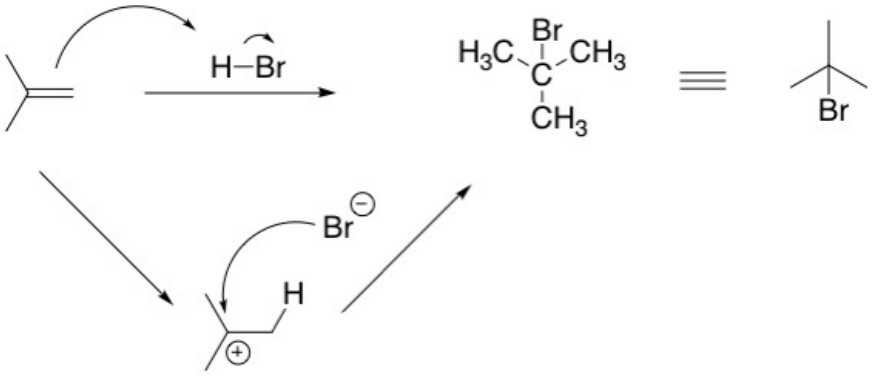
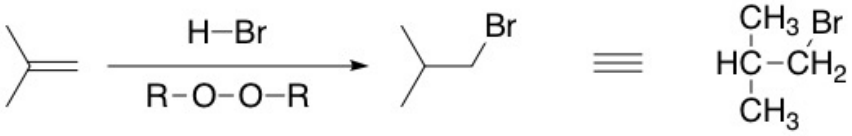
Recall:

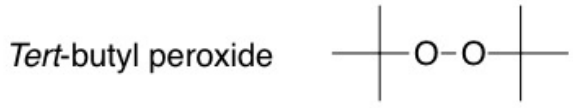
Addition Reactions of Alkenes (Markovnikov addition)



For alternate regiochemistry (addition of Br onto the less substituted carbon) need dialkyl peroxide (radical addition)

