

Amphiphilic Gold Nanoparticles with V-Shaped Arms

Eugene R. Zubarev,* Jun Xu,§ Arshad Sayyad, and Jacob D. Gibson

Department of Chemistry, Rice University, Houston, Texas 77005

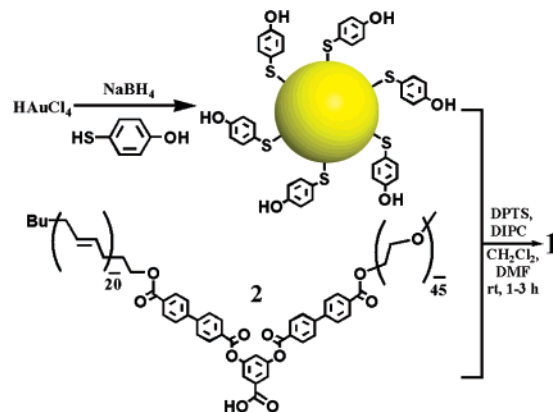
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The synthesis of hybrid metallic nanoparticles (NPs) is of great current interest and holds a significant promise in the areas of optoelectronics, catalysis, and biomedical applications.^{1–4} Despite the numerous reports on gold NPs functionalized with low molecular weight thiols,^{5–7} only a few examples of polymer-coated NPs are known. Mirkin et al.⁸ introduced a strategy for covalent attachment of DNA strands, and Murray et al.⁹ were the first to link PEG-SH to the surface of Au NPs. Several examples include Au particles with hydrophobic homopolymer chains.¹⁰ Very recently Kramer and Pine¹¹ reported on Au particles coated with a mixture of two different polymeric thiols, which created an amphiphilic shell as suggested by the observed accumulation of particles at the interface separating the domains of polystyrene and poly(2-vinyl pyridine). However, the distribution and exact ratio of polymers attached to the surface of Au NPs may be difficult to control in this method. These limitations could be overcome if an amphiphilic block copolymer with a fixed hydrophobe–hydrophile ratio were linked to Au NPs. Here we describe a simple and very efficient method to produce Au NPs with an equal number of hydrophobic and hydrophilic arms which are distributed along the surface of Au NP in an alternating fashion. The V-shaped amphiphilic arms used in this work render the hybrid gold particles soluble in water as well as in any organic solvent, including hexane. In addition, the amphiphilic arms provide an exceptional thermal (see SI) and solvent stability to Au clusters, which can stay in solution without precipitation, agglomeration, or decomposition for more than 2 years.

The synthesis of the amphiphilic Au NPs includes two stages. First, we prepared a V-shaped polybutadiene–poly(ethylene glycol) (PB–PEG) amphiphile **2** containing a carboxyl group at its junction point (Scheme 1). The diblock **2** was synthesized as described elsewhere ($MW_{PB} = 1000$, $MW_{PEG} = 2000$).¹² In a separate synthesis we prepared hydroxyl-terminated Au NPs (2 nm) using a modified procedure by Brust¹³ (see SI). The critical part of the synthesis involves the coupling between the amphiphile **2** and Au NPs which proceeds remarkably well under standard esterification conditions. Mercaptophenol-functionalized Au NPs are not soluble in dichloromethane, but the addition of 1,3-diisopropylcarbodiimide (DIPC) causes their gradual dissolution and the formation of brown solution in the presence of **2** and DPTS.¹⁴ The reaction can be monitored by thin-layer chromatography (12% MeOH in CH_2Cl_2) as the spot of the starting NPs (retention factor $R_f = 0$) disappears and a new product with $R_f \approx 0.6$ emerges. The latter has a characteristic dark-brown color which allows one to observe its motion when the plate is developed in a TLC chamber. More importantly, the reaction can be monitored by size-exclusion chromatography (SEC).

The coupling reaction occurs so rapidly that after 2 h there is only a small amount of starting material **2**, and a new peak with much higher molecular weight is present (Figure 1). The SEC traces taken after 12 and 24 h showed the same ratio of the peaks which

Scheme 1. Synthesis of Amphiphilic Au(PB–PEG)_n Nanoparticles



suggested that the amphiphile **2** was in excess and its maximum amount was attached to Au NPs within the first 2 h. The purification of the product, however, initially posed a formidable challenge. Attempts were made to isolate the product by column chromatography, dialysis, centrifugation, and preparative SEC. However, all these methods proved to be inefficient. The purification was finally achieved by centrifugal ultrafiltration of the DMF solutions through a regenerated cellulose membrane with MWCO 30 kDa. Only three rounds of centrifugation (each for 30 min) were enough to remove the excess of the amphiphile **2** and all the low molar mass components.¹⁴ The purity of the product **1** was confirmed by SEC (Figure 1, bottom). The polydispersity index (PDI) of Au(PB–PEG)_n, **1**, is remarkably low and suggests that their hydrodynamic

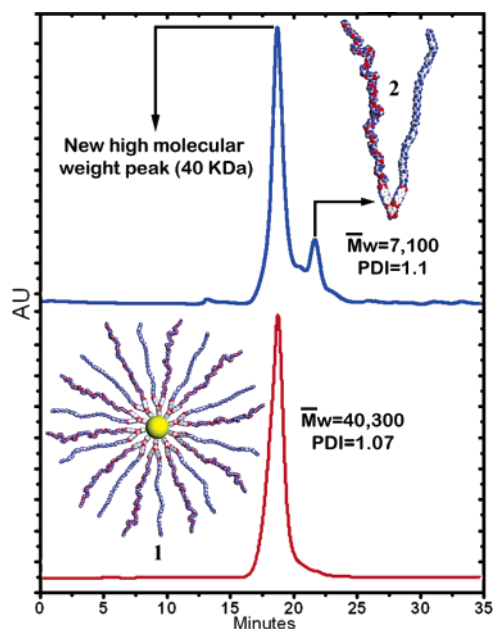


Figure 1. SEC of the reaction mixture after 2 h (top) and the isolated Au(PB–PEG)_n NPs **1** after purification (bottom).

