# Arborescent Polymers as Templates for the Preparation of Metallic Nanoparticles

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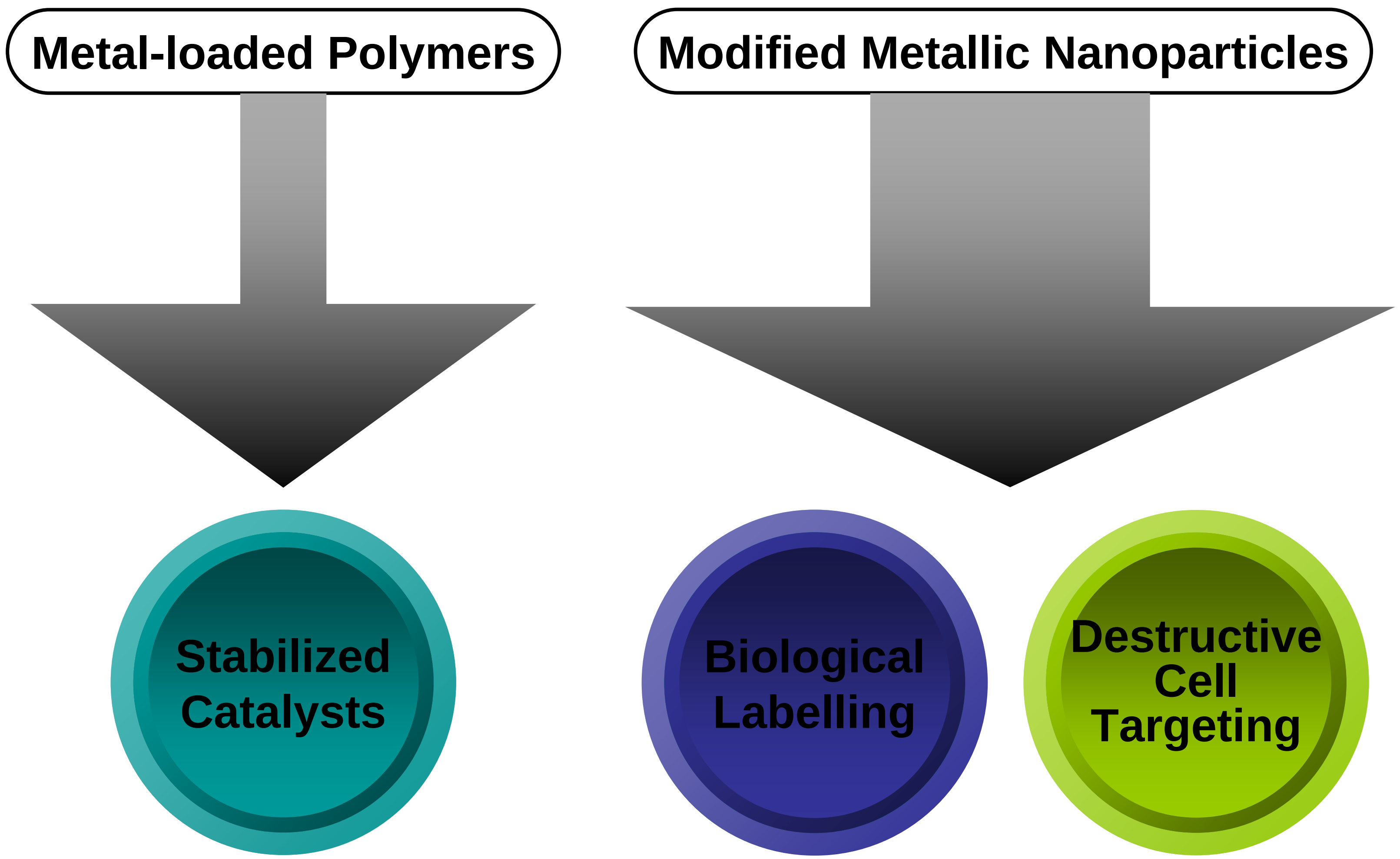
# Outline

1. Focus and Purpose of Research
2. The Template
3. Results
4. Conclusions & Future Work

# Main Focus

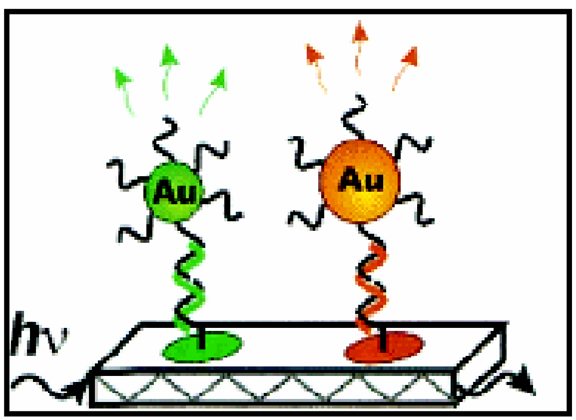
To synthesize and use amphiphilic arborescent copolymers as templates for the construction of metallic nanoparticles.

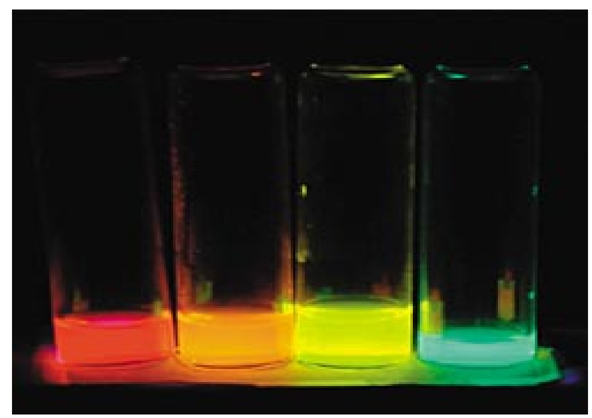
# Nanoparticle Applications



# Nanoparticle Applications

- **Biological labelling**
  - Jin, R.; Wu, G.; Li, Z.; Mirkin, C.; Schatz, G. *J. Am. Chem. Soc.* **2003**, *125*, 1643.



# Nanoparticle Applications

- **Destructive cell targeting**
  - Pitsillides, C.; Edwin, J.; Xunbin, W.; Anderson, R.; Lin, C. *Biophys. J.* **2003**, *84*, 4023.

- **Polymer stabilized colloid catalysts**
  - Schimpf, S. Lucas, M.; Mohr, C.; Rodemerck, U.; Brückner, A.; Radnik, J.; Hofmeister, H.; Claus, P. *Catalysis Today* **2002**, *72*, 63.

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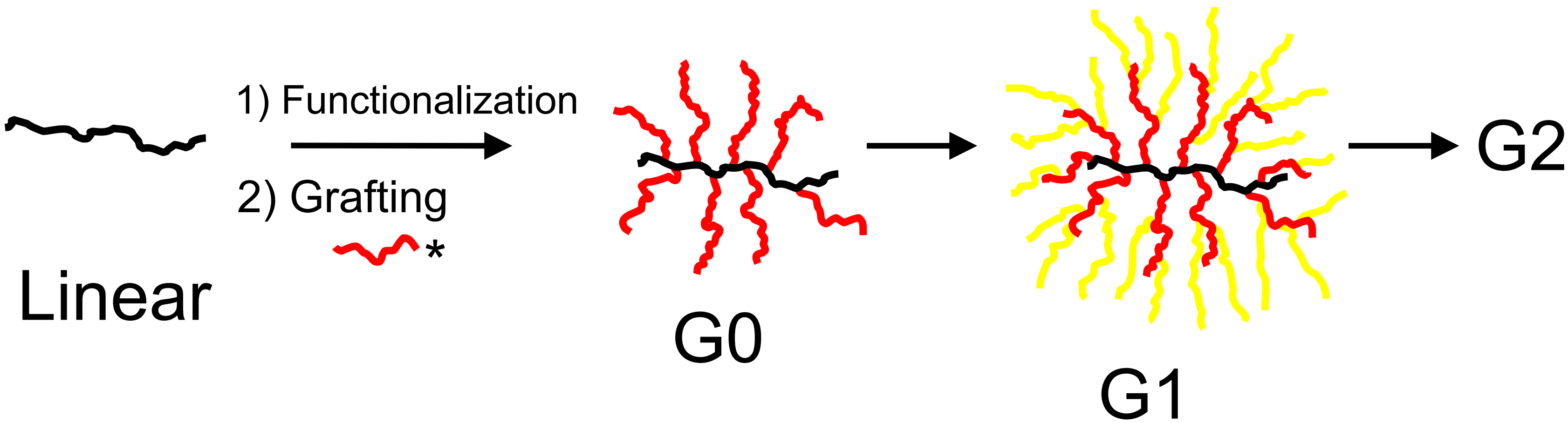
# Arborescent Polymers

