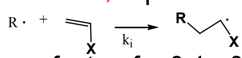
Fate of Initiator Radicals

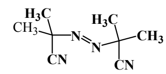
- Radical reactions
  - Recombination in solvent cage
    - Recombination in media
    - Reaction with polymer radicals (k_t)
    - Reaction with initiator (MIH)
    - Radical abstraction from polymer chains
    - Reaction with solvent or inhibitor
- Chain initiation, **R_i = 2 f kd [I]**



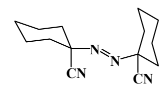
- Efficiency factor, f = 0.1 - 0.9

Radical Initiators

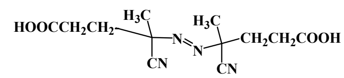
- Azo Initiators



azobisisobutyronitrile, AIBN
Td = 50-70°C



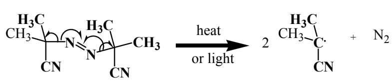
1,1'-azobis(1-cyclohexanenitrile)
80-100°C, High organic solubility



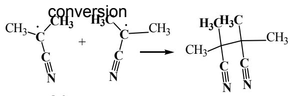
4,4'-azobis(4-cyanovaleric acid)
water soluble at pH > 7

Decomposition of Azo Initiators

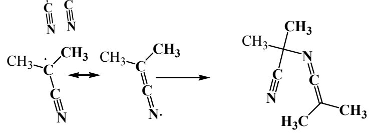
- 2- bond cleavage to liberate nitrogen



- Cage Recombination ---Side reaction- irreversible coupling of succinonitrile radicals, efficiency decreases at high conversion

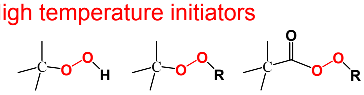


- or



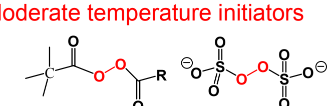
Peroxy Initiators

- High temperature initiators



Hydroperoxides Td = 155-175 C | Dialkyl Peroxides 100-135 C | Peresters 110-130 C

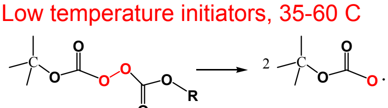
- Moderate temperature initiators



Diacyl Peroxides Td = 35-80 C | Persulfates 50-90 C

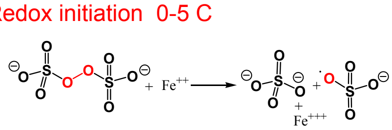
Peroxy Initiators

- Low temperature initiators, 35-60 C



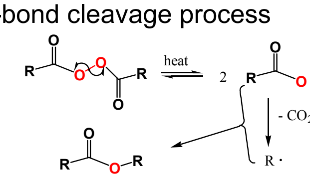
Peroxycarbonates

- Redox initiation 0-5 C



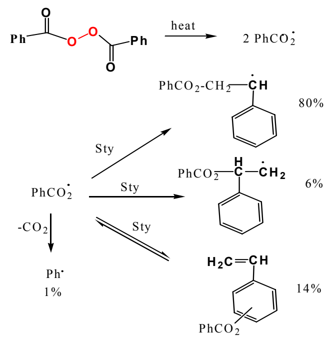
Decomposition of Peroxy Initiators

- 1-bond cleavage process



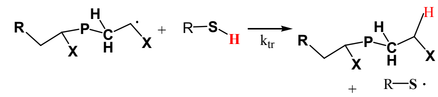
- If R = aryl, acyl radical initiates
  - = alkyl, CO_2 lost before initiation occurs

Reaction of Benzoyloxy radicals with styrene

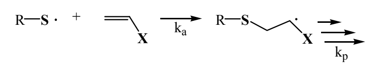


Chain Transfer

- Hydrogen transfer to growing polymer chain



- Reinitiation of growing chain using transferred radical



Effect of Chain Transfer on R_p and DP

Relative rate constants	Type of effect	Effect on R_p	Effect on DP
$k_p >> k_{tr}$ $k_a \sim k_p$	Normal	None	Decrease
$k_p << k_{tr}$ $k_a \sim k_p$	Telomerization	None	Large decrease
$k_p >> k_{tr}$ $k_a < k_p$	Retardation	Decrease	Decrease
$k_p << k_{tr}$ $k_a << k_p$	Inhibition	Large decrease	Large decrease

