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Letters

Preparation of Aggregation Stable Gold Nanoparticles Using Star-Block Copolymers

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Nanoparticles of improved stability against long-term aggregation were prepared using poly(styrene)-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) star-block copolymer architectures. The star-block copolymers, physically resembling diblock copolymer micelles, were synthesized by anionic polymerization and coupling with ethylene glycol dimethacrylate. They contain P2VP core segments that facilitated conversion of $HAuCl_4$ to single gold nanoparticles. The size distribution and long-term stability against aggregation of the gold nanoparticles were investigated both as solution and as films. UV−vis spectroscopy and transmission electron microscope images reveal long-term stability against aggregation up to 1 month.

Introduction

Nanoparticles of semiconductors and metals have been extensively studied in recent years due to their novel material properties which are greatly different from those of their bulk substances.[1] To achieve complete control of the properties of nanoparticles, it is necessary to prepare monodispersed particles with respect to size, shape, and internal structure. For example, the band gap of a semiconductor nanoparticle material is dependent on particle size and thus both its absorption and emission spectra are size dependent. A polydispersed semiconductor nanoparticle will show a broad emission spectrum, reflecting the overlap of multiple emission bands.[2−5]

One of the most widely studied nanoparticles, gold nanoparticles have attracted great attention due to their potential applications in optoelectronics, electronics, catalysis, and other areas.[1] For the preparation of gold nanoparticles with small sizes, narrow size distributions, and long-term stability, various stabilizers such as low molecular weight (MW) surfactants and various polymers have been used.[1,6−13] These materials are essentially classified as "nanoreactors", which allows for control of

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several parameters for nanoparticle synthesis. In the case of block copolymers, they offer some advantages compared to low MW surfactants with respect to stability of the self-organized structures, as well as in thin film formation. The critical micelle concentration (cmc) of block copolymers is typically smaller and their kinetic stability is larger than that of low MW surfactants. Other advantages offered by block copolymer micelles include some control over the diffusion of reagents into the micelles and the possibility of attaching coordinating ligands to the polymer in order to stabilize both precursors and nanoparticles within the micelles. It is also possible to control the micelle size through manipulation of MW composition, chemistry, and choices of solvent, as well as molecular architecture. Möller and co-workers[11,12] successfully prepared uniform gold nanoparticles and arranged them spatially in two-dimensional arrays by using poly(styrene)-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) diblock copolymer micelles. They also studied the association behavior and stability of the micelles containing gold nanoparticles. When an excess of hydrazine (N_2H_4) was not removed after reduction of tetrachloroauric acid ($HAuCl_4$), which was used for a gold nanoparticle precursor, the micelles started to coagulate immediately because N_2H_4 can swell the core volume of the micelles. The stability of the micelles containing gold nanoparticles was also dependent on the concentration of the polymer. As the concentration of the polymer decreased, the polymer chains were molecularly dispersed and gold nanoparticles started to aggregate to form anisomeric shapes and sizes. Thus, although single nanoparticles can be formed from the initial micelle, the long-term stability and preparation methods are very much dependent on micelle stability, which can be affected by concentration, temperature, solvent, and pressure.[13]

To overcome these drawbacks for the preparation of gold nanoparticles, PS-*b*-P2VP star-block copolymer architectures, physically resembling diblock copolymer micelles, can be used as a highly promising material in lieu of micelles.[14a] In this case, there is no more concern about the micelle instability with time and concentration because the core segments of the star-block copolymer are *covalently bound*. Furthermore, the star-block copolymer can be synthesized with a very narrow molecular weight distribution (MWD) and with a variety of macromolecular architectures and constitutions.[14b] In this case, nanoparticle synthesis can be confined within the core of the star-block copolymer compared to the core of a diblock copolymer micelle. This can be done by controlling the inner core polymer block length and constitution of the star. In this study, a PS-*b*-P2VP star-block copolymer was synthesized and gold nanoparticles were prepared within the core. The size distribution and long-term stability against aggregation of the gold nanoparticles were investigated.

Experimental Section

All the essential chemicals and reagents were purchased from Aldrich. Styrene was purified by sequential distillation over CaH_2 powder and dibutylmagnesium under high vacuum. 2-Vinylpyridine (2VP) was purified by sequential distillation over CaH_2 powder, sodium mirror, and trioctylaluminum. The coupling agent ethylene glycol dimethacrylate (EGDMA) was purified by distillation over CaH_2 powder and diluted with tetrahydrofuran (THF).

