

# PHOTODEGRADATION OF POLYOLEFINS

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Bachelor Thesis  
2006



Tomas Bata University in Zlín  
Faculty of Technology

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Univerzita Tomáše Bati ve Zlíně

Fakulta technologická

Ústav inženýrství polymerů

akademický rok: 2005/2006

## ZADÁNÍ BAKALÁŘSKÉ PRÁCE

(PROJEKTU, UMĚLECKÉHO DÍLA, UMĚLECKÉHO VÝKONU)

Jméno a příjmení: **Leoš VAŠEK**

Studijní program: **B 2808 Chemie a technologie materiálů**

Studijní obor: **Chemie a technologie materiálů**

Téma práce: **Photodegradation of Polyolefins**

Zásady pro vypracování:

**The aim of this Bachelor thesis is to create a compact view on the ageing of common polyolefins caused by UV irradiation. Many plastics products are used for outdoor applications, and UV light is one of the most severe sources of degradation changes in the material. Therefore, the study of photodegradation is of great interest. The main attention should be focused on the wide-spread polyolefins, polyethylene and polypropylene, and their different mechanism of photodegradation.**

Rozsah práce:

Rozsah příloh:

Forma zpracování bakalářské práce: **tištěná/elektronická**

Seznam odborné literatury:

**Wypych, G.: Handbook of Material Weathering (2nd Edition) - ISBN: 1-895198-12-7**

**Kutz, Myer: Handbook of Materials Selection - ISBN: 0-471-35924-6**

**Brydson, J.: Plastics Materials (7th Edition) - ISBN: 0-7506-4132-0**

**Wypych, G.: Weathering of Plastics - Testing to Mirror Real Life Performance - ISBN: 1-884207-75-8**

**dále odborné články dle doporučení vedoucí práce**

Vedoucí bakalářské práce:

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Ústav inženýrství polymerů

Datum zadání bakalářské práce:

**20. října 2005**

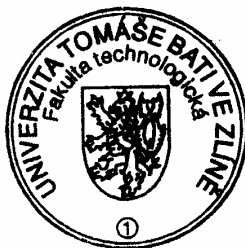
Termín odevzdání bakalářské práce:

**26. května 2006**

Ve Zlíně dne 7. února 2006



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## **ABSTRACT**

This bachelor thesis deals with photodegradation of polyolefins. The work consists of two main parts. The first part comprises the basic information about polyolefins, their polymerization, morphology, properties and applications. The second section is devoted to the polyolefins photodegradation. The fundamentals of photophysics and photochemistry are shortly described. Main attention is focused on the photodegradation of two most important polyolefins, polyethylene and polypropylene. The effect of morphology on photodegradation process is mentioned as well. Finally, the stabilization is briefly discussed.

## **ANOTACE**

Tato bakalářská práce se věnuje fotodegradaci polyolefinů. Skládá se ze dvou hlavních částí. První část obsahuje základní informace o polyolefinech, jejich polymerizaci, morfologii, vlastnostech a využití. Druhá část se již věnuje fotodegradaci polyolefinů. Stručně jsou vysvětleny základy fotofyziky a fotochemie. Hlavní pozornost je věnována fotodegradaci dvou nejvýznamnějších polyolefinů, polyetylenu a polypropylenu. Zmíněn je také efekt morfologie na proces fotodegradace. V neposlední řadě je krátce diskutována stabilizace polyolefinů.

## ACKNOWLEDGEMENTS

In the first place I would like to thank my supervisor Jana Výchopňová for her help in the course of full time of my work.

In the second place I would like to thank my girlfriend Lucie Pšenčíková, my mother Dagmar Vašková and my grandfather Jan Sedláček for kind support during my studies and making this thesis.

I declare I worked on this Bachelor thesis by myself and I have mentioned all the used literature.

Zlín, 16.5.2006

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## INTRODUCTION

Polymers are relatively new class of materials. They have been developed to take place of some natural materials for their specific properties. Initially the polymers were produced without the exhaustive knowledge of their properties. The result was the financial loss, which inspired distrust to this material. One of the causes of ineffectual applications of polymeric materials was the bad knowledge of their resistance in their surrounding environment. The plastics are not suitable for the universal use. The applicability depends on their chemical composition, structure, the amount and the composition of the fillers, impurities and admixtures. The way of processing, chemical composition and specifications of the environment have to be also considered [33].

This bachelor thesis is addressed to photodegradation of polyolefins. Polyolefins represent quantitatively the greatest group of synthetic polymers, especially due to great production volume of polyethylene and polypropylene (therefore, the main attention is devoted to them in this work). Reasons of their expansion are their availability, low price of raw materials for monomer production and their good properties. These materials are frequently used for outdoor applications. However, the sunlight radiation, with connection with other weather conditions like temperature or humidity, strongly influences durability of polyolefins and their useful properties. The loss of these properties is the reason of lifetime decrease of polyolefin products. Therefore, the study of degradation and possibilities of its retardation are on a main interest.

This work summarizes main knowledge of polyolefins and their photodegradation behaviour. Main attention is devoted to photodegradation of polyethylene and polypropylene.



## 1 POLYOLEFINS

Polyolefins are one of the most often used synthetic polymers, especially due to their good availability and low price. Moreover, polyolefins are very well processed by various technological processes and they have useful properties. Besides polyethylene and polypropylene, which are the most important representatives of polyolefins, also polybut-1-ene, polyisobutylene and poly-(4-methylpent-1-ene) represent interesting and perspective materials [1].

### 1.1 Polyethylene

Polyethylene (PE) has the largest volume use of any other plastic. Depending on the mode of polymerization, three basic types of polyethylene are frequently used: linear high-density polyethylene (HDPE), branched low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE) (Fig. 1.1) [2].

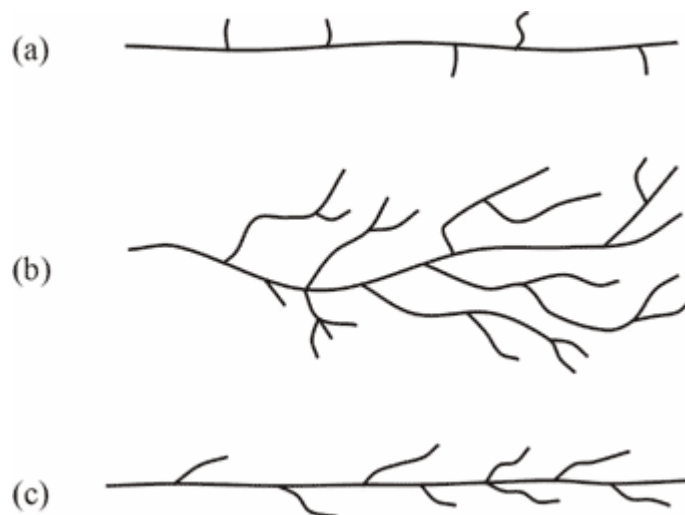


Figure 1. 1: Structure of polyethylene: a) HDPE; b) LDPE; c) LLDPE [3]

### 1.1.1 Polymerization and Structure

Polyethylene has the simplest basic structure of any polymer. Its molecule consists of long chain of carbon atoms, with two hydrogen atoms attached to each carbon. Commercially, it is produced from ethylene (Fig. 1.2).

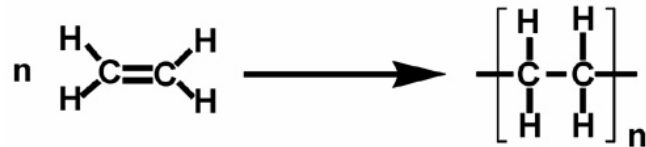


Figure 1. 2: Polymerization of ethylene [4]

There are five distinct routes of PE preparation:

- a) **High-Pressure Process:** Commercial high polymers are generally produced under conditions of high pressure (100-300 MPa) and at temperatures of 80-300°C. A free-radical initiator such as benzoyl peroxide, azodi-isobutyronitrile or oxygen is commonly used. By varying temperature, pressure, initiator type and composition and by incorporating chain transfer agents it is possible to vary independently polymer characteristics as branching and molecular weight without needing long reaction times. By this process, the LDPE is prepared.
- b) **Ziegler Process:** This polymerization is referred to as co-ordination polymerization since the mechanism involves the catalyst-monomer co-ordination complex controlling the way in which the monomer approaches the growing chain. The co-ordination catalysts are generally formed by the interaction of the alkyls of groups I-III metals with halides and other derivatives of transition metals in groups IV-VIII of the periodic table. The polymers produced by this technology are intermediate in density between LDPE and HDPE.
- c) **Phillips Process:** In this process ethylene, dissolved in a liquid hydrocarbon such as cyclohexane, is polymerized by a supported metal oxide catalyst at about 130-160°C and at about 1.4-3.5 MPa pressure. The solvent serves to dissolve polymer as it is formed and as a heat transfer medium but is otherwise inert. Commercial products (HDPE) have a melt flow index of only 0.2-5.0 and have the highest density of any commercial polyethylenes.

