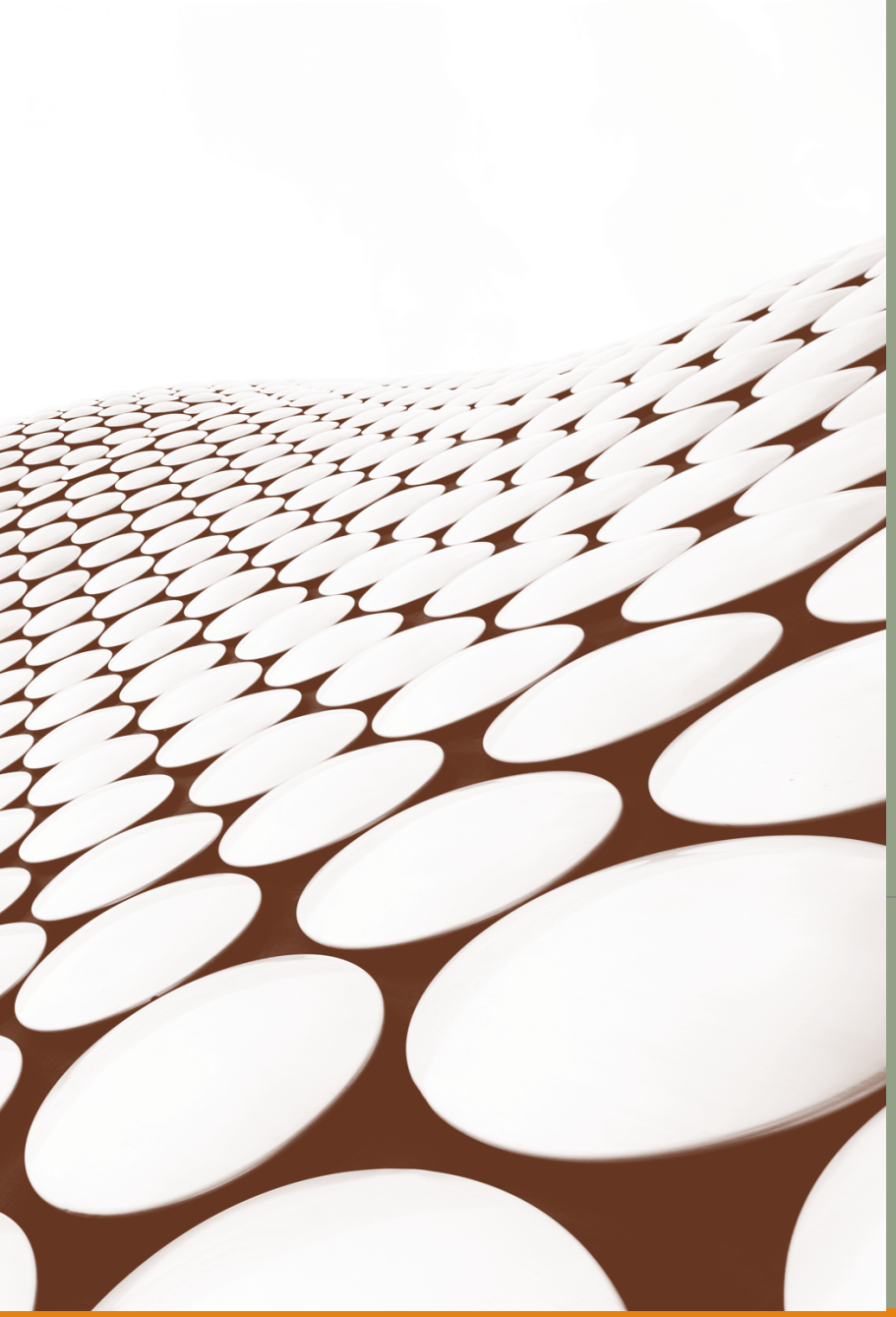


When Polymers Meet: Self-Assembled Amphiphilic Diblock Copolymers

CANDYCE COLLINS, DR. KATIE WEIGANDT, DR. AVANISH BHARATI

AUGUST 3RD ,2019

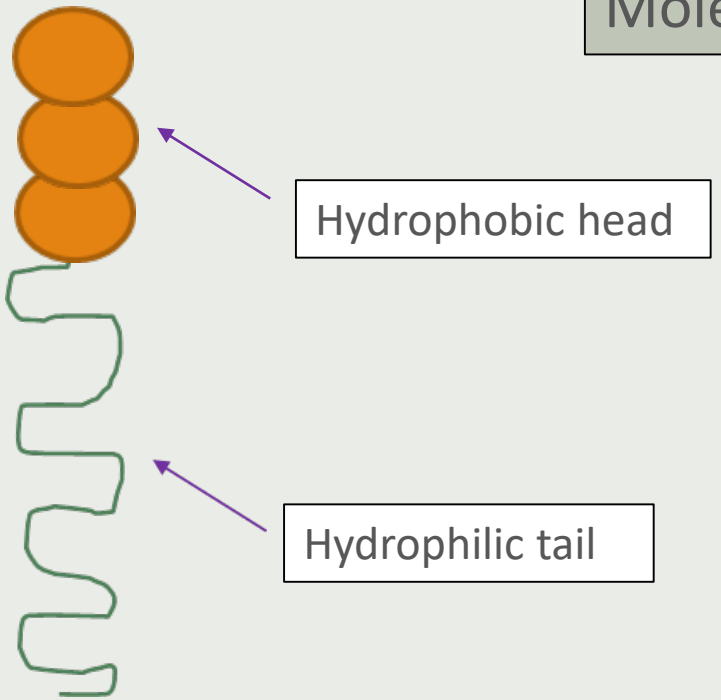
NIST-SURF

Self-Assembly

Colloids

Self-Assembly in micelles:

