Complex Arborescent Copolymer Architectures by Self-assembly

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Research on metallic nanoparticles has recently experienced much growth because of their unique physical properties and their multiple applications including imaging,[1-2] chemotherapy[1], sensing, biology, medicine,[2] and drug delivery.[3] The synthesis of nanoparticles with well-defined characteristics (e.g. composition, nanomorphology, size, size uniformity) is usually necessary to achieve the desired physical properties. Different methods have been investigated to prepare stable metallic nanoparticles with designed characteristics. This includes surfactants,[4] self-assembled block copolymer micelles,[5,6] star block copolymers,[7] and unimolecular micelle-like compounds.[8,9]

Arborescent copolymers, an unusual type of graft copolymers with a dendritic architecture, were also investigated as templates. Specifically, arborescent polystyrene-*graft*-[poly(2-vinylpyridine)-*block*-polystyrene] copolymers have been applied to the preparation of gold nanoparticles in our laboratory. The synthetic strategy used for these arborescent copolymers was a *grafting onto* procedure, whereby the functionalization of a linear or branched polystyrene (PS) substrate with acetyl groups was followed by grafting with anionic "living" polystyrene-*block*-poly(2-vinylpyridine) chains. The resulting dendritic species had a covalently bonded, layered structure with an inner shell of poly(2-vinylpyridine) (P2VP) chains.[10]

These unimolecular micelle architectures are much more stable as templates for loading polar compounds, such as metallic salts, than micelles formed by the self-assembly of linear block copolymers, since they have no critical micelle concentration. Aside from their inherent stability, arborescent polymer templates have the potential to offer other important advantages over other methods. For example, variations in the degree of polymerization of the side chain

building blocks and the number of grafting cycles (generation) provide control over the characteristics of the templates (e.g., core size, chain mobility, stabilizing layer thickness) beyond what is achievable by the self-assembly of block copolymer chains.[9] The manipulation of these nanostructures may be an advantageous for different applications.

We now present a new method for the preparation of arborescent core-shell-corona structures, namely polystyrene-*graft*-poly(2-vinylpyridine)-*graft*-poly(acrylic acid)-*block*-polystyrene, by the self-assembly of arborescent polystyrene-*graft*-poly(2-vinylpyridine) with poly(acrylic acid)-*block*-polystyrene via hydrogen bonding and electrostatic (weak acid-weak base) interactions as shown in Scheme 1. This methodology offers a simple but effective way to prepare the polymeric templates in nearly 100 % yield. It involves anionic grafting for the synthesis of the arborescent polystyrene-*graft*-poly(2-vinyl pyridine) substrates, atom transfer radical polymerization (ATRP) to synthesize the poly(acrylic acid)-*block*-polystyrene copolymer, and mixing of the two components, either in solution or in the solid state, in the appropriate ratio to prepare the core-shell-corona architectures.
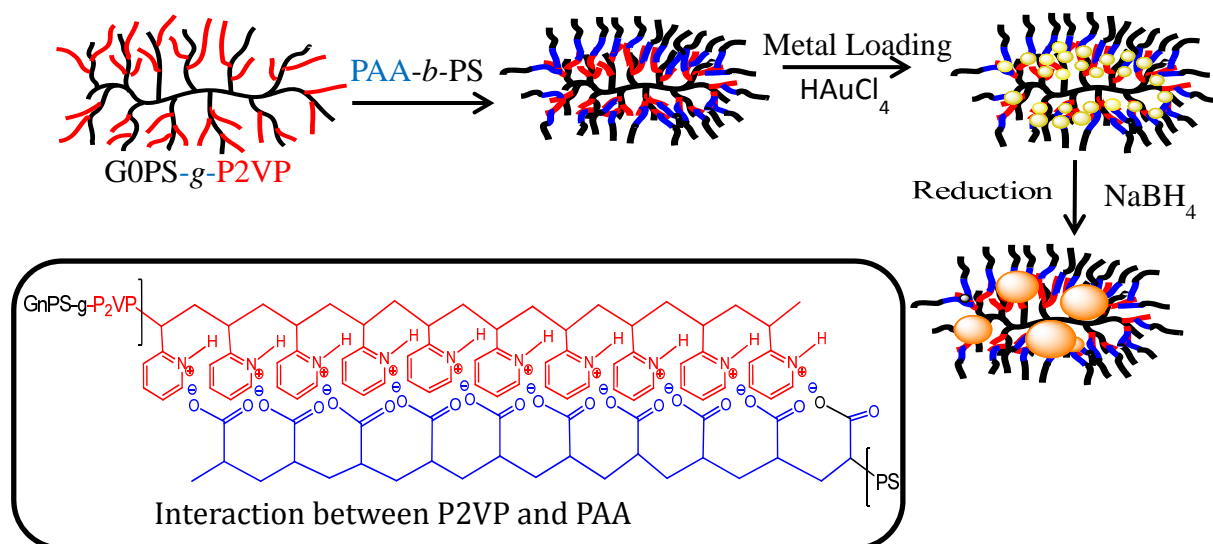
Scheme1. Schematic representation of the self-assembly of arborescent PS-*g*-P2VP with PAA-*b*-PS, metal loading, and reduction to obtain metallic nanoparticles.

