Characterisation of Thermally Aged Nitrocellulose by GPC.

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Introduction

- 100°C Aged Nitrocellulose
  - Chromatography
  - Mark-Houwink Plots
- Aged Nitrocellulose from a PBX Formulation
- Degradation Kinetics
- Conclusions

Analysis Conditions

- Nitrocellulose (cotton based) aged at 100°C in confined conditions for 4, 12, 18, 20 days.

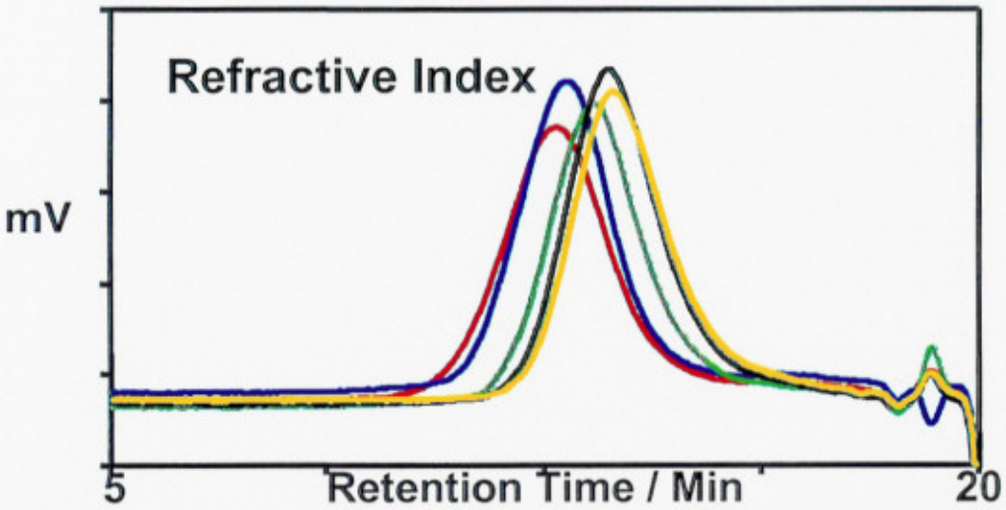
- All samples dissolved in THF for 7 days before GPC analysis (AWE Standard method).

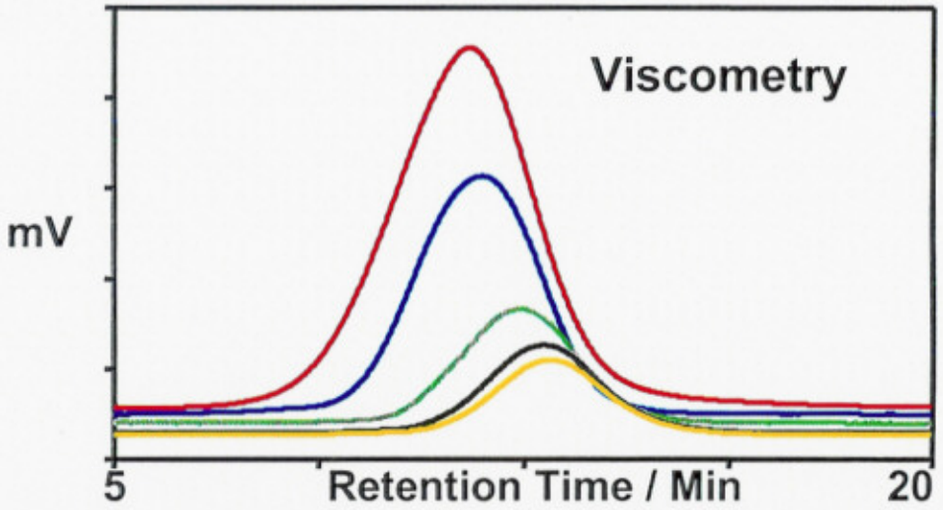
  Concentration ~2mg/ml.

