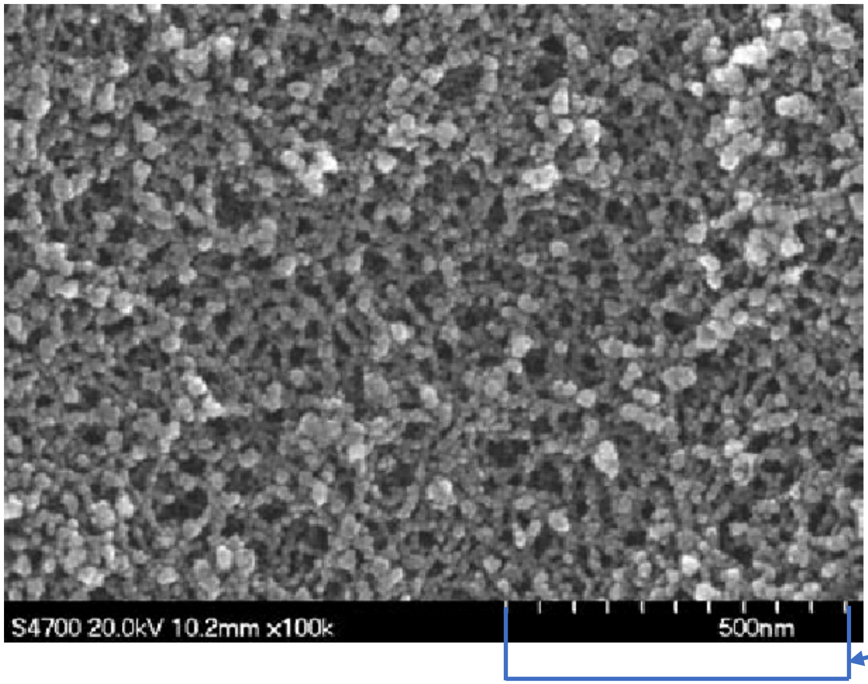
Crosslinking silica-based nanoporous networks under ambient conditions

Caleb Wigham
Ryan Murphy
Katie Weigandt
Yun Liu

Properties of Nanoporous Silica Networks

High Porosity
Low Thermal Conductivity

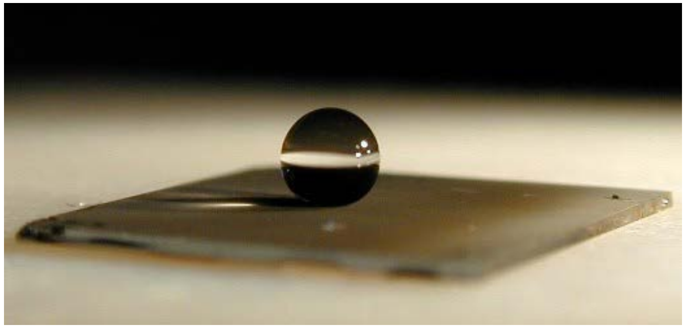
1



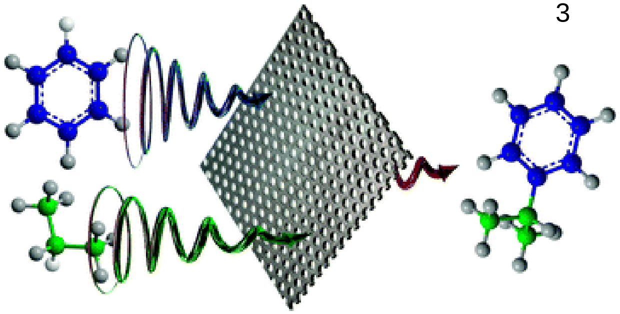
500 nm!

