Theoretical Aspects Regarding Polymer Photochemistry

Liliana Rosu, Cristian-Dragos Varganici and Dan Rosu

Abstract The chapter encompasses literature studies related to the basic photochemical decomposition processes occurring in polymers. Ultraviolet (UV) radiations from light, oxygen from air, temperature and humidity are the main factors producing chemical and/or physical irreversible damages in polymers. UVA radiations (λ = 315–400 nm) possess sufficiently high energy for generating most macromolecular chain bonds cleavage leading to initiation of important chemical modifications through radical intermediates such as oxides and hydroperoxides, chromophore carbonyl groups or conjugated double bonds. The presence of oxygen leads to occurrence of photo-oxidative processes through chained mechanisms.

1 Introduction

It is already known that electromagnetic radiations belonging to the visible and/or ultraviolet spectra consist of streams of very small discrete moving particles, characterized by wave-particle properties, named photons [1]. There is an inverse proportionality relationship between photon energy and wavalength of radiation, as described by Eq. (1), where h denotes Planck's constant (6.6249×10^{-27} erg s), λ is the wavelength of electromagnetic radiation, c is light velocity in vacuum (2.9979×10^{10} cm s^{-1}) and v is the radiation frequency.

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Table 1 Bond dissociation energy values of the main covalent bonds in commercially available organic polymers and the corresponding wavelength [2]

Chemical bond	Bond energy (kJ mol^{-1})	λ (nm)
C–Cl	327	366
C–O (ether)	331	361
C–C (aliphatic)	335	357
N–H	352	340
C–H (allyl)	356	336
S–H and C–O	364	328
Si–O	373	320
C–H (tertiary carbon)	381	314
C–H (secondary carbon)	395	302
C–H (primary carbon)	410	291

$$E = h\frac{c}{\lambda} = h\nu \tag{1}$$

The ultraviolet (UV) region was formally devided acording to wavelength and energetic content in three different domains: UVA, characterized by wavelengths in the range 315–400 nm, UVB, with wavelengths between 315 and 280 nm and UVC with wavelengths raging from 280 to 100 nm.

Based on Eq. (1) there was calculated the UV radiation energy contained within solar light. The radiation energy corresponding to wavelengths between 280 and 400 nm has values raging between 412 and 300 kJ mol^{-1}, these values being high enough to cleave the majority of covalent bonds specific to organic polymers, as one may observe from Table 1 [2].

Based on values from Table 1 one may conclude that UVA radiations are capable of generating macromolecular chain scissions in a former stage, which may lead to initiation of important chemical modifications via radical intermediates formation [3, 4].

2 Theoretical Aspects Regarding Polymer Photochemistry

Rabek suggested that during the initial stage of polymeric materials photodegradation there occurs the formation of an excited electronic state with singlet structure, resulting after photon absorbtion by the molecules present in the irradiated system [5]. Such a process is schematically given in relation (2):

$$S_0 \xrightarrow{h\nu} S^* \tag{2}$$

It is known that after absorbtion of luminuous energy any molecule passes from its fundamental electronic state (S_0), characterized by the positioning with spin electrons coupled in bonding orbitals (σ or π), into excited electronic states (S*), in which the chemical bonds electrons are promoted into different orbitals, such as the
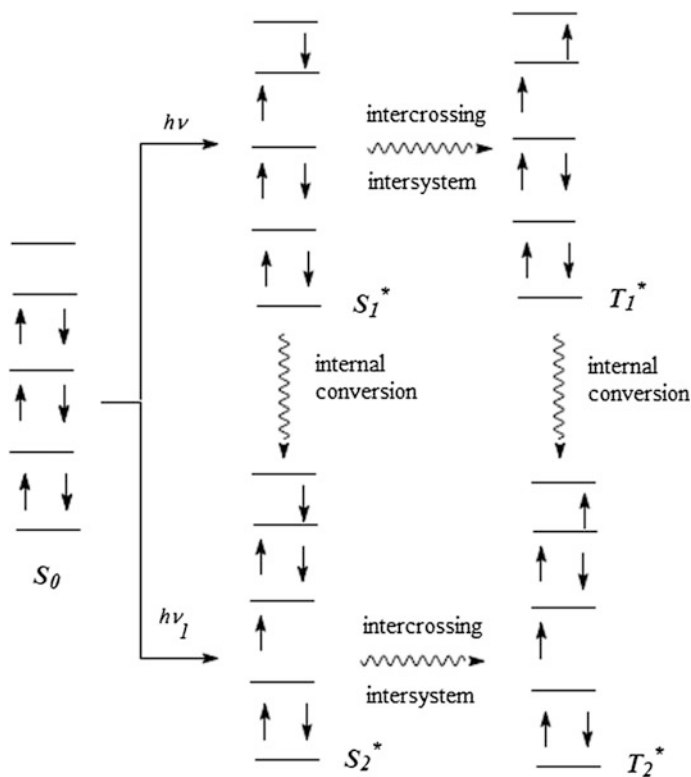
Fig. 1 Electronic excitation and dezexcitation processes, where S_0—fundamental state, S_1^* and S_2^*—singlet excited states, T_1^* and T_2^*—triplet excited states

nonbonding (n) or antibonding (π^* or σ^*) ones, which possess superior energetic content to that of fundamental state. In singlet states chemical bonds electrons decouple remaining antiparallel oriented, whilst in triplet states electronic spins are parallel positioned, as it may be observed from Fig. 1. Possible electronic excitation and dezexcitation processes for a irradiated molecule are also shown in Fig. 1.

Irradiated polymers may suffer the following photophysical processes:

- photon absorbtion and formation of singlet activated entities;
- nonradiative transitions of intercrossing systems with generation of excited triplet states;
- formation of free radicals from the two excited states (singlet and triplet);
- energetic transfer processes between excited molecules (donors) and other molecules present in the system (acceptors).

Basically, polymer photodegradation is an effect of the energy dissipated by photochemically excited molecules and represents one of the first stages of the *primary photochemical process*. This stage may lead to *scission of the excited*

macromolecule and appearance in the system of new macromolecular fragments $(P_1, P_2, \ldots, P_i)$. Such fragments are characterized by lower molecular weights, as compared to the initial macromolecules, which increase the system polydispersity. Apparition of macroradicals allow the establishing of chemical intercatenary bonding with neighbouring macromolecules leading to obtaining of crosslinked structures, having as consequences increasing of molecular weight and decreasing of solubility.

After initiation through this path, polymer degradation usually continues via *secondary photochemical processes* at which participate both initial macromolecules and products resulted from the *primary photochemical process*.

