

CHAPTER 2 - BACKGROUND INFORMATION

2.1 POLYOLEFINS STRUCTURE

2.1.1 POLYOLEFINS

Polymers are long chain macromolecules. Their properties depend on maintaining effective chain lengths. Mechanical properties are a function of morphology. Polyolefins are a subgroup of polymers that are obtained by polymerising α -olefins. They are commodity chemicals produced world wide on a large scale ($> 40 \times 10^6$ ton/year)[24]. They are cheap to produce, non-toxic and have a wide range of properties. End uses include film packaging, containers, textile fabrics, woven bags, sandwich bags, pipes, car bumpers, etc. Their use in our everyday lives is predicted to grow. Polyolefins are replacing other polymers/plastics in current use. It was predicted that more than 70 % of all thermoplastics will be polyolefin based by the new millennium [24]. Plastics are usually coloured or printed to make them more appealing (e.g. shopping bags). Environmental issues relating to polymer disposal can be minimised by recycling and other procedures. This will reduce a serious negative feature related to their presence in society as “visual” pollution.

The polyolefins enterprise is directly related to the development of appropriate additives for conversion of the starting materials (the polyolefin) into the required plastic. One of the main reasons for using polyolefins as raw materials is their chemical inertness and resistance to a large number of packaged products or contact media [3, 20, 24].

Physical changes in a polyolefin formulation due to its environment have been recognised as a prime reason for polymer failure [2, 13,15]. Most polyolefins are semi-crystalline materials. Their behaviour can be traced to this multiphase structure. Polypropylene and polyethylene are the most important polyolefins because they are used more frequently than

others. Polyolefin types include polypropylene (PP) that can be made in isotactic, syndiotactic or atactic form, low-density polyethylene (LDPE) (a randomly branched structure), high-density polyethylene (HDPE) (primarily linear chains with few branches and high crystallinity), crosslinked low-density polyethylene (CLDPE), and linear low-density polyethylene (LLDPE) (longer chains with small branches). The variations in morphology due to these chain structure differences contribute to the wide range of physical properties in polyolefins and are a key to their extensive use [13,25].

Usually they have glass transition temperatures (T_g 's) well below room temperature and, as a result, the amorphous regions are rubbery in nature. However the crystalline domains, which tend to be in the form of small platelets (lamellae), are nearly impermeable to small molecules due to the dense packing of the polymer chains. This mixture of rigid crystallites in a rubbery matrix gives the polyolefins their toughness [25].

[16 - 20]

Polyolefins have long passed the stage where they are regarded as a low-cost material that is useful for short-life applications only. Polyolefins (PP, HDPE, LDPE, CLDPE, and LLDPE) show a dramatic loss in strength when exposed to UV-radiation as experienced in outdoor weathering or exposure to sunlight. The degradation and stabilisation mechanisms are now fairly well understood [12]. By developing efficient stabilisers and sophisticated formulations, it has become possible to control their major disadvantages, namely degradation sensitivity during processing and poor long-term stability [3, 12].

2.1.1.2 POLYOLEFINS IN THE ENVIRONMENT

The polyolefins industry is permanently confronted with problems of quality and lifetime of its products. Initially, plastics came as a replacement for "traditional" materials; nowadays, they represent new materials with new properties. In order to meet the increasing

requirements, investigations of new synthesis and production technologies are needed [24].

UV degradation usually causes polymer embrittlement. They lose tensile properties and some polymers even become discoloured [7, 9, 15, 22, 26]. Because the useful lifetime of polymers depends on their retention of mechanical properties, it is important to counter the damage caused by UV light [12,17,26].

For this purpose, development is broadly supported by the use of effective additives. Stabilisers can frequently protect polyolefins, depending on what sorts of degradation reactions need to be interrupted. Therefore, the development of one of the most effective light stabiliser structures – Hindered Amine Light Stabilisers (HALS) – is directly linked to the expansion of polyolefin applications. In fact, in many applications, the stabilisation efficiency of this additive has still not been fully elucidated [16 - 20].

Polyolefins are displacing more expensive plastics from several applications. To compete, polyolefins require a significant improvement of performance such as durability, thermo-oxidative and light stability, colour, and gloss maintenance and impact resistance [24].

2.2 DEGRADATION OF POLYMERS

2.2.1 OVERVIEW OF POLYMER DEGRADATION

Degradation of polymers is a process that occurs with rupture of the main chain backbone or the side group bonds. The theory of polymer degradation is important in understanding polymer stability, durability, characterisation, synthesis, and recycling [12,13].

Polymeric materials have a high molecular weight which gives rise to their properties. Any foreign agent that gives rise to a change in this parameter can alter the properties significantly [12]. The types of degradation processes vary depending upon the environmental conditions in which the polymer is used, the manufacturing history as well as structure of the polymer. According to the literature, the types of degradation processes that polymers may undergo, are [8-10]:

- I- **Chemical degradation:** this occurs in polymers that are attacked by chemical agents, corrosive chemicals or gases. The basic structural functionalities in the polymers cause chain scission and oxidation.
- II- **Mechano-degradation:** this type of degradation happens to polymers by shearing forces, ultrasonic vibrations, repeated and rapid freezing of the solvent of a polymer solution, high-speed stirring. Chain scission may also occur here.
- III- **Thermal degradation:** this occurs during processing or during use at elevated temperatures (heat) and may involve either oxidative or non-oxidative degradation.
- IV- **Biodegradation:** this occurs to the polymers, which contain functional groups that are attacked by micro-organisms (enzymes, bacteria, and fungi).
- V- **Radiative degradation:** in this case degradation is initiated by high energy radiation (e.g. gamma rays).
- VI- **Photodegradation:** this happens to the polymers that are exposed to light. On exposure to sunlight, either the polymer itself or impurities in the polymer will absorb the radiation and induce reactions resulting in a loss of properties.
- VII- **Hydrolytic degradation:** this occurs in polymers containing functional groups that are sensitive to the effects of water.

The thermal degradation and photodegradation degradation are the most important among these different types of degradation in the use of polymers [12].

The degradation can be caused by mechanical stress or thermal treatment oxidation, γ -radiation, oxidation, or by the addition of peroxides. Traces of impurities and contaminants and various structural irregularities are often responsible for causing or accentuating the degradation of polymer chains [8]. Therefore, polymers are liable to degrade when they are subjected to natural weathering conditions such as sunlight, moisture and rain [24, 27].

Depending on the chemical structure and the degradation condition, polymers have been observed to degrade by chain scission occurring randomly along the chain, or by an unzipping depolymerisation, or by a combination of these.

2.2.2 GENERAL TYPES OF POLYMER DEGRADATION PROCESSES

The degradation and/or oxidation reactions depend upon the structure of the polymer, the presence of oxygen and temperature.

There are two general types of polymer degradation processes, corresponding roughly to the two types of polymerisation, step-reaction and chain-reaction [8, 9]:

- I- Random degradation is analogous to stepwise polymerisation. Here chain rupture or scission occurs at random points along the chain, leaving fragments, which are usually large, compared to monomer unit.
- II- Chain depolymerisation involves the successive release of monomer units from a chain end in a depropagation or unzipping reaction, which is essentially the reverse of chain polymerisation.

These two types may occur separately or in combination, may be initiated thermally or by ultraviolet, oxygen, ozone, or other foreign agent, and may occur entirely at random or preferentially at chain ends or at other weak links in the chain.

It is possible to differentiate between the two processes in some cases by following the molecular weight of the residue as a function of the extent of reaction. When polymers degrade and oxidise one of the most important changes in structure is in molecular weight [12]. Molecular weight drops rapidly as random degradation proceeds but may remain constant in chain depolymerisation, as whole molecules are reduced to monomer, which escapes from the residual sample as a gas. Examination of the degradation products also differentiates between the two processes: the ultimate product of random degradation is likely to be a polydisperse mixture of fragments of low molecular weight, whereas chain depolymerisation yields large quantities of monomer [8, 9].

Since the degradation and oxidation of polymers causes chain scission, one of the most important factors controlling polymer stability is the stability of their primary valence bonds. Thus, the stronger the chemical bond, the more stable will be the polymer. In fact, this is generally true where the C-F bond is stronger than either -C-H or -C-C- bonds. In this regard PTFE $-(CF_2-CF_2)-$ is more stable than polyethylene $-(CH_2-CH_2)-$ and this is a well-known commercial fact [12].

