The Affect of Water on the Stability of Nitrocellulose in THF Solution

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Explosive Materials, Ageing Mechanisms
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Introduction

- Nitrocellulose dissolution in THF
  - development of GPC analytical methodology
- What affects the stability of nitrocellulose in THF solution?
  - suspect temperature and water content
- Experimental observations
  - GPC observations in wet / dry THF over a range of low temperatures
- Ongoing mechanistic interpretation
  - further evaluating the role of water...

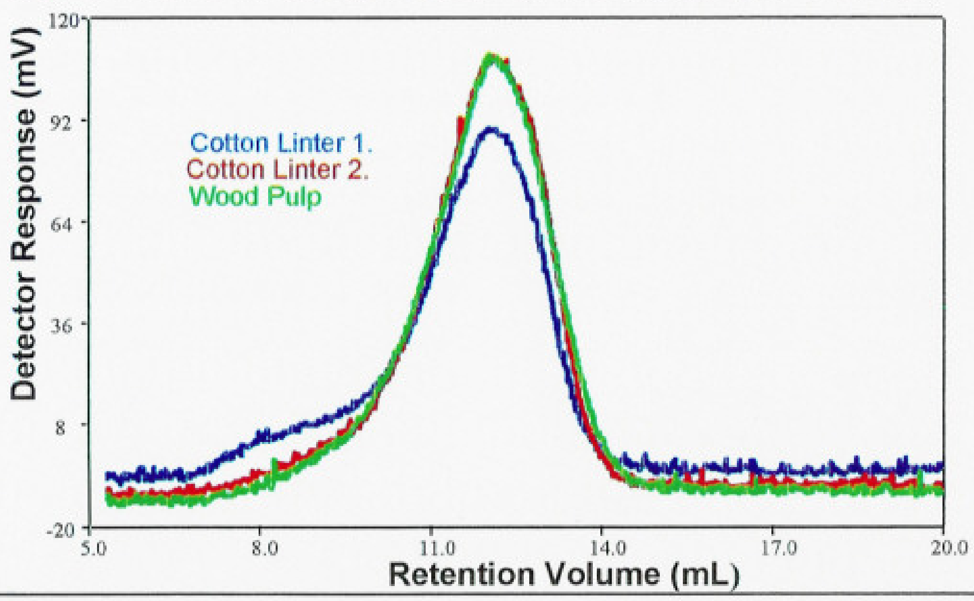
Nitrocellulose Dissolution

- Previous investigations have shown that nitrocellulose dissolution in THF is a very dynamic process
  - initially, fibres swell and form a colourless gel
  - gelatinous nitrocellulose then disperses into solution
  - dn/dc stabilises to an equilibrium value of ~ 0.074 after ~ 7 days
    - fast-eluting 'pre-peaks' in cotton linter derived nitrocellulose disappear over a similar timescale
- This work formed the basis for development of a new GPC method for nitrocellulose analysis in THF

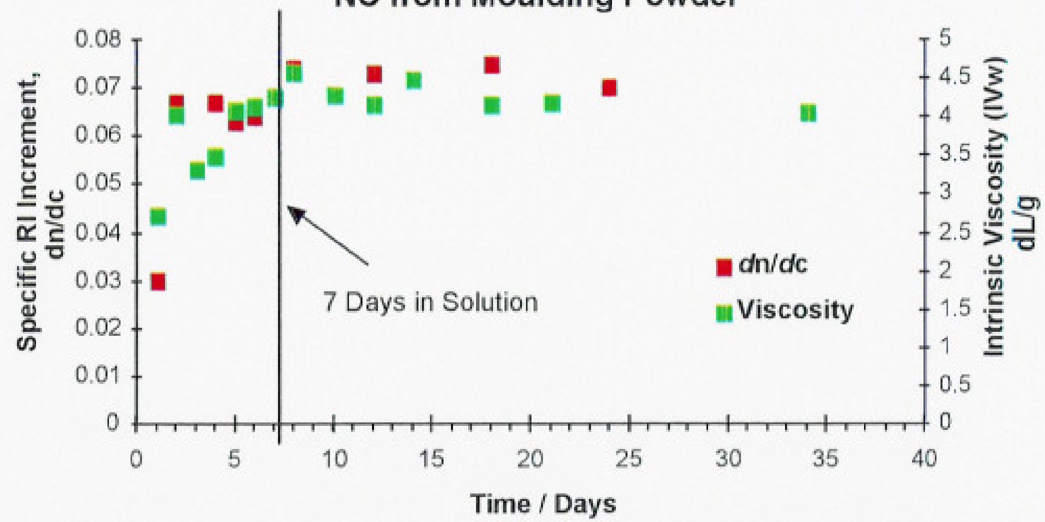
Validated Molecular Weight Determination

