

Arborescent Polymer-stabilized Palladium Nanoparticles as Green Catalysts for Suzuki-Miyaura Reaction

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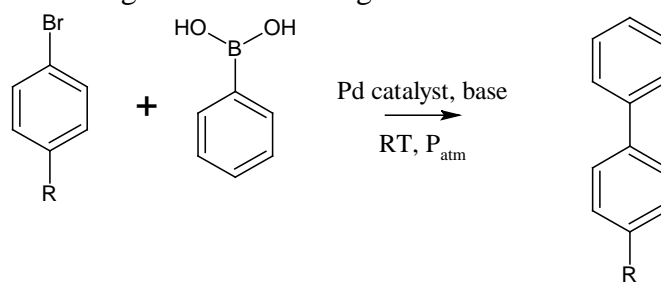
The important changes observed in the properties of materials as their size is decreased from the macroscopic to the atomic or molecular level have attracted a considerable interest from the research community. The effect on the surface reactivity of metals, in particular, has led to the development of nanocatalysis as a central field of nanoscience and nanotechnology.¹

Atoms at the surface of a solid often exhibit high chemical reactivity because of their unsatisfied coordination. As the size of a material diminishes, a rapid increase in the fraction of surface atoms can promote a greater catalytic activity.² However additional intrinsic changes in the nanometer size range, non-scalable from the bulk properties, also distinguish nanocatalysts from other large surface-area catalysts.^{3,4}

Transition metals such as palladium have attracted by far the most interest in catalysis, and significant efforts have been devoted to the elaboration of synthetic strategies offering control over the size but also over the structure, composition and shape of the nanoparticles (NP) obtained. The most common method employed consists in the reduction of a metal salt in solution in the presence of a stabilizer. Various stabilizing agents have been used such as ions, ligands, surfactants, linear polymers, and dendrimers.³

Investigations using dendritic polymers are less frequent, even though their unique properties make them promising candidates as catalysts supports. In particular, their well-defined three-dimensional structure presents a tunable template for the formation of monodispersed nanoparticles. Furthermore, the branches of dendritic polymers can selectively screen the access of substrate molecules to the metal active center, while providing dispersibility in the reaction medium.⁴

Pd catalysts are used in a variety of catalytic reactions, but carbon-carbon coupling represents its most important application in organic synthesis. Among the Pd-catalyzed cross-coupling reactions, the Suzuki-Miyaura (SM) reaction allows coupling between an aryl or vinyl boronic acid with an aryl or vinyl halide (or triflate), as illustrated in Scheme 1. This powerful cross-coupling method is particularly interesting for the synthesis of complex drug molecules, and other bioactive chemicals owing to the mild and 'green' conditions that can be employed.¹



Scheme 1: Suzuki-Miyaura reaction

Although dendritic structures - such as dendrimers, hyperbranched and star polymers - have been used in the preparation of NP, to the best of our knowledge, no report has demonstrated the utilization of arborescent (or dendrigraft) polymers as stabilizers and their application to catalysis. These molecules, with their distinctive unimolecular micelle architecture, exhibit a rapid increase in size with the number of grafting cycles used in their synthesis (or generation number, Gn), and expose a large number of functional groups to coordinate with metal atoms. Additionally, their open structure does not lead to steric crowding as observed with dendrimers. Furthermore, thanks to their large size, they are well suited for recovery after reaction, through microfiltration or precipitation.

We want to demonstrate the effective utilization of arborescent copolymers in the preparation and stabilization of Pd nanoparticles. The influence of the polymer generation on the catalytic activity in the SM cross-coupling reaction will also be examined. Characterization of the catalytic systems was performed using dynamic light scattering (DLS), atomic force microscopy (AFM), UV-visible spectrophotometry, transmission electron microscopy (TEM), as well as a novel characterization technique using a microplasma device (MPD) to quantify the metal content of the polymers in solution.

Experimental Procedures

The arborescent copolymers used in this study were synthesized by anionic polymerization and grafting techniques according to a procedure reported by Munam and Gauthier.⁶ They consisted of polystyrene (PS) substrates grafted with poly(2-vinylpyridine) (P2VP) chains at their periphery as shown in Figure 2.

