Polymer Size and Concentration Effects on the Size of Gold Nanoparticles Capped by Polymeric Thiols

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Gold nanoparticles stabilized by thiol-terminated poly(ethylene glycol) monomethy ether with molecular weights ranging from 350 to 2000 have been prepared at thiol-to-gold molar ratios ranging from 3:1 to 8. Particle size distributions have been constructed for these particles from transmission electron microscopy images of hundreds of particles for each variation in synthetic conditions. The mean diameters of these particles range from 1.5 to 3.2 nm, with a slight increase in particle size with decreasing thiol content; these particles are smaller than those prepared using alkanethiols at similar thiol-to-gold ratios. Particles prepared under thiol-poor conditions exhibit much greater polydispersity than those prepared under thiol-rich conditions and include numerically rare large-particle outliers that contain much of the gold in the sample. The mean diameters of the gold nanoparticles decrease slightly with increasing polymer weight, especially under thiol-rich conditions. A simple model is developed to predict the trends in nanoparticle diameter that would result were the polymer's steric bulk protecting the nanoparticles from additional growth the principal factor controlling nanoparticles size in this system. This model predicts a much stronger dependence on thiol concentration than has been experimentally observed and a dependence on polymer molecular weight opposite to that experimentally observed. This suggests that the polymers' steric bulk is not the principal reason that these polymers yield smaller nanoparticles than alkanethiols at similar thiol-to-gold ratios. It is instead proposed that polar polymers may yield small nanoparticles by accelerating particle nucleation via coordination between functional groups in the polymer and atomic gold.

Introduction

Due to their stability, coloration,1 chemical versatility, and facile one-pot syntheses in both nonpolar2 and polar3 media, thiol-stabilized gold nanoparticles have become a staple model system in nanomaterials research. When the thiol stabilizer is a functional polymer, these gold nanoparticles have found technological application as labels and sensors for heavy metal ions,4,5 carbohydrates,6 nanoparticles have found technological application as and other biomolecules.7

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In nonpolar solvents, the AuSR species aggregate,2 due to their stability, coloration,1 chemical versatility, and facile one-pot syntheses in both nonpolar2 and polar3 media, thiol-stabilized gold nanoparticles have become a staple model system in nanomaterials research. When the thiol stabilizer is a functional polymer, these gold nanoparticles have found technological application as labels and sensors for heavy metal ions,4,5 carbohydrates,6 and other biomolecules.7

AuSR

Although gold nanoparticles form quite rapidly upon addition of the reducing agent, and reaction times as short as 20 s have been reported in the literature,10 particle size measurements during the course of the reaction indicate that the initially formed particles ripen into larger ones for up to 60 h after the initial reduction.11 The final particle size is highly dependent on the thiol-to-gold ratio, with smaller particles resulting when more thiol is present.12,13 The smallest average particle diameter is achieved at a 3:1 thiol-to-gold ratio, where the initial Au(III) salt is completely converted to AuSR species before reduction.1 Mass spectrometry of these extremely small gold nanoparticles suggests that the small end of the nanoparticle size distribution is dominated by a few discrete cluster sizes, with core masses near 14 kDa, 22 kDa, and 28 kDa.14 Smaller particles are also generally achieved at lower temperatures or when the reducing agent is added more quickly.13 Large particles may be etched into small ones by heating in the presence of additional thiol; gold nanoparticles with core masses as small as 8 kDa, or

AuSR + BH₄⁻ → Auₙ(SR)ₘ n > m

In the presence of sodium borohydride, all gold species present are reduced to clusters of gold atoms surrounded by thiolates:

Au(III) + 3RSH → AuSR + RSSR

In nonpolar solvents, the AuSR species aggregate, imparting a cloudy appearance to the reaction mixture.

