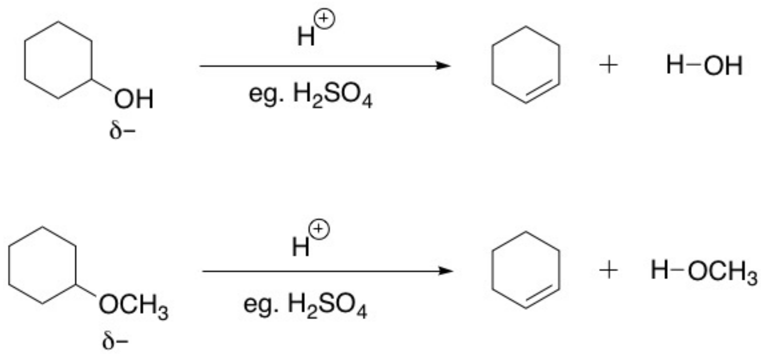
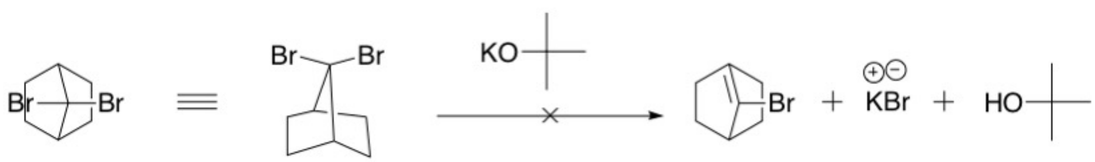
RECALL: Elimination reactions



-OH and -OCH_3 are bad leaving groups and so these reactions would not occur spontaneously without an acid catalyst.

To determine whether an elimination can occur, ask yourself three questions:



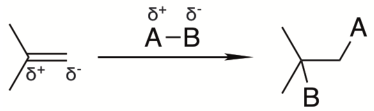
1. Is there a good leaving group present?
   Eg. Yes, Br is a good leaving group

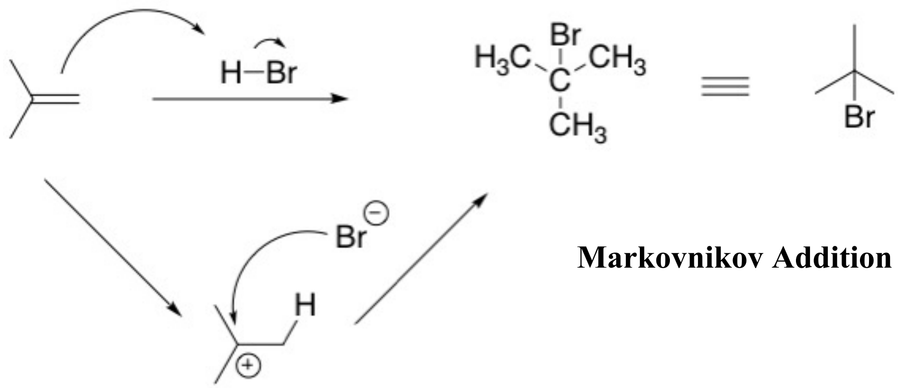
2. Is there a hydrogen on the carbon next to the carbon containing the leaving group?
   Eg. Yes, on the bridge-heads on either side of the carbon containing the Br.

3. Is Bredt's Rule being followed?
   Eg. No, if a double bond was being formed, it would be at a bridge-head and Bredt's rule states that a double bond cannot be formed at a bridge-head if the rings are small and all bridges >0. (double bond too strained)

   Substitution would likely not occur either as the electrophilic site is hindered (tertiary carbon).

