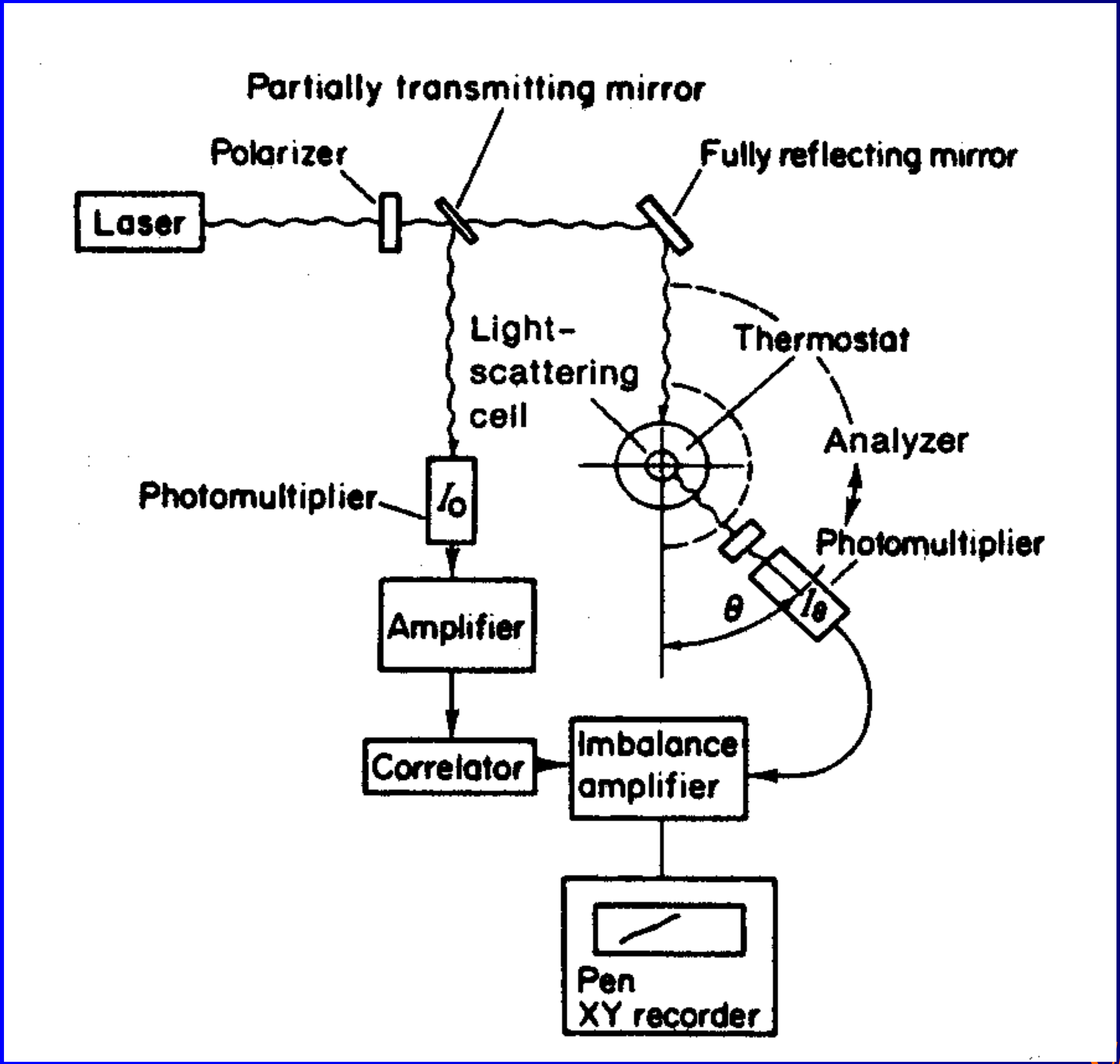
Macromolecular Chemistry

Lecture 11

Chemistry 367L/392N

Light Scattering Experiment

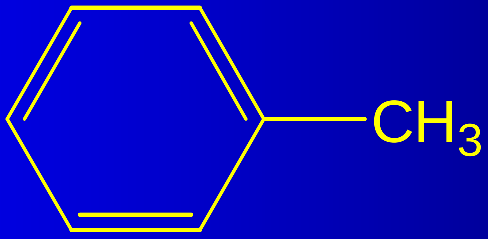


Measure

$I/I_0 = f(\theta)$

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 ot temperatures and wavelengths. Ratio is tabulated in many reference books.



Some Messy but accessible Constants

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

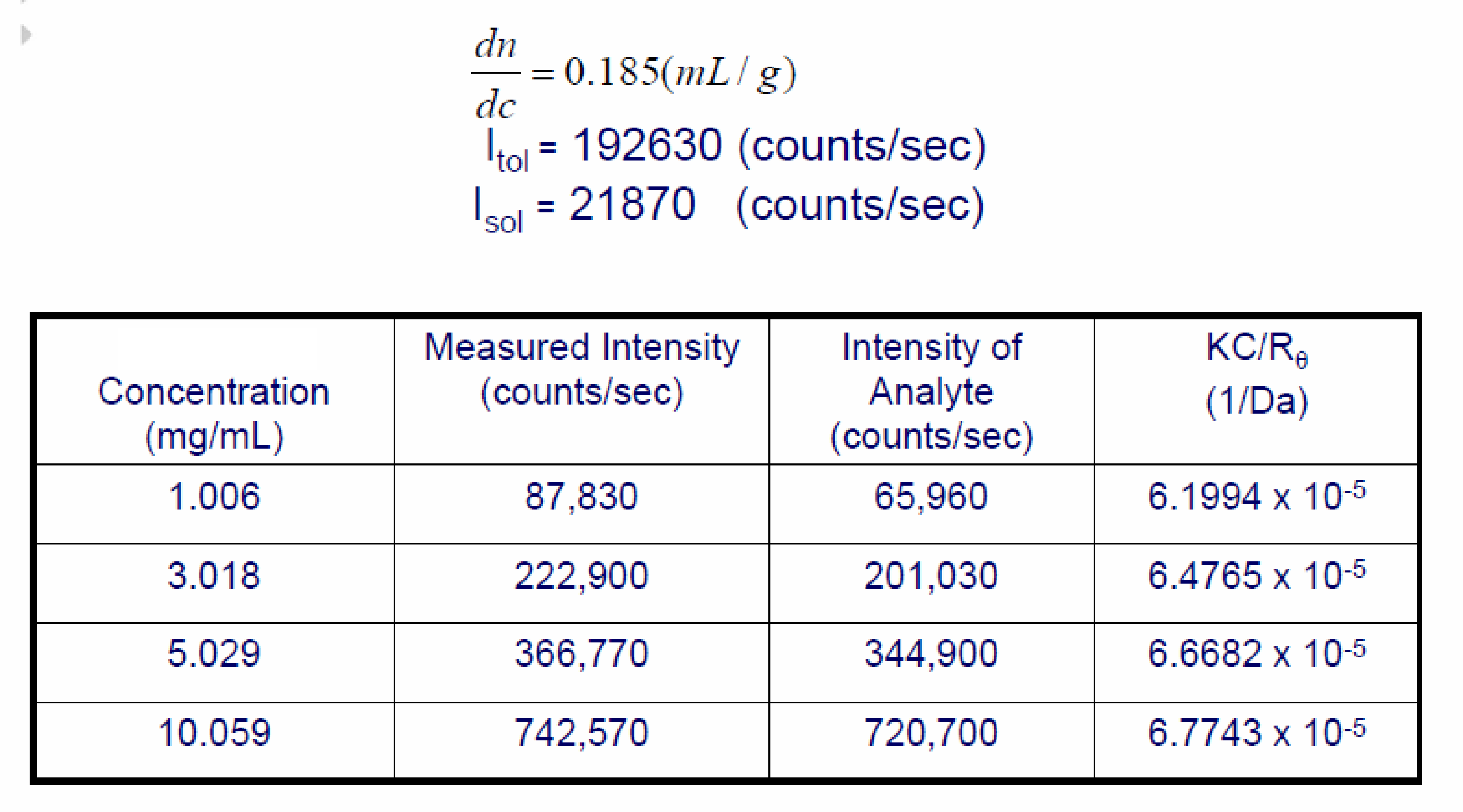
λ_o = laser wavelength
N_A = Avogadros number
n_o = Solvent RI
dn/dc = differential RI increment

