

Understanding the Mechanism of Star-Block Copolymers as Nanoreactors for Synthesis of Well-Defined Silver Nanoparticles

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Summary

Facile and large-scale synthesis of well-defined, thermally stable silver nanoparticles protected by polymer brushes for use in practical applications is still a challenge. Recent work has reported a nanoreactor approach that can be used to synthesize these silver nanoparticles. This approach uses amphiphilic star-block copolymers, which have a hydrophilic core surrounded by a hydrophobic exterior. These polymers thus can serve as the nanoreactors. In this study, we hypothesize that the local high concentration of silver ions in the inner hydrophilic cores of these star-block copolymers facilitates the nucleation and subsequent growth of silver nanoparticles. When all silver nanoparticles nucleate from the cores of the star-block copolymers in solution, the particle size can be controlled by the core size of the polymer. To test this hypothesis, a polyisoprene-*b*-poly(*p*-tert-butylstyrene) (PI-*b*-PtBS) star-block copolymer was functionalized with carboxylic acid groups using a high-efficiency, photo-initiated thiol-ene click reaction. We characterized this modified polymer using proton nuclear magnetic resonance spectroscopy, and the results indicated that ~60% of the double bonds in the polyisoprene block were successfully functionalized with carboxylic acid groups. When silver ions were added to a solution of these functionalized star-block copolymers, the negatively charged carboxylic acid groups would attract the positively charged silver ions. Subsequent reduction of these Ag⁺ by a *tert*-butylamine-borane complex at room temperature produced nanosized silver particles. However, transmission electron microscopy images showed that a significant amount of relatively large silver nanoparticles grew outside the star-block copolymer nanoreactors.

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Introduction

Metallic nanoparticles exhibit unique optical, electrical, and thermal properties due to the surface plasmon resonance effect. The surface plasmon resonance effect occurs when electrons in the conduction bands of metallic nanoparticles interact with light and emit large amounts of energy. Silver nanoparticles are one example of metallic nanoparticles that have this property. Silver nanoparticles commonly have applications in conductive inks/pastes and fillers for photovoltaics and electronics because of their high electrical conductivity, relative stability, and low sintering temperatures (1). Because of their unique optical properties, silver nanoparticles can also be potentially used in multilayer optical data storage, a form of future data storage technology that may store up to petabytes of information. Finally, silver nanoparticles exhibit unique antimicrobial properties because they can release a low level of silver ions, which are toxic to bacteria; therefore, they are widely used as antimicrobial coatings. There is a lot of ongoing research aiming to synthesize metallic nanoparticles with controlled sizes, uniform shape, and surface stabilization (2). Despite these tremendous research efforts, facile synthesis of large-scale silver nanoparticles with uniform size, shape, and surface stabilization still remains a challenge.

Recently, an elegant polymer nanoreactor approach was reported for facile synthesis of various inorganic nanoparticles, including metallic, metal oxide, and perovskite nanoparticles (3). Both spherical nanoparticles and nanorods have been synthesized through this approach, which utilizes amphiphilic (containing both hydrophobic and hydrophilic components) star- and bottle brush-block copolymers based on poly(acrylic acid) (PAA) and polystyrene (PS) (4). Because of the well-defined structure of the star and bottle-brush amphiphilic block copolymers, the synthesized nanoparticles exhibit a relatively high degree of uniformity in size, shape, and also surface stabilization. These nanoparticles have exhibited unique electrical, photonic, and optoelectronic properties, and thus are promising for future applications in nanotechnology. However, the special amphiphilic PS-*b*-PAA star block copolymers are not available commercially. It is more desirable to use a commercially available star block copolymer to scale up the synthesis

of silver nanoparticles.

