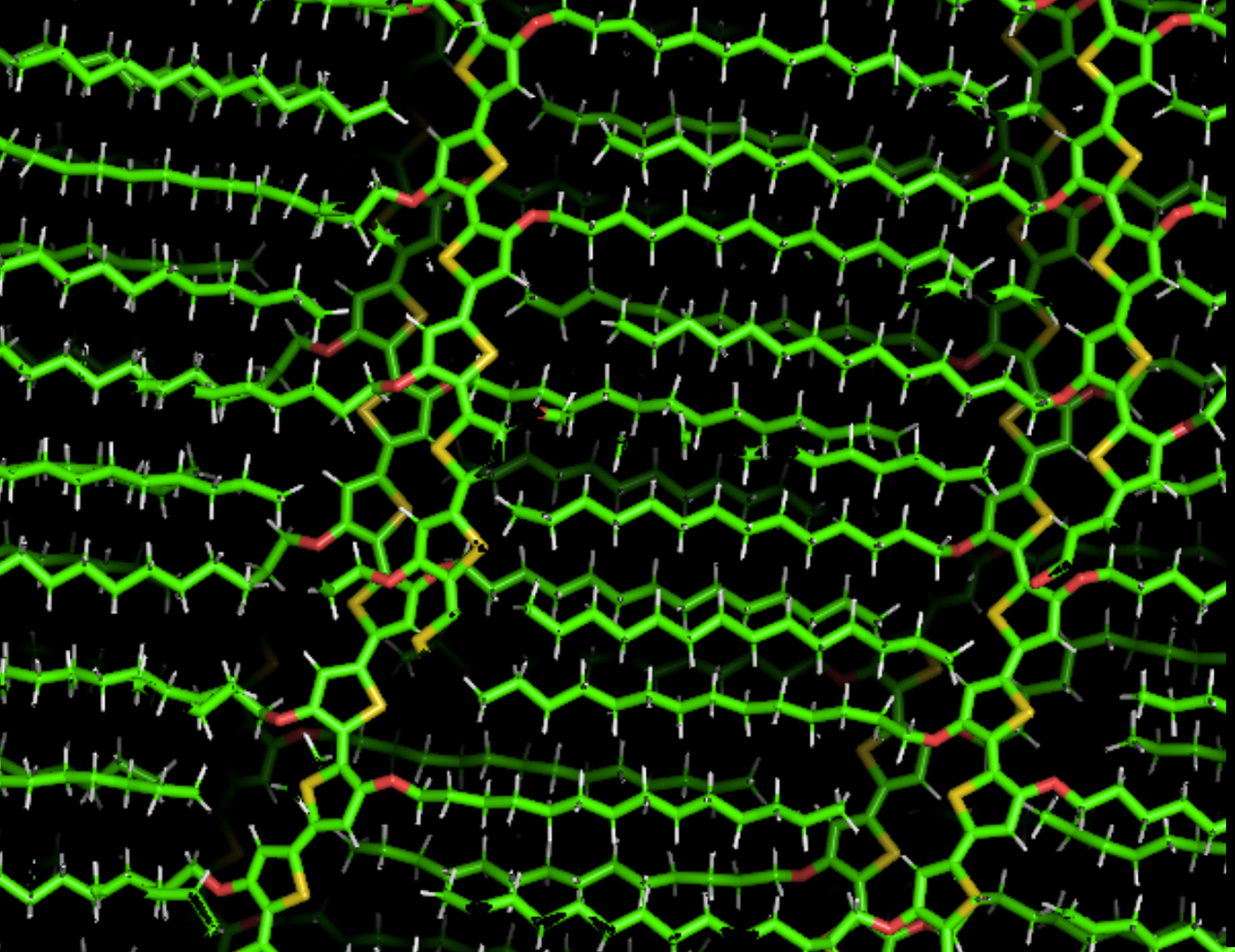
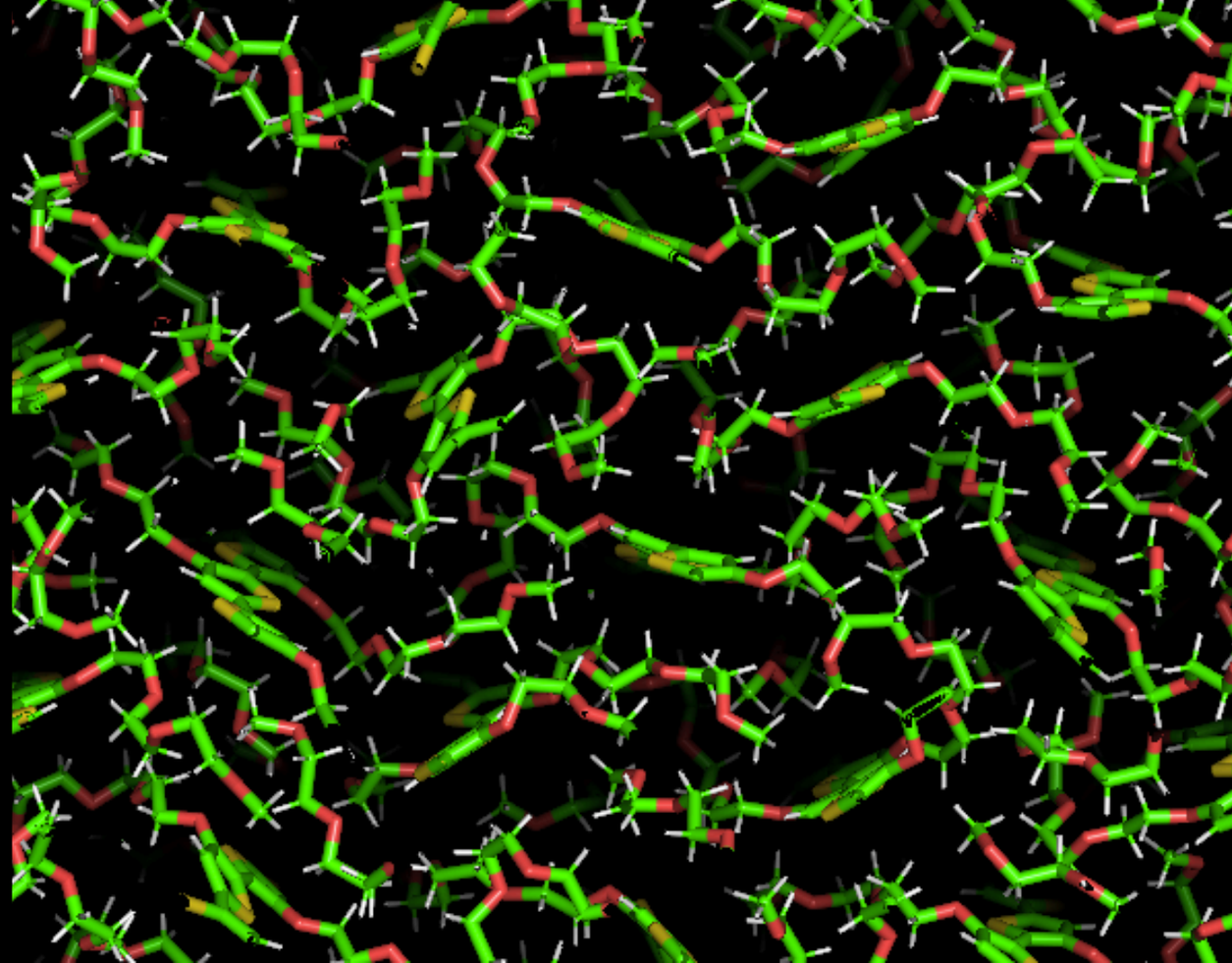
Investigating the Effect of side chain chemistry on polymer structure in solid state using Molecular Dynamics and Quantum Chemical Calculations

Nicholas Siemons, Jarvist Frost, Drew Pearce and Jenny Nelson
Imperial College, London
31/03/2020