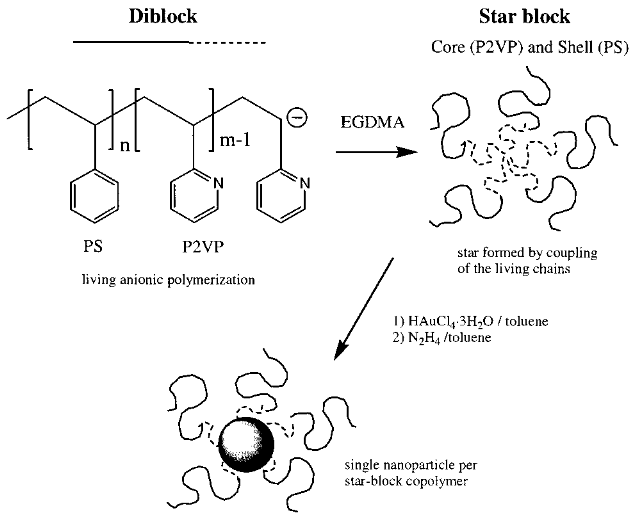

Figure 1. The chemical structure of the PS-*b*-P2VP diblock copolymer and the architecture of the PS-*b*-P2VP star-block copolymer.

PS-*b*-P2VP diblock copolymer was first synthesized by living anionic polymerization via a high-vacuum technique.[15] After flame-drying of the all-glass reactor, *n*-butyllithium was introduced, THF (purified with K/Na alloy) was distilled in by using liquid nitrogen, while THF was kept at −78 °C, and then styrene (St) and 2-vinyl pyridine (2VP) were introduced sequentially into the reactor by distillation. When 2VP was added, the solution color changed from light orange to dark red. Methanol was used to terminate the polymerization. For the synthesis of PS-*b*-P2VP star-block copolymer,[14a] a coupling agent, EGDMA, was added to the living anionic PS-*b*-P2VP arm (the reaction is described further in the Supporting Information). The resulting solution became colorless. Finally, the polymer was precipitated into hexane. Fractionation of the star-block copolymer was performed to remove unreacted diblock copolymers and to obtain a narrower MWD with THF and hexane as a solvent and a nonsolvent, respectively.

To prepare gold nanoparticles, a 5 mg/mL solution of PS-*b*-P2VP star-block copolymer in dry toluene was mixed with three different concentrations, 0.1, 0.3, and 0.5 equiv, of $HAuCl_4{\cdot}3H_2O$ per 2VP unit and stirred for 24 h. $HAuCl_4{\cdot}3H_2O$ is not soluble in toluene but was incorporated into the star-block copolymer cores by coordinating with 2VP copolymer units. Upon coordination, the star-block copolymer solution in toluene changes to light yellow in color. The inner P2VP chain can behave as a core in toluene, which is a solvent for PS but a nonsolvent for P2VP. Each of the 5 mL star-block copolymer solutions incorporated 0.1, 0.3, and 0.5 equiv of $HAuCl_4$ per 2VP unit and was added dropwise to 1, 3, and 5 mL of a 0.02 vol % solution of nonaqueous N_2H_4 in toluene, respectively. After reduction of $HAuCl_4$ for 12 h, the gold nanoparticle solution was diluted with dry toluene to 0.3 mg/mL on the basis of the star-block copolymer concentration.

To determine MW and MWD of polymers, size exclusion chromatography (SEC) was performed in THF using a Waters 510 pump, a Waters 410 differential refractometer, and an UV detector at 254 nm at room temperature (flow rate, 1 mL/min; columns: PSS 8 × 600 mm, 5 μm with pore size 100 Å, and Linear). SEC was calibrated with PS standards. ^1H NMR spectra were recorded on a Bruker 300 MHz ARX spectrometer in $CDCl_3$ at room temperature. UV−vis absorption spectra were obtained using a Perkin-Elmer UV−vis spectrometer (Lambda 20). The average size of gold nanoparticles was determined using a Hitachi transmission electron microscope (TEM, H-7000).

