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Recognition-Mediated Assembly of Nanoparticles into Micellar Structures with Diblock Copolymers

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Multiscale ordering of components is a key requirement for the application of molecular systems[1] to pragmatic devices.[2] Self-assembly provides a powerful tool for the creation of structured molecule-based systems. Application of self-assembly strategies to macromolecular systems[3] supplies a means for applying this methodology to both larger size scale regimes and hierarchical assembly strategies. Monolayer Protected Clusters (MPCs) provide a versatile building block for this method of assembly. Recent studies have demonstrated the formation of extended arrays and aggregates of MPCs using packing interactions;[4] similarly, control of aggregate structure based on covalent[5] and noncovalent[6] colloid-small molecule and colloid-DNA[7] shows promise in ordering MPC's.

In recent research, we have developed a polymer-mediated "bricks and mortar" strategy for nanoparticle assembly.[8] In this investigation, 2 nm gold nanoparticles featuring thymine functionality were assembled into spherical aggregates with use of a diaminotriazine-functionalized polymer. By varying the temperature during the assembly process, aggregates ranging from 100 to 1000 nm in diameter could be formed. The key limitation of this method, however, is that aggregate size and shape was controlled by the complex thermodynamics of the self-assembly process. This prevented access to structures smaller than 100 nm, and made formation of larger particles a trial-and-error process. To overcome these limitations, we have explored the utility of recognition element-functionalized diblock copolymers as mortar for the assembly of nanoparticles.[9] The use of diblock copolymers would exploit the microphase separation of the copolymer to provide control of aggregate size through changes in block length of the recognition element-functionalized block (Figure 1). We report here the application of this method to the size-controlled formation of nanoparticle aggregates in solution and in thin films.

The diblock copolymers required for the assembly process were synthesized using the nitroxide-mediated radical polymerization developed by Hawker et al.,[10] with the first block polystyrene and the second block a random copolymer of styrene and chloromethylstyrene. Incorporation ratios of the chloromethylstyrene units into the random copolymer block were determined to be 20 ± 4% by NMR integration. These polymers were then quantitatively converted into the diaminotriazine-functionalized polymers **1**−**3** through reaction with sodium cyanide followed by dicyandiimide.[11] The MPC "bricks", **Thy-Au**,[5] were made via place displacement[12] of a thymine-functionalized thiol into octanethiol-protected gold nanoparticle prepared with use of the Brust−Schiffern method,[13] with the control MMPC **MeThy-Au** produced in analogous fashion.

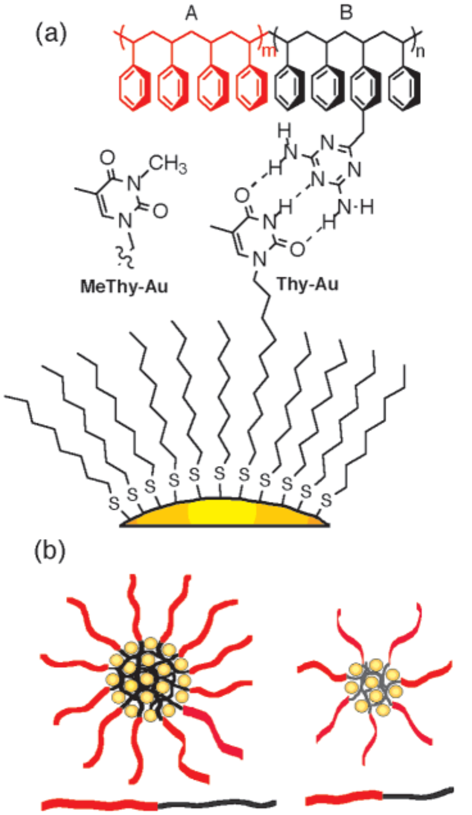

Figure 1. (a) Diblock copolymers **1**−**3** (see Table 1 for block lengths), **Thy-Au**, and non-hydrogen bonding control **MeThy-Au**.(b) Schematic demonstrating an increase in both core diameter and outer corona as the polymer size increases.

Aggregation in solution was demonstrated by using Dynamic Light Scattering (DLS) on dilute solutions[14] of **Thy-Au** and polymers **1**−**3**.[15] As hypothesized, the size of these aggregates increased with the size of the polymer (Table 1). The assembly process was recognition dependent: no evidence of aggregate formation was observed by DLS when polymers **1**−**3** were mixed with the control MPC **MeThy-Au**.