$$\frac{\boxed{K}C}{\boxed{R_\theta}} = \frac{1}{M} + 2A_2 c$$

$$R_\theta = \frac{I_A n_0^2}{I_s n_s^2} R_S$$

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



$$\frac{dn}{dc} = 0.185(mL/g)$$

I_{tol} = 192630 (counts/sec)

I_{sol} = 21870 (counts/sec)

Concentration (mg/mL)	Measured Intensity (counts/sec)	Intensity of Analyte (counts/sec)	KC/R_θ (1/Da)
1.006	87,830	65,960	6.1994×10^{-5}
3.018	222,900	201,030	6.4765×10^{-5}
5.029	366,770	344,900	6.6682×10^{-5}
10.059	742,570	720,700	6.7743×10^{-5}

Light Scattering

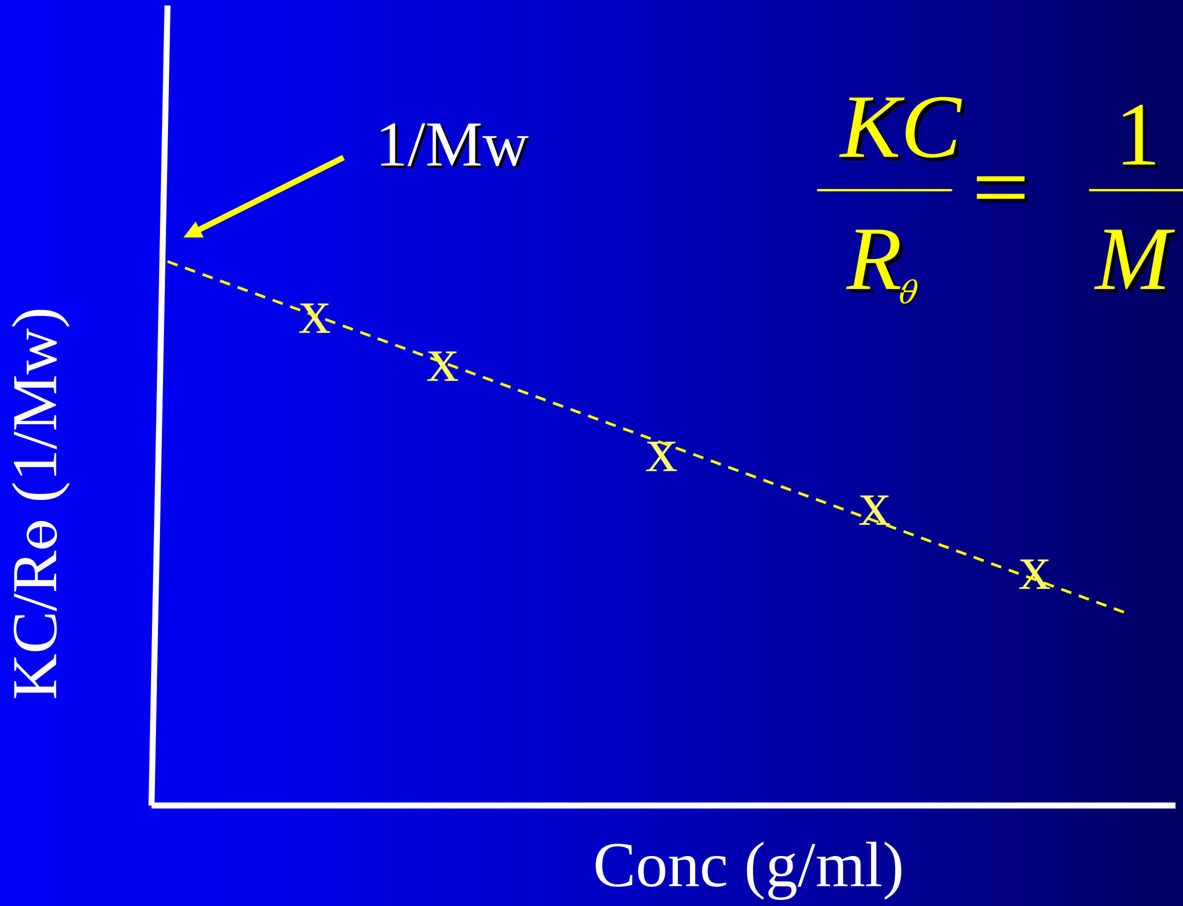
For Rayleigh scatterers,

$$\frac{KC}{R_\theta} = \frac{1}{M} + 2A_2c \qquad (y = b + mx)$$

Therefore a "Debye plot" of KC/R_θ versus c should give a straight line whose intercept at zero concentration will be $1/Mw$ and whose slope will be $2A_2$!

Note that the moment of the distribution is Mw !

