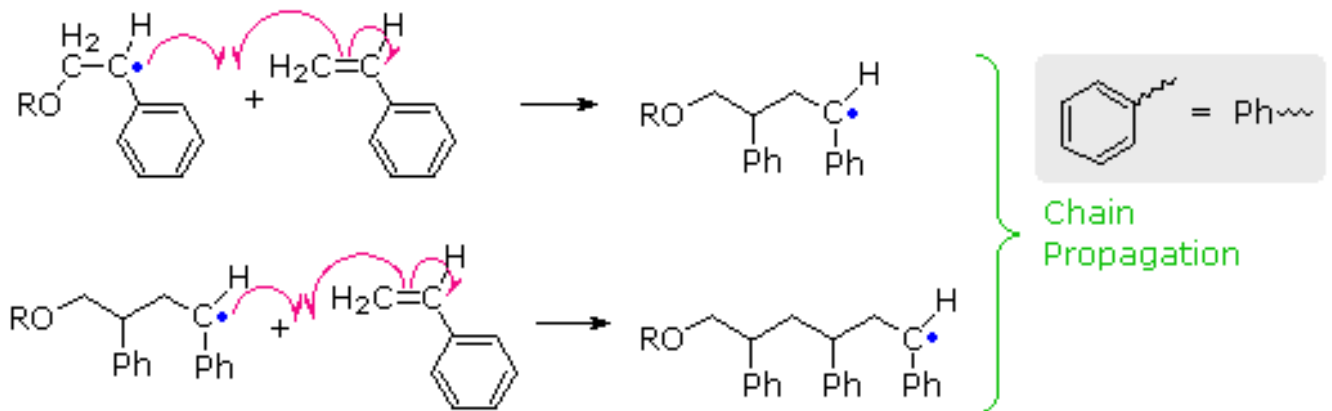
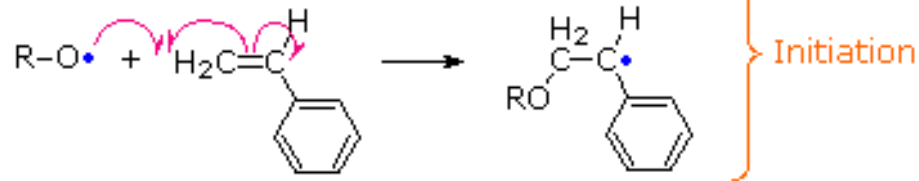
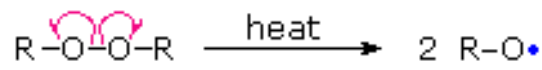


Mechanism of Polymerization



a growing polystyrene chain

Dr. Mainul

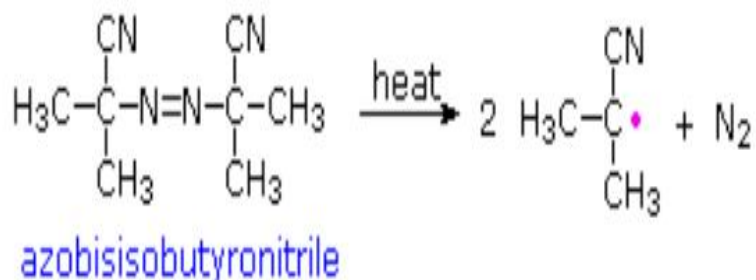
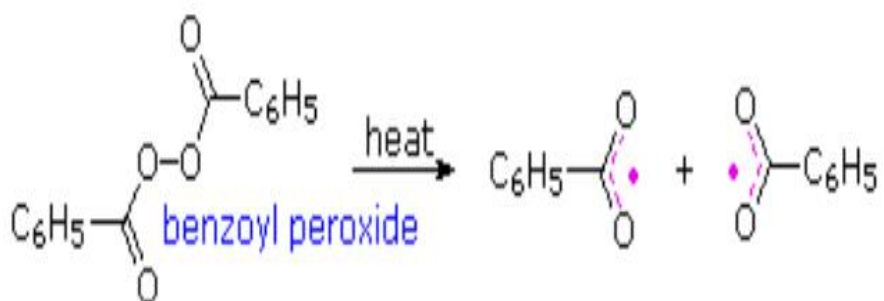
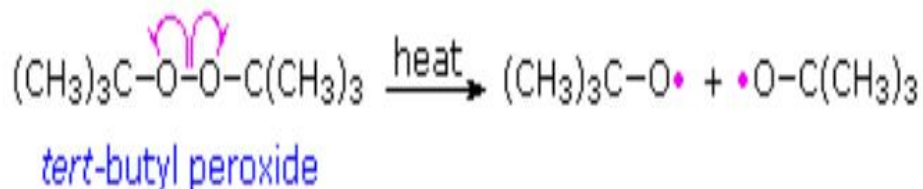
Mechanism of Chain Growth Polymerisation