Loading of the palladium catalyst was achieved by co-dissolution of the palladium catalyst with the polymer in ethanol. The polymer was first dissolved overnight in ethanol ($0.2 \text{ mg}\cdot\text{mL}^{-1}$) in a vial. The $\text{Pd}(\text{OAc})_2$ was dissolved in ethanol ($0.25 \text{ mg}\cdot\text{mL}^{-1}$), sonicated for 5 minutes, immediately added in the desired amount to the polymer solution to obtain a yellow or brown translucent solution.

SM reactions were conducted by dissolving 4-bromoanisole ($67 \mu\text{mol}$), phenylboronic acid ($100 \mu\text{mol}$), and K_2CO_3 ($0.13 \mu\text{mol}$) in about 1 mL of a mixture of ethanol/ D_2O (85/15 v/v), with acetone as an internal standard. The desired amount of polymer-stabilized catalyst was added to the solution which was transferred to a NMR tube which was mechanically stirred.

Results

Arborescent Polymers

Table 1: Characteristics of the arborescent copolymers used.

Generation	Description ^a	Molecular weight \bar{M}_n (10^6 g/mol) ^b	Diameter (nm) ^c	PDI ^c
<i>G1</i>	<i>G0PS-g-P2VP</i>	1.1	28.3 ± 0.2	0.07
<i>G2</i>	<i>G1PS-g-P2VP</i>	8.4	55.8 ± 0.2	0.09
<i>G3</i>	<i>G2PS-g-P2VP</i>	33	107.5 ± 0.6	0.08

a. The molecular weight of the PS and P2VP chains was *ca.* 5000 g/mol

b. Absolute values from SEC-MALLS and light scattering measurements

c. Z-average diameter and polydispersity index (PDI) obtained from DLS and cumulants analysis

The arborescent copolymers used incorporated a PS core of generation n (G_n) and a P2VP corona ($G_n\text{PS-g-P2VP}$, with $n = 1-3$, and overall generation is $G[n+1]$). Characterization of the molecules by DLS in ethanol revealed uniform structures with a narrow size distribution ($\text{PDI} \approx 0.08$). The hydrodynamic diameter was found to increase rapidly with the generation number of the copolymer from 28 nm to 108 nm, as summarized in Table 1.

AFM imaging could resolve individual molecules with a disk-like structure, resembling a ‘fried-egg’ topology with a sharp protruding globular center (Fig. 1). The height was measured to be *ca.* 2 nm and the diameter *ca.* 50 nm. The branched PS core retained its globular structure, while the P2VP chains spread into a thin layer. The hexagonal close-packing of the molecules is a further indication of the low size dispersity of the molecules.

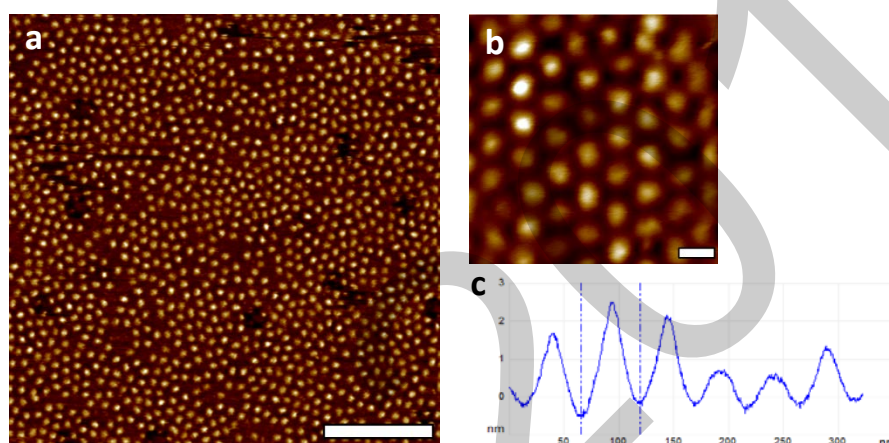


Figure 1: AFM imaging of $G_0\text{PS-g-P2VP}$ polymer deposited on a mica surface; a) phase imaging, bar is 500 nm b) height imaging, bar is 50 nm and c) height profile.

