Ionic Chain Polymerization
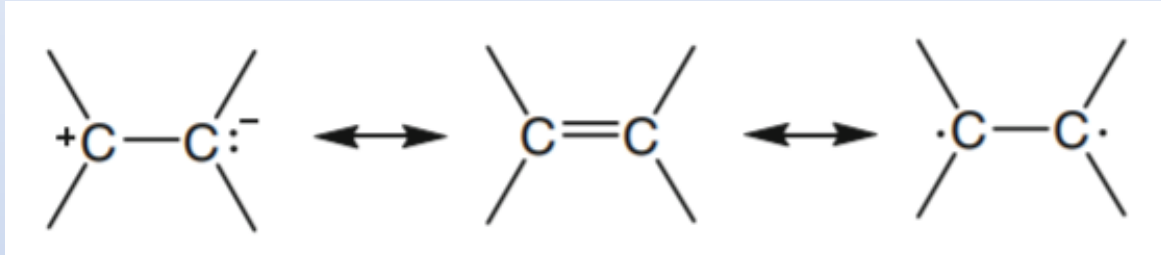
The carbon-carbon double bond can be polymerized either by free radical or ionic methods. The difference arises because the p-bond of a vinyl monomer can respond appropriately to the initiator species by either homolytic or heterolytic bond breakage a


Although radical, cationic, and anionic initiators are used in chain polymerizations, they cannot be used indiscriminately, since all three types of initiation do not work for all monomers. Monomers show varying degrees of selectivity with regard to the type of reactive center that will cause their polymerization. Most monomers will undergo polymerization with a radical initiator, although at varying rates. However, monomers show high selectivity toward ionic initiators [1]. Some monomers may not polymerize with cationic initiators, while others may not polymerize with anionic initiators.

Types of chain polymerization suitable for unsaturated monomers [3]

Monomer type	Radical	Cationic	Anionic	Coordination
Ethylene	+	−	−	+
1-Alkyl olefins (α-olefins)	−	−	−	+
1,1-Dialkyl olefins	−	+	−	+
1,3-Dienes	+	+	+	+
Styrene, α-methyl styrene	+	+	+	+
Halogenated olefins	+	−	−	−
Vinyl ethers	−	+	−	−
Vinyl esters	+	−	−	−
Acrylic and methacrylic esters	+	−	+	−
Acrylonitrile and methacrylonitrile	+	−	+	−
N-Vinyl carbazole	+	+	−	−
N-Vinyl pyrrolidone	+	+	−	−
Aldehydes, ketones	−	+	+	−

The carbon–carbon double bond in vinyl monomers and the carbon–oxygen double bond in aldehydes and ketones are the two main types of linkages that undergo chain polymerization
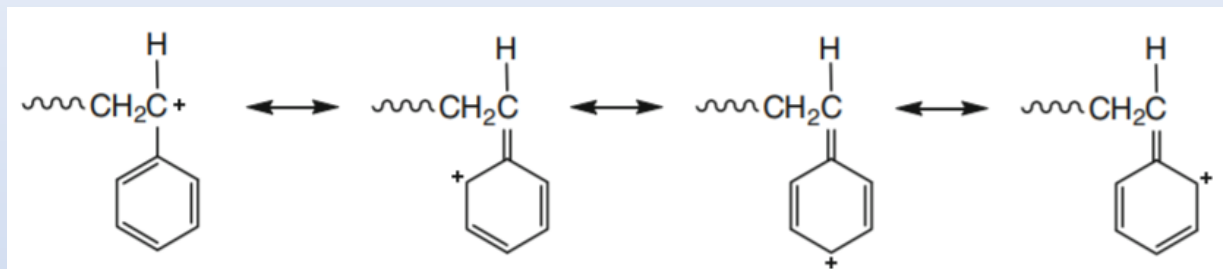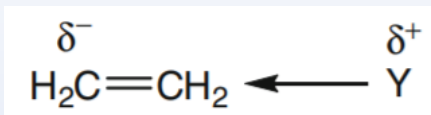
Certain vinyl compounds are best polymerized via cationic rather than freeradical intermediates.
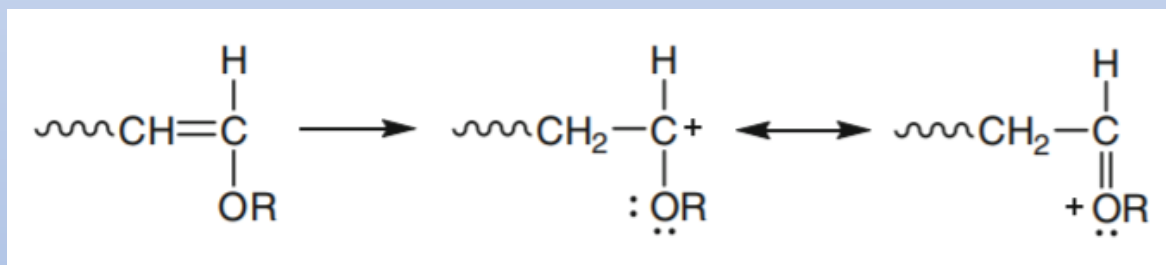