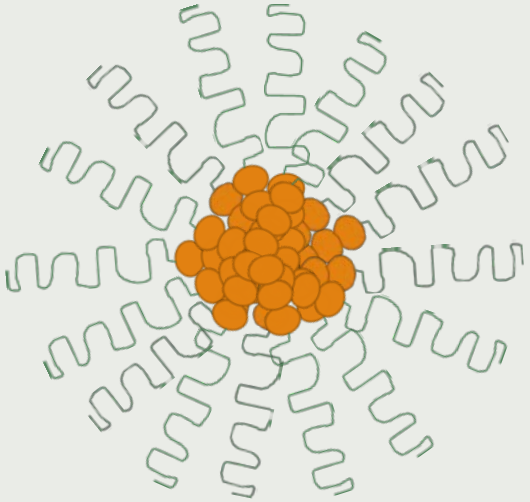
Molecular crystals



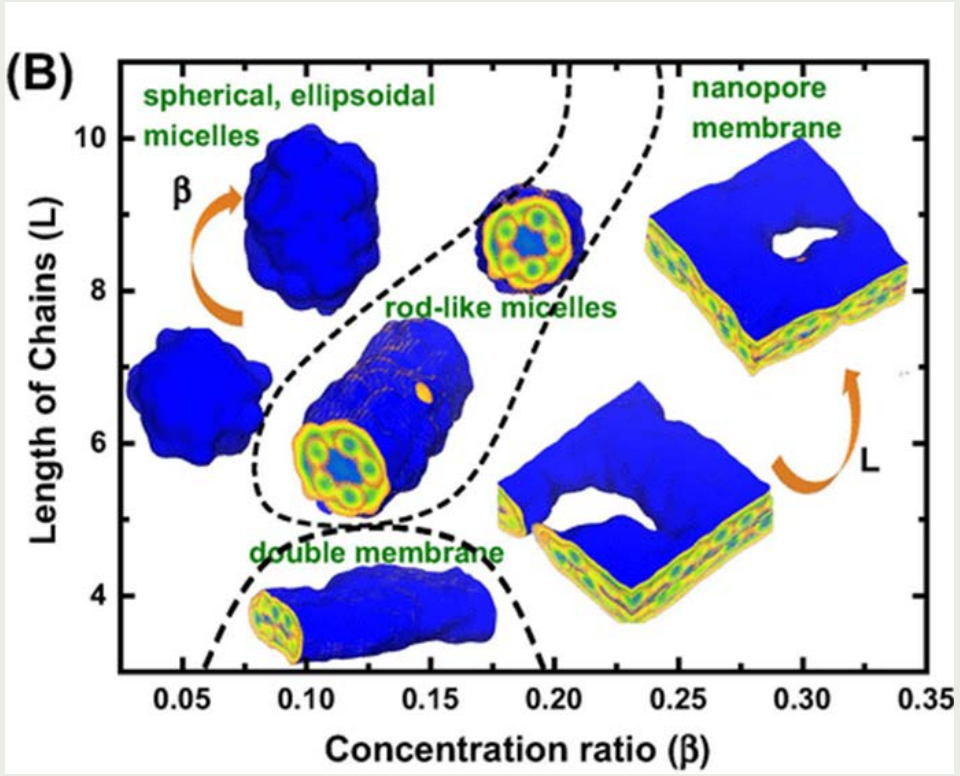
Hydrophobic head

Hydrophilic tail

Micelles



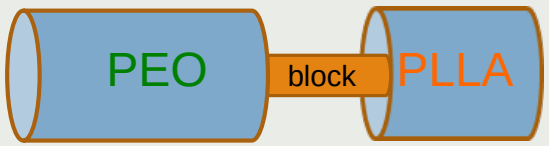
Lipid bilayers



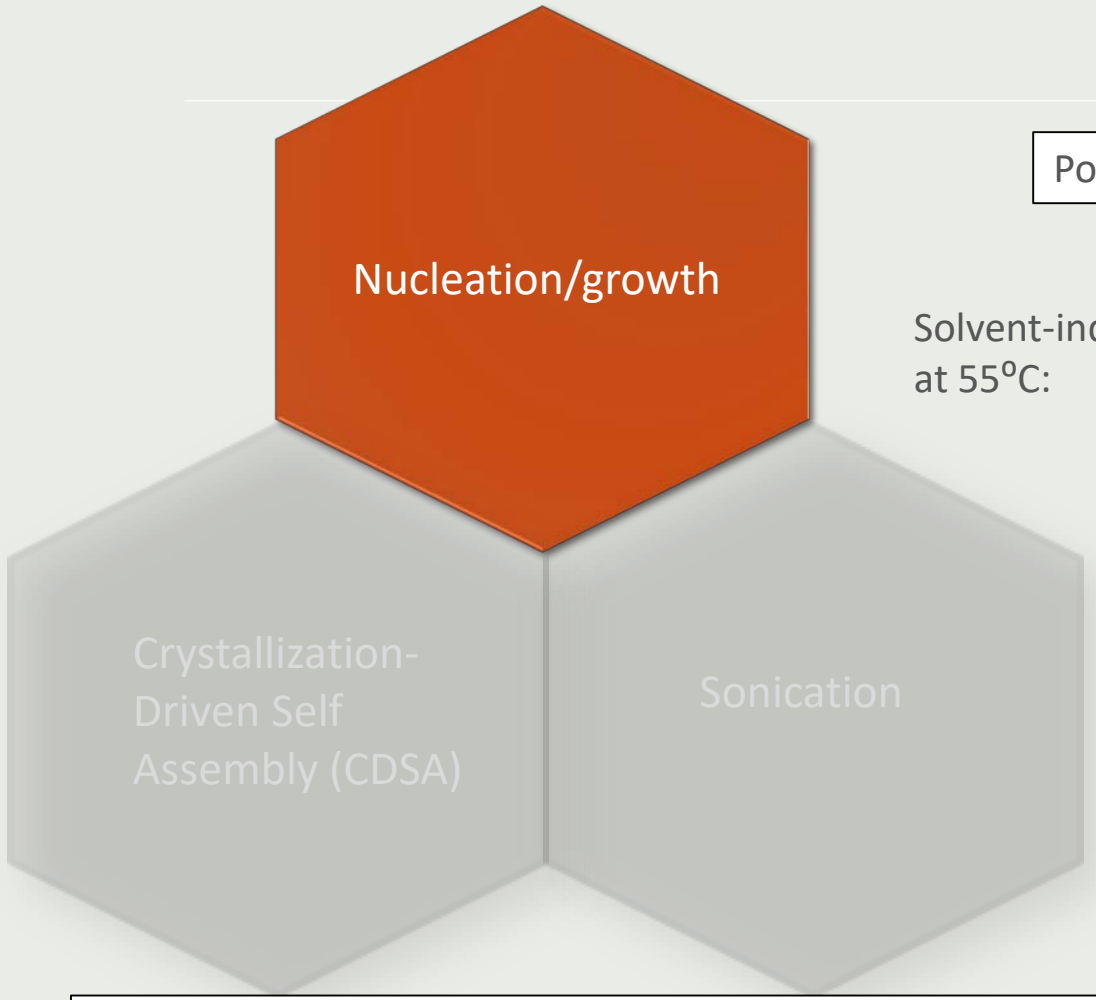
Song, Xianyu et. Al. (2018).