- d) **Standard Oil Company (Indiana) Process:** This process has many similarities to the Phillips process. It is based on the use of a supported transition metal oxide (Molybdenum oxide) in combination with a promoter (sodium or calcium as metals or hydrides). Reaction temperatures are 230-270°C and pressures are 4.0-8.0 MPa. The reaction is carried out in a hydrocarbon solvent. The products (HDPE) have a density similar to the Phillips polymers.
- e) **Preparation of LLDPE and Metallocene Polyethylene:** Over the years many methods have been developed in order to produce polyethylenes with short chain branches. One of them is a gas phase process. Gaseous monomers and catalysts are fed to a fluid bed reactor at pressures 0.7-2.1 MPa and at temperatures 100°C and below. The short branches are produced by including small amounts of propene, but-1-ene, hex-1-ene or oct-1-ene into the monomer feed. Application of metallocene catalysts is another way of LLDPE preparation. Such catalysts are transition metal compounds, usually zirconium or titanium, incorporated into a cyclopentadiene-based structure [2, 5].

### 1.1.2 Morphology

Polyethylene is used as a model semicrystalline polymer for morphological studies because it has the simplest chemical structure of any polymer. It has provided data and ideas valuable in the study of other semicrystalline polymers.

The most thermodynamically stable crystal structure of PE at ambient temperature and atmospheric pressure is the orthorhombic crystal symmetry. A monoclinic structure, which is thermodynamically less stable, has also been reported for PE, but it is present only in mechanically stressed samples, as in the stretching and orientation of films.

When PE is crystallized from a super cooled solution or the melt, the chains are organized by folding to form lamellae. These rapidly branch to form more complicated, filling space in 3 dimensions to form a structure known as a spherulite (Fig. 1.3).

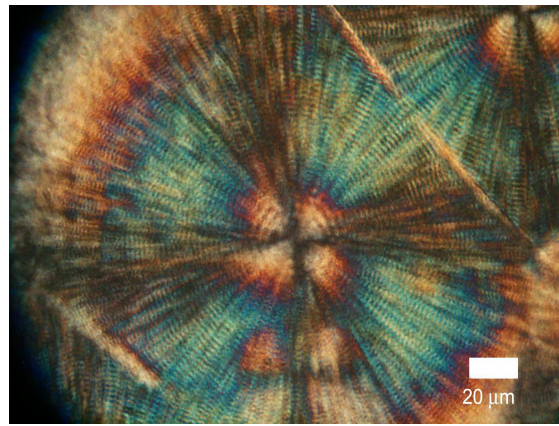


Figure 1. 3: Polyethylene spherulites [15]

### 1.1.3 Properties

Generally PE is a wax-like thermoplastic softening at about 80-130°C with a density less than that of water. PE exhibits near-zero moisture absorption, excellent chemical resistance, excellent electrical insulating properties and easy processing. In the mass it is opaque due to crystallization but thin films may be transparent [5]. Mechanical properties strongly depend on the molecular weight and on the degree of branching of the polymer. These properties are also dependent on the rate of testing, the temperature of test etc.

Table 1. 1: Effect of molecular weight and density (branching) on some mechanical and thermal properties of PE [5].

Property	Test	Density = 0.92 g/cm <sup>3</sup> high pressure polymers					Density = 0.94 g/cm <sup>3</sup> high pressure polymers	Density = 0.95 g/cm <sup>3</sup> Ziegler-type polymers			Density = 0.96 g/cm <sup>3</sup> Phillips-type polymers	Density = 0.98 g/cm <sup>3</sup> polymethylene
		0.3	2	7	20	70	0.7	0.02	0.2	1.5	~	~
Melt flow index (g/10 min)	BS2782	0.3	2	7	20	70	0.7	0.02	0.2	1.5	~	~
Tensile strength (MPa)	BS903	15.3	12.5	10.2	8.9	~	20.7	22.0	23.0	23.0	27.5	34.5
Elongation at break (%)	BS903	620	600	500	300	150	~	>800	380	20	500	500
Izod impact strength (J)	BS2782	13.5	13.5	13.5	13.5	13.5	~	4.3	2.7	2.0	6.8	~
Vicat softening point (°C)	BS2782	98	90	85	81	77	116	124	122	121	~	~
Softening temperature (°C)	BS1493	~	~	~	~	~	~	110	19.4	15.4	122	~
Crystalline melting point (°C)	~	108	108	108	108	108	125	130	130	130	133	136
Number average molecular weight	~	48000	32000	28000	24000	20000	~	~	~	~	~	~
CH <sub>3</sub> groups per 1000 C atoms	~	20	23	28	31	33	~	5-7	5-7	5-7	<1.5	unbranch.

Table 1.1 shows clearly the general effects of branching (density) and molecular weight on some polymer properties but under different test conditions different results may be obtained.

#### 1.1.4 Applications

Polyethylene is the polymer which is seen most in daily life. HDPEs major use is in blow-moulded bottles, drums, automotive gasoline tanks; injection-moulded crates, trash and garbage containers and extruded pipe products. LDPE/LLDPEs find major applications in plastic bags, films, cable insulations and bottles [2].

## 1.2 Polypropylene

The worldwide consumption of polypropylene occupies third place among commodity plastics, after low-density polyethylene and polyvinylchloride but before high-density polyethylene and polystyrene [6].

### 1.2.1 Polymerization

As early as 1869 propylene was polymerized by Berthelot by reaction with concentrated sulphuric acid. The resulting viscous oil, at room temperature, did not exhibit interesting properties for industrial application. Its industrial importance results from the appearance of crystalline high molecular weight polypropylene, which was first polymerized in 1955 by Natta from organo-metallic catalysts based on titanium and aluminium (Fig. 1.4). The resulting semi-crystalline polymer has strong mechanical properties which explain its rapid industrial development.

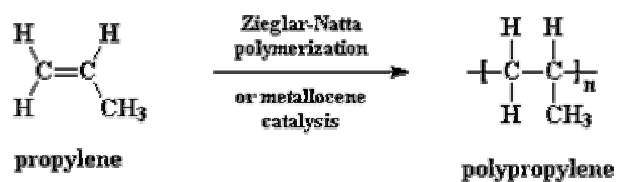


Figure 1. 4: Polymerization of propylene [7]

### 1.2.2 Structure and Morphology

Polymerization of the non-symmetrical propylene molecule leads to three possible sequences: head-to-head, head-to-tail and tail-to-tail. The steric effect of the methyl group highly favours the head-to-tail sequence, which gives a high chemical regularity of the PP chain [8].

Three stereo-configurations of polypropylene are known: isotactic, syndiotactic and atactic (Fig 1.5). Isotactic PP (iPP) has the methyl groups placed always on the one side of main chain whereas methyl groups of syndiotactic PP are varying regularly. Both previous types are stereoregular and semicrystalline unlike to atactic PP. Its methyl groups are placed randomly [10].

