# The General Questions We Can Ask

- **What are polymers?**
- **How they are synthesized?**
- **What are their applications?**

## 1. Significance of Polymers

- Polymer constitutes an important material for meeting demand in specialized fields.
- The human life would have been quite miserable without their applications. In fact, polymer forms the backbone of modern society.
- The idea is often expressed that we live in 'a plastic age‘.
- Polymers are large molecules built up by covalent linking of a large number of much smaller molecules.
- The volume of synthetic polymers produced worldwide is greater than the volume of steel.

- Therefore, the synthesis of tailor–made macromolecules with desired molecular design and understanding of the **Q**uantitative **S**tructure-**P**roperty **R**elationships (**QSPR**) have become main focus area for synthetic chemists.
- An increasing tendency to design “intelligent polymers”.

## 2. Background of present lectures

- Polymerization of vinyl monomers is of enormous industrial importance.
- Many vinyl monomers polymerized by free radical, ionic and ionic coordinate polymerization mechanism (Fig. 1).

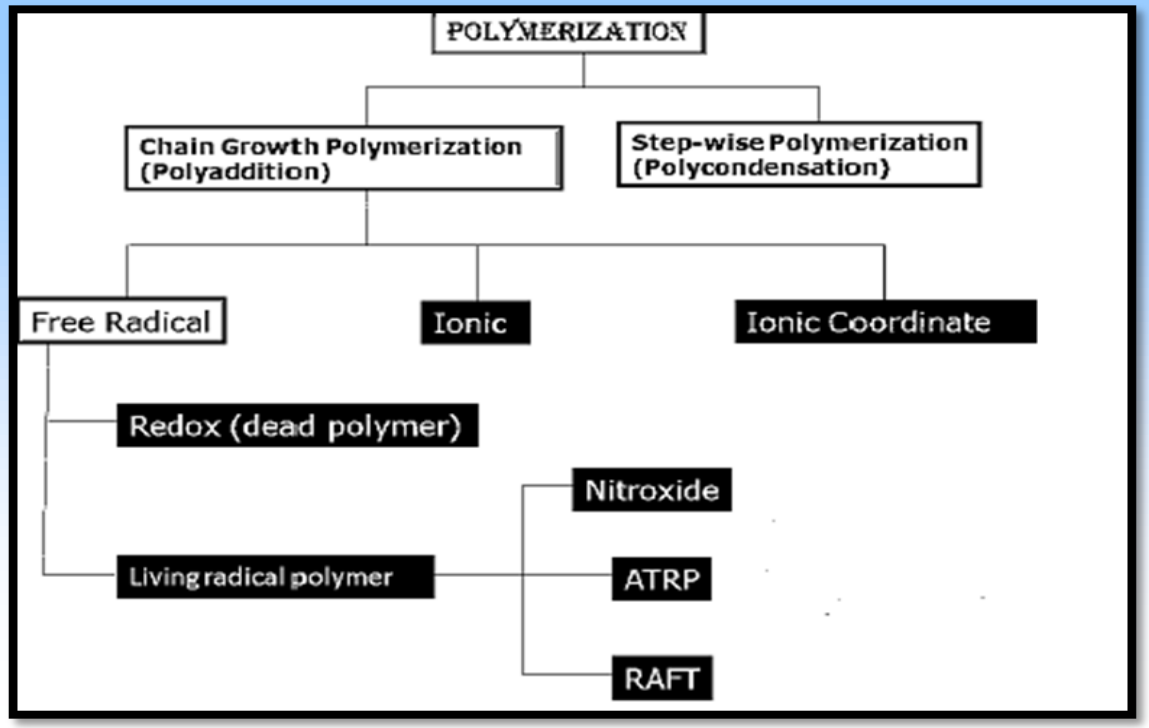



**Figure 1:** Route of the Polymerization

- For several reasons, radical polymerization has significant advantages over ionic and coordination polymerizations.

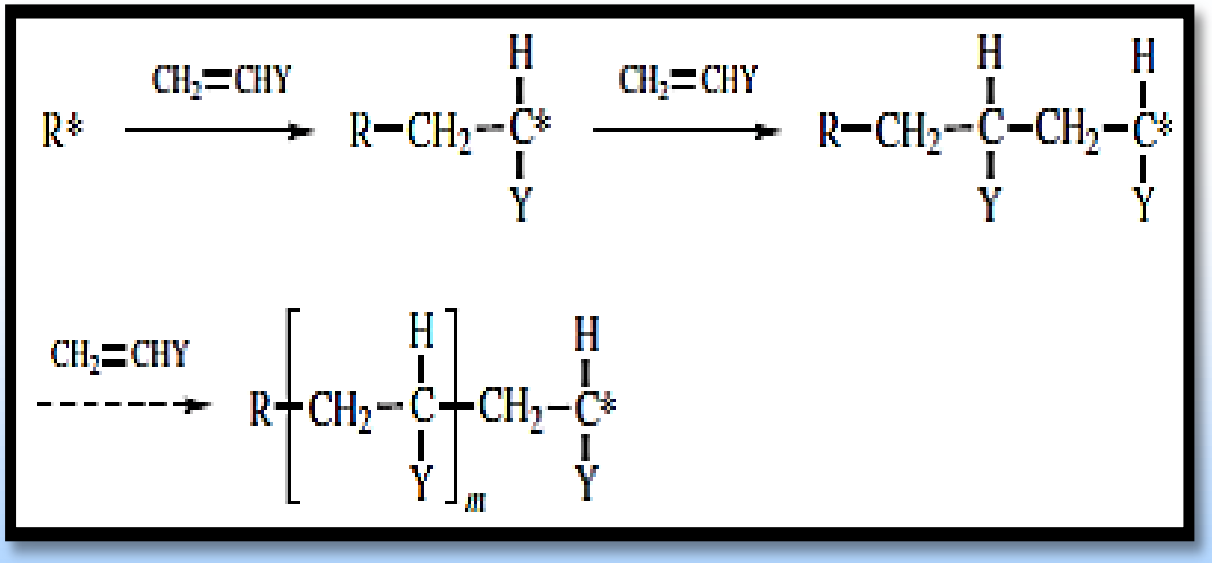
1. The reaction conditions are usually not as demanding,
2. They exhibit a tolerance of trace impurities, and
3. It is possible to polymerize a variety of monomers by radical polymerization.

- Because of these characteristics it is possible to prepare high molecular weight polymers without removing the stabilizers present in commercial monomers, in the presence of trace amounts of oxygen.
- In solvents, they have not been rigorously dried, or even in aqueous media, depending of course on their final applications.

- Today Free radical polymerization accounts for a large portion of mass-produced polymers.
- This technique is applied to prepare latexes to be used in paints, high molecular weight poly(methyl methacrylate) for safety glass (Plexiglas®) or foamed poly(styrene) to be applied in coffee cups.

# 3. Free radical polymerization

- FRP is a type of chain growth polymerization, along with anionic, cationic and coordination polymerization.
- FRP is one of the processes of polymer formation in which polymer grows by successive addition of the monomer units.




**Scheme 1:** Free radical polymerization.

- The overall kinetics can be described by eq. (1.1).

$$R_p = k_p [M] (f k_d [I]_o / k_t)^{1/2} \qquad (1.1)$$

- Molecular weights depend on the termination rate as well as the rate of transfer.

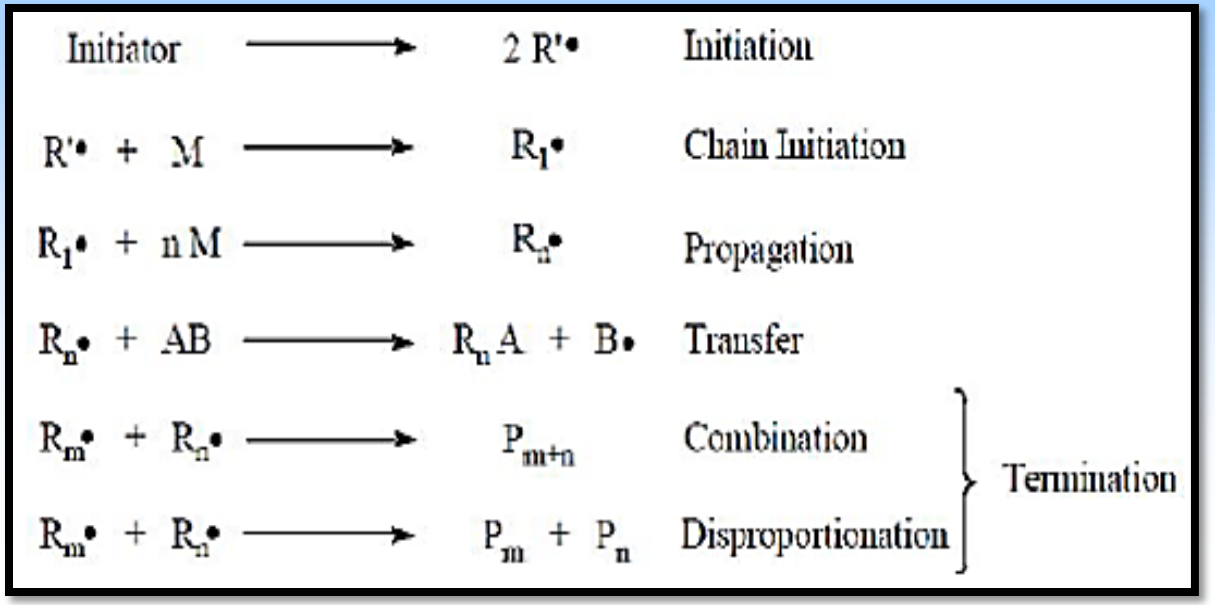
- The degree of polymerization depends reciprocally on the square root of radical initiator concentration when the contribution of transfer neglected, as shown in eq. (1.2):

$$DP_n = k_p [M] (f k_d [I]_o k_t)^{-1/2} \qquad (1.2)$$

- An advantage of free radical route is that the polymerization proceeds in a relatively facile manner: rigorous removal of moisture is unnecessary and polymerization carried out either in the bulk phase or in solution.

# 3.1 Mechanism of Free Radical Polymerization

1. Initiation:
2. Propagation:
3. Transfer:
4. Termination:




**Scheme 2:** Free radical polymerization mechanism

The limitations of the free radical polymerization are:

1. Due to diffusion-controlled termination reactions between growing radicals, little control over molar mass distribution,

2. Since, the typical life time of a propagating chain is very short, in the range of 1s, it is not possible to synthesize block copolymers or other chain topologies, and

3. There is no control over the polymer tacticity.

## 3.2 Advantages and Disadvantages of FRP

- Some advantages of radical polymerizations, with respect to other techniques, are

1. the relative insensitivity to impurities,
2. the moderate reaction temperatures and
3. the multiple polymerization processes available

- Some disadvantages related to the mechanism of free radical polymerization are

1. the poor control of the molecular weight and the molecular weight distribution, and
2. the difficulty (or even impossibility) of preparing well-defined copolymers or polymers with a predetermined functionality.

- To overcome these disadvantages, new techniques were developed based on either **reversible deactivation** of polymer radicals or a **degenerative transfer process**, called ‘living’ or Controlled Radical Polymerizations (CRP).

- It consist the following three type of polymerizations:

1. **A**tom-**T**ransfer **R**adical **P**olymerization (**ATRP**).
2. **S**table **F**ree-**R**adical **P**olymerization (**SFRP**).
3. **R**adical **A**ddition-**F**ragmentation **T**ransfer (**RAFT**).

## 4. Living/Controlled Radical Polymerization

- This method relies on completely pure reactions so that no termination caused by impurities occurs.
- These polymerizations stop only when there is no more monomer and not when termination occurs.
- The polymerization can continue upon the addition of more monomer.
- Block copolymers can be made by this way.
- This type of polymerization can be stopped and restarted at any time.

- Complete living radical polymerization allows for control of molecular weight and dispersity.

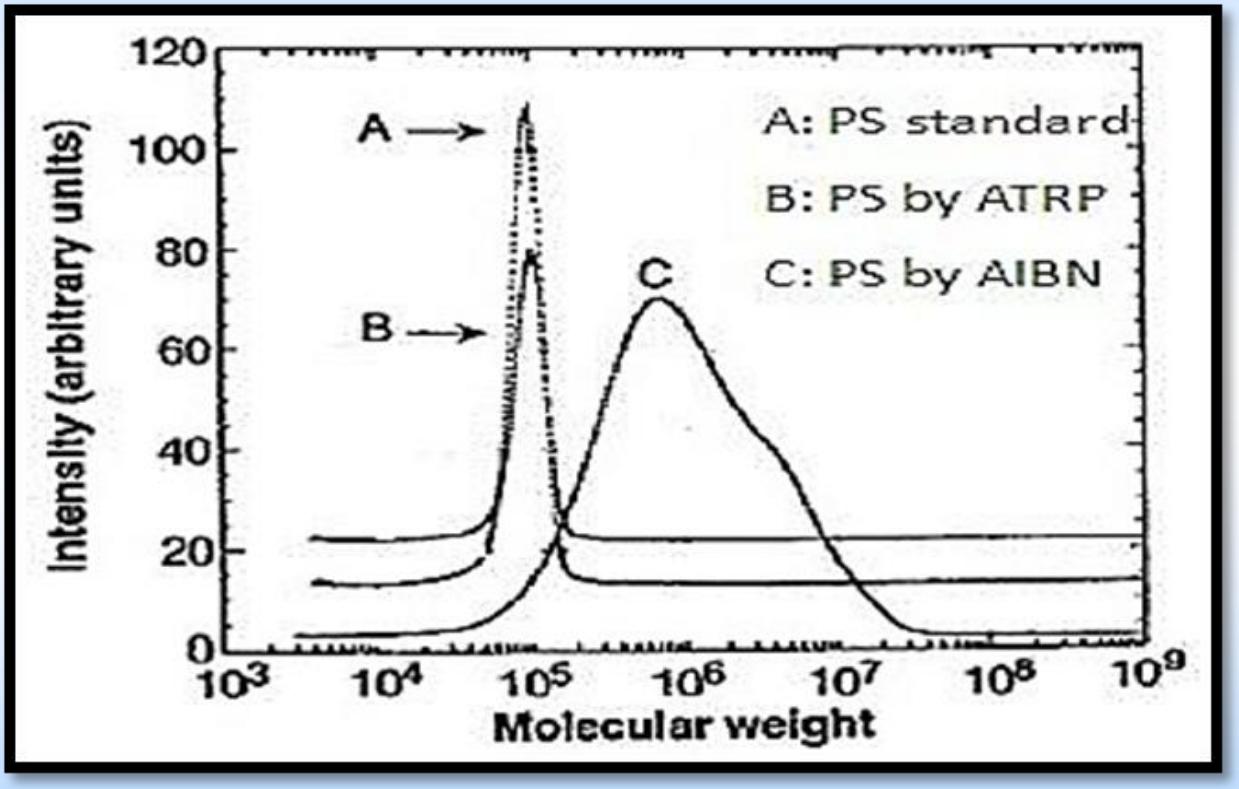



**Figure 2:** Specialty of living radical polymerization.

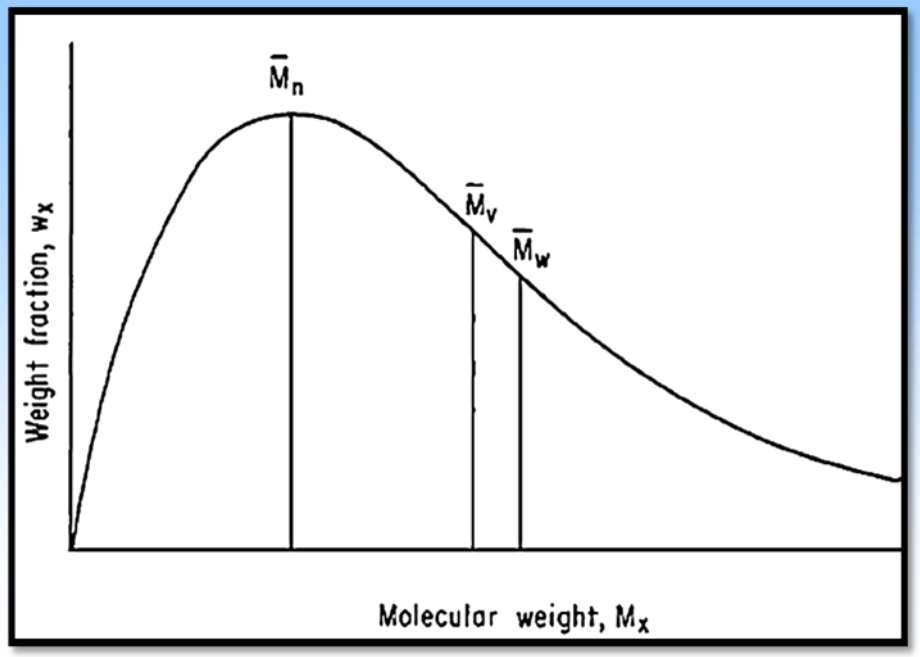



**Figure 3:** Polymer molecular weight distribution, Mw>Mv>Mn,

Dispersity = Mw/ Mn