* Present address: Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011.

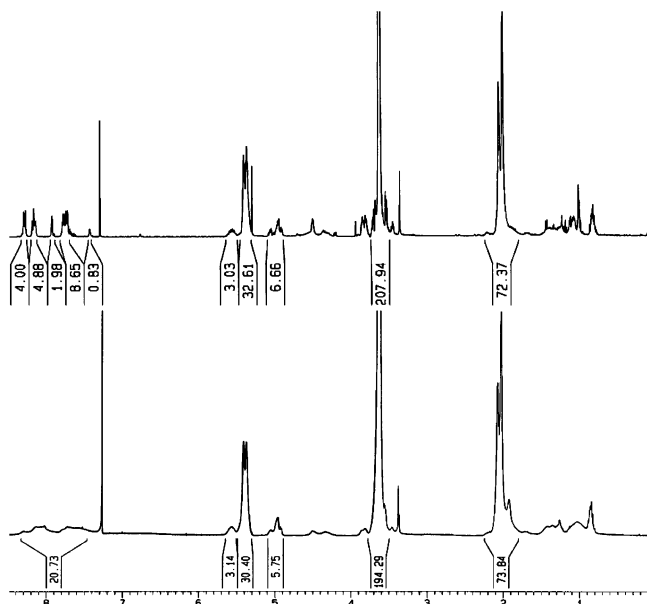


Figure 2. ^1H NMR spectra of V-shaped PB-PEG amphiphile **2** (top) and the isolated Au(PB-PEG) $_n$ NPs **1** (bottom) in CDCl_3 .

volume varies within a very narrow range. It appears that SEC does not sense the size distribution of the gold clusters (1.5–2.5 nm)¹⁴ because the PDI of the product is even lower than that of the starting diblock **2**. This result may be explained by a significant difference in the density of gold clusters and the swollen polymer shell in solution. The latter seems to dominate the overall hydrodynamic volume of the hybrid structure.

When the product is isolated, the average number of V-shaped molecules per particle can be estimated on the basis of the weight gain and the assumption that 2-nm gold clusters (based on TEM) contain 270 atoms.⁷ The observed increase in mass of the particles after the polymer attachment is 457% (from 7 to 37 mg). Given that the molar mass of **2** is 3500 Da, there are at least 65 V-shaped molecules attached to a given Au NP, and the grafting density is 2.94 chains/nm².¹⁴ This result was in good agreement with the elemental analysis data which showed that the content of gold in **1** was ~18%. This implies that the true molecular weight of the hybrid structures **1** is close to 280 kDa which includes 53 and 227 kDa for a 2-nm gold core and the amphiphilic arms, respectively. This number is significantly higher than that by SEC (40 kDa) which is known¹⁵ to underestimate the molar mass of branched structures when linear standards are used for calibration.

The high purity of the product also allows one to study its chemical composition by ^1H NMR. Figure 2 shows the spectra of the starting diblock **2** and **1**, the amphiphilic Au(PB-PEG) $_n$ NPs. The characteristic peaks of both PB and PEG are present in the isolated product **1**, and the integration shows that their ratio is the same as that in **2**. The main difference is the broadening of sharp signals in all three major regions,¹⁴ i.e., aromatic (biphenyls), vinyl (PB), and aliphatic (PB and PEO), which confirms that all amphiphilic arms are covalently attached and that there is essentially no free polymer. This is particularly evident from the aromatic region where signals of two biphenyls and dihydroxybenzoic acid turned into a series of broad humps, yet the integration gives a similar number of protons as in **2**. The aromatic moieties are near the attachment point which should cause a significant loss of their rotational mobility and the broadening of the NMR resonances.

The amphiphilic nature of Au(PB-PEG) $_n$ is expressed in their unique ability to dissolve in any conventional solvent. These include such extremes as pure hexane and pure water. Figure 3 shows the



Figure 3. Solutions of amphiphilic Au(PB-PEG) $_n$ NPs **1** in various solvents (0.1 wt %).

image of **1** dissolved in seven common solvents with very different polarities. The solutions are particularly stable and do not show any signs of precipitation or decomposition for more than 2 years.¹⁴ In most nonselective solvents, such as benzene, THF, and methanol, Au(PB-PEG) $_n$ form true molecular solutions which are highly transparent and nonviscous even at high concentrations. In contrast, solutions in hexane and water exhibit a characteristic Tyndall effect which is indicative of stable aggregates whose presence was confirmed by DLS.¹⁴ Importantly, these solutions are just as stable as those in nonselective solvents. There are no signs of precipitation, change in color, or transparency within a period of time as long as 25 months (see SI, Figure S5). Solutions of **1** are also exceptionally stable at high temperature.¹⁴ The properties of Au NPs **1** in selective solvents are under investigation and will be reported in due course.

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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