What does self-assembly have to do with this research?

How does diblock ratio and solvent quality effect the shape and size of particles?



Nucleation and Growth



Polymer solution

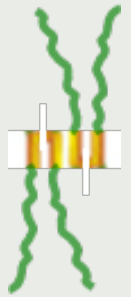
Solvent-induced crystallization at 55°C:

soluble insoluble

block A block B

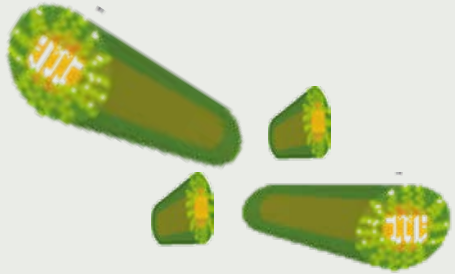
Crystallization in solution

Block B



Amorphous corona (flexible chains)

Crystalline core (folded chains)

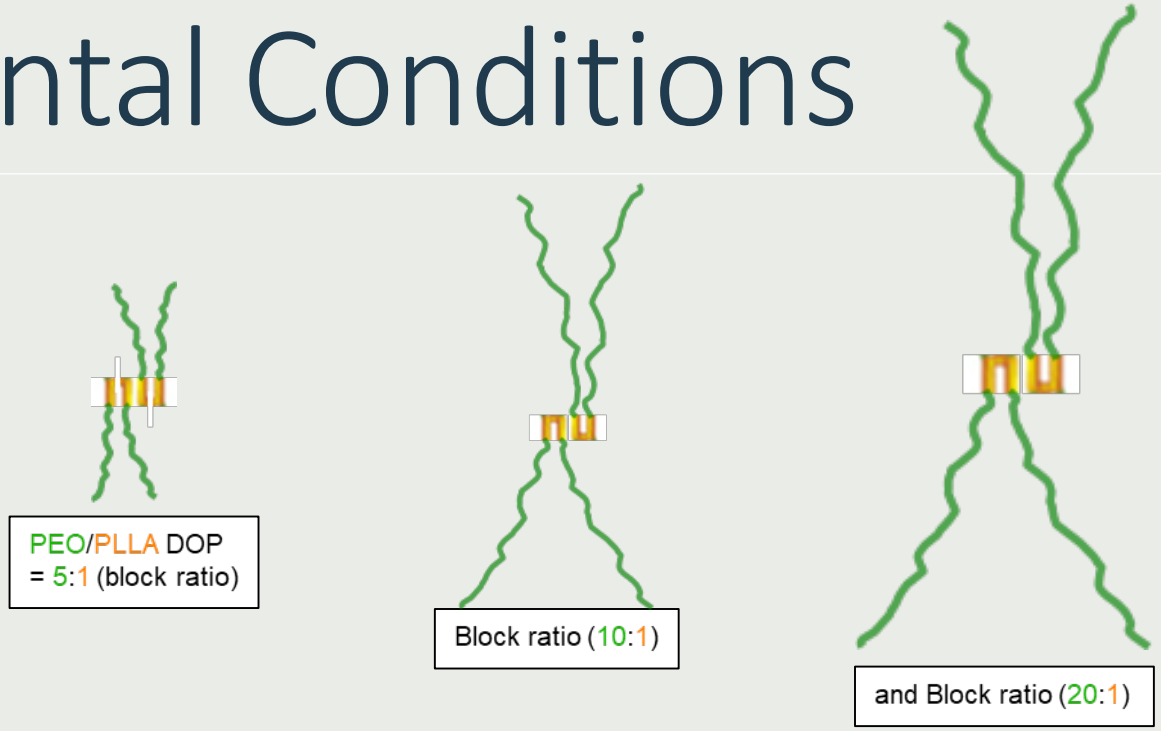


Poly-dispersed structures (pre-seed)

Near crystallization temperature slowly alter the solvent quality to a good solvent for the corona and theta solvent for the crystallizing core