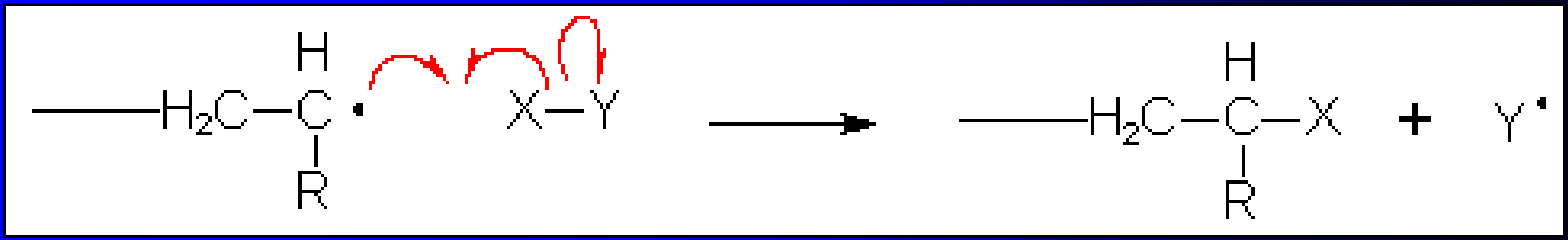
The Debye Plot



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

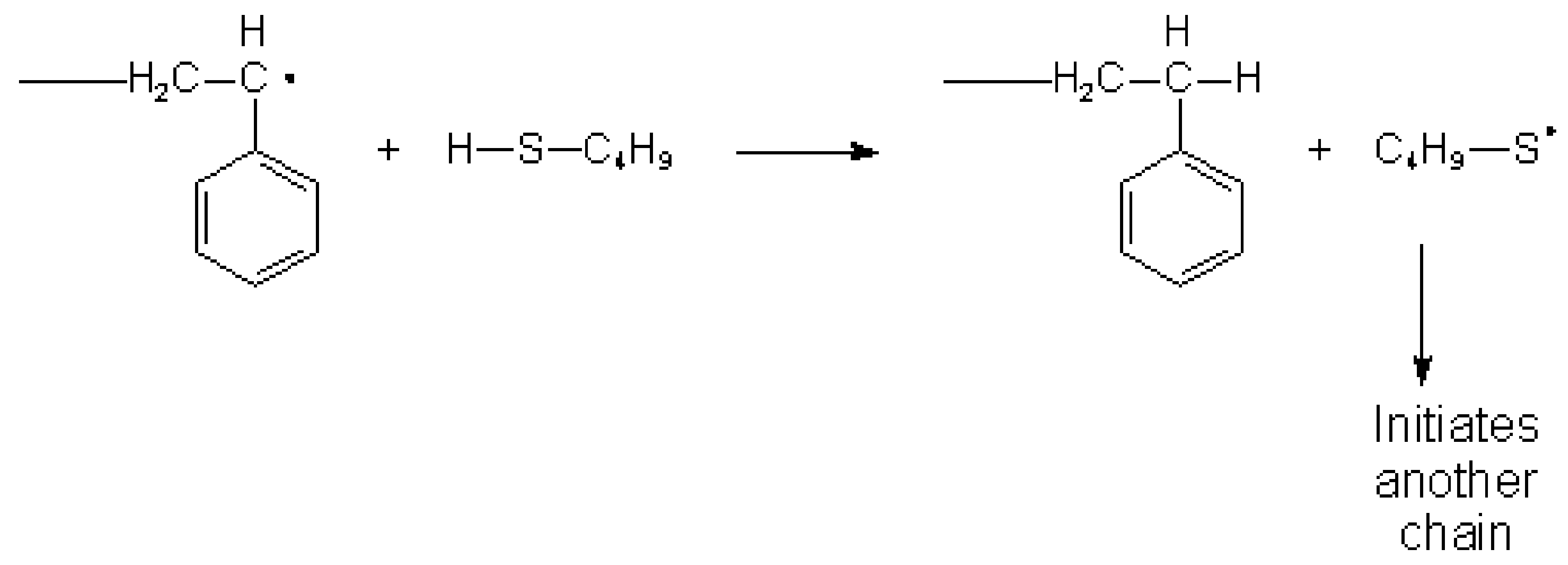
Chain Transfer in Free Radical Polymerization

- A termination and re-initiation reaction



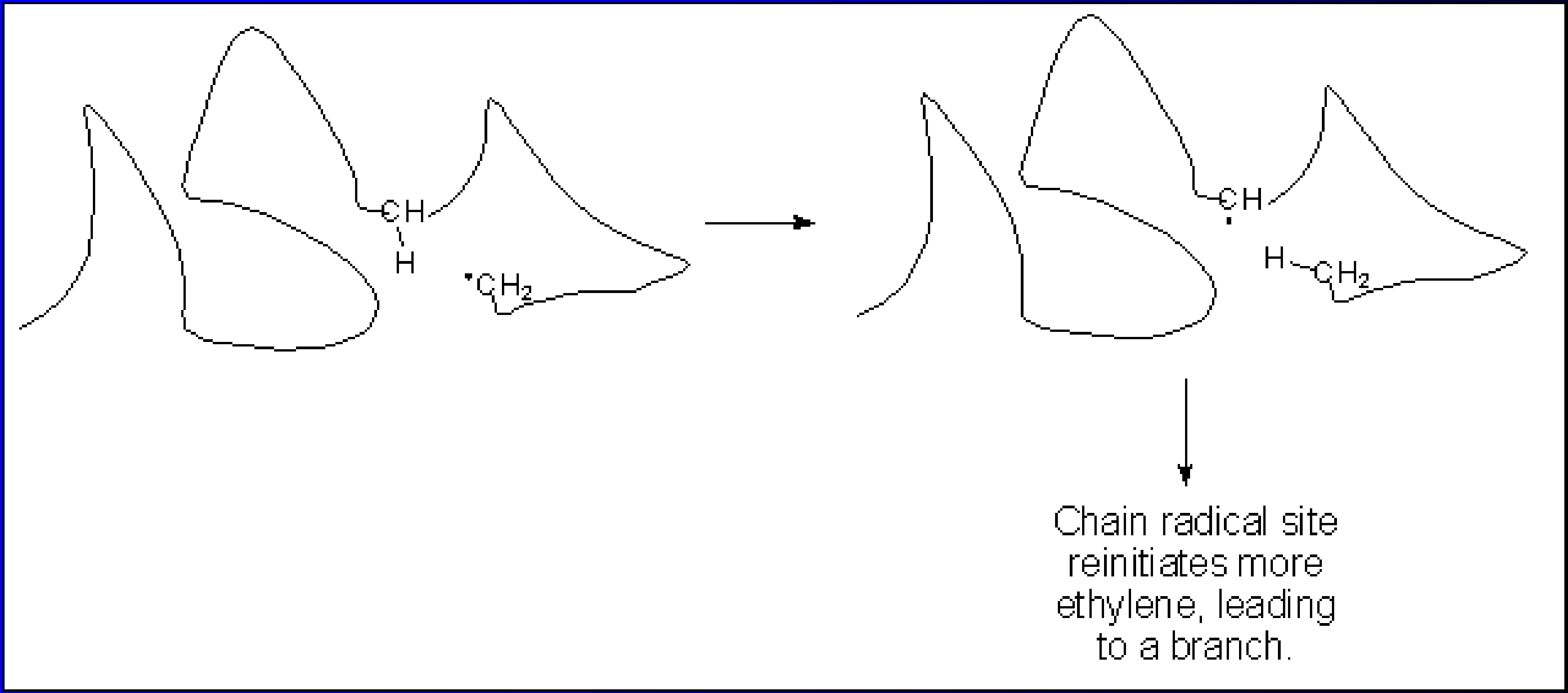
Chain Transfer Agents (CTAs)

