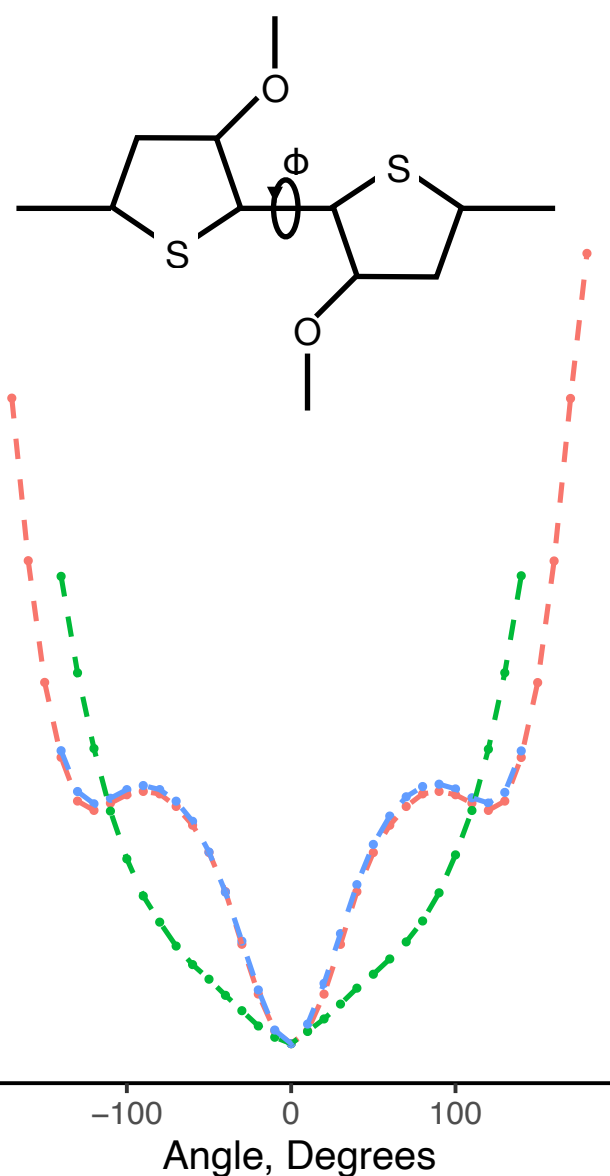


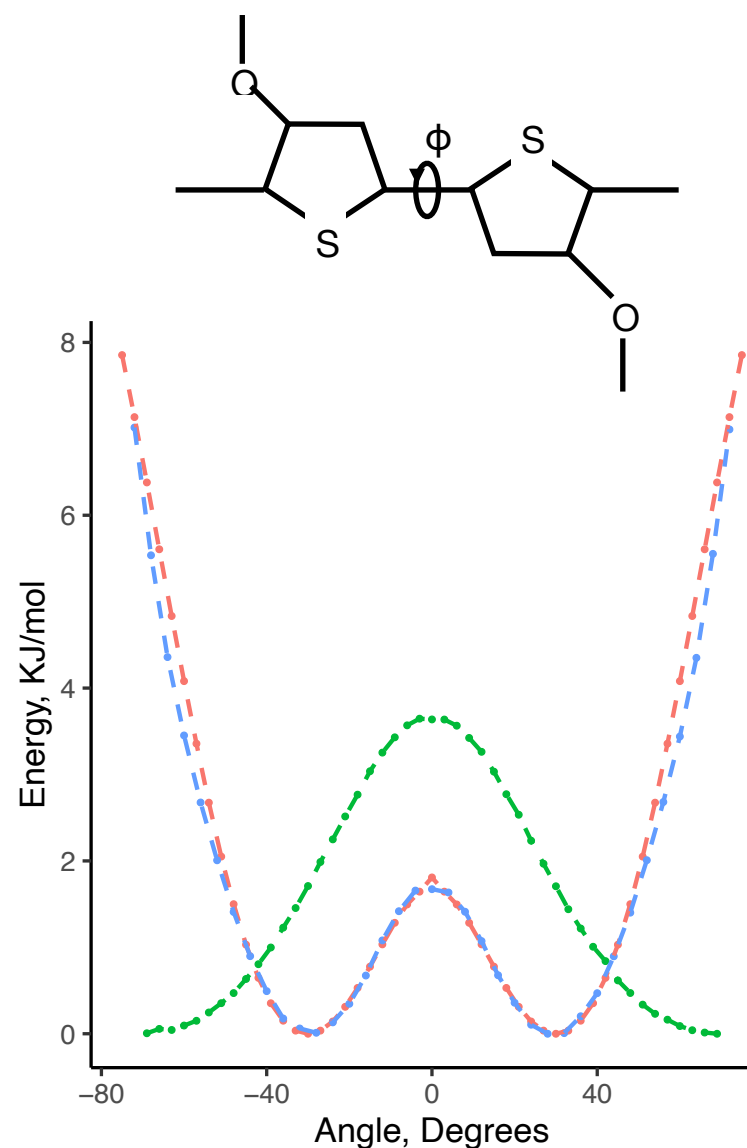
Force Field Design Principles

- 1) Forcefield based on OPLS
- 2) 'Important' DOFs re-parameterised. These are -
 - 1) 'inner dihedral'
 - 2) 'outer dihedral'
 - 3) C-O angle
- 3) Electrostatic parameters taken from mixture of OPLS and density functional theory (see next slide)

