



THE UNIVERSITY
of EDINBURGH

| School of Chemistry

Understanding the Structural Properties of Nitrocellulose

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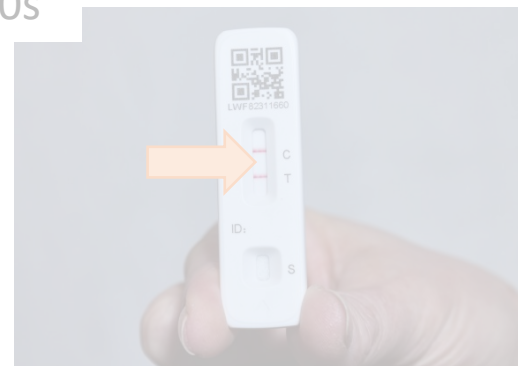
Nitrocellulose - Almost 200 Years of Use

Historic uses

1850s



1950s

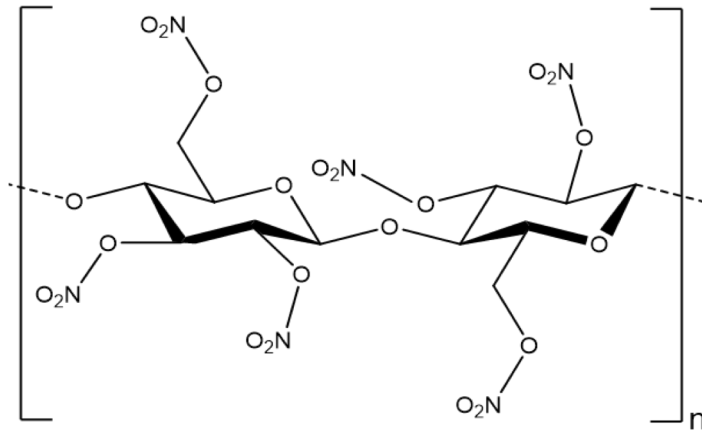


Current uses

Now

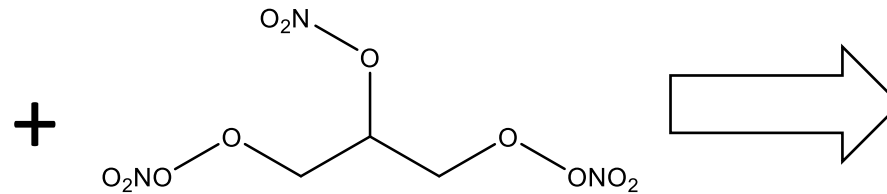


Nitrocellulose – Polymer binder



Naturally derived

Nitroglycerin – Liquid oxidiser

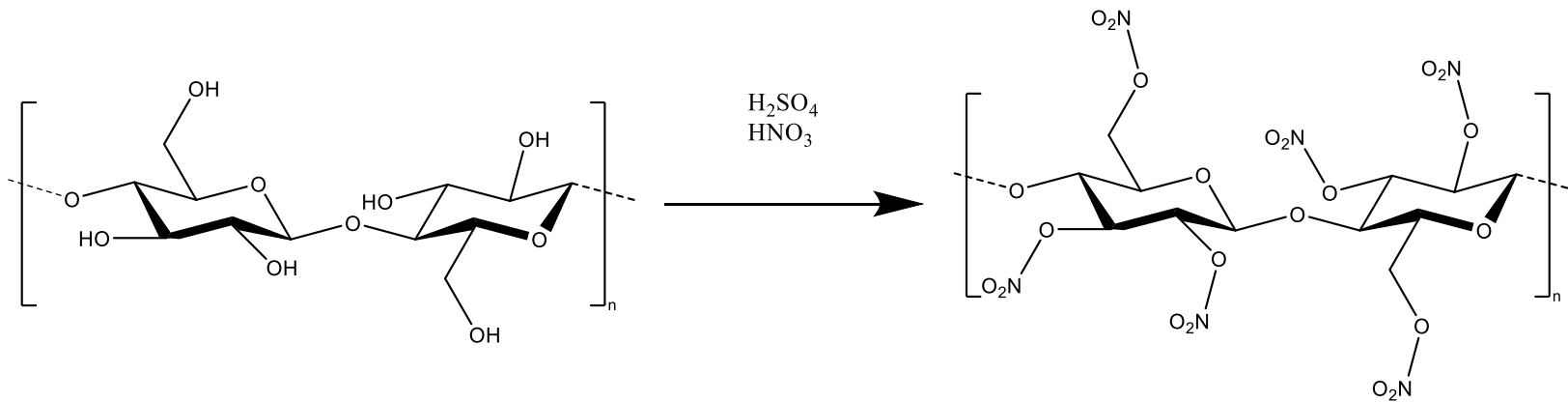
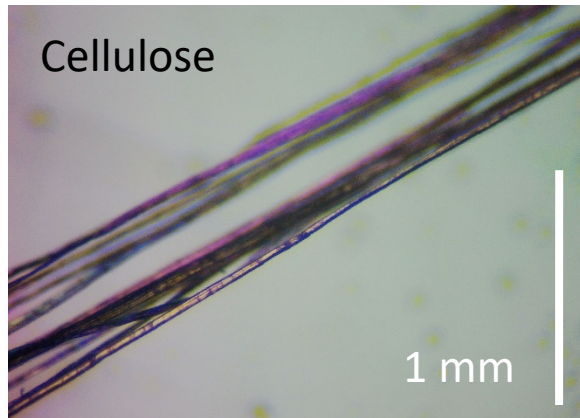


Solid Propellants



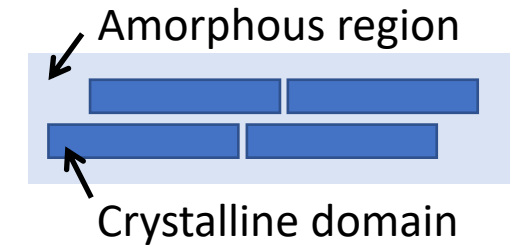
Supply chain and reliance issues

Structure of Nitrocellulose

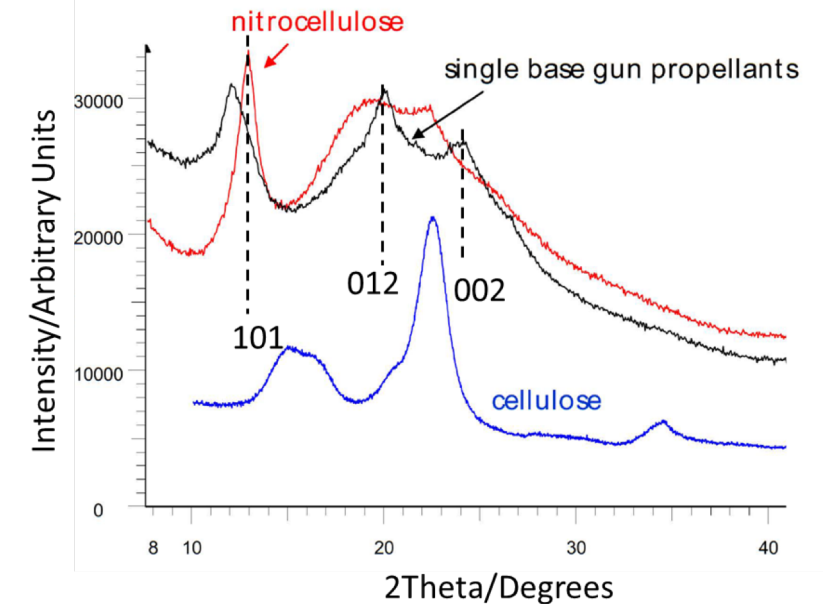


Heterogeneous reaction

Semicrystalline model of nitrocellulose



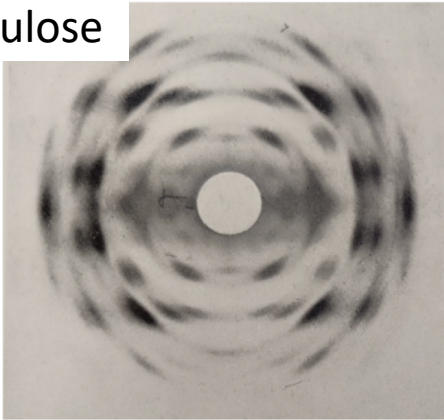
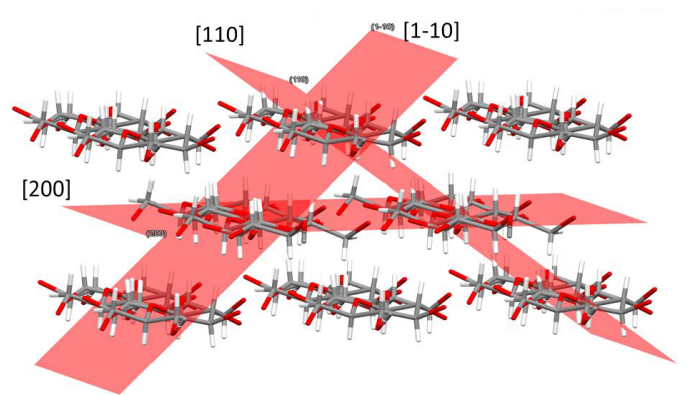
Powder X-Ray Diffraction