- Thiols are efficient examples



Chain Transfer to Polymer

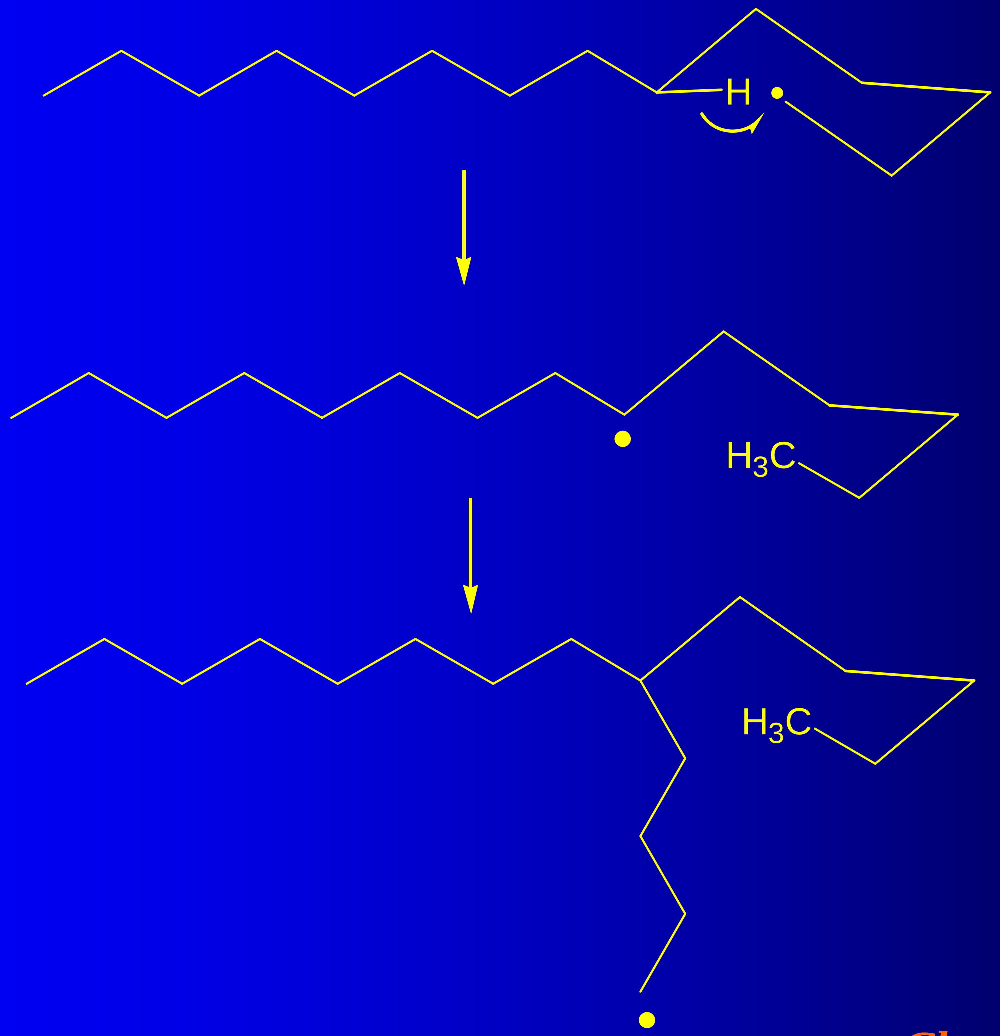
- Creation of branches
- “ Back biting”



Chain radical site reinitiates more ethylene, leading to a branch.

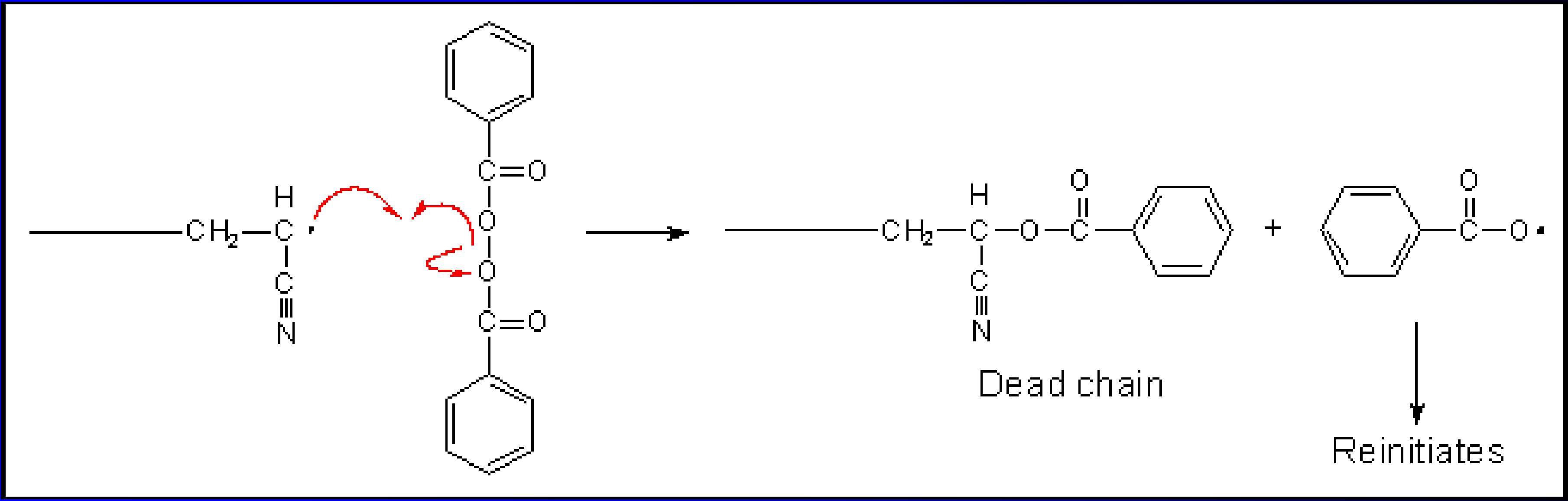
Branching in Polyethylene

- 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;

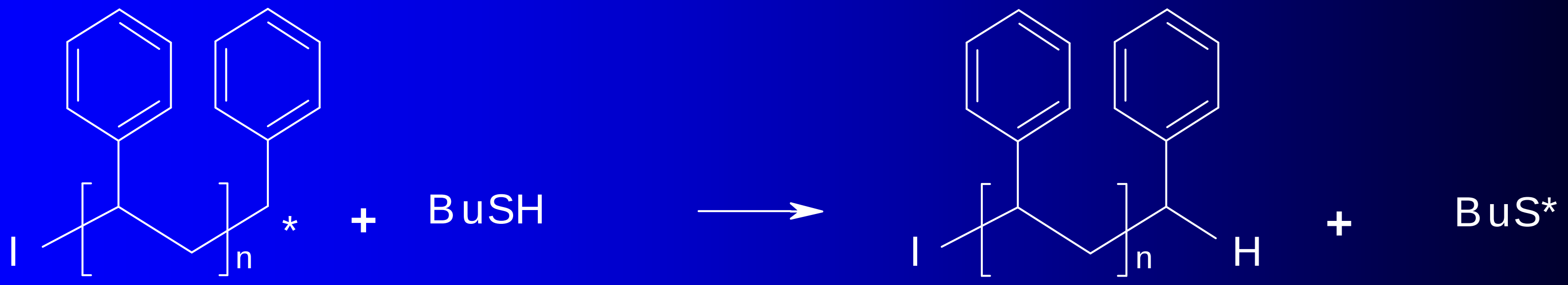
$$C = k_{tr}/k_p$$

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 $= {}^{k_{tr}}\!/_{k_p}$

$$C_I = {}^{k_{trI}}\!/_{k_p} \qquad C_S = {}^{k_{trS}}\!/_{k_p} \qquad C_M = {}^{k_{trM}}\!/_{k_p}$$



