Illustrate in various ways degradation of polymer take place. Also discuss mechanism & kinetics of degradation.

Introduction :-

Polymer degradation means change in the properties such as its lustre & strength either during the fabrication or during the daily usage.

The term 'degradation' implies a decrease in molecular weight of polymer.

As- we show that a plastic bucket left for long in the sun & rain & loses its lustre & strength. This deterioration in properties is due to a phenomenon called 'Polymer Degradation' which is due to by an uncontrolled change in the molecular weight or constitution of the polymer.

A polymer can suffer degradation mainly

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Many of the fabrication processes such as extrusion or moulding involve heating, which the polymer may not be able to endure and as a consequence, may just degrade.

similarly, plastics articles have to face mechanical stresses, solar radiations, atmospheric Oxygen, moisture, etc. These factors may degrade the polymer. The polymer degradation is not always undesirable, in some cases it is advantageous.

Example: when a space aircraft re-enters the earth's atmosphere, then intense heat is generated. This heat is capable of melting the metal and even it explode the aircraft.

To avoid such a situation, the space craft is covered by a 'heat shield' which is made of polymer based material. With the influence of heat, polymer may degrade but take away from the generated heat. In this way, the aircraft is protected.

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* Types of degradation:-
There are two types of degradation:-
(a) Chain end degradation.
(b) Random degradation.

(a) Chain end-degradation:-
This type of degradation starts from ends of chain due to which successive release of monomer units takes place. This type of degradation is actually the reverse of monomer the propogation step in chain polymerisation. So, due to this reason, this is called 'depolymer-isation'. We may imagine that the propagation step in polymerisation to represent the 'closing of a zip' & depolymerisation the 'opening of the zip'. So, it is also termed as 'unzipping'. The scission is almost like cutting off successively a long strip of paper into small bits from its end.
→ By which the molecular weight of the polymer decreases slowly & a large quantity of the monomer is liberated simultaneously.

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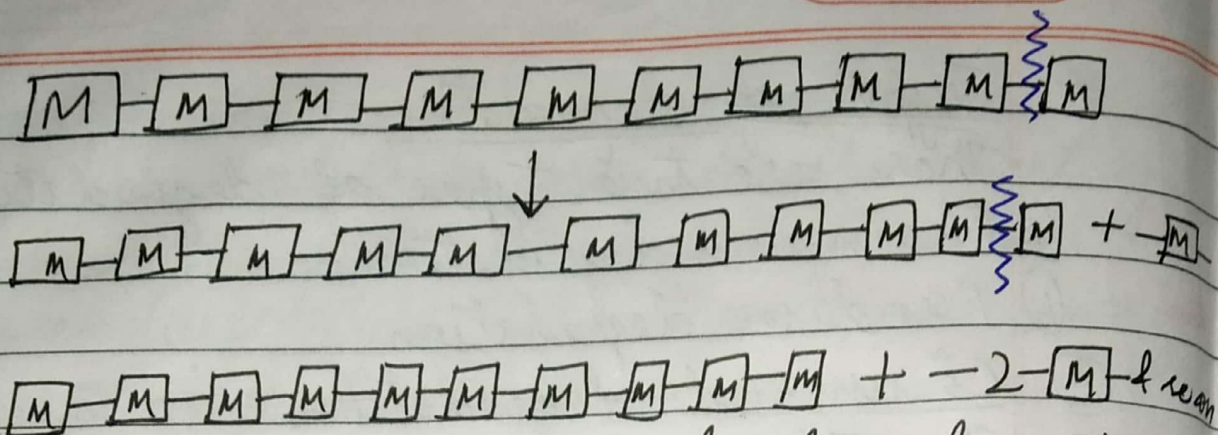

ntation of a polymer molecule undergoing end degradation.

Each block ⟶ show one monomeric unit

Polymers which are formed by chain polymerisation have been found to be more susceptible to unzipping or chain end degradation. But all such polymers do not undergo unzipping straightway.

Examples

When polymethylmethacrylate heated to 300°C under vacuum, depolymerises to give back the monomer in an almost quantitative yield.

The unzipping starts from the active chain ends formed. Infact, depolymerisation is a useful method for recovering the monomer from waste polymethyl methacrylate with recovery of almost 100%.

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In general, ~~too~~ it can be said that chain end degradation occurs when the back-bone bonds are weaker than the bonds of the side groups & only with polymer molecules carrying active chain ends with a free radical, cation, anion, etc.

Generally, chain end degradation may be represented as:-

$$M_n^{\cdot} \longrightarrow M_{n-1}^{\cdot} + M$$
$$M_{n-1}^{\cdot} \longrightarrow M_{n-2}^{\cdot} + M$$
$$M_{n-2}^{\cdot} \longrightarrow M_{n-3}^{\cdot} + M \quad \text{& so on}$$

where, $M_n^{\cdot}$, $M_{n-1}^{\cdot}$, $M_{n-2}^{\cdot}$ represents the polymer chain made up of so many monomer units & carrying on active end group where, (M) is the monomer

(b) Random Degradation:-

This takes place at any random point along the polymer chain instead of at the end chain.

