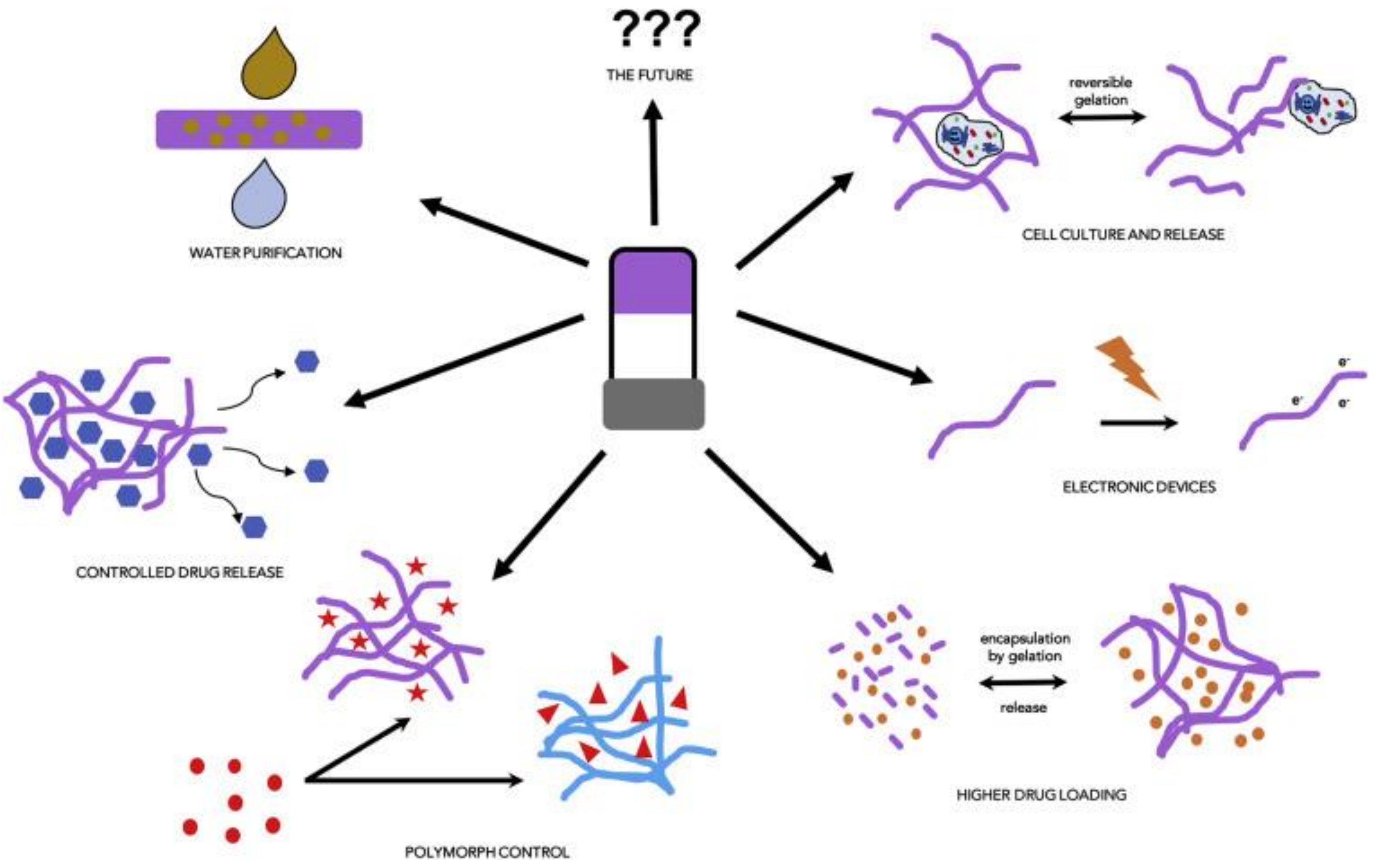
Self Assembled Soft Matter: Using SAXS

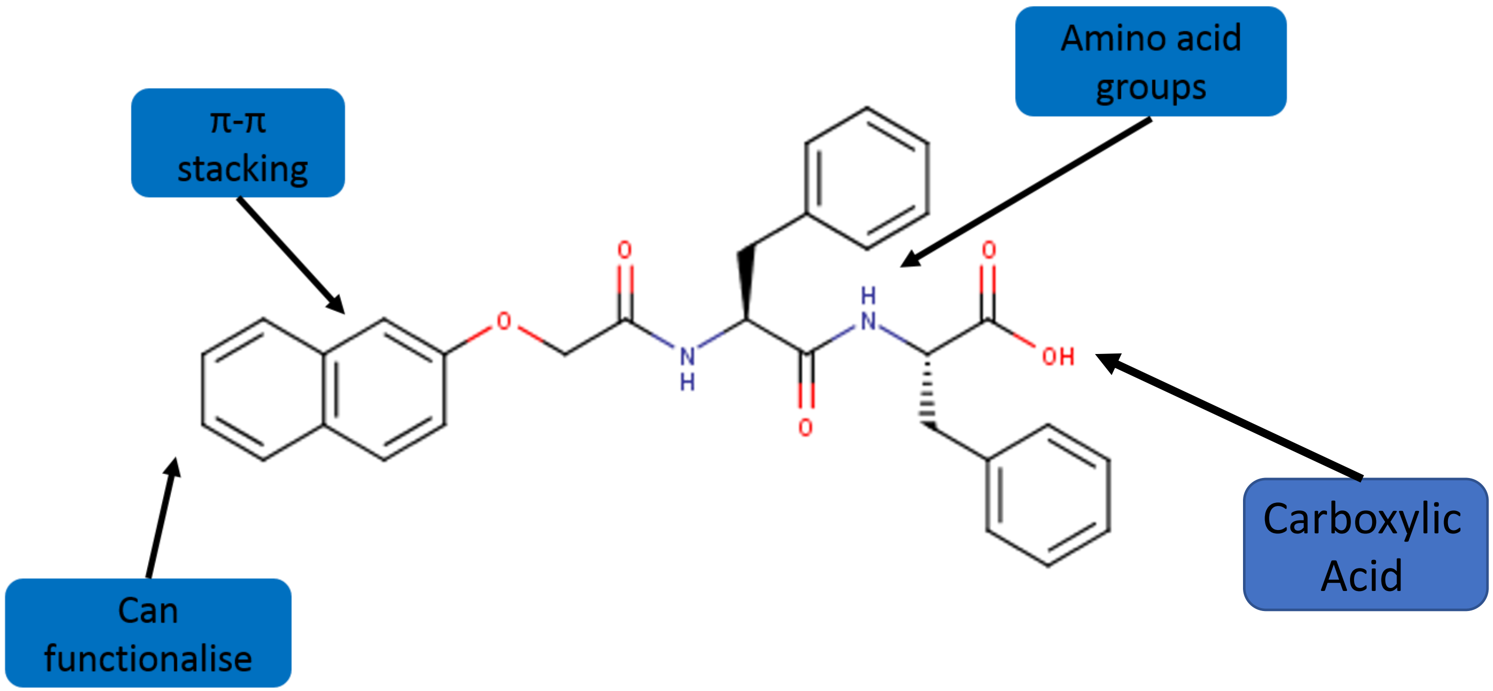
Kate McAulay, Ana Mari Fuentes Caparrós, Lisa Thomson and Dave Adams.

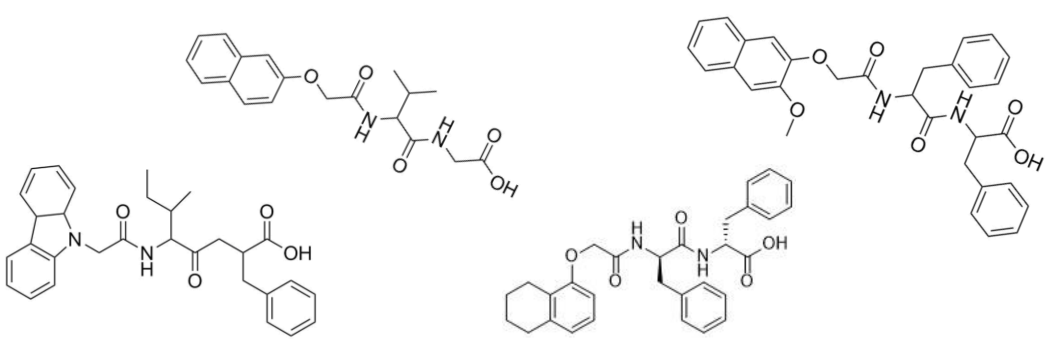
Background | Hydrogels



E. R. Draper and D. J. Adams, *Chem*, 2017, **3**, 390-410

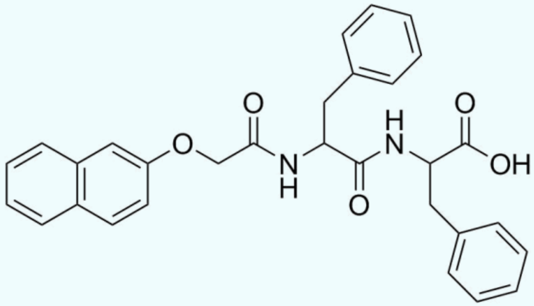
Background | Low Molecular Weight Gelators (LMWGs)