Results and Discussion

The chemical structure of the PS-*b*-P2VP diblock copolymer and the architecture of the PS-*b*-P2VP star-block copolymer are shown in Figure 1. The diblock

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Table 1. Characteristics of the Synthesized Polymers

polymer	M_w ($\times 10^{-4}$)	M_w/M_n
PS	3.53	1.20
PS-*b*-P2VP	5.32	1.22
PS-*b*-P2VP star-block copolymer	15.5	1.46

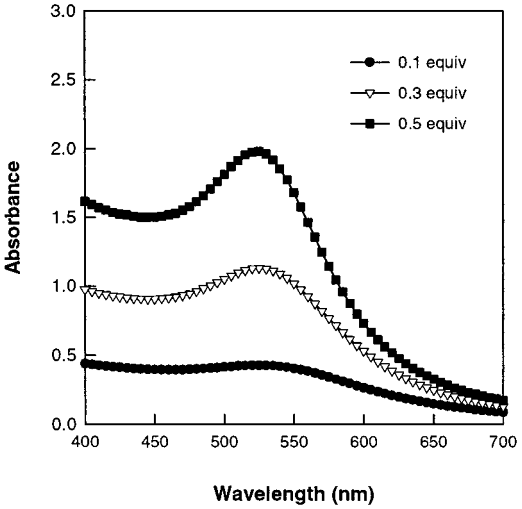

Figure 2. UV−vis absorption spectra of gold nanoparticles stabilized by the star-block copolymer.

copolymer was first synthesized by living anionic polymerization and coupled with EGDMA to form the star-block copolymer. The star-block copolymer consists of 65.1 wt % of PS and 34.9 wt % of P2VP inside, as determined by ^{1}H NMR. The star-block copolymer has a "core and shell" type structure by the self-micellization and partial cross-linking. The number of arms in the star-block copolymer should be of a distribution due to the nature of the coupling reaction with EGDMA (see Supporting Information).[14a] In this study, we used 2VP instead of 4-vinylpyridine (4VP) because the former yields a narrow MWD product and the use of a narrower MWD copolymer should lead to micelle cores having a more uniform size. The MW and polydispersity index as determined by SEC are listed in Table 1. Although the star-block copolymer was fractionated to remove unreacted diblock copolymers and to obtain a narrower MWD, its MWD was not ideally narrow due to the nature of the coupling reaction.

Figure 2 shows the UV−vis absorption spectra of various gold nanoparticle solutions. After addition of a reducing agent, N_2H_4, the yellowish colored solution of the star-block copolymer with incorporated $HAuCl_4$ changed immediately to a deep purple-red color. The absorption band at ~525 nm is assigned to the surface plasmon resonance of small gold nanoparticles.[16] The absorption bands were located around the same position irrespective of the incorporation ratio of $HAuCl_4$, and their intensity increased linearly with increasing incorporation ratio. Figure 3 shows TEM micrographs of gold nanoparticles for different incorporation ratios of $HAuCl_4$ 24 h after reduction with an excess of N_2H_4. Thin films were prepared by placing a drop of the solution onto a carbon-coated copper grid followed by contacting with a soaking tissue in order to make a liquid thin film. One gold nanoparticle was formed in the core of a star-block copolymer for all incorporation ratios of $HAuCl_4$. Most of the nanoparticles were spherically symmetric. The average sizes of gold nanoparticles were 4.1 ± 0.04, 5.5 ± 0.05, and 6.7 ± 0.06 nm for 0.1, 0.3, and 0.5 equiv of the incorporation ratio, respectively (see Supporting Information).

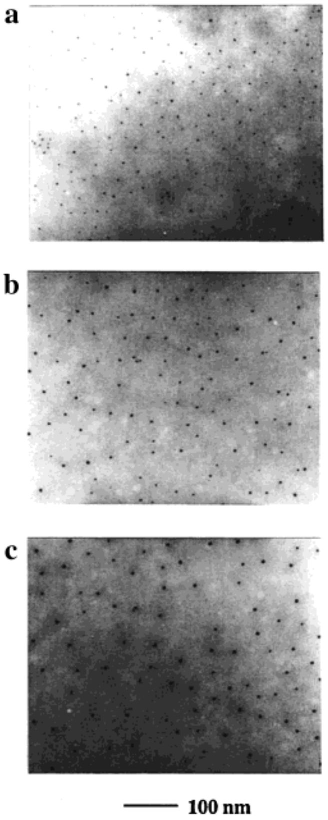

Figure 3. TEM micrographs of gold nanoparticles for different incorporation ratios of $HAuCl_4$ 24 h after reduction: (a) 0.1 equiv, (b) 0.3 equiv, and (c) 0.5 equiv.