Metal Loading

Loading of the unimolecular micelles was achieved by co-dissolution of the Pd(II) precursor with the arborescent copolymer in ethanol, acting both as a co-solvent and a reducing agent for $\text{Pd}(\text{OAc})_2$. Complexation of Pd(II) by the 2VP units in the corona of the molecules could be evidenced by UV-visible spectroscopy: The characteristic absorption band around 400 nm for $\text{Pd}(\text{OAc})_2$ was red-shifted and appeared as an intense band at 428 nm. Visually, the solution remained translucent yellow or brown for an extended amount of time, while $\text{Pd}(\text{OAc})_2$ in ethanol formed black Pd particles within 30 min.

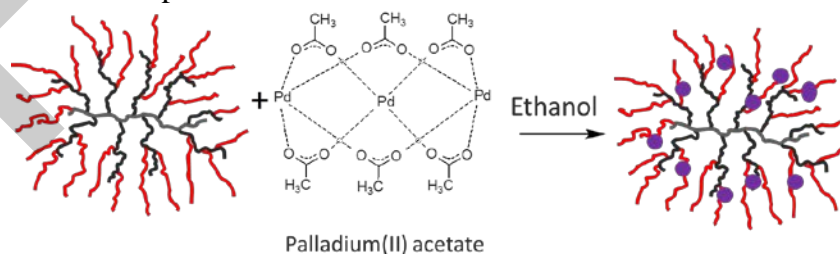


Figure 2: Illustration of the Pd loading of arborescent copolymers.

TEM imaging of the G_1 -Pd samples confirmed the presence of Pd-loaded arborescent polymer molecules with a diameter of 18 ± 2 nm, as shown in Fig. 3. Increasing the Pd content

from 0.24 to 1.5 equiv per 2VP unit led to enhanced image contrast, as expected for increased Pd content within the polymeric micelles. At 0.24 equiv, no indication of the formation of Pd NP could be revealed within the micelles at the TEM resolution used. Increasing the Pd content to 0.5 equiv led to the appearance of small NP 2 nm in diameter. At 0.9 equiv, a greater amount of 2 nm NP could be seen. A sample prepared with an excess of Pd (1.5 equiv) showed the presence of larger Pd NP (7 ± 2 nm diameter), constituted of smaller spherical nanoparticles of about 2 nm. These structures are reminiscent of the ‘raspberry’ morphologies observed for triblock terpolymers and for Au-loaded arborescent copolymers.^{7,8}

Quantitative measurement of the loading level of the arborescent copolymers was performed by a method recently developed by Karanassios *et al.*, using a microplasma device (MPD) for atomic emission spectroscopy. It was thus confirmed that all the 2VP units were available for coordination with the Pd(II) atoms.

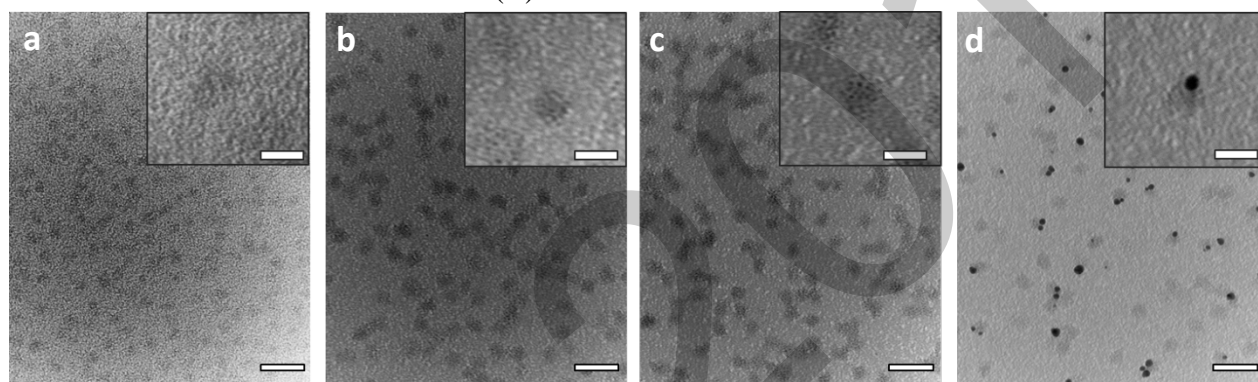


Figure 3: TEM images for the *G1* copolymer (*GOPS-g-P2VP*) with a Pd content per 2VP unit of a) 0.24 equiv, b) 0.5 equiv, c) 0.9 equiv, and d) 1.5 equiv. The scale bar represents 50 nm. Inset: Magnification over a single micelle; the scale bar represents 20 nm.

