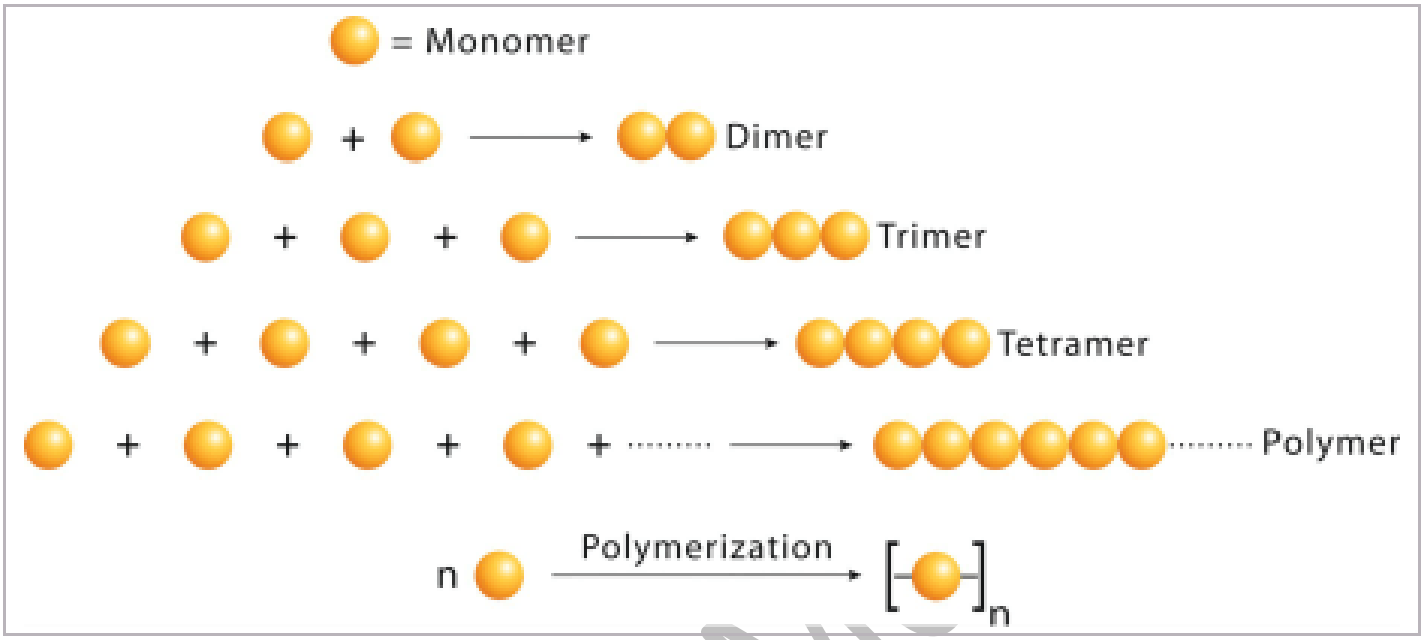
Polymerization Processes



A process of making the **monomer molecules react together** in a chemical reaction and produce three-dimensional networks or **polymer chains** is called **polymerization.**

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Types of polymerization

Based on the **mode of polymerization of polymers**, there are **two types** of polymerization. They are **addition polymerization** and **condensation polymerization**.

Addition polymerization

The formation of addition polymers occurs by the repeated **addition of monomer** molecules which possess **triple or double bonds**. For example, the formation of

$(C_3H_6)_n$ Poly-propene from (C_3H_6) propene, and **$(C_2H_4)_n$ Poly-ethene from (C_2H_4) ethene**.

Polymerization techniques

1. Addition polymerization:

   i. Bulk polymerization
   ii. Solution polymerization
   iii. Suspension polymerization
   iv. Emulsion polymerization

2. Condensation polymerization:

   i. Melt polycondensation
   ii. Solution polycondensation

Condensation polymerization

The formation of condensation polymers occurs by the **repeated condensation reaction** between **two different tri-functional or bi-functional monomeric units**. In this type of reaction, small molecules such as alcohol, water, hydrogen chloride, etc. are eliminated. Some examples are **nylon 6, nylon 6, 6, terylene (dacron)**, etc. Formation of nylon 6, 6 occurs due to the condensation of hexamethylene diamine ($C_6H_{16}N_2$) with adipic acid ($C_6H_{10}O_4$).

Degree of polymerization

The number of monomeric units present in a polymer is known as the degree of polymerization. They generally have high boiling and melting points.

How to calculate the degree of polymerization?

Step 1: Write the chemical formula of the polymer.

For example, let us consider **tetrafluoroethylene**. Its chemical formula is written as $-(CF_2\text{-}CF_2)_n-$. The monomer unit is put in the parentheses.

Step 2: Determine the atomic mass.

Determine the atomic mass of the elements composed in the **monomer unit** with the help of the periodic table. In the case of **tetrafluoroethylene**, the atomic mass of **carbon is 12** and the atomic mass of **fluorine is 19**.

Step 3: Evaluate the molecular weight.

To calculate the molecular weight, follow the sequence below:

- Multiply the atomic mass of carbon element by the number of carbon atoms in the monomer
- Multiply the atomic mass of fluorine element by the number of fluorine atoms in the monomer
- Add the products
- Therefore, the **molecular weight of tetrafluoroethylene is 12 x 2 + 19 x 4 = 100.**

Step 4: Divide.