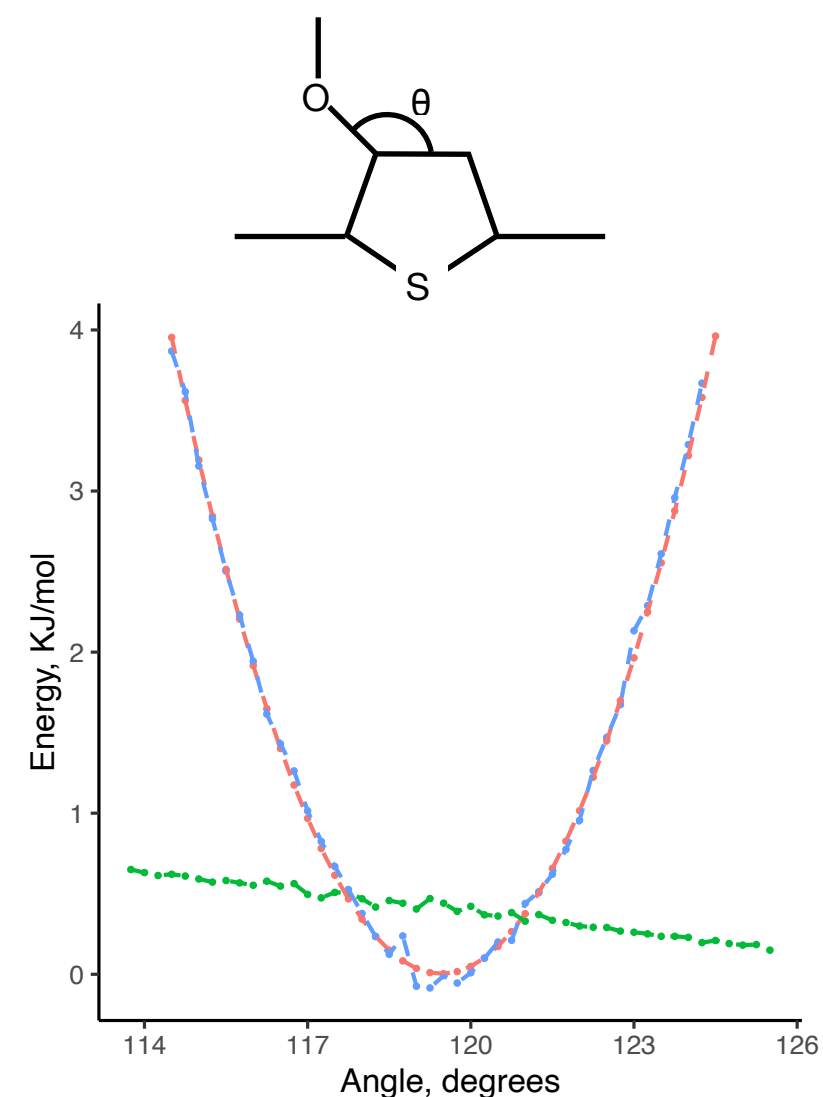
Inner dihedral



Outer dihedral



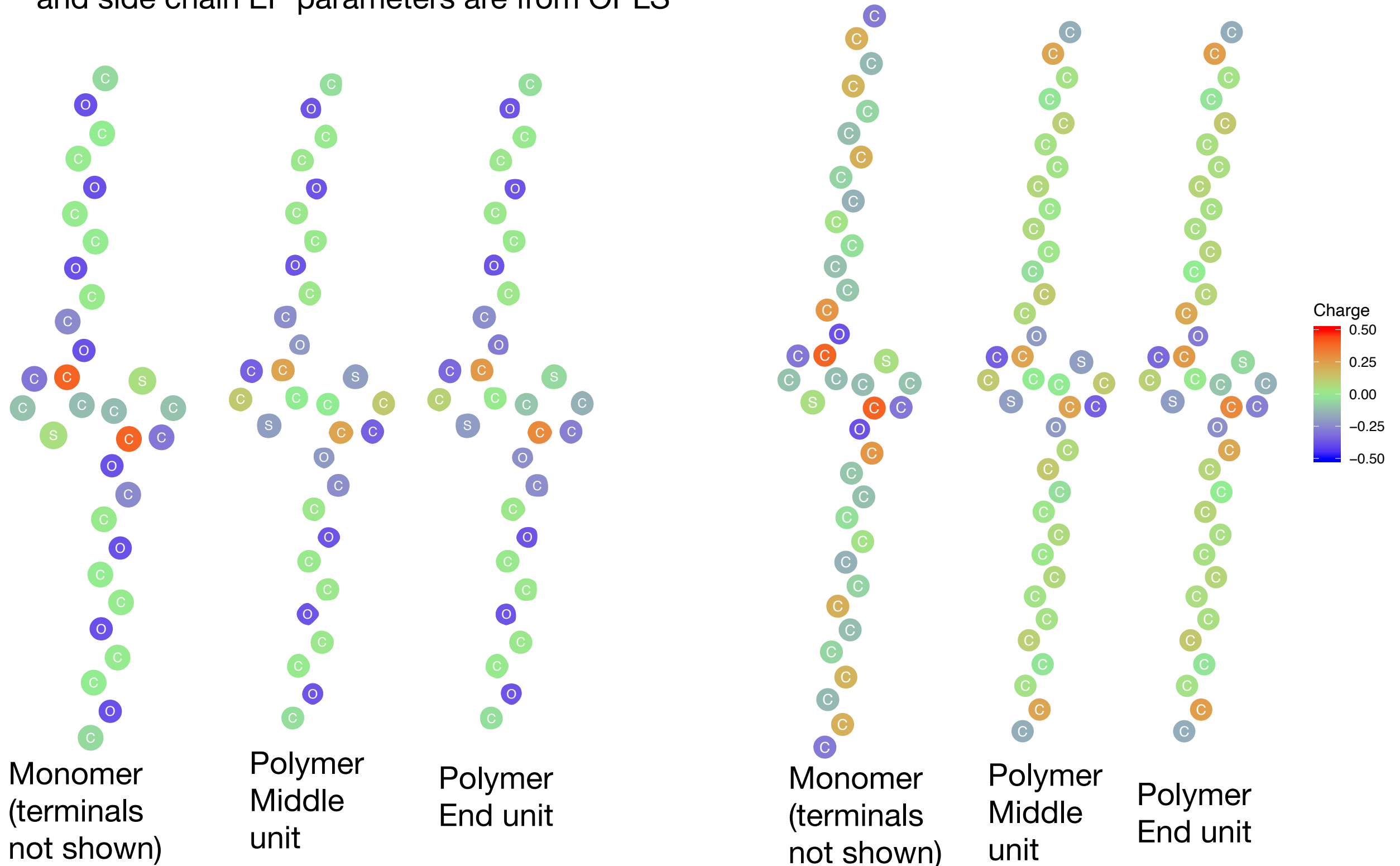
C-O angle



Green - Background potential in MD forcefield, Red - DFT energy scan, Blue - MD potential after parameterisation

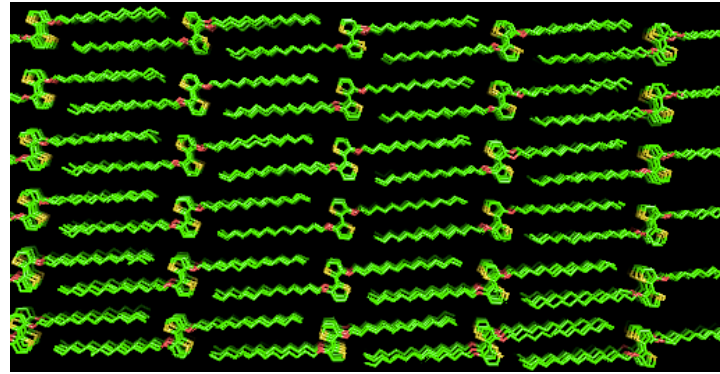
Electrostatic parameters (EP)

- 1) Alkoxyated monomer - EP parameters for entire molecule calculated using DFT
- 2) Alkoxyated polymer - EP parameters calculated for a set of representative oligomers using DFT
- 3) Glycoxyated monomer - EP parameters for the backbone are the same as for Alkoxyated monomer, and side chain EP parameters are from OPLS
- 4) Glycoxyated polymer - EP parameters for the backbone are the same as for Alkoxyated polymer, and side chain EP parameters are from OPLS



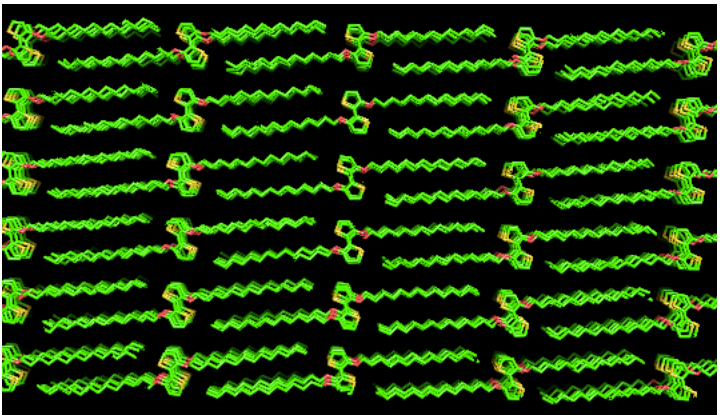
Alkoxyated monomer crystal structure - testing stability

Without annealing



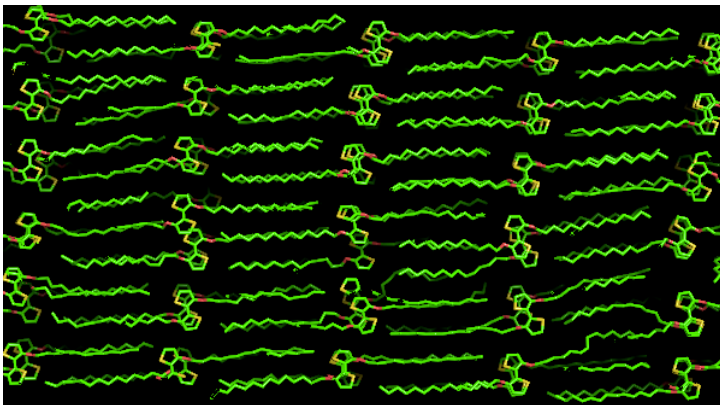
$a = 4.16$
 $b = 9.28$
 $c = 23.78$
 $\alpha = 91.97$
 $\beta = 91.28$
 $\gamma = 96.10$

Annealed at 350K



$a = 4.16$
 $b = 9.28$
 $c = 23.76$
 $\alpha = 92.21$
 $\beta = 91.70$
 $\gamma = 97.13$

Annealed at 400K

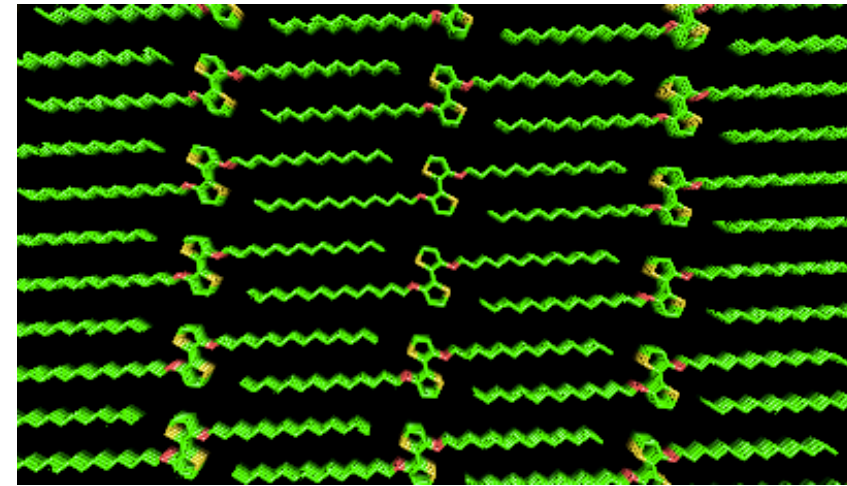


$a = 4.25$
 $b = 9.48$
 $c = 24.29$
 $\alpha = 90.71$
 $\beta = 88.89$
 $\gamma = 96.21$

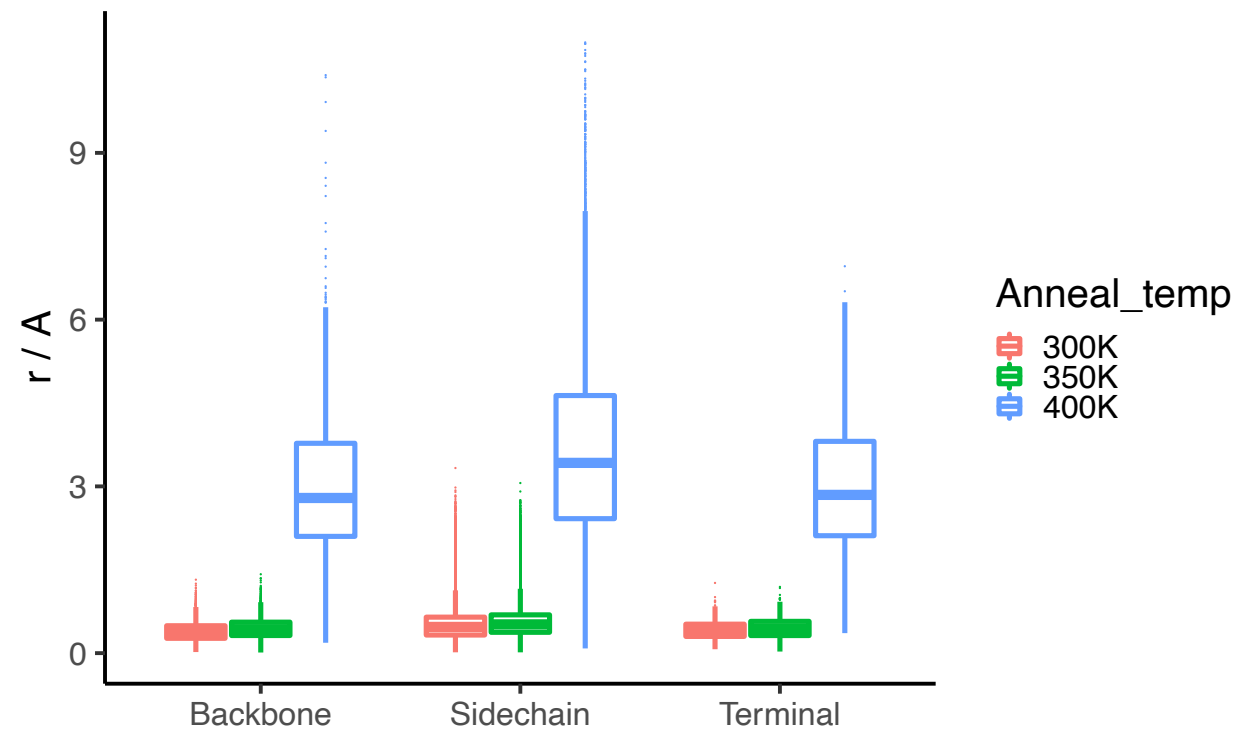
Annealing protocol -

- 1) Heat from 300K to annealing temperature over 1ns
- 2) Cool from annealing temperature to 300K at a rate of 10K/1ns

Before MD (structure from Andrew)



$a = 4.17$
 $b = 9.30$
 $c = 23.80$
 $\alpha = 91.86$
 $\beta = 91.48$
 $\gamma = 96.45$



Distribution of atomic displacement vectors, r , for each component of the system at the different temperatures

Annealing protocol Structure is stable at room temp, and after annealing at 350K. It still holds together after annealing at 400K, but some disorder is introduced into the system. Overall the alkoxyated monomer crystal is well reproduced.

Alkyl Monomer Crystal

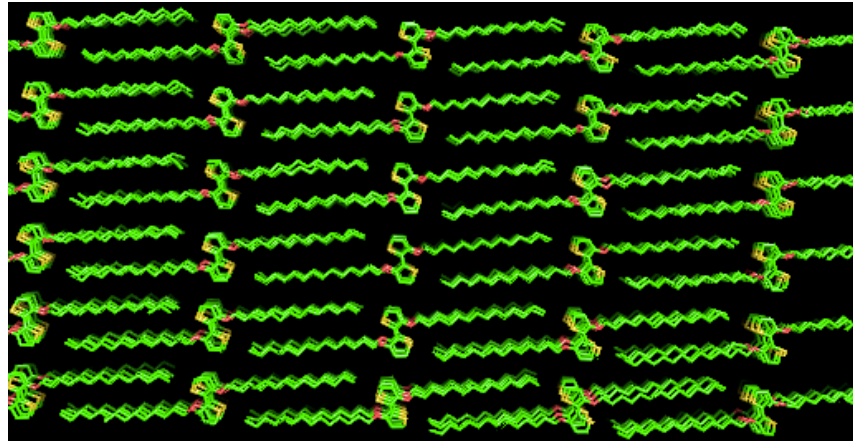
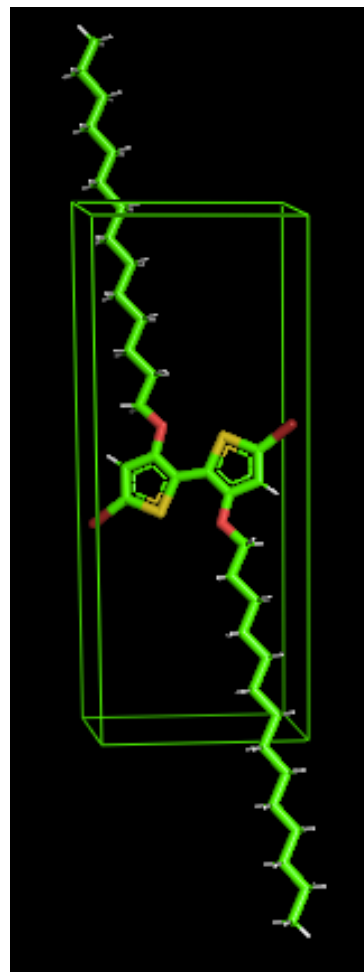


Image of super cell stabilised in MD



Parameters after MD

$a = 4.16$

$b = 9.28$

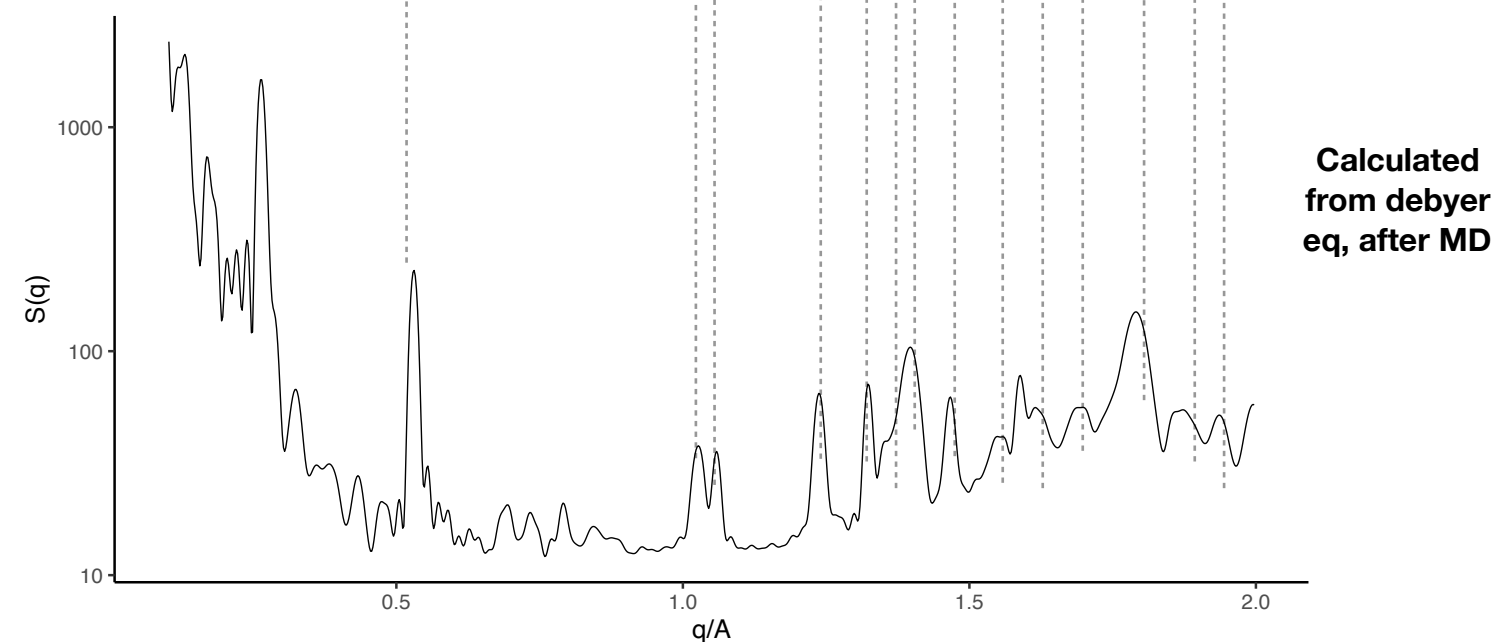
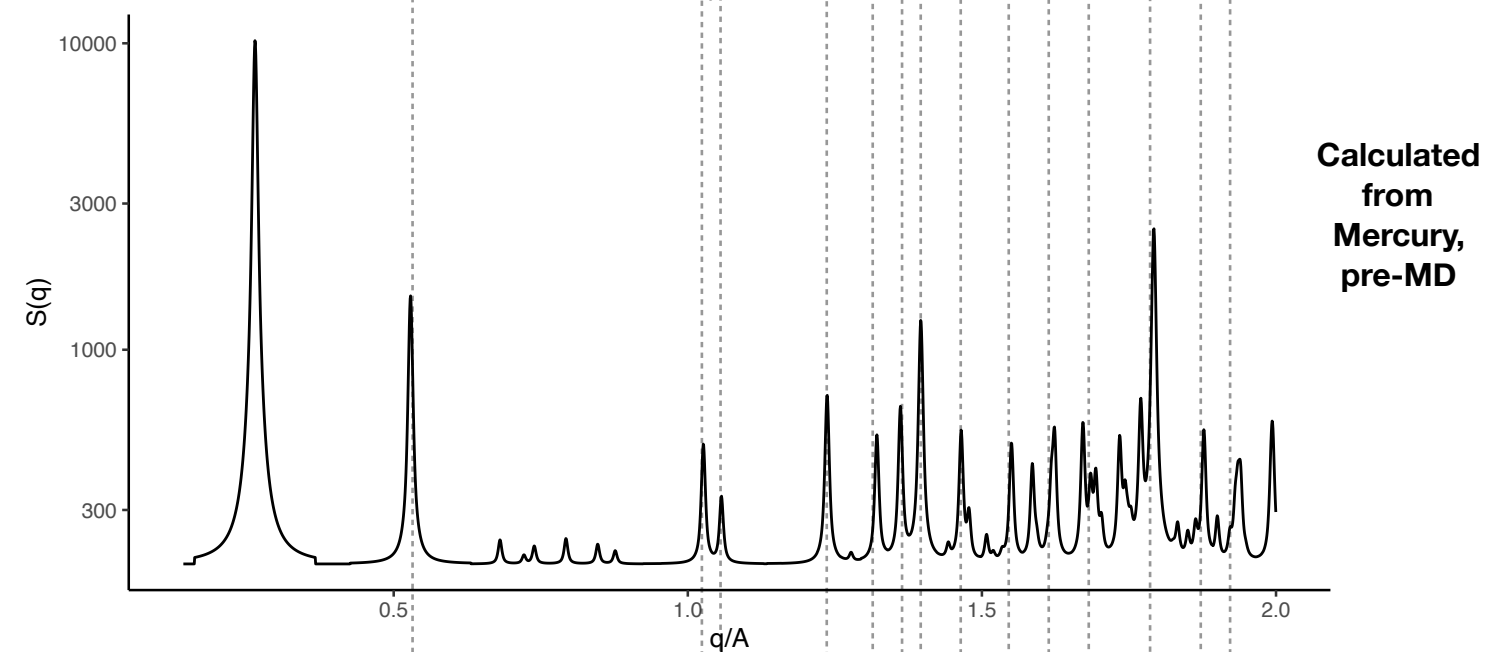
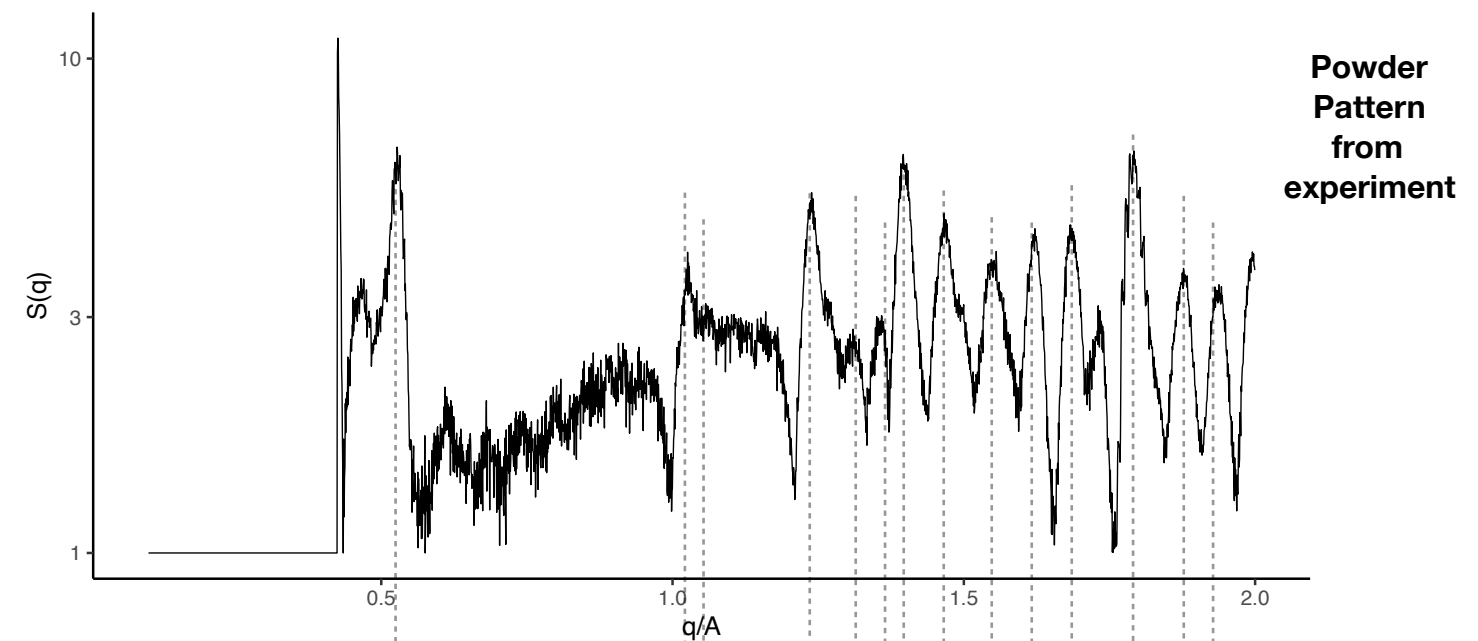
$c = 23.78$

$\alpha = 91.97$

$\beta = 91.28$

$\gamma = 96.10$

Strong agreement seen between the experiment, the theoretical structure factor and the calculated structure factor after equilibration in MD. Additionally the level of crystallinity seems to be in good agreement.



Alkoxyated Polymer Crystal

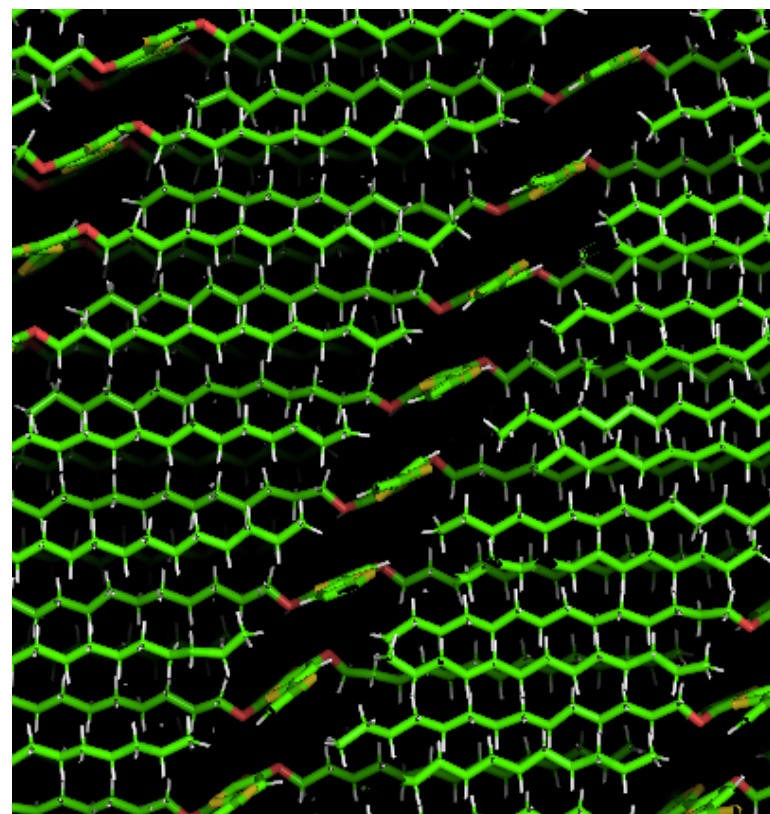
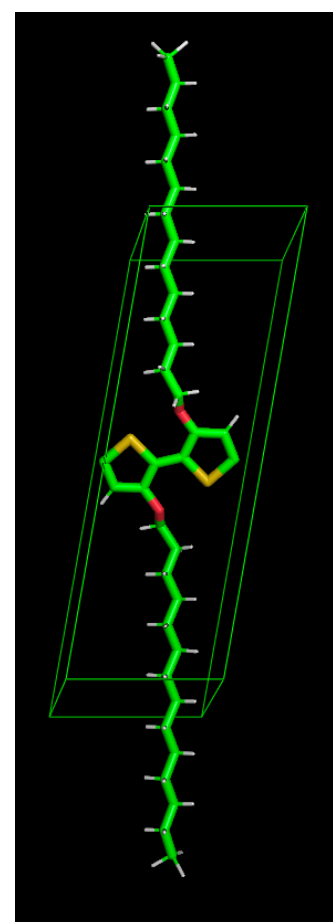
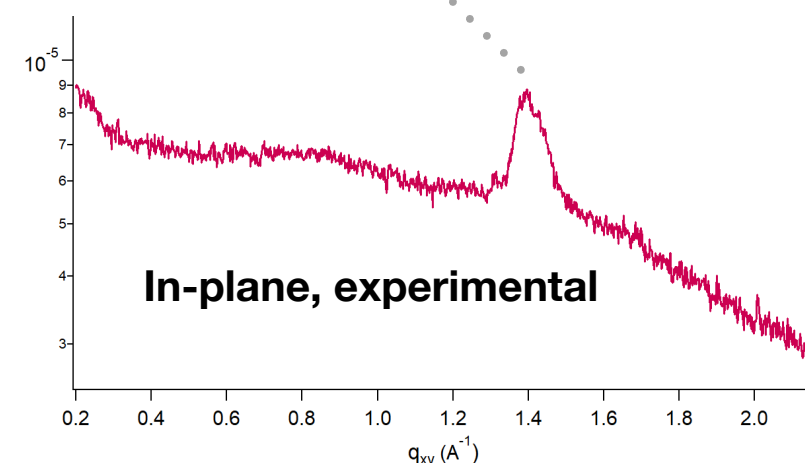
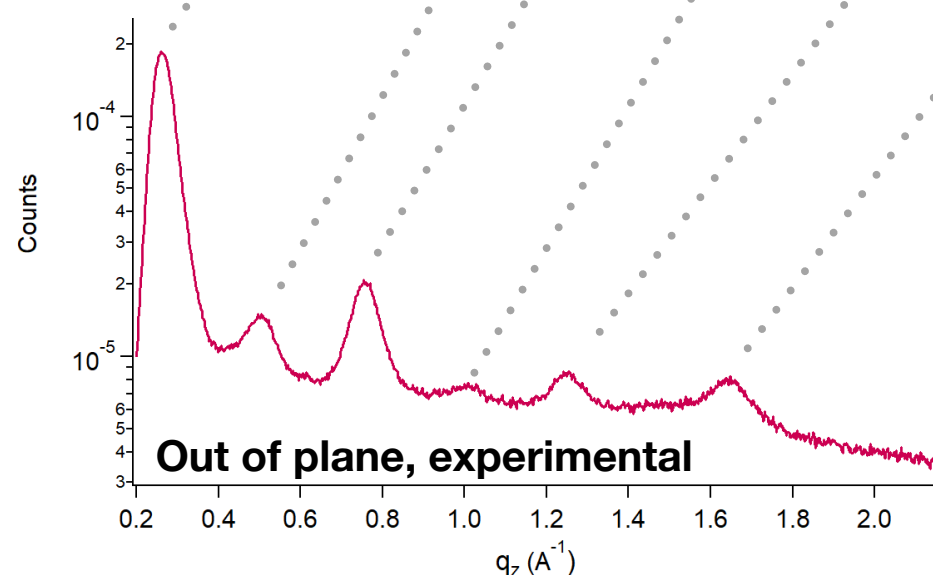
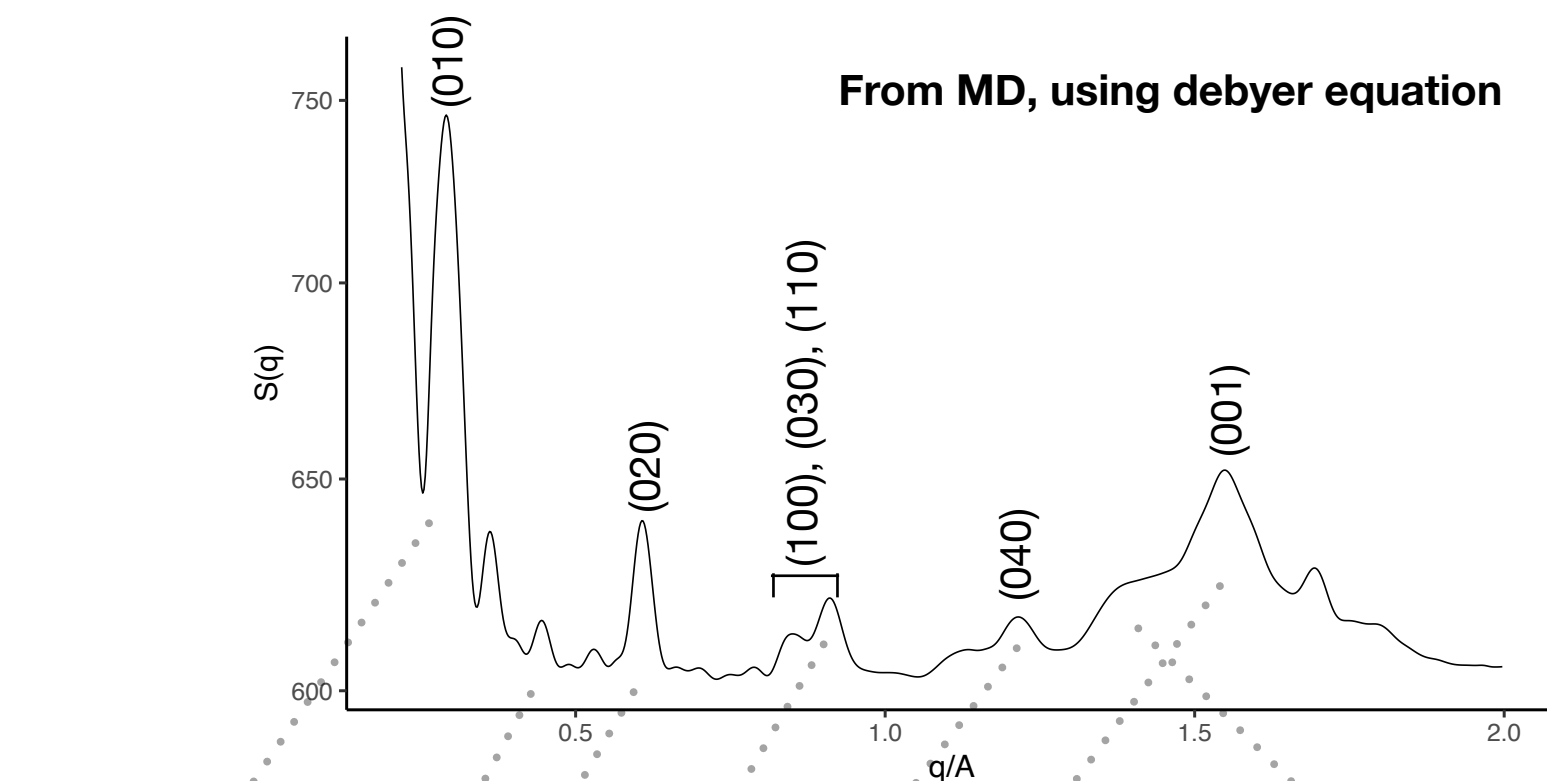


Image of crystal looking along backbones



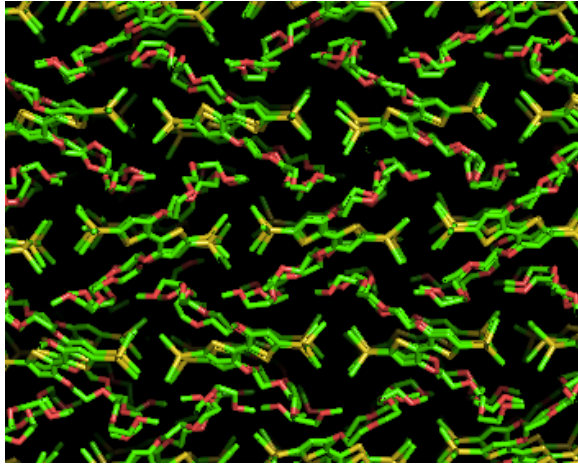
$a = 7.67$
 $b = 21.85$
 $c = 5.84$
 $\alpha = 65.27$
 $\beta = 79.60$
 $\gamma = 92.02$
 Symmetry = P1



In general the lamellar peaks, $(0n0)$, seem to be at lower q 's than in the data, suggesting the model over-predicts the lamellar stack distance. The pi-stack peak, (001) , is also at lower q value than the data, showing that it over-predicts the pi-stack distance. Peaks that I haven't labelled are because in the structure factor calculations there are many peaks in that area, so it is unclear which are showing peaks.

Glycoxylated monomer crystal structure - testing stability

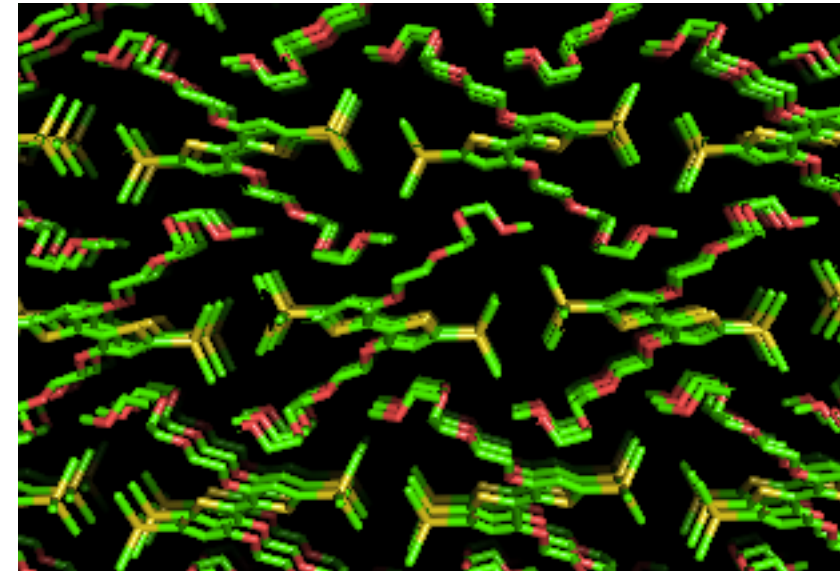
Without annealing



$a = 7.17$
 $b = 14.36$
 $c = 18.45$
 $\alpha = 89.25$
 $\beta = 96.78$
 $\gamma = 91.19$

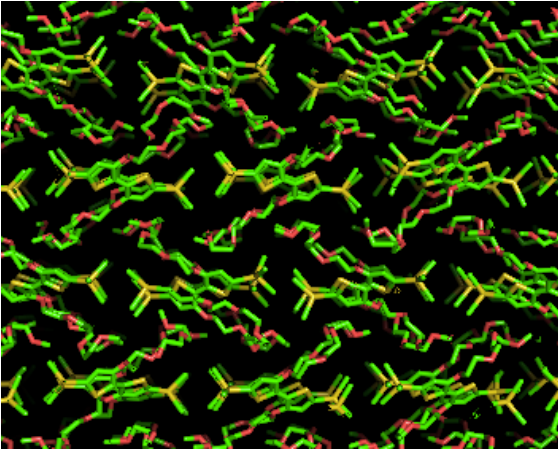
Annealing protocol -
1) Heat from 300K to annealing temperature over 1ns
2) Cool from annealing temperature to 300K at a rate of 10K/1ns

Before MD (structure from Andrew)



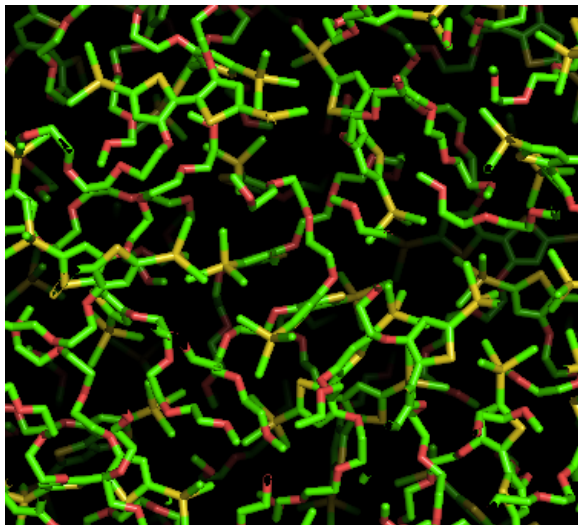
$a = 7.17$
 $b = 14.36$
 $c = 18.45$
 $\alpha = 89.25$
 $\beta = 96.78$
 $\gamma = 91.19$