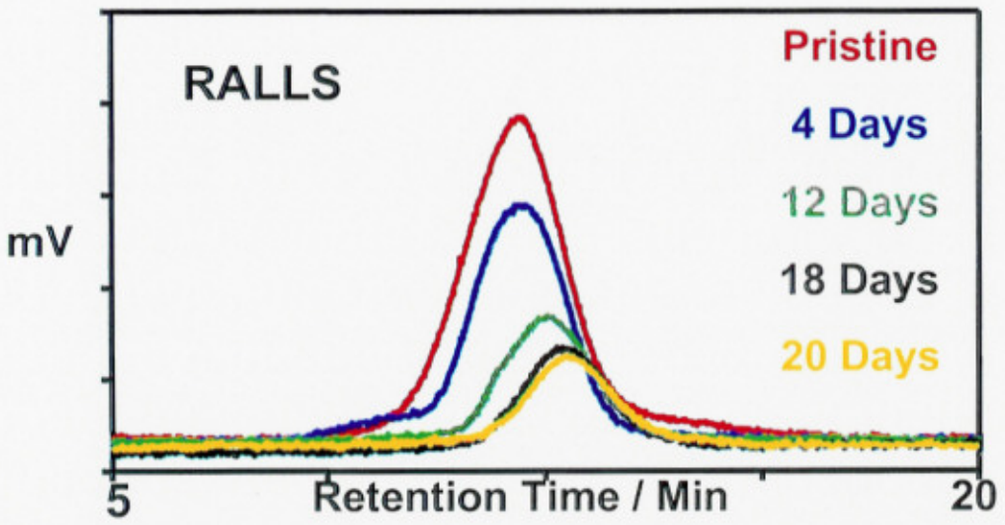
  Triplicate 100μl injections per sample

  1ml/min flow rate of THF

Aged (100°C) Nitrocellulose - Chromatography







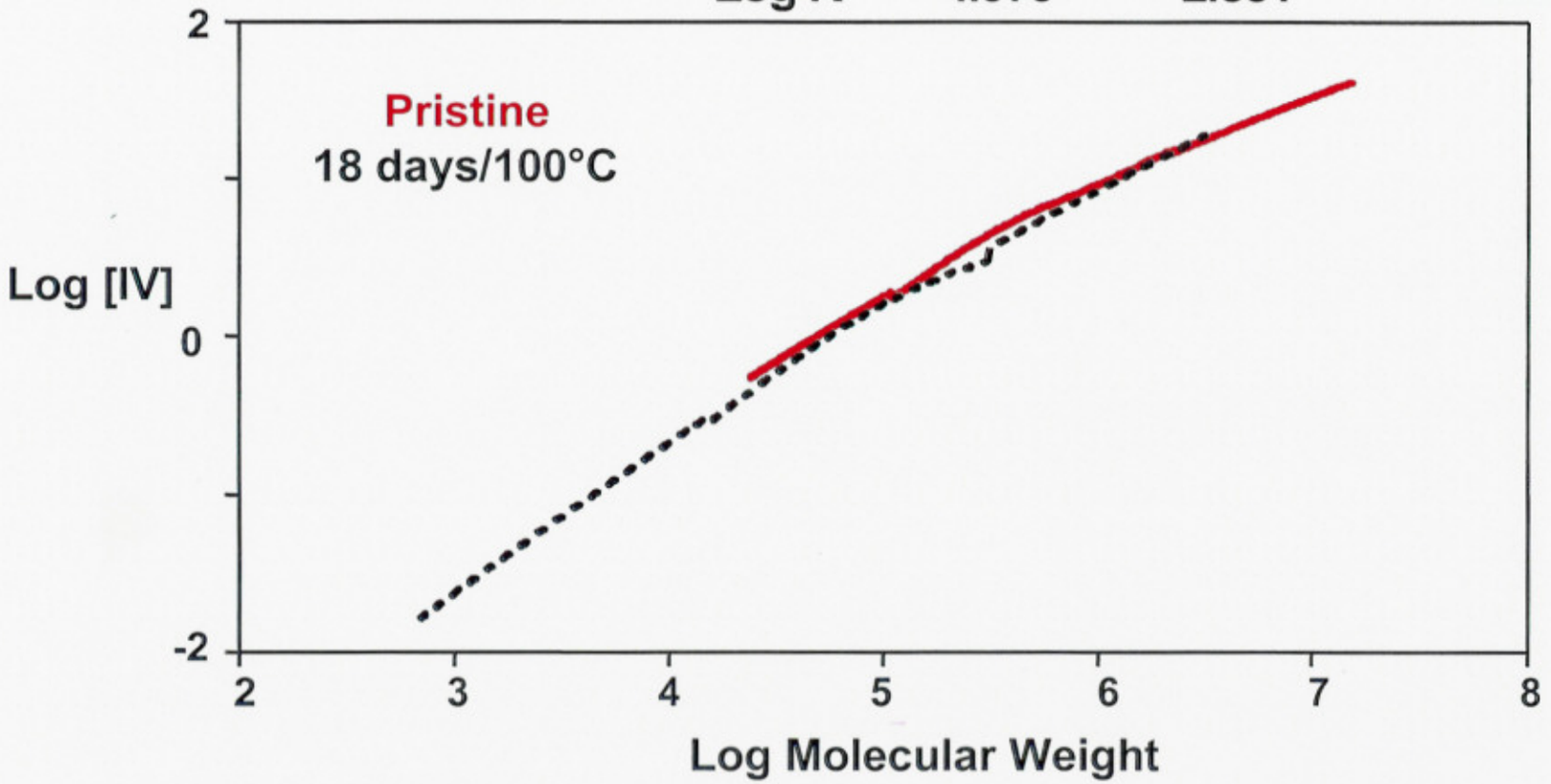
RI - Distribution tends to lower molecular weight as samples are aged and dn/dc is similar for all samples (Pristine 0.065, 20 Day aged 0.076)

