Controlled Interparticle Spacing through Self-Assembly of Au Nanoparticles and Poly(amidoamine) Dendrimers

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Multiscale engineering is a critical process in nanotechnology, providing a methodology for the integration of molecular systems into functional mesoscopic devices,[1] and macroscopic materials. One approach in the preparation of materials featuring multiscale order is self-assembly,[2] using molecular-level recognition events to provide systems ranging from the macromolecular to macroscopic scales.[3] Mixed monolayer protected clusters (MMPCs)[4] provide effective intermediates for these multiscale systems, providing order from the molecular to the nanometer scale within the self-assembled monolayer of the particle[5] that can be extended to meso- and macroscopic systems through the creation of structured nanoparticle aggregates.[6]

Particle spacing is a key determinant of the magnetic,[7] optical,[8] and electronic[9] properties of nanocomposite materials.[10] Particle spacing has been achieved using self-assembly techniques; however, systematic control remains a challange.[11] In recent studies, we have shown that recognition-mediated self-assembly of nanoparticles using linear copolymers provides structures featuring regular interparticle spacing.[12] Controlled variation of this spacing with flexible copolymers, however, is not straightforward. Dendrimers, in contrast, furnish preorganized systems,[13] providing the potential for systematic control of nanoparticle spacing.[14] We report here the formation of nanocomposites via dendrimer-mediated electrostatic self-assembly of MMPCs. In this approach, direct control of interparticle separation is provided through choice of dendrimer generation. Electrostatic self-assembly between the dendrimer and nanoparticle components was provided by salt bridge formation. For the nanoparticle component of this process, we used MMPC **1**, composed of a ~1.5 nm diameter Au core and a 70% octanethiol-30% 11-mercaptoundecanoic acid monolayer (Figure 1). Poly-(amidoamine) (PAMAM) dendrimers, generations 0, 1, 2, 4, and 6, provided the complementary "mortar" for the assembly process.

Addition of each of the dendrimers to solutions of MMPC **1** (0.5 mg/mL in 1:1 THF:MeOH) resulted in the rapid formation of a precipitate.[15] Preliminary examination of these precipitates using transmission electron microscopy (TEM) revealed that varying the ratios of MMPC to dendrimer resulted in two distinct morphologies. Low dendrimer to MMPC ratios led to networklike structures, which showed little evidence of spatial control (Figure 2a). In contrast, high ratios of dendrimer to MMPC (10:1 based on functional group equivalence) resulted in spherical aggregates ranging from 0.5 to 1.5 µm in diameter (Figure 2b). In these assemblies, *qualitative* differences in inter-MMPC spacing could be readily discerned (Figure 2c,d).[16]

Quantification of interparticle distance in the dendrimer MMPC nanocomposites was obtained using small angle X-ray scattering (SAXS). SAXS profiles were obtained on MMPC **1** assembled with
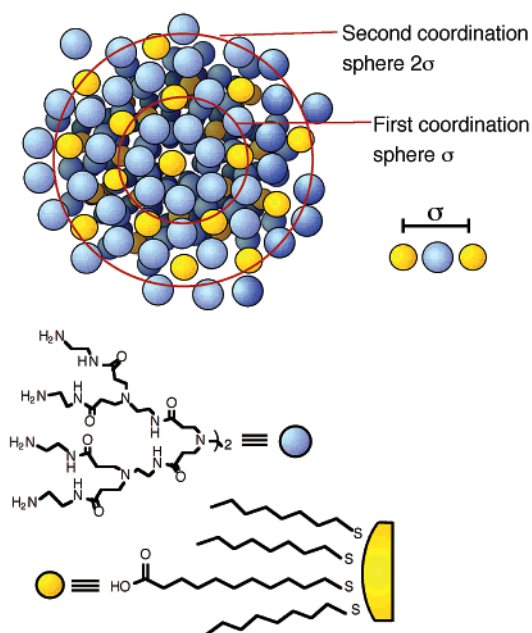
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Figure 1. Schematic representation of the assembly process between and excess of PAMAM generation 2 dendrimer (blue) and MMPC **1** (gold).
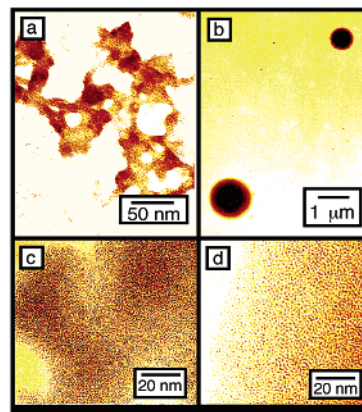

