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Degradation of Polymers by Photooxidation

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Abstract. Most of the commercially important polymers are prone to deterioration caused by oxidation reactions. Formation and subsequent photolysis of hydroperoxides as key intermediates cause chain scission and transformation of the polymer's initial molecular structure. Suitable stabilizers are needed to impart to the polymer acceptable service life time. UV-absorbers, triplet quenchers, radical scavengers, and hydroperoxide decomposers fulfill these requirements.

1. Introduction

Oxidative deterioration of polymers is known to be the source of changes in the appearance of the polymer leading to the loss, or a decrease, of mechanical and physical properties of the material. Heat and light are important physical factors in oxidation. Both processes involve formation of radicals followed by a breakdown of chemical bonds.

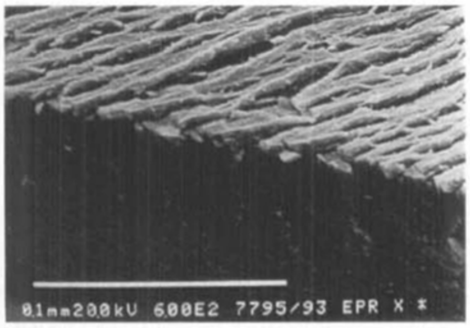

Fig. 1. *SEM Photo of the surface of a PP-EPR-copolymer, after being exposed to sunlight* (Florida, 3 years)

Fig. 1 shows the SEM picture of the surface of a polypropylene-EPR-copolymer which was exposed to sunlight. The destruction of the polymer surface can be clearly seen.

With increasing temperature, thermooxidation may overlap photooxidation. Therefore, we have to discuss to some extent the various factors influencing the oxidative deterioration of the polymers.

1.1. *Absorption of Light*

The lower wavelength limit of sunlight reaching the earth's surface is *ca.* 290 nm.

Many of the commercially important polymers, *e.g.* polyethylene or polypropylene, should not absorb any sunlight since the longest wavelength absorption band for the polyolefins is in the region below 200 nm, caused by a σ–σ* transition. The absorption of light by synthetic rubbers based on butadiene or isoprene copolymers is associated with a π–π* transition and occurs in the wavelength region of 180–240 nm, the longest absorption of polystyrenes are associated with the π–π* transition of the benzene ring and occurs in the wavelength region of 230–280 nm. The longest wavelenght absorption band for polyacetals can be associated with a partially forbidden η–σ* transition below 200 nm.

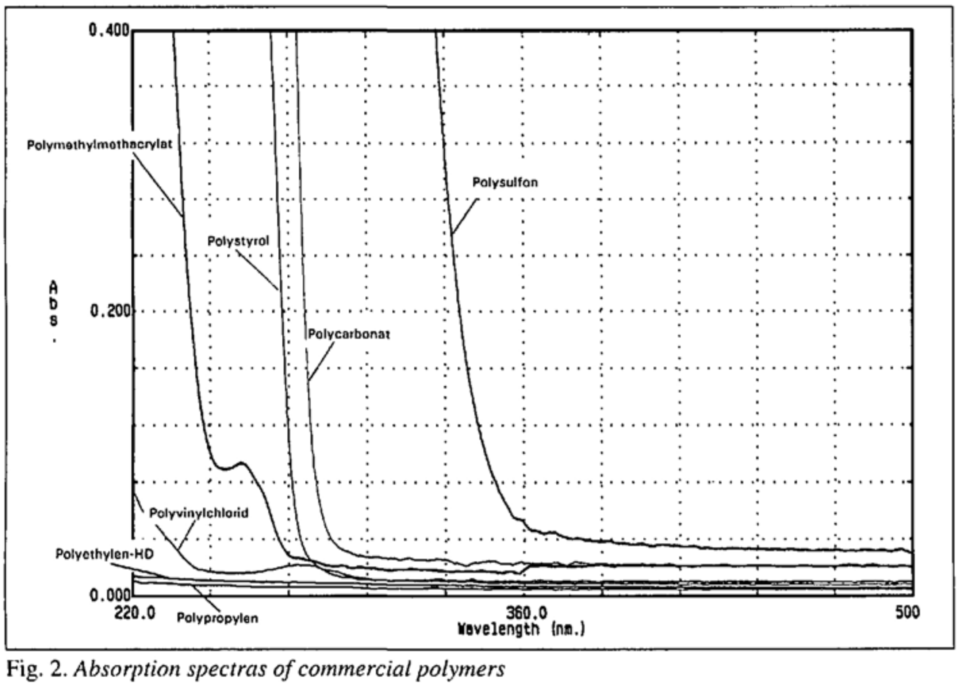

Fig. 2. *Absorption spectras of commercial polymers*

The longest-wavelenght absorption bands of polymers such as aliphatic polyamides, aliphatic polyesters or poly(meth)acrylics are in the region below 200 nm, associated with a η–π* transition [1][2].

