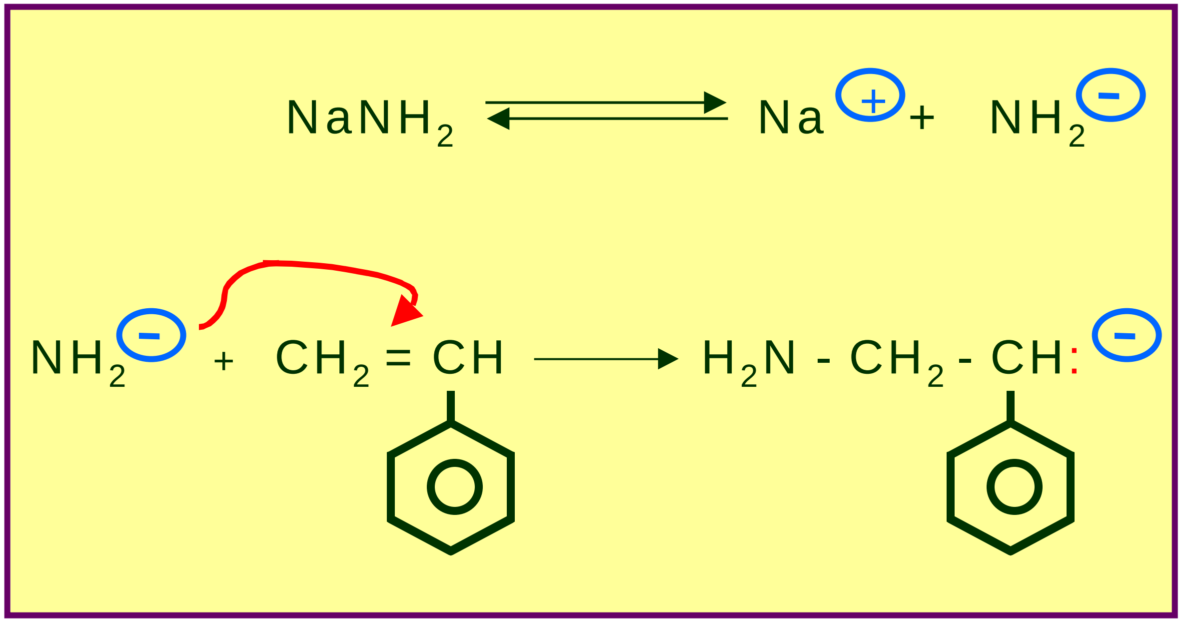
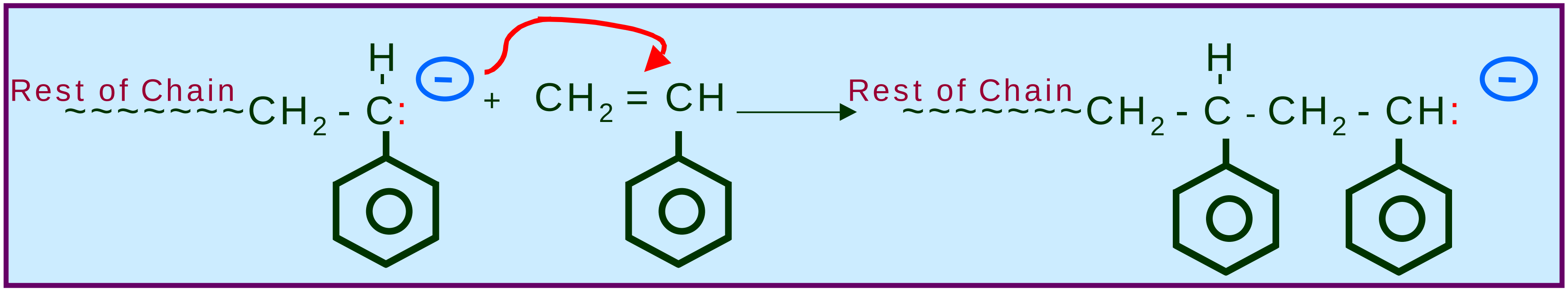
Anionic Polymerization - Initiation and Propagation

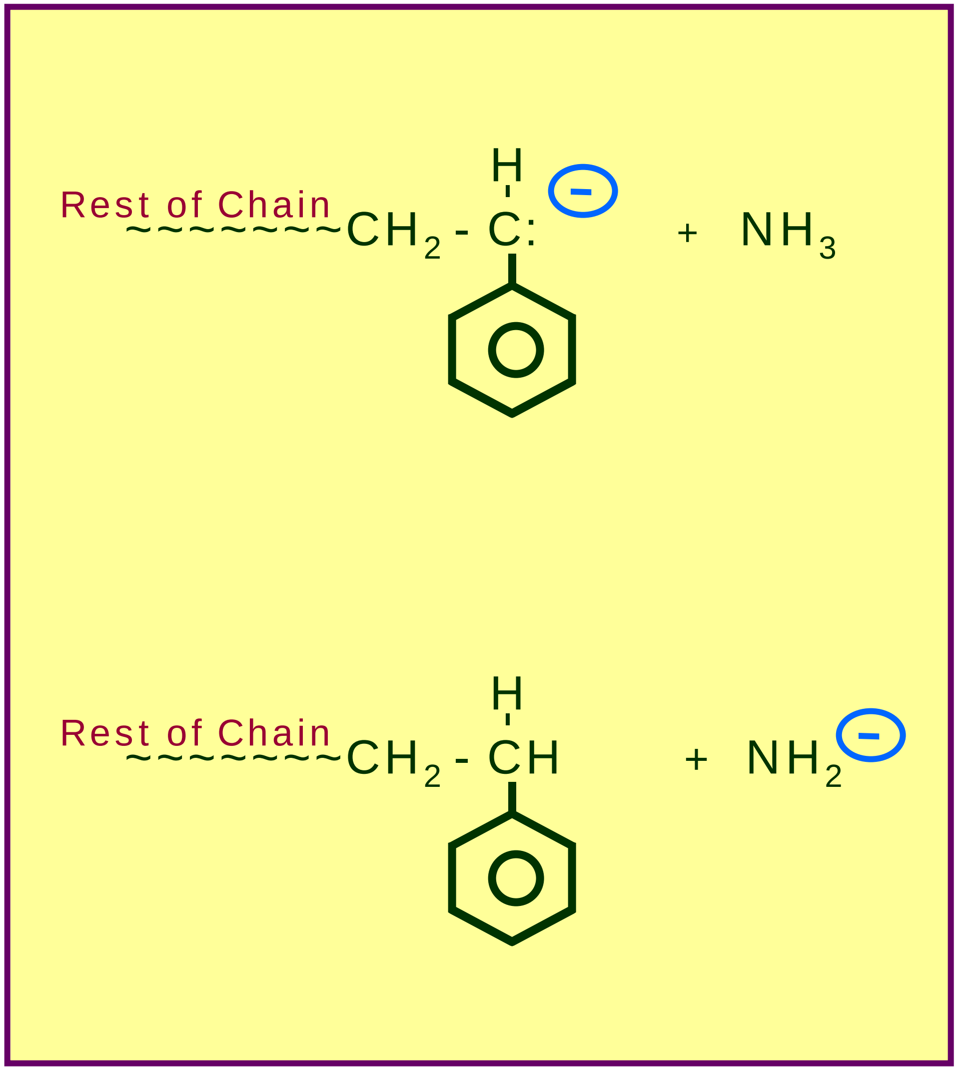
As in free radical polymerization, there are initiation and propagation steps.



Propagation proceeds in the usual manner, but there is no termination of the type that occurs when free radicals collide. (Why not?)