Viscometry reduces with ageing

RALLS response reduces with ageing
Change in conformation with degradation?

Aged (100°C) Nitrocellulose - Mark-Houwink Plot

		Lower	Upper
Pristine	a	0.907	0.540
	Log K	-4.346	-2.286
18 Days / 100°C	a	1.051	0.508
	Log K	-4.979	-2.331

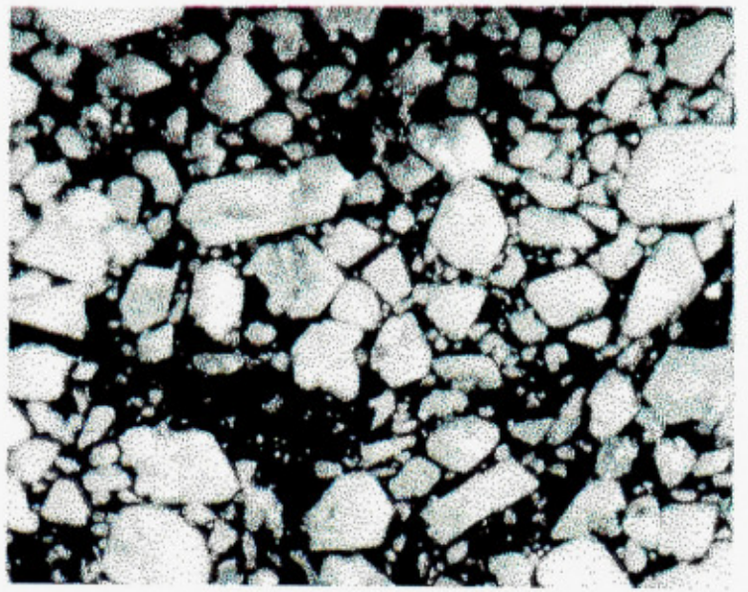


What is a Polymer Bonded Explosive?