However, there are many commercial polymers which absorb sunlight owing to the chromophoric groups that form part of the polymer structure, *e.g.* aromatic polyesters and polyamides, polysulphides, polyethersulphones, polycarbonate and other polymers containing aromatic moieties. The absorption spectra of some virgin polymers are shown in *Fig. 2.*

The first fundamental law of photochemistry formulated by *Grotthus* and *Draper* states that only light absorbed by a molecule can be effective in producing photochemical change in the molecule. As shown, a number of polymers do not absorb sunlight and no photochemically-induced reaction should, therefore, occur. However, a polymer undergoes different steps of transformation processes in order to produce the 'end-use' article. Most of these transformation steps involve melt processing such as extrusion, blow molding, injection molding, compression molding and others.

Shear, heat, and oxygen will cause oxidation, and hydroperoxides groups are formed. Subsequent chemical reactions lead to the formation of carbonyl groups which absorb sunlight. Some of these reactions are summarized in *Scheme 1.*

The stabilizers used (sterically hindered phenols, phosphites) that are added to the polymer to prevent degradation during melt processing have in most instances aromatic groups. Furthermore, catalysts are used to produce the polymers (transition metals, *Ziegler-Natta* catalysts [3]) and metals or metal compounds are, there-

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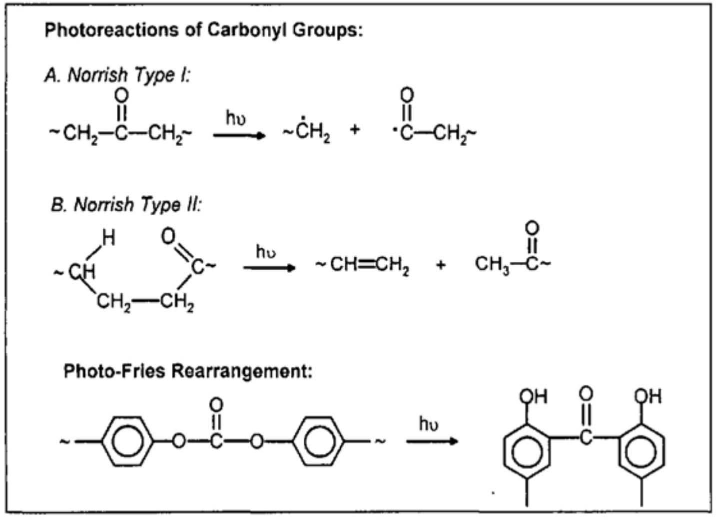
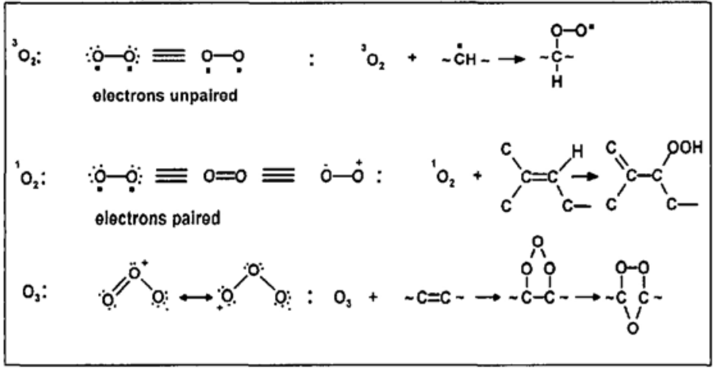
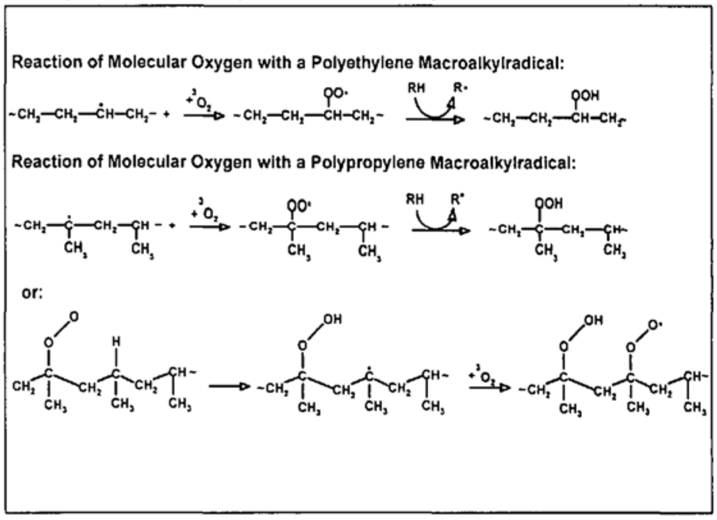
Scheme 1. *Photoreactions Leading to a Change in the Molecular Structure of the Polymer*