Studying Crystallinity in Nitrocellulose

Fiber X-Ray Diffraction

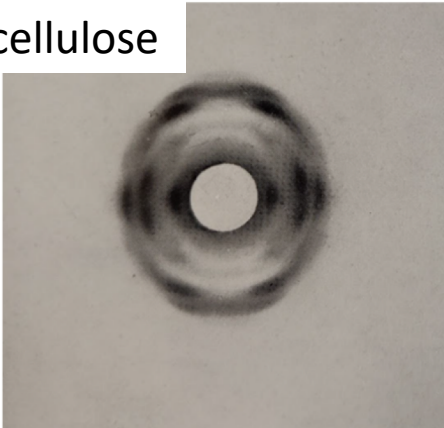
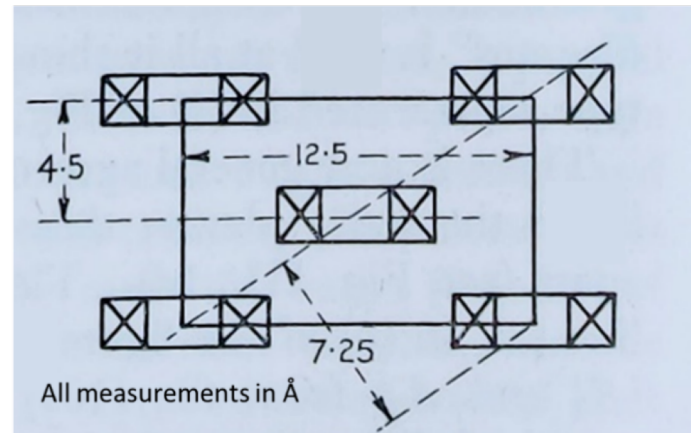
Cellulose



Challenges:

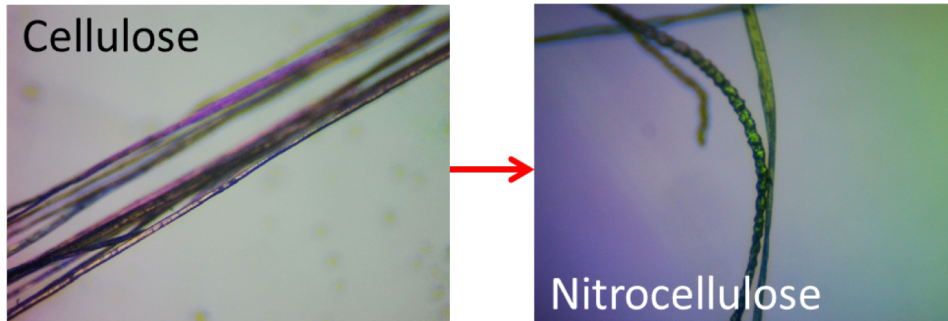
- Small crystalline domains
 - Broad peaks
- Chemically inhomogeneous
 - Tend to amorphous structure
- Weaker intermolecular interaction
 - Poor short-range order

Nitrocellulose



Accurately Describe the Structure of Nitrocellulose

What is the relationship between cellulose sources and nitrocellulose?



Develop structure-property relationships

What is the structure of nitrocellulose in composite materials?



Molecular dynamics simulations on composite materials

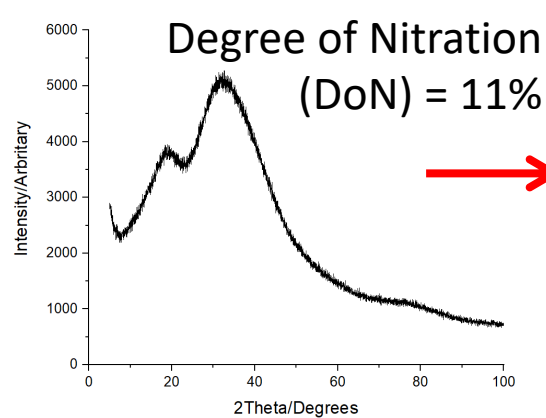
Produce a full atomistic crystal structure for nitrocellulose

☐ Optimise samples for high crystallinity

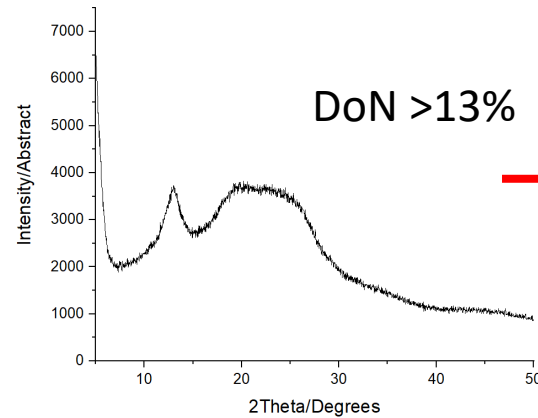
☐ Optimise for X-ray diffraction

Optimising for Crystalline Nitrocellulose

Compared through powder X-ray diffraction

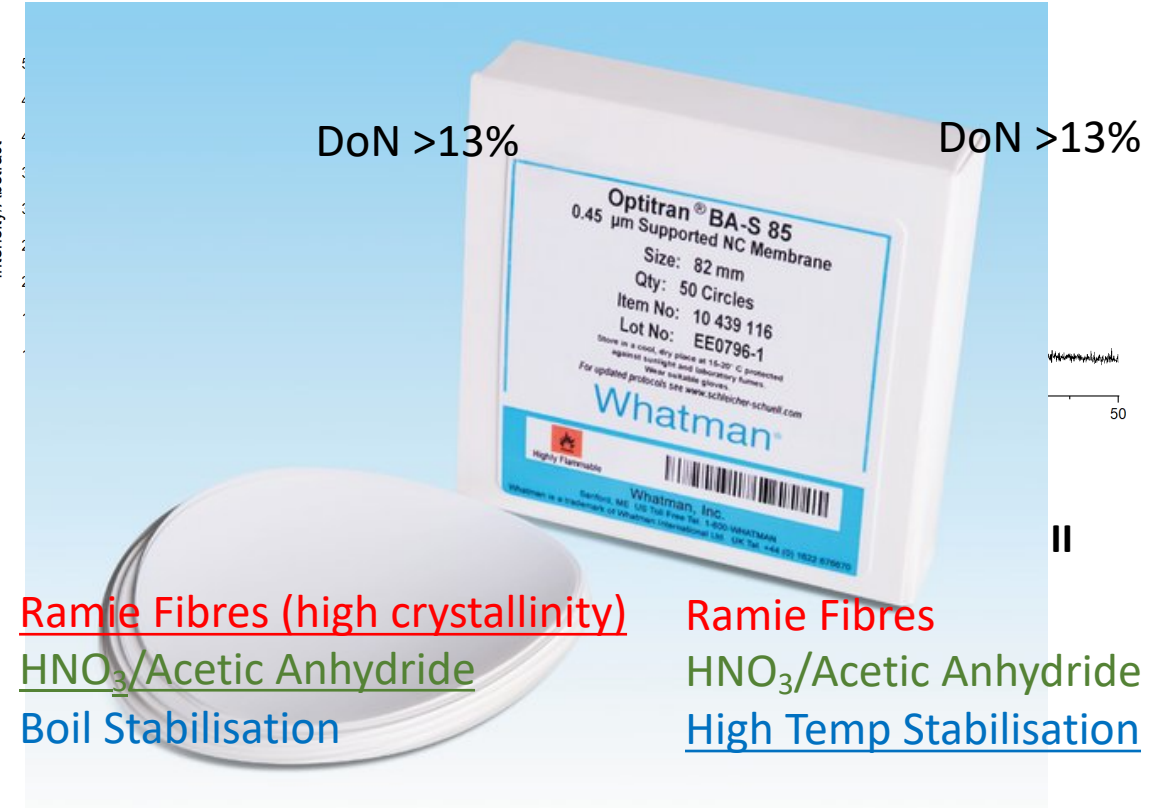


**Commercial
Nitrocellulose**



**In-House
Nitrocellulose I**

Cotton Linters
 $\text{HNO}_3/\text{H}_2\text{SO}_4$
Boil Stabilisation



Ramie Fibres (high crystallinity)
 HNO_3 /Acetic Anhydride
Boil Stabilisation

Ramie Fibres
 HNO_3 /Acetic Anhydride
High Temp Stabilisation

High crystallinity cellulose source

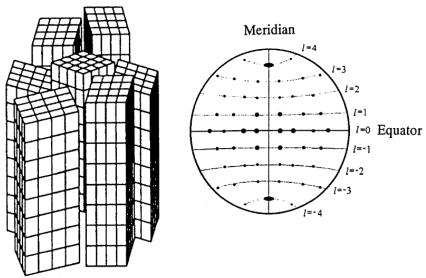
Optimising nitration method for
high **Degree of Nitration**

Stabilisation at **high temp** and **pressure**

Optimising for Structure Determination

☒ Samples optimised for high crystallinity ☐ X-ray diffraction at synchrotron facility

Orientated

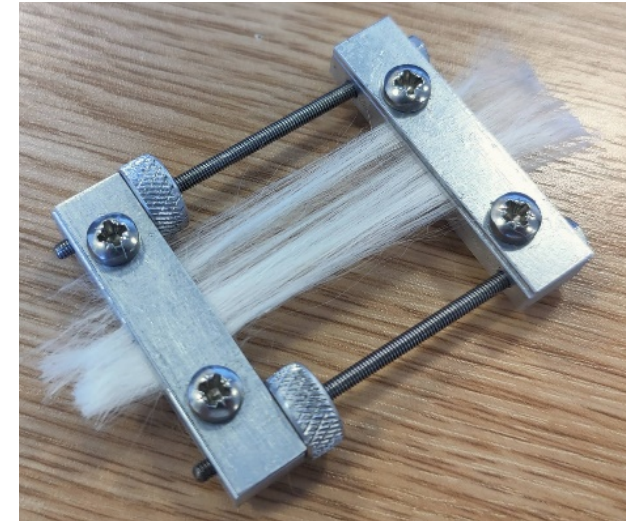


Fibre Diffraction of Nitrocellulose

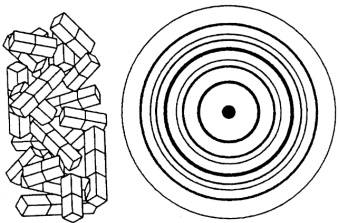
- Naturally orientation of crystalline domains

Challenges:

- Obtaining highly ordered samples
- Maintaining natural orientation



Non-orientated



Fibre diffraction to be continued at Diamond i19 (July 2023)

What next?