This type of degradation is the reverse of the polycondensation process. It is shown by the following equation.

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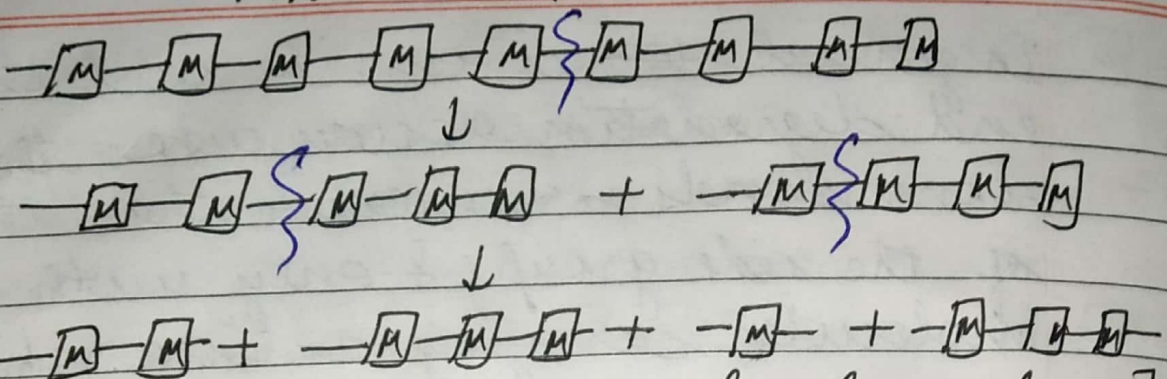
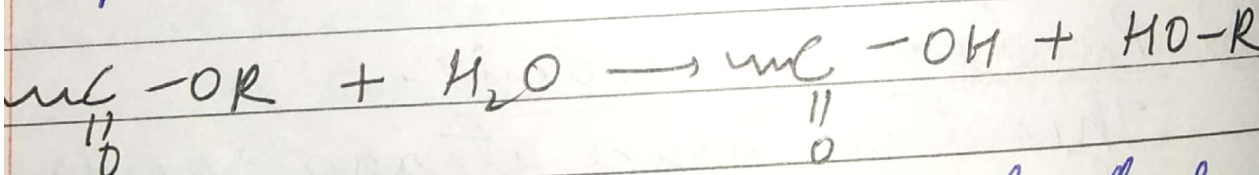
$M_n \longrightarrow M_n + M_1$



entation of a polymer molecule undergo] dam degradation.

In this type of degradation, polymer undergoes degradation into low molecular weight fragments but practically no monomer is liberated. Almost all polymers can undergo random degradation.

Random degradation of polyester can be represented as :-



In random degradation of polyethylene, a H-atom undergo migration from one C-atom to another resulting the formation of two fragments. It is shown as :-

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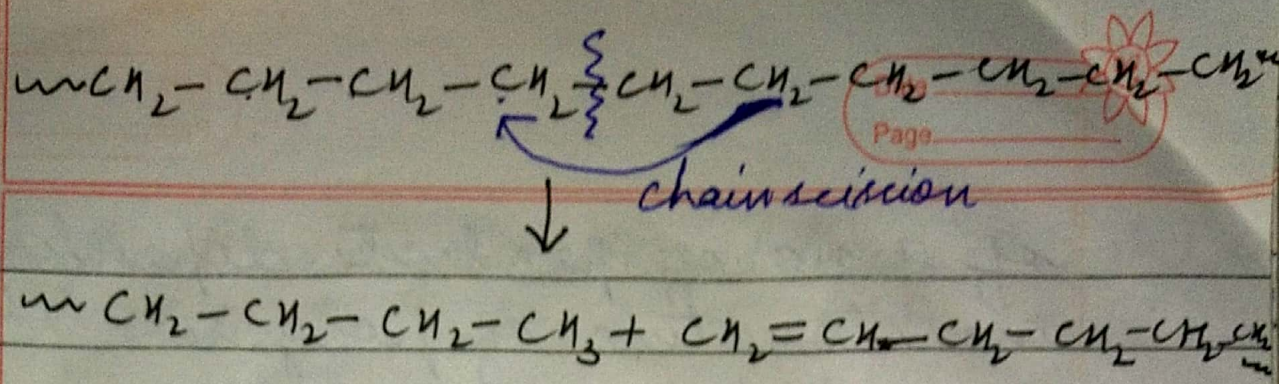

For random degradation to take place, it is not necessary for a polymer chain to have an active site. In random degradation, a sudden decrease in molecular weight takes place without release of the monomer.