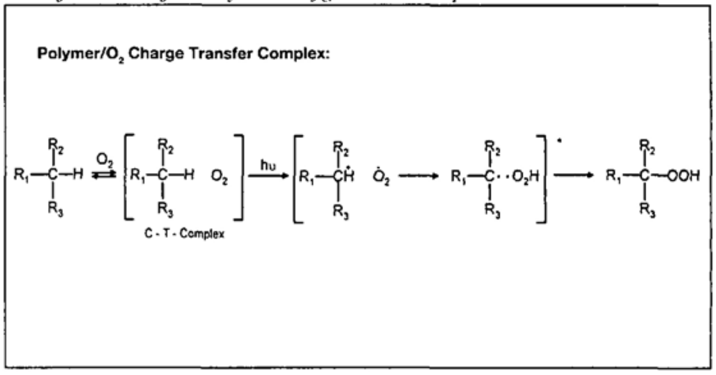
Scheme 2. *Reactions of Molecular Oxygen and Ozone with Suitable Groups Present in Polyolefins and Rubbers*



Scheme 3. *Reactions of Polyolefin Macroalkyl Radicals with $^3O_2$ and Subsequent Formation of Macroalkyl Hydroperoxides*



Scheme 4. *Formation of Macroalkyl Hydroperoxides by Light Induced Transfomation of a Polymer/Oxygen 'CT-Complex'*



fore, present in the resin. Pigments may be another source for impurities and atmospheric pollution can contribute to the formation of components or chromophoric groups which absorb sunlight.

1.2. *Diffusion and Solubility of Oxgen in Polymers*

The oxidation of a polymer is a reaction between a gas (oxygen) with a solid (polymer).

The solubility of oxygen in the polymer matrix and the rate of diffusion into the polymer play, therefore, an important role [4–6]. The diffusion coefficients and the solubilities of oxygen in some polymers are summarized in *Table 1*.

Diffusion is typically about two orders of magnitude lower compared with the values for liquid hydrocarbons. The concentration of oxygen, in equilibrium with the air, is *ca.* ten times lower then in liquid hydrocarbon. However, in semicrystalline polymers, *e.g.* polyolefins, oxygen is only soluble in the amorphous part of the polymer. Therefore, the solubility of oxygen is in simple linear dependence on crystallinity. Since the mechanical strength of a semicrystalline polymer depends on the chain entanglement in the amorphous phase, the breakdown of the mechanical properties of a polyolefin is caused by oxydative degradation in the amorphous phase of the polymer. Photo-oxidative degradation starts at the polymer's surface (see *Fig. 1*) and based on the work of *Gillen* and *Clough* [5] an oxidation profile can be established. The microcracks formed may propagate into the non-oxidized, ductile material when exposed to external stress or caused by physical aging processes.

2. Photooxidative Degradation of Polyethylene and Polypropylene

2.1. *Formation of Macroalkyl Hydroperoxides*

Oxygen is the key participant in the photooxidative degradation of polyolefins.

Two *Lewis* structures may be proposed for molecular oxygen (*Scheme 2*).

Molecular oxgen, $^3O_2$, reacts similar to a radical ('diradicaloid state'). Macroalkyl-radicals, R°, formed upon processing of polyolefins, are very easily transformed into macroperoxi-radicals ROO°. Singlet oxygen, $^1O_2$, can react in an 'ene'-type reaction in α-position to a C=C bond. It is still a matter of discussion whether singlet oxygen plays an important role in oxidative degradation processes [10]. The triplet photosensitized production of singlet oxygen caused by carbonyl groups is a possible reaction and *Gugumus* [11] found improved photostability of polyethylene in the presence of 1,4-diazabicyclo[2.2.2]-octane (DABCO), well known to act as a singlet oxygen quencher [12]. Ozone (O_3) reacts easily with C=C bonds. These reactions lead finally to the formation of the macroalkylhydroperoxides, as shown in *Scheme 3*. which are the precursors for all

Table 1. *Diffusion Coefficients and Solubilities of Oxygen in Some Polymers*

Polymer	Diffusion 10^7 cm^2 s^{-1}	Solubility $10^3 \cdot$ mol kg^{-1}	Temp. [°C]	Ref.
PE-LD	5.4	0.44	25	[7]
PE-HD	1.6	0.68	25	[7]
Natural rubber	16	5.0	25	[8]
PC	0,56	7.34	35	[9]

further degradation reactions. For polypropylene, a 'concerted' mechanism can be formulated, based on abstraction of tertiary hydrogen. For this reason, polypropylene is more prone to oxidation compared with polyethylene.

The formation of hydroperoxide groups is also postulated by a 'polymer/oxygen – charge-transfer complex' which may be transformed by excitation with light into the corresponding macroalkyl hydroperoxide [13], *Scheme 4.*

2.2. *Photochemistry of Hydroperoxides*

The polymeric hydroperoxides are the key intermediate in the breakdown of the polymer molecule. The thermal decomposition of polyolefin hydroperoxides has been frequently investigated, however, little work has been published on its photolysis. The photolytic decomposition of *t*-butyl hydroperoxide in an inert solvent occurs at 313 nm with high quantum yield [14]. *Fig. 3* shows the formation of carbonyl groups on irradiation of a polyethylene and a polypropylene film, using different 'cut-off' filters.