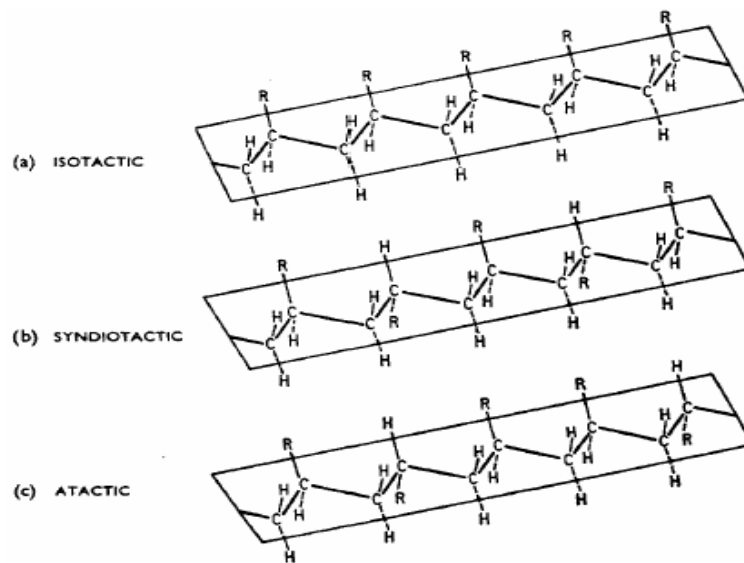


Figure 1. 5: Stereo-configurations of propylene sequences: a) isotactic; b) syndiotactic; c) atactic [9]

Commercially, predominantly iPP is produced. Its molecules cannot crystallize in a planar zigzag form because of the steric hindrance of the methyl group, but crystallize in a helix, with three molecules being required for one turn of the helix [5]. The helix can be either right- or left-handed, with a periodicity of 0.65 nm. The position of the methyl group with respect to the chain axis can be either up or down [12].

On the crystal lattice level, iPP exhibits three different morphological forms:  $\alpha$ ,  $\beta$  and  $\gamma$ , distinguished by the arrangement of the chains. Another form of iPP with a degree of order between crystalline and amorphous phases is a smectic form. Preparation of these forms depends on the crystallization conditions, such as pressure, temperature, cooling rate and addition of nucleators [11, 12].

The predominant crystal structure of pure isotactic polypropylene at atmospheric pressure is the monoclinic  $\alpha$ -structure. The equilibrium melting temperature of the  $\alpha$ -form of iPP crystals ( $T_m^0$ ) was reported between 185°C and 209°C [12, 16].

The  $\beta$ -form of iPP grows during melt-crystallization in only a small amount as a supplement of  $\alpha$ -phase. A higher content of  $\beta$ -phase can be obtained via intensive-melt cooling, shear-field crystallization, and particularly with the aid of specific nucleation [21, 22]. A number of nucleating agents, which differ in both nature and activity, is described. The  $T_m^0$  was extrapolated by several research groups, and values varied from 170°C to 200°C [9, 17].

The  $\gamma$ -form can be largely produced by crystallization at elevated pressures. It can be also produced at atmospheric pressure from low molecular weight fractions or from polypropylene-derived copolymers. The melting point of the  $\gamma$ -form is mostly reported in the range of 125 to 150°C for low molecular weight samples. In the case of pressure-crystallized samples of high molecular weight iPP, the melting occurs above 150°C [12].

### 1.2.3 Properties

Mechanical properties of PP are strongly dependent on its crystallinity. Increasing crystallinity enhances stiffness, yield stress, and flexural strength, however, decreases toughness and impact strength [11]. Some properties of commercial PP are summarized in Table 1.2.

Table 1. 2: Some mechanical and thermal properties of commercial polypropylenes

Property	Test method	Homopolymers			Copolymers	
Melt flow index (g/10 min)	( a )	3.0	0.7	0.2	3.0	0.2
Tensile strength (MPa)	( b )	34	30	29	29	25
Elongation at break (%)	( b )	350	115	175	40	240
Flexural modulus (MPa)	~	1310	1170	1100	1290	1030
Brittleness temperature (°C)	ICI/ASTM D.476	15	0	0	-15	-20
Vicat softening point (°C)	BS 2782	145-150	148	148	148	147
Rockwell hardness (R-scale)	~	95	90	90	95	88.5
Impact strength (J)	( c ) 13.5	34	46	46	57.5	~

( a ) Standard polyethylene grader: load 2.16 kg at 230°C

( b ) Straining rate 18 in/min

( c ) Falling weight test on 14 in diameter moulded bowls at 20°C

PP indicates some similar properties to polyethylene, particularly swelling and solution behaviour, and electrical properties. However, it differs in following:

- (1) It has a lower density ( $0.90\text{g/cm}^3$ ).
- (2) It has a higher softening point and hence a higher maximum service temperature.
- (3) It has a higher brittle point.
- (4) It is more susceptible to oxidation. The tertiary carbon atom provides a site for oxidation so that the polymer is less stable to the influence of oxygen [5].

#### 1.2.4 Applications

Polypropylene has enough high E-modulus, therefore it can be used for technical application. PP is often used for blow moulded bottles and automotive parts; injection-moulded closures, appliances, housewares, automotive parts, and toys. It can be also extruded into fibres and filaments for production of carpets, rugs, and cordage [2].

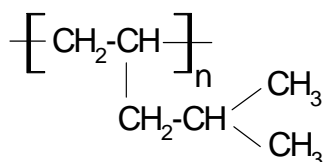


### 1.3 Poly-(4-methylpent-1-ene)

Of the numerous branched aliphatic polyolefins higher than the polybutenes developed in research laboratories since the mid fifties, only poly(4-methylpent-1-ene) (PMP), introduced in 1965 by ICI (England), has so far achieved commercial importance [14].

#### 1.3.1 Polymerization

PMP is produced using a Ziegler-Natta catalysts system of violet  $\text{TiCl}_3$  and diethyl aluminium chloride. The molecule of PMP is shown in Figure 1.6



*Figure 1. 6: Molecule of poly(4-methylpent-1-ene)*

#### 1.3.2 Structure and Morphology

PMP is a stereoregular polymer like polypropylene. There are three possibilities of its stereochemical arrangement: isotactic, syndiotactic and atactic. Isotactic and syndiotactic PMP are semicrystalline polyolefins. Moreover, isotactic PMP (iPMP) is polymorphic, i.e. it can crystallize in several modifications depending on crystallization conditions. Five crystal unit cells of PMP has been described.

The stereochemical configuration can strongly affect the physical and mechanical properties of the polymer.

The commercial PMP is usually an isotactic material which shows 65% crystallinity when annealed but under more common conditions about 40% [2].

### 1.3.3 Properties

PMP is linear  $\alpha$ -polyolefin with isobutyl branches and with very interesting properties. It has a high melting point of 240°C and low density. PMP presents relatively high thermal stability and chemical resistance, in addition to excellent dielectric characteristic and microwave transparency. But PMP is also a rather brittle, have poor aging characteristic, show a high gas permeability and is a rather expensive (about 3-4 times more than LDPE). Comparison of selected mechanical properties of iPMP, HDPE, and iPP is in Table 1.3.

Perhaps the most outstanding property of this material is the high degree of transparency. This is due to:

- a) both molecules and crystals show little optical anisotropy
- b) crystalline and amorphous zones have comparable densities; the crystalline phase has even lower density than that of amorphous. [2, 18, 19].

*Table 1. 3: Comparison of selected mechanical properties of iPMP, HDPE, and iPP [18]*

Property	iPMP	HDPE	iPP
Tensile modulus (GPa)	0.8-1.2	0.4-1.1	1.0-1.7
Tensile strength at yield (MPa)	23-28	~	~
Tensile strength at break (MPa)	17-20	18-33	29-30
Elongation at break (%)	10-25	12-700	500-900
Notched impact strength (kJ/m)	100-200	43-750	21-320

### 1.3.4 Applications

At the present time the major uses are in transparent chemical plant, in electrical equipment which can withstand soldering and encapsulation processes, in transparent sterilisable medical equipment and for lamp covers and covers of a car interior light [2].

## 1.4 Polybut-1-ene

Polybut-1-ene (PB) is the youngest member of the polyolefin family (1965) being linear in structure (Fig. 1.6) [13].

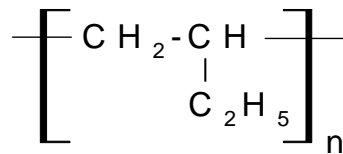


Figure 1. 7: Polybut-1-ene

### 1.4.1 Polymerization

The monomer butylene is obtained from the petrochemical industry [13]. PB is produced by Ziegler-Natta system and the commercial material have very high molecular weight of 770 000 to 3 000 000, that is about ten times higher than that of the normal LDPE [5].