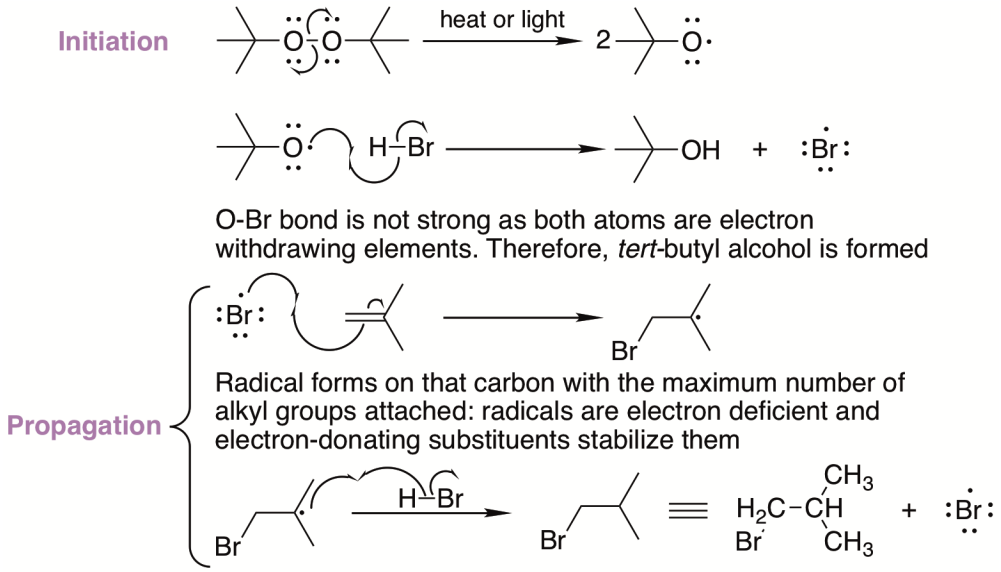


Examples of peroxides

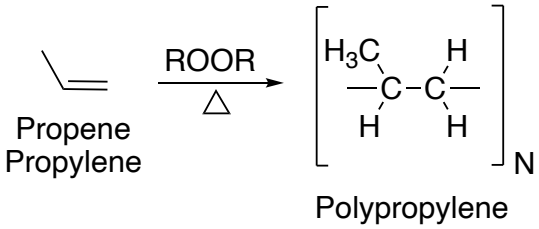


Hydrogen peroxide HO–OH

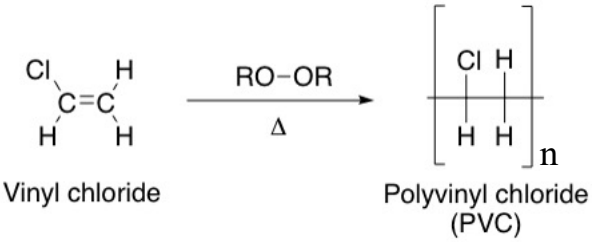
Radical mechanism



Polypropylene

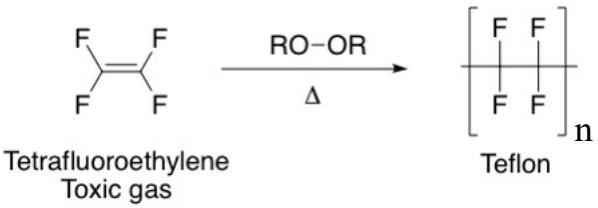


Polyvinyl chloride



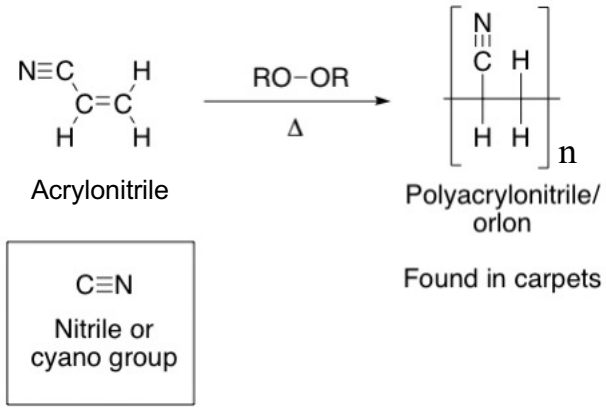
Such polymers containing chloride can form HCl if decomposed.

Teflon (Polytetrafluoroethylene)



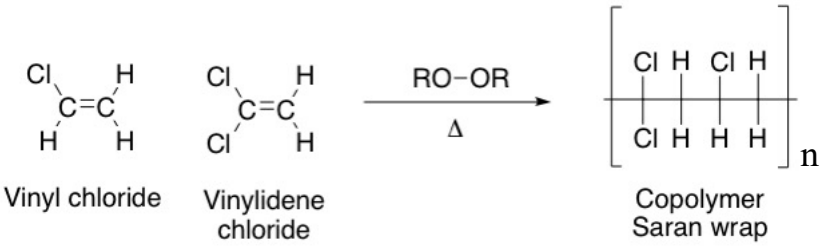
Teflon is very unreactive and does not adhere substances
Many polymers degrade into their components if heated enough, and can further decompose.

Polyacrylonitrile



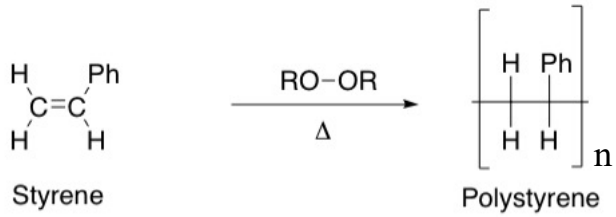
Polyacrylonitrile can form HCN if it is heated to decomposition.

Copolymers



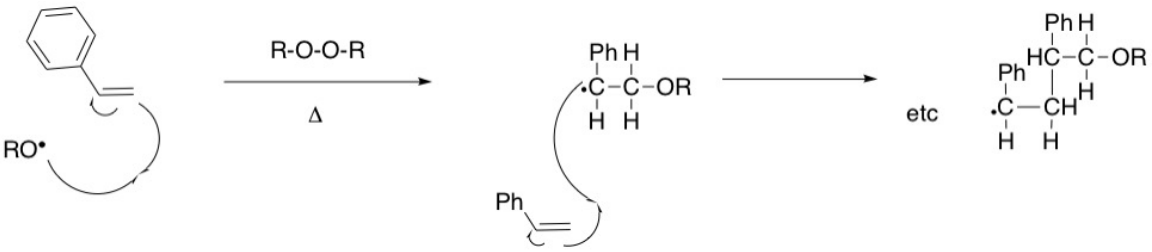
Copolymers are composed of two different subunits.

