Science Symposium, ISS Inc. 61-62

Advanced Colloids Experiment (Temperature controlled) – ACE-T5

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Presented by:

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September 2019

New Bijel Chemistries for Long-Duration Microgravity and Ground-Based Experiments

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Department of Chemical and Biomolecular Engineering

NASA Research Opportunities in Complex Fluids
and Macromolecular Biophysics
80NSSC18K1554

Outline

- **Science Team**
- **Science Background, Hypothesis, and Objectives**
  - Introduction to bijels
  - Unresolved scientific questions
  - Need for new chemistries
  - Importance of long-duration microgravity
- **Earth Benefits and Applications**
  - Applications in energy materials
  - Applications in tissue engineering and biomaterials
- **Ongoing Ground-Based Experiments**

Science Team

Ali Mohraz (Principal Investigator)

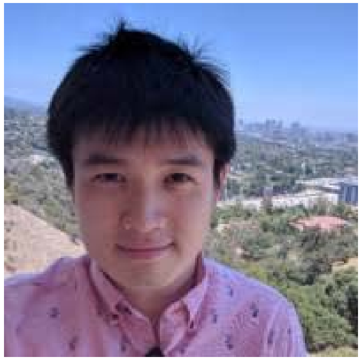
Associate Professor of Chemical and Biomolecular Engineering

University of California, Irvine

Herman Ching (Graduate Student Researcher)

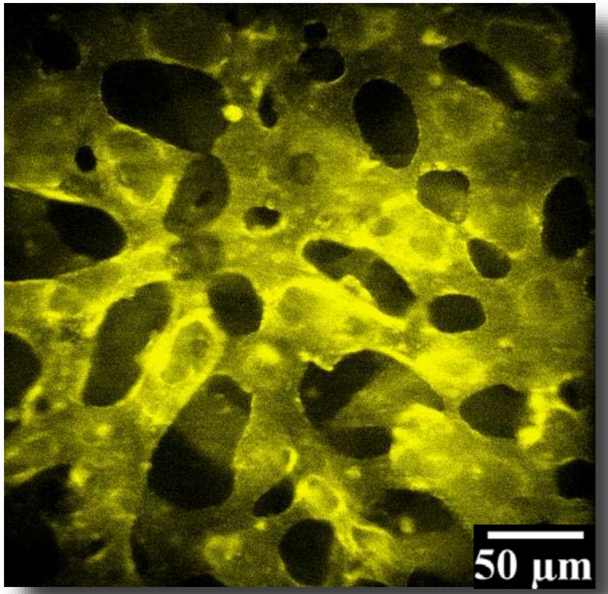
PhD Student in Chemical and Biochemical Engineering

University of California, Irvine



Abstract

Bijels (bicontinuous interfacially jammed emulsion gels) were discovered in 2007 at the University of Edinburgh. These materials feature a tubular, bicontinuous arrangement of two fluid phases separated by a monolayer of jammed colloidal particles at the interface.

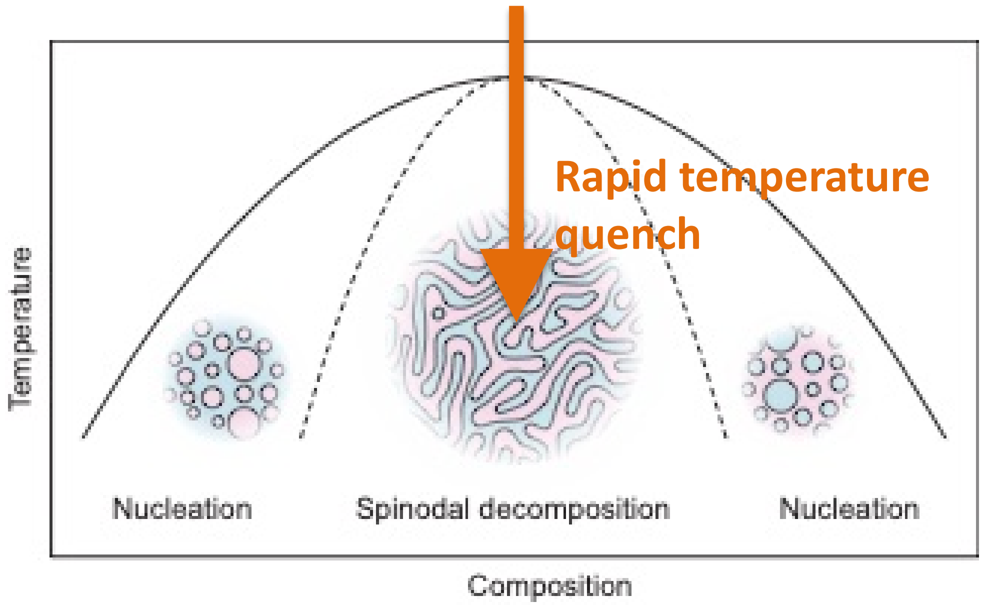


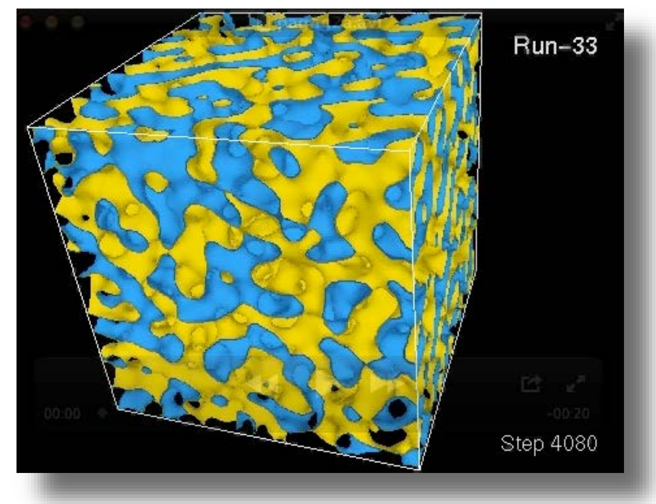
Because of their unique morphological characteristics, bijels hold significant promise as next-generation materials for energy and biotechnology applications. But in order to fully realize their potential, their physics and mechanical properties must be better understood.

The mechanical properties and stability of bijels is mediated by an interplay between interfacial forces that impart elasticity to the system, and external stresses. Unfortunately, the interfacial forces are inherently coupled with density differences and cannot be studied systematically in the presence of gravity.

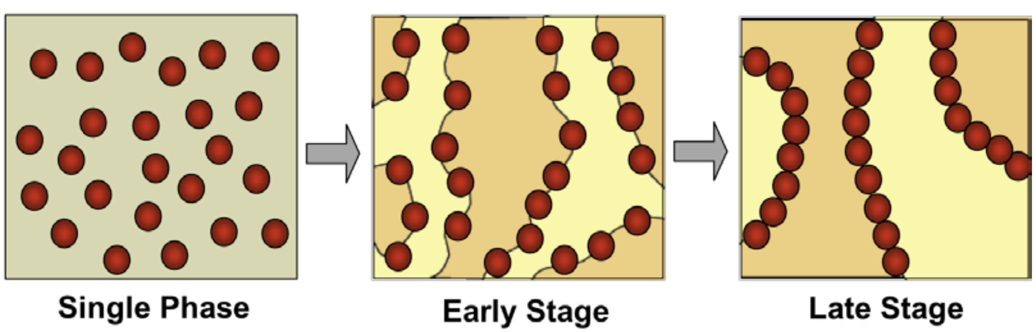
Bicontinuous Interfacially Jammed Emulsion Gels

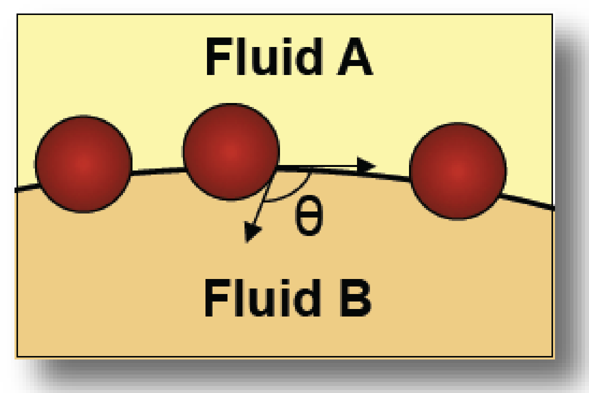
Spinodal Decomposition Arrested by Particle Jamming at the Interface





I. Pagonabarraga et al.
New J. Phys. (2001)

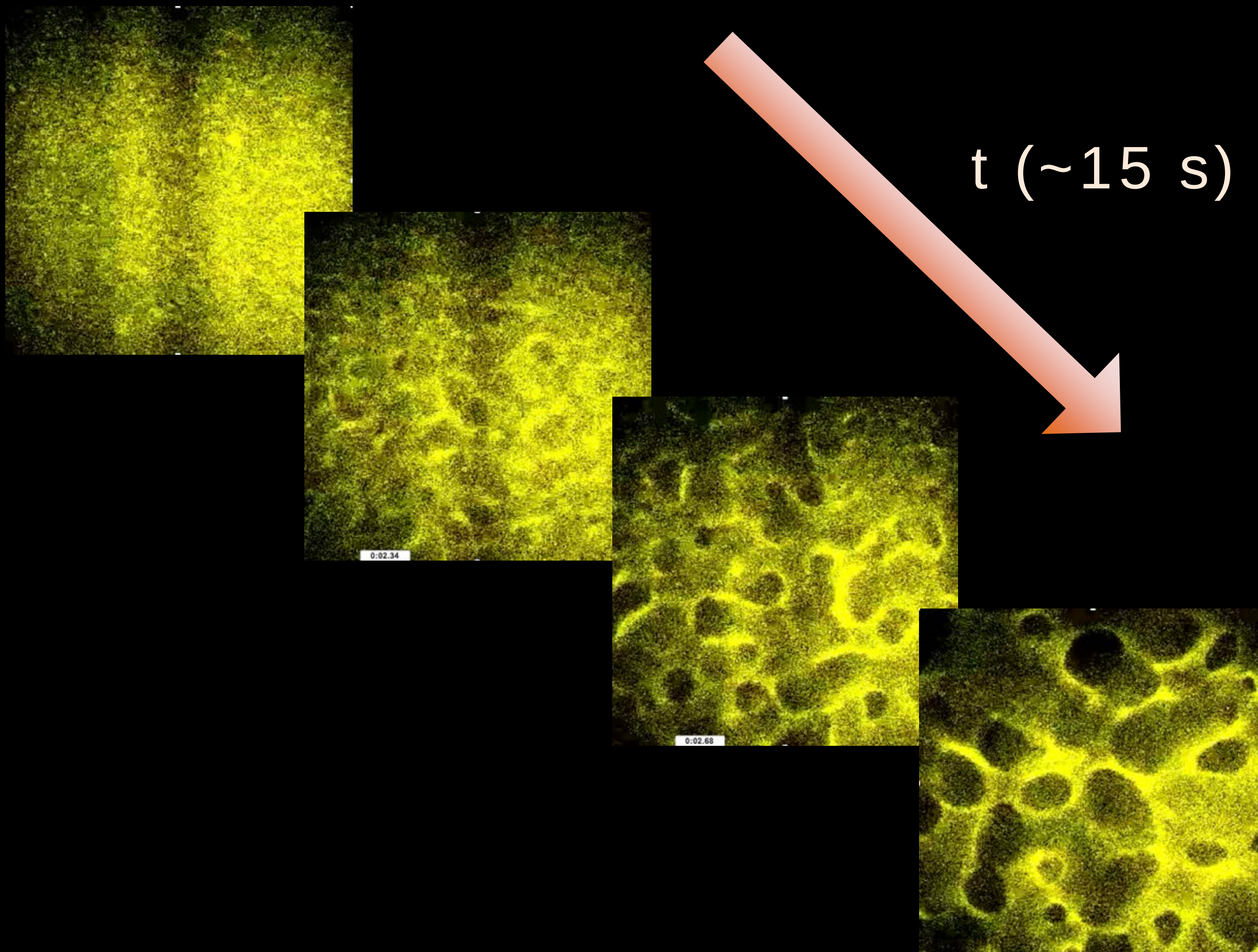




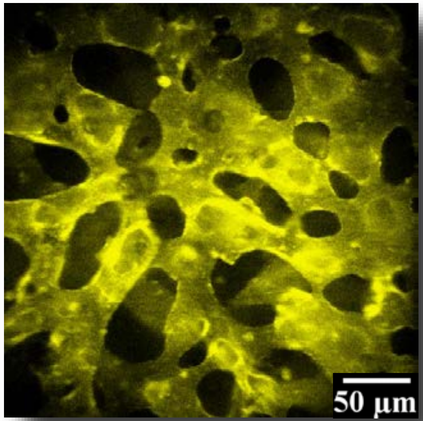
K. Stratford et al, *Science* (2005)
A. Herzig et al, *Nature Materials* (2007)

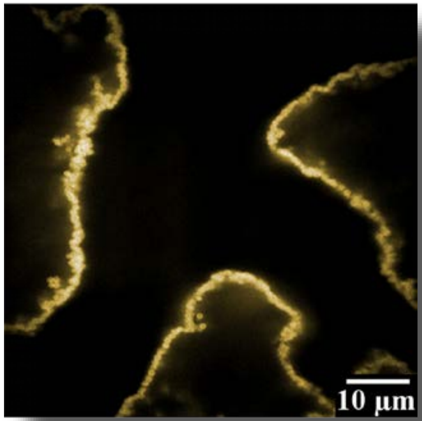
$$\Delta G = \pi r^2 \gamma \left(1 - \left|\cos\theta\right|\right)^2 \sim 10^4 kT$$

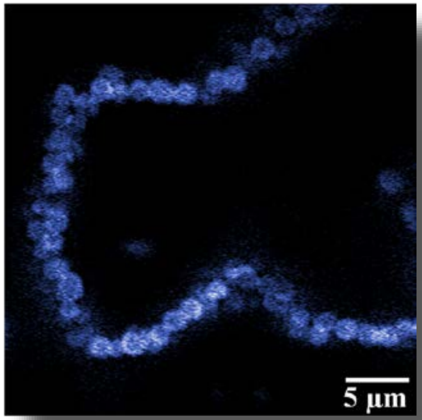
Bijel Formation (Confocal Video)



