

Block Copolymer Self-assembly: Exploitation of Hydrogen Bonding for Nanoparticle Morphology Control via Incorporation of Triazine-Based Comonomers by RAFT Polymerization

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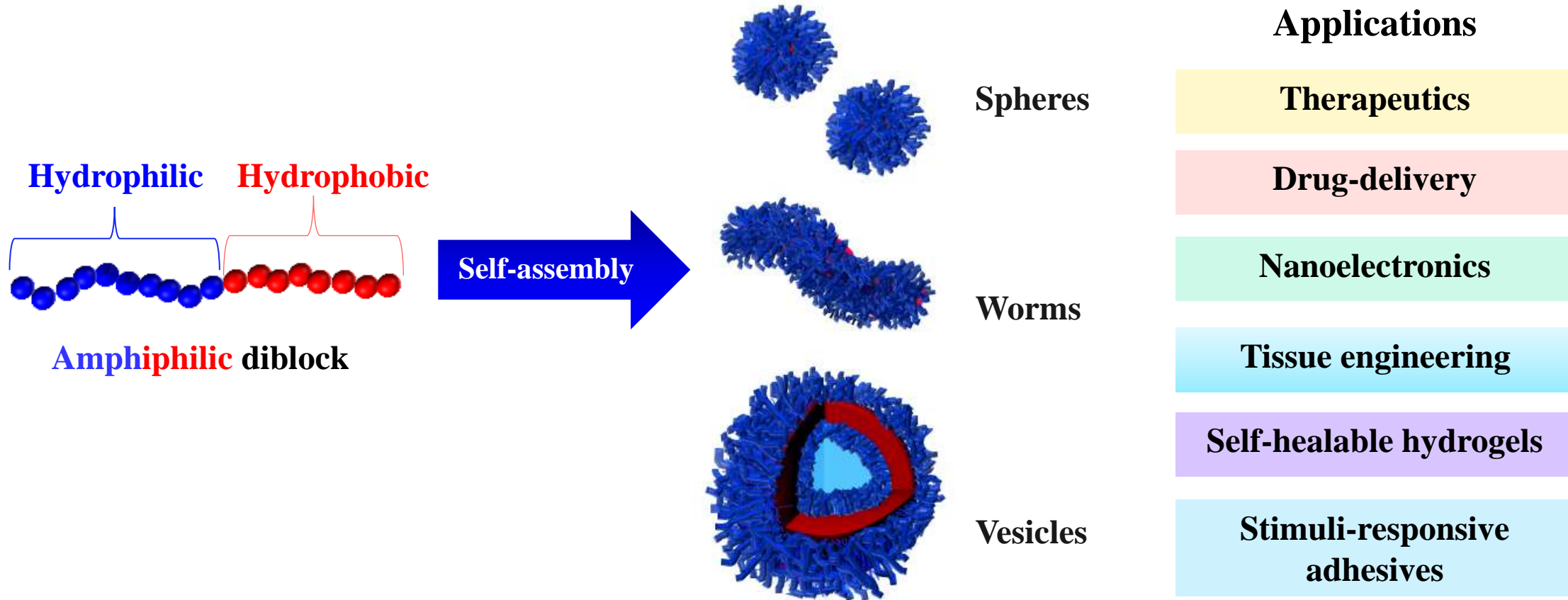
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Self-assembly of amphiphilic block copolymers



Driving force: Chemical incompatibility of one of the blocks with the continuous phase

(typically, aggregation occurs due to the insolubility of the hydrophobic block in water)

Incorporation of hydrogen bonding interactions

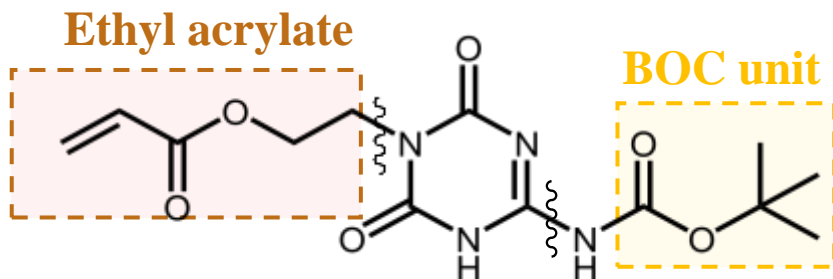
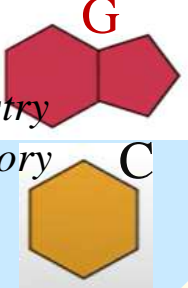



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A

G

C



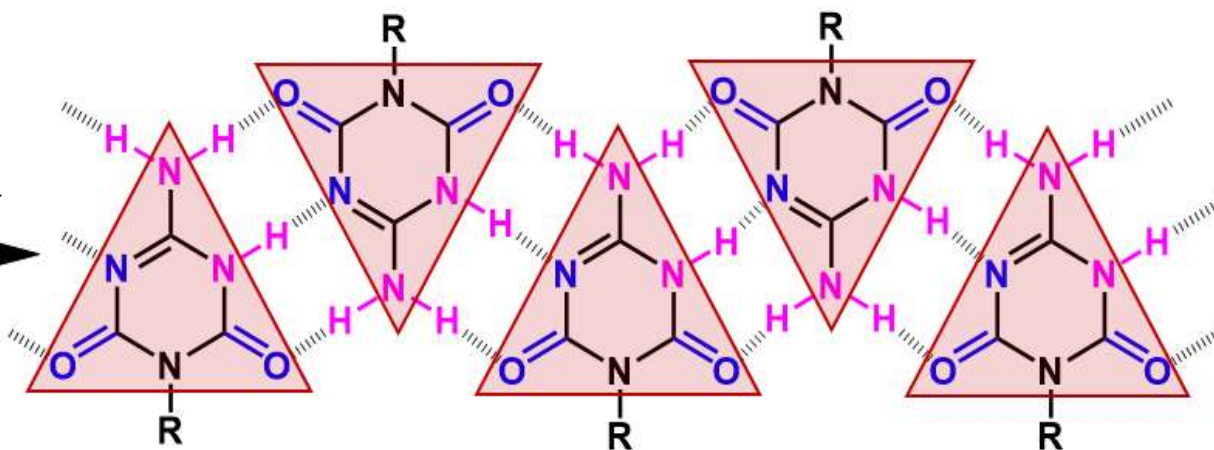
Triazine based Janus Guanine-Cytosine nucleobase