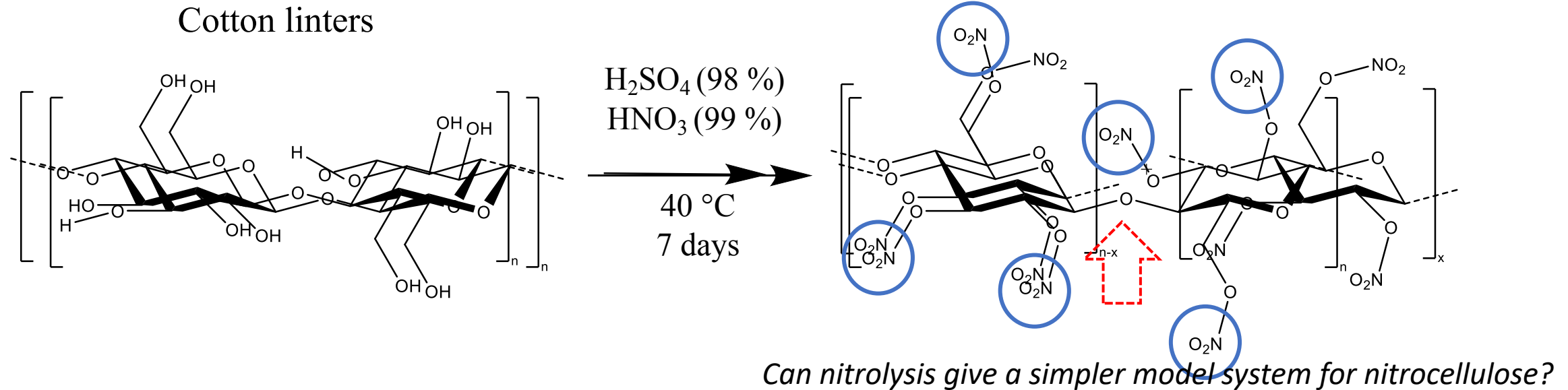
Simplifying the System

Polymers - Tend to be amorphous – Difficult to produce homogeneously
 Small molecule – Tend to crystallinity – Easier to produce in pure form

Nitrate ester substitution

Nitrolysis of Cellulose

Hydr**ol**ysis of glycosidic bond



Nitrolysis – What do we Expect?

Rate of Hydrolysis

Assumptions:

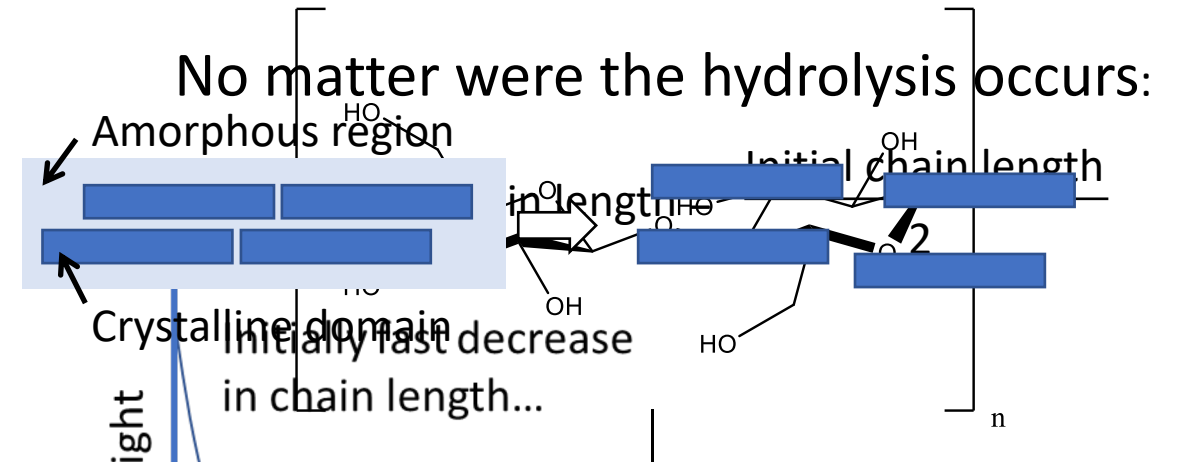
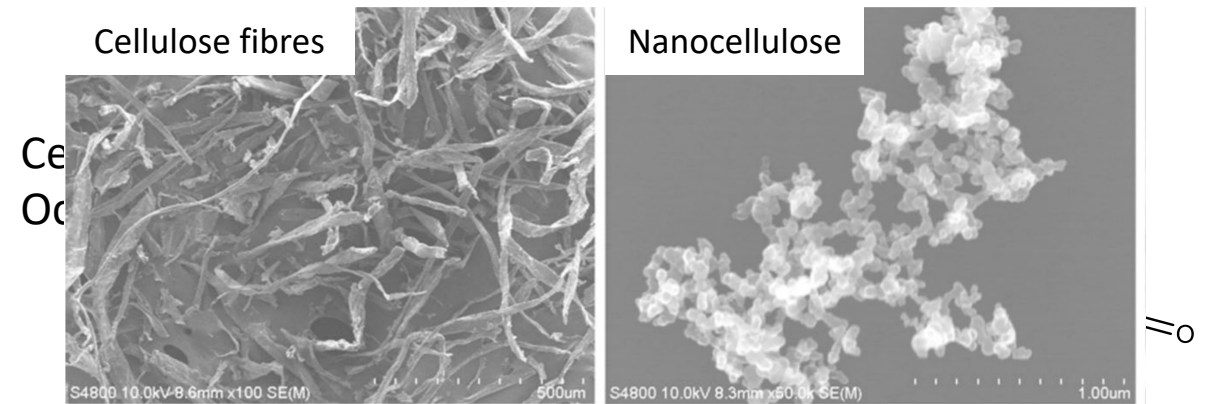
- Random hydrolysis breaks
- Constant rate of hydrolysis

Crystallinity vs. Amorphous

Amorphous cellulose preferentially hydrolysed
Good morphological control

Protecting Groups

Good chemical control over exact product

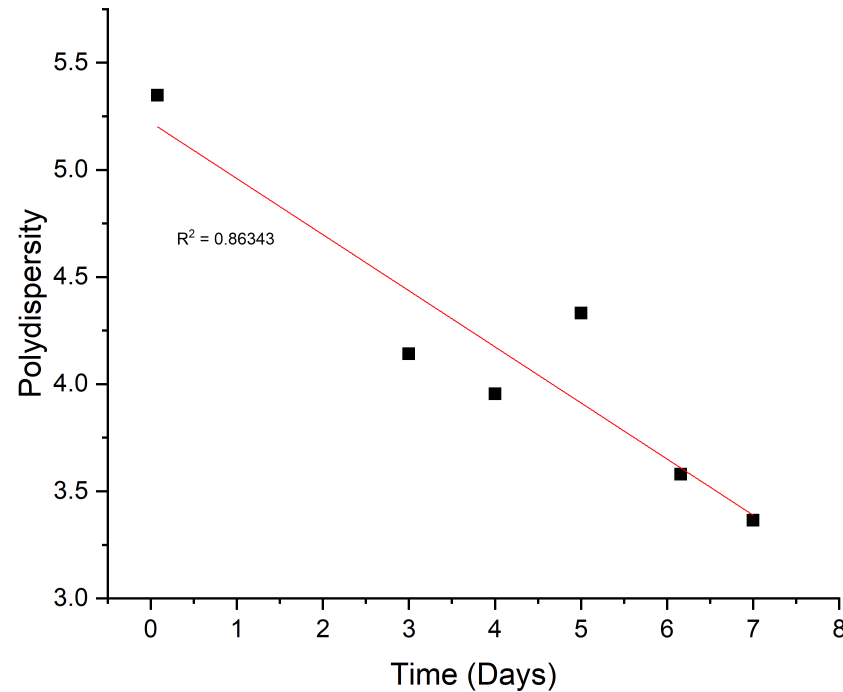
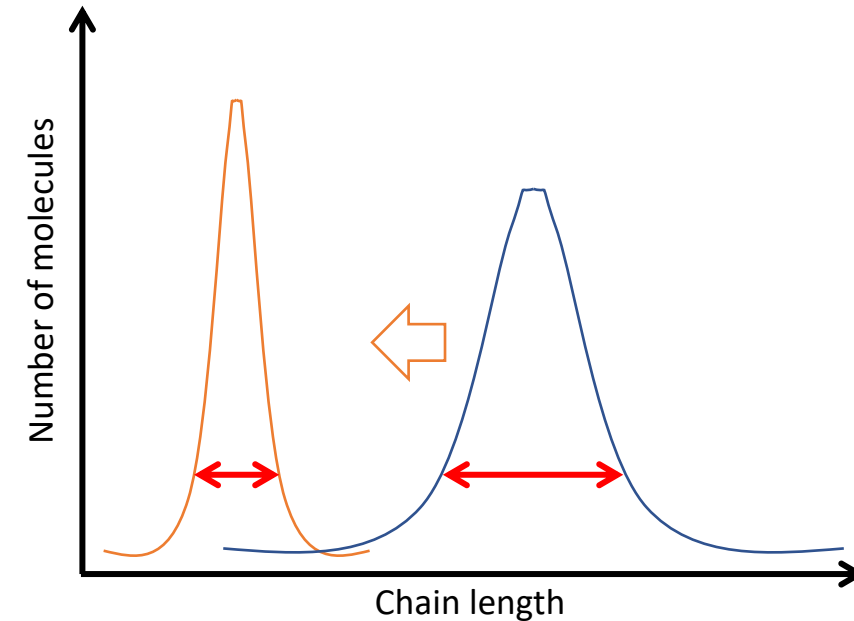


Electron microscopy images reproduced from Zhang *et al.*

Time

Nitrolysis – Chain Length

Polydispersity is measure of distribution of chain lengths



Decrease of ~5 in polydispersity per day
Decrease in polydispersity

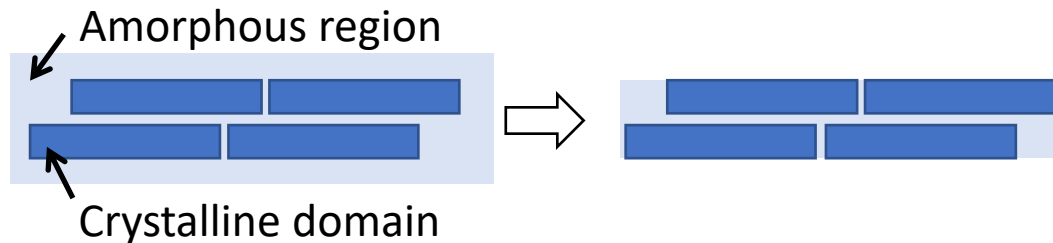
Shorter chain length, smaller distribution -> Ultimate product?