Figure 2. (a,b) TEMs of MMPC **1**/G_4 dendrimer composites with (a) excess MMPC **1** and (b) excess dendrimer. (c,d) MMPC **1** assembled with PAMAM G_0 (c) and G_4 (d) qualitatively indicating an increase in particle–particle spacing.

an excess of PAMAM dendrimers ranging from G0–G6 (Figure 3).[17] When MMPC **1** was assembled with PAMAM dendrimers, the primary peak (Q_1) shifts to lower Q values as the particle is assembled with larger dendrimers, confirming the expected increase in spacing distance (Table 1). A secondary scattering peak (Q_2) is representative of medium-range order, with maxima ~2σ for
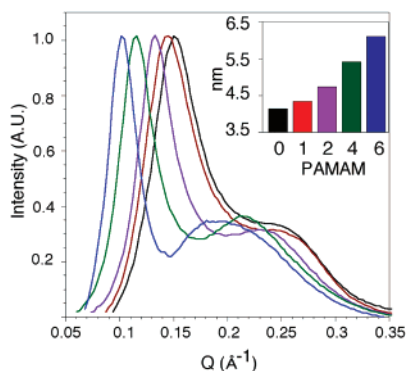
Figure 3. SAXS plot of MMPC **1** assembled with G_0–G_6 PAMAM dendrimers. Inset graph shows the correlation between generation and spacing.

Table 1. Spacing Values for PAMAM Dendrimer Assembled with MMPC **1**

	G_0	G_1	G_2	G_4	G_6
$Q_1{}^a$	0.152	0.145	0.133	0.116	0.103
$Q_2{}^a$	0.257	0.261	0.241	0.220	0.200
D_1 (nm)	4.1	4.3	4.7	5.4	6.1
D_2 (nm)	2.4	2.4	2.6	2.9	3.1

^{a} Q values taken from SAXS plots and spacing values obtained using d $(nm^{-1}) = 2\pi/Q$.

dendrimer generations 2, 4, and 6. Generation 0 and 1, in contrast, gave a peak ratio closer to 1.7σ, suggesting an internal structure intermediate between a liquid (2σ) and solid packing model ($\sqrt{2}\sigma$).[18] Assembly in these systems is thermodynamic: inverse addition of reagents provided materials identical by SAXS (see the Supporting Information).

In summary, we have demonstrated a dendrimer-mediated "bricks and mortar" method for the self-assembly of nanoparticles. This process is based on acid/base chemistry between the MMPC and dendrimer and provides direct control of interparticle separation. The application of this methodology to the creation of nanocomposite materials with customizable magnetic and optical properties is currently underway and will be reported in due course.

Supporting Information Available: TEM images of MMPC **1** with varying ratios of G_4 dendrimer, IR spectroscopy of salt bridge formation, and additional SAXS profiles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Salt bridge formation in the aggregates was established using IR spectroscopy: the broad peak observed in the N−H for hydrogen bound amine in the dendrimer becomes sharper, and a new peak at 3069 cm^{-1} arising from the RNH$_3{}^+$ stretch appears. Concurrently, a decrease in the CO stretching frequency of the carbonyl region arising from the deprotonation of the MMPC-bound carboxylic acids was observed (see the Supporting Information for spectra).
(16) Selective dendrimer staining with sodium phosphotungstate further demonstrates the role of the dendrimer as a spacer in these assemblies (see the Supporting Information).
(17) A sealed tube source was used to produce the Cu Kα radiation ($\lambda = 0.154$ Å). The scattering intensity is presented as a function of the wave vector $q = (4\pi/\lambda)\sin(2\theta/2)$, where 2θ is the scattering angle, and λ is the Cu Kα radiation wavelength.
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