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approximately 40 gold atoms, have been prepared using this technique.15

However, there has been little research as to what extent these results remain true when the stabilizing thiol is not a small molecule but an oligomer or polymer. It has been observed16 that gold nanoparticles prepared using thiol-functionalized polymers can be small even when the gold concentration greatly exceeds that of the thiol on a molar basis. This phenomenon has been noted for thiolated poly(ethylene glycol)16 (PEG) and thiolated poly(N-isopropylacrylamide),17 although not for thiolated polystyrene.18 Similar effects occur for nonpolymeric but nonetheless bulky thiols.19 Miyaake and co-workers have prepared gold nanoparticles using poly(N-vinyl-2-pyrrolidone) (PVP) and thiolated PVP copolymers under a variety of conditions,20 but always with a large molar excess of polymer over gold. To our knowledge, no systematic study has been published on the effect of the polymeric thiol-to-gold ratio on nanoparticle diameter, nor has there been any report on the relationship between polymer molecular weight and nanoparticle diameter in such systems.

In this paper, we report what is to our knowledge the first systematic study on the size effect of polymeric thiols on gold nanoparticle diameter, acquiring rigorous statistics through the analysis of hundreds of nanoparticles for each variation in experimental conditions. In this study, we employed gold nanoparticles passivated with thiol-terminated PEG. These particles' solubility in water and a broad range of polar organic solvents lends them a greater potential for biochemical and other applications than the more widely studied alkanethiols, which are soluble only in nonpolar solvents. Also, the use of PEG thiols allowed gold nanoparticles to be prepared via a single-phase synthesis in polar solvent, without the use of phase transfer agents that may also influence nanoparticle size. At large thiol-to-gold ratios, small (<2 nm) particles result regardless of polymer molecular weight, with very few large objects observed. Also at large thiol-to-gold ratios, particle size decreases with increasing polymeric thiol molecular weight. At low thiol-to-gold ratios, the particle size distribution is both broader and larger with a tail of large outliers, and the dependence of particle size on molecular weight is not so evident.

Experimental Section

Materials. Triphenylphosphine, diisopropyl azodicarboxylate, and poly(ethylene glycol) monomethyl ethers (Me-PEG) were purchased from Aldrich. Thiolacetic acid, sodium borohydride, hydrogen tetrachloroaurate trihydrate, anhydrous tetrahydrofuran, and all other solvents were purchased from Fisher. The poly(ethylene glycol) monomethyl ethers were heated to 60 °C for 10 min under a 200 mTorr vacuum to drive off water before use. All other materials were used as received.

Synthesis of Me-PEG Thiols (Me-PEG-SH). Thiolated Me-PEGs were prepared via a modified version of the Mitsunobu reaction. A method described by Nicol and co-workers21 for diisopropyl azodicarboxylate was used in place of the diethyldi-azodicarboxylate used in that synthesis, and the intermediate thiolactates were cleaved by overnight reflux in 0.1 M HCl in methanol instead of by LiAlH₄ reduction. Approximately 90% purity was obtained. ¹H NMR, 400 MHz, CDCl₃: Me-PEG-SH (350) δ 1.56 (triplet, 0.98, SH), δ 2.68 (quartet, 1.94, CH₃SH), δ 3.37 (singlet, 3.00, CHO), δ 3.5–3.7 (PRP, 30.67, OCH₃CHO); Me-PEG-SH (550) δ 1.59 (triplet, 0.90, SH), δ 2.69 (quartet, 1.88, CH₃SH), δ 3.37 (singlet, 3.00, CHO), δ 3.5–3.7 (PRP, 44.24, OCH₃CHO); Me-PEG-SH (750) δ 1.58 (triplet, 0.89, SH), δ 2.68 (quartet, 1.84, CH₃SH), δ 3.36 (singlet, 3.00, CHO), δ 3.5–3.7 (PRP, 65.08, OCH₃CHO); Me-PEG-SH (1000) δ 1.59 (triplet, 0.93, SH), δ 2.69 (quartet, 1.68, CH₃SH), δ 3.37 (singlet, 3.00, CHO), δ 3.5–3.7 (PRP, 156.01, OCH₃CHO).