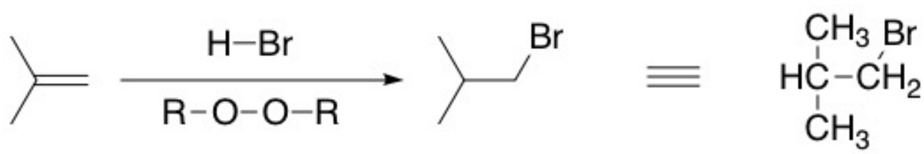
<u>RECALL: Addition reactions</u>





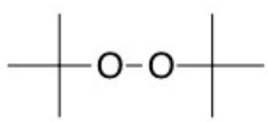
Markovnikov Addition

For alternate regiochemistry (addition of Br onto the less substituted carbon) need dialkyl peroxide – Anti-Markovnikov Addition



<u>Examples of peroxides</u>

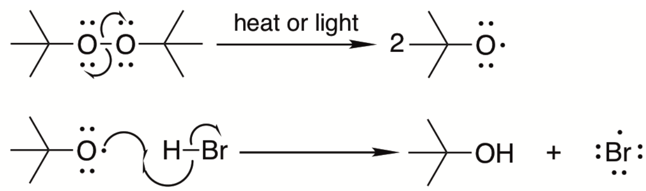
Tert-butyl peroxide



Hydrogen peroxide HO–OH

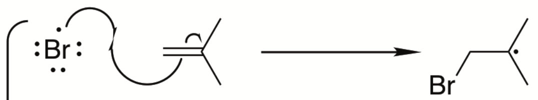
Radical mechanism

Initiation

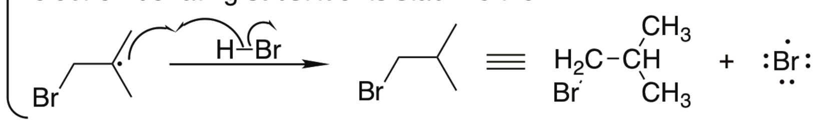


O-Br bond is not strong as both atoms are electron withdrawing elements. Therefore, *tert*-butyl alcohol is formed

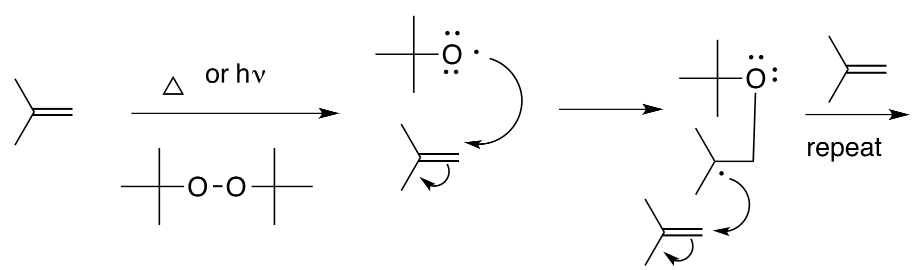
Propagation

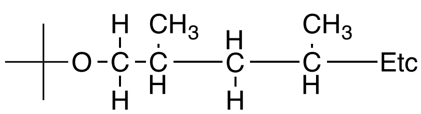


Radical forms on that carbon with the maximum number of alkyl groups attached: radicals are electron deficient and electron-donating substituents stabilize them

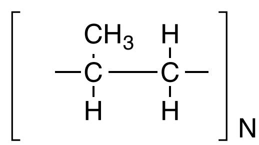


Example without HBr – a polymerization reaction occurs





polypropylene



shorthand notation for polypropylene

Note: more stable radical (in this case tertiary) is always formed by addition onto double bond

There is a termination step (not shown) that ends this polymerization. It is the combination of two radicals. It could be two growing chain radicals meeting or peroxide radicals. If less peroxide is used in the reaction, the polymer chain will be longer.