Polystyrene

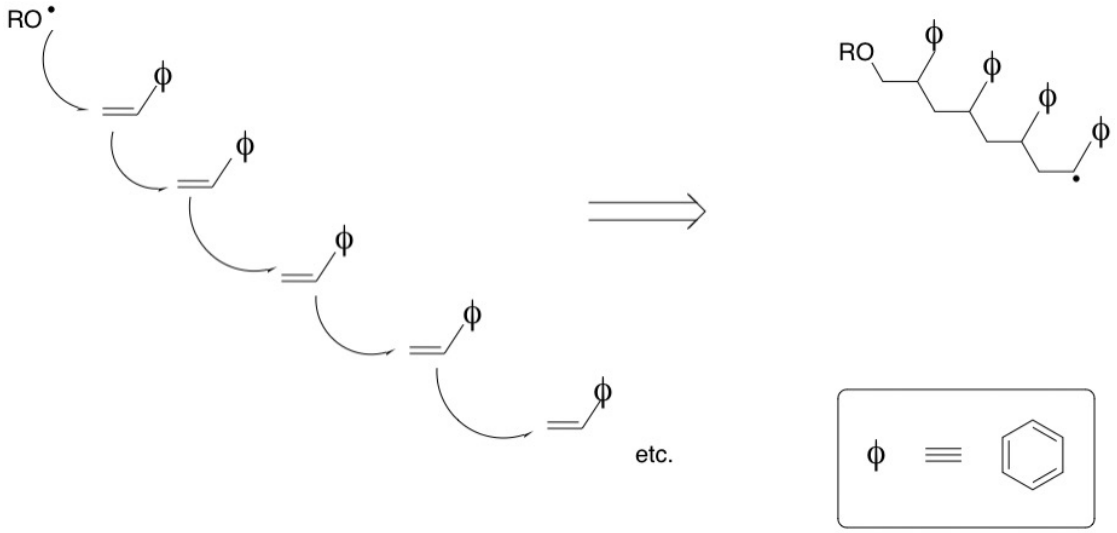


Ph = phenyl group

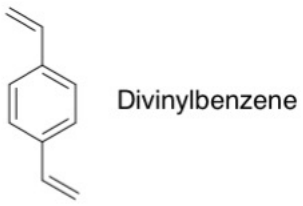
Example: Mechanism of polystyrene formation

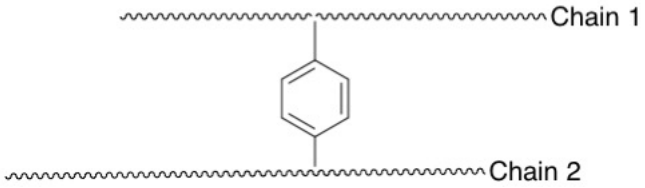


Short-hand for mechanism of polystyrene formation



Divinyl benzene can be added as a cross-linker so chains link on both of its double bonds This make the copolymer more solid (as you encounter in many products) – typically about one part in 100 to one part in 6 of divinylbenzene may be added





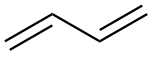
Conjugated Systems

Definition: Systems that are separated by exactly one single bond from a double bond

Compounds containing conjugated systems:

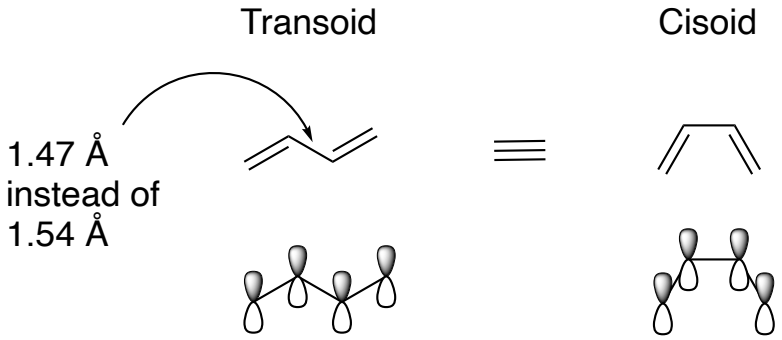
Polyenes:

Example 1: 1,3-butadiene

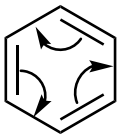


Double bonds are separated by one single bond

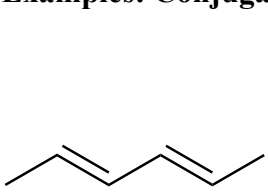
Tends to be planar; p orbitals want to be aligned, even though rotation along the sigma bond is not restricted. Transoid conformation is in equilibrium with cisoid conformation.