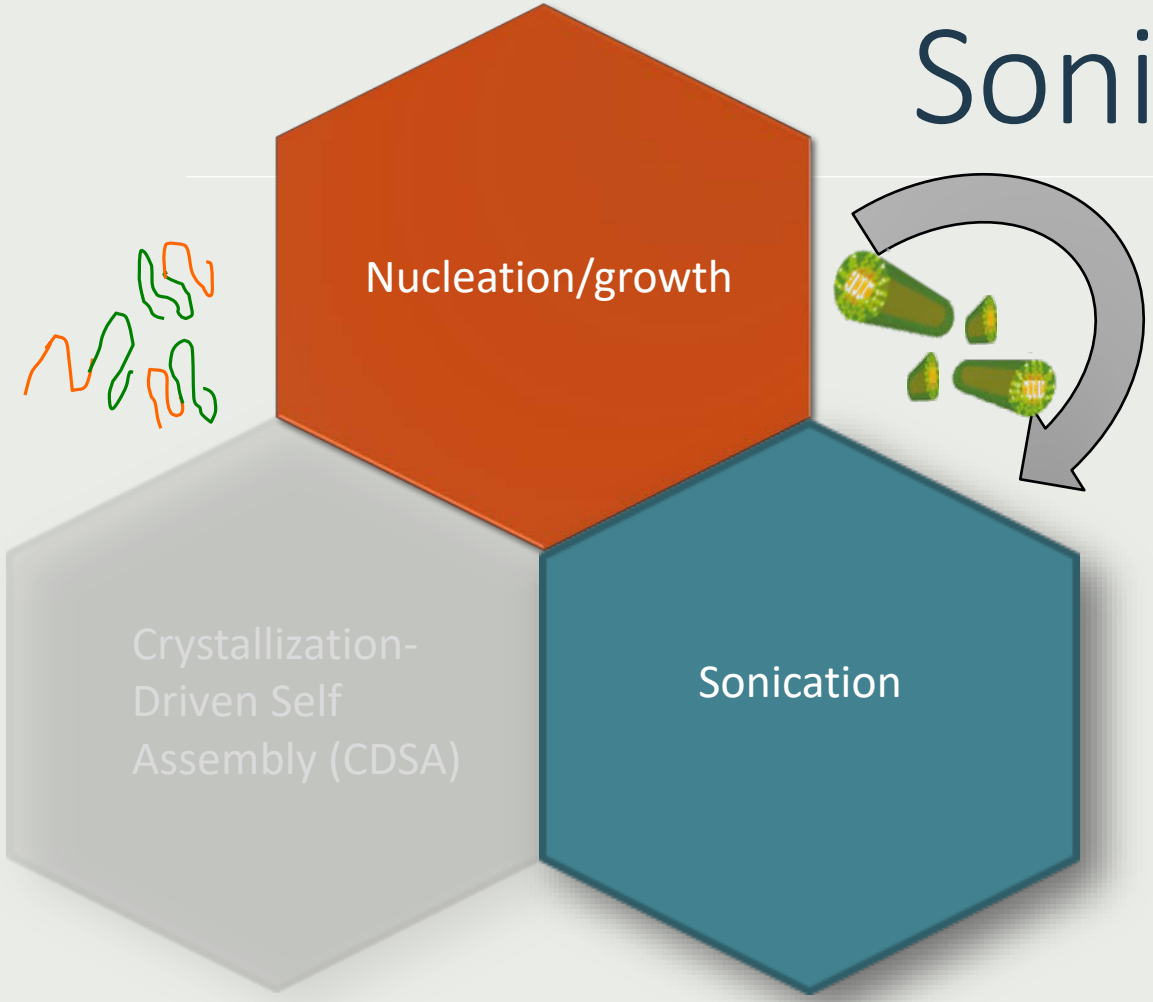
Experimental Conditions

Conditions/Parameters varied:

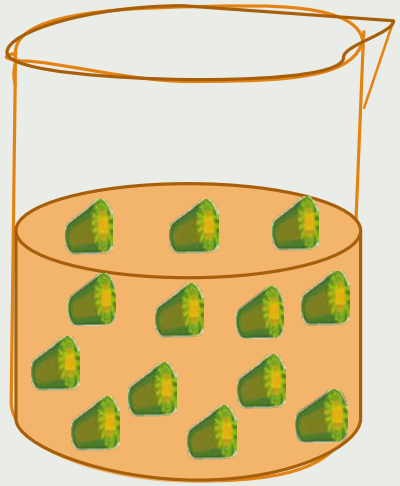


- Solvent quality
  - THF/D_2O ✗
  - Acetone/D_2O ✔ (forms a homogeneous mixture at all experimental temperatures and compositions – inferred from Dynamic Light Scattering and Small-angle Neutron Scattering)

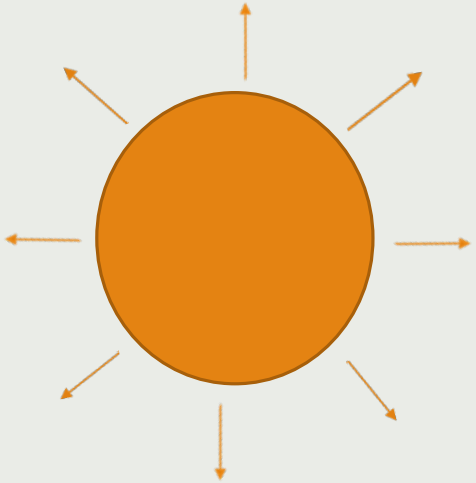
Sonication



Mono-dispersed structures (seed)

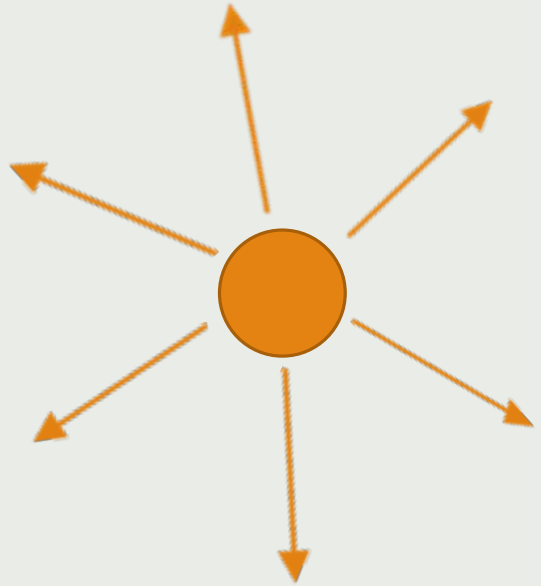


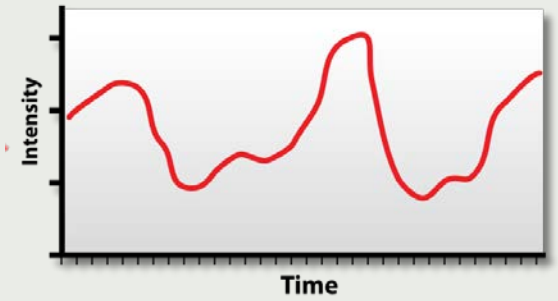
Dynamic Light Scattering (DLS)



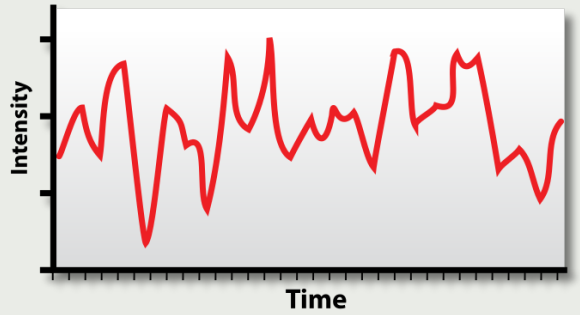
$$D = \frac{k_B T}{6\pi\eta r}$$

D – Diffusion constant
K_B – Boltzmann's constant
T – Temperature
η – Viscosity (solvent)
r – Radius of the spherical particle