The alkoxy substituent allows a delocalization of the positive charge. If the substituent was not present, the positive charge would be localized on the single a-carbon atom. The presence of the alkoxy group leads to stabilization of the carbocation by delocalization of the positive charge over two atoms—the carbon and the oxygen. Similar delocalization effects occur with phenyl, vinyl, and alkyl substituents, for example, for styrene polymerization.

The most common commercial cationic polymerization is the polymerization of isobutylene (CH_3–$C(CH_3)$=CH_2) which can be polymerized with Friedel–Crafts catalysts in a reaction

Characteristics of Ionic Chain Polymerization

Ionic polymerizations are highly selective. The cationic polymerization will undergo cationic intermediate as shown below:
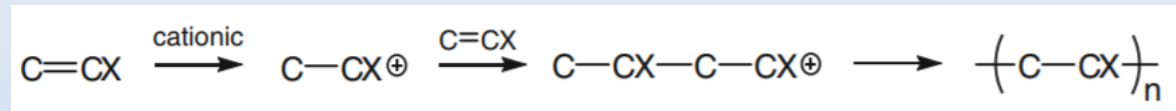
The X has to be an electron donating group such as alkoxy, phenyl, vinyl, 1,1- dialkyl, and so on to stabilize the cationic intermediate. The anionic polymerization will undergo anionic intermediate as shown below:
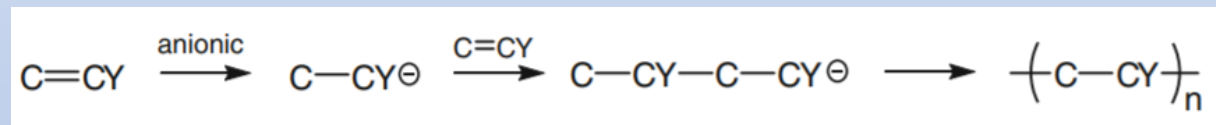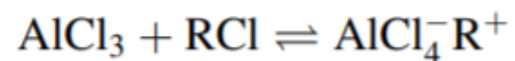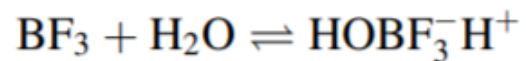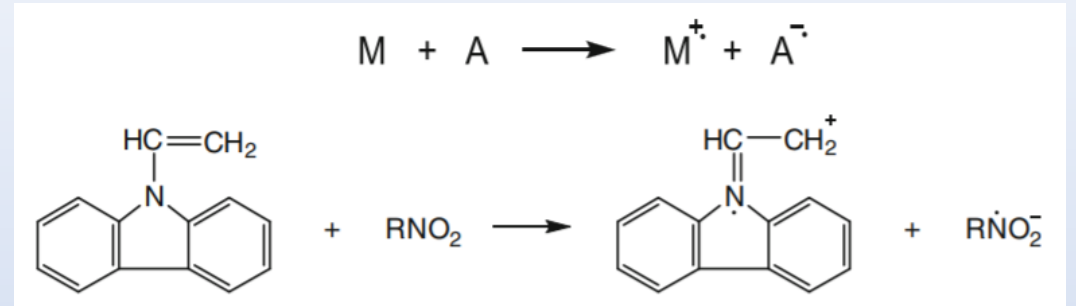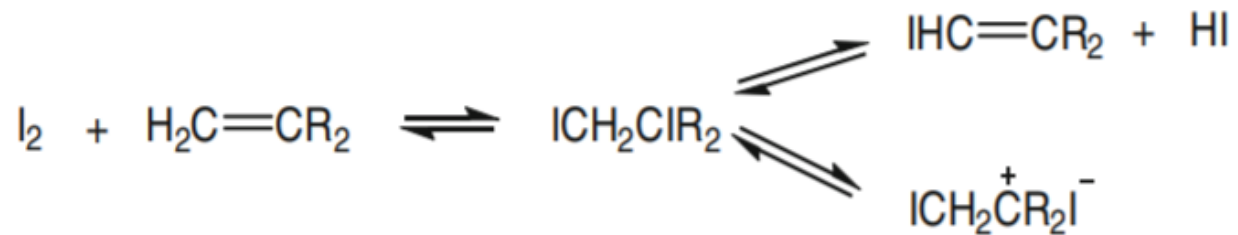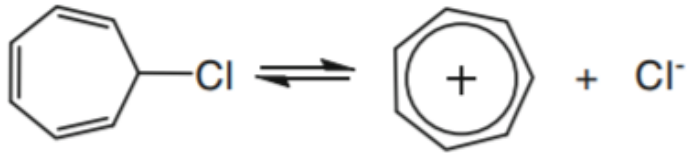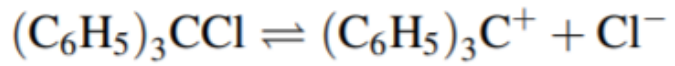