Hydrophobic
Low Surface Energy and High Contact Angle

2



3

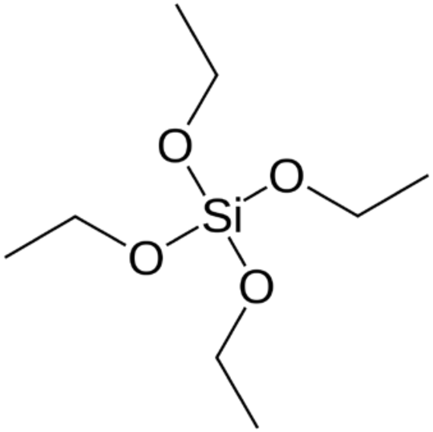


Catalysis - High Surface Area

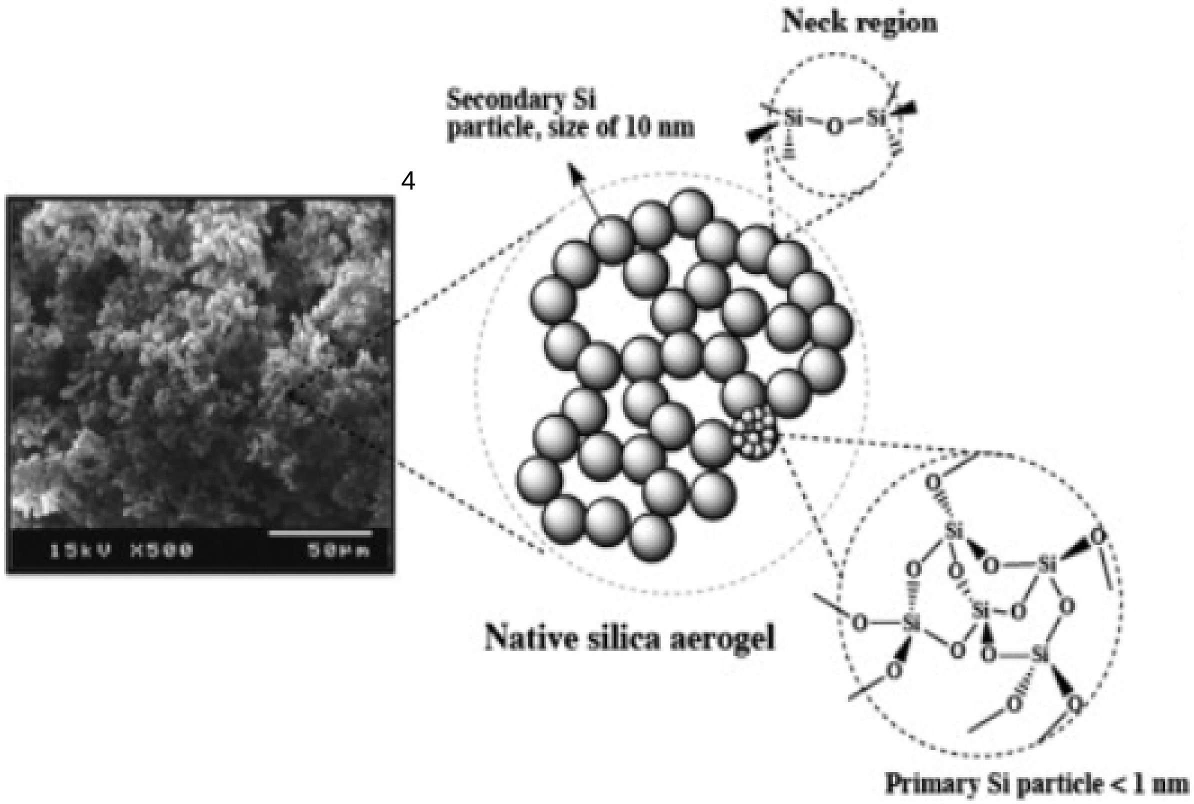
1. Zhang, H.; Gu, W.; Li, M.-J.; Fang, W.-Z.; Li, Z.-Y.; Tao, W.-Q. Influence of Environmental Factors on the Adsorption Capacity and Thermal Conductivity of Silica Nano-Porous Materials. *J. Nanosci. Nanotechnol.* **2015**, *15* (4), 3048–3054.
2. https://news.softpedia.com/news/Omniphobic-Material-Repels-Any-Liquid-97625.shtml
3. Catal. Sci. Technol., 2016,6, 2465-2466

Building Nanoporous Silica Networks

Tetraethyl orthosilicate monomer

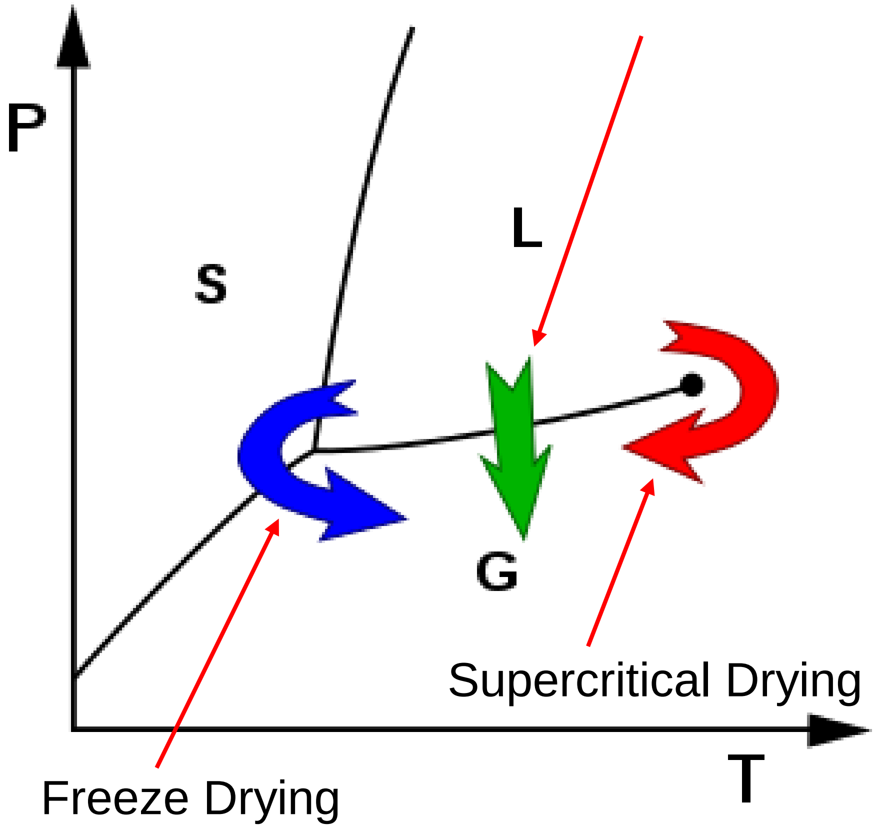


TEOS + Water + Base



[4]