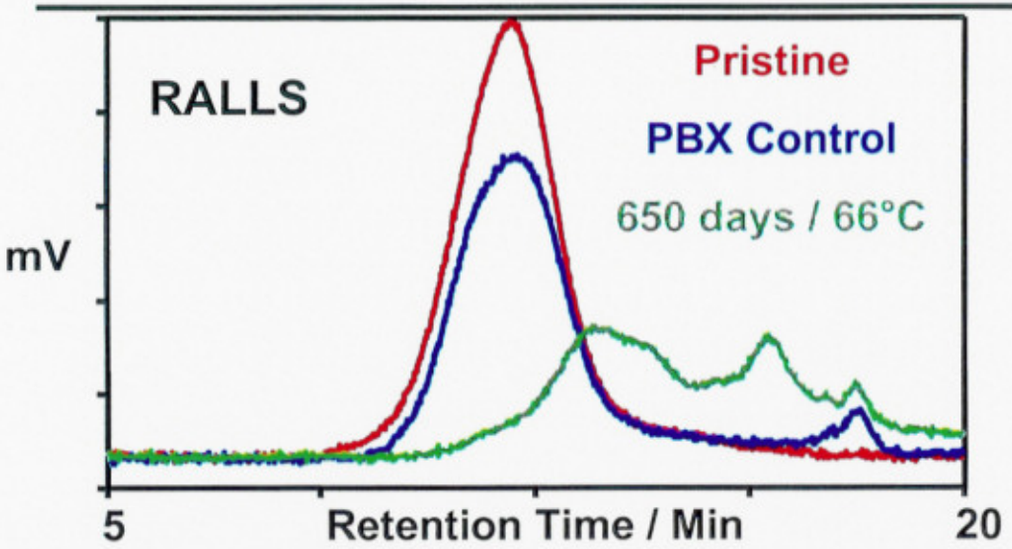
- A PBX contains:
  - Explosive filler - 91%
  - Polymeric binder

    Nitrocellulose - 1%
  - Plasticiser - 8%
  - Stabiliser

    Ethyl Centralite - 0.02%



Aged Nitrocellulose - from a PBX



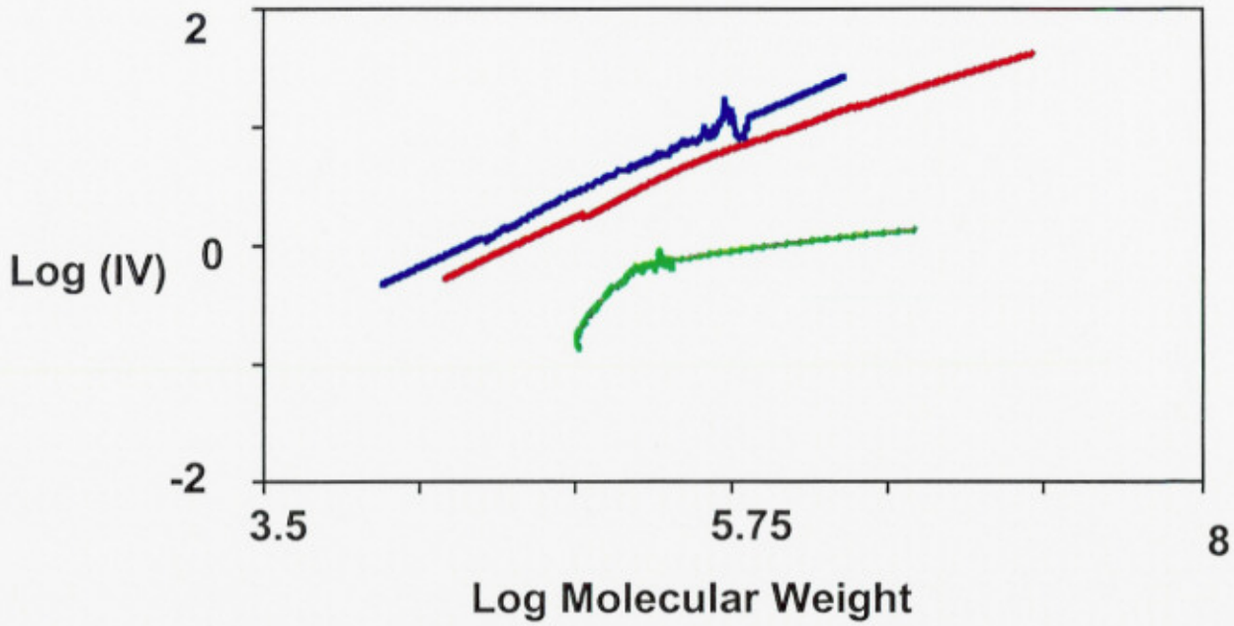
Some molecular weight change on formulation / pressing / machining