Currently, only hydrophobic star-block copolymers based on polydienes [e.g. polybutadiene (PB) and polyisoprene (PI)] and PS have been commercialized in large quantities (5). They need to be converted to amphiphilic star block copolymers for the synthesis of silver nanoparticles. There are many research studies about chemical functionalization of polydiene-based polymers (6). If these hydrophobic star-block copolymers can be chemically modified to contain carboxylic acid groups, then it is possible to scale up the synthesis of well-defined silver nanoparticles using these polymers. In particular, the silver nanoparticles can be "tethered" to the hydrophobic PS blocks or brushes of the polymer. If the silver nanoparticles are blended in a polymer matrix, their photothermal effects from the surface plasmon property can be used for optical data storage (7). For example, upon laser light excitation, the silver nanoparticles can heat up and release large amounts of energy to quench fluorescent dyes on a data storage structure, forming digital 0 (quenched) and 1 (unquenched) states.

Regardless of the recent report on well-defined silver nanoparticles (3), the fundamental mechanism for the controlled synthesis of silver nanoparticles using amphiphilic star-block copolymer nanoreactors

is still unclear. We hypothesize that the local high concentration of silver ions in hydrophilic cores of the star-block copolymer facilitates the nucleation and subsequent growth of silver nanoparticles. When all silver nanoparticles nucleate within the star-block copolymers suspended in solution, the particle size can be controlled by the core size. In this study, we explored the thiol-ene click reaction (8) to modify a star block copolymer of PI-*b*-poly(4-*tert*-butylstyrene) (PI-*b*-PtBS). By reacting 3-mercaptopropionic acid (3MP) with double bonds using a photo-radical initiation reaction, the PI block of the polymer can be successfully functionalized with carboxylic acid groups. These negatively charged carboxylic acid groups will be able to attract positively charged silver ions that are added to a solution of the functionalized polymer. Based on proton nuclear magnetic resonance (^1H NMR) spectroscopy results, the functionalization degree is about 60%. The rest of the double bonds most likely undergo an internal cyclization reaction. Using these carboxylic acid-functionalized star-block copolymers, silver nanoparticles can be prepared by reducing AgNO_3 with *tert*-butylamine borane (TBAB) in a mixture solution of *N,N*-dimethylformamide (DMF) and dioxane at room temperature. Both UV-Vis spectroscopy and transmission electron microscopy (TEM) results showed the successful preparation of silver nanoparticles. However, TEM images suggested that a relatively large amount of silver nanoparticles nucleated/grew outside the star-block nanoreactors. The strength of the ionic interaction between the silver ions and the carboxylic acid groups and also the strength of the reducing agent (TBAB) are a few of the possible factors that may have affected the results.

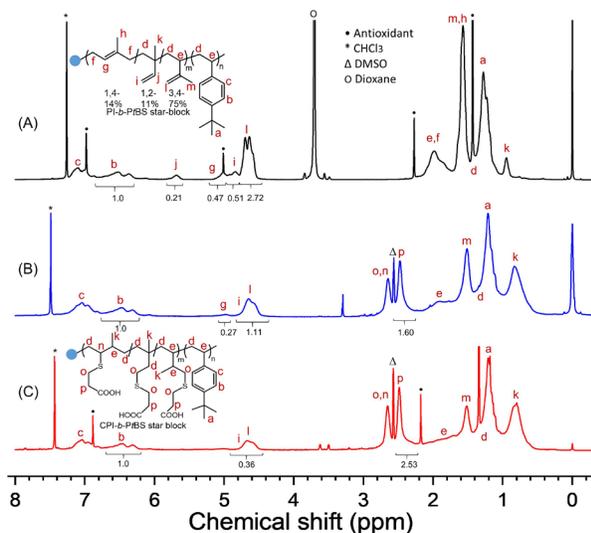


Figure 1. ^1H NMR Spectra. (A) PI-*b*-PtBS and CPI-*b*-PtBS star block copolymers synthesized with the 3MP to double bond ratio being (B) 10 : 1 and (C) 50 : 1 (mol./mol.). For PI-*b*-PtBS, CDCl_3 was the solvent, and 1,4-dioxane was used as an external reference to determine the content of double bonds. For CPI-*b*-PtBS, a mixture of CDCl_3 and DMSO- d_6 in an 80 : 20 ratio (by volume) was used as the solvent. Tetramethylsilane (TMS) was used as the internal reference at 0 ppm. Solvent (i.e., CHCl_3 and DMSO) peaks and antioxidant (i.e., BHT) peaks are labeled in the spectra.

