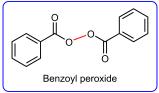
CONCEPT: RADICAL POLYMERIZATION

- Radical initiators catalyze radical polymerization of alkenes.
 - □ ___ or ___ can start the reaction.



• The reaction mechanism is ______ to that of free-radical halogenation of alkanes.

Radical Polymerization Mechanism



STEP 1: Radicals form when the initiator undergoes homolytic cleavage.

□ Initiator radicals react with monomers to form monomer radicals.

Chain Initiation

RO—OR

$$\Delta \text{ or } hv$$

RO—CH₂—CH

CH₃
 CH_3

STEP 2: The monomer radical reacts with a monomer molecule and forms a new radical through *head-to-tail addition*.

□ The chain grows at the i_____ site.

Chain Propagation

$$RO-CH_2-\dot{C}H + H_2C=CH \longrightarrow RO-CH_2-CH-CH_2+\dot{C}H \longrightarrow CH_3 \longrightarrow CH_3$$

CONCEPT: RADICAL POLYMERIZATION

STEP 3: Chain termination can occur by:

- 1 Radical Combination: Any two radicals can combine to form a ___ bond.
- **2 Disproportionation:** A radical can abstract ____ from another radical.

Chain Termination

(1a)
$$\frac{1}{3}$$
 CH_2 CH_3 CH_2 CH_3

(1b) $\frac{1}{3}$ CH_2 CH_4 CH_5 CH_5 CH_5 CH_6 CH_7 CH_8 CH_8

EXAMPLE: Rank the following monomers from the highest to the lowest ability to undergo radical polymerization.

PRACTICE: Write a mechanism for the peroxide-catalyzed radical polymerization of vinyl acetate.

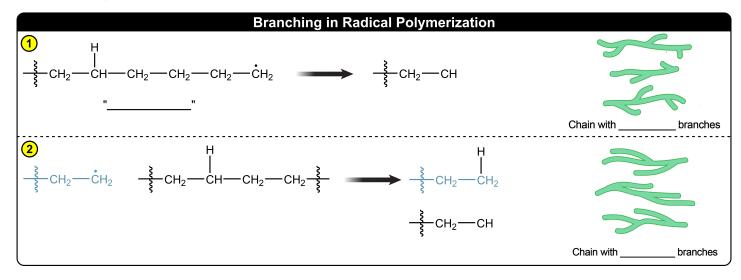
CONCEPT: RADICAL POLYMERIZATION

Branching During Chain Growth

- Radical polymerization _____ produces branched polymers.
 - □ Branching occurs due to a _____ transfer reaction.
 - 1 Intramolecular: results in _____ branches.
 - H abstraction occurs at the ____ C from the propagation site.
 - 2 Intermolecular: results in _____ branches.

Chain Transfer

Change in active site during radical polymerization.



• Branching affects the _____ properties of the polymer.

EXAMPLE: Which one of the following statements is true about radical polymerization?

- a) Impurities in the reaction mixture induce branching during polymerization.
- b) Chain branching occurs by an inter- or intramolecular chain transfer reaction.
- c) Chain branching occurs if the termination step is slow.
- d) The initiator determines the amount of branching in the polymer chain.

PRACTICE: Why does back-biting result in the formation of short branches?

- a) Back-biting results in short branches because it is faster than intermolecular chain transfer.
- b) Intramolecular chain transfer is a controlled reaction and results in a uniform distribution of branches.
- c) Back-biting only takes place in short chains, and therefore produce shorter branches.
- d) Intramolecular H abstraction at the 5^{th} carbon produces a stable transition state.