Degradation of polymer may be brought by:-

1. By physical factors like heat, light or mechanical stress.
2. By chemical agents as oxygen, ozone, acid or alkalies.

(A) Thermal Degradation:-

Degradation of polymer under the influence of heat is known as thermal degradation. It may take place either by unzipping or randomly. The unzipping mechanism leads to the formation of pure monomer, while random degradation leads to the formation

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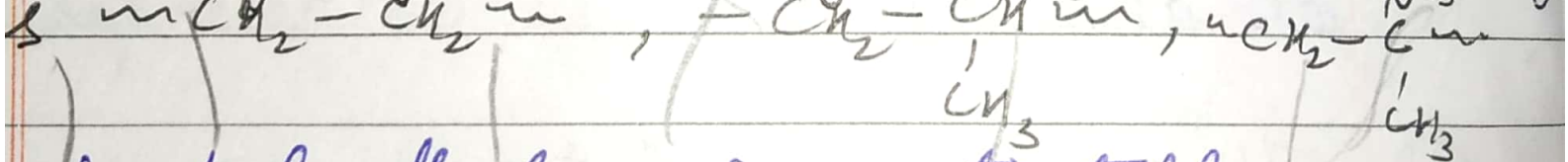
of a no. of products, depending on the structure of polymer.

Factors affecting the C-C bond stability:-

The presence of substituents on the C-C chain:-

Because many polymers have a C-C chain or backbone, so their thermal stability depends on the stability of C-C bonds. As the no. of substituents increase, the stability of polymer backbone decrease as:-

polyethylene > polypropylene > polyisobutylene



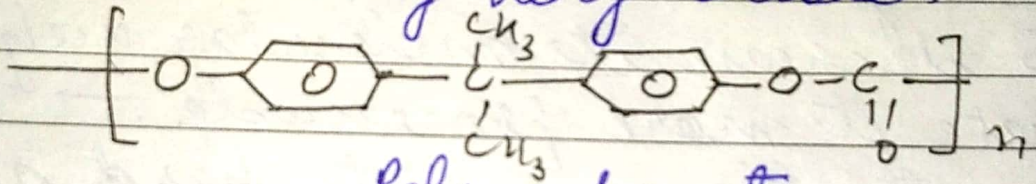
ie polyethylene is most stable.

Although, all the substituents do not always decreases the thermal stability of the polymer.

Example: Polytetrafluoroethylene (PTFE) or Teflon is the most stable polymer. It is thermally stable upto 400°C

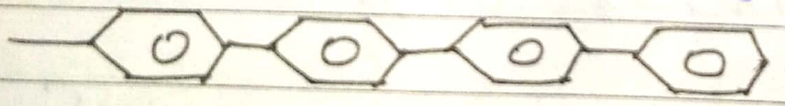
without undergoing degradation. This thermal stability is due to the high bond dissociation energy of C–F bonds.

② Presence of aromatic ring :-
The thermal stability of the polymer has been found to increase by the presence of aromatic groups in the polymer backbone, as Polycarbonate is thermally very stable.



Polycarbonate.

Polyphenylene is thermally very stable than polycarbonate since backbone chain is formed by aromatic rings.



(Polyphenyl
-ene

③ The presence of oxygen atom in the polymer chain & branching also make polymers susceptible to thermal degradation.

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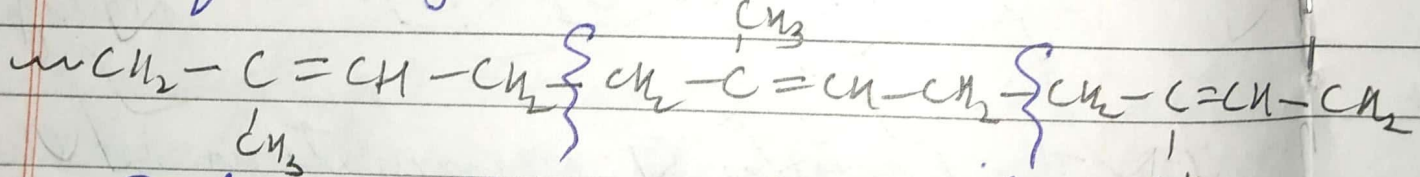
(B) **Mechanical Degradation**

(a) (b) (c)

When a polymer, such as polystyrene is dissolved in a suitable solvents & subjected to vigorous stirring or beating, it undergoes considerable molecular degradation. This process is known as 'Mechanical Degradation'.

Ans: In rubber industry, the rubber is actually masticated by passing it through two rotating roller in order to decrease its molecular weight and make it more processable. → This mastication converts hard and tough rubber into a soft, supple & semisolid mass.

We know that rubber is polyisoprene with the following structure:-



Isoprene unit Isoprene unit Isoprene unit.