It was reported that when PS-*b*-P4VP diblock copolymer was used for the preparation of gold nanoparticles, some of the micelles contained two gold nanoparticles due to a collision-induced aggregation of particles, resulting in a broad size distribution of gold nanoparticles.[1,11] To prevent such events and to keep the micelle cores as molecular entities, the micelle cores have to be slightly cross-linked with *p*-xylenedibromide (5% per 2VP) and small amounts of methanol were added to provide a higher mobility of the inner micelle cores.[1] In our case, the synthesis of a well-defined PS-*b*-P2VP star-block copolymer does not necessitate this extra step. It is a much more rational approach to the preparation of monodispersed gold nanoparticles since the degree of cross-linking is controlled a priori. Thus, control of the size, shape, and internal structure of the core should be possible by macromolecular design of the star copolymer.

The long-term stability of gold nanoparticles against aggregation is very important for their applications. The control of particle−particle interaction is critical for the preparation of a stable particle dispersion resulting in quantum confinement effects. The stability of gold nanoparticles prepared using PS-*b*-P2VP diblock copolymer was briefly reported by Möller and co-workers.[11] Excess N_2H_4 used for the reduction of $HAuCl_4$ swelled the micelles and resulted in aggregation mostly pairwise even at 30 min after reduction. Therefore, they had to remove the excess of N_2H_4 directly after reduction by adding 38% aqueous HCl. Only then were they able to obtain identical TEM images after many days.

In our case, stable nanoparticles were observed even after *1 month* both as solution and films. Figure 4 shows TEM micrographs of gold nanoparticles for different incorporation ratios of $HAuCl_4$ 1 month after reduction with 4.1 ± 0.06, 5.6 ± 0.1, and 6.8 ± 0.25 nm sizes for 0.1,

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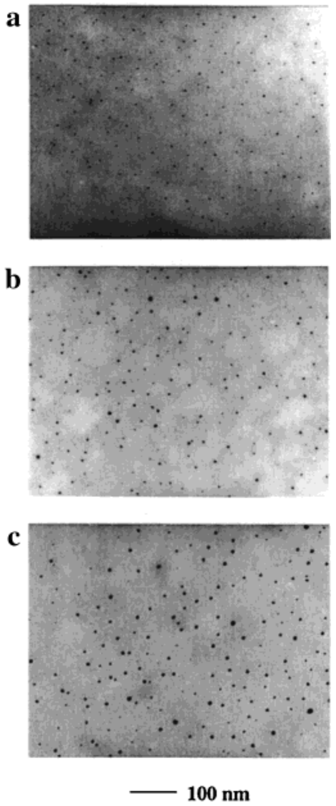

Figure 4. TEM micrographs of gold nanoparticles for different incorporation ratios of $HAuCl_4$ 1 month after reduction: (a) 0.1 equiv, (b) 0.3 equiv, and (c) 0.5 equiv.

0.3, and 0.5 equiv, respectively. In the case of 0.3 and 0.5 equiv samples, interestingly, larger gold nanoparticles than those observed 24 h after reduction were observed due to some aggregation and residual reduction, that is, resulting in a much broader size distribution of gold nanoparticles. Some of the gold nanoparticles were even larger than 5 times the initial average size due to the aggregation. However, in the case of the 0.1 equiv sample, the size distribution of gold nanoparticles remained unchanged for 1 month. This result was also confirmed using UV−vis spectroscopy. The absorption band at 525 nm observed 24 h after reduction was red-shifted by ∼10 nm for 0.3 and 0.5 equiv samples. This shift is most likely due to the size increase of gold nanoparticles.[17−19] These results indicate that gold nanoparticles above a certain size can be aggregated due to the particle−particle interaction although there is a PS shell protecting their aggregation. However, it is a very promising result that we can successfully improve the long-term stability of gold nanoparticles against aggregation even after a month by controlling the size of the PS shell.

Thus, we have found that star-block copolymers can provide some potential advantages over diblock copolymer micelles in single-nanoparticle preparation. Nanocomposite materials prepared by incorporation of nanoparticles in a polymer matrix are of great interest in terms of their potential applications as electronic and optical materials.[20,21] For the preparation of nanocomposite materials as films and fibers, blending of nanoparticles into the matrix is the most desirable approach. In this case, their miscibility with a polymer matrix and their resulting stability are essential. As we have shown in this study, star-block copolymers can successfully stabilize gold nanoparticles over longer periods of time. This has the potential for providing a wide variety of matrix materials by changing the core and shell composition of star-block copolymers. Also, selective decoration in a phase-separated block copolymer system can provide a variety of structures having a unique spatial distribution of nanoparticles in the matrix polymers.[22−24]

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Supporting Information Available: Description of the size distribution and estimation, explanation on the use of the term “stable”, and description of the formation of a cross-linked star copolymer structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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