Harsh ageing leads to bimodal distribution - seen in all detectors

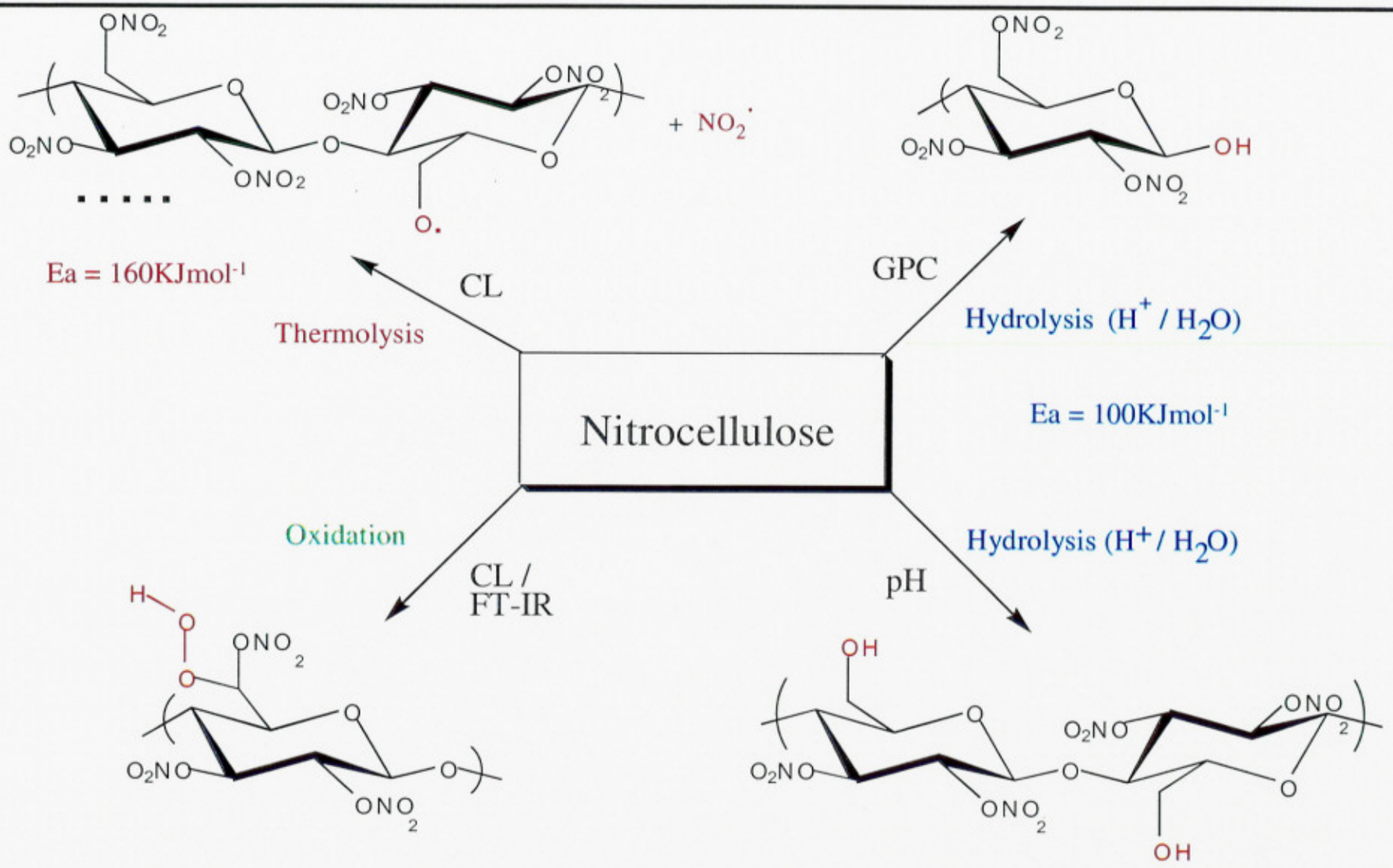
Mark-Houwink Plots

Pristine and PBX extracted NC are similar.