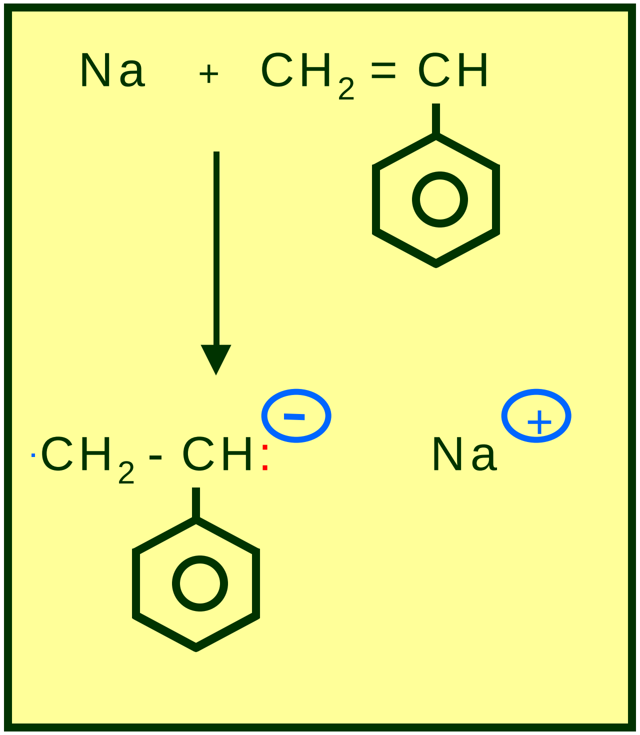


Anionic Polymerization - Chain Transfer to Solvent



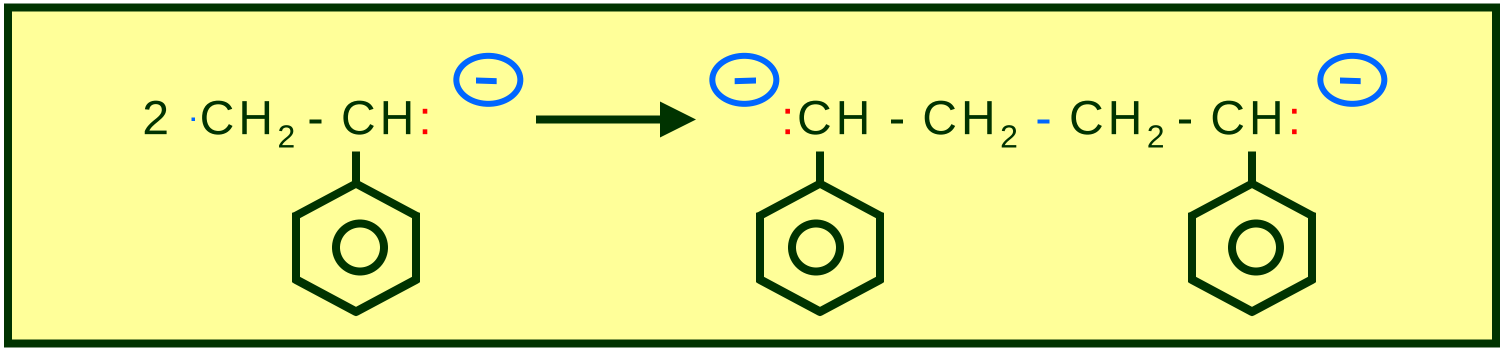
If a solvent that is able to release a proton is used it can react with the active site. Ammonia is an example of such a protic solvent and the reaction results in the formation of a negatively charged NH_2 ion, which can initiate the polymerization of a new chain. In other words, we have chain transfer to solvent.

Anionic Living Polymerization



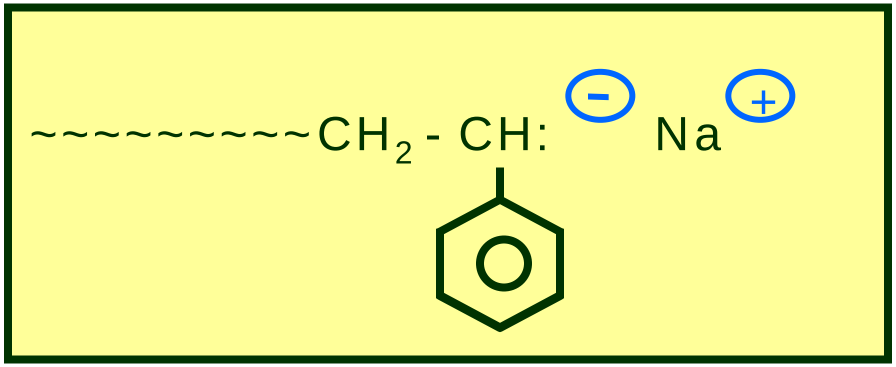
$$\mathrm{Na} + \mathrm{CH_2{=}CH} \longrightarrow \cdot\mathrm{CH_2{-}CH}{:}^{\ominus} \quad \mathrm{Na}^{\oplus}$$

Let's consider the polymerization of styrene initiated by metallic sodium in an "inert" solvent in which there are no contaminants (i.e. there are no molecules with active hydrogens around).



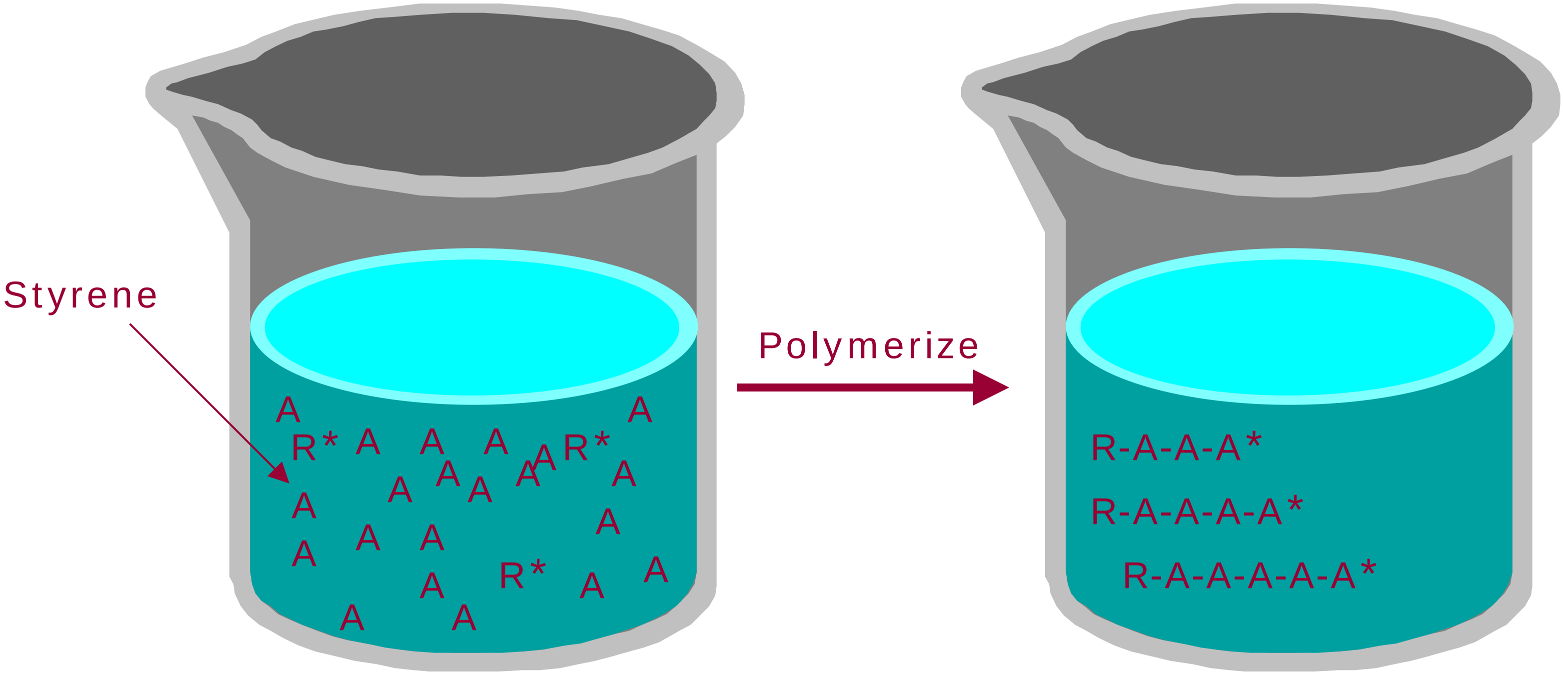
$$2\ \cdot\mathrm{CH_2{-}CH}{:}^{\ominus} \longrightarrow {}^{\ominus}{:}\mathrm{CH{-}CH_2{-}CH_2{-}CH}{:}^{\ominus}$$

