Waterborne Multi-lobed Particle Morphology for Directed-Assembly Towards 3D Hierarchical Structures

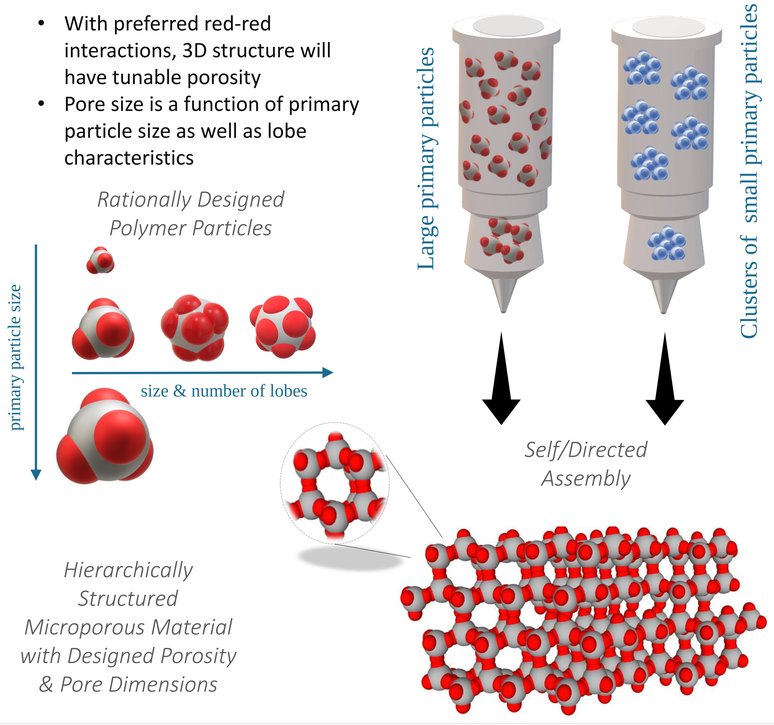
Yung-Chun Lin[1], John Tsavalas[1,2]

(1) Department of Chemistry and (2) Materials Science Program, University of New Hampshire, Durham, NH

Introduction

Particle based building blocks are ubiquitous in applications in material science [1] and biomedical engineering [2]. Performance of such materials is highly related to the particle morphology. Our idea behind microparticles (and microgels) as building blocks for scaffolds for regenerative medicine has been proposed. We introduced a two-stage seeded emulsion polymerization method to create multi-lobed composite polymer nanoparticles by restricting second-stage polymer chain diffusion to the surface of seed particles[3]. Here, we targeted both nano- and micro-size particles suited for tissue engineering scaffolds. Different techniques are also explored for self-assembly and direct-write 3D printing with latex.

- With preferred red-red interactions, 3D structure will have tunable porosity
- Pore size is a function of primary particle size as well as lobe characteristics



Goal

Our goal is to produce porous 3D scaffolds for tissue engineering through rational design of particles with tunable assembly properties amenable to additive manufacturing technique.

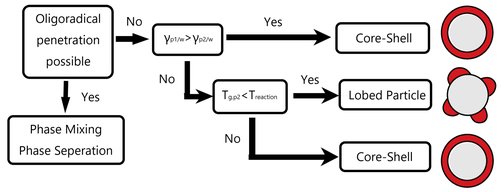
Experimental

Emulsion Polymerization

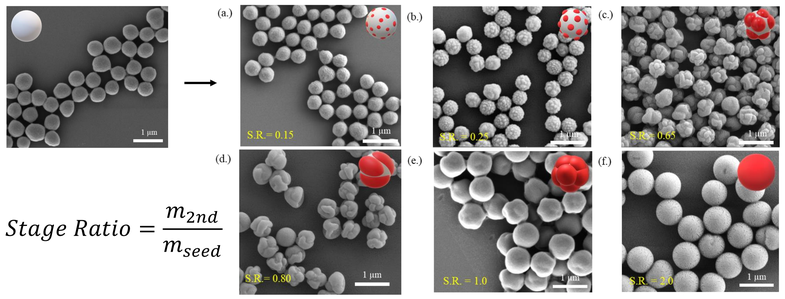
- Initiator: Potassium persulfate
- Surfactant: Sodium dodecyl sulfate
- Monomer: 1st stage → Methyl methacrylate
  2nd stage → Styrene, Hexyl methacrylate

Experimental Results

Asymmetric Pre-Structured Particles

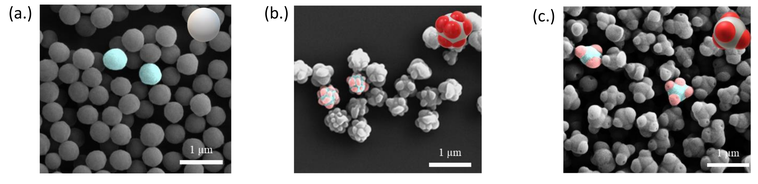


Seeded Emulsion Polymerization route to Multi-Lobed Particles: key to this procedure is to have a glassy polar seed particle (e.g. methyl methacrylate), and a rubbery (Tg lower than reaction temp) hydrophobic second stage (e.g. styrene-co-hexyl methacrylate) to enable surface diffusion (red)