In this mechanical degradation following steps are followed:-

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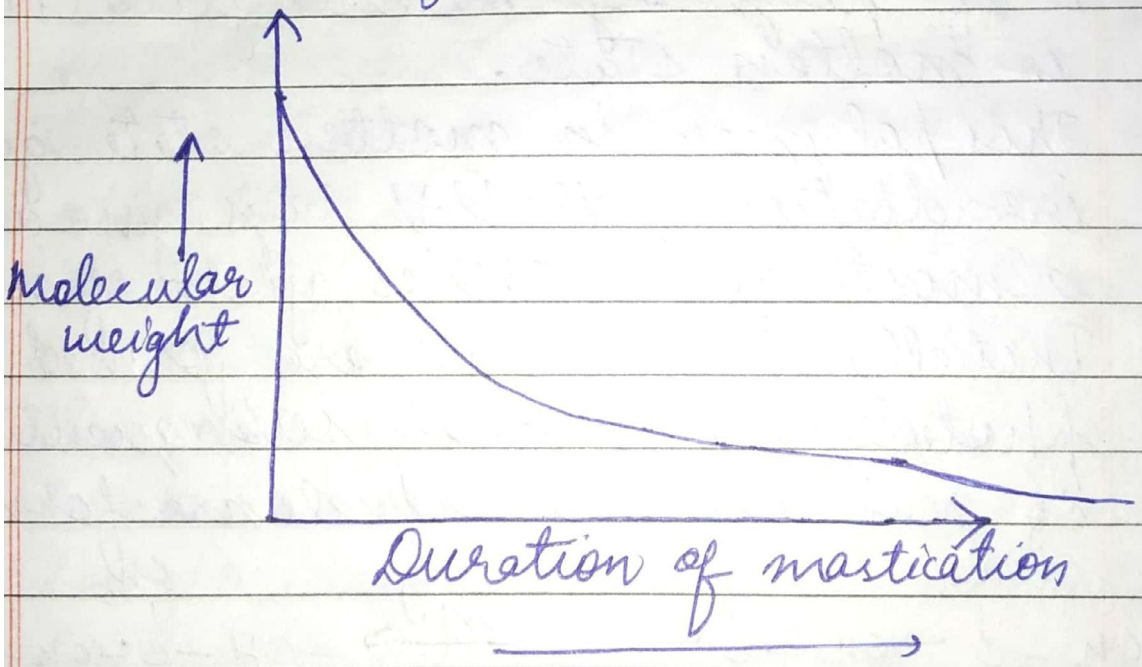
Can reduce the average molecular weight
Gives a narrower molecular weight distribut-ion.
Makes the polymer more processable.

When rubber is subjected to mastication in an atmosphere of N_2 at an ambient temperature, no degradation takes place. But degradation is takes place, very quick in presence of O_2 or air.



Effect of mastication time on molecular weight of a polymer undergo mechanical degradation.

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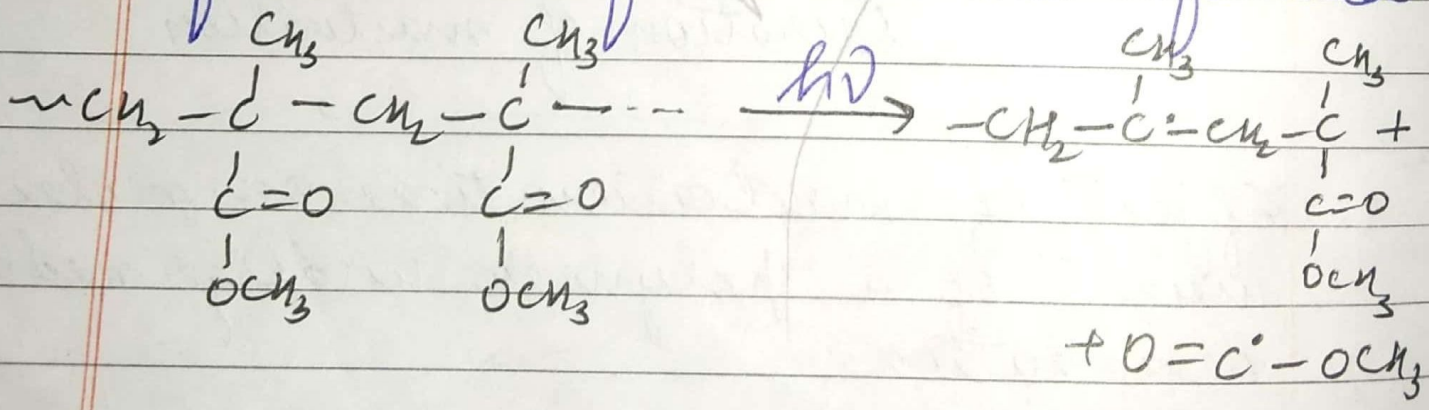
(c) Photodegradation:

Photodegradation process brought about by U.V. light. The yellowing & the embrittlement on storage, of some of the transparent plastics or coloured rubber articles are also due to their interaction with U.V. light (ie. this because of photodegradation).

Example of Photodegradation: By U.V. radiation is of polymethyl methacrylate (PMAA). in molten state.

This polymer in molten state gives on irradiation with U.V. rays give an almost quantitative yield of monomer. Initially free radicals are formed during photodegradation and subsequent course of reaction, free radicals are formed.