Removing the Solvent



Ambient Pressure Drying (APD)

<u>Advantages</u>

- Lower Cost
- Fewer Synthesis Steps
- Easier Scalability

<u>Disadvantages</u>

- Harder to Control
- Destructive Capillary Forces

Ambient Pressure Drying

$$p_c = \frac{2\gamma\cos(\theta)}{r_c}$$

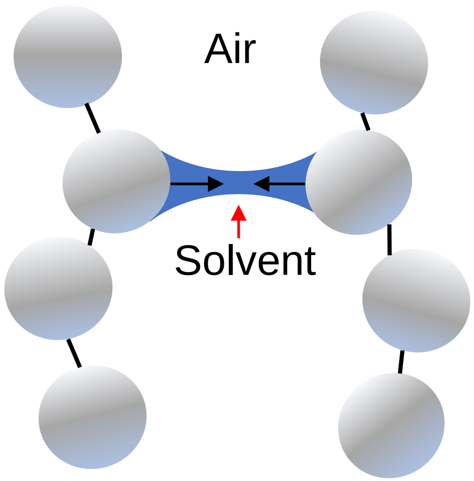
$p_c = capillary\ pressure$

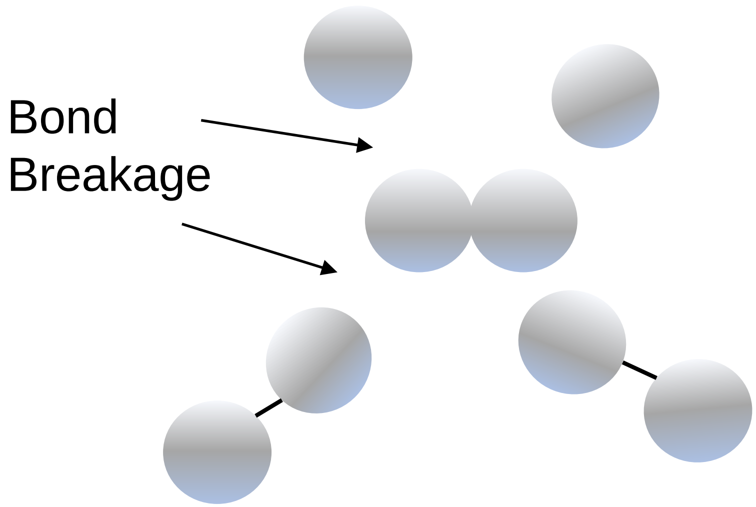
$\gamma = interfacial\ tension$

$r_c = radius\ of\ interface$

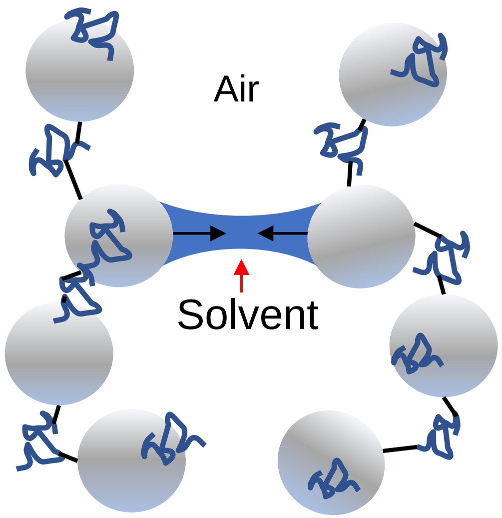
r_c = 100 µm → p_c = 0.0056 atm

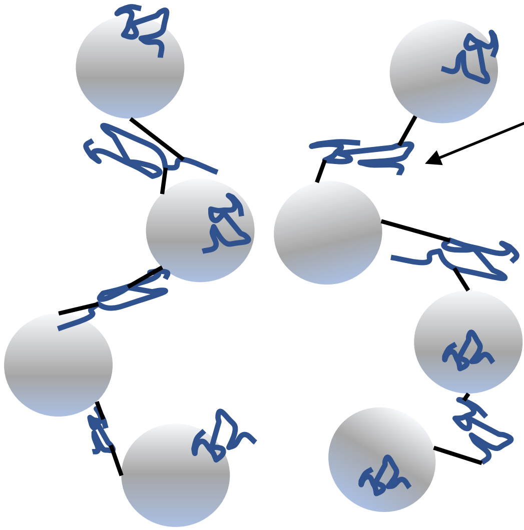
r_c = 10 nm → p_c = 56 atm

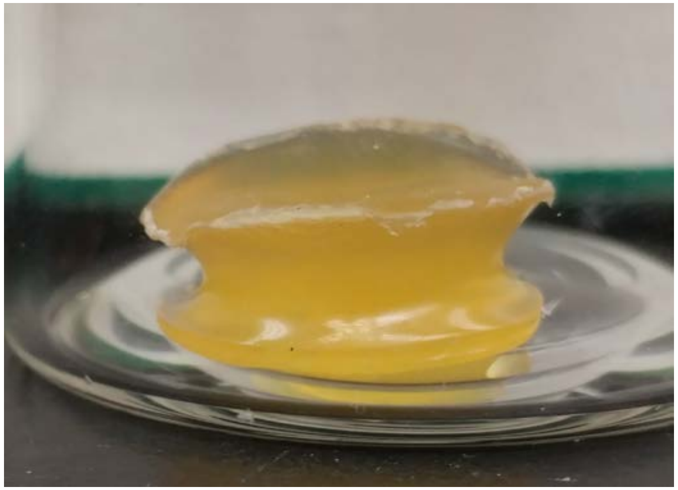




New Synthetic Approach

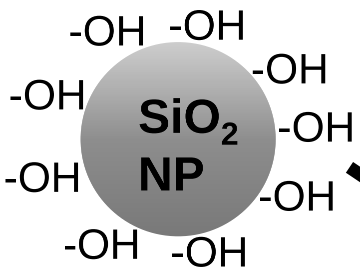




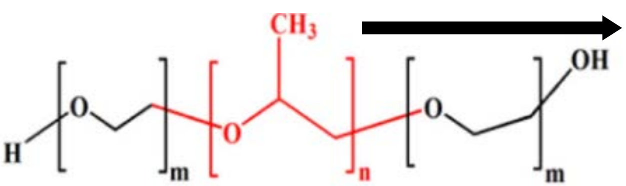


Our Approach

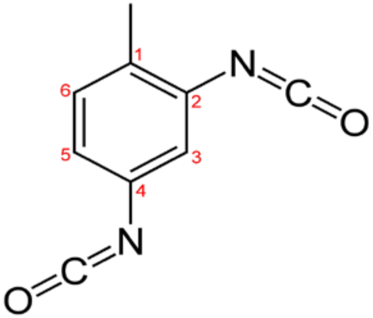
Silica Nanoparticles



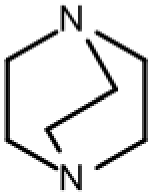
Pluronic Block-Copolymer



Toluene
Diisocyanate (TDI)

