Chapter 1

Building the Model

1.1 Introduction

A wide range reaction products are experimentally observed during the low temperature degradation and slow ageing of **NC!** (**NC!**). These can be partially attributed to the range of susceptible attack sites on the polysaccharide backbone, as well as the myriad of possible secondary reactions following denitration, depolymerisation or ring-cleavage.

When probing the details of individual chemical reactions using computational methods, the extended polymer structure becomes unweildy due to the large number of atoms.

In practice, *ab initio* and density functional methods used to determine the reaction energies are limited to between XX - XX atoms.

The polymer structure was truncated to a single-ring monomer by Shukla *et al.* for the purposes of investigating the alkaline hydrolysis behaviour of **NC!**.[**?**] The study analysed the **sn2!** nucleophilic attack at the nitrate carbon, releasing the nitrate ion in favour of a hydroxyl group, at the C2, C3 and C6 nitrate sites (FIG. X).

Insert fig X

Comparisons between the monomer, dimer and trimer found the dimeric structure to be the smallest suitable model for the chemical behaviour of the polymer. This is also observed when considering the minimum unit encompassing all bonding interactions necessary for parameterisation for a forcefield, for implementation in molecular dynamics simulations.

In this chapter, the electronic properties of the monomer, dimer and trimer truncations of the polymer are compared. The monomer model The fully nitrated dimer structure used in this study consists of two non-planar β-D-glucopyranose rings joined by a glycosidic bond, with six nitrate groups attached at the 2,3,6 positions on each ring (FIG XX). as in cellulose chains "observed during SEM / X-ray diff measurements" (FIG).

Comparisons between the monomer, dimer and trimer found the dimeric structure to be the minimum model required to accurately represent the chemical behaviour of NC in the alkaline hydrolysis pathway.

1.2   Methodology

Monomer, dimer and trimer starting structures were drawn as closely matching literature geometries as possible. Starting with the oxygen of the glucopyranose ring in the chair position, the hydroxy groups are sequentially substituted by nitrate groups at the C2, C3 and C6 positions, retaining their equatorial conformation. The order of nitration and denitration us explored in [Results chap 2].For dimer and trimer, individual saccharide rings were alternating (FIG above)

In order to explore the limitations of different capping groups, chain ends were capped with either methoxy or hydroxy groups (FIG.), as were employed in Shukla's study. The differences in the charge distribution and intra-molecular interactions were probed using **QTAIM!** (**QTAIM!**) methods to look at critical points and the Laplacian of electron density. When regarding partial charges and to a limited extent, steric considerations, methoxy groups were expected to provide a better approximation for the extended polysaccharide.

Structures underwent geometry optimisation in vacuum and implicit solvent, using various methods detailed in section XX.

1.2.1   Computational details

The **B3LYP!** (**B3LYP!**) density functional was chosen for initial exploration of electronic properties for the system. It is an efficient and well-benchmarked method for calculating electronic properties for main group elements and appropriate for the model system size, which would extend to around 80 atoms for the trimer. All electronic structure calculations, including geometry optimisation and thermodynamic calculations were performed to the level of **B3LYP!** 6-311+G(d,p), using **G09!** (**G09!**).

Structures were built using z-matrix notation or the **GView!** (**GView!**) graphical interface. Molden 5.0.2 and **GView!** packages were used for visualisation. Electrostatic potential (**ESP!**) surface maps were also visualised using **G09!**, using the CubeGen utility.

QTAIM! analyses, including generation of Laplacian electron density maps and **CP!** (**CP!**) analysis on the optimised structures were performed using MultiWFN 3.6

Partial charges were obtained via PyRed (R.E.D. Server version 3.0).

1.3 Truncating the polymer

1.3.1 Model size

- Variation in partial charges, with different capping groups - Variation in ESP with different capping groups - Variation in Critical bonding points with diff capping groups

And all of the above with different sized systems

Repeat for solvent and vacuum, if there is time (there isn't)

[FIX ME]

1.4 Truncating the polymer model

obvs mention Shukla's studies here.

Looked at QTAIM for interaction with capping groups

[FIX ME]

The dimer ends are capped by methoxy groups rather than hydroxyl groups as were employed in Shukla's study. From the perspective of partial charges, and to an extent steric considerations, methoxy groups are expected to provide a better approximation for the extended polysaccharide.

Shukla's work identified the nitrate group attached to carbon three (C3) as the most susceptible to denitration and the first to be removed. This is supported by the distribution of partial charges in the molecule, with disregard of the capping groups. Thus, the nitrate group on C3 was used as the target site for degradation studies.

1.5 Summary

In this section