

- The addition polymerization can divide into three types:-
- 5.2.1. Free Radical Vinyl Polymerization.
- 5.2.2. Cationic Vinyl Polymerization.



5.2.3. Anionic Vinyl Polymerization.







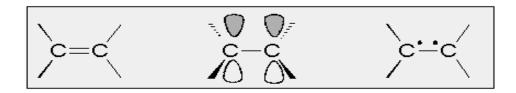


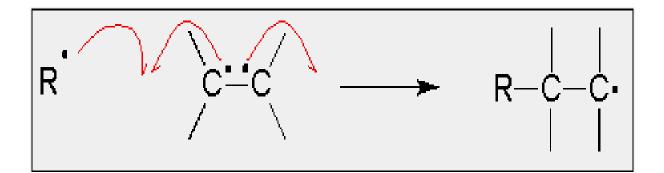
- It go through three steps:
- 1- Initiation Step. خطوة البداية
- 2-Propagation Step.خطوة التكاثر
- 3- Termination Step.خطوة النهاية





#### 5.2.1. Free Radical Vinyl Polymerization







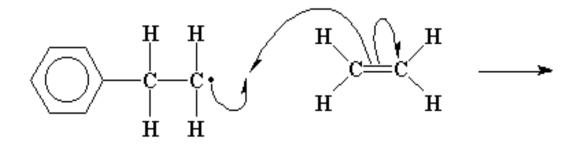


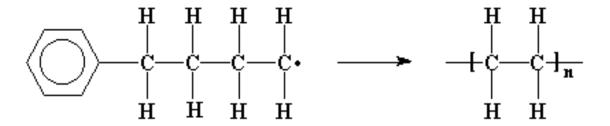
#### 5.2.1.1. Initiation Step:





#### 5.2.1.2. Propagation step:





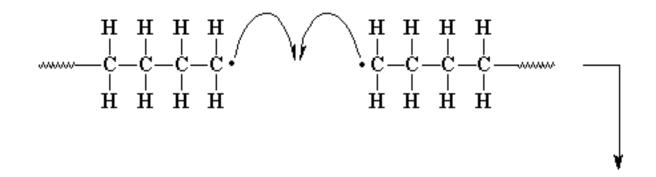


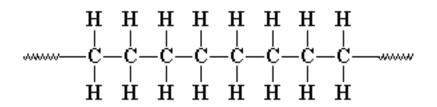


- This is called *coupling*. Coupling is one of two main types of *termination* reaction.
- Termination is the third and final step of a chain-growth polymerization.
- Initiation and propagation are the first two steps, of course.











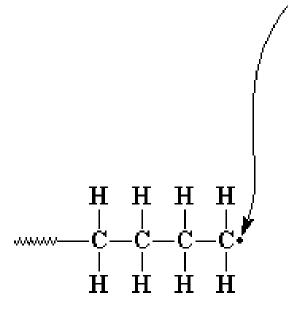


Another way in which our unpaired electrons can shut down the polymerization is called <u>disproportionation</u>.

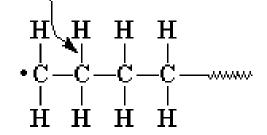




#### 5.2.1.3.2. Disproportionation



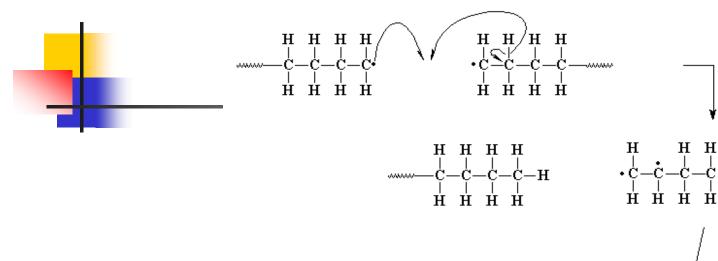
<u>This</u> electron can find a mate by swiping an electron from the pair of electrons which makes up <u>this</u> bond.

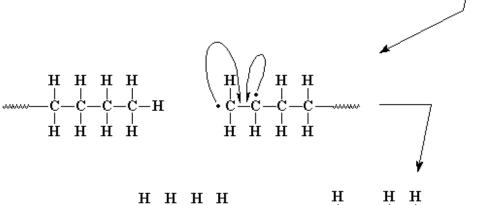




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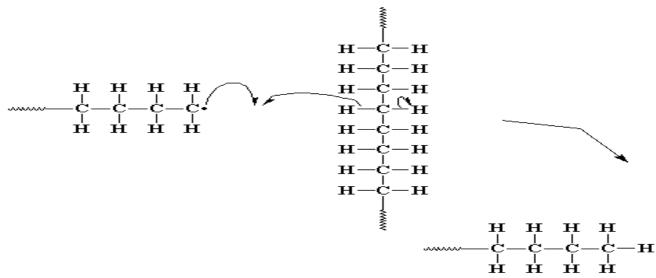


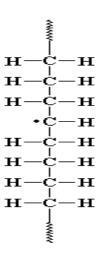


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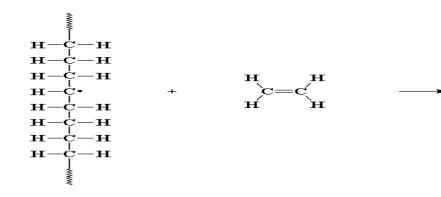


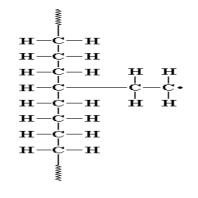




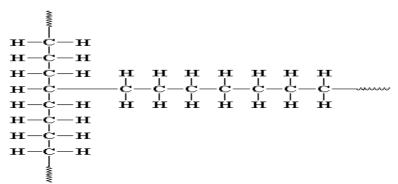














This branching has a big effect on how polyethylene behaves. To find out how, and how getting rid of branching helped make lowly polyethlyene better than Kevlar in <u>bullet proof vests</u>.









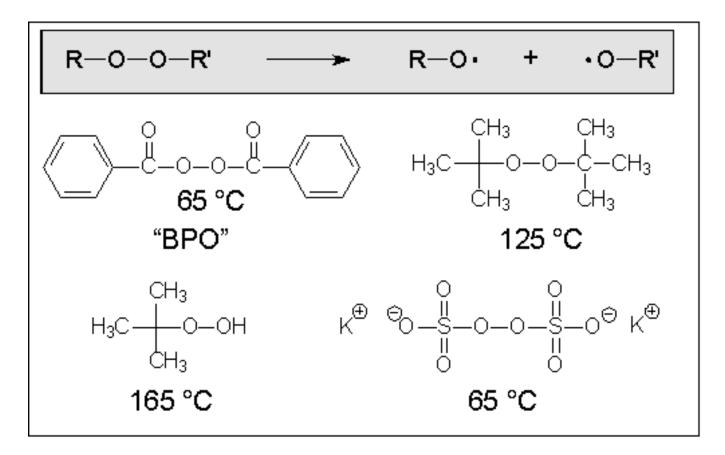


# Types of Initators:

- 1.Thermal initiators:
- Most common kind of FR initiator.
- Unimolecular decomposition.
- First order kinetics.
- Most common examples: peroxides or azo compounds.



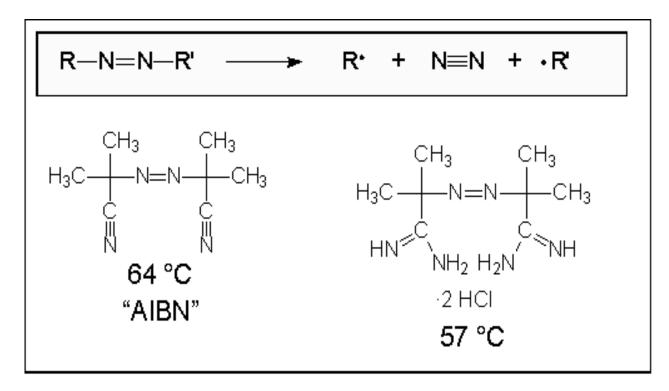
#### i) Peroxides:







#### ii) Azo compounds:





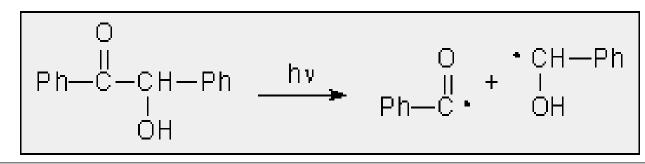
(Temperatures are for 10 hour half-lives.)

## 2-Redox initiators:

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + HO^{-} + HO^{-}$$



## 3- Photo-initiators:







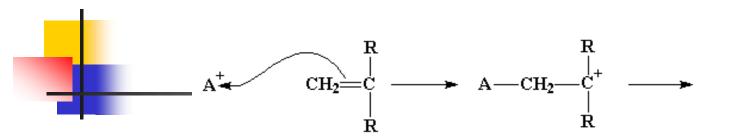




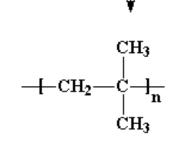


- Cationic vinyl polymerization is a way of making polymers from small molecules, or monomers, which contain carboncarbon double bonds.
- Its primary commercial use is for making polyisobutylene.



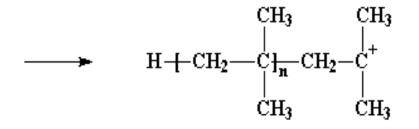


Note: When a line is drawn between two atoms, this represents a pair of electrons the atoms share. Sharing one pair of electrons makes a single bond. Sharing two pairs makes a double bond, shown by two lines. The curved arrows show the motion of a pair of electrons.



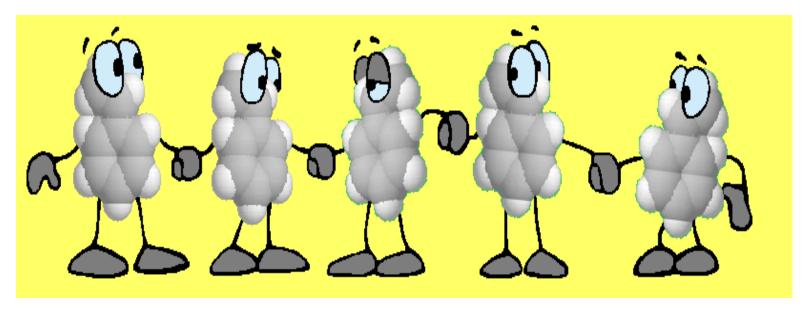




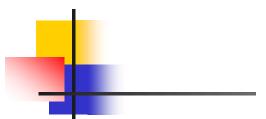


















# butyl lithium





- Now a little bit of the butyl lithium will always fall apart. Not a lot, but some.
- It falls apart to form a positive lithium cation and a negative butyl anion. We call an anion like this where the negative charge is on a carbon atom a carbanion





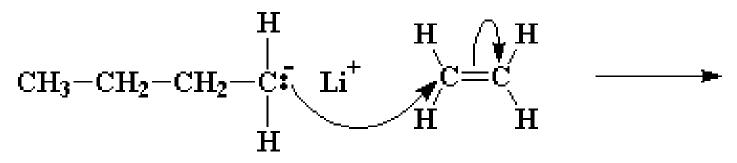




- This forms a new carbanion, with the negative charge resting on that carbon.
- The process in which the butyl lithium falls apart, and the butyl anion reacts with a monomer molecule is called <u>initiation</u>.















#### The Chain That Wouldn't Die

- Now while you may get this nagging feeling that this can't go on forever, that something has to put a stop to this convenient process. Funny thing, though: it doesn't stop!
- In many cases, the only thing that stops monomers from adding to the growing chain is that eventually there are no more monomer molecules in the beaker left to add!



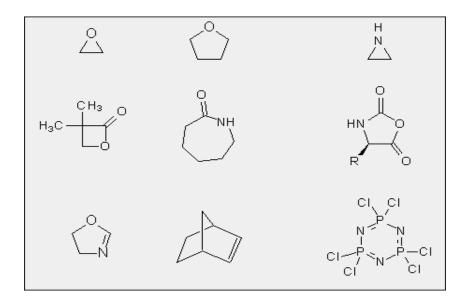


• And even then, if someone came along some time later and dumped *more* monomer into the beaker, they would add to the chain and the chain would grow some more!





## 5.3. Ring Opening Polymerization.







- Examples of Ring Opening Polymerization
- Polyesters:

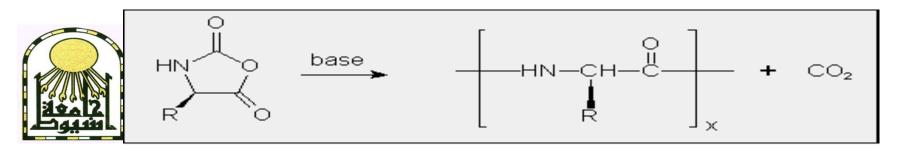
$$\begin{array}{c|c} CH_3 & O \\ H_3C & \xrightarrow{base} & \begin{array}{c|c} CH_3 & O \\ \hline \\ CH_2 & C \\ \hline \\ CH_3 & \end{array} \end{array}$$





## Polyamides:

#### • Ring Opening Polymerization of N-Carboxy Anhydrides





### Silicones:

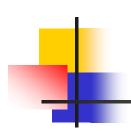
$$\begin{array}{c|c} CH_3\\ H_3C \searrow_{i-0}^{l} CH_3\\ O & Si \searrow_{CH_3}\\ H_3C \longrightarrow_{i-0}^{l} O & or\\ CH_3 & O & base & CH_3\\ CH_3 & CH_$$





 An example of a completely inorganic polymer that can be functionalized with organic groups after polymerization.





## 6. Copolymers

 1- Statistical Copolymers (Random)

 Also called random copolymers. Here the monomeric units are distributed randomly, and sometimes unevenly, in the polymer chain:



~ABBAAABAABBBABAABA~.



## 2- <u>Alternating Copolymers</u> (<u>Regular</u>):

 Here the monomeric units are distributed in a regular alternating fashion, with nearly equimolar amounts of each in the chain:





## 3- Block Copolymers

Instead of a mixed distribution of monomeric units, a long sequence or block of one monomer is joined to a block of the second monomer:



~AAAAA-BBBBBBBB~AAAAAA~BBB~.



## 4- Graft Copolymers

- As the name suggests, side chains of a given monomer are attached to the main chain of the second monomer:
- ~AAAAAA(BBBBBBBB~)AAAAAA(BBBB ~)AAA~.





Some Useful Copolymers			
Monomer A	Monomer B	Copolymer	Uses
H2C=CHCI	H2C=CCI2	Saran	films & fibers
H2C=CHC6H5	H2C=C- CH=CH2	SBR styrene butadiene rubber	tires
H2C=CHCN	H2C=C- CH=CH2	Nitrile Rubber	adhesives hoses(خراطیم)
H2C=C(CH3)2	H2C=C- CH=CH2	Butyl Rubber	inner tubes
F2C=CF(CF3)	H2C=CHF	Viton	(وسائد)Gaskets