Aged shows very steep gradient a= 2.061, logK = -10.678

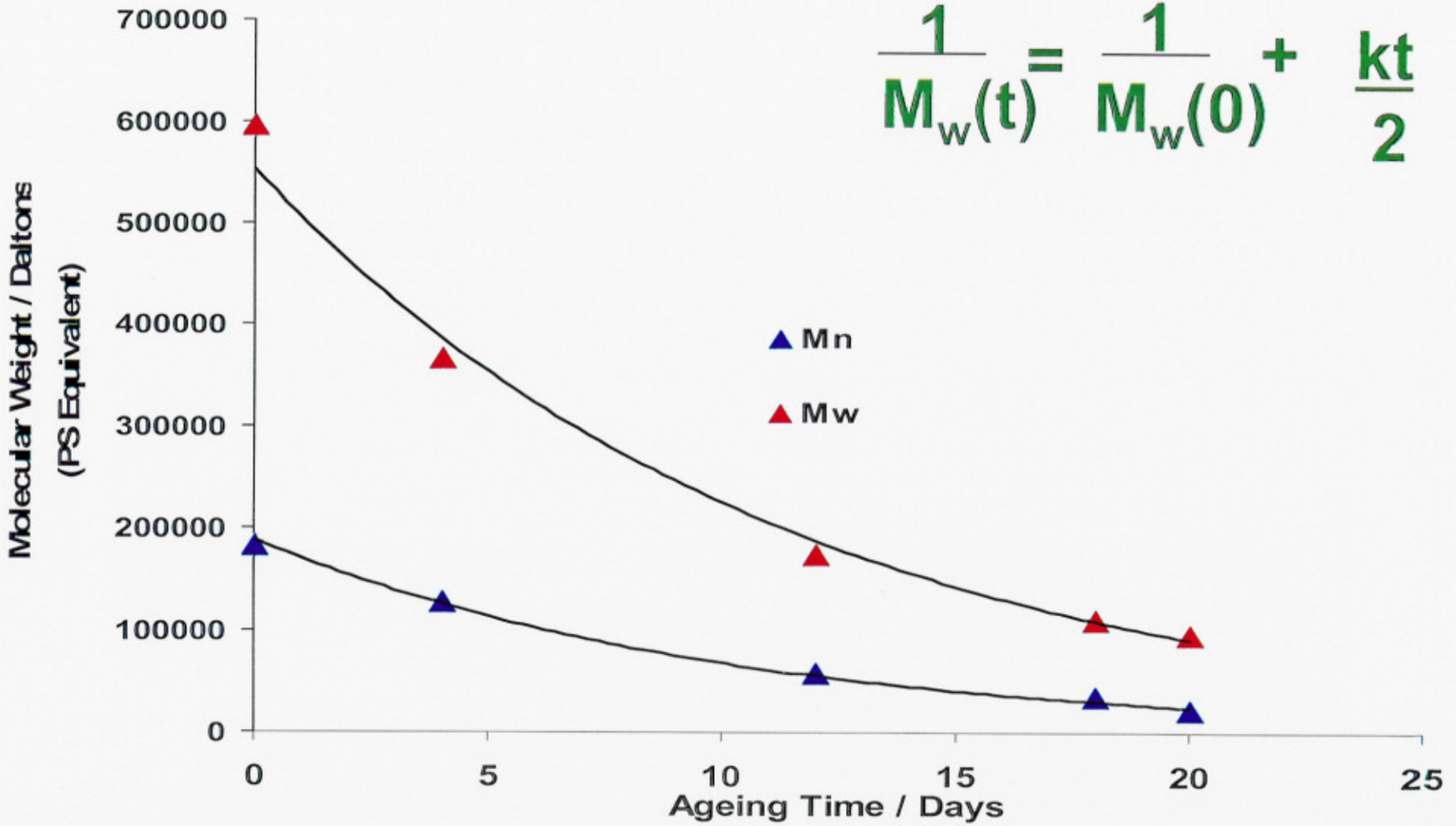


Nitrocellulose Degradation Routes

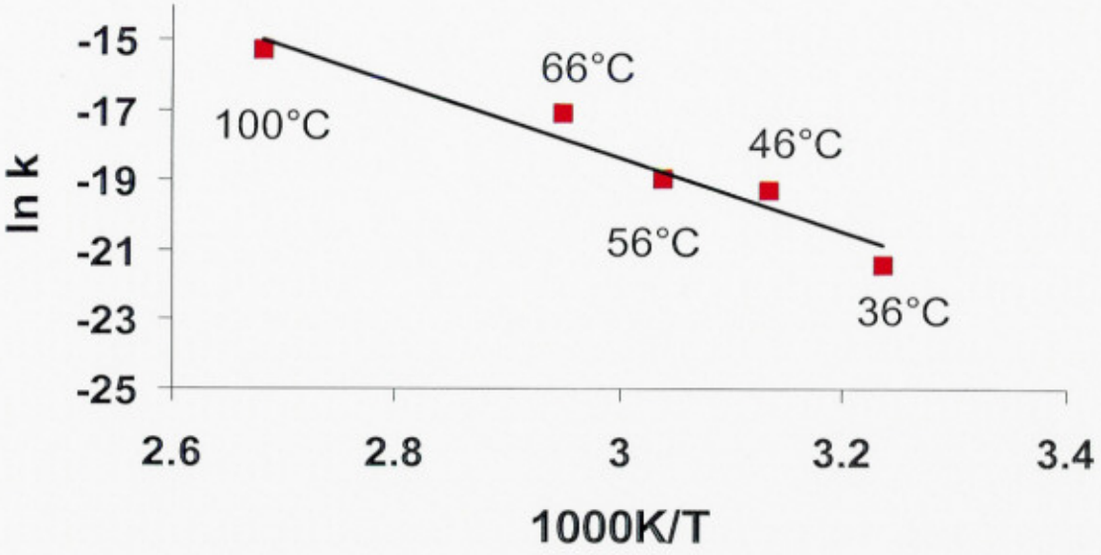


Aged (100°) Nitrocellulose - Degradation

$$\frac{1}{M_w(t)} = \frac{1}{M_w(0)} + \frac{kt}{2}$$



Arrhenius Analysis of Rate Data



$$k = Ae^{-Ea/RT}$$

$$\ln k = -10.627/T + 13.52$$

$$R^2 = 0.94$$

Cellulose [1]	113 KJmol^{-1}	Chain Scission – H_3O^+ catalysed
Nitrocellulose [2]	100 KJmol^{-1}	Chain Scission – H_3O^+ catalysed
Nitrocellulose	100 KJmol^{-1}	Nitrate ester loss – H_3O^+ catalysed
Nitrocellulose [3]	160 KJmol^{-1}	Thermolysis @ > 80°C
Nitrocellulose [4]	101± 11 KJmol^{-1}	AWE Ageing Trials

(1) Emsley *et al* (2000); (2) Bohn & Volk (1992) ; (3) Voltrauer & Foutijn (1981);
(4) Deacon, Kennedy, Lewis & Macdonald (2001)

Conclusions

Ageing at elevated temperatures produces nitrocellulose of a lower molecular weight distribution in solution.

Observations from RALLS and Viscosity (M-H plots) suggest conformation changes of nitrocellulose on ageing. Becomes more rigid - how / why?

Kinetics analysis shows that nitrocellulose degradation; as measured by GPC; fits a Random Chain Scission model.

Ref: The application of Gel Permeation Chromatography to the Investigation of the Ageing Processes of Nitrocellulose. P R Deacon, G R A Kennedy, A L Lewis and A F Macdonald. Symp Chem Probl Connected Stabil Explos, 12th 2001.)