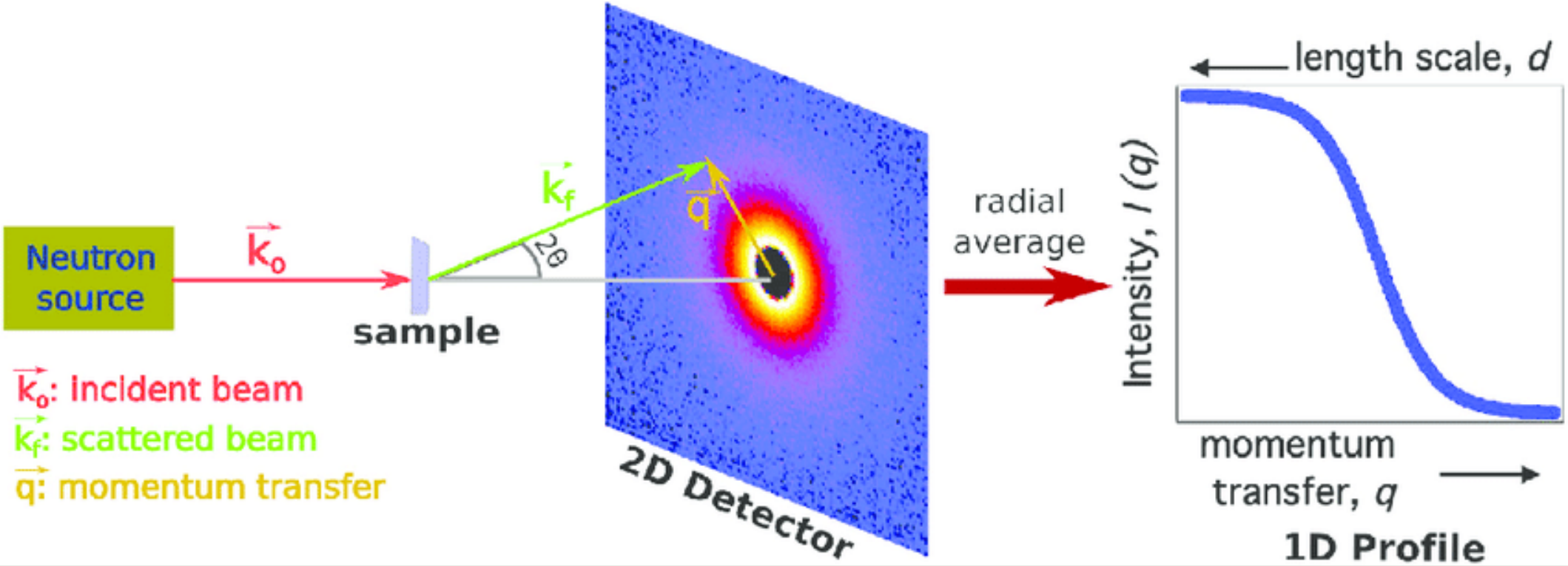




Conditions	Hydrodynamic radius in nm [r]	% Polydispersity (in size)
Pre Seeds	~ 450	~ 45
Seeds	~ 80.0	~ 8.0



Small-Angle Neutron Scattering (SANS)

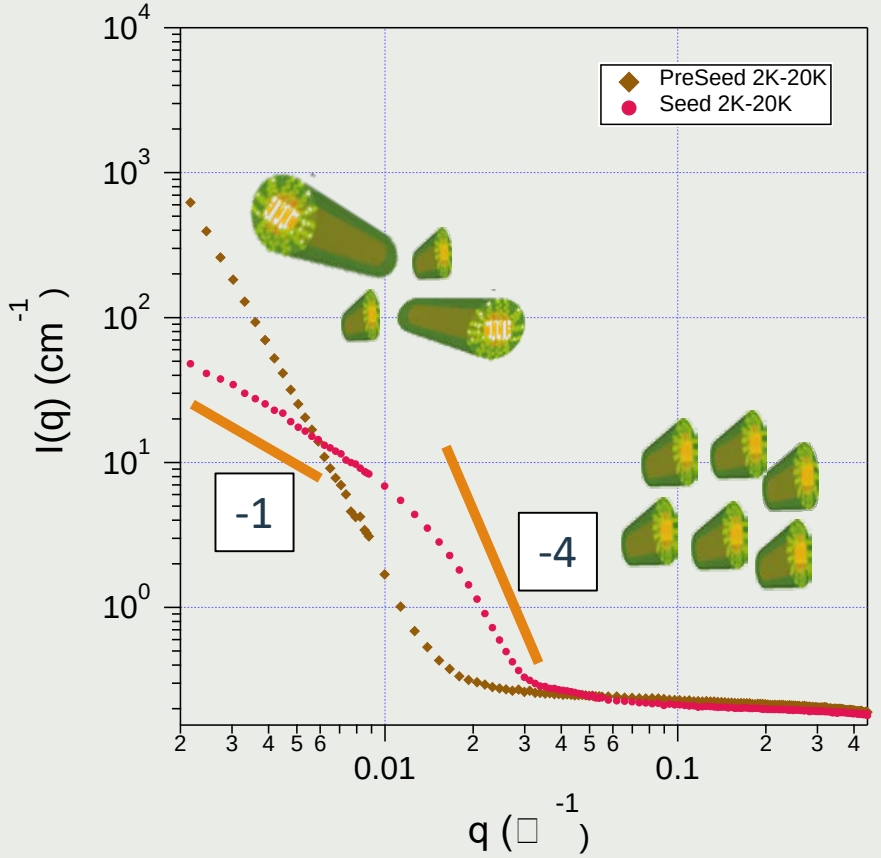


Monica Castellanos, et. Al.(2016)

Neutron beam source → sample → 2D detector and reads the information with intensity (I, q) and momentum transfer (q)

1D Small-Angle Neutron Scattering (SANS)

Preseeds vs seeds



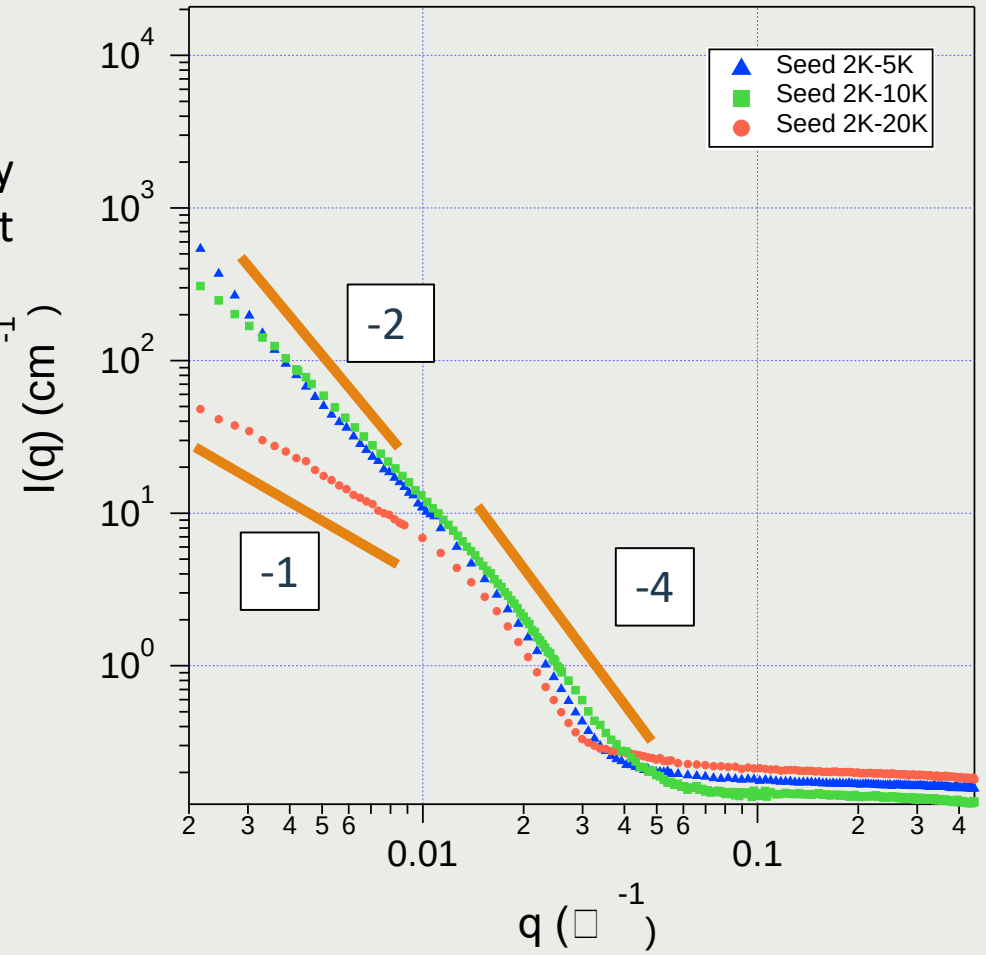
Sonication resulted in smaller structures.