Bijel Morphology



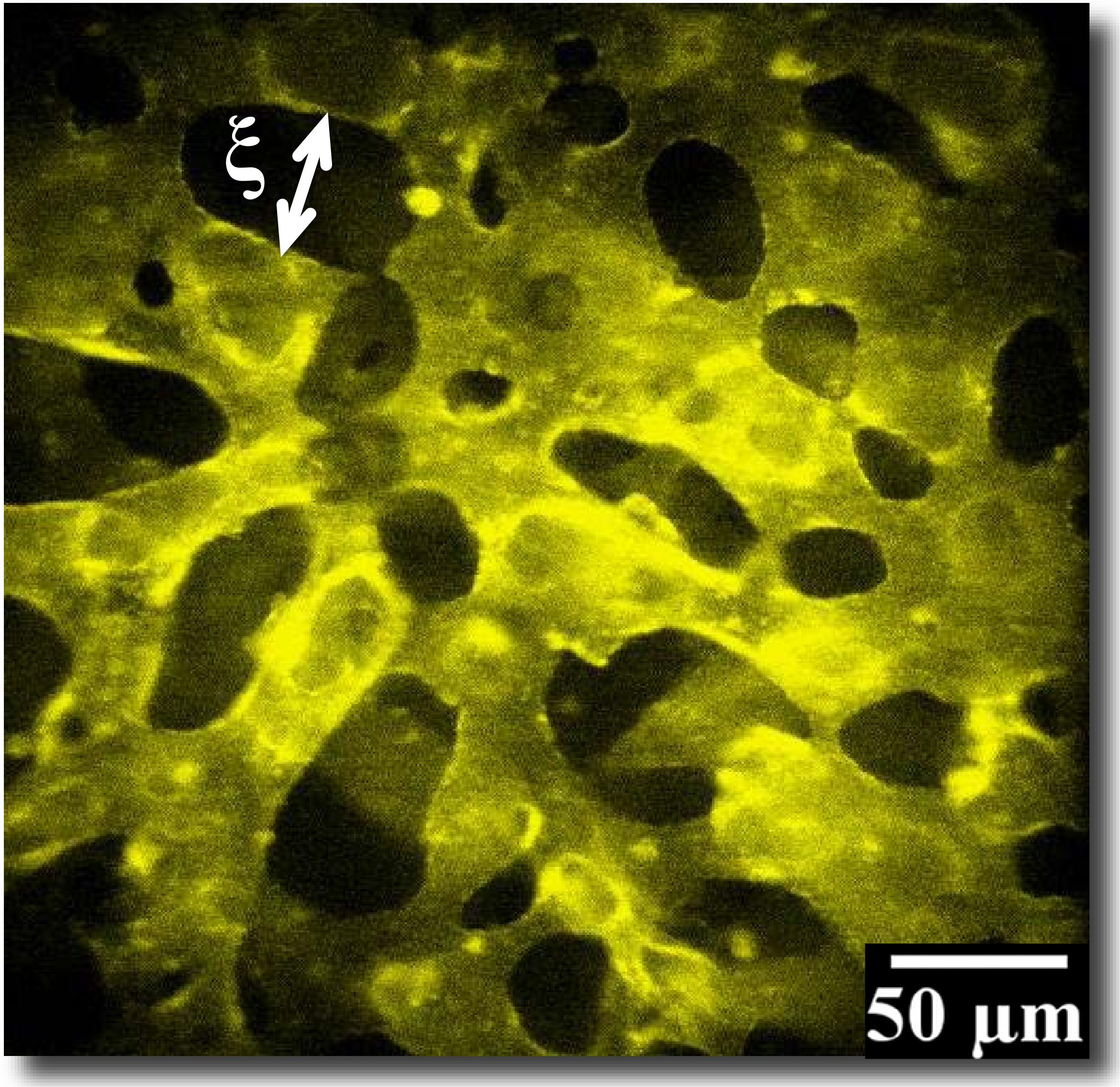




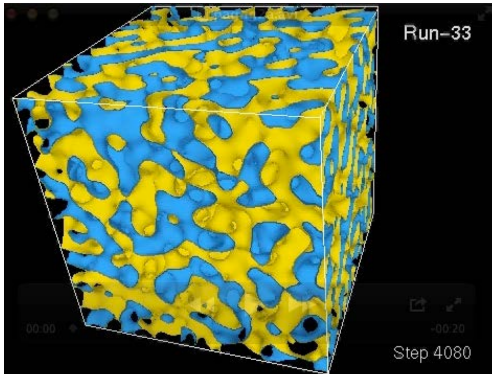
Magnification

Bicontinuous emulsion mechanically stabilized by a jammed particle monolayer in macroscopic (several mm) samples

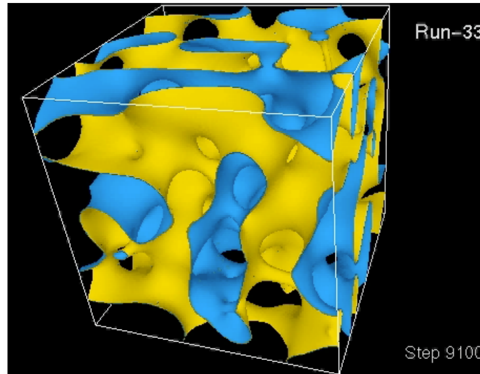
Unique Opportunity for Materials Synthesis



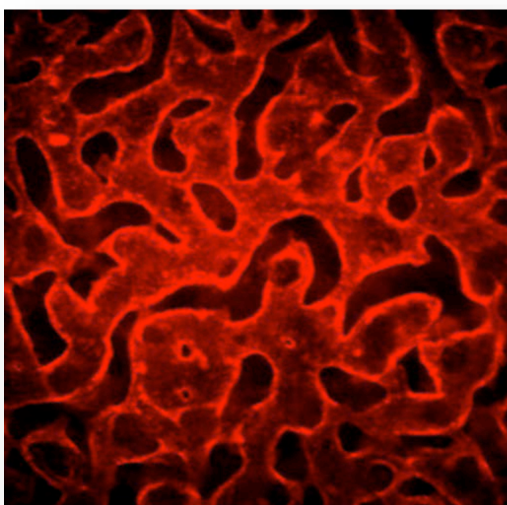
Control of Domain Size

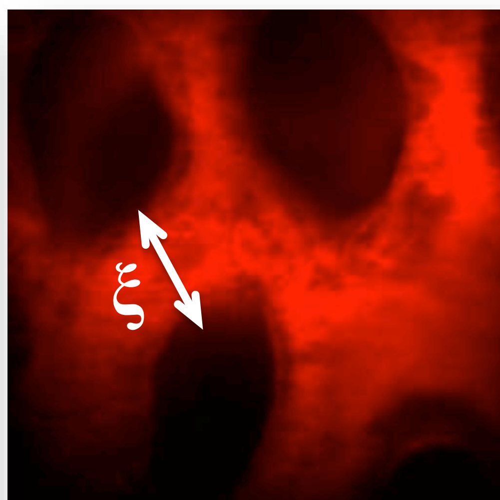


Early Stage

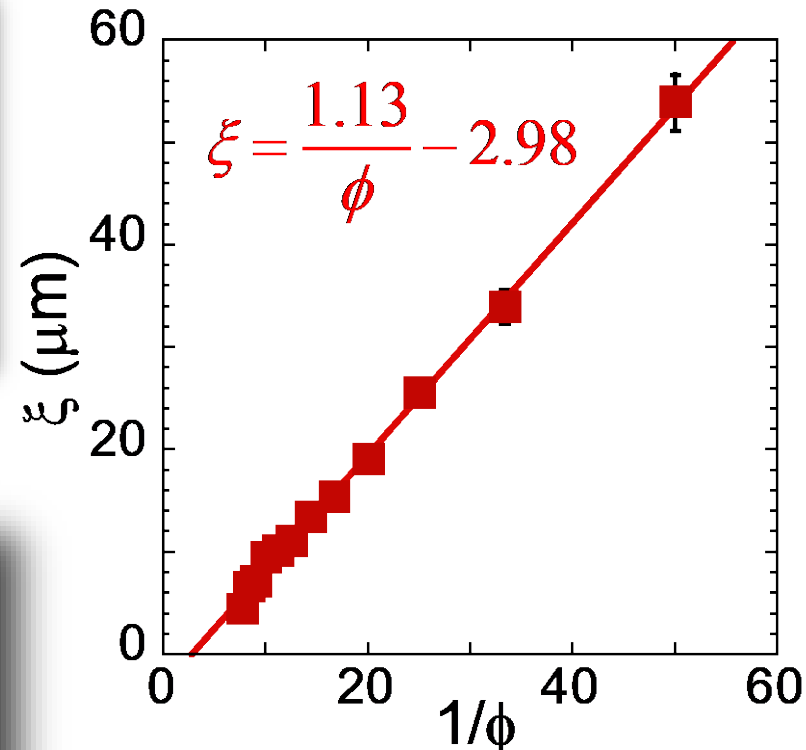


Late Stage



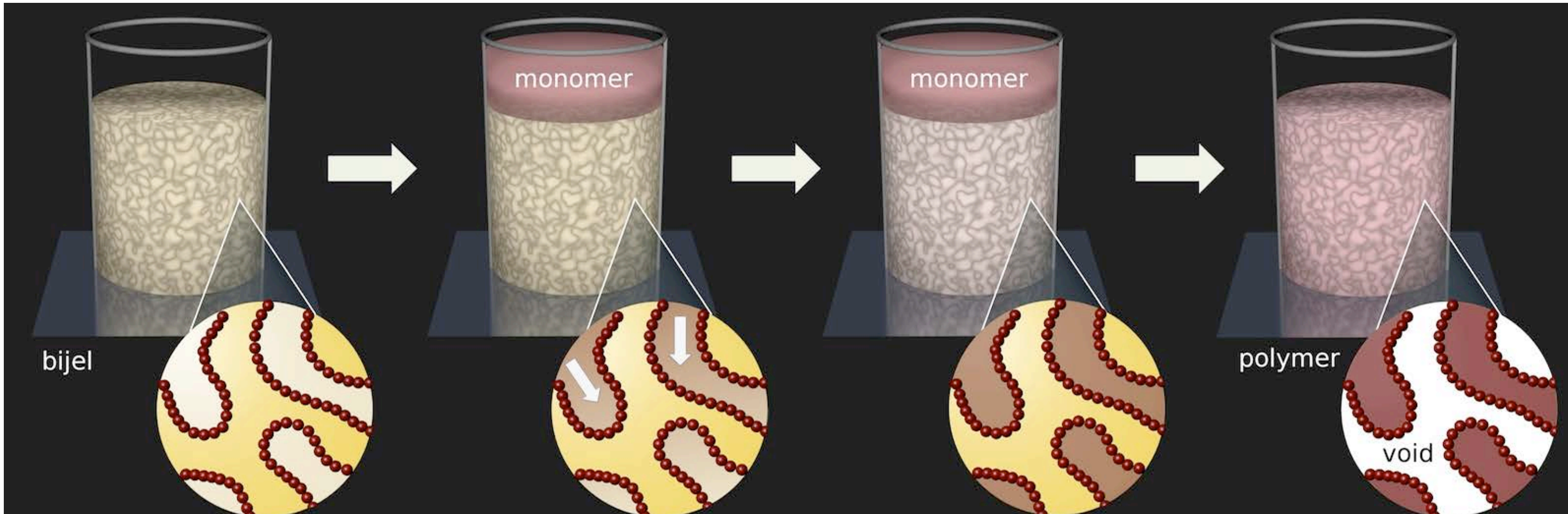


Decreasing ϕ

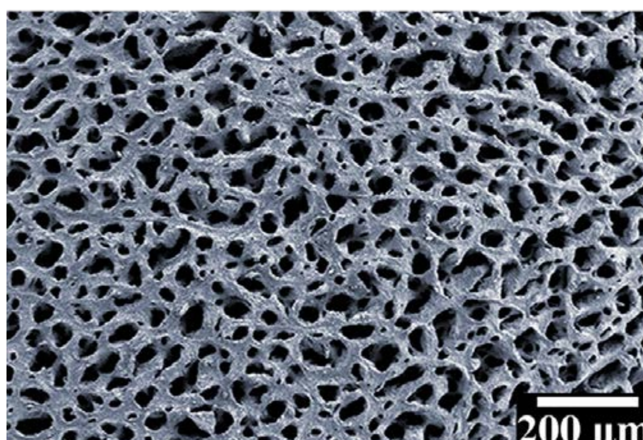


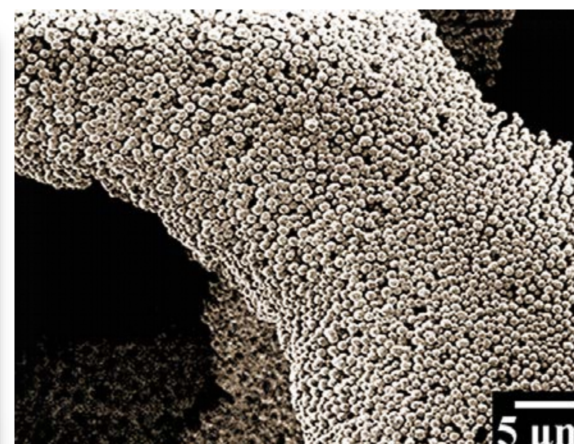
For monolayer coverage, $\xi \sim \frac{1}{\phi}$

Bijel Processing Method Pioneered at UC Irvine



Monomer: 1,6 hexanediol diacrylate; polyethyleneglycol diacrylate, and more
Photoinitiator: Darocur 1173



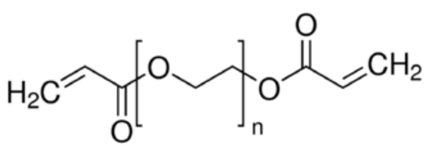


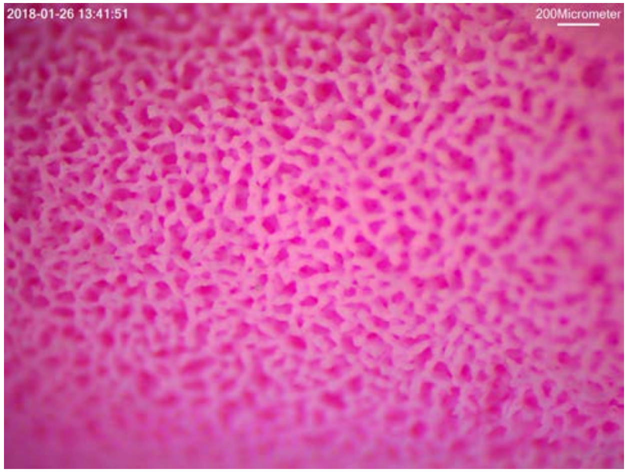
Magnification

Lee and Mohraz, *Advanced Materials* (2010

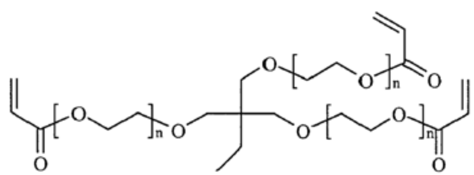
Biocompatible Bijel-Templated Sponges

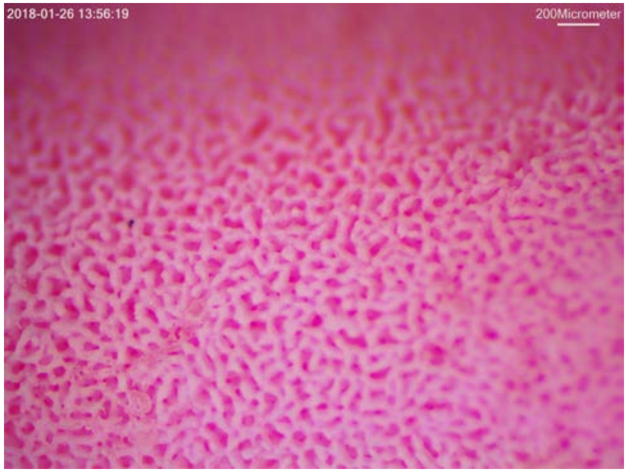
(PEGDA, 2 repeat units on average)



