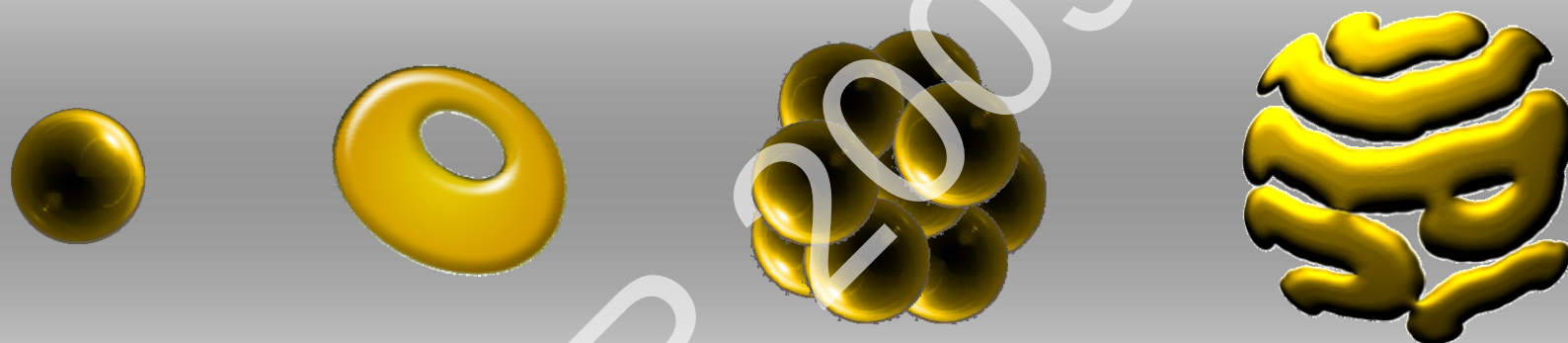


Unique Morphology of Metal-loaded Arborescent Copolymers



31st Annual Institute for Polymer Research Symposium

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Department of Chemistry



Outline

- **Introduction**

- Arborescent polymers
- Metal templating
- Potential applications

- **Results**

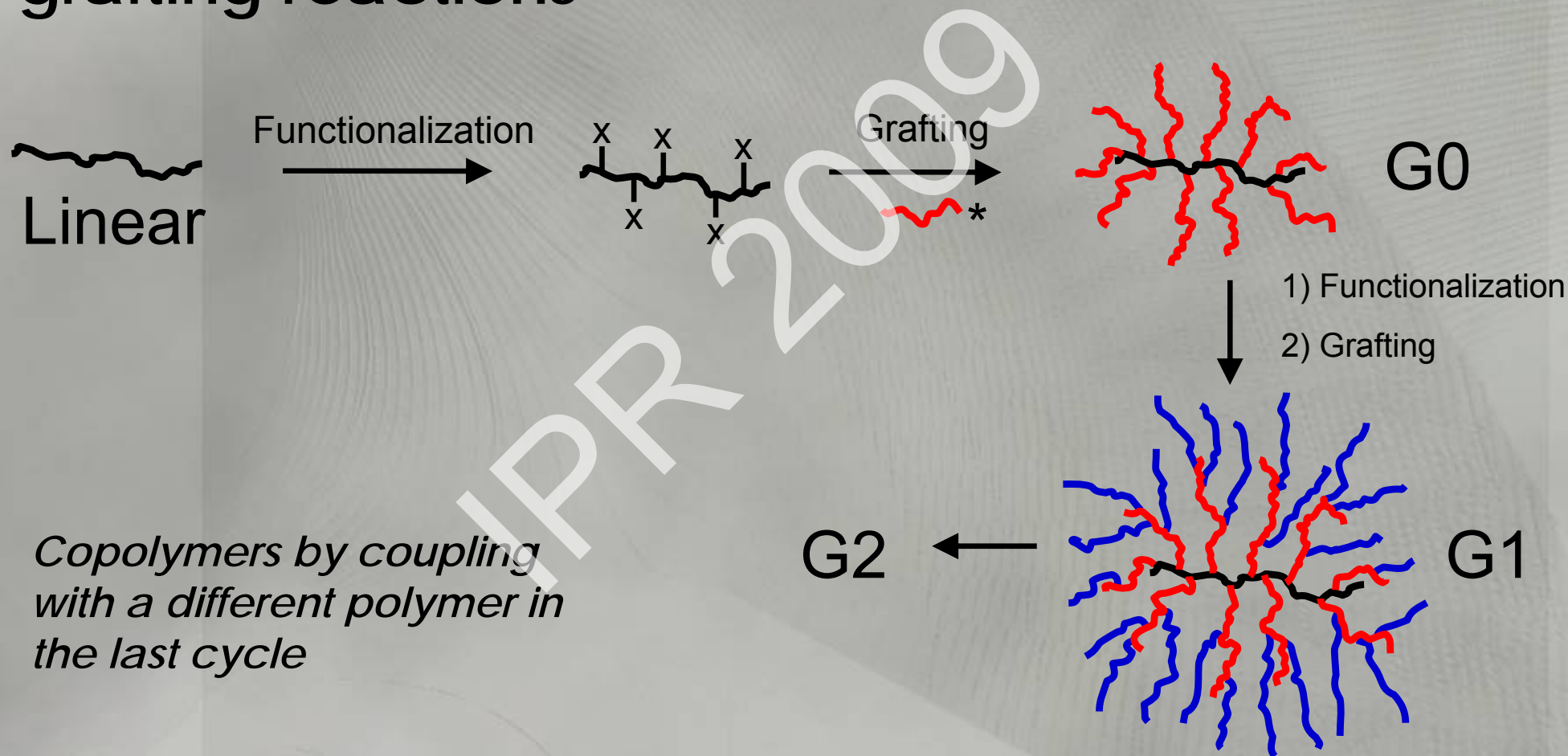
- Morphologies observed
- Stability and counterion dependence
- Block copolymer ratio variation