Measurement of Chain Transfer Constants

The Mayo Equation:

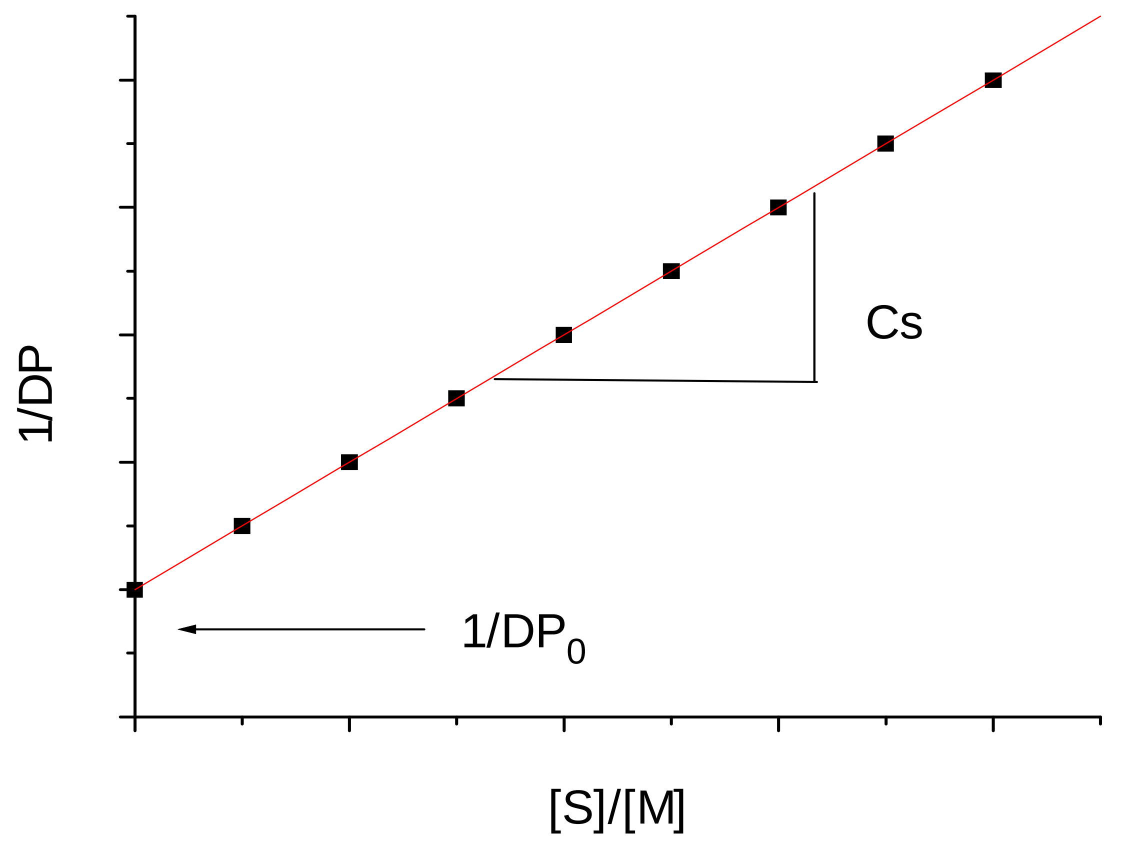
$$\frac{1}{DP_n} = \frac{1}{DP_0} + Cs\left[\frac{Transfer\ agent}{monomer}\right]$$

DP_n = degree of polymerisation WITH transfer agent

DP_o = degree of polymerisation WITHOUT transfer agent

C_S = 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

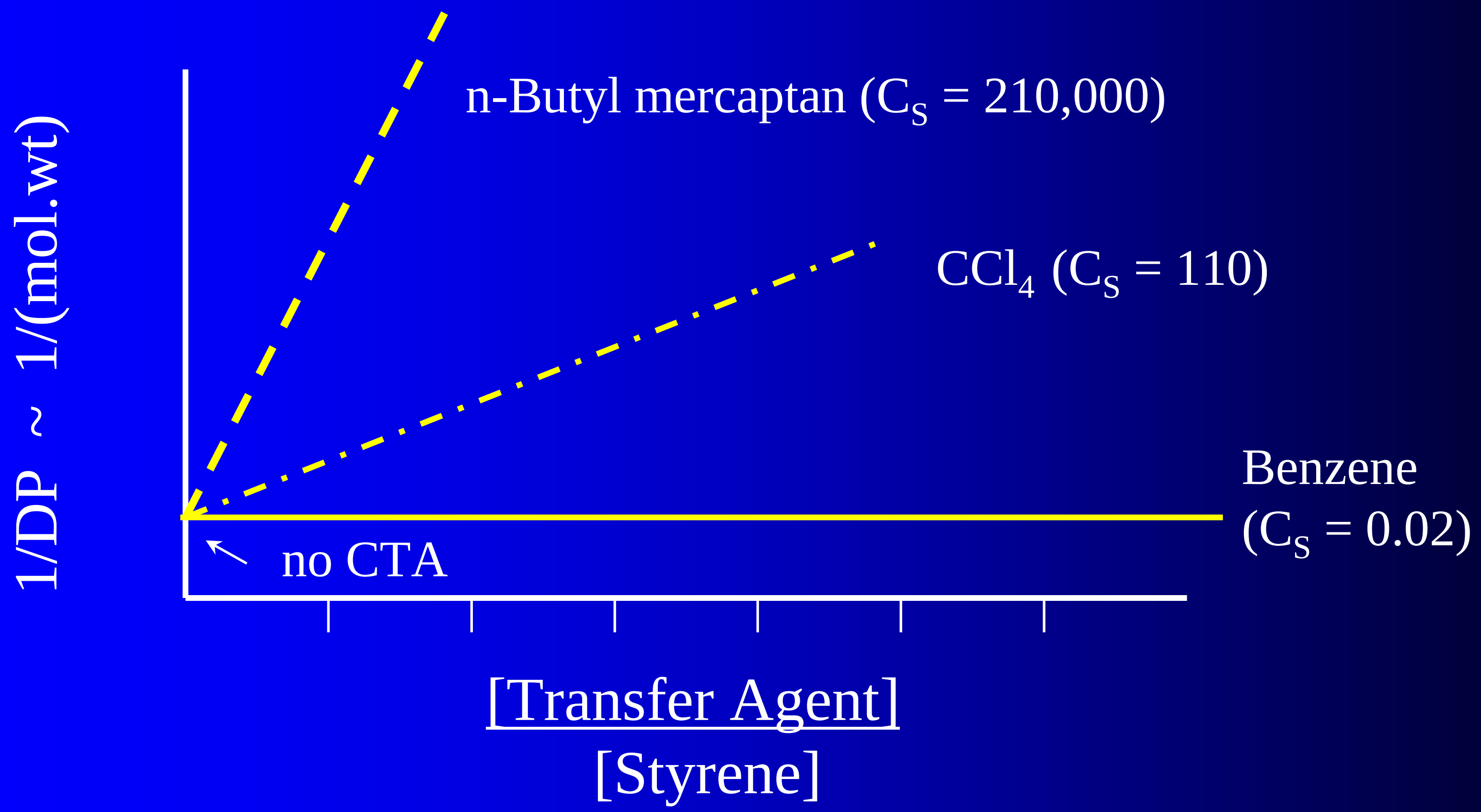
For Styrene @ 60°C

CTA	C_s x 10^4	Comment
Benzene	0.02	Addition to propagating radical
Toluene	0.1	Resonance stabilized
Ethyl Benzene	0.7	Weakening of C-H Bond
Acetone	4.1	
CCl_4	110	Weak C-C1 Bond
$CH_3(CH_2)_3SH$	210,000	Weak S-H Bond