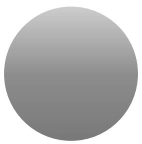


Catalyst



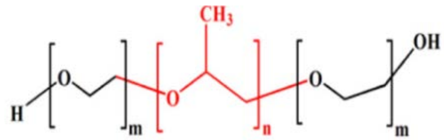
Problems Encountered

Particle and Polymer Effects
Shape and Molecular Weight



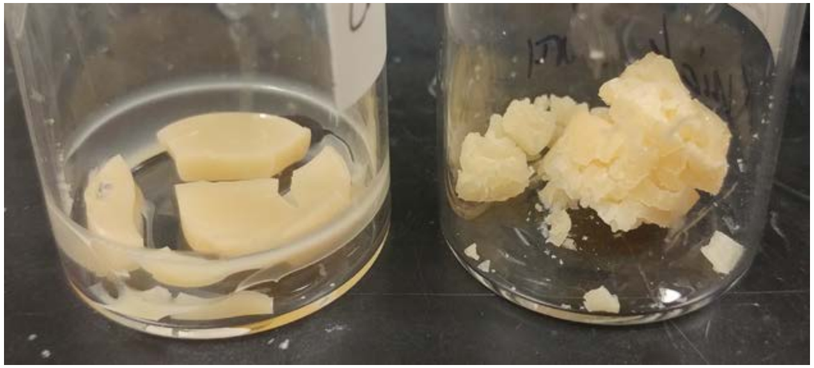
Spherical

Random



Difunctional Block-Copolymer

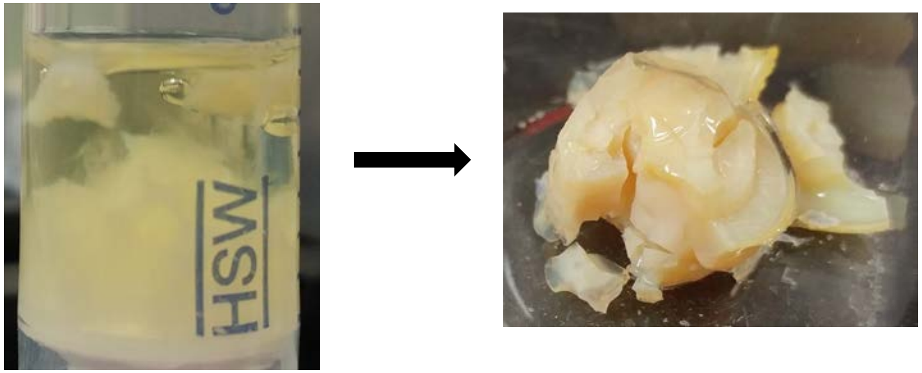
Rate of Solvent Evaporation