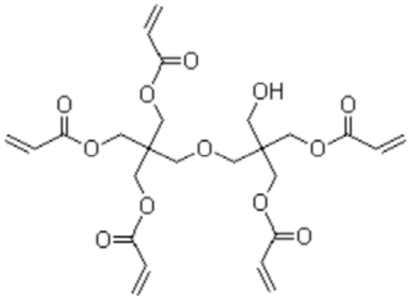


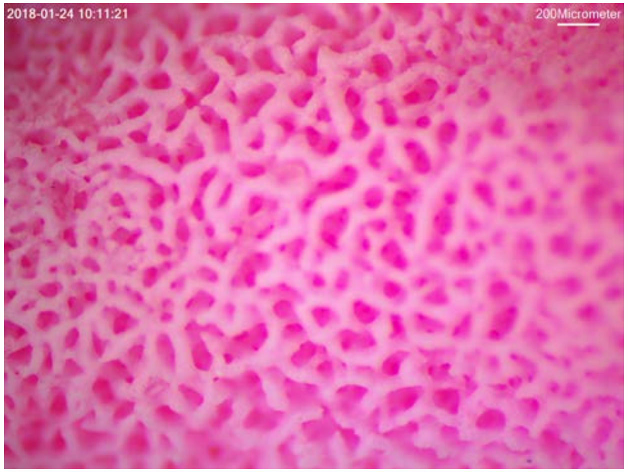
Ethoxylated Trimethylolpropane Triacrylate Esters
(ETA, 20 total repeat units)



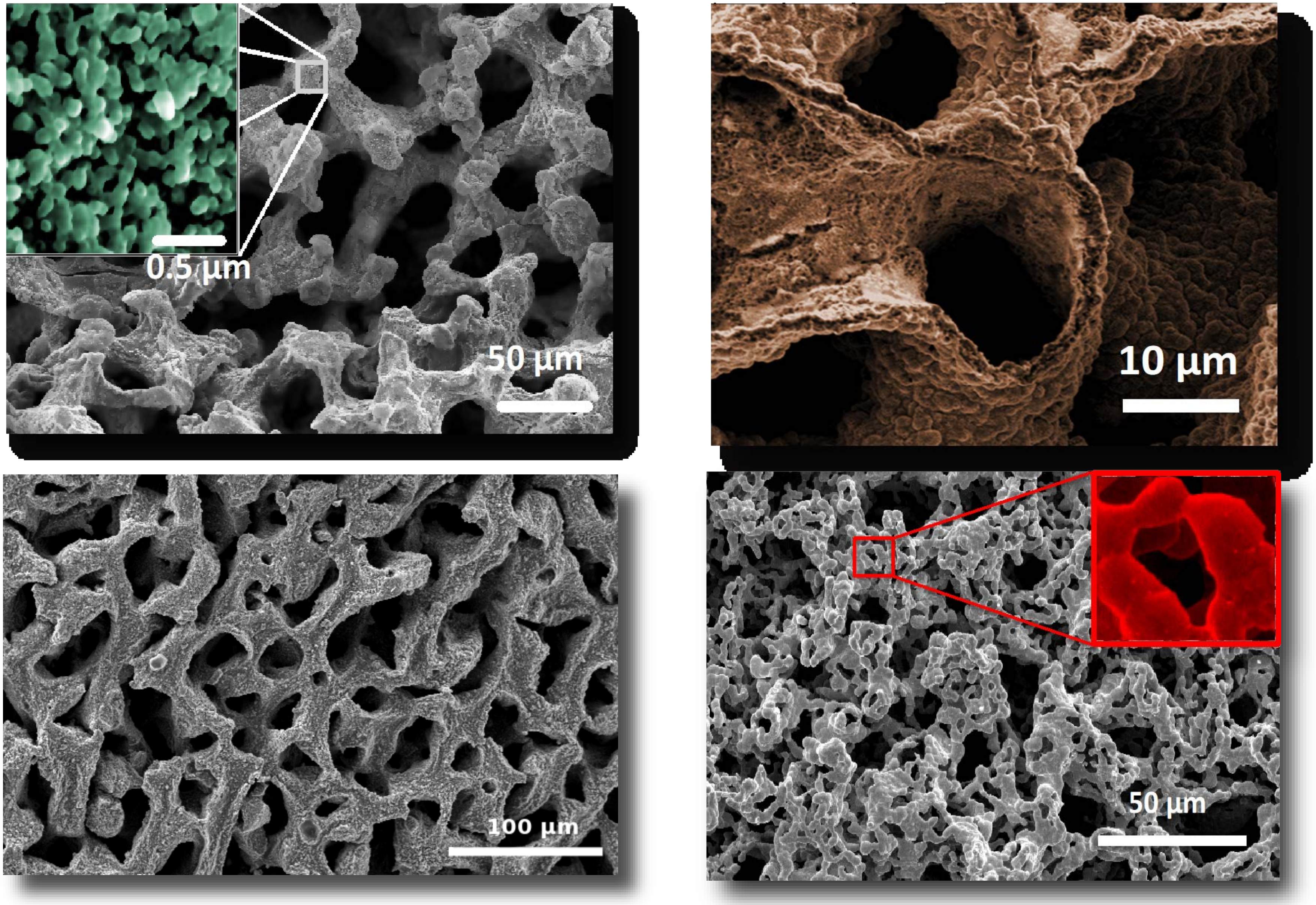


Dipentaerythritol Pentaacrylate Esters



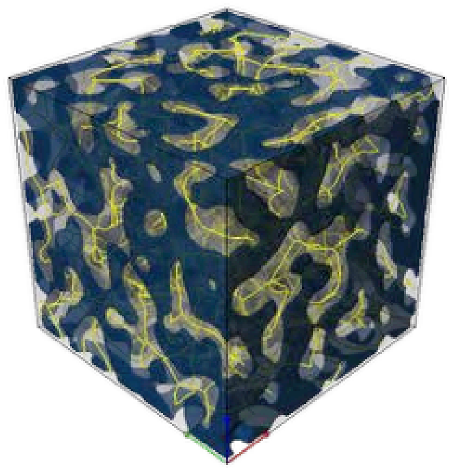


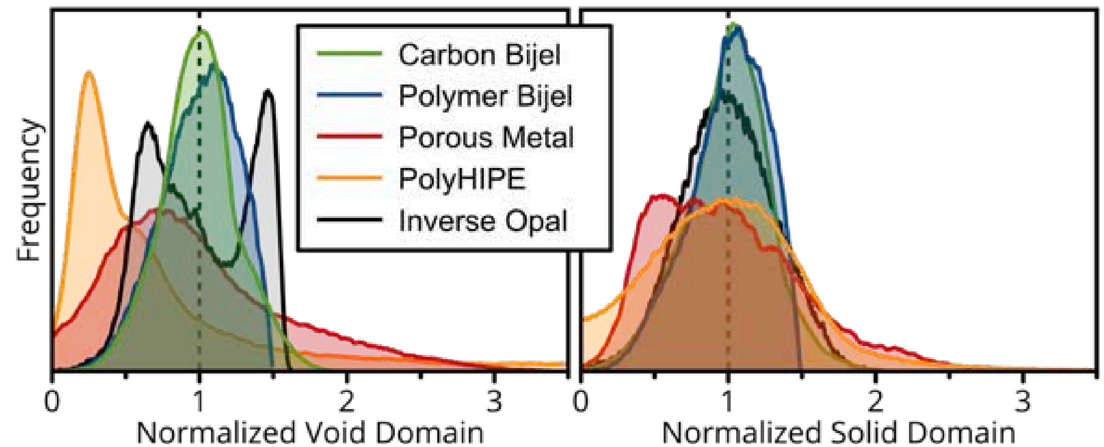
Bijel-Derived Porous Metals and Ceramics

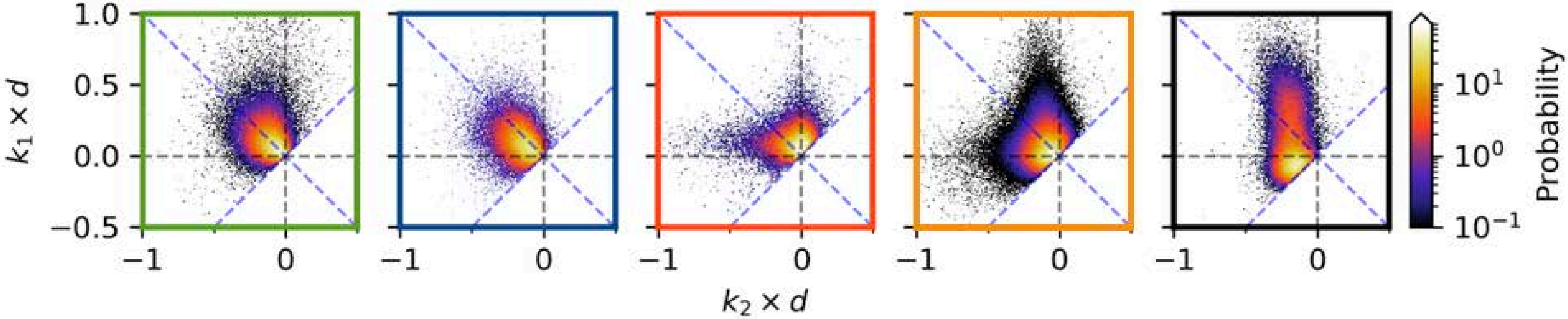


Lee and Mohraz, *Advanced Materials* (2010); *J. Amer. Chem Soc.* (2011

Morphological Characteristic of Bijel-Derived Materials, Compared to Other Relevant Systems





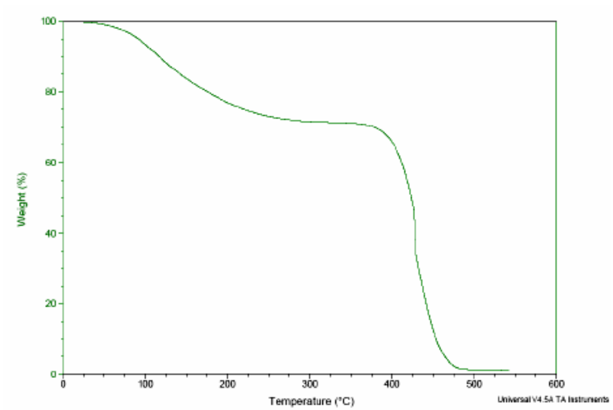


- Bicontinuity
- Negative Gaussian Curvatures
- Uniform Domain Size
- Low Degree of Branching

