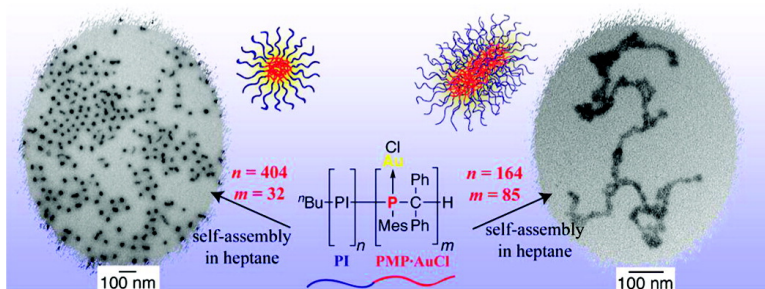


## Phosphorus-Containing Block Copolymer Templates Can Control the Size and Shape of Gold Nanostructures

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## Phosphorus-Containing Block Copolymer Templates Can Control the Size and Shape of Gold Nanostructures

Kevin J. T. Noonan, Bronwyn H. Gillon, Vittorio Cappello, and Derek P. Gates\*

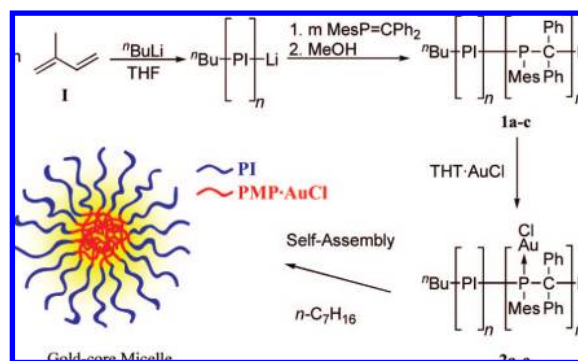
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The solution self-assembly of amphiphilic block copolymers provides a powerful tool to access ordered structures in the nano- and microdomain.<sup>1</sup> Through careful tuning of the polymer microstructure and tailoring polymer–solvent interactions, shaped micelles, vesicles, and inverse structures can be obtained.<sup>2</sup> Most previous research in this area has focused on organic block copolymers; however, there is increasing demand for organized inorganic nanoassemblies due to their exciting electronic, magnetic, and optical properties.<sup>3</sup> In particular, the use of block copolymers to stabilize and assemble metal nanoparticles is particularly desirable.<sup>4</sup> For example, chemically functional amphiphilic block copolymers can mediate the assembly of gold nanoparticles from gold(I) precursors; however discrete gold(I)–polymer complexes are presumed but not generally characterized.<sup>5</sup> The assembly of well-defined polymeric coordination complexes offers the prospect to provide greater size and shape control. In this regard, phosphine-containing polymers are particularly attractive;<sup>6</sup> however the development of convenient methods to incorporate phosphine moieties into block copolymers poses a significant challenge.<sup>5i,7</sup>

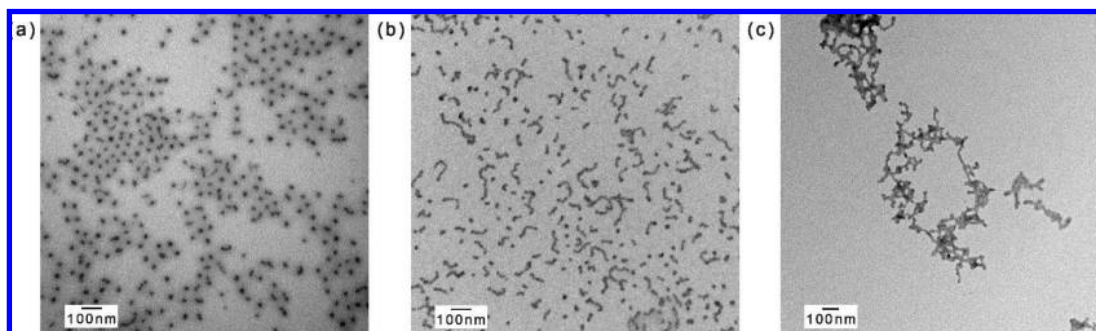
Our group has been interested in the analogy between P=C and C=C bonds and have shown that phosphalkenes, like olefins, can be polymerized using radical or anionic methods of initiation.<sup>8</sup> The addition polymerization of P=C bonds leads to poly(methylenephosphine) (PMP), an unprecedented functional phosphine-containing polymer. Remarkably, the anionic polymerization of phosphalkenes affords living homo- and block copolymers.<sup>9,10</sup> PMP homopolymers are readily soluble in polar organic solvents and are insoluble in nonpolar solvents. Given the ability of PMPs to form macromolecular metal complexes,<sup>11</sup> we hypothesized that block copolymers containing nonpolar-soluble blocks should self-assemble to give metal-rich micelles.

