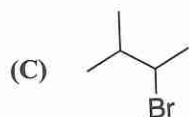
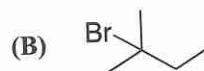
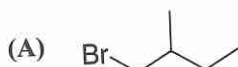
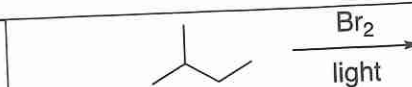


Choice (A) is not correct because it is an initiation step or formation of radicals from non-radicals. Choices (C) and (D) are not correct because they are propagation steps where radicals are in both the starting material and products.

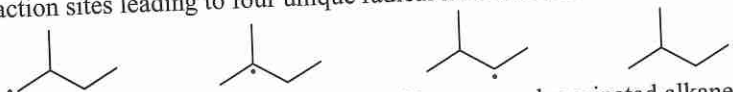
Practice Problems: PQ-1, PQ-2, PQ-3, PQ-4, and PQ-5

SQ-2. What is the major product of this reaction?

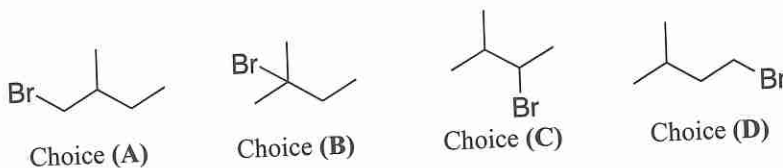


Knowledge Required: (1) Functionalization of alkanes through free-radical halogenation. (2) Stability trend of radical intermediates.

Thinking it Through: You are asked to determine which product is formed from the free-radical bromination of 2-methylbutane. You recall that the initiation step of this reaction is the homolytic cleavage of bromine (Br_2) to form two bromine radicals. The first propagation step is the abstraction of a proton from 2-methylbutane. There are four possible abstraction sites leading to four unique radical intermediates:



Each of these radical intermediates can lead to a different monobrominated alkane upon reaction with a bromine (Br_2):

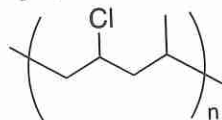


You recall that free-radical bromination proceeds through the most stable free-radical intermediate. Choices (A) and (D) are formed from primary radicals. Choice (C) is formed from a secondary radical. Choice (B) is formed from a tertiary radical. Of primary, secondary, and tertiary radicals, you recall that radicals follow the same stability trend as carbocations (resonance stabilized $> 3^\circ > 2^\circ > 1^\circ > \text{methyl}$).

Choice (B) is correct because it is formed from the most stable, or tertiary radical intermediate. Choices (A), (C), and (D) are not correct because they are formed from less stable radical intermediates.

Practice Problems: PQ-6, PQ-7, PQ-8, PQ-9, and PQ-10

SQ-3. What two monomers are used to form the polymer via a free-radical reaction?



(A) chloroethane and propene

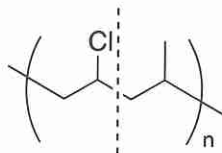
(B) chloropropene and ethene

(C) chloroethene and propane

(D) chloroethene and propene

Knowledge Required: (1) Formation of polymers via a free radical mechanism.

Thinking it Through: You are asked to consider which two monomers are used to form a given polymer. You note that there are four carbons in the backbone of the polymer unit provided, and thus assume that the polymer is formed from two monomers that include an ethenyl, or alkene, moiety ($-\text{CHCH}-$). You draw a dotted line through the central carbon-carbon bond to determine the two monomers:



You conclude that chloroethene (CH_2CHCl) is the monomer on the left side of the dotted line. You conclude that propene (CH_2CHCH_3) is the monomer on the right side of the dotted line.

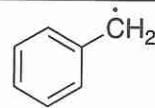
Choice (D) is correct because the two monomers both contain alkenes and the chlorine group is on the correct monomer.

Choice (A) is not correct because the two monomers do not both contain an alkene. Choice (B) is not correct because the chlorine group is on the wrong monomer. Choice (C) is not correct because the two monomers do not both contain an alkene.

Practice Problems: PQ-11, PQ-12, PQ-13, PQ-14, and PQ-15

Practice Questions (PQ)

PQ-1. What is the hybridization and geometry of the benzylic carbon radical?



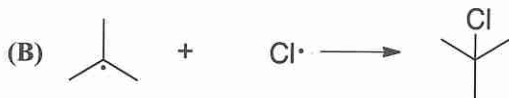
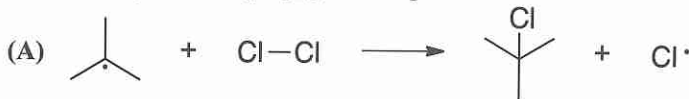
(A) sp^2 ; trigonal planar

(B) sp^2 ; tetrahedral

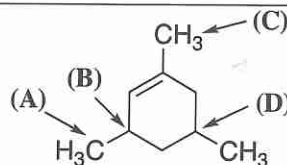
(C) sp^3 ; trigonal planar

(D) sp^3 ; tetrahedral

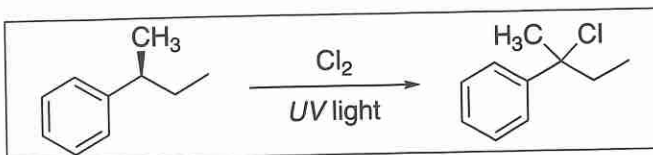
PQ-2. What represents a propagation step of a radical reaction?



PQ-3. Which site would most readily undergo hydrogen atom abstraction to generate a radical?