Catalytic Activity Testing: Suzuki-Miyaura Reaction

The activity of the *GnPS-g-P2VP*-stabilized Pd(0) catalyst system was investigated in the SM coupling reaction between phenylboronic acid and 4-bromoanisole as shown in Scheme 1. The conversion could be conveniently monitored *in operando* by ¹H NMR spectroscopy. As depicted in Fig. 4a, high conversions (above 50%) were obtained in less than 2 h with the higher generation arborescent copolymer stabilizers. The smaller *G1* copolymers apparently did not offer sufficient steric stabilization for the Pd(0) species, which aggregated as black Pd particles during the reaction. Comparison of the apparent rate constant for the reactions, shown in Fig.4b, highlight the high activity obtained for the *G2* and *G3* stabilizers. Free Pd(OAc)₂ in solution displays a very high catalytic activity initially but the conversion reaches a plateau in less than 1 h. It is likely that large, non-stabilized Pd(0) particles formed during these reactions, with a concomitant loss in activity. Furthermore, the catalyst cannot be recovered from these reactions and recycled. Enhanced selectivity was also achieved for *G2*- and *G3*-stabilized Pd(0), with higher conversions obtained.

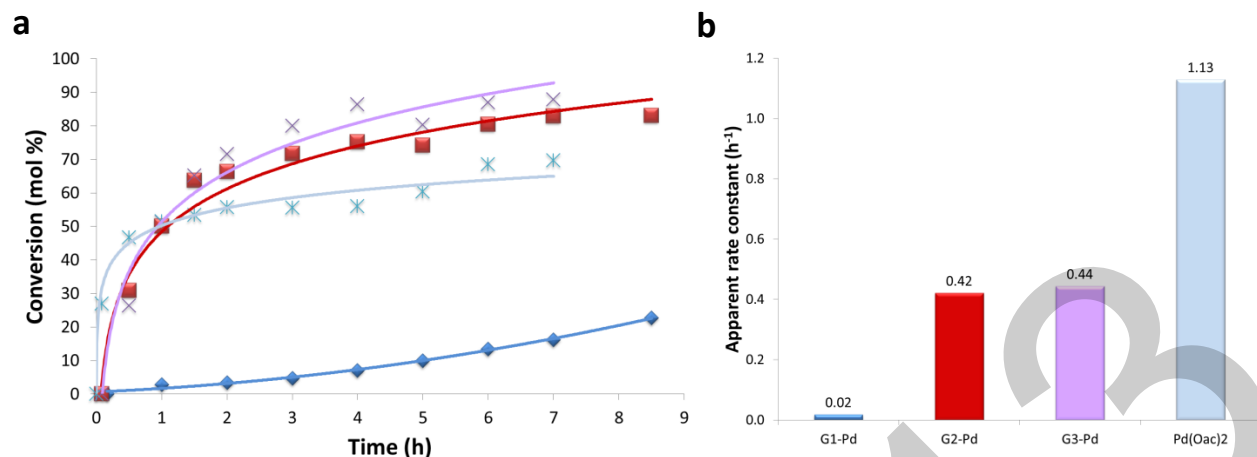



Figure 4: a) Conversion of the biphenyl product formed during the reaction, and b) apparent rate constant using G1 (dark blue diamonds), G2 (red squares), G3 (purple crosses) arborescent copolymers, and no stabilizer (light blue stars).

Conclusions

We demonstrated the utilization of well-defined arborescent copolymers, *Gn*PS-*g*-P2VP, with sizes varying from 28 to 108 nm, to synthesize Pd NP. By selecting the generation number (*Gn*) and the loading level, control was achieved over the size and the structure of the nanoparticles. Analysis by DLS, AFM, and TEM revealed the formation of Pd NP with a diameter of about 2 nm when more than 0.5 equiv of Pd per 2VP was used. The addition of an excess of Pd led to the formation of larger Pd domains of about 7 nm diameter. In all cases, raspberry-type morphologies were observed. Catalytic testing of the polymer-stabilized Pd in the SM reaction revealed the beneficial effects of the dendritic structures. The smaller *G1* arborescent copolymer could not provide sufficient steric stabilization under the reaction conditions used and displayed poor catalytic activity. The larger arborescent copolymer (*G2* and *G3*) structures, however, were effective stabilizers and displayed good catalytic activity.