Returning of the excited macromolecule to its fundamental energetic state is made through *physical radiative photoluminiscence phenomena*, *heat release*, *nonradiative transitions* or even by *energy transfer towards another acceptor molecule* existing in the system (Fig. 2).

There were established three laws which govern photochemical processes [1]. The first one is *the photochemical equivalent law*, also known as the *Einstein–Stark law*. According to it, each molecule participating to a chemical reaction involved in the primary photochemical process absorbs the photon as a necessary condition in initiating photochemical transformations. The photochemical equivalent law is completed by the *Grothus–Draper afirmation* which expresses the necessity of light absorbtion by at least one of the reactants participating in a photophysical process or a photochemical reaction. In conformity with this law, only the light absorbed by the molecule which endures photochemical transformation may determine chemical bond dissociation or generation of structural modifications, such as transpositions.

Although most polymer structures are mainly comprised of C–X type covalent bonds, where X may be C, O, N, P or halogen, and these bonds do not absorb light with wavelengths higher than 200 nm, the observation that polymer photodegradation is generated even at exposure to irradiation wavelengths higher than 300 nm is not considered to disobey the two previous mentioned laws. It was observed that the simple presence of some chromophore carbonyl type groups or conjugated
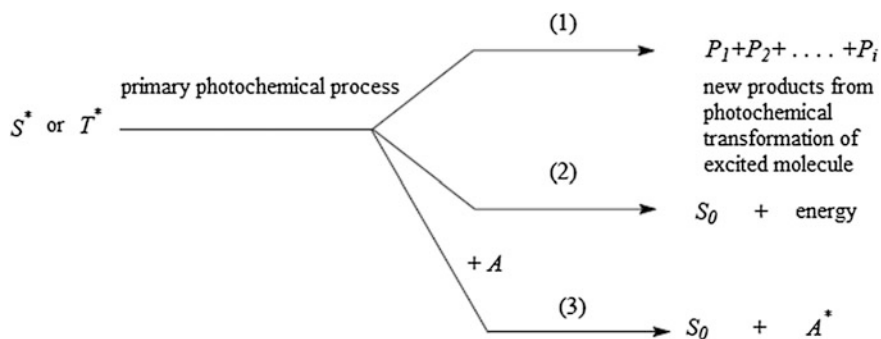

Fig. 2 Dissipation of excited molecule energy during primary photochemical process

double bonds, either in the molecular structure or in the form of impurities in the polymer molecular weight, assure absorbtion of light with wavelengths between values of 300 and 360 nm.

The third law, also known in the literature as the *reciprocity law* was initially elaborated by Bunsen and Roscoe.

From what was previously presented one may conclude that photodegradation of polymeric materials is the result of the following two types of reactions [5]:

- *Primary photochemical reactions* produced under direct absorbed light action, having as result free radicals or transposition products formation;
- *Secondary reactions* initiated by free radicals generated in primary photochemical processes. These reactions are independent of absorbed light. Such an example consists of photooxidation reactions.

The quantitative evaluation of photochemical reactions is expressed through the quantum yield (Φ) which is defined as the relationship between the number of cleaved polymer molecules and number of absorbed photons in the time unity [1, 5]:

$$\Phi = \frac{number\ of\ cleaved\ macromolecules}{number\ of\ absorbed\ photons\ by\ the\ polymer} \quad (3)$$

The *quantum crosslinking yield* (Φ_c) is defined following a similar manner in Eq. (4):

$$\Phi_c = \frac{number\ of\ crosslinked\ macromolecules}{number\ of\ absorbed\ photons\ by\ the\ polymer} \quad (4)$$

Quantum yields specific to common photochemical processes are subunitary. An exception consists of the photodegradation reactions occurring through chain mechanism, characterized by supraunitary quantum yields values.

Quantum cleavage yields values of the main commercially available polymers are given in Table 2 [2, 5].

The *quantum cleavage yield* (Φ_{cl}) may be evaluated from experimental data by using the Eq. (5), where I_a is the number of absorbed photons by the polymer and $(M_n)_0$ and $(M_n)_t$ are the averaged numeric molecular weights of the polymer measured before and after irradiation [6]:

$$\Phi_{cl} = \frac{1}{I_a}\left[\left(\frac{1}{\overline{M_n}}\right)_t - \left(\frac{1}{\overline{M_n}}\right)_0\right] \quad (5)$$

The polymer solution viscosity measured before and after exposure to light may also be used in evaluating the quantum cleavage yield of the macromolecular chain, through Eq. (6) in which $(M_v)_0$ and $(M_v)_t$ are viscosity-averaged molecular weights of the initial and irradiated polymer:

Table 2 Quantum cleavage yields of the main commercially available polymers [2, 5]

Name	Wavelength (nm)	Quantum yield
Poly(ethylene terephthalate)	254	1.6×10^{-3}
Poly(methyl methacrylate)	254	1.7×10^{-3}
Poly(acrylonitrile)	254	$2.0–7.7 \times 10^{-4}$
Poly(vinyl acetate) (in air)	254	5×10^{-3}
Poly(α-methylstyrene)	254	7×10^{-3}
Polystyrene	254	5.5×10^{-4}
Poly(methyl vinyl ketone)	254	2.5×10^{-2}
Poly(phenyl isopropyl ketone)	254	1.7×10^{-2}
Polyurethanes	313	5×10^{-3}
	365	2×10^{-3}
Epoxy resins	365	4.5×10^{-4}
Polysulfones	254	8.4×10^{-4}
Poly(ether sulfones)	254	7.7×10^{-4}
Poly(methyl phenyl) silane	313	1.7×10^{-2}

$$\Phi = \frac{1}{I_a} \left[\left(\frac{1}{\overline{M_v}} \right)_t - \left(\frac{1}{\overline{M_v}} \right)_0 \right] = \frac{1}{I_a} \left[\frac{(\overline{M_v})_0}{(\overline{M_v})_t} - 1 \right] \tag{6}$$

By plotting the linear dependence of $\frac{(\overline{M_v})_0}{(\overline{M_v})_t} - 1$ as function of absorbed photons number, the value of Φ may be determined.