2.2.3 DEGRADATION REACTIONS

The three general types of degradation reactions at high temperatures are [8, 12]:

- 1- Depolymerisation reactions where the polymer chain is

scissioned such that the products are similar in structure to that of the polymer but of a lower molecular weight.

- 2- Elimination reactions where degradation usually results in the formation of lower molecular weight fragments or molecules that are sometimes unrelated to that of the original polymer.
- 3- Substituent reactions where the main chain substituents undergo reactions such that the chemical nature of the repeat unit is changed although the chemical structure remains intact.

Most degradation reactions at high temperature are of free radical type. Scheme 2.1 shows the general types of free radical degradation reactions, where P_i represents unreactive polymer molecule, P_i^\bullet represents a macro-radicals and the subscripts denote the number of monomer units in the polymer chain. Thus random initiation involves splitting of the polymer chain into unequal lengths to give two macro-radicals. Terminal initiation results in the loss of a single monomer radical fragment from the end of the polymer chain. Transfer in this case shows that one macro-radical can transfer its activity to another chain unit. Scission may occur randomly to give two more active radicals and termination may be due to the formation of two 'dead' polymer chains or the recombination of two macro-radicals giving a higher molecular weight fragment [9, 12].

Scheme 2.1

Random Initiation



Terminal Initiation



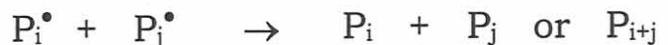
Transfer



Scission



Termination



2.2.4 THERMAL OXIDATIVE REACTIONS OF POLYMERS

Molecular oxygen exists in its ground state as a triplet $^3\text{O}_2$. Oxygen has the ability to diffuse through the amorphous regions of the polyolefins. The crystalline regions are not accessible as they are too closely packed. In the solid state amorphous polymers are more susceptible to oxidation than crystalline polymers. This is illustrated for amorphous, semi-crystalline and single crystals of polypropylene in Figure 2.1.

The rate of diffusion of oxygen will be faster in the amorphous material which will oxidise faster followed by the moulded film and then the single crystals (act as a barrier to diffusion). In the presence of oxygen most polymers will undergo rapid chain scission reactions below their melting points [12]. In their study of the effect of structure on oxidation of polyolefins, Hanssen et al. observed that the greater the number of branches, the more easily the polymer is attacked by the oxygen. Consistent with this is the observation that the order of ease of oxidation is: PP > LDPE > HDPE [28]. However, bulky side groups that reduce the access of oxygen to the chain backbone modify this situation, implying that both the existence of and the accessibility to tertiary carbons are important in the oxidation reaction.

A typical mechanistic scheme for the oxidation of polymer systems is as follows:

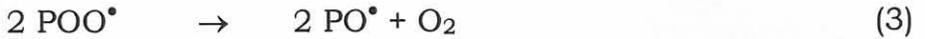
- Molecular oxygen has a biradical nature, and reacts easily with other organic or polymer – free radicals (P^\bullet) giving polymer peroxy radicals (POO^\bullet):



- The peroxy radical rapidly abstracts hydrogen from another polymer molecule (PH) to form a polymer hydroperoxide (POOH):



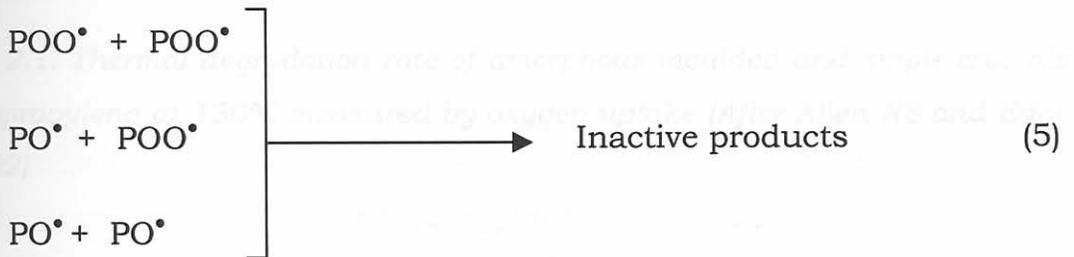
- Alternatively two peroxy radicals may react with each other to produce polymer oxyradicals (PO[•]):



- The polymer oxyradical can also be formed from the decomposition of polymer hydroperoxides (POOH):



- Termination occurs by the following reactions:



The inactive products include for example ether, ester and peroxide i.e.

$P-O-P$, $P-O-\overset{\overset{O}{||}}{C}-P$, $P-O-O-P$. They contain either bridges or peroxide bridges depending on the reactions, which participate in the termination reaction.

2.3 DETAILED PHOTO-OXIDATION AND PHOTODEGRADATION
MECHANISM FOR POLYETHYLENE AND POLYPROPYLENE

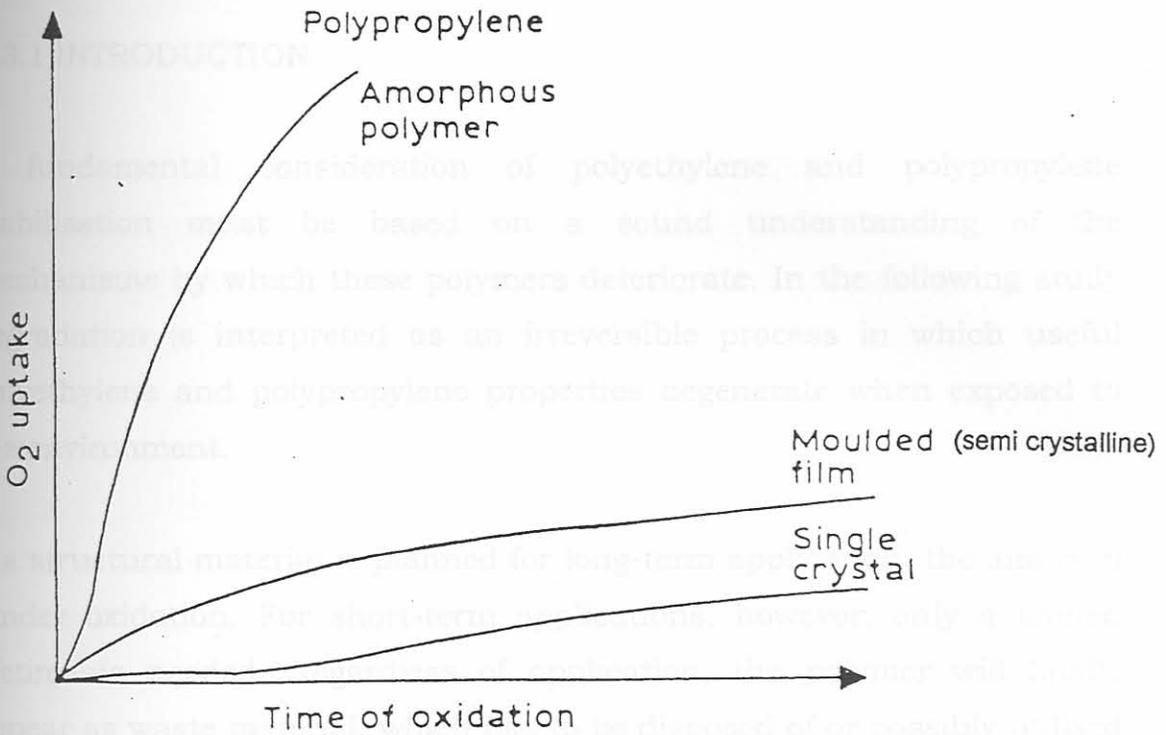


Figure 2.1. Thermal degradation rate of amorphous moulded and single crystals of polypropylene at 130°C measured by oxygen uptake (After Allen NS and Edge M, 1992).

Metal ions are invariably present in many polymer systems, especially the polyolefins, and they can accelerate (or i.e. catalyse) the decomposition of hydroperoxides as shown in scheme 2.2 producing alkoxy and peroxyradicals [12].

Scheme 2.2



2.3 DETAILED PHOTO-OXIDATION AND PHOTODEGRADATION MECHANISM FOR POLYETHYLENE AND POLYPROPYLENE

2.3.1 INTRODUCTION

A fundamental consideration of polyethylene and polypropylene stabilisation must be based on a sound understanding of the mechanisms by which these polymers deteriorate. In the following study degradation is interpreted as an irreversible process in which useful polyethylene and polypropylene properties degenerate when exposed to the environment.