General Procedure for Au Nanoparticle Preparation. Following an established procedure,22 30 mg of HAuCl₄·3H₂O was dissolved in a mixture of 16 mL of 2-propanol and 0.5 mL of acetic acid. Neat Me-PEG-SH was melted if solid and then added to the liquid form, and the solution was vigorously stirred for 15–30 min. Next, the gold was reduced by rapid addition of 0.12 g of NaBH₄ in 5 mL of water. The solution turned dark immediately, indicating the formation of gold nanoparticles, and was stirred for at least 1 h. The solution was then centrifuged for 1 h at 4000g to remove all large sediment, such as the aggregate presented in Figure 6. Assuming Stokes flow, single particles larger than ~40 nm would be expected to be removed by centrifugation. Also, charged gold nanoparticles larger than 10 nm can be expected to aggregate due to van der Waals attractions,23 and such aggregates would also be expected to be removed by centrifugation.

Instrumentation. ¹H NMR spectra were taken on a Varian U400 spectrometer. Microscopy was performed on a Phillips CM-12 transmission electron microscope operating at 120 keV. For the transmission electron microscopy (TEM) sample preparation, a fraction of each nanoparticle solution was diluted about 20-fold with water before being dripped onto holey carbon grids lying on filter paper. When the nanoparticles were dried from other solvents, including 2-propanol, ethanol, or dichloromethane, branched nanoparticle aggregates24 were seen instead of discrete nanoparticles.

TEM Image Analysis. Particle diameter statistics were obtained from TEM images using the software package Imagej, freely available from NIST over the Internet. This program treats particles as regions of contiguous pixels whose gray scale values lie between user-defined thresholds (Figure 1). Carbon background speckle that would otherwise be counted as unrealistically small particles was filtered out by setting a minimum particle size in pixels. We used Feret’s diameter (the greatest distance between any two pixels on the particle boundary) as the particle size metric, as this measurement appeared relatively insensitive to small changes in image analysis thresholds. While yielding reproducible statistics, this approach does inflate the size of asymmetric particles over more spherical particles of similar mass and it does select against smaller particles that appear in poor contrast against the background.

Results and Discussion

Nanoparticle Size Distributions. This study was conducted to determine the effect of polymer molecular weight and the thiol-to-gold ratio on the size of gold nanoparticles capped by polymeric thiols. The mean diameter of the particles formed in our modified one-phase Brust synthesis ranged from 1.5 to 3.2 nm as a function of the PEG molecular weight and thiol-to-gold ratio (Figure 2, Table 1). The smallest particles were formed using higher molecular weight polymers and larger thiol-to-gold ratios. With decreasing thiol-to-gold ratios, both the average diameter and polydispersity of the particles increased. At the smallest thiol-to-gold ratio used in this study, the trend of decreasing particle size with increasing

polymer molecular weight seen at larger thiol-to-gold ratios was not observed. Previous authors\textsuperscript{16,17} have observed that gold nanoparticles prepared from polymeric thiols at small thiol-to-gold ratios are substantially smaller than those prepared from alkanethiols at similarly small thiol-to-gold ratios. This work corroborates that observation. However, the mean diameter gives an incomplete view of the particle size distribution. Figure 2 also presents the mean diameter of the largest 10% of particles observed from each synthesis. As the thiol-to-gold ratio decreases, the size of these large particles increases faster than the mean particle diameter. The TEM micrographs in Figure 3 show gold nanoparticles prepared using Me-PEG-SH(750) at thiol-to-gold ratios of 1:8 and 3:1. The thiol-rich conditions result in a relatively narrow distribution of small (1.7 ± 0.5 nm diameter) gold nanoparticles, while under thiol-deficient conditions, a larger, broader diameter distribution (2.3 ± 1.2 nm) results, and several large outliers are present.