The Y has to be an electron withdrawing group such as –CN, CO, phenyl, vinyl, and so on to stabilize the anionic intermediate. Thus the selectivity of ionic polymerization is due to the very strict requirements for stabilization of anionic and cationic propagating species.

Cationic and anionic polymerizations have many similar characteristics. The formation of ions with sufficiently long lifetimes for propagation to yield highmolecular-weight products generally requires stabilization of the propagating centers by solvation. Relatively low or moderate temperatures are also needed to suppress termination, transfer, and other chain-breaking reactions which destroy propagating centers

Cationic Polymerization

Compounds used most frequently to initiate cationic polymerization are mineral acids, particularly H_2SO_4 and H_3PO_4, and Lewis acids such as: $AlCl_3$, BF_3, $TiCl_4$, and $SnCl_4$. Lewis acids need the presence of trace amounts of water (proton or cation source) which form the electrophilic species to initiate polymerization. Examples are the reactions of BF_3 with water and aluminum chloride with an alky chloride. Water is called initiator, and the Lewis acid is called coinitiator. They form an initiating system. With certain very active Lewis acids, autoionization may occur.

$$BF_3 + H_2O \rightleftharpoons HOBF_3^- H^+$$

$$AlCl_3 + RCl \rightleftharpoons AlCl_4^- R^+$$

$$2AlBr_3 \rightleftharpoons AlBr_4^- AlBr_2^+$$

$$(C_6H_5)_3CCl \rightleftharpoons (C_6H_5)_3C^+ + Cl^-$$

$$M + A \longrightarrow M^{+\cdot} + A^{-\cdot}$$

Cations can also be formed by photo initiation. Aryldiazonium salt (ArN2 + Z-), diaryliodonium salt (Ar2 + IZ-), and triarylsulfonium salt (Ar2S+ Z-) are effective photoinitiators of cationic polymerization, where Z- is a nonnucleophilic and photostable anion such as tetrafluoroborate (BF4 -), hexafluoroantimonate (SbF6 -), and tetraperfluorophenylborate [(C6F5)4B-], and hexafluorophosphate (PF6 -).