If a structural material is planned for long-term application, the aim is to hinder oxidation. For short-term applications, however, only a limited lifetime is needed. Regardless of application, the polymer will finally appear as waste material, which has to be disposed of or possibly utilised for some other uses. A potential of the latter is controlled oxidation in which low molecular weight organic intermediates can be obtained. The first aim can be achieved by the use of a stabiliser-sensitiser system, while oxidising agents or initiators under special conditions can oxidise the waste materials. Whatever the practical aim is, the process to be controlled is the degradation reaction [2, 7, 11, 14, 22, 26].

2.3.2 LIGHT ABSORPTION PROCESSES

There are two types of photodegradation of polymers depending on the mode of light absorption, which itself is governed by the cut-off point for terrestrial sunlight, i.e. wavelengths > 290 nm [12].

- (i) Direct photodegradation, when macro-molecules absorb light directly, and free radicals are formed after photo-excitation;

- (ii) Sensitised photodegradation, when the degradation of macromolecules is initiated by the free radicals which are formed from the photo-decomposition of low molecular weight photo-initiators (sensitisers).

Most polymers contain C-C, C-H, C-O, C-N and C-Cl bonds, and they do not absorb light with a wavelength longer than 190 nm. When polymers contain different types of chromophoric group, they can absorb light with wavelengths of 250 – 400 nm and higher [8, 9, 10].

A necessary condition for the dissociation of a particular bond into free radicals is the excitation of a molecule by the absorption of light of sufficient energy [10]. Pure polyolefins (PE and PP) do not absorb light in the wavelength region shorter than 200 nm. Thus generation of free radicals in them due exposure to light is only possible if impurity groups (carbonyl, peroxide, hydroperoxide groups, etc.) are present. The latter are formed in the polymer or entering into it in the course of synthesis, processing, usage. They may act as initiators or sensitisers when excited [12].

The formation of radical species in polyolefins also occurs under the action of ionising radiation, mechanical loads and other energetic factors, several types of macro-radicals (alkyl, allyl, polyene, peroxide, acyl, etc.) being formed in polyolefins of different chemical structures.

2.3.3 GENERAL FEATURES OF POLYETHYLENE AND POLYPROPYLENE OXIDATION: QUALITATIVE CHARACTERISATION OF PROCESS

The uptake of oxygen causes the formation of RO_2^\bullet radicals in the chain. Some are transformed to end products and further R^\bullet and RO_2^\bullet radicals, while others abstract hydrogen from the CH_2 segments and are transformed into hydroperoxides. The latter are active intermediates,

which decompose at higher temperatures. After an additional series of elementary steps, the hydroperoxides cause additional changes in the polymer, namely [2]:

- (i) Formation of oxidised structures in the chain,
- (ii) Fragmentation of the polymer chain, and
- (iii) Formation of low molecular weight products.

2.3.4 MECHANISM OF POLYETHYLENE AND POLYPROPYLENE OXIDATION

Most authors have been treated polyolefin oxidation in terms of the basic mechanism of Bolland and Gee [29, 30]. A version of it is given in Scheme 2.3. (a). It can be applied to describe oxidation at low and medium oxygen pressure when the rate of the process is determined by the reactions of hydrocarbon (R^\bullet) and peroxy (RO_2^\bullet) radicals.

At high oxygen partial pressure the oxidation of the radicals is very fast compared to the other propagation steps (process 2b). In this case, the reactions of RO_2^\bullet radicals are rate determining. This mechanism is suitable for describing the main features of kinetics in the oxidation of some polyolefins, but it does not give any information about the non-rate-determining elementary steps of the reaction.

If, however, the composition of the products formed in the oxidation is investigated, it is found that the reactions leading to the end products of the oxidation are just these non-rate-determining processes.

The detailed mechanisms of these processes and consequently the composition of the products depend on the chemical structure of the polymer [2, 9].

Scheme 2.3 Simplified mechanism scheme of polyolefin oxidation.

(f = radical efficiency factor.)

(a) Low and medium O ₂ pressure	(b) high O ₂ pressure
<u>(1) Initiation</u>	
(1.1) $RH + O_2 \rightarrow RH + 2R^\bullet + H_2O_2$	$RH + O_2 + RH + 2O_2 \rightarrow 2RO_2^\bullet + 2H_2O$
(1.2) $I + 2f RH \rightarrow 2f R^\bullet + \text{products}$	$I + 2f RH + 2f O_2 \rightarrow 2f RO_2^\bullet + \text{products}$
<u>(2) Radical propagation</u>	
$R^\bullet + O_2 \rightarrow RO_2^\bullet$	Very fast, non-rate-determining
<u>(3) Chain propagation</u>	
(3.1) $RO_2^\bullet + RH \rightarrow R^\bullet + RO_2H$	$RO_2^\bullet + RH + O_2 \rightarrow RO_2^\bullet + RO_2H$
(3.2) $RO_2^\bullet + RH \rightarrow R^\bullet + \text{products}$	$RO_2^\bullet + O_2 \rightarrow RO_2^\bullet + \text{products}$
<u>(4) Degenerated branching</u>	
$RO_2H + 2fRH \rightarrow 2fR^\bullet + H_2O$ + other products	$RO_2H + 2fRH + 2fO_2 \rightarrow 2fRO_2^\bullet$ + H ₂ O + products
<u>(5) Termination</u>	
(5.1) $R^\bullet \rightarrow \text{products}$	slow, rate is negligible
(5.2) $RO_2^\bullet \rightarrow \text{products}$	$RO_2^\bullet \rightarrow \text{products}$
(5.3) $R^\bullet + R^\bullet \rightarrow \text{products}$	slow, rate is negligible
(5.4) $R^\bullet + RO_2^\bullet \rightarrow \text{products}$	slow, rate is negligible
(5.5) $RO_2^\bullet + RO_2^\bullet \rightarrow \text{products}$	$RO_2^\bullet + RO_2^\bullet \rightarrow \text{products}$

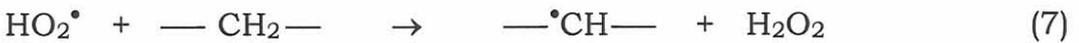
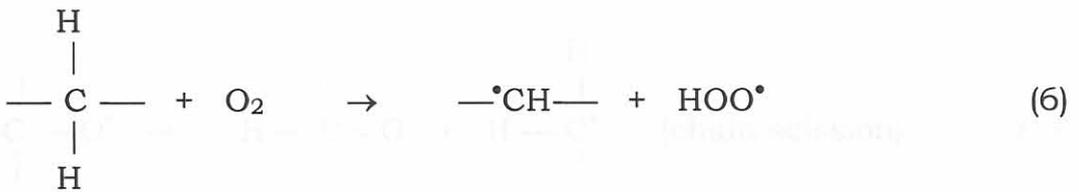
The majority of the oxidation product result from hydroperoxide decomposition processes [31]. In addition, a considerable proportion is formed in the transformation of peroxy radicals and a smaller fraction from radical termination processes. Most of the free radicals formed in hydroperoxide decomposition recombine within the molecular structure. About 80% of the end products resulting from PE-hydroperoxides and 90% of those from PP-hydroperoxides are formed in the structure processes. A smaller proportion, which is likely to be responsible for the broad spectrum of products, is formed by the reactions of radicals

escaping the cage and of active intermediate products formed from them [2, 7, 9, 28].

In the following scheme, we will survey the main processes leading to formation and decomposition of hydroperoxides and the structure of the active intermediate products in the cases of PE and PP. We will assume that the kinetic conditions of scheme 2.3 (b) are fulfilled, i.e. every macroradical formed is oxidised.

