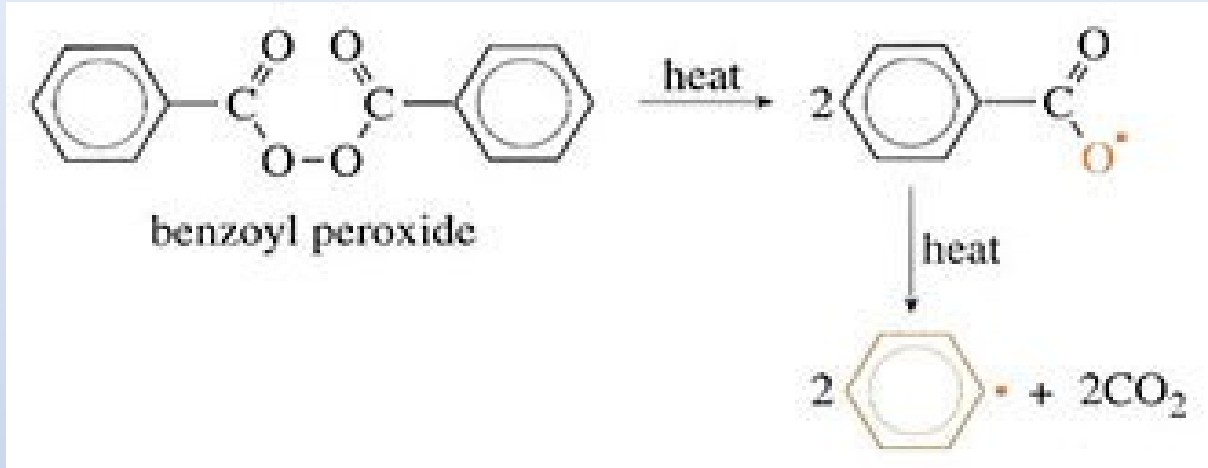# Kinetics of radicalic chain polymerization-2:

Thermal Initiators


benzoyl peroxide

This free radical is very reactive and will attack monomer molecules when introduced into a polymerization vessel.

This is an unstable chemical which produces active species that attack the monomer. A good example is benzoyl peroxide which splits up when heated:

phenyl radical   styrene
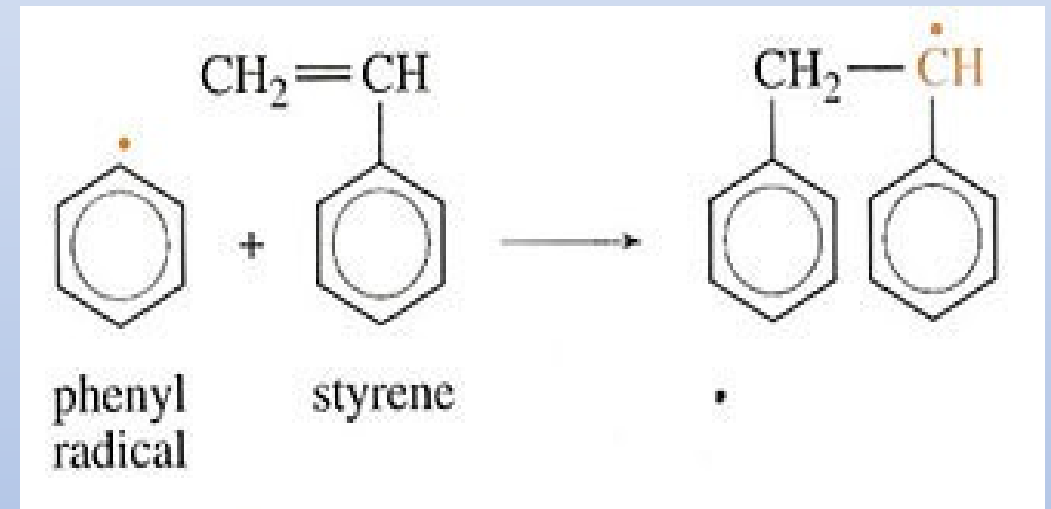
Two other common peroxide initiators are diacetyl peroxide 2 and di-t-butyl peroxide 3.