Initiation

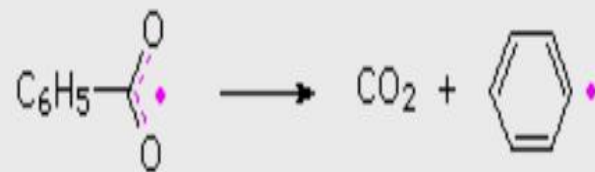
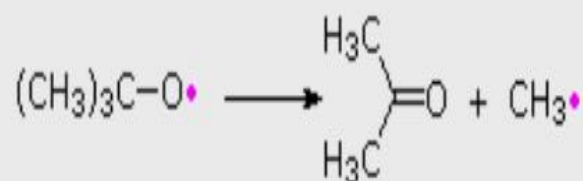
1. The formation of free radicals from an initiator.
2. The addition of one of these free radicals to monomer molecules.

Free radical can be formed by Homolytic scission (homolysis) or breakage of a single bond.

Homolytic can be achieved by heat (thermolysis) or by light such as U.V. (photolysis).



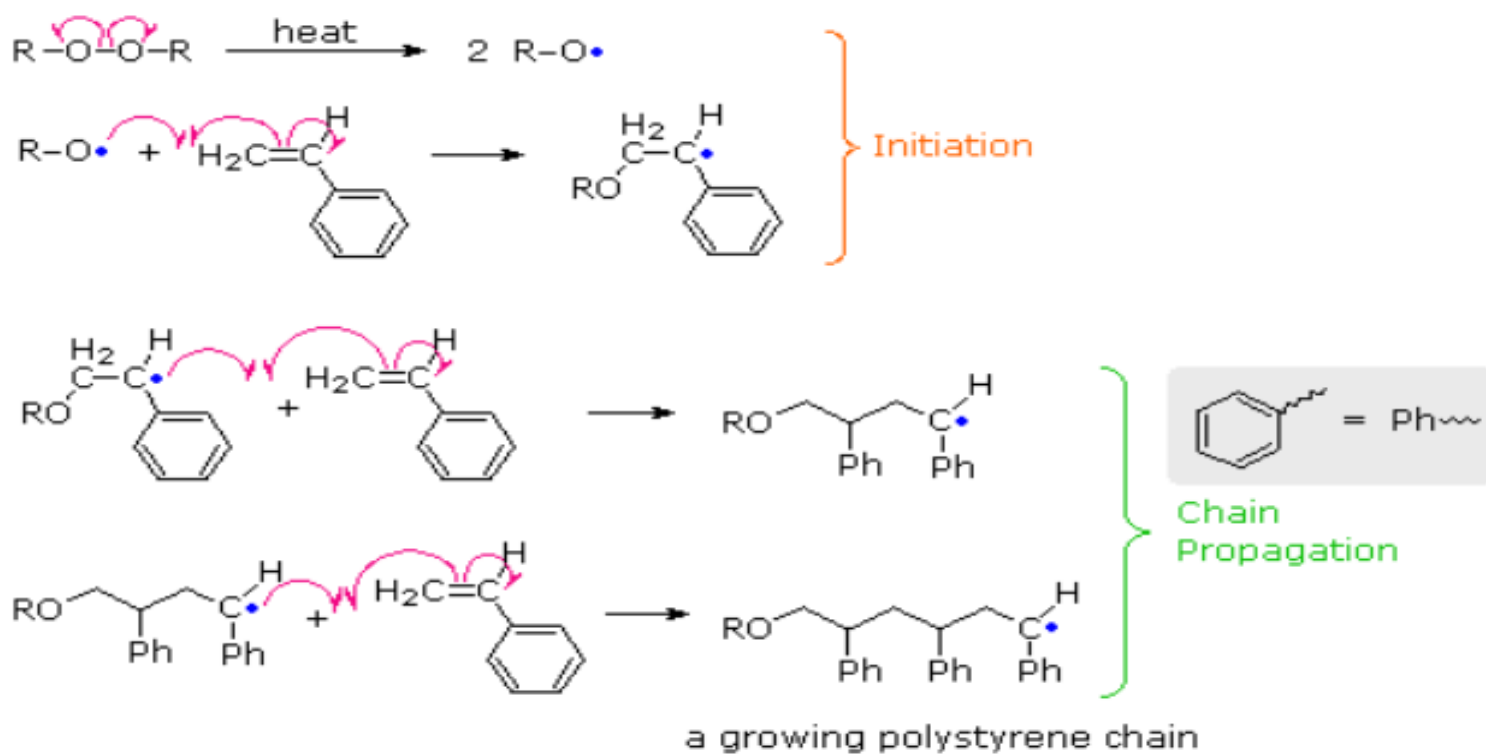
Subsequent Reactions



Propagation