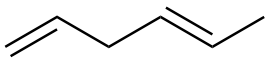
Example 2: Benzene



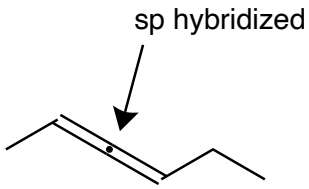
Examples: Conjugated or Not?



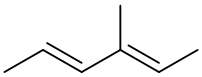
conjugated



not conjugated

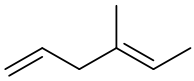


not conjugated



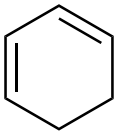
3-methyl-2,4-hexadiene

Conjugated

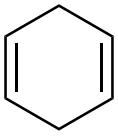


4-methyl-1,4-hexadiene

Not conjugated

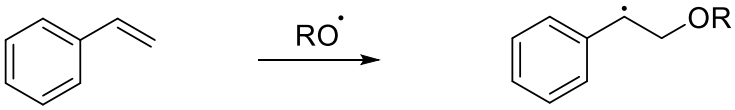


1,3-cyclohexadiene
conjugated



not conjugated

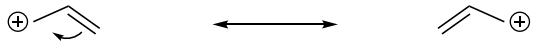
Conjugated (relatively unreactive)



A conjugated radical intermediate

Conjugated Intermediates:

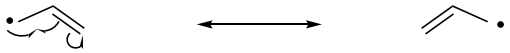
1) Cation:



Allyl Cation

Conjugation stabilizes the positive charge

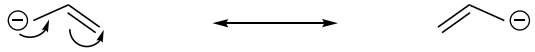
2) Radical:



Allyl Radical

Conjugation stabilizes the radical

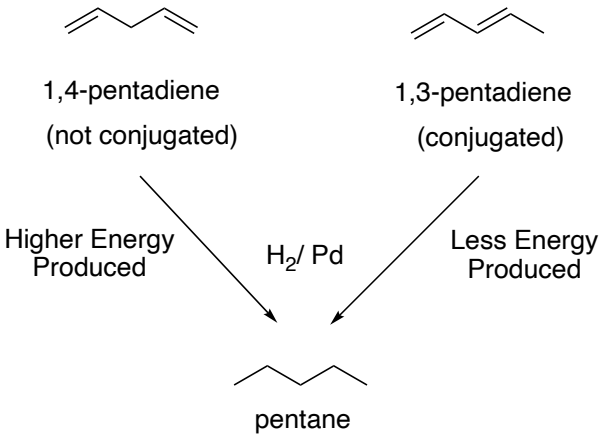
3) Anion:

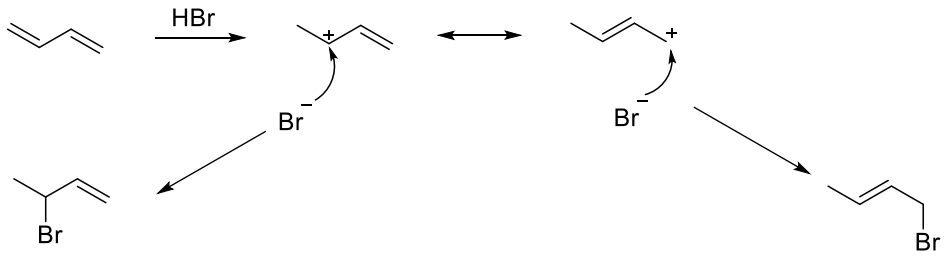


Allyl Anion

Conjugation stabilizes the negative charge

Example of conjugated and not conjugated system:





1,2-addition

1,2-addition product is less stable
Kinetic product

1,4-addition

1,4-addition product is more stable
Thermodynamic product