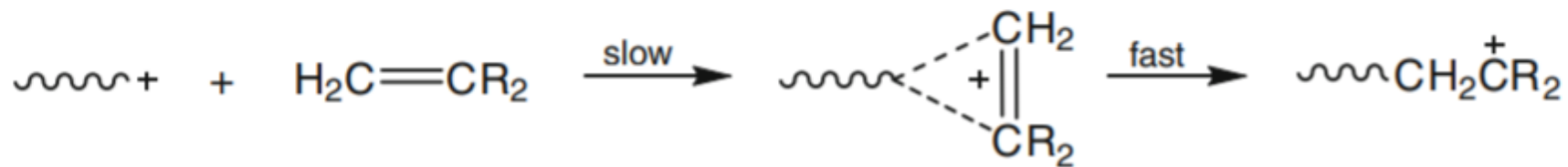# Reaction Mechanisms of Cationic Polymerization

The cationic polymerization is a chain polymerization that involves three steps: (1) initiation, (2) propagation, and (3) termination. The rate of addition to aliphatic monomers is of the order of

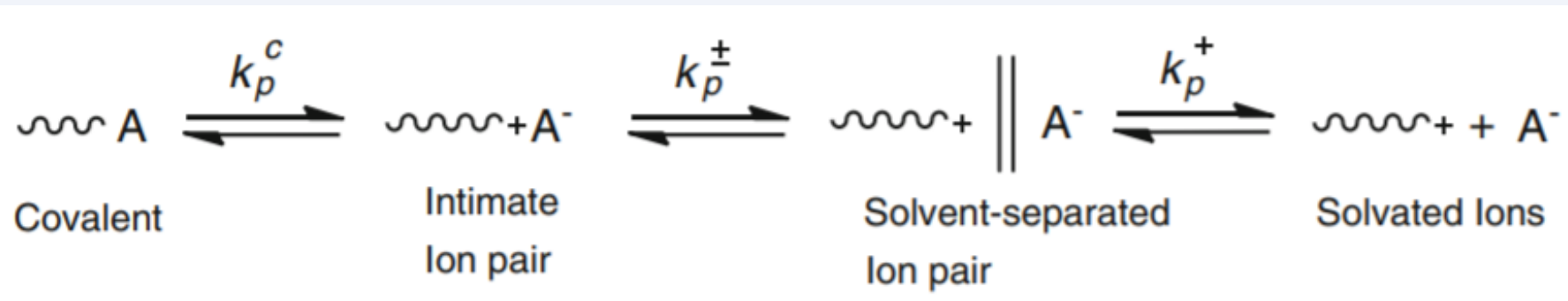$$(CH_3)_2C = CH_2 > CH_3CH = CH_2 > CH_2 = CH_2$$
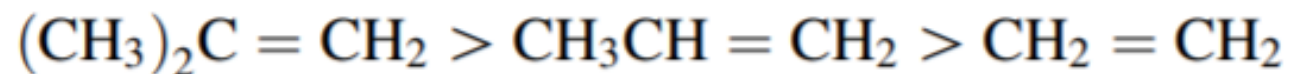
Ortho substituents retard the addition regardless of whether they are activating or deactivating.