Temperature: 55°C
Solvent: 10 wt % Acetone to D_2O

SANS on Seeds

Effect of block ratio:

Increasing the block asymmetry resulted in particles of different shapes.

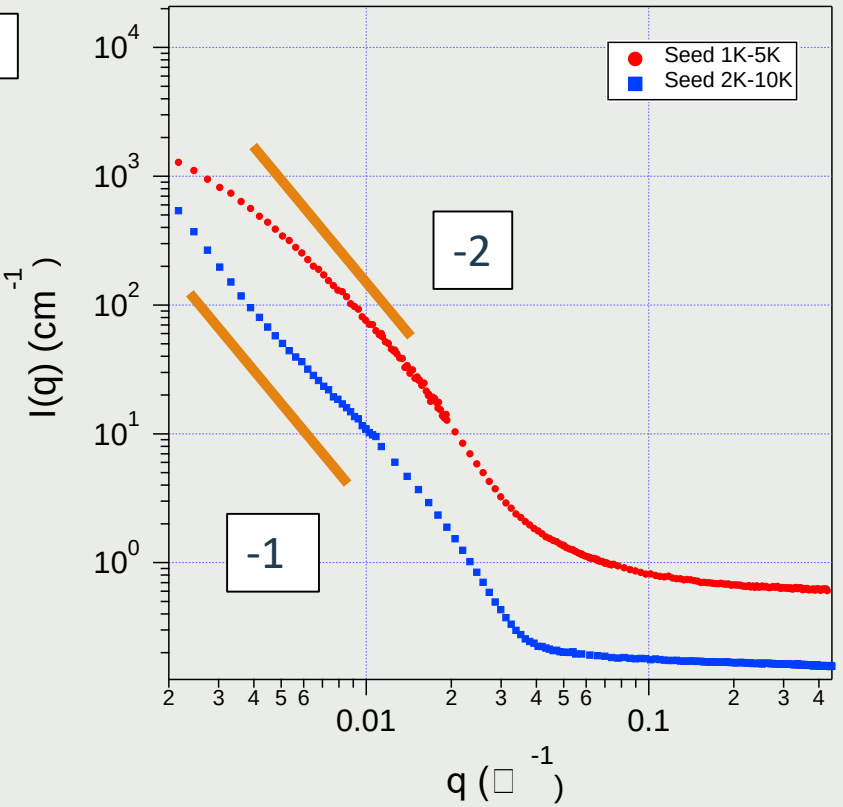


Temperature: 55°C
Solvent: 10 wt % Acetone to D_2O

SANS on Seeds

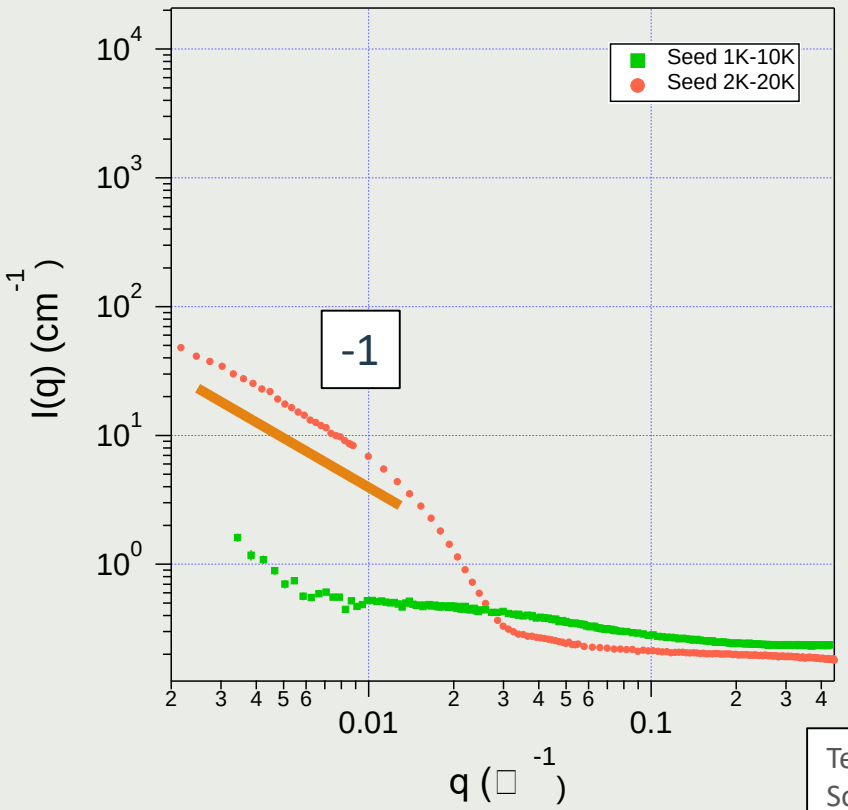
Effect of PLLA length for a fixed block ratio