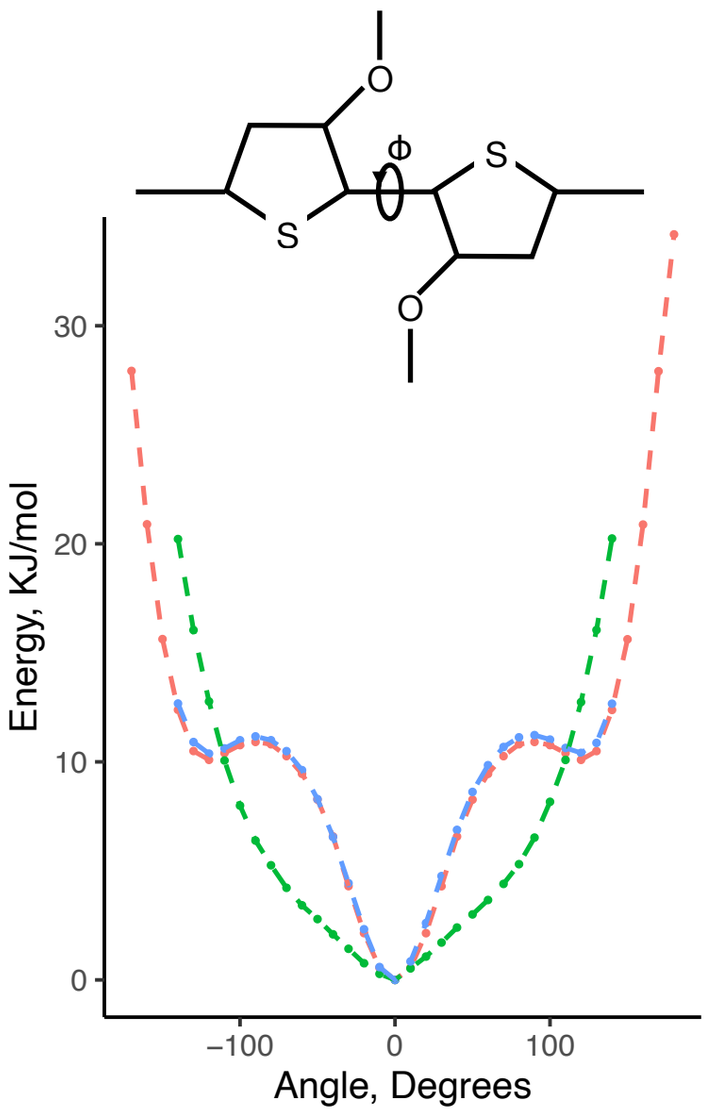




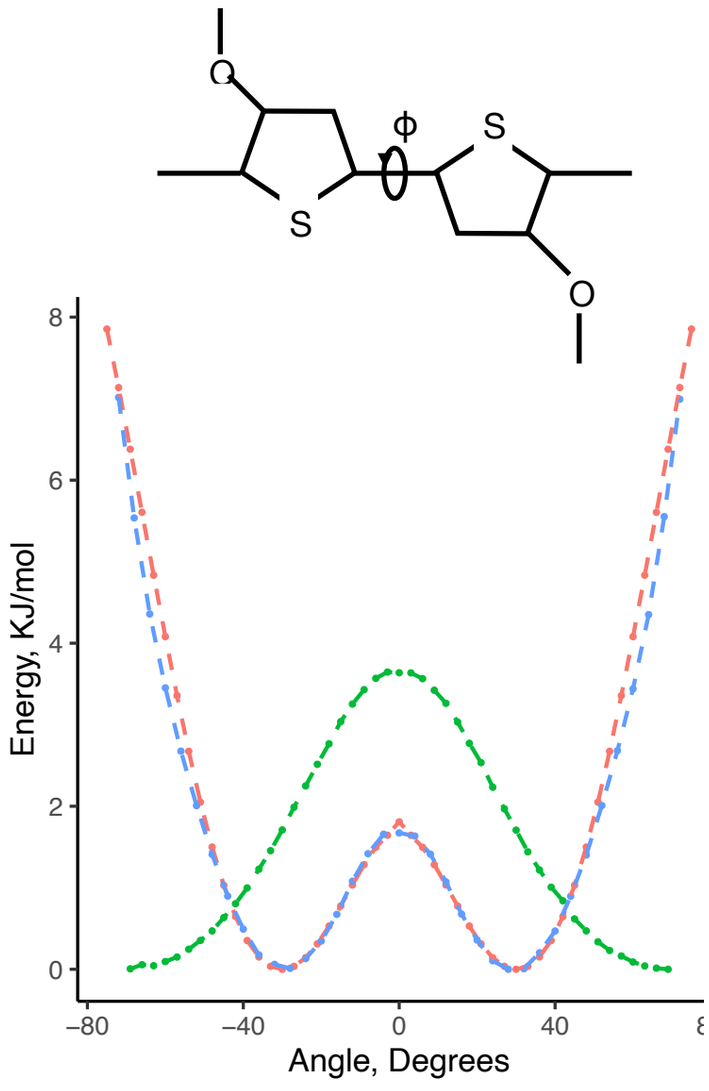
Force Field Design Principles

1) Forcefield based on OPLS. OPLS on its own is not enough however, as it typically does not model pi conjugated systems very well. Therefore specific re-parameterisation needs to be done.
2) 'Important' DOFs re-parameterised. These are -
    1) 'inner dihedral'
    2) 'outer dihedral'
    3) 'C-O angle'