- RALLS - GPC identified previously unseen chromatographic features
  - fast-eluting pre-peak - a small but important fraction..?
- As sample dissolves, 'high molecular weight' pre-peak collapses

Nitrocellulose from Different Source Materials (RALLS Data)



Solution *dn/dc* and Intrinsic Viscosity Affects NC from Moulding Powder

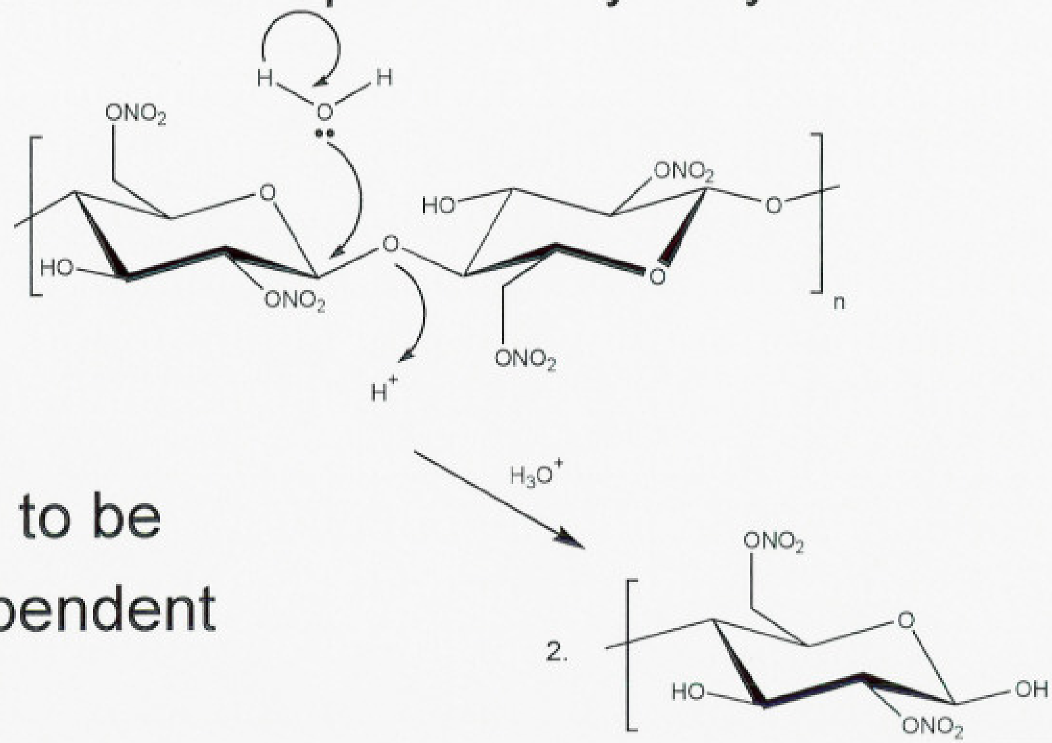


- *dn/dc* and viscosity (η) plateau
- Constant *dn/dc* reached after 7 days
  - measured M_w critically dependent on dn/dc. RALLS $M_w \propto (dn/dc)^2$

⇨ **Robust analytical technique for Arrhenius kinetics analysis**

What Affects the Dissolution of Nitrocellulose?