Polyethylene

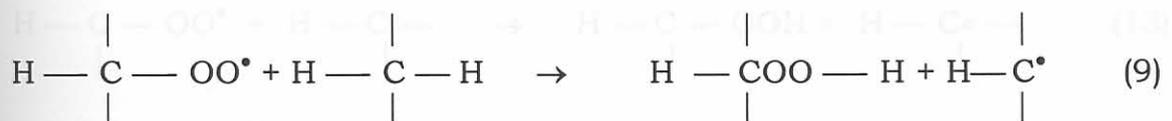
Primary initiation



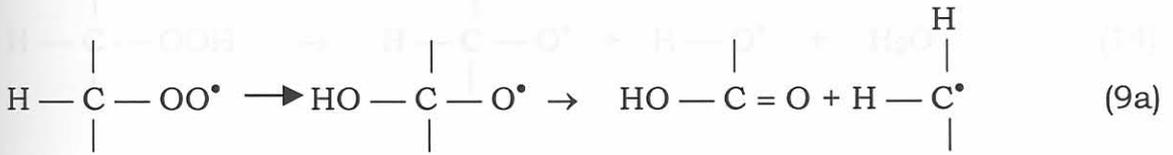
Radical oxidation



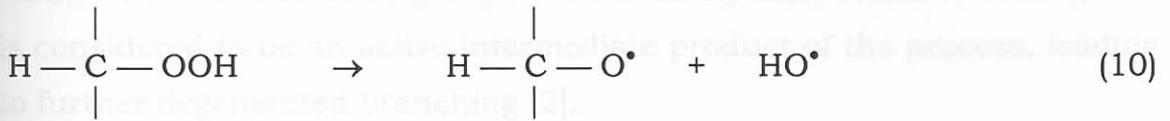
Polymer hydroperoxide formation



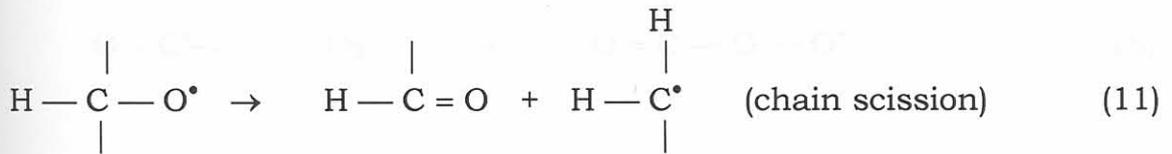
Peroxy radical transformation (formation of chain-end radicals and chain scission)



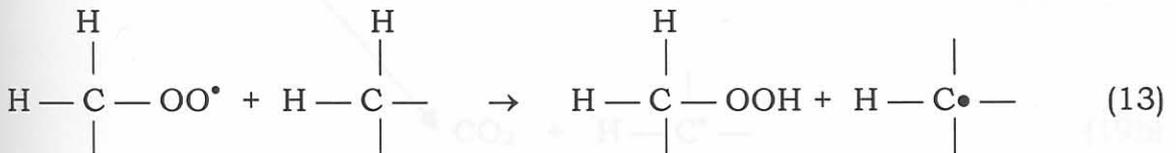
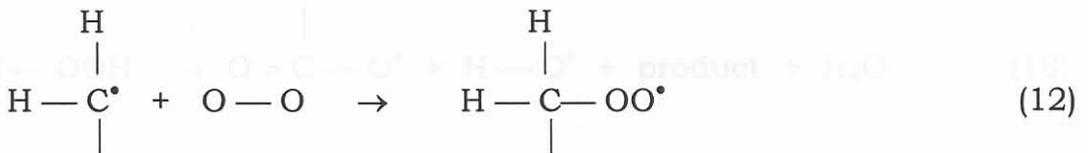
Hydroperoxide decomposition

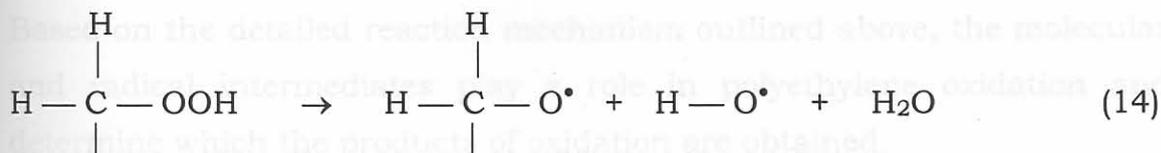


Transformation of alkoxy radical, formation of chain-end radicals



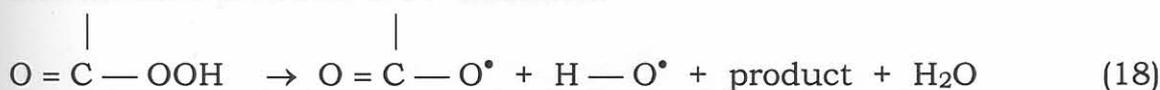
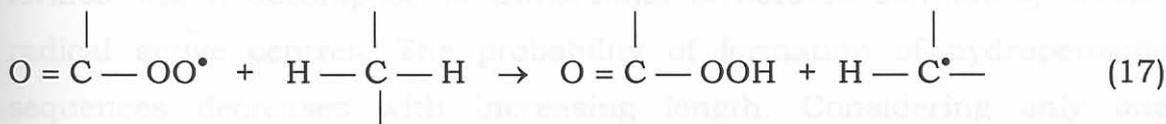
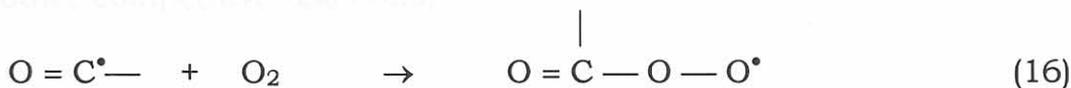
Formation of chain-end intermediate products





Polypropylene

The reactions of $\text{H}-\text{C}=\text{O}$ groups formed in process (11) can be regarded as secondary processes. However, both the formation and further oxidation of these groups are extremely fast. Therefore this group is considered to be an active intermediate product of the process, leading to further degenerated branching [2].



Based on the detailed reaction mechanism outlined above, the molecular and radical intermediates play a role in polyethylene oxidation and determine which the products of oxidation are obtained.

products in a molecular process.

Polypropylene

In PP oxidation the number of propagating radicals and active intermediate products is higher than in PE oxidation. The polymer contains a very reactive tertiary hydrogen atom. The consequences of this fact for the degradation mechanism are the following [32]:

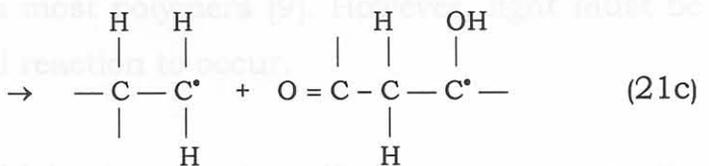
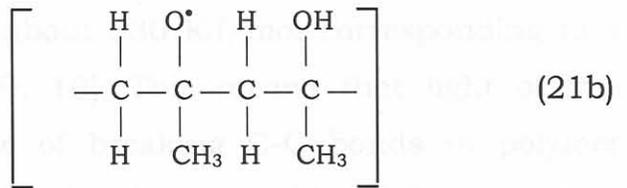
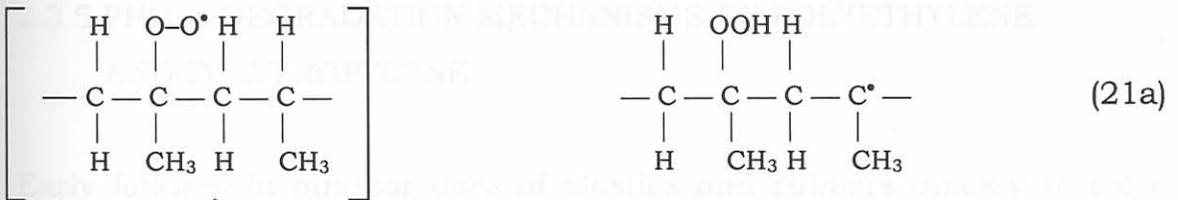
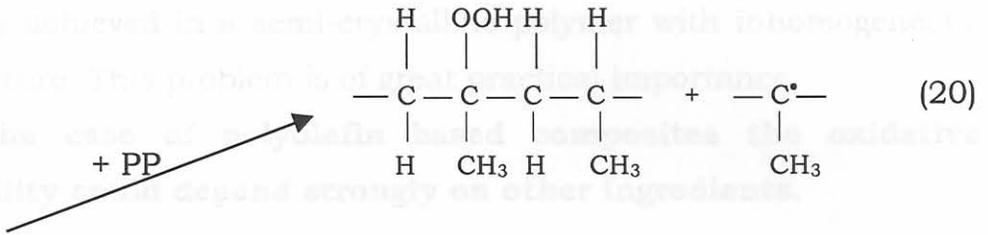
- (1) High probability of intramolecular chain transfer,
- (2) The oxidation rate of hydrocarbon radicals is in proportion to the rates of other competitive reactions.