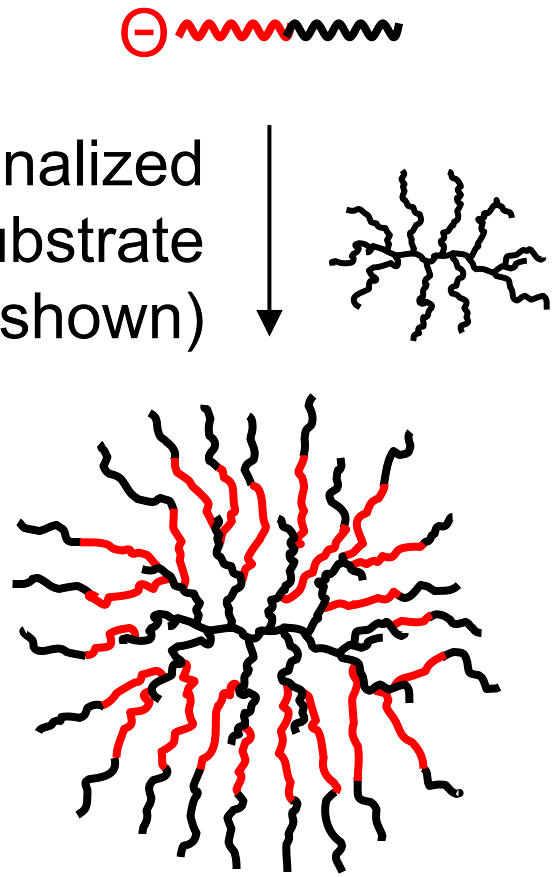
- Branched structure obtained from successive grafting reactions




Copolymers obtained by coupling with a different polymer in the last cycle


- Li, J.; Gauthier, M. *Macromolecules* **2001**, *34*, 8918.
- Kee, R.A.; Gauthier, M. *Macromolecules* **1999**, *32*, 6478.

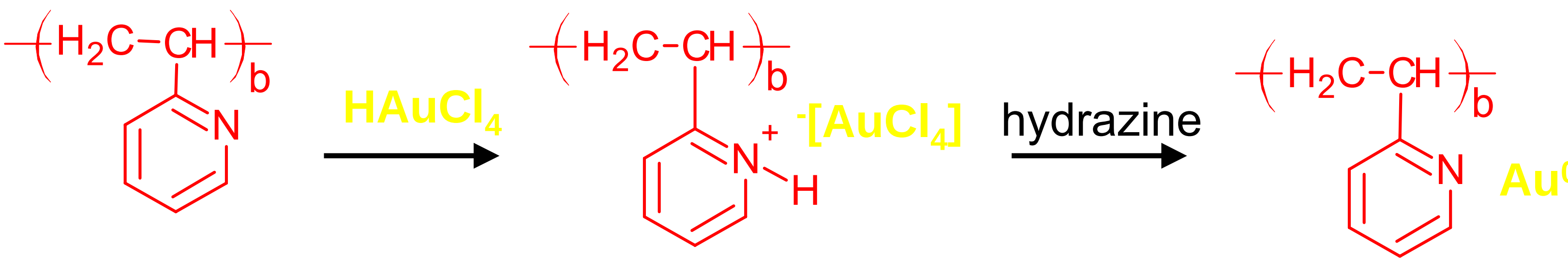
# Synthesis



Amphiphilic block copolymer (P2VP-*block*-PS)
Functionalized substrate (G0 PS shown)
amphiphilic arborescent copolymer
G0 PS-*graft*-(P2VP-*block*-PS)

# Selective Reactions

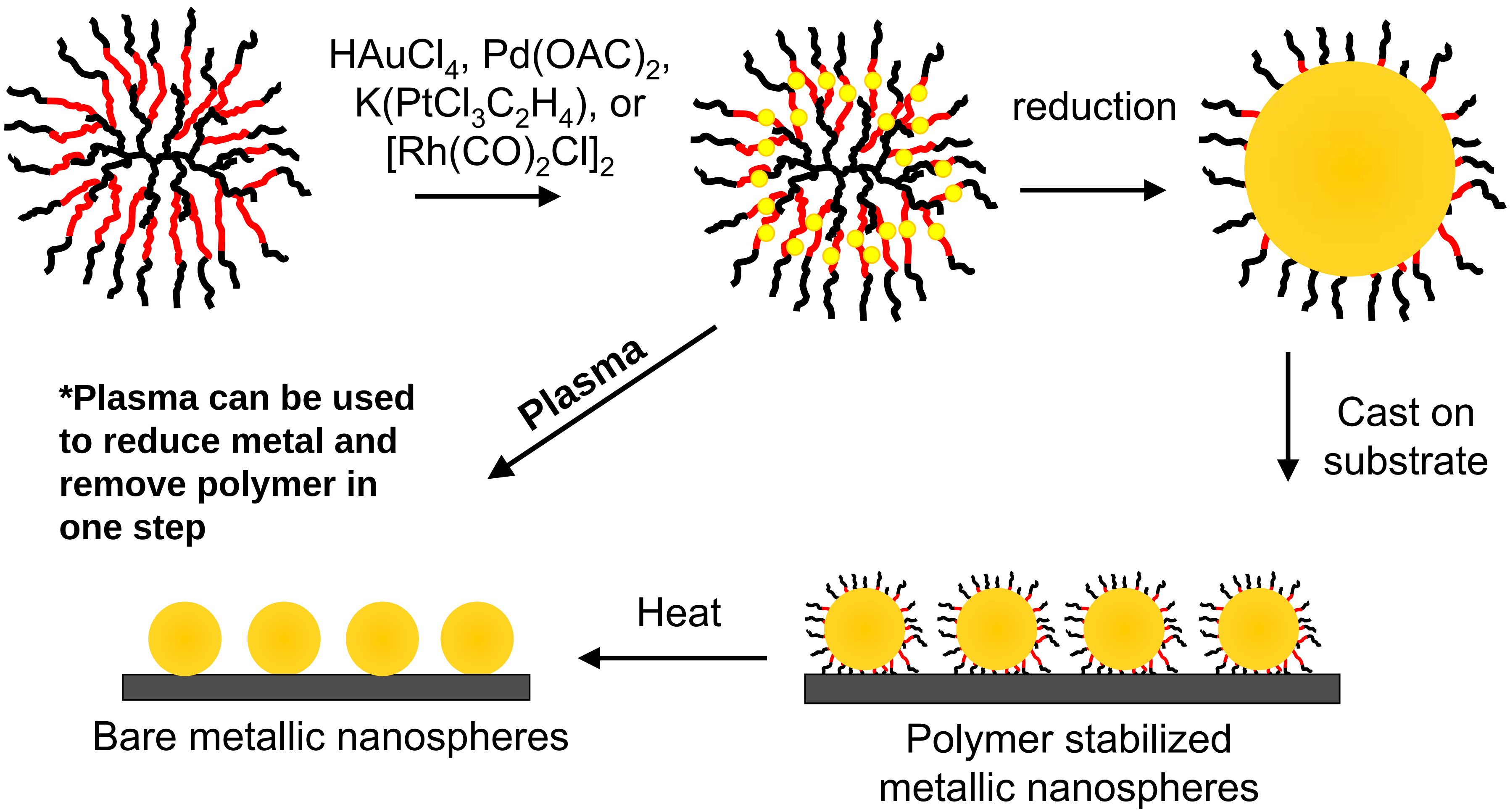
Polymer loading and reduction




Other loadable metal salts:

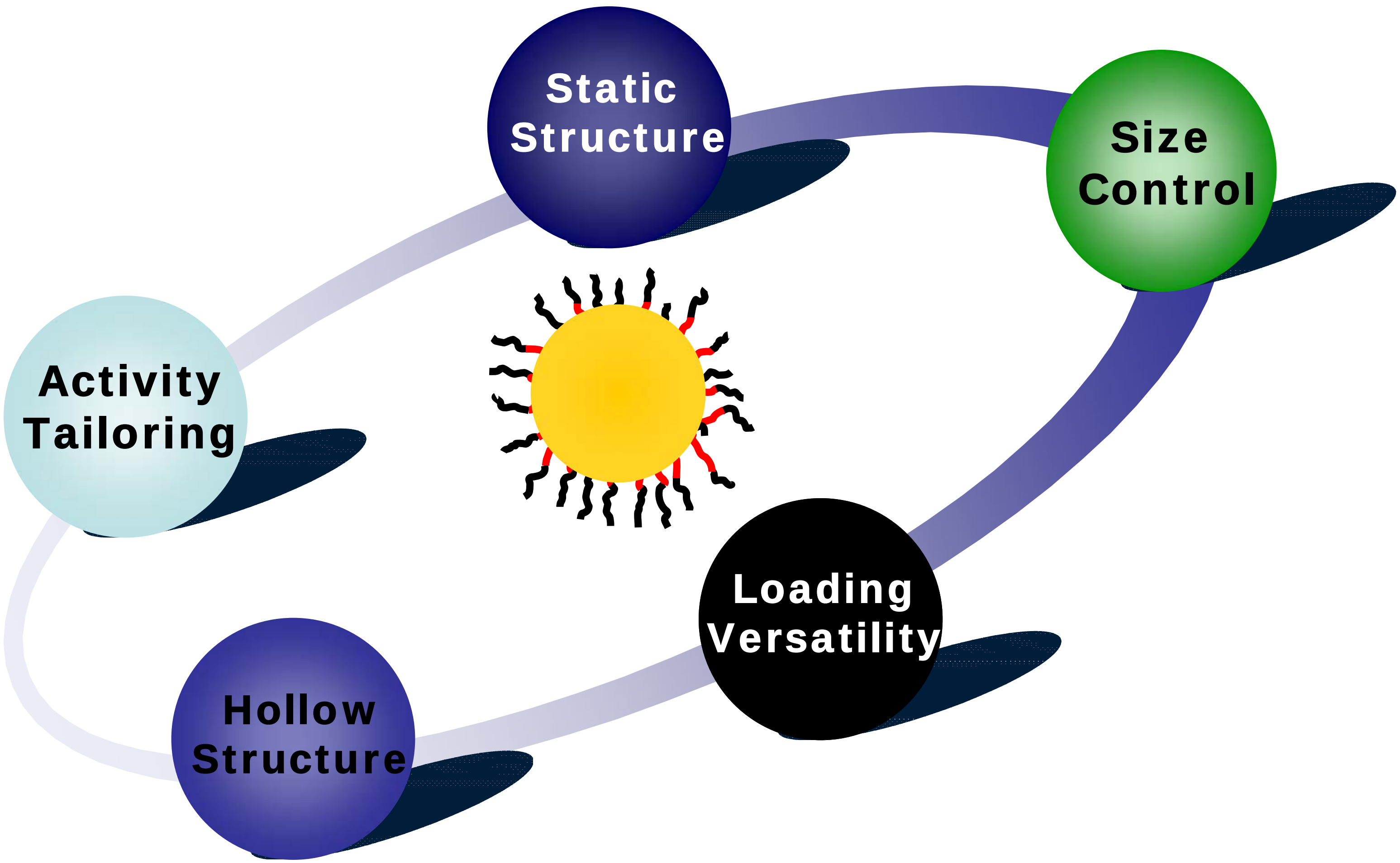
- Palladium - $Pd(OAC)_2$
- Platinum - $K(PtCl_3C_2H_4)$
- Rhodium - $[Rh(CO)_2Cl]_2$

# Loading and Deposition



# Arborescent Polymer Templates

## Unique Characteristics



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# Preliminary tests

Linear block copolymer used to validate loading procedure

**PS-*b*-P2VP**

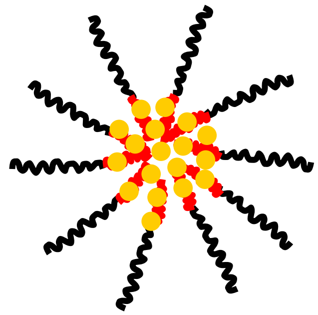
$M_w$(PS) = *29 000 (DP=277)*

$M_w$(P2VP)= *33 500 (DP=320)*

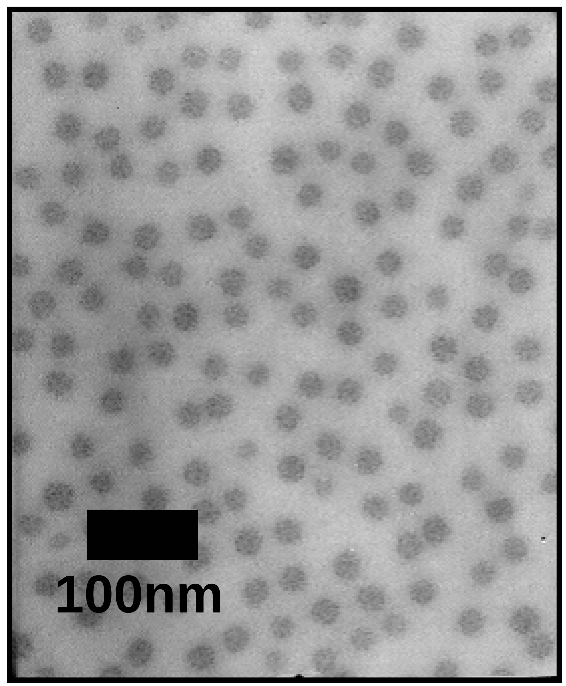
**PS*(277)*-*b*-P2VP*(320)***

**DP – Degree of Polymerization**

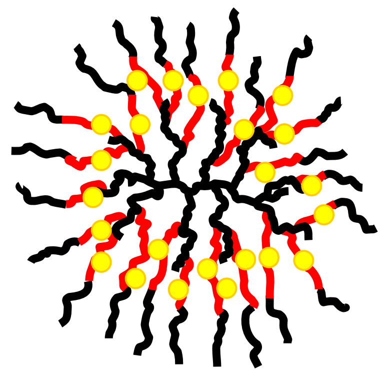
**PS*(277)*-*b*-P[2VP*(HAuCl$_4$)$_{0.5}$(320)*]**



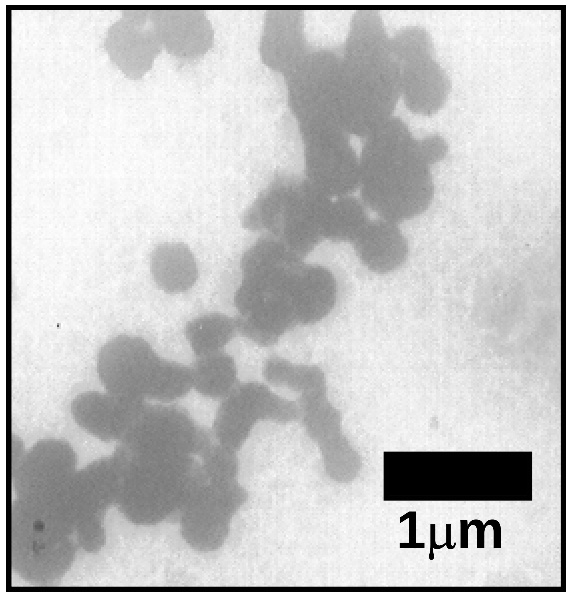
0.5 eq loading



# Arborescent Polymer Loading

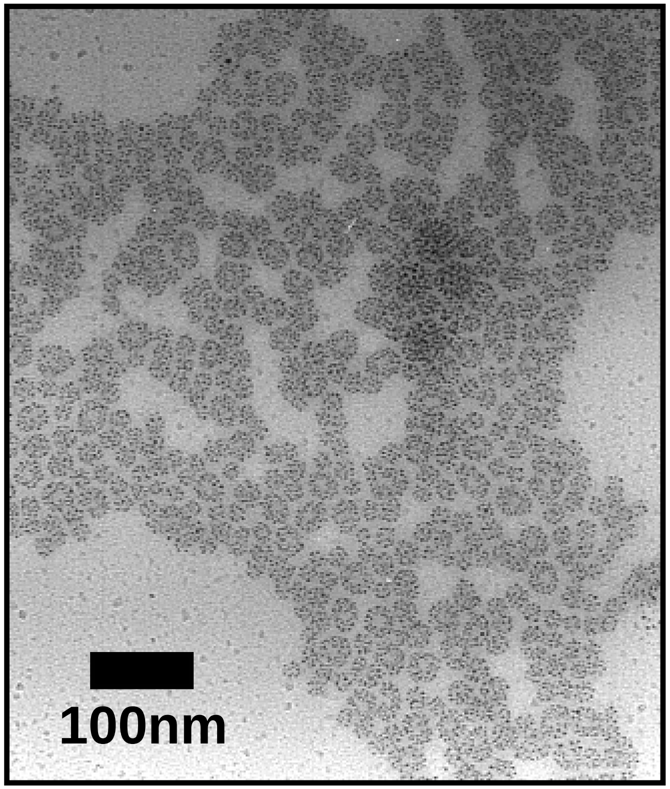


**G1PS-*g*-{PS*(66)*-*b*-P[2VP*(HAuCl$_4$)$_{0.5}$(89)*]}**

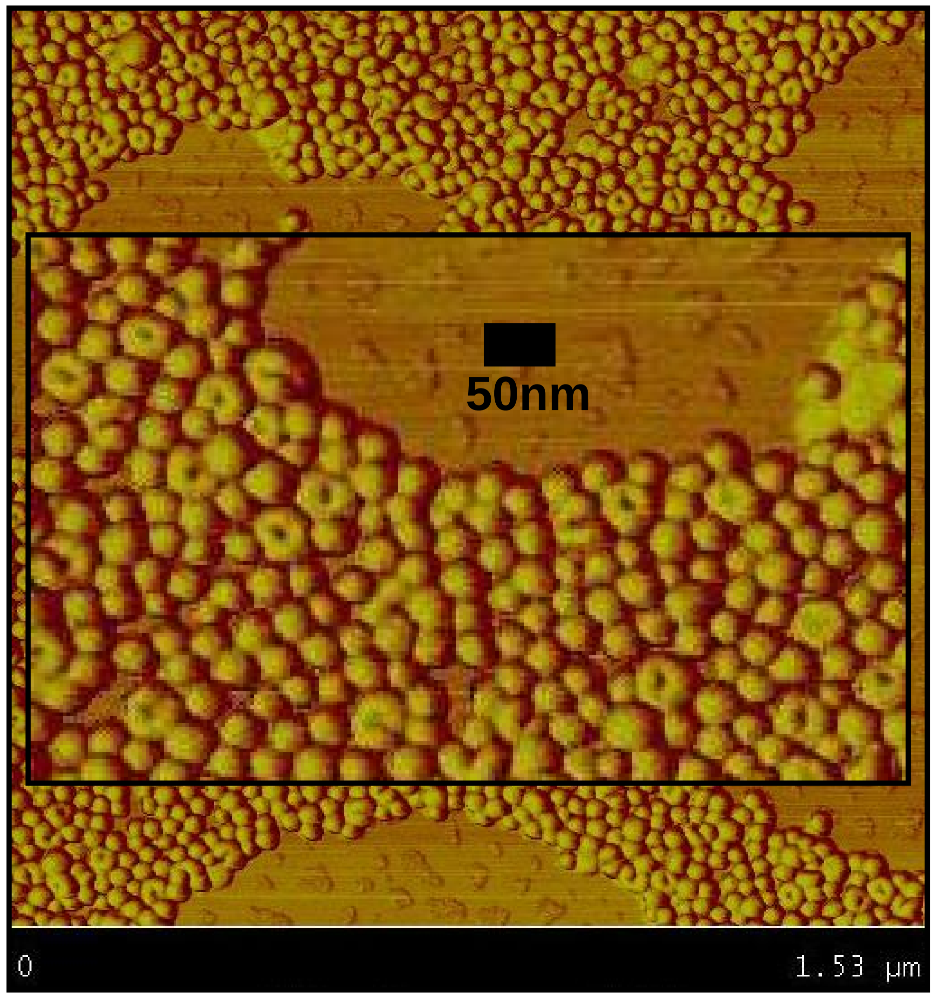



**Extensive aggregation → Increase length of PS chains in corona to shield charges**

**G1PS-*g*-{PS*(144)*-*b*-P[2VP*(HAuCl$_4$)$_{0.5}$(144)*]}**



# G1PS-*g*-{PS*(144)*-*b*-P[2VP*(HAuCl$_4$)$_{0.5}$(144)*]}

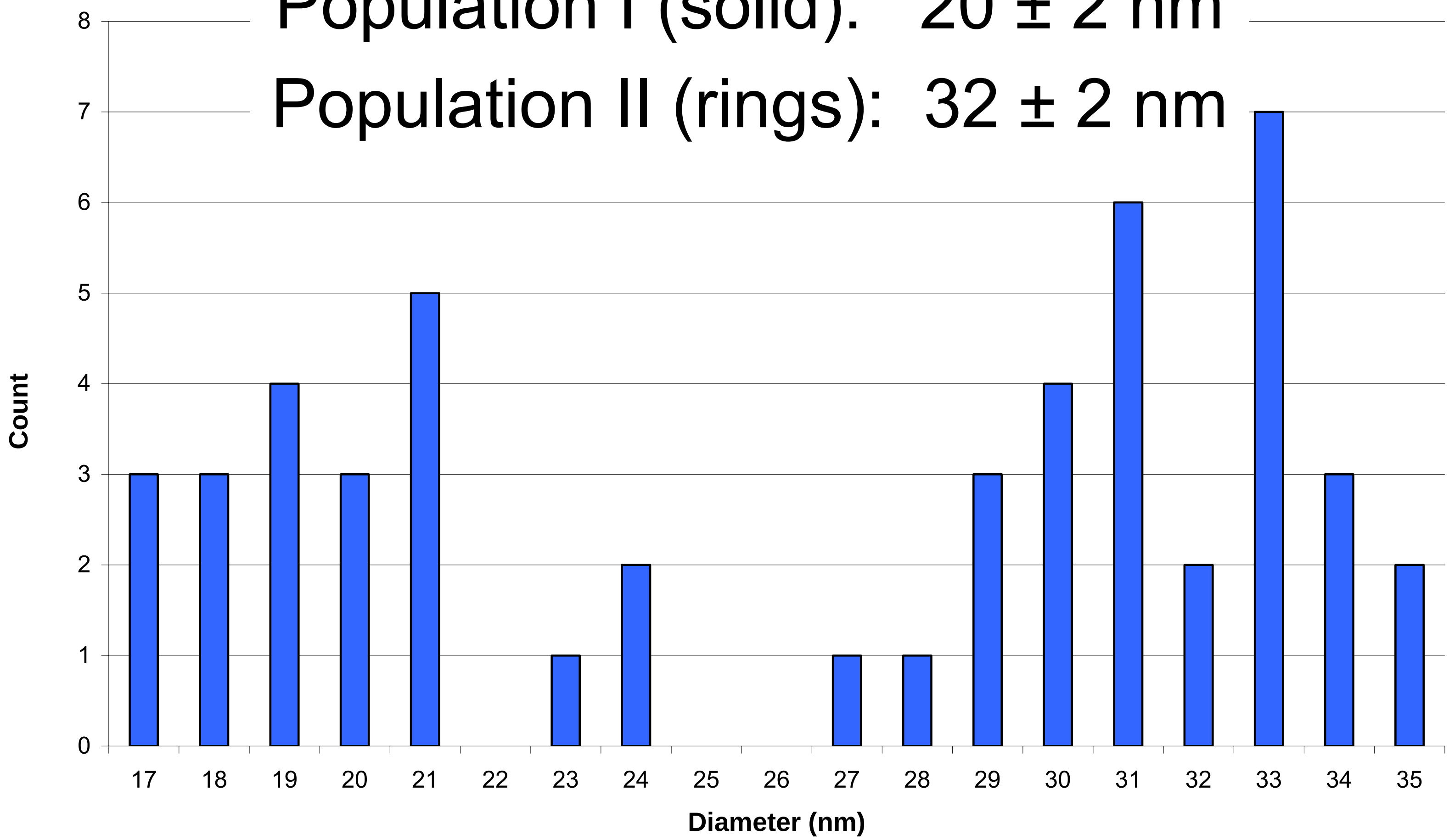


# Size Populations

**G1PS-*g*-{PS*(144)*-*b*-P[2VP*(HAuCl$_4$)$_{0.5}$(144)*]}**

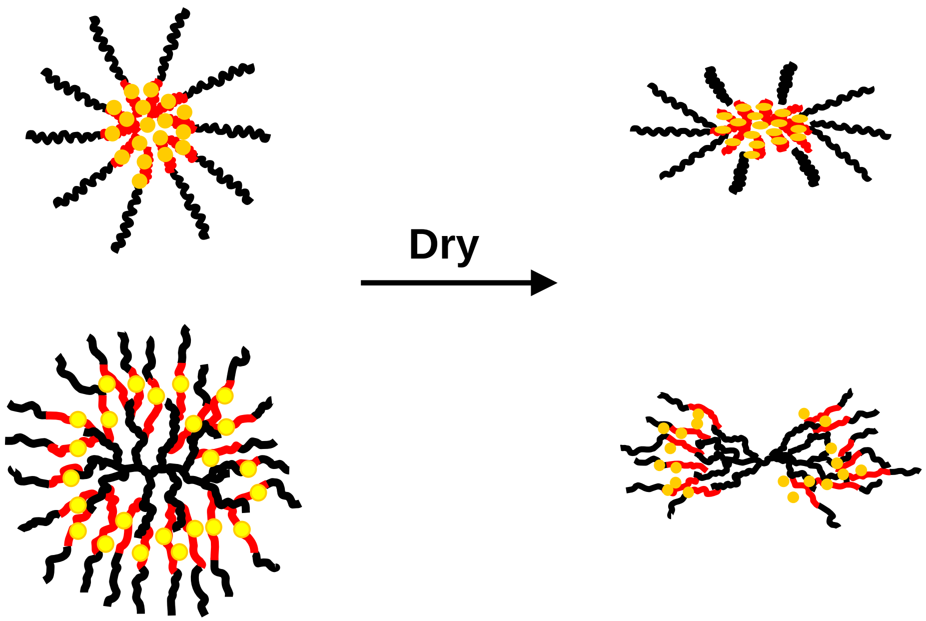
Population I (solid): 20 ± 2 nm

Population II (rings): 32 ± 2 nm

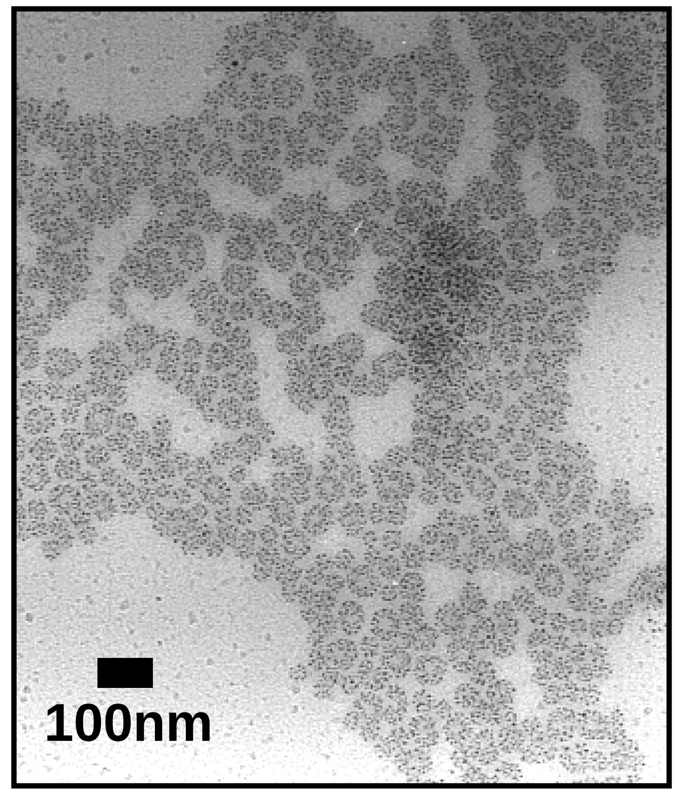


# Structure Analysis

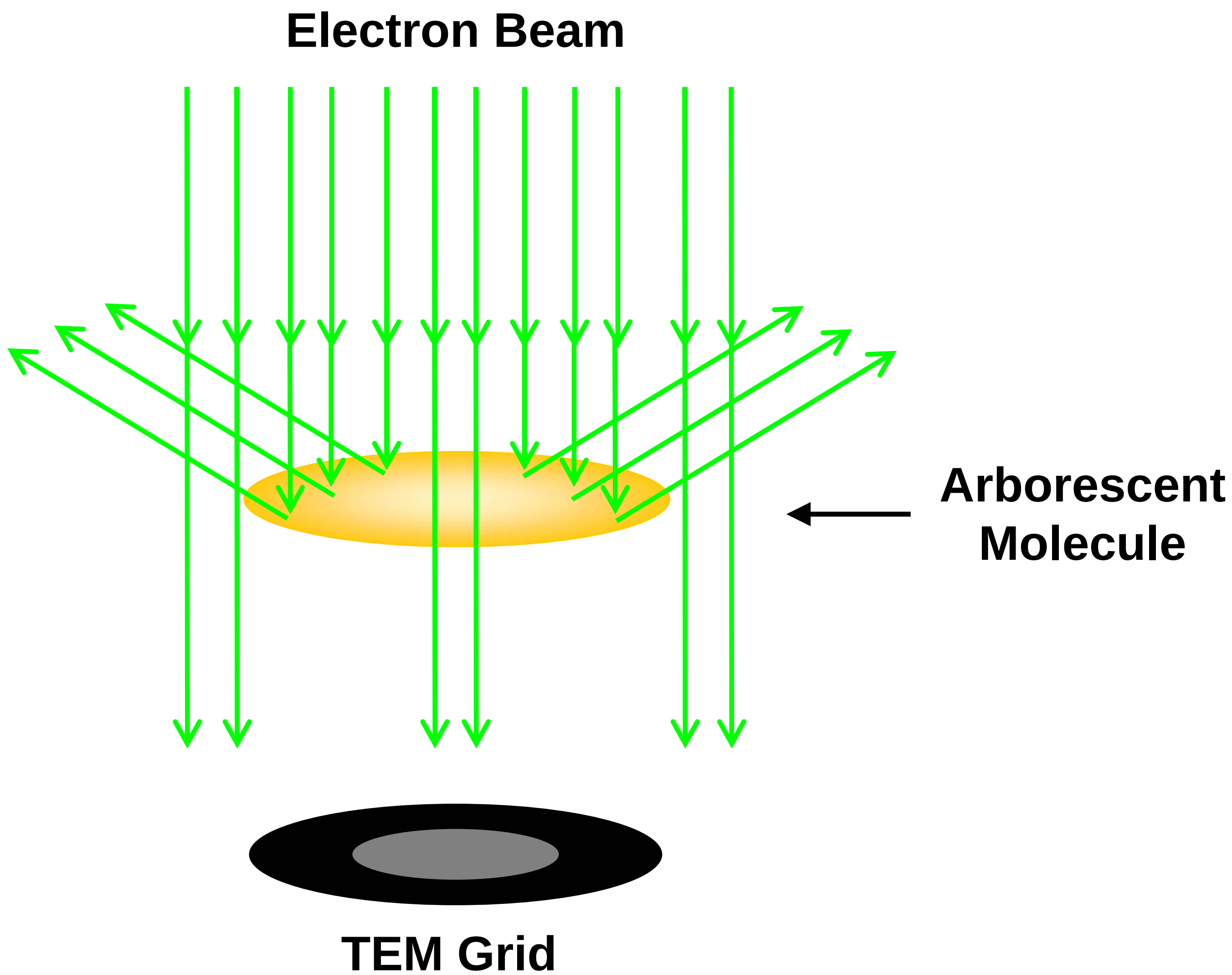
**Solid Structures: Linear side-chain micelles**




**Ring Structures: Graft copolymer**

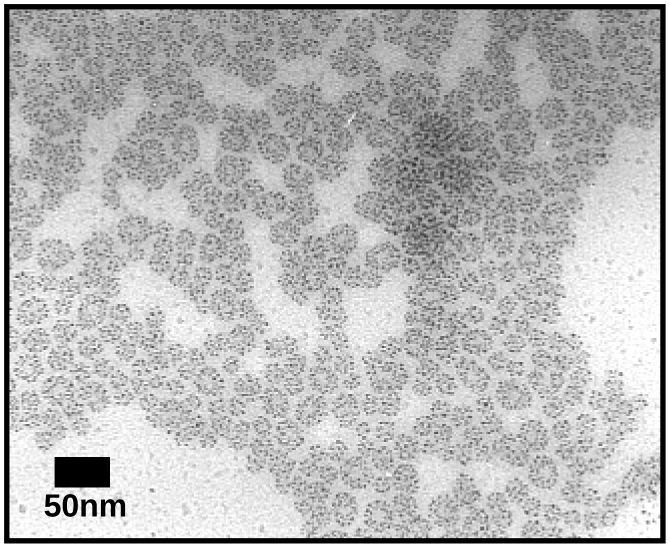


# Structure Analysis

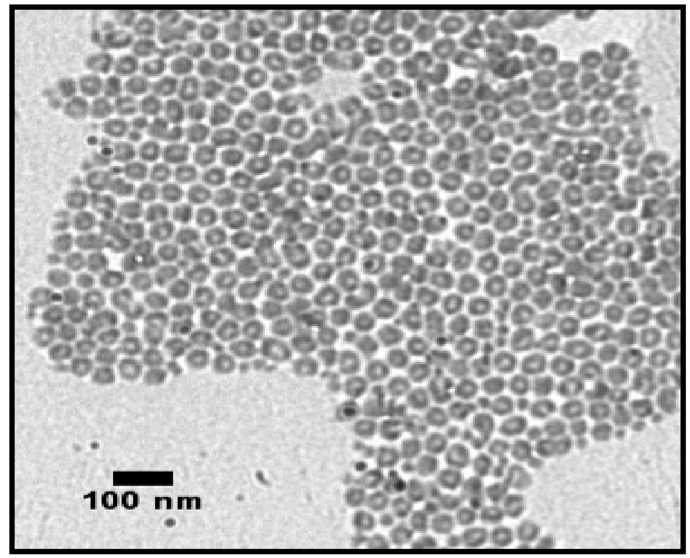


# Structure Analysis

Could the rings be aggregates of side-chain micelles?

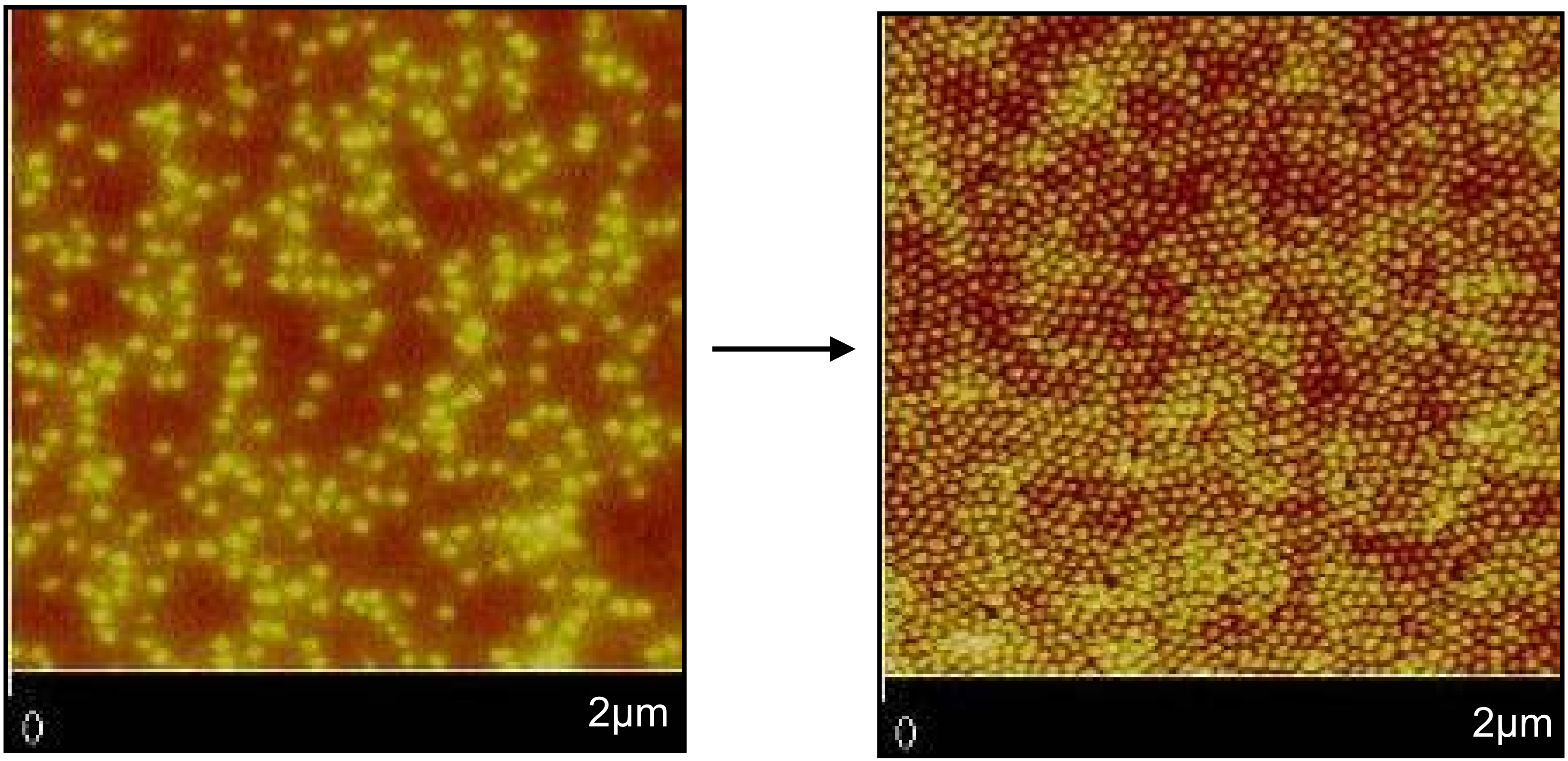



**Toluene**



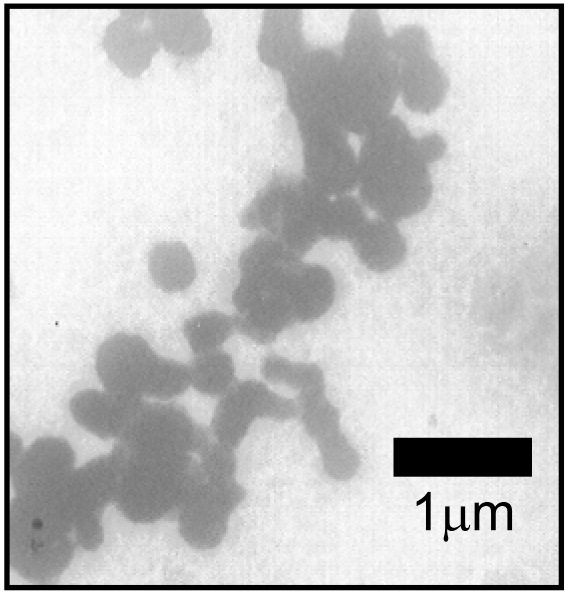

**THF**

# Purification

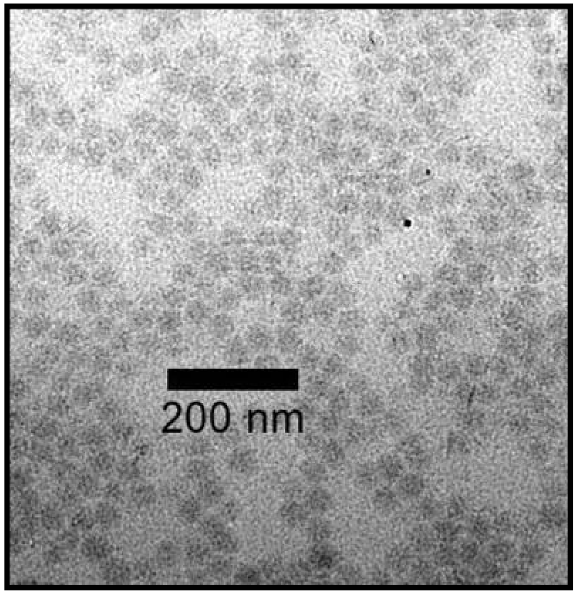


# Size and Aggregation

Can aggregation be controlled using a more polar solvent?




**Toluene**



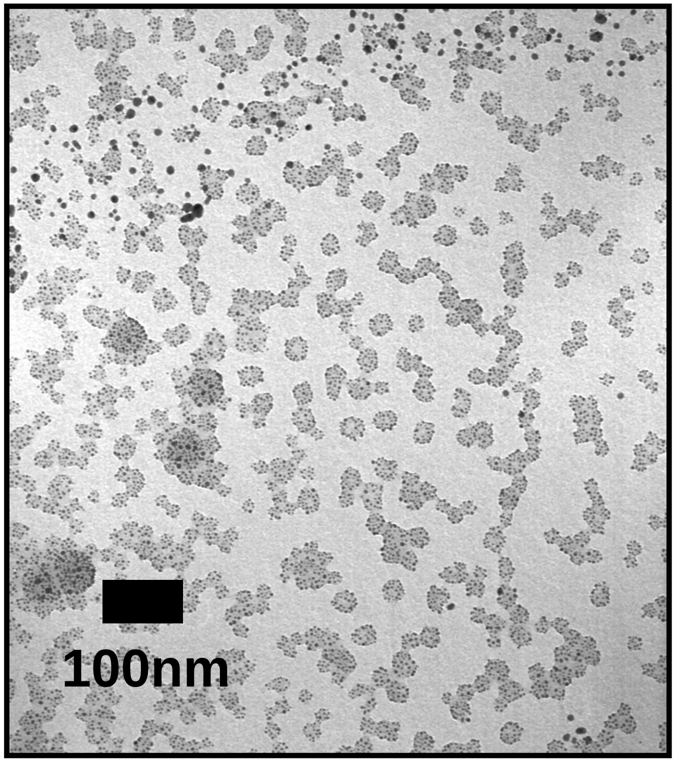

**THF**

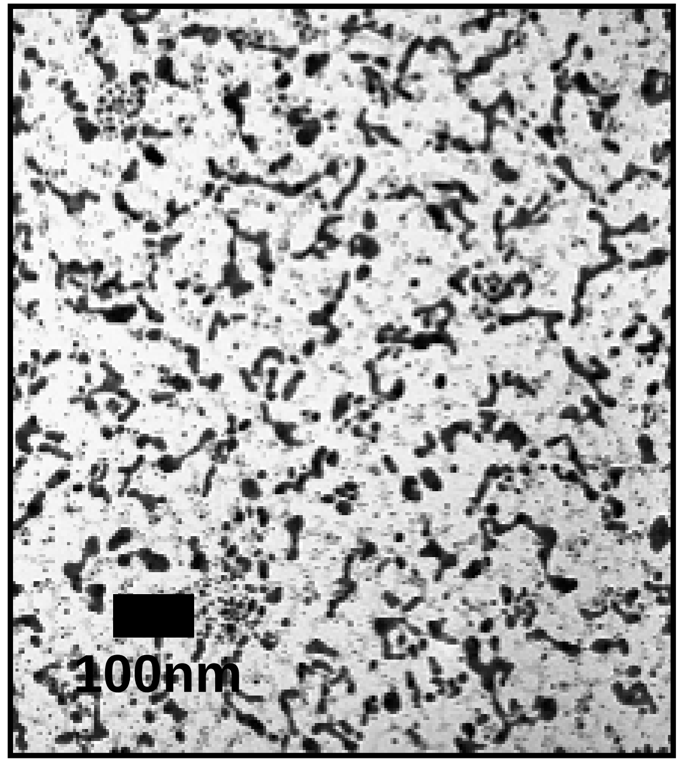
# Size and Aggregation

| Sample | Toluene 1st | Toluene 2nd | THF 1st | THF 2nd |
|---|---|---|---|---|
| **Core (G1PS)** | 24.4 ± 0.3 | 23.8 ± 0.6 | → 26.9 ± 0.1 | 26.3 ± 0.2 |
| **PS(*66*)-*b*-P2VP(*89*)** | 50.0 ± 0.4 | 49.5 ± 0.4 | → 56.1 ± 0.2 | 55.3 ± 0.4 |
| **+ 0.5eq Au** | 85 ± 7 | 61 ± 4 | → 51.7 ± 0.6 | ↓ 50.8 ± 0.4 |
| **Core (G1PS)** | 28.2 ± 0.1 | 26.6 ± 0.2 | → 29.6 ± 0.3 | 28.2 ± 0.2 |
| **PS(*95*)-*b*-P2VP(*95*)** | 53.2 ± 0.2 | 52 ± 1 | → 63.2 ± 0.2 | 61.5 ± 0.2 |
| **+ 0.5eq Au** | 90 ± 1 | 77 ± 2 | → 56.2 ± 0.4 | ↓ 54.5 ± 0.5 |
| **PS(*144*)-*b*-P2VP(*144*)** | 72.9 ± 0.9 | 67 ± 1 | → 76.3 ± 0.5 | 74.2 ± 0.9 |
| **+ 0.5eq Au** | 122 ± 3 | 97 ± 3 | → 64.1 ± 0.2 | ↓ 63.1 ± 0.4 |