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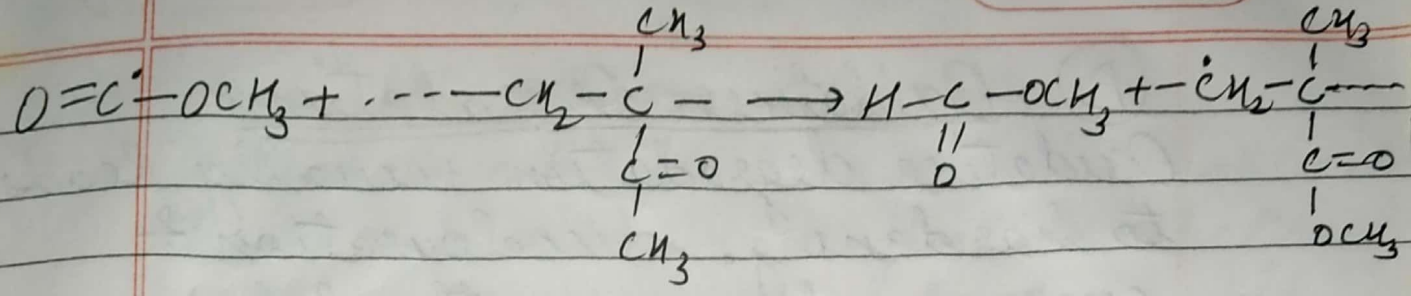
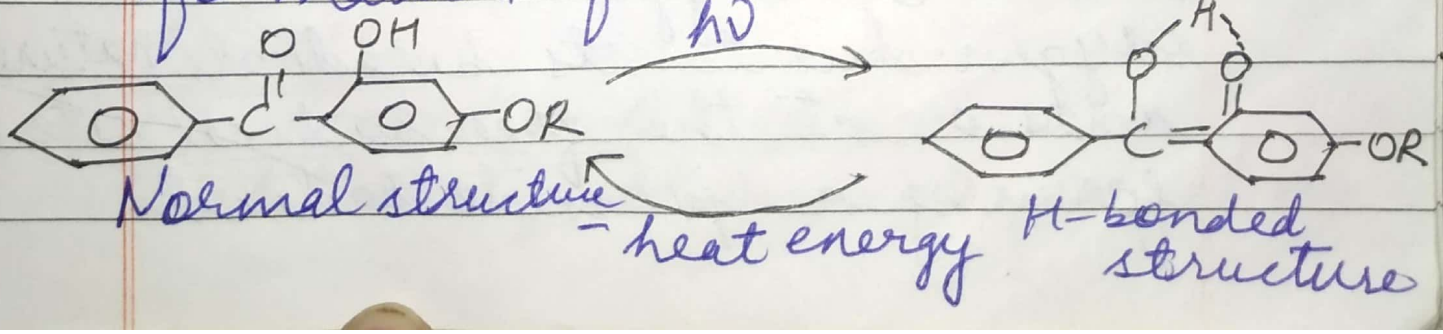


→ Use of photostabilisers in photodegradation:-
In order to protect the polymers from photodegradation, some photostabilisers are added to the plastics.
Common photostabilisers are:-

- Phenyl salicylate known as 'Salol'
- 2,4-hydroxy benzophenone (Uvinal 400)

The function of a photostabiliser is to absorb the U.V radiation & dissipate the energy thus absorbed to the environment in some harmless form. The absorbed energy is transmitted back as heat or radiation of a longer wavelength. Most stabilisers have the -OH & -CO group in the O-position, which encourages the formation of the H-bond as:-



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(D) Oxidative Degradation:-

Oxidative degradation usually leads to hardening, discolouration & surface change in the polymer molecule. Oxidative degradation of polymer is mainly depends on its structure.

Example:- Polyisoprene or polybutadiene having double bonds are easily attacked by oxygen. In early stage of oxidative degradation, free radical sites are formed on the chain backbone as a result of attack of O_2, O_3 or some free radical are formed by thermal decomposition of some radical are formed by thermal decomposition of some additives.

$M \longrightarrow M^{\cdot}$ (where M is a polymer chain)

Once the free radical sites are formed, attack by oxygen becomes easier, oxygen due to its biradical nature, adds on at the free radical site, forming a peroxide radical.

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$$M^{\cdot} + O_2 \longrightarrow MOO^{\cdot}$$

The peroxide radical so formed, attacks the neighbouring reagent & abstract 1-atom to form Hydroperoxide.

$$MOO^{\cdot} + M \longrightarrow MOOH + M^{\cdot}$$

It can also attack a neighbouring double bond →:

$$MOO^{\cdot} + -C=C- \longrightarrow MO^{\cdot} + ---\underset{O}{C}-C-$$

The hydroperoxide is capable of forming a no of free radical sites.

$$MOOH \longrightarrow MO^{\cdot} + {}^{\cdot}OH$$

$$M^{\cdot} + MOOH \longrightarrow MO^{\cdot} + MOH$$

$$MO^{\cdot} + MOOH \longrightarrow MOH + MOO^{\cdot}$$

The free radical so formed can also recombine & leads to formation of chain.