Scheme 1



Herein, we report the synthesis and solution self-assembly of well-defined gold(I) complexes of isoprene-phosphaalkene block copolymers to access gold(I) nanostructures with tunable shapes and sizes.

Polyisoprene (PI) is readily soluble in nonpolar organic solvents, and therefore, we set out to prepare PI-*b*-PMP **1** as outlined in Scheme 1. Living PI was prepared by treating carefully purified isoprene (**I**) with *n*-BuLi (M/I = 480:1). To determine the chain length of the isoprene segment, a drop was removed from the reaction mixture and the absolute molecular weight was determined using triple-detection GPC (THF:  $M_n = 27\,500$ ; PDI = 1.05; approx  $DP_n = 404$ ). Subsequently, a THF solution of phosphalkene monomer (MesP=CPh<sub>2</sub>) (M/I = 22:1) was added to the yellow reaction mixture which immediately turned deep red, characteristic of the living  $-P(\text{Mes})-CPh_2^-$  chain end. Conveniently, the progress of polymerization may be followed by <sup>31</sup>P NMR spectroscopy and terminated by adding MeOH (1 drop) when complete. Copolymer **1a** was isolated by precipitation from THF into MeOH (2 × 100 mL).



**Figure 1.** TEM micrographs showing the nanostructures obtained from the solution self-assembly of block copolymers: (a) **2a**: PI<sub>404</sub>-*b*-PMP<sub>32</sub>•AuCl (b) **2b**: PI<sub>222</sub>-*b*-PMP<sub>77</sub>•AuCl; (c) **2c**: PI<sub>164</sub>-*b*-PMP<sub>85</sub>•AuCl. Dark areas represent regions of high gold(I) content.

**Table 1.** Selected Characterization Data for Polyisoprene-*block*-poly(methylenephosphine)s (PI-*b*-PMP-*m*) Prepared by the Successive Living Anionic Polymerization of Isoprene and MesP=CPh<sub>2</sub>

sample	PI		PI- <i>b</i> -PMP- <i>m</i> (1)			PI- <i>b</i> -PMP- <i>m</i> -AuCl (2)			
	$M_n$ (g mol <sup>-1</sup> )	PDI	$M_n$ (g mol <sup>-1</sup> )	PDI	<i>n</i> : <i>m</i> (expt) <sup>a</sup>	$M_n$ (g mol <sup>-1</sup> )	PDI	$R_h$ (THF) <sup>b</sup>	$R_h$ (C <sub>7</sub> H <sub>16</sub> ) <sup>c</sup>
<b>a</b>	27 500	1.05	38 500	1.12	404:35	43 500	1.18	5 nm	82 nm
<b>b</b>	15 100	1.06	39 400	1.06	222:77	44 800	1.10	5 nm	75 nm
<b>c</b>	11 200	1.09	38 200	1.24	164:85	57 900	1.15	5 nm	>400 nm <sup>d</sup>

<sup>a</sup> The approximate chain lengths (*n* and *m*) are determined from the absolute  $M_n$  of each homo- and copolymer sample. <sup>b</sup> Hydrodynamic radius ( $R_h$ ) was determined using viscometer data from the triple detection GPC analysis. <sup>c</sup>  $R_h$  was determined from dynamic light scattering (DLS) data for the solutions used to prepare TEM samples. <sup>d</sup> Due to the large distribution of sizes an exact value could not be determined.