- Does temperature affect the rate of dissolution?
- Does moisture content of solvent cause chemical degradation?
  - nitrocellulose known to be susceptible to hydrolytic chain scission
  - chain scission known to be very temperature dependent

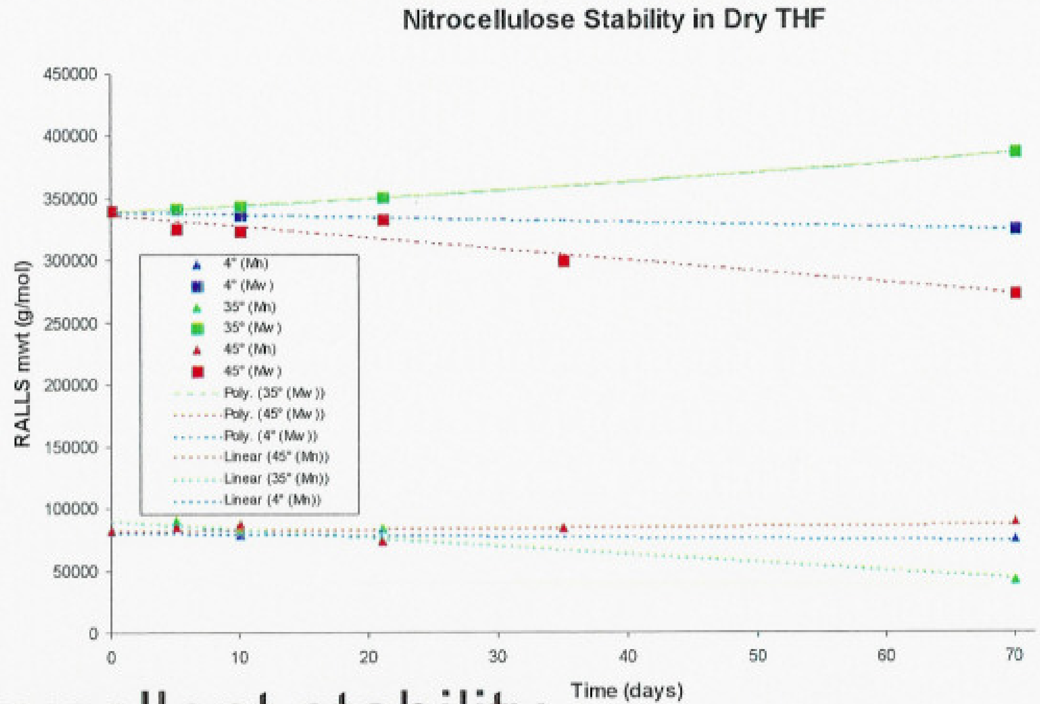


Experimental Investigation

- The solution phase stability of nitrocellulose has been investigated under the following conditions:-
  - thoroughly dried cotton nitrocellulose (11.7 - 12.2 % N)
  - stabilised THF (low level of BHT stabiliser)
  - 3 temperatures -
    - 4 °, 35 ° and 45 °C
  - 2 water contents within the THF
    - ~ 0 % (w/v) (distilled from Na and stored over NaH)
    - 1.0 % (w/v) (doped with 10 $mgml^{-1}$ H_2O)
- Individual, sealed vials withdrawn periodically over a 10 week timescale
  - analysed by triple detector GPC

Results in Dry THF...