Block ratio of 1:5



PLLA length effects the shape of particles

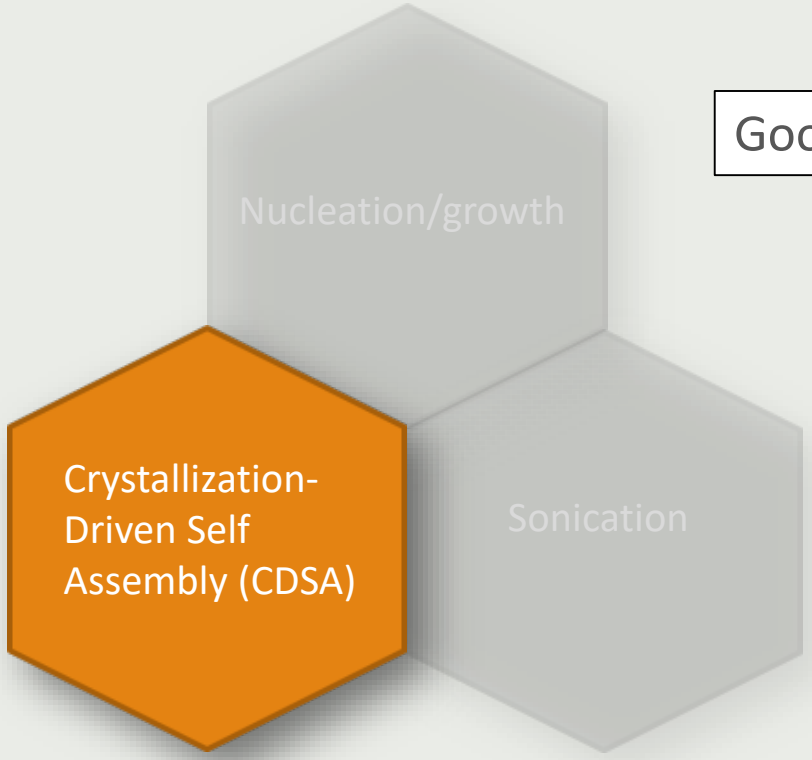
Block ratio of 1:10



Temperature: 55°C
Solvent: 10 wt % Acetone to D_2O

Small PLLA in highly asymmetric blocks do not undergo self-assembly

Crystallization-Driven Self Assembly (CDSA): Tuning aspect ratio



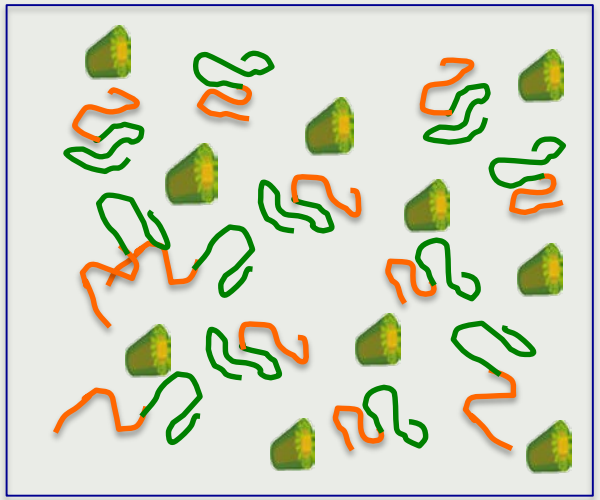
Good solvent for PEO corona and marginal to bad solvent for PLLA core

Basic idea:

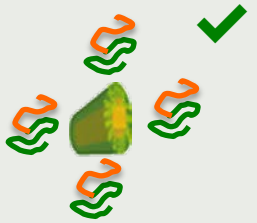
Minimize self-nucleation of micelles

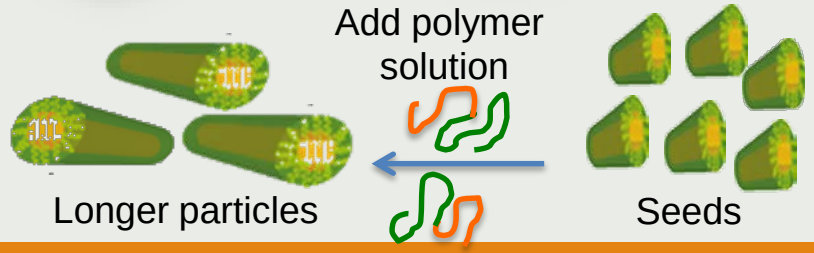
Minimize the propensity of seeds to attach and grow

Promote stable seeds and epitaxial growth of polymers on seeds



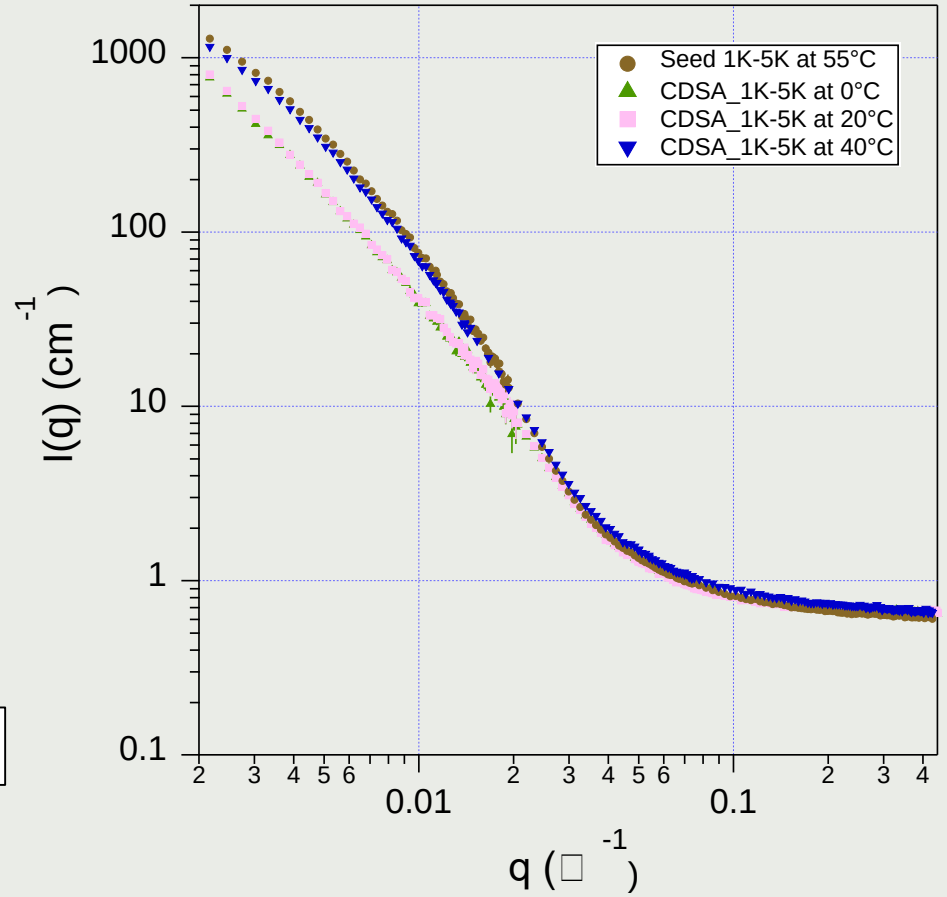
Aim: Long fairly Mono-dispersed structures