Slow

Fast

Phase Separation

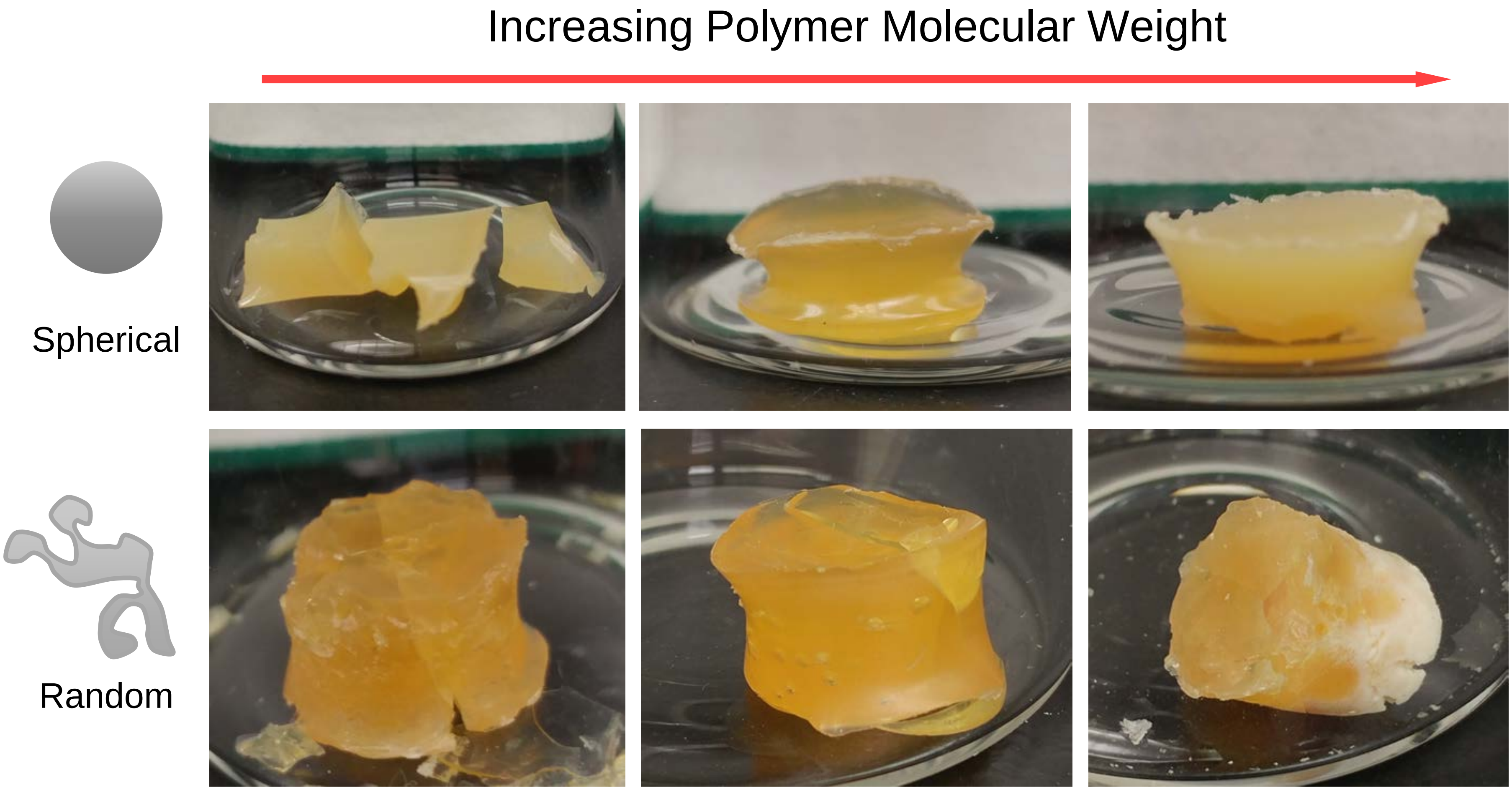


Catalyst Addition Delay after Reaction

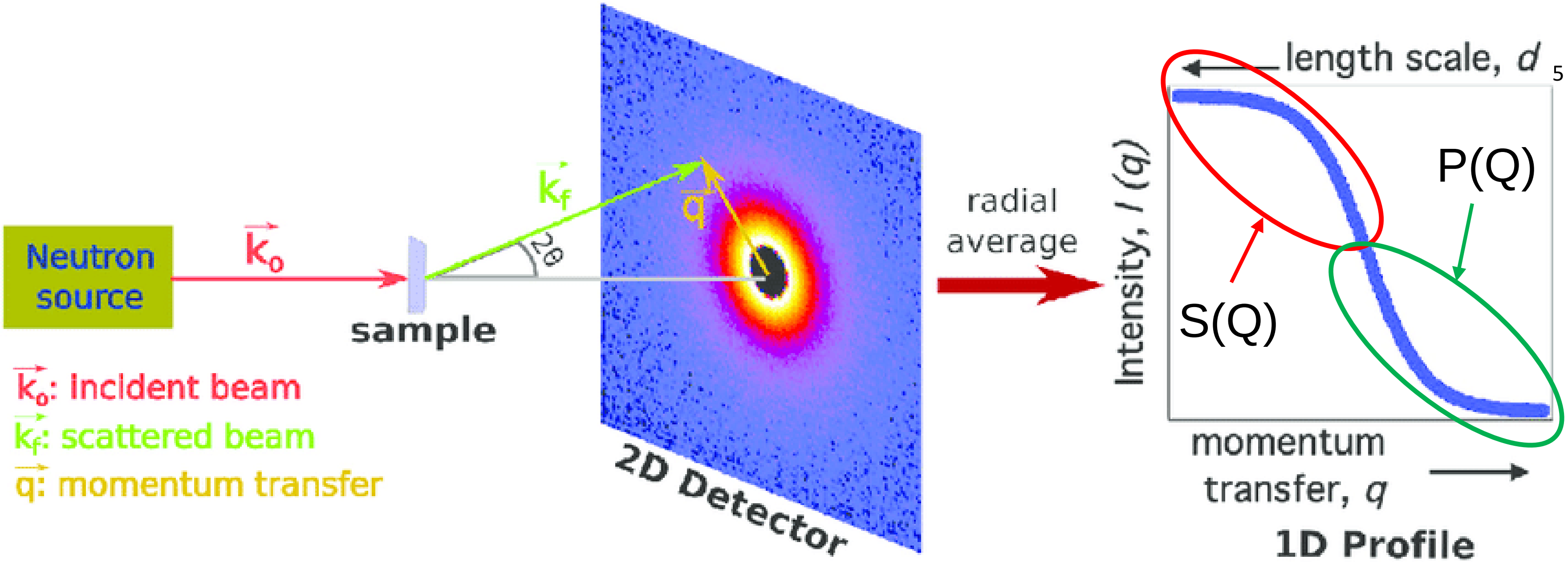
0 Hours

2 Hours

Particle and Polymer Effects



What is SANS?



[5]

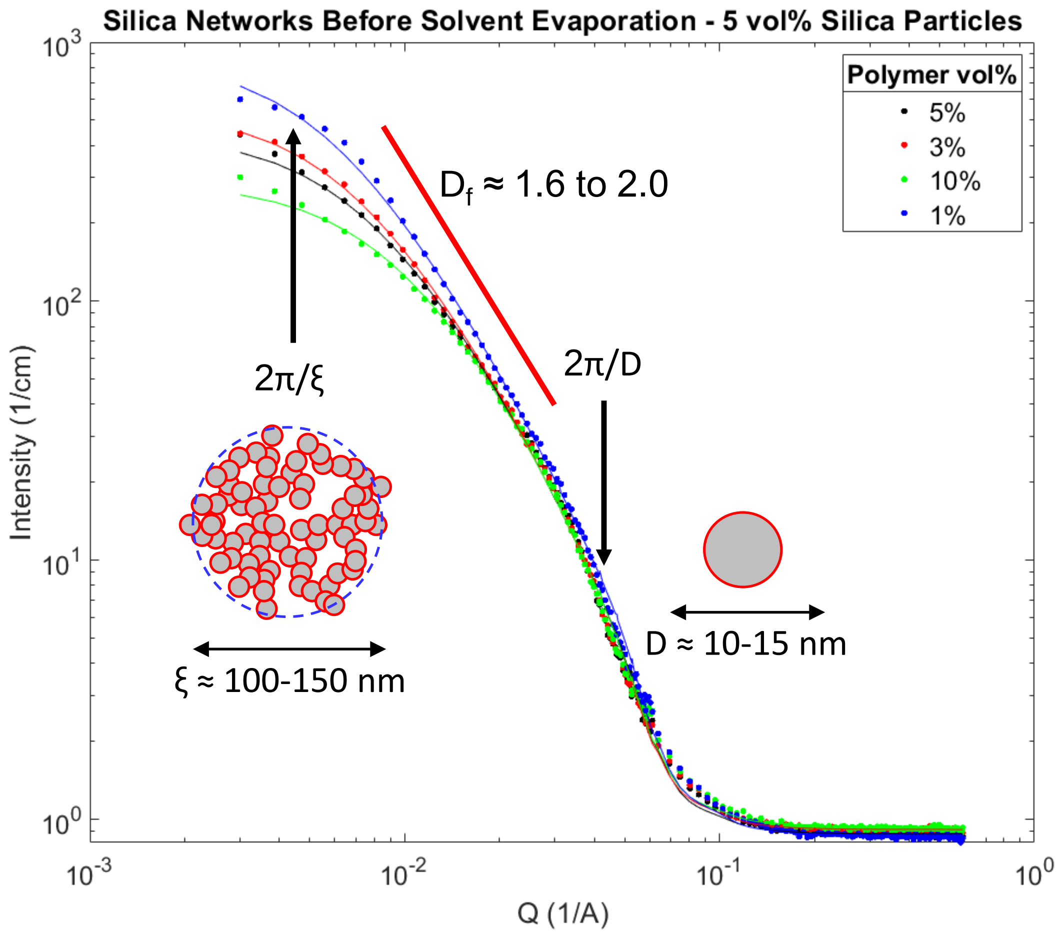
P(Q): Form Factor – particle shape, size, dispersity