- **Conclusions**

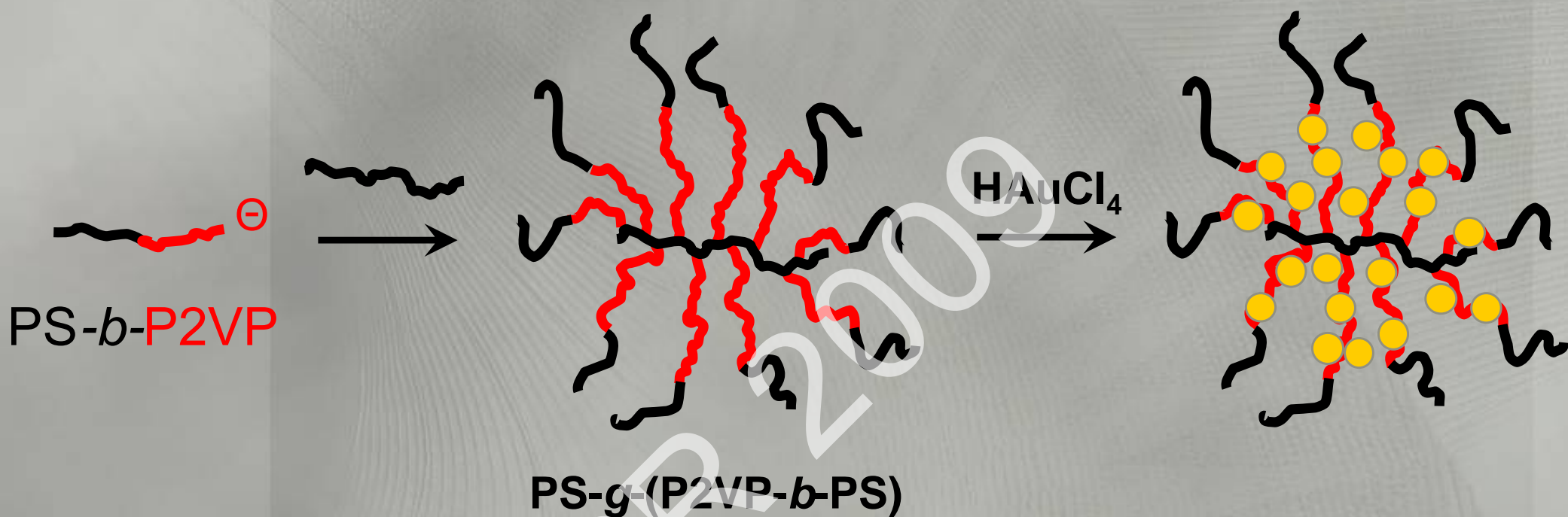
- **Future work**

Arborescent Polymers

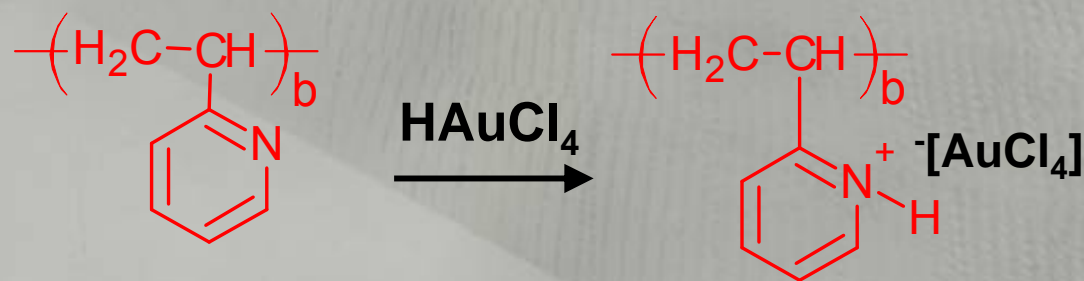
Branched structure obtained from successive grafting reactions



Nanoparticle Template



*Core-shell-corona
(CSC) architecture*



Applications

- **Polymer-stabilized catalysts**
 - Easily recovered from reaction medium
 - Compatible with many metal catalysts
 - Stable covalent structure, concentration-independent
- **Biological applications**
 - Targeted cell delivery or destruction
 - Optical markers or sensors
 - Biocompatible systems are being investigated

Results

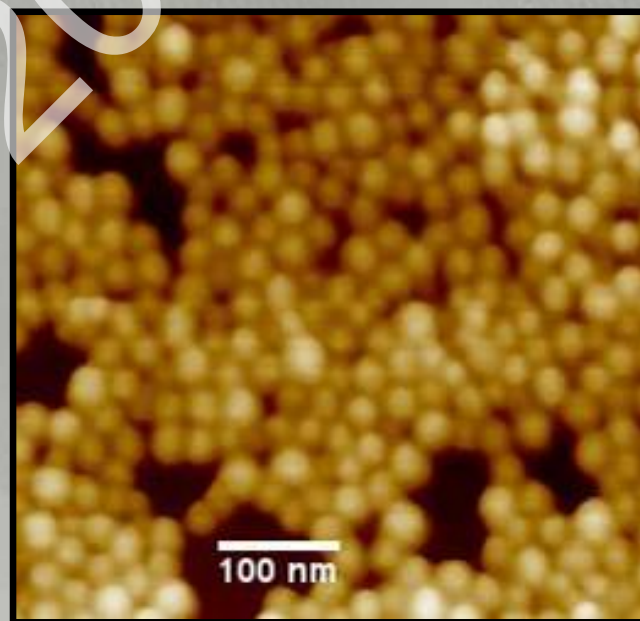
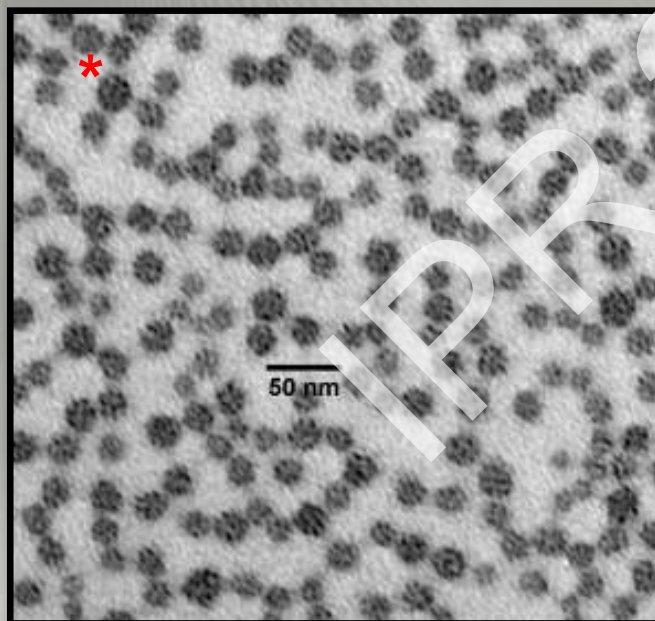
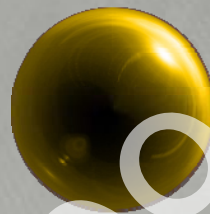
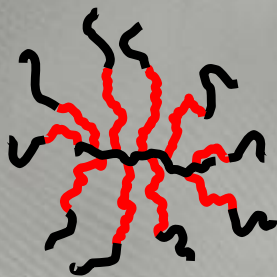
Templates