$$2\,MOO^{\cdot} \longrightarrow MOOM + O_2$$

$$2\,MO^{\cdot} \longrightarrow MOOM$$

$$M^{\cdot} + OH^{\cdot} \longrightarrow MOH$$

$$2M^{\cdot} \longrightarrow M-M, \text{ etc.}$$

Example:-

Ozone oxidation Degradation:-

Oxidative degradation is also caused by

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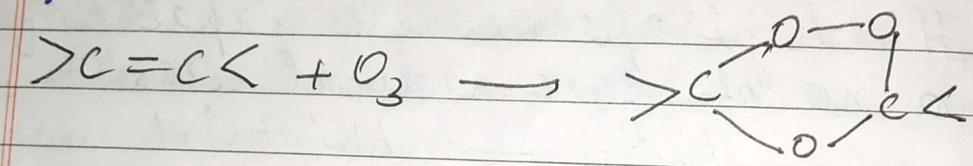
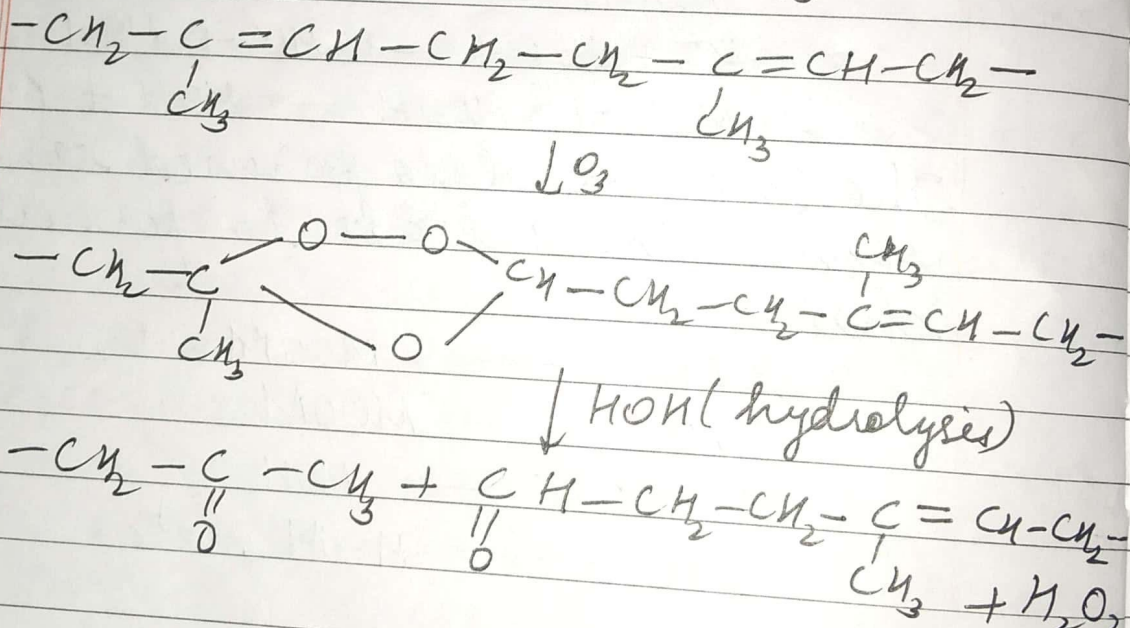
(b)

O_3 and many elastomer when exposed to ozone, they have been found to crack on stretching. The cracks, in rubber articles due to the ozone present in the atmosphere.
O_3 adds double bond to form ozonide. The the ozonide undergo HOH & undergo cleavage to form ketonic & aldehydic groups.





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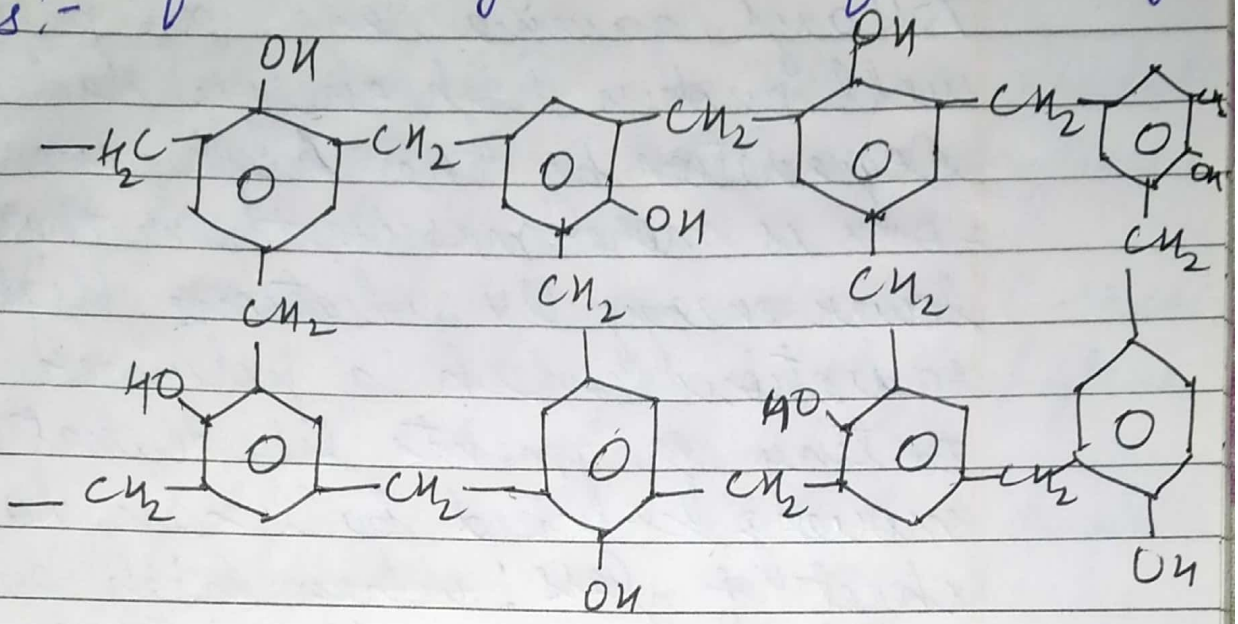
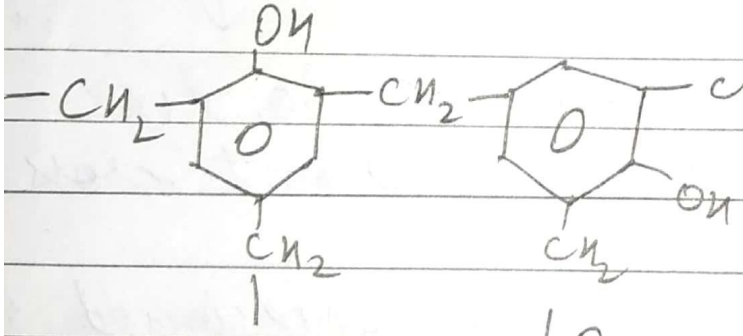
Oxidation of Phenal formaldehyde:-