The light-induced oxidation of the polymers occurs at wavelengths around 300 nm but even at wavelenghts of 360 nm, the yield of carbonyl groups is considerable. Polypropylene undergoes faster photooxidation compared with polyethylene because of the concerted mechanism of hydroperoxide formation. The photolysis of hydroperoxide groups under solar irradiation is a slow process, the average lifetime of an –OOH group under constant irradiation is reported to be ~25 h [15–17]. Therefore, the most probable mechanism of photodecomposition of hydroperoxide groups is an energy transfer process from the exited carbonyl or aromatic hydrocarbon groups to the hydroperoxide groups as acceptors [15]. The resulting ketones can photolyze according *Norrish* Type-I or *Norrish* Type-II reaction as shown in *Fig. 3.* Recently, *Gugumus* [11] has proposed intra- and intermolecular decomposition mechanism based on the photolysis of the secondary and tertiary hydroperoxides as shown in *Scheme 5.*

2.3. *Thermo-oxidative Reactions Involving Peroxy, Alkoxy, and Alkyl Radicals*

The photolysis of the hydroperoxide group yields a primary or secondary alkoxy radical, $RO^{\bullet}$. The alkoxy radical are im-

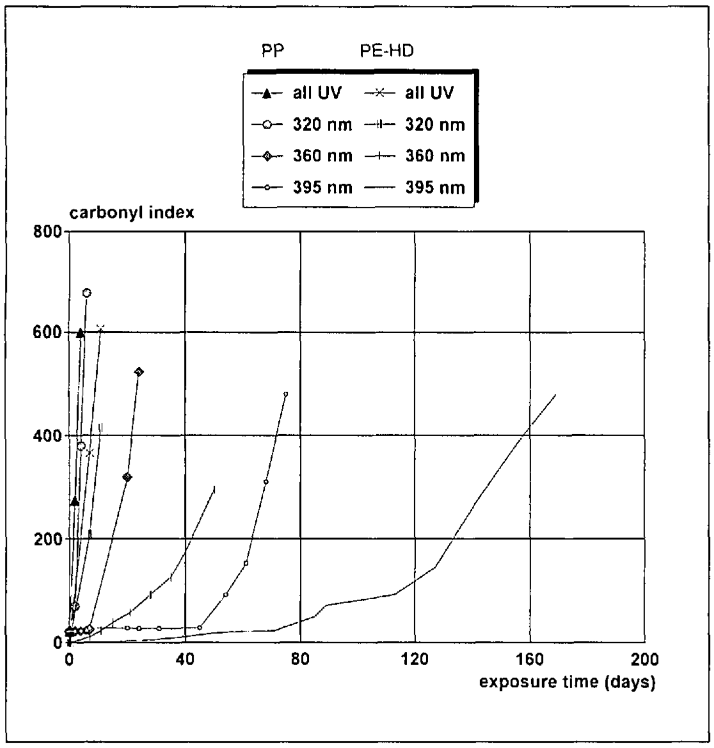
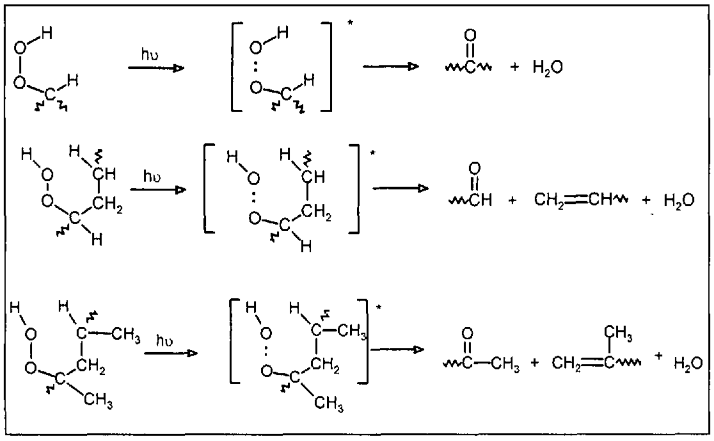
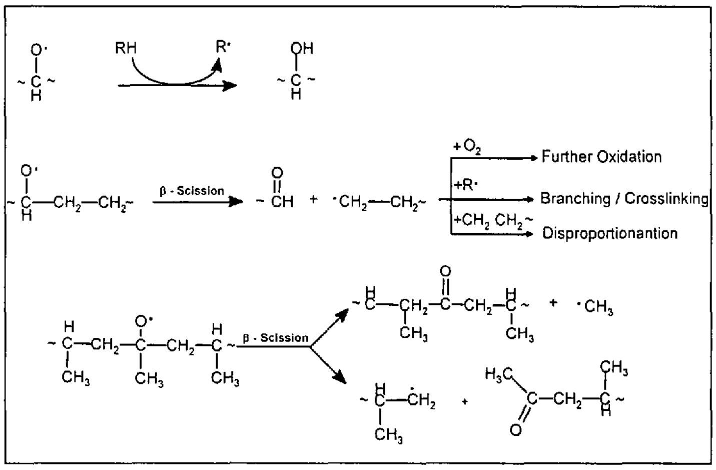