As a result of intramolecular chain transfer, hydroperoxide sequences are formed which decompose to transitional structures containing several radical active centres. The probability of formation of hydroperoxide sequences decreases with increasing length. Considering only one intramolecular step, let's survey the reactions leading to active intermediate products of PP oxidation.

The primary initiation process is similar to those shown in processes (6) – (8). The peroxy radical formed may then part in several competitive reactions.

Even in a system protected by an antioxidant, the following processes
In practice, PE and PP are almost always protected against oxidation by additives. The additives are molecules of different structure depending on application (melt stabilisers, antioxidants, UV stabilisers). The initiating step of thermal oxidation cannot be avoided by the use of stabilisers. The primary process (1.1) always takes place and an RO_2^\bullet radical is formed. One group of antioxidants hinders the chain reaction by substituting for the polymer in process (3.1) as an oxidation substrate. One of the

reaction products is, even in this case, a polymer hydroperoxide. This then may initiate a new oxidation chain, unless the system contains an antioxidant, which is also able to decompose peroxides to inactivate products in a molecular process.



Even in a system protected by an antioxidant, the following processes should be reckoned with:

- (i) **The primary process of oxidation;** will occur and a slight structural change of the polymer is inevitable.
- (ii) **Gradual stabiliser consumption in the primary process;** the protection is, therefore, transitional. The stabiliser system should

be chosen after a careful analysis of the demand and of the required lifetime.

- (iii) **Unexpected local degradation due to the inhomogeneous distribution of the additives even in an optimally designed composition.** Homogeneous distribution, on the other hand, is not easily achieved in a semi-crystalline polymer with inhomogeneous structure. This problem is of great practical importance.
- (iv) **In the case of polyolefin based composites the oxidative stability could depend strongly on other ingredients.**

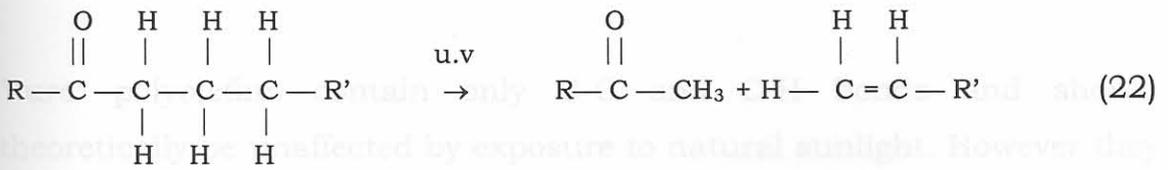
2.3.5 PHOTODEGRADATION MECHANISMS OF POLYETHYLENE AND POLYPROPYLENE

Early failures in outdoor uses of plastics and rubbers quickly revealed the severe effect of ultraviolet light on many polymers in the presence of oxygen. The C-C bond energy is about 330 KJ/mol corresponding to a photon wavelength of 360 nm [9, 10]. This means that light of this wavelength or shorter is capable of breaking C-C bonds in polymer molecules by which it is absorbed. It has been considered that quantum energies associated with light wavelengths 300 – 400 nm are sufficient to break the chemical bonds in most polymers [9]. However, light must be absorbed for a photochemical reaction to occur.

The shortest wavelength (highest energy) radiation present in the ultraviolet spectrum of the sun at ground level may be taken as 290 nm. Radiation of shorter wavelength is removed by molecular oxygen and ozone in the atmosphere [10].

The mechanisms of oxidative photodegradation are probably diverse, and it is only possible to indicate the kind of processes involved. In fact the direct breaking of single C-C and C-H bonds is relatively uncommon. The C=O bond absorbs more strongly and it appears that the following

reaction is important in initiating photo-oxidation in polymers containing CO groups.



Many engineering polymers including polyesters, polyurethanes and polyamides contain CO groups. In addition, CO groups are present as impurities in polyethylene and polypropylene, and also in other hydrocarbon polymers. The observation that radiation of wavelength longer than 340 nm does not produce photodegradation in polyethylene is one important piece of evidence for this [9]. Photo-oxidation leads generally to discoloration, surface cracking and deterioration of mechanical and electrical properties.

The term 'photodegradation' covers reactions carried out in the absence of oxygen and is often described as 'photolysis'. Photo-oxidation reactions, on the other hand, occur in the presence of air or oxygen. A third reaction arises when degradation or oxidation occurs under irradiation at an elevated temperature, but below the temperature necessary for purely thermal breakdown. This type of process is referred to as 'photothermal' degradation or oxidation [12,14].

Stability to sunlight exposure is one of the most important criteria in determining the practical application of all polymeric materials out of doors [12]. All unstabilised organic polymers are degraded upon exposure to terrestrial sunlight in the presence of oxygen [9,10]. However, the rates of photodegradation vary enormously with polymer structure, and range from a few months out-of-doors for polypropylene to, say, several years for poly(methyl methacrylate) and poly(tetrafluoroethylene) [12].

The basic mechanisms of photo-oxidation and photodegradation of commercial synthetic polymers are highly controversial and to a degree are not yet completely solved.

'Pure' polyolefins contain only C-C and C-H bonds and should theoretically be unaffected by exposure to natural sunlight. However they photo-oxidise through a number of impurity groups introduced during polymerization and/or processing. The main light-absorbing species are believed to be carbonyl groups, unsaturated carbonyl groups, hydroperoxides, unsaturated hydroperoxides, metallic impurities, aromatic compounds and oxygen-polymer charge-transfer complexes [8-10]. Much recent research indicates that carbonyl and hydroperoxide groups are the two most important species in the photo-oxidation of commercial polymers [2, 9].

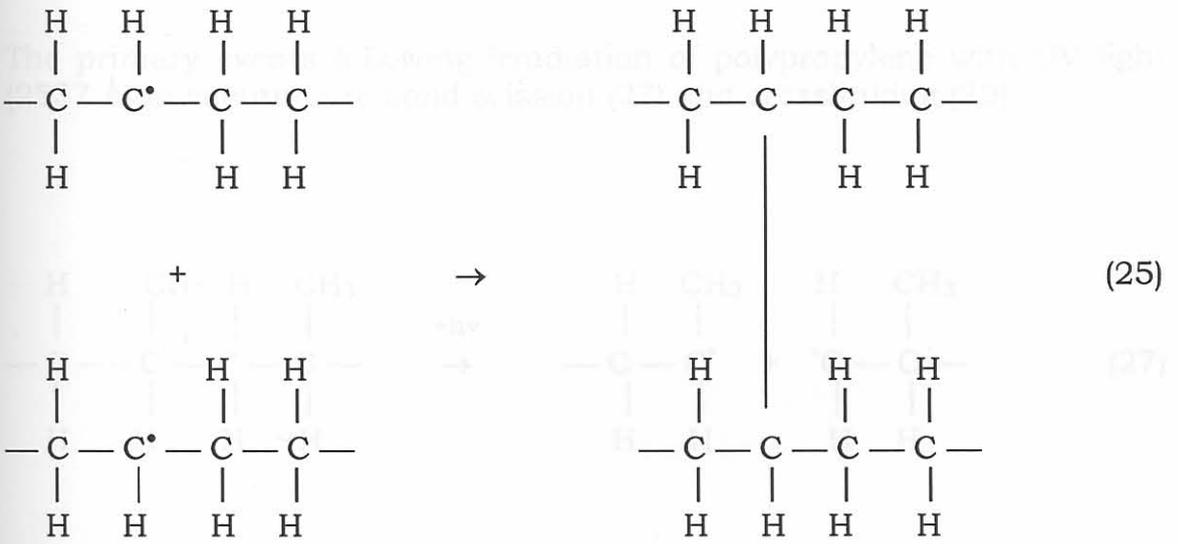
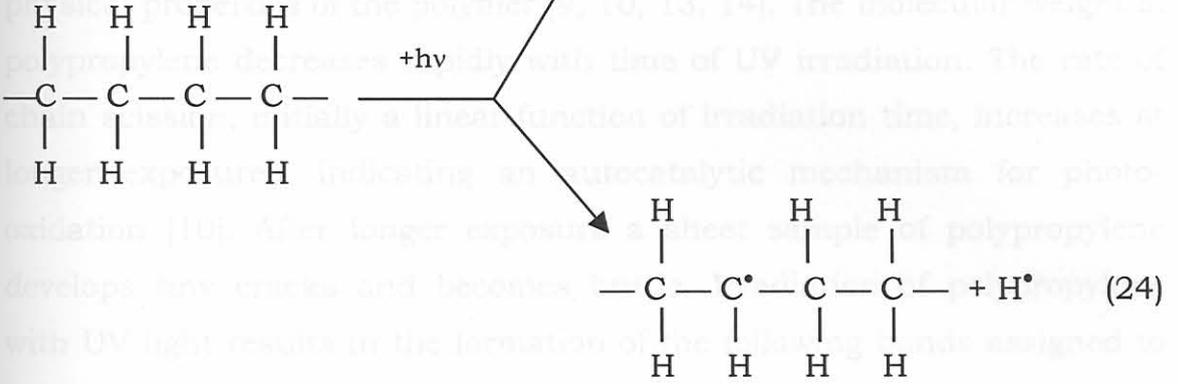
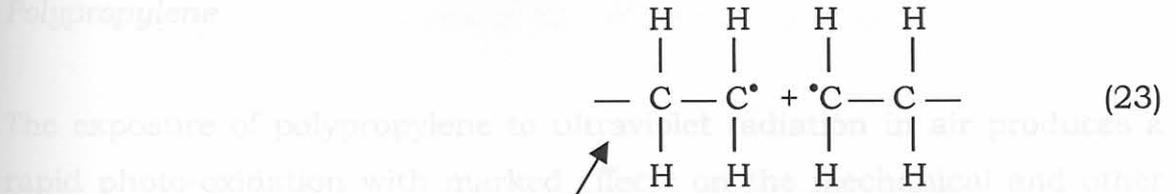
Polyethylene