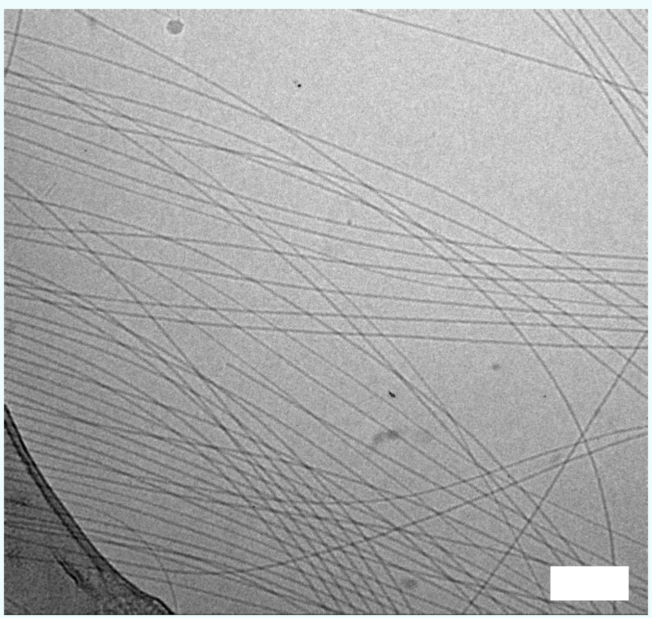


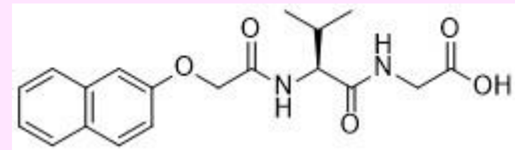
2NapFF Solutions at pH 11:

Background | Micelles at High pH

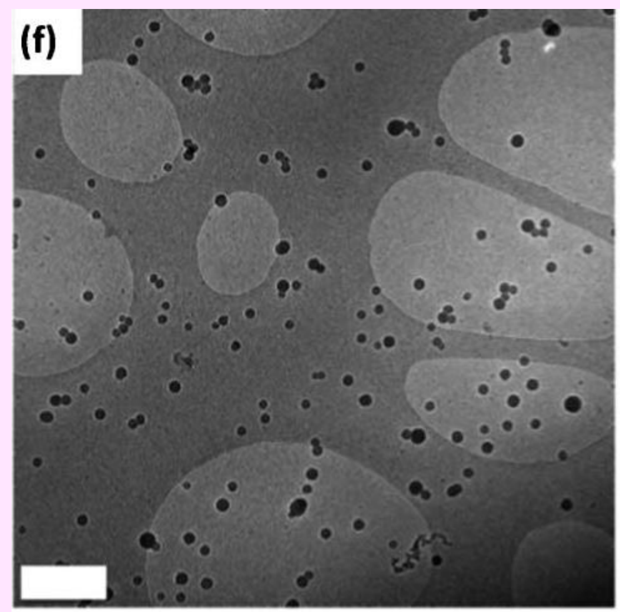


Very hydrophobic = anisotropic, persistent structures (worm-like micelles)

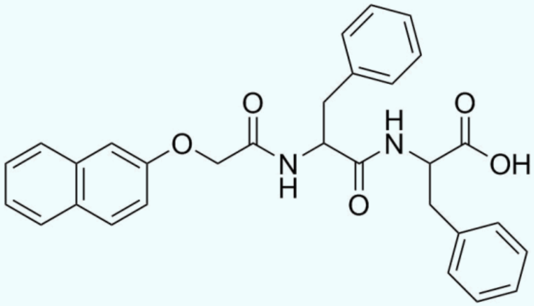




Less hydrophobic = less persistent structures (spherical micelles/aggregates)



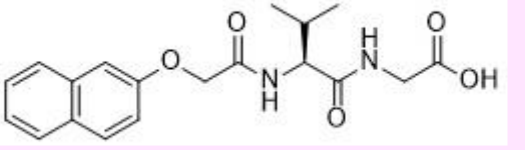
Background | Micelles at High pH



Very hydrophobic = anisotropic, persistent structures (worm-like micelles)

SAXS/SANS: Highly scattering at high pH

Normally fit to flexible cylinder or hollow cylinder

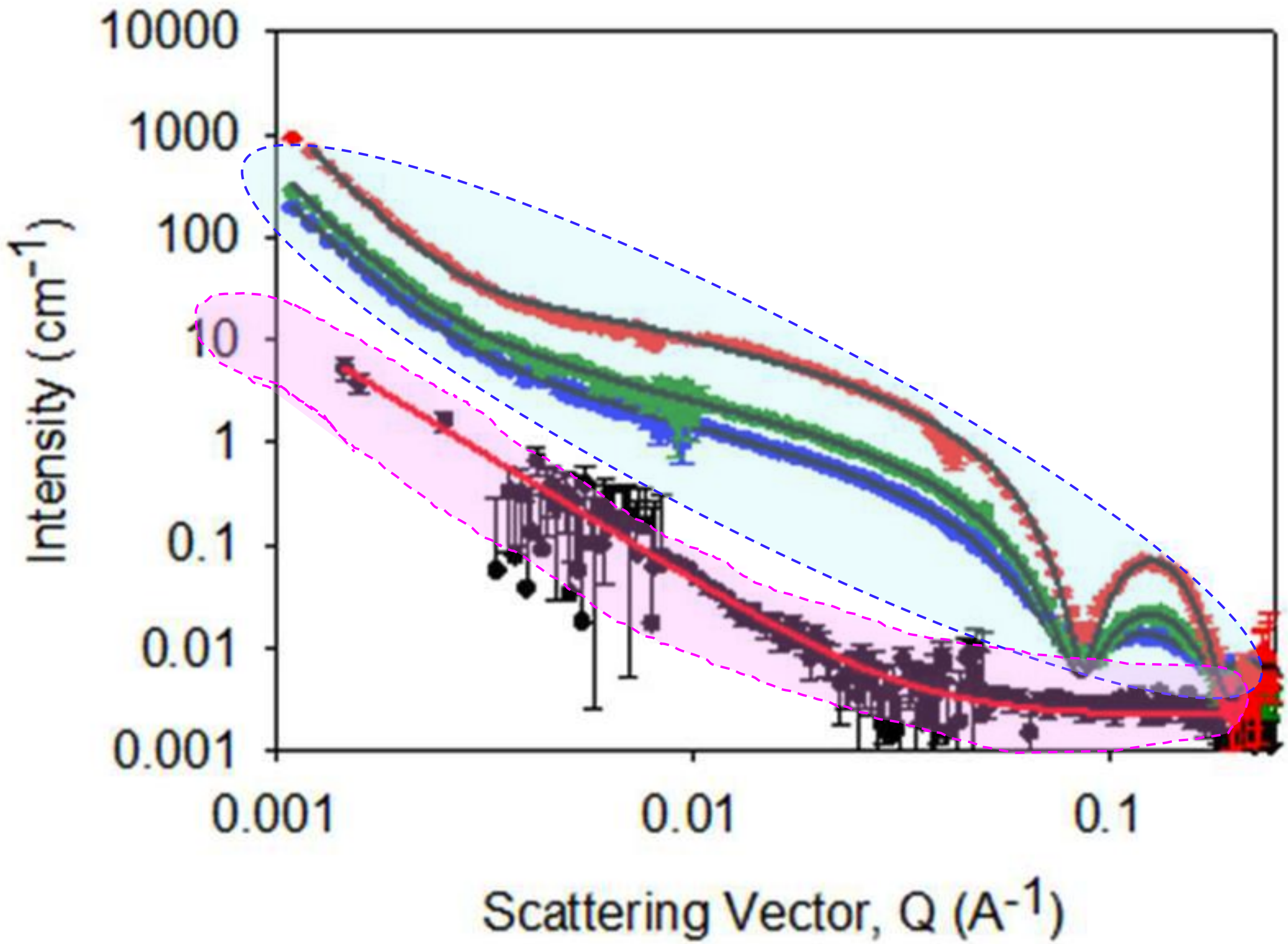


Less hydrophobic = less persistent structures (spherical micelles/aggregates)

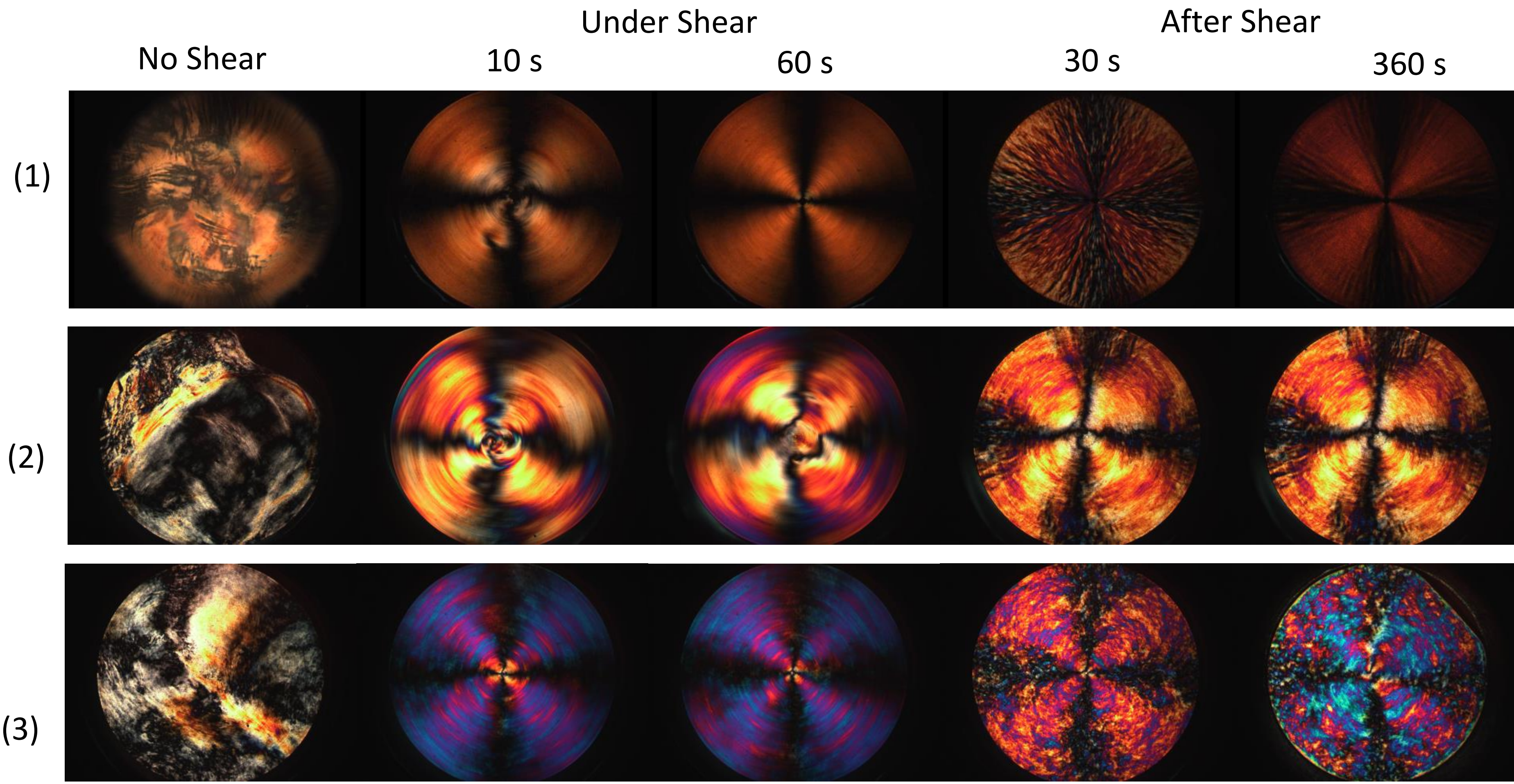
SAXS/SANS: Weakly scattering at high pH

Generally fit to a power law only.

Background | Micelles at High pH



Experimental | Aligning Micelles



Can put the rheometer in the beam!

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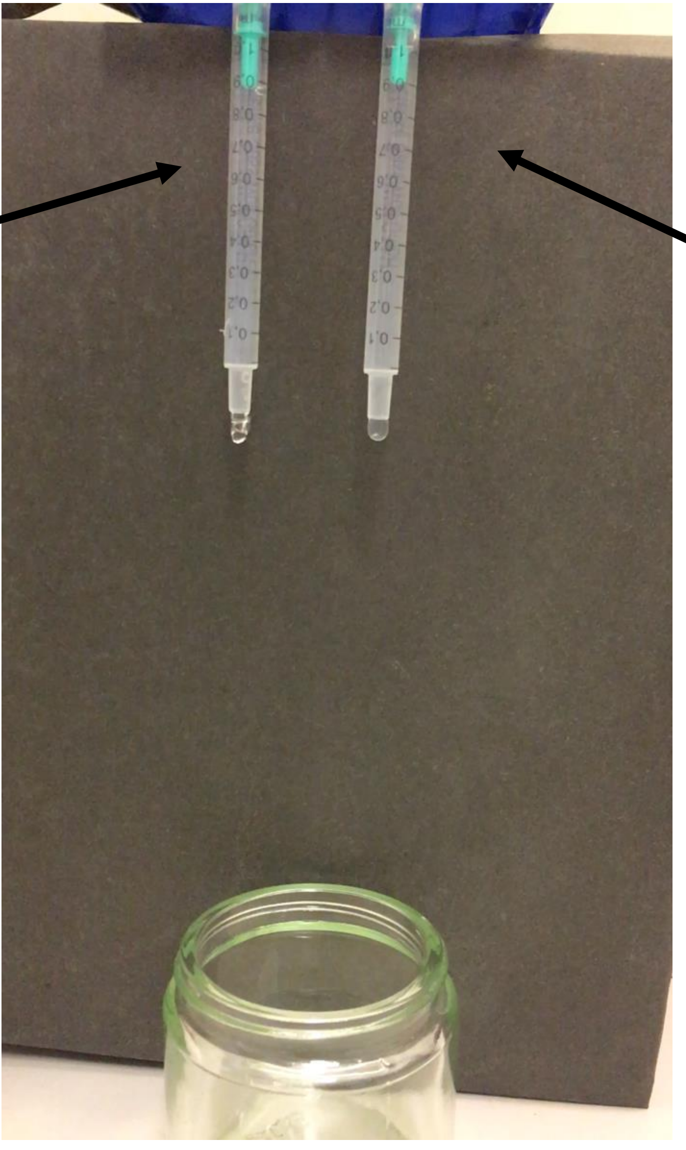
Experimental | Heating and Cooling

Before Heating

More viscous



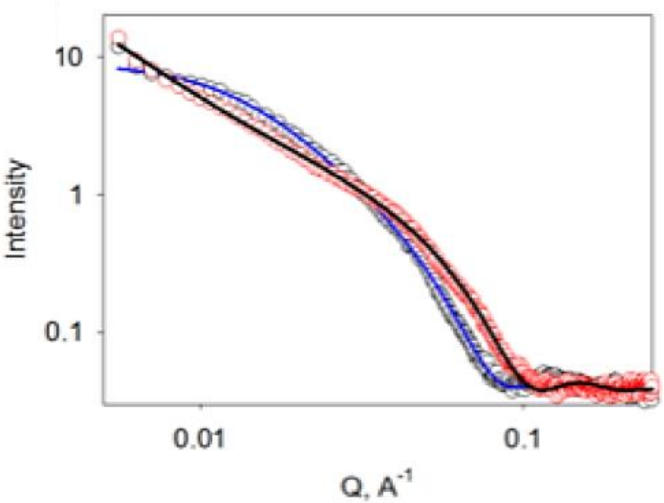
After Heating

Less Viscous

Draper et al., *Angew. Chem. Int. Ed.*, 2017, *129*, 10603

SAXS | Heating and Cooling

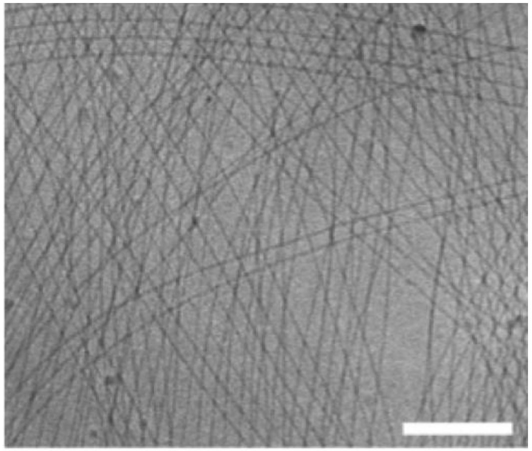
SAXS:

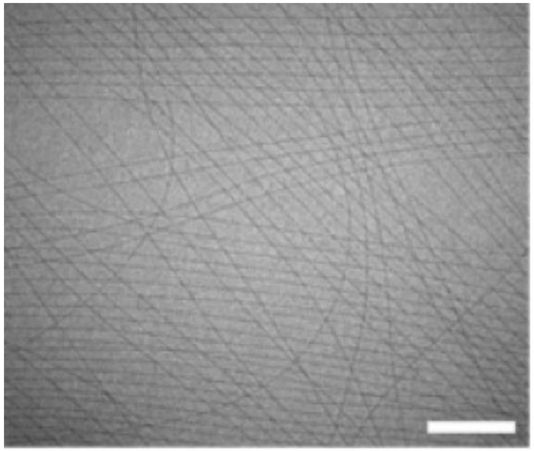


Before Heating:
Flexible Cylinder
Radius 40.5 ± 0.2 Å
Kuhn length 63.0 ± 2.4 Å
Length 949.6 ± 5.6 Å.

After Heating:
Flexible Cylinder
34.0 ± 0.1 Å
Kuhn length of 339.7 ± 3.4 Å
Length of 4976.4 ± 232.8 Å

Cryo-TEM:

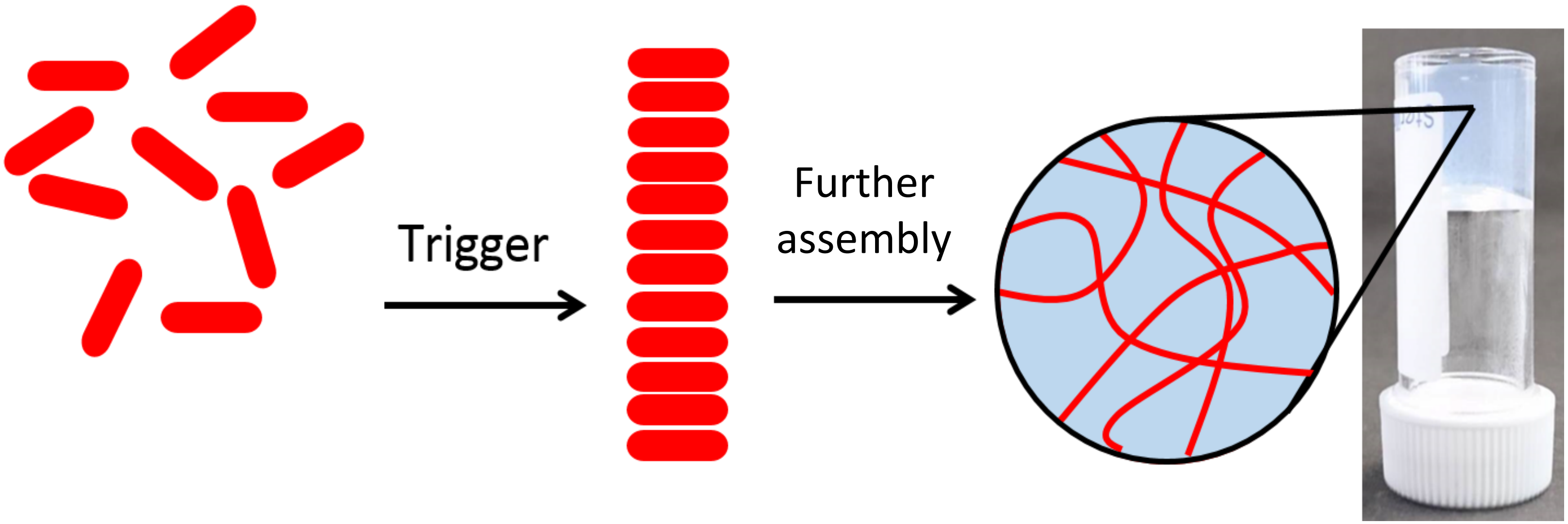




In both cases, the absolute length is beyond the resolution of the fit,
The length increases after the heat/cool cycle.
The radius decreases after the heat/cool cycle.
The Kuhn length increases after the heat/cool cycle so the flexibility decreases.

Draper et al., *Angew. Chem. Int. Ed.*, 2017, *129*, 10603

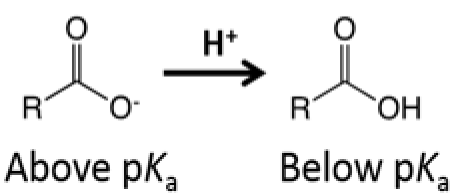
Background | Self-assembly



LMWG
in solution at
High pH

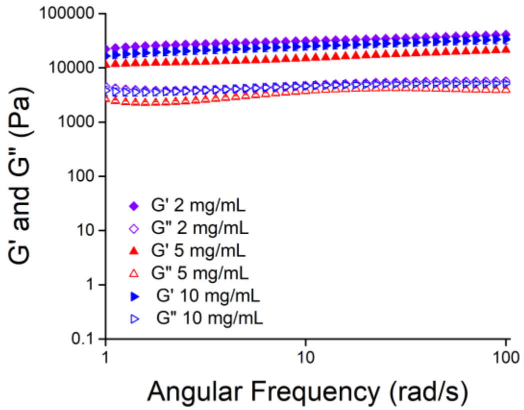
pKa = pH
Assembly into 1-D fibre
structures

Fibre 3-D network
giving a self-supporting
gel

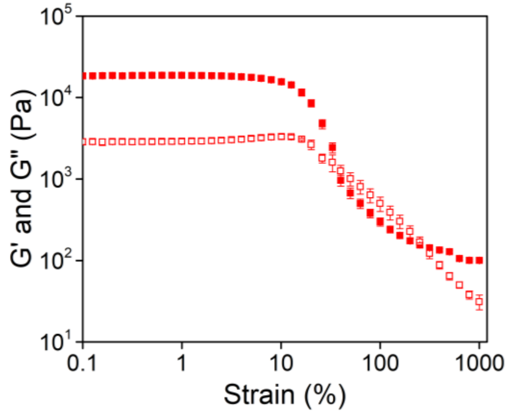


Background | Self-assembly

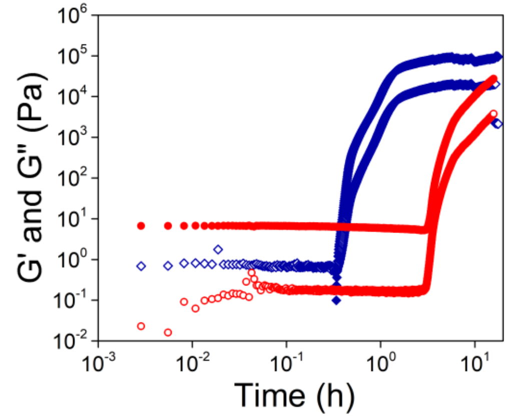
Frequency Sweep



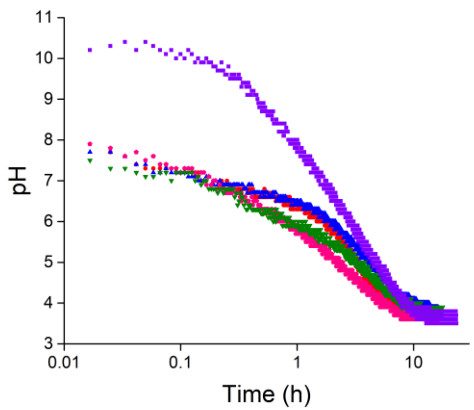
Strain Sweep:



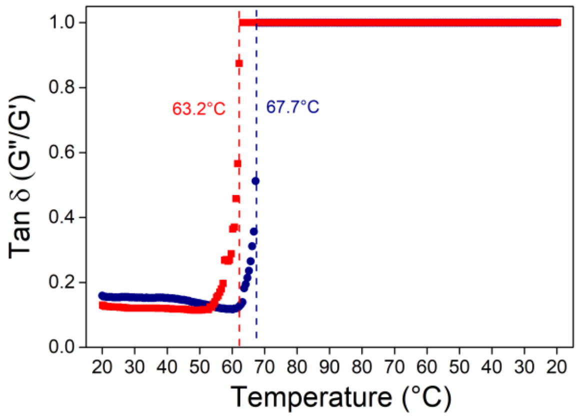
Time Sweep:



pH Measurements:

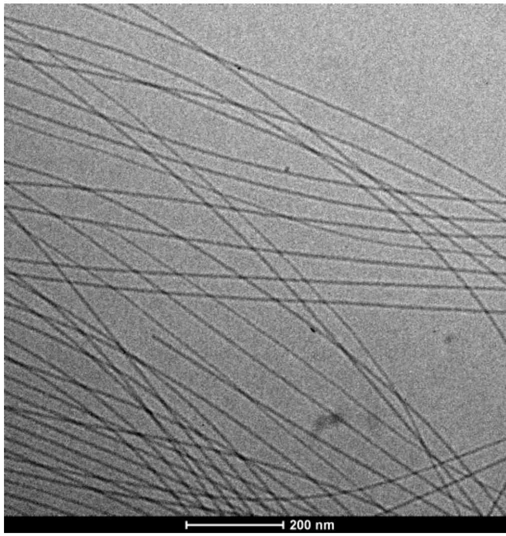


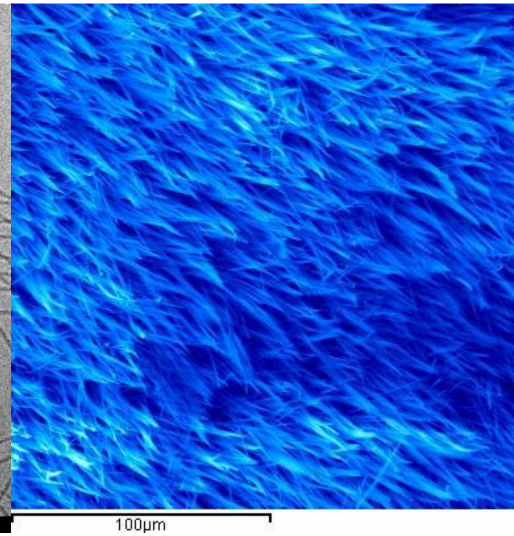
Heat/Cool:

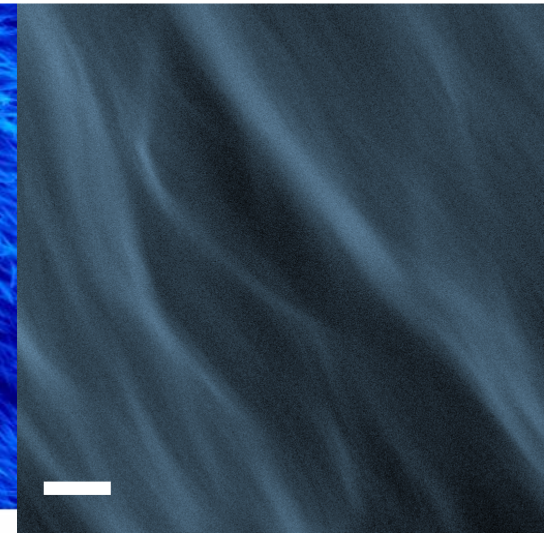


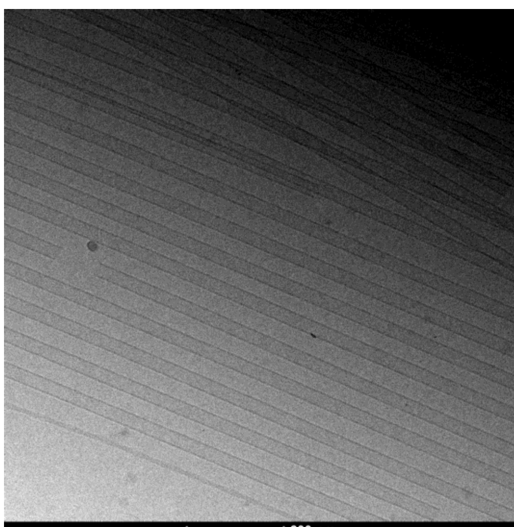
Techniques | Microscopy

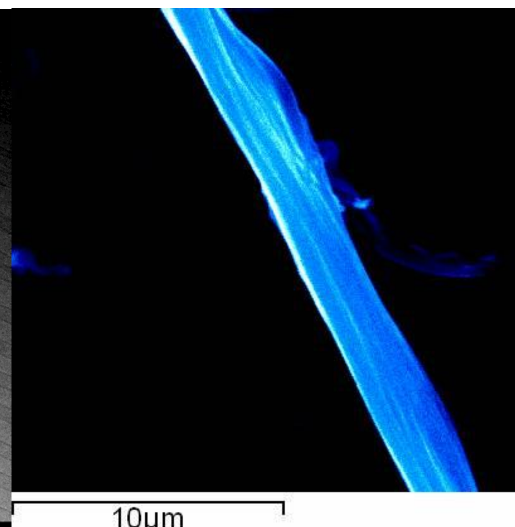
Cryo-TEM	SEM	Confocal Microscope

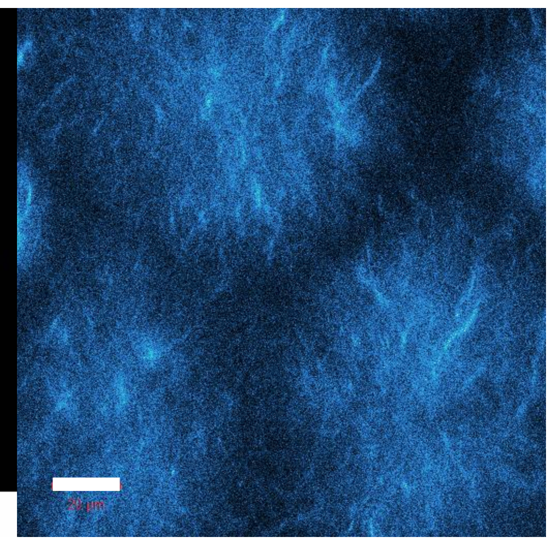






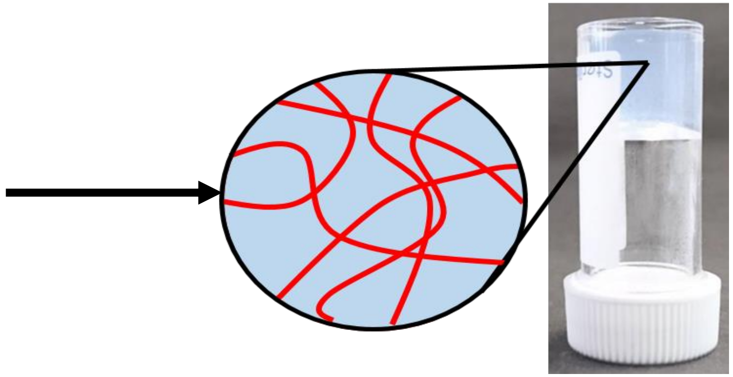






SAXS | What does it tell us?

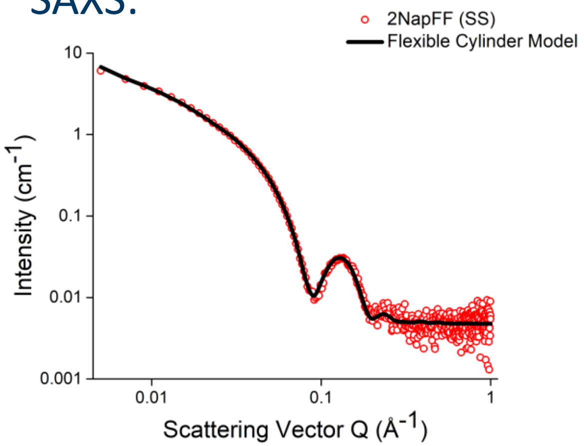
Small angle scattering can be used to probe the primary fibres.

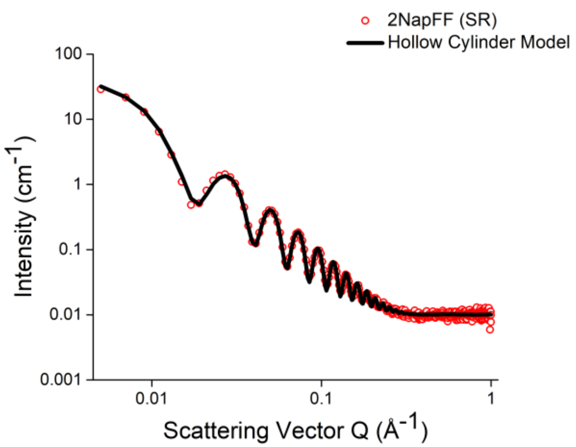


The fit provides information as to the radius of the structure, the length, persistence, Kuhn length *etc.*

LMWGs, the best fits usually are best to a cylinder, a flexible cylinder, a hollow cylinder, or some other long, anisotropic structure.

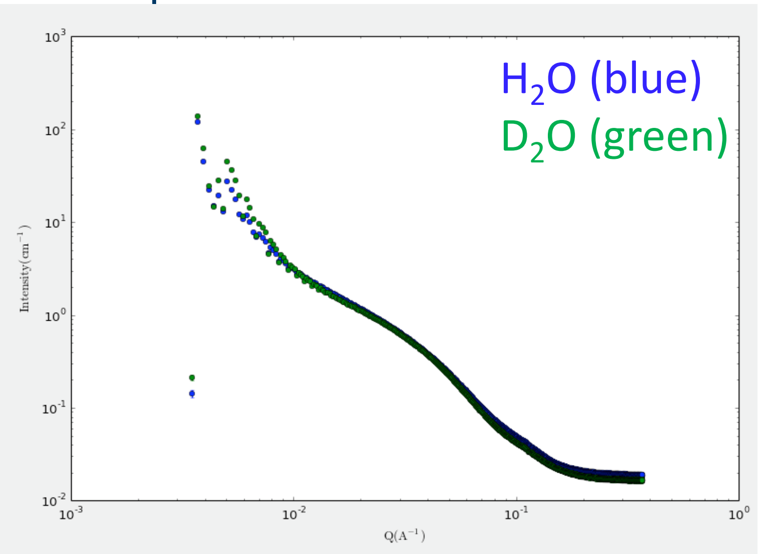
SAXS:





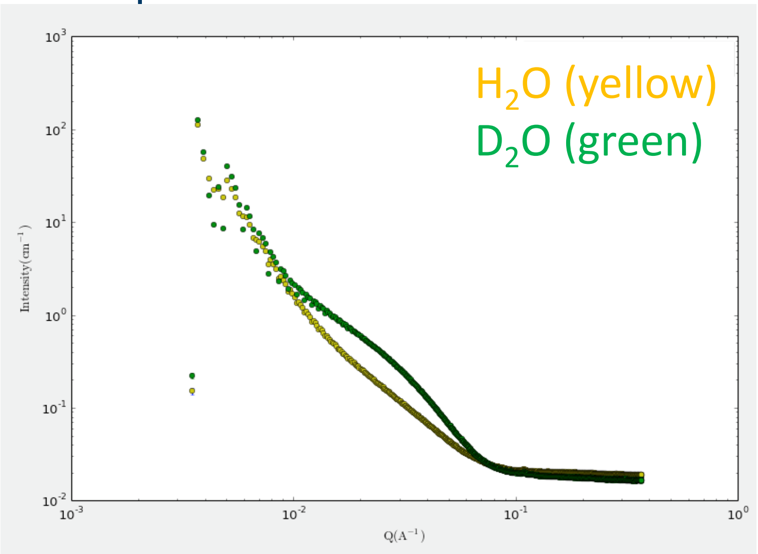
SAXS | Advantages no D_2O!

BrNapAG

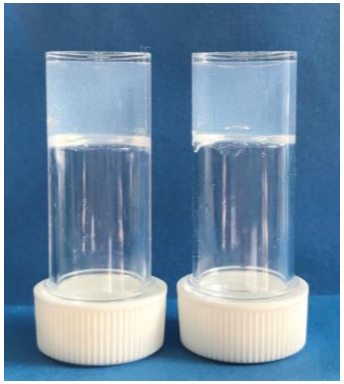


Very similar scattering.

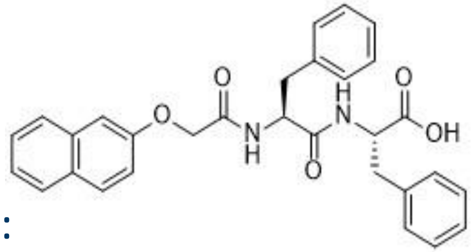
BrNapIF



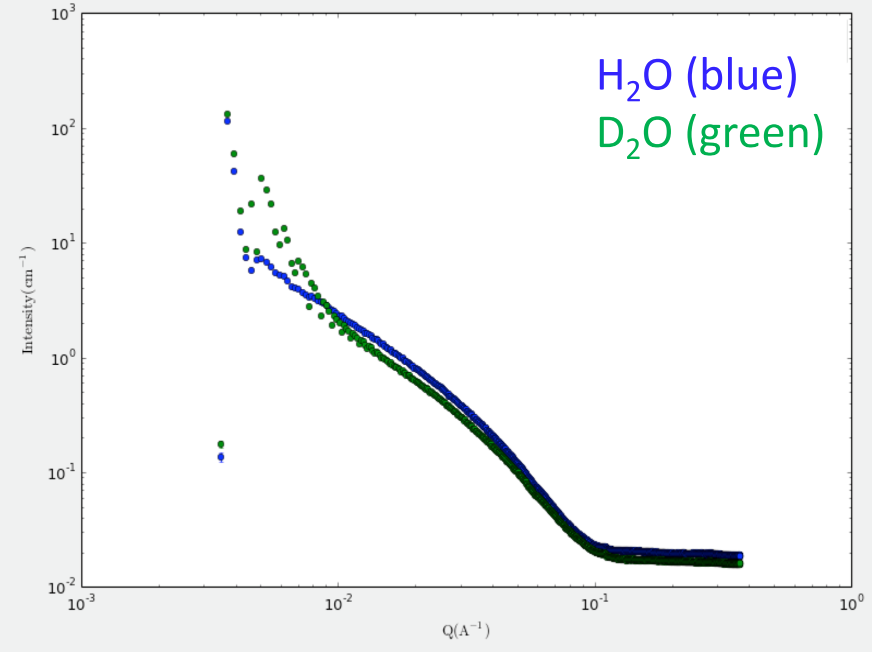
Differences in scattering.



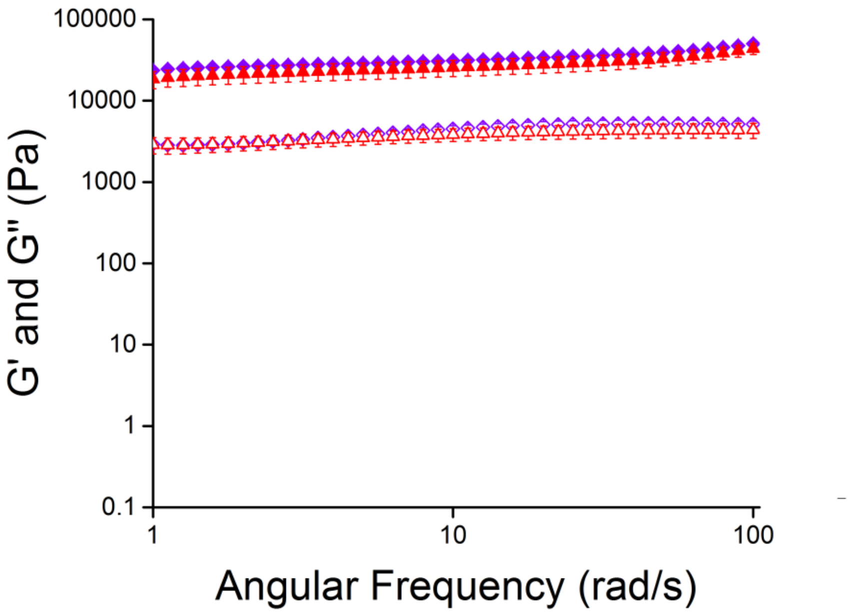
SAXS | 2NapFF Gels



SAXS:



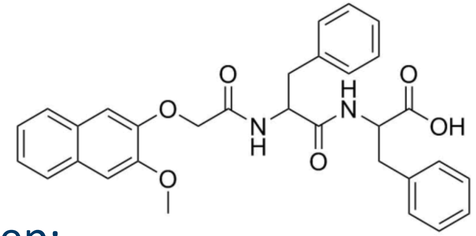
Frequency Sweep:



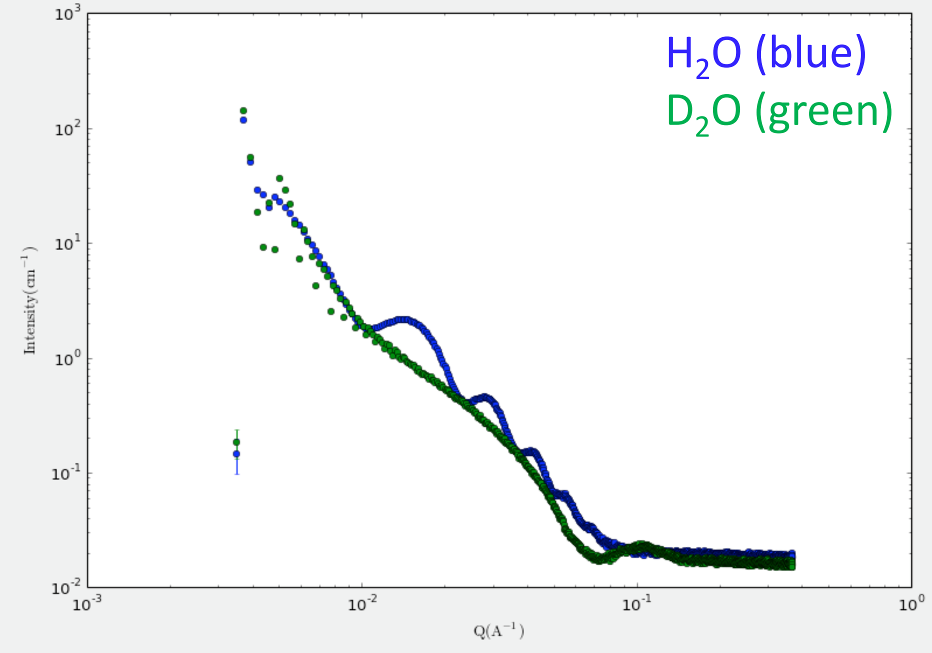
H_2O (purple) and D_2O (Red)
closed symbols G' and open G"

- Very similar in general as expected from previous data.

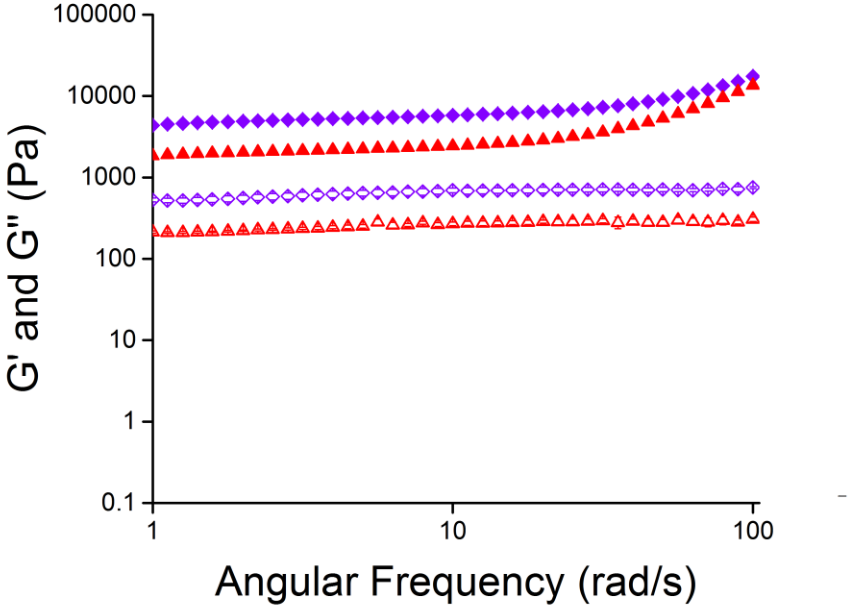
SAXS | 3MeONapFF Gels



SAXS:



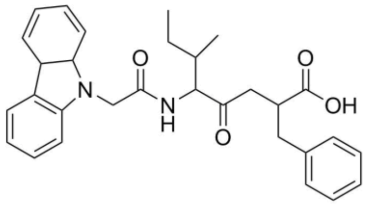
Frequency Sweep:



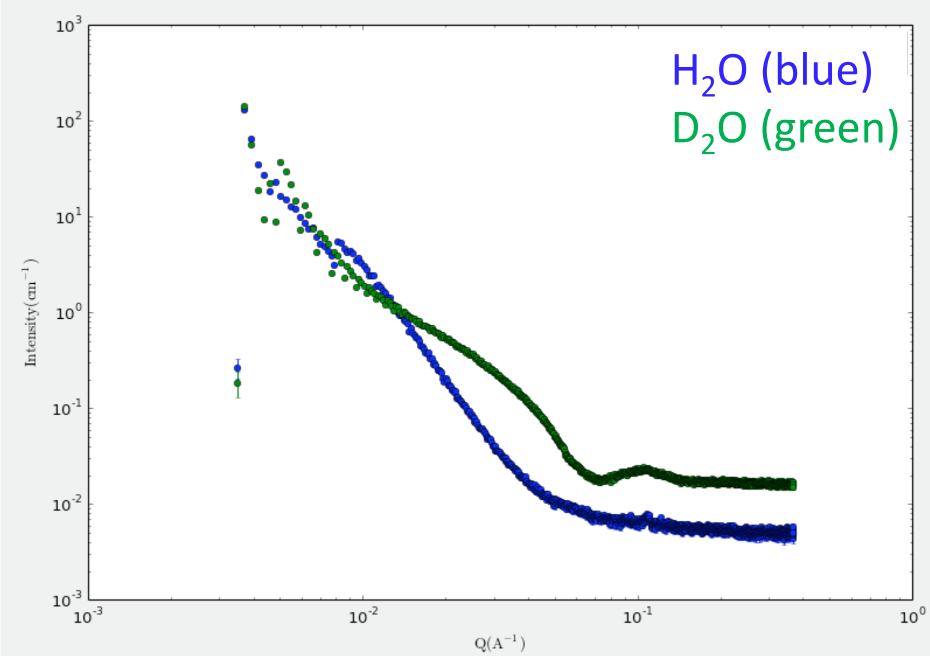
H_2O (purple) and D_2O (Red)
closed symbols G' and open G"

- Different structures AND different rheology data!
- H_2O fits to a hollow cylinder with a radius of around 3.6 nm and a thickness of 1.6 nm
- D_2O fits to a hollow cylinder with a radius of around 21 nm and a thickness of 7.6 nm

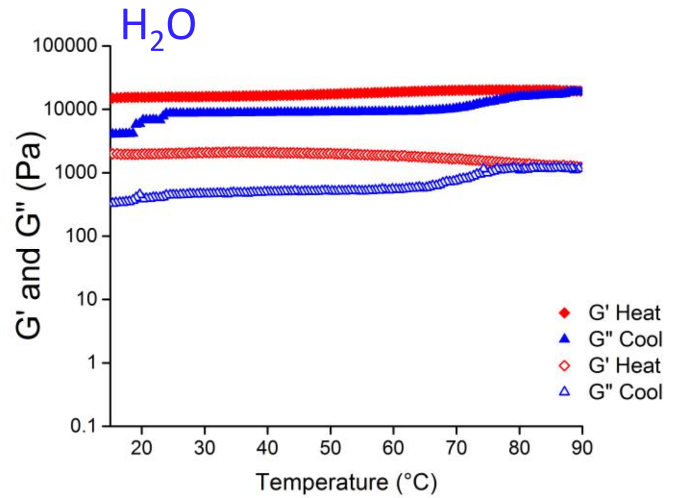
SAXS | CarbIF Gels

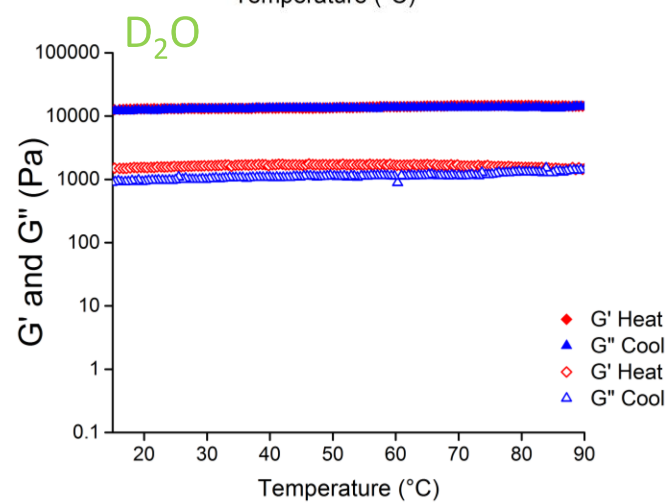


SAXS:



Temperature Sweep:

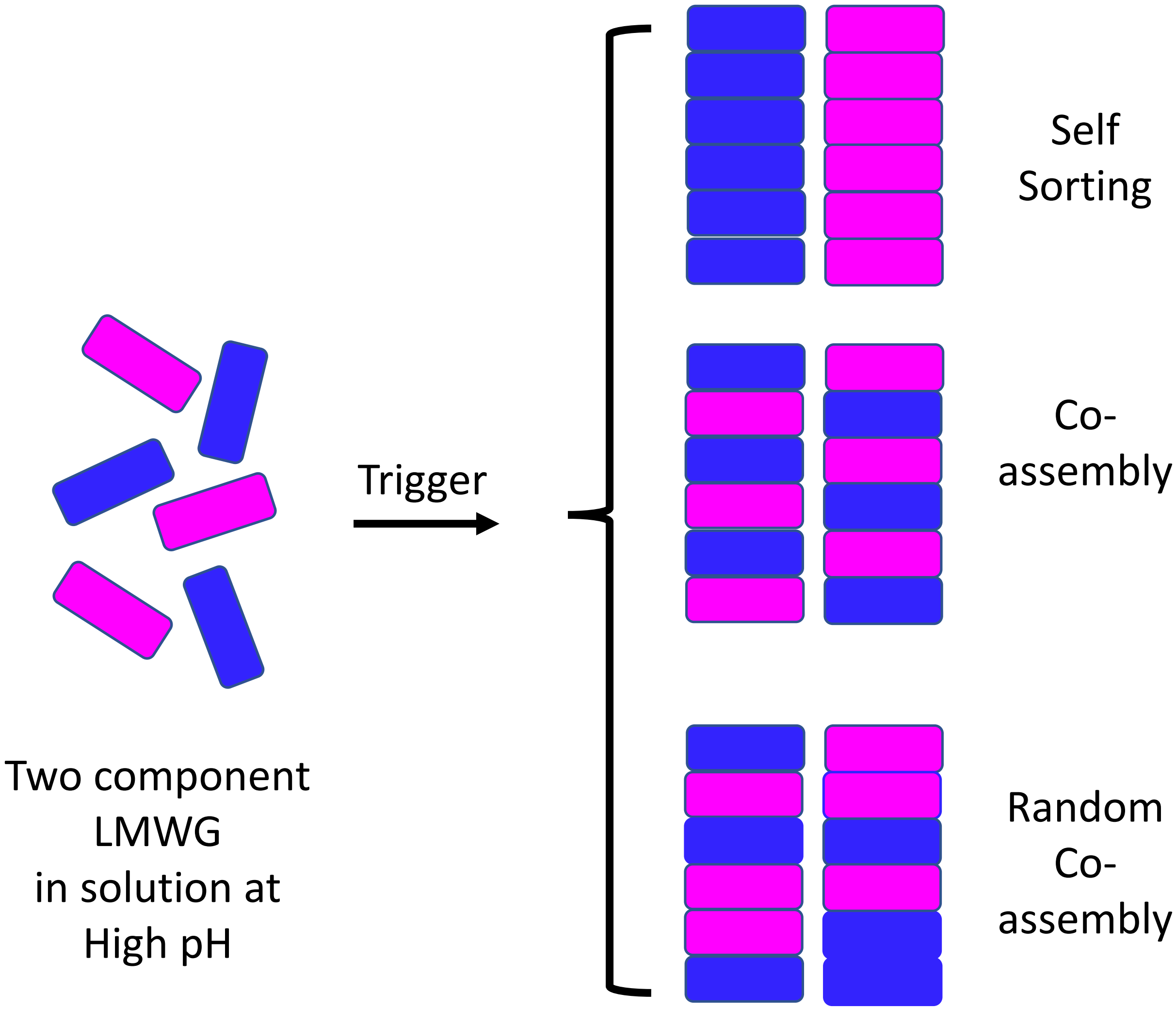




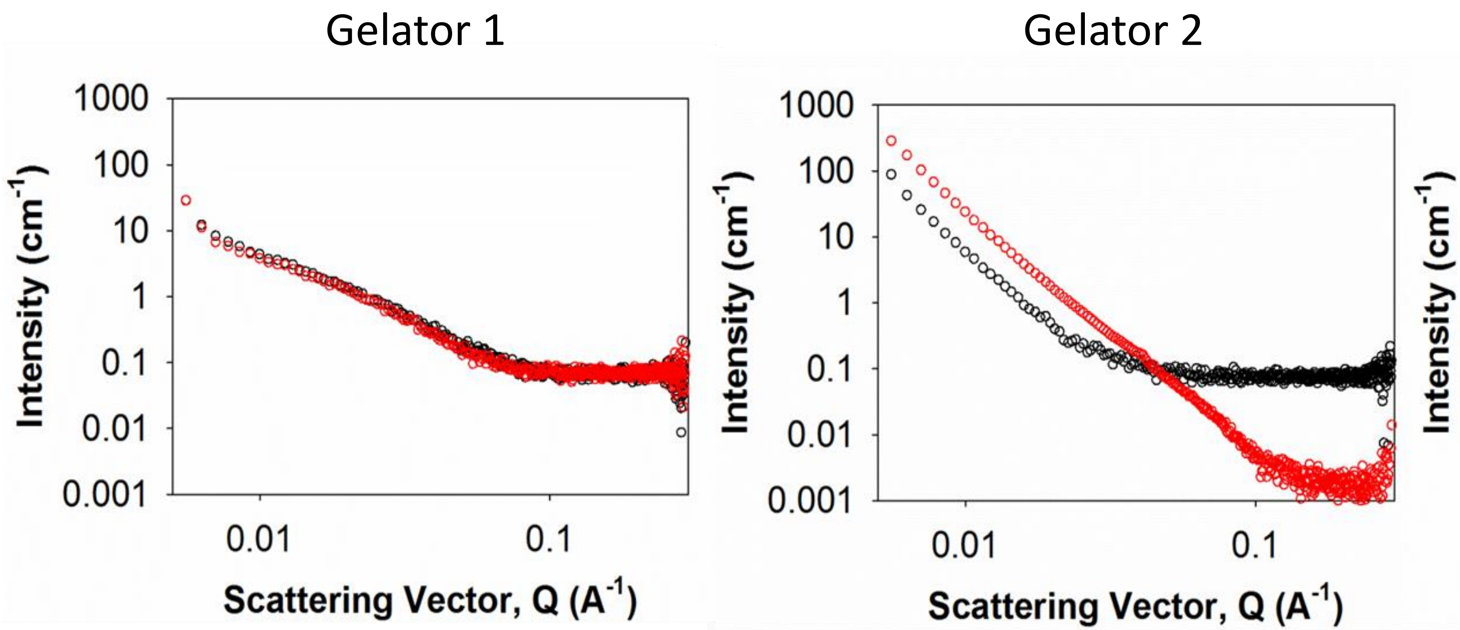
Significant difference!

- H_2O fits to a polydisperse flexible cylinder with a radius of around 16 nm.
- D_2O fits to a hollow cylinder with a radius of around 3 nm and a thickness of 1 nm.

SAXS | Multicomponent Systems



SAXS | Annealing Multicomponent Supramolecular Gels



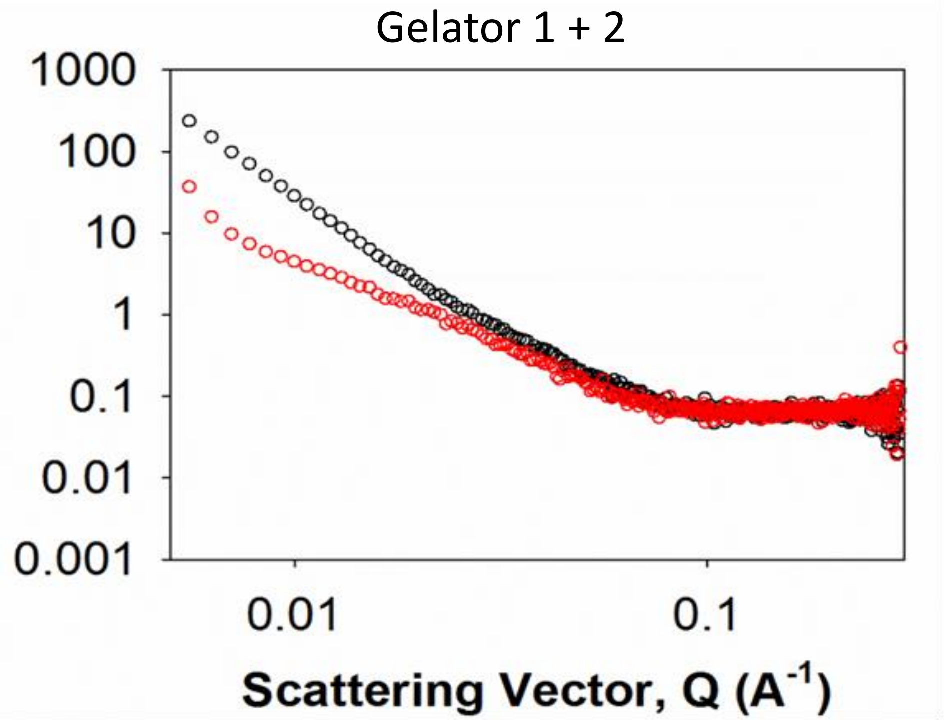
SAXS data before (black) and after (red) annealing.

For **Gelator 1** the data fits to a flexible cylinder model with a radius of 4.3 ± 0.07 nm.

The baseline for **Gelator 2** drops after annealing as there is crystallisation and a small amount of precipitation, meaning that there is less sample in the beam after annealing.

A. M. Fuentes-Caparrós *et al*, *Nanoscale*, 2019, 11, 3275-3280

SAXS | Annealing Multicomponent Supramolecular Gels



SAXS data
Before (black)
After (red)
annealing.

For the multicomponent system, the SAXS data is different before and after annealing.

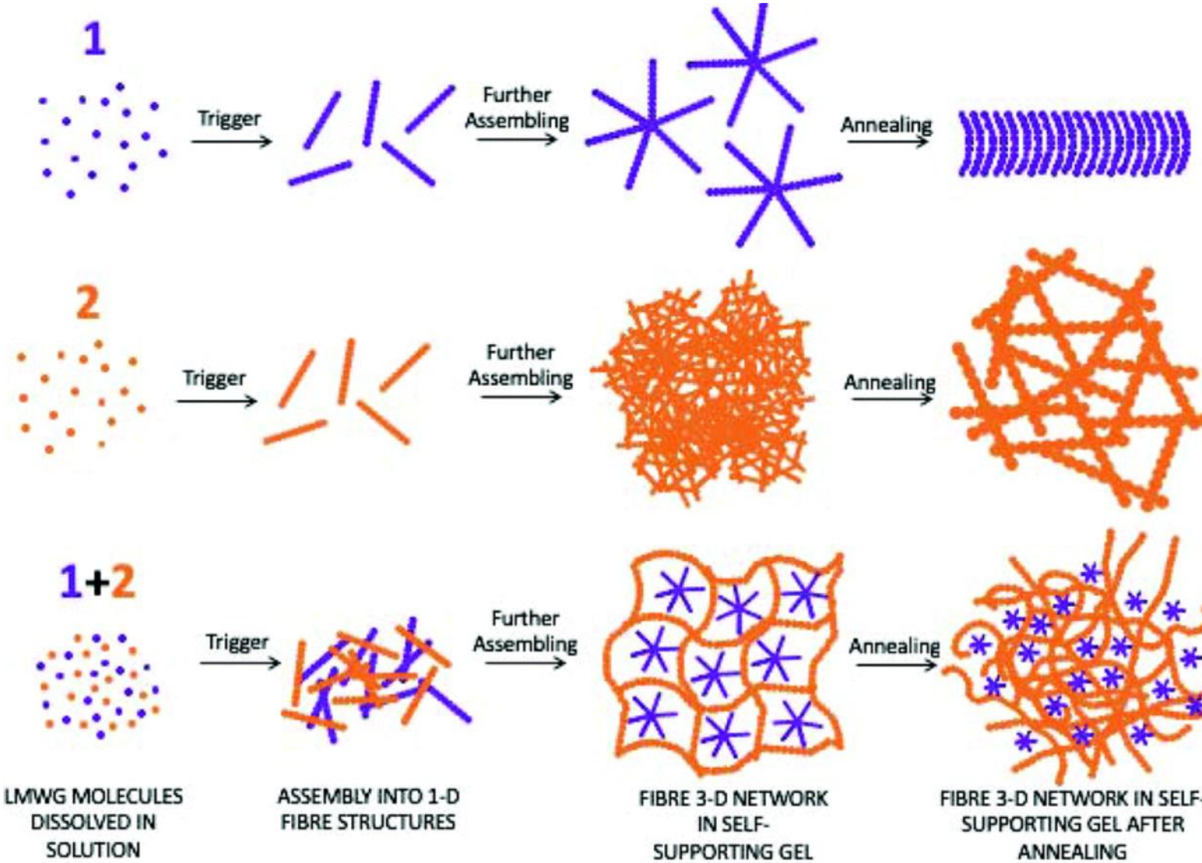
Before heating, the data are reminiscent of that of **2**

After annealing, the data are very similar to that of **1**

A. M. Fuentes-Caparrós *et al, Nanoscale*, 2019, 11, 3275-3280

SAXS | Annealing Multicomponent Supramolecular Gels

Gelator	Gradient	Description
1 before and after	-2	mass fractal network
2 before	-4	objects too large to be resolved by SAXS
1+2 Before	-3	mass fractal with a tight interconnected structure
1+2 After	-2	mass fractal network



A. M. Fuentes-Caparrós *et al*, *Nanoscale*, 2019, 11, 3275-3280

Conclusions

- We are using SAXS to look at the self-assembled LMWG structures in solutions and gels.
- Can investigate structural information without modifying the samples.
- Don’t need to use D_2O.
- Relate these structures to the physical and mechanical properties of the samples.

University of Glasgow

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- Hao Su
- Honggang Cui

- Nikul Khunti
- Nathan Cowieson

diamond

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