The number of photons absorbed by the polymer is evaluated with the help of light sensitive substances known as chemical actinometers. Such a compound, noted A, transforms into another compound, noted B, after exposure to luminous radiation with known wavelength λ and quantum yield Φ_B. The number of absorbed photons by compound A is determined with relation (7) in which I_a is the number of absorbed photons, I_0 is the number of photons characterizing the incident radiation, ε_A is the molar absorptivity of compound A, c is concentration of compound A and l is the length of the luminous radiation.

$$1 - \left(\frac{I_a}{I_0} \right) = 1 - 10^{\varepsilon} \cdot A^c \cdot A^l \tag{7}$$

The fraction absorbed by the polymer from the incident light may be evaluated either experimentally, by photometric methods, or by the known parameters of Eq. (7).

2.1 General Photodegradation Mechanisms of Polymers

2.1.1 Photo-Oxidative Mechanism

As previously stated, primary photochemical reactions occur as a result of macromolecules activation through direct light absorbtion. In inert atmosphere of argon or nitrogen there exists the possibility of specific degradative processes occurence, such as macromolecules scissions and crosslinking, whilst in air oxygen also participates to the photodegradation processes. The oxygen in air may initiate photo-oxidative processes. Photo-oxidative degradation of polymeric materials occurs through radical intermediates, mostly as a chained mechanism [6], as further shown.

2.1.2 Initiation

Initiation is the photodegradation stage in which free radical species are generated and consists of light absorbtion, either by chromophore groups present in the macromolecule structure or by ones present in impurities in the polymer. Thus activated structures with variable stability are generated, capable of reacting with oxygen [reactions (8), (9)]. In the two reactions R and P represent new alkyl radicals resulted from R–H and P–H macromolecules decomposition and $HO_2\cdot$ is hydroperoxide radical.

$$R-H + O_2 \xrightarrow{h_v} R\cdot + HO_2\cdot \tag{8}$$

$$P-H + O_2 \xrightarrow{h_v} P\cdot + HO_2\cdot \tag{9}$$
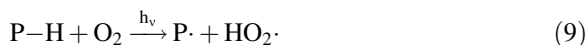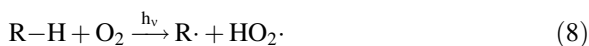
There exists the possibility of the newly formed alkyl radicals to react with unactivated macromolecules generating new reactive radicals resulted by hydrogen extraction from the polymer structure, as shown in reaction (10):

$$R\cdot + P-H \rightarrow R-H + P\cdot \tag{10}$$
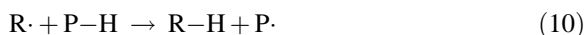
Hydrogen atoms are extracted in increasing order of bond energies, the most susceptible being the entities containing tertiary carbon atoms, followed by the ones containing secondary carbon atoms and primary ones.

Also, there exists the possibility of hydroperoxide radicals to react between them leading to H_2O_2 formation and, under H_2O_2 action, even more stable macromolecules may generate new alkyl radicals:

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$$
$$H_2O_2 \xrightarrow{h_v} 2HO\cdot \qquad (11)$$
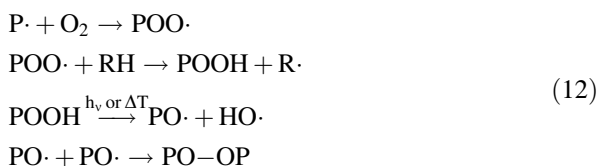$$R-H + HO\cdot \rightarrow R\cdot + H_2O$$
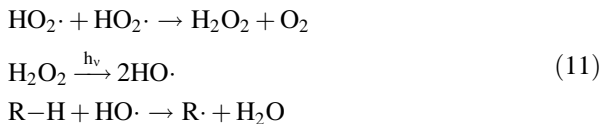
Free radical generation during initiation is also sustained by other authors. Feller also considers that by exposing the polymeric materials to UV irradiation hydroperoxides and peroxides are generated under oxygen influence through a similar mechanism [7], however the author also stating that free radicals are formed exclusively as result of a C–H bond scission from the macromolecular structure. Such an initiation path is also sustained by data in Table 2 which demonstrate that even UV radiations possess sufficient energy in order to assure a C–H bond scission.

Hydroperoxide formation is essential for explaining photodegradative processes of polymers with aliphatic structure. The presence of hydroperoxides was evidenced during polyethylene, polypropylene and poly(vinyl chloride) photodegradation [8].

2.1.3 Propagation

In the propagation stage the resulted radicals react with oxygen from air to yield new reactive oxi- or peroxi- structures or other macroradicals which finally transform in hydroperoxide and peroxide structures as shown in Eq. (12):

$$P\cdot + O_2 \rightarrow POO\cdot$$
$$POO\cdot + RH \rightarrow POOH + R\cdot$$
$$POOH \xrightarrow{h_v\ or\ \Delta T} PO\cdot + HO\cdot \qquad (12)$$
$$PO\cdot + PO\cdot \rightarrow PO-OP$$

Apparition of peroxi radicals is a rapid stage controlled by oxygen diffusion in the polymer bulk. Photodegradation efficiency during propagation is related to the rate of hydroperoxide decomposition and to their capacity of generating new free oxi- and peroxi- radicals, as given in relation (13):

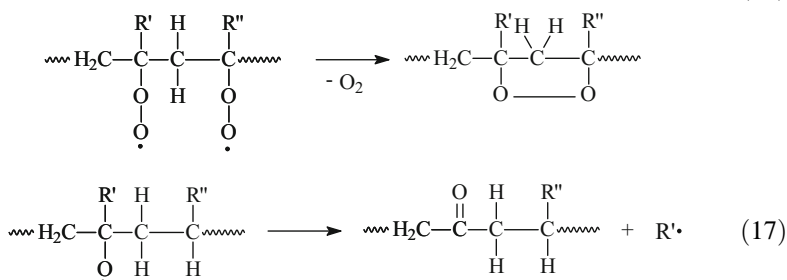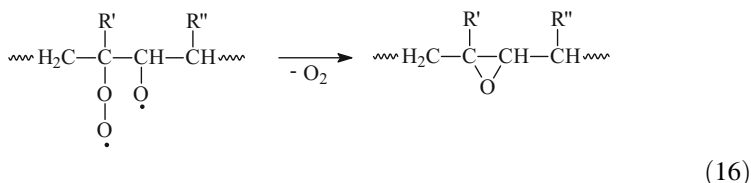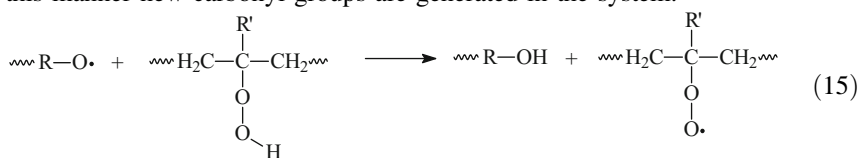$$PO-OH \xrightarrow{hv} PO\cdot + \cdot OH \qquad (13)$$