In the absence of oxygen, pure polyethylene is relatively stable material under ultraviolet radiation [10]. After long exposure to UV light of short wavelength (2537 Å) in a vacuum or in a nitrogen atmosphere, chain scission (23) and hydrogen abstraction (24) occur. Also crosslinking (25) and evolution of hydrogen (26) are observed.

The mechanism of the degradation of polyethylene by UV light is complicated. At present this mechanism has not been satisfactorily established [8-10].

The photophysical processes affect the physical properties of polymers. It has been shown that the crosslinking of polyethylene chains is increased when the film thickness and the crystallinity decrease. The crosslinking promotes gel formation predominantly in the amorphous regions of the polymer [10].

Polypropylene

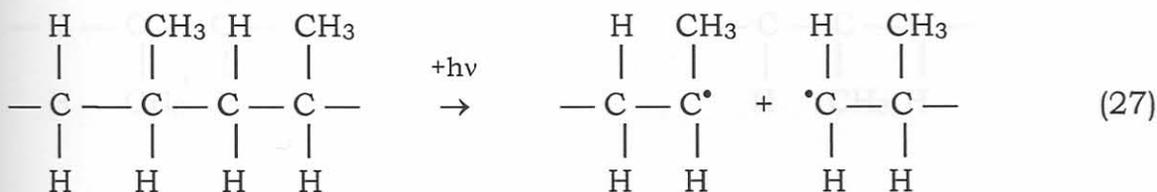


The weathering resistance of polyethylene of commercial grades has been related to the photo-oxidation reactions. They predominately occur close to the surface of the specimen [8] and are due to the presence of impurities or extraneous carbonyl groups [12, 22, 23].

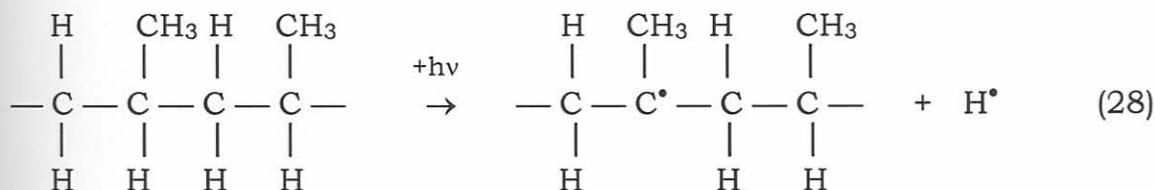
Polypropylene

The exposure of polypropylene to ultraviolet radiation in air produces a rapid photo-oxidation with marked effects on the mechanical and other physical properties of the polymer [9, 10, 13, 14]. The molecular weight of polypropylene decreases rapidly with time of UV irradiation. The rate of chain scission, initially a linear function of irradiation time, increases at longer exposures, indicating an autocatalytic mechanism for photo-oxidation [10]. After longer exposure a sheet sample of polypropylene develops tiny cracks and becomes brittle. Irradiation of polypropylene with UV light results in the formation of the following bands assigned to specific groups: Hydroxyl and hydrogen-bonded hydroperoxides at 3400cm^{-1} , carbonyl at $1715\text{-}1720\text{cm}^{-1}$, γ -lactone at 1728cm^{-1} , carboxylic acid at 1715cm^{-1} , and vinyl alkene at 1645cm^{-1} [10, 12, 13, 14].

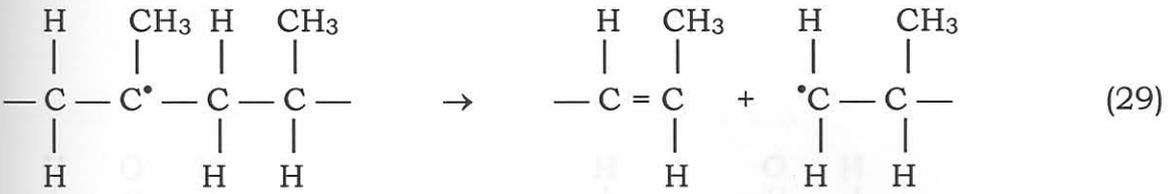
The primary events following irradiation of polypropylene with UV light (2537 \AA) in vacuum are bond scission (27) and crosslinking (30):



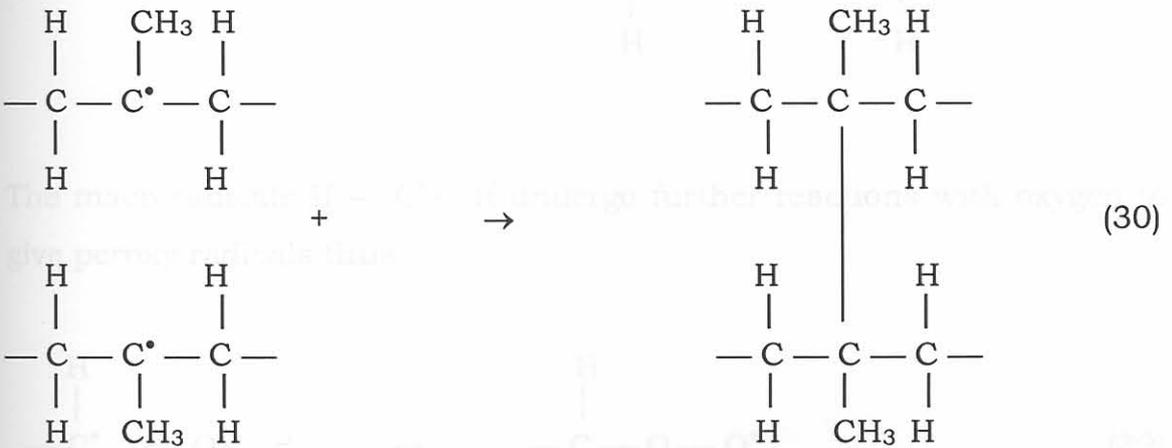
Another probable reaction is the dissociation of carbon - hydrogen bonds at the tertiary carbon:



which may lead to chain scission by a disproportionation reaction:

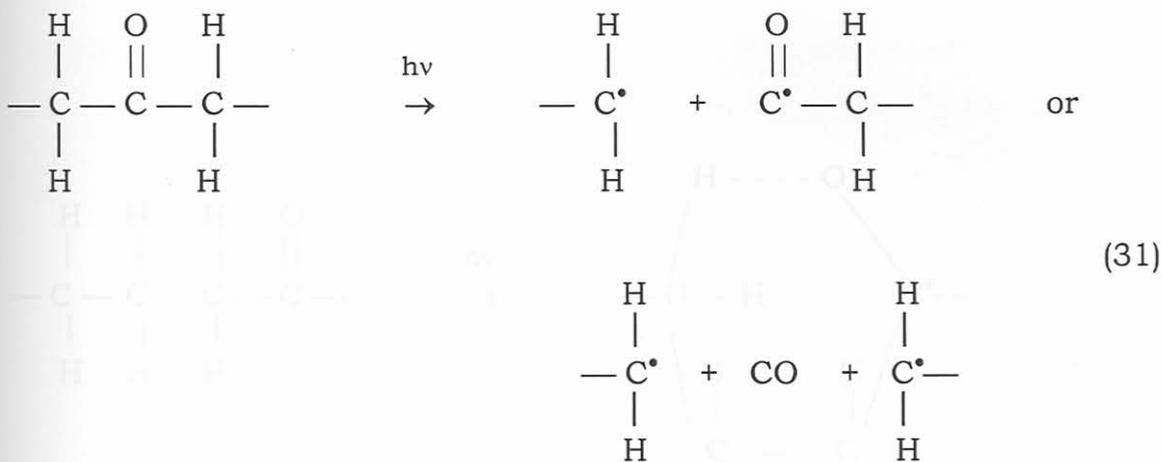


When two polypropylene radicals react by combination a crosslink is formed:

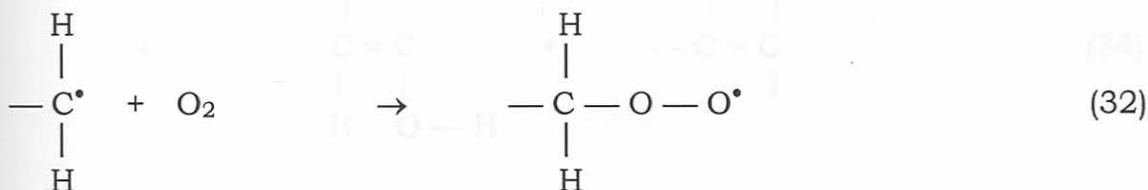


Two main primary photochemical processes are believed to be responsible for the carbonyl-initiated photo-oxidation of polyolefins [2]. Their nomenclature originates from the early pioneering work of Norrish on the photochemistry of liquid-phase aliphatic ketones [8-10].

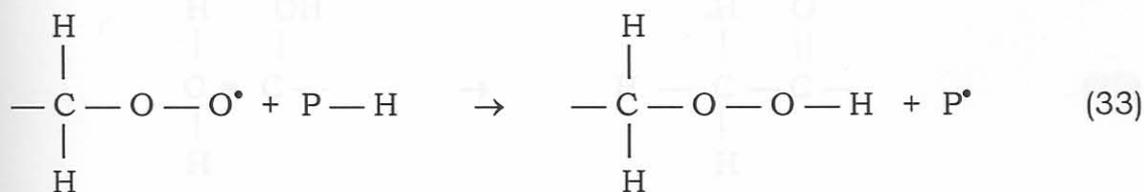
Norrish type - I process: This leads to the formation of free radicals in which the excited singlet or triplet states of the carbonyl groups are precursors [10].



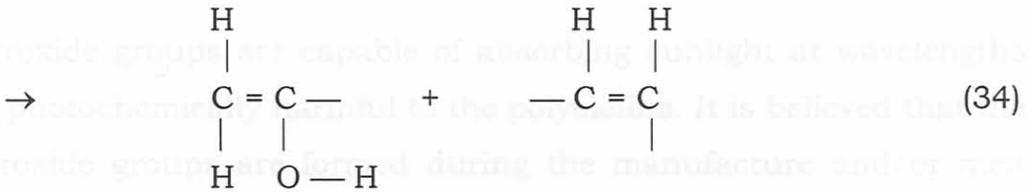
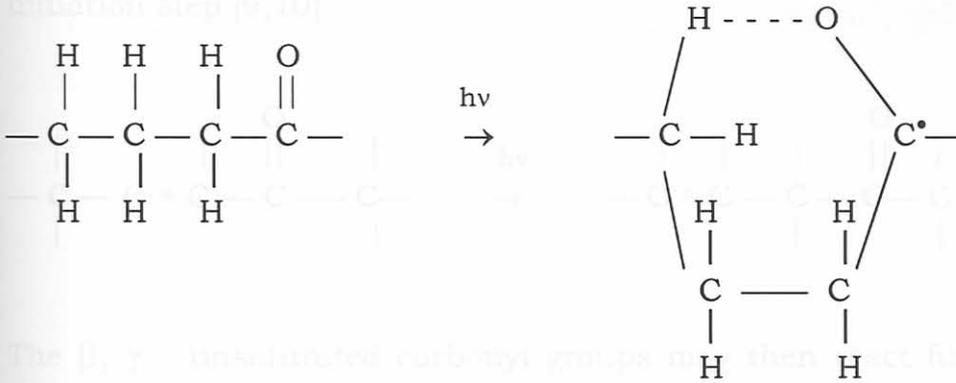
The macroradicals $\text{H}-\text{C}^\bullet-\text{H}$ undergo further reactions with oxygen to give peroxy radicals thus



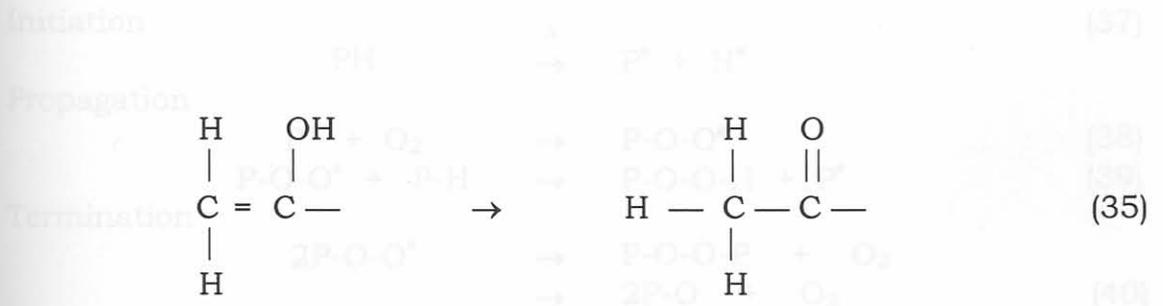
The peroxy radicals may then abstract hydrogen atoms from the polymer substrate, P-H, to form hydroperoxide groups thus



Norrish - type II process: This only occurs when the ketone possesses at least one hydrogen atom on a γ -carbon with respect to the carbonyl group. The reaction occurs via a six-membered cyclic intermediate involving intramolecular hydrogen-atom abstraction and produces one olefinic and one enolic group in the polymer [8-12].

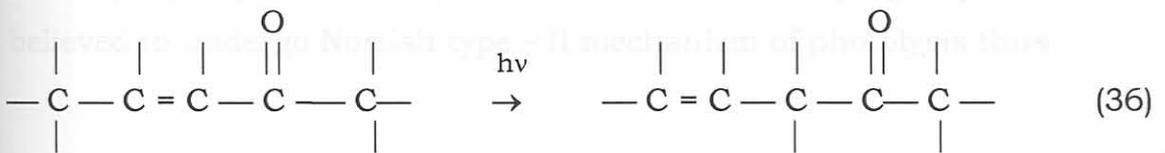


The enolic group then rearranges to give a ketone group thus



Although the Norrish type-II process does not directly produce free radicals, it is nevertheless considered to be the most important primary reaction at ambient temperatures in the mechanism of the oxidative photodegradation of polyethylene containing carbonyl groups randomly distributed along the hydrocarbon chain [9].

On photo-oxidation, the luminescent α , β - unsaturated carbonyl groups are converted into β , γ - unsaturated carbonyl groups via the following initiation step [9,10]



The β , γ - unsaturated carbonyl groups may then react further via the Norrish type - I and II processes to give aliphatic carbonyl products, e.g. carboxylic acids and esters.