2

3
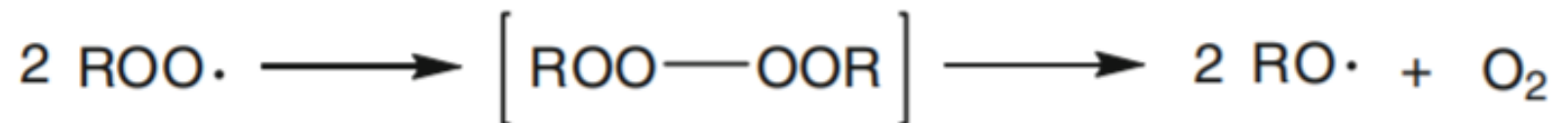

4

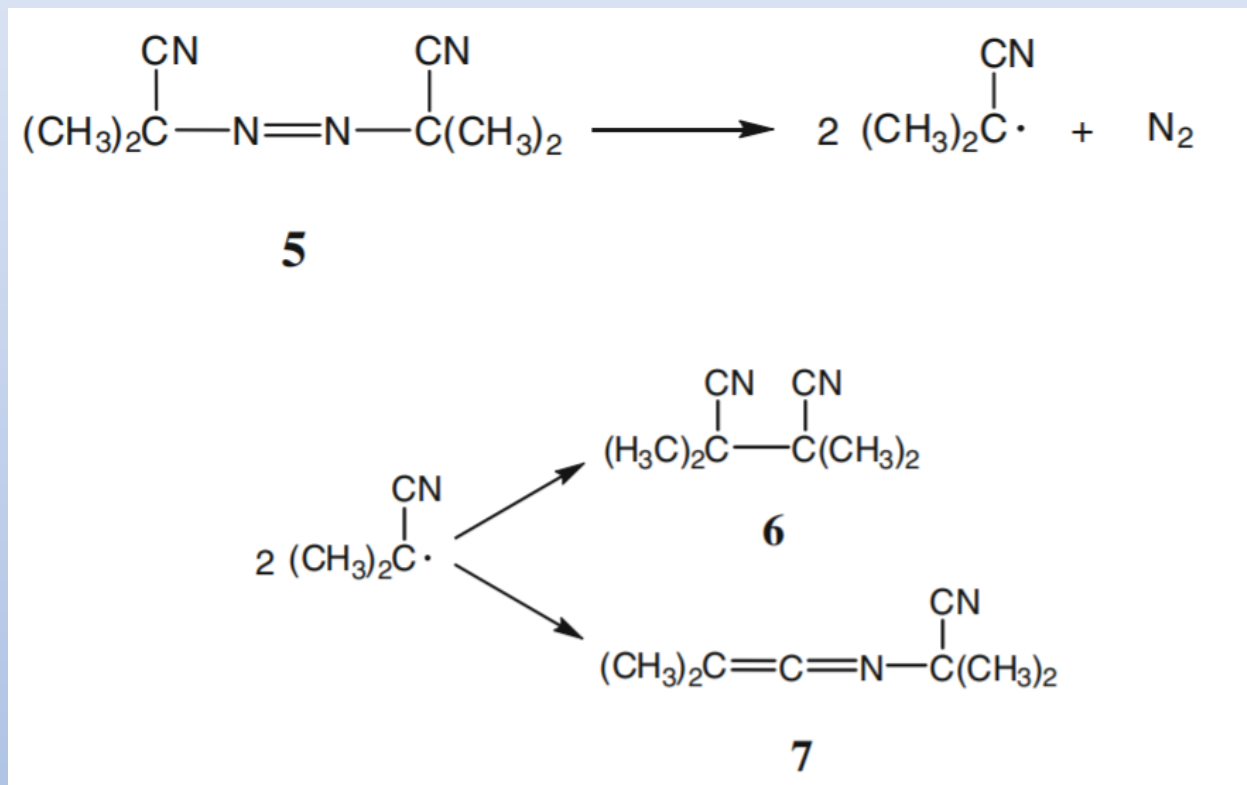$$ROOH \longrightarrow RO\cdot \; + \; \cdot OH$$
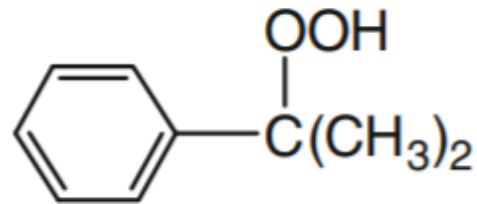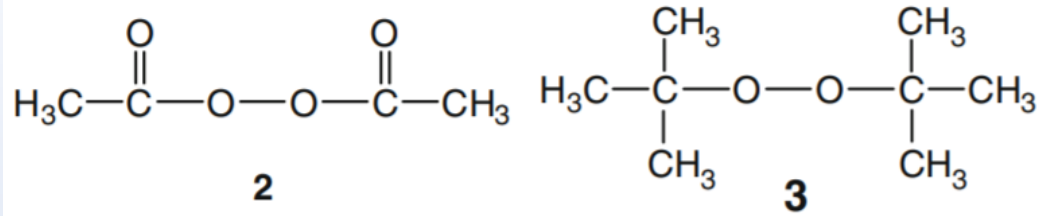
Hydroperoxides such as cumyl hydroperoxide 4 decompose to form alkoxy and hydroxyl radicals. Because hydroperoxides contain an active hydrogen atom, induced decomposition occurs readily, for example, by a chain-end radical. Peroxy radicals may also combine with subsequent formation of oxygen.