Day 0 = 7 days dissolution

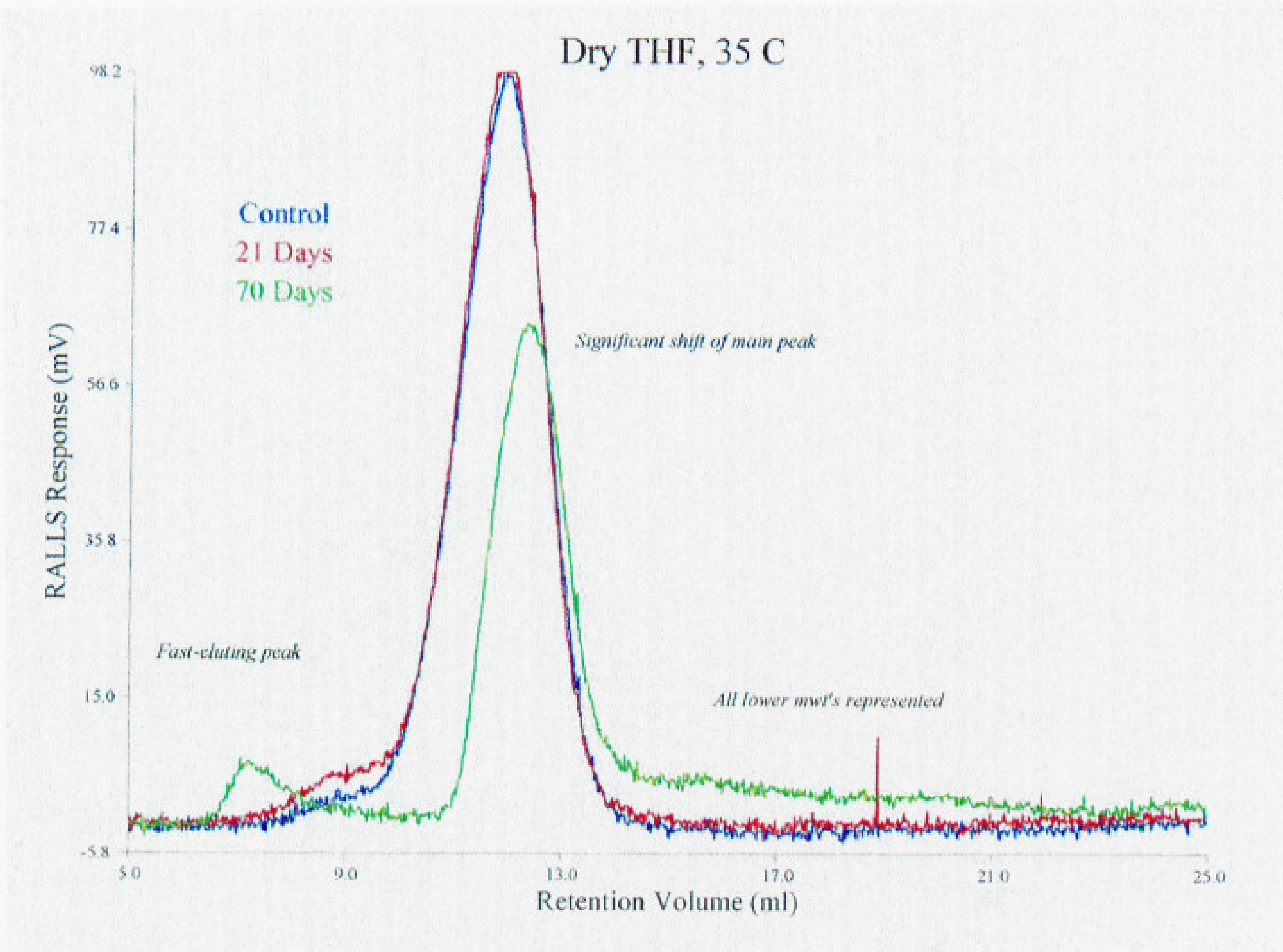


- Nitrocellulose exhibits excellent stability
  - no significant changes at 4 °C
  - slight degradation at 45 °C
  - mwt *increase* at 35 °C
    - this has been witnessed elsewhere! (NC and cellulose)