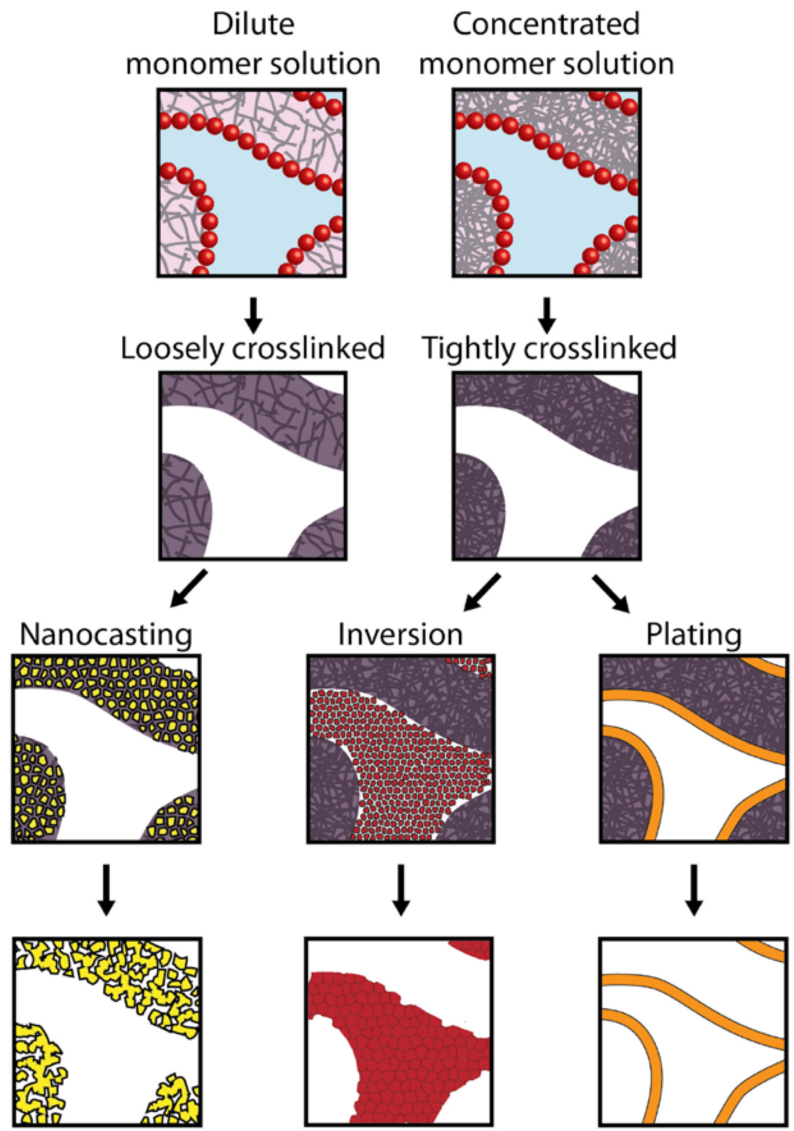
EARTH BENEFITS AND APPLICATIONS

Materials Processing

Control over crosslinking density opens new routes for materials processing

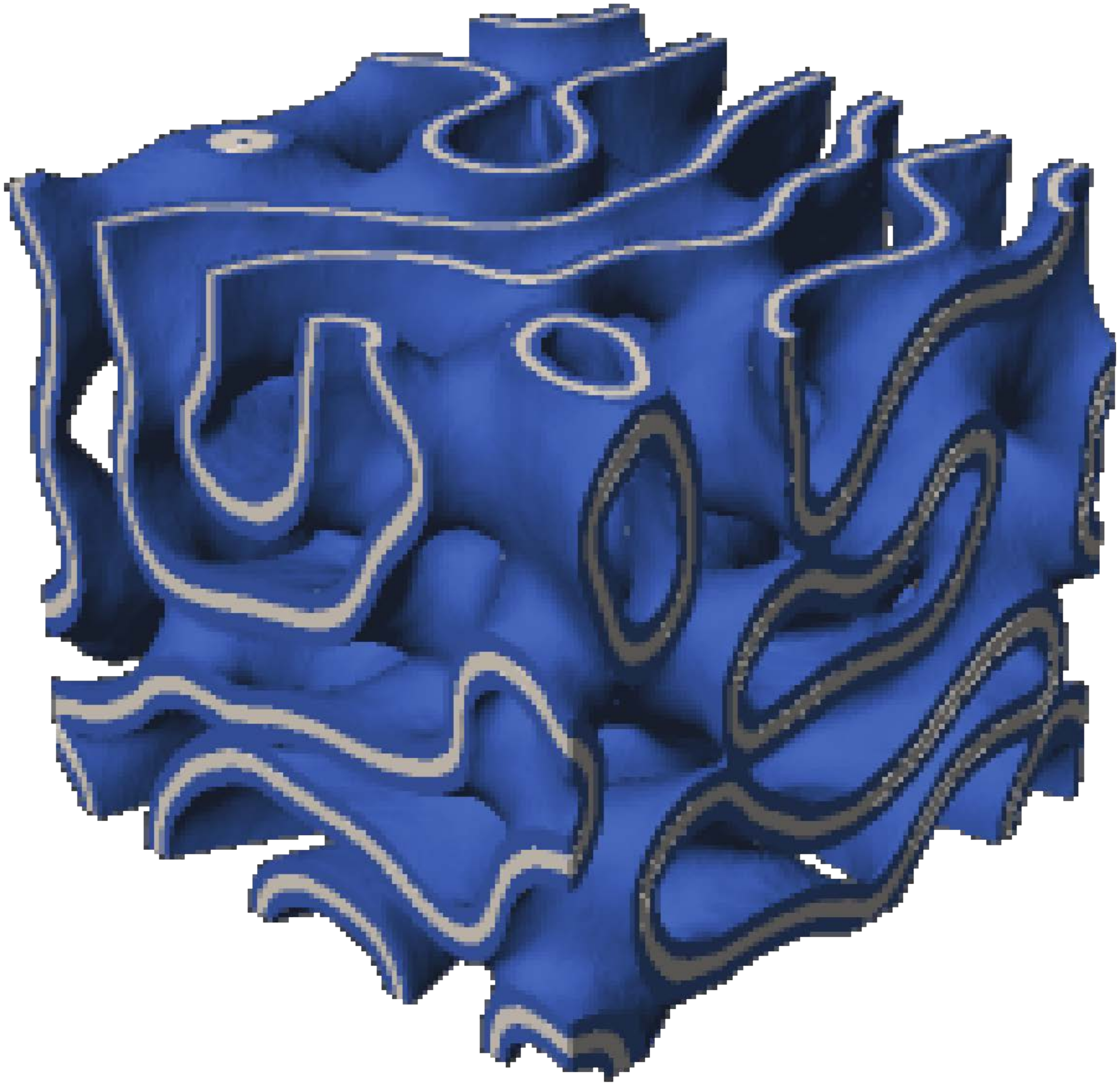


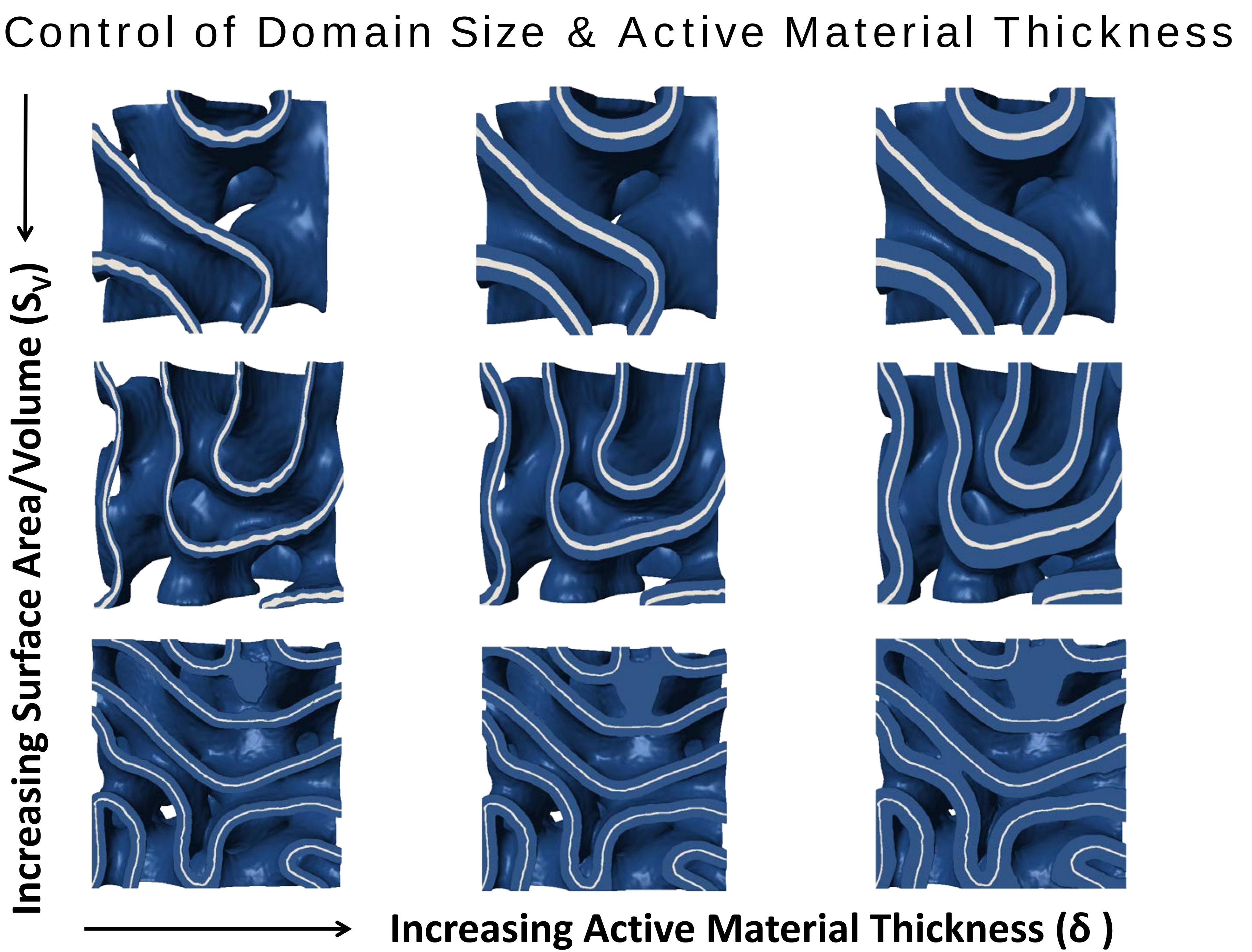
Polymer removed completely at T ~ 450°C



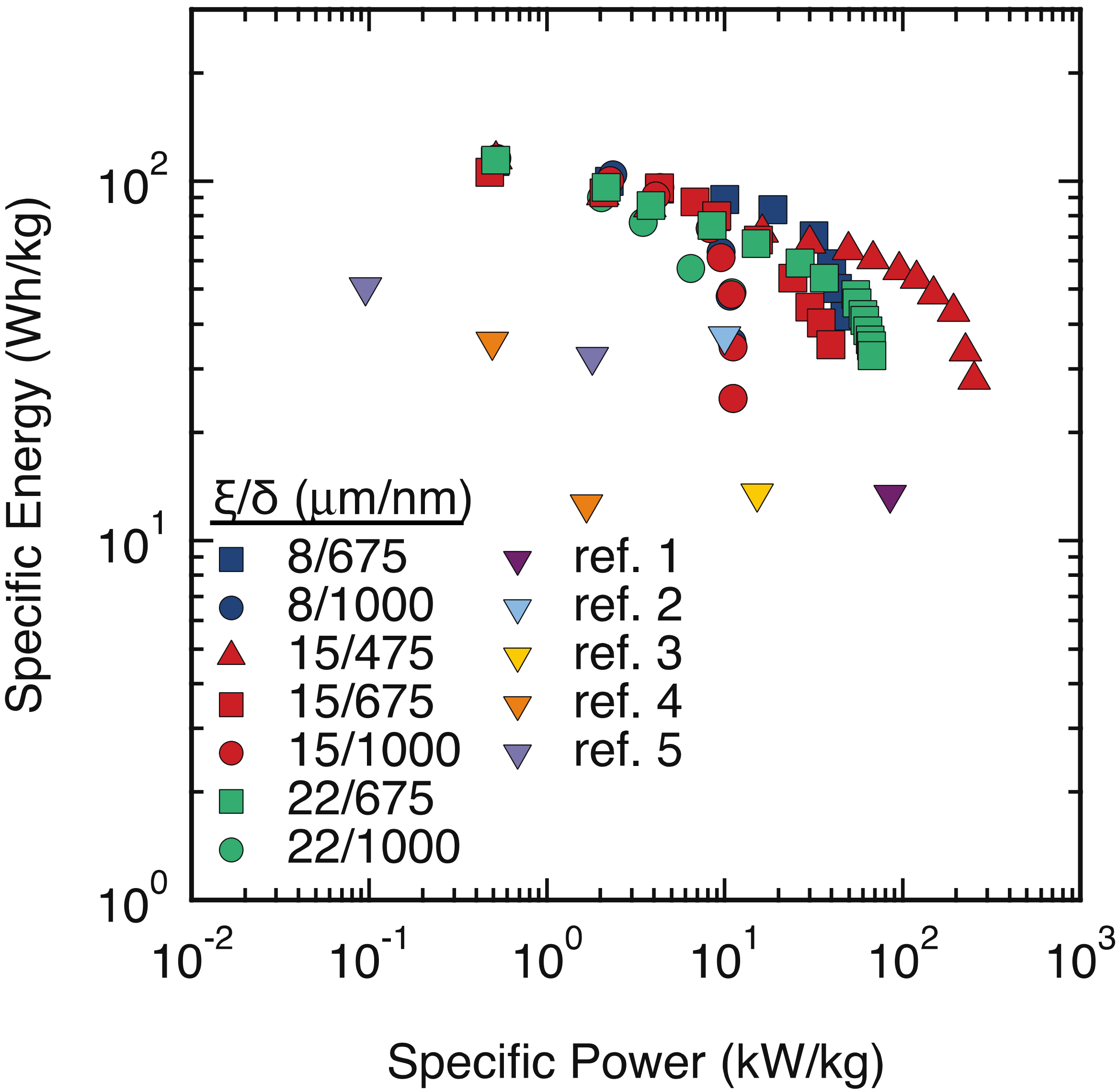
Lee and Mohraz, *Advanced Materials* (2010)

Electrochemical Energy Storage

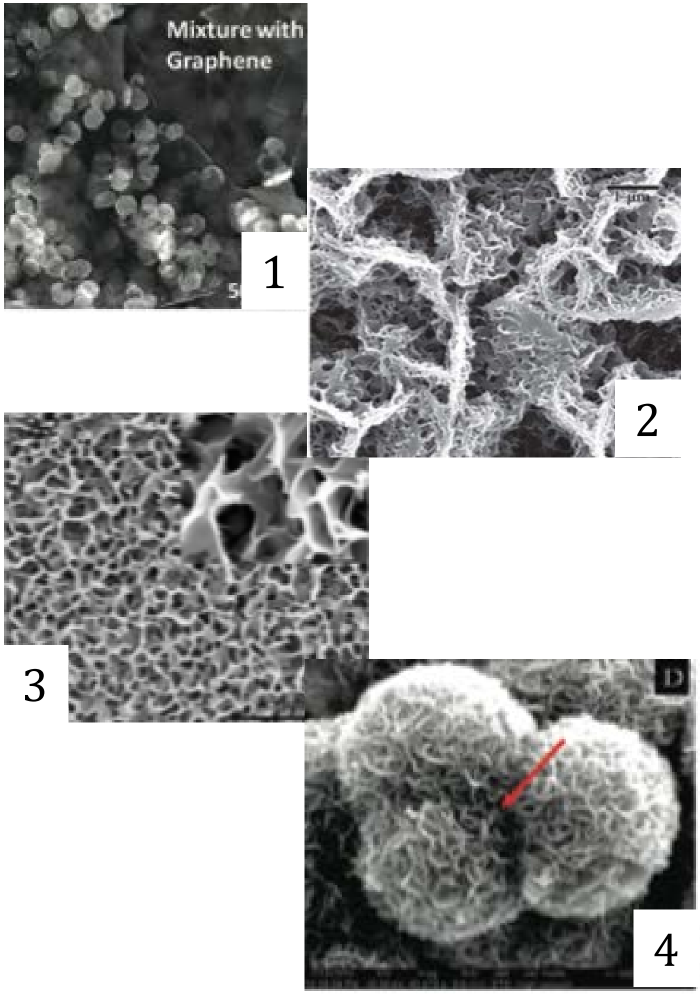



Control of Domain Size & Active Material Thickness
Increasing Surface Area/Volume (S_V)
Increasing Active Material Thickness (δ)

Gravimetric Ragone Plot

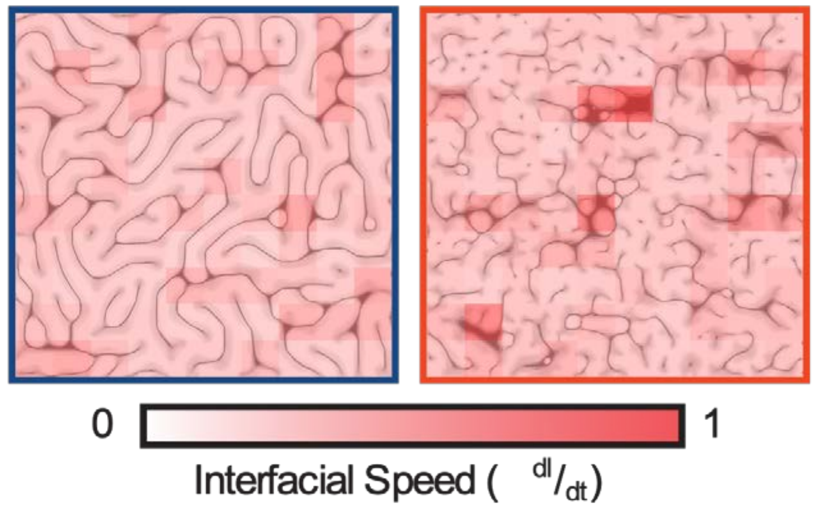


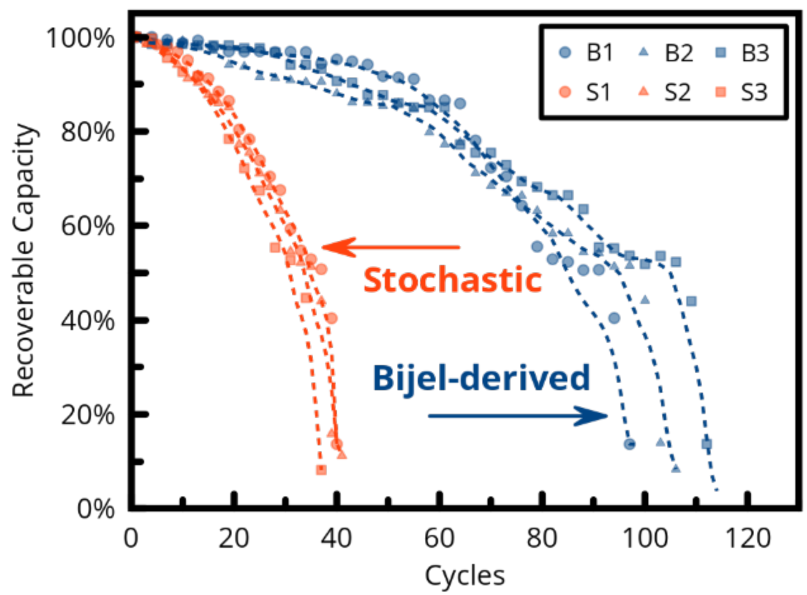
J. A. Witt, D. R. Mumm, A. Mohraz, *J. Mat. Chem. A* (2016)