a, a -Azobis(isobutyronitrile) 5, is the most widely used azo compound which decomposes at relatively low temperatures. The driving force for decomposition is the formation of nitrogen and the resonance-stabilized cyanopropyl radical. The initially formed radicals can also combine in the solvent cage to deplete initiator concentration as with the peroxide decomposition.

$$(CH_3)_2\underset{\underset{CN}{|}}{C}-N{=}N-\underset{\underset{CN}{|}}{C}(CH_3)_2 \longrightarrow 2\ (CH_3)_2\underset{\underset{CN}{|}}{C}\cdot\ +\ N_2$$

5

$$2\ (CH_3)_2\underset{\underset{CN}{|}}{C}\cdot$$

$$(H_3C)_2\underset{\underset{CN}{|}}{C}-\underset{\underset{CN}{|}}{C}(CH_3)_2$$

6

$$(CH_3)_2C{=}C{=}N-\underset{\underset{CN}{|}}{C}(CH_3)_2$$

7

Decomposition Temperature and Half-Life of Thermal Initiators

The thermal, homolytic dissociation of initiators is the most widely used mode of generating radicals to initiate polymerization for both commercial polymerization and theoretical studies. Polymerizations initiated in this manner are often referred to as thermal initiated or thermal catalyzed polymerizations. Thermal initiators are usually having dissociation energies in the range 100–170 kJ mol-1. The peroxides are most extensively used as radical sources. Several common peroxy compounds are tabulated in Table 7.5. The differences in the decomposition rates of various initiators are conveniently expressed in terms of the initiator half-life (t1=2) defined as the time for the concentration of I to decrease to one half its original value. The rate of initiator disappearance is

$$\frac{-d[I]}{dt} = k_d[I]$$

Table 7.5 Peroxides and their decomposition temperature [3]

| Peroxide	Decomposition temperature (°C)
Acyl peroxide	70–90
Benzoyl peroxide	80–95
Cumyl peroxide	120–140
Di-t-butyl peroxide	120–140