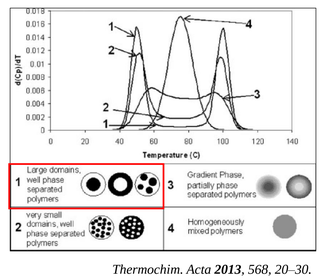
$$Stage\ Ratio = \frac{m_{2nd}}{m_{seed}}$$

*Scanning electron microscopy of Multi-Lobed Particles grown from **480 nm** seed sizes by seeded emulsion polymerization to show various morphologies*

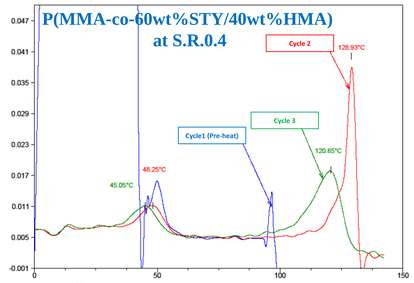


False colored SEM images of (a) poly(methyl methacrylate) (b) poly(methyl methacrylate-co-Styrene/Hexyl methacrylate (c) poly(methyl methacrylate-co-Styrene/Hexyl methacrylate after annealing

Thermal Profile of Composite particles



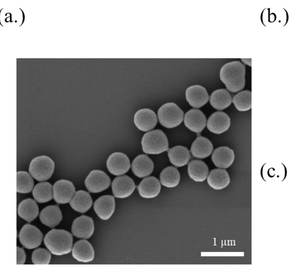
*Thermochim. Acta **2013**, 568, 20–30.*



Differentiation Scanning calorimetry data

Characterization Pre-structured Particles

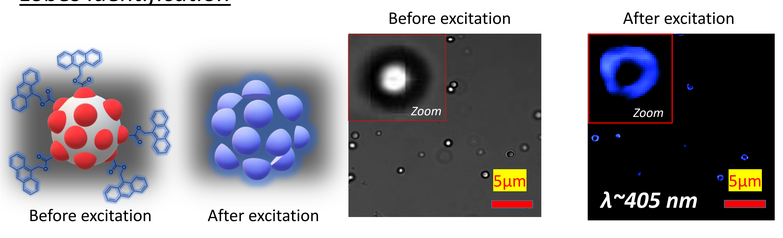
Particle Size Analysis



	Mean	25%	Median	75%	Max	Std. Dev
By Number	521.7	517.7	524.7	535.4	524.7	19.2
By Area	523.1	517.7	524.7	535.4	524.7	18
By Weight	523.7	517.7	528.3	535.4	524.7	17.5

Seed particle size analyzed by capillary hydrodynamics fractionation (CHDF2000)

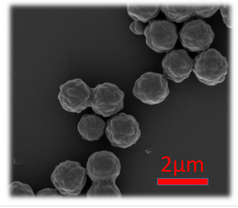
Lobes identification



*Confocal microscopy of Multi-Lobed Particles grown from **1200 nm** seed sizes by seeded emulsion polymerization to show 2nd stage polymer by using fluorescence*

Ongoing & Next Steps

- Induce aggregation/assembly of multilobes
- Development of robust 3D printing method
- Surface functionalization of multi-lobed particles
- Pre-coagulation to large-clusters for self-assembly resulting in large pores
- Multilobed particles in micro-size



References

[1] Tripathi, A. K.; Tsavalas, J. G.; Sundberg, D. C. Quantitative measurements of the extent of phase separation during and after polymerization in polymer composites using DSC *Thermochim. Acta* **2013**, 568, 20–30

[2] Bracaglia, L.G., B.T. Smith, E. Watson, N. Arumugasaamy, A.G. Mikos, and J.P. Fisher. 3D printing for the design and fabrication of polymer-based gradient scaffolds. *Acta Biomaterialia* **2017**, 56: p. 3-13.

[3] Blenner, D, Stubbs, J.M, Sundberg, D.C., Multi-lobed composite polymer nanoparticles prepared by conventional emulsion polymerization, *Polymer **2017*** 114, 2017 54-63

Acknowledgements

This research is supported by National Science Foundation EPSCoR award #1757371, NH BioMade

Other Collaborators on this research include:

- **UNH**: Erik Berda (Chem), Harish Vashisth (ChE) , Kyung Jae Jeong (ChE)
- **Dartmouth**: Chenfeng Ke (Chem)