Fig 3. *Build-up of carbonyl groups upon irradiation of a polyethylene and a polypropylene film, using different 'cut-off' filters*

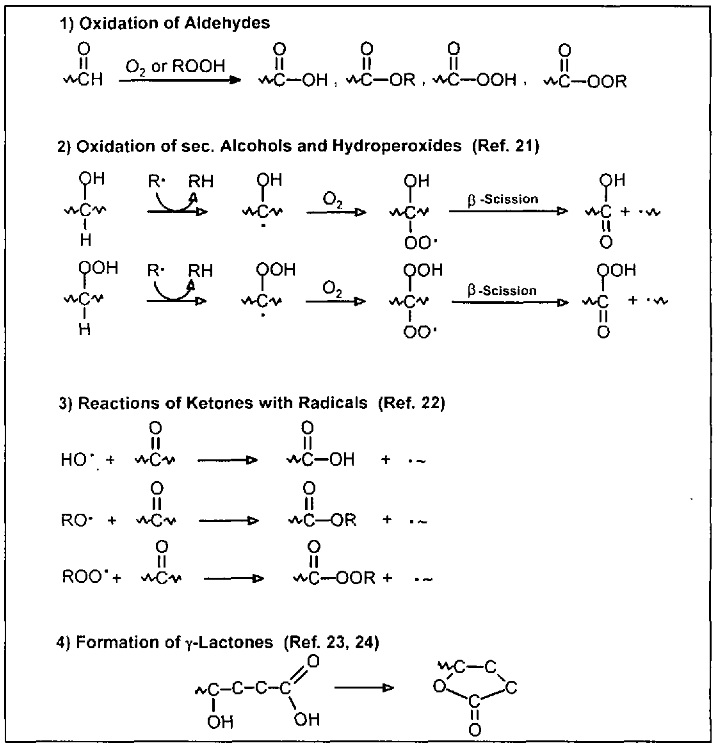
Scheme 5. *Intramolecular Decomposition of Secondary and Tertiary Hydroperoxides*



Scheme 6. *Reactions of Secondary and Tertiary Alkoxy Radicals*



Scheme 7. *Formation of Acid-, Ester-, Peracid-, Perester and γ-Lactone Groups*



portant in the autoxidation of hydrocarbons [18]. They may, as shown in *Scheme 6*, abstract hydrogen from the substrate, combine with available free radicals or undergo β-scission to give a ketone and an alkyl radical which will be transformed by further oxidation reactions into various oxidation products [19][20].

Further oxidation of the intermediate degradation products occurs and the formation of acid, ester, peracid, perester, and γ-lactone groups is observed [21–24].

Some of the proposed reaction mechanism are summarized in *Scheme 7*.

Oxidation reactions close to the end of the polymer chain yield volatile products [25].

Figs. 4–6 show the IR spectra (carbonyl region) of unstabilized polypropylene after multiple extrusion, oven aging at 135° and irradiation in a *XENO 1200* exposure device.

All IR spectra show the formation of oxidation products following exposure. The absorption band at 1780 cm^{-1} is attributed to the γ-lactone group, the absorption at 1745 cm^{-1} to ester groups, the absorption at 1725 cm^{-1} to aldehyde groups, the absorption at 1720 cm^{-1} to ketone groups, and the absorption band at 1710 cm^{-1} to acid groups.

Caused by oxygen-deficient conditions in an extruder [26], the amount of oxidation products formed from the unstabilized PP after the fifth pass is *ca.* 30–40 times lower then the amount of oxidation products after oven aging of unstabilized PP-plaques (thickness 1mm) for 7 h at 135° or aging of similar PP-plaques in a *XENO 1200* exposure device for 253 h. The yield of γ-lactone groups is higher when the polymer sample was exposed at elevated temperatures, *e.g.* extrusion at 260° or oven aging at 135°, compared with the irradiation at 55°. These findings are in good agreement with the mechanism proposed for the formation of the lactone group (*Scheme 7*).

2.4. *Changes in Molecular Weight and Molecular-Weight Distribution of Polypropylene upon Processing, Thermal Aging or Exposure to Light*

Changes in molecular weight and molecular-weight distribution exhibit a detrimental effect on the polymer's mechanical properties. Oxidative degradation reactions, such as photolysis of a ketone (*Norrish* Type I and II reactions), β-scission of a peroxy radical, intramolecular reactions involving secondary and tertiary hydroperoxides and reactions of radicals with ketones lead to polymer chain scission, chain branching or cross-linking.