Hydrogen bonding interactions

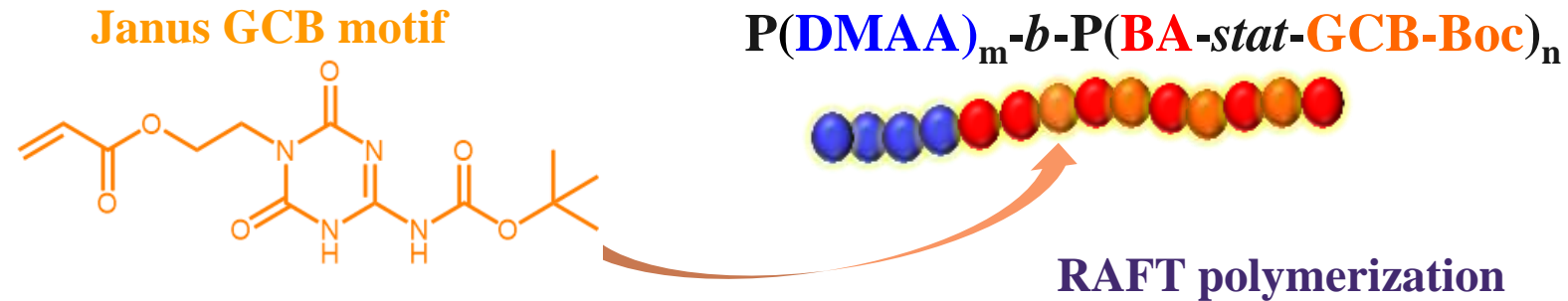
— H-bonding donor
— H-bonding acceptor

Hydrogen bonding interaction

- Dynamic and reversible nature
 - High fidelity
 - Molecular recognition
 - Smart and adaptive functionality
- Self-assembly



Strategy



DP of hydrophilic block (20, 40)

DP of hydrophobic block (40, 80, 100, 120, 140)

Variable amount of GCB content (0, 5, 10, 15 mol%)

DP of hydrophobic block, without GCB (40, 80, 100, 120, 140)

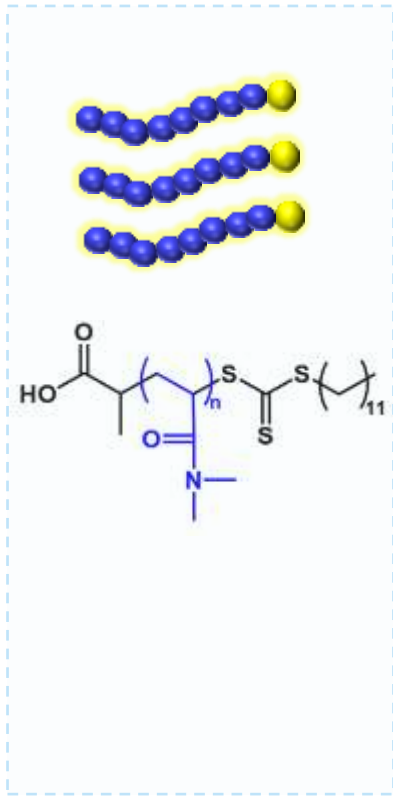
Effect of deprotection (Self-assembly of protected polymers)