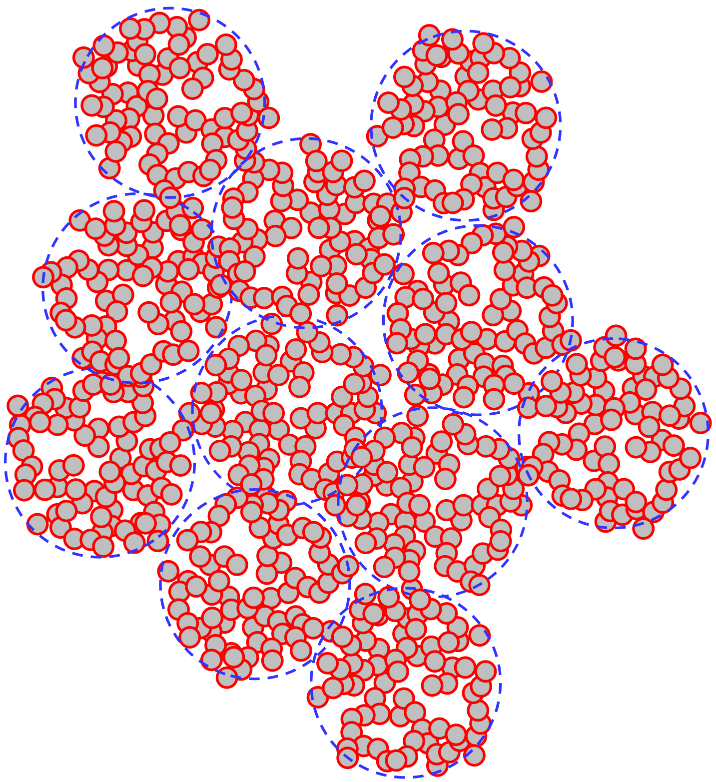
S(Q): Structure Factor – spatial distribution of particles, interactions between particles

$$q = \frac{4\pi}{\lambda}\sin(\theta)$$

5. Monica Castellanos, Maria & Mcauley, Arnold & Curtis, Joseph. (2016). Investigating Structure and Dynamics of Proteins in Amorphous Phases Using Neutron Scattering. Computational and Structural Biotechnology Journal. 15. 10.1016/j.csbj.2016.12.004.