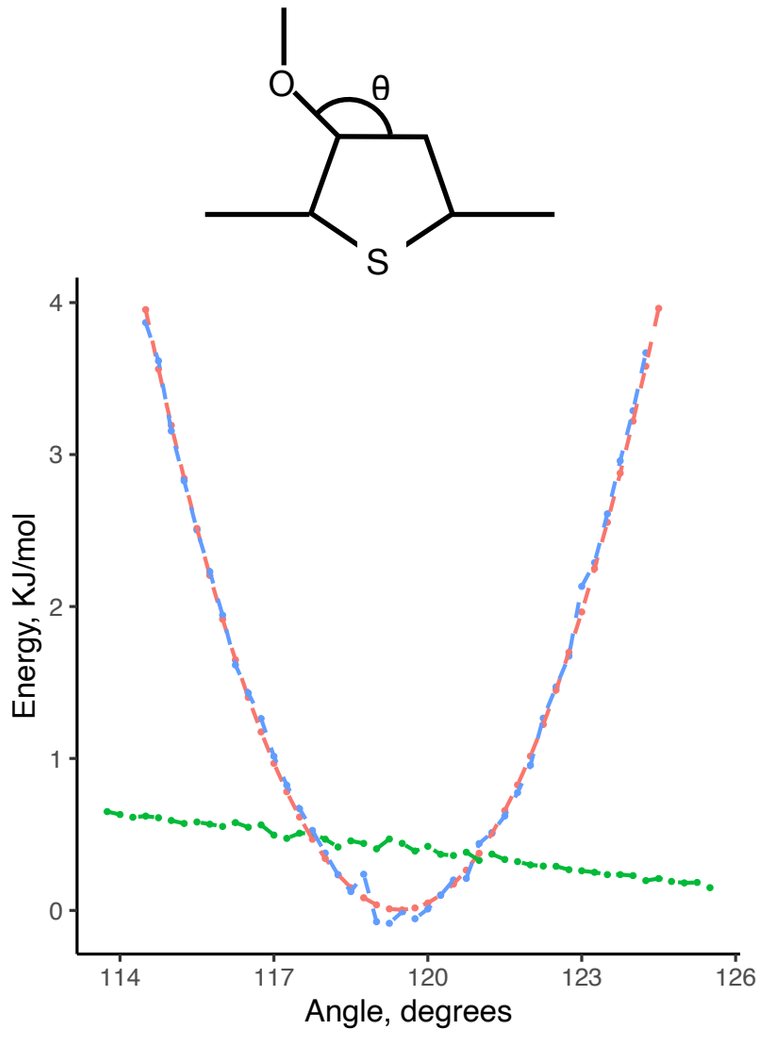
Inner dihedral



Outer dihedral



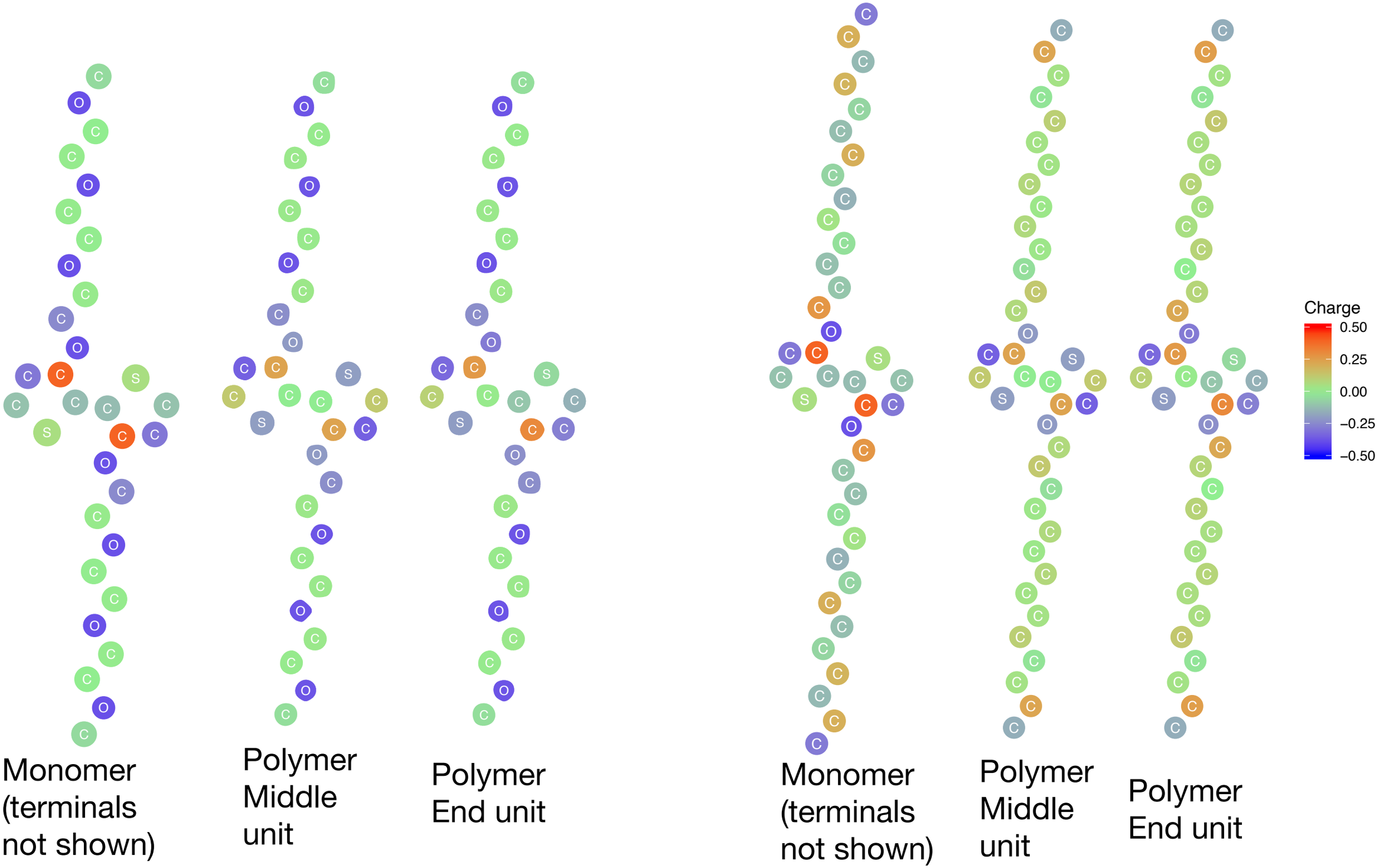
C-O angle



Green - Background potential in MD forcefield, Red - DFT energy scan, Blue - MD potential after parameterisation. B3LYP functional used for inner dihedral and C-O angle, wB97XD used for Outer Dihedral.

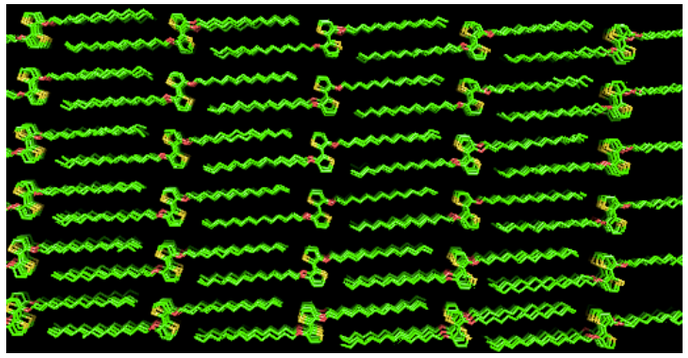
Electrostatic parameters (EP)

1) Alkoxylated monomer - EP parameters for entire molecule calculated using DFT, B3LYP functional
2) Alkoxylated polymer - EP parameters calculated for a set of representative oligomers using DFT, B3LYP functional
3) Glycoxylated monomer - EP parameters for the backbone are the same as for Alkoxylated monomer, and side chain EP parameters are from OPLS
4) Glycoxylated polymer - EP parameters for the backbone are the same as for Alkoxylated polymer, and side chain EP parameters are from OPLS



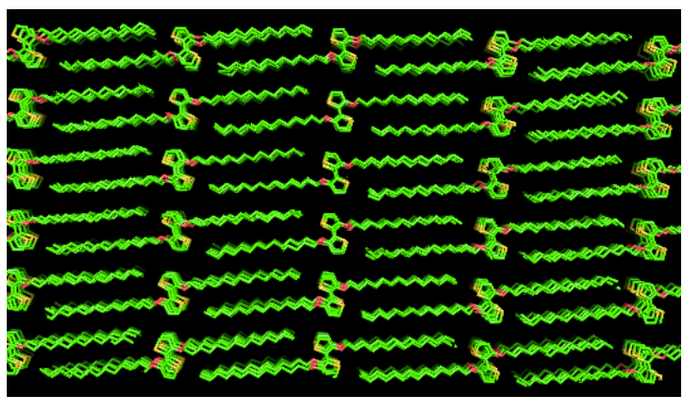
Alkoxylated monomer crystal structure - testing stability

Without annealing



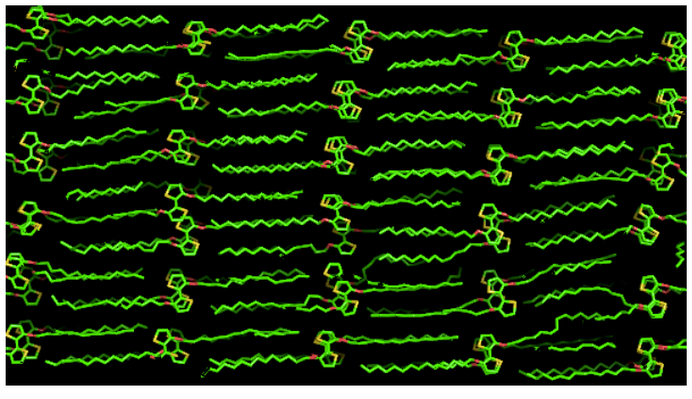
a = 4.16
b = 9.28
c = 23.78
α = 91.97
β = 91.28
ɣ = 96.10

Annealed at 350K



a = 4.16
b = 9.28
c = 23.76
α = 92.21
β = 91.70
ɣ = 97.13

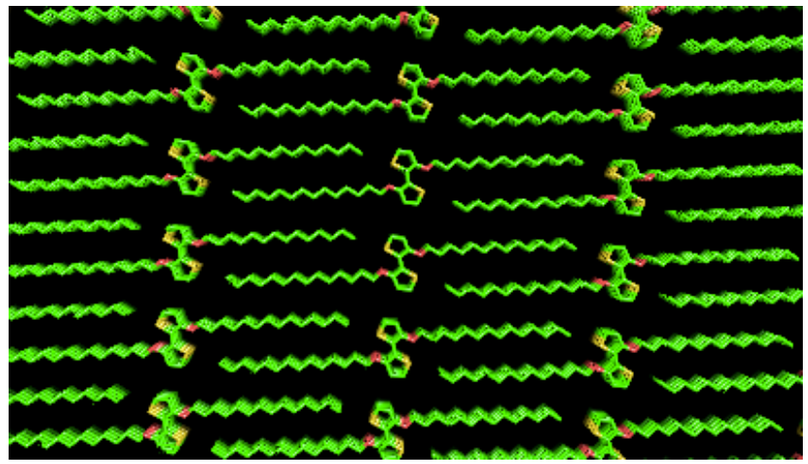
Annealed at 400K



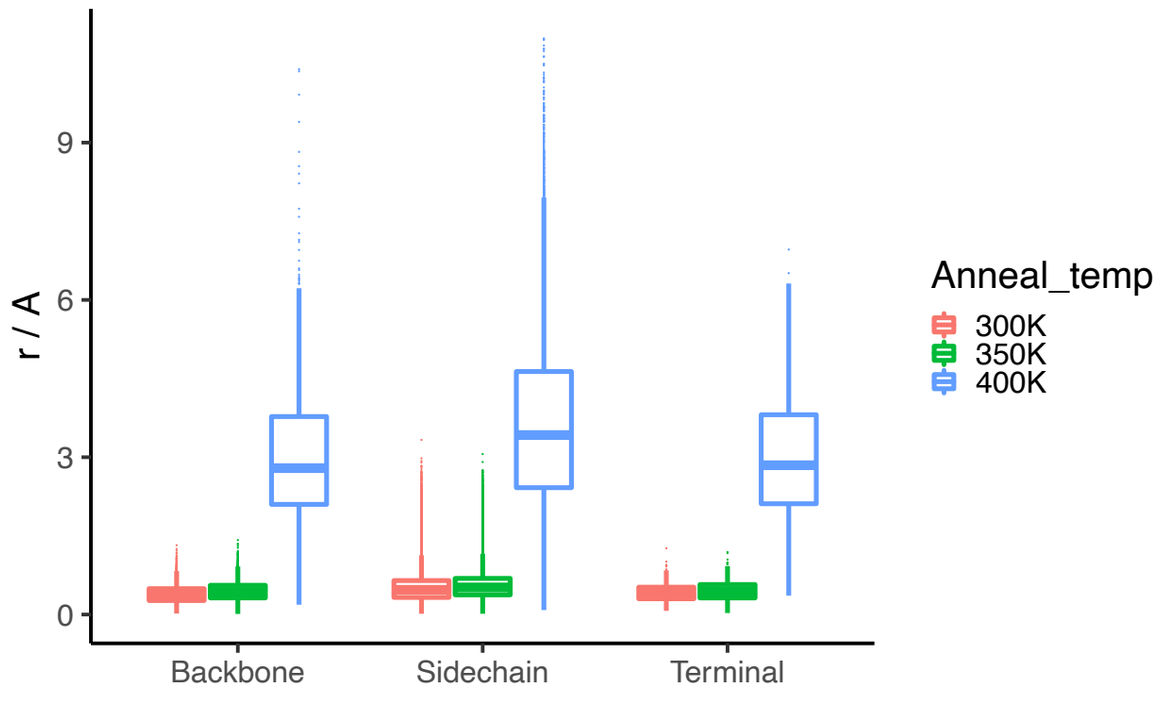
a = 4.25
b = 9.48
c = 24.29
α = 90.71
β = 88.89
ɣ = 96.21

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
α = 91.86
β = 91.48
ɣ = 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 alkoxylated monomer crystal is well reproduced.