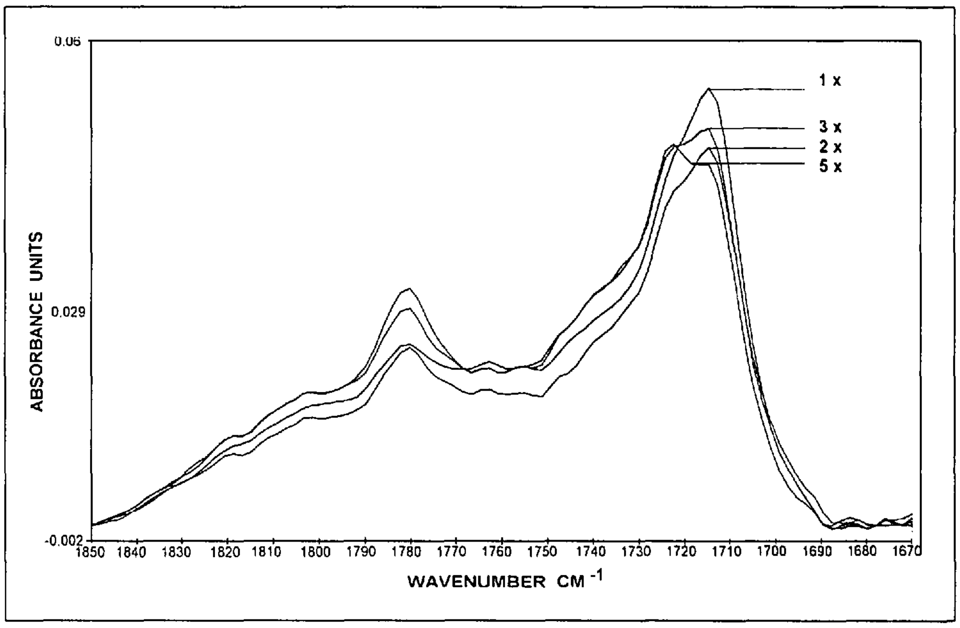


Fig. 4. *IR Spectrum of polypropylene after different passes in an extruder* (260°)