1. H. Wang et al, *J. Am. Chem. Soc.* (2010)
2. K Liang et al, *J. Mater. Chem.* (2012)
3. K Liang et al, *Mater. Res. Bull.* (2013)
4. S. Meher et al, *ACS Appl. Mater. Interf.* (2011)
5. T. Zang et al, Adv. Funct. Mater (2012)

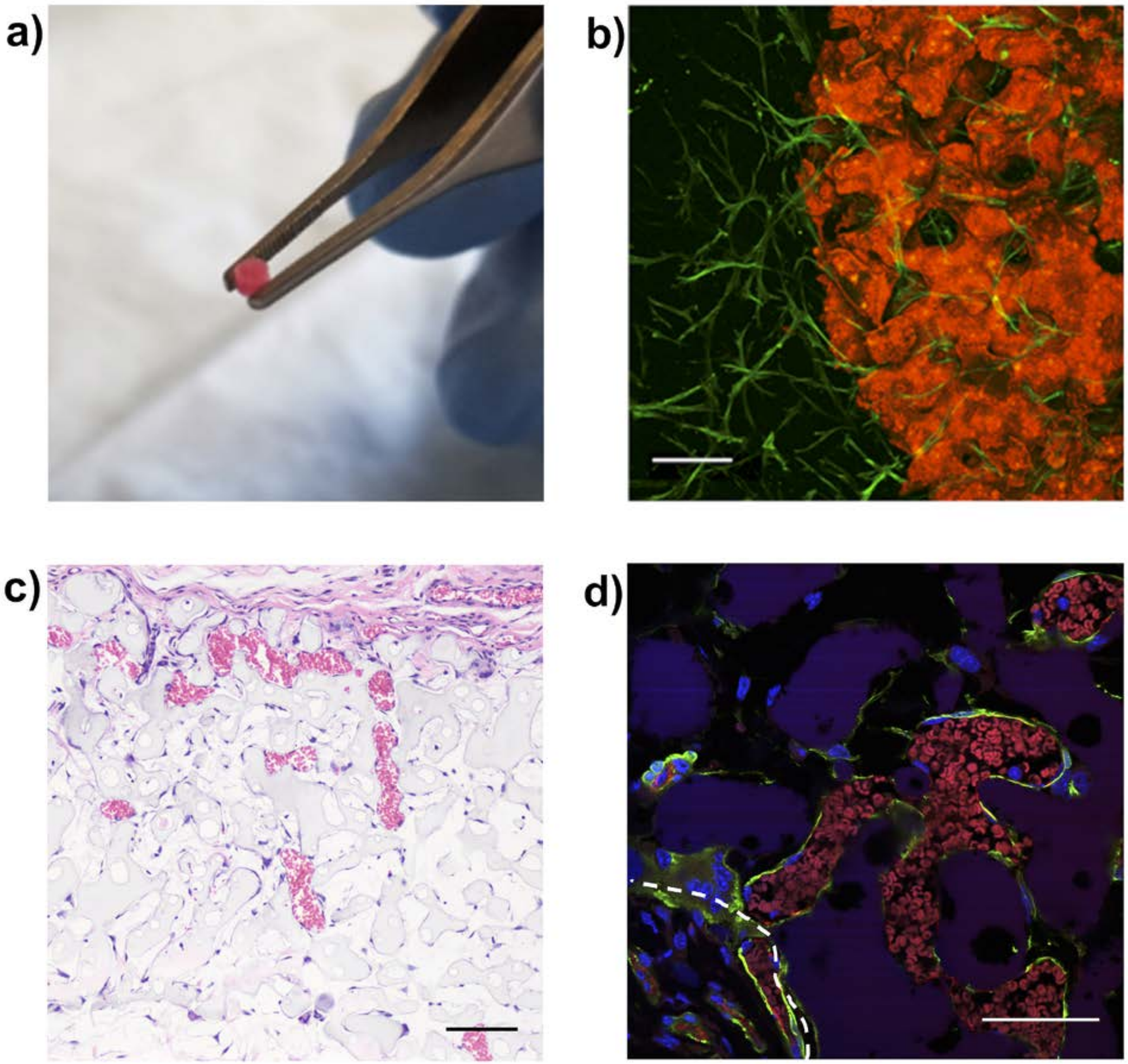
Extension to Other Chemistries (ZnO here)





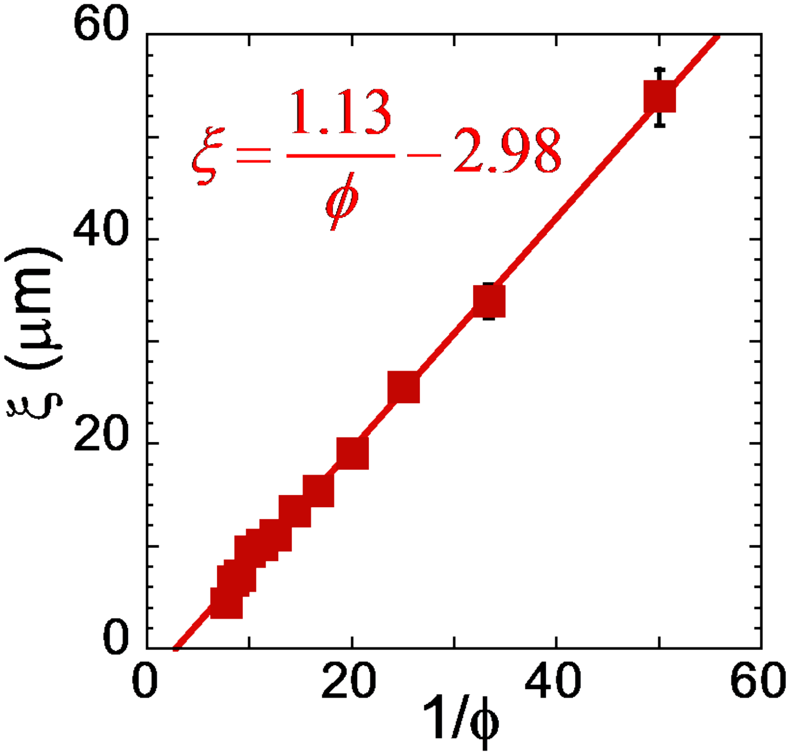
K. McDevitt, D.R. Mumm, A. Mohraz, to be submitted

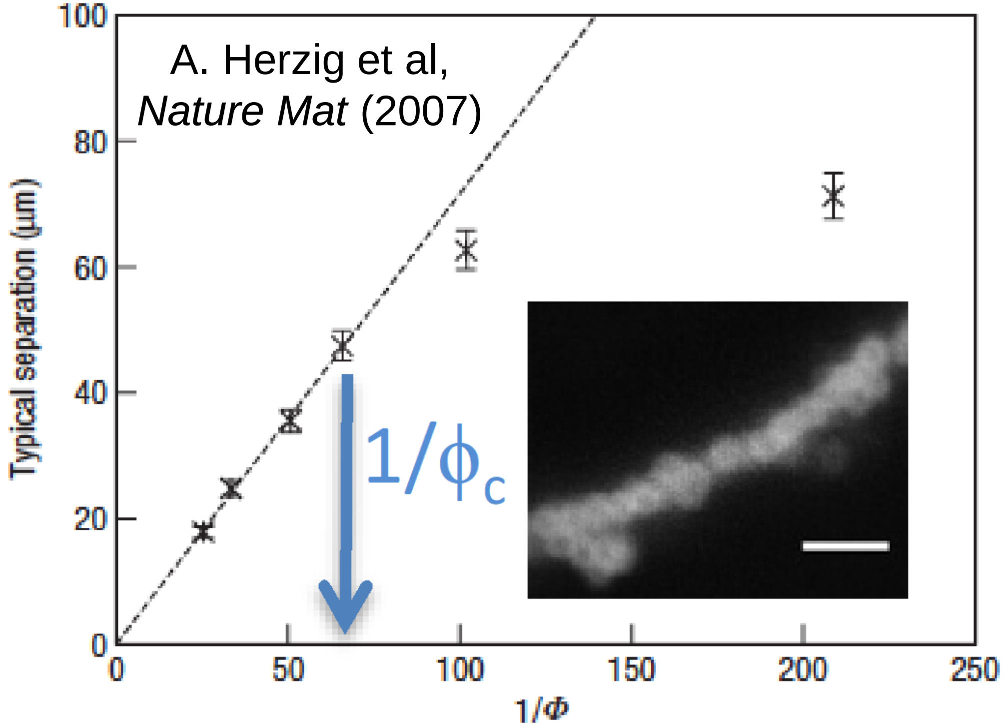
Application in Biomaterials



T.J. Thorson, E.L. Botvinick and A. Mohraz, *ACS Biomat Sci & Eng* (2018)
T.J. Thorson et al, *Acta Biomaterialia*, to appear (2019)

Control of Domain Size





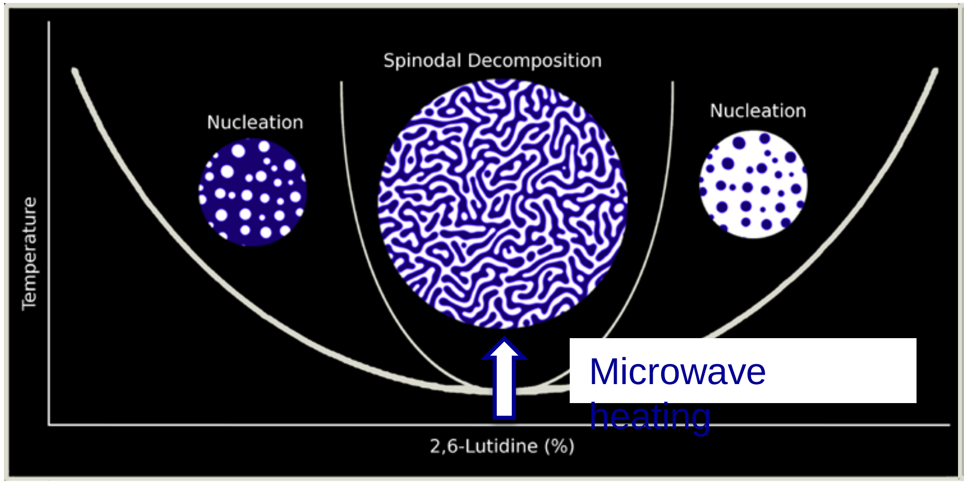
For monolayer coverage, $\xi \sim \frac{1}{\phi}$

Outstanding Question: What causes the deviation from the expected linear scaling?

Hypothesis: A matter of mechanical stability against gravity.