Alkyl Monomer Crystal

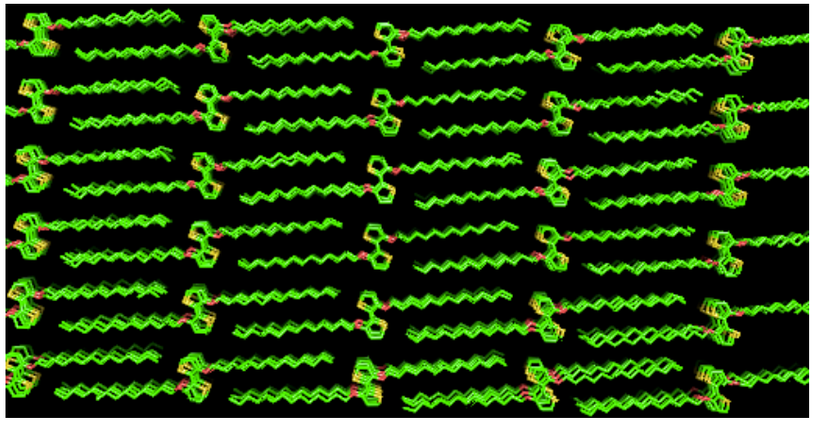
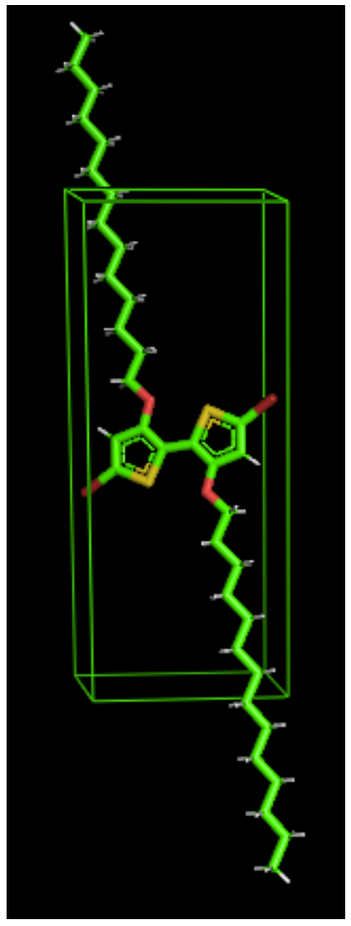