References

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May 8, 2013

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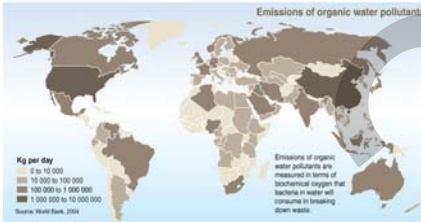



Outline

Green Chemistry Growing Need

- » Chemical industry is a major contributor to environmental pollution
- » Growing demand, and stricter legislation for the development of environmentally acceptable processes
- » Rapid development of "Green Chemistry"



Emissions of organic water pollutants


Kg per day

- 0 to 100 000
- 100 000 to 1 000 000
- 1 000 000 to 10 000 000
- 10 000 000 to 100 000 000

Emissions of organic water pollutants are measured in terms of biochemical oxygen that bacteria in water will consume in breaking down waste.

Source: World Bank, 2004


Emissions of organic water pollutants. (2004). In UNEP/GRID-Arendal Maps and Graphics Library.



Green Chemistry 12 Principles

1. Waste prevention
2. Atom efficiency
3. Less hazardous/toxic chemicals
4. Safer products by design
5. Innocuous solvents and auxiliaries
6. Energy efficient
7. Renewable raw materials
8. Reduction of derivatives
9. **Catalysis**
10. Design for degradation
11. Real-time analysis for pollution prevention
12. Inherently safer processes


P. Anastas, J. C. Warner, 1998, *Green Chemistry: Theory and Practice*, Oxford.



Green Chemistry 12 Principles

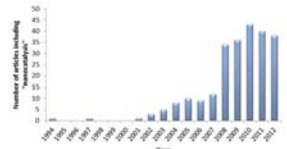
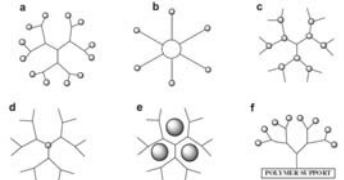
1. **Waste prevention**
2. **Atom efficiency**
3. **Less hazardous/toxic chemicals**
4. Safer products by design
5. **Innocuous solvents and auxiliaries**
6. **Energy efficient**
7. Renewable raw materials
8. **Reduction of derivatives**
9. **Catalysis**
10. Design for degradation
11. Real-time analysis for pollution prevention
12. **Inherently safer processes**

P. Anastas, J. C. Warner, 1998, *Green Chemistry: Theory and Practice*, Oxford.




Nanocatalysis Emerging Field

- » Nanoparticles:
 - » Size-dependent properties
 - » Large surface area
 - » Enhanced intrinsic surface reactivity
- » Stabilizers
 - » Prevent aggregation
 - » Increase activity (e.g. polymeric field)
 - » Increase selectivity
 - » Ease recovery

Types of dendrimer-stabilized catalysts

P. Serp, K. Philippot, Eds. 2013. *Nanomaterials in Catalysis*. Vol. 1. Wiley-VCH: Weinheim.

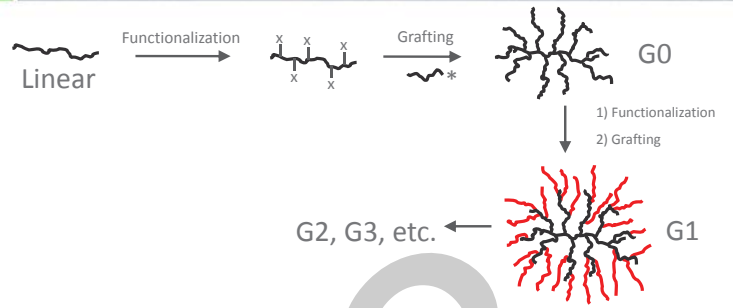




Arborescent Polymers Micelles Synthesis

Anionic polymerization, DLS, AFM

Arborescent Polymers Synthesis



» Copolymers obtained by attaching a different type of polymer in the last cycle

» Rapid increase in molecular weight

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Arborescent Polymers DLS Characterization in Ethanol

