Light Scattering Experiment

Measure
$I/I_0 = f(\theta)$
Standard Approach

- Measure scattering of an analyte relative to a well characterized very pure liquid

- Toluene is often used due to good scattering signal and values well characterized for a range of temperatures and wavelengths. Ratio is tabulated in many reference books.
Some Messy but accessible Constants

\[ K = \frac{2\pi^2}{\lambda_0^4 N_A} \left( n_0 \frac{dn}{dc} \right)^2 \]

\[ \frac{KC}{R_\theta} = \frac{1}{M} + 2A c \]

\( \lambda_0 \) = laser wavelength
\( N_A = \) Avogadros number
\( n_0 = \) Solvent RI
\( dn/dc = \) differential RI increment

\[ R_\theta = \frac{I_A n_0^2}{I_S n_s^2} R_s \]

\( I_A = \) Intensity of analyte (sample I – solvent I)
\( n_o = \) Solvent RI
\( I_S = \) Intensity of standard (Toluene?)
\( n_S = \) RI of Standard
\( R_s = \) Rayleigh ratio of standard
Molecular Weight Example

\[
\frac{dn}{dc} = 0.185 \text{ (mL/g)}
\]
\[
l_{\text{tol}} = 192630 \text{ (counts/sec)}
\]
\[
l_{\text{sol}} = 21870 \text{ (counts/sec)}
\]

<table>
<thead>
<tr>
<th>Concentration (mg/mL)</th>
<th>Measured Intensity (counts/sec)</th>
<th>Intensity of Analyte (counts/sec)</th>
<th>KC/R$_{\theta}$ (1/Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.006</td>
<td>87,830</td>
<td>65,960</td>
<td>6.1994 x 10$^{-5}$</td>
</tr>
<tr>
<td>3.018</td>
<td>222,900</td>
<td>201,030</td>
<td>6.4765 x 10$^{-5}$</td>
</tr>
<tr>
<td>5.029</td>
<td>366,770</td>
<td>344,900</td>
<td>6.6682 x 10$^{-5}$</td>
</tr>
<tr>
<td>10.059</td>
<td>742,570</td>
<td>720,700</td>
<td>6.7743 x 10$^{-5}$</td>
</tr>
</tbody>
</table>
Light Scattering

For Rayleigh scatterers,

\[
\frac{KC}{R_\theta} = \frac{1}{M} + 2A_2c \quad (y = b + mx)
\]

Therefore a “Debye plot” of \( KC/R_\theta \) versus \( c \) should give a straight line whose intercept at zero concentration will be \( 1/M_w \) and whose slope will be \( 2A_2 \)!

**Note that the moment of the distribution is \( M_w \) !**
The Debye Plot

\[ \frac{KC}{R_\theta} = \frac{1}{M} + 2A_2c \]

- \( KC \) vs \( 1/Mw \)
- \( KC/Re (1/Mw) \) vs Conc (g/ml)
Chain Transfer in Free Radical Polymerization

- A termination and re-initiation reaction
Chain Transfer Agents (CTAs)

- Thiols are efficient examples

\[ \text{H}_2\text{C} - \text{C} - \text{C}^\bullet + \text{H} - \text{S} - \text{C}_6\text{H}_9 \rightarrow \text{H}_2\text{C} - \text{C} - \text{H} + \text{C}_6\text{H}_9 - \text{S}^\bullet \]

Initiates another chain
Chain Transfer to Polymer

- Creation of branches
- “Back biting”
Branching in Polyethylene

- Common Branch length is 4 or 5....why ???
Chain Transfer to Initiator

- Example for acrylonitrile and BPO
- What effect does this process have on DP, PDI??
Chain Transfer Kinetics

The chain transfer constant, $C$ is defined as the ratio of the chain transfer and propagation rate constants:

$$C = \frac{k_{tr}}{k_p}$$

There is some C, which includes a term for transfer to a CTA, and one to monomer, solvent, polymer, etc.