### 1.4.2 Structure and Morphology

PB is stereoregular polyolefin as well as PP and PMP. Commercially, PB is manufactured via a stereospecific mechanism into an isotactic structure, of 50%-55% crystallinity. Isotactic polybut-1-ene is polymorphic, thus, it exhibits three crystalline forms. One form is produced on crystallization from the melt but this is unstable and on standing for 3-10 days this is replaced by a second crystal form. A third modification may be obtained by crystallizing from solution. The first crystalline form has a density of 0.89 g/cm<sup>3</sup> and a melting point of 124°C but on reversion to the second form the density rises to 0.95 g/cm<sup>3</sup> and the melting point to 135°C. During the crystalline phase transformation the crystallinity increases.

### 1.4.3 Properties

This polymer is typical of the aliphatic polyolefins in its good electrical insulations and chemical resistance. It has a melting point and stiffness intermediate between

polyethylene and polypropylene, but it is less resistant to aliphatic hydrocarbons than PE and PP. Because it has very high molecular weight, polymer has a very high resistance to creep. One advantage of this is that the wall thicknesses of PB pipes may be much less than for corresponding PE and PP pipes [5].

#### 1.4.4 Applications

The main interest of PB is in its use as a piping material. The principal application is for small-bore cold and hot water piping (up to 95°C) for domestic plumbing [5].

### 1.5 Polyisobutylene

In chronological terms polyisobutylene (PIB) was the first of the polyolefins. Low polymers were prepared as early as 1873. PIB is made from the monomer isobutylene by cationic vinyl polymerization (see Fig. 1.8).

The pair of opposing methyl groups leads to a low  $T_g$  of about -73°C (-20°C for polybut-1-ene). The methyl groups do, however, hinder rotation about the main chain bonds so the resulting material is, at sufficiently high molecular weights, a rather sluggish rubber.

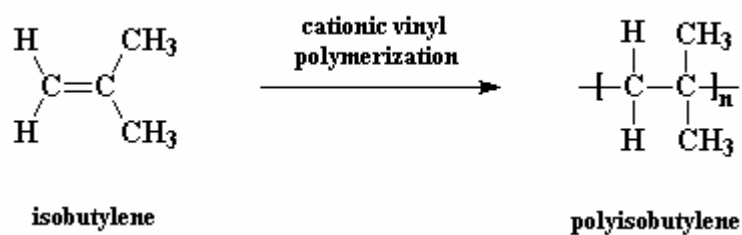


Figure 1. 8: Polymerization of PIB

The homopolymer finds uses as an adhesive component, as a base for chewing gum, in tank linings, as a motor oil additive to provide suitable viscosity characteristics and to improve the environmental stress-cracking resistance of polyethylene. It has been

incorporated in quantities of up to 30% in HDPE to improve the impact strength of heavy duty sacks [2].

## 2 PHOTODEGRADATION

Polyolefins are often used for outdoor applications. By virtue of the weather conditions, the material age and change its properties (embrittlement, cracking of the surface, color changes, decrease of the mechanical features etc.) Weathering of polymers may be caused by various factors as for example mechanical stress, oxidation, heat- or biodegradation. One of the most severe factors contributing to degradation is ultraviolet radiation.

### 2.1 Photophysics

Visible light, infrared, ultraviolet (UV), and  $\gamma$ -rays are each a distinct form of electromagnetic radiation (Fig. 2.1). Each propagates in space as waves of electronic and magnetic fields. Electromagnetic waves carry a discrete amount of energy depending on their frequency, as stated by Planck's Law [20]:

$$E = h\nu \quad (1)$$

where

- $E$  = energy of radiation [J]
- $\nu$  = frequency of radiation [1/s]
- $h$  = Planck's constant [J.s]

The frequency of radiation depends on the conditions in which this radiation was formed. With a temperature increase, the light spectrum is shifted to the left, meaning that more UV and visible light is emitted [20].

It is evident that radiation with higher frequency, ergo with lower wavelength, carries a greater amount of energy. At the earth's surface lies the most energetic solar radiation in region of ultraviolet wavelength in electromagnetic spectrum.

Ultraviolet wavelengths from sunlight are an important component in outdoor degradation. The energy from sunlight is mainly visible and infrared light; ultraviolet makes up less than 5% of sunlight. However, the photodegradation of exterior plastic materials is caused mainly by UV light.

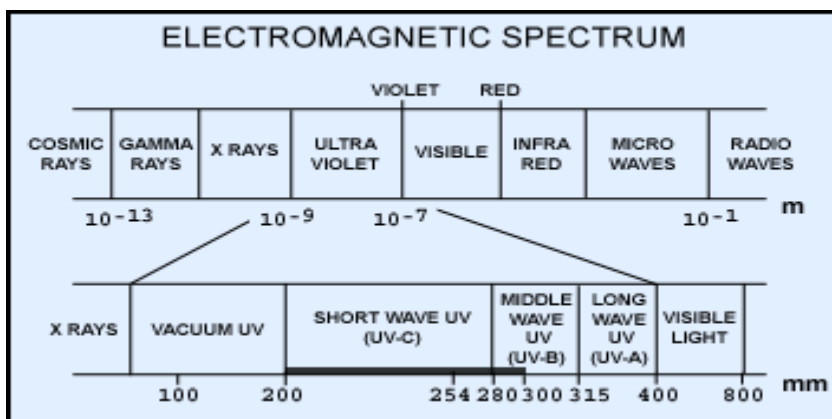


Figure 2. 1: Electromagnetic spectrum

Under normal conditions, most organic molecules are in the ground state ( $S_0$ ). The lowest energy state for these molecules is a singlet state in which electrons with opposing spins are paired in the molecular orbitals. The frequently-used Jablonski diagram shows the possible outcomes when molecules absorb energy (Fig. 2.2) [20]

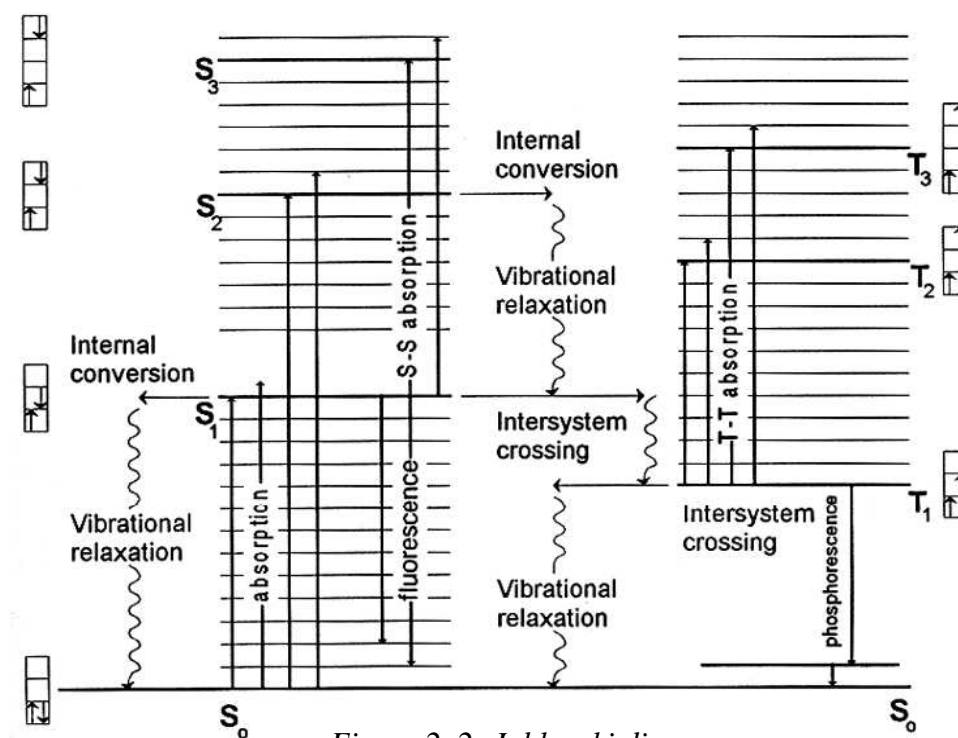


Figure 2. 2: Jablonski diagram

At first electrons in molecule of polymer absorb the radiation energy. Depending on the energy absorbed by the molecule, the electrons are promoted from ground state to higher energy state levels. The absorbed energy is then dissipated either in radiative processes as fluorescence and phosphorescence or in non-radiative processes. In them is absorbed energy converted. This process, in dependence on the balance of energy available in a particular molecule and in the chemical structure of the excited molecule, can lead to cleavage into free radicals, abstraction of hydrogen atom, photosensitization, decomposition with formation of two or more molecules, photodimerization or crosslinking, intramolecular rearrangement or photoisomerization. Which reaction type predominates partly depends on the environment. These primary photochemical reactions are mostly followed by secondary reactions; prevailing with oxygen or ozone and photooxidation is realized.