Transmission Electron Microscopy (TEM) provided further insight into the structure of the aggregates. Solutions of copolymers **1**−**3** (0.5 mg/mL) and MPC **Thy-Au** (2 mg/mL) were dropcast onto TEM grids.[16] Microscopy of the resultant thin films confirms the self-assembly process and the formation of spherical micellar aggregates (Figure 2b−d).[17]

TEM not only allows confirmation of micellar shape but also provides an efficient way to analyze aggregate core size. Concurrent with the trend observed between the polymer M_w and the solution R_h, the core radius increases with increasing polymer length. The core radii were ∼60% of the R_h for the combined core and corona

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Table 1. Size Data for Copolymer **Thy-Au** Aggregates

polymer	block A/B (M_w)	PDI	R_h[a] (nm)	core radii[b] (nm)
1	14k/14k	1.29	18.7	13.2[d] ± 1.3[c]
2	26k/24k	1.27	27.1	13.9 ± 1.2[c]
3	30k/28k	1.12	31.1	19.4 ± 1.8[c]

[a] DLS. [b] Determined from TEM images of aggregate core. [c] Standard deviation obtained from ~100 aggregates/sample. [d] Diffuse micelles.

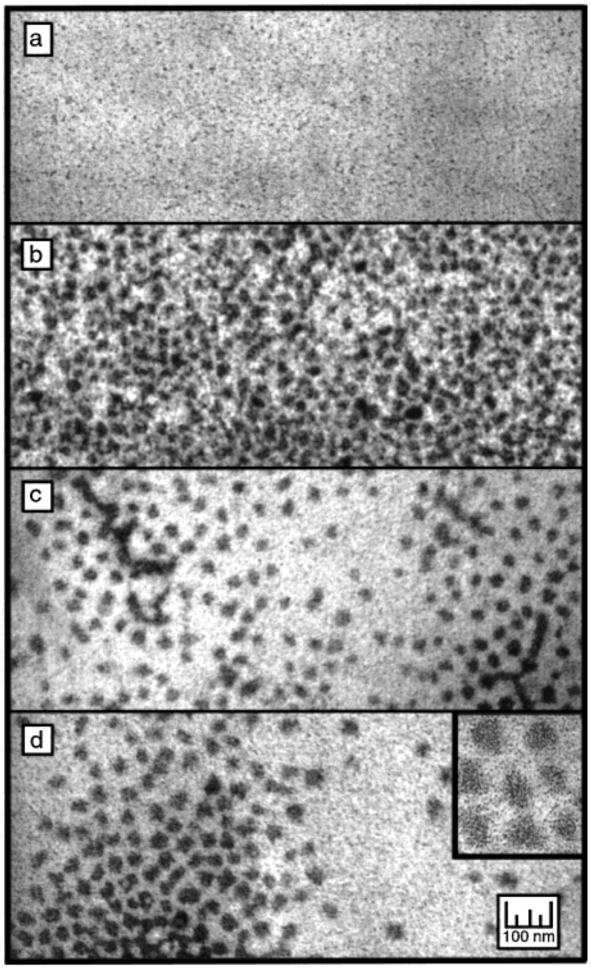

Figure 2. (a) **MeThy-Au** control with polymer **2** showing complete lack of aggregation. (b–d) Spherical micellar structures formed by assembly of **Thy-Au** by polymers **1** (b), **2** (c), and **3** (d, inset 2× magnification to show individual MPCs).

as determined by DLS, indicating that the polymer chains within the core are somewhat extended relative to the polystyrene corona.

Examination of the micrographs reveal that both core size and structure are polymer length dependent. Diffuse cores were observed with the **Thy-Au**-polymer **1** micelles, while more substantial cores were formed with polymers **2** and **3**. The diffuse aggregates observed with polymer **1** probably arise from the lower number of recognition sites present on this shorter system. In agreement with solution studies, the micellar morphology observed with **Thy-Au** and polymers **1**–**3** is strictly recognition dependent: no aggregation of **MeThy-Au** was observed when mixed with polymers **1**–**3** (Figure 2a).

In summary, we have a system where recognition element-functionalized diblock copolymers are used to self-assemble complementary nanoparticles. Using this strategy, the size of the aggregate both in solution and in thin films is controlled through block length. Further characterization of the relationship between block lengths and aggregate size, as well as application of these aggregates to electrically and magnetically active systems is currently underway, and will be reported in due course.

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Supporting Information Available: Synthesis and characterization of polymers **1**–**3**, and additional TEM micrographs of Thy-Au and MeThyAu-polymer systems (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) **Thy-Au** solutions of 0.25 mg/mL and polymer solutions of 0.5 mg/mL in $CHCl_3$. DLS data were collected using standard techniques.

(15) The radii of the aggregates as determined by DLS remained relatively constant from 0.2 to 0.6 mole fraction of polymers **1-3**:**Thy-Au**, indicating that the size of the aggregates is controlled by polymer structure, not concentration.

(16) Polymers **1**–**3** were titrated with the **Thy-Au** solution. Four solutions of increasing **Thy-Au** ratios were analyzed by TEM: 1 to 40, 1 to 2, 1 to 1.33 and 1 to 1 polymer to **Thy-Au**. Micellar aggregates were observed in each case, with the optimal ratio depending on polymer length.

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