Stimuli-responsive behavior

Strategy

Step 1

Hydrophilic
macroRAFT

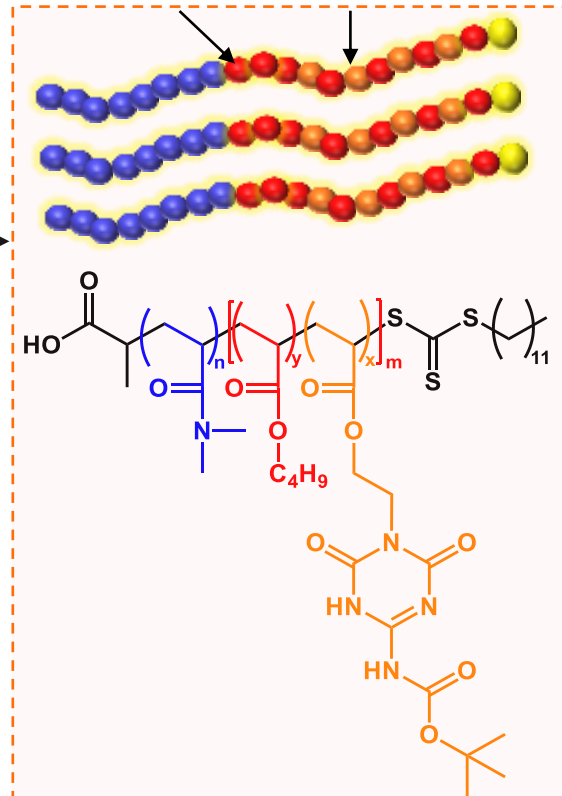


PDMAA

AIBN
DMF
70°C

Step 2

Chain extension with
BA and GCB-Boc

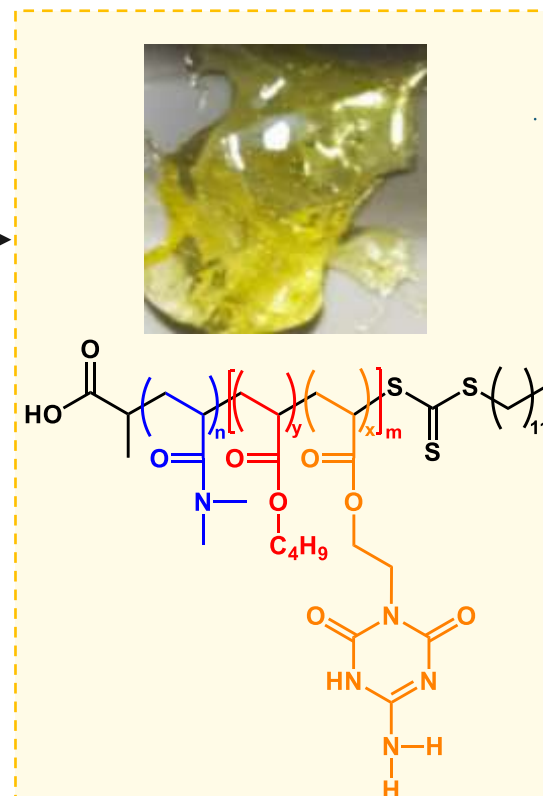


PDMAA_m-b-P(BA-stat-GCB-Boc)_n

TFA
DCM
0°C

Step 3

Boc deprotection

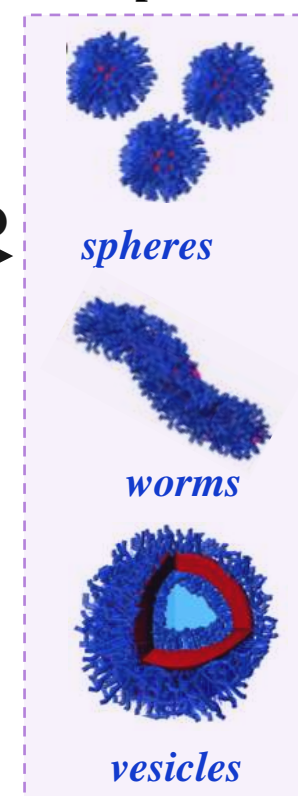


PDMAA_m-b-P(BA-stat-GCB)_n

DMSO
Water

Step 4

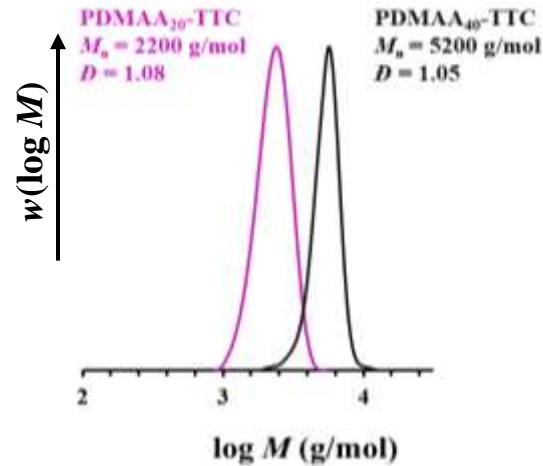
Self-assembled
nanoparticles



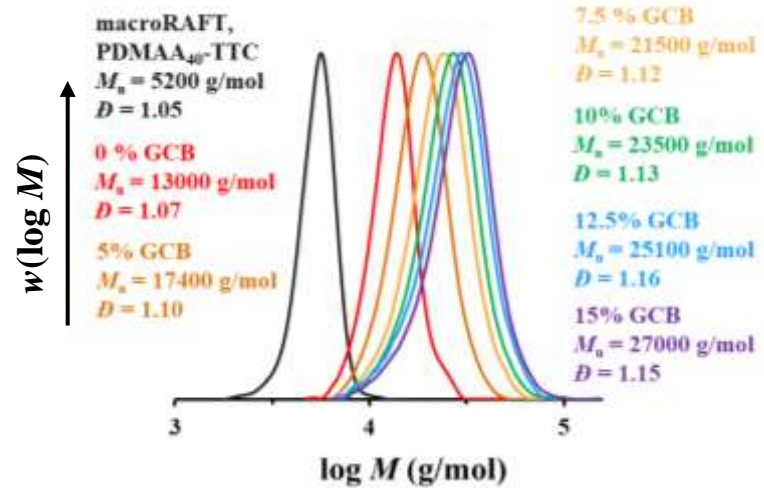
MWDs of macroRAFT and amphiphilic block copolymers

PDMAA_n macroRAFT

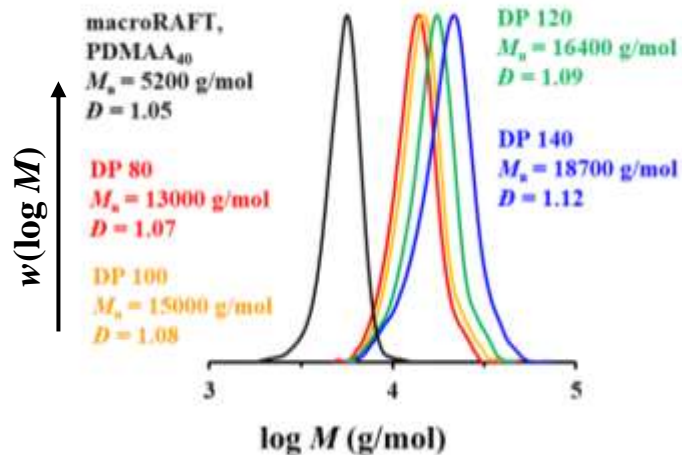
(a)