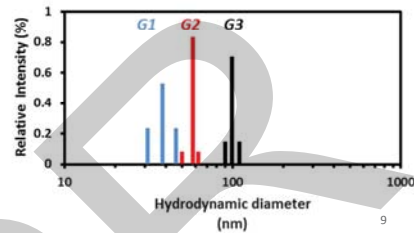
- » Unimolecular micelles
 - Static globular structure
 - Good colloidal stability

- » Control over
 - Size
 - Composition
 - Structure

- » Control over
 - Rigidity
 - Solubility
 - Polymeric field

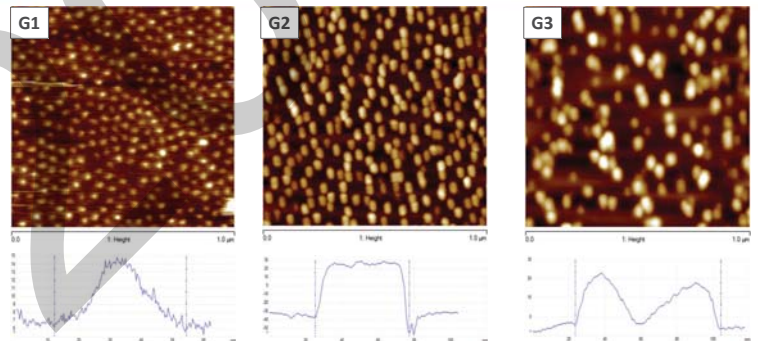
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G2	G1PS-g-P2VP	55.8 ± 0.2	0.09
G3	G2PS-g-P2VP	107.5 ± 0.6	0.08

PS and P2VP chains = 5000 g/mol



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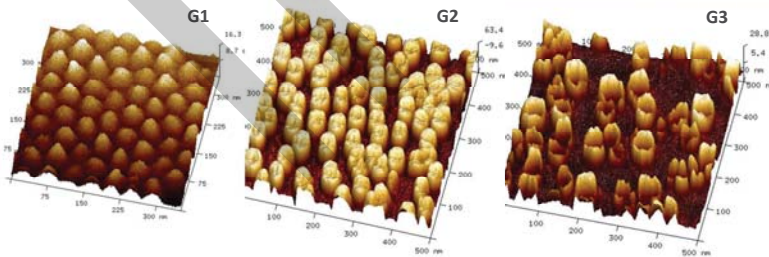
Arborescent Polymers AFM Imaging - Height and Phase Modes



- » Monodispersed spherical micelles
- » Phase segregation observed

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Arborescent Polymer AFM Imaging - Phase Mode



- » G1: Flat, "fried-egg" morphology
 - Polar P2VP adsorbed on the mica surface
 - Rigid PS core
- » G2: No visible phase separation
- » G3: Phase segregation between PS core and P2VP corona

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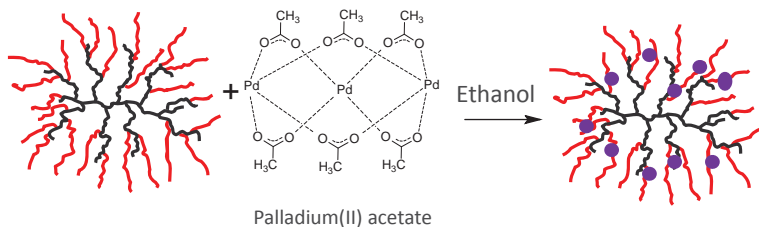


Pd Loading Synthesis and Characterization

TEM, DLS, MPD

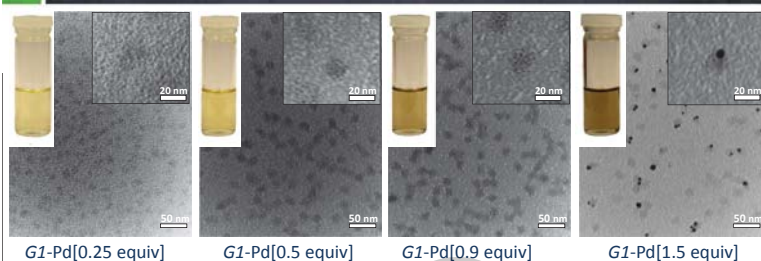
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Polymer Loading Reaction Scheme