Control by Chain Transfer

- Add chain transfer processes to termination processes

$$\frac{1}{DP} = \frac{k_t[M\cdot]^2 + k_{tr}[SH][M\cdot] + k_{tm}[M][M\cdot] + k_{ti}[I][M\cdot]}{k_p[M\cdot][M]}$$

- Assume chain transfer to monomer and initiator are small

$$\frac{1}{DP} = \frac{k_t[M\cdot]^2 + k_{tr}[SH][M\cdot]}{k_p[M\cdot][M]} = \frac{k_t[M\cdot]}{k_p[M]} + \frac{k_{tr}[SH]}{k_p[M]}$$

$$\frac{1}{DP} = \frac{1}{DP_0} + Ctr\frac{[SH]}{[M]}$$

- Where Ctr is the chain transfer constant

Common Chain Transfer Agents

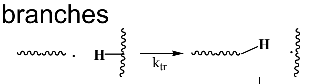
Transfer agent	Styrene, Ctr x 10^4	Vinyl Acetate Ctr x 10^4
Toluene	0.125	21.6
Di-n-butyldisulfide	24	10,000
Carbon tetrabromide	22,000	390,000
n-butyl mercaptan	210,000	480,000

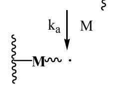
Additional Chain Transfer Processes

- Chain transfer to monomer, Ctr x 10^4
  - Ethylene, 0.4- 4.0; Styrene, 0.3-0.6
  - Vinyl acetate, 1.75-2.8
  - Vinyl chloride, 10.8-16
  - Allyl systems, 50-100
- Chain transfer to polymer --branching
  - Polyethylene
  - Vinyl acetate
  - Vinyl chloride

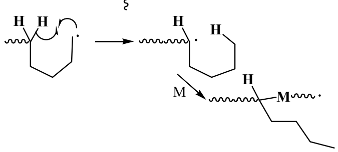
Transfer to Polymer

- Polyethylene branching
- Long branches





- Short branches



Inhibition of Radical Polymerization

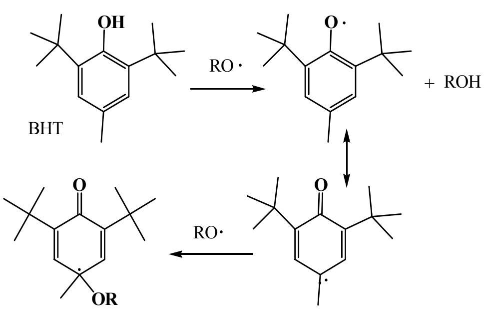
- Must stop oxygen- and carbon centered radicals

$R\cdot + O_2 \longrightarrow ROO\cdot$; $ROO\cdot + RH \longrightarrow ROOH + R\cdot$

$ROOH \longrightarrow RO\cdot + \cdot OH$

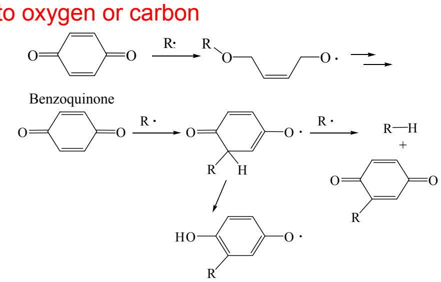
- Oxygen centered radicals stopped by hydrogen transfer
- Carbon centered radicals stopped by addition
- Inhibitor should not add to, abstract from or otherwise reach with monomer or solvent
- Inhibitors should not undergo self reaction or unimolecular decomposition
- Inhibitors must react rapidly with the propagating and/or initiator derived radicals to terminate polymer chains

Trapping Oxygen Centered Radicals

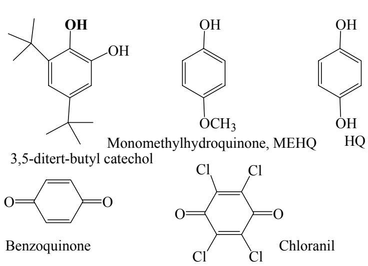


Trapping carbon centered radicals

- Carbon centered radicals stopped by addition to oxygen or carbon



Typical Inhibitors



O_2 $FeCl_3$ $CuCl_2$ S

Stable Radical Inhibitors