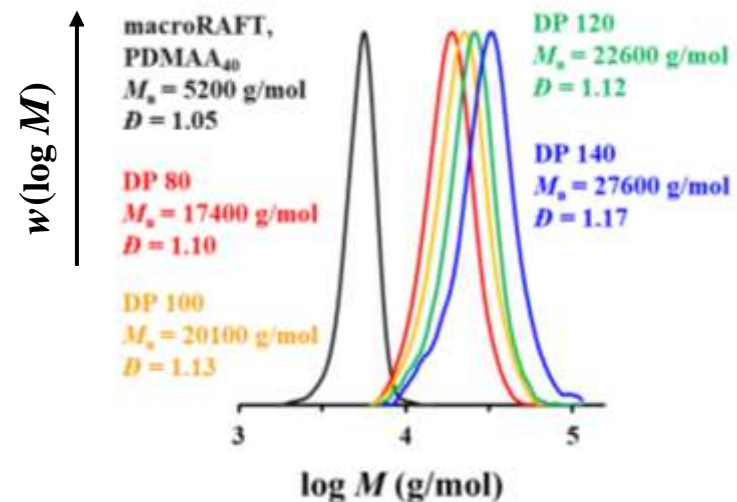
PDMAA₄₀-b-P[BA-stat-GCB-Boc(x%)]₈₀



PDMAA₄₀-b-PBA_m

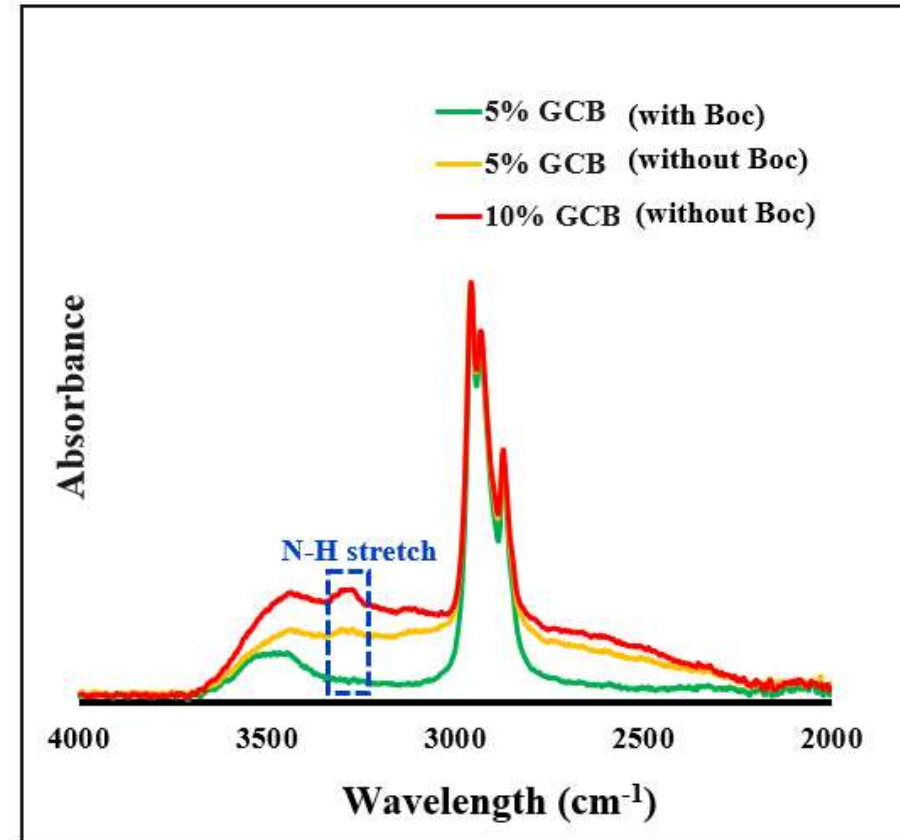
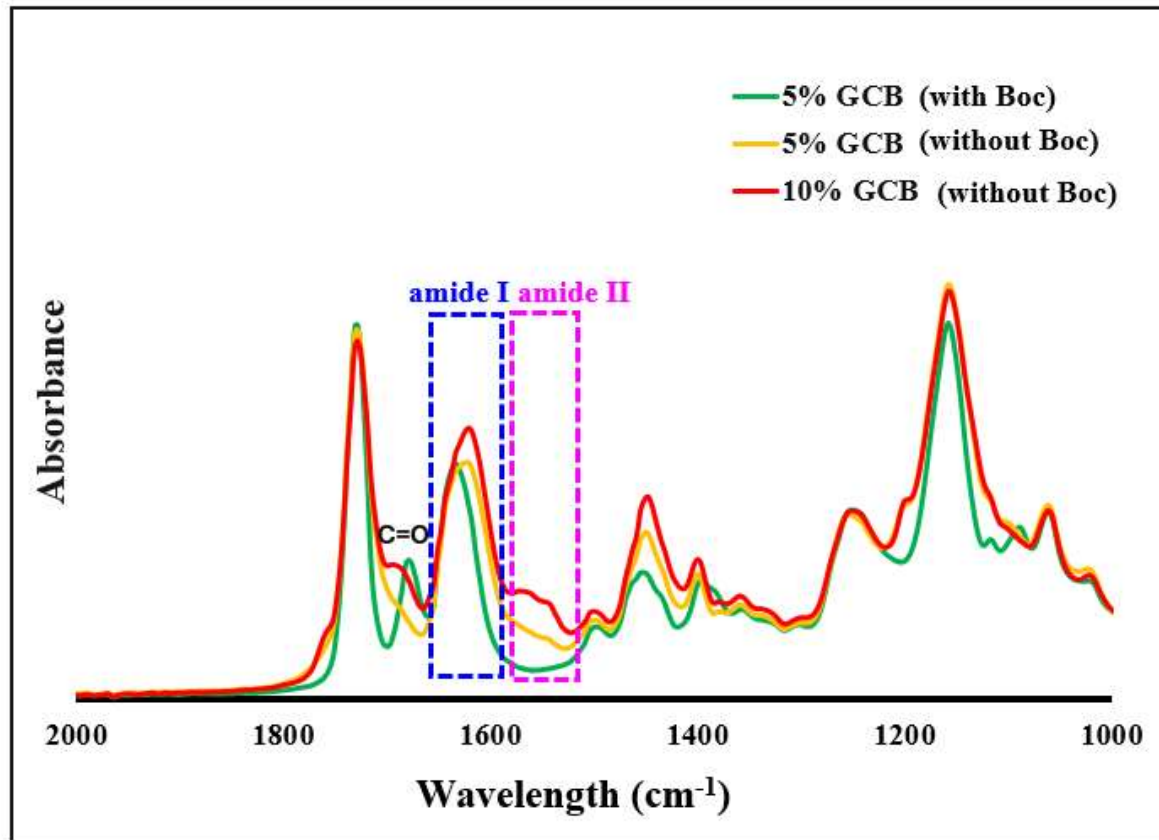


PDMAA₄₀-b-P[BA-stat-GCB-Boc(5%)]_m

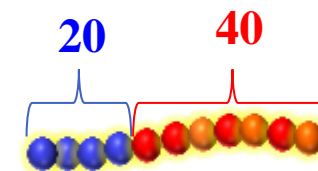
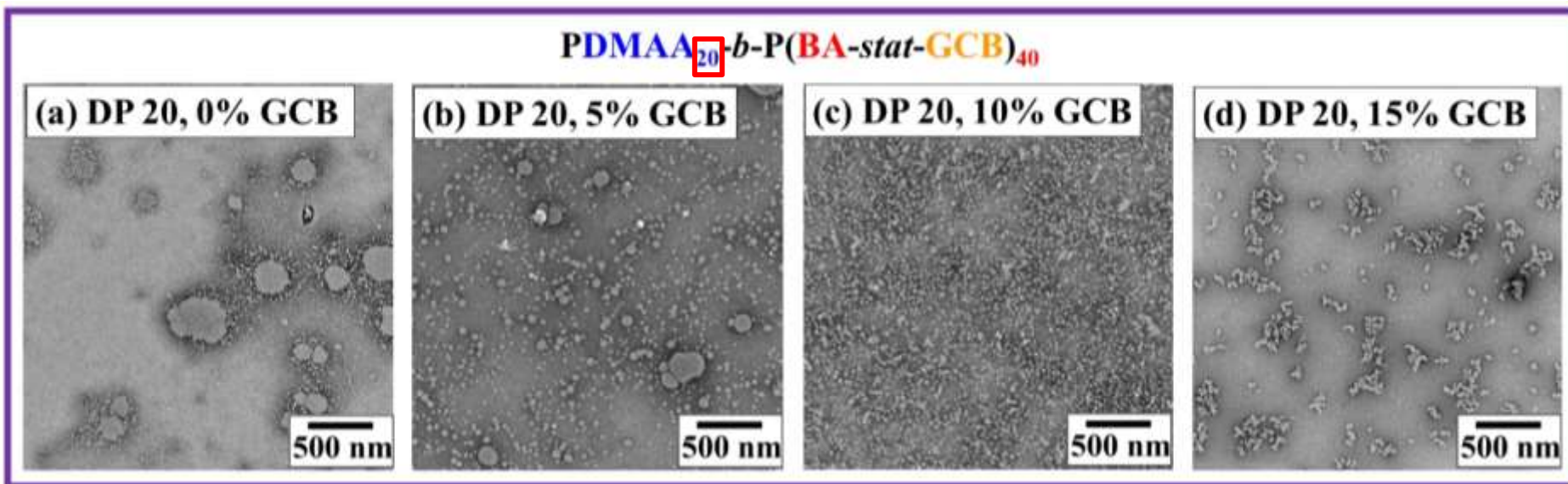