Results

Synthesis of CPI-*b*-PtBS Star-Block Copolymer via Thiol-ene Click Reaction

The result of the thiol-ene click reaction was examined by ^1H NMR spectroscopy. **Figure 1** compares the ^1H NMR spectra for the unmodified PI-*b*-PtBS and the modified PI-*b*-PtBS (abbreviated as CPI-*b*-PtBS) samples. The microstructure of the PI block could be determined from peak assignments and their integration values (**Figure 1A**). The relative amounts of 1,4-, 1,2- and 3,4-microstructures were determined to be 14%, 11%, and 75%, respectively. After the UV-initiation at RT, the intensities of the *l* and *e/f* proton peaks decreased significantly, whereas the *i* and *j* proton peaks did not change much. These results indicated that the 3,4- and 1,4-double bonds reacted with 3MP more than the 1,2-double bonds did. Two new proton peaks appeared between 2.4 and 2.8 ppm (the sharp peak at 2.6 ppm is from DMSO), which could be assigned to protons *o/n*

and p in the chemical structure of CPI- b -P t BS. On the basis of the decrease in proton peaks l and g , it was concluded that approximately 90% of the double bonds reacted, and from the integration of proton peaks o/n and p , it was concluded that approximately 60% of the double bonds were grafted with 3MP (**Figure 1C**). The difference suggested that about 30% of the double bonds underwent internal crosslinking or cyclization, as mentioned previously (6).

Note that this thiol-ene click reaction was carried out at a 50:1 molar ratio of 3MP to the amount of double bonds in the PI blocks (*i.e.*, 3MP was largely in excess). When this molar ratio was decreased to only 10:1, much less 3MP was grafted to the double bonds (about 38%) and about 22% double bonds underwent intramolecular crosslinking/cyclization, *i.e.*, as much as 40% double bonds unfunctionalized (**Figure 1B**). This result suggests that the outer P t BS blocks have a certain “shielding effect”; they prevented 3MP molecules from reaching the inner PI blocks for the thiol-ene click reaction.

Unimolecular Micelles Studied by DLS

For the nanoreactor approach to work effectively, it is important to make sure that unimolecular micelles are dispersed individually in solution. Dynamic light scattering (DLS) was used to determine how dispersed the micelles were. Because of their amphiphilic nature, the unimolecular micelles might aggregate due to strong intermolecular interactions, depending on different solvents. For example, when PI- b -P t BS was dissolved in toluene, a hydrodynamic diameter of 26 nm was detected. When CPI- b -P t BS was dissolved in DMF, two hydrodynamic diameters of 18.4 and 63.2 nm were obtained. The 63.2 nm diameter could have occurred due to the aggregation of unimolecular micelles since the polar DMF is a poor solvent for the nonpolar P t BS outer blocks. By adding less polar dioxane (a good solvent for P t BS) to the DMF solution to form a mixture solvent that was 70% DMF and 30% dioxane by volume, a single hydrodynamic diameter of 36-40 nm was observed. In this study, the 70:30 DMF:dioxane mixed solvent was used for the synthesis of silver nanoparticles.

Synthesis of Silver Nanoparticles using CPI- b -P t BS Star-Block Copolymers

As mentioned previously, silver nanoparticles were synthesized by “loading” different amounts of silver ions (1, 5, and 10 equivalents compared to the amount of carboxylic acid groups in CPI- b -P t BS) into the star-block copolymers. They were then reduced using TBAB. A few minutes after the reduction of the silver ions started, the solution turned from clear to yellow, light brown, and then brown. The final colors after overnight reduction for 1, 5, and 10 equivalents of Ag⁺ are shown in **Figure 2**. The