## 2.2 Photochemistry

Most commercial organic polymers undergo chemical reaction upon irradiation with ultraviolet light, because they possess chromophoric groups (as regular constituents or as impurities) capable of absorbing UV light. Carbonyl groups play a prominent role among these chromophoric groups [23]. Therefore, the photochemistry of ketone polymers was selected to demonstrate how light-induced chemical reactions proceed. As can be seen from Fig. 2.3, light absorbed by carbonyl groups can include bond scission by either Norrish type I or type II processes.

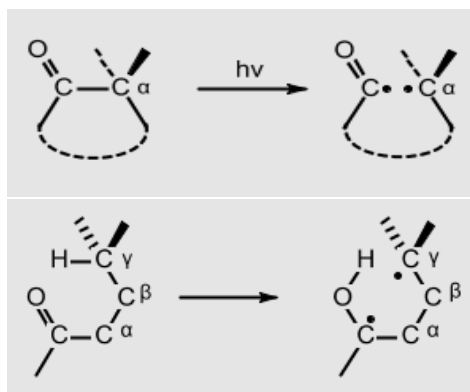


Figure 2. 3: Norrish I and II reactions [24]



The fraction of absorbed photons, utilized for chemical transformation, depends significantly on polymer mobility. The importance of molecular mobility derives from the fact that in type II processes the close approach of excited carbonyl groups to H atom at  $\gamma$ -carbons is a prerequisite for reaction. Moreover, cage recombinations of radical pair (produced e.g., in type I processes) become less probable, as the mobility increases [23].

The most common photoreaction for all materials is photooxidation. Usually, free radicals are generated as transient species in photolytic processes. Since oxygen reacts readily with most free radicals, peroxy radicals will be formed. Photolysis, therefore, can give rise to autoxidative free radical chain reaction. The primary reaction steps are following (Fig. 2.4):

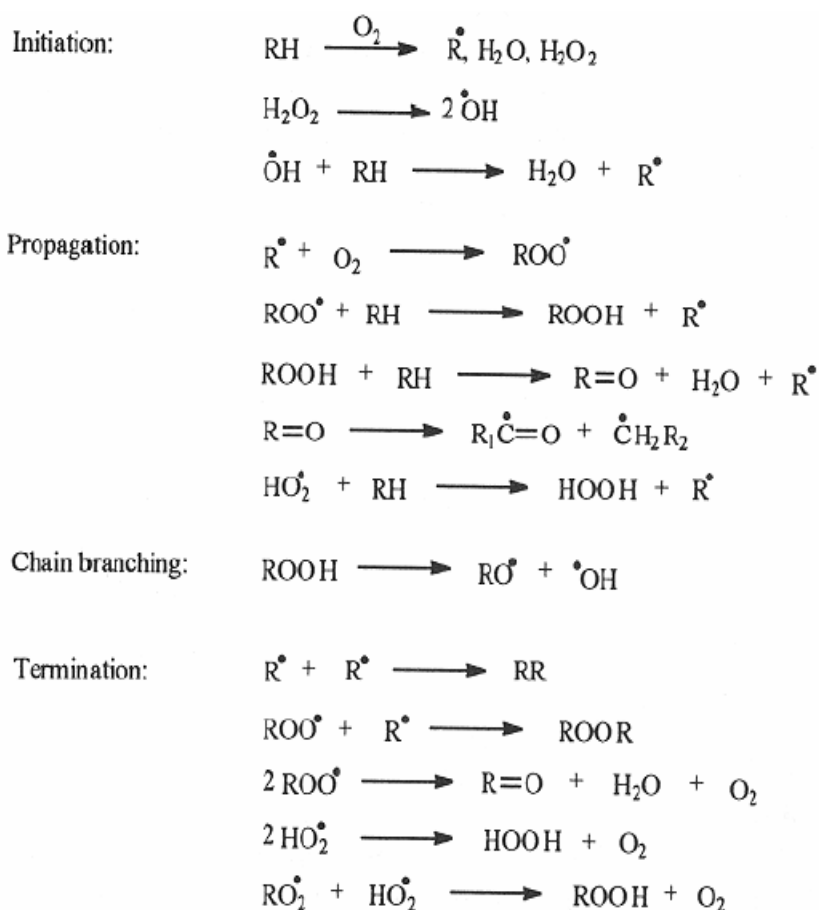
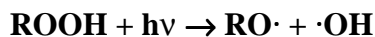


Figure 2. 4: Photooxidation of polyolefins [20]

Hydroperoxide groups are formed in the propagation reaction. At wavelengths below 300 nm hydroperoxides are photolytically decomposed (Fig 2.5).



*Figure 2. 5: Formation of hydroperoxide groups*

This reaction is considered to be very important in the photoinitiated oxidation of many commercial polymers because of presence of peroxide groups as chemically bound impurities, originating from processing at elevated temperature in the presence of oxygen [23].

Since polyethylene and polypropylene are the most important polyolefins the photooxidation process of such materials is described in next chapters. Nevertheless, the photooxidation of PMP and PB is very similar to that of PP. These three materials (e.g. PP, PMP and PB) contain tertiary carbons in the chains and therefore are very sensitive to oxidation.

Unlike PE or PP, the mechanism of photooxidation of PIB is complicated by the fact that at temperatures above 50°C, depolymerisation may occur [31].

### 2.3 Photodegradation of Polyethylene

Information on polyethylene degradation is available from model studies done because of the commercial interest in photodegradable polyethylene for applications, such as, garbage bags, agricultural films, etc [20].

In the absence of oxygen, pure polyethylene is a relatively stable material under ultraviolet radiation. After long exposure to UV light of short wavelength (254 nm) in a

vacuum or in a nitrogen atmosphere, chain scission and hydrogen abstraction occur. Also crosslinking and evolution of hydrogen are observed (Fig. 2.6) [25].

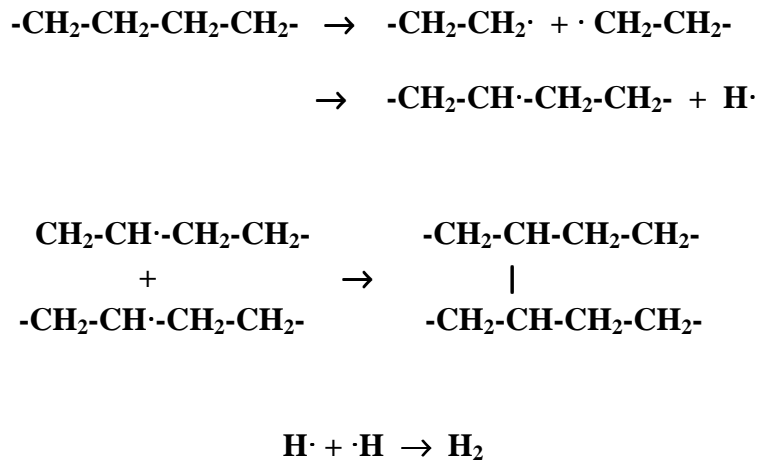


Figure 2. 6: Chain scission and crosslinking of PE

Copolymerization of ethylene monomer with small amount of carbon monoxide forms an ethylene-carbon monoxide copolymer, known to degrade on sunlight exposure by Norrish type I and II reactions (Fig. 2.7). Both cases are equivalently dangerous to the durability of the polymer. If the polymer degrades according to Norrish I mechanism, two free radicals are formed simultaneously. When the Norrish II mechanism controls degradation, two molecules capable of absorbing sunlight are formed [20].

