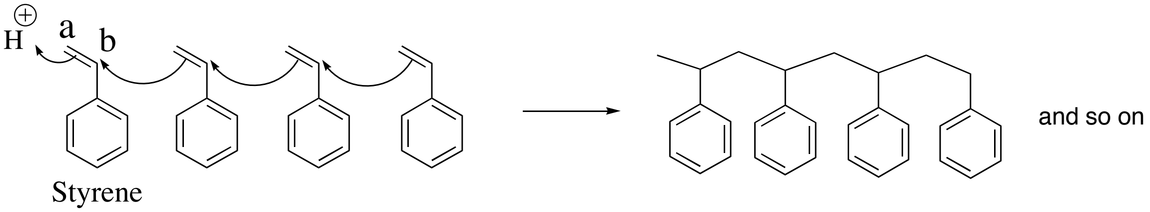
Practical Applications for Conjugated Addition Reaction:

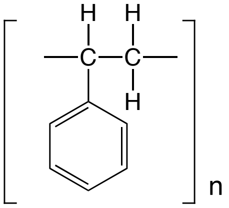
Example: Polystyrene formation



In which position of styrene will the carbocation form: a or b?

The answer is b, because the resulting carbocation is conjugated with the benzene ring and is also 2°.

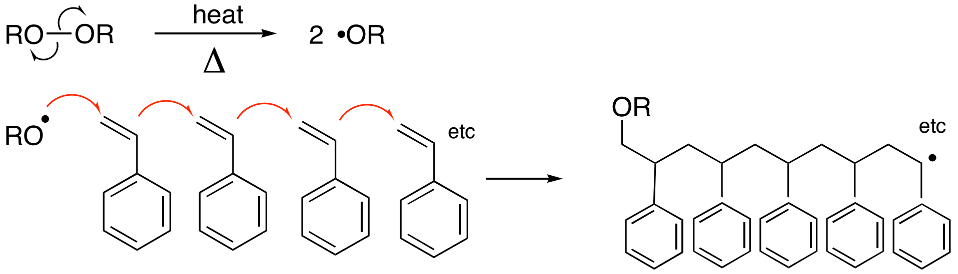
Drawing convention for polymers



Polystyrene

Example: Polystyrene formation via a radical mechanism

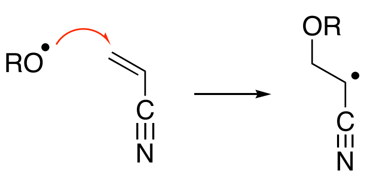
When peroxides are heated, peroxy radicals can be formed:



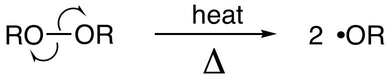
The peroxy radical can add on to the double bond, forming a carbon-based radical. The radical formed is more stable in the benzylic position adjacent to the phenyl ring. This radical can then add onto another molecule of styrene, thus forming a polymer.

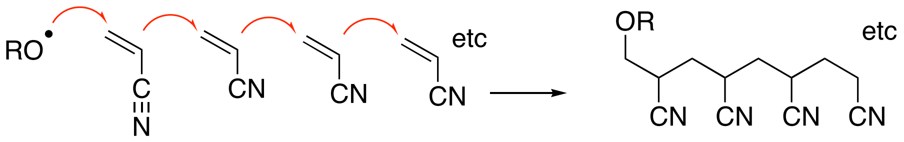
Example: Polyacrylonitrile (Orlon) synthesis (by a conjugated radical process)

This example is similar to the radical mechanism of polystyrene formation.



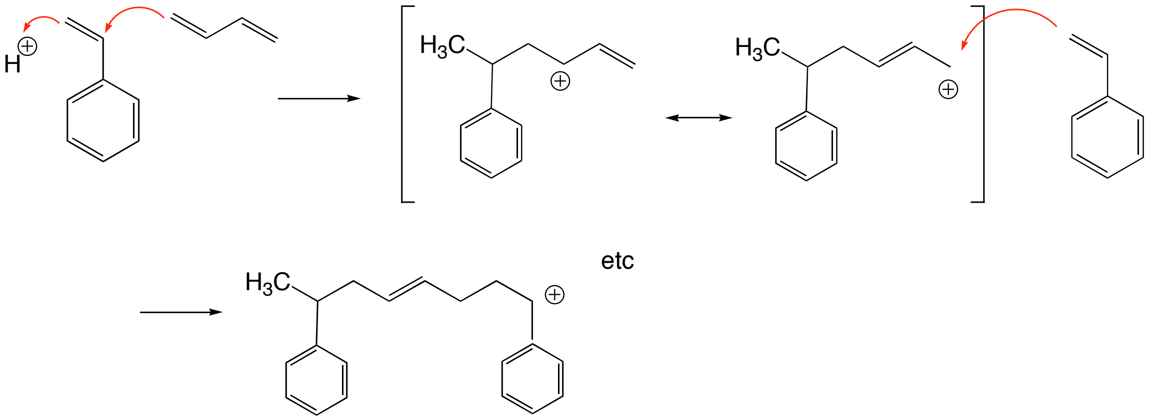
The radical formed on the carbon is stabilized by the adjacent cyano group.



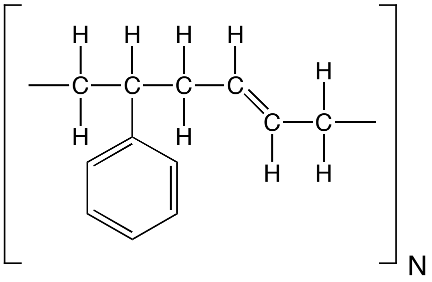


Example: Styrene Butadiene Rubber (SBR) synthesis

SBR is a **copolymer**.

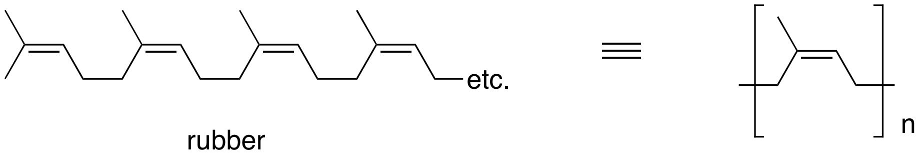


Another representation:

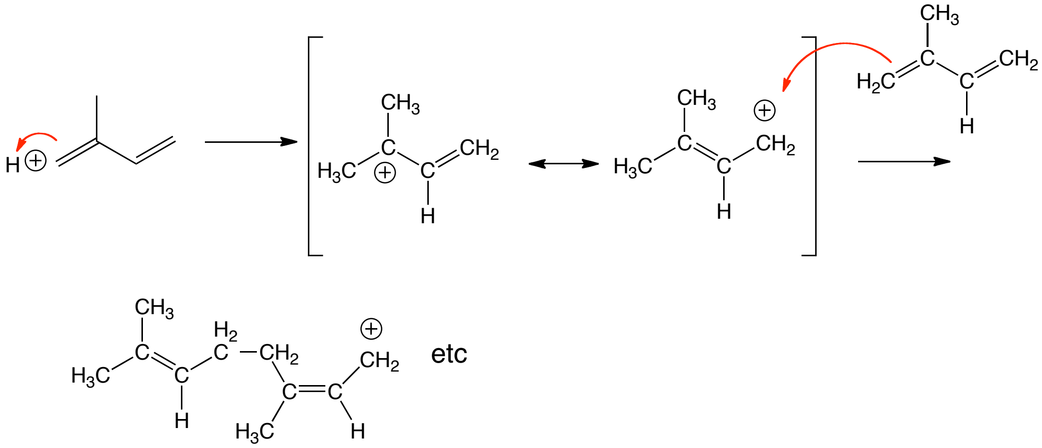


Example: Rubber formation

Rubber is a natural product produced by rubber tree *Hivea brasiliensis*. The rubber is collected in the form of syrup (latex) and after concentration as raw rubber it is very sticky (like chewing gum). This is not very useful.

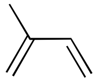


rubber

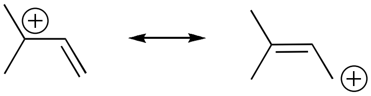


Rubber can be viewed as a polymer of 2-methyl-1,3-butadiene, which is also known as isoprene. Addition of acid will form a resonance-stabilized cation.

Charles Goodyear found that by adding sulfur and coal (carbon) to rubber in presence of heat, sulfur cross-linked rubber or vulcanized rubber is formed. This rubber is not sticky or plastic, but rather is elastic (like a rubber band). Such forms of rubber are widely used.



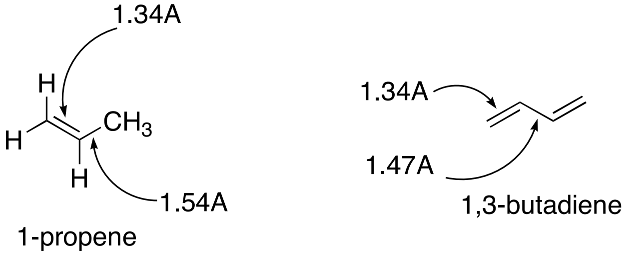
2-methyl-1,3-butadiene
isoprene



However, rubber cannot be synthesized using the same reaction as use for making polystyrene.

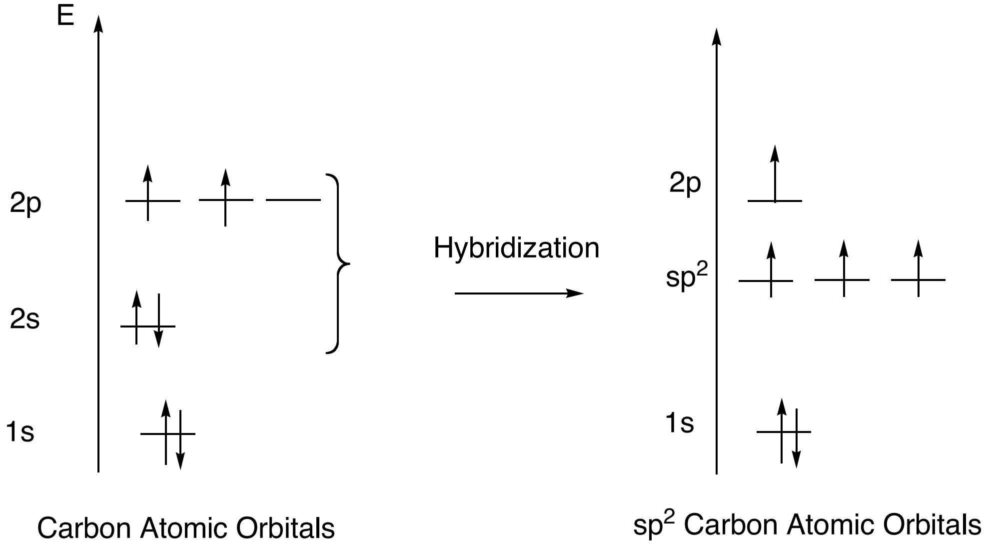
Why? Because the geometry of the double bond is *cis* in rubber, whereas *trans* is usually the more stable configuration. The double bond formed by making polymerizing isoprene would have a *trans* geometry. Rubber biosynthesis is controlled by enzymes which provides control over the product that is formed.

Bond and Energy Characteristics of Conjugated System

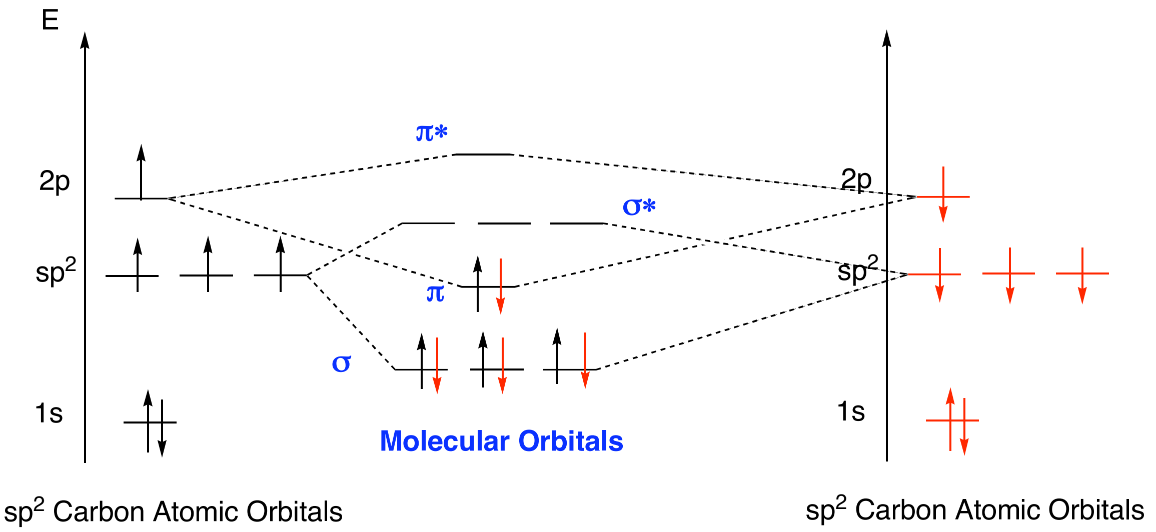


The bond length between the double bond carbons in propene is ca. 1.34 Å (remembering that 1 Å is equal to 10^{-8} cm). In 1,3-butadiene, the bond length of the double bond is 1.34 Å, and the bond length between the two singly bonded carbons is 1.47 Å. Compared to a normal C-C bond length of 1.54 Å, the central single bond in 1,3-butadiene is shorter (has some small amount of double bond character) and is therefore stronger than a normal single bond.