Polymers
Poly = many
Meros = parts

Examples of Biopolymers

1. Polysaccharides
   - polymers of sugars

2. Proteins and peptides
   - polymers of amino acids

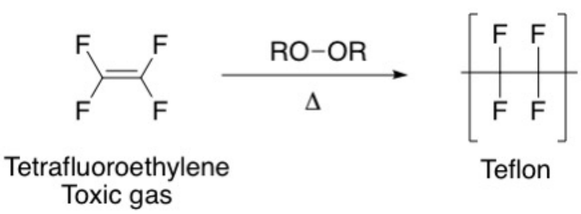
3. Nucleic acid polymers (DNA and RNA)
   - polymers of nucleotides

4. Fats and polyketides
   - polymers of fatty acids

5. Polyisoprenoids/terpenoids
   - polymers of isoprene (i. e. natural compound rubber)

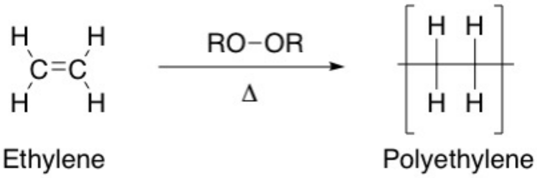
<u>Polymer formation</u>

Teflon (Polytetrafluoroethylene)

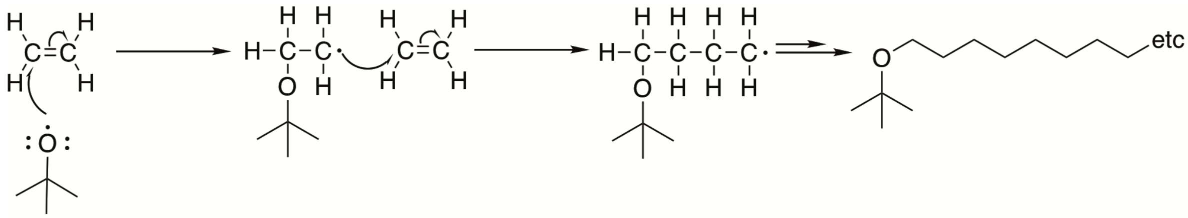


Teflon is very unreactive and does not adhere substances
Many polymers degrade into their components if heated enough, and can further decompose.

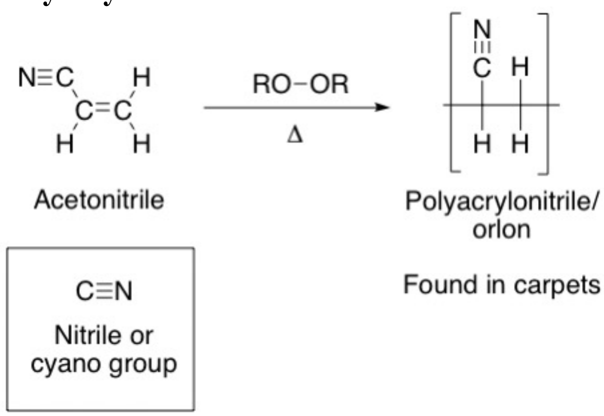
Polyethylene



Mechanism:

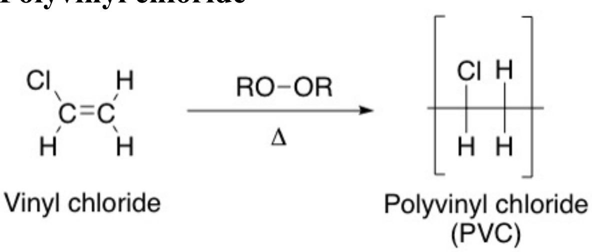


Polyacrylonitrile



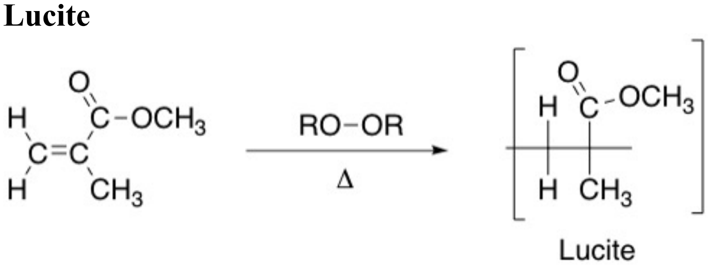
Polyacrylonitrile can form HCN if it is heated to decomposition.