Expanding the Synthesis Platform

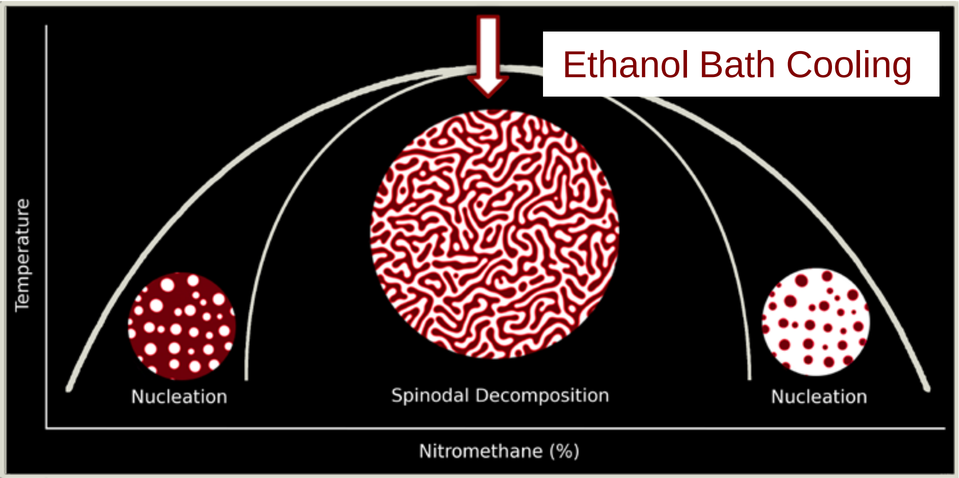
Water + 2,6-Lutidine



Critical point: $x_L = 0.064$ Tc = 34.1°C

A. Herzig et al, *Nature Mat* (2007)

Ethylene Glycol + Nitromethane

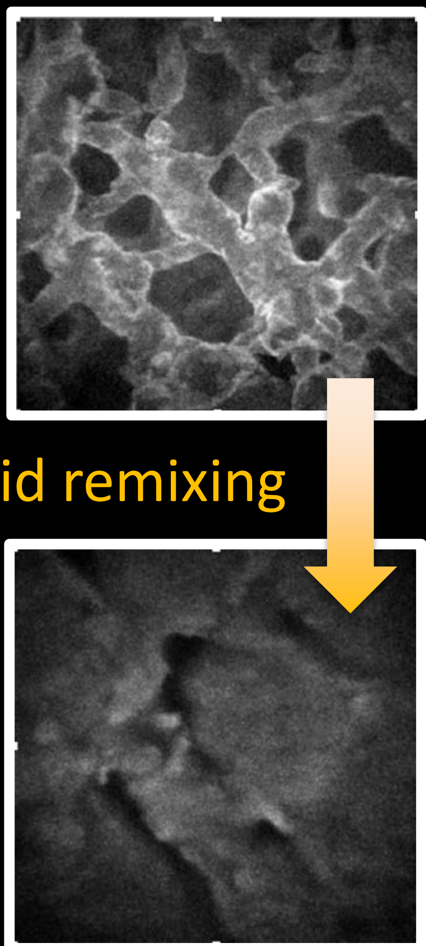


Critical point: $x_{NM} = 0.64$ Tc = 40°C

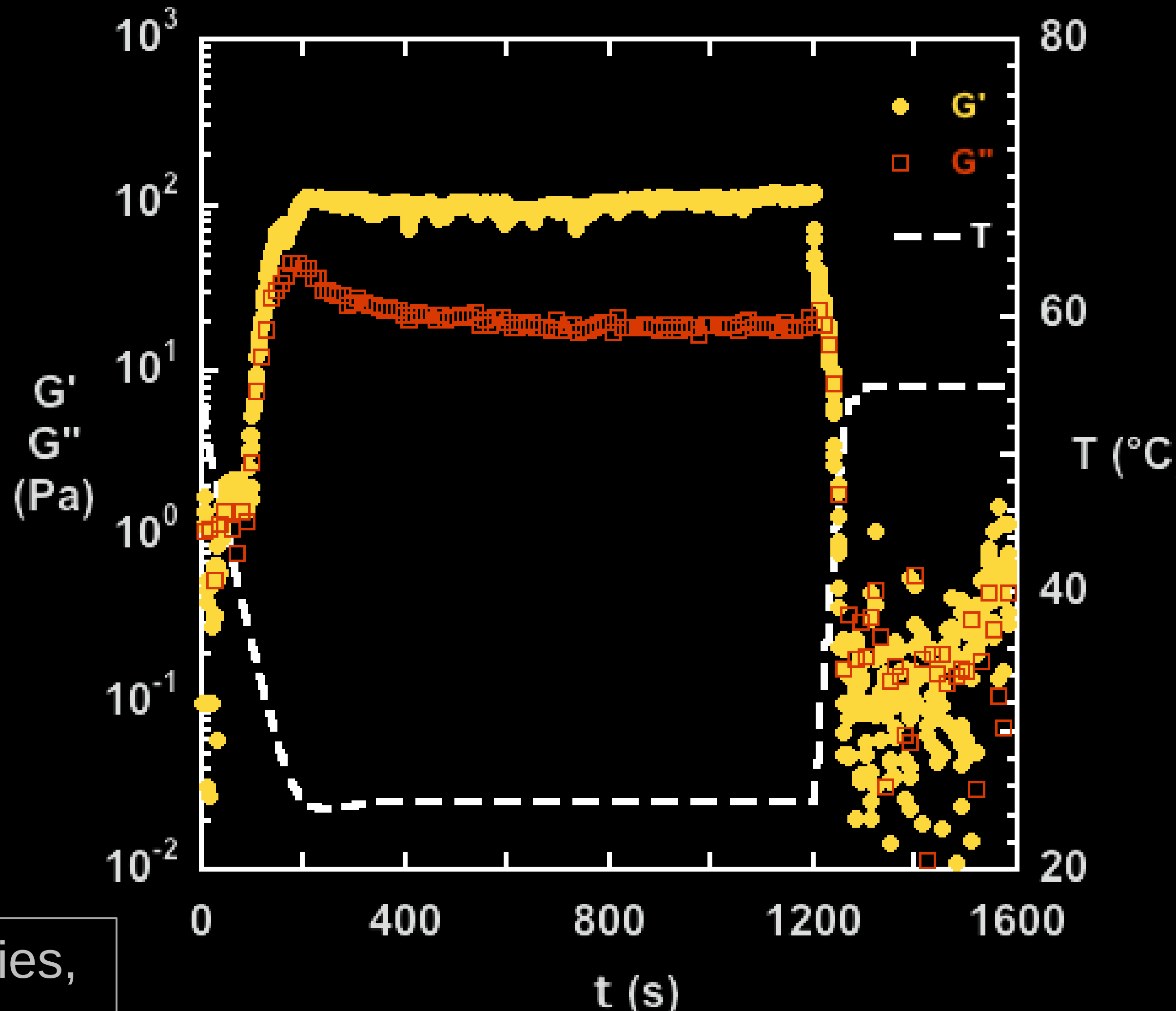
J.W. Tavacoli et al, *Adv Func Mat* (2011)

New bijel chemistries can expand the range of materials possible. However, so far our materials processing methods have **only been successful with the W/L system**.

Clues from Bijel Rheology



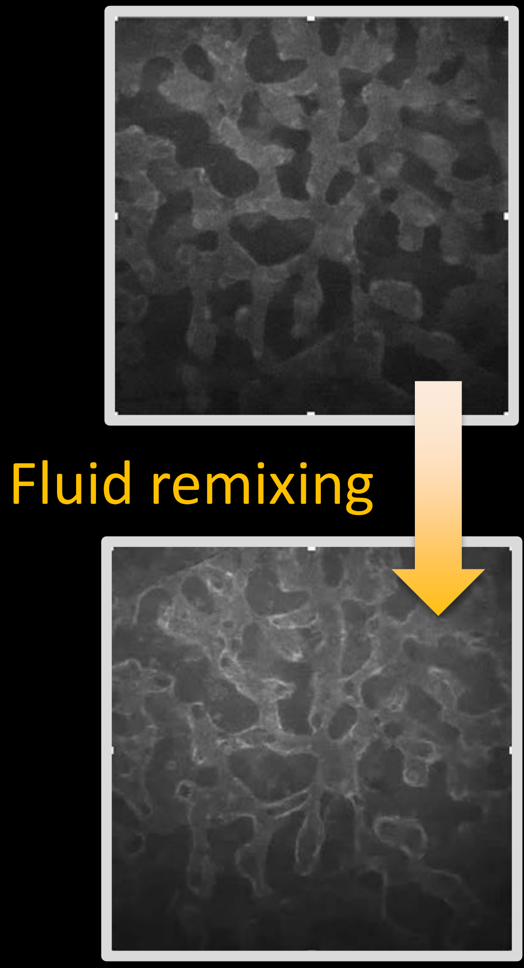
Fluid remixing

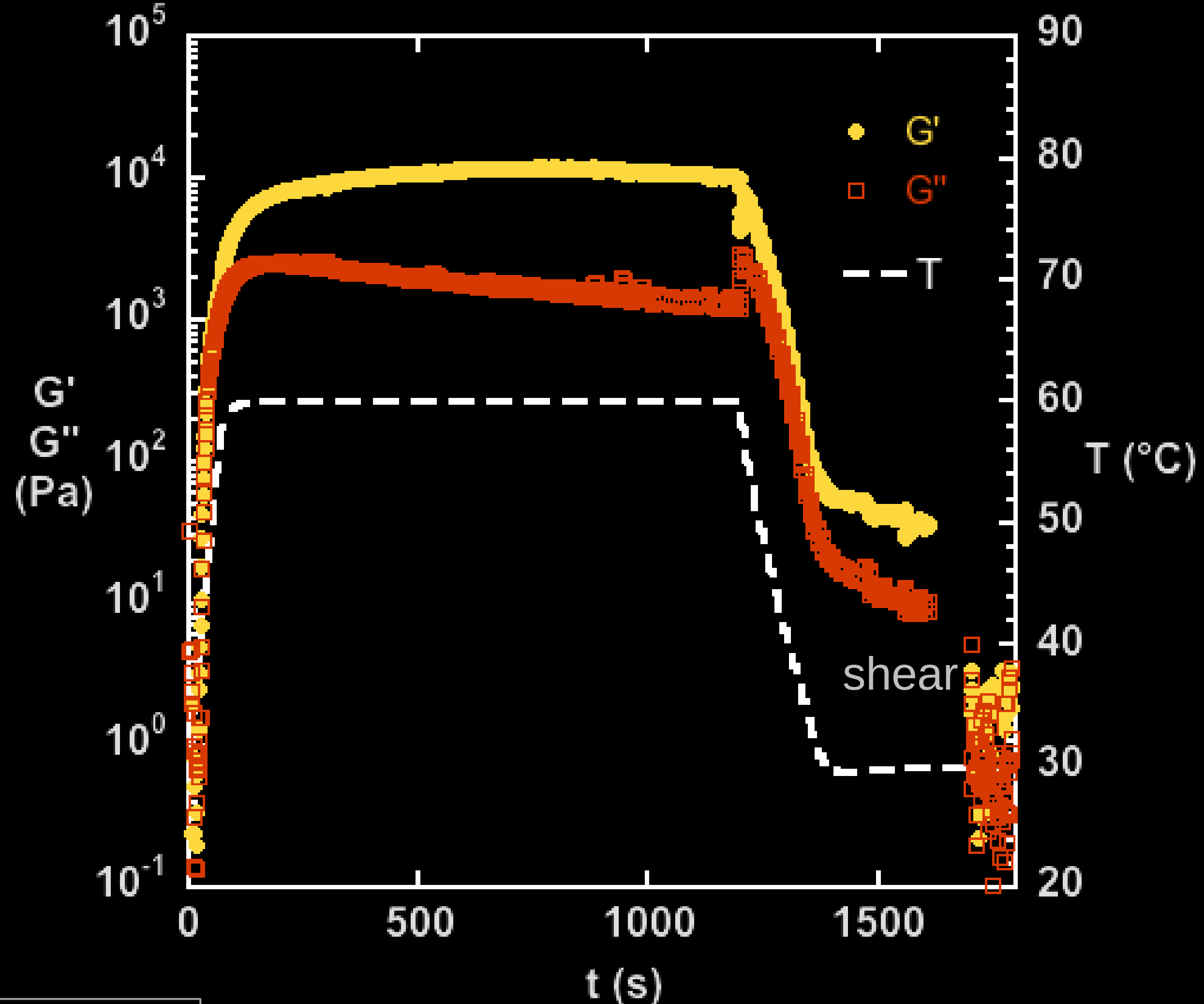


With most bijel chemistries, the scaffold breaks down upon fluid remixing

Lee et al, *Advanced Functional Materials* (2013)

Clues from Bijel Rheology

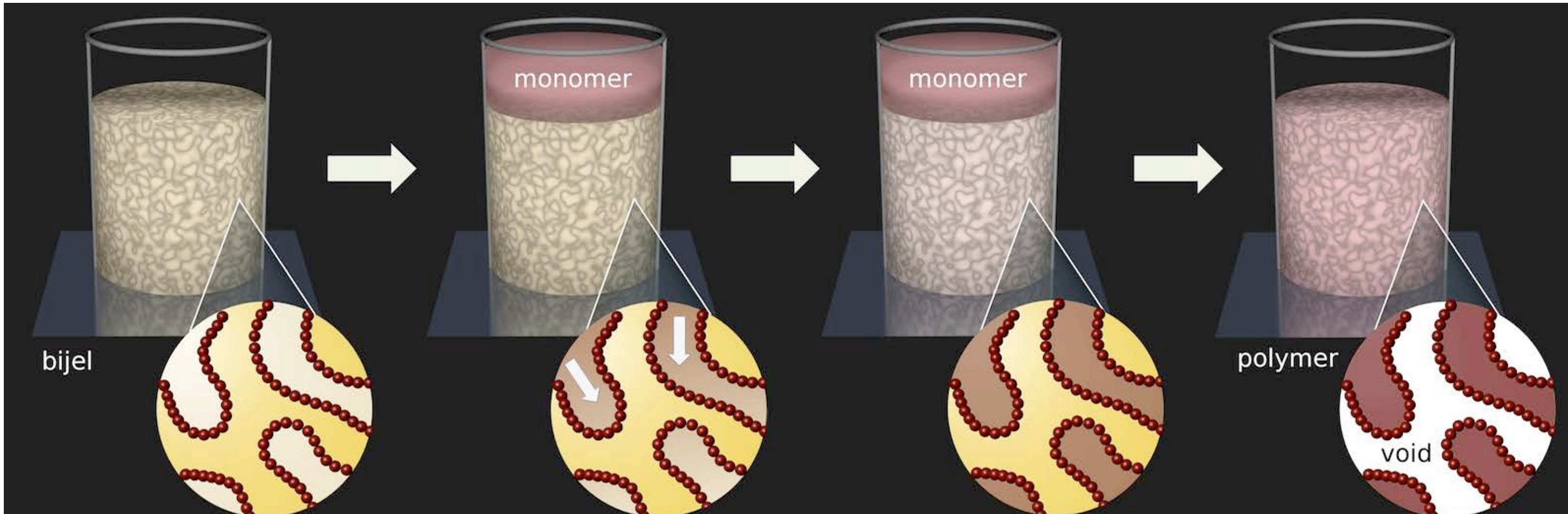




The W/L system can form a monogel (withstands remixing)

Lee et al, *Advanced Functional Materials* (2013)

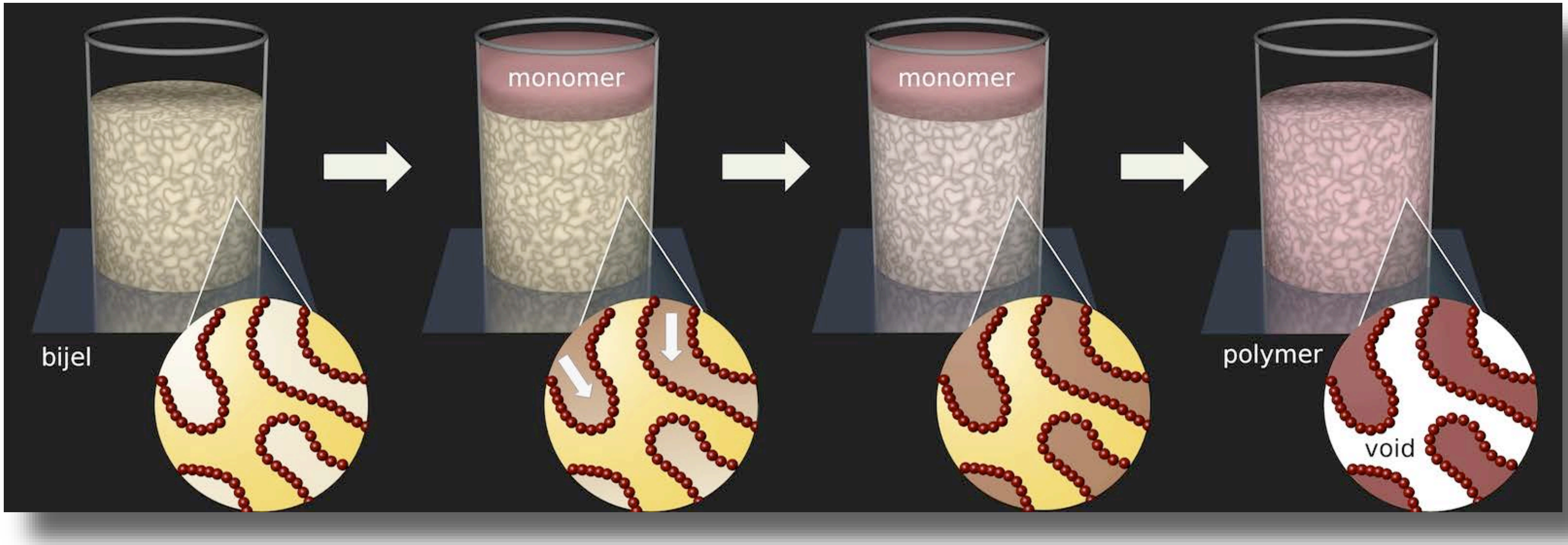
Bijel Rheology and Processability



Outstanding Question: Why can't we process bijels with other chemistries into co-continuous composites?
Hypothesis: During monomer diffusion, concentration gradients lead to Marangoni forces along the interface and cause structural breakdown in <u>weak samples</u>.