The newly generated very reactive radicals stabilize themselves rapidly through extraction of hydrogen atoms from neighbouring macromolecules and continue the degradative process:
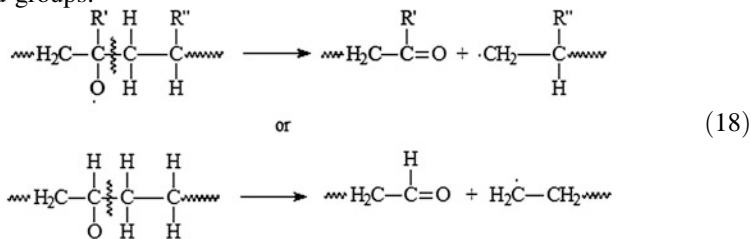
$$\text{www R—H} + \text{HO•} \longrightarrow \text{ww R•} + H_2O$$

$$\text{ww R—O•} + \text{H—P} \longrightarrow \text{ww R—OH} + \text{P•}$$

(14)
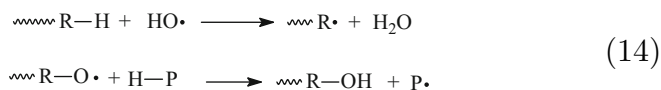
Radicals formed through such paths possess the capacity to continue macro-molecules cleavage or crosslinking reactions. Another known reaction, produced with the participation of oxi radicals is the one of hydroperoxide decomposition (Eq. 15).

In the case of vicinal peroxide groups, these may stabilize through cyclization when epoxide or peroxide entities are formed (Eq. 16) [5].

In the situation in which the formation of cyclic structures is not sterically favored radical stabilization is achieved via intramolecular interactions (Eq. 17) [5]. In this manner new carbonyl groups are generated in the system.

$$\text{ww R—O•} + \text{ww } H_2C\text{—}\overset{R'}{\underset{\underset{O-H}{\overset{|}{O}}}{\overset{|}{C}}}\text{—}CH_2\text{ww} \longrightarrow \text{ww R—OH} + \text{ww } H_2C\text{—}\overset{R'}{\underset{\underset{O•}{\overset{|}{O}}}{\overset{|}{C}}}\text{—}CH_2\text{ww}$$

(15)

$$\text{ww } H_2C\text{—}\overset{R'}{\underset{\underset{\overset{|}{O•}}{\overset{|}{O}}}{\overset{|}{C}}}\text{—}\overset{R''}{\underset{\overset{|}{O•}}{CH}}\text{—}CH\text{ww} \xrightarrow{\text{- }O_2} \text{ww } H_2C\text{—}\overset{R'}{\underset{O}{\overset{|}{C}}}\text{—}\overset{R''}{CH}\text{—}CH\text{ww}$$

(16)

$$\text{ww } H_2C\text{—}\overset{R'}{\underset{\underset{\overset{|}{O•}}{\overset{|}{O}}}{\overset{|}{C}}}\text{—}\overset{H}{\underset{H}{C}}\text{—}\overset{R''}{\underset{\underset{\overset{|}{O•}}{\overset{|}{O}}}{C}}\text{www} \xrightarrow{\text{- }O_2} \text{ww } H_2C\text{—}\overset{R'H}{C}\overset{H}{C}\text{—}\overset{R''}{C}\text{www}$$

(17)

$$\text{ww } H_2C\text{—}\overset{R'}{\underset{\overset{|}{O•}}{\overset{|}{C}}}\text{—}\overset{H}{\underset{H}{C}}\text{—}\overset{R''}{\underset{H}{C}}\text{www} \longrightarrow \text{ww } H_2C\text{—}\overset{O}{\underset{H}{\overset{||}{C}}}\text{—}\overset{H}{\underset{H}{C}}\text{—}\overset{R''}{C}\text{www} + R'•$$

Another way to stabilize oxi radicals is represented by the β-scission reactions [5]. These transformations result in macromolecular scission and formation of new carbonyl end groups:

$$\text{ww}H_2C\text{—}\overset{R'}{\underset{\overset{|}{O}}{C}}\overset{H}{\underset{H}{C}}\text{—}\overset{R''}{\underset{H}{C}}\text{www} \longrightarrow \text{ww}H_2C\text{—}\overset{R'}{C}=O + \cdot CH_2\text{—}\overset{R''}{\underset{H}{C}}\text{www}$$

or

(18)

$$\text{ww}H_2C\text{—}\overset{H}{\underset{\overset{|}{O}}{C}}\overset{H}{\underset{H}{C}}\text{—}\overset{H}{\underset{H}{C}}\text{www} \longrightarrow \text{ww}H_2C\text{—}\overset{H}{C}=O + H_2\dot{C}\text{—}CH_2\text{ww}$$

The photolysis of ketone or ester products, formed via β-scission reactions, occurs through Norrish reactions which may be of type I, when free radicals are generated through decarbonylation, or of type II, occurring via chain scission [9]:

$$\tag{19}$$
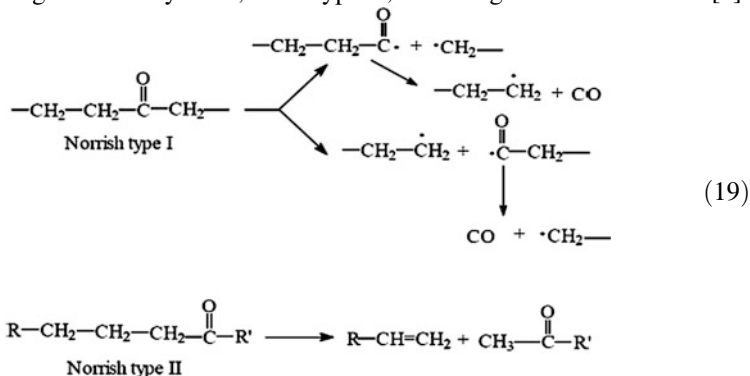
In Fig. 3 there is given the general photo-oxidation cycle of polymers [9].

2.1.4 Other Aspects Concerning Hydroperoxides Photodecomposition

Solar light may generate sufficient energy to polymeric materials in order to cleave RO–OH and R–OOH bonds in hydroperoxides. So the dissociation energy value of RO–OH bond in hydroperoxides is 176 kJ mol^{-1} and that of R–OOH is 377 kJ mol^{-1} [7]. That is why it is considered that during hydroperoxide irradiation the formation of RO· and HO· radicals is predominant.