Annealed at 350K

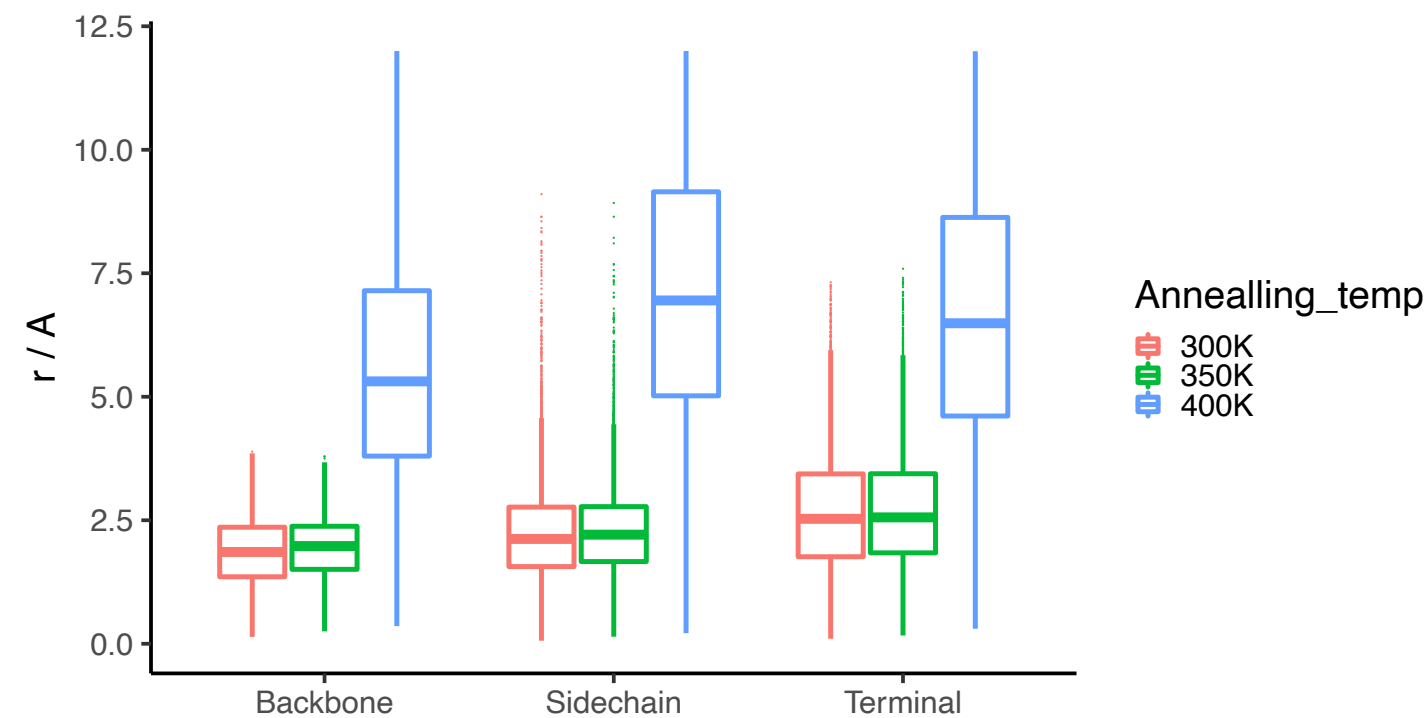


$a = 7.17$
 $b = 14.36$
 $c = 18.29$
 $\alpha = 89.35$
 $\beta = 98.08$
 $\gamma = 90.23$

Annealed at 400K



Too
amorphous
to
characterise
A unit cell



Distribution of atomic displacement vectors, r , for each component of the system at the different temperatures

Same as alkoxyated crystal structure. Holds together well at 300K and 350K, with average atomic displacements around 2Å. The crystal melts and fails to reform after annealing at 400K. Overall, crystal structure is well reproduced.

Glycol Monomer Crystal

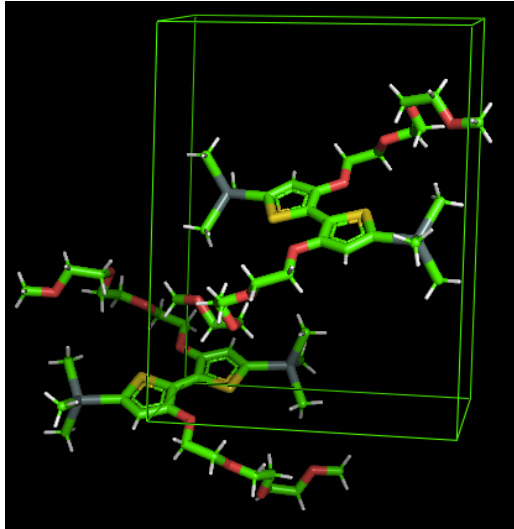
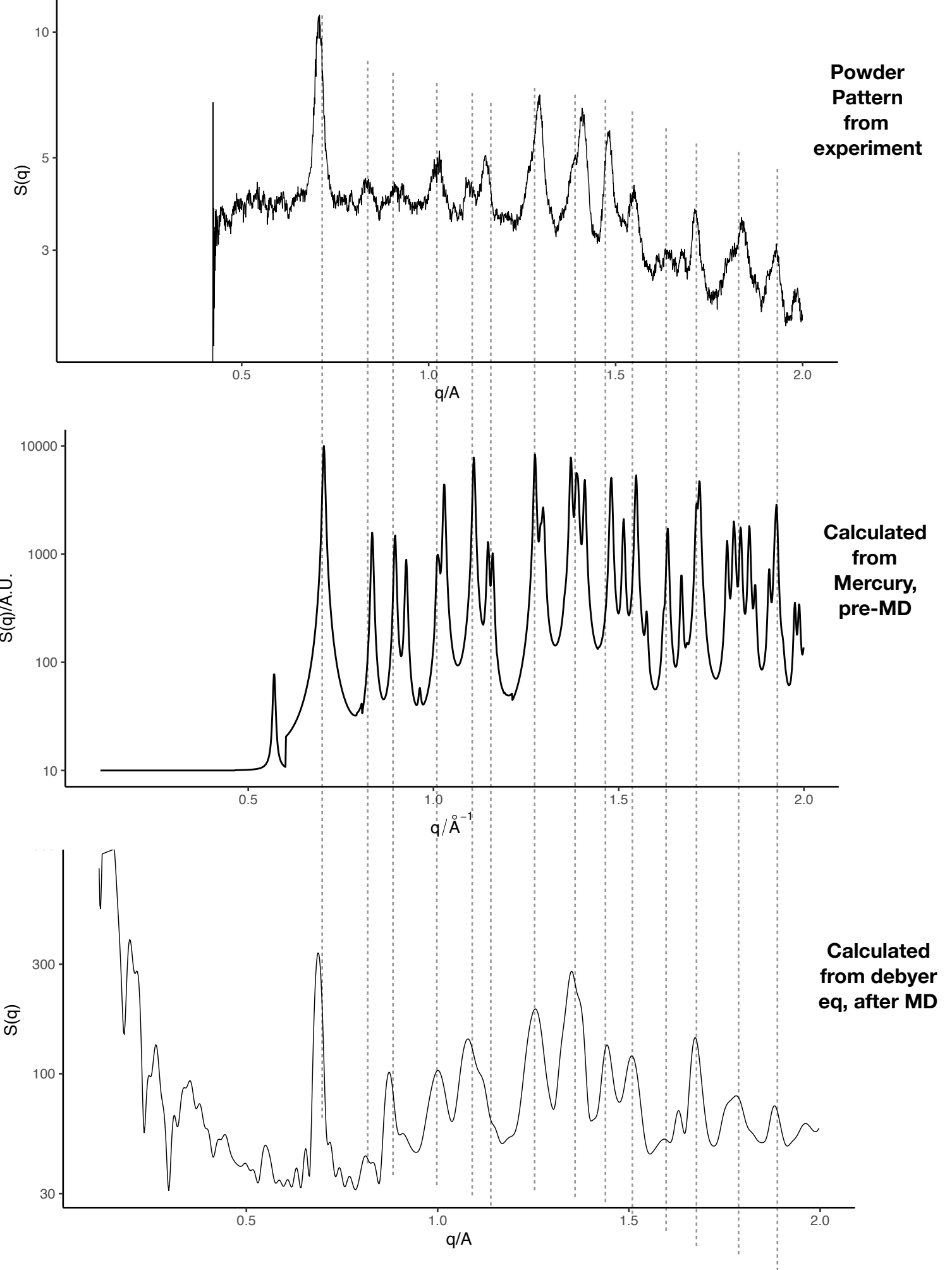


Image of super cell
stabilised in MD

Parameters
after MD

$a = 7.17$
 $b = 14.36$
 $c = 18.45$
 $\alpha = 89.25$
 $\beta = 96.78$
 $\gamma = 91.19$

Strong agreement seen between the
experiment, the theoretical structure
factor and the calculated structure factor
after equilibration in MD.