The addition of monomer molecules to the active center to grow the polymer chain.

Time of addition for each monomer is of the order of a millisecond. Thus several thousands of additions can take place in a few seconds.



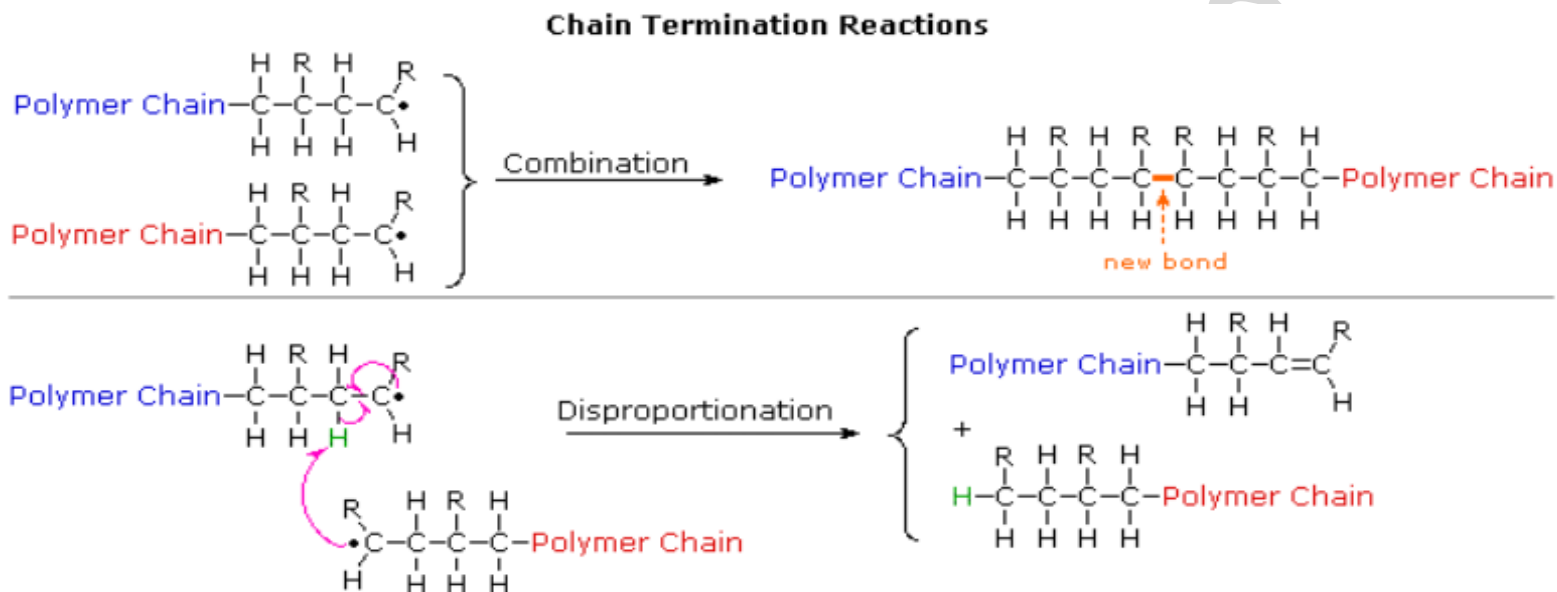
Termination

The last stage of chain reaction in which the growth of the polymer chain terminated (or stopped).

There are two mechanisms of termination:

i) Combination:

Coupling together two growing chains to form a single polymer molecule.