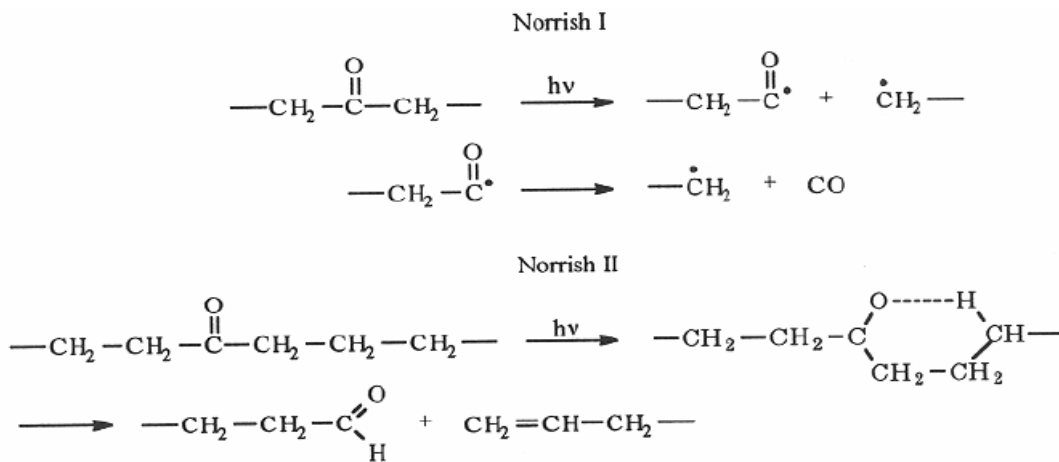


Figure 2. 7: Degradation of ethylene-carbon monoxide copolymer [20]

Photooxidation of polyethylene proceeds by a free radical chain mechanism outlined in chapter 2.2. First, primary initiation step may produce three free radicals, then secondary processes also give rise to compounds containing hydroxyl, carbonyl, and vinyl groups which also absorb radiation and undergo further degradative processes. The structure of polyethylene determines the probability of further conversion [20].

High-density PE and low-density PE contain unsaturations. The presence of these unsaturations (vinylidene groups) leads to formation of allylic hydroperoxides during the thermooxidative processes, and this becomes the major mechanism of initiation (Fig. 2.8).

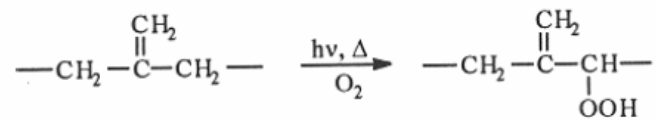


Figure 2. 8: Formation hydroperoxides in PE [20]

This structure can be further converted by heat, UV, or other radicals to free radicals and/or to structures containing UV-absorbing groups (e.g., carbonyl). Unsaturations then usually predominantly lead to chain scission reactions, but crosslink formation also occurs (Fig. 2.9) [20].

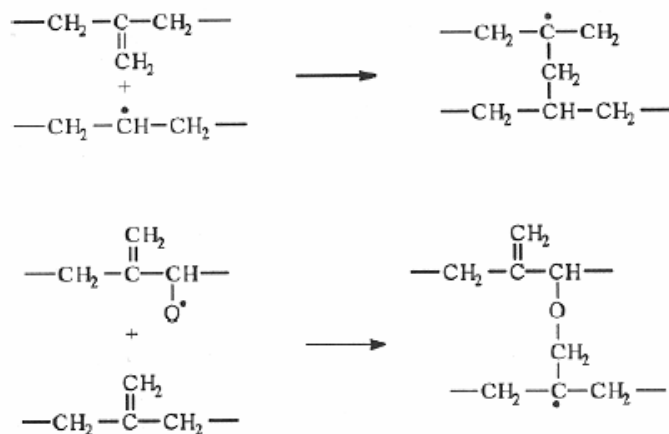


Figure 2. 9: Crosslinking vinylidene groups and hydroperoxides in PE [20]

In summary, three major functional groups are accumulated during degradation: ketones, carboxylic acids, and vinyl groups. During photolysis, ketones and vinyl groups increase linearly with time of exposure, whereas carboxylic acids accumulate exponentially.

### 2.3.1 Effect of Morphology on Photodegradation

Degradation of PE is influenced by a great extent of its crystallinity. It has long been known that branched polyethylene oxidizes faster than linear polyethylene, and it has been discovered that its oxidation rate is roughly proportional to the amount of amorphous fraction present (Fig. 2.10). This suggests that the oxidation of semicrystalline polyethylene is restricted to its amorphous region. It was subsequently discovered that the crystalline region absorbs practically no gas which implies that oxygen is simply not available in the crystalline region. Based upon these facts, polyethylene of low crystallinity has a high rate of carbonyl formation and a low concentration of radicals.

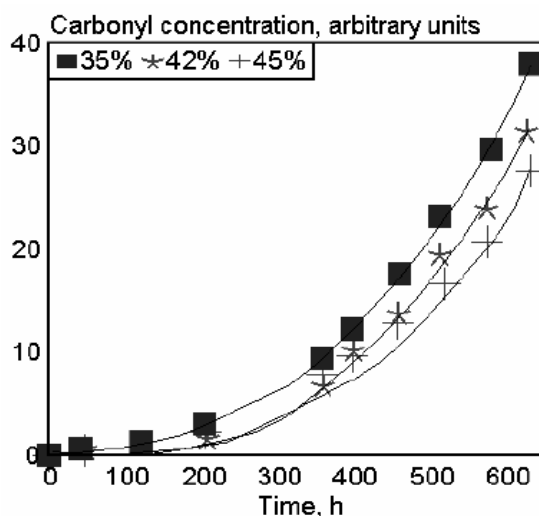
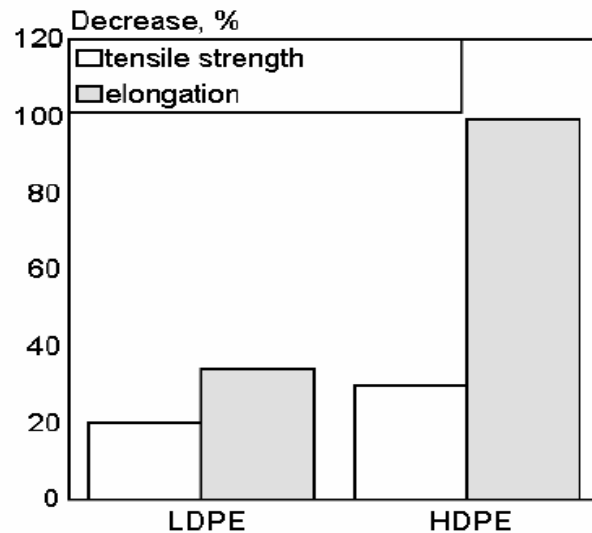


Figure 2. 10: Carbonyl formation during Xenotest irradiation of LDPE samples varying in degree of crystallinity [20]

Crystallinity changes during the course of degradation. In the initial stages of photodegradation, chain scission prevails which reduces molecular weight. Shorter chains are more mobile and are thus able to crystallize more readily. Therefore, embrittlement of PE is controlled by two associated processes: reduction of molecular weight and increased crystallinity [20].

### 2.3.2 Changes in Properties and Stabilization

If polyethylene is exposed for long periods outdoors, it is degraded by the concerted action of atmospheric oxygen and radiation at the UV end of the solar spectrum. The degradation leads to a deterioration in impact resistance and ultimate elongation, and possibly, to discoloration [32]. Elongation of HDPE especially is reduced to almost zero (Fig. 2.11) [20].



*Figure 2. 11: Percentage decrease of PE tensile strength and elongation during natural weathering in Queensland, Australia for 1 year [20]*

The outdoor stability can be increased by finishing the polyethylene with special light stabilizers. Good results are obtained by the HALS type (hindered amine light stabilizers), in some cases in combinations with benzotriazole compounds [32]. Their effectiveness is due to their transformation products, the corresponding nitroxyl radicals, which is the real stabilizing species. Hindered nitroxyl radicals are effective chain breaking-acceptor antioxidants which act by trapping the macroalkyl radicals to give hydroxylamines and / or alkylhydroxylamines [27].