$$H_2C=CH\ddot{O}R \xrightarrow{R'^+} R'CH_2-\overset{+}{CH}-\ddot{O}R \longleftrightarrow R'CH_2-CH=\overset{+}{\ddot{O}}R$$
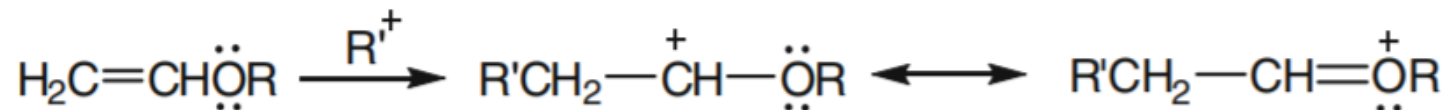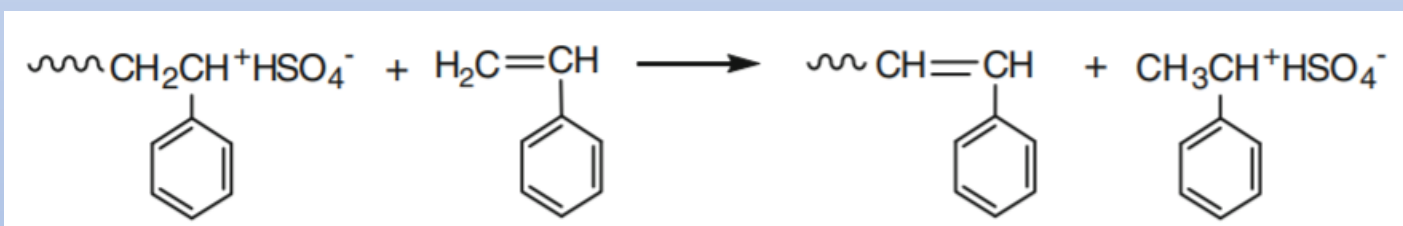
In free radical polymerization, the covalent bond formation is a rate limiting step.

$$\text{\large\textasciitilde}^+ \ + \ H_2C{=}CR_2 \xrightarrow{\text{slow}} \text{\large\textasciitilde}\!\!\underset{CR_2}{\overset{CH_2}{\big\langle}}^+ \xrightarrow{\text{fast}} \text{\large\textasciitilde}CH_2\overset{+}{C}R_2$$
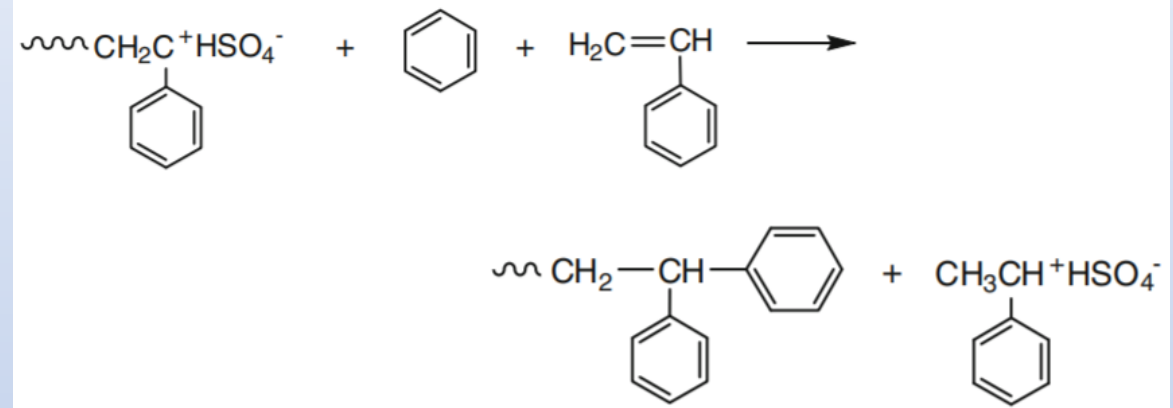
The initiator ion pair (consisting of the carbocation and its negative counterion) produced in the initiation step proceeds to propagate by successive additions of monomer molecules.