Glycoxylated Bithiophene Polymer Crystal

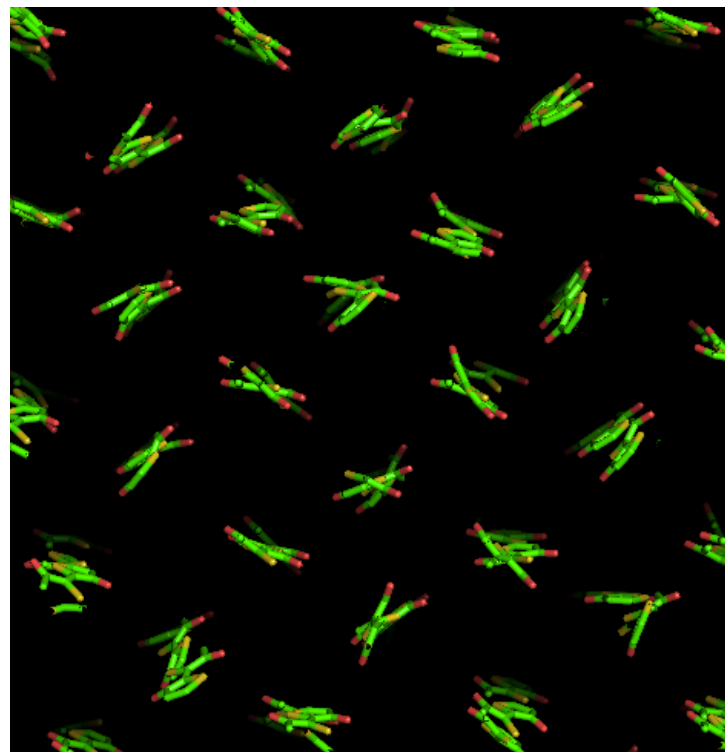
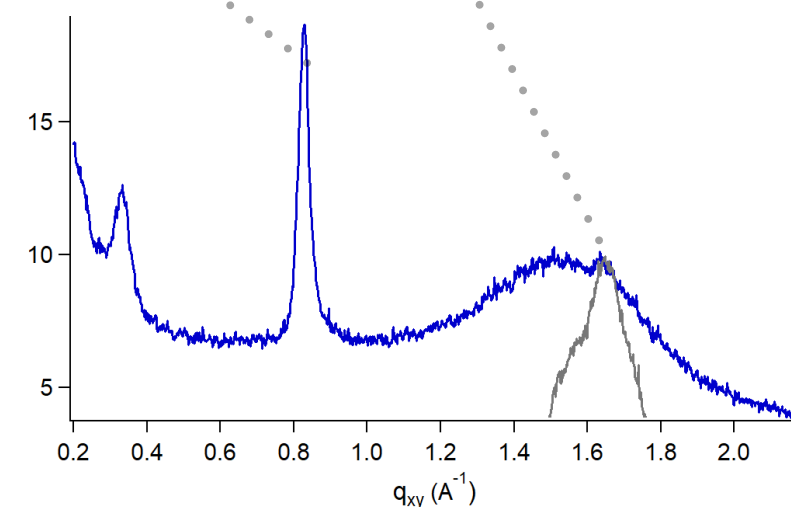
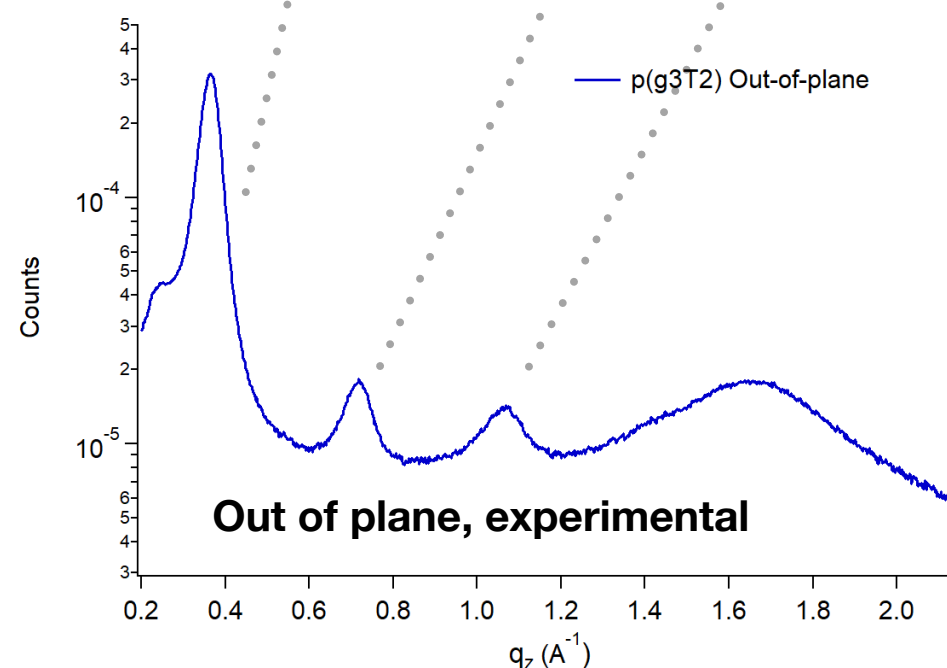
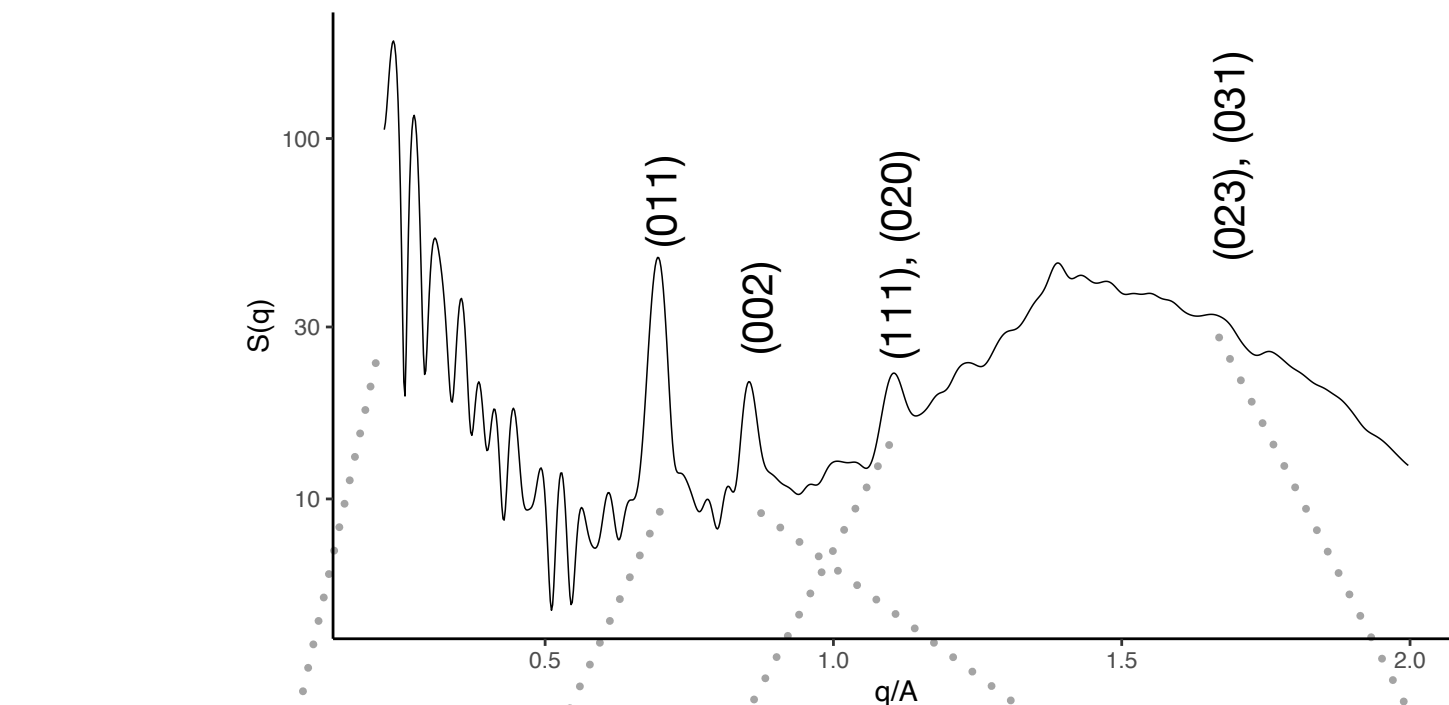


Image of crystal looking along backbones. Only backbone structure shown for clarity



$a = 7.96$
 $b = 12.2$
 $c = 15.7$
 $\alpha = 90.00$
 $\beta = 97.71$
 $\gamma = 90.00$
 Symmetry = P21/n

Oscillations at low- q in the simulated pattern may be occurring due to artefacts from the limited size of the box that is simulated. The lattice parameters are only approximate, as further analysis of the MD structure files are needed to extract the exact ones. The polymer crystal adopts a herringbone structure, as opposed to a pi stack. Worthwhile to keep testing other structures with pi stacks to see if good agreement is reached with other structures. So far these haven't been stable in MD however.

Questions moving forward -

- 1) How can we screen for other possible crystal structures for the polymers? I am currently working on some other structures for the glycoxylated polymer which contain a more traditional pi-stack, however so far these have shown to be unstable in MD (thats not to say its the pi-stack thats making them unstable).
- 2) Is there significant side chain-backbone interactions occurring in the glycoxylated polymers? For example some sort of weak hydrogen-bonding that could influence redox potentials?
- 3) How do these crystal structures affect the interaction with an aqueous electrolyte (subject of future simulations)
- 4) What is the implications of these crystal structures for devices? Both in terms of hole transport and ion penetration into the bulk.