$$[I] = [I]_0 e^{-k_d t}$$

$$\ln \frac{[I]_0}{[I]} = k_d t$$

$$t_{1/2} = \frac{0.693}{k_d}$$

Redox Initiators

The redox initiators are useful in initiation of low temperature polymerization and emulsion polymerization. Reaction rates are easy to control by varying the concentration of metal ion or peroxide. For nonaqueous polymerization, metal ions: Co^{2+}, Mn^{2+}, Cu^{2+}, and Fe^{2+} are generally introduced as the naphthenates shown in below. Cobalt naphthenate is commonly used as unsaturated polyester (Alkyd resin) drying agents for the autoxidative crosslinking of the double bond.
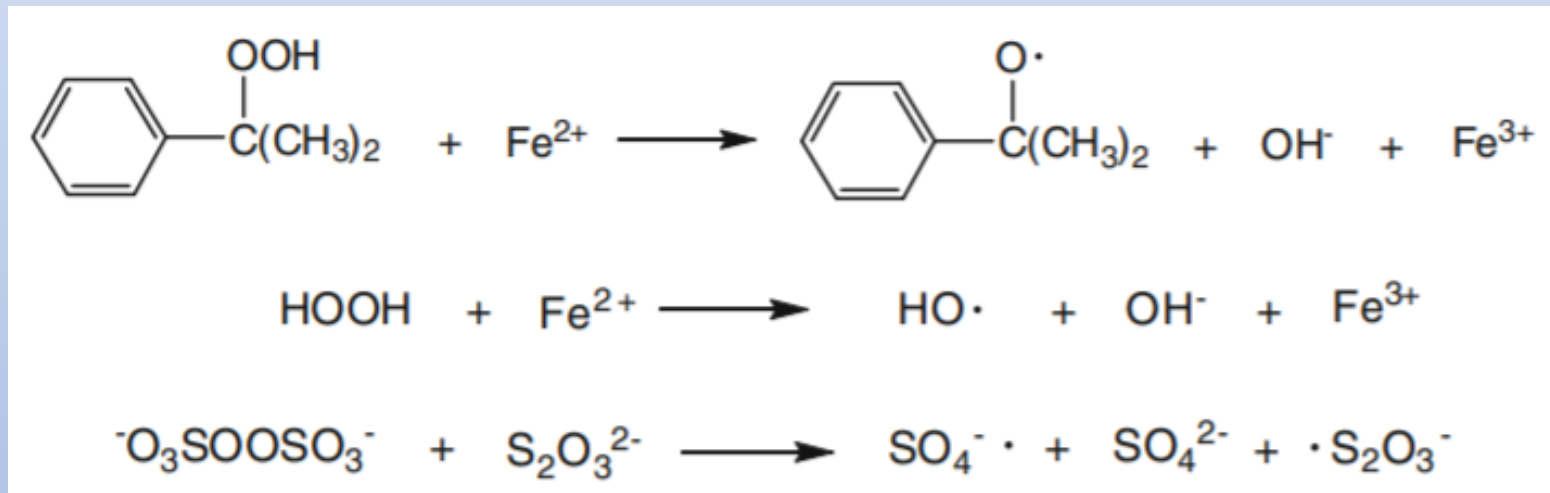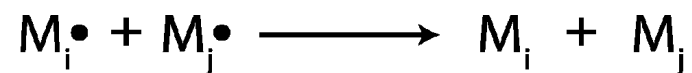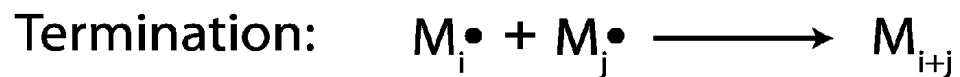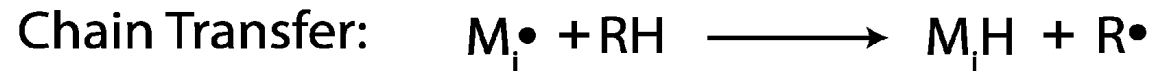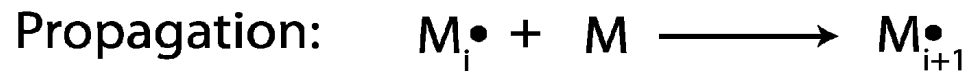
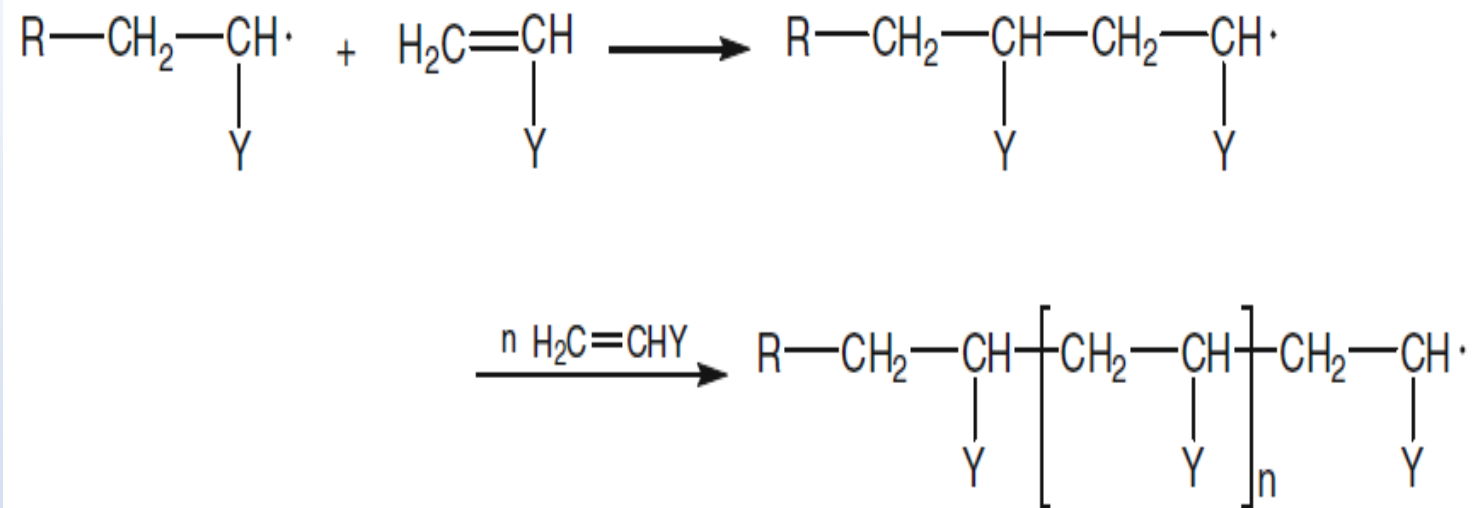**Reaction Mechanism of Free Radical Chain Polymerization**