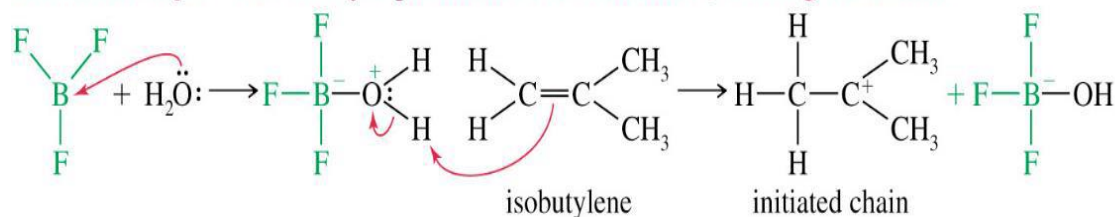


ii) Disproportionation:

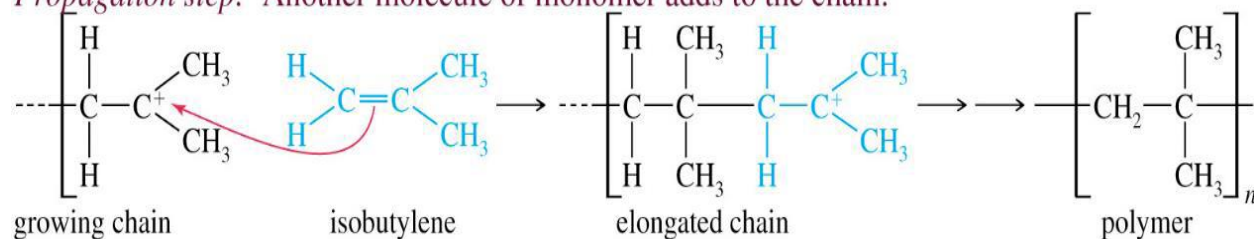
When a hydrogen atom move from one growing chain to another.

Cationic Polymerization Mechanism

Initiation steps: The catalyst protonates the monomer, starting the chain.



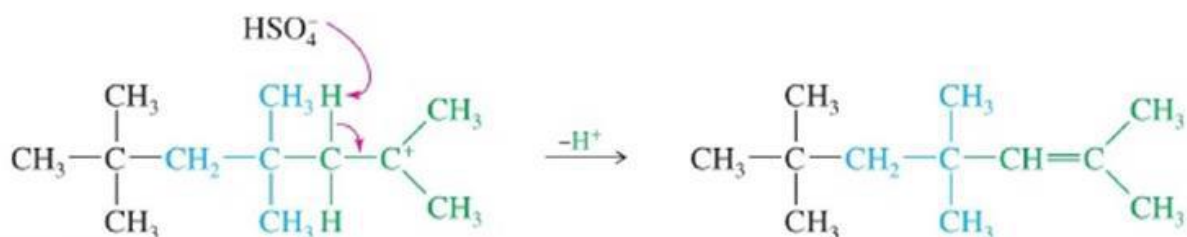
Propagation step: Another molecule of monomer adds to the chain.



- Strongly acidic catalysts are used to initiate cationic polymerization.
- BF_3 is a particularly effective catalyst, requiring a trace of water or methanol as a co-catalyst. Intermediate must be a stable carbocation.

Dr. Maini

Termination Step of Cationic Polymerization



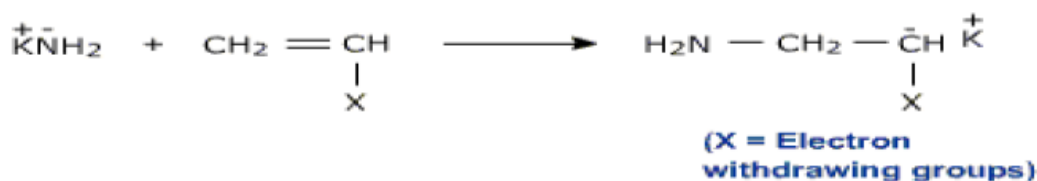
- The chain growth ends when a proton is abstracted by the weak base of the acid used to initiate the reaction.
- The loss of a hydrogen forms an alkene and ends the chain growth, so this is a termination step.

Dr. Mainul

Anionic Polymerization Mechanism

- An anionic initiator will generate a **carbanion intermediate** and thus the polymerization is of anionic addition type.
- Here the active centre of the **propagating** species is **negatively** charged.
- Hence it occurs easily with **monomers** containing **electron withdrawing groups** such as phenyl, nitrile etc., which are able to stabilize the propagating species.

Initiation can be brought about by reagents such as **n-butyl lithium** or **potassium amide**. In the initiation step, the base adds to a double bond to form a **carbanion**.



In the **chain propagation**, this carbanion adds to the double bond and the process repeats to form a polymeric carbanion.



The chain reaction can be **terminated** by **addition** of an **acid**.