Thank you

SANS data on Seeds and CDSA: Choosing the appropriate temperature



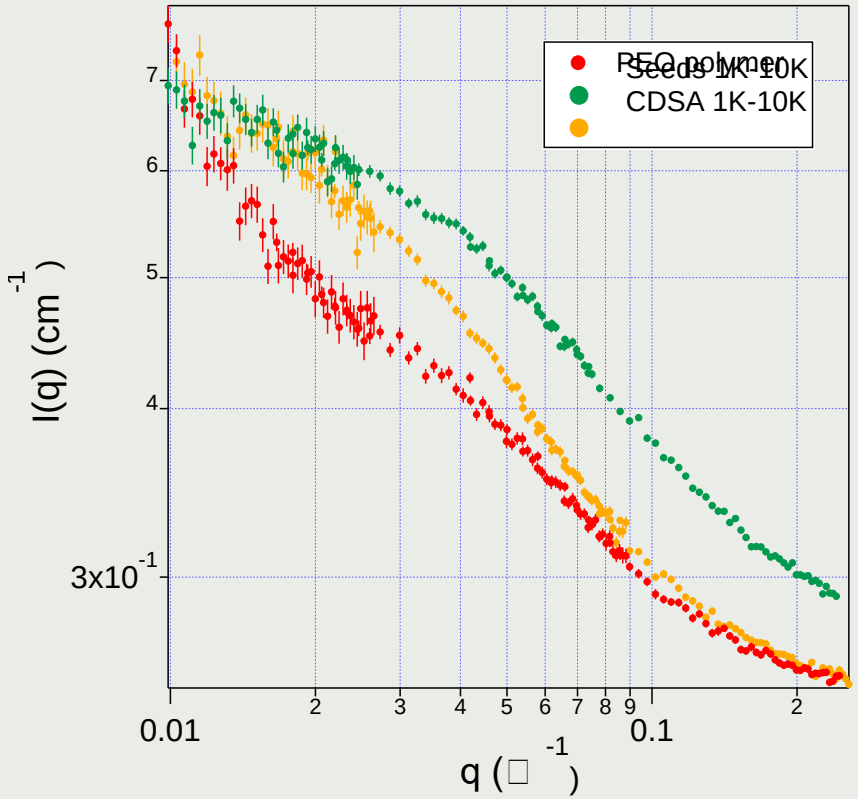
Effective concentration: ~5-10 mg/mL
Solvent: 10 wt % Acetone to D_2O

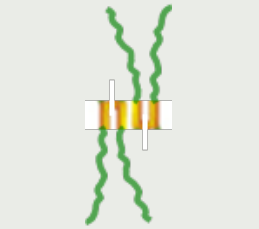
Seeds (1K-5K) vs CDSA (1:1)

The shape of the particle is unaffected at 40°C

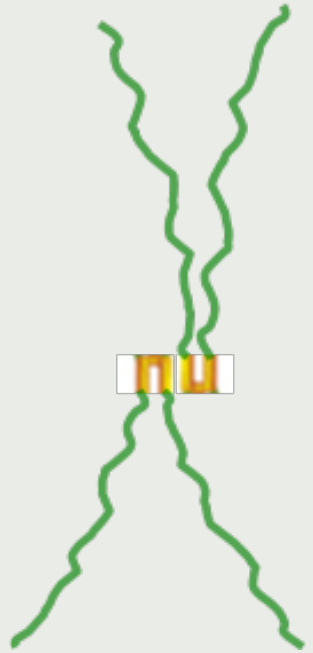
SANS data on Seeds and CDSA for short and highly asymmetric diblocks

CDSA temperature is 40°C





PEO/PLLA DOP
= 5:1 (block ratio)



and Block ratio (20:1)

Seed response is similar to that of PEO of the corresponding length: no self-assembly occurs

On-going and Future Research

- Preparing seeds and CDSA for 1K-7.5K and 2K-15K to form 1D particles with varying aspect ratio.
- In the future, the findings will provide a toolbox of particles with varying aspect ratio to answer the fundamental questions relevant to the flow behavior of soft materials.

Acknowledgements

NCNR:
Julie Borchers
Joe Dura
Katie Weigandt
Avanish Bharati
Ryan Murphy
Elizabeth Kelley
SURF Fellows NCNR Soft Matter Group

Fayetteville State University:
Cevdet Akbay
Zhiping Luo
Gibin George

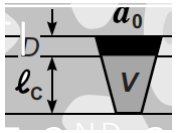
Facilitate the formation of 1-dimensional rod-like structures

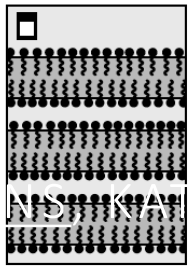
Decrease the thickness to broaden the accessible length

Currently used

PEO/PLLA DOP
= 5:1 (block ratio)

$$P = \frac{V}{a_0 l_c}$$

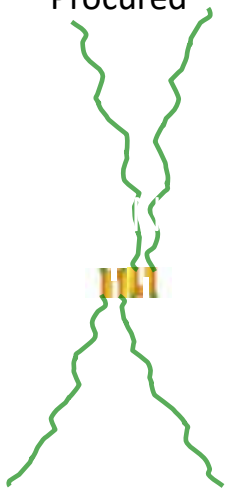




Lamellar

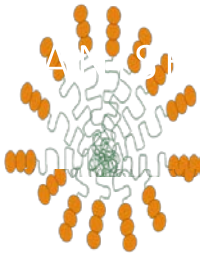
$$\frac{V}{a_0 \ell_c} \approx 1$$

Procured



Block ratio (10:1)

Increase l_c more rapidly than V



and Block ratio (20:1)

Procured

$$P = \frac{V}{a_0 l_c}$$

Increasing the length of PEO block for fixed PLLA block

Reference samples

Only PLLA polymer

PEO with increasing M_n as in the diblocks