Triple detection GPC analysis of the pure block copolymer in THF reveals a monomodal molecular weight distribution ( $M_n = 38\,500$ ; PDI = 1.12).<sup>12</sup> Comparison of the relative molecular weight of the copolymer and the isoprene homopolymer suggests that the approximate formulation of copolymer **1a** is PI<sub>404</sub>-*b*-PMP<sub>35</sub>.

To test our hypothesis that chemically functional and amphiphilic isoprene-phosphaalkene block copolymers would provide an excellent template for metal nanostructures, the gold(I) complex **2a** was prepared. Treating a CH<sub>2</sub>Cl<sub>2</sub> solution of **1a** with THT·AuCl (THT = tetrahydrothiophene) results in complete conversion of the broad <sup>31</sup>P NMR signal for **1a** ( $\delta = -5$ ) to a new resonance at 25 ppm which is consistent with **2a** (cf. PMP·AuCl:  $\delta = 25$ ).<sup>11</sup> The macromolecular gold(I) complex was analyzed by triple-detection GPC (THF:  $M_n = 43\,500$ ; PDI = 1.18). The molecular weight increase observed is consistent with the incorporation of AuCl moieties into the polymer.

The self-assembly properties of this new class of block copolymer were evaluated by dynamic light scattering (DLS) analysis of dilute solutions of **2a** in *n*-heptane (ca. 0.5 mg mL<sup>-1</sup>). Remarkably, the hydrodynamic radius ( $R_h$ ) in *n*-heptane (82 nm) is much larger than that observed in THF (5 nm). Confirmation of the self-assembled structures of **2a** is provided by transmission electron microscopy (TEM). The *n*-heptane solution was drop cast onto a copper TEM grid coated with Formvar. The striking results are shown in Figure 1a. Spherical morphologies are observed and the uniform size distribution of the dark spots is particularly fascinating (range: 28–32 nm). Close examination of the micrograph reveals that light gray regions encapsulate the dark spheres. This is consistent with a micelle comprised of a PMP·AuCl core (dark) and a PI corona (light), exactly what is expected when assembled in a PI-selective solvent.

Changing the relative block lengths of amphiphilic block copolymers is known to enable the fine-tuning of the morphologies of micelles.<sup>13</sup> Therefore, two additional polymers were prepared with longer PMP blocks and similar overall molecular weights to **1a** (Table 1: **1b**, PI<sub>222</sub>-*b*-PMP<sub>77</sub>; **1c**, PI<sub>164</sub>-*b*-PMP<sub>85</sub>). Neither **2b** nor **2c** are soluble in pure heptane; however the addition of THF (12 and 25%, respectively) to dissolve the samples affords large self-assembled structures.<sup>14</sup> The TEM images of drop-cast **2b** and **2c** reveal that the increase in the PMP chain length relative to PI imparts dimensionality to the nanostructures (Figure 1). In the case of **2b**, oblong-shaped structures (worms) with an average length of 53 nm (range: ca. 15 to 150 nm) and average width of 21 nm (range: 15 to 30 nm) are observed. Particularly fascinating are the large intertwined wormlike structures observed for the sample possessing the greatest PMP/PI ratio (**2c**) which approach the micron scale.

In summary, a new bottom-up approach to well-defined gold(I) nanostructures is reported which exploits the self-assembly and ligand properties of amphiphilic PI-*b*-PMP copolymers. Remarkably, changing the relative block lengths enables the fabrication of spheres, worms, and large aggregates. These findings provide a

foundation for the future reduction of gold(I) and cross-linking of isoprene to afford exciting gold nanostructures with insulating coatings.

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**Supporting Information Available:** Experimental details, NMR spectra, additional TEM images. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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