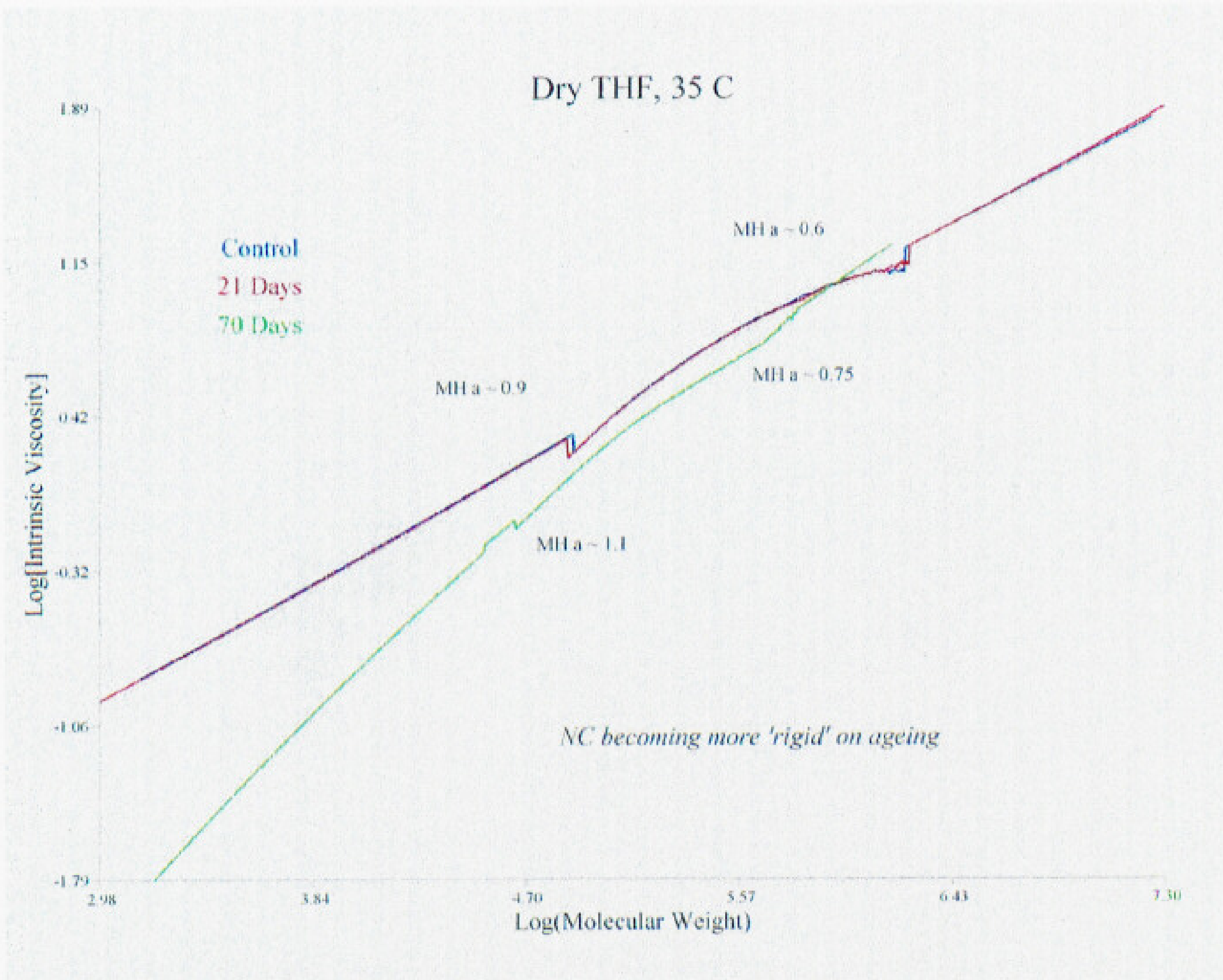
Stability in Dry THF...

- Fast-eluting RALLS pre-peak gradually reappears at the exclusion limit of the column
  - dn/dc remains constant at 0.075 (± 0.02)
  - aggregation or gellation?
  - conformational changes?
    - is the pre-peak physically large or of high mass?
- Mark-Houwink plot suggests that NC molecules become more conformationally rigid as a function of storage time
  - initial high mass fraction has markedly lower *a* value
    - chain branching or poor solvation?
  - on storage, M-H ‘steepens’ and ‘straightens’