Two reactions are involved in the initiation of free radical chain polymerization: formation of the initiator radical, and addition of the initiator radical to monomer. The end group analysis of propagating chain shows the initiator radicals are incorporated into the polymer. The propagation reactions comprise addition of monomer radical to another monomer molecule, followed by successive additions of oligomer and polymer radicals to available monomer.

Propagation continues until some reaction occurs to terminate it. Two radicals are easily be terminated by a combination (coupling) reaction as shown.

On the other hand, more rarely, they can be terminated by a disproportionation reaction, in which a hydrogen radical that is beta to one radical center is transferred to another radical center. This results in the formation of two polymer molecules.

Initiation: $I \xrightarrow{\text{stimulus}} I\bullet$

$I\bullet + M \longrightarrow IM\bullet$

Propagation: $M_i\bullet + M \longrightarrow M_{i+1}\bullet$

Chain Transfer: $M_i\bullet + RH \longrightarrow M_iH + R\bullet$

Termination: $M_i\bullet + M_j\bullet \longrightarrow M_{i+j}$

$M_i\bullet + M_j\bullet \longrightarrow M_i + M_j$

Oxygen Inhibition: $M_i\bullet + O_2 \longrightarrow M_iOO\bullet$

$M_iOO\bullet + M \xrightarrow{\quad\times\quad} \textit{(no reaction)}$

The two different modes of termination can be represented in general term by

Propagation continues until some reaction occurs to terminate it.