G	Description	Block Copolymer Side Chains							
		PS			P2VP		Copolymer		
		DP	M_n	PDI	DP	M_n	M_n	%2VP	PDI
0	PS- <i>g</i> -(P2VP14- <i>b</i> -PS11)	108	11200	1.04	130	13500	24700	0.55	1.11
1	G0PS- <i>g</i> -(P2VP8- <i>b</i> -PS8)	76	7910	1.04	75	7760	15700	0.50	1.19
2	G1PS- <i>g</i> -(P2VP5- <i>b</i> -PS6)	64	6620	1.06	54	5580	12200	0.46	1.14
2	G1PS- <i>g</i> -(P2VP11- <i>b</i> -PS11)	106	11000	1.02	113	11800	22800	0.52	1.14
2	G1PS- <i>g</i> -(P2VP20- <i>b</i> -PS25)	192	20000	1.02	235	24500	44500	0.55	1.13
3	G2PS- <i>g</i> -(P2VP15- <i>b</i> -PS11)	105	10900	1.06	142	14700	25700	0.57	1.01
3	G2PS- <i>g</i> -(P2VP8- <i>b</i> -PS11)	110	11500	1.17	78	8130	19600	0.41	1.02
3	G2PS- <i>g</i> -(P2VP15- <i>b</i> -PS20)	191	19900	1.12	148	15500	35400	0.39	1.05
4	G3PS- <i>g</i> -(P2VP14- <i>b</i> -PS11)	109	11400	1.03	131	13700	25000	0.55	1.01

Morphologies

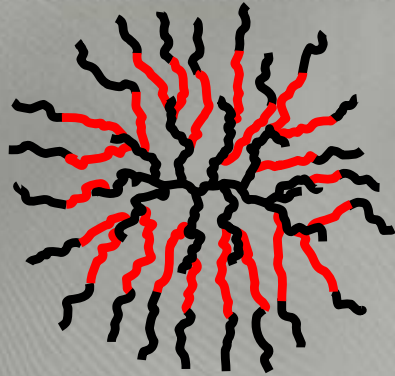
- What can we expect for different architectures and generations of these templates?
 - Loading with 0.5 eq of HAuCl_4 per 2VP unit in toluene

G0: PS-*g*-(P2VP-*b*-PS)

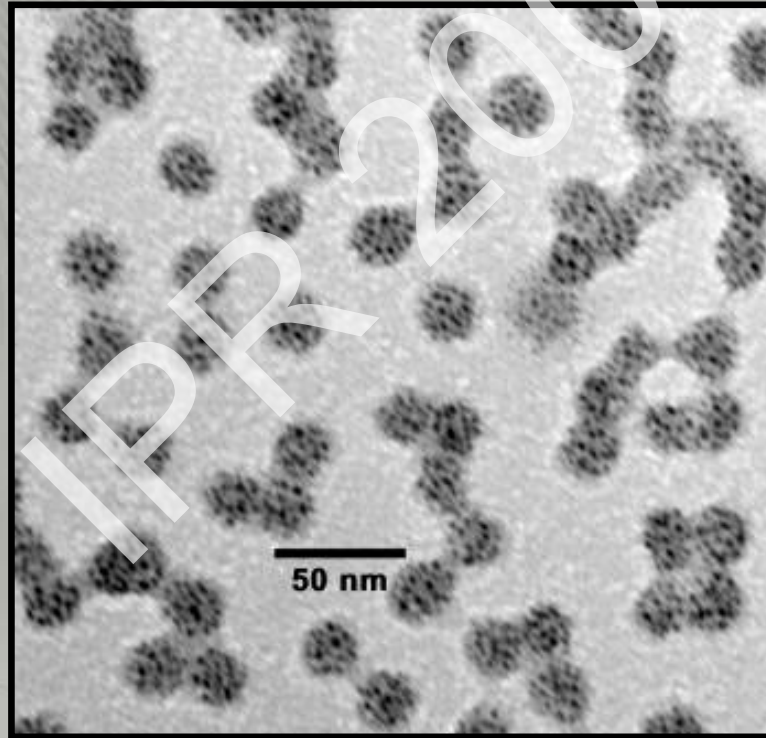


19 ± 2 nm

G1: G0PS-*g*-(P2VP-*b*-PS)



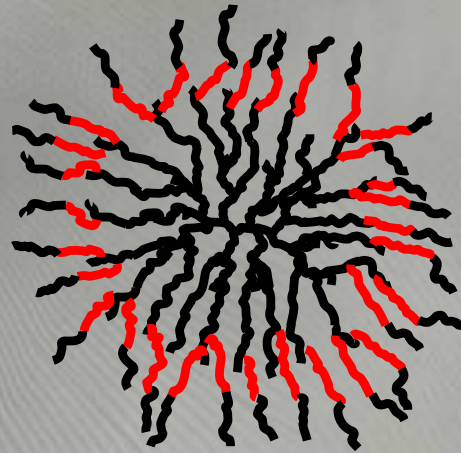
Hollow?



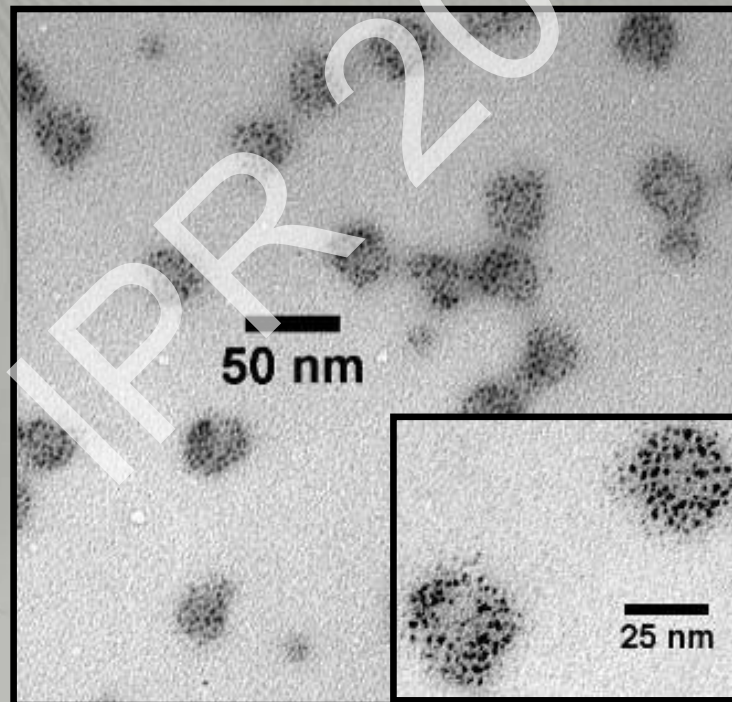
23 ± 2 nm

**No evidence of
hollow
morphology**

G2: G1PS-*g*-(P2VP-*b*-PS)