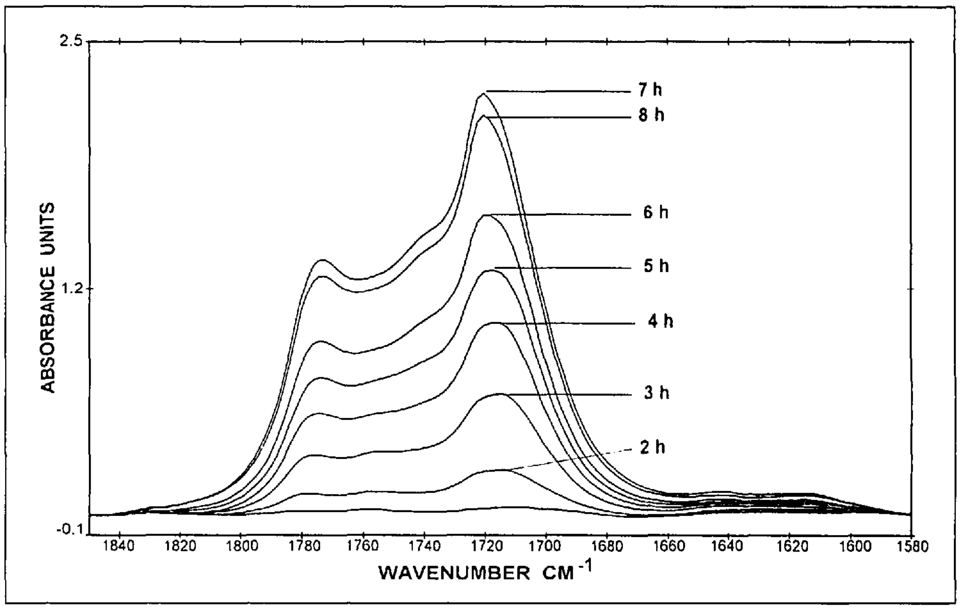


Fig. 5. *IR Spectrum of polypropylene after oven aging at 135°*

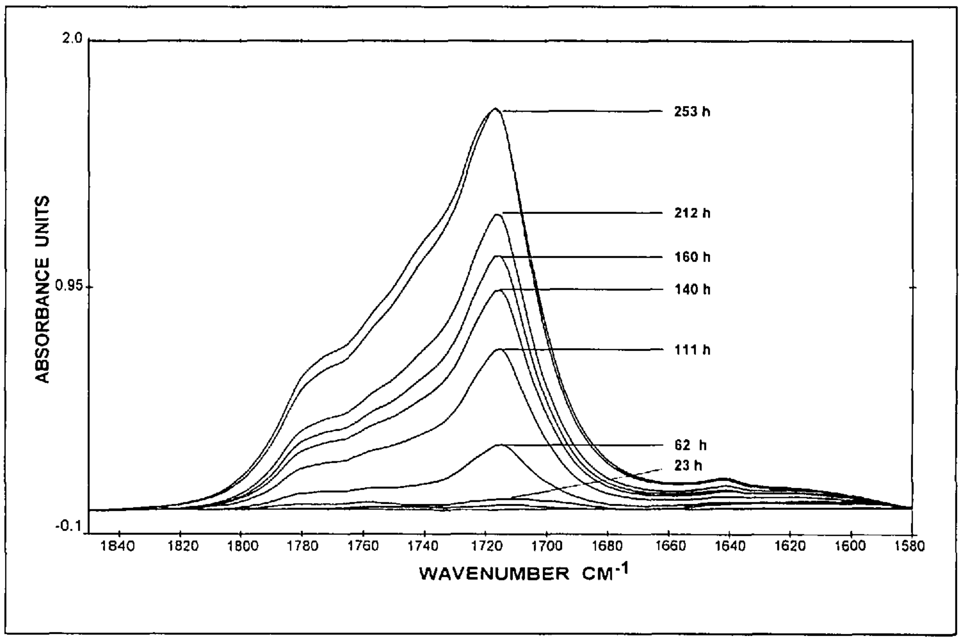


Fig. 6. *IR Spectrum of polypropylene after irradiation in a* XENO 1200 *exposure device* (b.p. 55°)

Table 2. *Changes in Molecular Weight*, M_w, *Molecular-Weight Distribution*, M_w/M_n, *of Unstabilized PP-Homopolymer, after Multiple Extrusion Passes at 260°*

Extrusion Pass#	M_w	M_w/M_n
1[a])	178 000	2.99
2[b])	106 000	2.48
3	72 000	1.92
5	60 000	1.71

[a]) Powder.
[b]) 2nd – 5th Extrusion: pellets.

Table 3. *Changes in Molecular Weight*, M_w, *Molecular-Weight Distribution*, M_w/M_n, *of Unstabilized PP-Homopolymer*[a]) *after Oven Aging at 135°* (draft air oven)

Hours, at 135 °C	M_w	M_w/M_n
0	178 000	2.99
1	121 000	2.92
2	106 000	2.94
3	98 000	3.27
5	95 000	4.32

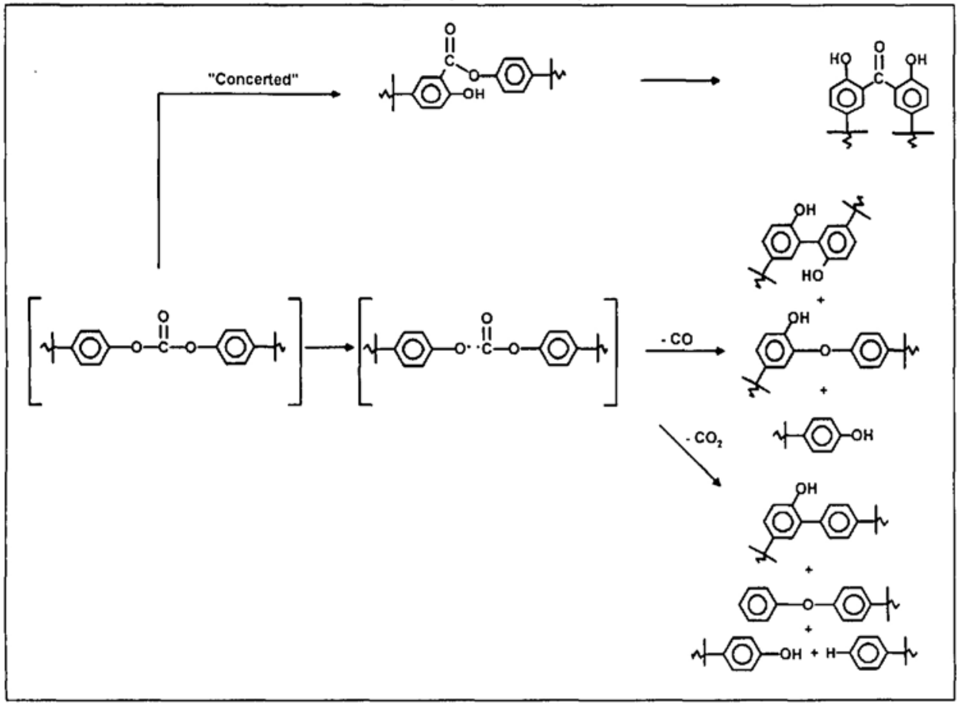
[a]) 1 mm compression molded plaques.

Table 4. *Changes in Molecular Weight*, M_w, *Molecular-Weight Distribution*, M_w/M_n, *of Unstabilized PP-Homopolymer*[a]) *after Irradiation in a* XENOTEST 1200 *Exposure Device, b.p. Temperature: 55°*

Hours	M_w	M_w/M_n
0	178 000	2.99
5	168 000	3.06
24	133 000	3.33
64	102 000	2.55
160	77 000	3.30

[a]) 1 mm compression molded plaques.

Scheme 8. *Photo-*Fries *Reaction Involving Bisphenol-A Polycarbonate*



All these reactions occur when the polymer is exposed to high temperature, shear, and light and during the polymer life time. The changes in molecular weight and molecular-weight distribution of unstabilized polypropylene after multiple extrusion passes, after oven aging at 135° and after irradiation in a *XENO 1200* exposure device are listed in *Tables 2–4*.