Oxygen attacks a common resin as phenolformaldehyde. Phenolformaldehyde is:-

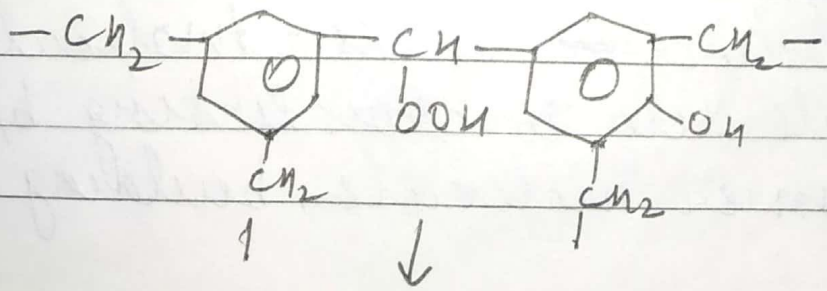


Attack by O_2 commences at 200°C. Methylenic linkage are the ones susceptible to oxidation.



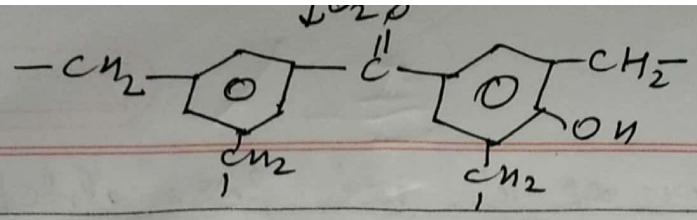
② Resin structure

$\downarrow O_2$



③ Hydroperoxide formation

$\downarrow$



④ Benzophenone formation

(E) Degradation by High Energy Radiation

X-Rays, gamma rays, α & β rays are well known high energy radiation. Degradation by the high-energy radiations is more massive than that by the lower energy UV radiations. High energy radiations smash a polymer molecule to tiny fragments like what a fast moving bricked ball can do to a sheet of glass. When high-energy radiations are so 'brutal' the polymer responds in a complex manner.

On this it lets all sorts of things to happen :-

(a) from breaking of its bonds or
(b) Scission of its chain to cross linking

of the molecule is scissioned, the polymer degradation is associated with a reduction in the molecular weight while due to cross linking b/w the polymer molecule, building up the

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polymer network with a resultant increase in the molecular weight.

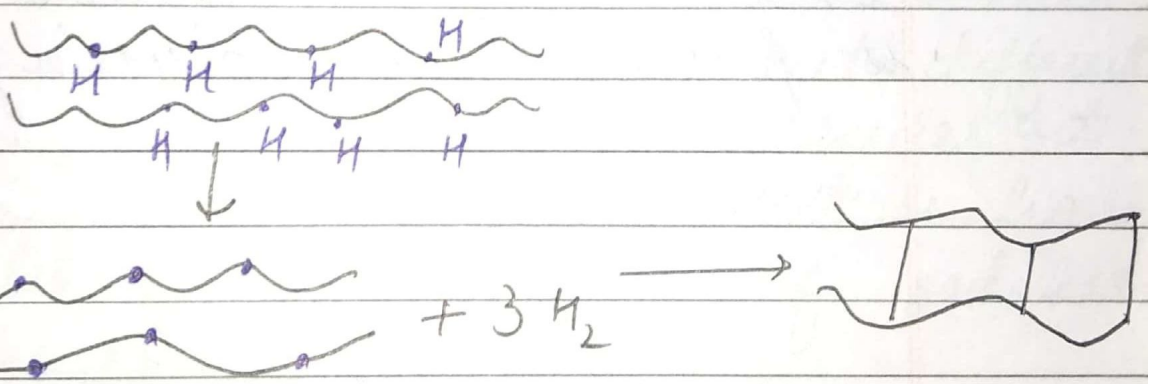
Example:-

Those polymers which degrade on irradiation are :- PTFE, Tetrafluoroethylene, cellulose, etc.