RALLS Data

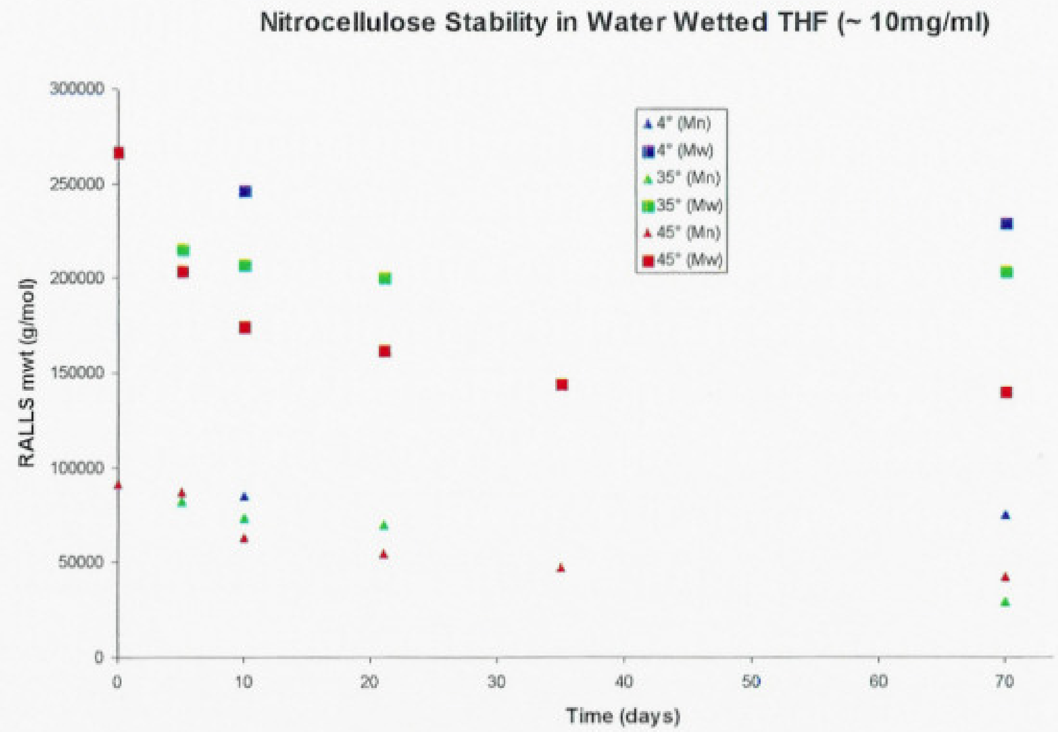

Dry THF, 35 C
RALLS Response (mV)
98.2
77.4
56.6
35.8
15.0
-5.8
Control
21 Days
70 Days
Significant shift of main peak
Fast-eluting peak
All lower mwt's represented
5.0
9.0
13.0
17.0
21.0
25.0
Retention Volume (ml)

Mark-Houwink



Results in Wetted THF...