Crystalline Morphology

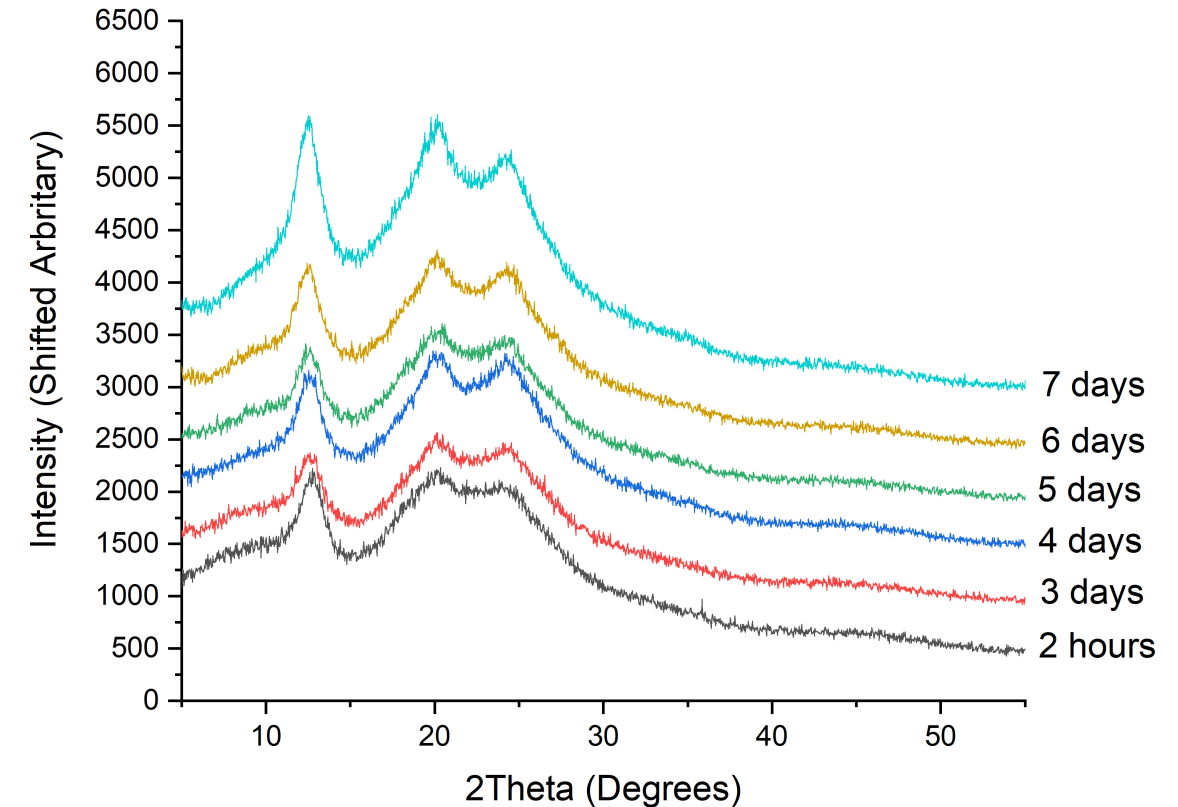
Nitrolysis:

Maintains crystallinity with lower background

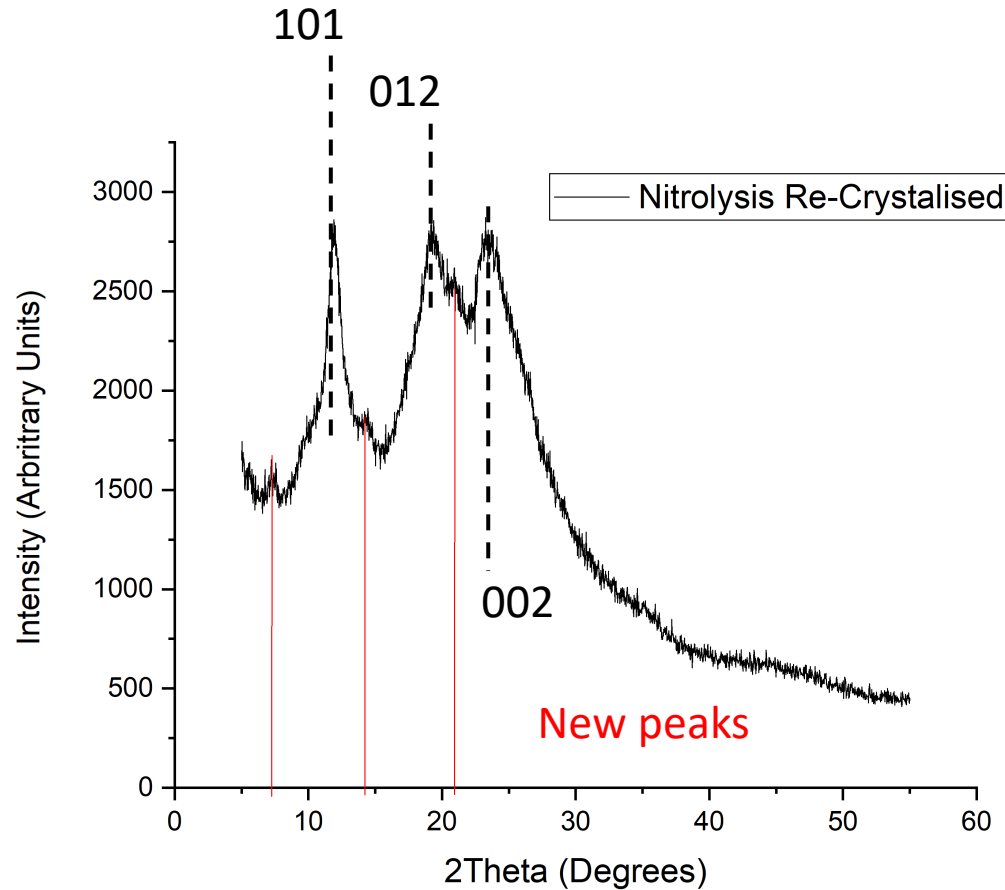
No peak broadening



Powder X-ray diffraction of nitrolysis product



Moving to More Crystalline Product



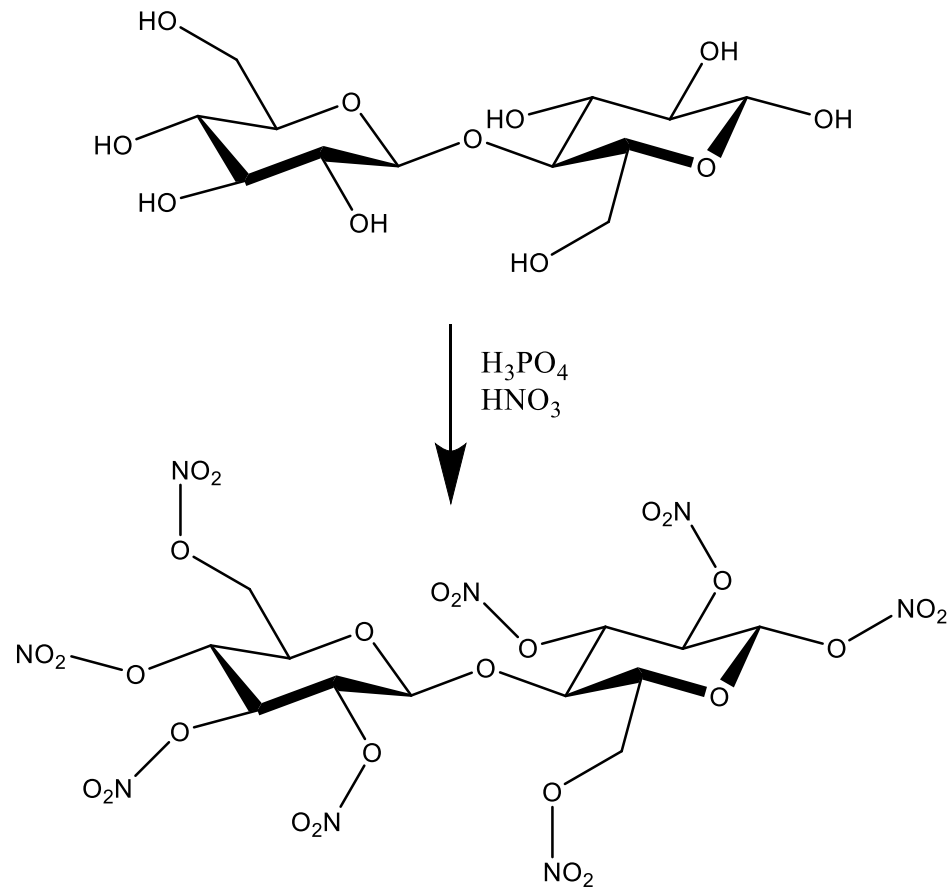
Recrystallised from acetone/methanol

Three new peaks – more structural information

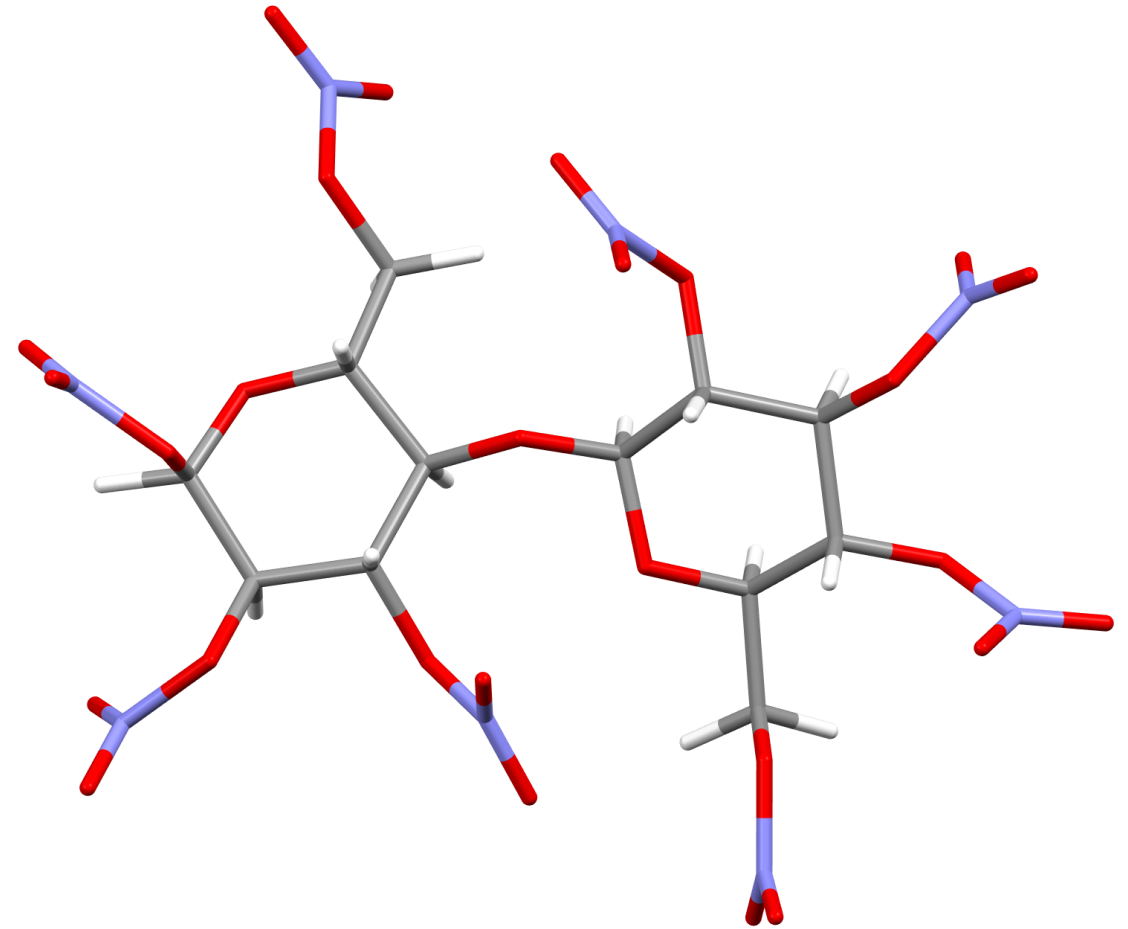
How to improve this further?

Singular product easier to characterise

Nitration of Cellobiose



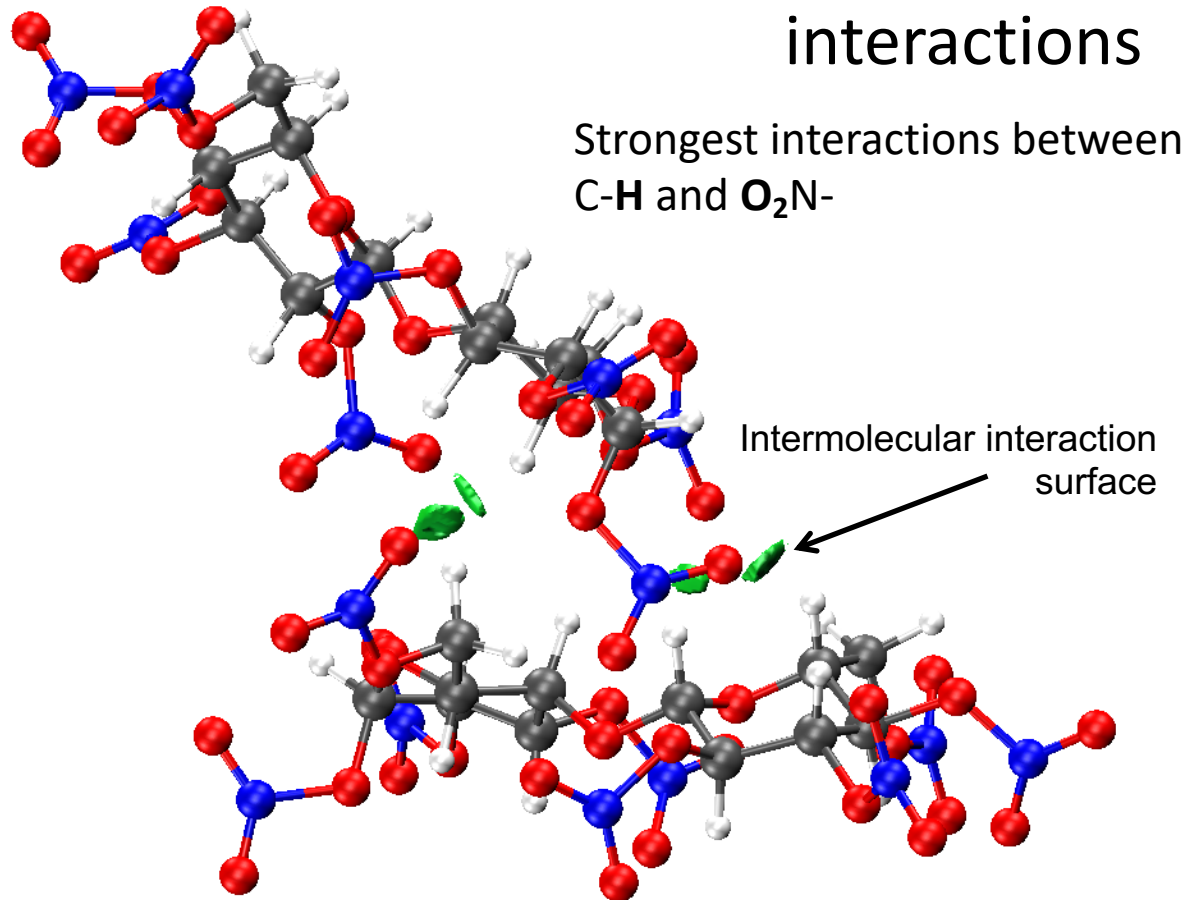
Cellobiose Octanitrate (CON)