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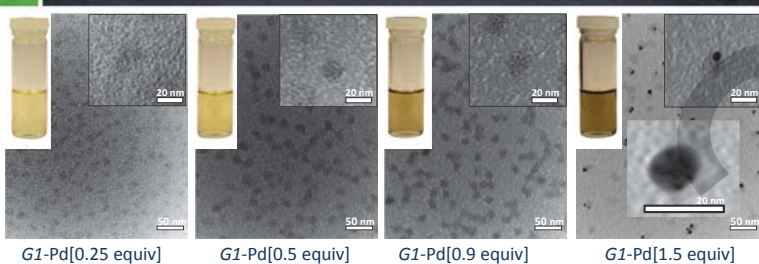
Polymer-stabilized Pd TEM Characterization



- » Homogeneous solutions obtained in ethanol
 - Arborescent polymer-stabilization of Pd(II)
- » Nanoparticles (ca. 2 nm) formation above 0.5 equiv Pd
- » "Raspberry" morphologies observed

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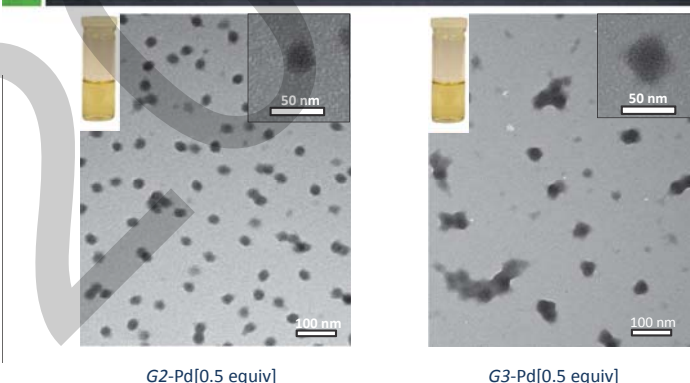
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Polymer-stabilized Pd TEM Characterization (cont'd)

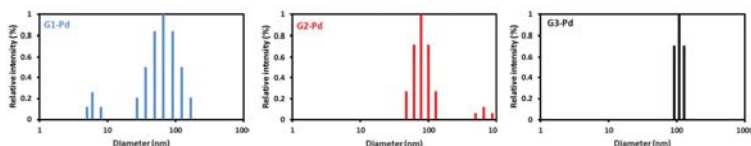


- » Homogeneous solutions with G2 and G3
- » "Raspberry" morphology
- » Some aggregates formed in G3 copolymer films

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Polymer-stabilized Pd DLS Characterization in Ethanol

Generation	Description	Diameter (nm)	Diameter polymer alone (nm)	PDI
G1	G0PS-g-P2VP-Pd(II)	61.5 ± 0.5	28	0.23
G2	G1PS-g-P2VP-Pd(II)	83.6 ± 0.5	56	0.20
G3	G2PS-g-P2VP-Pd(II)	104.9 ± 0.5	108	0.10

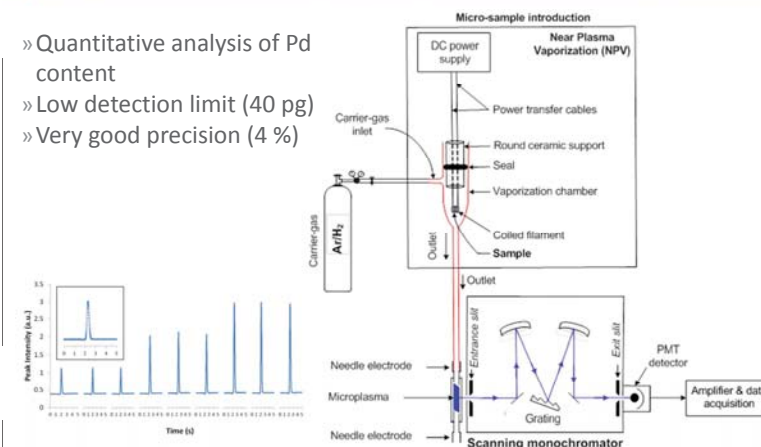


- » Some aggregation observed for smaller micelles (G1 and G2)
- » Good stabilization in solution for larger G3 micelles