Confirmation of hydrogen bonding by FTIR spectroscopy

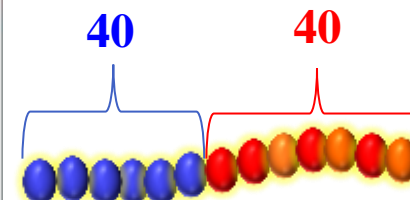
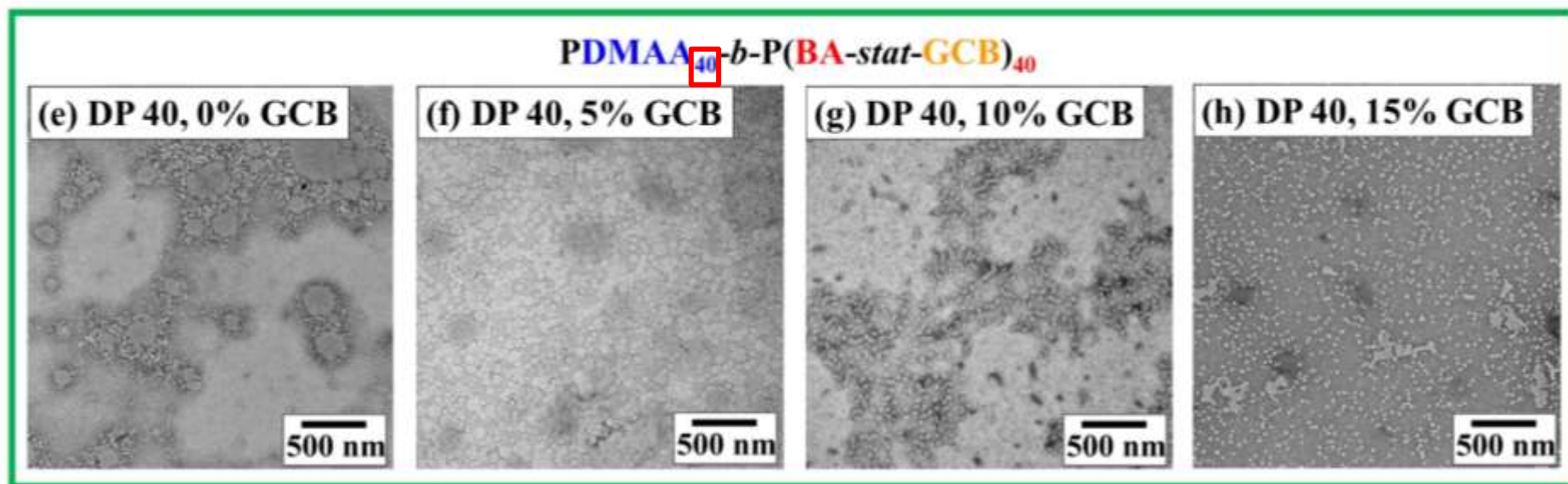
- PDMAA₄₀-*b*-P[BA-*stat*-(GCB-Boc(5%))]₈₀ in the solid state (green curve),
- PDMAA₄₀-*b*-P[BA-*stat*-GCB(5%)]₈₀ (yellow curve) and
- PDMAA₄₀-*b*-P[BA-*stat*-GCB(10%)]₈₀ (red curve) in the amide region (Left) and N-H stretching region(right).



Morphology of self-assembled polymers: Effect of GCB content

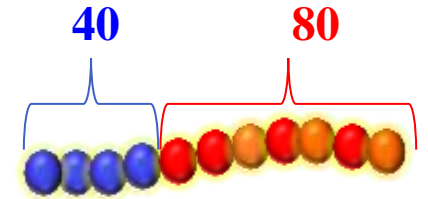
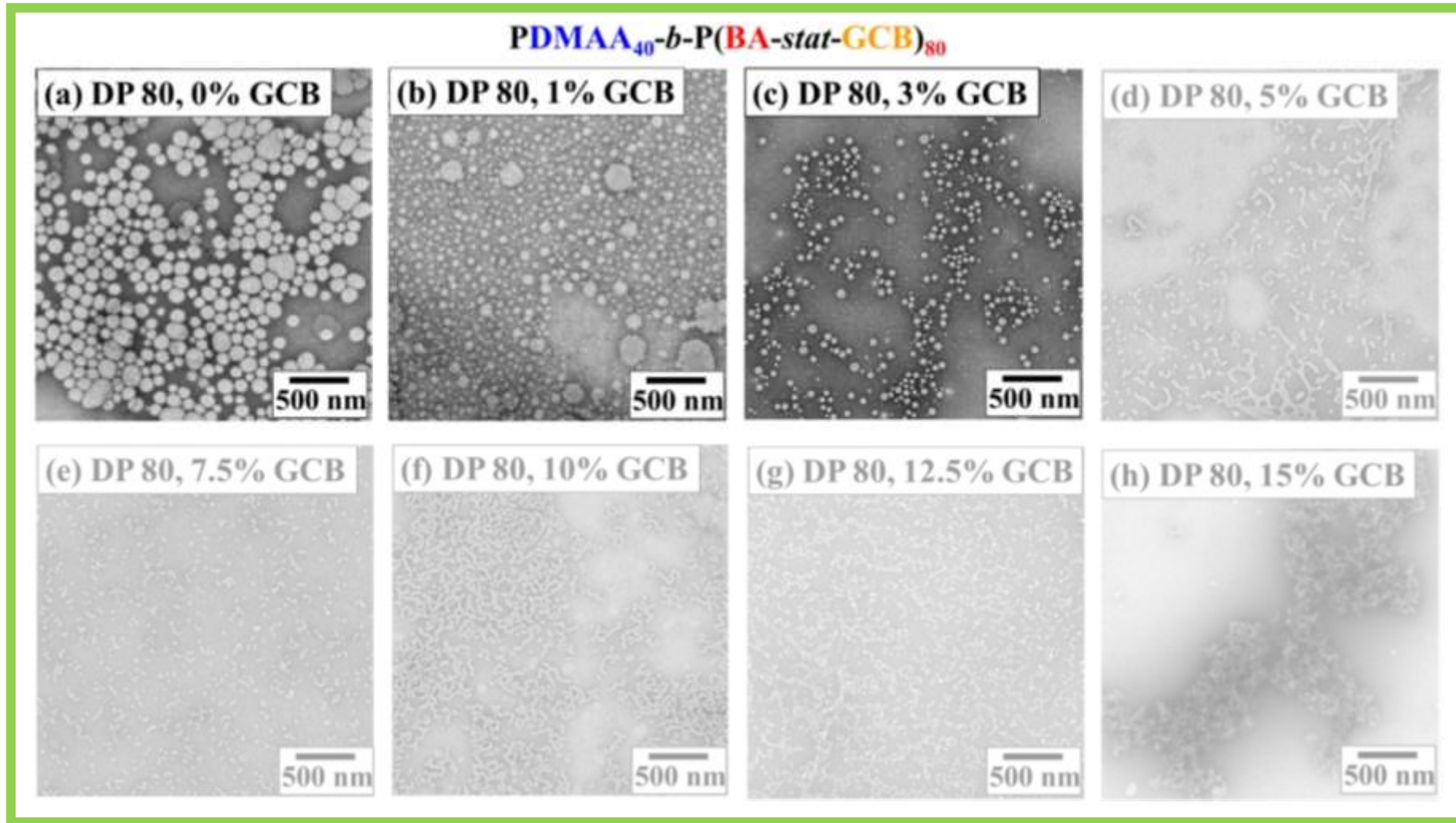