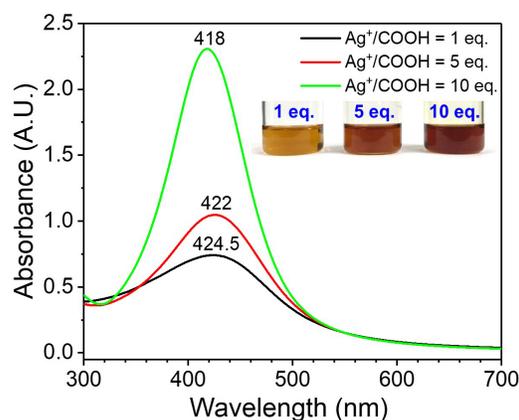


Figure 2. UV-Vis Spectra. Synthesized silver nanoparticles in the DMF:dioxane 70:30 (by volume) suspension when the Ag⁺/COOH ratio is 1, 5, and 10 equivalents, respectively.

solutions exhibited plasmonic UV absorption around 420 nm, indicating the presence of silver nanoparticles. By increasing the amount of Ag⁺, the plasmonic absorption peak became more intense, and the peak shifted to a slightly smaller wavelength.

The morphology of the reduced silver nanoparticles was examined by TEM, and results are shown in **Figure 3**. From these results, it can be seen that by increasing the amount of Ag⁺, the amount of synthesized silver nanoparticles increased. This is consistent with the darker color and increased plasmonic absorption peak in the UV-Vis spectra. Additionally, the particle size decreased from 48±13 nm for 1 equivalent Ag⁺ (**Figure 3A**), to 12±5 nm for 5 equivalents Ag⁺ (**Figure 3B**), and finally to 10±5 nm for 10 equivalents Ag⁺ (**Figure 3C**). As a test to determine if this trend in size would continue, a trial with more than 20 equivalents of Ag⁺ was conducted. This trial resulted in the precipitation of black particles in the solution upon reduction. This most likely occurred because when silver ions are in too large of an excess, the size of the synthesized silver nanoparticles continues to grow until precipitation occurs. It is therefore probable that 10 equivalents of Ag⁺ is the optimal condition for the facile synthesis of silver nanoparticles using this method.

Discussion

On the basis of the above experimental results, there may be many factors that can affect the synthesis of silver nanoparticles. First, during the synthesis, the amphiphilic star-block copolymer should form an open unimolecular micelle system, which means the outer polymer brushes should be solvated in solution and maintain their extended brush shape, rather than collapsing. In such a way, the reactants (*i.e.*, Ag⁺ and TBAB) can readily

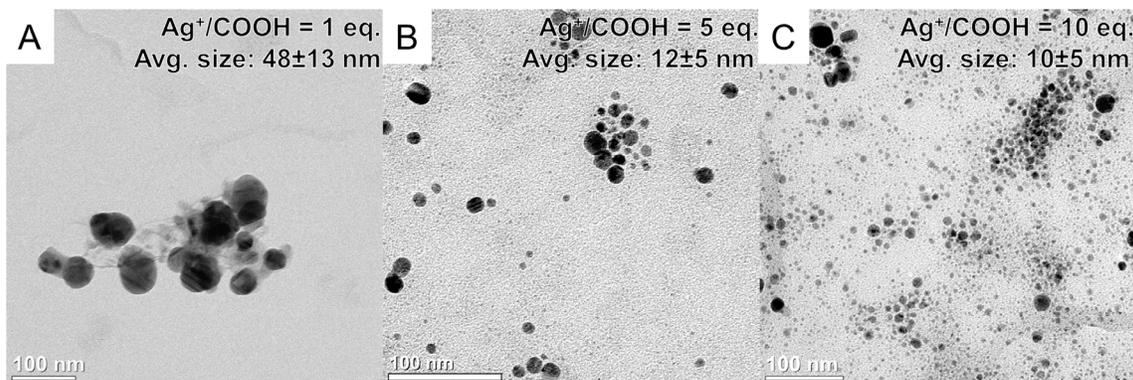


Figure 3. TEM Micrographs of Silver Nanoparticles. Silver nanoparticles synthesized with Ag^+/COOH ratios of (A) 1, (B) 5, and (C) 10 equivalents, respectively. The amount of TBAB was kept at 10 equivalents of Ag^+ .

diffuse in and out of the unimolecular micelle, although the outer brushes might still have a moderate shielding effect. Secondly, it is the ionic interaction of the Ag^+ with the carboxylic acid groups that loads and concentrates Ag^+ in the core of the unimolecular micelle (**Figure 4A**). For example, assuming that Ag^+ complexes in a 1:1 molar ratio with the carboxylic acid groups in the 40 nm unimolecular micelle, the concentration of Ag^+ inside the micelle is 5.34 mg/mL. In contrast, the concentration of Ag^+ in the solution outside the polymers is only 0.15 mg/mL. Obviously, the Ag^+ concentration inside the unimolecular micelle is much higher (~35 times) than that in solution.