a 11.36 Å, b 8.96 Å, c 13.15 Å
 β 104.5°, Monoclinic
Space group $P2_1$

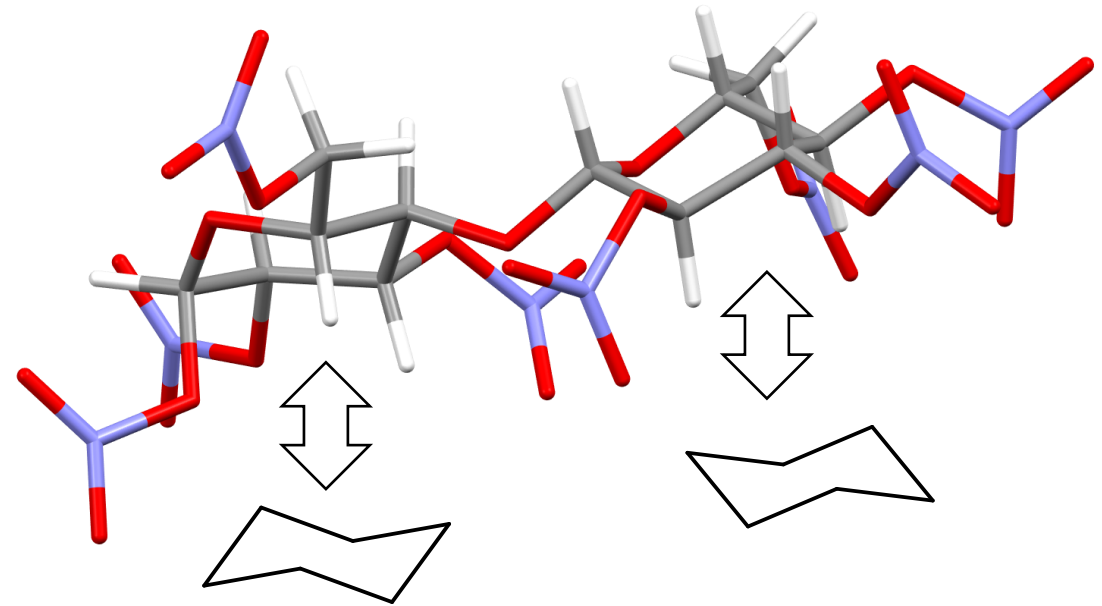
Cellobiose Octanitrate

Non-covalent intermolecular interactions



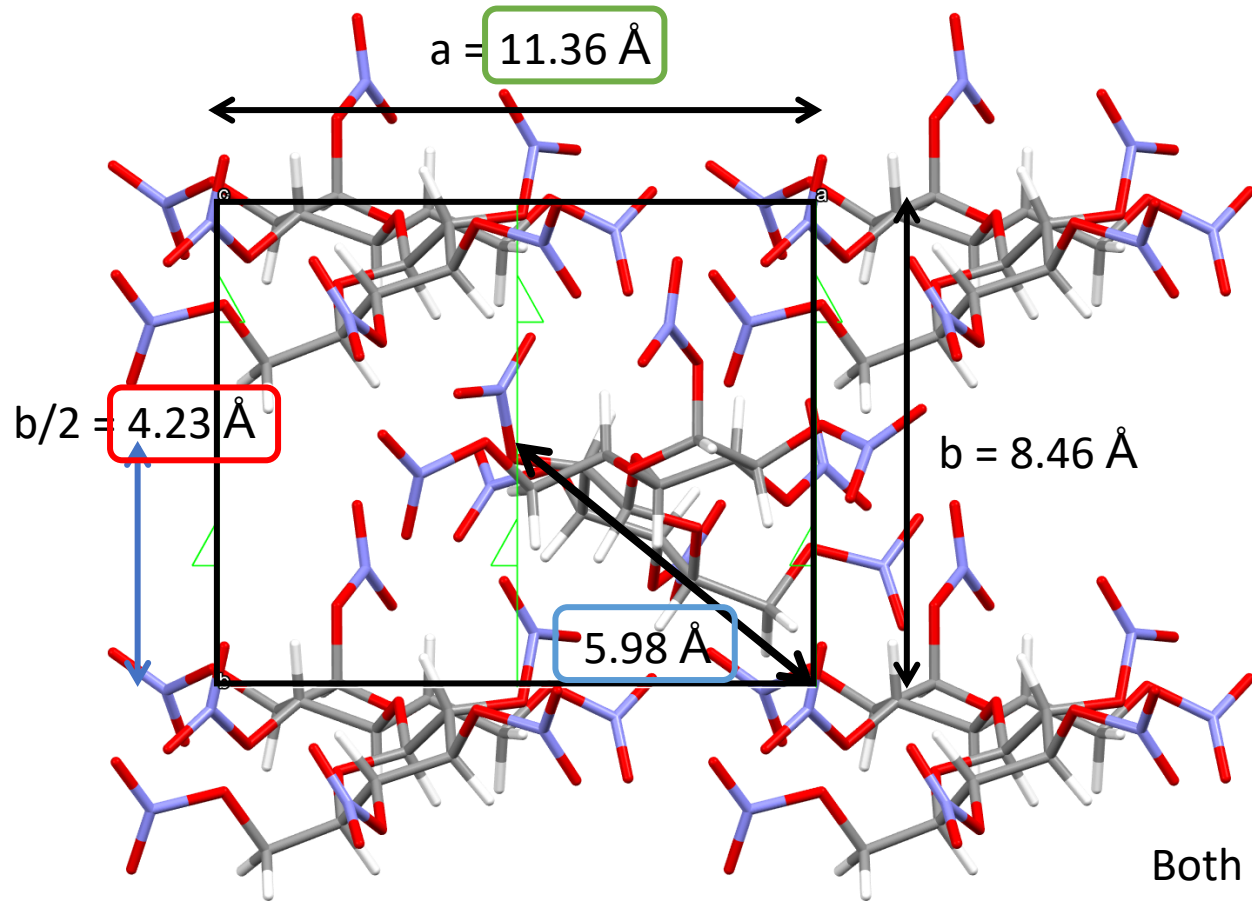
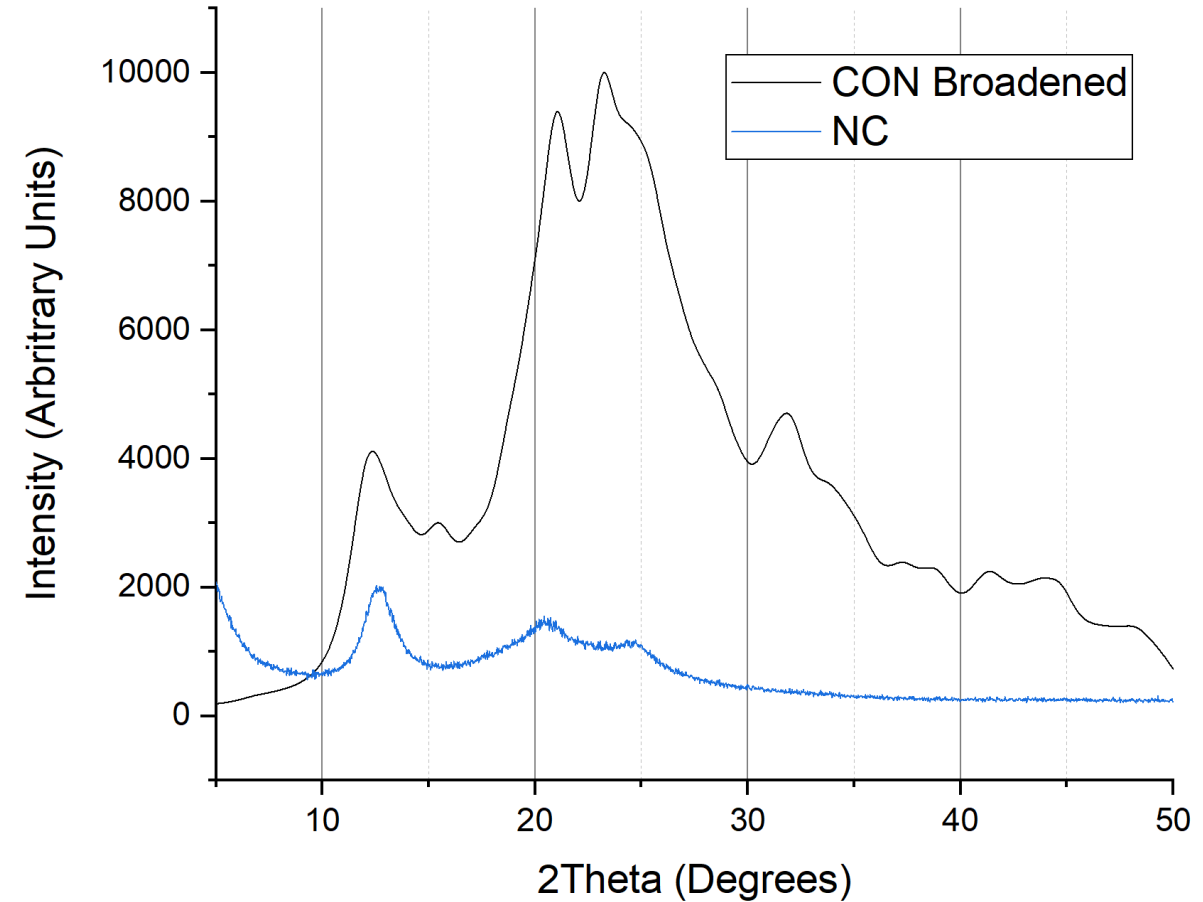
Molecular conformation

Slightly distorted chair – contrary to literature



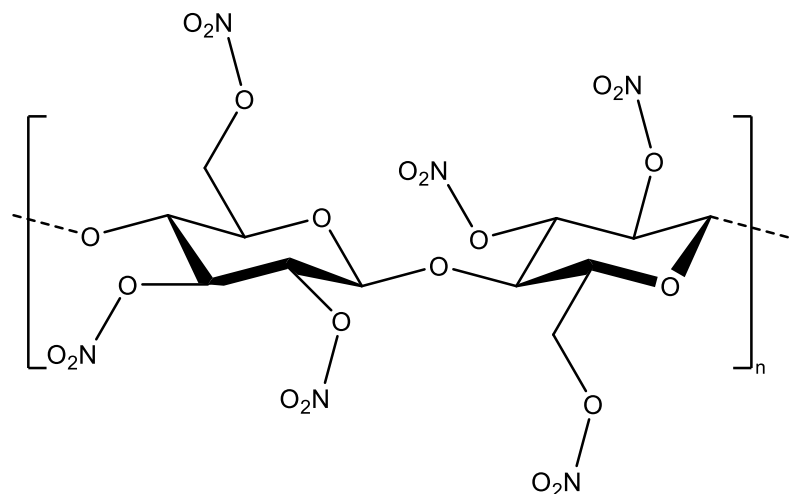
A Representative Model for Nitrocellulose?

Cellobiose Octanitrate (CON)

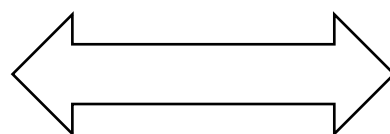


Both viewed along "fibre" axis

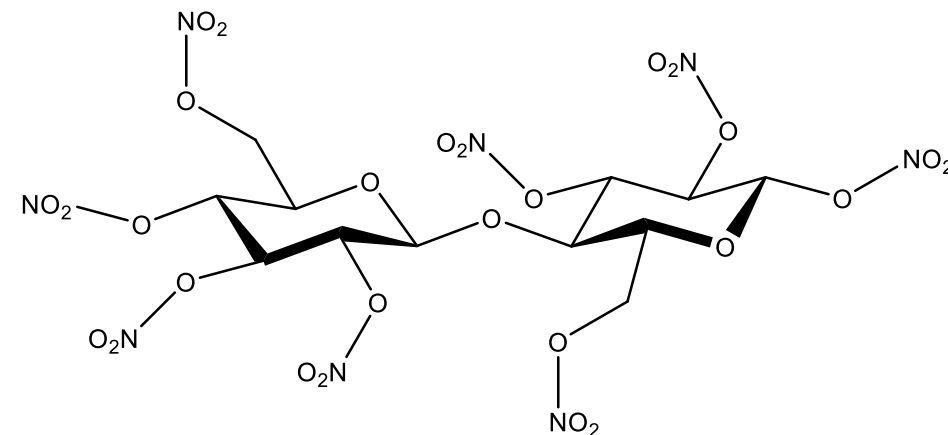
Shorter Chains Models for Nitrocellulose



Nitrocellulose – 100's to 1000's of monomer units



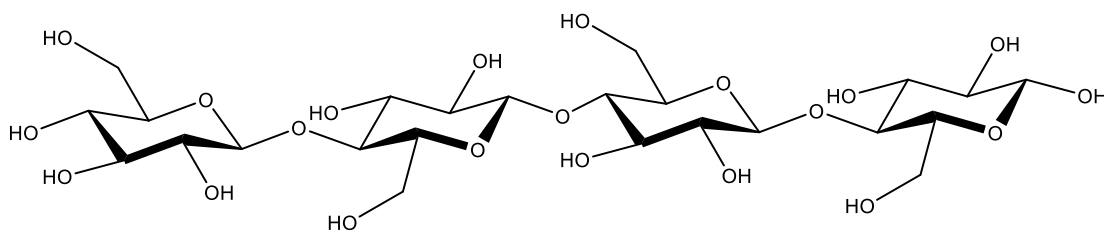
Short chain models
of nitrocellulose



CON - 2 monomer units

Change starting material

Cellotetrose etc...