Divide the molecular mass of the polymer by the molecular weight of the monomer. For example, **if the molecular mass of tetrafluoroethylene is 1,20,000, then its degree of polymerization is calculated as 1,20,000 / 100 = 1,200.**

Therefore, the **degree of polymerization is 1,200.**

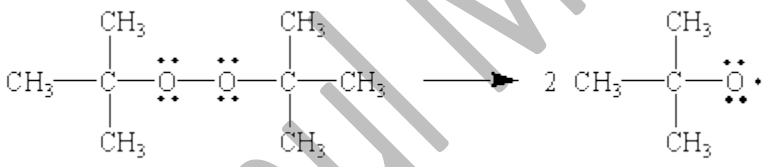
Initiator: a **molecule** that can react with a **monomer molecule** to start a chain growth polymerization. Usually a **free-radical generator** (e.g., peroxide, peroxydicarbonate, azo-compound) or, in some cases, a carbon-centered cation.

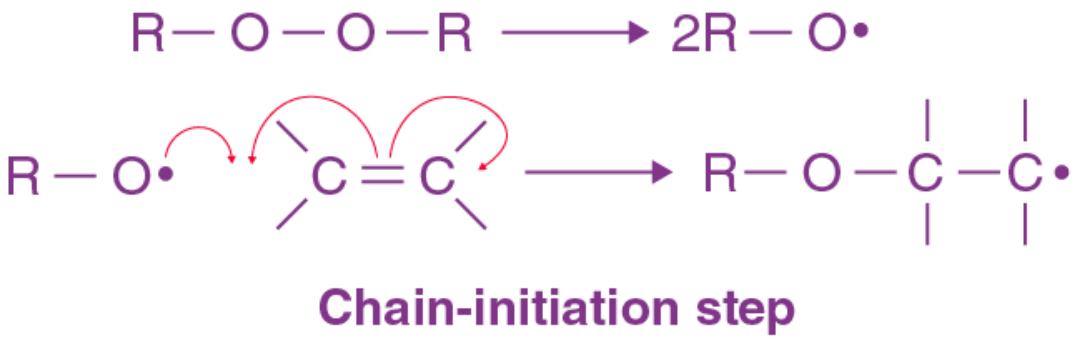
Stages of Addition Polymerization

1) Initiation

Initiation is the **foremost step** in the polymerization process. An active center is generated in this process to begin polymerization.

A source of **free radicals** is needed to initiate the chain reaction. These free radicals are usually produced by **decomposing a peroxide** such as di-tert-butyl peroxide or benzoyl peroxide, shown below. In the presence of either **heat or light**, these peroxides decompose to **form a pair of free radicals** that contain an unpaired electron.



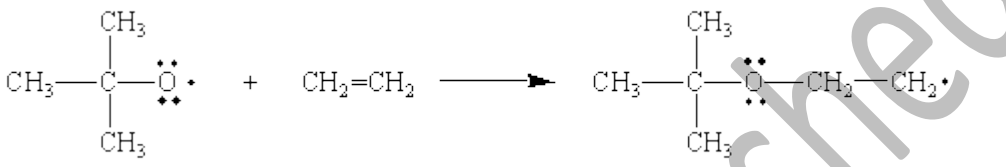


Chain-initiation step

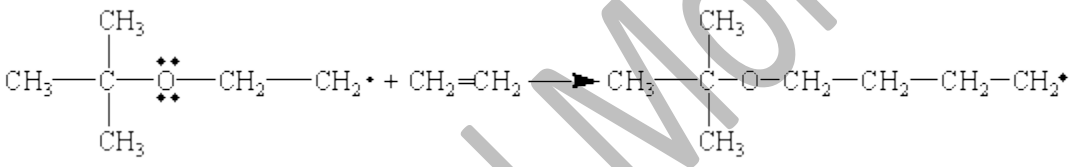
2) Propagation:

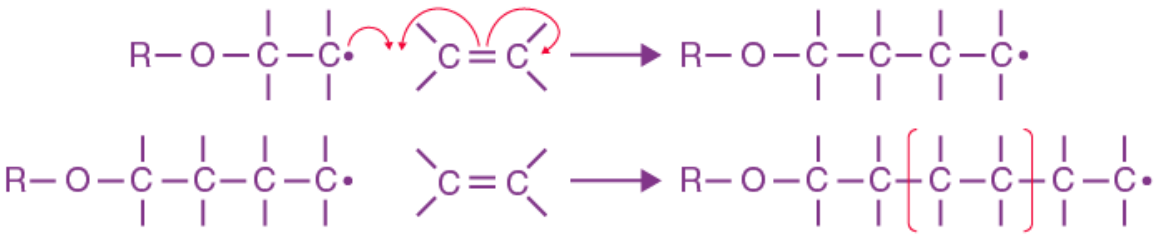
The free radical produced in the chain-initiation step adds to an alkene to form a new free radical.

A polymer spends most of its time **expanding its chain** length or propagating. After initiation of free radical, it attacks another **monomer subunit**. It uses one of the **pi bond electrons to form a stable bond** with another carbon atom. The other electron returns to the second carbon atom, turning the whole molecule into a radical.



The product of this reaction can then add additional monomers in a chain reaction.





Chain-propagating step

3) Termination

Termination is the **final step** in the polymerization process. Termination occurs in different stages. If **longer chains are expected**, the **initiator concentration should be less; otherwise, many short chains will form**.

Termination occurs whenever two free radicals come in contact with one another (not shown). The two free electrons form a covalent bond and the free radical on each molecule no longer exists.