Fig. 3 The general photo-oxidation cycle of polymers [9]
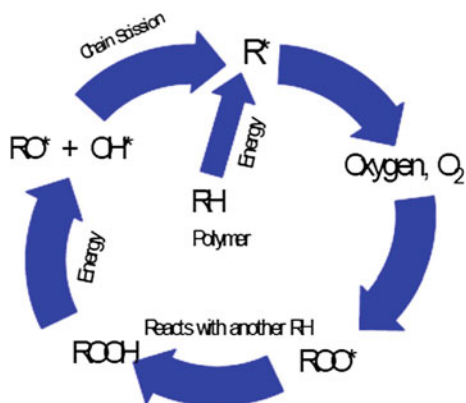
Radiation effect of wavelengths of 254 and 313 nm over photo-oxidation reactions of some elastomers with low aromatic entities content was monitored [8–10]. Authors reported the formation of more or less reactive hydroperoxide groups, dependent on the occupied position in the polymer structure. It was thusly observed that active peroxide groups situated in the vicinity of aromatic entities possess the capacity of easily generating radical species as a result of photolysis reactions and these generated radicals during such dissociations (RO· and HO·) are capable of initiating oxidation reactions in the polymer. The presence of inactive hydroperoxide structures was evidenced by their constant concentration increase with exposure time. Authors also noticed a more increased tendency of active hydroperoxide formation at lower wavelength values. Authors were thus able to demonstrate that the total fraction of active hydroperoxides was higher (0.93) when irradiation was undertaken with radiations at 254 nm in comparison to 0.60, which was the total hydroperoxide fraction at 313 nm exposure of material. Gardette and Lemaire have also debated on different hydroperoxide group types and their different sensitivities to photochemical reactions [11].

It is currently considered that hydroperoxide decomposition represents the main stage involved in the photo-oxidative degradation of polymers.

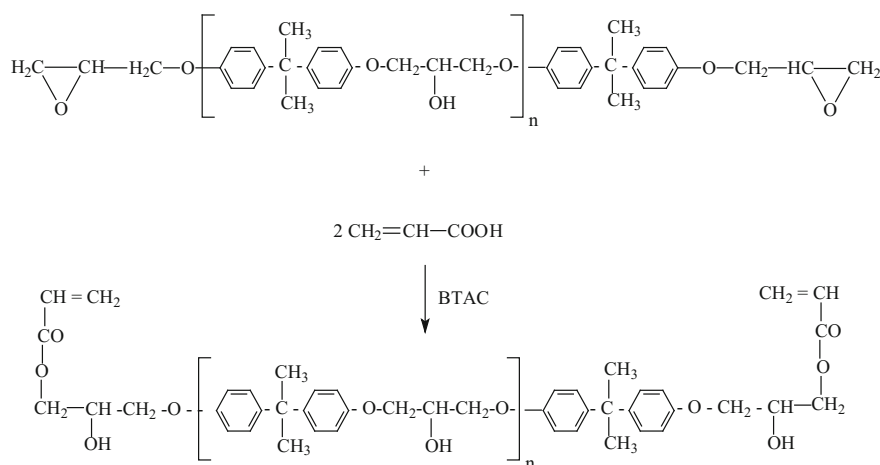### 2.1.5 The Energy Transfer Between Carbonyl Groups and Hydroperoxide Structures

As already mentioned, it was observed that during photo-oxidative degradation of polymers there occur accumulations of new carbonyl groups with ketonic, carboxylic or ester structure [5]. It was noticed that, whilst in most cases carbonyl structure concentrations from polymer bulk increase with exposure time, concentration of hydroperoxide and peroxide structures rapidly reaches a stationary state at relatively low concentrations. An exemplification of such behavior is given in Table 3, in which the variation of hydroperoxide concentration with exposure time (luminous radiation with $\lambda \geq 300$ nm) is represented in the case of photo-oxidative degradation of a vinyl-ester based polymeric structure, crosslinked by end double bonds, where BTAC is benzyltributylammonium chloride (Schemes 1, 2—reproduced with kind permission from Elsevier—license no. 3842460646409) [12].

The increase in hydroperoxide concentration led to a gloss retention decrease and roughness increase of sample surface, as it may be seen from Fig. 4 [12] (reproduced with kind permission from Elsevier—license no. 3842460646409).

Through FTIR and UV–Vis spectroscopy methods there were identified diverse products resulted during photo-oxidative degradation, such as carbonyls, hydroxyl entities and peroxides and hydroperoxides, and photo-oxidative degradation mechanisms were given in Schemes 3 and 4 [12] (reproduced with kind permission from Elsevier—license no. 3842460646409).

Table 3 Hydroperoxide concentration variation during UV exposure [12] (reproduced with kind permission from Elsevier—License no. 3842460646409)

Irradiation time (min)	Hydroperoxydes content mol (–OOH)/g polymer $\times 10^{-5}$
10	7.0
50	9.4
100	12.6
150	14.3
200	15.2
250	15.8
300	16.3
350	16.9
400	17.5
450	17.9
500	17.7
550	17.5
600	17.5

Scheme 1 Synthesis of the vinyl-ester resin [12] (reproduced with kind permission from Elsevier—license no. 3842460646409)

2.1.6 The Photo-Fries Rearrangement

The photo-Fries rearrangement was described as being a rearrangement of phenyl ester entities with their transformation in ortho hydroxy ketones and para hydroxy ketones. The reaction occurs in three steps: formation of two radicals, recombination and hydrogen extraction [13–15]. The general implied reactions are depicted in Scheme 5 [2].
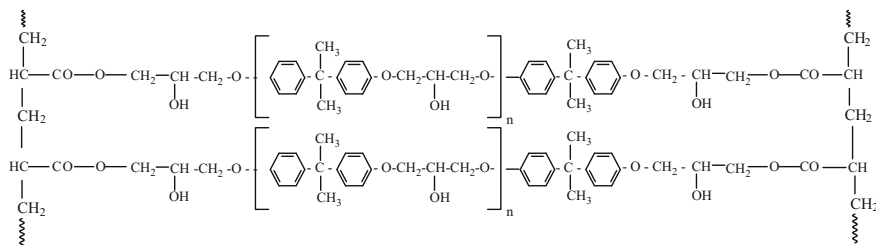
Scheme 2 Structure of the crosslinked vinyl-ester resin [12] (reproduced with kind permission from Elsevier—license no. 3842460646409)
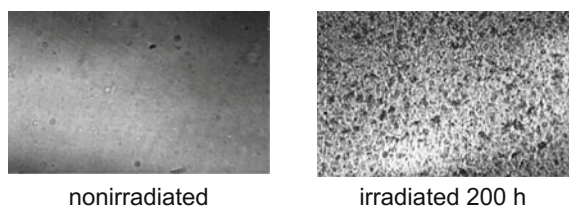

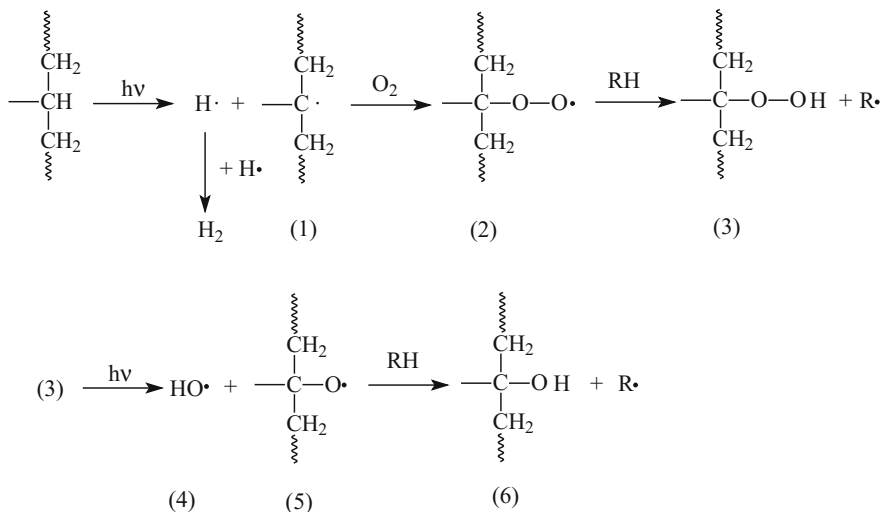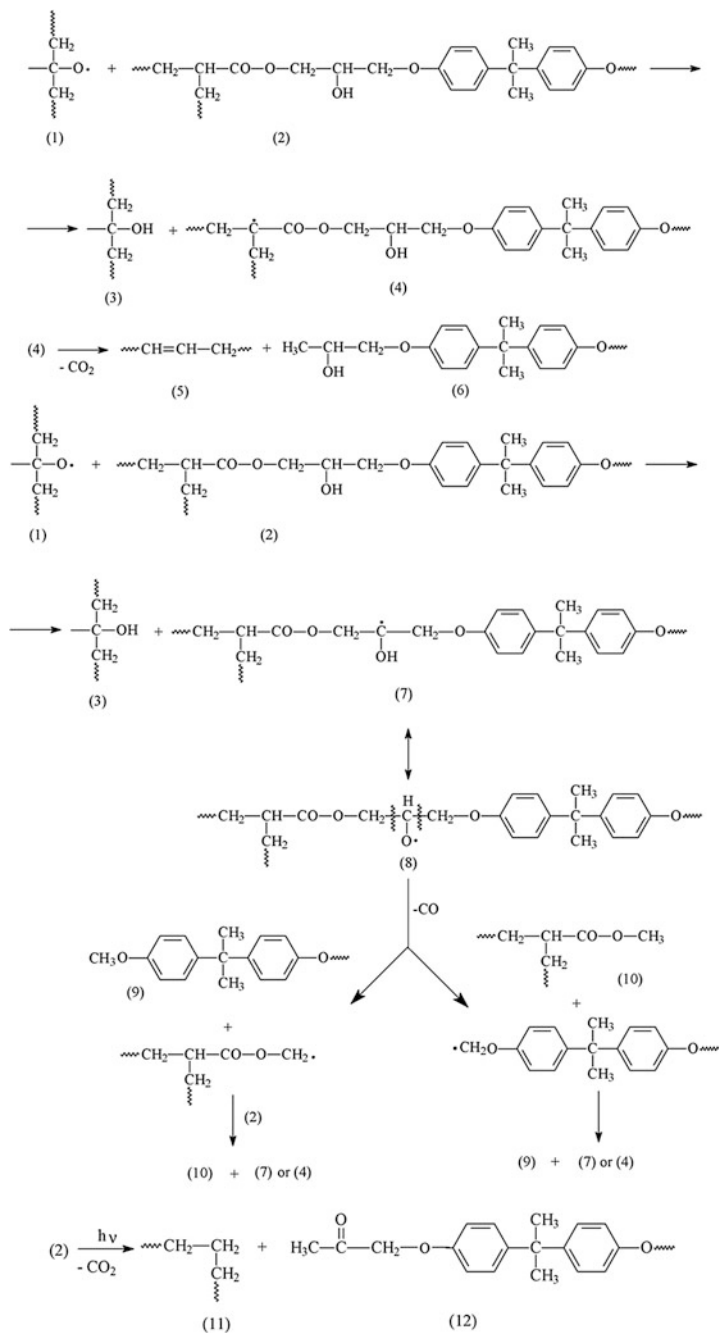
nonirradiated   irradiated 200 h

Fig. 4 Optical micrographs of crosslinked vinyl-ester resin film [12] (reproduced with kind permission from Elsevier—license no. 3842460646409)

Scheme 3 New hydroxyls, peroxides and hydroperoxides resulted during UV irradiation [12] (reproduced with kind permission from Elsevier—license no. 3842460646409)
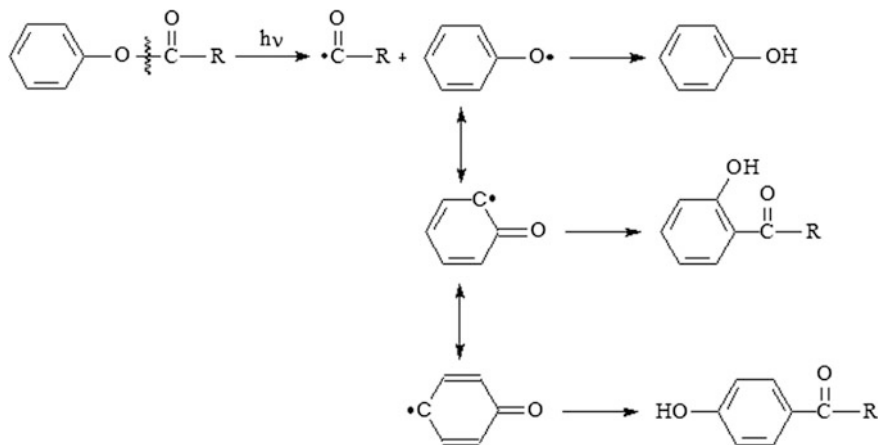
Scheme 4 Photo-oxidative degradation mechanism [12] (reproduced with kind permission from Elsevier—license no. 3842460646409)
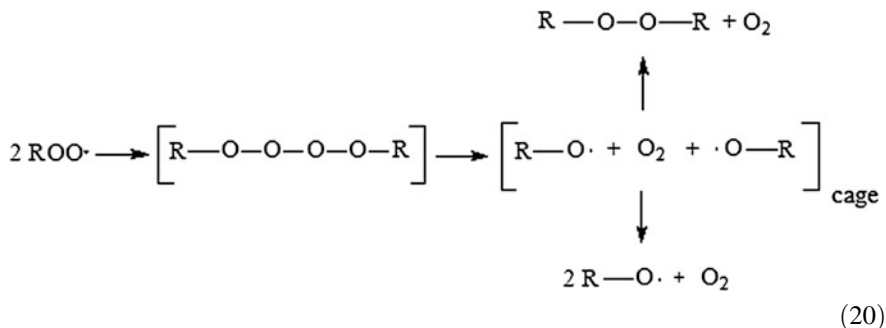
Scheme 5 The photo-Fries rearrangement [2]