Must better understand bijel rheology and response to Marangoni forces

Bijel Rheology and Processability

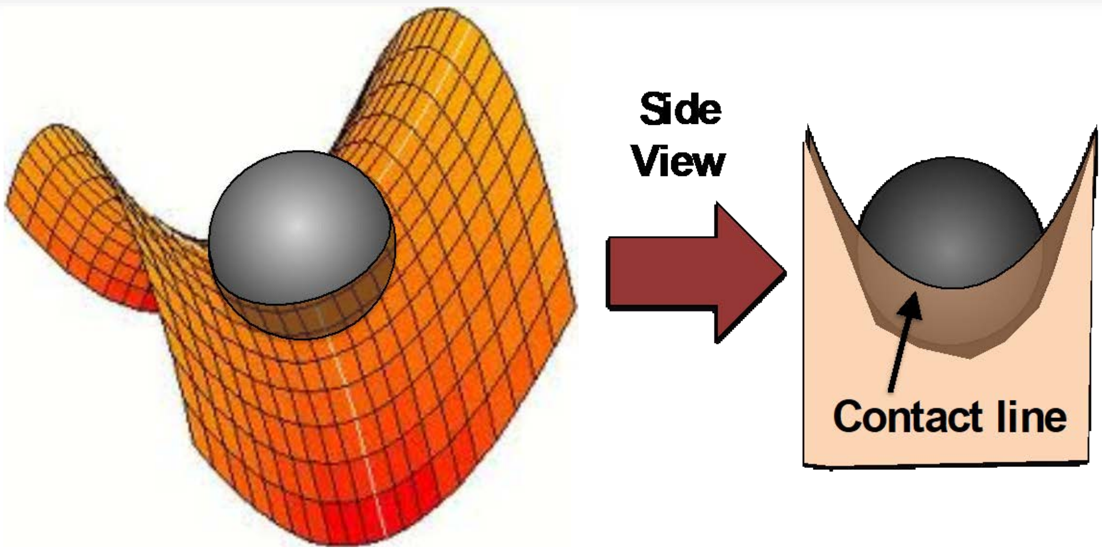


$$G_0' \sim n_2 r_m^2 \left. \frac{d^2U}{dr^2} \right|_{r_m}$$

Patel and Russel,
J. Coll Int Sci (1989)

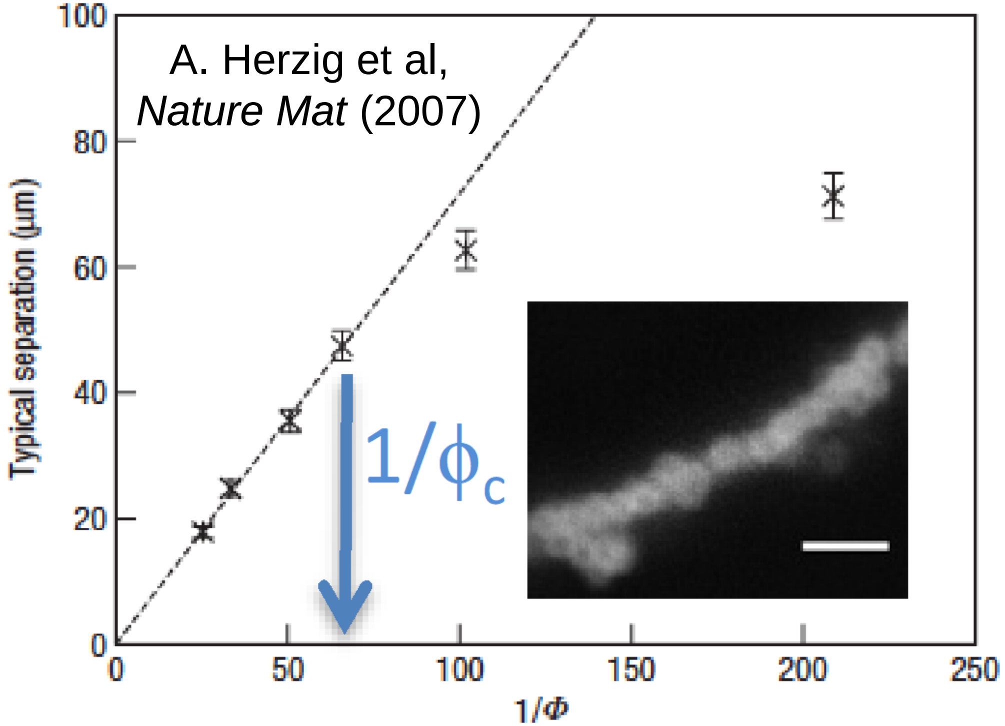
Interactions in BIJELs:

- Van der Waals
- Electrostatic
- Capillary



Interparticle interactions are quite complicated!

Role of Microgravity - 1

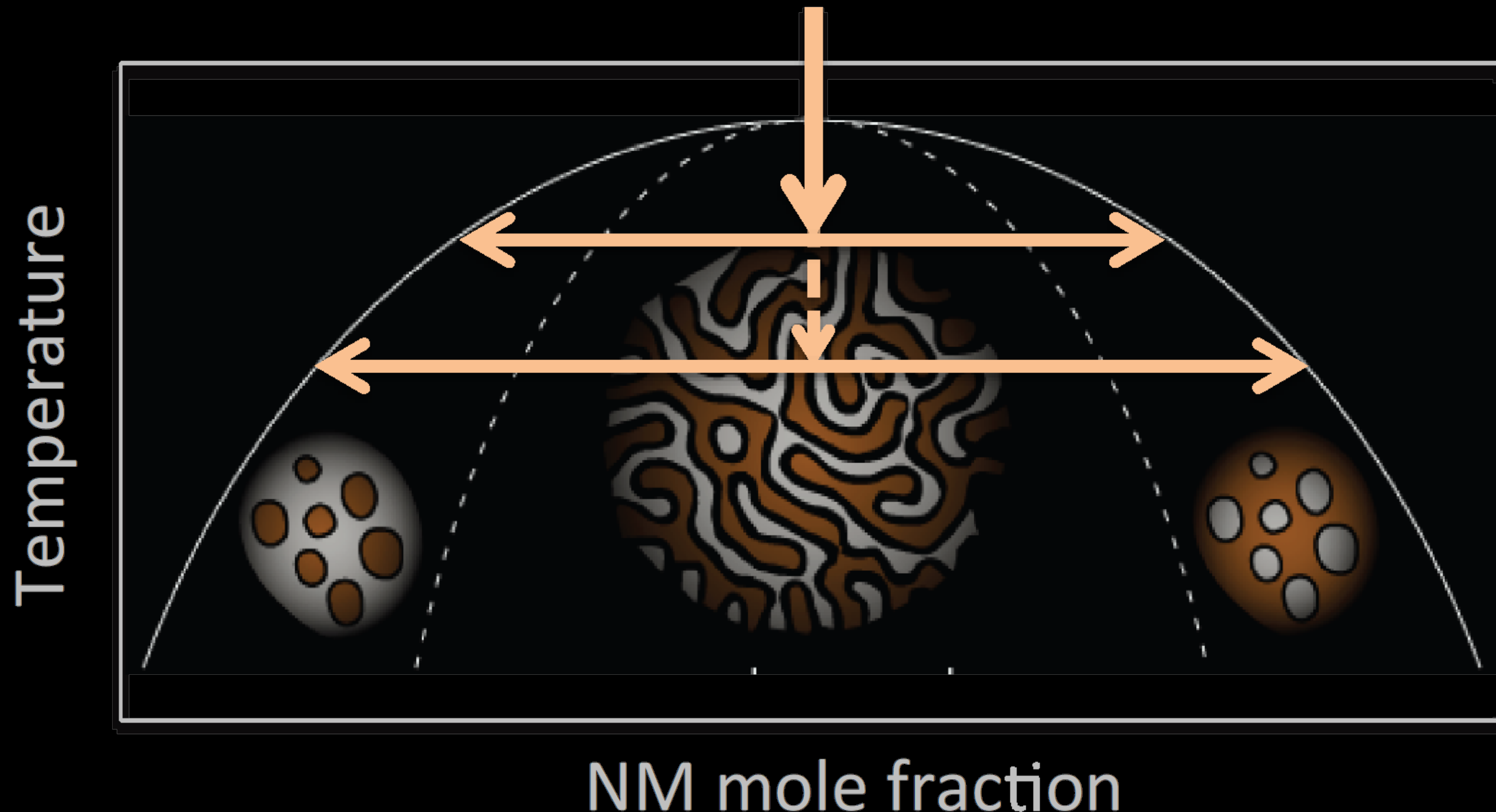


Mechanical stability hypothesis can be tested by preparing in microgravity at least one bijel at volume fractions below Φ_c

For monolayer coverage, $\xi \sim \frac{1}{\phi}$

Outstanding Question: What causes the deviation from the expected linear scaling?
Hypothesis: A matter of mechanical stability against gravity.

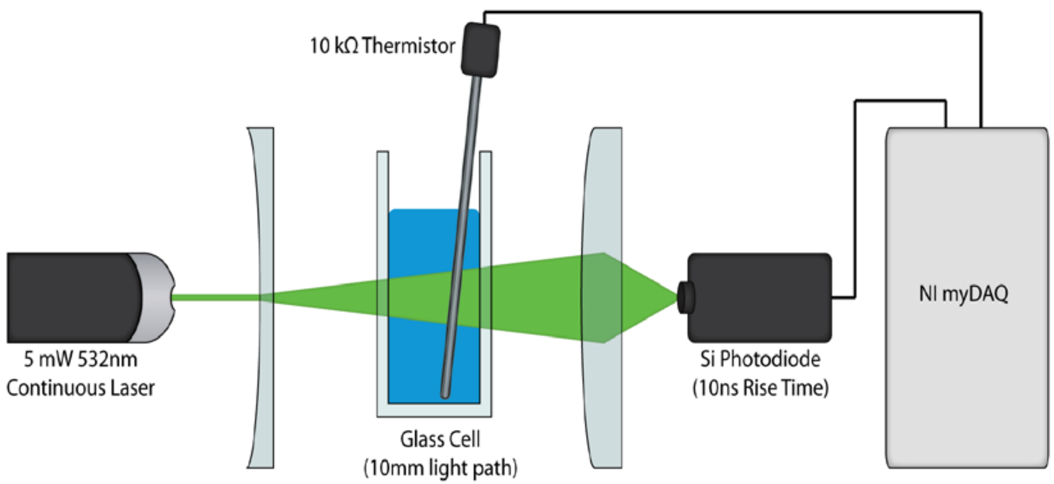
Role of Microgravity - 2

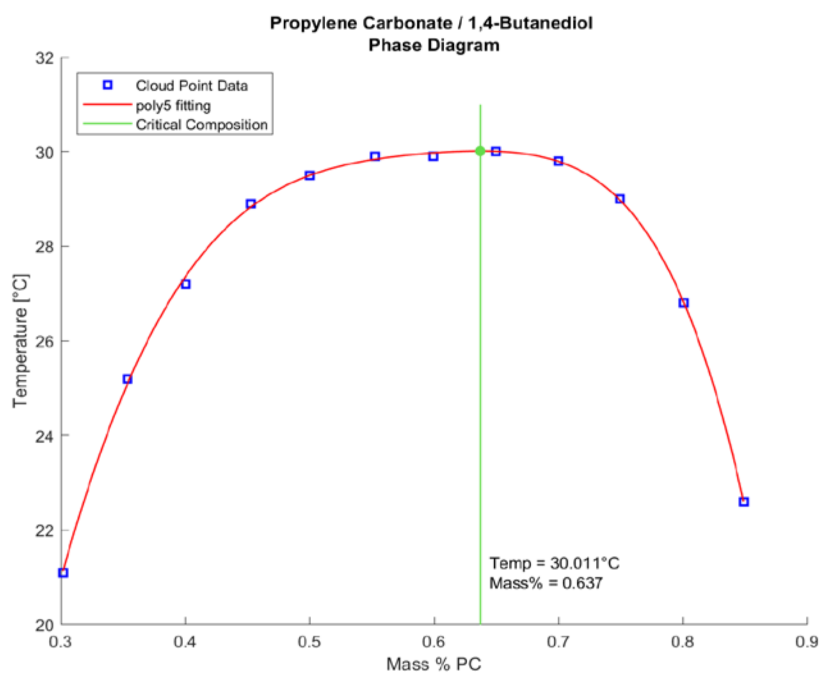


Temperature dependence of σ can be exploited to systematically study the effect of Marangoni forces on bijels. However, such effects must be decoupled from density differences.

NEW CHEMISTRIES FOR LONG-DURATION MICROGRAVITY EXPERIMENTS (REQUIRED FOR ASTRONAUT SAFETY)

Cloud Point Measurements for Phase Diagram





Candidate Binary Fluid Mixtures Considered

Fluid 1	Fluid 2	Phase behavior	T_c [°C]	X_c (fluid 1) [wt%]	P^{sat}_1 @25°C [mmHg]	P^{sat}_2 @25°C [mmHg]	Bijel formation
Nitroethane	Propylene Glycol	UCST	14.1	62.5	20.8	0.13	Yes
Propylene Carbonate	1,4-Butanediol	UCST	30.0	63.7	0.045	0.011	Yes
Propylene Carbonate	Ethyl Decanoate	UCST	34.3	45.0	0.045	0.02	Yes
Propylene Carbonate	Water	UCST	61.1	57.5	0.045	23.8	Yes
Propylene Carbonate	Di-n-octyl phthalate	UCST	28.0	59.5	0.045	1.0×10^{-7}	Yes
Ethylene Carbonate	1,4-Butanediol	UCST	42.3	60.0	9.8×10^{-3}	0.011	No
Ethylene Carbonate	Isopropyl Alcohol	UCST	41.2	48.0	9.8×10^{-3}	45.4	No

*Propylene Carbonate/Water phase diagram was published by: A. Williamson and N. Catherall, J. Chem. Eng. Data 16, 3, 335-336 (1971)

*Vapor pressure for Ethyl Decanoate was published by D. Zaitsau, et al. J. Chem. Eng. Data 54, 3026-3033 (2009)

*All other vapor pressure data were obtained from PubChem

PROPOSED EXPERIMENTS

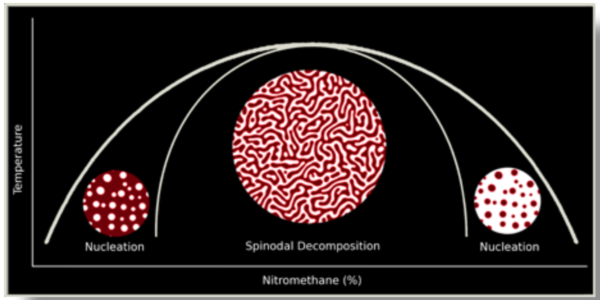
Materials and Methods

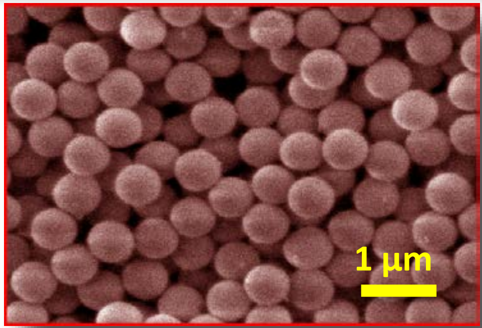
Propylene Glycol + Nitroethane, prepared at critical composition of $x_{NE} = 0.64$

Fluorescent silica particles, diameter *D* ~ 400 nm
Surface chemistry modified by grafting hydrophobic moieties hexamethyldisilazane (HMDS) onto the surface

2 × 3 cells, prepared at volume fractions ranging from $\Phi = 0.005$ to $\Phi = 0.04$, ($\Phi = 0.005, 0.01, 0.025$; $\Phi = 0.005, 0.0075, 0.015$)