Day 0 = 7 days dissolution

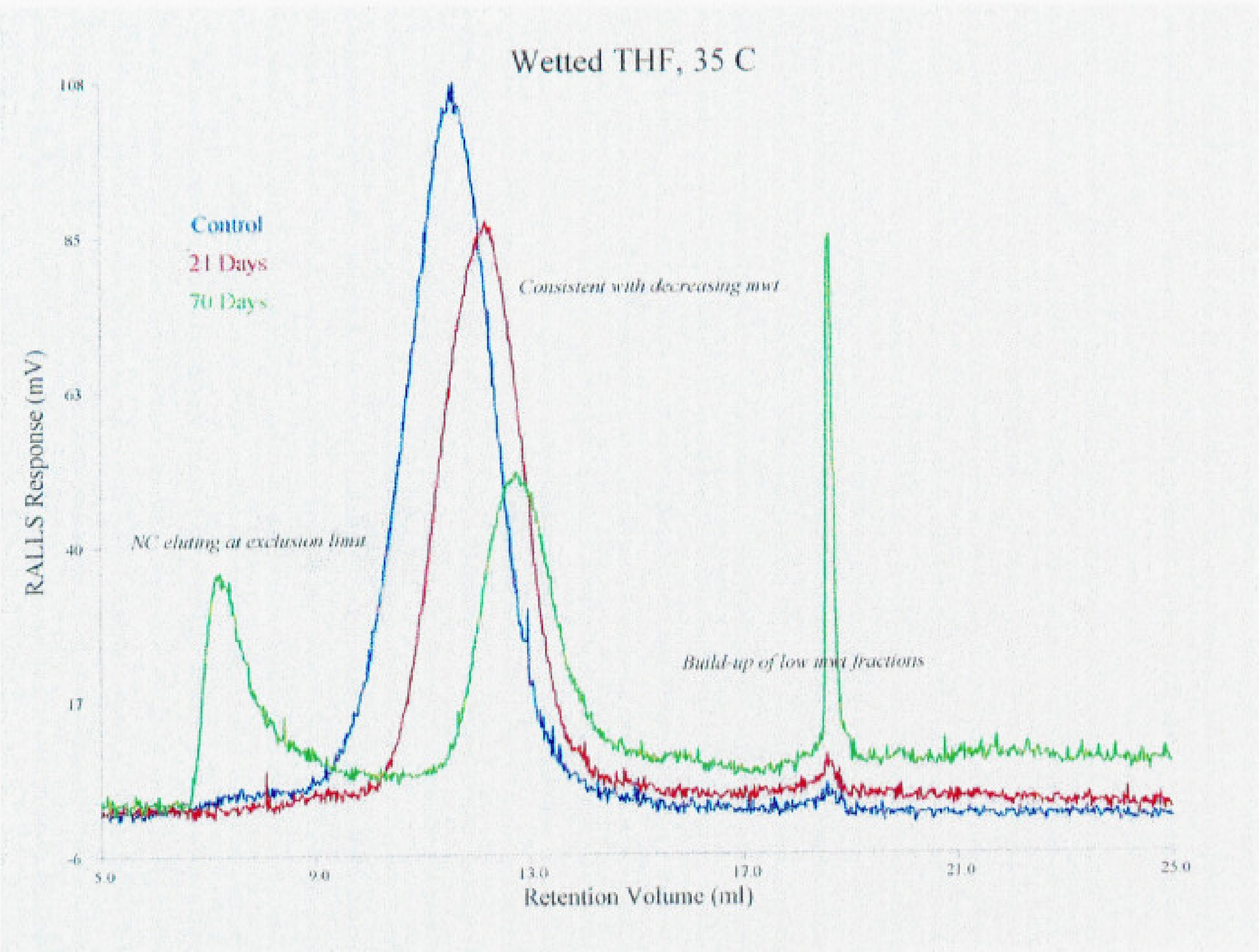


- Significant depolymerisation at *all* temperatures
  - as expected, very temperature dependent
  - mwt plateau observed
    - limit likely to be defined by initial water content