- (a) Large aggregates
- (b) Aggregates+ spheres
- (c) Spheres
- (d) Spheres+ nuggets



- (e) Aggregates
- (f) Aggregates
- (g) Spheres+ nuggets
- (h) Spheres+ worms

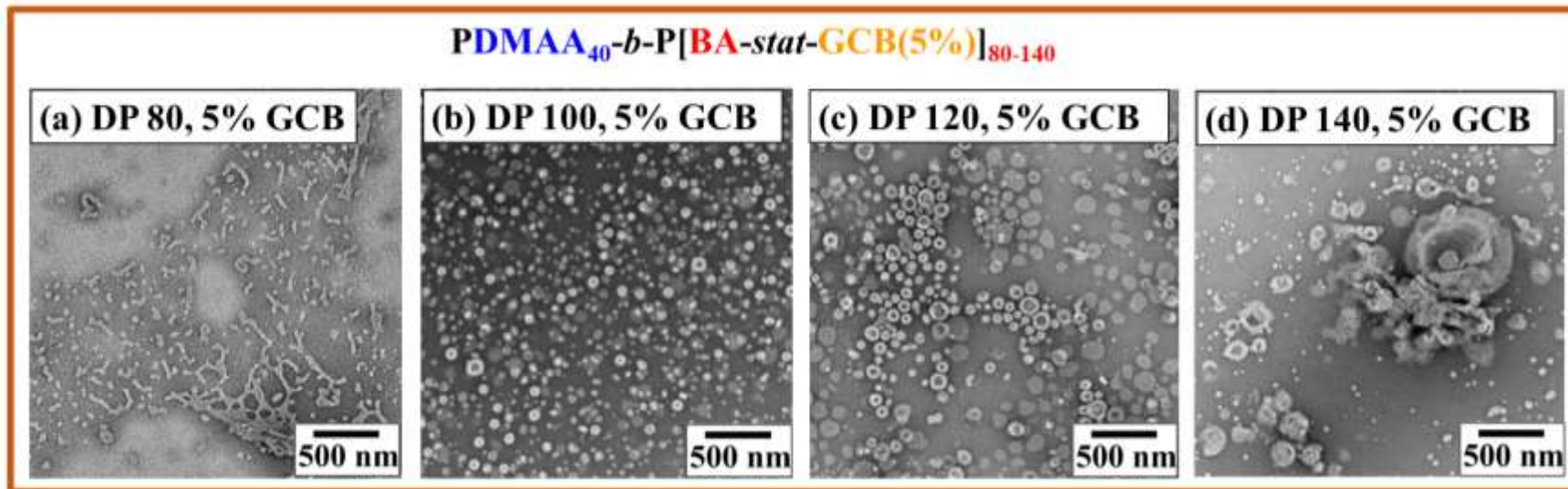
Morphology of self-assembled polymers: effect of GCB content



- (a) Aggregates
- (b) Aggregates + spheres
- (c) Spheres
- (d) Spheres + worms
- (e) Spheres + worms
- (f) Worms
- (g) Branched worms
- (h) Branched worms

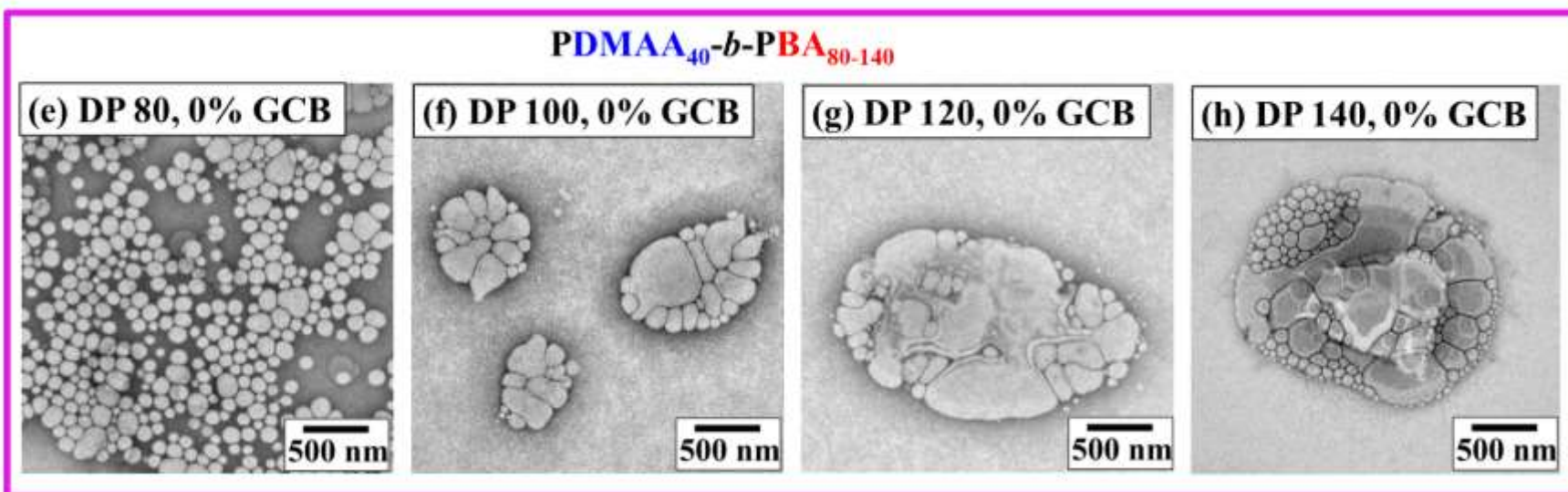
- Initial increase in GCB leads to reduction in particle size; formation of spheres
- Further increasing GCB content results in transition towards higher order morphologies