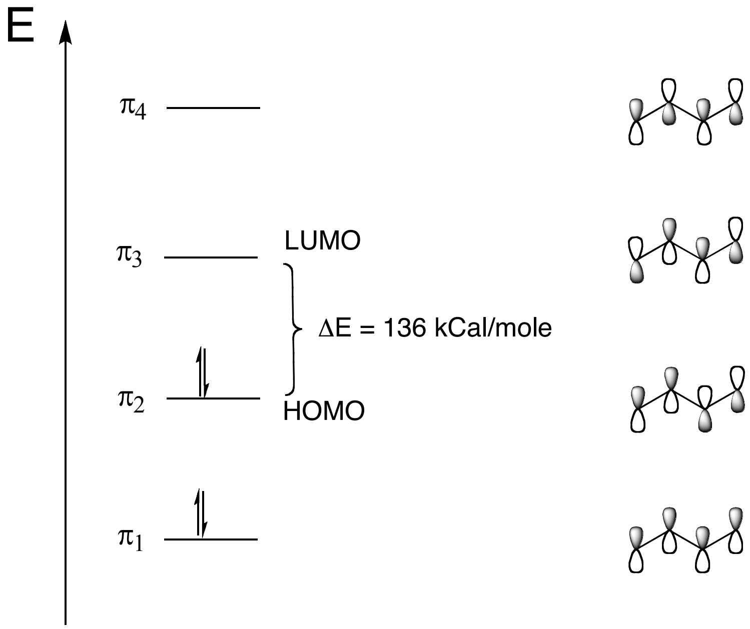
Recall how we can show the energy levels of the atomic orbitals of C. If the C is sp^2 hybridized, two of the 2p orbitals "combine" with the 2s orbital to form two sp^2 hybrid orbitals.



The following molecular orbital (MO) diagram shows the construction of molecular orbitals from the hybrid orbitals of two sp^2 hybridized carbons doubly bonded together (i.e., ethane). One electron pair in the σ MO represents the single bond between the two carbons (and the other two represent C-H bonds), while the electron pair in the π MO represents the double bond (i.e., the π bond) between the two carbons.

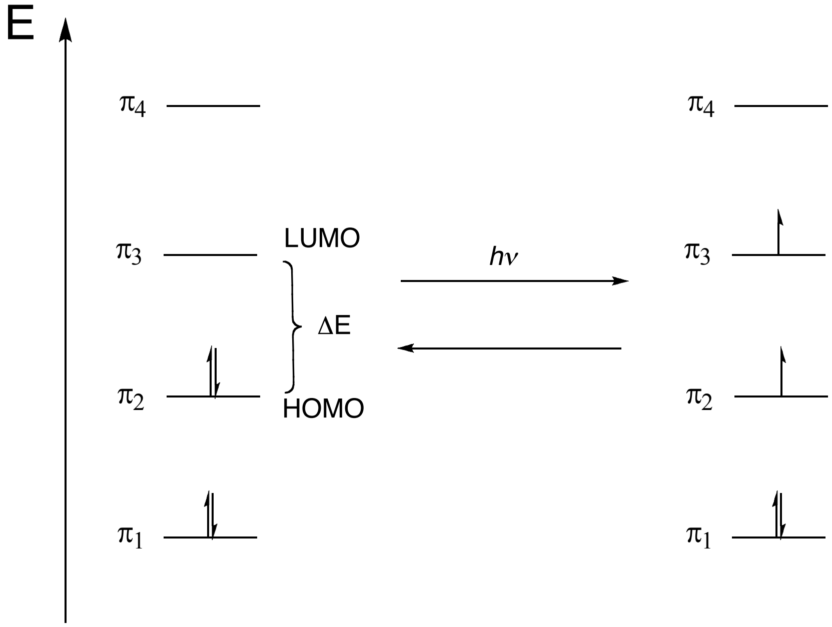


In butadiene, all four carbon atoms have a *2p* orbital. These **atomic** *2p* orbitals will combine to produce 4 π **molecular** orbitals (the number of atomic orbitals combined equals the number of molecular orbitals formed). Since there are two double bonds, there are two bonding and two antibonding π molecular orbitals (recall each π bond system is made by combining two *2p* atomic orbitals). A bonding and an anti-bonding molecular orbital result. As well, two double bonds means that there are 4 π electrons in the conjugated system (1 double bond has 2 π electrons), we can fill the 4 **molecular** orbitals with these electrons starting from the lowest energy level.



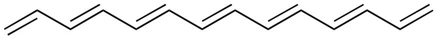
HOMO stands for Highest Occupied Molecular Orbital
LUMO stands for Lowest Unoccupied Molecular Orbital

Molecules absorb energy at the specific wavelength corresponding to the ΔE between the HOMO and LUMO. This is the basis for colour (absorption of light with a wavelength corresponding to visible light) and photosynthesis.



As the molecule becomes more conjugated, the energy gap (ΔE) between the HOMO and LUMO become smaller.

A molecule with ≥ 7 conjugated double bonds absorbs light between 4000 – 8000 Å in the visible region such as the compound shown below.



In this molecule, there are 7 bonding and 7 anti-bonding π molecular orbitals. The energy gap between the LUMO and HOMO is very small. Since E = hc/λ, the wavelength at which this molecule absorbs would be long. It absorbs blue-violet and we see it as yellow.