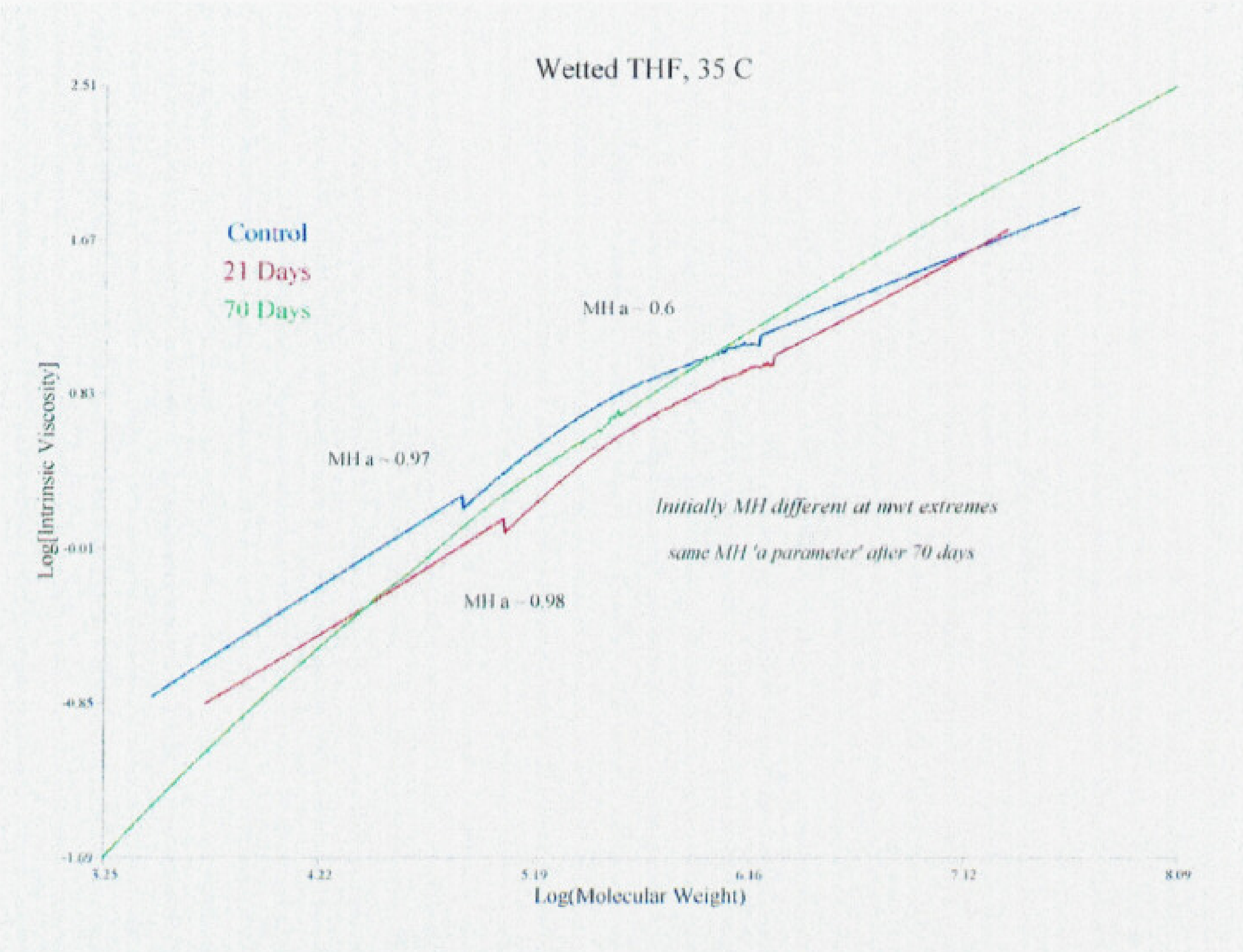
Stability in Wetted THF

- Again, fast-eluting RALLS pre-peak reappears
  - after 70 days, pre-peak is very large but still **RALLS only**
  - dn/dc remains constant at 0.074 (± 0.02)
  - main peak reduces in size dramatically
    - 'aged' NC must become a less efficient light-scatterer
  - aggregation, gellation or conformational changes?
    - is pre-peak material physically large or of high mass?
- Mark-Houwink plot does suggest that NC molecules become very rigid as a function of storage time
  - does this account for the reduced RALLS peak size?
  - initial high mass fraction has markedly lower *a* value
    - on storage, M-H is much steeper and near linear (*a* ~ 1.1)

RALLS Data


Wetted THF, 35 C
Control
21 Days
70 Days
Consistent with decreasing mwt
NC eluting at exclusion limit
Build-up of low mwt fractions
RALLS Response (mV)
108
85
63
40
17
-6
5.0
9.0
13.0
17.0
21.0
25.0
Retention Volume (ml)

Mark-Houwink



Conclusions

- dn/dc does not shift from equilibrium value of ~ 0.074
- Nitrocellulose proves very stable in dry THF
- Under dry conditions, effect of depolymerisation is off-set by grow-in of 'aggregate'
  - mwt increase at 35 °C
- Addition of water causes significant hydrolytic depolymerisation
  - lots of low mwt material formed
  - pronounced 'aggregate' peak forms on storage
- Hydrolytic degradation very temperature sensitive