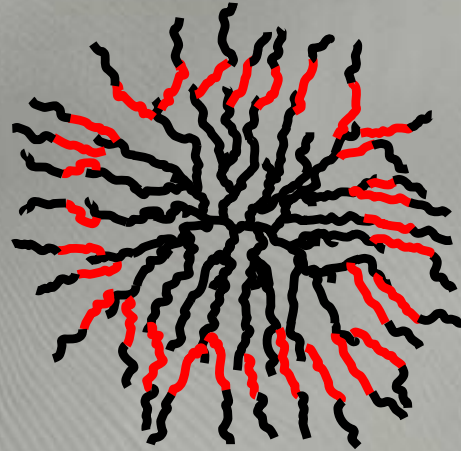


Hollow?

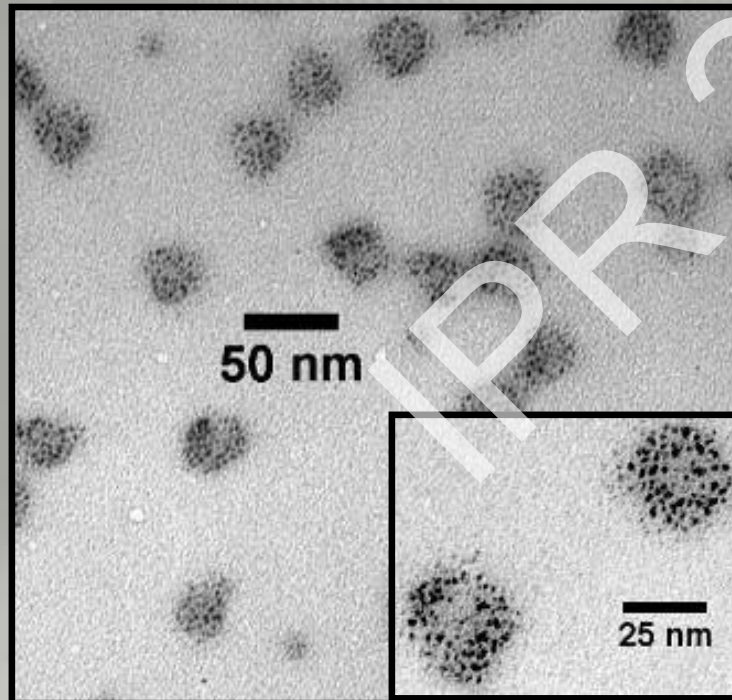


30 ± 3 nm

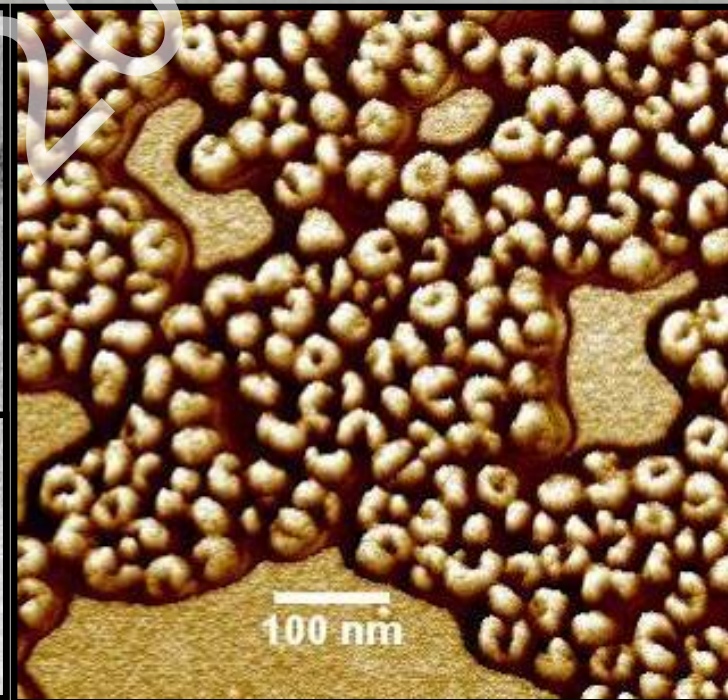
G2: G1PS-*g*-(P2VP-*b*-PS)



Ring-like
organization
of Au



30 ± 3 nm

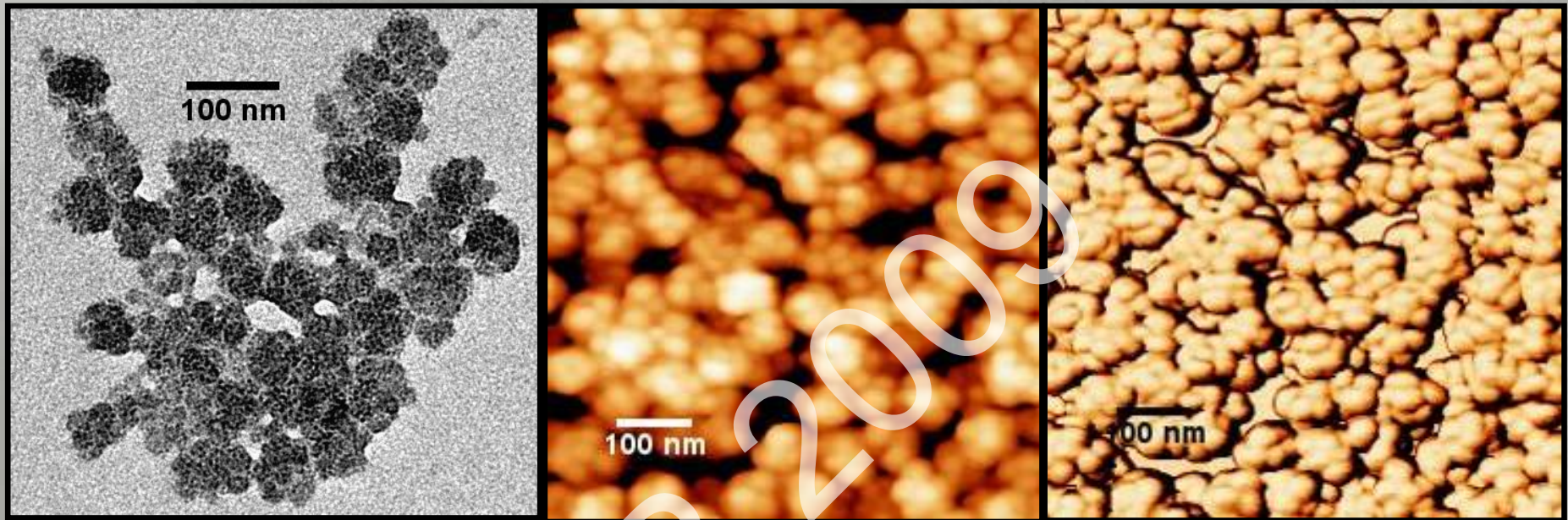


Higher Generations (G3, G4 ...)



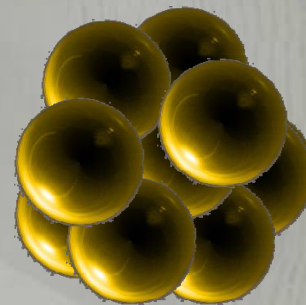
Higher generation core → larger ring structure?

G3: G2PS-*g*-(P2VP-*b*-PS)



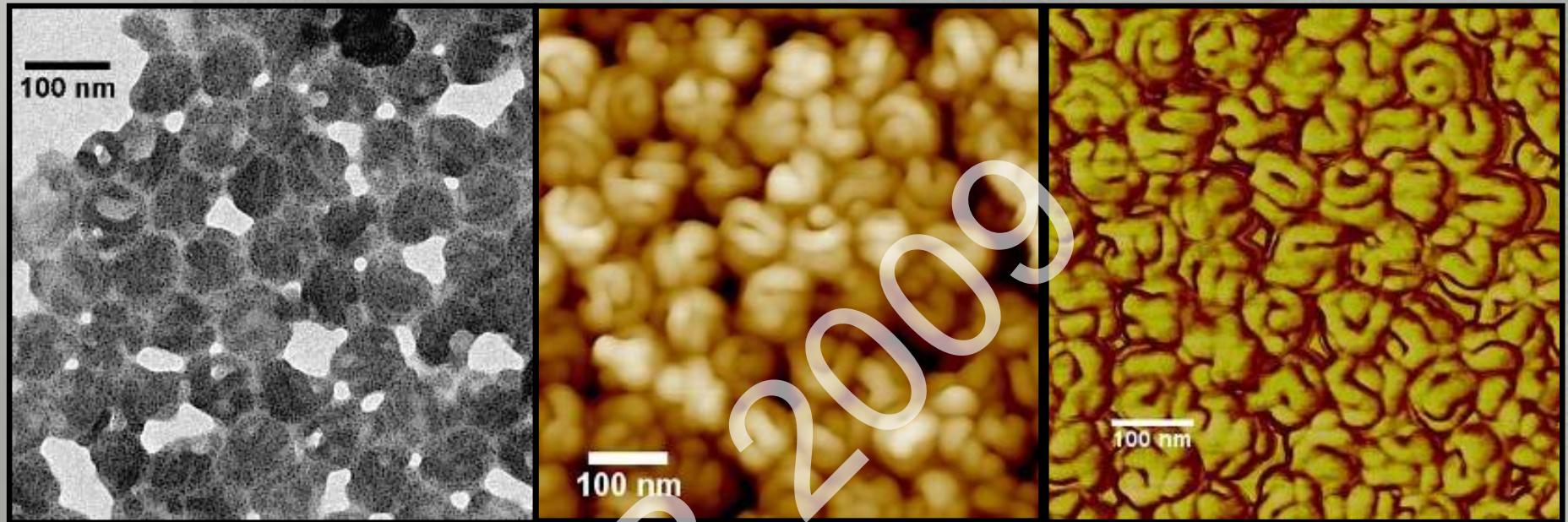
58 ± 5 nm

Globular phase separation



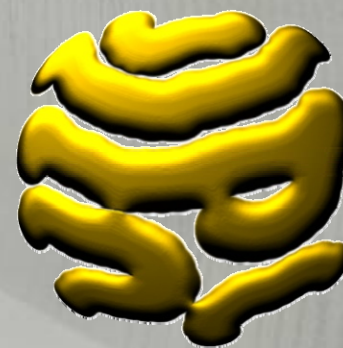
Intramolecular self-assembly!!

G4: G3PS-*g*-(P2VP-*b*-PS)



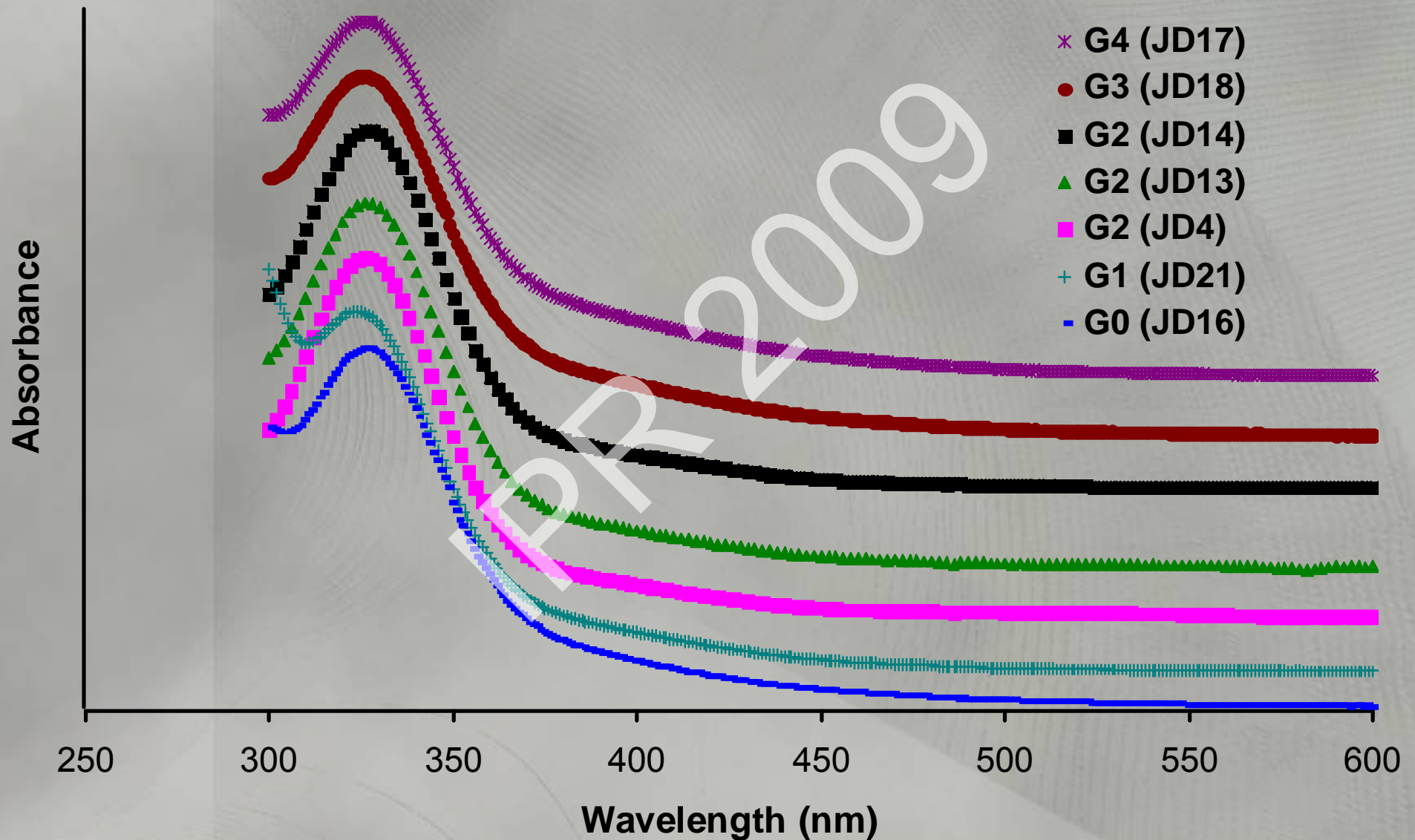
$75 \pm 3 \text{ nm}$

Cylindrical phase separation



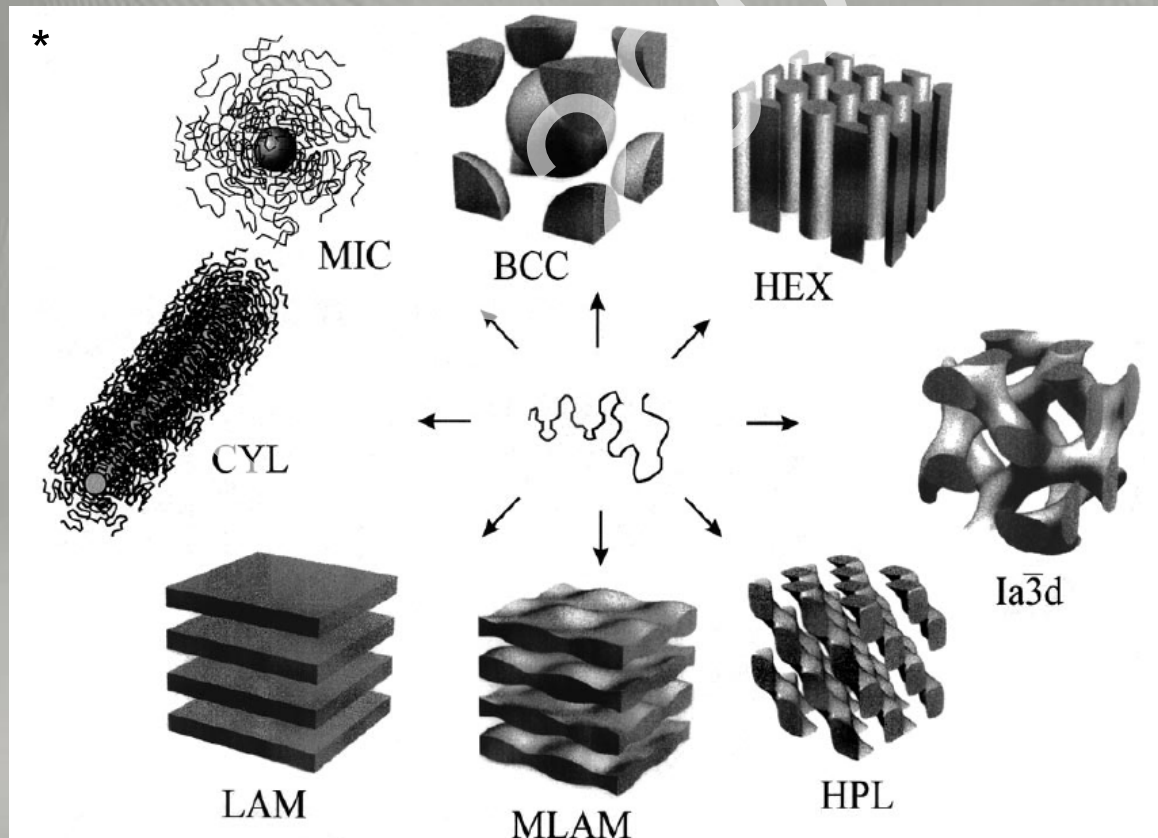
Intramolecular self-assembly

Optical Properties



Comparisons

- Block copolymers assemble into various morphologies depending on composition and solvency conditions



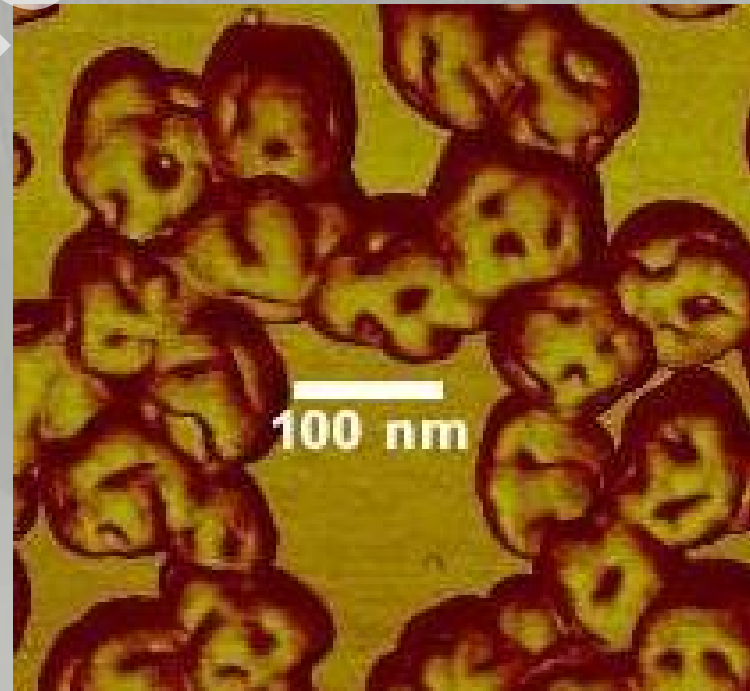
Comparisons

- Can PS-*b*-P2VP arborescent copolymers form similar structures?
- Related to tethered systems?
- Can the morphology in the arborescent systems be altered (controlled)?
 - Solvent composition
 - Annealing
 - Counterion type
 - PS : P2VP ratio in block copolymer

Domain Stability

- Nano-domains are resistant to solvent change or annealing
 - Feature enhancement or domain interpenetration observed

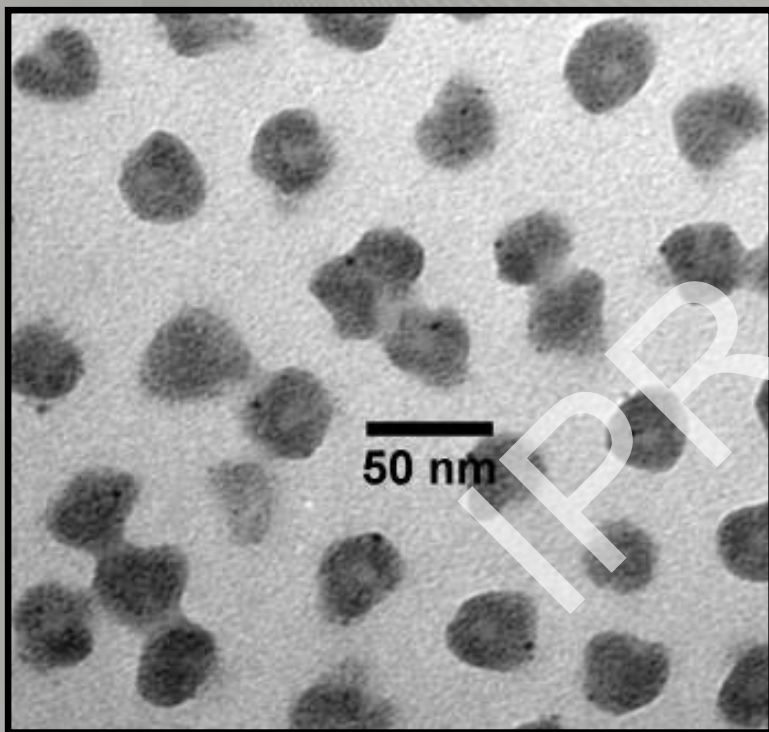
G2



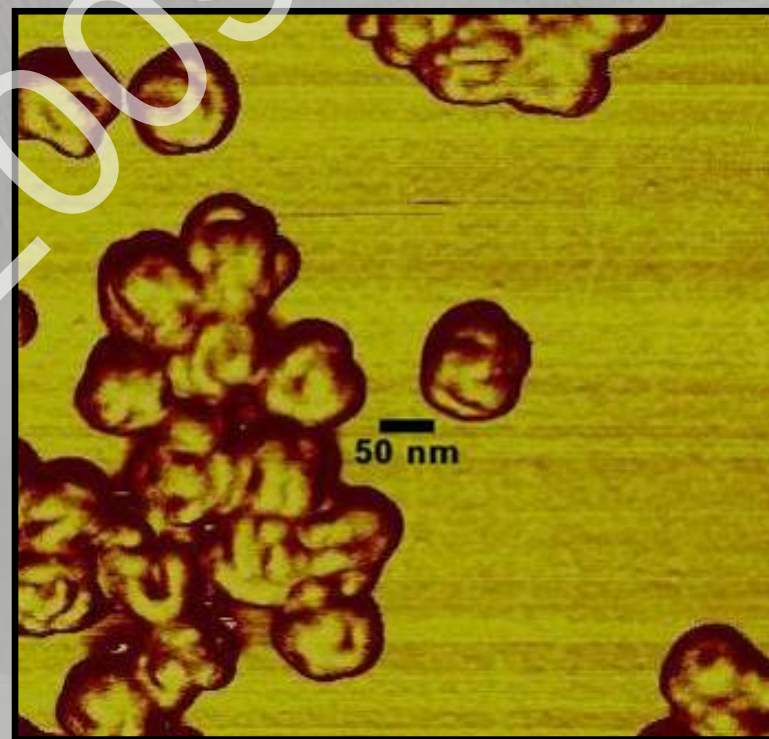
G4

Counterion

- Nano-domains present for different metals or bimetallic loading



G2 - Pd(OAc)₂

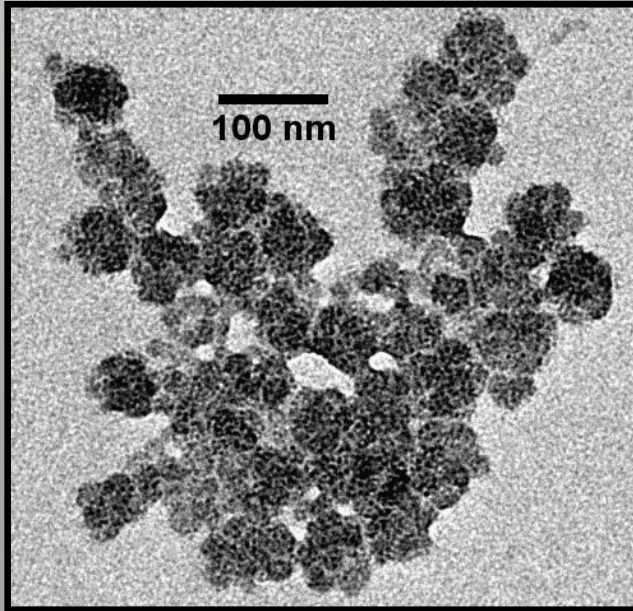


G4 – HAuCl₄ / H₂PtCl₆

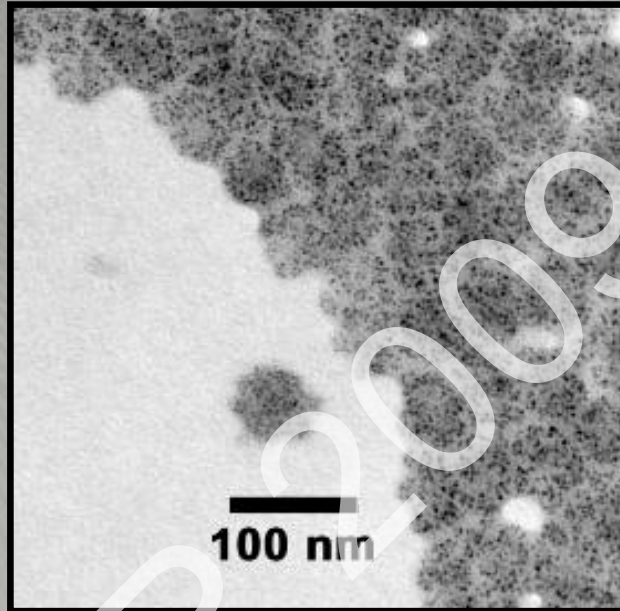
Side Chain Variation

- **G2: Morphology not well-defined, poor for visual comparison**
 - PS11-P2VP11, PS20-P2VP25 both show ring structures
 - PS6-P2VP5 does not
- **G3: Better-defined morphology**

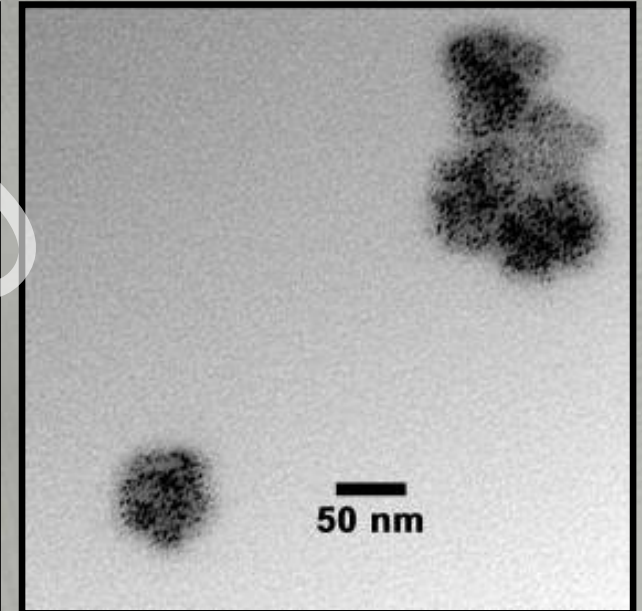
G3



PS 11 - P2VP 15



PS 11 - P2VP 8



PS 20 - P2VP 15

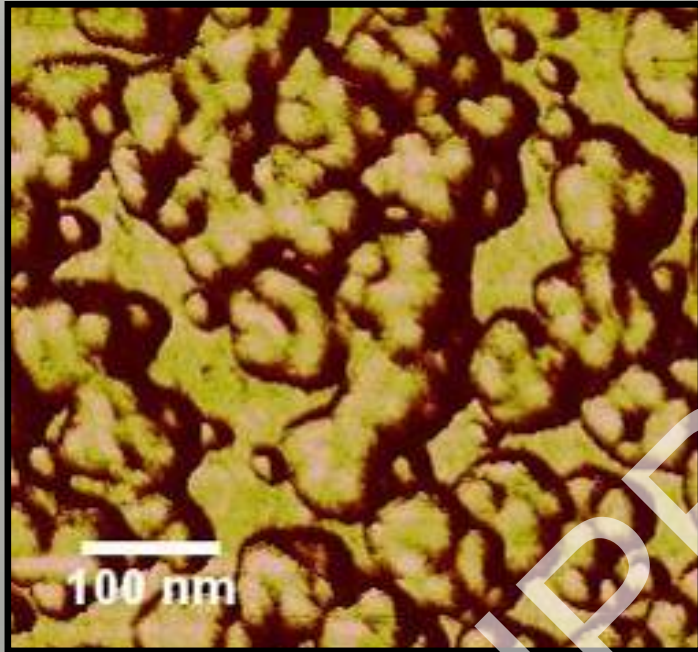
- No major change in nano-domains
 - Core generation-dependent

Potential Applications

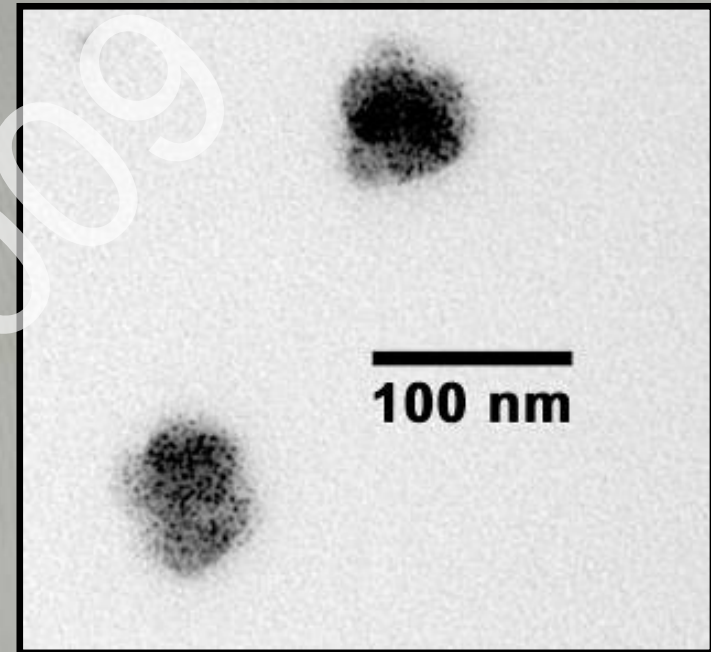
- The unusual behaviour of these templates could provide new physical properties and applications
 - Bimetallic loading
 - Alloy formation or discrete metal loading of separate compartments?
 - Catalysis
 - Optics
- Do the compartments form simultaneously or one at a time?

Loading Level & Time

G3 - 0.05 eq Au



G3 – 5 min, 0.5 eq Au



- Domains are time- or loading level-dependent
- All domains form simultaneously

Conclusions & Future Work

Conclusions

- *Intramolecular* self-assembly observed on this scale for the first time
- Nanodomain formation results from metal coordination
- Domains form in non-selective solvents
- Domains are stable, resistant to annealing or solvent changes
- Similar morphologies observed for different metals

Conclusions

- **Change in ratio of block copolymer components has limited influence on nano-domain morphology**
 - Morphology is mainly mediated by the core generation
- **Nanodomains appear to form simultaneously and are not strongly correlated to loading level or equilibration time**

Future Work

- Further characterization of templates required
- Relationships with block copolymer systems: Can the morphologies be predicted?
- Bimetallic loading and elemental mapping
- Reduction studies

Acknowledgements

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