

Polymerization by Addition

Addition polymerization can be divided into two main types:

- 1- Polymerization with chain growth by free radicals.
- 2- Ionic polymerization : { Anionic polymerization and
 Cationic polymerization.

If the aggregates large substitutes, it hinders the polymerization process due to steric hindrance. While If the stereochemistry of the kind that pulls the electrons it would lead to reducing the carbon density electronic connected double bonds , this case polymerization of monomer preferably anionic polymerization, like (Acrylonitrile).

If the aggregates and substitutes (electron donating groups), they increase the electron density at the double bond, and preferably monomer polymerized by cationic polymerization, like polypropylene.

Generally , the most monomer can polymerize by free radical polymerization because it is not steric hindrance as in table;

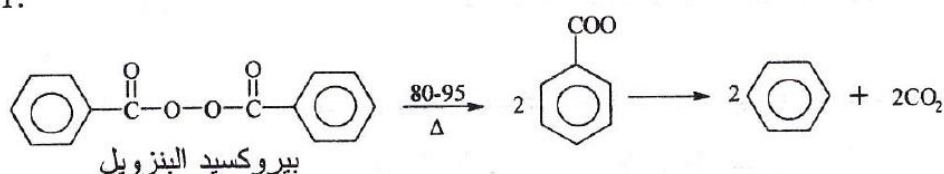
نوع البلمرة			التركيب الكيميائي	المونومير
أنيونية	كاتيونية	جذور حرة		
√	√	√	$\text{CH}_2=\text{CH}_2$	إيثيلين
√	√	√	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	١، ٣ - بيوتاديين
×	√	×	$\begin{array}{c} \text{R} \\ \diagup \\ \text{C}=\text{CH}_2 \\ \diagdown \\ \text{R} \end{array}$	١، ١ - داي الكيل أوليفين
√	√	√	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array}$	ستيرين
×	×	√	$\begin{array}{c} \text{HC}=\text{CH}_2 \\ \\ \text{X} \end{array}$	أوليفين أحادي الهالوجين
×	×	√	$\text{R}-\text{C}(=\text{O})-\text{O}-\text{CH}=\text{CH}_2$	أسترات الفينيل
√	×	√	$\text{H}_2\text{C}=\text{CH}-\text{C}(=\text{O})-\text{OMe}$	أكريلات الميثيل
√	×	√	$\text{CH}_2=\text{CH}-\text{CN}$	أكريلونتريل
√	×	√	$\begin{array}{c} \text{CH}_3\text{C}=\text{CH}_2 \\ \\ \text{CN} \end{array}$	ميثيل أكريلونتريل
√	×	√	$\text{H}_2\text{C}=\text{CH}-\text{C}(=\text{O})-\text{NH}_2$	أكريل أميد
√	×	√	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C}-\text{C}(=\text{O})-\text{NH}_2 \end{array}$	ميثيل أكريل أميد
×	√	×	$\text{H}_2\text{C}=\text{CH}-\text{O}-\text{R}$	إيثر الفينيل

Type of Initiators Used in Free Radical Polymerization

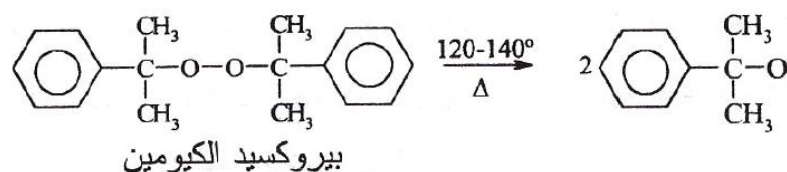
There are many types of initiators which used in addition polymerization for starting this reaction by its decomposition to free radical and active center as following:

Thermal decomposition: The initiator is heated until a bond is homolytically cleaved, producing two radicals (Figure 1). This method is used most often with organic peroxides or azo compounds. At some times this type called (Thermal Catalysts) , such as (benzoyl peroxide) and (cumene peroxide).

1.



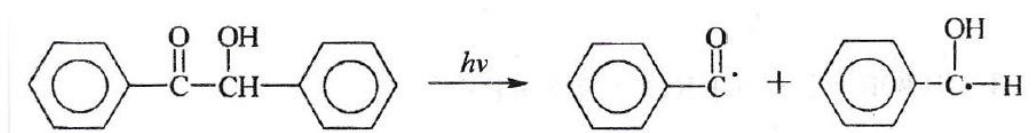
2.



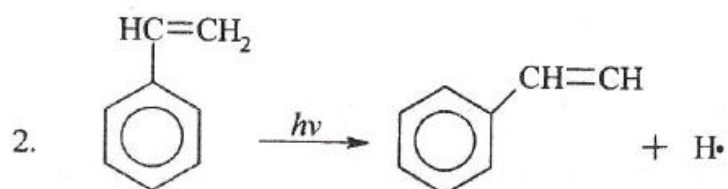
Photolysis: Radiation cleaves a bond homolytically, producing two radicals (Figure 2). This method is used most often with metal iodides, metal alkyls, and azo compounds.

Photoinitiation can also occur by bi-molecular H-abstraction when the radical is in its lowest triplet excited state.[4] An acceptable photoinitiator system should fulfill the following requirements:[4]

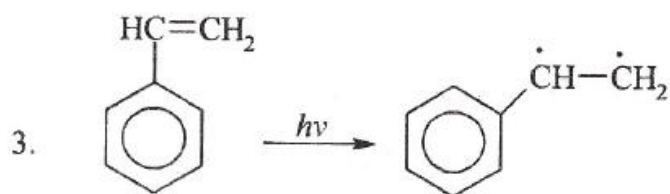
- High absorptivity in the 300-400 nm range.
- Efficient generation of radicals capable of attacking the olefinic double bond of vinyl monomers.
- Adequate solubility in the binder system (prepolymer + monomer).
- Should not impart yellowing or unpleasant odors to the cured material.
- The photoinitiator and any byproducts resulting from its use should be non-toxic.



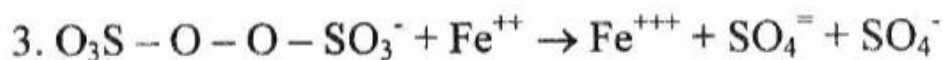
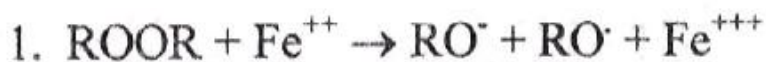
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Redox reactions: Reduction of hydrogen peroxide or an alkyl hydrogen peroxide by iron (Figure 3).



CHAIN-GROWTH POLYMERIZATION

Chain-growth polymerizations require the presence of an initiating molecule that can be used to attach a monomer molecule at the start of the polymerization. The initiating species may be a radical, anion, or cation, as discussed in the following sections. Free-radical, anionic, and cationic chain-growth polymerizations share three common steps—initiation, propagation, and termination. Whether the polymerization of a particular monomer can occur by one or more mechanisms (i.e., free radical, anionic, or cationic) depends, in part, on the chemical nature of the substituent group. In terms of general guidelines, monomers with an electronwithdrawing group can polymerize by an anionic pathway, while those with an electrondonating group follow a cationic pathway. Some important vinyl monomers such as methyl methacrylate and styrene can be polymerized by more than one pathway (e.g., free-radical and anionic).

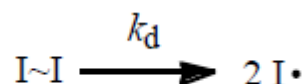
Free-Radical Polymerization mechanism and Copolymerization

Like other chain-growth polymerizations, a free-radical polymerization has three principal steps:

- Initiation of the active monomer
- Propagation or growth of the active (free-radical) chain by sequential addition of monomers
- Termination of the active chain to give the final polymer product

These steps and their associated kinetics are described next in general terms for free-radical polymerizations, with the polymerization of styrene used as an example.

The Initiation Step. Initiation in a free-radical polymerization consists of two steps—a dissociation of the initiator to form two radical species, followed by addition of a single monomer molecule to the initiating radical (the association step). The dissociation of the initiator ($I-I$) to form two free-radical initiator species ($I\cdot$) can be represented as



where k_d is the dissociation rate constant. The dissociation rate constant follows an Arrhenius dependence on temperature given as

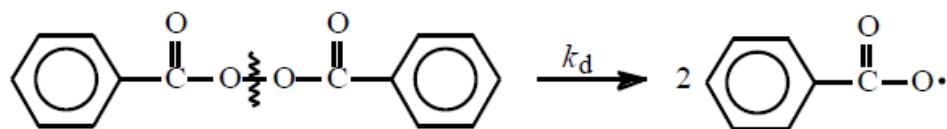
$$k_d = A \exp(-E_a / RT)$$

where E_a is the activation energy for dissociation. In addition to a strong dependence on temperature, dissociation rate constants for different initiators vary with the nature of the solvent used in solution polymerization, as shown by data given in Table:

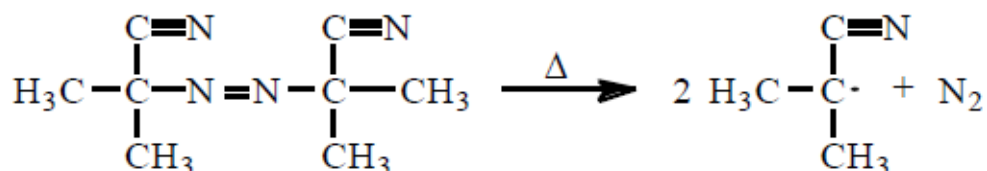
Dissociation Rate Constants for Some Common Initiators in Solution

Initiator	Solvent	$T (^{\circ}\text{C})$	$k_d (\text{s}^{-1})$	$E_a (\text{kJ mol}^{-1})$
Benzoyl peroxide	Benzene	30	4.80×10^{-8}	116
		70	1.38×10^{-5}	
	Toluene	30	4.94×10^{-8}	121
		70	1.10×10^{-5}	
AIBN	Benzene	40	5.44×10^{-7}	128
		70	3.17×10^{-5}	
	Toluene	70	4.00×10^{-5}	121

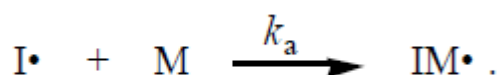
Initiators for free-radical polymerizations include any organic compound with a labile group, such as an azo ($-N=N-$), disulfide ($-S-S-$), or peroxide ($-O-O-$) compound. The labile bond of the initiator can be broken by heat or irradiation, such as UV- or γ -irradiation. An important example of a free-radical initiator is benzoyl peroxide that dissociates as



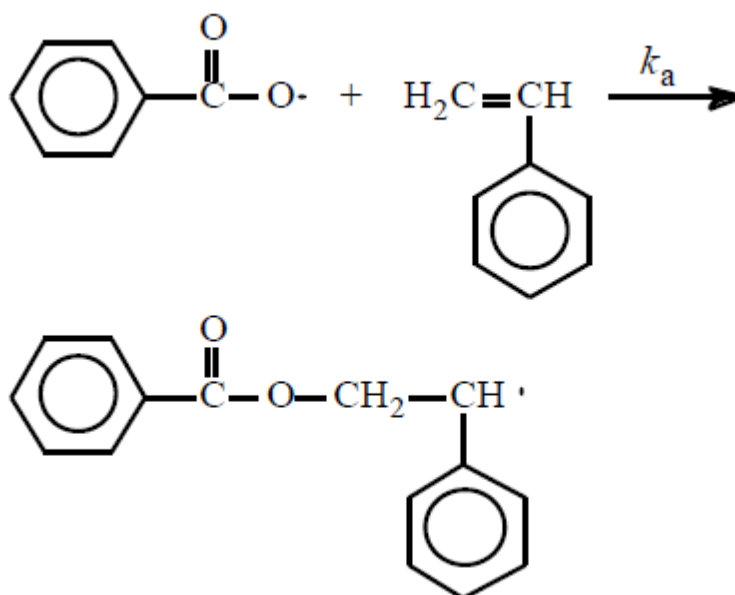
Another important group of free-radical initiators are the azo ($\text{R}-\text{N}=\text{N}-\text{R}$) compounds such as 2,2'-azobis(isobutyronitrile) (AIBN), which thermally decomposes to yield nitrogen and two cyanoisopropyl radicals ($\text{R}\cdot$) as



In the second step of initiation (i.e., association), a monomer molecule (M) is attached to the initiator radical. This addition step may be represented as:



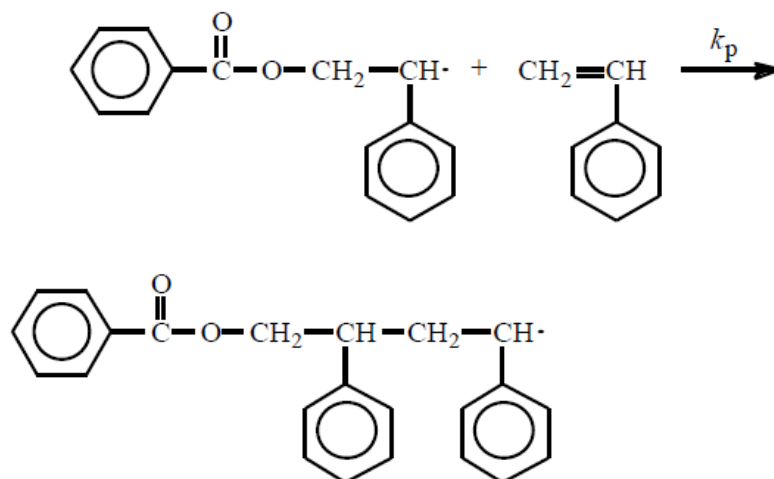
where k_a is the rate constant for monomer association. In the specific case of the polymerization of styrene initiated by benzoyl peroxide, the addition occurs as



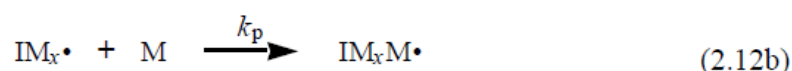
The Propagation Step. In the next step, called propagation, additional monomer units are added to the initiated monomer species as:



where k_p is the *propagation rate constant*. For styrene addition with benzoyl peroxide initiation, the first propagation step is

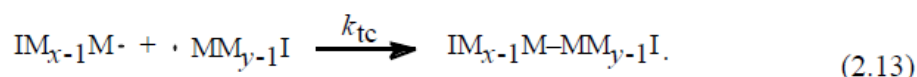


Additional monomers are added sequentially during subsequent propagation steps, as represented by the generalized equation

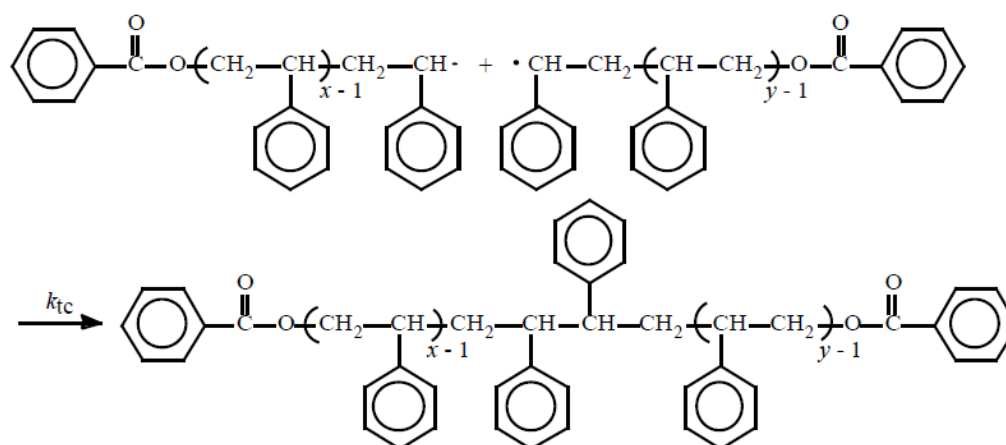


During the propagation step in vinyl polymerization, the energetically preferred placement of monomers is head-to-tail where the more substituted carbon atom is designated as the “head.” Head-to-head placement may occur, for example, during termination by combination as discussed in the next section.

Termination. Propagation will continue until some termination process occurs. One obvious termination mechanism occurs when two propagating radical chains of arbitrary degrees of polymerization of x and y meet at their free-radical ends. Termination in this manner occurs by *combination* to give a single terminated chain of degree of polymerization $x + y$ through the formation of a covalent bond between the two combining radical chains, as illustrated by the following reaction:

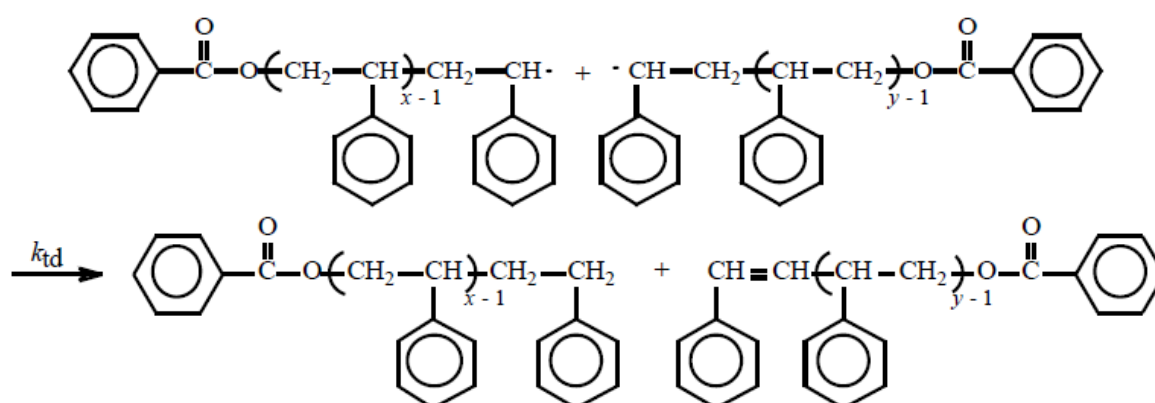
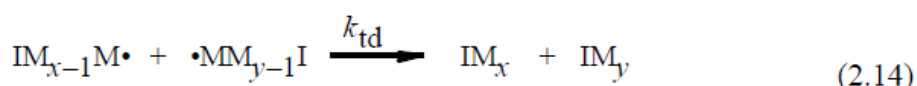


For the example of styrene polymerization, termination by combination gives the following chemical structure:

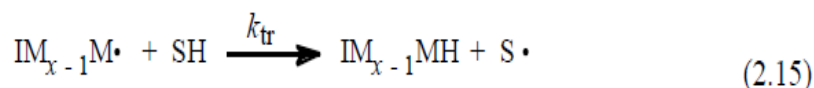


The above structure shows a single head-to-head placement of styrene units at the combination site.

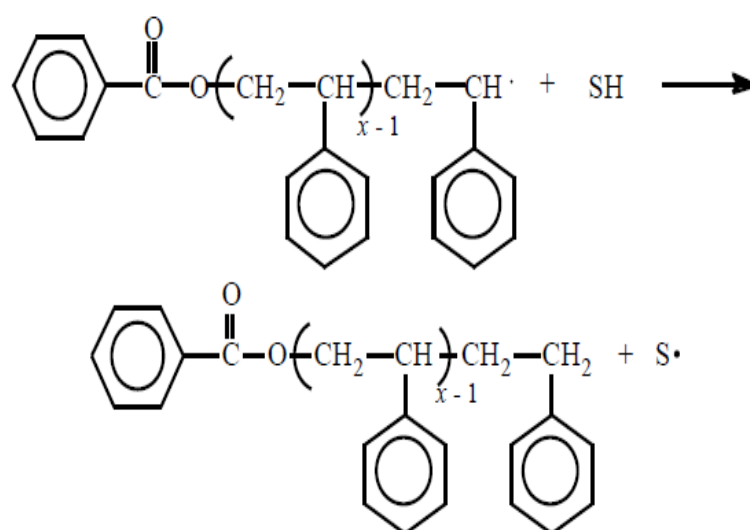
Termination also can occur by a *disproportionation* reaction to give two terminated chains, as illustrated below. In this case, one terminated chain will have an unsaturated carbon group while the other terminated end is fully saturated. In both cases of termination, one end (i.e., in termination by disproportionation) or both ends (i.e., in termination by combination) contain the initiating free-radical group of the initiator molecule. In the case of termination by combination, the benzoyl peroxide group caps *both* ends of the chain. This indicates the important difference between an initiator, which becomes part of the terminated chain, and a polymerization *catalyst*, which promotes the polymerization but is fully recovered at the end of the polymerization. Catalysts are used in cationic and coordination polymerizations as discussed in Sections 2.2.2 and 2.2.3.



In addition to termination by combination and disproportionation, another mechanism of termination is *chain transfer* by hydrogen abstraction from an initiator, monomer, polymer, or solvent molecule. In general terms, this process may be represented as



where SH represents a solvent or any other molecule with an abstractable hydrogen atom. In the specific case of the benzoyl peroxide-initiated polymerization of styrene, termination by chain transfer occurs as



As illustrated, the radical site is transferred to the chain-transfer agent (S^\bullet), which can then add monomer units to continue the polymerization process. Subsequent termination of the growing chain-transfer radical chain (SM_x^\bullet) will result in a terminated chain having one (i.e., termination by disproportionation) or two (i.e., termination by combination) chain-transfer (S) groups at the polymer ends.

Examples of propagation and termination rate constants are given in Table 2-3. Both k_p and k_t show a strong (Arrhenius) dependence upon temperature, as illustrated by data for styrene. Rate constants can vary by several orders of magnitude depending on monomer type (i.e., vary with the chemical nature of the substituent group in vinyl polymerization).