Ultraviolet screening can be provided by pigments. The pigments have the ability to reflect or absorb the radiation and avoid the penetration of the radiation inside the material. The efficiency depends on their concentration. There are several kinds of pigments. For instance the white (titanium dioxide and zinc oxide), yellow (cadmium yellow), red, blue and green pigments. These pigments may improve the light stability of polyethylene but

can equally well impair it [30, 32].

Best outdoor performance is achieved by adding special grades of carbon black. Mass fractions of 2-3% of carbon black uniformly distributed in the matrix improves the outdoor performance by a factor higher than 15 [32].

## 2.4 Photodegradation of Polypropylene

The degradation mechanism of polypropylene is very similar to polyethylene. The primary events following irradiation of polypropylene with UV light in vacuum are bond scission and crosslinking (Fig. 2.12) [20, 25].

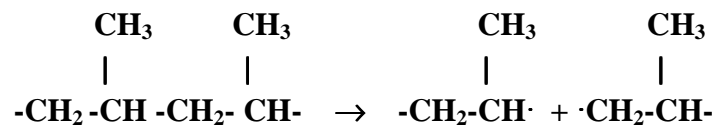


Figure 2. 12: Chain scission of PP

Another probable reaction is the dissociation of carbon-hydrogen bonds at the tertiary carbon (Fig 2.13).

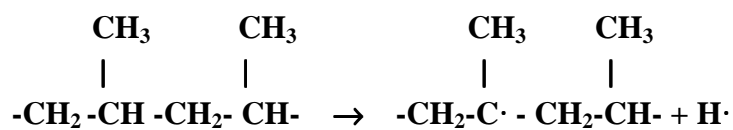


Figure 2. 13: Dissociation of carbon-hydrogen bonds

This may lead to chain scission by a disproportionation reaction (Fig 2.14) [25].

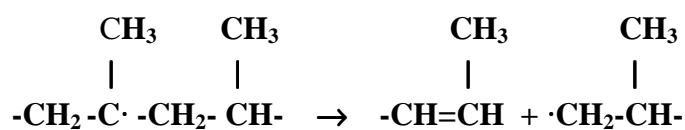


Figure 2. 14: Chain scission of PP by a disproportionation reaction

When two polypropylene radicals react, crosslink is formed (Fig. 2.15).

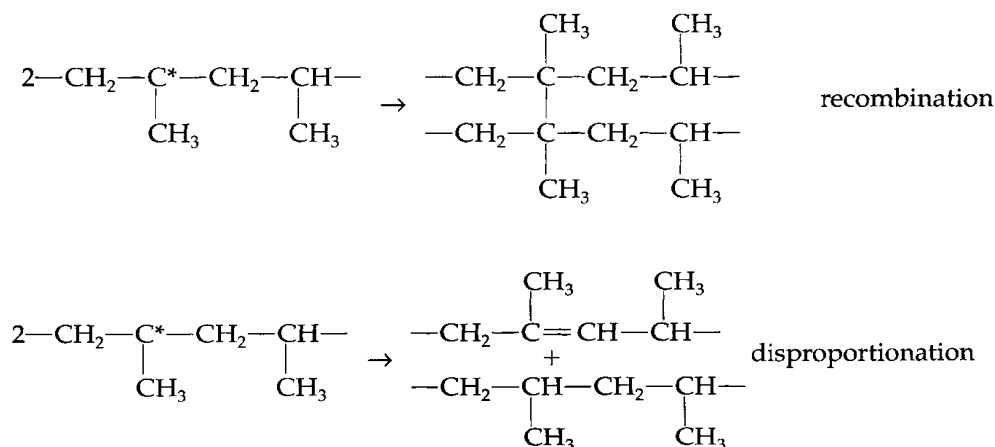


Figure 2. 15: Crosslinking of polypropylene radicals [26]

Degradation reactions during outdoor exposure are others than during irradiation in vacuum. Saturated hydrocarbon polymers (e.g. 'pure' PP) are intrinsically transparent to the incident sun spectrum and should not be affected by the solar radiation. Commercial PP, however, absorbs weakly at wavelengths above 285nm and its sensitivity to sunlight is a consequence of light absorbing impurities, particularly oxygen-containing species and other species present arising from production processes, i.e. polymer manufacture, melt processing and fabrication. These impurities sensitize and accelerate PP photooxidative degradation under service conditions involving exposure to light (outdoors and indoors) resulting in changes of properties [27].

Hydroperoxides formed during melt processing are the most important impurities (photoinitiators). They play a major initiating role during the early stages of PP photooxidation, while the derived carbonyl-containing products exert deleterious effects during later stages of photooxidation (e.g. by Norrish types I and II reactions), see Fig. 2.16. Hydroperoxides and their decomposition products are responsible for the changes in molecular structure and overall molar mass of PP which are manifested in practice by the loss of mechanical properties and by changes in the physical properties of the polymer surface [27].



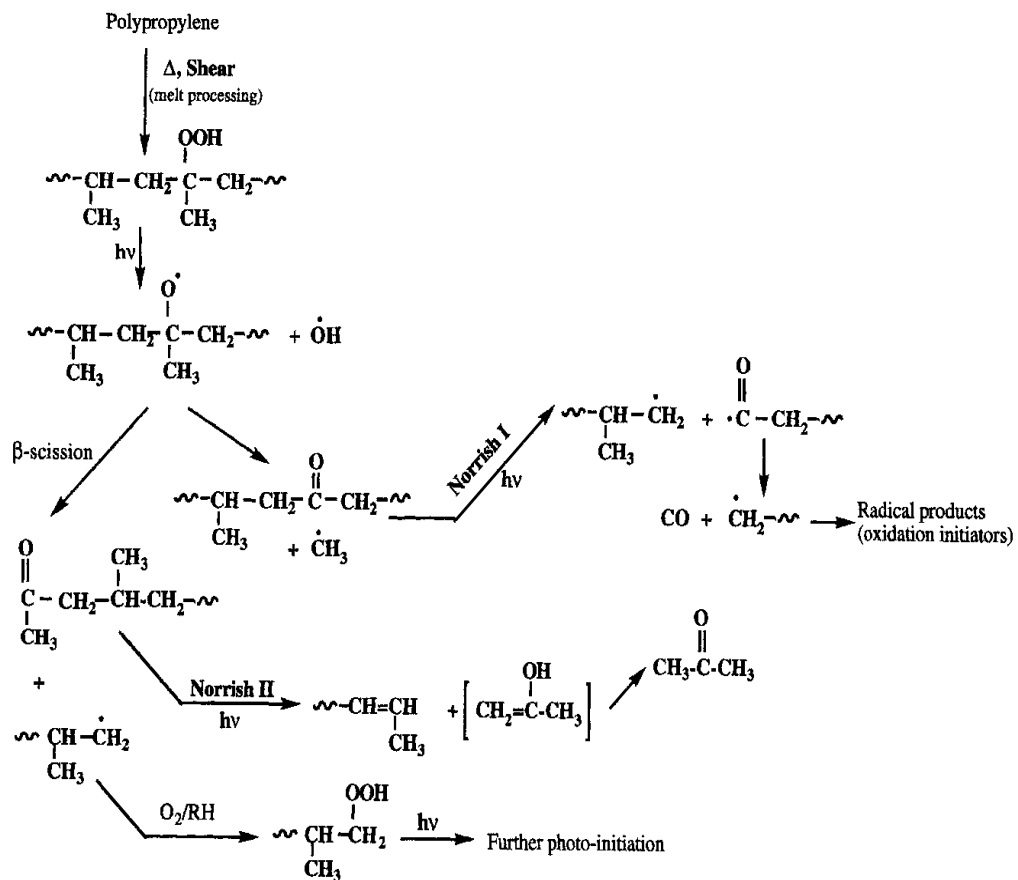


Figure 2. 16: Polymer hydroperoxidation during processing and further photoinitiation by the hydroperoxides and the derived carbonyl compounds [27].

A higher temperature of oxidation speeds both the formation rate and the decomposition rate of hydroperoxides. When carbonyl concentration is high, the rate of formation of hydroperoxides is dependent on the initial thermooxidative processes. As a result of photodegradation, more ester groups are formed and an aldehyde group is also generated. Carbonyl groups and hydroxyl groups are preferentially formed on the exposed surface, and their concentrations increase almost linearly with time of exposure.