Under these thiol-deficient conditions, more gold becomes concentrated in a few large particles. Figure 4 presents histograms of the particle size distributions for all thiol-to-gold ratios we studied in the Me-PEG-SH(350)

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**Figure 1.** Image analysis with ImageJ: (a) original image; (b) image broken into regions of similar background darkness; (c) nanoparticle outlines; (d) particle diameter histogram.

**Figure 2.** Mean particle diameters for all syntheses. White bars represent mean diameter of the largest 10% of particles observed from each synthesis.

**Table 1.** Particle Sizes and Standard Deviations for All Syntheses

<table>
<thead>
<tr>
<th>Me-PEG-SH mol wt</th>
<th>thiol/Au ratio</th>
<th>mean diameter, nm</th>
<th>std dev, nm</th>
<th>no. of particles</th>
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<tr>
<td>350</td>
<td>3:1</td>
<td>1.95</td>
<td>0.50</td>
<td>301</td>
</tr>
<tr>
<td>350</td>
<td>1:1</td>
<td>2.32</td>
<td>0.72</td>
<td>340</td>
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<td>0.80</td>
<td>420</td>
</tr>
<tr>
<td>350</td>
<td>1:4</td>
<td>2.63</td>
<td>1.02</td>
<td>407</td>
</tr>
<tr>
<td>350</td>
<td>1:8</td>
<td>2.18</td>
<td>0.95</td>
<td>378</td>
</tr>
<tr>
<td>550</td>
<td>3:1</td>
<td>1.79</td>
<td>0.50</td>
<td>402</td>
</tr>
<tr>
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<td>1:1</td>
<td>2.52</td>
<td>0.76</td>
<td>272</td>
</tr>
<tr>
<td>550</td>
<td>1:2</td>
<td>2.16</td>
<td>0.66</td>
<td>304</td>
</tr>
<tr>
<td>550</td>
<td>1:4</td>
<td>2.63</td>
<td>0.93</td>
<td>389</td>
</tr>
<tr>
<td>550</td>
<td>1:8</td>
<td>2.16</td>
<td>1.36</td>
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<td>1.11</td>
<td>477</td>
</tr>
<tr>
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<td>1:4</td>
<td>1.88</td>
<td>0.57</td>
<td>283</td>
</tr>
<tr>
<td>750</td>
<td>1:8</td>
<td>2.30</td>
<td>1.22</td>
<td>417</td>
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<tr>
<td>2000</td>
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<tr>
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<td>328</td>
</tr>
<tr>
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<tr>
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<td>1:8</td>
<td>3.19</td>
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system. The concentration of gold in a few large objects is reflected in the emergence of a large-particle tail in the particle size distribution at small thiol-to-gold ratios. Figure 5 shows this more dramatically by reploting the particle size histograms for the 3:1 and 1:8 thiol-to-gold cases of the Me-PEG-SH(350) system on a mass-weighted basis, under the assumption that particle mass varies as the cube of particle linear dimension. For the 3:1 case, the mass-weighted distribution remains sharply peaked, with a population only moderately skewed toward larger particles versus the number-weighted distribution shown in Figure 4a, whereas for the 1:8 sample, the mass-weighted histogram is markedly distorted by a few large objects. Similar results were also observed for the particles prepared using higher molecular weight polymers.

The large-particle tail shown in Figure 4 may extend to still larger objects, unobserved by TEM but present in the precipitated byproduct of the reaction. It has been reported that uncharged monothiols are ineffective in protecting larger gold nanoparticles (>10 nm) against van der Waals-driven flocculation,23 and any precipitate of these larger particles was removed by the centrifugation step of our synthesis. Due to the small mass of gold used in these preparations, the mass of this precipitate was too small to be accurately determined on a laboratory balance; however, after centrifugation, the supernatant solutions from samples prepared using a 1:8 thiol-to-gold ratio were visibly less colored than those prepared under more thiol-rich conditions, indicating the loss of a significant amount of gold in this flocculated precipitate.