Chain Transfer constants at 60 °C

CTA	Sryrene	Vinyl acetate	
Benzene	0.023	1.2	
Toluene	0.125	21.6	
n-Butanol	1.6	20	
$CHCl_3$	3.4	150	
n-Butyl amine	7.0		
CCl_4	110	10,700	
n-Butyl Mercaptan	210,000	480,000	

Effect of CTA on DP of Styrene @ 60^{O}C



Transfer to Polymer

Intramolecular reaction/backbiting →

- short chain branches

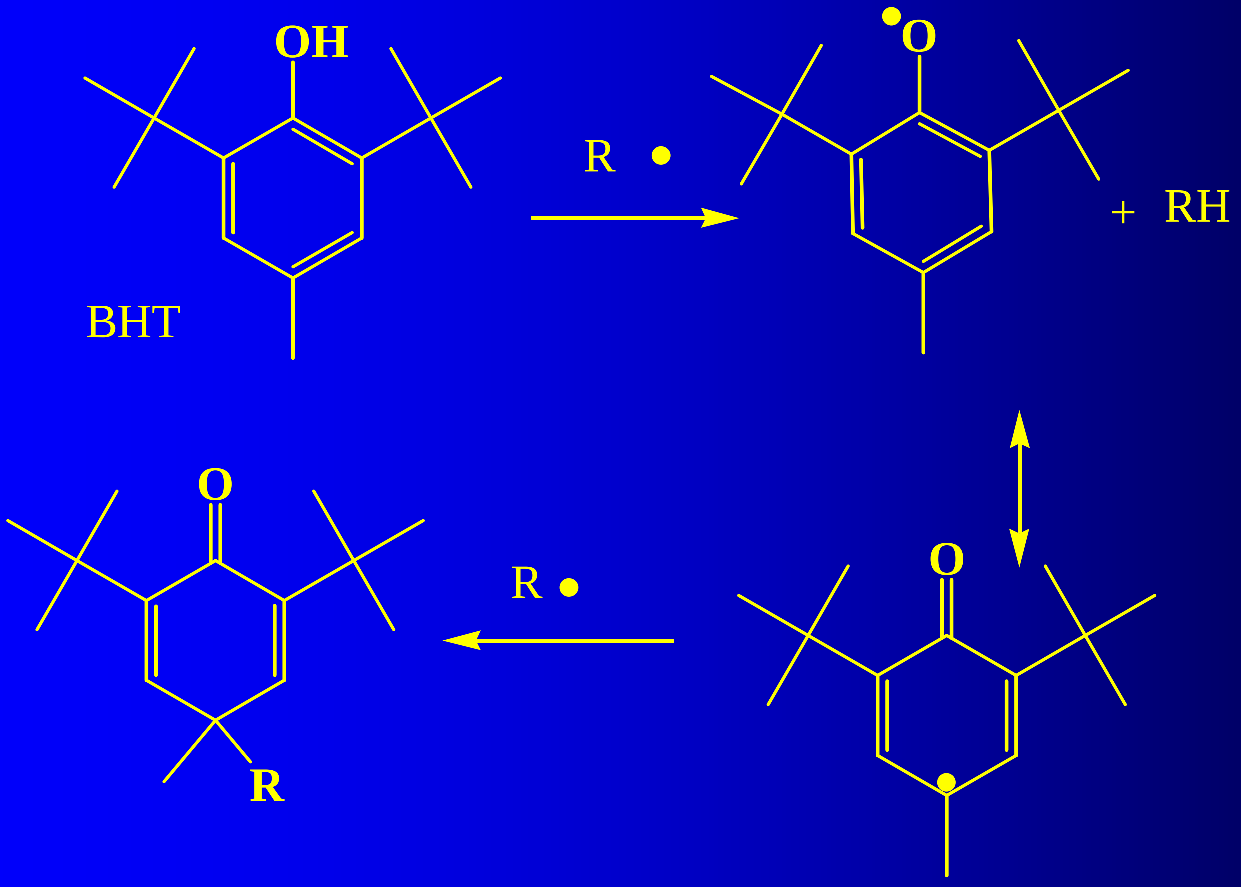
Intermolecular reaction →

- long chain branches

$C(\text{Psty}) = 10 * 10^4$

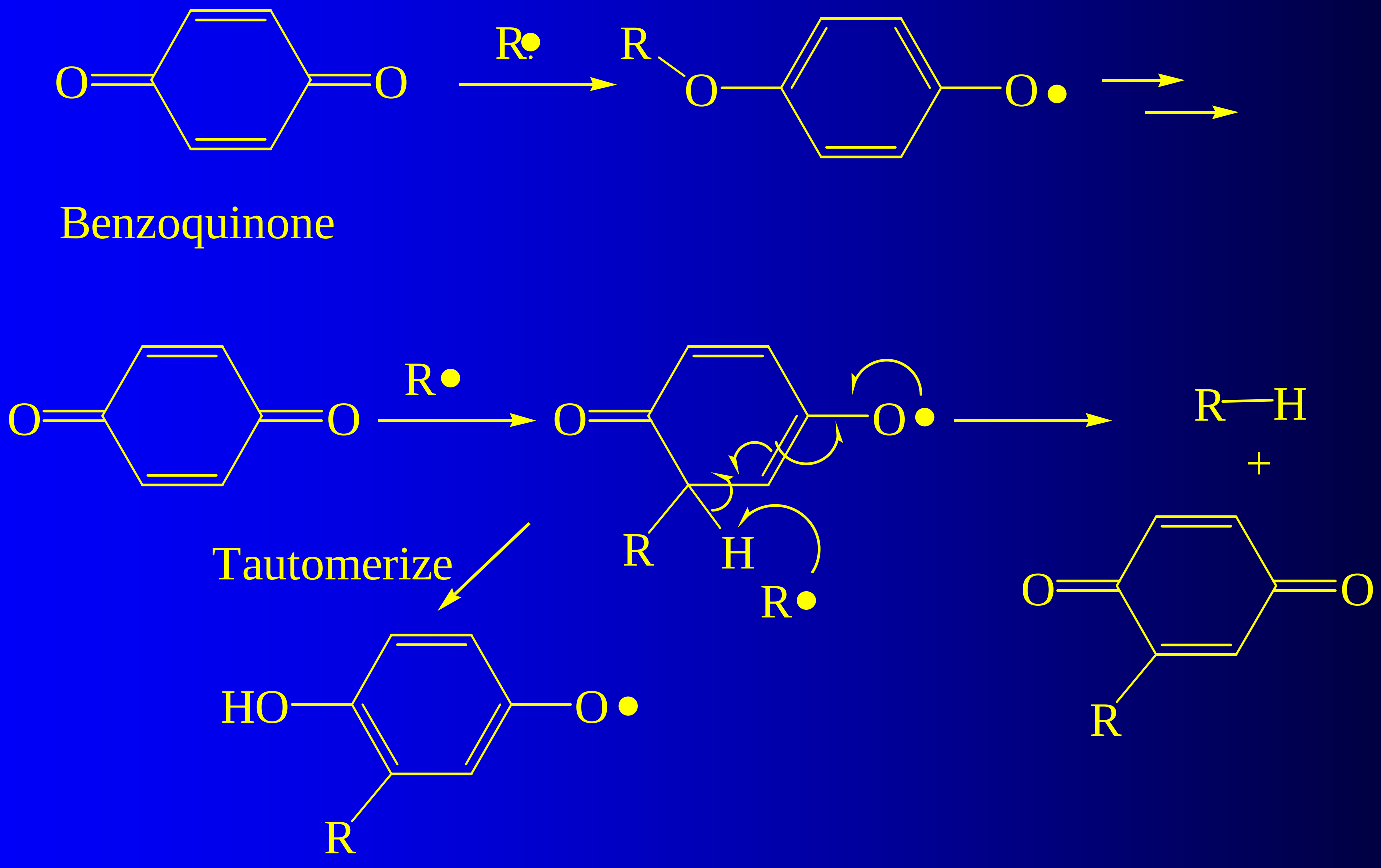
