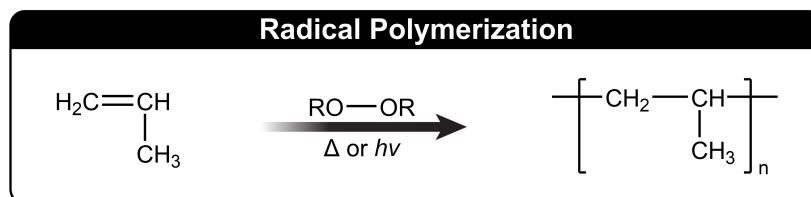
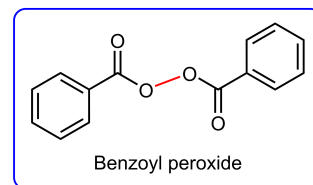


CONCEPT: RADICAL POLYMERIZATION

- 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

Initiation

Step 2

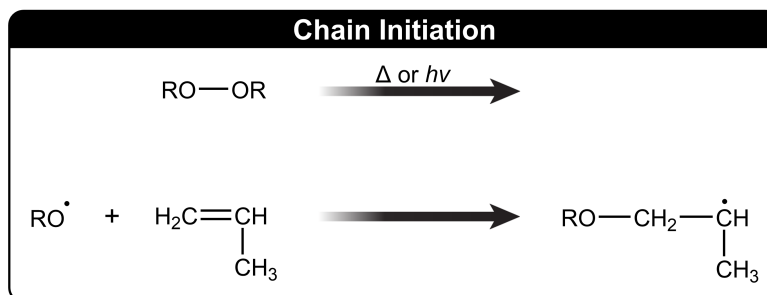
Propagation

Step 3

Termination

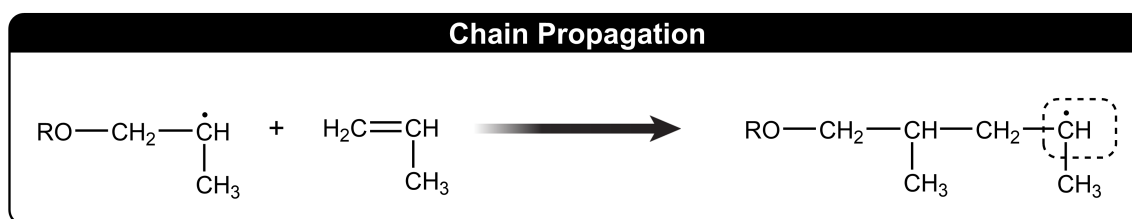
STEP 1: Radicals form when the initiator undergoes homolytic cleavage.

□ Initiator radicals react with monomers to form monomer radicals.



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 _____ site.

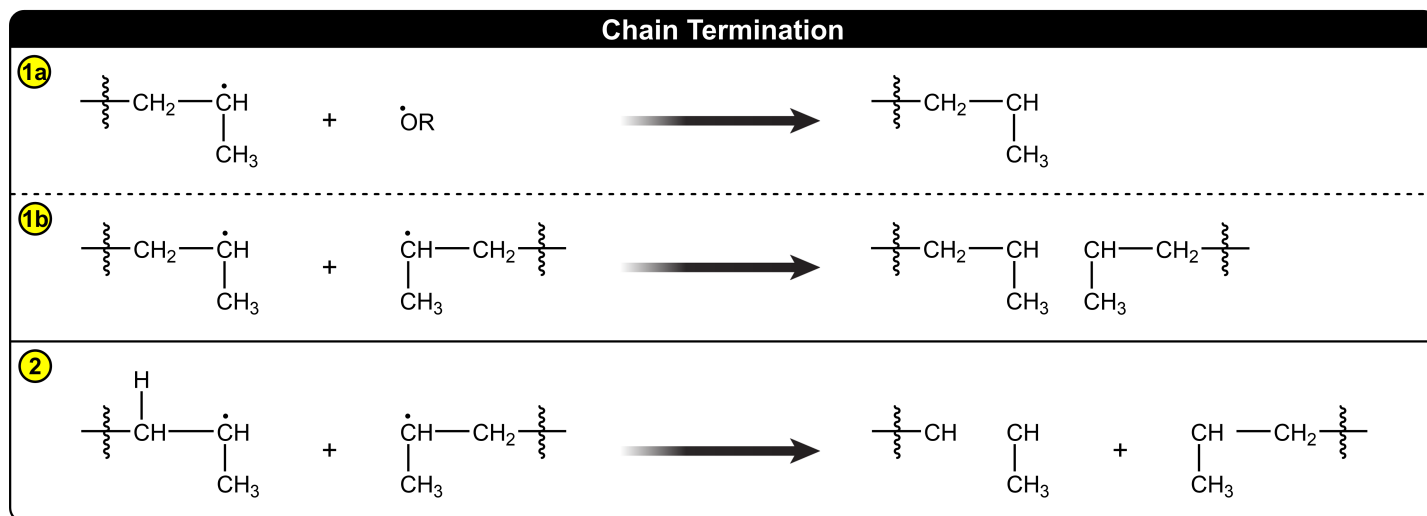


CONCEPT: RADICAL POLYMERIZATION

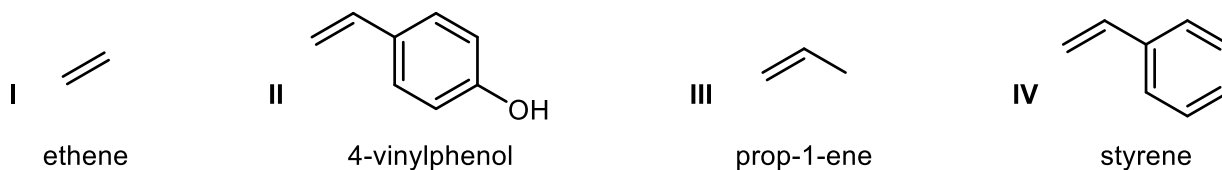
STEP 3: Chain termination can occur by:

① **Radical Combination:** Any two radicals can combine to form a ____ bond.

② **Disproportionation:** A radical can abstract ____ from another radical.



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.

- 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 5th carbon produces a stable transition state.