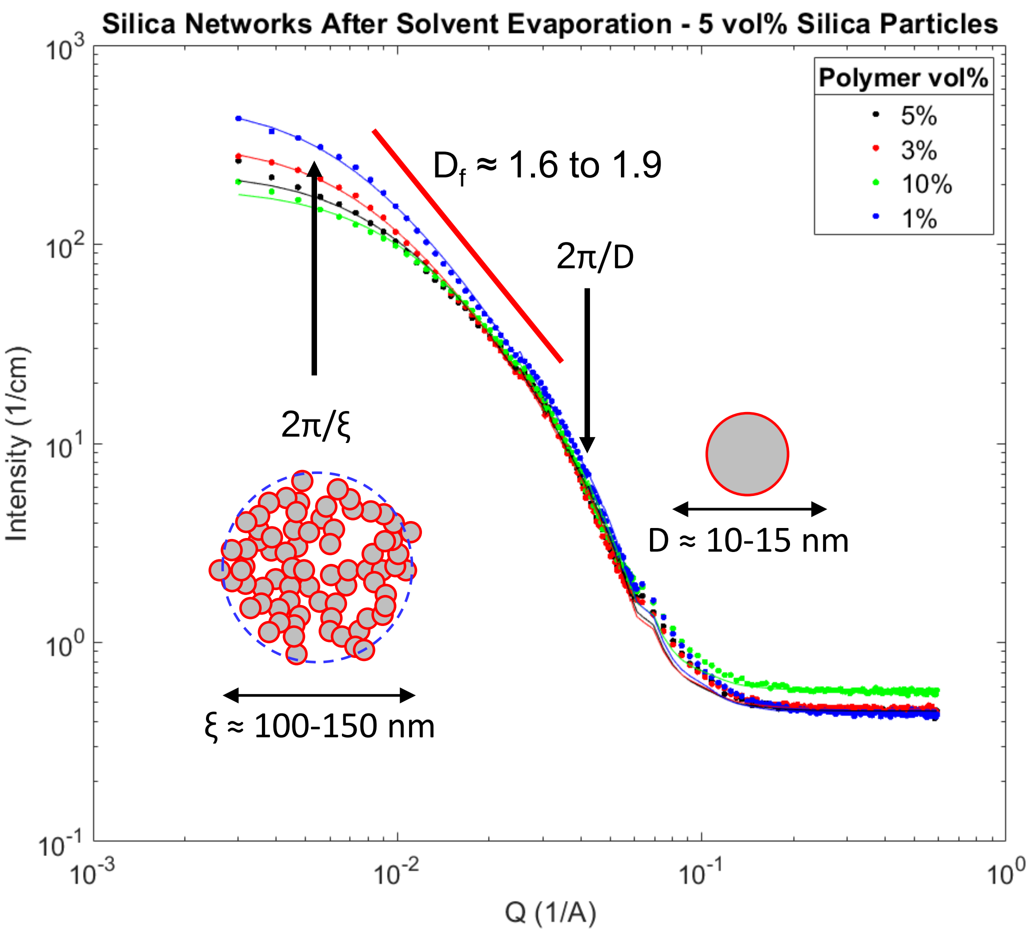
SANS *Before* Solvent Evaporation



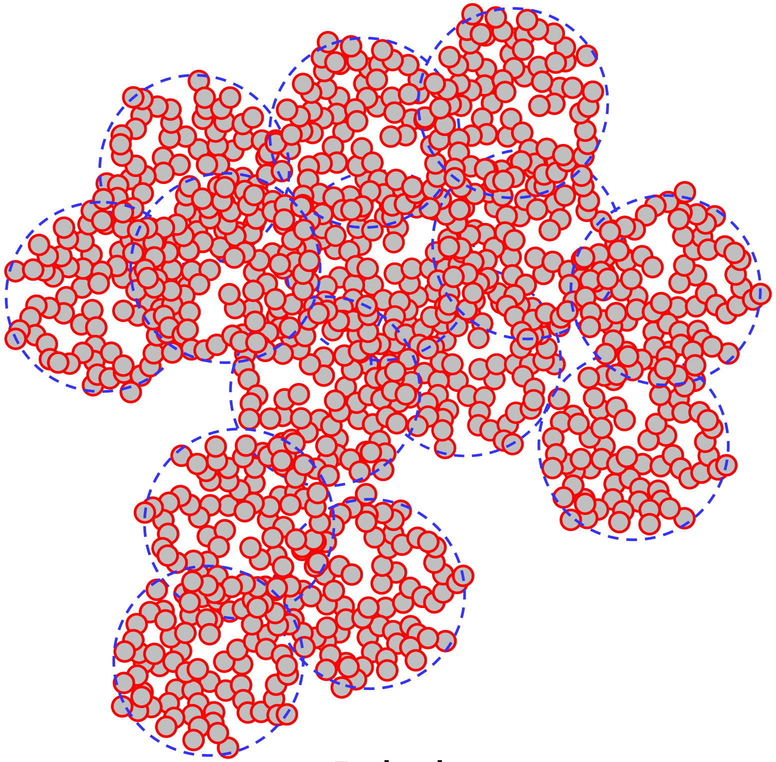


Solvated
Silica Particle
Network

SANS *After* Solvent Evaporation



Do more significant structural changes occur at larger lengths (smaller q)?

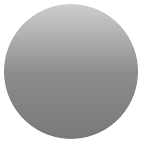


Dried
Silica Particle
Network

No major structural changes on the nanoscale

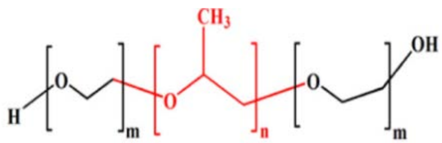
Problems Encountered

Particle and Polymer Effects
Shape and Molecular Weight



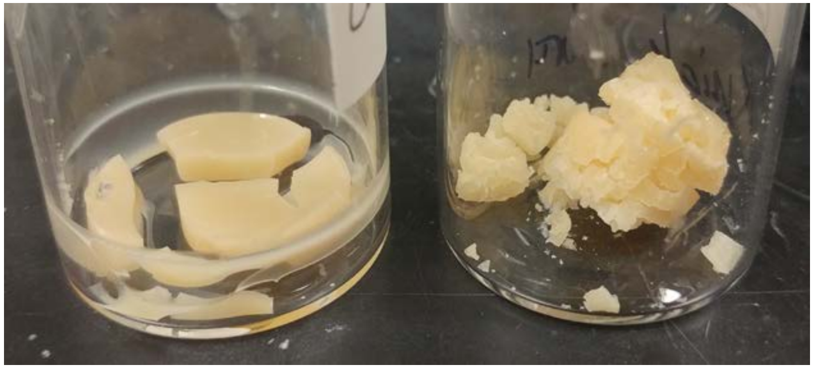
Spherical

Random



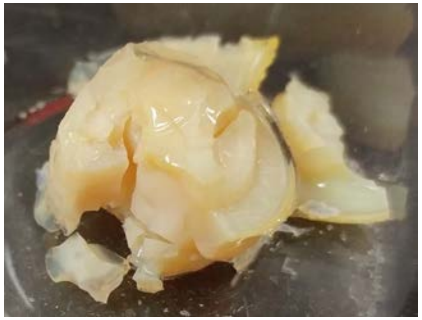
Difunctional Block-Copolymer

Rate of Solvent Evaporation



Slow Fast

Phase Separation