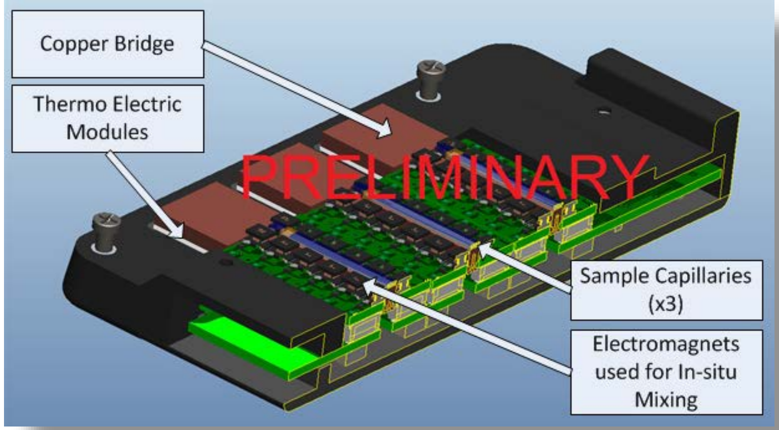
ACE-T Hardware at the ISS utilized to prepare bijels and subject them to controlled temperature gradients
Using 10x and 20x air objectives, images recorded after bijel formation to assess domain size dependence on Φ, and after temperature gradient to assess stability against Marangoni forces





REQUIRED HARDWARE

- Transparent cuvettes with inner dimensions (50 mm x 3 mm x 0.5 mm) and wall thickness 0.3 mm or lower
- Capability to heat sample to 25°C and perform mixing at this temperature
- Capability to rapidly and uniformly quench sample at a rate of at least 10°C/min, to a final temperature of 0°C
- Confocal imaging with rhodamine filter
- 2.5x air objective for overall sample inspection
- 10x (and potentially 20x or 40x) air objectives for microstructural imaging
- Capability to apply a temperature gradient of 12°C or more along the cuvette length
- Capability to record videos at 2 fps, ideally while end temperatures are being changed



Images courtesy of NASA

EXPERIMENTAL PROTOCOL

- Heat sample up to 25°C
- Perform in-situ mixing
- Apply a temperature quench at 10°C/min from 25°C to 0°C (phase separation)
- Define XYZ offsets, adjust camera parameters using 2.5x objective and B/S cube
- Survey capillary cell at 2.5x; determine test locations (away from stir bar or bubble)
- Adjust and record best camera parameters using 10x air objective and dye filter
- Survey and record best z depth where bicontinuous domains can be observed at least 150 μm away from the cell walls at each primary test location
- Record one full frame image at this location and z depth
- Back off the height to the cell wall
- Collect a z-stack of 100 images at spacing Δz = 5 μm (stack covers entire cell width)
- Return to recorded z location where bicontinuous domains were seen
- While recording images at 1 fps, increase the temperature at one end from 0°C to 4°C at a rate of 1°C/min
- Back off the height to the cell wall
- Collect a z-stack of 100 images at spacing Δz = 5 μm (stack covers entire cell width)
- Return to recorded z location where bicontinuous domains were seen
- While recording images at 1 fps, increase the temperature at one end from 4°C to 8°C at a rate of 1°C/min

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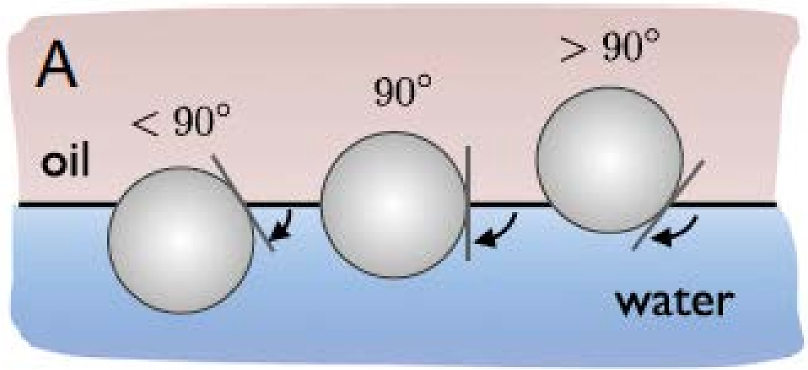
EXPERIMENTAL PROTOCOL Continued

- Back off the height to the cell wall
- Collect a z-stack of 100 images at spacing $\Delta z = 5\ \mu m$ (stack covers entire cell width)
- Return to recorded z location where bicontinuous domains were seen
- While recording images at 1 fps, increase the temperature at one end from 8°C to 12°C at a rate of 1°C/min
- Back off the height to the cell wall
- Collect a z-stack of 100 images at spacing $\Delta z = 5\ \mu m$ (stack covers entire cell width)
- Shutter lamp between image sets to prevent sample bleaching

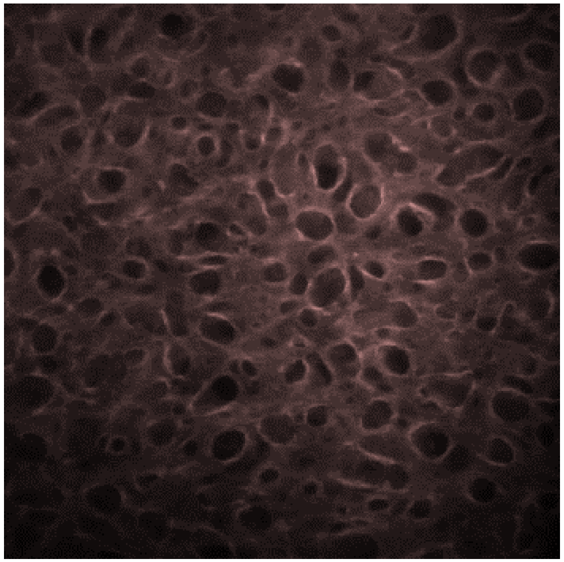
ONGOING GROUND-BASED EXPERIMENTS

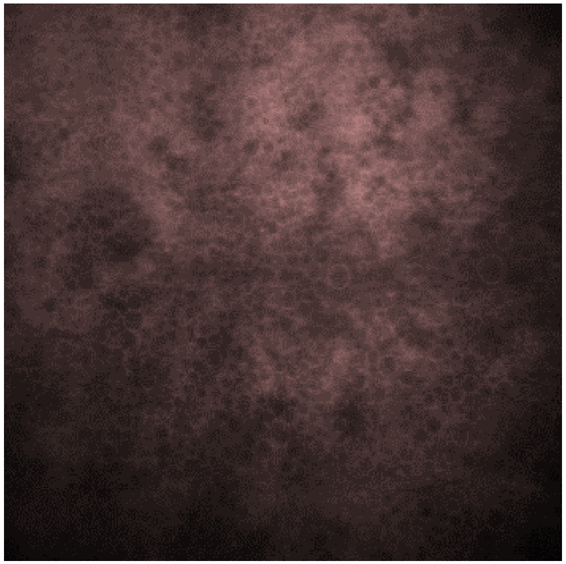
PARTICLE SURFACE CHEMISTRY



1 gr of particles (*D* ~ 600 nm) treated with 1.75 mL HMDS during synthesis

Day 0

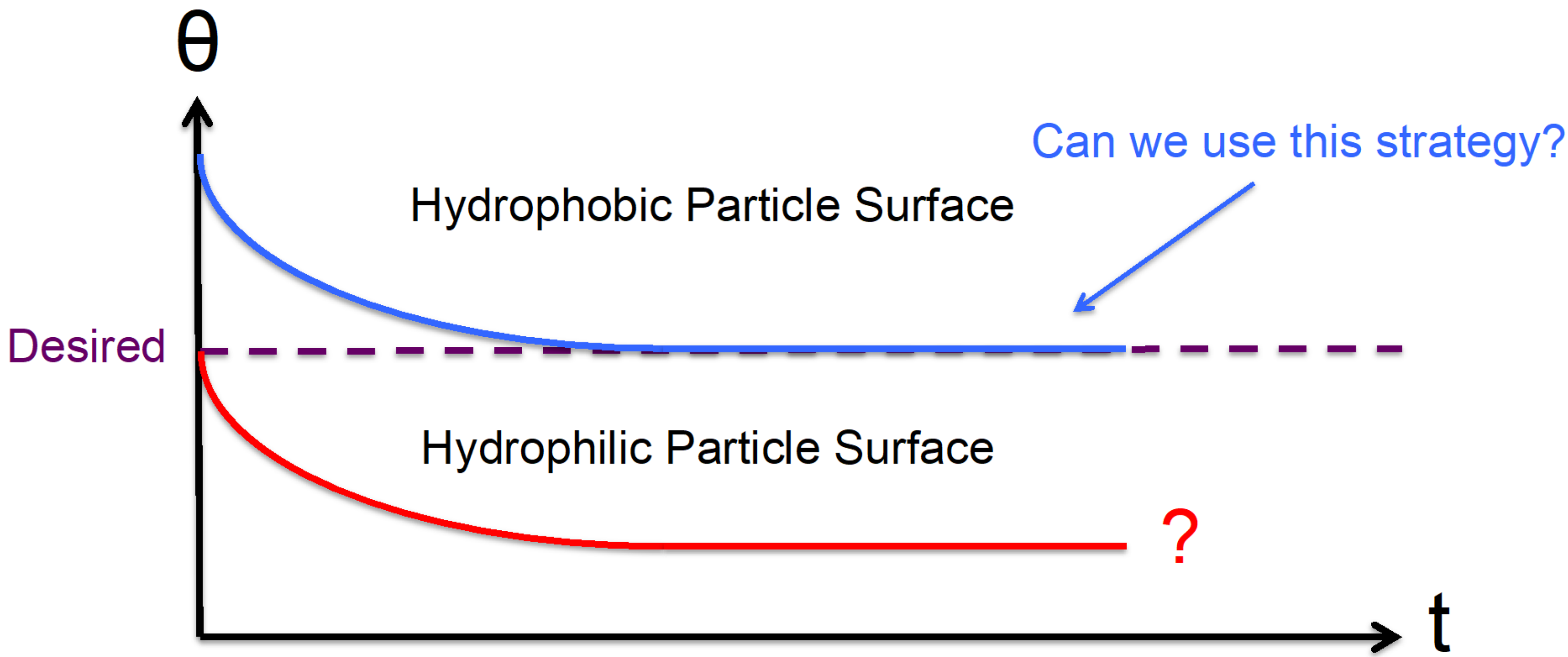




Day 2

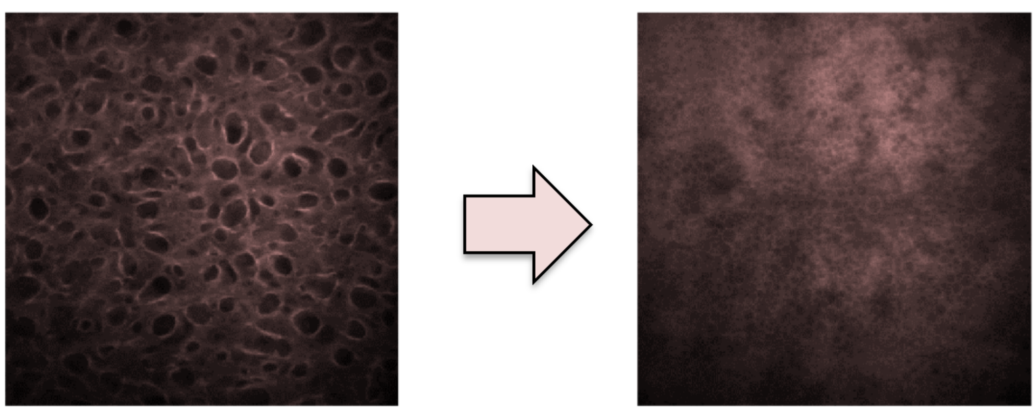
Particle surface chemistry is dynamic, changing to more hydrophilic behavior over time

PARTICLE SURFACE CHEMISTRY



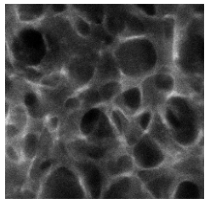
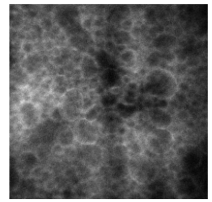
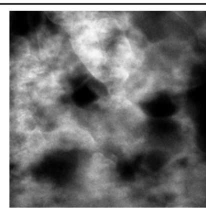
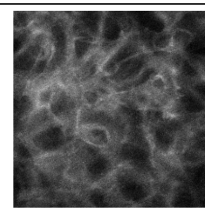
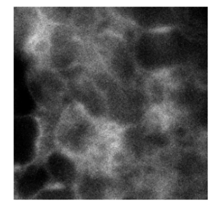
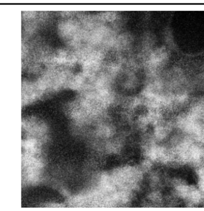
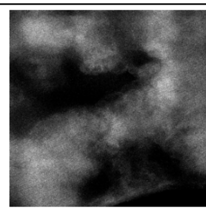
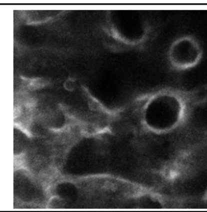
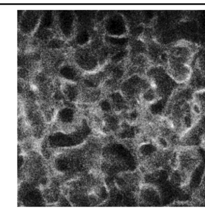
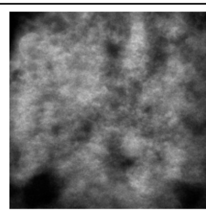
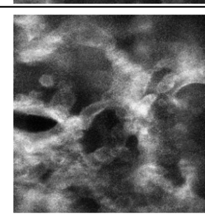
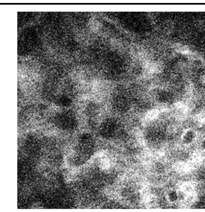
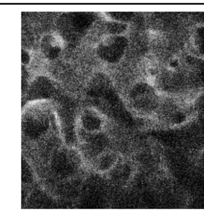
1 gr of particles (*D* ~ 600 nm) treated with **1.75 mL HMDS** during synthesis

Day 0



Day 2

SURFACE CHEMISTRY AGING TESTS

Surface Chemistry Modification	Day 0	Month 1	Month 3	Month 5
• 2.0mL of HMDS/gram of silica • Tuned for 17hr			No interfacial activity	No interfacial activity
• 6.0mL of HMDS/gram of silica • Tuned for 17hr				
• 6.25mL of HMDS/gram of silica • Tuned for 18hr				To be tested
• 7.0mL of HMDS/gram of silica • Tuned for 17hr				

QUESTIONS?

SUCCESS CRITERIA

Minimum Success

- Homogenize samples completely, apply a temperature quench to initiate phase separation, and observe bijel formation in 33% of the samples.
- Have images with sufficient quality and clarity to determine the characteristic domain size for at least two different colloid volume fractions.
- Be able to demonstrate the breakdown of at least one bijel structure under Marangoni forces (temperature gradients).

Significant Success

- Homogenize samples completely, apply a temperature quench to initiate phase separation, and observe bijel formation in 66% of the samples
- Have images with sufficient quality and clarity to determine the characteristic domain size for at least four different colloid volume fractions.
- Be able to demonstrate the breakdown of at least two bijel structures at different colloid volume fractions under Marangoni forces.

Complete Success

- Homogenize samples completely, apply a temperature quench to initiate phase separation, and observe bijel formation in all samples.
- Have images with sufficient quality and clarity to determine the characteristic domain size for all samples.
- Be able to demonstrate the temperature gradient needed to cause structural breakdown for each colloid volume fraction tested.