According to the literature there exist two types of products which the phenoxy radical may generate during the photodegradation process. In a first instance there is the possibility of the phenoxy radical to generate phenol via extraction of a hydrogen atom from vicinal entities. In a second instance the phenoxy radical may lead to the formation of an acyl phenol through recombination with an acyl radical and hydrogen extraction, after previously passing in the form of one of the two cyclohexadienonic intermediates. Two important factors in radicals rearrangements are temperature and the nature of the substitutes, since high temperatures influence formation of the ortho isomer [13–15].

Norrish type reactions and photo-Fries rearrangements were together observed by Rosu et al. in accelerated ageing studies on semi-interpenetrating polymer networks based on linear semi-aromatic polyurethane and crosslinked epoxy resin, whilst only Norrish type reactions were reported for poly(vinyl alcohol) and cellulose based cryogels by Varganici et al. Further general aspects on the outcome of the two recently reported studies were given in this book.

2.1.7 Termination

Chain termination stage of photo-oxidative processes occurs through recombination of different radical types resulting in linear, branched or crosslinked products. It is already known that during photo-oxidative degradation weak reactive hydroperoxide radicals may accumulate in sufficiently high concentrations. Through their

recombination there results a tetraoxyde intermediate which gradually transforms into macroradicals and oxygen [16], as shown in Eq. (20):

$$R\!-\!O\!-\!O\!-\!R \;+\;O_2$$

$$2\,ROO^\cdot \longrightarrow \left[R\!-\!O\!-\!O\!-\!O\!-\!O\!-\!R\right] \longrightarrow \left[R\!-\!O^\cdot \;+\; O_2 \;+\; ^\cdot O\!-\!R\right]_{cage}$$

$$2\,R\!-\!O^\cdot \;+\; O_2$$

$$\tag{20}$$

Small macroradicals reactivity is dependent on electronic density of the atom containing the unpaired electron. If the macroradical reactivity is low, the probability for the macroradical to be encaged before extraction increases with reactivity decrease [17]. The reactivity of radicals formed by polymer degradation decreases in the order: $R^\cdot > R\!-\!O^\cdot > R\!-\!O\!-\!O^\cdot$.

Light induced degradative effects on the polymeric materials are visible on their surfaces and the depth at which their properties are affected represents an interesting subject [7]. It is why the most affected materials are the transparent or translucid ones. Systems which totally absorb luminous radiation, without occurring of diffusion phenomena, respect the *Lambert–Beer law*, where I_0 is the incident light intensity, I is light intensity at depth x and α is light absorptivity:
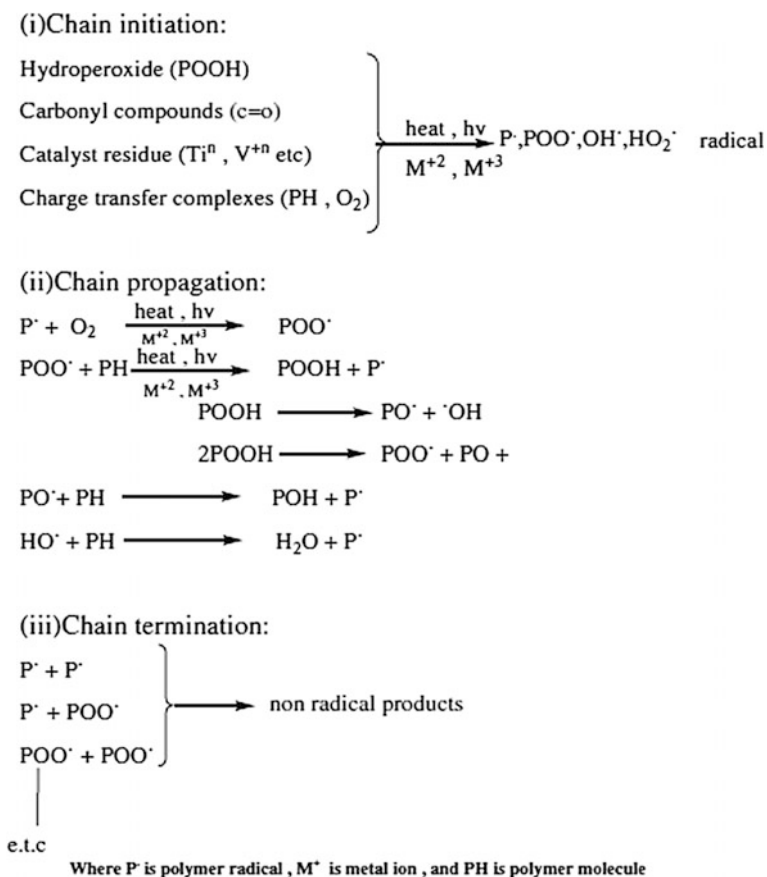
$$I = I_0 e^{-\alpha x} \quad \text{or} \quad ln\frac{I_0}{I} = \alpha x \tag{21}$$