Image of super cell stabilised in MD



Parameters after MD

a = 4.16

b = 9.28

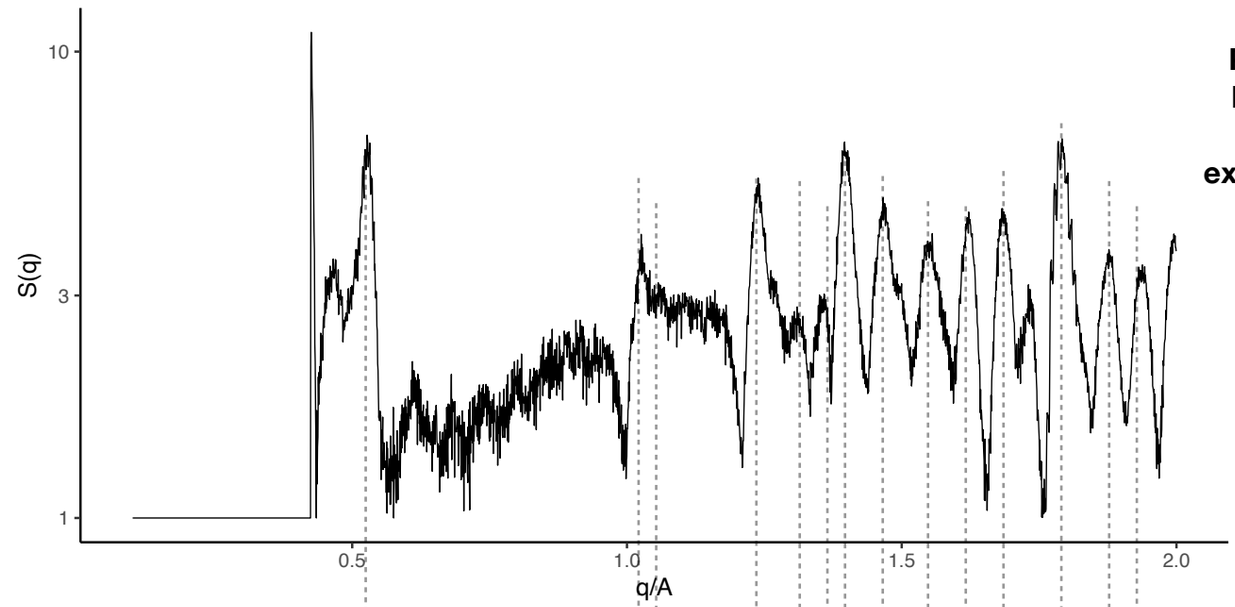
c = 23.78

α = 91.97

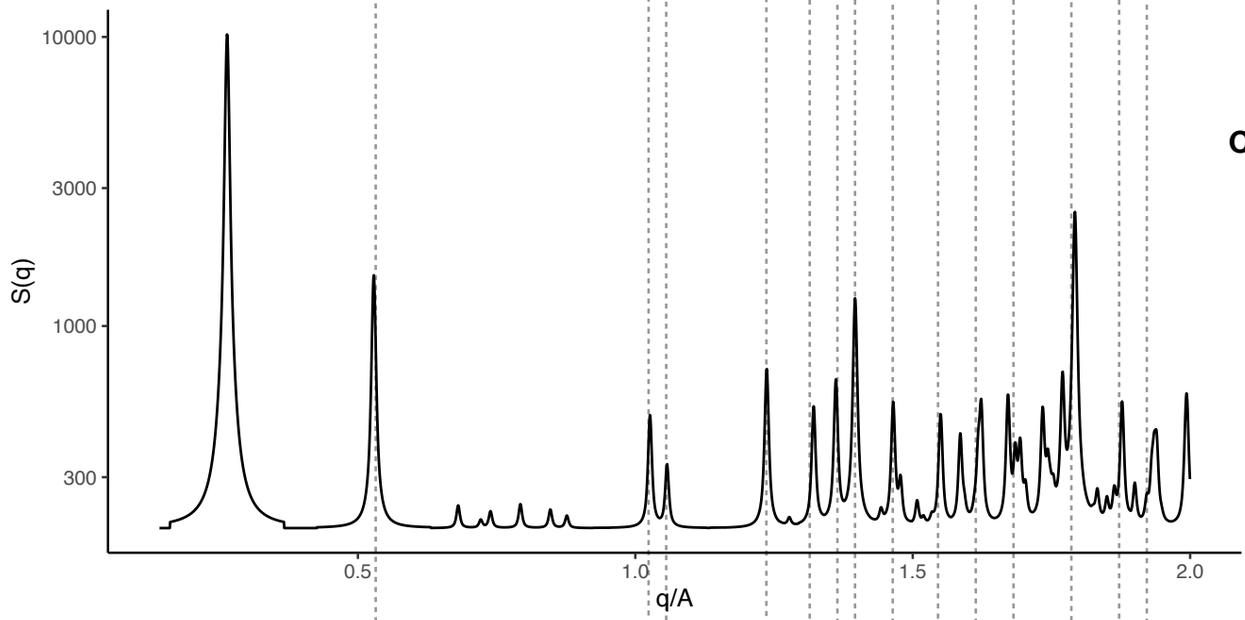
β = 91.28

ɣ = 96.10

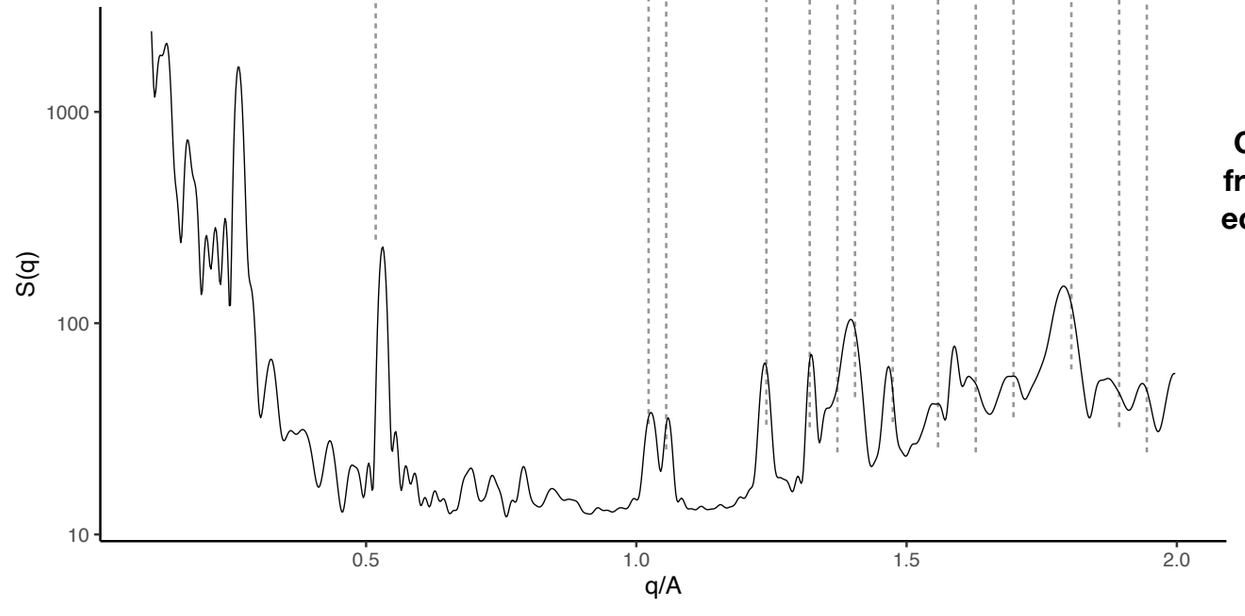
Strong agreement seen between the experiment, the theoretical structure factor and the calculated structure factor after equilibration in MD. Additionally the level of crystallinity seems to be in good agreement.



Powder Pattern from experiment



Calculated from Mercury, pre-MD



Calculated from debyer eq, after MD

Alkoxylated Polymer Crystal

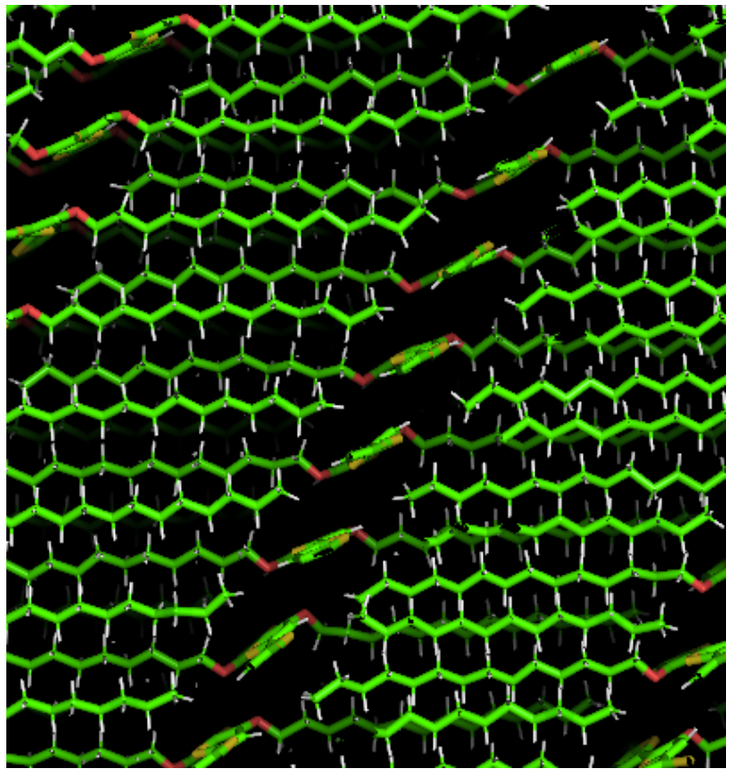
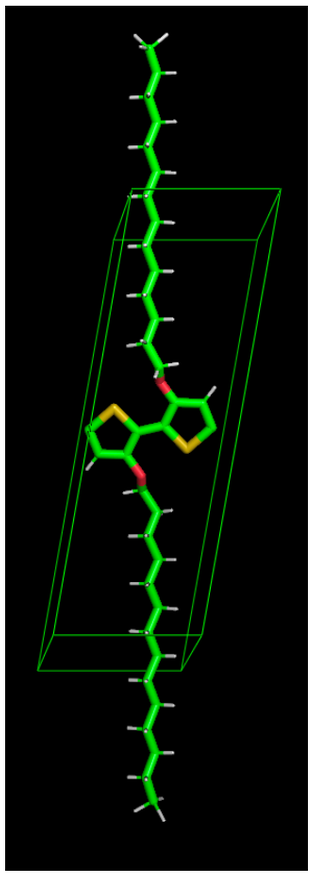
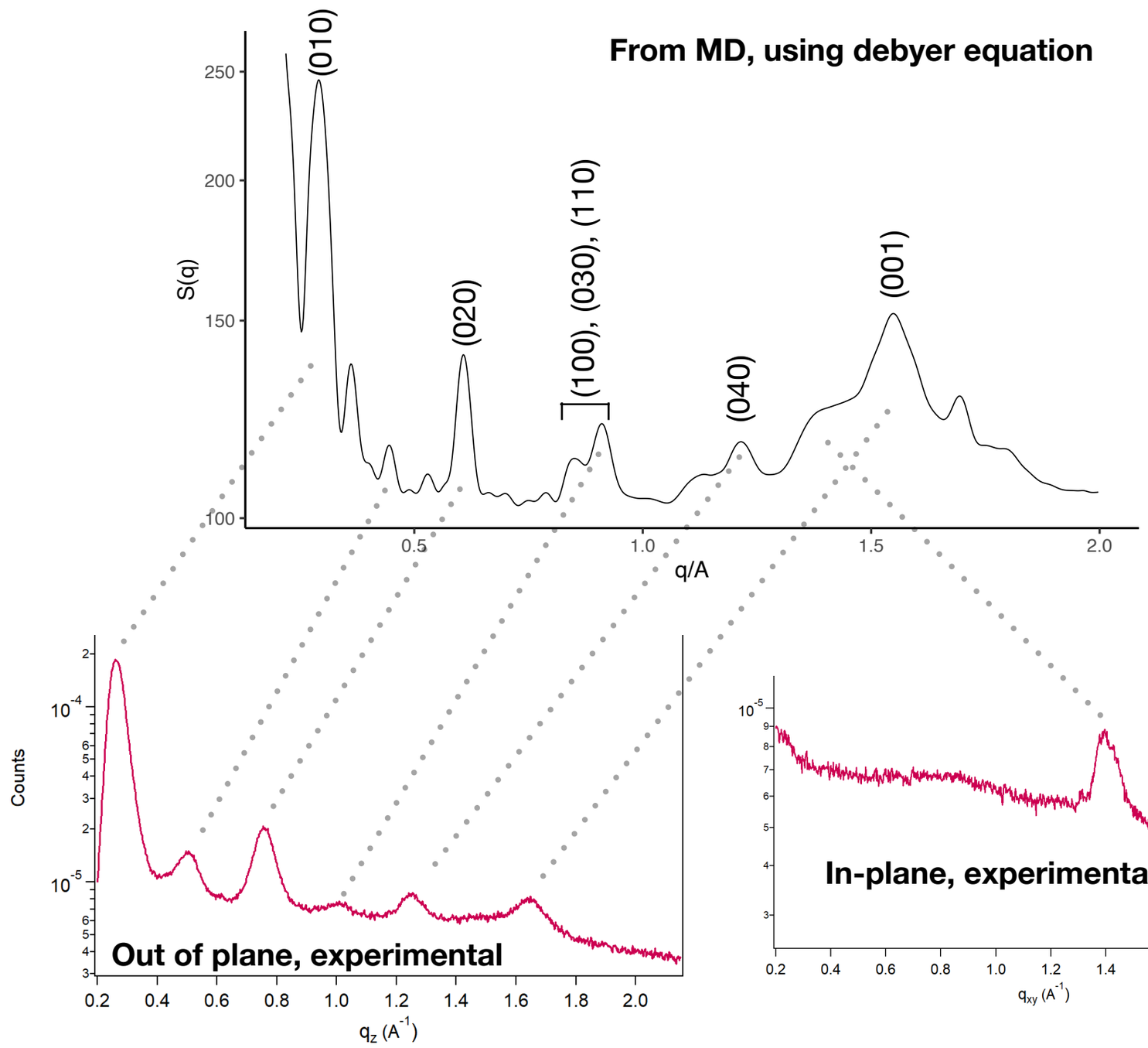


