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AWE

Activities Complimentary to GPC

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- Mass measurement techniques
  - triple detector GPC
  - ultracentrifugation
  - MALDI-TOF mass spectroscopy
- Hyphenated GPC - FTIR
  - LC-Transform combined with molecular modelling
    - potential pre-peak characterisation
- Computational modelling of molecular weight distributions as polymers degrade
  - mechanistic diagnostics

GPC Mass Measurement Techniques

Enhanced GPC techniques:-
- Triple-detector GPC capability
  - not tried Universal (hydrodynamic volume) calibration mwt's
  - attempting to optimise light scattering mwt's
  - viscosity data useful (the *only* absolute measurement)
  - conformation (R_g, Mark-Houwink etc) used by modellers
- Light scattering theoretically superior to conventional and universal GPC
  - "near absolute" calibration-free mwt data (M_n & M_w)
  - for NC, light scattering M_w values much lower that PS equivalents (~ 30%) - why?
    - *very* dependant upon dn/dc values ($M \propto (dn/dc)^{0.5}$)

Alternative Mass Measurement Techniques (I)

Ultracentrifugation at (UK)NCMH, Nottingham

- 3 high viscosity nitrocellulose(s) analysed as solutions in THF (concentration *cf.* GPC)
  - Velocity Sedimentation
    - samples centrifuged at relatively high speed (~10,000rpm) for short period of time (~ 12hrs)
    - all samples showed a very narrow (almost monodisperse) distribution (when expressed as sedimentation coefficient)
    - conversion to mass yields average Mw values ~ 150,000 (!)
    - "easily confused for a partially degraded protein"
  - Equilibrium Sedimentation (slower but absolute technique)
    - analysis now complete for all 3 NC samples
    - data analysis confirms velocity observations ~ monodisperse, low mwt!

Alternative Mass Measurement Techniques (II)

MALDI-TOF mass spectroscopy

- Samples of nitrocellulose are being transferred to LLNL in the US for MALDI-TOF analysis
  - no reported molecular weight for nitrocellulose by MALDI-TOF
    - no published starting protocol to work from
  - reported that dipole polarisation of nitrate ester groups means that analysis best performed in "negative ion mode"
- Nitrocellulose films have been used as the inert matrix material for MALDI analysis of oligonucleotides!
  - suggests that the NC molecular weight was either very high or very low (i.e. outside the analysis "window" (~150,000))
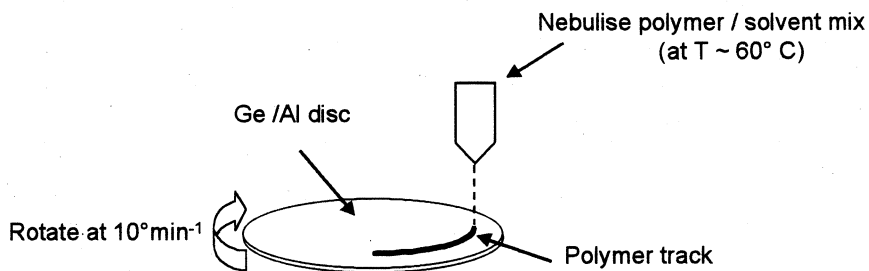
Use of LC-T to Characterise Pre-peak

Nebulise polymer / solvent mix
(at T ~ 60° C)

Ge /Al disc

Rotate at 10°min⁻¹

Polymer track

- Apparent 'high mass' pre-peak in cotton linter NC
- FTIR fingerprints showed both peaks were nitrocellulose
  - pre-peak potentially fully nitrated, *i.e.* pure trinitrocellulose
  - consistent with molecular modelling predictions

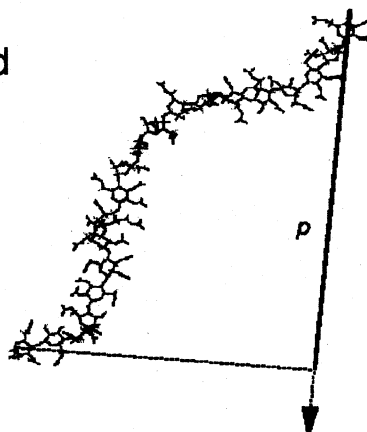# Molecular Modelling of Nitrocellulose

- Molecular modelling predicted
  an extended linear structure
  for nitrocellulose chains
- Trinitrate clusters thought
  to be the most extended
  - may be high *hydrodynamic volume* not high *mass*
  - explanation for pre-peak?
  - rod-like trinitrocellulose, high hydrodynamic volume & good light scattering efficiency

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Ageing - Computer Modelling of MWD

- Emsley *et al* (Surrey) have used modelling codes to predict how *cellulose* MWD might change as the material ages
  - technique can distinguish between random and systematic degradation processes
- We are applying these techniques to the degradation of nitrocellulose
  - early indication that nitrocellulose degrades by a non-random chain scission reaction
  - "systematic weaknesses" preset in pristine nitrocellulose
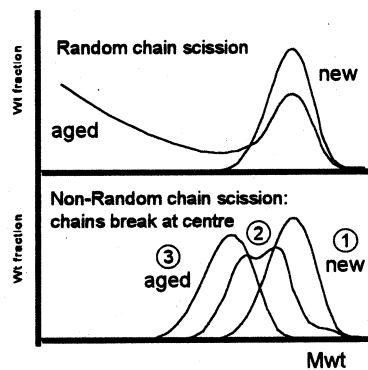   - does this account for the ultracentrifuge results...?

Random *vs.* Systematic Scission

Cellulose - ageing at 120°C in air

Computer simulation
(repetitive random model)
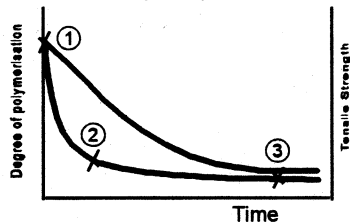
- Cellulose depolymerisation,
- Drs Brendan Howlin & Alan Emsley, Surrey University

Iterative computer simulation can be compared with experimental data

→ **cellulose scission is non-random**