$C(\text{PMMA}) = 0.1 - 360 * 10^4$

Trapping Radicals

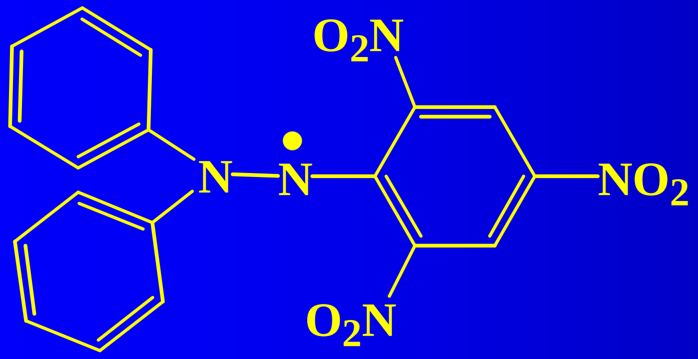


Trapping carbon centered radicals

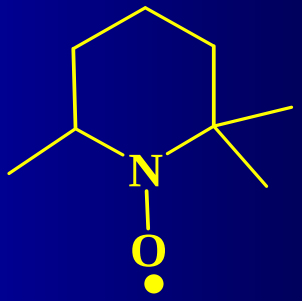
- Carbon centered radicals stopped by addition to oxygen or carbon



Stable Radical Inhibitors



Diphenylpicrylhydrazyl, DPPH



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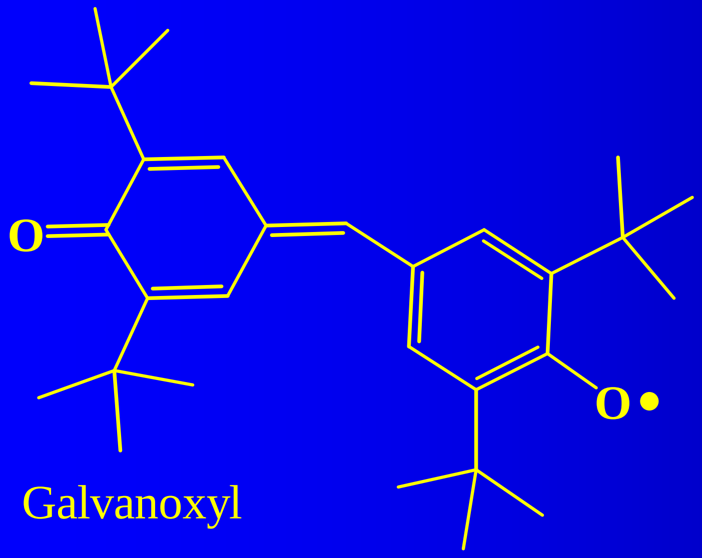
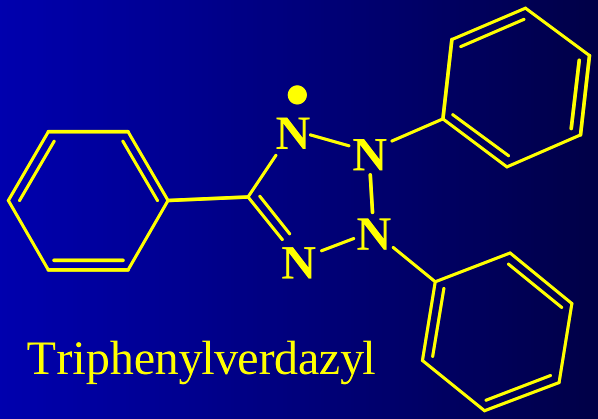
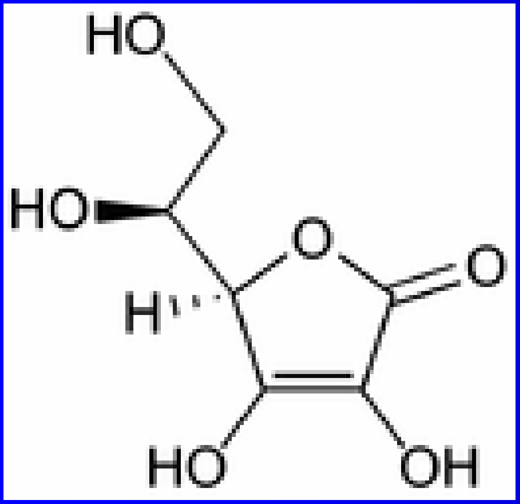