While those polymers which get cross linked are polyethylene, polypropylene etc.

Many polymers when exposed to high energy radiation, give out gases as H_2, CO_2, CO, CH_4 etc. As

Polyethylene & polypropylene
↓ High energy
gives H_2. It is indicated as



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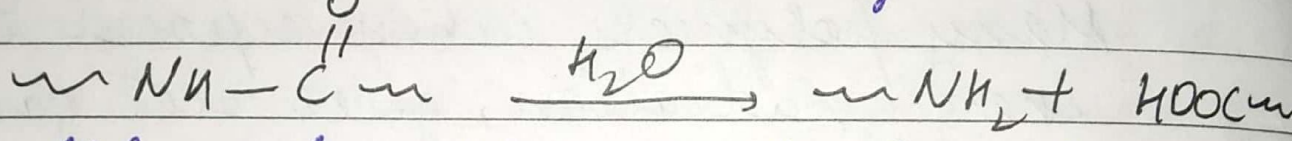
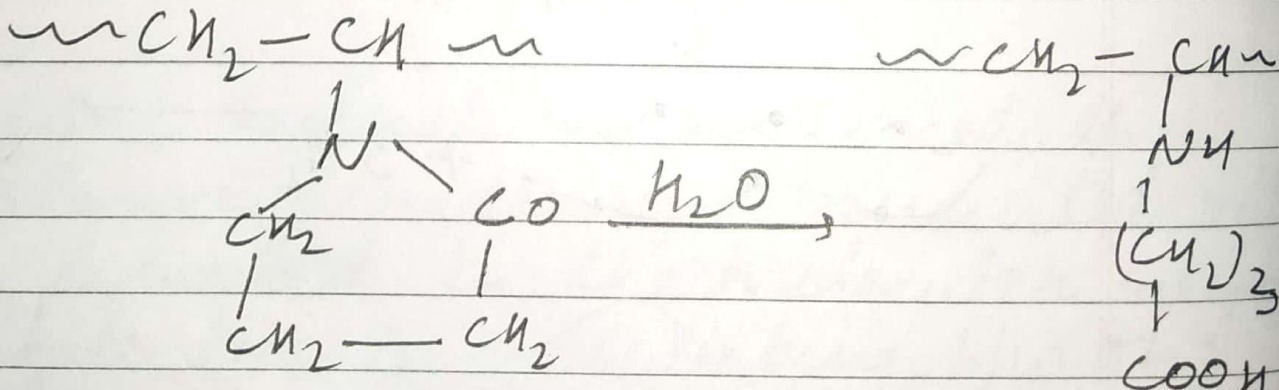
(F) Hydrolytic Degradation:-

Polymers with amide, ester & acetal linkages can be easily hydrolysed in the presence of acids & alkalies. Acidolysis & aminolysis of these polymers also lead to random degradation of the polymer chain. When above groups are present in the chain backbone, the HOH leads to chain scission or degradation as,



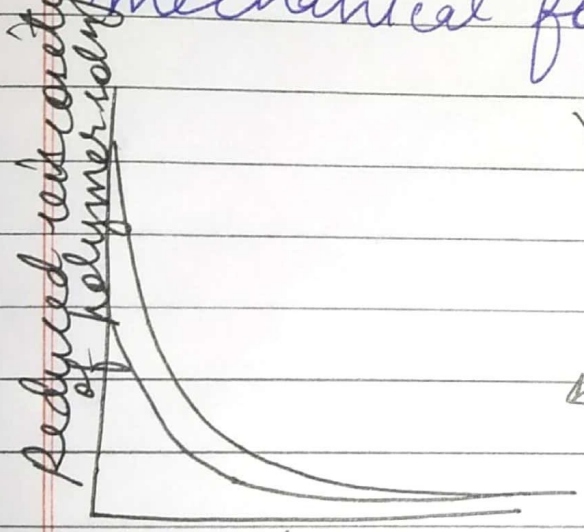
while, when these hydrolysable groups from the side groups of the polymer chain, HOH leads only to a change of functional group & not to any chain scission as this type of HOH is provided by polyvinylpyrrolidone



(4) Degradation by Ultrasonic Waves:

These are of very high frequencies (above 20,000 Hz) when a dil. soln of a high molecular weight polymer is subjected to ultrasonic waves, the polymer begins to degrade by reducing its molecular weight.

Ultrasonic degradation is a special case of mechanical degradation as the polymer here is subjected to very high vibrations, which are only mechanical forces.



Effect of ultrasonic degradation of two sample of the same polymers with different initial molecular wt. The mol. wt is shown in term of reduced viscosity