Polyvinyl chloride



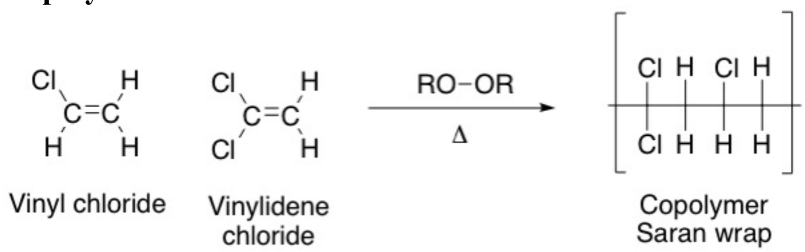
Such polymers containing chloride can form HCl if decomposed.

Lucite



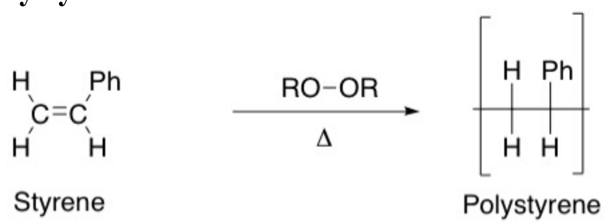
Found in windshields

Copolymers



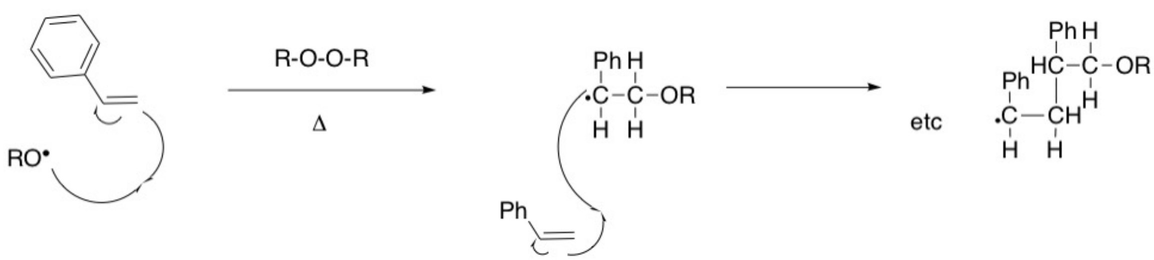
Copolymers are composed of two different subunits.