PQ-4. What is the expected stereochemistry of the organic product from this reaction?

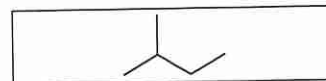


- (A) (*S*)-isomer only
 (B) (*R*)-isomer only
 (C) equal amounts of (*R*)-isomer and (*S*)-isomer
 (D) unequal amounts of (*R*)-isomer and (*S*)-isomer

PQ-5. How is the regioselectivity and stereospecificity in the hydrobromination of an alkene with catalytic peroxide best described?

- (A) Markovnikov orientation with both *syn* and *anti* products
 (B) Anti-Markovnikov orientation with both *syn* and *anti* products
 (C) Markovnikov orientation with only *syn* product(s)
 (D) Anti-Markovnikov orientation with only *anti* product(s)

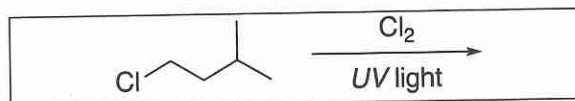
PQ-6. What is the major product obtained from radical monobromination of this molecule?



- (A) 1-bromo-2-methylbutane
 (C) 2-bromo-3-methylbutane

- (B) 2-bromo-2-methylbutane
 (D) 1-bromo-3-methylbutane

PQ-7. How many products, including stereoisomers, result from this monochlorination?



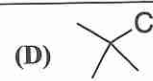
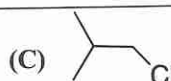
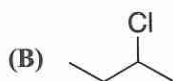
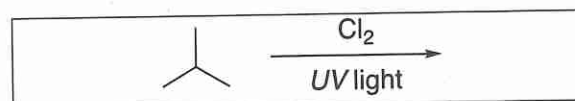
(A) 3

(B) 4

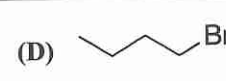
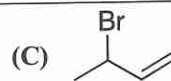
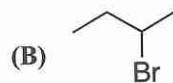
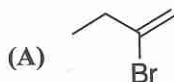
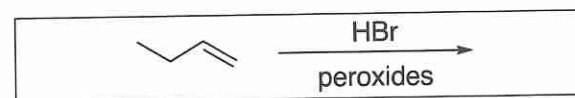
(C) 5

(D) 6

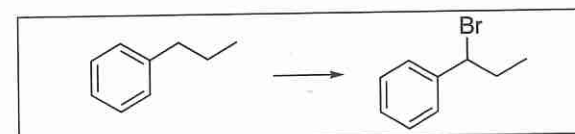
PQ-8. What is the major monochlorination product of this reaction?



PQ-9. What is the major product of this reaction?



PQ-10. Which reagents would be used to carry out this transformation?



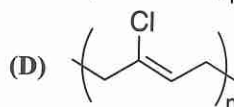
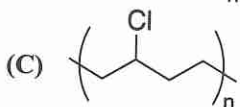
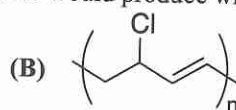
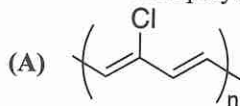
(A) $\text{Br}_2, \text{FeBr}_3$

(B) HBr, HOOH

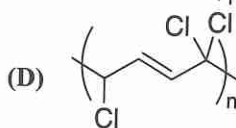
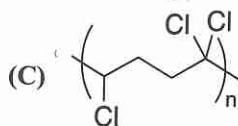
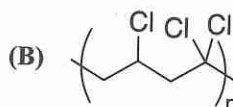
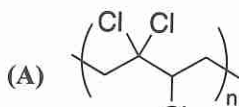
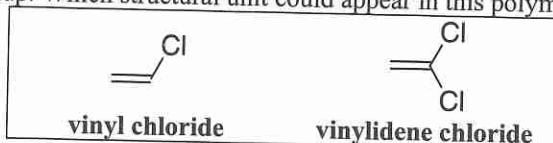
(C) $\text{Br}_2, \text{light}$

(D) $\text{Br}_2, \text{H}_2\text{O}$

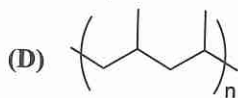
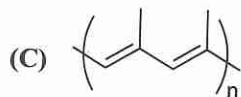
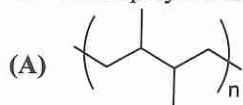
PQ-11. Free-radical polymerization of 2-chloro-1,3-butadiene would produce which polymer?



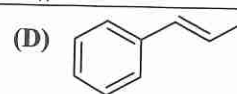
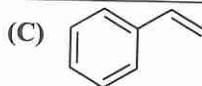
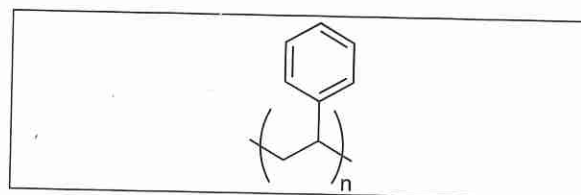
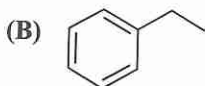
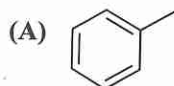
PQ-12. The copolymerization of vinyl chloride and vinylidene chloride by free radical catalysis produces a polymer used in food wrap. Which structural unit could appear in this polymer?



PQ-13. Which polymer is formed by free-radical polymerization of propene?



PQ-14. Polystyrene is made from what monomeric unit?



PQ-15. Polyvinyl chloride is made from what monomeric unit?