When these experiments were extended to even smaller thiol-to-gold ratios (1:16 and smaller), the supernatant solutions after centrifugation were to the eye either colorless or only barely perceptibly colored, and substantial amounts of a black solid had precipitated. Figure 6 shows TEM images prepared from a dispersion of the precipitate formed using Me-PEG-SH(750) at a thiol-to-gold ratio of 1:16. The open, branching morphology of these aggregates suggests that they formed via the diffusion-limited aggregation and subsequent partial sintering of large (>12 nm) gold nanoparticles.

With respect to the body of previous work that shows small nanoparticles resulting from gold reduction in the presence of polymeric thiols, even at small thiol-to-gold ratios.
ratios, this study suggests that while small gold nanoparticles do form under these conditions, they are the minority product in a synthesis that produces particles across the nanometer size regime, including large particles that, although numerically rare, do contain much of the gold, and the largest of which are colloidally unstable. This should perhaps be considered when reading some of the earlier work on gold nanoparticles stabilized by polymeric thiols.

For all thiol-to-gold ratios greater than 1:8, the data in Figure 2 show that smaller particles resulted when higher molecular weight polymers were used as the passivant. The syntheses performed at a thiol-to-gold ratio of 3:1 in particular show a steady decrease in nanoparticle size with increasing polymer molecular weight. This trend may tentatively be regarded as an extension of the observation that polymeric thiols produce smaller nanoparticles than small-molecule alkanethiols.

Observations Regarding Polymer Layer Thickness. Micrographs such as those in Figure 3 show a 1.2-1.7 nm spacing between the metal core of each particle and that of its nearest neighbor. This interspace was too close to be compatible with the 0.35 nm² footprint measured by Murray and co-workers for Me-PEG(5000)-SH on 2.8 nm gold nanoparticles and implies that our synthesis leads to Me-PEG-SH monolayers that are less dense than those prepared in that study. At the same time, this spacing is too great to be compatible with a model wherein strong attraction between PEG and the gold surface causes the PEG molecules to lie flat on the gold.

Evaluation of Steric Effects of Passivant on Nanoparticle Size. When comparing the gold nanoparticles produced using polymeric thiols to those produced using alkanethiols, previous authors have remarked that the smaller size of the nanoparticles produced using polymeric thiols indicates that macromolecular thiols are better passivants against core growth, presumably as a consequence of the polymer's greater bulk. However, to our knowledge there have been no attempts to derive testable predictions from this hypothesis.

In the synthesis of gold nanoparticles by reduction of gold salts, two particle growth mechanisms may coexist. Particles may grow by the aggregation of nanoparticles of similar size, or by the addition of individual gold atoms or small clusters thereof to comparatively large particles. It may readily be accepted that polymeric thiols are better passivants against particle–particle aggregation than small-molecular thiols; fewer polymer molecules are needed to coat the nanoparticle surfaces sufficiently densely to provide a steric barrier against aggregation. Indeed, on the basis of the long-term stability (months) of the PEG-stabilized particles produced for this work, the PEG polymer layers formed in this synthesis do appear to be quite effective in passivating gold nanoparticles in the size range studied against particle–particle aggregation.