The higher the value of $C$ the smaller the amount required to lower the molecular weight.
Chain transfer constant \( = \frac{k_{tr}}{k_p} \)

\[ C_I = \frac{k_{trI}}{k_p} \quad C_S = \frac{k_{trS}}{k_p} \quad C_M = \frac{k_{trM}}{k_p} \]

\[ \text{I} \quad \text{BuSH} \quad \rightarrow \quad \text{I} \quad \text{BuS}^* \]
Measurement of Chain Transfer Constants

The Mayo Equation:

\[
\frac{1}{DP_n} = \frac{1}{DP_0} + C_s \left[ \frac{\text{Transfer agent}}{\text{monomer}} \right]
\]

- $DP_n = \text{degree of polymerisation WITH transfer agent}$
- $DP_0 = \text{degree of polymerisation WITHOUT transfer agent}$
- $C_s = \text{Chain Transfer “constant” or “coefficient”}$
Generic Mayo plot
**CHAIN TRANSFER AGENTS**

Chain transfer activity dependent upon the monomer being polymerised and the structure of the CTA

For **Styrene @ 60°C**

<table>
<thead>
<tr>
<th>CTA</th>
<th>$C_s \times 10^4$</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.02</td>
<td>Addition to propagating radical</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.1</td>
<td>Resonance stabilized</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>0.7</td>
<td>Weakening of C-H Bond</td>
</tr>
<tr>
<td>Acetone</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>$\text{CCl}_4$</td>
<td>110</td>
<td>Weak C-Cl Bond</td>
</tr>
<tr>
<td>$\text{CH}_3(\text{CH}_2)_3\text{SH}$</td>
<td>210,000</td>
<td>Weak S-H Bond</td>
</tr>
</tbody>
</table>
## Chain Transfer constants at 60 °C

<table>
<thead>
<tr>
<th>CTA</th>
<th>Sryrene</th>
<th>Vinyl acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.023</td>
<td>1.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.125</td>
<td>21.6</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>1.6</td>
<td>20</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>3.4</td>
<td>150</td>
</tr>
<tr>
<td>n-Butyl amine</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>CCl₄</td>
<td>110</td>
<td>10,700</td>
</tr>
<tr>
<td>n-Butyl Mercaptan</td>
<td>210,000</td>
<td>480,000</td>
</tr>
</tbody>
</table>
Effect of CTA on DP of Styrene @ 60°C

\[ \frac{1}{\text{DP}} \sim \frac{1}{(\text{mol.wt})} \]

- n-Butyl mercaptan (\(C_S = 210,000\))
- \(\text{CCl}_4\) (\(C_S = 110\))
- Benzene (\(C_S = 0.02\))

[Transfer Agent]
[Styrene]
Transfer to Polymer

**Intramolecular reaction/backbiting** →
- short chain branches

**Intermolecular reaction** →
- long chain branches

$C(\text{Psty}) = 10 \times 10^4$
$C(\text{PMMA}) = 0.1 - 360 \times 10^4$
Trapping Radicals

BHT + R → RH

R + → R
Trapping carbon centered radicals

- Carbon centered radicals stopped by addition to oxygen or carbon

![Chemical structures showing the trapping of carbon centered radicals using benzoquinone.](image_url)
Stable Radical Inhibitors

Diphenylpicrylhydrazyl, DPPH

Galvanoxyl

Triphenylverdazyl

Chemistry 367L/392N
Some Familiar CTA’s

Ascorbic acid  Vit C  Butylated HydroxyAnisole  BHA

α-tocopherol  Vit E
**Butylated HydroxyToluene**

- BHT radical will not initiate new chains

BHT radical will not initiate new chains.

Decomposes, does not reinitiate.
Interesting CTA’s

Phenyl-a-t-butyl nitronate (PBN)

TEMPO
Antioxidant treatment with phenyl-\(\alpha\)-tert-butyl nitrone (PBN) improves the cognitive performance and survival of aging rats

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Received 30 May 1995; revised version received 26 January 1996; accepted 26 January 1996

Abstract

Accumulating evidence has implicated free radical production and resultant oxidative damage as a major contributing factor in brain aging and cognitive decline. In the present study, aging 24-month-old rats were chronically treated with the synthetic spin-trapping antioxidant phenyl-\(\alpha\)-tert-butyl nitrone (PBN) for up to 9.5 months. Chronic PBN treatment (1) improved the cognitive performance of aged rats in several tasks, (2) resulted in greater survival during the treatment period, and (3) decreased oxidative damage within brain areas important for cognitive function. These results not only provide a direct linkage between free radicals/oxidative damage and cognitive performance in old age, but also suggest that synthetic brain antioxidants could be developed to treat or prevent age-associated cognitive impairment and Alzheimer’s disease.

Keywords: Antioxidants; Phenyl-\(\alpha\)-tert-butyl nitrone (PBN); Aging rats; Cognition; Survival; Free Radicals; Oxidative damage; Alzheimer’s disease
Radical Theory of Aging

Recent Review: Mechanisms of Ageing and Development Volume 125, Issues 10-11, October- November 2004