Galvanoxyl

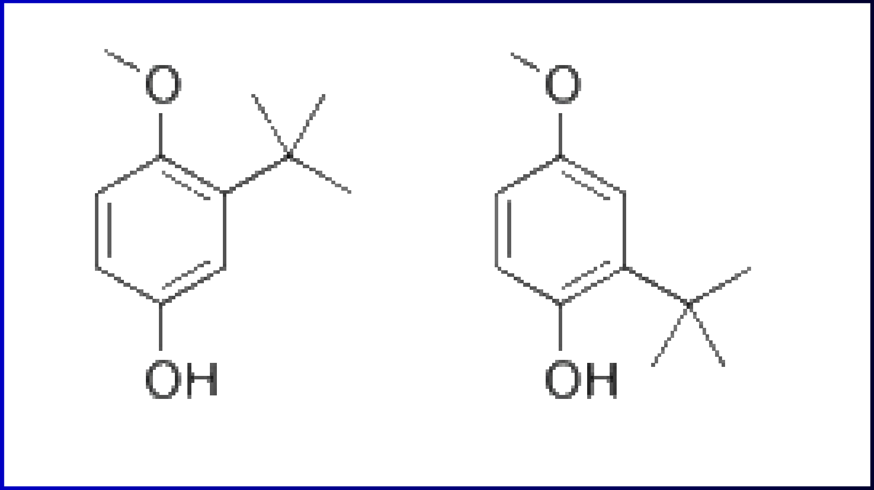


Triphenylverdazyl

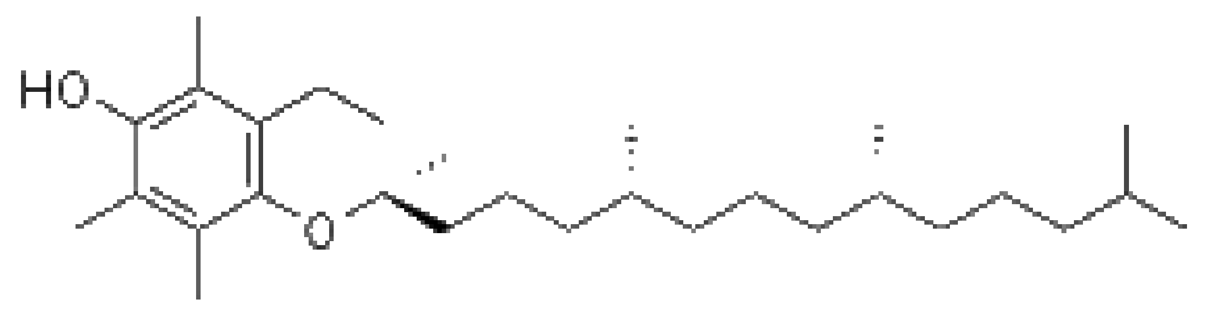
Some Familiar CTA’s



Ascorbic acid Vit C



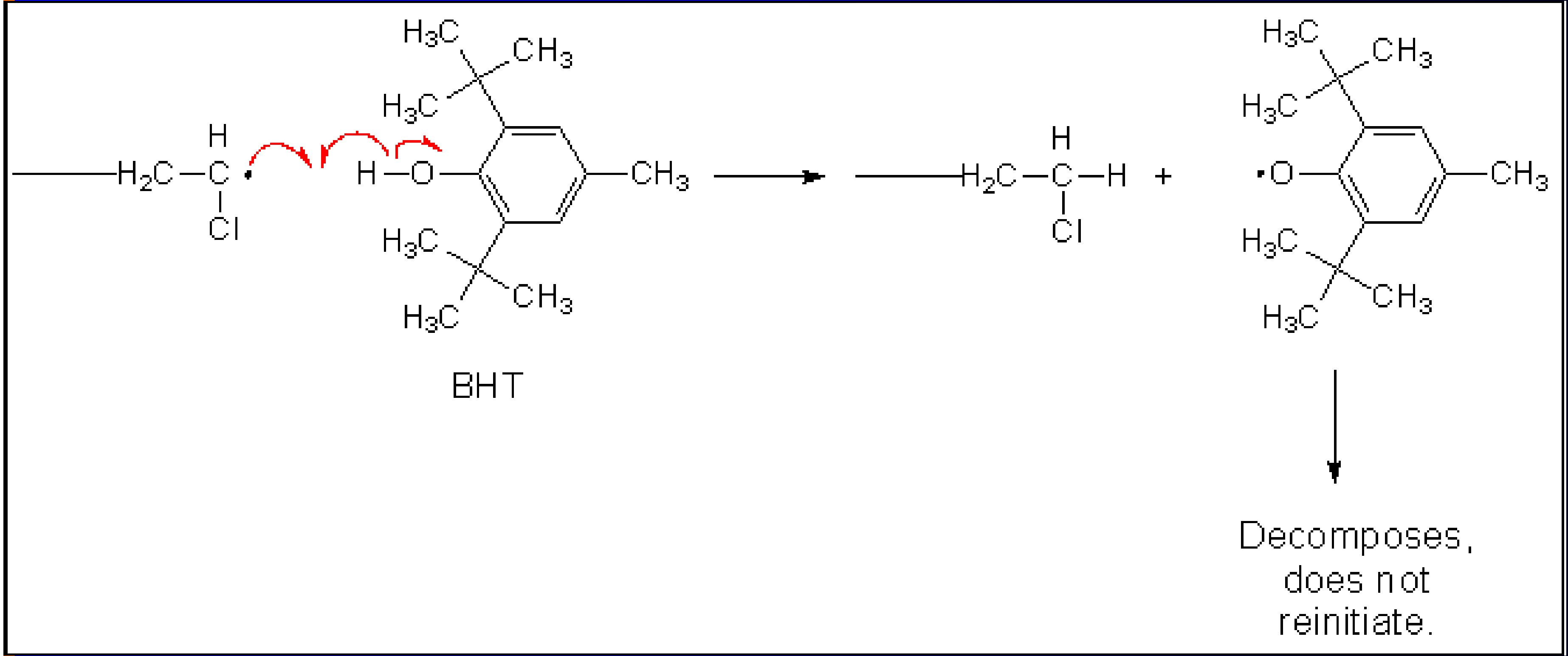
Butylated HydroxyAnisole BHA



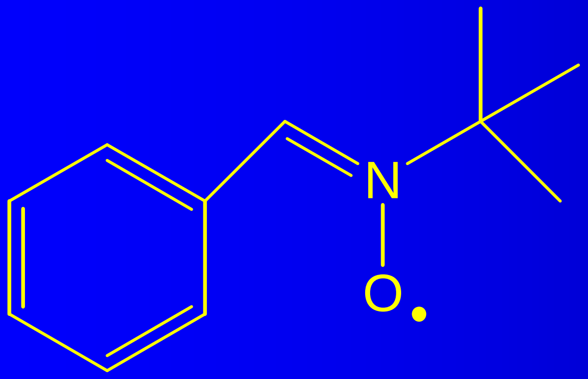
α-tocopherol   Vit E

Butylated HydroxyToluene

- BHT radical will not initiate new chains

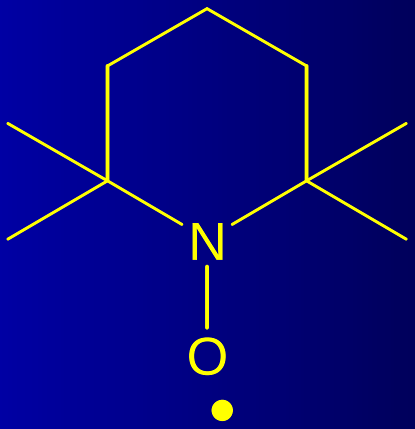


Interesting CTA’s



Phenyl-a-t-butylnitrone

PBN



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Neuroscience Letters 205 (1996) 181–184

NEUROSCIENCE LETTERS

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

Candice A. Sack, Debra J. Socci, Blane M. Crandall, Gary W. Arendash*

Department of Biology and Institute on Aging, University of South Florida, Tampa, FL 33620, USA

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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-α-*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-α-*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