The polymers synthesized were analysed by nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC), dynamic light scattering (DLS), transmission electron microscopy (TEM), and atomic force microscopy (AFM). An increase in size is observed after the substrate was complexed with the block copolymers to yield self-assembled structures with a single, narrow size population, and nanomorphologies were observed that were similar to the systems previously obtained in our laboratory by anionic block copolymer grafting.

These complexes were successfully loaded with tetrachloroauric acid (HAuCl$_4$), and subsequent reduction of the HAuCl$_4$-loaded (G1PS-g-P2VP30K)-g-(PAA-b-PS) complex with sodium borohydride (NaBH$_4$) yielded aggregation-free gold nanoparticles with a size ranging from 6 to 17 nm inside the polyion complexes.
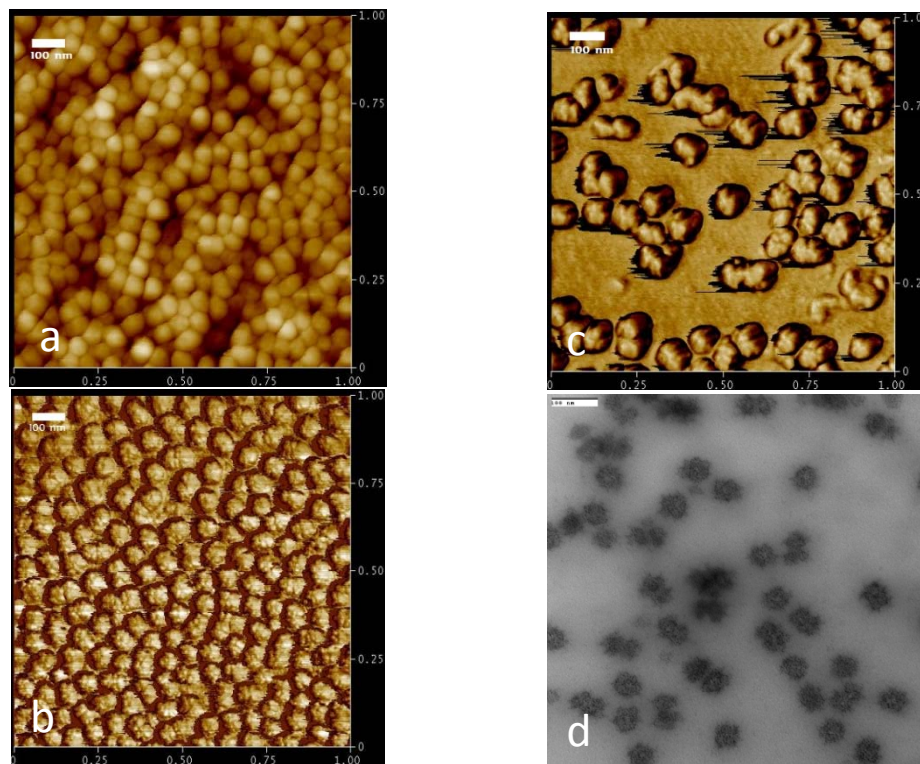

Figure 1 (a) AFM images showing the spherical morphology of G2PS-g-P2VP13K in THF, (b) AFM image showing the raspberry-like morphology of G2PS-g-P2VP-g-(PAA10-b-PS260) in toluene, and (c) AFM and (d) TEM images for the raspberry like morphology obtained for HAuCl$_4$- loaded (G2PS-g-P2VP)-g-(PAA10-b-PS260) in toluene (the scale bars are 100 nm).

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