Image of crystal looking along backbones



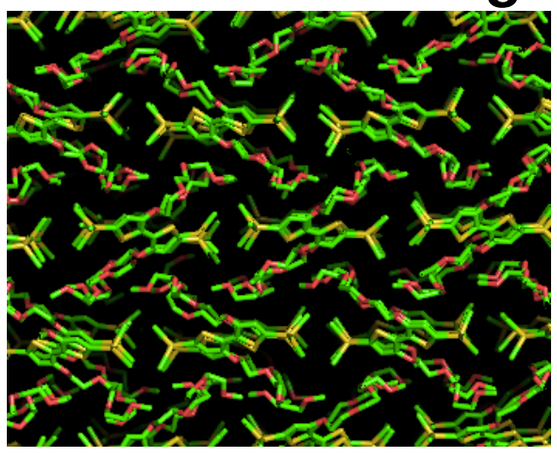
a = 7.67
b = 21.85
c = 5.84
α = 65.27
β = 79.60
γ = 92.02
Symmetry = P1



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

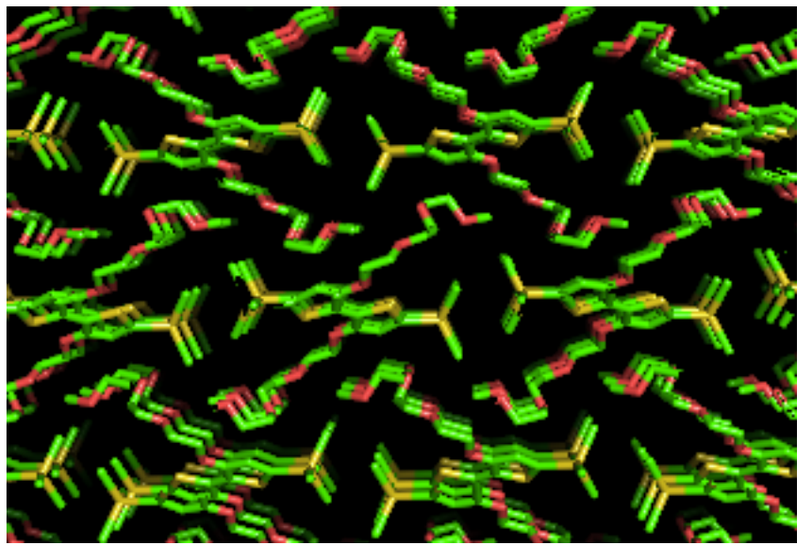
Without annealing



a = 7.1
b = 14.4
c = 18.5
α = 89.2
β = 96.8
ɣ = 91.2

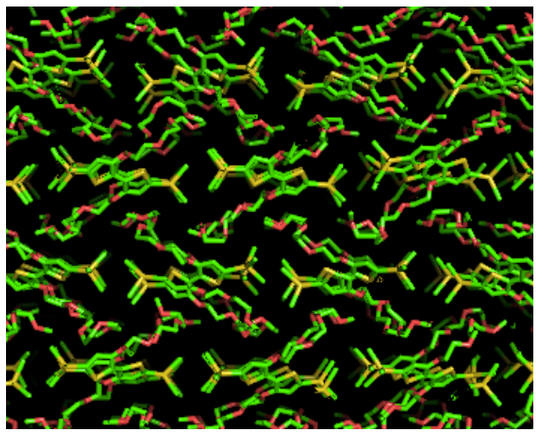
Annealing protocol -
1) Heat from 300K to annealing temperature over 1ns
2) Cool from annealing temperature to 300K at a rate of 10K/1ns

Before MD (structure from Andrew)



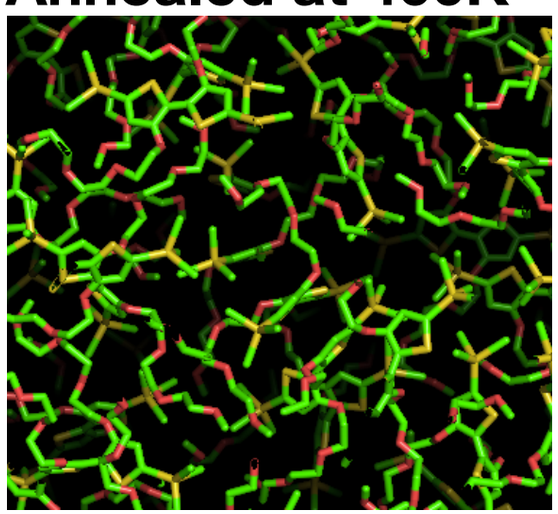
a = 7.17
b = 14.36
c = 18.45
α = 89.25
β = 96.78
ɣ = 91.19

Annealed at 350K

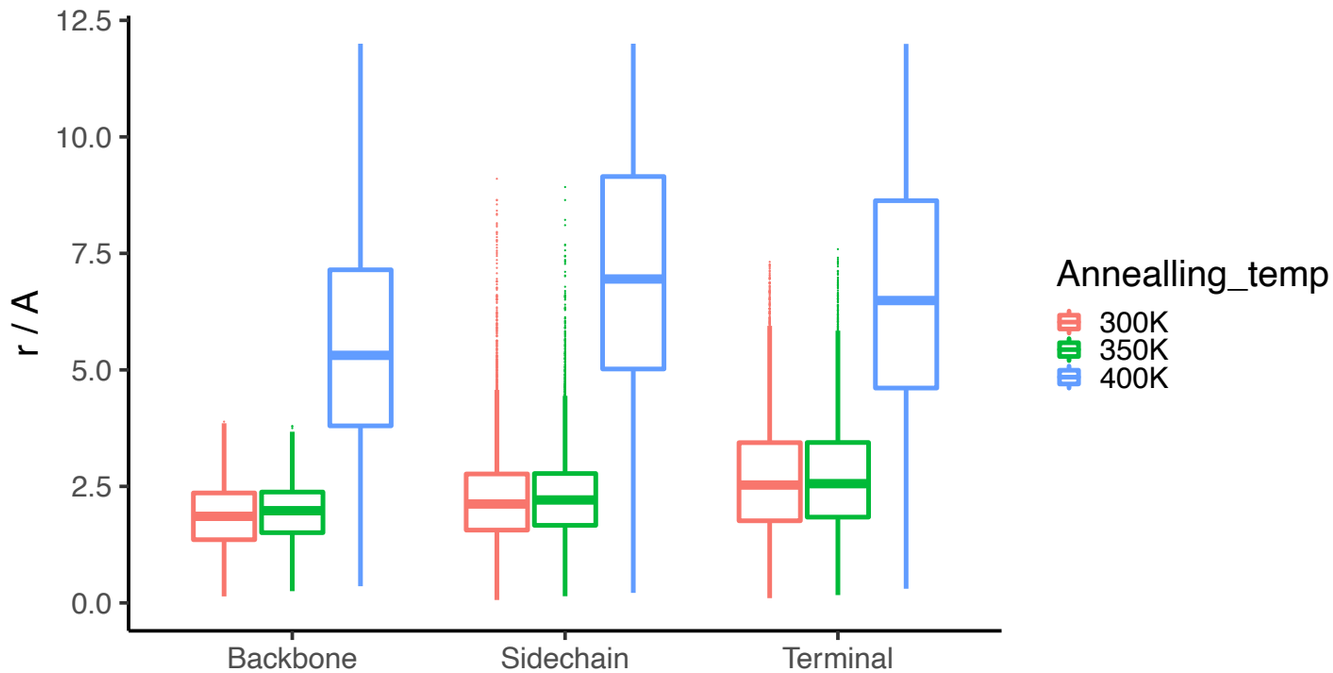


a = 7.2
b = 14.4
c = 18.3
α = 89.4
β = 98.1
ɣ = 90.2

Annealed at 400K



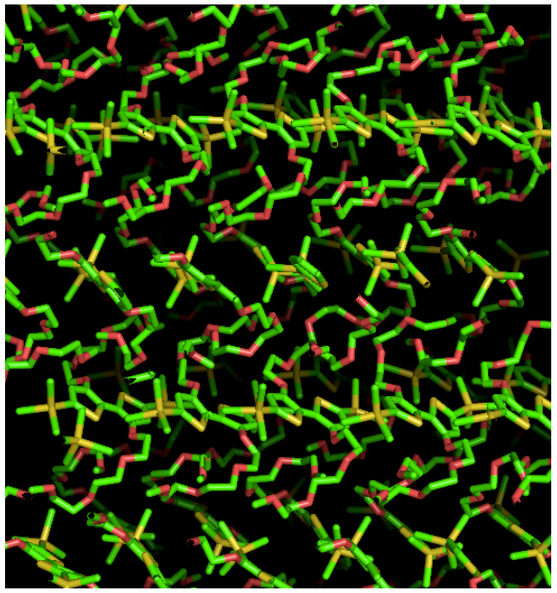
Too amorphous to characterise A unit cell



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

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

Glycol Monomer Crystal



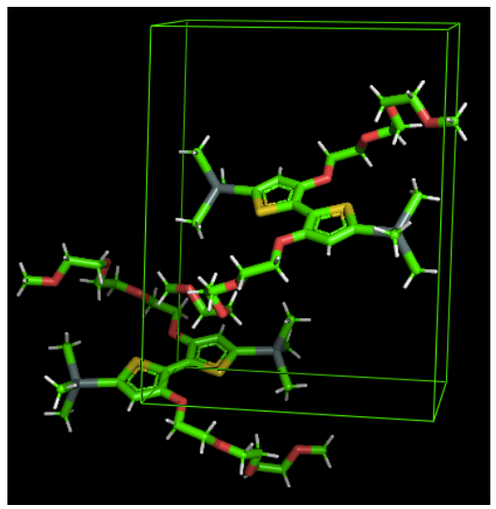
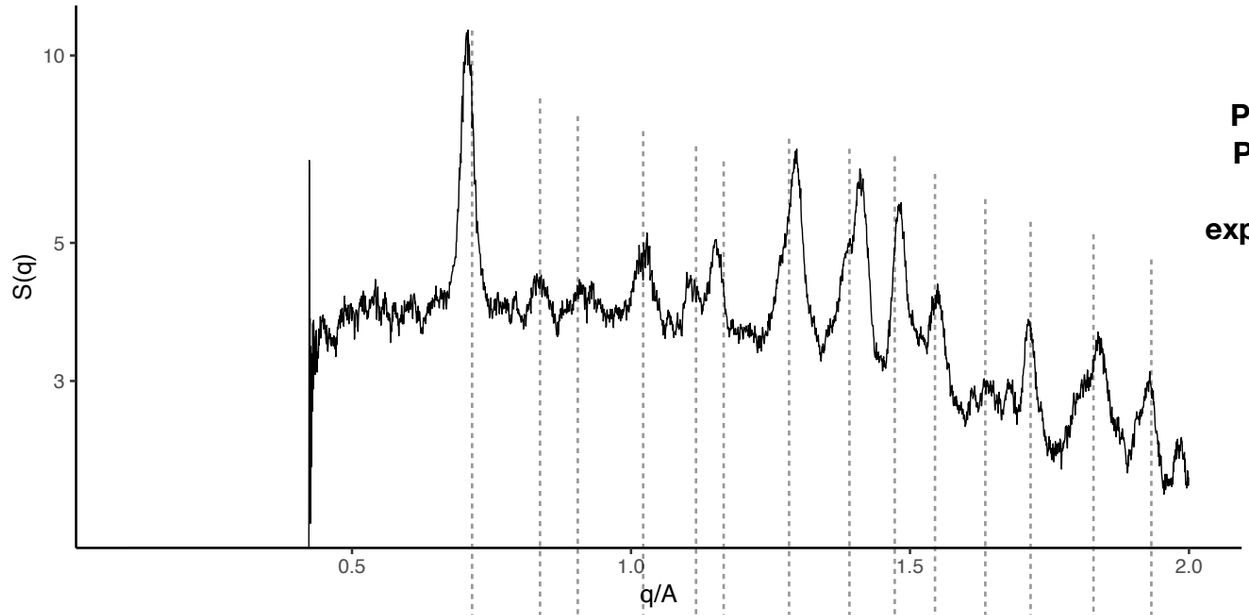


Image of super cell stabilised in MD

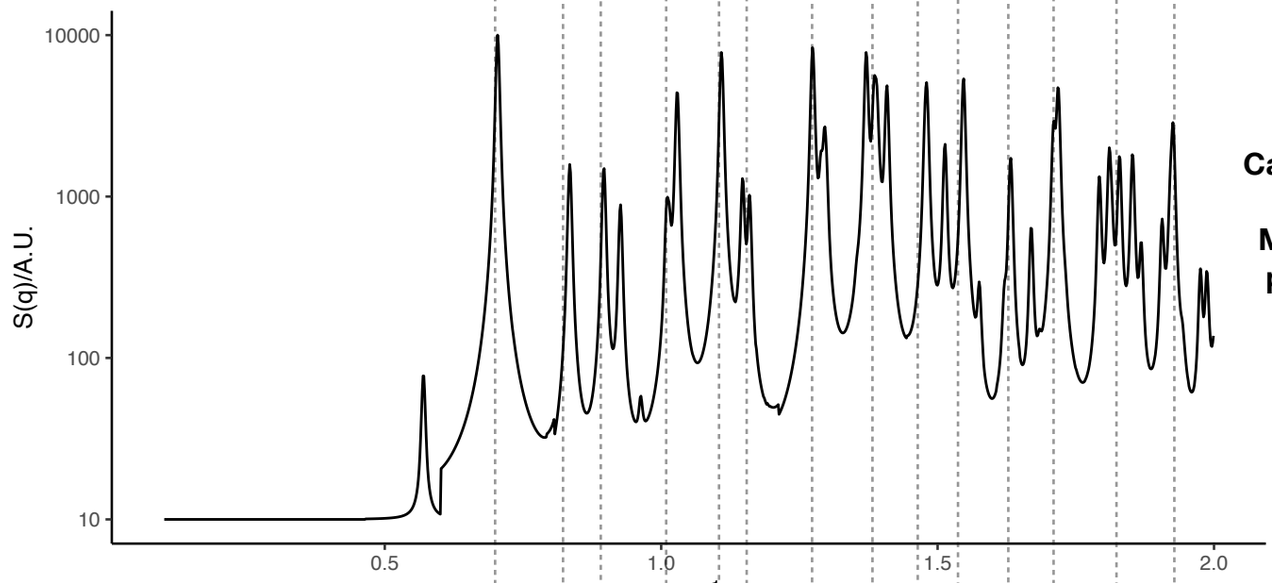
Parameters after MD

a = 7.17
b = 14.36
c = 18.45
α = 89.25
β = 96.78
γ = 91.19

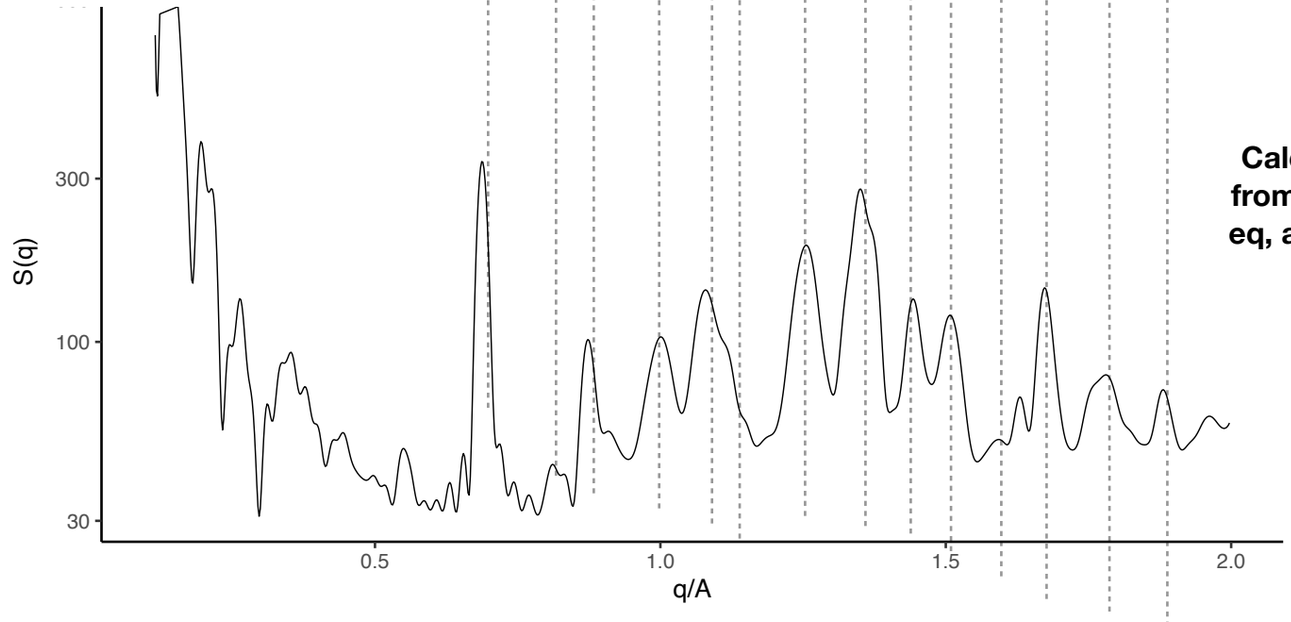
Strong agreement seen between the experiment, the theoretical structure factor and the calculated structure factor after equilibration in MD.