In addition, the relative concentrations of the TBAB reducing agent in the unimolecular micelles and outside in the solution depends on the interaction between the reducing agent and carboxylic acid groups in the core of the unimolecular micelle. Whether the Ag^+ will be reduced inside or outside the unimolecular micelle will be determined by the balance between the reducing power and the diffusion of the reducing agent into the unimolecular micelle. What this means is that if the reducing power of reducing agent is low and the diffusion of reducing agent into the unimolecular micelle is high, the Ag^+ will be preferentially reduced inside the core (**Figure 4B**). This is actually the mechanism for nanoreactors. The open unimolecular micelle system allows continuous attraction of reactants in the core. Continued reduction of the attracted Ag^+ will lead to the growth of silver nanoparticles until the inner hydrophilic core is fully occupied. In this sense, the size of silver nanoparticles would be determined by the core size of the unimolecular micelle, which is exactly observed in a previous report (3).

On the contrary, if the reducing power of the reducing agent is high and/or the diffusion of the reducing agent into the unimolecular micelle is low, Ag^+ will be reduced outside the micelle, even though the concentration of Ag^+

in solution is lower than that in the micelle (**Figure 4C**). Subsequent growth of the unstabilized Ag^0 in solution could lead to a broad distribution of particle size, and most likely large Ag^0 particles will precipitate out from the solution. Meanwhile, it is possible that the Ag^+ inside the unimolecular micelle could diffuse out of the core and get reduced in the solution. For example, when a strong reducing agent such as NaBH_4 or hydrazine is used, large silver aggregates precipitated out of the solution very quickly (in a few minutes).

Judging from the relatively broad distribution of silver nanoparticles in **Figure 3**, we conclude that a large portion of the reduction of Ag^+ may have happened outside the unimolecular micelles of the CPI-*b*-PtBS star-block copolymer. Therefore, the reducing power of TBAB may still be too strong. Ethanol and ethylene glycol are weaker reducing agents that can possibly be used. However, if ethanol or ethylene glycol is used as the reducing agent, no reduction happens at RT. When heated to high temperatures such as 100°C to accelerate the reduction, side reactions happen. Currently, we are trying to figure out what side reactions occur and potential methods to avoid them.

Although the silver nanoparticles prepared in this work are less well-defined than those reported before (3), this study provides a deeper understanding of the fundamental mechanism of nanoreactors using amphiphilic star block copolymers. This will help the design and development of better systems to prepare well-defined silver nanoparticle in the future. The use of commercially available star-block copolymers still holds the promise of scaling up the synthesis of silver nanoparticles.

In summary, the hypothesis of a high concentration-induced nanoreactor mechanism for the synthesis of well-defined silver nanoparticles was tested in this study. Chemical modification of a commercially-available PI-*b*-PtBS star block copolymer was first carried out via