What is not so obvious is that macromolecular thiols should be more effective passivants than alkanethiols against growth by atomic addition. Thiol monolayers on gold are not necessarily impervious to gold atoms; recent work has demonstrated the growth of gold nanoparticles stabilized with 2-mercaptosuccinate by the addition of additional HAuCl₄ and reducing agents capable of reducing gold at a gold surface, but not of nucleating new particles. Similarly, a study of alkanethiol-stabilized gold nanoparticle growth dynamics found that despite the extremely rapid formation of gold nanoparticles upon the addition of the reducing agent, the particle size distribution continued to evolve toward larger particles for up to 60 h after the initial reduction, for which one possible mechanism is ripening by transport of individual atoms from small particles to larger ones. If gold atoms can penetrate monolayers of small-molecular thiols, then they may penetrate monolayers of polymeric thiols even more readily, since steric effects between polymer chains may hamper a polymeric thiol's ability to efficiently pack on a gold surface; previous authors have measured the footprint of Me-PEG-SH(5000) on 2.8 nm gold nanoparticles as 0.35 nm² per thiol, compared to 0.21 nm² for dodecanethiol, and the polymer layers we have prepared are less dense than those prepared in that study. If gold atoms may readily penetrate the polymer layer surrounding the nanoparticles in this study, then the smaller size of gold nanoparticles stabilized by polymeric thiols relative to those stabilized by alkanethiols is not due to the polymeric thiols preventing further nanoparticle growth by atomic addition.

If, however, particles do stop growing because the thiol monolayer prevents gold atoms from adding to the nanoparticle surface, as is implied by a steric model of nanoparticle size control, then the following highly simplistic model can make some predictions about the expected dependence of particle size on thiol-to-gold ratio and passivant size.

We first assume that particle growth is primarily by atomic or small-cluster addition and that due to the slower diffusion of nanometer-sized particles relative to individual atoms, particle–particle aggregation is a secondary process that occurs on longer time scales after primary particle formation is essentially complete. If sufficient passivant is present, the primary particles may be expected to become stabilized against aggregation on a time scale faster than aggregation itself, and particle–particle aggregation should be a negligible process.

We also assume that gold atoms and passivant molecules diffuse independently to the growing nanoparticle surface. In light of recent work on gold nanoparticles passivated with mixtures of thiols implying that the AuSR intermediate breaks up immediately upon reduction, this is a tenable assumption. The rate of delivery of a species in solution to a growing surface is proportional to the

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concentration $c$ and diffusivity $D$ of that species, so provided that both atomic gold and passivant molecules readily stick to the growing nanoparticle upon contact, then the ratio of gold atoms to passivant molecules in the nanoparticle will be given by the ratio

$$\frac{N_{Au}}{N_{pass}} = \frac{c_{Au} D_{Au}}{c_{pass} D_{pass}}$$

(1)

If, as is implied by a steric model of nanoparticle size control, the particle stops growing because its surface has been completely covered with passivant molecules, then from geometric considerations, the ratio of gold atoms to passivant molecules in a completely covered particle, neglecting any distortion of the passivant’s shape upon binding, is

$$\frac{N_{Au}}{N_{pass}} = \frac{\frac{4}{3} \pi R_p^3 \rho_{Au}}{4\pi (R_p + R_G)^2 / k R_G^2}$$

(2)

where $R_p$ is the radius of the gold core, $R_G$ is the radius of gyration of a passivant molecule, $\rho_{Au}$ is the number density of gold atoms in the particle, and the geometrical constraint defining complete coverage is each passivant molecule occupying a footprint of area $k R_G^2$ upon a spherical shell $R_p + R_G$ distant from the particle center. Setting these two expressions equal to each other yields a particle radius of

$$R_p^3 = \frac{3}{k \rho_{Au} c_{pass} D_{pass}} \left( \frac{R_p + R_G}{R_G} \right)^2$$

(3)

where $R_p \gg R_G$, the quantity $(R_p + R_G)/R_G$ is approximately $R_p/R_G$, and so particle size is inversely dependent on the thiol-to-gold ratio. Also, since for polymers in dilute solution $D_{pass} \propto R_G^{-1}$, this implies that in this large-particle limit, $R_p \ll R_G^{-1}$. That is, in the large-particle limit, a higher passivant concentration results in smaller particles because the particle surface is passivated more quickly, and larger passivant molecules result in smaller particles because fewer of them are required to passivate the surface.