Nitrolysis

Very low molecular weight nitrocellulose as
model for nitrocellulose

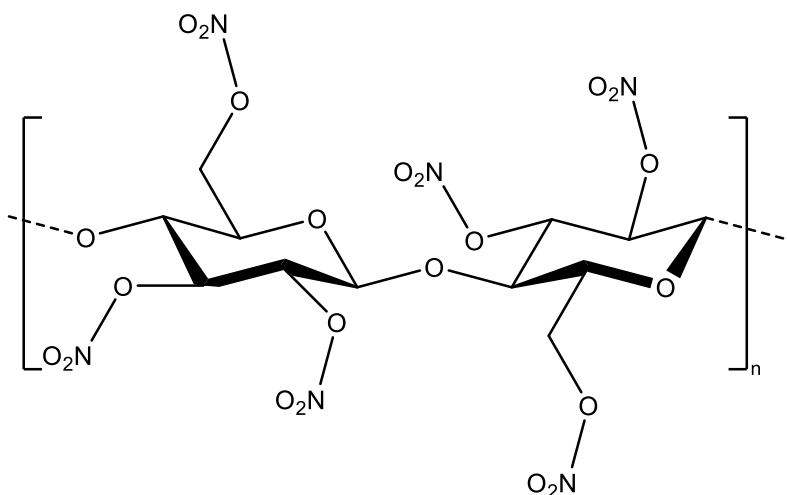
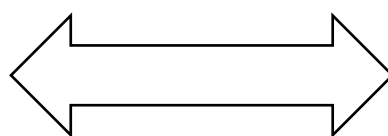
Exciting Uses for Model Nitrocellulose System

Study **composite materials**:

- Co-Crystals of CON

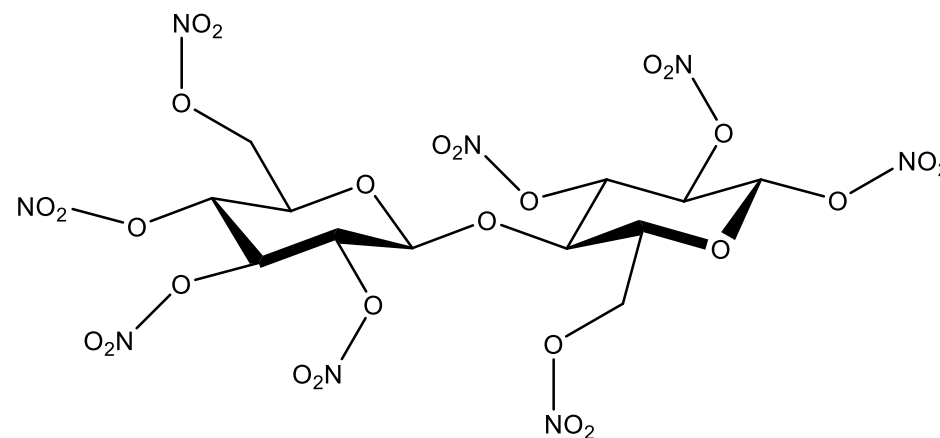
A **new standard** for nitrocellulose tests:

- Polymers are variable: morphology, molecular weight, homogeneity...

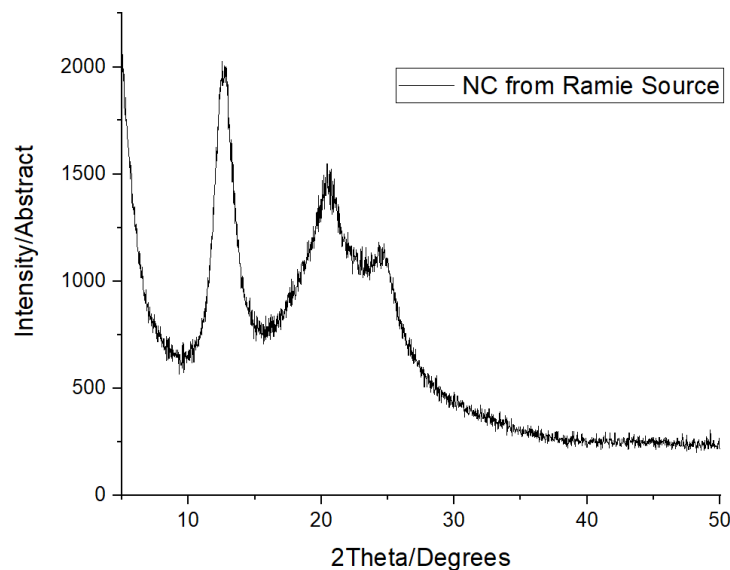


Short chain models
for nitrocellulose

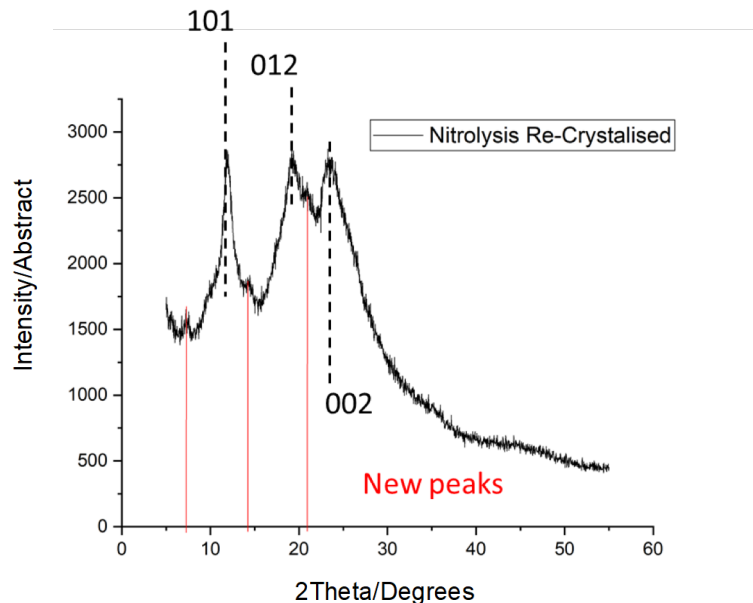
Cellobiose Octanitrate (CON)



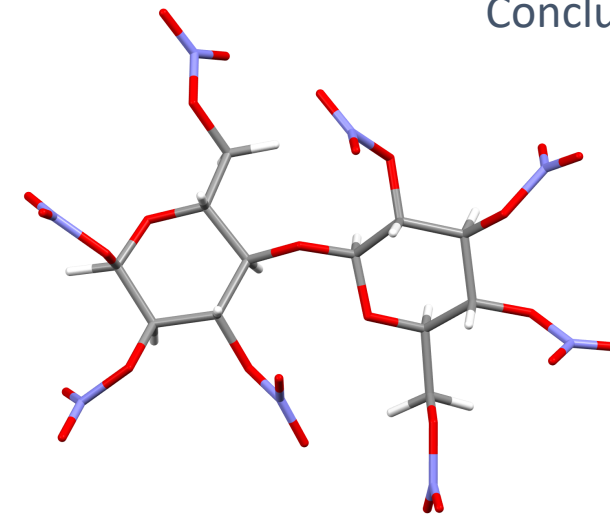
Optimising Nitrocellulose for Fibre Diffraction



Simplifying Nitrocellulose Through Nitrolysis



Conclusions



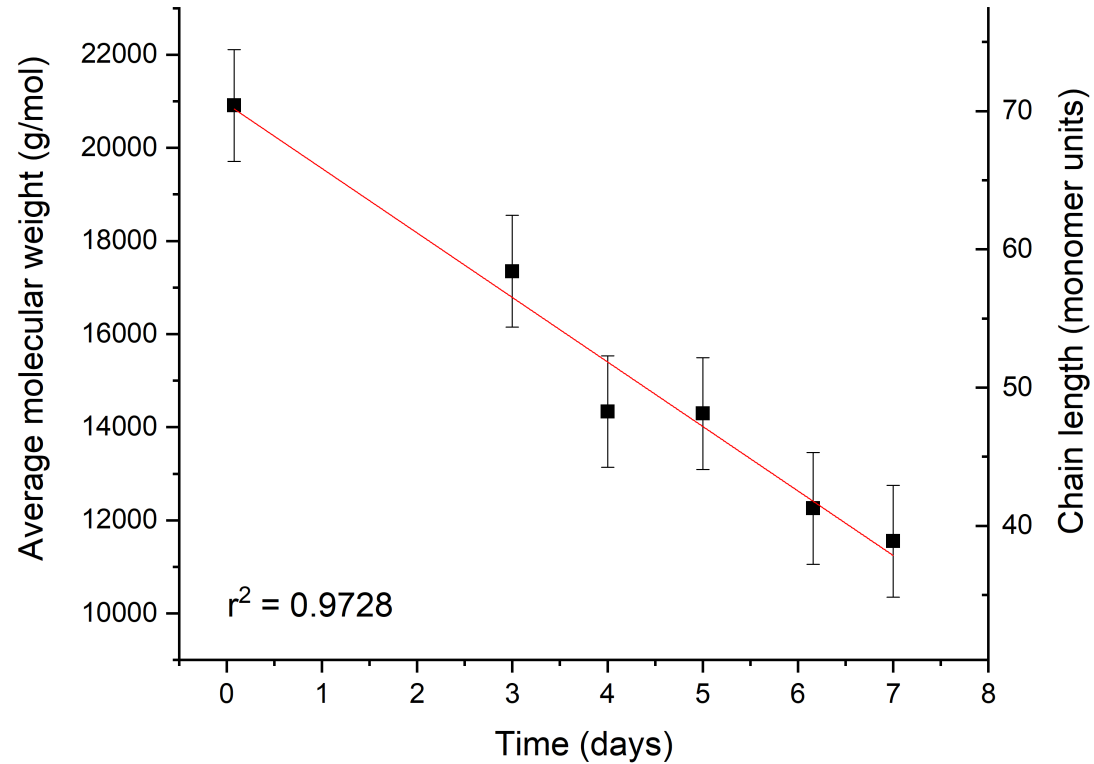
Model System for Nitrocellulose

Acknowledgements

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Thanks to Dr Gary Nichol for CON crystal data collection and structure determination; to Dr Xiaojiao Liu for room temperature CON crystal data collection and to Mr George Steedman for preparing and designing specialist tools.