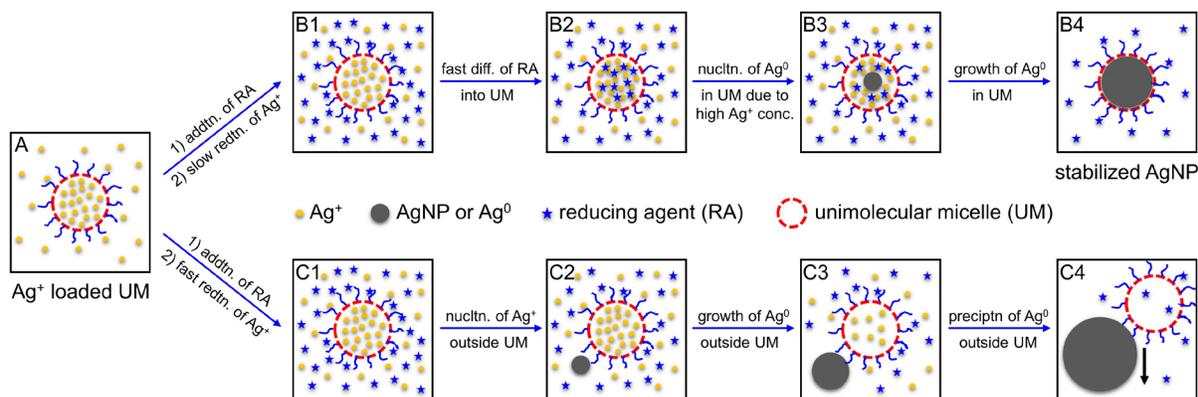


Figure 4. Schematic Representations. (A) Ag⁺-loaded unimolecular micelle (UM), subsequent synthesis of (B) 1-4: UM-stabilized silver nanoparticles via slow reduction of Ag⁺ and fast diffusion of reducing agent (RA), and (C) 1-4: precipitated Ag⁰ outside the UM from fast reduction of Ag⁺ and slow diffusion of RA.

a photo-initiated thiol-ene click reaction to prepare the CPI-*b*-P*t*BS star block copolymer. From ¹H NMR results, the degree of 3MP grafting onto the double bonds in the PI blocks was about 60%. These amphiphilic CPI-*b*-P*t*BS star-block copolymers were used as nanoreactors for the synthesis of silver nanoparticles in a mixed DMF:dioxane solution. TBAB was chosen as the reducing agent at RT. TEM images displayed some large silver nanoparticles (>10 nm), suggesting that many particles were primarily nucleated and grown outside the nanoreactors. It was possible that the reducing power of TBAB was somewhat too strong to induce reduction and nucleation outside the nanoreactors. Currently, we are searching for more appropriate reagents with a moderate reducing power to test our hypothesis for the synthesis of well-controlled silver nanoparticles using the nanoreactor approach.

Methods

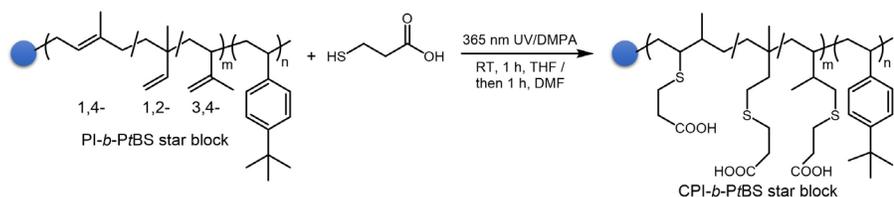
The reagents, 3MP, 2,2-dimethoxy-2-phenylacetophenone (DMPA), TBAB, AgNO₃, and anhydrous P₂O₅, were purchased from Aldrich. All solvents, such as anhydrous tetrahydrofuran (THF), anhydrous DMF, and dioxane, were purchased from Fisher Scientific, and were used without further purification. The PI-*b*-P*t*BS star-block copolymer was kindly supplied by Tongji University, China and was synthesized using the method outlined in literature report (5). In this method, *sec*-butyllithium (*s*-BuLi) was used as an initiator to start the anionic polymerization of 4-*tert*-butylstyrene (*t*BSt) in purified *n*-hexane. This was done under an oxygen and moisture-free condition. After all of the *t*BSt monomers reacted, a predetermined amount of purified isoprene, along with a small amount of purified [2,2,2]cryptand as a catalyst, was introduced into the living polymerization solution to initiate polymerization of the polyisoprene block. Afterwards, purified

divinylbenzene was added as the crosslinking agent to form the final star-block copolymer. The molecular weights and molecular weight distribution for the PI-*b*-P*t*BS diblock copolymer and the star-block copolymer were characterized by size-exclusion chromatography (SEC). The number-average molecular weights (M_n) for the P*t*BS and PI blocks were 9 and 14 kDa, respectively. The M_n for the star block copolymer was 212 kDa and the molecular weight distribution was 1.17. Therefore, each star-block copolymer contained about 10 diblock arms, each consisting of a P*t*BS block and a PI block.