Where $R_p \gg R_G$, however, the quantity $(R_p + R_G)/R_G$ is approximately unity, and so in the small-particle limit, the particle size is less dependent on the thiol-to-gold ratio, depending on this quantity only as $R_p \propto (c_{pass}/c_{Au})^{-1/3}$, while the dependence on passivant size is reversed, as $R_p \propto R_G$.

In the small-particle limit, the number of passivant molecules needed to surround the negligibly sized particle becomes constant, the dependence on particle size on passivant concentration is weak because the same constant number of passivant molecules will passivate the particle regardless of the particle's growth in the meantime, and larger passivant molecules result in a larger particle because they require more time to diffuse to and passivate the growing nanoparticle.

The above model is highly schematic. It treats the ratio $c_{Au}/c_{pass}$ as a constant, which in fact since the gold atoms diffuse to the particle surfaces faster than passivant molecules, it will decrease throughout the reaction. On the other hand, it treats the sticking probabilities for gold atoms and passivant molecules as constant, equal, and close to unity, whereas in truth as the particle becomes partially covered, it will be harder for either species to reach the particle surface, and because a partially passivated surface is more likely to reject additional passivant molecules than the smaller gold atoms, the sticking probability for passivant molecules will decrease faster than that for gold atoms. Perhaps most glaringly, the geometric constraint used to define a completely covered surface is most appropriate for dense spherical objects, and any effects of the passivant’s shape or deformability must be incorporated into the “constant” $k$, which may actually be a function of $R_p$ and $R_G$. However, the consequences of this geometric constraint should nonetheless be sound: in the small-particle regime, the number of passivant molecules required to surround the particle is the number of passivant molecules that can be arranged into a small region of space rather than the number of passivant molecules that be arranged upon a surface of a given area, and so, in the small-particle regime, the number of passivants needed to passivate the particle is a weaker function of either $R_p$ or $R_G$ than in the large-particle regime. As a result, the particle size dependence on both $c_{pass}/c_{Au}$ and $R_G$ becomes weaker and, in the case of $R_G$, may even be reversed.

However, these predictions are not borne out by our experimental data. Figure 7 compares the mean particle diameters predicted by eq 3 (given $k = \pi$) to the experimental data of Figure 2. It is immediately apparent that the experimental particle sizes depend on the thiol-to-gold ratio is much weaker than that predicted by the steric model of eq 3. While it may be readily granted that eq 3 must fail both in the thiol-rich extreme (where particles may be expected to reach a minimum cluster size of perhaps 1.1 nm$^3$) and in the thiol-poor extreme (where the primary particle size will be controlled by the number of particles nucleated, regardless of the now-negligible thiol content), its predictions regarding the dependence of particle size on the thiol-to-gold ratio are a plausible consequence of a steric model over the range of the experimental data, yet not supported by the experimental data.

The weaker dependence of particle size on the thiol-to-gold ratio is also seen in previous authors’ work. Figure 8 plots particle sizes for dodecanethiol-stabilized gold nanoparticles from Murray and co-workers’ thorough investigation of that system,13 compared to eq 3’s predictions for Me-PEG-SH(200). Again the experimental particle sizes are less strongly dependent on the thiol-to-gold ratio than would be predicted from steric considerations alone.

Nor does the steric model of eq 3 correctly predict the dependence of particle size on passivant size. Figure 9 compares the particle size vs polymer weight predictions
Nucleation Enhancement as an Alternative Explanation of Nanoparticle Size. While a model as simplistic as that of eq 3 should not be expected to give quantitative accuracy, it might at least be expected to capture the qualitative trends that would result were the role of the steric bulk of the thiol in preventing particle growth by atomic addition the principal factor that yields smaller nanoparticles when more thiol or polymeric thiols are used in gold nanoparticle preparations. Yet it does not do so. We propose in light of this that the passivant’s steric bulk protecting the particle from additional growth is not the principal factor at work in this phenomenon. Rather, we propose that particles stop growing not because the passivant layer cuts off the supply of additional gold atoms from solution but because the solution has been exhausted of gold, and the presence of more thiols or polymeric thiols enhances the particle nucleation rate and causes the same amount of gold to be distributed among a larger number of particles.

