micrometers, with an average size of 0.92 ± 0.33 μm. However, as the cross-linked Au NPs are added to the PS/PMMA blends, it can be clearly observed that the size of droplets decreases significantly. In this case, average sizes of droplets were 0.46 ± 0.14 and 0.32 ± 0.09 μm for addition of 5.0 and 10.0 wt % of cross-linked Au NPs, respectively. Furthermore, we did not observe any aggregation of Au NPs into larger particles within the polymer domain during the thermal annealing of these polymer blends. Therefore, it can be concluded that most of cross-linked Au NPs are located at the interface of PS/PMMA blends and effectively retard droplet phase coarsening.[54]

In summary, we have designed thermally stable Au NPs using well-defined photo-cross-linkable block copolymers, P(S-*b*-S-N_3)-SH, as polymeric ligands. The thermal stability was achieved via a formation of cross-linked PS-N_3 shell on the Au surface, preventing aggregation and thermal dissociation between Au core and thiol group upon heating coupled with the presence of a PS brush layer attached to the cross-linked shell. These covalently stabilized nanostructures exhibited remarkable thermal stability with no aggregation being observed on heating to 200 °C for extended periods of time in both solution and the solid state. This allows the cross-linked Au NPs to serve as compatibilizers for thermally annealed PS/PMMA blends with the cross-linked Au NPs being located at the PS/PMMA interface resulting in the reduction in the droplet size. Since the design of the photo-cross-linkable polymeric ligands is modular, the surface property of the Au NPs can be readily tuned and applied to other functional metal nanoparticles, providing a versatile route to the fabrication of a variety of nanocomposite systems.

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Supporting Information Available: Size exclusion chromatography traces of PS-SH, PS-RAFT macroinitiator, and P(S-*b*-S-N_3)-SH, UV−vis spectra, and additional TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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