Nitrolysis – Chain Length



Hydrolysis towards end of chain

Nitrocellulose chain



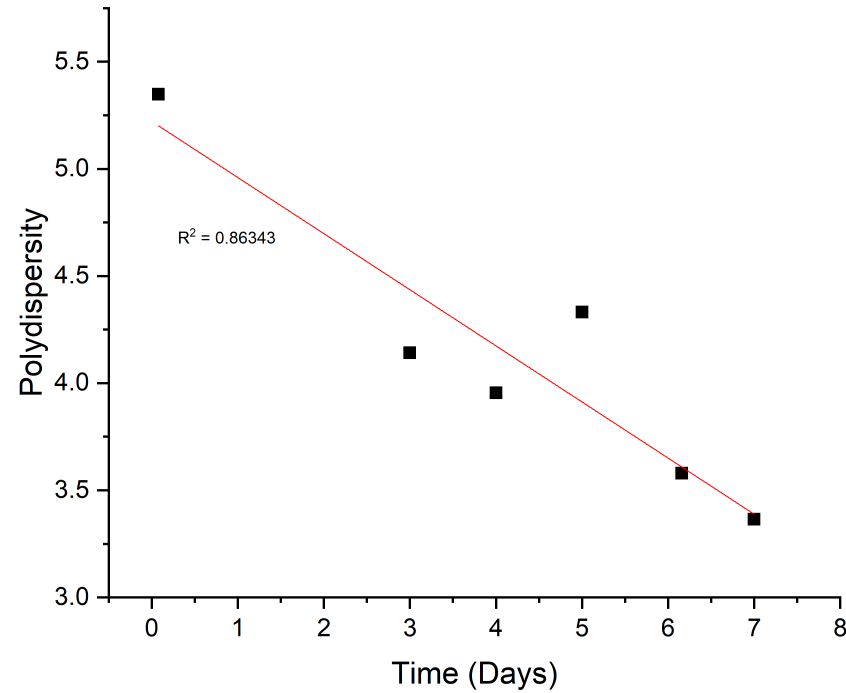
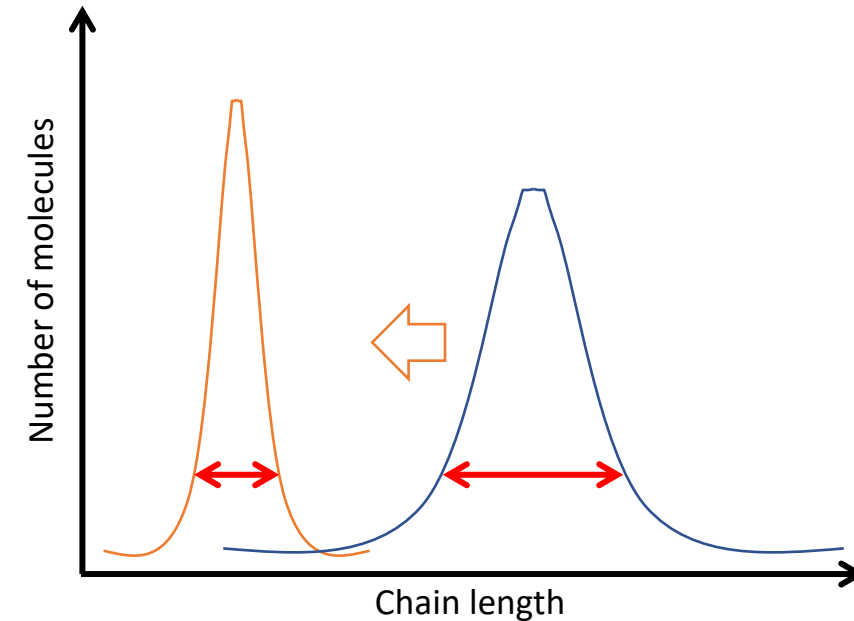
Monomer

GPC calibrated for 5 – 500 monomer units

Decrease of ~5 monomer units per day

Nitrolysis – Chain Length

Polydispersity is measure of distribution of chain lengths

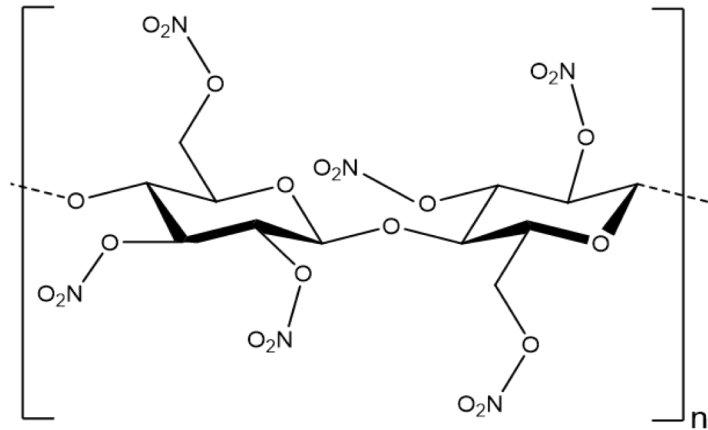


Decrease in polydispersity

Shorter chain length, smaller distribution -> Ultimate product?

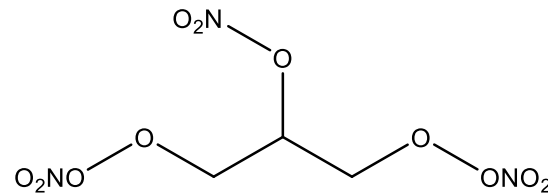
Nitrocellulose in Solid Propellants

Nitrocellulose – Polymer Binder

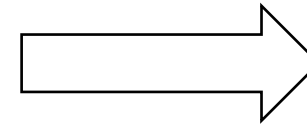


Strong but brittle polymer

Nitroglycerin – Liquid oxidiser



Plasticiser



Solid Propellants



Strong but mouldable composite

Naturally derived -> Natural variation

Supply chain and reliance issues

Nitrolysis – What do we Expect?

Rate of Hydrolysis

No matter where the hydrolysis occurs:

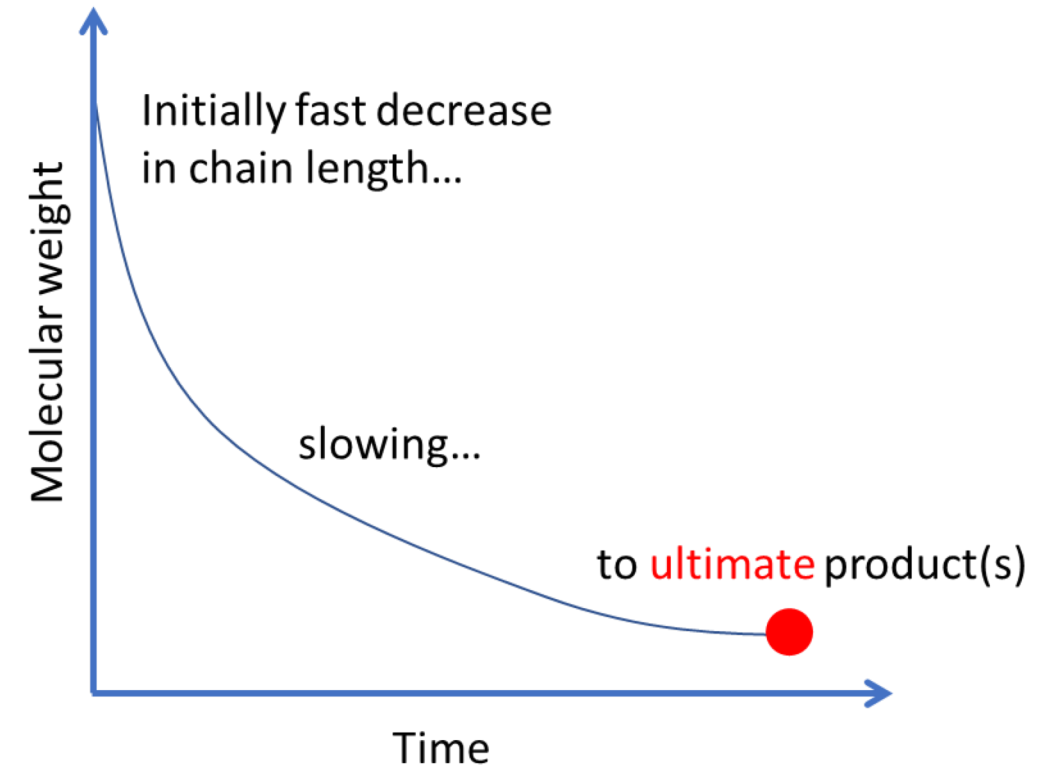
$$\text{Average final chain length} = \frac{\text{Initial chain length}}{2}$$

Crystallinity vs. Amorphous

Morphological control

Protecting Groups

Chemical control



Assumptions:

- Random hydrolysis breaks
- Constant rate of hydrolysis