Such an explanation might also help explain the previously observed result that when the reducing agent is added to the gold salt/thiol mixture slowly (over the course of several minutes), a larger, broader particle size distribution results than when the reducing agent is added rapidly, even at large thiol-to-gold ratios where nanoparticle formation early in the addition should not significantly deplete the thiol supply. From a steric basis, one would predict that slow addition of reducing agent would increase the effective thiol-to-gold ratio in the reaction mixture, yielding a smaller particle distribution. From a nucleation-based viewpoint, however, slow addition would result in fewer nanoparticles being nucleated early in the reaction, and at later stages of reduction, growth of these particles may occur at the expense of nucleation of additional particles.

In speculating why polymeric thiols might enhance the nucleation rate, it may be useful to recall from the literature that when thiol-terminated polystyrene was used to prepare gold nanoparticles at a thiol-to-gold ratio of 1:3.5, the resulting gold nanoparticles had a mean diameter of 6.2 ± 1.7 nm. If a polar polymer is necessary to prepare the anomalously small gold nanoparticles discussed in this paper, then it may be through weak coordination between Au(0) and the lone pair electrons on heteroatoms in the polymer, such a polymer accelerates rather than retards the growth of an attached particle by acting as a "net" to capture additional gold atoms. In support of this hypothesis, quartz crystal microbalance studies have shown that PEG does adsorb to a gold surface in the presence of small (≤ 20 ppm) quantities of chloride ions, such as are supplied in our synthesis through the use of HAuCl₄ as the gold source. Furthermore, Murray and co-workers have demonstrated that gold atoms do not remain irreversibly fixed to a single thiol molecule throughout the course of reduction, suggesting that even under thiol-rich conditions, irreversible coordination to thiols does not prevent gold from becoming coordinated to PEG. If this is the case, then we tentatively suggest that PEG and possibly other polar polymers assist particle nucleation by more rapidly supplying gold atoms to unstably small gold clusters, helping them to acquire more atoms (and more stability) before they disintegrate. Moreover, larger polymers enhance this effect by being larger nets. Through increasing the effective cross section of small gold clusters, polymers capable of weakly coordinating atomic gold may cause more rapid particle nucleation and thus a smaller particle population from a fixed supply of gold.

Especially in light of observations that thiolated gold surfaces are not imperious to additional growth, we suggest that the role of polymeric thiols in producing small gold nanoparticles may lie not in their steric bulk preventing further nanoparticle growth but in their enhancement of the particle nucleation rate at very early stages of reduction. If this hypothesis is correct, steric considerations may become important only late in the reaction, when steric interactions between thiols on separate particles prevent aggregation of those particles that have already formed. We suggest that study of the gold nanoparticle nucleation process may be a fruitful venue for further research in gold–thiol chemistry.

**Conclusion**

This research represents the first systematic study of the effects of polymer molecular weight and the thiol-to-gold ratio on the size of gold nanoparticles capped by polymeric thiols. We have found that, as for small molecular thiols, nanoparticle size decreases with increasing thiol concentration and that larger polymers yield smaller nanoparticles. We have also found that as the thiol content decreases, the polydispersity of the particles increases, and our data suggest that previous reports of small nanoparticles being prepared using polymeric thiols at small thiol-to-gold ratios should be qualified by the statement that under these conditions, small (~2 nm) nanoparticles do form, but only as part of a broad size distribution whose large-particle tail may contain much of the mass of the sample. The observation that particle size decreases with increasing polymer molecular weight, even for very small particle sizes, suggests that the polymer's steric bulk in blocking particle growth may not be the principal limit on these particles' size, and we suggest instead that the presence of polar polymeric thiols accelerates nanoparticle nucleation, yielding more small particles rather than fewer large ones.

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**Supporting Information Available:** Particle size histograms for all samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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