Polystyrene

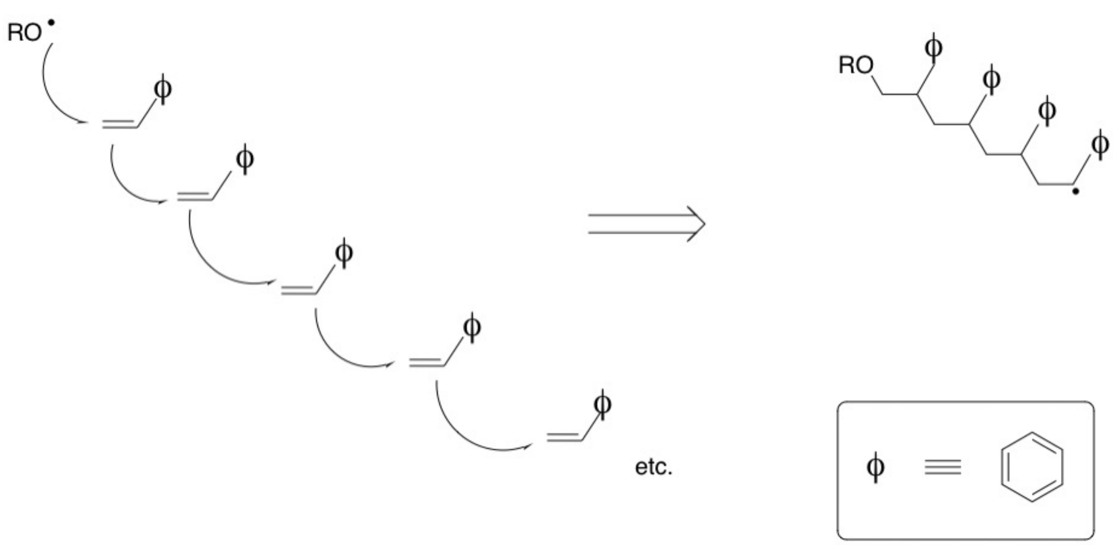


Ph = phenyl group

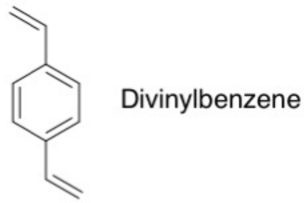
Example: Mechanism of polystyrene formation

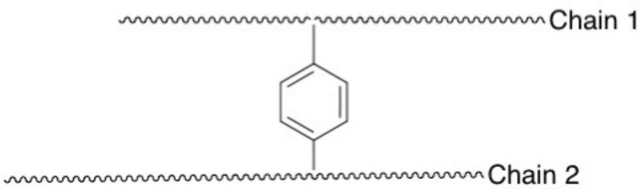


Short-hand for mechanism of polystyrene formation



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





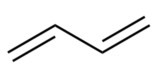
<u>Conjugated Systems</u>

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

Compounds containing conjugated systems:

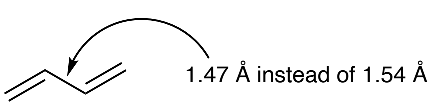
Polyenes:

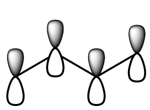
Example 1: 1,3-butadiene



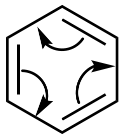
Double bonds are separated by one single bond

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.

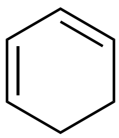




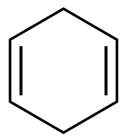
Example 2: Benzene



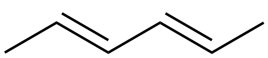
Examples: Conjugated or Not?



1,3-cyclohexadiene
conjugated

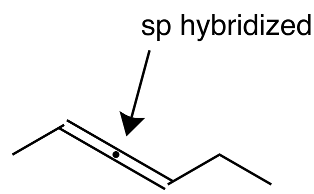


not conjugated



conjugated

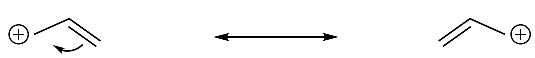
not conjugated



not conjugated

Conjugated Intermediates:

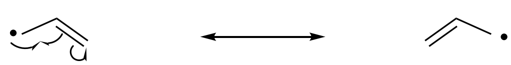
1) Cation:



Allyl Cation

Conjugation stabilizes the positive charge

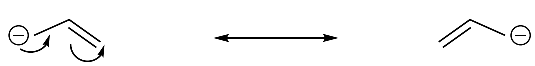
2) Radical:



Allyl Radical

Conjugation stabilizes the radical

3) Anion:

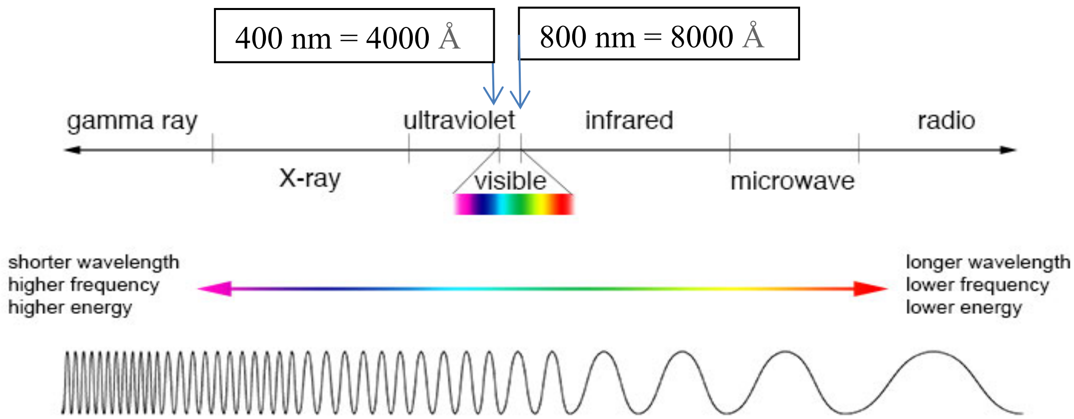


Allyl Anion

Conjugation stabilizes the negative charge

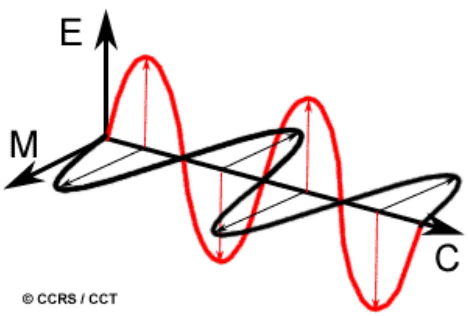
Electromagnetic Spectrum:

1nm = 10 angstrom



UV and visible light: conjugated double bond systems absorb UV light and some visible light

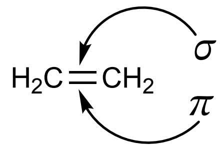
$$\mathbf{E = h\nu = \frac{hc}{\lambda}}$$



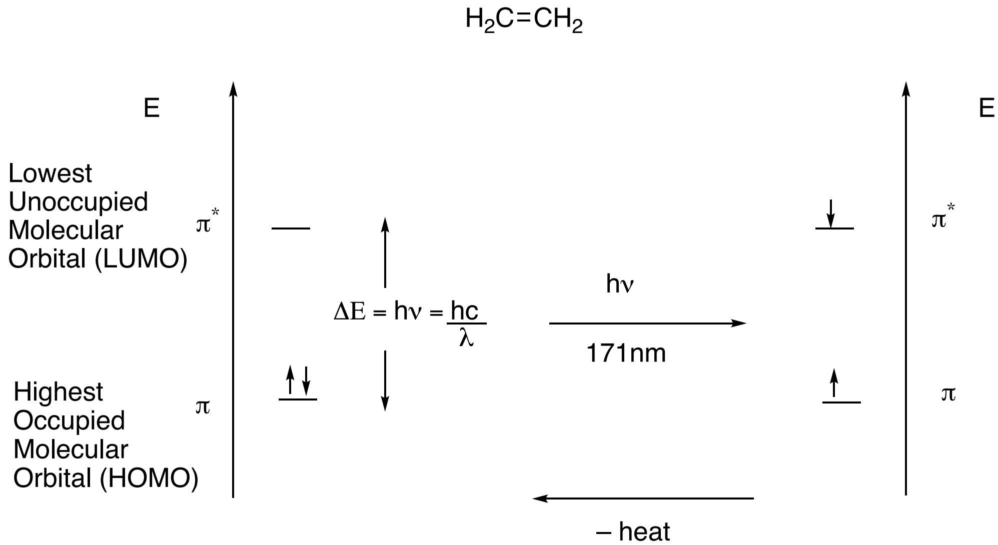
E = energy
H = Planck's Constant (6.6×10^{-34} Joules•sec
ν = frequency
λ = wavelength
c = speed of light (3.0×10^{10} cm/sec)

Molecular Orbitals:

Example 1: Ethylene



Looking only at the π orbitals:



An electron can be excited from the HOMO to the LUMO using light of a precise wavelength dependent on the energy difference between the two orbitals (since the orbitals are quantized). The electron can go back to its original orbital and heat (or light) is produced in the process.