The validity of the *Lambert–Beer law* in polymers represented the subject of several photodegradation studies. Jellinek associated this relation with photochemical scissions in macromolecules [18, 19]. Heller used the Lambert–Beer relation for testing protective action efficiency of some UV radiation absorbant materials [20]. The energy absorbed by the vast majority of polymeric materials increases disproportionally with wavelength of the absorbed incident luminous radiation. An example was offered by Müller even from back in 1983, which demonstrated the increase of carbonyl groups content as a consequence of photo-oxidative degradation of polyethylene foils with exposure time increase in a Xenotest device [21]. The author noticed that photodegradation effects significantly decrease after exceeding 200 µm in depth. The increase of nondegraded material content in polymer bulk was also demonstrated through calculus [22, 23]. Polymer surface layers changed their color due to chromophore accumulation. Immediately after their formation, chromophores supplement the absorbed light and favor polymer photodegradation.
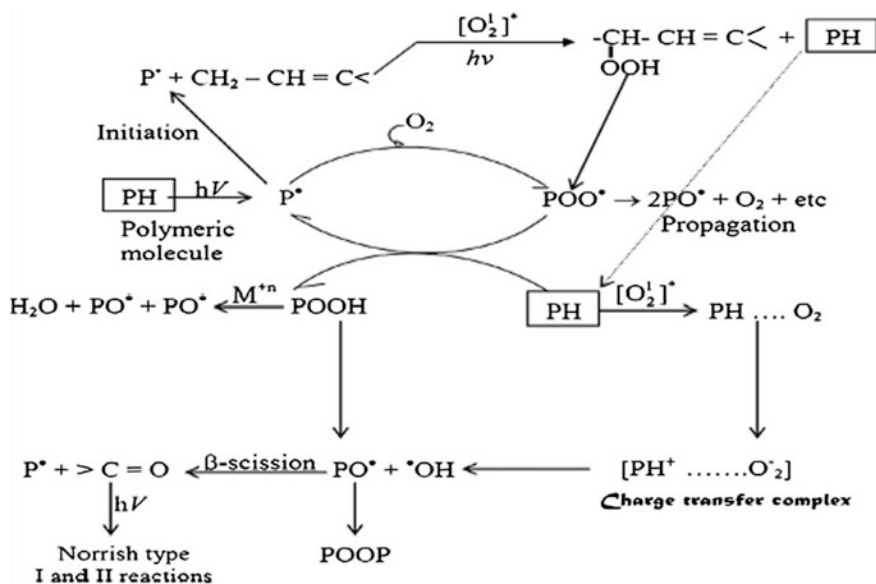
Photodegradative processes and the depth to which they affect polymeric materials are dependent on the wavelength of exposure. R.L. Feller demonstrated that the presence of UV radiations with low wavelengths in the light spectrum of a carbon arc lamp determines a in depth crosslinking of butyl acrylate and isobutyl acrylate films, as opposed to high wavelengths radiations, present in the solar light, which only generate crosslinking of thinner films [24].

General photodegradation mechanisms of the most common classes of polymers were vastly detailed by Rabek [5]. These mechanisms include: polyketones, polyolefins, polycarboxylic acids and analogues, poly (vinyl alcohol), polyacrylates and polymethacrylates, polyvinylpyrrolidone, polyacrylonitrile, polystirenes, polydienes, and polyacetylenes.

General oxidation and photooxidation mechanisms of polymers were overviewed in Schemes 6 and 7 [9].

(i)Chain initiation:

Hydroperoxide (POOH)

Carbonyl compounds (c=o)

Catalyst residue (Ti^n, V^{+n} etc)

Charge transfer complexes (PH, O_2)

$$\xrightarrow[M^{+2},\ M^{+3}]{heat,\ hv} P^{\cdot}, POO^{\cdot}, OH^{\cdot}, HO_2^{\cdot}\quad radical$$

(ii)Chain propagation:

$$P^{\cdot} + O_2 \xrightarrow[M^{+2},M^{+3}]{heat,\ hv} POO^{\cdot}$$

$$POO^{\cdot} + PH \xrightarrow[M^{+2},M^{+3}]{heat,\ hv} POOH + P^{\cdot}$$

$$POOH \longrightarrow PO^{\cdot} + {}^{\cdot}OH$$

$$2POOH \longrightarrow POO^{\cdot} + PO +$$

$$PO^{\cdot} + PH \longrightarrow POH + P^{\cdot}$$

$$HO^{\cdot} + PH \longrightarrow H_2O + P^{\cdot}$$

(iii)Chain termination:

$$P^{\cdot} + P^{\cdot}$$

$$P^{\cdot} + POO^{\cdot} \longrightarrow non\ radical\ products$$

$$POO^{\cdot} + POO^{\cdot}$$

e.t.c

Where P' is polymer radical, M⁺ is metal ion, and PH is polymer molecule

Scheme 6 General oxidation and photooxidation mechanisms of polymers [9]

Scheme 7 Photooxidation of polymers [9]

3   Conclusions

Electromagnetic radiations from visible and/or UV spectra are comprised of streams of very small moving particles with wave-particle properties, named photons.

The UV region is devided based on wavelength and corresponding energy in three domains: UVA (315–400 nm), UVB (315–280 nm) and UVC (280–100 nm). The radiation energy of wavelengths in the range 280–400 nm presents values which cleave the majority of covalent bonds in polymers (412–300 kJ mol^{-1}).

Light energy absorbtion leads to the passing of any molecule from its electronic fundamental state into an excited energetically superior electronic state.

During irradiation polymers may undergo different photophysical processes, such as: photon absorbtion and activated singlet entities formation, generation of free radicals from singlet and triplet excited states, energy transfer between donor and acceptor molecules present in the system or nonradiative transitions of inter-crossing systems with excited triplet states formation.

Polymer photodegradation occurs through primary and secondary photochemical processes. A first stage of any primary photochemical process consists of energy dissipation by excited molecules leading to excited macromolecules scissions with formation of new macromolecular fragments of lower molecular weights, increasing the system polydispersity. Higher molecular weight crosslinked fragments may also be generated through chemical intercatenary bonding, leading to decrease in solubility.

Polymer photodegradation continues through secondary photochemical processes with participation of both macromolecules and products resulted during primary photochemical processes. Afterwards, the excited macromolecule returns to its fundamental energetic state via different processes such as heat release, physical radiative photoluminiscence phenomena, nonradiative transitions or energy transfer towards another acceptor molecule in the system.

Carbon–halogen covalent bonds or covalent bonds of carbon with C, O, N and P atoms do not absorb light at higher than 200 nm wavelengths. It is only through the presence of chromophore carbonyl groups or conjugated double bonds that light absorbtion is assured with wavelengths in the rage 300–360 nm.

In inert atmosphere there may occur specific degradative processes (macromolecules scissions and crosslinking). In air atmosphere oxygen also influences photodegradation through photo-oxidative processes occurring via radical intermediates as chained mechanisms.

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