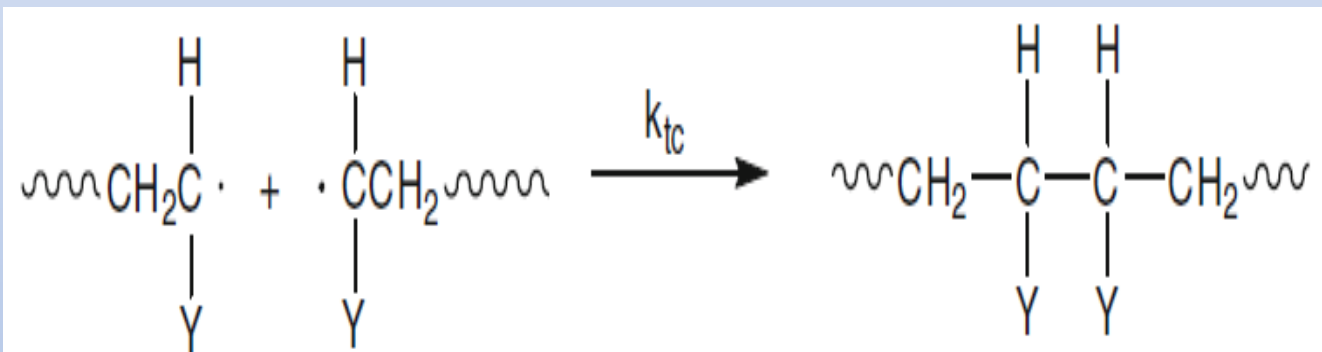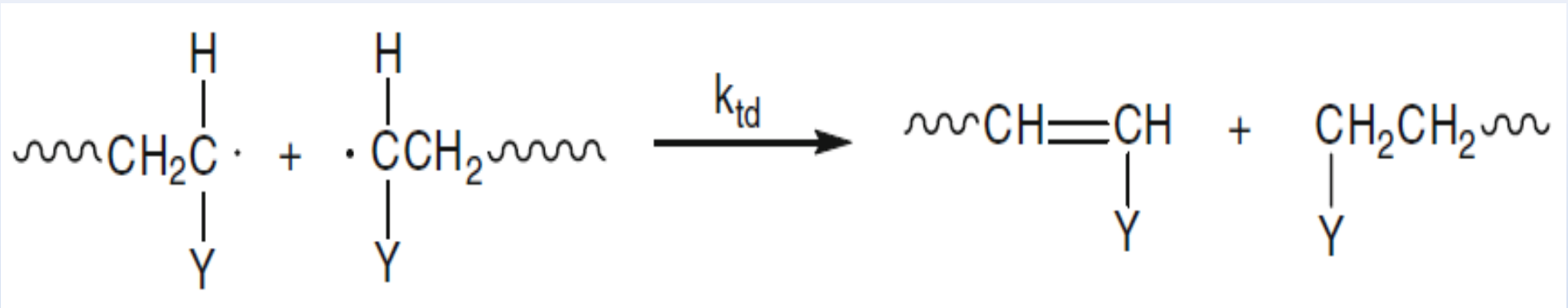Two radicals are easily be terminated by a combination (coupling) reaction as shown

On the other hand, more rarely, they can be terminated by a disproportionation reaction, in which a hydrogen radical that is beta to one radical center is transferred to another radical center. This results in the formation of two polymer molecules—one saturated and one unsaturated as shown

REF: Lecture Notes In Chemistry 82 Principles of Polymer Design and Synthesis

The two different modes of termination can be represented in general term by

$$M_n \cdot + M_m \cdot \xrightarrow{k_{tc}} M_{n+m}$$

$$M_n \cdot + M_m \cdot \xrightarrow{k_{td}} M_n + M_m$$
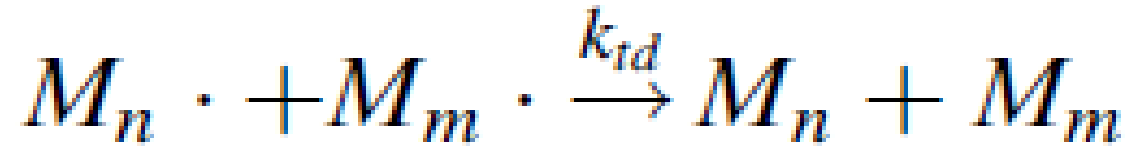
where ktc and ktd are the rate constants for termination by coupling and disproportionation, respectively. One can also express the termination step by

$$M_n \cdot + M_m \cdot \longrightarrow \text{dead polymer}$$