Hydroperoxide groups are capable of absorbing sunlight at wavelengths that are photochemically harmful to the polyolefins. It is believed that the hydroperoxide groups are formed during the manufacture and/or melt processing of the polyolefin by the Bolland - Gee auto-oxidation mechanism thus [29, 30]:

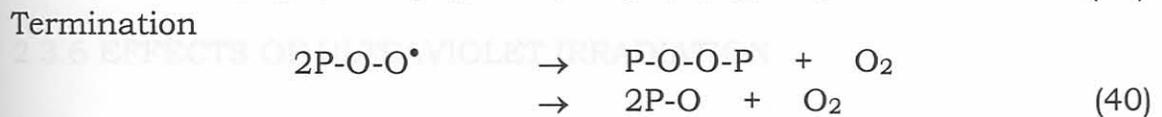
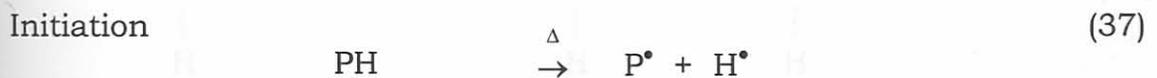
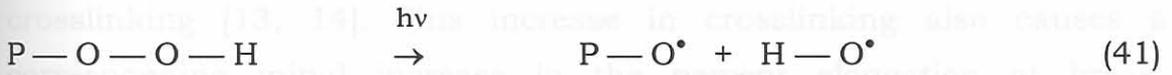


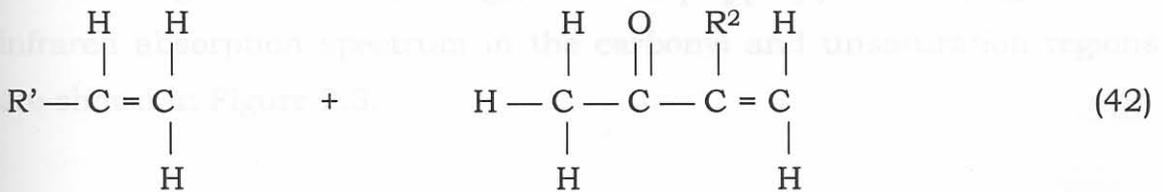
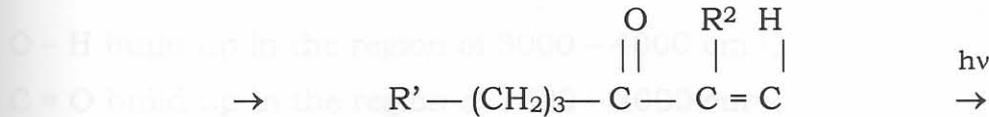
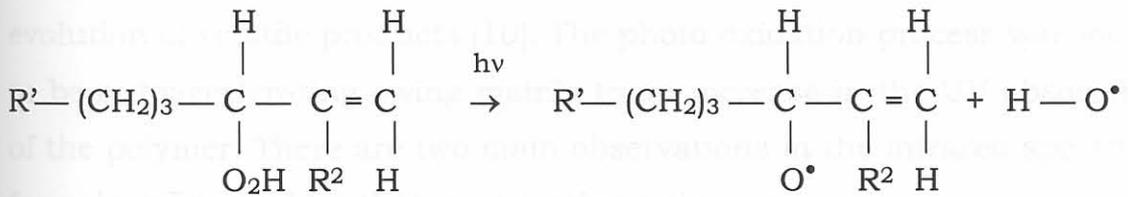
Photo-oxidation of polyolefins results in marked changes in both the physical and mechanical properties of the polymers. It leads to chain scission and a consequent reduction in the molecular weight of the

On exposure to light, the hydroperoxides dissociate in the excited state to give alkoxy and hydroxyl radicals thus



The radicals PO^\bullet and HO^\bullet can then start the free - radical chain process.

On irradiation these groups are photolysed initially to α, β - unsaturated carbonyl groups. The α, β - unsaturated carbonyl groups are then believed to undergo Norrish type - II mechanism of photolysis thus



Thus, the carbonyl absorption band produced during the photo-oxidation of polyolefins is very broad and consists of various types of carbonylic product (6, 12).

2.3.6 EFFECTS OF ULTRAVIOLET IRRADIATION

Attenuated total reflectance spectroscopy which analyses the surface Photo-oxidation of polyolefins results in marked changes in both the physical and mechanical properties of the polymers. It leads to chain scission and a consequent reduction in the molecular weight of the

polymer [9]. Further exposure results in an increase in the rate of degradation, indicating that an autocatalytic mechanism is dominant. Accompanying chain scission is a significant increase in the degree of crosslinking [13, 14]. This increase in crosslinking also causes a corresponding initial increase in the percent elongation at break. Continued irradiation, however, eventually results in a marked decrease of the elongation at break.

There is considerable chain restructuring during the irradiation of polyolefins [9, 10]. Photo-oxidation of polyolefins also results in a marked deterioration in the electrical resistivity of the polymer [13].

Exposure of polyolefins to ultraviolet light in air leads to the uptake of oxygen, formation of carbonyl, hydroxyl, and vinyl groups and the evolution of volatile products [10]. The photo-oxidation process was found to be autoaccelerating owing mainly to an increase in the UV absorption of the polymer. There are two main observations in the infrared spectrum for polyolefins and for that matter other polymers:

O – H build up in the region of 3000 – 4000 cm^{-1} ,

C = O build up in the region of 1500 – 2000 cm^{-1} .

These changes are shown in Figure 2.2 for polypropylene. Changes in the infrared absorption spectrum in the carbonyl and unsaturation regions are shown in Figure 2.3.

Thus, the carbonyl absorption band produced during the photo-oxidation of polyolefins is very broad and consists of various types of carbonylic product [8,12].

Attenuated total reflectance spectroscopy which analyses the surface layers of the polymer indicates that photo-oxidation occurs at the surface layers where oxygen has access and it is believed that the carbonyl group

formation decreases with increasing effective depth of light penetration on both sides of the film [12].

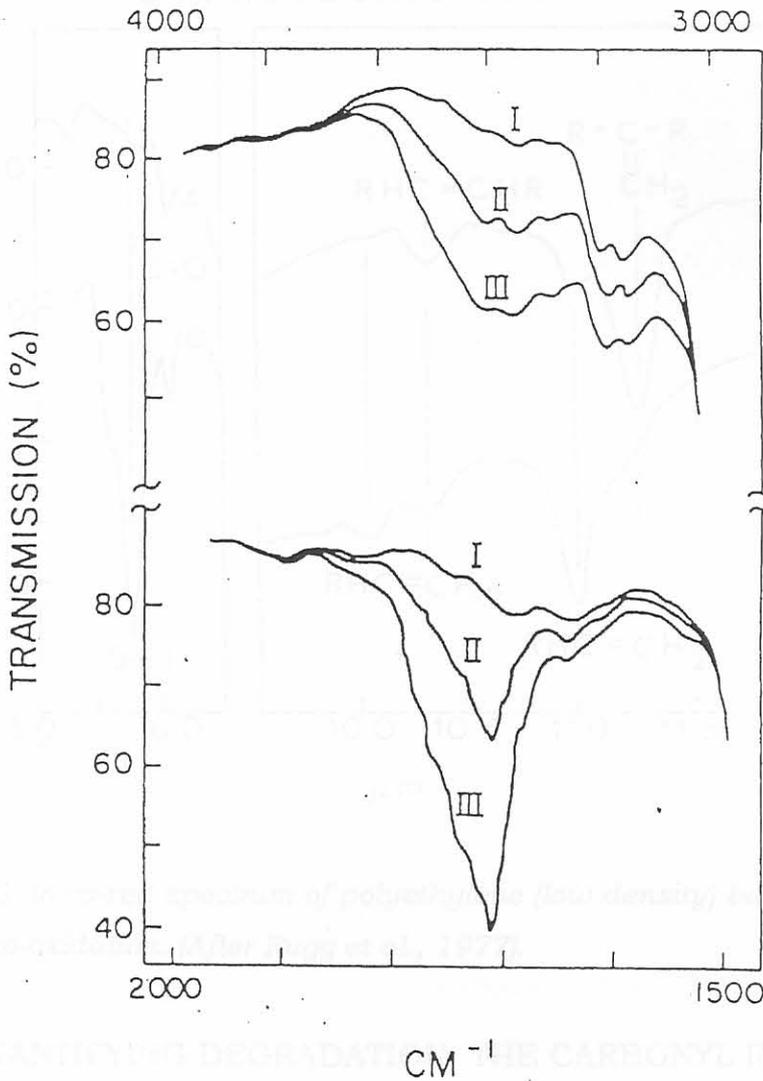


Figure 2.2. Formation of photo-oxidation products in polypropylene film monitored by infrared after irradiation for: I, 0h, II, 6h, III, 110h. (After Wiles, 1973).

As seen from the figure, the carbonyl absorption band is very broad extending from 1650 to 1850 cm^{-1} and is resolvable into six overlapping peaks. The main broad hydroxyl band at 3400 cm^{-1} contains a small band at 3340 cm^{-1} which has been attributed to the formation of hydrogen - bonded hydroperoxides produced by oxidation of the tertiary C - H bonds [8-10].