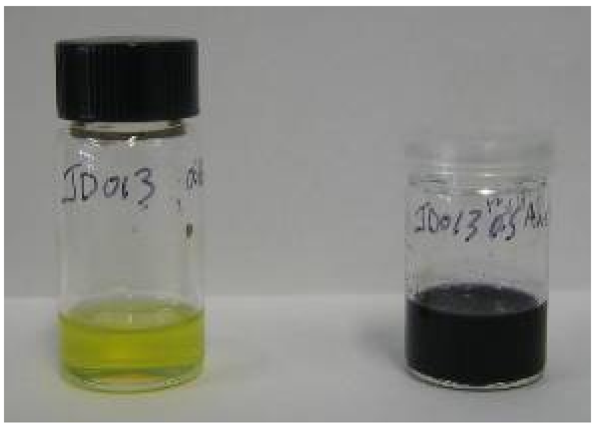
# Plasma Etching and Reduction

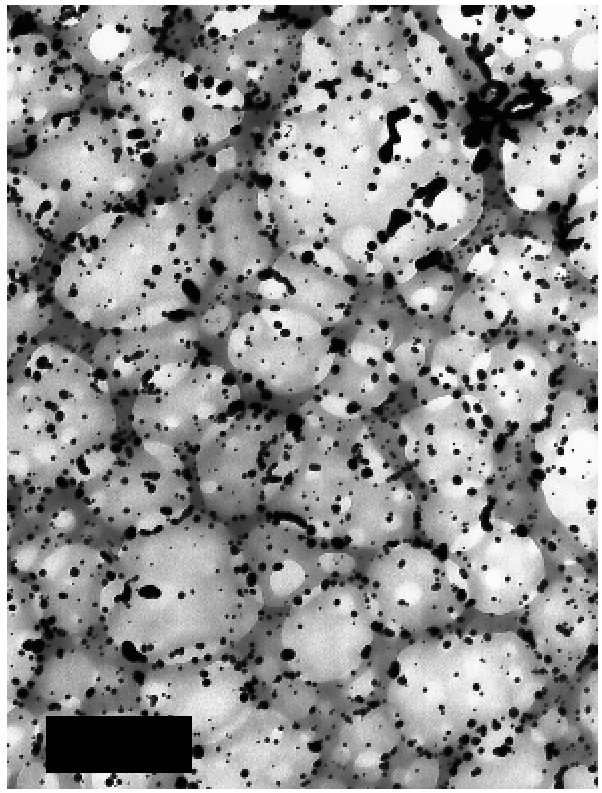
# Hydrogen Plasma Etching



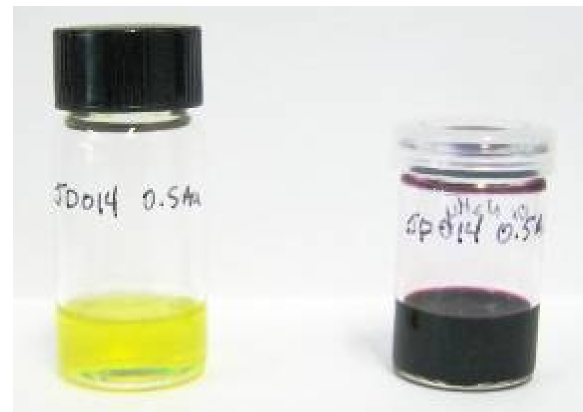



# Hydrazine Reduction

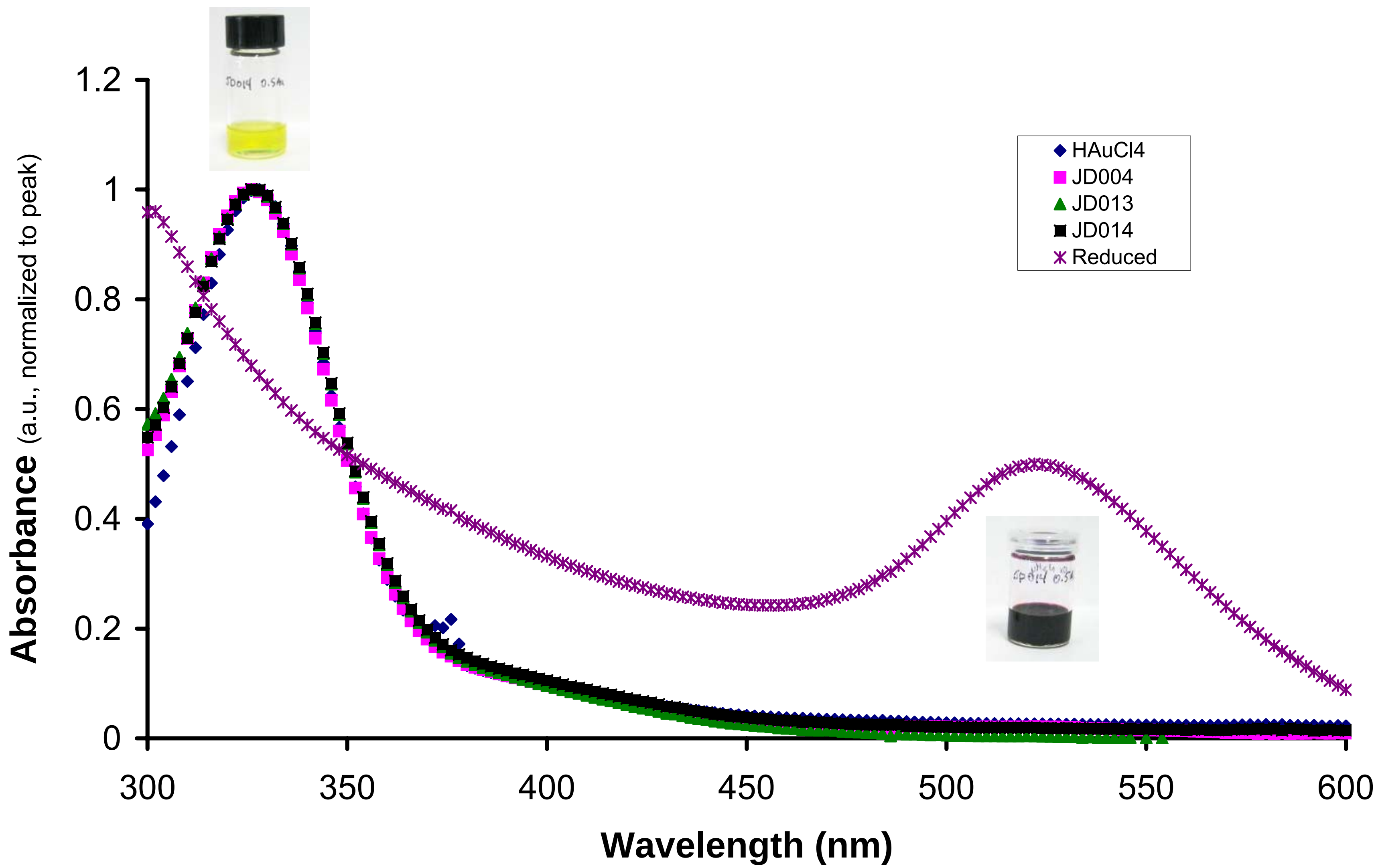


250nm



# UV-Vis Absorbance



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# Conclusions

- Different arborescent copolymer templates successfully loaded with gold
- Ring-like structures observed, consistent with hollow metallic nanosphere morphology
- Aggregation can be controlled through synthetic procedure and/or solvent changes

# Future Work

- Optimization and control of metal reduction and polymer etching to yield one metallic particle per micelle.

- Load templates with catalytic materials and test for stability, selectivity, and reactivity

- Synthesize a series of arborescent copolymers with systematic variations in dimensions of core and shell

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University of Waterloo

# Thank you!

Questions?