Catalyst Addition Delay after Reaction

0 Hours

1.5 Hours

Summary of Key Results

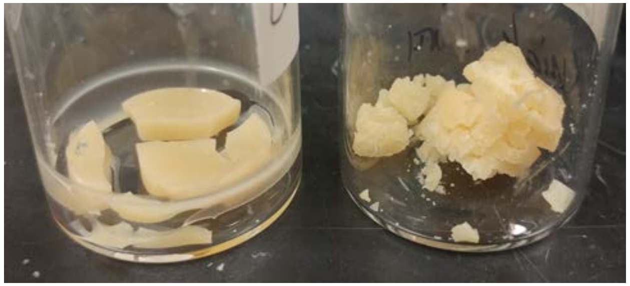
- Incubation time of ~2 hours greatly increases structural integrity

0 hours

1.5 hours

- Slow solvent evaporation dispenses stresses

Slow Fast



- Optimum polymer additive molecular weight ~ 3800 g/mol

1100 g/mol

3750 g/mol

Future Work

- Quantify effect of particle shape, size, and structure
- Mitigate phase separation using incubation times and solvent variations
- Use uSANS for larger length-scale probing
- Measure accessible surface area and thermal conductivity

Acknowledgements

- Ryan Murphy – Mentor
- Katie Weigandt - Co-Mentor
- Julie Borchers, Joe Dura – NCNR SURF Directors