Carboxylation of the PI-*b*-P*t*BS Star Block Copolymer by Thiol-ene Click Reaction

In a typical synthesis process (Figure 5), 200 mg of the PI-*b*-P*t*BS star block copolymer, 2.04 mL (23.4 mmol, 50 eq. of the double bonds in PI) of 3MP, and 20 mg (0.078 mmol) of DMPA were dissolved in 20 mL THF in a 100 mL round-bottom flask. The reaction mixture was irradiated with a 10 W, 365 nm UV light-emitting diode (LED) for 1 h at room temperature (RT). Afterwards, the THF was evaporated using a rotary evaporator and 20 mL DMF was added into the flask to perform a second click reaction, which also lasted for 1 h at RT. The second click reaction had to be done in DMF because the solubility of the star-block copolymer became poor in THF after grafting some polar 3MP onto the PI blocks. Changing the solvent from THF to DMF could increase the overall degree of grafting of 3MP. After the click reaction, the carboxylated PI-*b*-P*t*BS (abbreviated as CPI-*b*-P*t*BS) star-block copolymer was purified for 2 days using a dialysis tube with a molecular weight cutoff of 12-14 kDa. The purified CPI-*b*-P*t*BS was dried in a vacuum oven in the presence of anhydrous P₂O₅ for 1 day until a constant weight was reached.

Figure 5. Chemical Modification of PI-*b*-P*t*BS Star-Block Copolymer. Modified by the thiol-ene click reaction using DMPA as the photoinitiator under 365 nm UV irradiation.



Synthesis of Silver Nanoparticles using TBAB

In a typical process (Figure 6), 10 mg of CPI-*b*-P*t*BS was dissolved in 10 mL of a DMF:dioxane (70% DMF by volume) mixture solvent, forming a clear solution. A certain amount of AgNO₃ (1, 5, and 10 equivalents compared to the amount of COOH groups in the CPI-*b*-P*t*BS) was added to the mixture solution under magnetic stirring at ~600 rpm. About 12 hours were given for the AgNO₃ to dissolve and the Ag⁺ to complex with the COOH groups in the star-block copolymers. Afterwards, the clear, ion-loaded polymer solution was added dropwise to 10 equivalents of TBAB (with respect to Ag⁺) under magnetic stirring. TBAB was chosen as the reducing agent for the synthesis of silver nanoparticles because it had a moderate reducing power between NaBH₄ / hydrazine (which are too powerful) and ethanol (which is too weak) at RT. After a few minutes of stirring, the solution became light yellow, and over the course of a couple hours, gradually turned into a brown or wine color, depending on the amount of silver salt added. The silver nanoparticle dispersions were stable for several days.

Characterization Methods and Instrumentation

SEC was performed on a Waters Breeze 2 HPLC system, using THF as the solvent at a flow rate of 1.0 mL/min and PS as standards. ¹H NMR spectra were recorded using a Bruker 500 MHz NMR spectrometer. Dynamic light scattering (DLS) experiments were carried out using a Wyatt DynaPro NanoStar DLS instrument. UV-Vis spectroscopy was carried out on a Jasco V-670 spectrophotometer. TEM was performed on an FEI Tecnai F30 electron microscope operating at an accelerating voltage of 300 kV. Particle size was analyzed using the open source ImageJ software.

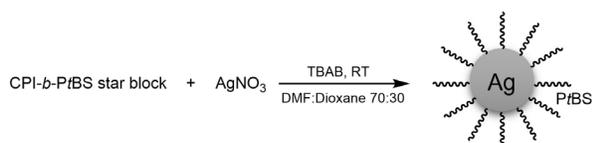


Figure 6. Synthesis of Silver Nanoparticles. Using CPI-*b*-P*t*BS star block copolymers as nanoreactors.

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