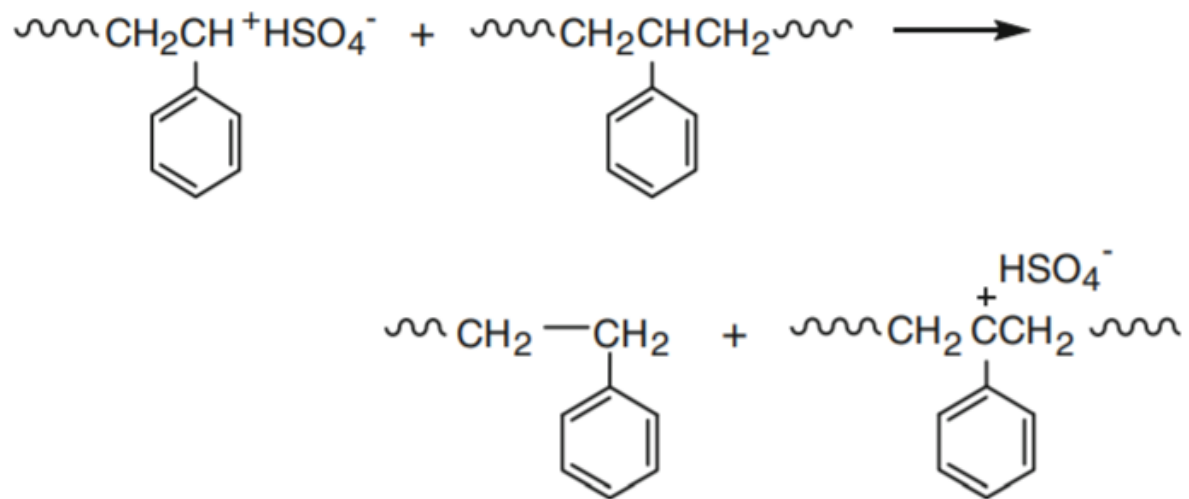$$\mathrm{HMn^+\,(IZ)^- + M \xrightarrow{\ k_p\ } HMnM^+\,(IZ)^-}$$
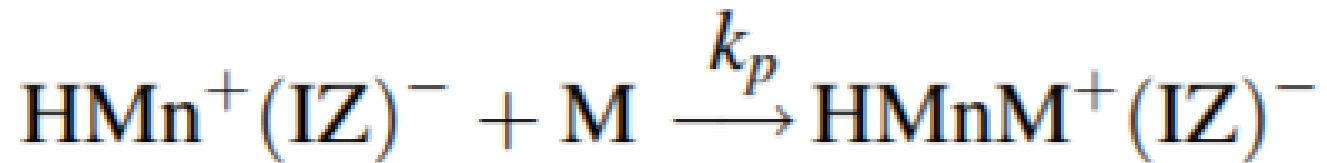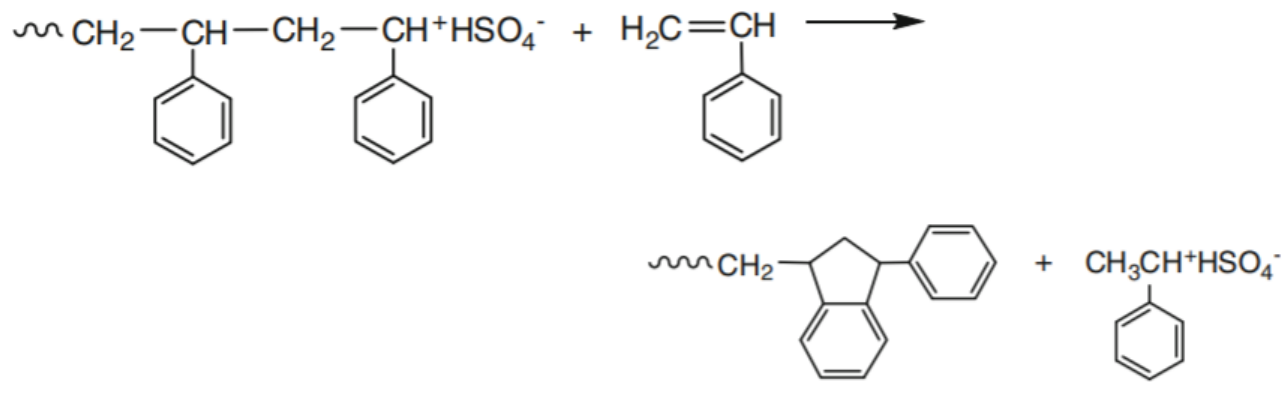
By ring alkylation:

By hydride abstraction from the chain to form a more stable ion:

With solvent, for example, with benzene by electrophilic substitution: