Lecture 43

Types of Addition Polymerization

There are three types of addition polymerization:

1. Free Radical
2. Cationic
3. Anionic

Free Radical Polymerization:

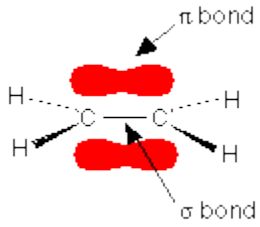
A variety of alkenes and their derivatives are polymerized in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. A free radical may be defined as an intermediate compound containing an odd number of electrons, but which do not carry an electric charge and are not free ions. For example, the polymerization of ethylene.

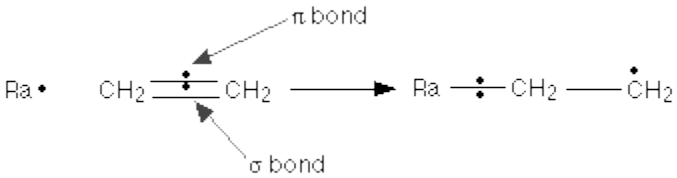
Initiation:

The oxygen reacts with some of the ethene to give an organic peroxide. Organic peroxides are very reactive molecules containing oxygen-oxygen single bonds which are quite weak and which break easily to give free radicals.

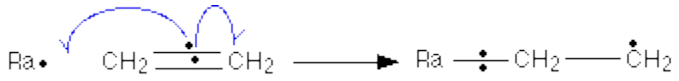
Chain Propagation:

In an ethene molecule, $CH_2=CH_2$, the two pairs of electrons which make up the double bond aren't the same. One pair is held securely on the line between the two carbon nuclei in a bond called a sigma bond. The other pair is more loosely held in an orbital above and below the plane of the molecule known as a $\pi\pi$ bond.





The sigma bond between the carbon atoms isn't affected by any of this. The free radical, Ra•, uses one of the electrons in the ππ bond to help to form a new bond between itself and the left hand carbon atom. The other electron returns to the right hand carbon. You can show this using "curly arrow" notation if you want to:

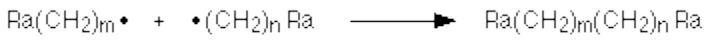


This is energetically worth doing because the new bond between the radical and the carbon is stronger than the ππ bond which is broken. You would get more energy out when the new bond is made than was used to break the old one. The more energy that is given out, the more stable the system becomes. What we've now got is a bigger free radical - lengthened by CH_2CH_2. That can react with another ethene molecule in the same way:

So now the radical is even bigger. That can react with another ethene - and so on and so on. The polymer chain gets longer and longer.

Chain Termination:

The chain does not, however, grow indefinitely. Sooner or later two free radicals will collide together.



That immediately stops the growth of two chains and produces one of the final molecules in the poly(ethene). It is important to realise that the poly(ethene) is going to be a mixture of molecules of different sizes, made in this sort of random way.

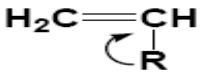
Ionic Polymerization:

The addition polymerization that takes place due to ionic intermediate is called ionic polymerization. Based on the nature of ions used for the initiation process. ionic polymerization is classified into two types; Cationic polymerization and Anionic polymerization

Anionic Initiation:

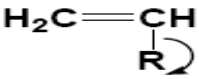
Anionic initiation is the polymerization of monomers. Here the R group is electron-withdrawing and Promotes the formation of a stable carbanion.

Cationic



R - Electron donating

Anionic



R - Electron withdrawing

Propagation Parameters:

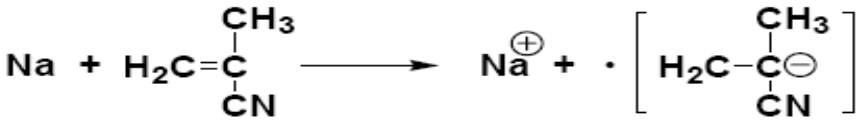
It involves the polymerization of monomers that have strong electron-withdrawing groups. Examples are acrylonitrile, vinyl chloride, Methyl methacrylate and styrene. Propagation of chain depends on ion separation, the nature of the solvent and nature of the counter Ion.

Electron Withdrawing Group:

In organic chemistry, an electron donating group (EDG) or electron releasing group (ERG) is an atom or functional group that donates some of its electron density into a conjugated π system via resonance or inductive electron withdrawal, thus making the π system more nucleophilic. Weak electron-withdrawing group requires a strong base initiator. While strong electron-withdrawing groups only a weak base initiator is required.

Electron Transformation to Donor:

Initiation mechanism (c) requires the direct transfer of an electron. It is transferred from donor to the monomer in order to form a radical anion. This can be achieved by using an alkali metal.



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