Effect of hydrophobic block length on morphology



Presence of GCB

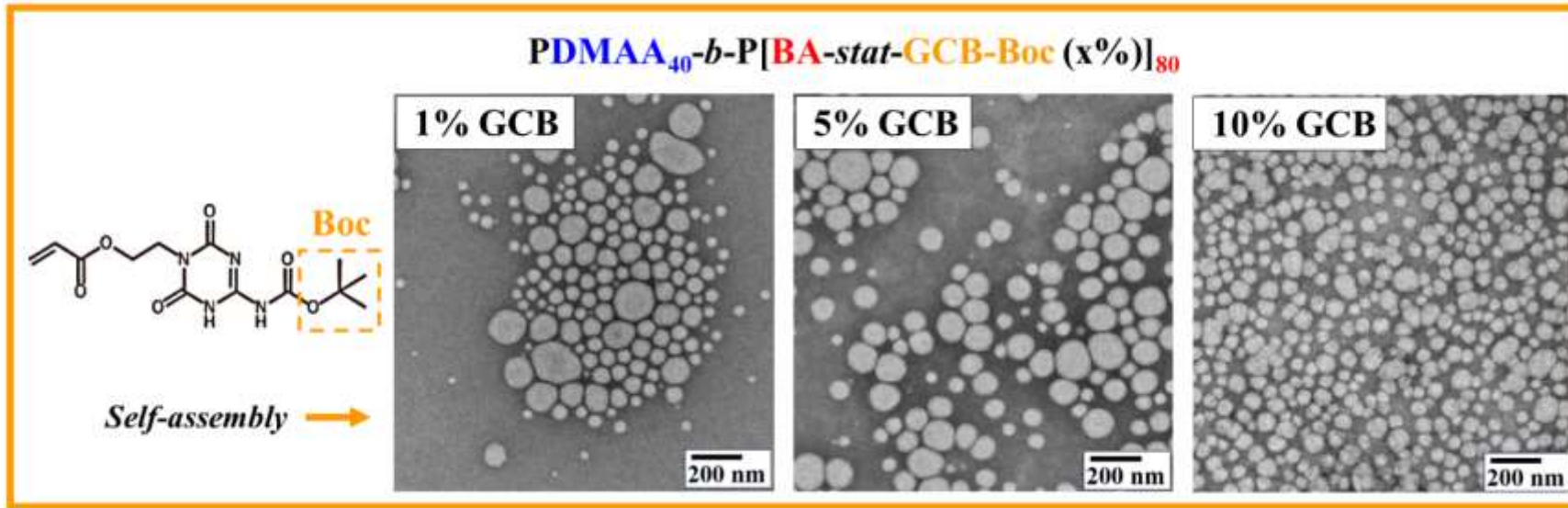
- (a) Worms
- (b) Small vesicles
- (c) Large vesicles
- (d) Multi-layered vesicle



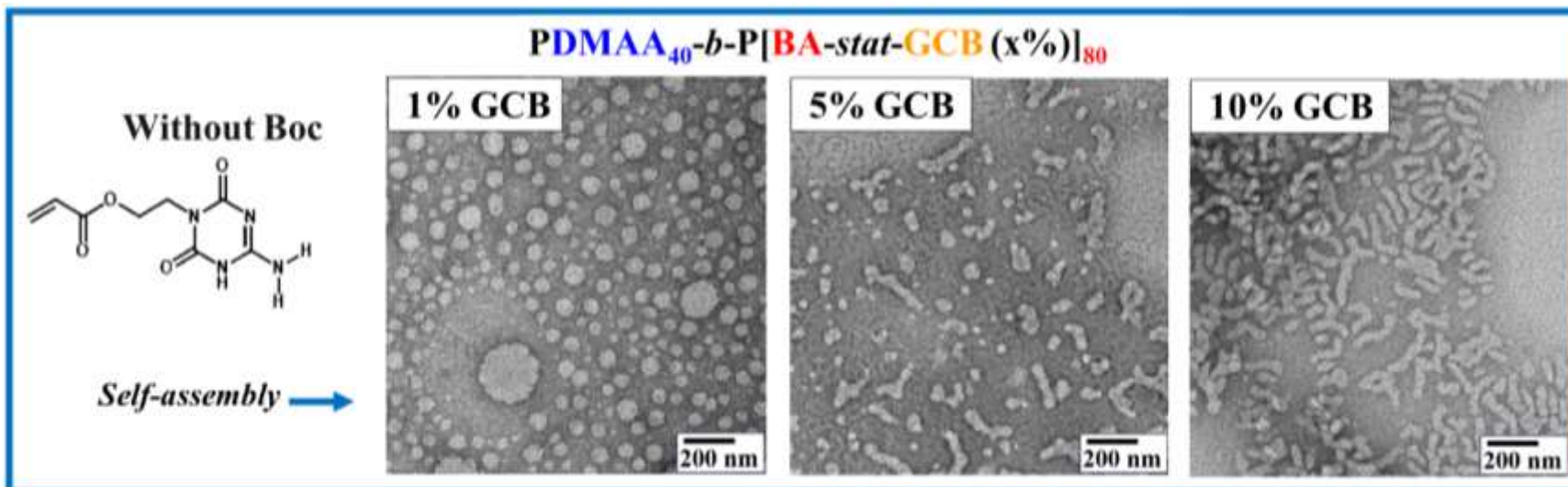
Absence of GCB

- Unstable system
- Aggregate formation
- Due to low T_g of polymers

Effect of Boc deprotection on morphology



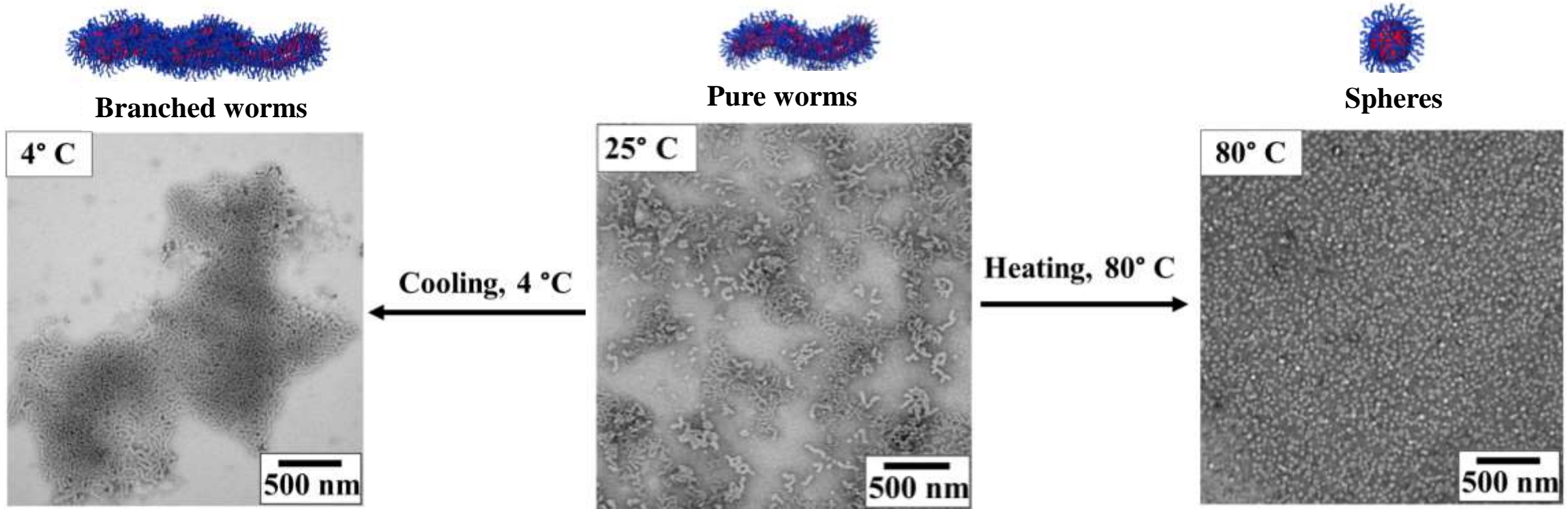
Spherical morphologies



Higher-order morphology transition

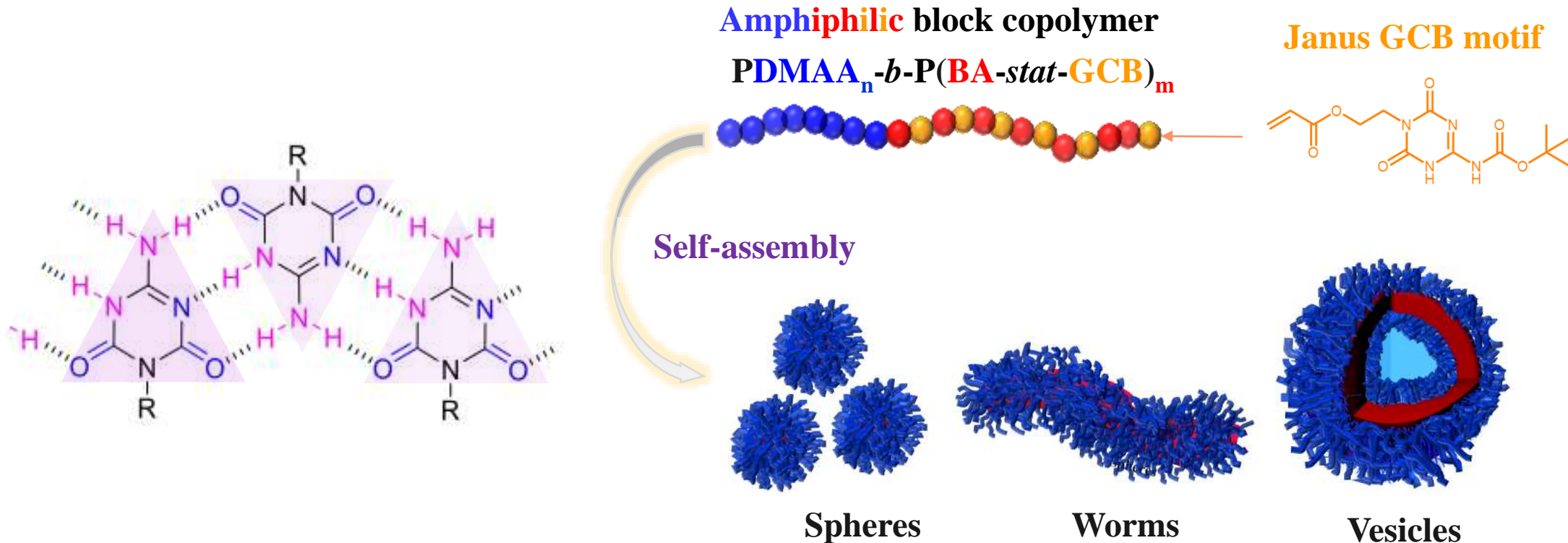
Stimuli-responsive behavior of polymeric nanoparticles

Polymer: PDMAA₄₀-*b*-P[BA-*stat*-GCB(10%)]₈₀



- Temperature ↑ thermal energy leads to the breakage of hydrogen bonds, allowing chains to rearrange into smaller particles
- Temperature ↓ hydrogen bonds are reformed with the formation of long and branched worms

Summary



- Incorporation of low mole fraction (15 mol%) nucleobase containing monomer
- Highly directional complementary nucleobase hydrogen bonding interactions generated by GCB monomer
- Combined effect of hydrogen bonding and solvent immiscibility drives the self-assembly to higher-order morphology
- Stimuli-responsive behavior makes it potential candidate for emerging applications

Acknowledgments

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Dr. Fumi Ishizuka

Collaborators: Dharmendra Singh

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