Powder Pattern from experiment



Calculated from Mercury, pre-MD



Calculated from debyer eq, after MD

Glycoxylated Bithiophene Polymer Crystal

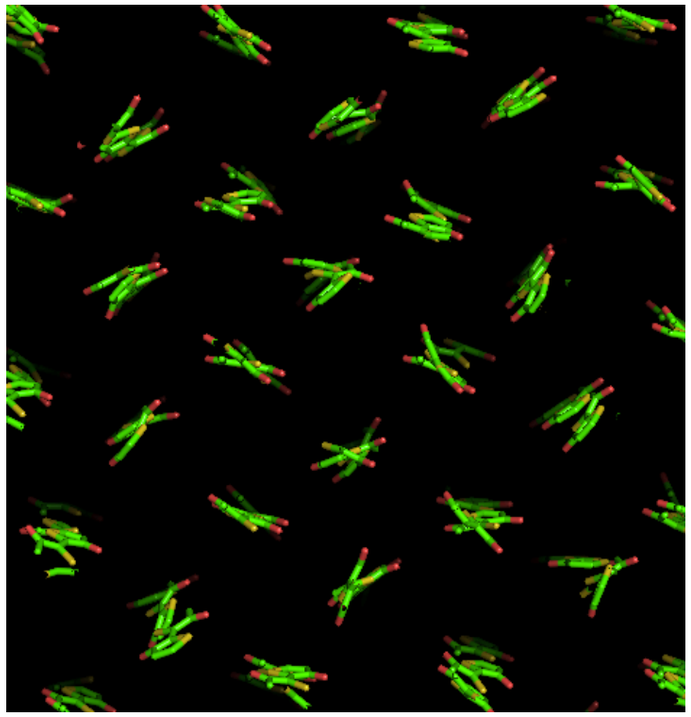
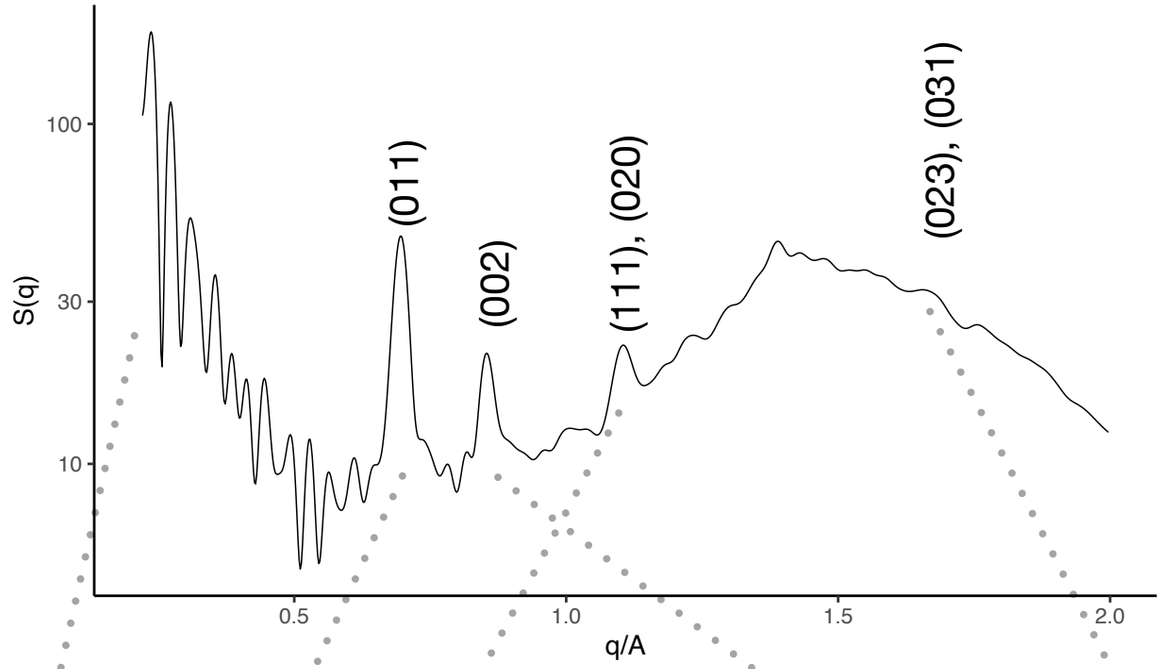
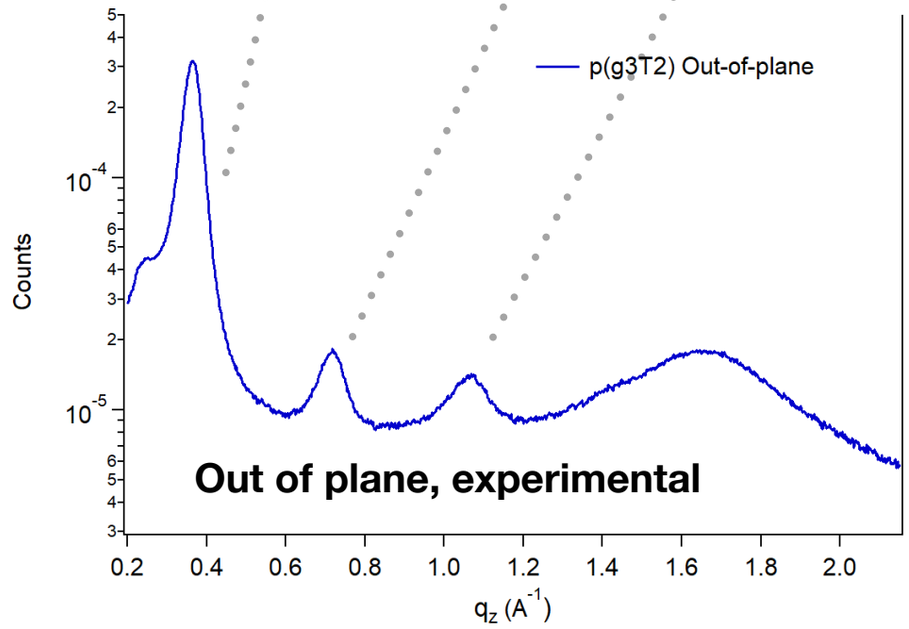
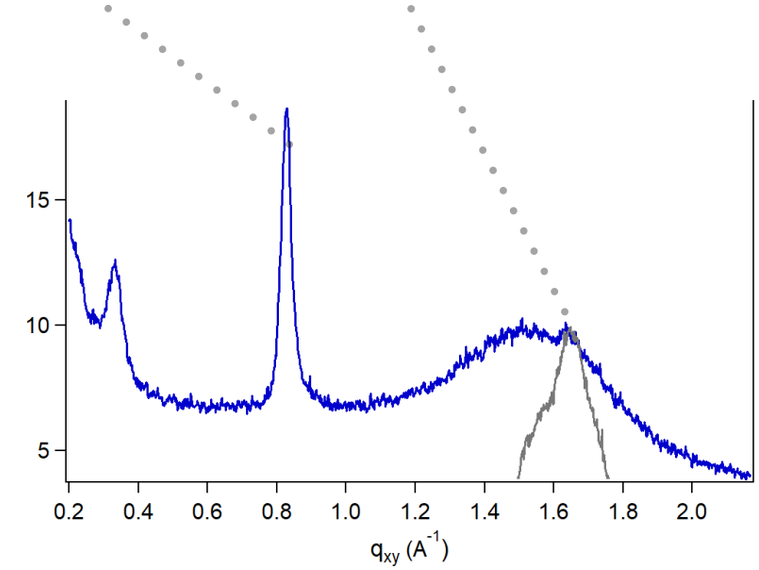


Image of crystal looking along backbones. Only backbone structure shown for clarity

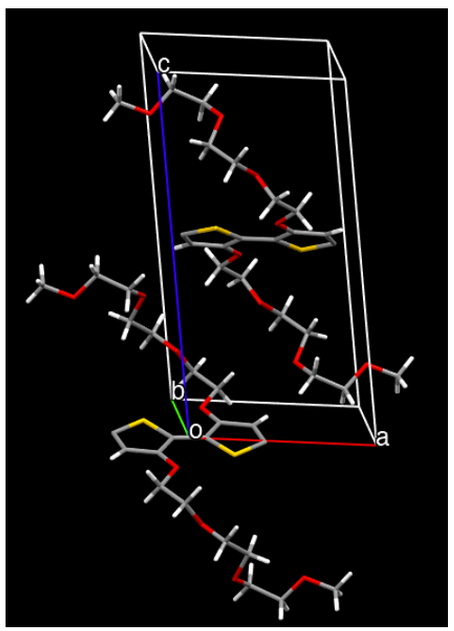




Out of plane, experimental



In-plane, experimental



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 pic 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.