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

Metal-loaded Polymers

Modified Metallic Nanoparticles

Stabilized Catalysts

Biological Labelling

Destructive Cell Targeting
Nanoparticle Applications

• Biological labelling
Nanoparticle Applications

• **Destructive cell targeting**

• **Polymer stabilized colloid catalysts**
Arborescent Polymers

• Branched structure obtained from successive grafting reactions

1) Functionalization
2) Grafting

Linear

G0

G1

G2

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

Synthesis

Amphiphilic block copolymer (P2VP-block-PS)

Functionalized substrate (G0 PS shown)

G0 PS-graft-(P2VP-block-PS)

amphiphilic arborescent copolymer
Selective Reactions

Polymer loading and reduction

Other loadable metal salts:
- Palladium - Pd(OAC)$_2$
- Platinum - K(PtCl$_3$C$_2$H$_4$)
- Rhodium - [Rh(CO)$_2$Cl]$_2$
Plasma can be used to reduce metal and remove polymer in one step.

**Loading and Deposition**

- HAuCl₄, Pd(OAC)₂, K(PtCl₃C₂H₄), or [Rh(CO)₂Cl]₂
- Cast on substrate
- Heat
- Bare metallic nanospheres
- Polymer stabilized metallic nanospheres
Arborescent Polymer Templates

Unique Characteristics

Static Structure

Size Control

Activity Tailoring

Hollow Structure

Loading Versatility
Agenda

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Preliminary tests

Linear block copolymer used to validate loading procedure

\[
\text{PS-}b\text{-P2VP}
\]

\[
M_w(\text{PS}) = 29\,000\ (DP=277)
\]
\[
M_w(\text{P2VP}) = 33\,500\ (DP=320)
\]

\[
\text{PS}(277)-b\text{-P2VP(320)}
\]

DP – Degree of Polymerization
PS(277)-b-P[2VP(HAuCl₄)₀.₅(320)]

0.5 eq loading

100nm
Arborescent Polymer Loading
G1PS-\(g-\{PS(66)-b-P[2VP(HAuCl_4)_{0.5}(89)]\}\)

Extensive aggregation $\rightarrow$ Increase length of PS chains in corona to shield charges
G1PS-g-{PS(144)-b-P[2VP(HAuCl₄)₀.₅(144)]}
G1PS-g-{PS(144)-b-P[2VP(HAuCl₄)₀.₅(144)]}
Size Populations

G1PS-g-\{PS(144)-b-\text{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

Electron Beam

TEM Grid

Arborescent Molecule
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?
## Size and Aggregation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Toluene 1st</th>
<th>Toluene 2nd</th>
<th>THF 1st</th>
<th>THF 2nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core (G1PS)</td>
<td>24.4 ± 0.3</td>
<td>23.8 ± 0.6</td>
<td>26.9 ± 0.1</td>
<td>26.3 ± 0.2</td>
</tr>
<tr>
<td>PS(66)-b-P2VP(89)</td>
<td>50.0 ± 0.4</td>
<td>49.5 ± 0.4</td>
<td>56.1 ± 0.2</td>
<td>55.3 ± 0.4</td>
</tr>
<tr>
<td>+ 0.5eq Au</td>
<td>85 ± 7</td>
<td>61 ± 4</td>
<td>51.7 ± 0.6</td>
<td>50.8 ± 0.4</td>
</tr>
<tr>
<td>Core (G1PS)</td>
<td>28.2 ± 0.1</td>
<td>26.6 ± 0.2</td>
<td>29.6 ± 0.3</td>
<td>28.2 ± 0.2</td>
</tr>
<tr>
<td>PS(95)-b-P2VP(95)</td>
<td>53.2 ± 0.2</td>
<td>52 ± 1</td>
<td>63.2 ± 0.2</td>
<td>61.5 ± 0.2</td>
</tr>
<tr>
<td>+ 0.5eq Au</td>
<td>90 ± 1</td>
<td>77 ± 2</td>
<td>56.2 ± 0.4</td>
<td>54.5 ± 0.5</td>
</tr>
<tr>
<td>PS(144)-b-P2VP(144)</td>
<td>72.9 ± 0.9</td>
<td>67 ± 1</td>
<td>76.3 ± 0.5</td>
<td>74.2 ± 0.9</td>
</tr>
<tr>
<td>+ 0.5eq Au</td>
<td>122 ± 3</td>
<td>97 ± 3</td>
<td>64.1 ± 0.2</td>
<td>63.1 ± 0.4</td>
</tr>
</tbody>
</table>
Plasma Etching and Reduction
Hydrogen Plasma Etching
Hydrazine Reduction
UV-Vis Absorbance

Absorbance (a.u., normalized to peak)

Wavelength (nm)

- HAuCl₄
- JD004
- JD013
- JD014
- Reduced
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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Thank you!

Questions?