The results clearly demonstrate that upon exposure of the polymer, chain scission reaction occur. Since the values of *Tables 2–4* can be directly related to oxidation as shown in *Figs. 4–6*, the following statements can be made:

- Upon thermal- and photoaging of following unstabilized PP-homopolymer, polymer-chain scission reactions caused by oxidative degradation occur. The polydispersity slightly increases upon exposure, thus indicating that the oxidation takes place randomly.
- During processing, the level of oxidation is much lower owing to oxygen-deficient conditions. However, significant chain scission takes place. Molecular weight as well as polydispersity decrease, indicating that chain scission is caused by thermo-mechanical processes, involving high shear [26]. The low level of oxidation products, especially carbonyl groups, can act at a later stage as 'sensitizers' for the photolysis of the hydroperoxide groups. Thus, thermal history is of great importance for the polymer's service life time.

3. Photooxidative Degradation of Bisphenol-A Polycarbonate

3.1. *Photo-*Fries *Pathway*

Unstabilized bisphenol-A polycarbonate, when exposed to sunlight, undergoes discoloration, cross-linking occurs and cracks are formed on the surface. Since the polymer, by its structure, can absorb light in the region above 295 nm, photon-induced processes can occur.

Early investigations on the photoaging of BPA-PC suggested that the 'photo-*Fries*' reaction, as shown in *Scheme 8*, is the key mechanism [27][28].

Recent investigations by *Factor* and coworkers [29] indicate that upon exposure to sunlight, small amounts of photo-*Fries* products, some products assigned to ring oxidation [30] and large amounts of side-chain oxidation products are found in the aged material. A general scheme for the photooxidative reaction pathway is shown in *Scheme 9*.

The photooxidation mechanism, promoted by light absorption in the region of 310–350 nm, caused by photo-*Fries* prod-

Scheme 9. *Photooxidative Reactions Involving Bisphenol-A Polycarbonate*

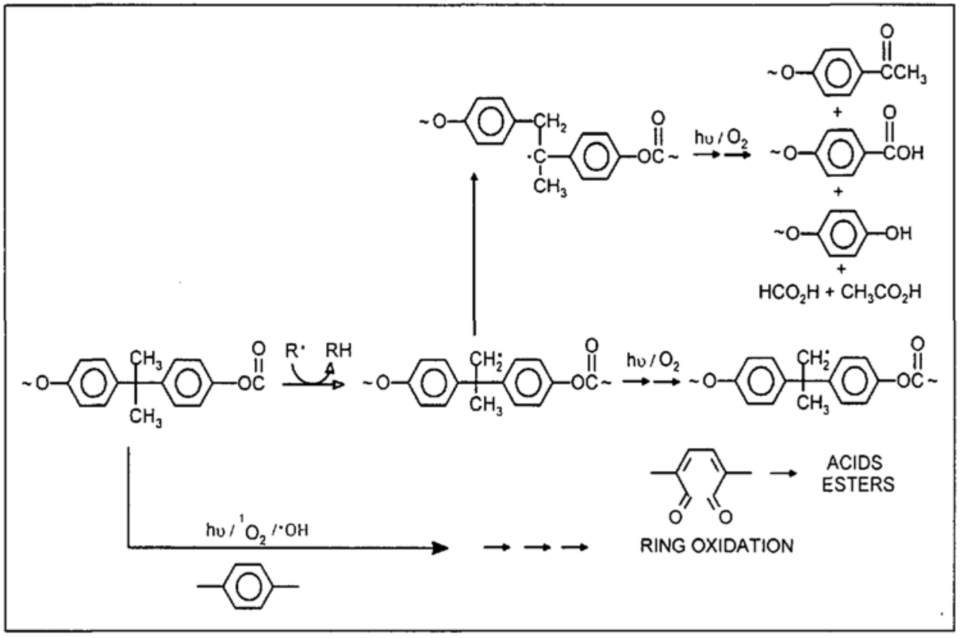


Table 5. *Changes in Molecular Weight,* M_w, *and Elongation of BPA-Polycarbonate after Irradiation in a* 340 FL *Exposure Device*

Hours	M_w	% Elongation
0	29 900	96
285	25 000	42
535	24 550	26
800	102 000	15
970	77 000	0

25 µm films

Table 6. *Changes in Yellowness Index (YI) of BPA Polycarbonate, after Irradiation in a* 340 FL *Exposure Device*

Hours	YI
0	3.00
285	4.54
535	6.54
800	8
970	11

25 µm film

ucts [29], defects and impurities in the polymer [31] leads finally to colored photoproducts. The low amount of photo-*Fries* products may be explained by the work of *Lemaire* [32][33] who demonstrated that such products are easily photodegraded.

BPA-PC undergoes chain scission reactions upon irradiation, leading to a decrease in molecular weight [28]. Results of changes in molecular weight and discoloration are listed in *Tables 5* and *6* [34].

The water content in the resin may influence the deterioration of the polymer.

Therefore, reactions caused by photooxidation of BPA-PC need further elucidation.

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