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Microplasma Device (NPV-MPD) Instrumentation

- » Quantitative analysis of Pd content
- » Low detection limit (40 pg)
- » Very good precision (4 %)



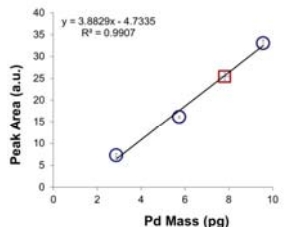
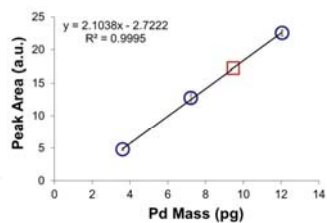
S. Weagant, V. Chen, V. Karanassios, *Anal. Bioanal. Chem.* 2011, 401, 2865.

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NPV-MPD Pd Quantitative Analysis

» Quantitative coordination of Pd(II) with 2VP units

Sample	G1Pd[0.25 equiv]	G1Pd[1.5 equiv]
Pd/2VP (mol%) Initial	25.4	149.0
Pd/2VP (mol%) After dialysis	23.6 ± 0.3	99.8 ± 7.2
Pd recovered (%)	93 ± 1	68 ± 6



○ G1Pd Standards □ G1Pd[0.25 equiv] (dialysis)

○ G1Pd Standards □ G1Pd[1.5 equiv] (dialysis)

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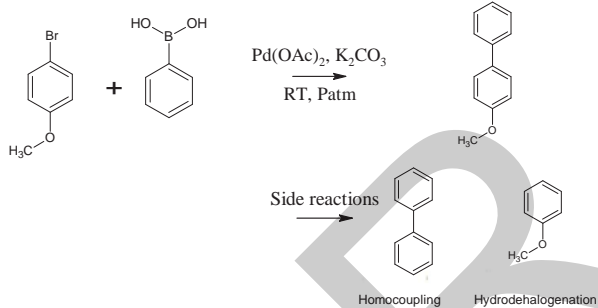


Testing Catalytic Activity

Suzuki reaction

Suzuki-Miyaura Pd-catalyzed Cross-coupling

- » Cross-coupling between alkenylboranes and organic halides
- » One of the commonly used reactions for carbon-carbon bond formation
- » Catalyzed by Pd(II)_L, usually poorly soluble in water

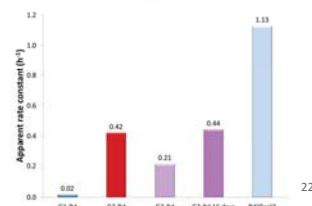
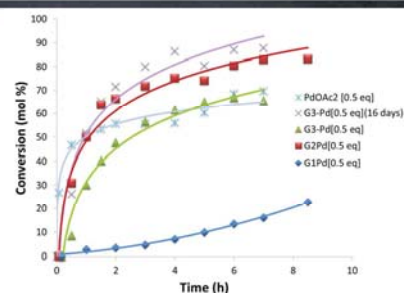


R. Heck, E. Negishi, A. Suzuki, 2010, Nobel Prize in Chemistry.

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Suzuki-Miyaura Influence of Generation

- » G1: Low catalytic activity, poor Pd stabilization
- » G2: Good catalytic activity
- » G3: Induction time before high catalytic activity
- » Pd(OAc)₂: High activity, but precipitates during reaction (hence lower conversion)



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Conclusions and Future Work

Conclusions:

- Arborescent copolymers provide well-defined templates (30 – 100 nm) for the preparation of metallic nanoparticles
- Formation of NP (2 nm) and raspberry morphologies observed
- Quantitative analysis achieved by new MPD technique
- Good catalytic activity observed for higher generation copolymers

Future Work:

- Catalyst recycling studies
- Influence of P2VP chain length on catalytic activity
- Development of water-soluble templates

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