Anionic Living Polymerization

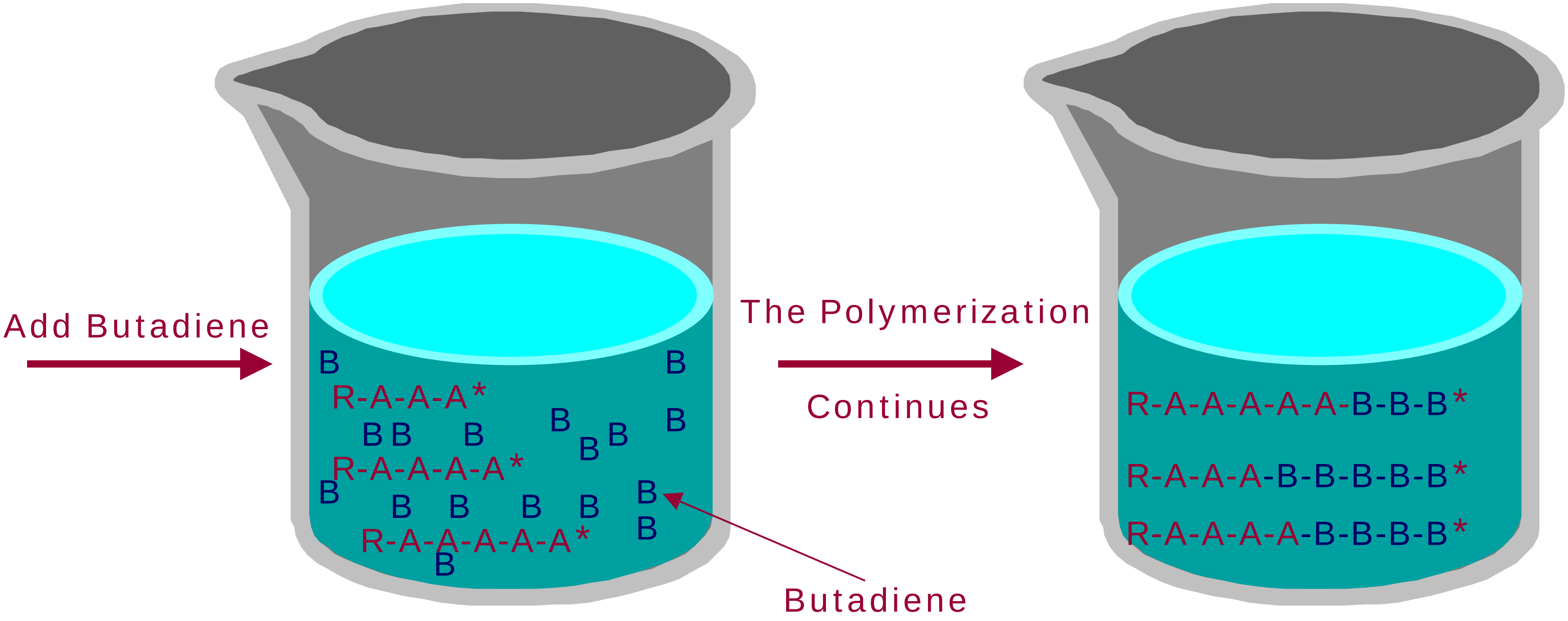

$\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim CH_2-CH{:}^{\ominus}\ Na^{\oplus}$

Then if there is nothing for the anion to react with, there is no termination (combination with the counterion occurs in only a few instances; the ions hang around one another and their attractions are mediated by solvent)

This allows the synthesis of block copolymers. Because the active site stays alive, one can first polymerize styrene, for example:



Anionic Living Polymerization



Add Butadiene

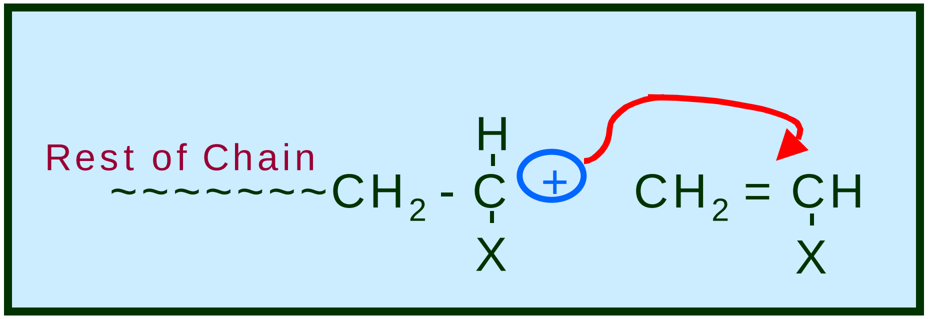
The Polymerization Continues

Butadiene

Some Final Notes on Anionic Polymerization

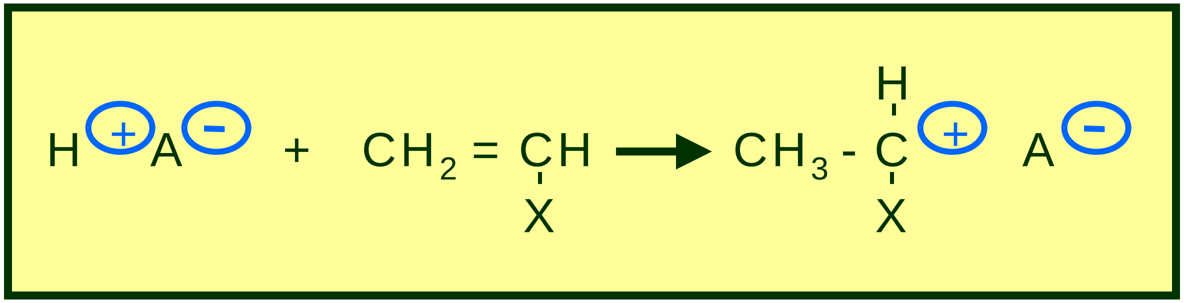
There are a lot more interesting things about anionic polymerization - the effect of polar groups, the fact that not all monomers can be used to make block copolymers, the ability to make certain polymers with very narrow molecular weight distributions, and so on - but these topics are for more advanced treatments, so now we will turn our attention to cationic polymerization .