#### 2.4.1 Effect of Morphology on Photodegradation

The process of degradation of PP depends on the physical structure, as well as for other semicrystalline polymers. Accordingly to PE, the degree of crystallinity strongly influences the degradation kinetics. The higher is the crystallinity, the lower is the oxygen permeability and thus the lower is the rate of oxidation.

The effect of PP polymorphism on the degradation of polypropylene (especially induced by UV irradiation) is also observed. It is found, that the  $\beta$ -nucleation specifically affect the processes of UV degradation of isotactic polypropylene [29]. The molecular degradability of  $\beta$ -nucleated polypropylene ( $\beta$ -iPP) is lower as compared to common  $\alpha$ -polypropylene ( $\alpha$ -iPP). Figure 2.17 shows the micrographs of surfaces of degraded  $\alpha$ -iPP and  $\beta$ -iPP. Deep and relatively distant macroscopic cracks on the surface of  $\alpha$ -iPP specimen are seen while the surface of  $\beta$ -iPP is damaged by a dense network of fine cracks, only microscopically observable [29].

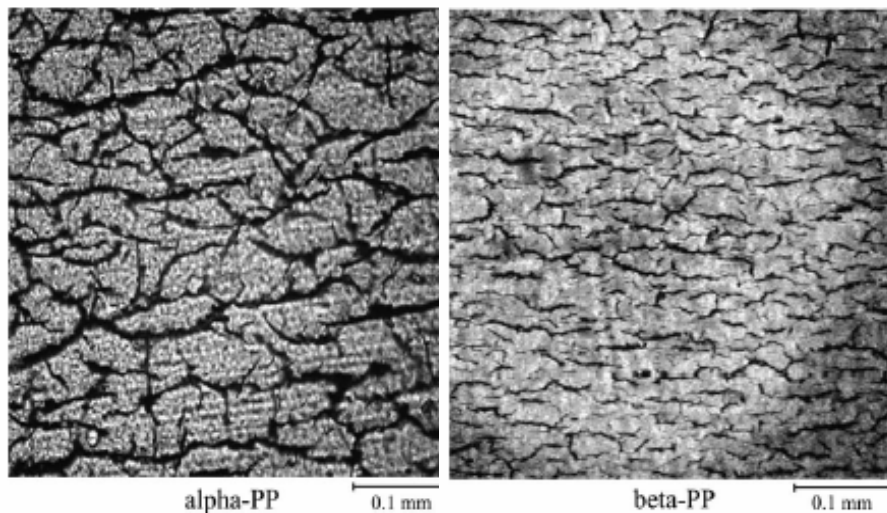


Figure 2. 17: Surface cracks on  $\alpha$ -PP and  $\beta$ -PP specimens after 240 h UV exposure [29].

#### 2.4.2 Changes in Properties and Stabilization

In the natural atmospheric conditions insulating of PP generally causes embrittlement of the material, cracking of the surface (during the exposition the number of the crack increases), color changes (PP gets yellow or brown, over the further ageing the color gets darker), contractions of the material and decrease of the mechanical features (Fig 2.18, 2.19) [30].

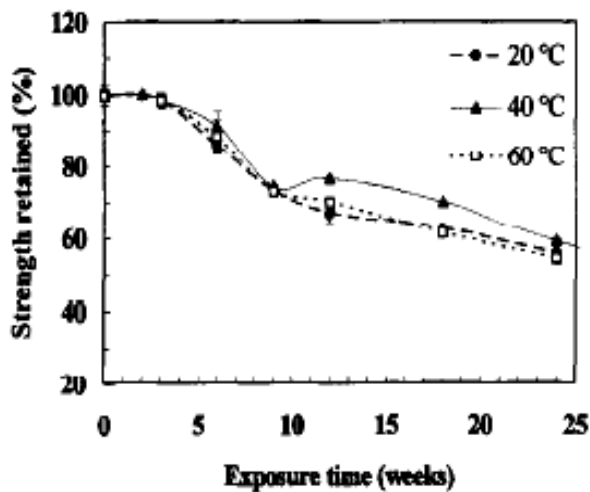


Figure 2. 18: Tensile strength as a function of exposure time for injection moulded PP produced using different mould temperatures [28]

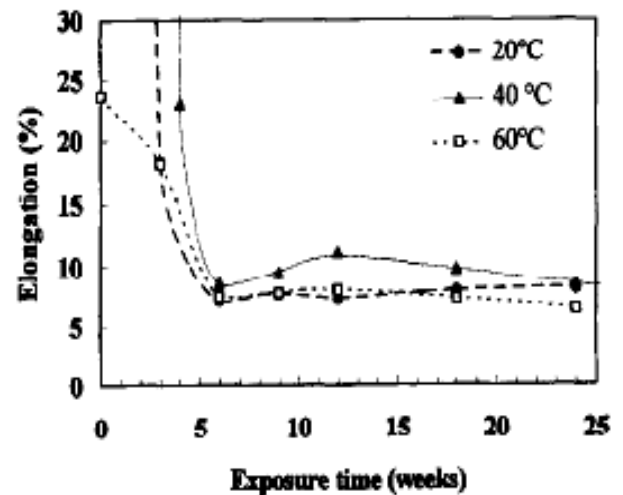


Figure 2. 19: The maximum elongation of PP exposed to ultraviolet radiation. The values of elongation for 20PP and 40PP were 310 and 520%, respectively [28].

Commercial polypropylene is highly sensitive to UV light and its photostabilization is essential for outdoor and indoor end-use applications. Photostabilizers are incorporated in PP during its melt processing and are generally used at higher concentration levels than that of thermal antioxidants [9].

Three different classes of compounds form the major and most important commercial categories of photostabilizers for PP. These are based on nickel complexes (those containing sulfur ligands function primarily as peroxide decomposers), UV-absorbers, e.g. based on 2-hydroxybenzophenone and 2-hydroxyphenylbenzotriazole, and sterically hindered amine light stabilizers (HALS) [9].

## CONCLUSION

This Bachelor thesis is focused on the photodegradation of polyolefins, their stabilization and influence of its morphology on the extent of the degradation.

The photodegradation proceeds mainly by photoinitiated oxidation reactions. Although photooxidation mechanisms of polyolefins are very similar, their weather resistance is different. Unlike polyethylene polypropylene, poly(4-methylpent-1-ene) and polybut-1-ene contains tertiary carbons in the polymer chain, which are very susceptible to formation of radicals leading to faster degradation. Therefore, these materials have to be protected by addition of stabilizers.

The photodegradation of polyolefins is strongly influenced by their morphology. Oxidation rate is roughly proportional to the amount of amorphous fraction present, which suggests that the oxidation of more crystalline polymer is slower than that of lower crystallinity. The effect of polymorphism on the degradation is also observed. Regarding isotactic polypropylene the  $\beta$ -nucleation affect the processes of its UV degradation. The molecular degradability of  $\beta$ -nucleated isotactic polypropylene is lower as compared to common  $\alpha$ -isotactic polypropylene.

Finally, it should be overall noted, that the research of ageing of polyolefins, favourable polymeric materials due to their low cost and good mechanical properties, is still in progress. The improving of its photostability has to lead to enlargement of its use outdoor.

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## REVIEW OF SYMBOLS

PE	Polyethylene
LDPE	Low-density polyethylene
HDPE	High-density polyethylene
LLDPE	Linear low-density polyethylene
PP	Polypropylene
iPP	Isotactic polypropylene
$\alpha$	Monoclinic crystalline form of polypropylene
$\beta$	Trigonal crystalline form of polypropylene
$\gamma$	Orthorhombic crystalline form of polypropylene
$T_m^0$	Equilibrium melting temperature [°C]
PMP	Poly(4-methylpent-1-ene)
iPMP	Isotactic poly(4-methylpent-1-ene)
PB	Polybut-1-ene
PIB	Polyisobutylene
$T_g$	Glass transition temperature [°C]
E	Energy of radiation [J]
$\nu$	Frequency of radiation [1/s]
h	Planck's constant [J.s]
UV	Ultraviolet
HALS	Hindered amine light stabilizers
$\alpha$ -PP	Polypropylene containing mainly $\alpha$ -phase
$\beta$ -PP	Polypropylene containing mainly $\beta$ -phase



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