Cationic Polymerization



$$\sim\sim\sim\sim\sim\sim\sim\sim CH_2-\overset{H}{\underset{X}{C}}{}^{\oplus} \quad CH_2=\underset{X}{CH}$$

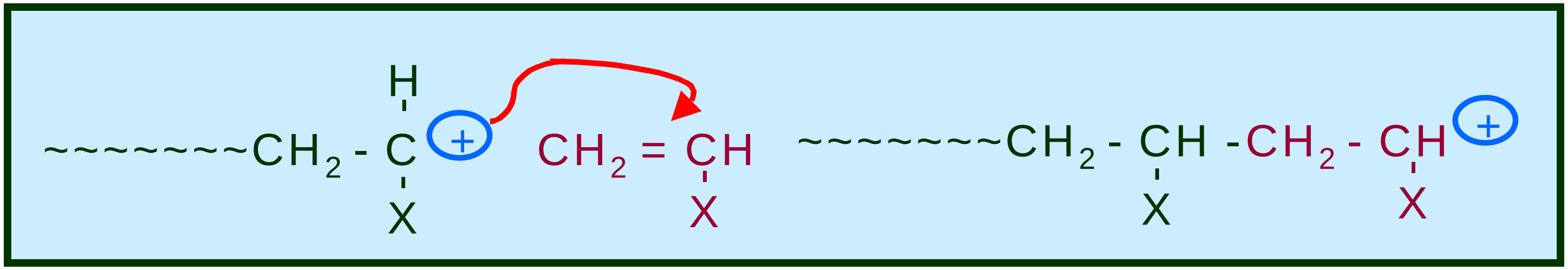
As you by now have doubtless anticipated, cationic polymerizations involve an active site where there is a positive charge because, in effect, there is a deficit of one electron at the active site.



$$H^{\oplus}A^{\ominus} + CH_2=\underset{X}{CH} \longrightarrow CH_3-\overset{H}{\underset{X}{C}}{}^{\oplus} \quad A^{\ominus}$$

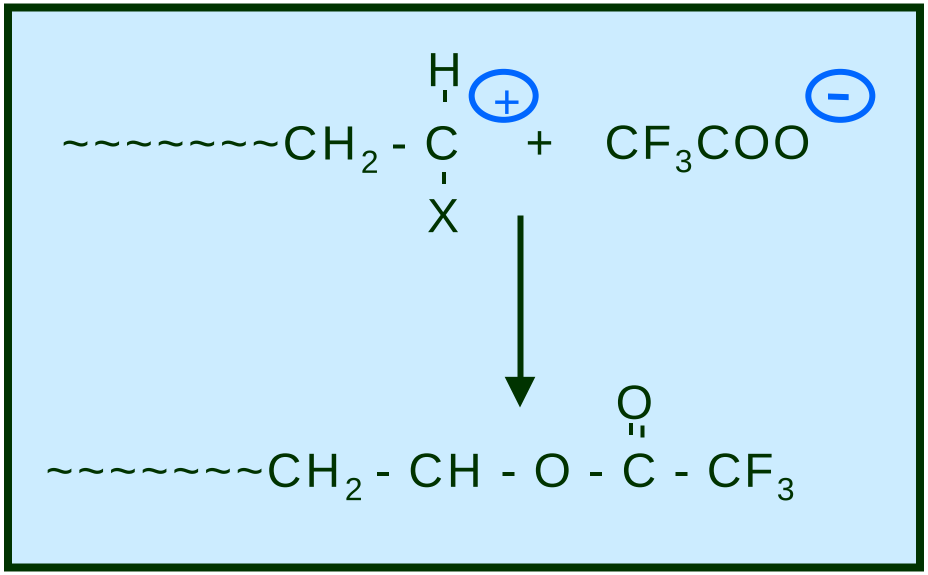
Cationic polymerizations can be initiated by protonic acids or Lewis acids (the latter sometimes combined with certain halogens).

Propagation then proceeds in the usual way.



$$\sim\sim\sim\sim\sim\sim\sim\sim CH_2-\overset{H}{\underset{X}{C}}{}^{\oplus} \quad CH_2=\underset{X}{CH} \quad \sim\sim\sim\sim\sim\sim\sim\sim CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}{}^{\oplus}$$

Cationic Polymerization - Termination and Chain Transfer

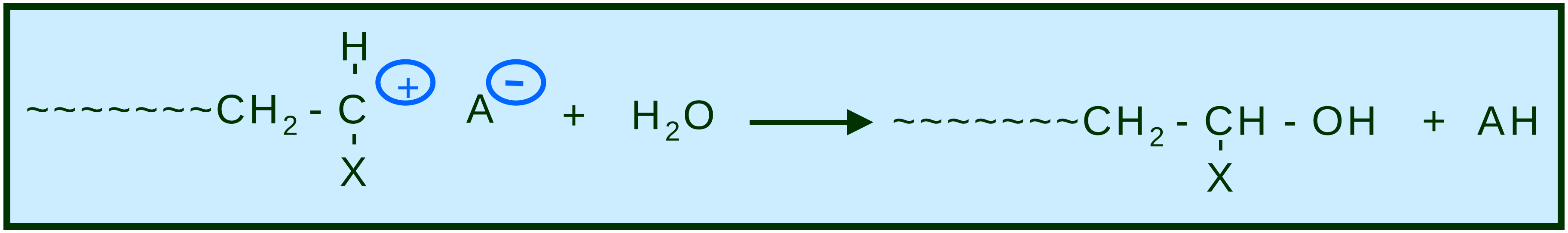


$$\sim\sim\sim\sim\sim\sim\sim\sim CH_2 - \underset{X}{\overset{H}{C}}{}^{\oplus} \quad + \quad CF_3COO^{\ominus}$$

$$\Big\downarrow$$

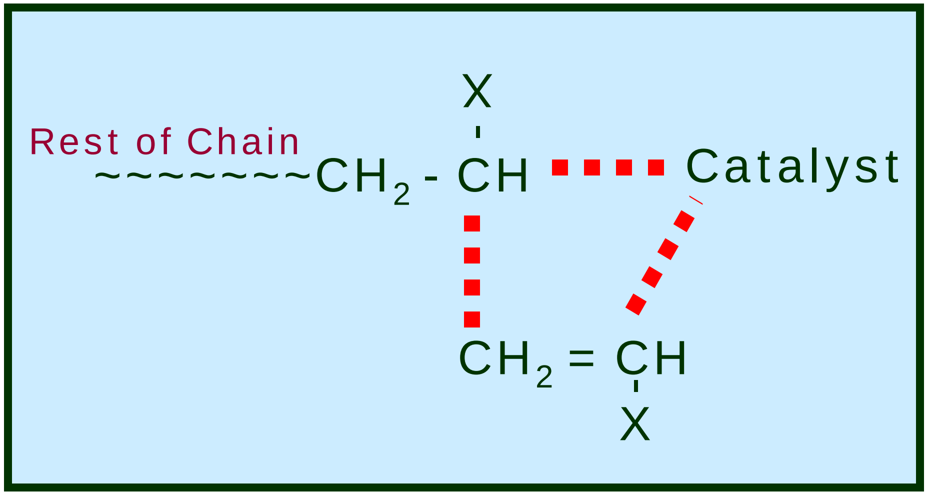
$$\sim\sim\sim\sim\sim\sim\sim\sim CH_2 - CH - O - \overset{O}{\overset{\|}{C}} - CF_3$$

Unlike anionic polymerization, termination can occur by anion - cation recombination, for example, as illustrated opposite. Lots of other side reactions can occur, with trace amounts of water, as illustrated below, chain transfer to monomer, and so on. This makes it much more difficult to make a living polymer using cationic polymerization.



$$\sim\sim\sim\sim\sim\sim\sim\sim CH_2 - \underset{X}{\overset{H}{C}}{}^{\oplus} \quad A^{\ominus} \quad + \quad H_2O \longrightarrow \sim\sim\sim\sim\sim\sim\sim\sim CH_2 - \underset{X}{CH} - OH \quad + \quad AH$$

Coordination Polymerization

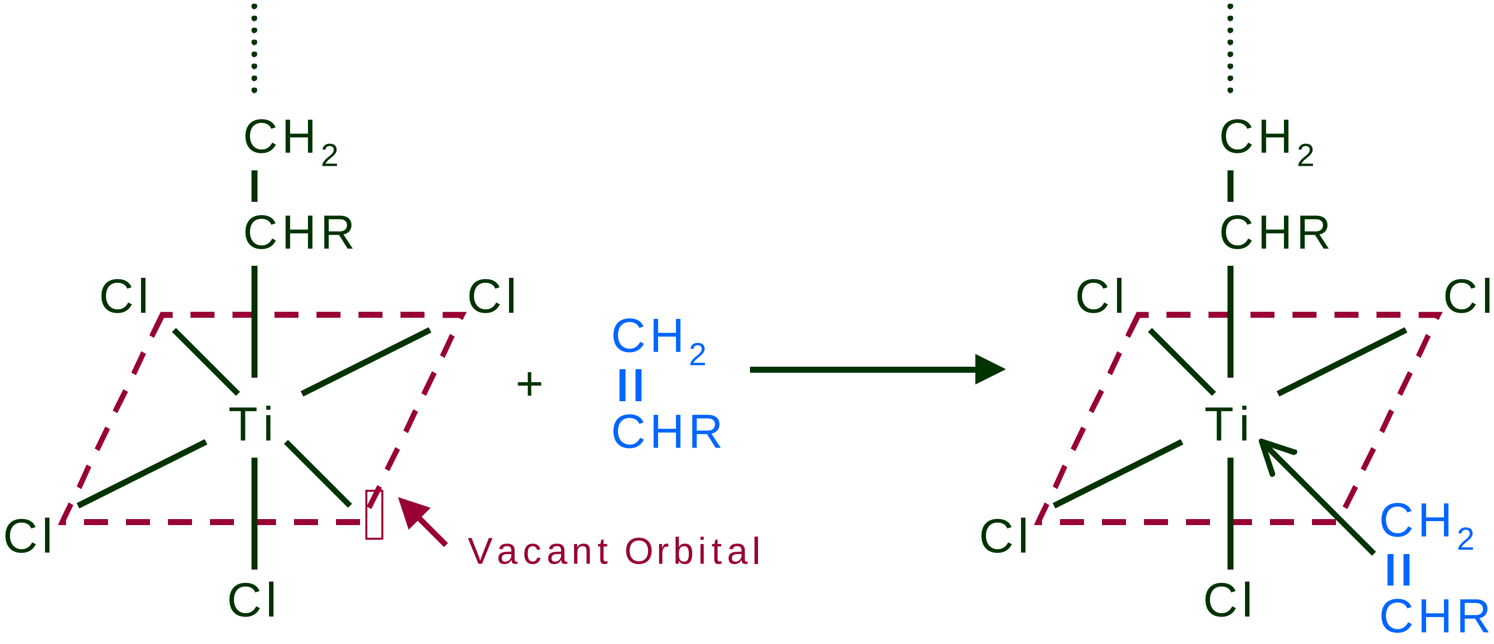


Some reactions are best described as coordination polymerizations, since they usually involve complexes formed between a transition metal and the π electrons of the monomer (many of these reactions are similar to anionic polymerizations and could be considered under that category).

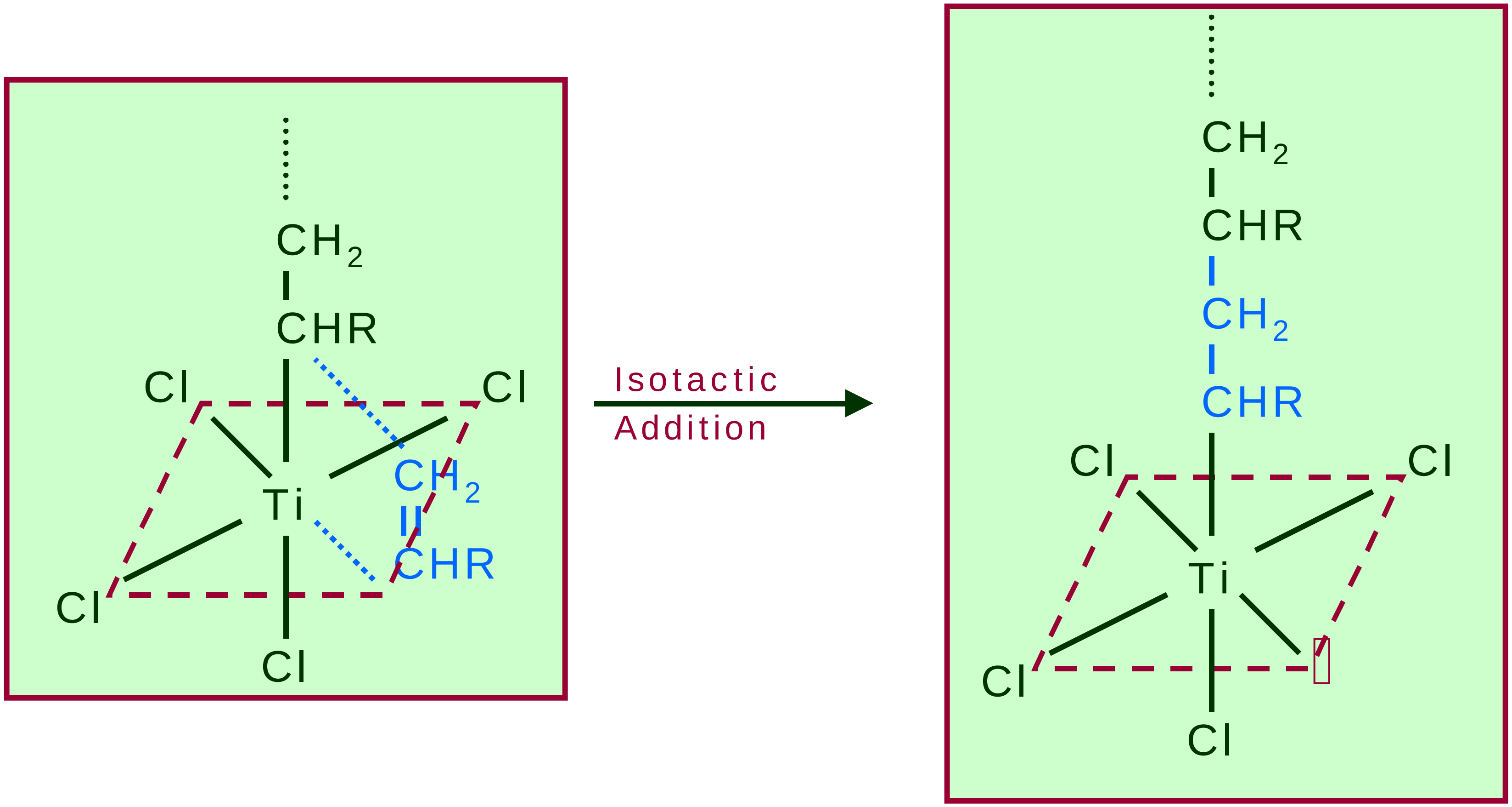
These types of polymerizations usually lead to linear and stereo-regular chains and often use so-called Ziegler - Natta catalysts, various metal oxides, or, more recently, metallocene catalysts.

Ziegler - Natta Catalysts

Ziegler-Natta catalysts generally consist of a metal organic compound involving a metal from groups I - III of the periodic table, such as triethyl aluminium, and a transition metal compound (from groups IV - VIII), such as titanium tetrachloride. The metal organic compound acts as a weak anionic initiator, first forming a complex whose nature is still open to debate. Polymerization proceeds by a process of insertion. The transition metal ion (Ti in this example) is connected to the end of the growing chain and simultaneously coordinates the incoming monomer at a vacant orbital site. Two general mechanisms have been proposed and for simplicity here we simply illustrate the so-called monometallic mechanism (the other is bimetallic)



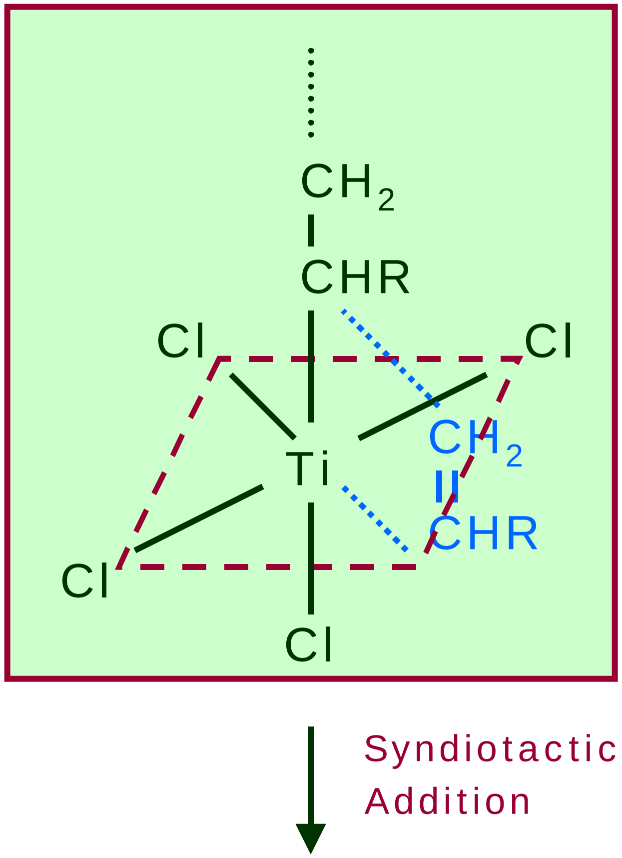
Ziegler - Natta Catalysts

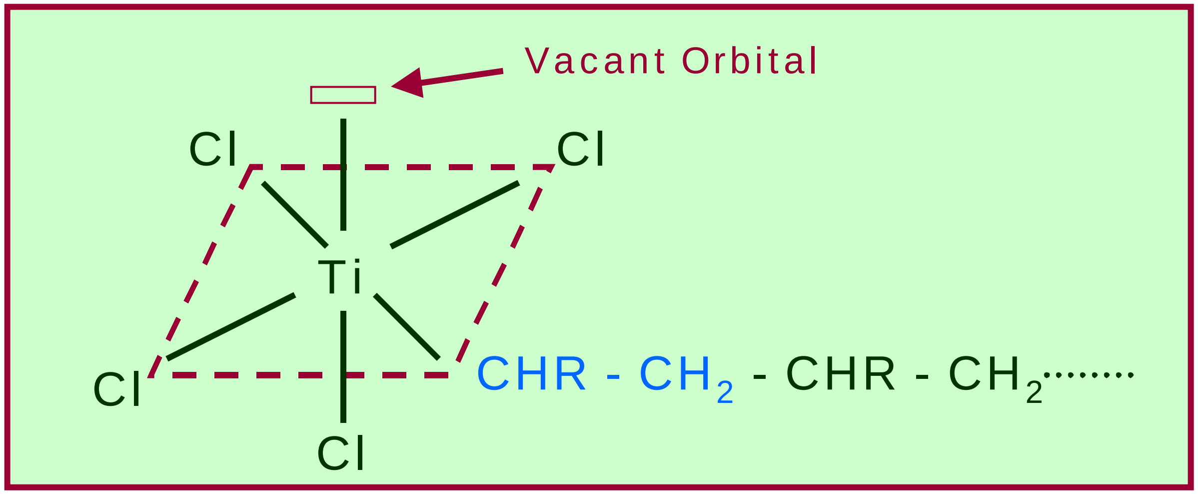


Isotactic placement can then occur if the coordinated monomer is inserted into the chain in such a way that the growing chain remains attached to the transition metal ion in the same position.

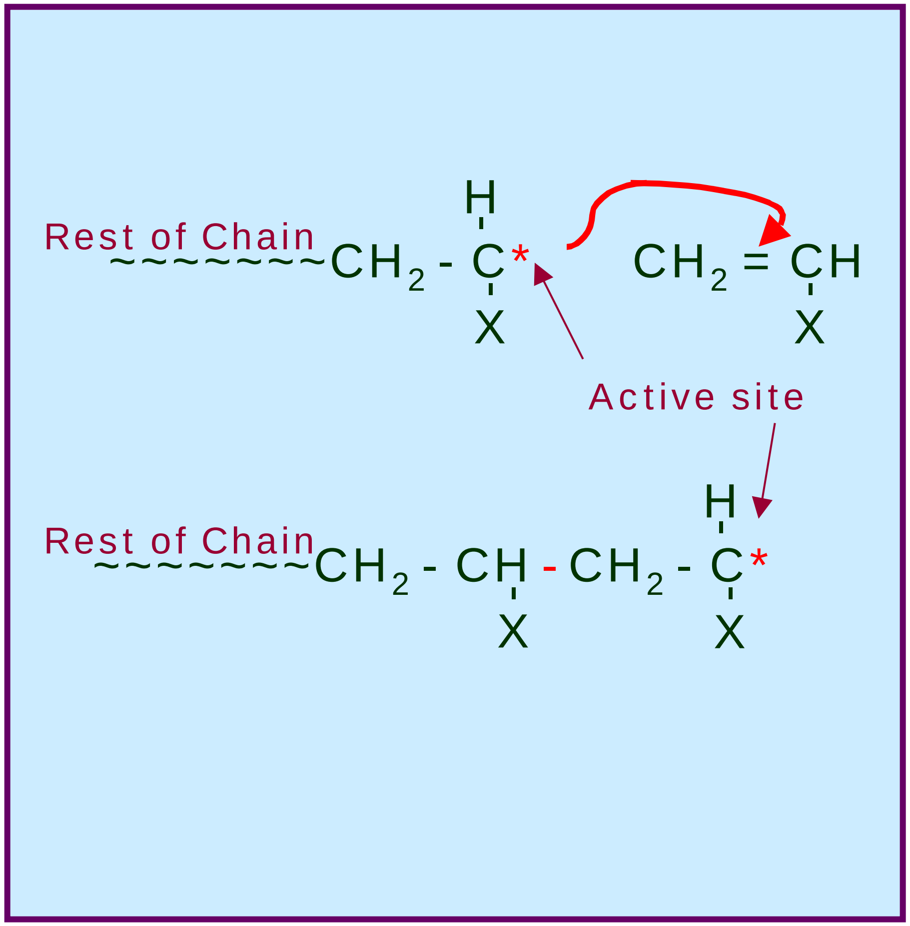
Ziegler - Natta Catalysts

Or, if the chain becomes attached to the transition metal ion in the position of the orbital that was initially vacant, syndiotactic addition will occur. This becomes more favoured at lower temperatures, but vinyl monomers usually form isotactic chains with these catalysts. Because of the heterogeneous nature of the geometry of the catalyst surface atactic and stereoblock polymers can also be formed



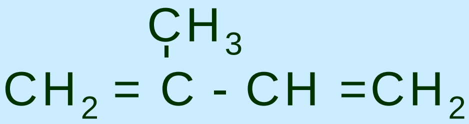
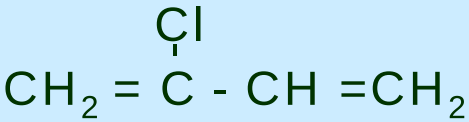
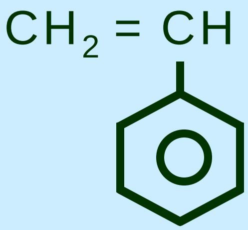


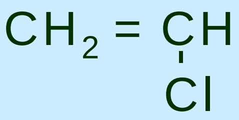
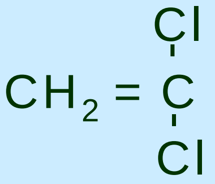
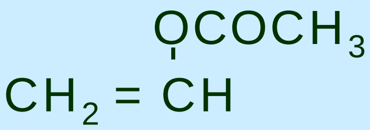
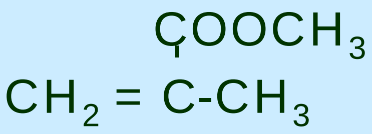
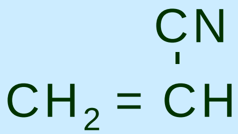
Chain Polymerization Methods and Monomer Type



As you might guess, not all monomers can be polymerized by a given chain polymerization method. There is a selectivity involved that depends upon chemical structure (i.e. the inductive and resonance characteristics of the group X in the vinyl monomer shown opposite). With the exception of α-olefins like propylene, most monomers with C=C double bonds can be polymerized free radically, although at different rates

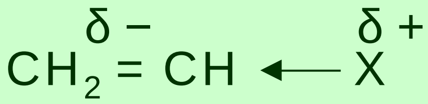
Some Monomers that can be Polymerized Free Radically

Monomer	Chemical Structure
Ethylene	$CH_2 = CH_2$
Tetrafluoro-ethylene	$CF_2 = CF_2$
Butadiene	$CH_2 = CH - CH = CH_2$
Isoprene	 $CH_2 = \overset{CH_3}{C} - CH = CH_2$
Chloroprene	 $CH_2 = \overset{Cl}{C} - CH = CH_2$
Styrene	

Monomer	Chemical Structure
Vinyl Chloride	 $CH_2 = \underset{Cl}{CH}$
Vinylidene Chloride	 $CH_2 = \underset{Cl}{\overset{Cl}{C}}$
Vinyl Acetate	 $CH_2 = \overset{OCOCH_3}{CH}$
Methyl Methacrylate	 $CH_2 = \overset{COOCH_3}{C} - CH_3$
Acrylonitrile	 $CH_2 = \overset{CN}{CH}$

Chain Polymerization Methods and Monomer Type

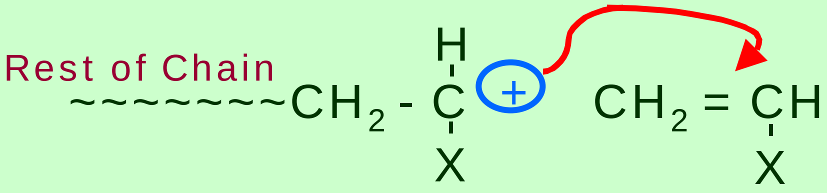
Monomers are much more selective with respect to ionic initiators. Electron donating substituents, such as alkyl, alkoxy and phenyl groups increase the electron density on the C=C double bond



$$\overset{\delta -}{CH_2 = CH} \longleftarrow \overset{\delta +}{X}$$

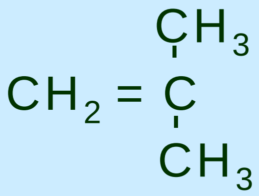
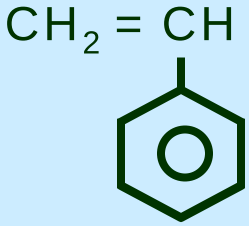
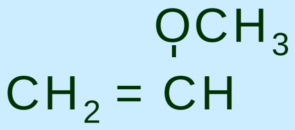
Electron donating substituent

and facilitate cationic polymerization



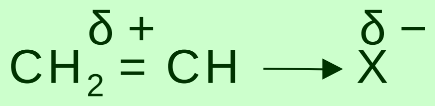
$$\sim\sim\sim\sim\sim\sim\sim\sim CH_2 - \underset{X}{\overset{H}{C}}{}^{\oplus} \quad CH_2 = \underset{X}{CH}$$

Some Monomers that can be Polymerized Cationically

Monomer	Chemical Structure
Isobutylene	 $CH_2 = \underset{CH_3}{\overset{CH_3}{C}}$
Styrene	
Vinyl Methyl Ether	 $CH_2 = \overset{OCH_3}{CH}$

Monomers that can be Polymer Anionically

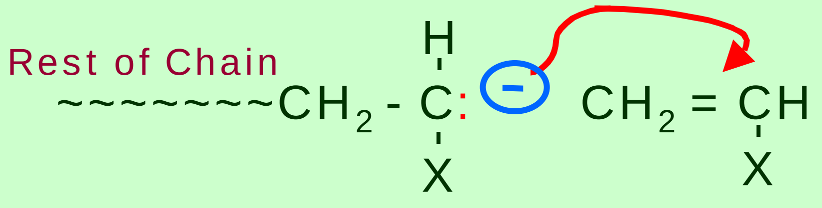
While substituents that are electron withdrawing,

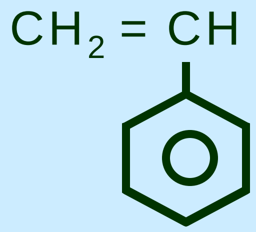
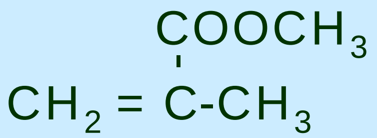
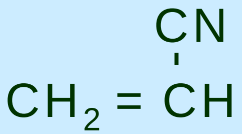
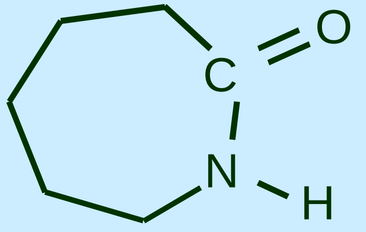
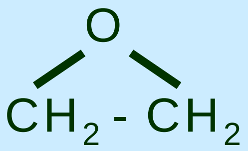


$$\overset{\delta +}{CH_2 = CH} \longrightarrow \overset{\delta -}{X}$$

Electron withdrawing substituent

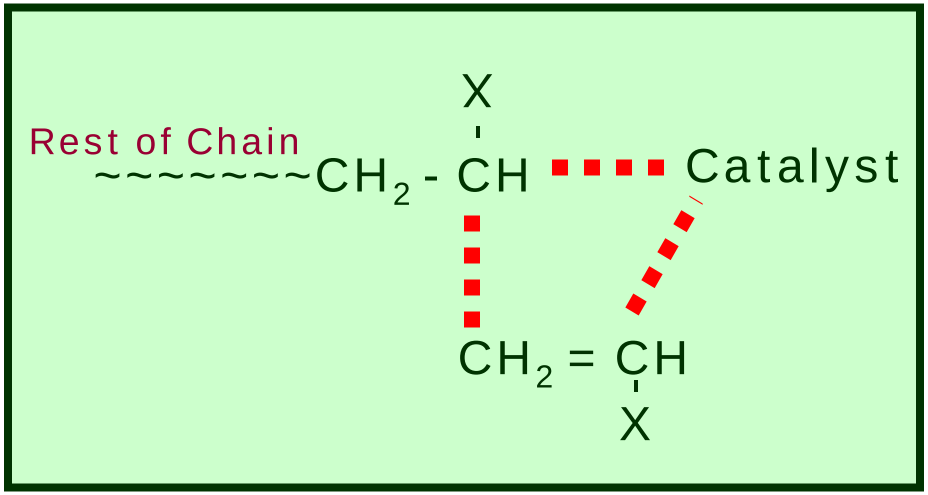
such as cyano, acid or ester, facilitate anionic polymerization



Monomer	Chemical Structure
Styrene	
Butadiene	$CH_2 = CH - CH = CH_2$
Methyl Methacrylate	 $CH_2 = \overset{COOCH_3}{C}\text{-}CH_3$
Acrylonitrile	 $CH_2 = \overset{CN}{CH}$
Caprolactam	
Ethylene Oxide	

Monomers that can be Polymerized using Ziegler - Natta Catalysts

Finally, Ziegler - Natta catalysts are used to polymerize a variety of a-olefins (e.g. ethylene and propylene) and styrene, but many polar monomers cannot be polymerized this way as they inactivate the initiator, either through complexation or reaction with the metal components



POLYMERIZATION PROCESSES

TWO USEFUL DISTINCTIONS ;

- **BETWEEN** BATCH **AND** CONTINUOUS
- **AND BETWEEN** SINGLE - PHASE **AND** MULTI - PHASE

SINGLE - PHASE

Bulk or Melt Polymerization

Solution Polymerization

BATCH VS. CONTINUOUS -

Depends on polymerization time
ie kinetics - coming up next!

SINGLE - PHASE

Bulk or Melt Polymerization

Solution Polymerization

MULTI - PHASE

Gas / Solid

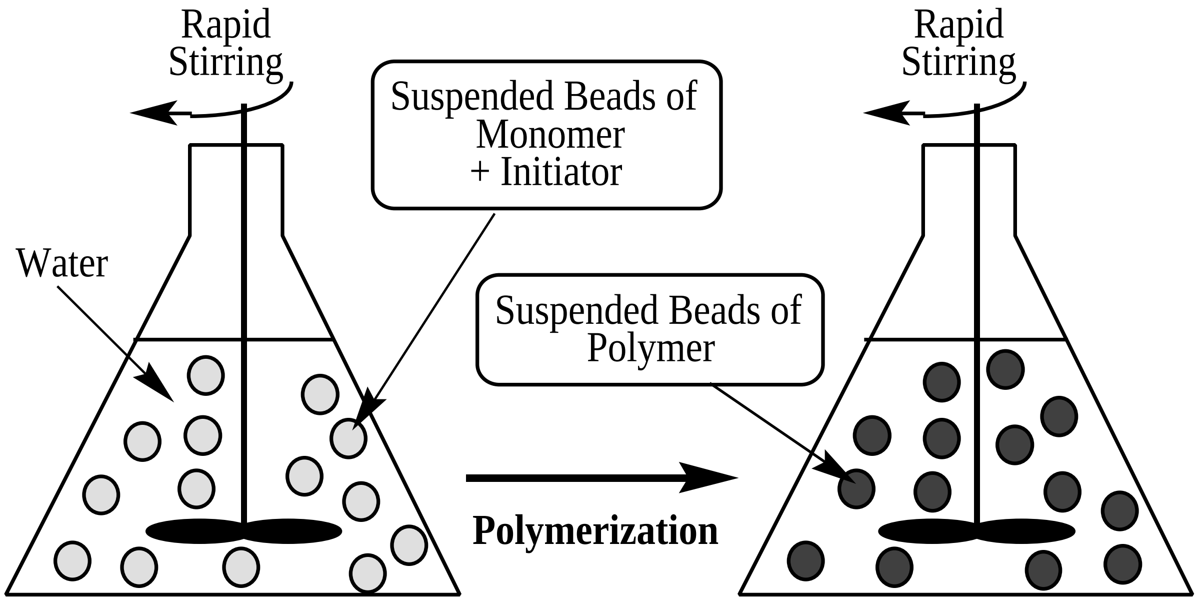
Liquid / Solid

Suspension

Emulsion

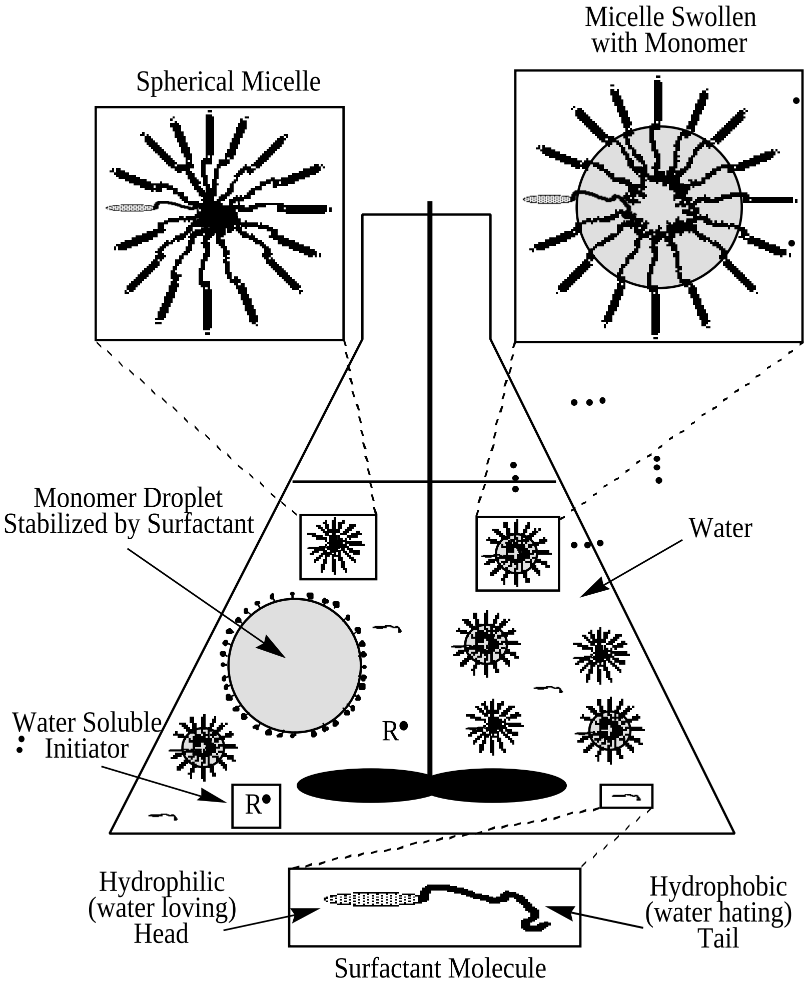
Etc

Polymer Processes—
Free Radical Suspension Polymerization



Schematic representation of suspension polymerization.

Polymer Processes—
Free Radical Emulsion Polymerization



Schematic representation of the initial stages of an emulsion polymerization.